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Evaluation of Health Risks Associated with Potential Toxic Elements in Selected Vegetables Consumed in the Western Black Sea Region of Turkey

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ABSTRACT: Vegetables with useful phytochemicals, vitamins, protein, carbohydrates, and minerals are nutritional sources and play an important role in the prevention of many chronic diseases. However, vegetables are contaminated with potentially toxic elements caused by anthropogenic and natural activities. Therefore, this study is the first attempt to analyze 14 potentially toxic elements in some of the most consumed vegetables in Kastamonu province located in the Western Black Sea Region of Turkey by using an ICP-OES for the evaluation of the potential human health risks of adults due to potentially toxic elements via ingestion. The concentrations (μg/kg, dw) of Fe, Al, Sr, Mn, Zn, Ti, Cu, Ni, Pb, V, As, Cr, Cd, and Co analyzed in sixty-nine samples belonging to thirty-six different vegetable types varied from 3995 to 968073, 569 to 616664, 2730 to 144287, 843 to 51417, 268 to 34344, <LOD to 65115, <LOD to 21506, <LOD to 44230, <LOD to 3671, <LOD to 4582, <LOD to 2996, 198 to 5548, 284 to 1289, and <LOD to 856, respectively. The Pb and Cd concentrations analyzed in the studied vegetable samples were above the maximum levels recommended by the Turkish Food Codex. The hazard index and total cancer risk index were estimated to evaluate noncarcinogenic and carcinogenic health risks, respectively. Evaluation of potential noncarcinogenic risk reveals no risk for consumption of the studied vegetables (except for eggplant, potato, and sugar beet) for adult consumers. However, values of the total cancer risk index estimated for Pb, Ni, Cr, Cd, and As analyzed in 15 vegetable samples are higher than the safety limit ($\geq 10^{-4}$).
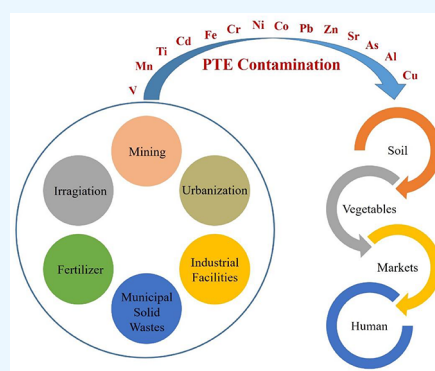
1. INTRODUCTION

Consuming adequate and balanced food is a basic human need and is very important for a sustainable life. Changing diet diversity is the most important factor in maintaining a wide range of macro and micronutrients, and this requires adequate supply, access, and consumption of a variety of foods.[1] Plant-based foods are of vital importance for human nutrition and the protection of human health. Human nutrition is not possible without crop production, which itself must be promoted by sufficient and proper plant nutrients.[2] Vegetables are plant foods that contain various edible parts such as leaves, shoots, roots, tubers, flowers, fruits, seeds, and stems. Therefore, they consist of several categories such as root, tuberous, fruit, and leafy vegetable.[3] These categories containing high amounts of vitamins, proteins, oils, minerals, phytochemicals, essential elements, and dietary fiber are an important food group for the human diet and are also among the main nutritional sources.[3−7] Thus, they play an important role in preventing cancer, cardiovascular and other chronic disease risk.[4]

Vegetables constitute an essential part of the human diet worldwide, and the most significant portion of the total vegetable crop is consumed fresh. Handling vegetables after harvest is detrimental to their quality. Because many vegetables have a short shelf life, they undergo microbial spoilage, in most cases losing sugar, essential oil, other nutrients (e.g., vitamins B and C) and water.[8] Therefore, it is important to handle them in the most hygienic way and under the appropriate conditions to prevent the loss of essential nutrients. The handling process of vegetables contains freezing, canning, blanching and dehydrating.[8] In addition, various processes are applied to the production and distribution of vegetables. Various growth fertilizers can be applied to the soil before planting. In general, fertilizers consist of some combination of nitrogen compounds (ammonium salts, nitrates, or urea), phosphates, and potassium compounds. Planted seeds may have been subjected to one of several protection methods, usually insecticides or fungicides, before the plant germinates and grows. Thus, vegetables can be polluted with potentially toxic elements
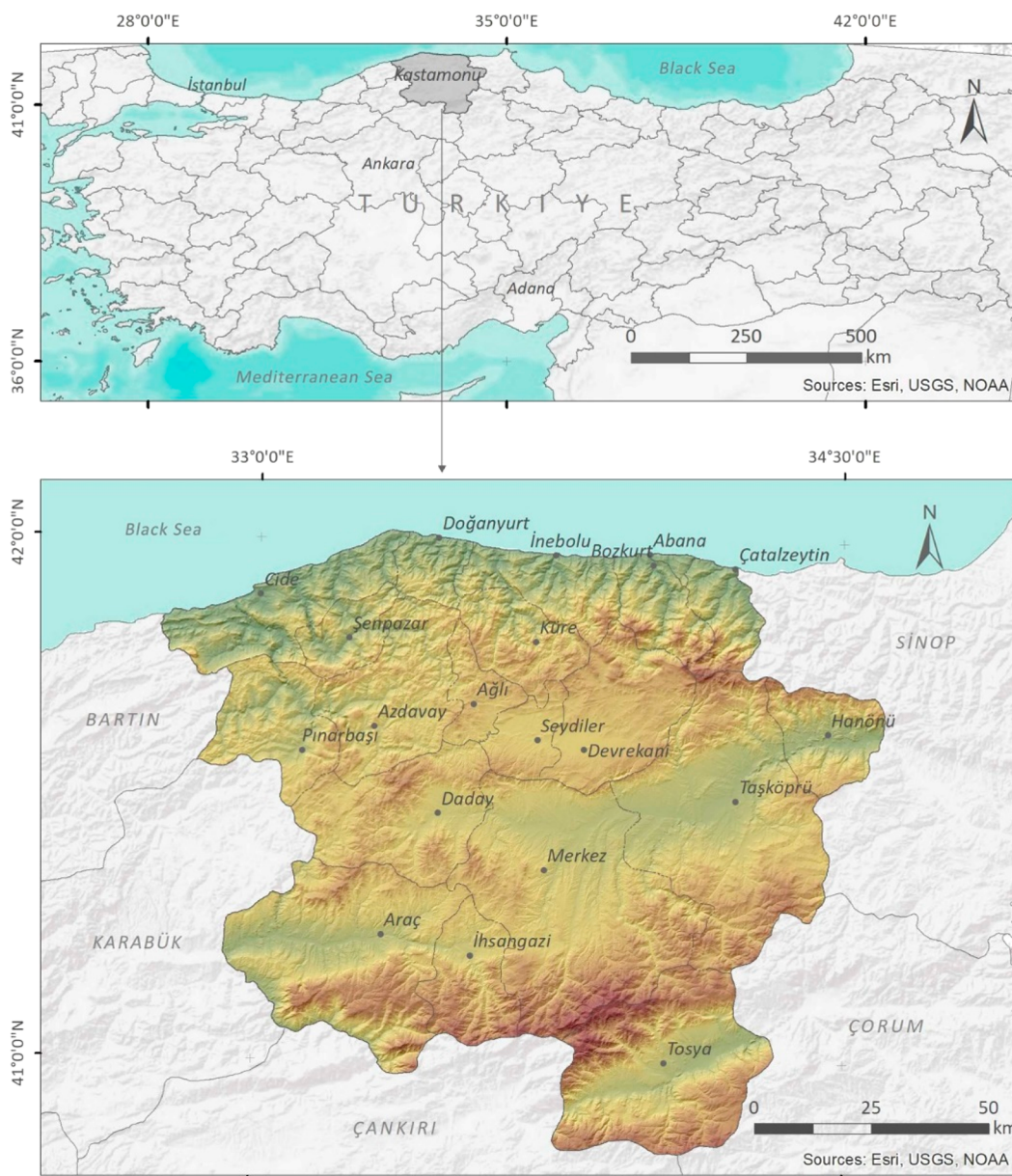
Figure 1. Location of sampling sites.

(PTEs) due to the chemicals applied during these processes and the contamination of soil, irrigation water and air in many regions as a result of human activities sources (sewage irrigation, municipal solid wastes, mining, urbanization, industrial and vehicle emissions, etc.).[9−13]

Vegetables absorb PTEs with long half-lives and accumulate them in high quantities in their edible and inedible parts. The accumulation of PTE in different parts of the vegetable depends on various factors such as plant species, climatic conditions, soil characteristics, geographical location, and agricultural practices.[14] Excessive accumulation of PTE in vegetables not only has consequences for food and water quality and safety, but also causes serious human and animal health problems.[9,14−21] On the other hand, vegetables can contain varying amounts of elements (Fe, Mn, Cu, Zn, Co, Ni, Cr III, etc.) that are biologically essential trace elements (micronutrients) and can also be harmful as well as elements (Pb, Hg, As, Cr, and Cd) that can be highly toxic in even small amounts without any defined biological role.[10,14,22] Pb, Hg, As,

Cr IV, and Cd have carcinogenic effects and are on the WHO's list of the chemicals of major health concern.[22,23] PTE toxicity depends on the element, element concentration and duration, intensity and frequency of exposure, as well as routes of exposure.[14] In this context, more than 90% of human exposure to PTEs is associated with the consumption of polluted water and food.[14] Ingestion of food products (vegetables, fruit, cereals, etc.) polluted with these PTEs can initiate a variety of impairments such as carcinogenicity, genotoxicity, teratogenicity, mutagenicity, neurotoxicity, as well as immunological distress, endocrine disorders, and psychosocial dysfunctions.[14,23] Therefore, consumers must be protected against high levels of PTEs in foodstuffs by regulating them to the maximum levels specified in the framework of national and international regulations.[22] However, not all PTEs or types of foodstuffs are listed in these regulations. For this reason, the observation and determination of the concentrations of different PTEs or heavy metals (HMs) in various food products and the evaluation of the potential health risks

associated with consumption are very important for consumers to have an idea about the safety of foods and to understand their harmful effects. In recent years, much attention has been paid to investigating the PTEs or HMs concentrations in the types of vegetables consumed in different countries and evaluation of their potential health risks, and many studies have been published on this subject.[7,10,22,24−39] However, there is very little information about this subject in Turkey. To date, studies on the contents of PTEs of vegetables grown in Kayseri and Istanbul, Van provinces, and Marmara region were published in the literature. Türkdoğan et al.[40] determined levels of Cu, Co, Pb, Cd, Zn, Ni, and Mn in vegetable samples collected from the Van region in Eastern Turkey, where upper gastrointestinal cancers are endemic using a flame atomic absorption spectrometer (FAAS). Yilmaz and Aksoy[41] determined Zn, Pb, Ni, Cd and Cu in some vegetables (eggplant cucumber, green pepper, tomato, lettuce, onion, bean, parsley, pumpkin, peppermint, and okra) consumed in Kayseri province of Turkey using inductively coupled plasma−optical emission spectrometry (ICP-OES). Osma et al.[42] determined the levels of Cd, Cu, Cr, Ni Zn, and Pb in three different vegetables (bean, pepper, and eggplant) collected from six sites in Istanbul using ICP-OES. Leblebici and Özyürek[43] determined levels of Ni, Cu and Pb in tomato, pepper, onion, and bean collected in Nevşehir province using an ICP-OES. İslamoğlu et al.[44] analyzed the concentrations of As, Pb, Hg, and Cd in spinach, carrot, and potato consumed in Istanbul province using an ICP-MS. Zor and Kocaoba[45] analyzed mineral (Na, Mg, Al, P, K, Ca, and Se) and heavy metal (Zn, Fe, Cu, Cd, Zn, As, Hg, Sn, and Pb) contents of lettuce, spinach, and parsley samples consumed in Marmara region of Turkey using an inductively coupled plasma mass spectrometry (ICP-MS). As can be seen, none of these studies evaluated the health risks caused by PTEs in vegetables consumed in Turkey. Therefore, this study aimed to determine the concentrations of PTEs (Fe, Al, Sr, Mn, Zn, Ti, Cu, Ni, Pb, V, As, Cr, Cd and Co) in sixty-nine samples belonging to thirty-six different vegetable types consumed in Kastamonu province located in the Western Black Sea Region of Turkey by using an ICP-OES and to evaluate the potential non-carcinogenic and carcinogenic health risks for adults estimating average daily intake, hazard quotient, hazard index and excess lifetime cancer risk, and total cancer risk indexes. The novelty of this study is that it is the first inclusive and detailed investigation related to the determination of PTEs in mostly consumed vegetables collected from markets in Kastamonu and evaluation of the potential health risks. The data obtained from this study will provide a scientific basis for local governance to make food pollution more serious and raise awareness among the public.

2. MATERIALS AND METHODS

2.1. Study Area and Sample Collection. This study was performed in Kastamonu province, which is located in the Western Black Sea region of Turkey at a latitude of 41°21′ N and a longitude of 33°46′ E (Figure 1). Kastamonu is approximately 240 km away from Ankara, the capital city of Turkey. Kastamonu province, whose altitude is 775 m above sea level, has a surface area of 13108 km², of which 74.6% is mountainous and forested, 21.6% is plateau and 3.8% is plain.[46] There are Western Black Sea Mountains in the north of the province. Isfendiyar (Küre) Mountains, located to the north of the city center, are parallel to the Black Sea coast. In

the south of the province are the Ilgaz Mountains, which have an east−west extension. With a coastline of 170 km, Kastamonu is a city having the widest coastline in the Black Sea. Since Kastamonu province has a long coastline to the Black Sea, it can be expected to have a maritime climate (humid/temperate). However, as you move from the coast to the inner regions, it takes on a continental climate structure. The average annual rainfall and average temperature are 488.4 mm and 10.3 °C, respectively.[46] Kastamonu province is one of the most important nature tourism destinations in Turkey due to its nature and coastline.[5] According to the last census, the population of Kastamonu province is 378115, of which 155286 live in the center. Kastamonu province's rugged land structure, 59% of the available land being forests and shrubs, limited land suitable for first-class agriculture, long and harsh winters, and inadequate irrigation facilities reduce the diversity in crop production. In this region, mostly rice, corn, barley, garlic, chickpea, wheat, sugar beet, and potato are cultivated.[5]

Kastamonu people living in the city center generally prefer the local markets held on certain days of the week and the markets where these products are sold to supply vegetables from different farms in their districts and nearby provinces. Therefore, vegetable consumption is purchased and consumed without consulting the source of production. Samples of the most preferred and consumed vegetable types were collected by purchasing them from local markets and large supermarkets in Kastamonu. Sixty-nine samples belonging to thirty-six different vegetable types, including three from some samples, were collected in 2021−2022. Vegetable samples collected in sufficient quantities for PTE analysis were brought to the sample preparation laboratory of Kastamonu University in plastic bags and coded by dividing them into groups as given in Table 1. The collected vegetable samples were divided into four groups: Group I: Leafy or edible stem vegetables; Group II: Vegetables cultivated for their fruits; Group III: Potatoes, root, and tuberous vegetables; and Group IV: Leguminous and other vegetables. Only the edible parts of each vegetable were included, and any bruised or rotten parts were also removed. Each sample was washed with ultrapure water and dried for 24 h. The samples were then cut into very small pieces and then dried in an oven at 60 °C until they reached a constant weight. The dried samples were then pulverized with a porcelain mortar and pestle and stored frozen until chemical analysis.[9]

2.2. Sample Preparation and Instrumental Analysis. The analysis of 14 elements (Fe, Al, Sr, Mn, Zn, Ti, Cu, Ni, Pb, V, As, Cr, Cd, and Co) in collected vegetable samples were carried out using an ICP-OES technique via microwave digestion system (CEM MARS 6) equipped with pressure and temperature control to 45 bar and 200 °C. The digestion was achieved by following the procedure previously described by Turhan.[9,44] All chemicals utilized in the study were analytical reagent grade (Merck, Darmstadt, Germany). Shortly, 10 mL of nitric acid (HNO₃, 65% v v⁻¹) was poured into each 0.25 g homogenized powdered vegetable sample into a Teflon vessel. Then, the tightly closed vessel was placed in a microwave digestion system with the process program containing: up to 200 °C at 45 bar pressure in 15 min and constant at 200 °C for 15 min; cooling step for 30 min to reach the room temperature. After the cooling step, the digestive solution was filtered with a Whatman filter (No. 42). Then the solution was transferred to a 50 mL volumetric flask with ultrapure water (18.2 MΩ cm⁻¹) supplied by a New Human

Table 1. Information on the Samples Analyzed within This Study[a]

sample code	vegetable type	annual consumption (kg y^{-1})	dry/wet
	Leafy or Edible Stem Vegetables (Group I)		
VEG1	white cabbage ($N = 2$)	7.97	0.10
VEG2	purslane ($N = 2$)	0.15	0.05
VEG3	swiss chard	0.10	0.10
VEG4	spinach ($N = 3$)	2.74	0.08
VEG5	parsley	1.36	0.15
VEG6	dill ($N = 2$)	0.15	0.11
VEG7	mint	0.31	0.09
VEG8	rocket	0.47	0.10
VEG9	lettuce (cos)	2.43	0.03
VEG10	mushroom	0.81	0.15
	Vegetables Cultivated for Their Fruits (Group II)		
VEG11	eggplant ($N = 3$)	90.25	0.08
VEG12	squash ($N = 3$)	6.83	0.04
VEG13	okra	0.35	0.08
VEG14	bell pepper ($N = 2$)	4.72	0.07
VEG15	tomato	155.37	0.06
VEG16	cucumber ($N = 2$)	24.30	0.03
VEG17	green pepper ($N = 3$)	11.48	0.08
VEG18	pumpkin ($N = 2$)	1.07	0.06
VEG19	capia pepper ($N = 2$)	17.94	0.07
	Potatoes, Root, and Tuberous Vegetables (Group III)		
VEG20	potato ($N = 3$)	62.70	0.24
VEG21	leek ($N = 3$)	1.95	0.19
VEG22	celeriac ($N = 2$)	0.29	0.22
VEG23	red beets	0.26	0.06
VEG24	carrots ($N = 2$)	9.29	0.13
VEG25	sugar beet ($N = 2$)	237.50	0.33
VEG26	turnip	0.03	0.09
VEG27	dry onion ($N = 3$)	27.70	0.05
VEG28	green onion ($N = 2$)	1.42	0.08
VEG29	red radish ($N = 2$)	2.00	0.09
VEG30	white radish ($N = 2$)	0.04	0.10
VEG31	Jerusalem artichoke	0.02	0.35
	Leguminous and Other Vegetables (Group IV)		
VEG32	Borlotti bean	0.87	0.91
VEG33	bean	0.42	0.91
VEG34	green bean ($N = 3$)	1.54	0.19
VEG35	broccoli ($N = 3$)	1.28	0.12
VEG36	cauliflower ($N = 3$)	2.85	0.08

[a]N: number of samples.

Power I Scholar UV Water Purification System and kept at 4 °C before PTE analysis.[9,47]

Detailed information about ICP-OES (SpectroBlue II, Torch box: $1 \times 200-300$ m^3 h^{-1}) used in PTE analysis was given in the studies by Turhan.[9,47] The spectrometer uses revolutionary UV-PLUS gas purification technology that eliminates optical system cleaning. The plasma consisted of Argon, and the RF generator power varied from 0.7 to 1.7 kW. Plasma flow rate, auxiliary gas flow rate, nebulizer flow rate, coolant flow, sample pump speed, and RR power were 13 L min^{-1}, 0.8 L min^{-1}, 0.8 L min^{-1}, coolant flow, 13 L min^{-1} and 1.2 kW, respectively. Solutions for the calibration of ICP-OES were prepared by diluting the multielement standard stock

solution (1000 mg L^{-1}) (Merck, Germany) containing twenty-three elements (Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl, and Zn). The correlation coefficients were equal to 0.999 for all PTEs. The PTE analysis was repeated in triplicate. The limit of detection (LOD) was calculated by using the following formula:[47]

$$\text{LOD} = \frac{3 \times C \times \text{RSD}_{\text{B}}}{\text{SBR}} \tag{1}$$

where C is the concentration of PTE, RSD_{B} is the relative standard deviation of the background, and SBR is the signal-to-background ratio. The limit of detections (LODs) of Fe, Al, Sr, Mn, Zn, Ti, Cu, Ni, Pb, V, As, Cr, Cd, and Co were 0.21, 0.34, 0.10, 0.47, 0.22, 0.49, 0.62, 0.66, 0.83, 6.08, 2.79, 0.27, 0.64, and 0.34 μg kg^{-1}, respectively.

2.3. Potential Health (PH) Risk Evaluation. Generally, the PH risk evaluation of food consists of four steps. The first step involves the formulation and identification of hazards that may pose a threat to human health. Since PTEs (or HMs) are primary contaminants in foods, PH risk evaluation is often extrapolated to such contaminants.[48,49] The second step involves a dose−response evaluation. For each PTE there is a specific intake dose that causes harmful effects to occur. Therefore, it is necessary to determine the amount of PTEs that cause health consequences and also, the frequency of exposure to food, duration of exposure, and route of exposure should be described.[48,49] The third step is the exposure path, such as ingestion, inhalation, and dermal contact. The final step is risk characterization. PH risk evaluation in this study was performed according to the point estimation method developed by USEPA.[50] In this study, the PH risks resulting from ingestion of the investigated vegetable samples were evaluated in two categories for adults: noncarcinogenic risk (non-CR) and carcinogenic risk (CR). The first step of non-CR and CR evaluation is the calculation of daily PTE intake from food, which forms the basis for subsequent estimations and the final PH risk evaluation. Until now, different terms such as chronic daily intake (CDI), estimated daily intake (EDI), daily intake of metals (DIM), average daily intake (ADI), and average daily dose (ADD) were used to describe chronic intake of PTEs, although the calculation method is the same.[50] In this study, the average daily intake (ADI in mg kg^{-1} day^{-1}) of PTEs was calculated as follows:[37,48]

$$\text{ADI} = \frac{C \times \text{IR} \times \text{FE} \times \text{ED}}{\text{BM} \times \text{AT}} \tag{2}$$

where C is the concentration of PTE analyzed in the vegetable samples (mg kg^{-1}), IR is the average daily intake rate given in the third column of Table 1, ED is the average exposure duration of adults, FE is the frequency of exposure, BM is the average body weight, and AT is the average exposure time.[51]

Estimation of non-CR indicates the determination of the impact of PTEs in foods on noncarcinogenic effects in humans.[49] In this study, the evaluation of the non-CR due to PTE analyzed in the investigated vegetable samples evaluation was carried out based on the estimation of hazard quotient (HQ) and hazard index (HI) values (USEPA 1989).[50] If the values of HQ or HI are higher than one (HQ or HI > 1), there is a significant health risk for humans, and if lower than one (HQ or HI < 1), the impact of PTEs is insignificant.[49] Then, based on ADI value, HQ and HI were estimated using the following formulas:[48,50]

$$HQ = \frac{ADI}{R_fD} \tag{3}$$

$$HI = \sum_{i=1}^{n} HQ_i \quad i = 1, 2, 3, ..., n \tag{4}$$

where n is the number of PTEs and R_fD is the PTE oral reference dose determined by the USEPA.[52]

Cancer risk measures the impact of PTEs in foods on their carcinogenic effect on humans, and CR evaluation was performed to evaluate the potential risk associated with exposure to carcinogenic substances over a lifetime exposure period. In this study, CR evaluation was done by estimating excess lifetime cancer risk (ELCR) and the total cancer risk (TCR) index. Based on ADI value, the ELCR and TCR were estimated for Pb, Ni, Cr, Cd, and As by using the following formulas:[48,49,53]

$$ELCR = ADI \times SF \tag{5}$$

$$TCR = \sum_{i=1}^{n} ELCR_i \quad i = 1, 2, 3, ..., n \tag{6}$$

where SF is the slope factor determined by the USEPA 2012.[52] TCR levels are evaluated in four groups as follows:[54] $TCR \leq 10^{-6}$: no risk; $10^{-6} < TCR < 10^{-5}$: acceptable risk; $10^{-5} < TCR < 10^{-4}$: low priority risk and $TCR \geq 10^{-4}$: high priority and unacceptable risk. The units and values of the parameters used in the PH risk evaluation are given in Table 2.

Table 2. Values of Parameters Used for Potentially Health Risk Evaluation

parameters	units	values
avg life (ED)	y	70
frequency of exposure (FE)	day y^{-1}	365.2425
avg body mass (BM)	kg	70.0
avg exposure time (AT)	day y^{-1}	25567

PTE	ref dose (R$_F$D; mg kg^{-1} day^{-1})	cancer slope factor (SF; kg day mg^{-1})
Al	1	
As	0.0003	1.5
Cd	0.0005	6.1
Cr	0.003	0.5
Co	0.0003	
Cu	0.037	
Fe	0.7	
Pb	0.0035	0.0085
Mn	0.14	
Ni	0.02	1.7
Sr	0.6	
V	0.009	
Zn	0.3	
Ti		

2.4. Statistical Analysis. The statistical analysis employed in this study was conducted to assess the data distribution, investigate variance homogeneity, and discern potential differences among groups concerning the concentrations of PTEs. To ensure the robustness of our analysis, initially, the raw data were subjected to two fundamental tests: The Shapiro-Wilk test for normality and the Bartlett test for variance homogeneity. The results of these tests indicated that a significant portion of the data did not conform to the normal

distribution or exhibit homogeneity of variances, which can lead to unreliable parametric analysis. Thus, logarithmic transformation was applied to the data set to address the challenges of non-normality and variance heterogeneity.

Following the logarithmic transformation, the data were re-evaluated using the Shapiro-Wilk test and Bartlett test. Remarkably, the transformed data demonstrated substantial improvements with a majority of the variables now adhering to normal distribution assumptions and displaying variance homogeneity. Nevertheless, a small subset of the transformed variables continued to exhibit deviations from normality or lacked homogeneity of variances.

For variables that met the normality and variance homogeneity criteria after transformation, a one-way analysis of variance (ANOVA) was performed to investigate potential differences among groups. If the ANOVA yielded a significant result ($p < 0.05$), posthoc Turkey tests were employed to identify specific groups that differed significantly.

Conversely, the Kruskal−Wallis test was employed as a nonparametric alternative. If the Kruskal−Wallis test produced a significant p-value ($p < 0.05$), subsequent pairwise Wilcoxon rank-sum tests were conducted to pinpoint the specific groups displaying significant differences. All statistical analyses were conducted by R studio version 2023.06.[55]

In addition, the logarithmic transformed data was used to conduct Principal Component Analysis (PCA) to explore the underlying patterns and relationships within the data set of analyzed PTEs in vegetables. The calculations of PCA analysis were done R studio version 2023.06.2, and the biplot resulting the PCA analysis was obtained by Orange Data Mining version 3.[56]

3. RESULTS AND DISCUSSION

3.1. Concentration of PTE in Vegetables. The concentrations of the PTEs analyzed in vegetable samples are given in Table 3, and the results of the statistical analyses are given in Table 4. As can be seen from Table 3, PTE concentrations of vegetable samples showed a wide variation. The decreasing order of the average concentration of PTEs analyzed in all vegetable samples were Fe > Al > Sr > Mn > Zn > Ti > Cu > Ni > Pb > V > Cr > As > Cd > Co. From the information given in Tables 1 and 3, according to the average concentrations analyzed in vegetable samples in Groups I, II, II, and IV, PTEs are also listed as follows: Fe > Al > Sr > Mn > Ti > Zn > Cu > Ni > V > Pb > Cr > As > Cd > Co (Figure 2a), Fe > Sr > Al > Zn > Mn > Cu > Ni > Pb > Ti > Cr > V > As > Cd > Co (Figure 2b); Fe > Al > Sr > Mn > Ti > Zn > Cu > Ni > V > Pb > Cr > As > Cd > Co (Figure 2c), and Fe > Sr > Ni > Mn > Al > Zn > Cu > Pb > Ti > Cr > As > V > Cd > Co (Figure 2d), respectively. The boxplot for logarithmic transformed data is also given in Figure 3.

Iron (Fe) is both an essential micronutrient and a toxic metal for living organisms because Fe is toxic due to its high ability to produce free radicals that can damage the biological system.[57] On the other hand, iron deficiency is the most common nutritional deficiency and a major trigger of anemia, and approximately 1.2 billion people suffer from iron deficiency anemia.[58] However, excess Fe can accumulate in the organs in the body, which can bring about damage to the organs such as the heart, liver, and endocrine glands.[57] Fe concentrations in the vegetable samples varied from 3995 (white radish cocoated VEG30) to 968073 (purslane cocoated VEG2) μg kg^{-1} with an average value of 162713 μg kg^{-1}. The

Table 3. PTE Concentrations Analyzed in Vegetable Samples

sample code	concentration ($\mu g\ kg^{-1}$ dw)													
	Al	As	Cd	Cr	Co	Cu	Fe	Pb	Mn	Ni	Sr	V	Zn	Ti
VEG1	6387	2663	446	2584	247	1075	27572	2816	10656	1115	22486	1439	6637	1429
VEG2	554605	2281	606	5548	856	9938	968073	3671	43725	3628	98088	4319	15536	52326
VEG3	40463	1634	662	1028	446	4065	95004	2522	42559	3173	8659	2843	9789	6220
VEG4	224842	2035	483	2077	382	9758	332540	2967	30126	1898	43177	2065	12499	30518
VEG5	74819	2738	482	1504	614	6749	110484	3106	51417	2945	36920	3959	13472	5457
VEG6	43763	391	490	1010	202	7464	77115	1540	22459	1012	82737	1015	9800	11104
VEG7	69370	732	543	1452	443	2765	112177	1926	24748	1581	81761	1307	10545	7400
VEG8	258124	2996	824	1860	697	4847	388430	3405	29655	2396	144287	4582	18630	21580
VEG9	26120	<LOD	626	1825	370	7413	279846	1158	24163	33227	26234	<LOD	24200	1664
VEG10	58238	1282	955	1839	584	21506	64322	2886	10043	1505	4114	3109	18718	5892
VEG11	39800	369	495	1884	386	5673	68944	1976	12317	1832	6136	1956	8735	5097
VEG12	6503	581	421	1901	209	7753	31463	2362	7473	1082	24880	1151	9425	1124
VEG13	18543	1242	678	2092	469	5083	42411	2285	16259	3415	56507	1357	34344	1226
VEG14	608	<LOD	407	3752	<LOD	4976	17269	1593	2259	825	9310	<LOD	516	68
VEG15	796	<LOD	438	198	<LOD	6671	8731	1633	2422	<LOD	8103	<LOD	1023	332
VEG16	4997	<LOD	491	696	276	3386	28155	1634	7635	724	19372	<LOD	6120	577
VEG17	11452	<LOD	479	797	138	6224	34737	2446	7868	1609	5576	860	7300	1193
VEG18	11736	<LOD	1289	800	195	3502	29108	1724	3942	2341	30753	1208	3884	2320
VEG19	11952	<LOD	537	921	218	4347	142255	1567	6306	14501	2812	1107	5442	1431
VEG20	109491	564	478	1814	323	3372	178573	2278	5650	2111	2730	1609	4062	14059
VEG21	53247	1855	410	606	170	2310	75075	2294	8726	1236	30019	1058	7140	5834
VEG22	5557	<LOD	399	803	<LOD	<LOD	38203	1624	3454	1891	17821	<LOD	406	3003
VEG23	91457	<LOD	578	1762	510	5561	111111	1707	30670	1457	46361	2478	21699	7425
VEG24	8009	629	477	1707	304	4011	15735	2354	6314	1810	62811	1365	7150	784
VEG25	44956	<LOD	555	1239	505	7045	71288	2875	47912	1730	18984	3403	7088	2535
VEG26	932	<LOD	410	254	<LOD	<LOD	6278	1635	843	<LOD	28007	<LOD	629	168
VEG27	2801	<LOD	479	381	143	3644	7330	1604	4211	452	24568	608	3099	82
VEG28	616664	1965	573	3471	811	1993	933524	2915	30197	4327	101624	3439	8969	65115
VEG29	190997	2739	621	1999	561	2863	544499	3172	25855	12334	44385	2289	10492	7647
VEG30	569	<LOD	404	718	<LOD	<LOD	3995	1686	1090	<LOD	29887	<LOD	268	<LOD
VEG31	230710	<LOD	577	3208	557	3165	296196	1893	11994	4609	6422	3494	8883	18727
VEG32	696	<LOD	388	489	<LOD	<LOD	13251	1583	1787	<LOD	4460	<LOD	939	1304
VEG33	1307	<LOD	284	2917	<LOD	<LOD	45316	<LOD	2116	<LOD	17702	<LOD	542	773
VEG34	14554	1413	432	758	346	4411	579320	2161	15419	44230	33796	1234	8336	1992
VEG35	9132	230	436	818	225	957	56524	1517	9753	4458	31002	745	7585	4100
VEG36	2603	1555	433	591	273	1067	22829	2238	12938	928	7698	914	8100	813
avg	79078	1495	536	1592	395	5277	162713	2193	15971	5174	33894	2034	8944	8323
median	16549	1484	482	1478	370	4411	66633	2161	10350	1891	25557	1439	7842	2535
std error	23834	149	30	188	33	636	40370	106	2389	1594	5440	198	1236	2393
min	569	<LOD	284	198	<LOD	<LOD	3995	<LOD	843	<LOD	2730	<LOD	268	<LOD
max	616664	2996	1289	5548	856	21506	968073	3671	51417	44230	144287	4582	34344	65115

order of average concentrations of Fe in vegetable groups is as follows: Group I > Group III > Group IV > Group II, but there is no statistically significant difference in terms of Fe concentrations in the four vegetable groups (Table 4).

Aluminum (Al) is widely found in the environment, and aluminum in foods can reach the human brain after being digested. Short-term exposure to high levels of Al can bring about clear signs of neurological damage. Epidemiological and experimental findings reveal that exposure to Al leads to higher levels of inflammatory activity in the brain and may contribute to the inception and progression of Alzheimer's disease.[59] Al concentrations in the vegetable samples varied from 569 (white radish cocoated VEG30) to 616664 (green onion cocoated VEG28) $\mu g\ kg^{-1}$ with an average value of 77078 $\mu g\ kg^{-1}$. The order of average concentrations of Al in vegetable

groups is as follows: Group I > Group III > Group II > Group IV.

According to the statistical analysis in Table 4, the Al concentrations in Groups I and III were similar, which is also true for Groups II and IV. The statistical analysis also showed that the aluminum concentrations in Group I/Group III are statistically different from those in Group II/Group IV.

Strontium (Sr) is toxic at certain levels and can cause nervous disorders due to the body's low Sr threshold.[60] At different stages of the life cycle, organisms differ in their ability to discriminate between Sr and Ca, which may result in age-related differences in gastrointestinal absorption, which may affect health, the immune system, and chromosomal abnormalities.[60] Sr concentrations in the vegetable samples varied from 2730 (potato cocoated VEG20) to 144287 (rocket

Table 4. Summary of Statistical Analyses for the Logarithmic Transformed Data of Potentially Toxic Elements

PTE	Shapiro–Wilk test p-value	Bartlett test p-value	ANOVA/Kruskal–Wallis test p-value	group differences (Tukey/Wilcoxon) p-value[a]
Al	0.3157	0.2163	0.0059	GI vs GIII: S (0.4845)
				GII vs GIV: S (0.8796)
				GI vs GII: D (0.0236)
				GI vs GIV: D (0.0122)
As	0.0711	0.8427	0.2750	-
Cd	0.0039	0.1129	0.9654	-
Cr	0.4923	0.4090	0.2540	-
Co	0.6442	0.5087	0.1030	-
Cu	0.2291	0.0206	0.0289	GI vs GII: S (0.9608)
				GI vs GIII: S (0.2591)
				GI vs GIV: D (0.0149)
				GII vs GIV: D (0.0361)
Fe	0.8053	0.1029	0.1300	-
Pb	0.0971	0.2255	0.1570	-
Mn	0.2235	0.0541	0.0075	GI vs GII: D (0.0136)
				GI vs GIII: D (0.0338)
				GI vs GIV: D (0.0414)
Ni	0.0049	0.4337	0.7320	-
Sr	0.2759	0.9426	0.1200	-
V	0.2191	0.2340	0.0265	GI vs GIII: S (0.7605)
				GI vs GII: D (0.0866)[b]
				GI vs GIV: D (0.0502)[b]
Zn	0.0003	0.0064	0.0078	-
Ti	0.7693	0.1008	0.0167	GI vs GII: D (0.0127)

[a]GI: Group I; GII: Group II; GIII: Group III; GIV: Group IV; S: similar; D: different, "-": All groups are similar. [b]The difference can be accepted as borderline significant.

cocoated VEG8) μg kg^{-1} with an average value of 33894 μg kg^{-1}.

The order of average concentrations of Sr in vegetable groups is as follows: Group I > Group III > Group IV > Group II, but there is no statistically significant difference in terms of Sr concentrations in the four vegetable groups (Table 4).

Manganese (Mn) is an essential nutrient for many indispensable biochemical processes in the human body and an important cofactor for many enzymatic processes.[61] Adverse health effects may occur due to inadequate intake or overexposure. Mn toxicity can lead to serious pathologies in the central nervous system, and the typical symptom of overexposure to Mn is Parkinsonism.[61] Mn concentrations in the vegetable samples varied from 843 (turnip codded VEG26) to 51417 (parsley codded VEG5) μg kg^{-1} with an average value of 15971 μg kg^{-1}. The order of average concentrations of Mn in vegetable groups is as follows: Group I > Group III > Group IV > Group II. According to the statistical analysis in Table 4, the Mn concentration in Group I is statistically different from those in the other three groups.

Zinc (Zn) is an essential element of great importance for human health and has the capacity to bind to more than 300 enzymes and more than 2000 transcriptional factors.[62] The deficiency of Zn can lead to increased prostate swelling and cancer. However, overdoses of Zn can cause gastrointestinal disorders.[63] Zn concentrations in the vegetable samples varied from 268 (white radish cocoated VEG30) to 34344 (okra cocoated VEG13) μg kg^{-1} with an average value of 8944 μg kg^{-1}. The order of average concentrations of Zn in vegetable groups is as follows: Group I > Group II > Group III > Group IV, but there is no statistically significant difference in terms of Zn concentrations in the four vegetable groups (Table 4).

Titanium (Ti) has no known biological role. However, Ti or its corrosive byproducts may cause harmful reactions in humans.[64] Ti concentrations in the vegetable samples varied from < LOD (white radish codded VEG35) to 65115 (green onion VEG28) μg kg^{-1} with an average value of 8323 μg kg^{-1}. The order of average concentrations of Ti in vegetable groups is as follows: Group I > Group III > Group IV > Group II. According to the statistical analysis in Table 4, the Ti concentration in Group I is statistically different from that in Group II. On the other hand, the other two groups, namely, Groups III and IV, are similar.

Copper (Cu) is an essential element for humans and plays a role in many physiological processes such as infant development and growth, fetal brain development, bone strength, cholesterol metabolism, and immune function. However, Cu can pose risks to human health with elevated exposure and negatively affects the functions of important organs such as the brain, kidneys and liver.[65] Cu concentrations in the vegetable samples varied from <LOD to 21506 (mushroom codded VEG10) μg kg^{-1} with an average value of 5277 μg kg^{-1}. Cu was observed below the detection limit in celeriac (VEG22), turnip (VEG26), white radish (VEG30), Borlotti bean (VEG32), and bean (VEG33). The order of average concentrations of Cu in vegetable groups is as follows: Group I > Group II > Group III > Group IV. According to the statistical analysis in Table 4, the Cu concentration in Group IV is statistically different from those in Groups I and II.

Nickel (Ni) is an essential mineral that can prevent anemia, regulate prolactin, and stabilize DNA and RNA structures. However, Ni is a toxic element that can affect many organs. Excessive Ni intake may trigger cancer, allergic reactions and respiratory problems.[63] IARC (International Agency for Research on Cancer) has classified soluble and insoluble Ni compounds as Group 1 (carcinogenic to humans) and Ni and its alloys as Group 2B (possibly carcinogenic to humans).[66] Ni concentrations in the vegetable samples varied from <LOD to 44230 (green bean codded VEG34) μg kg^{-1} with an average value of 5174 μg kg^{-1}. Ni was observed below the detection limit in tomato (VEG15), turnip (VEG26), white radish (VEG30), Borlotti bean (VEG32), and bean (VEG33). The order of average concentrations of Ni in vegetable groups is as follows: Group IV > Group I > Group II > Group III, but there is no statistically significant difference in terms of Ni concentrations in the four vegetable groups (Table 4).

Lead (Pb) is a nonessential and highly toxic element that occurs naturally in the environment. IARC has classified Pb as probable human carcinogens (group 2B) and its inorganic compounds as probable human carcinogens (Group 2A).[67] Bioaccumulation of Pb in the human body can cause detrimental effects on the hematological and cardiovascular systems.[67] Pb concentrations in the vegetable samples varied
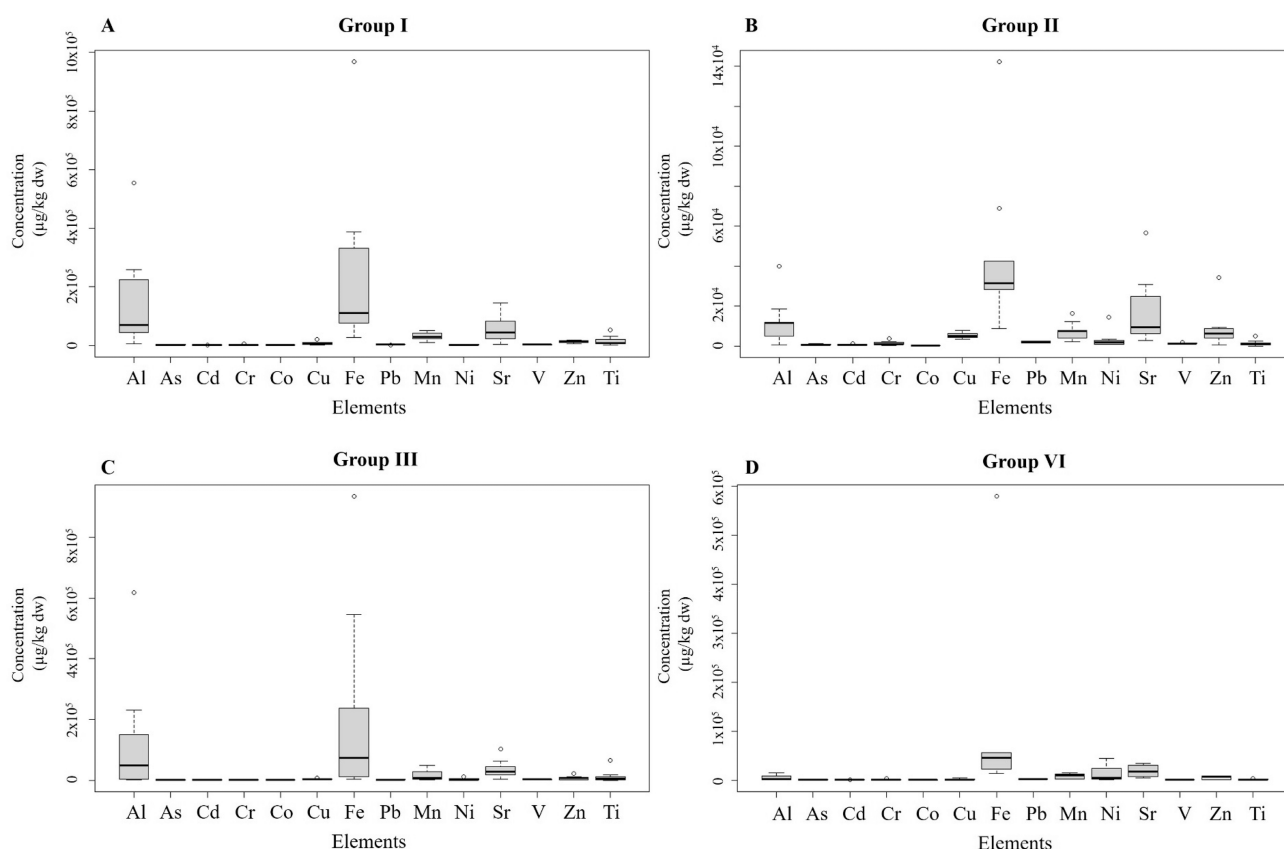
Figure 2. Element contents of groups (A) Group I, (B) Group II, (C) Group III, and (D) Group IV.

from <LOD to 3671 (purslane codded VEG2) μg kg^{-1} with an average value of 2193 μg kg^{-1}. Pb was observed below the detection limit in bean. The order of average concentrations of Pb in vegetable groups is as follows: Group I > Group III > Group II > Group IV, but there is no statistically significant difference in terms of Pb concentrations in four vegetable groups (Table 4). World Health Organization (WHO; WHO 1995), European Commission legislation (EC 2006), and Turkish Food Codex (OG, 2008) have determined the maximum level (ML) values of Pb as 300 μg kg^{-1} for cabbage and similar vegetables, leafy vegetables, and cultivated mushrooms and 100 μg kg^{-1} for other vegetables.[68−70] The Pb concentrations analyzed in all vegetable samples are greater than the ML values.

Vanadium (V) and its alloys do not pose any health or safety hazards, and even it has beneficial effects on humans.[71] V deficiencies can cause various pathologies. However, an excessive concentration of V can lead to irreversible damage to various tissues and organs.[71] V concentrations in the vegetable samples varied from <LOD to 4582 (rocket codded VEG8) μg kg^{-1} with an average value of 2034 μg kg^{-1}. V was observed below the detection limit in lettuce (VEG9), bell pepper (VEG14), tomato (VEG15), cucumber (VEG16), celeriac (VEG22), turnip (VEG26), white radish (VEG30), Borlotti bean (VEG32), and bean (VEG33). The order of average concentrations of V in vegetable groups is as follows: Group I > Group III > Group II > Group IV. According to the statistical analysis in Table 4, the V concentrations in Groups I and III are similar, where the V concentration difference between Group I and Groups II and IV can be accepted as borderline significant.

Chromium (Cr) is both an essential and a toxic element. Cr ions occur in two forms: Cr(III) (essential) and Cr(VI) (potentially toxic). Cr(III) is a biologically necessary element due to its role in carbohydrate and sugar metabolism and protein. It helps convert glucose into energy, supporting blood pressure levels and healthy blood glucose.[63] However, IARC has classified Cr(VI) as a known human carcinogen based on sufficient evidence that Cr(VI) compounds cause lung cancer.[72] Cr concentrations in the vegetable samples varied from 198 (tomato codded VEG15) to 5548 (purslane codded VEG2) μg kg^{-1} with an average value of 1592 μg kg^{-1}. According to WHO guidelines (WHO, 2003), food products (especially vegetables, fruits, meat and fish) include Cr in concentrations ranging from <10 to 1300 μg kg^{-1}.[73] The order of average concentrations of Cr in the vegetable groups is as follows: Group I > Group III > Group II > Group IV, but there is no statistically significant difference in terms of Cr concentrations in four vegetable groups (Table 4).

Arsenic (As) is a nonessential and very toxic element for humans. IARC has classified As and its compounds as Group 1 (carcinogenic to humans).[74] As concentrations in the vegetable samples varied from <LOD to 296 (rocket codded VEG8) μg kg^{-1} with an average value of 1495 μg kg^{-1}. Arsenic was observed below the detection limit in lettuce (VEG9), bell pepper (VEG14), tomato (VEG15), cucumber (VEG16), green pepper (VEG17), pumpkin (VEG18), capia pepper (VEG19), celeriac (VEG22), red beet (VEG23), sugar beet (VEG25), turnip (VEG26), dry onion (VEG27), white radish (VEG30), Jerusalem artichoke (VEG31), Borlotti bean (VEG32), and bean (VEG33). The order of average concentrations of As in vegetable groups is as follows: Group
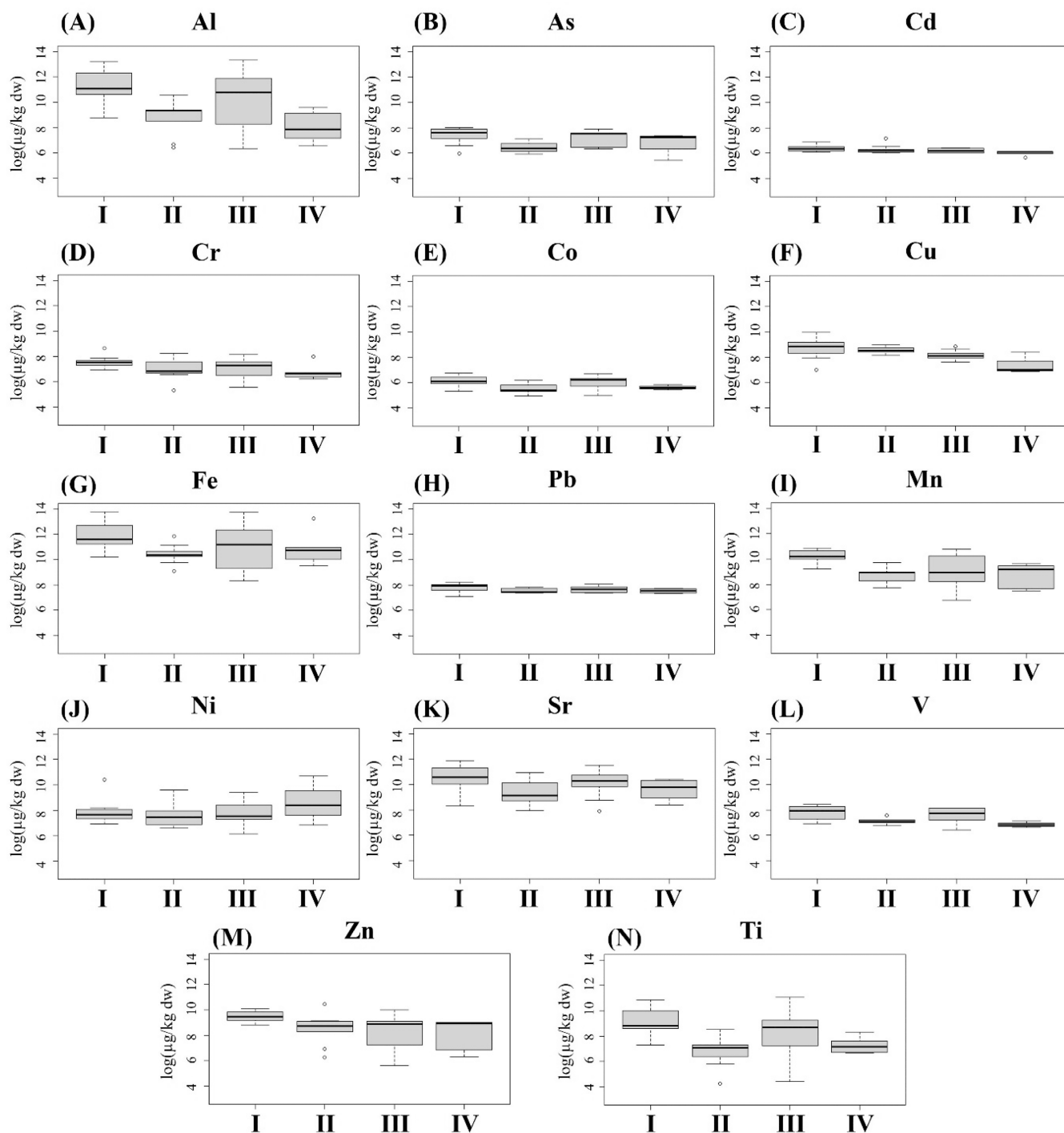
Figure 3. Comparison between element contents of groups according to logarithmic transformed data (A) Al, (B) As, (C) Cd, (D) Cr, (E) Co, (F) Cu, (G) Fe, (H) Pb, (I) Mn, (J) Ni, (K) Sr, (L) V, (M) Zn, and (N) Ti.

I > Group III > Group IV > Group II, but there is no statistically significant difference in terms of As concentrations in the four vegetable groups (Table 4).

Cadmium (Cd) is a nonessential and highly toxic element having an extremely long biological half-life. Chronic low-level exposure to Cd has been associated with a higher risk of many diseases, including cancer, bone damage, cardiovascular disease, diabetes, renal tubular disease, and obstructive pulmonary disease.[75] Cd concentrations in the vegetable samples varied from 284 (bean codded VEG33) to 1289 (pumpkin codded VEG18) μg kg^{-1} with an average value of

536 μg kg^{-1}. World Health Organization (WHO; WHO 1995), European Commission legislation (EC 2006), and Turkish Food Codex (OG, 2008) have determined the ML values of Cd as 200 μg kg^{-1} for leaf vegetables, fresh herbs, cultivated fungi, and celeriac, 100 μg kg^{-1} stem vegetables, root vegetables, and potatoes, and 50 μg kg^{-1} for other vegetables.[68−70] The Cd concentrations analyzed in all vegetable samples are greater than the ML values. The order of the average concentrations of Cd in vegetable groups is as follows: Group I > Group II > Group III > Group IV, but there
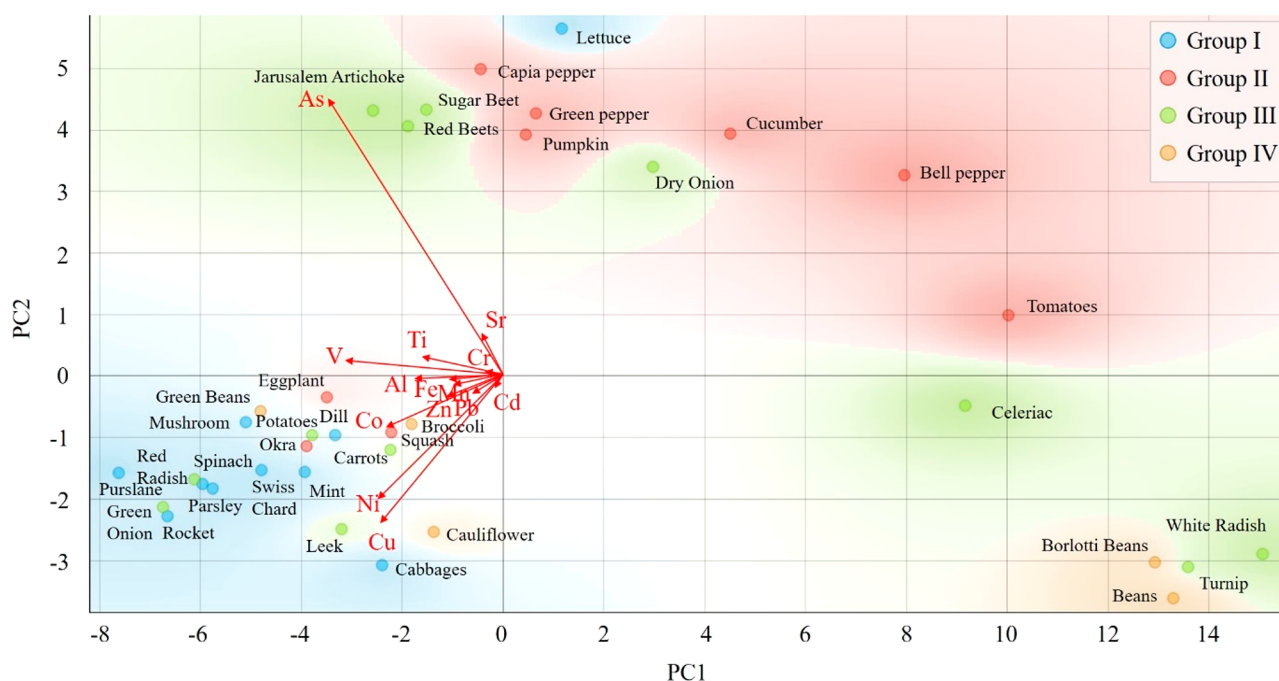
Figure 4. Biplot resulting from PCA analysis.

is no statistically significant difference in terms of Cd concentrations in four vegetable groups (Table 4).

Cobalt (Co) is an essential metal component of vitamin B12 and is also a toxic element. Excessive Co exposure causes a complex clinical syndrome that includes a variety of cardiovascular, neurological, and endocrine deficits.[76] Co concentrations in the vegetable samples varied from <LOD to 856 (purslane coded VEG2) μg kg^{-1} with an average value of 395 μg kg^{-1}. Co was observed below the detection limit in bell pepper (VEG14), tomato (VEG15), celeriac (VEG22), turnip (VEG26), white radish (VEG30), Borlotti bean (VEG32) and bean (VEG33). The order of average concentrations of Co in vegetable groups is as follows: Group I > Group III > Group IV > Group II, but there is no statistically significant difference in terms of Co concentrations in the four vegetable groups (Table 4).

The results of PCA are presented in Figure 4. The PCA was employed to explore the intricate relationships among the analyzed PTEs within the diverse spectrum of vegetables under investigation. In this analysis, a total of five principal components were derived. Remarkably, the initial two principal components, PC1 and PC2, elucidated a significant proportion of the data set's overall variance.

Figure 4, a biplot, was generated to visually depict the relationships between the original PTE variables and the principal components. In the biplot, the directional vectors of variable loading arrows indicate the magnitude and direction of the influence of each PTE on the principal components. The length of these arrows signifies the strength of the association.

From this biplot, distinct patterns can be discerned among the vegetable groups (Groups I, II, III, and IV) in terms of PTE concentrations. Notably, Group I, excluding lettuce, exhibited a notable concentration of PTEs, as evidenced by the direction of the variable loading arrows. Conversely, Group II, with the exception of eggplant, okra, and squash, positioned itself on the opposing sides of the variable loading arrows, signifying comparatively lower PTE concentrations.

However, discerning clear patterns regarding PTE concentrations for Groups III and IV from the biplot proved challenging. The distribution and orientation of the variables in relation to the principal components did not yield readily interpretable patterns for these groups. But some vegetables in Group III that are directly in contact with soil, such as potatoes, leek, carrots, green onion, and red radish, presented high PTE concentrations.

This intricate interplay of PTEs within different vegetable groups underscores the importance of considering multiple principal components to gain insights into the underlying structure of the data. Further investigations and targeted analyses may be necessary to elucidate the factors contributing to the observed variations in the PTE concentrations among these vegetable groups.

In addition, a comprehensive correlation analysis was conducted to investigate potential relationships among the concentrations of PTEs within four distinct vegetable groups. The results of this analysis are given in Figure 5, which illustrates a correlogram reflecting the element contents of these vegetable groups. This examination revealed noteworthy findings within each plant group, where several pairs of elements exhibited statistically significant correlations at the $p < 0.05$ level.

In Group I, positive correlations were observed among the following element pairs: Al−Co ($p = 0.0205$), Al−Fe ($p = 0.0019$), Al−Ti ($p = 8.1122 \times 10^{-5}$), As−V ($p = 0.0278$), Cd−Zn ($p = 0.0420$), Co−V ($p = 0.0009$), Cu−Zn ($p = 0.0258$), Fe−Ti ($p = 0.0216$), Ni−Zn ($p = 0.0341$), Pb−V ($p = 0.0034$), and Ti−Zn ($p = 0.0225$). These positive correlations suggest that as the concentration of one element increases, the concentration of the other element tends to increase as well.

Conversely, within Group I, there was a negative correlation observed between Ni and V ($p = 0.0059$), indicating that as the concentration of one element increased, the concentration of the other decreased. These correlations provide valuable
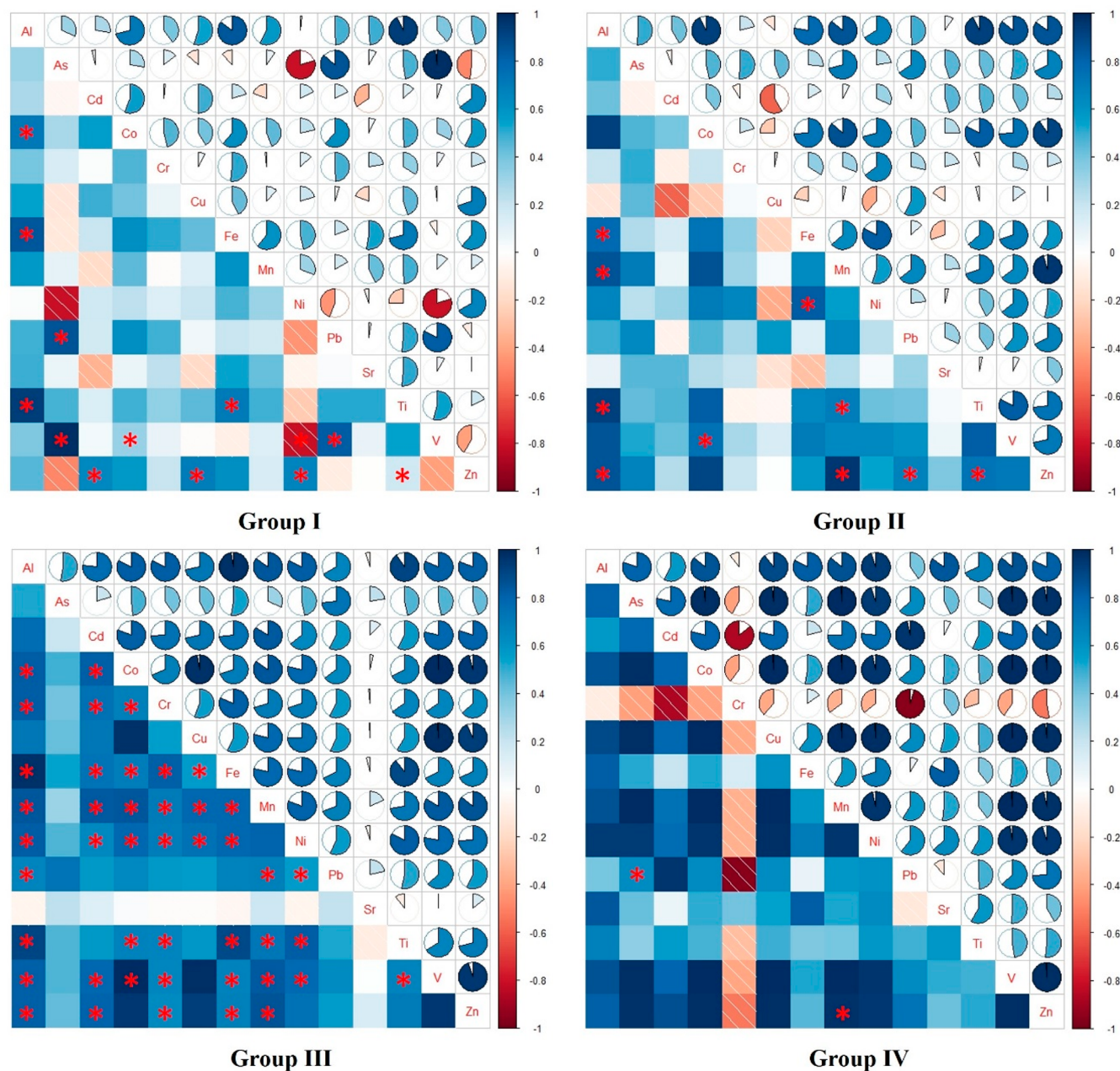
Figure 5. Correlogram plots on PTE content in all four groups. * denotes a statistically significant correlation ($p < 0.05$)

insights into the potential interactions and dependencies between PTEs within Group I.

In Group II, the correlation analysis unveiled a distinct pattern characterized by positive correlations between several pairs of elements, all of which exhibited statistical significance at the $p < 0.05$ level. These notable positive correlations included Al−Fe ($p = 0.0140$), Al−Mn ($p = 0.0032$), Al−Ti ($p = 0.0003$), Al−Zn ($p = 0.0035$), Co−V ($p = 0.0477$), Fe−Ni ($p = 0.0066$), Mn−Ti ($p = 0.0381$), Mn−Zn ($p = 7.3099 \times 10^{-5}$), Pb−Zn ($p = 0.0472$), and Ti−Zn ($p = 0.0253$).

Group II did not exhibit any negative correlations among its elements compared with Group I. This distinct pattern suggests a consistent and concurrent increase in the concentrations of these elements within the vegetable samples of Group II.

While Group I displayed positive and negative correlations, Group II demonstrated a more homogeneous relationship characterized solely by positive correlations. These findings underscore the variability in element interactions between different vegetable groups, emphasizing the unique compositional characteristics of each group.

In Group III, the correlation analysis revealed a distinct pattern reminiscent of Group II, characterized by exclusively positive correlations among various pairs of elements. These correlations exhibited statistical significance at the $p < 0.05$ level and included Al−Co ($p = 0.0108$), Al−Cr ($p = 0.0010$), Al−Fe ($p = 9.8732 \times 10^{-8}$), Al−Mn ($p = 0.0005$), Al−Ni ($p = 0.0196$), Al−Pb ($p = 0.0175$), Al−Ti ($p = 3.9372 \times 10^{-5}$), Al−V ($p = 0.0106$), Al−Zn ($p = 0.0013$), Cd−Co ($p = 0.0032$), Cd−Cr ($p = 0.0052$), Cd−Fe ($p = 0.0068$), Cd−Mn ($p = 0.0006$), Cd−V ($p = 0.0179$), Cd−Zn ($p = 0.0017$), Co−

Cr ($p = 0.0009$), Co−Fe ($p = 0.0108$), Co−Mn ($p = 0.0128$), Co−N ($p = 0.0172$), Co−Ti ($p = 0.0245$), Co−V ($p = 9.572 \times 10^{-5}$), Cr−Fr ($p = 0.0013$), Cr−Mn ($p = 0.0105$), Cr−Ni ($p = 0.0094$), Cr−Ti ($p = 0.0013$), Cr−V ($p = 0.0042$), Cr−Zn ($p = 0.0281$), Fe−Mn ($p = 0.0025$), Fe−Ni ($p = 0.0031$), Fe−Ti ($p = 0.0013$), Fe−V ($p = 0.0042$), Fe−Zn ($p = 0.0281$), Mn−Pb ($p = 0.0131$), Mn−Ti ($p = 0.0355$), Mn−V ($p = 0.0085$), Mn−Zn ($p = 0.0004$), Ni−Ti ($p = 0.0258$), Ni−V ($p = 0.0412$), and Ti−V ($p = 0.0188$).

Similar to Group II, Group III did not exhibit any negative correlations among its constituent elements. This distinctive correlation pattern underscores the coherent and parallel variations in the concentrations of these elements within Group III vegetables.

In Group IV, a notably distinct correlation pattern emerged, distinguishing it from the preceding groups. The analysis identified only two statistically significant positive correlations within this group, such as As−Pb ($p = 0.0232$) and Mn−Zn ($p = 0.0060$).

Unlike Groups I, II, and III, which exhibited multiple positive correlations, Group IV stands out for its limited associations among the potentially toxic elements. This scarcity of significant correlations suggests that elements within Group IV vegetables do not closely track one another's concentrations.

This finding underscores the divergent composition and interaction dynamics within Group IV compared with the other vegetable groups. While Groups I, II, and III predominantly displayed positive correlations, Group IV presents a unique profile marked by fewer significant associations. This insight highlights the heterogeneous nature of potentially toxic element relationships across various vegetable groups.

These findings underscore the complexity of element relationships within different vegetable groups, shedding light on the intricate interplay of PTE concentrations and offering valuable information for further exploration and understanding of the factors influencing the PTE distribution in edible vegetables.

3.2. Evaluation of Noncarcinogenic and Carcinogenic Health Risk.

The noncarcinogenic and carcinogenic health risks from ingestion of PTEs analyzed in the studied vegetable samples were evaluated using the data given in Table 2. The values of the ADI estimated for all PTEs, HQ estimated for all PTEs, except for Ti, and ELCR estimated for As, Cd, Cr, Ni, and Pb are summarized in Table 5. The variation of HI and TCR values according to vegetables is presented in Table 6. The ADI values estimated for adults varied from 1.8×10^{-8} (Ti) to 2.2×10^{-1} (Fe) mg kg^{-1} day^{-1}. The average ADI values of the PTEs are listed as Fe > Al > Mn > Sr > Cu > Zn > Ti > V > Pb > Ni > Cr > Cd > Co > As. The HQ values estimated for PTEs (except for Ti) varied from 8.9×10^{-8} (Al) to 5.2 (Co). The average HQ values of the PTEs are ranked as Co > Cd > As > Pb > Cr > V > Mn > Cu > Fe > Ni > Al > Sr > Zn. While all average values of HQ are lower than the risk limit of 1, the HQ values of Co, Cd, As, Pb, Cr, V, and Mn are above the risk limit. It can be seen from Table 6 that HI values estimated for PTEs in vegetable samples varied from 1.5×10^{-4} (VEG26) to 16.0 (VEG25). All HI values are lower than the risk or safety limit of 1, except for VEG11 (eggplant), VEG20 (potato), and VEG25 (sugar beet). HI values for eggplant, potato, and sugar beet samples were found as 1.5 (66% due to As, Cd, and Co), 3.5 (75% due to As, Cd, Co, and

Table 5. Values of indexes estimated for non-carcinogenic and carcinogenic PH risk evaluation

PTE		ADI (mg kg^{-1} day^{-1})	HQ	ELCR
As	Average	3.5×10^{-5}	1.2×10^{-1}	5.2×10^{-5}
	Range	2.5×10^{-7} - 3.3×10^{-4}	8.4×10^{-4} - 1.1	3.8×10^{-7} - 5.0×10^{-4}
Cd	Average	6.9×10^{-5}	1.4×10^{-1}	4.2×10^{-4}
	Range	4.3×10^{-8} - 1.7×10^{-3}	8.6×10^{-5}- 3.4	2.6×10^{-7} - 1.0×10^{-2}
Cr	Average	1.7×10^{-4}	5.5×10^{-2}	8.3×10^{-5}
	Range	2.7×10^{-8} - 3.8×10^{-3}	8.9×10^{-6}- 1.3	1.3×10^{-8} - 1.9×10^{-3}
Pb	Average	3.5×10^{-4}	9.9×10^{-2}	2.9×10^{-6}
	Range	1.7×10^{-7} - 8.8×10^{-3}	4.9×10^{-5}- 2.5	1.5×10^{-9} - 7.5×10^{-5}
Ni	Average	2.9×10^{-4}	1.4×10^{-2}	4.9×10^{-4}
	Range	6.5×10^{-7} - 5.3×10^{-3}	3.3×10^{-5}- 0.3	1.1×10^{-6} - 9.0×10^{-3}
Co	Average	6.7×10^{-5}	2.2×10^{-1}	
	Range	1.1×10^{-7} - 1.5×10^{-3}	3.8×10^{-4}- 5.2	
Cu	Average	9.4×10^{-4}	2.5×10^{-2}	
	Range	6.5×10^{-7} - 2.2×10^{-2}	1.8×10^{-5}- 0.6	
Zn	Average	8.2×10^{-4}	2.7×10^{-3}	
	Range	4.2×10^{-8} - 2.2×10^{-2}	1.4×10^{-7}- 7.2×10^{-2}	
Al	Average	6.2×10^{-3}	6.2×10^{-3}	
	Range	8.9×10^{-8} - 1.4×10^{-1}	5.9×10^{-3}- 0.1	
Fe	Average	1.1×10^{-2}	1.5×10^{-2}	
	Range	6.3×10^{-7} - 2.2×10^{-1}	8.9×10^{-7}- 0.3	
Mn	Average	4.4×10^{-3}	3.1×10^{-2}	
	Range	8.9×10^{-8} - 1.5×10^{-1}	6.4×10^{-7}- 1.0	
V	Average	4.6×10^{-4}	5.1×10^{-2}	
	Range	6.5×10^{-7} - 1.0×10^{-2}	7.3×10^{-5}- 1.2	
Sr	Average	2.1×10^{-3}	3.4×10^{-3}	
	Range	1.3×10^{-6} - 5.8×10^{-2}	2.2×10^{-6}- 9.7 $\times 10^{-2}$	
Ti	Average	5.4×10^{-4}	-	
	Range	1.8×10^{-8} - 8.33×10^{-3}	-	

Cr), and 16.0 (78% due to Cd, Cr, Co, and Pb), respectively. The order of the HI average concentrations estimated for the vegetable groups is as follows: Group III (1.69) > Group II (0.29) > Group I (0.07) > Group IV (0.06).

The values of ELCR estimated for As, Cd, Cr, Ni, and Pb varied from 1.5×10^{-9} (Pb) to 1.0×10^{-2} (Cd). The values for ELCR are ranked as follows: Ni > Cd > Cr > As > Pb. While all ELCR values for Pb are in the acceptable risk range (10^{-9} to 10^{-5}), approximately 85%, 78%, 92%, and 76% of the ELCR values for As, Cd, Cr, and Ni are in the safety or low priority risk range (10^{-8} to 10^{-5}), respectively. As can be seen from Table 6, the TCR values estimated for As, Cd, Cr, Ni, and Pb analyzed in vegetable samples varied from 2.8×10^{-7} (VEG26) to 2.1×10^{-2} (VEG25). TCR values estimated for approximately 42% of the vegetable samples (15 vegetable samples) were in the unacceptable risk range (CR ≥ 10^{-4}). The order of TCR average concentrations estimated for the vegetable groups is as follows: Group III (2.3×10^{-3}) > Group

Table 6. Values of the Health Index and Cancer Risk Index Estimated for Vegetables

sample code	HI	TCR
VEG1	0.40	3.1×10^{-4}
VEG2	5.3×10^{-3}	4.7×10^{-6}
VEG3	4.1×10^{-3}	4.9×10^{-6}
VEG4	0.10	8.8×10^{-5}
VEG5	0.12	1.0×10^{-4}
VEG6	3.0×10^{-3}	3.8×10^{-6}
VEG7	7.5×10^{-3}	8.6×10^{-6}
VEG8	0.03	2.7×10^{-5}
VEG9	0.02	1.7×10^{-4}
VEG10	0.05	5.3×10^{-5}
VEG11	1.53	2.2×10^{-3}
VEG12	0.06	6.7×10^{-5}
VEG13	0.01	1.4×10^{-5}
VEG14	0.04	7.5×10^{-5}
VEG15	0.60	1.0×10^{-3}
VEG16	0.08	1.3×10^{-4}
VEG17	0.10	2.2×10^{-4}
VEG18	0.01	3.1×10^{-5}
VEG19	0.19	1.4×10^{-3}
VEG20	3.51	4.9×10^{-3}
VEG21	0.13	1.1×10^{-4}
VEG22	4.3×10^{-3}	1.5×10^{-5}
VEG23	3.1×10^{-3}	4.2×10^{-6}
VEG24	0.28	3.7×10^{-4}
VEG25	16.02	2.1×10^{-2}
VEG26	1.5×10^{-4}	2.8×10^{-7}
VEG27	0.12	2.1×10^{-4}
VEG28	0.07	6.9×10^{-5}
VEG29	0.11	2.1×10^{-4}
VEG30	2.5×10^{-4}	4.4×10^{-7}
VEG31	1.3×10^{-3}	2.7×10^{-6}
VEG32	0.04	8.1×10^{-5}
VEG33	0.02	4.8×10^{-5}
VEG34	0.13	9.2×10^{-4}
VEG35	0.02	6.6×10^{-5}
VEG36	0.07	6.1×10^{-5}
avg	0.7	9.5×10^{-4}
min	1.5×10^{-4}	2.8×10^{-7}
max	16.0	2.1×10^{-2}

II (5.7×10^{-4}) > Group IV (2.4×10^{-4}) > Group I (7.8×10^{-5}).

4. CONCLUSIONS

The analysis results revealed that the concentrations of PTEs in thirty-six different vegetable types belonging to four vegetable groups strongly varied. The average concentration of PTEs analyzed in all vegetable samples are ranked as Fe > Al > Sr > Mn > Zn > Ti > Cu > Ni > Pb > V > Cr > As > Cd > Co. As a result, Group I (leafy or edible stem vegetables) contains higher levels of PTEs compared to other vegetable groups. The Pb and Cd concentrations analyzed in all vegetable samples are above the maximum levels set by the Turkish Food Codex, FAO/WHO, and the European Commission.

All HI values estimated for noncarcinogenic health risk evaluation are lesser than the safety limit of 1, except for eggplant, potato, and sugar beet. Since dangerous PTEs such as As, Pb, Cd, Cr, and Co were detected in high amounts in eggplant, potato, and sugar beet samples, HI values were greater than unity, exhibiting noncarcinogenic health effects. According to the average HI values, vegetable groups are ranked as Group III > Group II > Group I > Group IV.

Carcinogenic risk index TCR values estimated for As, Cd, Cr, Ni, and Pb analyzed in 15 vegetable (cabbage, parsley, lettuce, eggplant, tomato, cucumber, green pepper, capia pepper, potato, leek, carrots, sugar beet, dry onion, red radish, and green bean) samples were higher than an unacceptable risk value of 10^{-4}, which is considered unsafe for regular human consumption. According to the average TCR values, vegetable groups are ranked as Group III > Group II > Group IV > Group I.

As is known, long-term consumption of PTEs can cause various health hazards in humans. Therefore, regular monitoring of PTEs in vegetables (especially leafy vegetables) is vital to prevent the accumulation of such PTEs in the human food chain. This study recommends considering not only whether PTE levels in vegetables exceed maximum levels, but also the human health risks caused by the consumption rates of substances in these vegetable samples. In conclusion, the data obtained from this study will raise awareness among consumers and contribute to paying due attention to the safety of vegetables grown and distributed in the region. Going forward, it is of great importance to conduct such studies on other food products.

■ ASSOCIATED CONTENT

Data Availability Statement

All data generated or analyzed during this study are included in this published Article. Data sets are available from the corresponding author on reasonable request.

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Author Contributions

B.Ş. collected vegetable samples and prepared the sample for PTE analysis. Ş.T., A.K., and A.A. ensured the successful completion of the analysis measurements. E.M.A. completed the statistical analysis. Ş.T. wrote the manuscript, and all the authors approved the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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