



Assessment of Heavy Metal Contents of Mulberry Samples (Fruit, Leaf, Soil) Grown in Gumushane Province

Ozgun Kalkisim¹ · Duygu Ozdes² · Cemalettin Baltaci³ · Celal Duran⁴

Received: 19 July 2017 / Accepted: 6 July 2018 / Published online: 31 July 2018
© Springer-Verlag GmbH Deutschland, ein Teil von Springer Nature 2018

Abstract

The present study aims to identify the heavy metal contents of white mulberry (*Morus alba* L.) and black mulberry (*Morus nigra* L.) that are grown in the city center of Gumushane province and its neighboring counties. Heavy metal analyzes were performed in the fruits, leaves and soils of the plants. The control samples, on the other hand, were collected from the mulberry trees located 3 km away from the highway where the vehicle traffic and industrial activities are at their lowest. Sample collection was performed twice a year, namely during the ripening period and fully ripening period of the fruits. The analyses of the heavy metals were performed by using inductively coupled plasma-mass spectrophotometry (ICP-MS). The obtained results were compared with the acceptable limits of heavy metal for humans as established by the World Health Organization (WHO), Turkish Food Codex (TFC) and the literature and an opinion was submitted as to whether they present any risk in terms of human health. When the available data is evaluated, the mulberries grown in Gumushane province, were found to have presented a health risk in terms of Pb, Cd, Ni, Cu, Zn, Mn and Co metals.

Keywords Gumushane · Mulberry · *Morus alba* L. · *Morus nigra* L. · Heavy metal

Beurteilung des Schwermetallgehaltes bei Maulbeeren (Frucht, Blatt, Boden) aus der Region Gumushane

Schlüsselwörter Gumushane · Maulbeere · *Morus alba* L. · *Morus nigra* L. · Schwermetall

Introduction

Rapid development of industrial activities and technology, coupled by rapid increase in population, has given rise to environmental and soil pollution, which is regarded as one of the most important problems that the world faces today

(Talio et al. 2011). In parallel to the environmental and soil pollution, which has the potential to reach hazardous levels for both humans and other organisms, foodstuffs are subject pollution through food chain (Vural 2013; Vural et al. 2017). In this respect, heavy metals are considered the chief foodstuff polluter that threaten the human health (Gürdal 2011).

Heavy metals grouped as biological and non-biological heavy metals depending on the way in which they involve in the biological processes inside the metabolism of the organism. Biological heavy metals that are supposed to be present in the metabolism of the organism at certain concentrations (such as Fe, Cu, Zn and Mn) are compulsorily consumed through foodstuff on a regular basis as they involve in biological reactions. Non-biological heavy metals, on the other hand, (such as Hg, Pb, Cd and Sb) lead to serious health problems by affecting the metabolic structure even if they are taken in very little concentration (Mizuike 1983; Ahmed and Uddin 2007; Wen et al. 2009; Xing et al. 2016). The tolerable limits of some heavy metal

✉ Duygu Ozdes
duyguozdes@hotmail.com

¹ Department of Agricultural Biotechnology, Faculty of Agriculture and Natural Sciences, Recep Tayyip Erdogan University, 53100 Rize, Turkey

² Department of Chemical and Chemical Processing Technologies, Gumushane Vocational School, Gumushane University, 29100 Gumushane, Turkey

³ Department of Food Engineering, Faculty of Engineering and Natural Sciences, Gumushane University, 29100 Gumushane, Turkey

⁴ Department of Chemistry, Faculty of Sciences, Karadeniz Technical University, 61080 Trabzon, Turkey

Table 1 The tolerable limits of some heavy metal ions in foods and drinking water

	Weekly intake level ^a (mg kg ⁻¹)	TFC ^b (mg kg ⁻¹)	RWHC ^c (µg L ⁻¹)	EPA ^d (µg L ⁻¹)	WHO ^e (µg L ⁻¹)
Pb	0.025	0.2	10	1.3	10
Hg	0.0016	1	1	2	1
Cd	0.007	0.05	5	5	3
As	0.015	–	10.0	6	10
Cu	0.5	10	2000	1300	2000
Ni	0.035	–	20	–	20
Cr	1.4	–	–	–	50
Zn	105	5–50	–	–	3000
Fe	126	52	–	300	2000
Mn	35	–	–	–	500

^aDetermined by World Health Organization and Food Additives Food and Agriculture Organization (WHO/FAO)

^bDetermined by Turkish Food Codex Regulation (TFC)

^cThe tolerable limits of heavy metal ions in drinking water determined by Regulation on Waters for Human Consumption (RWHC)

^dThe tolerable limits of heavy metal ions in drinking water determined by Environmental Protection Agency (EPA)

^eThe tolerable limits of heavy metal ions in drinking water determined by World Health Organization (WHO)

ions in foods and drinking water determined by the Turkish Food Codex (TFC), Regulation on Waters for Human Consumption (RWHC), Environmental Protection Agency (EPA), and World Health Organization (WHO) are given in Table 1.

Industrial activities, exhaust gases released by motor vehicles, mineral deposits and mining operations, volcanic activities, fertilizers and pesticides used in agriculture and urban waste are some of the factors that cause the spread of heavy metals into the environment. Depending on the type and concentration of the heavy metal being exposed to, the consumption of food stuff that is polluted by heavy metals lead to development of various cancer types, organ failures, neurological illnesses and musculoskeletal diseases that are of chronic nature. For this reason, determining heavy metal levels in the foodstuff samples consumed by humans is highly important (Xiong et al. 2006; Espada-Bellido et al. 2013; Pourjavid et al. 2016).

Gumushane is located in Eastern Black Sea Region with an approximate altitude of 1100m above sea level. Gumushane hosts rich mineral deposits and there are extensive mining operations conducted in the province. Owing to the fact that it is surrounded by mountains and thus has limited air circulation, it suffers from intense air pollution. For this reason, it is wondered whether the heavy metal contents of white mulberries (*Morus alba* L.) and black mulberries (*Morus nigra* L.), which are grown in the province of Gumushane and used in the manufacturing of commonly consumed food products such as molasses, jams, dried fruit

rollups, mulberry pulp, fruit ice cream, churchkhela, vinegar and fruit juice concentrate, pose a health risk.

This study aims to establish the heavy metal contents of the white mulberries (*Morus alba* L.) and black mulberries (*Morus nigra* L.) that are grown in the city center of Gumushane province and its neighboring counties. Since the plants acting, as producers in ecosystems are not capable of displacing themselves, they are heavily affected by the heavy metal pollution in their respective area. Soil, on the other hand, is the chief source of toxic heavy metals that are permeated into the foodstuff. Fertile soils contain the elements that are required for the cultivation of plants in addition to a wide variety and varying amounts of heavy metals. Heavy metals received from air and soil are accumulated on the surfaces and in various tissues of the plants and passed on to humans and other living organisms through the food chain. For this reason, in this study the heavy metal analyzes were performed in the fruits, leaves and soil of the plants. According to the literature review, so far no heavy metal pollution study has been conducted on the white and black mulberries grown in the city center of Gumushane and its neighboring counties and the soil in which the plants are cultivated. In this study, the heavy metal contents of the mulberry fruits grown in Gumushane were established and the results obtained were compared with the acceptable limits of heavy metal for humans as established by the World Health Organization (WHO), Turkish Food Codex (TFC) and the literature and an opinion was submitted as to whether they present any risk in terms of human health.

Materials and Methods

Collection of Research Materials

Deriving its name from the ‘silver’ mineral, Gumushane is located in Eastern Black Sea Region with an approximate altitude of 1100m above sea level. Despite the fact that only one fourth of Gumushane province has cultivatable lands, the economy of the province nevertheless generally relies on agriculture. Agricultural activities are mostly conducted in the not so wide lowlands of Kelkit and Şiran counties largely in the form of crop plantation. Lentil, figs, potatoes and sugar beets are cultivated as well. Gumushane is one of the least industrialized provinces of the country. The number of industrial businesses is less than 300, which are small-scale business ventures that employ a small number of laborers. Gumushane has rich mineral deposits of iron, copper, zinc, gold, lead and lignite and thus there are extensive mining operations conducted in the province. Owing to the fact that it is surrounded by mountains and thus has limited air circulation, it suffers from intense air pollution.

Table 2 Sample station information

Station	Coordinate	Altitude (m)	
1	Torul 1	N40°33.736 E039°17.268	984
2	Torul 2	N40°33.736 E039°17.268	984
3	Torul 3 (Black mulberry)	N40°33.658 E039°17.624	998
4	Torul 4	N40°33.608 E039°17.636	949
5	Torul 5	N40°33.742 E039°17.265	986
6	Torul 6	N40°33.698 E039°17.333	969
7	Torul 7	N40°33.677 E039°17.677	967
8	Torul 8	N40°33.591 E039°17.632	963
9	Kürtün 1	N40°42.090 E039°05.132	590
10	Kürtün 2	N40°40.258 E039°08.549	700
11	Kürtün 3	N40°42.026 E039°05.238	586
12	Kürtün 4	N40°40.397 E039°08.389	706
13	Hasköy 1 (Control Sample)	N40°26.202 E039°20.631	1166
14	Hasköy 2	N40°25.787 E039°20.898	1178
15	Arzular 1	N40°24.927 E039°39.677	1325
16	Arzular 2	N40°24.924 E039°39.865	1360
17	Pirahmet	N40°24.207 E039°36.405	1261
18	Boyluca 1	N40°22.225 E039°19.754	1340
19	Boyluca 2	N40°22.580 E039°20.088	1329
20	Mescitli	N40°30.209 E039°25.745	988
21	Org. Ind	N40°24.643 E039°39.277	1276
22	University 1	N40°26.193 E039°30.813	1152
23	University 2 (Black mulberry)	N40°26.186 E039°30.811	1149
24	Kelkit 1	N40°07.647 E039°22.415	1376
25	Kelkit 2 (Black mulberry)	N40°07.506 E039°26.242	1408
26	Kelkit 3	N40°07.539 E039°22.312	1376
27	Kelkit 4	N40°11.443 E039°07.321	1388
28	Şiran 1	N40°12.902 E039°08.624	1457
29	Şiran 2	N40°14.768 E039°10.430	1578
30	Şiran 3	N40°12.038 E039°07.145	1455

The samples of mulberry fruits, leaves and the soil in which the plant is cultivated—which are to be analyzed in terms of their heavy metal contents—were collected from Kelkit, Torul, Şiran, Kürtün, Hasköy, Arzular, Pirahmet, Boyluca, Gumushane University central campus, organized industrial zone, and Mescitli that are located in Gumushane province. The details of the locations from which the samples were collected are presented in Table 2. Care was taken to collect the materials from the areas that are in close proximity to the mineral deposits and the areas that are situated approximately 100 m away from the busy highway. Control samples, on the other hand, are collected from the mulberry trees located in Hasköy that is 3 km away from the highway where the vehicle traffic and industrial activities are at their lowest. Sample collection was performed twice a year,

namely during the ripening period and fully ripening period of the fruits.

The leaves and fruits of mulberry trees were collected from the branches facing the roadside without using any metal equipment. The samples were left to dry on blotting papers in a shaded and airless room and in order to achieve complete dryness certain amounts thereof were taken into petri plates to be dried in the drying oven for further 12 h at 105 °C. The fruits and leaves were not cleaned before analysis. Soil samples were collected from an approximate depth of 15–20 cm in the projection area of petals without using any metal equipment, which were put in plastic bags to be kept in a deep freezer at –21 °C until the analyses. The certain amounts of soil samples put in petri plates prior to the analysis were dried in the drying oven for 16 h at 105 °C. Each of the dried samples were pulverized and homogenized in a porcelain press and filtered through a 160 µm sieve.

Methods

Prior to heavy metal analysis, the fruit, leaf and soil samples were digested in a closed microwave digestion system (Milestone Start D model) using appropriate solvent mixtures. For that purpose 0.500 g of fruit, leaf and soil samples were placed in Teflon vessels, separately. 6.0 mL of HNO₃ and 2.0 mL of H₂O₂ for fruit and leaf samples and 4.5 mL of HCl, 1.5 mL of HNO₃, 1 mL of HF and 2 mL of H₂O₂ for soil samples were added into the vessels. Digestion conditions for the samples were performed according to the literature (Bulut et al. 2009). The volumes of the obtained clear solutions were made up 50 mL with distilled/deionized water and then the analyses of heavy metal ions including Pb, Hg, As, Cd, Ni, Cu, Fe, Cr, Zn, Co and Mn were carried out by using ICP-MS (Agilent 7700 Series).

The limit of quantitation (LOQ) values (three times the detection limits) were calculated as 0.033, 0.055, 0.059, 0.043, 0.016, 0.035, 0.083, 0.018, 0.013, 0.025 and 0.023 µg L⁻¹ for Pb, Hg, As, Cd, Ni, Cu, Fe, Cr, Zn, Co and Mn ions, respectively. The accuracy of the method was investigated by spike/recovery tests and the obtained recovery values were higher than 95% for each metal ions.

Results and Discussion

The Pb ions levels of unripe mulberry, ripe mulberry, leaf and soil samples were obtained in the ranges of 0.09–247.18 µg g⁻¹, 0.29–41.48 µg g⁻¹, 3.85–101.37 µg g⁻¹ and 0.16–3.07 mg g⁻¹, respectively (Table 3). The unripe mulberry, ripe mulberry, and leaf samples taken from the university campus have the highest average Pb ions levels. Notwithstanding, in soil samples the highest average Pb

Table 3 The Pb and Cd levels of unripe mulberry, ripe mulberry, leaf and soil samples

Station	Pb				Cd			
	Unripe Mulberry ^b	Ripe Mulberry ^b	Leaf ^b	Soil ^c	Unripe Mulberry ^b	Ripe Mulberry ^b	Leaf ^b	Soil ^b
Torul 1	9.29±0.17	2.42±0.07	6.66±0.02	0.92±0.02	0.14±0.01	0.03±0.01	0.06±0.01	8.22±0.13
Torul 2	7.26±0.39	4.73±0.08	7.23±0.09	0.31±0.01	0.13±0.01	0.03±0.01	0.06±0.01	3.08±0.12
Torul 3 ^a	6.48±0.53	2.46±0.10	6.76±0.11	1.15±0.03	0.13±0.01	0.02±0.01	0.07±0.01	7.19±0.22
Torul 4	0.09±0.01	2.68±0.11	7.63±0.15	0.77±0.00	0.09±0.01	0.09±0.01	0.16±0.01	6.18±0.30
Torul 5	4.04±0.25	3.17±0.06	5.75±0.16	0.91±0.03	0.11±0.01	0.02±0.01	0.05±0.01	8.47±0.62
Torul 6	5.33±0.22	2.36±0.20	7.84±0.08	0.71±0.01	0.09±0.01	0.06±0.01	0.07±0.01	7.27±0.36
Torul 7	3.43±0.16	1.06±0.03	8.36±0.14	1.46±0.06	0.06±0.01	0.03±0.01	0.14±0.01	8.83±0.33
Torul 8	5.49±0.17	2.14±0.07	8.47±0.03	1.06±0.04	0.07±0.01	0.01±0.01	0.07±0.01	6.60±0.58
Kürtün 1	BDL ^d	5.92±0.29	9.40±0.13	0.77±0.02	BDL	0.17±0.01	0.11±0.01	4.57±0.07
Kürtün 2	BDL	8.43±0.74	7.04±0.09	0.83±0.02	BDL	0.03±0.01	0.09±0.01	9.39±0.18
Kürtün 3	BDL	2.60±0.11	10.71±0.43	3.07±0.08	BDL	0.03±0.01	0.10±0.01	4.51±0.05
Kürtün 4	BDL	BDL	10.69±0.06	0.63±0.01	BDL	BDL	0.13±0.01	3.84±0.05
Hasköy 1	BDL	BDL	4.73±0.04	0.72±0.01	BDL	BDL	0.08±0.01	4.29±0.07
Hasköy 2	BDL	BDL	4.57±0.09	0.53±0.01	BDL	BDL	0.12±0.01	6.41±0.17
Arzular 1	BDL	BDL	8.24±0.19	0.35±0.01	BDL	BDL	0.06±0.01	3.29±0.18
Arzular 2	BDL	BDL	6.57±0.13	0.16±0.01	BDL	BDL	0.03±0.01	3.39±0.07
Pirahmet	BDL	0.29±0.01	9.05±0.09	0.33±0.01	BDL	BDL	0.05±0.01	2.15±0.11
Boyluca 1	BDL	1.86±0.04	7.58±0.24	1.13±0.04	BDL	0.06±0.01	0.14±0.01	25.3±0.48
Boyluca 2	4.37±0.18	6.27±0.10	4.04±0.09	0.57±0.02	0.11±0.01	0.04±0.01	0.05±0.01	10.38±0.35
Mescitli	2.43±0.10	2.45±0.08	12.77±0.37	1.01±0.02	0.22±0.01	0.02±0.01	0.06±0.01	3.19±0.20
Org. Ind.	26.62±0.54	6.51±0.27	21.41±1.65	0.28±0.01	0.25±0.01	0.07±0.01	0.10±0.01	1.81±0.18
University 1	59.8±1.45	22.72±0.22	54.37±2.86	0.86±0.03	0.44±0.01	0.11±0.01	0.34±0.03	2.86±0.16
University 2 ^a	247.18±1.63	41.48±2.48	101.37±1.22	0.32±0.01	1.75±0.02	0.43±0.01	0.53±0.02	1.66±0.07
Kelkit 1	2.22±0.06	2.07±0.04	10.89±0.30	0.57±0.02	0.02±0.01	0.02±0.01	0.05±0.01	12.32±1.02
Kelkit 2 ^a	27.99±0.62	5.93±0.03	3.85±0.19	0.22±0.01	0.08±0.01	0.26±0.01	0.04±0.01	2.62±0.09
Kelkit 3	6.77±0.09	3.05±0.03	8.58±0.22	0.23±0.01	0.15±0.01	0.07±0.01	0.06±0.01	4.69±0.17
Kelkit 4	2.11±0.04	4.09±0.10	4.35±0.25	0.19±0.01	BDL	0.05±0.01	0.02±0.01	1.91±0.05
Şiran 1	2.36±0.02	2.95±0.05	4.85±0.13	0.16±0.01	0.02±0.01	0.07±0.01	0.14±0.01	1.03±0.02
Şiran 2	3.65±0.03	6.45±0.12	15.83±0.43	0.22±0.01	0.10±0.01	0.03±0.01	0.11±0.01	2.17±0.05
Şiran 3	1.85±0.03	5.41±0.08	5.68±0.15	0.21±0.01	BDL	0.02±0.01	0.02±0.01	1.84±0.07

^aBlack Mulberry^b($\mu\text{g g}^{-1}$)^c(mg g^{-1})^dBelow detection limit

ions level was obtained in Kürtün. When average Pb concentration data were taken into consideration, it is seen that the Pb ions were not observed in unripe mulberry, sampled from both Kürtün and Pirahmet and it was not obtained in both unripe and ripe mulberry, sampled from Hasköy and Arzular. When Pb ions concentrations given in Table 3 are compared with national and international quality control criteria, it is seen that the levels of Pb ions in mulberry samples grown in Gumushane province are much higher than the tolerable limits and therefore it is considered a serious threat to health. The detection of high Pb ions levels in the samples is thought to be caused by the exhaust gases from motor vehicles, worn rubber dust, engine and grease oils as well as mining activities. The tolerable limit

of Pb ions in soils is determined as $100\mu\text{g g}^{-1}$ and in the analyzed soil samples the Pb ions concentrations are also above this level. The Pb ions spread into the air, water and soils by the gases resulting from industrial activities, fossil fuels, fertilizers and pesticides, and eventually, this pollution reaches to the plants. It is also known that the Pb ions levels are found in high levels in the soils near the roads where traffic is intense. In a study carried out in China, the researchers have determined the heavy metal contents of 268 vegetables, grown in the soils polluted by various reasons such as agricultural, industrial and mining activities and traffic intensity. The levels of Pb, Cd, Cr, Hg, and As in colza, celery, cabbage, carrot, asparagus, lettuce, tomato, and red pepper were found higher than

Table 4 The Ni and Cu levels of unripe mulberry, ripe mulberry, leaf and soil samples

Station	Ni				Cu			
	Unripe Mulberry ^b	Ripe Mulberry ^b	Leaf ^b	Soil ^c	Unripe Mulberry ^b	Ripe Mulberry ^b	Leaf ^b	Soil ^c
Torul 1	28.4±0.34	13.67±0.54	9.34±0.15	0.45±0.02	75.76±0.42	58.89±3.20	87.43±2.24	0.30±0.00
Torul 2	15.6±0.12	15.75±0.26	13.98±0.22	0.17±0.00	109.06±1.62	65.11±3.13	95.21±3.83	0.49±0.03
Torul 3 ^a	29.08±2.36	5.01±0.23	8.36±0.16	0.18±0.00	54.53±0.99	42.48±1.26	77.51±6.06	0.65±0.02
Torul 4	0.09±0.01	6.76±0.16	10.59±0.40	0.18±0.00	0.09±0.01	40.54±1.24	60.35±2.48	0.82±0.02
Torul 5	34.78±0.27	31.96±3.36	7.71±0.14	0.42±0.01	69.95±1.52	41.76±0.59	73.81±6.16	2.82±0.04
Torul 6	16.11±0.48	15.49±0.47	24.58±1.66	0.62±0.00	63.87±4.86	36.42±0.94	74.73±1.17	0.51±0.02
Torul 7	19.04±0.32	4.51±0.19	104.74±1.22	0.21±0.00	68.49±2.21	21.20±0.27	76.13±1.95	0.60±0.03
Torul 8	35.94±1.83	9.80±0.18	10.59±0.28	0.31±0.00	119.24±8.78	45.45±0.94	76.04±2.03	0.69±0.02
Kürtün 1	2.07±0.16	17.52±0.30	15.76±0.23	0.41±0.01	BDL ^d	101.69±1.24	115.08±1.96	0.53±0.01
Kürtün 2	2.32±0.16	12.62±1.23	62.27±5.50	0.42±0.01	BDL	76.64±0.62	60.61±1.10	2.27±0.08
Kürtün 3	2.88±0.01	19.93±0.20	13.34±0.42	0.16±0.01	BDL	71.00±0.58	98.96±3.68	0.66±0.03
Kürtün 4	3.44±0.02	0.64±0.01	17.34±0.35	0.18±0.00	BDL	BDL	91.96±3.76	0.85±0.01
Hasköy 1	3.59±0.14	1.05±0.01	16.12±0.56	0.27±0.01	BDL	BDL	55.32±2.59	0.29±0.00
Hasköy 2	2.68±0.08	1.66±0.07	15.91±1.53	0.34±0.00	BDL	BDL	75.16±2.78	0.24±0.00
Arzular 1	2.24±0.08	2.09±0.08	27.42±1.65	0.21±0.01	BDL	BDL	63.61±3.26	0.59±0.00
Arzular 2	1.84±0.02	2.28±0.22	13.54±0.46	0.17±0.01	BDL	BDL	78.58±1.36	0.49±0.00
Pirahmet	1.97±0.21	3.50±0.17	8.54±0.10	0.25±0.01	BDL	2.05±0.06	58.48±1.16	0.20±0.00
Boyluca 1	1.96±0.13	13.98±0.22	24.29±0.67	0.15±0.01	BDL	73.77±0.79	81.60±4.49	0.20±0.01
Boyluca 2	38.13±0.48	13.98±0.38	13.82±0.35	0.20±0.01	94.63±4.51	27.45±0.54	33.48±0.82	0.22±0.00
Mescitli	11.73±0.62	12.14±0.24	19.24±0.38	0.18±0.00	83.04±3.29	34.64±1.26	58.95±2.51	0.26±0.01
Org. Ind.	20.22±1.33	36.43±0.52	16.28±1.16	0.57±0.01	117.5±4.10	43.50±2.31	58.17±2.55	0.26±0.00
University 1	17.16±0.38	28.48±2.75	6.25±0.06	0.19±0.01	85.61±0.99	34.49±0.40	65.72±0.99	0.24±0.00
University 2 ^a	25.50±0.83	9.19±0.39	10.69±0.16	0.10±0.00	221.69±3.41	54.91±0.34	74.70±4.90	0.24±0.00
Kelkit 1	49.08±2.93	80.65±1.35	25.88±0.47	1.04±0.03	93.30±2.23	63.34±1.23	51.42±1.25	0.27±0.01
Kelkit 2 ^a	59.2±0.08	70.26±1.21	19.40±0.45	0.84±0.06	304.41±2.04	63.68±4.30	63.46±1.51	0.24±0.02
Kelkit 3	88.55±3.83	147.39±2.81	37.62±0.64	0.94±0.03	118.02±1.87	109.25±7.0	57.21±0.64	0.22±0.01
Kelkit 4	22.66±0.77	21.87±0.63	17.86±0.75	0.22±0.01	89.08±2.04	83.87±8.14	69.39±2.80	0.20±0.01
Şiran 1	48.16±0.36	12.64±0.56	8.70±0.20	0.25±0.01	36.87±1.01	78.82±5.53	42.89±0.21	0.18±0.00
Şiran 2	52.55±0.65	29.05±1.41	15.40±0.17	0.15±0.03	39.28±0.96	41.66±2.43	29.56±1.04	0.20±0.02
Şiran 3	32.64±0.82	23.69±0.86	21.15±0.19	0.32±0.04	31.95±0.99	49.31±1.80	44.39±0.64	0.16±0.00

^aBlack mulberry^b($\mu\text{g g}^{-1}$)^c(mg g^{-1})^dBelow detection limit

the non-hazardous level determined by the Environmental Protection Agency (EPA) and the researchers have investigated that the level of heavy metal contamination varied according to the vegetable type (Liu et al. 2013). Hamurcu et al. (2010) have observed the Pb ions levels of the fruits grown on the roadside in the range of 1.54–2.86 $\mu\text{g g}^{-1}$. Duru et al. (2011) have used *Verbascum sinuatum* L. as a biomonitor to evaluate the heavy metal pollution caused by vehicles on the Black Sea coastline and they have found Pb ions levels in the range of 9.12–83.6 $\mu\text{g g}^{-1}$. In a study carried out in Hamburg, the researchers have reported the Pb ions levels of the soils, sampled from the regions where traffic density is high, more than 1000 $\mu\text{g g}^{-1}$ (Aid 1987).

The Cd ions levels of unripe mulberry, ripe mulberry, leaf and soil samples were obtained in the ranges of 0.02–1.75, 0.01–0.43, 0.02–0.53 and 1.03–12.32 $\mu\text{g g}^{-1}$ respectively (Table 3). The highest average Cd ions levels in unripe mulberry and leaf samples were obtained in university campus and in ripe mulberry and soil samples, it was observed in Kelkit and Boyluca, respectively. On the other hand, the lowest Cd concentrations in unripe mulberry, ripe mulberry, leaf, and soil samples were determined in Şiran, Arzular, Pirahmet and organized industrial zone, respectively. Cd ions were not detected in unripe mulberry, sampled from Kürtün, Hasköy and Arzular, and it was not observed in both unripe and ripe mulberry, sampled from Pirahmet. When considered the tolerable limit of

Cd ions in foods ($0.05 \mu\text{g g}^{-1}$) specified by Turkish Food Codex, it is seen that the Cd ions concentrations of unripe mulberry sampled from Torul ($0.10 \mu\text{g g}^{-1}$), Mescitli ($0.22 \mu\text{g g}^{-1}$), organized industrial zone ($0.25 \mu\text{g g}^{-1}$), and university campus ($1.10 \mu\text{g g}^{-1}$) and ripe mulberry sampled from university campus ($0.13 \mu\text{g g}^{-1}$) and Kelkit ($0.15 \mu\text{g g}^{-1}$) exceed the permissible limits. The high levels of Cd ions in the samples taken from close to the main road with high traffic intensity are thought to be caused by the emissions spreading into the environment by motor vehicles, the wearing of vehicle tires (rubber materials containing $20\text{--}90 \mu\text{g g}^{-1}$ Cd), the burning of engine oil and the releasing of the diesel fuel into the air. The permissible limit of Cd ions in soils is determined as $5.0 \mu\text{g g}^{-1}$. The Cd ions levels of the soils, sampled from Torul ($6.98 \mu\text{g g}^{-1}$), Kürtün ($6.39 \mu\text{g g}^{-1}$), Hasköy ($5.63 \mu\text{g g}^{-1}$) and Boyluca ($8.23 \mu\text{g g}^{-1}$) have obtained above this limit. The Cd ions reach to the ground because of industrial and human activities such as phosphorus and farm fertilizer applications. It is thought that these applications are intense in the places where the level of Cd ions is high in soils. It has been determined that the water leaking from the mining activities is responsible for the high Cd levels of the vegetables grown in England (Atafar et al. 2010). Zhao et al. (2016) have reported the Cd ions concentrations of the medicinal plants (*Alpinia oxyphylla* and *Morinda officinalis*) as 0.03 and $0.16 \mu\text{g g}^{-1}$, respectively. Noli and Tsamos (2016) have observed the Cd ions concentration of the soils, sampled from the areas where lignite coal extracted, in the range of $0.55\text{--}3.3 \mu\text{g g}^{-1}$.

The Ni ions were determined in the ranges of $0.09\text{--}88.55$, $0.64\text{--}147.39$, $6.25\text{--}104.74 \mu\text{g g}^{-1}$ and $0.10\text{--}1.04 \text{mg g}^{-1}$ in unripe mulberry, ripe mulberry, leaf and soil samples, respectively (Table 4). The mean values show that the highest Ni levels in both unripe and ripe mulberry were obtained in Kelkit and in leaf and soil samples, it was observed in Kürtün and organized industrial zone, respectively. Conversely, the lowest Ni ions levels in unripe mulberry, ripe mulberry, and leaf samples were obtained in Pirahmet and in soil samples, it was determined in Mescitli. The limit value for Ni ions in fruits and vegetables was given as $10 \mu\text{g g}^{-1}$ by Herrick and Freidland (1990). According to this, it is seen that this limit value is exceeded in all samples except the ripe and unripe mulberry sampled from Hasköy, Arzular and Pirahmet. It is considered that the high Ni ions concentration of the analyzed samples is caused by diesel fuel and gasoline, engine oils, and dust of brake lining. Kaya (2010) reported the Ni ions concentrations of apple, walnut, and grape samples, which grown on the soils formed on parent materials spewed out Erciyes strato volcano, in the ranges of $5.47\text{--}58.22 \mu\text{g g}^{-1}$, $21.97\text{--}57.88 \mu\text{g g}^{-1}$ and $5.27\text{--}149.30 \mu\text{g g}^{-1}$, respectively. The tolerable Ni ions level in the soil is determined as $100 \mu\text{g g}^{-1}$. The Ni ions concentrations were found above this limit in all of the

analyzed soil samples. Chehregani et al. (2009) have determined the Ni ions level as $1730 \mu\text{g g}^{-1}$ in the study, which was conducted by the side of Angouran mine in Iranian.

In unripe mulberry, ripe mulberry, leaf and soil samples, the Cu ions levels were found in the ranges of $0.09\text{--}304.41$, $2.05\text{--}109.25$, $29.56\text{--}115.08 \mu\text{g g}^{-1}$ and $0.16\text{--}2.82 \text{mg g}^{-1}$, respectively (Table 4). By the evaluation of the mean values, it is seen that the highest Cu ions levels in unripe and ripe mulberry were obtained in university campus and Şiran, respectively and in both leaf and soil samples it was determined in Kürtün. The lowest Cu ions concentrations in both unripe mulberry and leaf samples were obtained in Şiran, and in both ripe mulberry and soil samples, it was determined in Pirahmet. Cu ions were not obtained in unripe mulberry, sampled from Kürtün, Hasköy, Arzular and Pirahmet. The Cu ions levels of other samples were obtained above the amount of the tolerable limits in food samples ($10 \mu\text{g g}^{-1}$) determined by Turkish Food Codex. The emissions and atmospheric deposits resulting from human activity, assessment of sewage wastes as fertilizer, fossil fuels, traffic and mining operations are considered as responsible factors of the obtained high Cu ions concentration in the samples. Because of the Cu ions levels of the analyzed samples exceed the daily tolerable limits ($1.5\text{--}3.0 \text{mg}$), by taking into consideration the potential toxic effects of this heavy metal ion, the mulberry grown in Gumushane should be consumed carefully (Korfali et al. 2013; Deveci 2012). In addition, Cu ions play an important role in the carbohydrate and lipid metabolism of the plants. According to some scientific sources, the tolerable Cu ions level in plants varies in the range of $2\text{--}30 \text{mg kg}^{-1}$. The excess amount of Cu ions causes toxic effects in the plants by disrupting the physiological incidents (Alaoui-Sosse et al. 2004). The Cu ions concentrations of apple, pear, quince, almond and walnut samples, which grown on the soils formed on parent materials spewed out Erciyes strato volcano, were determined in the ranges of $8.74\text{--}63.01$, $9.38\text{--}60.18$, $32.71\text{--}44.59$, $85.20\text{--}170.60$ and $64.10\text{--}222.1 \mu\text{g g}^{-1}$, respectively (Kaya 2010). The values obtained in also this study are higher than the limits determined by Turkish Food Codex. In other study performed in China, the Cu ions levels of soils, sampled from regions where mining activities are conducted intensely, have been determined as $1486 \mu\text{g g}^{-1}$ (Jian-Min et al. 2007).

The Zn ions concentrations of unripe mulberry, ripe mulberry, leaf and soil samples were found in the ranges $0.09\text{--}845.25$, $24.71\text{--}730.94$, $209.19\text{--}568.24 \mu\text{g g}^{-1}$ and $0.88\text{--}14.33 \text{mg g}^{-1}$, respectively (Table 5). The calculated mean values show that the highest Zn ions levels in unripe and ripe mulberry samples were obtained in organized industrial zone and Kelkit, respectively and in both leaf and soil samples it was determined in Boyluca. The lowest Zn concentrations in unripe mulberry, ripe mulberry, leaf

Table 5 The Zn and Cr levels of unripe mulberry, ripe mulberry, leaf and soil samples

Station	Zn				Cr			
	Unripe Mulberry ^b	Ripe Mulberry ^b	Leaf ^b	Soil ^c	Unripe Mulberry ^b	Ripe Mulberry ^b	Leaf ^b	Soil ^b
Torul 1	344.85±0.89	204.95±3.11	347.69±5.45	3.24±0.09	4.29±0.08	1.67±0.08	4.09±0.17	505.88±119.87
Torul 2	377.41±13.54	464.59±7.12	358.14±9.52	3.03±0.06	5.53±0.08	2.74±0.16	5.18±0.31	189.43±22.96
Torul 3 ^a	237.87±4.58	228.42±1.92	437.57±19.03	3.05±0.05	2.76±0.06	0.99±0.03	2.67±0.01	297.11±35.02
Torul 4	0.09±0.01	274.89±0.53	337.45±10.72	2.50±0.03	0.09±0.01	1.61±0.02	3.21±0.14	257.89±15.32
Torul 5	222.56±4.34	443.13±7.84	358.21±14.01	3.88±0.10	3.11±0.10	1.97±0.03	3.88±0.13	542.61±10.58
Torul 6	303.89±0.73	181.37±3.99	367.30±1.43	2.87±0.03	4.80±0.35	1.65±0.09	4.31±0.03	853.1±15.13
Torul 7	334.59±2.80	103.39±2.33	568.24±9.43	4.59±0.20	2.44±0.13	0.40±0.02	4.81±0.06	267.32±2.27
Torul 8	486.26±26.95	270.11±6.56	399.48±3.74	3.02±0.06	3.71±0.24	2.05±0.06	3.86±0.10	388.62±21.45
Kürtün 1	BDL ^d	603.55±14.25	532.28±11.41	3.19±0.13	BDL	4.41±0.14	4.01±0.35	325.35±10.16
Kürtün 2	BDL	424.37±10.28	401.73±4.05	3.28±0.08	BDL	9.21±0.13	5.08±0.08	480.16±13.74
Kürtün 3	BDL	296.52±9.54	512.03±12.43	4.70±0.05	BDL	1.87±0.05	9.10±0.42	308.97±26.65
Kürtün 4	BDL	BDL	539.81±14.85	2.26±0.02	BDL	BDL	8.20±0.15	240.01±4.69
Hasköy 1	BDL	BDL	352.90±8.81	3.11±0.02	BDL	BDL	2.55±0.08	690.26±60.61
Hasköy 2	BDL	BDL	378.93±7.58	2.87±0.01	BDL	BDL	2.37±0.06	466.92±41.29
Arzular 1	BDL	BDL	418.57±29.87	1.61±0.02	BDL	BDL	6.12±0.27	141.07±15.24
Arzular 2	BDL	BDL	336.88±3.32	1.50±0.01	BDL	BDL	5.43±0.20	140.64±1.95
Pirahmet	BDL	24.71±0.16	396.91±6.06	1.47±0.01	BDL	BDL	3.15±0.12	396.52±6.14
Boyluca 1	BDL	332.76±7.56	549.18±9.92	6.28±0.30	BDL	1.30±0.01	2.77±0.10	201.28±4.50
Boyluca 2	845.25±2.16	234.27±5.45	478.53±11.05	5.10±0.10	5.71±0.13	0.98±0.01	1.44±0.02	265.83±13.55
Mescitli	194.70±12.51	175.91±2.63	334.10±5.67	1.63±0.03	1.50±0.17	1.15±0.22	3.00±0.31	208.3±16.46
Org. Ind.	613.93±17.55	409.84±17.57	287.31±18.87	1.25±0.02	5.17±1.75	2.54±1.49	3.15±0.12	662.98±7.63
University 1	526.60±10.41	327.06±3.27	497.21±23.14	1.66±0.04	4.37±1.03	1.50±0.10	3.42±0.04	189.06±3.99
University 2 ^a	107.56±0.59	294.41±10.34	469.78±8.86	1.03±0.02	7.08±0.39	2.06±0.11	4.32±0.11	244.67±13.25
Kelkit 1	734.38±33.90	534.75±9.47	376.33±8.36	14.33±0.62	2.66±0.06	2.03±0.06	1.31±0.03	809.24±30.12
Kelkit 2 ^a	561.37±4.65	387.71±11.69	317.46±26.09	2.10±0.02	5.00±0.14	6.12±0.59	2.98±0.05	697.57±7.13
Kelkit 3	628.65±6.47	730.94±15.85	515.88±4.19	2.06±0.02	3.18±0.06	5.49±0.27	1.72±0.03	815.51±56.26
Kelkit 4	334.74±1.60	342.79±14.51	230.19±3.78	0.98±0.01	2.96±0.21	2.69±0.04	1.79±0.64	284.65±1.71
Şiran 1	340.94±2.15	477.00±7.52	230.77±9.34	1.03±0.03	2.72±0.32	4.18±0.11	3.61±0.05	529.1±16.02
Şiran 2	400.48±10.02	499.75±10.49	551.14±6.18	1.50±0.05	3.37±0.04	4.49±0.09	2.40±0.12	212.21±2.85
Şiran 3	399.50±2.20	450.68±5.03	209.19±0.97	0.88±0.02	1.28±0.06	2.07±0.03	2.51±0.23	325.89±6.29

^aBlack mulberry^b($\mu\text{g g}^{-1}$)^c(mg g^{-1})^dBelow detection limit

and soil samples were established in Mescitli, Pirahmet, organized industrial zone and Şiran, respectively. Zn ions were not determined in unripe mulberry sampled from Kürtün and Hasköy, and it was not observed in both unripe and ripe mulberry sampled from Arzular and Pirahmet. There was no Zn ions detected in unripe mulberry sampled from Kürtün and Hasköy, and in both unripe and ripe mulberry sampled from Arzular and Pirahmet. In a study in which heavy metal pollution was investigated in Konya city center, roads and parks, the Zn ions concentrations of plants in the city center were determined in the range of 184.3–884.5 $\mu\text{g g}^{-1}$ (Keleş 2007). Zhao et al. (2016) have reported Zn ions concentration of soils, sampled from the

region where mining activities are conducted in China, as 2516 $\mu\text{g g}^{-1}$.

The Cr levels of unripe mulberry, ripe mulberry, leaf and soil samples were determined in the ranges 0.09–7.08, 0.40–9.21, 1.31–9.10 and 140.64–853.10 $\mu\text{g g}^{-1}$, respectively (Table 5). The unripe mulberry, ripe mulberry, leaf and soil samples collected from university campus, Kelkit, Kürtün, and organized industrial zone, respectively have the highest Cr level according to mean data. The lowest Cr concentrations in unripe mulberry, ripe mulberry, leaf and soil samples were found in Mescitli, Boyluca, Kelkit and Arzular, respectively. Cr ions were not detected in unripe mulberry sampled from Kürtün, and in both unripe and ripe mulberry sampled from Arzular, Pirahmet and

Table 6 The Mn and Fe levels of unripe mulberry, ripe mulberry, leaf and soil samples

Station	Mn				Fe			
	Unripe Mulberry ^b	Ripe Mulberry ^b	Leaf ^b	Soil ^b	Unripe Mulberry ^b	Ripe Mulberry ^b	Leaf ^b	Soil ^b
Torul 1	3.36±0.04	2.65±0.02	13.14±0.31	2.06±0.08	2.78±0.02	2.00±0.02	4.89±0.06	90.21±10.51
Torul 2	4.75±0.22	3.66±0.07	14.38±0.95	2.45±0.08	5.59±0.05	2.71±0.02	6.02±0.06	85.21±4.33
Torul 3 ^a	3.24±0.07	2.95±0.05	12.04±0.44	2.35±0.02	2.78±0.04	11.66±0.18	3.44±0.13	6.87±0.11
Torul 4	3.93±0.05	5.42±0.10	15.68±0.41	1.52±0.05	2.52±0.07	17.85±0.13	3.69±0.16	55.21±1.82
Torul 5	2.82±0.07	2.02±0.05	10.19±0.12	2.08±0.03	2.17±0.01	14.06±0.24	4.85±0.15	9.32±1.15
Torul 6	2.68±0.02	1.86±0.07	10.59±0.07	2.11±0.03	2.84±0.00	12.36±0.20	5.17±0.189	10.59±0.28
Torul 7	2.66±0.01	1.06±0.04	14.85±0.44	2.28±0.02	18.31±0.09	4.80±0.05	4.33±0.14	7.11±0.14
Torul 8	8.37±0.07	3.22±0.11	15.41±0.37	2.33±0.05	3.52±0.18	15.18±0.16	4.18±0.12	77.67±5.18
Kürtün 1	BDL ^c	2.12±0.13	31.91±0.28	3.55±0.11	BDL	5.77±0.20	4.80±0.13	7.32±0.11
Kürtün 2	BDL	5.43±0.12	13.22±0.68	19.85±0.19	BDL	4.14±0.05	4.19±0.14	7.81±0.22
Kürtün 3	BDL	6.69±0.18	17.86±1.32	2.35±0.03	BDL	2.28±0.04	6.33±0.08	7.14±0.08
Kürtün 4	BDL	BDL	3.93±0.41	17.94±0.38	BDL	BDL	5.54±0.48	6.87±0.10
Hasköy 1	BDL	BDL	5.88±0.15	7.14±0.09	BDL	BDL	2.40±0.04	5.23±0.10
Hasköy 2	BDL	BDL	10.37±0.39	16.23±0.33	BDL	BDL	2.61±0.07	6.03±0.04
Arzular 1	0.001±0.00	BDL	6.12±0.06	14.60±0.19	BDL	BDL	3.99±0.09	7.50±0.05
Arzular 2	0.003±0.00	BDL	8.02±0.25	13.30±0.81	BDL	BDL	3.92±0.07	7.98±0.26
Pirahmet	0.006±0.00	0.09±0.01	6.92±0.12	14.27±0.09	BDL	0.45±0.01	2.67±0.01	5.73±0.08
Boyluca 1	0.006±0.00	5.81±0.10	14.94±0.76	16.83±0.91	BDL	15.71±0.29	2.74±0.06	5.82±0.42
Boyluca 2	6.43±0.18	1.82±0.04	6.30±0.43	12.23±0.16	3.28±0.07	10.19±0.16	17.62±0.13	4.08±0.04
Mescitli	1.96±0.08	2.39±0.04	14.06±0.22	14.38±0.04	15.02±0.74	10.62±0.23	2.62±0.03	5.43±0.28
Org. Ind.	7.22±0.60	2.05±0.10	9.42±0.41	11.40±0.01	4.94±0.14	10.85±0.50	3.22±0.18	4.99±0.03
University 1	11.52±0.07	3.51±0.90	18.61±1.24	13.11±0.42	6.37±0.04	2.10±0.02	4.50±0.18	5.16±0.16
University 2 ^a	2.21±0.03	5.07±0.12	15.19±0.38	10.54±0.09	13.49±0.08	4.00±0.15	7.30±0.47	5.29±0.07
Kelkit 1	3.30±0.07	3.13±0.04	3.46±0.05	9.51±0.30	3.22±0.14	2.16±0.02	1.75±0.02	4.30±0.20
Kelkit 2 ^a	7.10±0.04	4.74±0.52	10.32±0.34	11.56±0.31	4.91±0.02	4.98±0.43	7.24±0.11	4.90±0.39
Kelkit 3	3.38±0.02	4.72±0.17	4.38±0.19	9.64±0.37	2.95±0.03	2.80±0.08	3.07±0.08	4.18±0.13
Kelkit 4	4.52±0.01	4.58±0.45	8.53±0.22	13.06±0.23	3.21±0.01	2.82±0.13	5.38±0.08	2.81±0.02
Şiran 1	2.58±0.02	12.69±1.00	8.87±0.06	8.70±0.26	2.57±0.01	6.00±0.12	11.52±0.42	4.57±0.05
Şiran 2	3.49±0.07	6.09±0.33	6.98±0.20	10.72±0.17	4.58±0.06	8.35±0.24	5.87±0.03	4.93±0.05
Şiran 3	3.22±0.08	8.64±0.15	10.12±0.14	8.12±0.27	13.13±0.40	2.20±0.04	3.31±0.02	3.28±0.01

^aBlack mulberry^b(mg g⁻¹)^cBelow detection limit

Hasköy. Alloway (1990) reported that the concentration of 0.03–14.0 µg g⁻¹ Cr in the dry matter of plants is normal value. Accordingly, the Cr levels obtained in mulberry samples grown in Gumushane do not pose a significant health risk. The permissible level of Cr ions in soils is determined as 100 µg g⁻¹. The Cr ions concentrations detected in the analyzed soil samples are higher than this limit. In the study on determination of heavy metals and mineral elements in some plants in Eskişehir, the Cr ions concentrations of clustered dock, *Urtica dioica* and *Rosmarinus officinalis* were obtained as 24.10, 425.0 and 5.77 µg g⁻¹, respectively (Saltan and Canbay 2015).

The Mn ions levels of unripe mulberry, ripe mulberry, leaf and soil samples were found in the ranges of 0.001–11.52, 0.09–12.69, 3.46–31.91 and 1.52–19.85 mg g⁻¹,

respectively (Table 6). According to the mean values, the highest Mn levels in unripe mulberry, ripe mulberry, leaf and soil samples were obtained in organized industrial zone, Şiran, university campus and Boyluca, respectively. The lowest Mn concentrations in unripe and ripe mulberry were observed in Pirahmet, and in leaf and soil samples, it was determined in Kelkit and Torul, respectively. Mn ions were not observed in unripe mulberry sampled from Kürtün district, and in both unripe and ripe mulberry sampled from Arzular and Hasköy. It is considered that the Mn pollution is mainly caused by the mining activities, fossil fuels, traffic, and pesticides. Mn plays a role in the photosynthesis of plants and it is situated as a cofactor in the structure of some enzymes in human body. In case of the excessive intake of Mn causes significant diseases such as Parkinson

Table 7 The As and Hg levels of unripe mulberry, ripe mulberry, leaf and soil samples

Station	As				Hg			
	Unripe Mulberry ^b	Ripe Mulberry ^b	Leaf ^b	Soil ^b	Unripe Mulberry ^b	Ripe Mulberry ^b	Leaf ^b	Soil ^b
Torul 1	0.79±0.04	0.31±0.01	1.05±0.05	109.17±0.83	0.04±0.00	BDL	BDL	5.43±0.08
Torul 2	1.13±0.08	0.43±0.01	1.04±0.06	70.22±3.02	BDL	BDL	0.11±0.01	0.84±0.01
Torul 3 ^a	1.77±0.03	0.30±0.02	0.98±0.07	97.27±9.32	BDL	BDL	BDL	0.24±0.00
Torul 4	0.09±0.01	1.51±0.05	6.34±0.37	187.78±4.12	0.09±0.00	BDL	0.08±0.00	0.22±0.00
Torul 5	0.53±0.01	0.25±0.02	1.02±0.03	104.51±9.13	BDL	BDL	0.33±0.01	0.66±0.01
Torul 6	0.88±0.01	0.22±0.02	1.12±0.03	75.35±3.57	BDL	BDL	BDL	0.35±0.00
Torul 7	0.32±0.01	0.11±0.01	1.04±0.07	150.77±2.02	BDL	BDL	0.01±0.00	0.40±0.01
Torul 8	0.52±0.01	0.36±0.02	2.56±0.12	128.46±4.57	0.02±0.00	BDL	BDL	0.50±0.01
Kürtün 1	0.01±0.00	0.69±0.07	1.01±0.04	68.55±1.03	BDL	0.29±0.01	0.41±0.01	0.79±0.01
Kürtün 2	0.01±0.00	0.54±0.01	0.74±0.01	96.95±4.46	BDL	BDL	0.06±0.00	0.52±0.01
Kürtün 3	BDL ^c	0.31±0.01	1.49±0.07	69.49±1.22	BDL	BDL	BDL	1.16±0.03
Kürtün 4	BDL	BDL	1.14±0.02	93.65±1.67	BDL	BDL	0.12±0.01	0.49±0.00
Hasköy 1	BDL	BDL	0.62±0.04	63.33±3.19	BDL	BDL	0.06±0.00	0.21±0.02
Hasköy 2	BDL	BDL	0.80±0.05	105.98±1.15	BDL	BDL	BDL	0.46±0.00
Arzular 1	BDL	BDL	1.20±0.05	114.58±1.64	BDL	BDL	BDL	0.72±0.01
Arzular 2	BDL	BDL	1.03±0.03	29.86±1.05	BDL	BDL	BDL	0.34±0.01
Pirahmet	BDL	BDL	0.92±0.03	132.27±2.65	0.01±0.00	BDL	BDL	0.46±0.03
Boyluca 1	BDL	0.26±0.02	0.86±0.04	171.86±1.62	0.14±0.01	0.03±0.00	BDL	1.51±0.06
Boyluca 2	2.55±0.38	0.34±0.02	1.04±0.02	176.85±2.43	0.26±0.01	BDL	BDL	0.60±0.01
Mescitli	0.37±0.07	0.40±0.01	2.20±0.02	121.08±4.26	BDL	BDL	BDL	0.62±0.05
Org. Ind.	2.20±0.24	0.40±0.01	1.83±0.13	70.42±2.60	0.05±0.00	BDL	BDL	0.34±0.00
University 1	5.47±0.10	1.79±0.02	4.51±0.22	101.44±8.14	0.09±0.01	BDL	BDL	1.14±0.01
University 2 ^a	18.54±0.36	3.68±0.17	7.12±0.40	93.71±2.86	0.29±0.01	BDL	0.33±0.01	0.11±0.00
Kelkit 1	0.59±0.06	0.53±0.02	1.34±0.06	109.56±6.33	BDL	BDL	BDL	0.70±0.02
Kelkit 2 ^a	1.69±0.02	1.40±0.02	2.21±0.08	117.5±3.47	BDL	BDL	BDL	0.15±0.02
Kelkit 3	0.92±0.08	0.94±0.06	1.68±0.12	95.17±4.00	BDL	BDL	BDL	0.36±0.00
Kelkit 4	1.32±0.12	1.24±0.02	1.49±0.05	50.04±3.15	BDL	BDL	BDL	0.28±0.02
Şiran 1	0.85±0.07	2.19±0.16	2.42±0.03	72.43±1.00	BDL	BDL	BDL	0.39±0.00
Şiran 2	1.96±0.12	3.89±0.16	3.08±0.23	73.74±4.44	BDL	BDL	BDL	0.45±0.02
Şiran 3	0.28±0.01	0.65±0.04	0.96±0.08	73.43±1.16	BDL	BDL	BDL	BDL

^aBlack mulberry^b($\mu\text{g g}^{-1}$)^cBelow detection limit

in humans (Erdoğan et al. 2005; Meraler 2010). Rattan et al. (2005) have determined the Mn levels of rice, wheat, corn, cucumber and turnip, grown in the soils irrigated with urban and industrial wastes, as 53.3, 15.3, 26.0, 19.9 and 16.7 mg kg⁻¹, respectively. The weekly intake level of Mn is determined as 35.0 mg kg⁻¹ by WHO/FAO. On the other hand, it is foreseen that the critical level of Mn is 200–3000 mg kg⁻¹ in soils. The total Mn ions concentrations of alluvial soils in İzmir have been determined in the range of 300–1420 mg kg⁻¹ (Saatçi et al. 1988) and the aqua regia extracted total Mn ions levels of the soils sampled from Samsun have been obtained in the range of 831.20–5421.40 mg kg⁻¹ (Kızılkaya et al. 1998).

The Fe ions levels of unripe mulberry, ripe mulberry, leaf and soil samples were established in the ranges of

2.17–18.31, 0.45–17.85, 1.75–17.62 and 2.81–90.21 mg g⁻¹, respectively (Table 6). The highest Fe levels in unripe mulberry were obtained in Mescitli, in ripe mulberry and leaf samples it was determined in Boyluca and in soil samples, it was found in Arzular, according to the calculated mean data. In other respects the lowest Fe concentrations in unripe mulberry, ripe mulberry, leaf and soil samples were obtained in Şiran, Arzular, Pirahmet and organized industrial zone, respectively. Fe ions were not observed in unripe mulberry sampled from Kürtün and Pirahmet, and in both unripe and ripe mulberry sampled from Arzular and Hasköy. The weekly intake of Fe is determined as 126 mg kg⁻¹ and the tolerance limits of Fe ions stated by TFC (as 52 mg kg⁻¹ in foods), EPA (as 300 $\mu\text{g L}^{-1}$ in drinking waters) and WHO (as 2000 $\mu\text{g L}^{-1}$ in drinking waters) are higher than the limits

Table 8 The Co levels of unripe mulberry, ripe mulberry, leaf and soil samples

Station	Co			
	Unripe Mulberry ^b	Ripe Mulberry ^b	Leaf ^b	Soil ^b
Torul 1	0.86 ± 0.02	0.55 ± 0.06	0.84 ± 0.02	239.05 ± 7.45
Torul 2	1.17 ± 0.02	0.55 ± 0.04	1.11 ± 0.05	153.60 ± 10.62
Torul 3 ^a	0.81 ± 0.06	0.29 ± 0.04	0.46 ± 0.01	148.30 ± 12.98
Torul 4	0.09 ± 0.01	0.60 ± 0.06	0.82 ± 0.03	106.97 ± 4.24
Torul 5	0.56 ± 0.01	0.30 ± 0.01	0.80 ± 0.04	228.34 ± 4.89
Torul 6	0.59 ± 0.06	0.37 ± 0.01	0.96 ± 0.03	292.32 ± 8.72
Torul 7	0.39 ± 0.02	0.16 ± 0.01	0.61 ± 0.02	161.81 ± 11.44
Torul 8	0.84 ± 0.05	0.22 ± 0.04	0.56 ± 0.01	159.63 ± 6.93
Kürtün 1	BDL ^c	1.01 ± 0.16	0.66 ± 0.03	145.02 ± 5.71
Kürtün 2	BDL	1.71 ± 0.05	0.65 ± 0.01	202.99 ± 6.30
Kürtün 3	BDL	0.47 ± 0.01	1.42 ± 0.06	110.99 ± 4.11
Kürtün 4	BDL	BDL	1.40 ± 0.03	109.78 ± 10.30
Hasköy 1	BDL	BDL	0.37 ± 0.01	132.44 ± 11.50
Hasköy 2	BDL	BDL	0.39 ± 0.01	147.33 ± 10.08
Arzular 1	BDL	BDL	0.71 ± 0.05	162.79 ± 3.36
Arzular 2	0.02 ± 0.01	BDL	0.70 ± 0.03	176.98 ± 4.67
Pirahmet	0.06 ± 0.01	0.06 ± 0.01	0.31 ± 0.01	104.45 ± 6.93
Boyluca 1	0.09 ± 0.01	0.30 ± 0.01	0.31 ± 0.04	83.32 ± 4.00
Boyluca 2	0.63 ± 0.05	0.19 ± 0.01	0.19 ± 0.01	59.71 ± 1.83
Mescitli	0.44 ± 0.01	0.27 ± 0.01	0.45 ± 0.01	91.16 ± 7.52
Org. Ind.	0.97 ± 0.04	0.17 ± 0.01	0.48 ± 0.12	115.88 ± 4.09
University 1	1.25 ± 0.01	0.33 ± 0.01	0.62 ± 0.22	81.68 ± 1.76
University 2 ^a	2.08 ± 0.12	0.65 ± 0.04	0.92 ± 0.01	77.87 ± 1.48
Kelkit 1	0.59 ± 0.02	0.29 ± 0.01	0.26 ± 0.01	112.25 ± 1.82
Kelkit 2 ^a	1.01 ± 0.10	1.97 ± 0.04	0.54 ± 0.05	122.15 ± 1.76
Kelkit 3	0.76 ± 0.02	0.64 ± 0.02	0.36 ± 0.14	114.61 ± 2.46
Kelkit 4	0.74 ± 0.04	0.72 ± 0.02	0.38 ± 0.09	58.82 ± 6.13
Şıran 1	0.59 ± 0.02	1.51 ± 0.02	1.16 ± 0.14	82.28 ± 6.62
Şıran 2	0.88 ± 0.02	1.50 ± 0.03	0.74 ± 0.03	78.22 ± 0.80
Şıran 3	0.30 ± 0.01	0.55 ± 0.01	0.50 ± 0.04	71.35 ± 7.13

^aBlack mulberry^b(µg g⁻¹)^cBelow detection limit

of most of the heavy metal ions. In addition, the permissible Fe ions levels in foods reached to 200 mg kg⁻¹ in WHO/FAO reports. Noli and Tsamos (2016) have determined the mean Fe ions contents of the soils sampled from the Anargiri, Perdikas, Filotas and Lehova regions of Greece, where lignite mines and thermal power plants are located, as 28.01, 29.32, 36.97 and 22.62 mg g⁻¹, respectively. In the same study, the Fe ions contents of parsleys, sampled from Anargiri, Filotas and Lehova regions, were reported as 261, 166 and 233 mg kg⁻¹, respectively (Noli and Tsamos 2016).

The As levels of unripe mulberry, ripe mulberry, leaf and soil samples were determined in the ranges of 0.01–18.54, 0.11–3.89, 0.62–7.12 and 29.86–187.78 µg g⁻¹, respectively (Table 7). When taking into consideration the average values, it is seen that the highest As levels in unripe mulberry, ripe mulberry, and leaf samples were obtained in university

campus and in soil samples it was determined in Boyluca. On the other hand, the lowest As levels in unripe mulberry and leaf samples were observed in Kürtün ve Hasköy, respectively, and in ripe mulberry and soil samples, it was determined in organized industrial zone. The As ions were not observed in both unripe and ripe mulberry sampled from Arzular, Pirahmet and Hasköy. Although there is no limit value was given in the Turkish Food Codex Regulation for As ions, in the literature the weekly intake level of it was determined as 0.015 mg kg⁻¹ (Korolczuk et al. 2015).

The Hg concentrations of unripe mulberry, ripe mulberry, leaf and soil samples were found in the ranges of 0.01–0.29, 0.03–0.29, 0.01–0.41 and 0.11–5.43 µg g⁻¹, respectively (Table 7). The mean data show that the highest Hg levels in unripe mulberry, ripe mulberry, leaf and soil samples were obtained in Boyluca, Kürtün, university campus and Torul,

respectively. The lowest Hg levels in unripe mulberry, ripe mulberry, leaf and soil samples were observed in Pirahmet, Boyluca, Hasköy and Şiran, respectively. Hg ions were not detected in unripe mulberry sampled from Kürtün and in both unripe and ripe mulberry sampled from Torul, Hasköy, Arzular, Pirahmet, Mescitli, organized industrial zone, university, Kelkit and Şiran. The weekly intake level of the Hg ions is $0.0016 \text{ mg kg}^{-1}$ and the tolerance limit of it stated by the TFC is 1.0 mg kg^{-1} (Li et al. 2016). Accordingly, it is seen that the Hg ions detected in mulberry samples does not pose a significant risk to health.

In unripe mulberry, ripe mulberry, leaf and soil samples, the Co concentrations were detected in the ranges of 0.02–2.08, 0.06–1.97, 0.19–1.42 and 58.82–292.32 $\mu\text{g g}^{-1}$, respectively (Table 8). When considering the average values, it is seen that the highest Co levels in unripe mulberry, ripe mulberry, leaf and soil samples were obtained in university campus, Şiran, Kürtün and Torul, respectively. The lowest Co levels in unripe mulberry was obtained in Arzular, in ripe mulberry it was observed in Pirahmet and in leaf and soil samples it was found in Boyluca. Co ions were not detected in unripe mulberry sampled from Kürtün and in both unripe and ripe mulberry sampled from Arzular and Hasköy. The permissible limit of Co ions is stated as 0.2 mg kg^{-1} by the Turkish Food Codex. When taking into consideration this limit value, it is seen that the Co ions detected in ripe and unripe mulberry samples, except the samples taken from Hasköy, Arzular and Pirahmet, pose a risk for health. On the other hand, the amount of tolerable Co ions in soils is $50 \mu\text{g g}^{-1}$, and the Co levels of all the analyzed soil samples are higher than this value. Keleş (2007) has determined the Co ions concentrations of the plants and soils, sampled from Konya city center, in the ranges of 0–7.1 $\mu\text{g g}^{-1}$ and 0.3–102.5 $\mu\text{g g}^{-1}$, respectively.

Conclusion

In this study, the heavy metal contents of the fruits, leaves and soils of the white mulberries (*Morus alba* L.) and black mulberries (*Morus nigra* L.) that are grown in the city center of Gumushane province and its neighboring counties were established.

When the results obtained are reviewed, it is observed that the amounts of Pb, Cd, Ni, Cu, Zn, Mn and Co found in the mulberry fruit grown in province of Gumushane are generally higher than the tolerable levels. The factors causing such heavy metals to spread into the environment are mainly listed as the industrial activities, mineral deposits and mining operations and the exhaust gases released by motor vehicles. Gumushane has rich mineral deposits. Therefore, the presence of mining activities is believed to be one of the most important reasons for the heavy metal

pollution. Motor vehicles account for 50% of the heavy metal pollution. The Pb and Ni are released into the air because of those metals being included in the fuel while heavy metals of Cd and Zn are released into the air because of car tire wear, burning motor oils and particularly diesel fuels. Due to the fact that Gumushane is surrounded by high mountains, it has a limited air circulation and thus the heavy metals brought about by pollution can be adsorbed by the vegetables and fruits cultivated in the area. The mulberry fruits that are considered to be control samples are collected from Hasköy that has a very little vehicle traffic. It is observed that the heavy metal contents of the mulberries collected from that particular area are lower than the samples from other areas. The pollution of soil samples by heavy metals, on the other hand, is believed to be the result of the dissolution of the rocks that contain heavy metals for various reasons and their spread into water and soil.

As can be seen from the result of this study, heavy metals can contaminate our foodstuff from various sources and increasingly threaten our health. For this reason, preventive strategies should be developed. In this respect, the sources of contamination should first of all be thoroughly identified and eliminated and the traceability of their environmental exposure and hazard risks should be maintained. Heavy metals should be monitored in all foodstuff samples on a continuous basis by the relevant unit. Washing foodstuff thoroughly is another step that can help reduce heavy metal exposure. Washing food thoroughly will further remove the pesticide and herbicide residue that contain heavy metals away from the food and reduce exposure to such materials.

Acknowledgements The authors wish to thank the Research Council of the Gumushane University (Project No:16.B0110.02.01) for the financial support of this study.

Conflict of interest O. Kalkisim, D. Ozdes, C. Baltaci and C. Duran declare that they have no competing interests.

References

- Ahmed MJ, Uddin MN (2007) A simple spectrophotometric method for the determination of cobalt in industrial, environmental, biological and soil samples using bis(salicylaldehyde)orthophenylenediamine. *Chemosphere* 67:2020–2027
- Aid H (1987) *Bodenschutz und Moderne Landwirtschaft*, Bielefeld.
- Alaoui-Sosse B, Genet P, Vinit-Dunand F, Toussaint ML, Epron D, Badot PM (2004) Effect of copper on growth in cucumber plants (*Cucumis sativus*) and its relationships with carbohydrate accumulation and changes in Ion contents. *Plant Sci* 166:1213–1218
- Alloway BJ (1990) *Heavy metal in soils*. Blackie and Sou, Glasgow, London
- Atafar Z, Mesdaghinia A, Nouri J, Homae M, Yunesian M, Ahmadi Moghaddam M (2010) Effect of fertilizer application on soil heavy metal concentration. *Environ Monit Assess* 160(1–4):83–89
- Bulut VN, Ozdes D, Bekircan O, Gundogdu A, Duran C, Soyлак M (2009) Carrier element-free coprecipitation (CEFC) method for the separation, preconcentration and speciation of chromium using an isatin derivative. *Anal Chim Acta* 632:35–41

- Chehregani A, Noori M, Yazdi HL (2009) Phytoremediation of heavy-metal-polluted soils: Screening for new accumulator plants in Angouran mine (Iran) and evaluation of removal ability. *Ecotoxicol Environ Saf* 72:1349–1353
- Deveci T (2012) Gaziantep'te Atık Sulardan Etkilenen Toprak ve Bitkilerde Eser Element (Cu, Co, Mn ve Zn) ve Fe Konsantrasyonlarının ICP-MS ile Tayini. Kilis 7 Aralık University, Kilis (Master Thesis)
- Duru N, Türkmen Z, Çavuşoğlu K, Yalçın E, Yapar K (2011) *Verbascum sinuatum* L. (Scrophulariaceae) (Sığırkuyruğu) Türü Kullanılarak Karadeniz Sahil Şeridinde Taşlıların Sebep Olduğu Ağır Metal Kirliliğinin Araştırılması. *Sakarya Univ J Sci* 15(2):89–96
- Erdogru Ö, Tosyalı C, Erbilir F (2005) Kahramanmaraş'ta Yetişen Bazı Sebzelerde Demir, Bakır, Mangan, Kadmium ve Nikel Düzeyleri. *Kahramanmaraş Sütçü İmam Univ Sci Eng J* 8(2): 27–29
- Espada-Bellido E, Bi Z, Berg C (2013) Determination of chromium in estuarine waters by catalytic cathodic stripping voltammetry using a vibrating silver amalgam microwire electrode. *Talanta* 105:287–291
- Gürdal G (2011) Abundances and modes of occurrence of trace elements in the Çan coals (Miocene), Çanakkale-Turkey. *Int J Coal Geol* 87:157–173
- Hamurcu M, Özcan MM, Dursun N, Gezgin S (2010) Mineral and heavy metal levels of some fruits grown at the roadsides. *Food Chem Toxicol* 48(6):1767–1770
- Herrick G, Freidland T (1990) Patterns of trace metal concentration and acidity in mountain forest soils of northeastern US. *Water Air Soil Pollut* 53:151–157
- Jian-Min Z, Zhi D, Mei-Fang C, Cong-Qiang L (2007) Soil heavy metal pollution around the Dabaoshan mine, Guangdong province, China. *Pedosphere* 17(5):588–594
- Kaya BB (2010) Erçiyas strato volkanından püsküren ana materyaller üzerinde oluşmuş topraklarda yetiştirilen meyvelerin ağır metal içeriklerinin belirlenmesi. Gaziosmanpaşa University, Tokat (Master Thesis)
- Keleş CT (2007) Konya Şehir Merkezi Yol ve Parklarında Ağır Metal Kirliliği. Selçuk University, Konya (Master Thesis)
- Korfali SI, Hawi T, Mroueh M (2013) Evaluation of heavy metals content in dietary supplements in Lebanon. *Chem Cent J* 7(10):1–13
- Korolczuk M, Ochab M, Rutyna I (2015) Determination of As(III) by anodic stripping voltammetry following double deposition and stripping steps at two gold working electrodes. *Talanta* 144:517–521
- Kızılkaya R, Karaca, Arcaç S (1998) Samsun yöresi topraklarında Zn/Cd oranı ve bu oran ile iz element ve ağır metaller (Fe, Cu, Mn, Pb, Ni) arasındaki ilişkiler. I. Ulusal Çinko Kongresi Bildiriler Kitabı s: 501–509.
- Li Z, Xia S, Wang J, Bian C, Tong J (2016) Determination of trace mercury in water based on N-octylpyridinium ionic liquids preconcentration and stripping voltammetry. *J Hazard Mater* 301:206–213
- Liu X, Song Q, Tang Y, Li W, Xu J, Wu J (2013) Human health risk assessment of heavy metals in soil–vegetable system: A multi-medium analysis. *Sci Total Environ* 463:530–540
- Meraler SA (2010) Mahlep (*Prunus mahaleb* L.)'in Bitki Kısımlarında Mineral Bileşiminin Belirlenmesi. Kilis 7 Aralık University, Kilis (Master Thesis)
- Mizuike A (1983) Enrichment techniques for inorganic trace analysis. Springer, New York
- Noli F, Tsamos P (2016) Concentration of heavy metals and trace elements in soils, waters and vegetables and assessment of health risk in the vicinity of a lignite-fired power plant. *Sci Total Environ* 563–564:377–385
- Pourjavid MR, Arabieh M, Yousefi SR, Sehat AA (2016) Interference free and fast determination of manganese(II), iron(III) and copper(II) ions in different real samples by flame atomic absorption spectroscopy after column graphene oxide-based solid phase extraction. *Microchem J* 129:259–267
- Rattan RK, Datta SP, Chhonkar PK, Suribabu K, Singh AK (2005) Long-term impact of irrigation with sewage effluents on heavy metal content in soils, crops and groundwater a case study. *Agric Ecosyst Environ* 109:310–322
- Saatçi F, Hakerlerler H, Tuncay H, Okur B (1988) İzmir ili civarındaki bazı önemli endüstri kuruluşlarından tarım arazileri ve sulama sularında oluşturdukları çevre kirliliği sorunu üzerinde bir araştırma. Ege Üniversitesi Araştırma Fonu Proje No:127, Bornova-İzmir
- Saltan FZ, Canbay HS (2015) Eskişehir'de Halk Arasında Kullanılan Bazı Bitkilerdeki Ağır Metal ve Besin Elementlerinin Belirlenmesi. Süleyman Demirel Univ J Nat Appl Sci 19(1):83–90
- Talio MC, Luconi MO, Fernández LP (2011) Determination of nickel in cigarettes smoke by molecular fluorescence. *Microchem J* 99:486–491
- Vural A (2013) Assessment of heavy metal accumulation in the roadside soil and plants of robinia pseudoacacia, in Gumushane, north-eastern Turkey. *Ekoloji* 22(89):1–10
- Vural A, Gundogdu A, Akpınar I, Baltacı C (2017) Environmental impact of Gümüşhane city, Turkey, waste area in terms of heavy metal pollution. *Natural Hazards* 88:867–890
- Wen X, Wu P, Chen L, Hou X (2009) Determination of cadmium in rice and water by tungsten coil electrothermal vaporization–atomic fluorescence spectrometry and tungsten coil electrothermal atomic absorption spectrometry after cloud point extraction. *Anal Chim Acta* 650:33–38
- Xing H, Xu J, Zhu X, Duana X, Lu L, Wang W, Zhang Y, Yang T (2016) Highly sensitive simultaneous determination of cadmium (II), lead (II), copper (II), and mercury (II) ions on N-doped graphene modified electrode. *J Electroanal Chem (Lausanne)* 760:52–58
- Xiong C, Jiang Z, Hu B (2006) Speciation of dissolved Fe(II) and Fe(III) in environmental water samples by micro-column packed with N-benzoyl-N-phenylhydroxylamine loaded on microcrystalline naphthalene. *Anal Chim Acta* 559:113–119. <https://doi.org/10.1016/j.aca.2005.11.051>
- Zhao X, Wei J, Shu X, Kong W, Yang M (2016) Multi-elements determination in medical and edible *Alpinia oxyphylla* and *Morinda officinalis* and their decoctions by ICP-MS. *Chemosphere* 164:430–435