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Original Research

Assessment of Heavy Metal Accumulations (Cd, Cr, Cu, Ni, Pb, and Zn) in Vegetables and Soils

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Abstract

This study measured levels of cadmium, chromium, copper, nickel, lead, and zinc in fruits of *Capsicum annuum* L., *Phaseolus vulgaris* L., and *Solanum melongena* L. during the 2007 vegetation period, to determine levels of metal pollution in Istanbul Province. Plant and soil samples were collected from six sites in Istanbul (Brook Coast area, inner city, industrial area, suburban, roadside, and rural – control – areas). Unwashed and washed leaf and soil samples were analyzed using inductively coupled plasma optical emission spectrometry. The highest and lowest values were as follows: Cd (0.28-0.89 $\mu g \cdot g^{-1}$), Cr (5.33-14.04 $\mu g \cdot g^{-1}$), Cu (1.47-5.19 $\mu g \cdot g^{-1}$), Ni (3.06-13.65 $\mu g \cdot g^{-1}$), Pb (29.28-86.20 $\mu g \cdot g^{-1}$), and Zn (3.70-5.74 $\mu g \cdot g^{-1}$). The unwashed samples were more contaminated than the washed samples. Contamination was higher in the vegetables grown in industrial areas and along roadsides. The overall metal concentration pattern in vegetables was Pb > Cr > Ni > Zn > Cu > Cd.

Keywords: heavy metal, ICP-OES, soil, vegetables

Introduction

Heavy metals are extremely persistent in the environment. They are non-biodegradable and non-thermo degradable and therefore readily accumulate to toxic levels [1]. Heavy metals can accumulate in the soil at toxic levels due to the long-term application of wastewater. The contamination of vegetables with metals due to soil and atmospheric contamination poses a threat to their quality and safety [2].

Dietary intake of metals also poses risks to animals and human health. Metals such as Cd and Pb have been shown to have carcinogenic effects. A high concentration of metals (Cu, Cd, and Pb) in vegetables is related to a high prevalence of upper gastrointestinal cancer [3]. For most people, the main route of exposure to metals is through diet, except for occupational exposure. Many countries have regulated a range of industrial sectors in order to control the emission of metals. Uptake and bioaccumulation of metals in vegetables are influenced by a number of factors such as climate, atmospheric depositions, concentrations of metals in soil, the nature of the soil in which the vegetables are grown, and the degree of maturity of the plants at the time of harvest [4].

Air pollution has the potential threat to post-harvest vegetables during transportation and marketing, causing elevated levels of metals in vegetables [5, 6]. Elevated levels of heavy metals in vegetables are reported from areas with long-term use of treated or untreated wastewater [6, 7]. Other anthropogenic sources of metals include the addition of manures, fertilizers, sewage sludge, and pesticides that uptake metals by modifying the physico-chemical proper-

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ties of the soil such as pH, organic matter, and bioavailability of metals in the soil [6, 8, 9]. Also, cultivation areas near highways are exposed to atmospheric pollution in the form of metal-containing aerosols [6, 10]. These aerosols can be accumulated on soil and vegetables, or alternatively accumulated on leaves and fruits and then absorbed by vegetables. Because of atmospheric deposition high accumulations of Pb, Cr, and Cd can occur in leafy vegetables [4, 6, 10]. Field studies have found positive relationships between atmospheric metal deposition and elevated concentrations of metals in plants and topsoil. Unwashed leafy vegetables sold on roadsides in Riyadh, Saudi Arabia, had higher levels of metals than their washed ones [6, 11].

Materials and Methods

Istanbul is located in northwestern Turkey (41º01.2' N, 28º58.2' E) and is one of the largest metropolitan areas in the world. Istanbul covers an area of approximately 5,100 km^2 and has the largest and fastest growing population (12.9 million inhabitants) in Turkey [12, 13]. Istanbul expands toward both Europe and Asia through the Bosphorus and has coasts on the Marmara and Black seas. Summer is generally hot and humid, with an average temperature of 28ºC between July and August. Winter is cold, wet, and often snowy, averaging 5ºC. Similar to other fast-developed cities, the air, water and soil quality are affected by the increase of activities such as construction, traffic, and industrial production [14].

Samples of vegetables were collected from parts of Istanbul representing six different station types: brook coast, suburban area, industrial area, inner city, roadside, and rural area (Fig. 1).

In total, 18 different samples of 3 different vegetables were studied, including pepper (*C. annuum* L.), bean (*P. vulgaris* L.), and eggplant (*S. melongena* L.) (Table 1).

Samples were taken by hand using vinyl gloves and carefully packed into polyethylene bags [15]. Only the edible parts of each vegetable were analyzed. In addition, soil samples were collected from the sampling sites. Samples were divided into two sub-samples: one sub-group was thoroughly washed several times with tap water (followed by distilled water) to remove dust particles in a standardized procedure, while the rest of the vegetables were untreated and then oven dried at 80ºC for 24 h. At each site, soils were sampled from the top 10 cm by means of a stainless steel trowel to avoid contamination. To ensure consistent distribution of metals in the soil samples, all materials were ground in a micro-hammer cutter and filtered via a 1.5-mm sieve [16].

Table 1. The names of vegetables in English, Turkish, and their Latin names.

English name	Local name (Turkish)	Latin name
Pepper	Biber	*Capsicum annuum* L.
Bean	Fasulye	*Phaseolus vulgaris* L.
Eggplant	Patlıcan	*Solanum melongena* L.

Dried and milled samples were powdered and kept in clean polyethylene bottles. In addition, the soil samples were collected with a stainless steel crab. These samples were dehydrated in open air and passed through a 2-mm sieve. After homogenization, soil samples were stored in clear paper bags prior to analysis [16].

Samples (0.5 g dry weight) were digested with 10 ml pure HNO_3 (65%) using a CEM MARS 5 (CEM Corporation Mathews, NC, USA) microwave digestion system. The digestion conditions were as follows: maximum power was 1200 W, the power was at 100%, the ramp was set for 20 min, the pressure was 180 psi, the temperature was 210ºC, and the hold time was 10 min. After digestion, solutions were evaporated to near dryness in a beaker. The volume of each sample was adjusted to 10 mL using 0.1 M HNO_3. The determination of the elements in all samples was

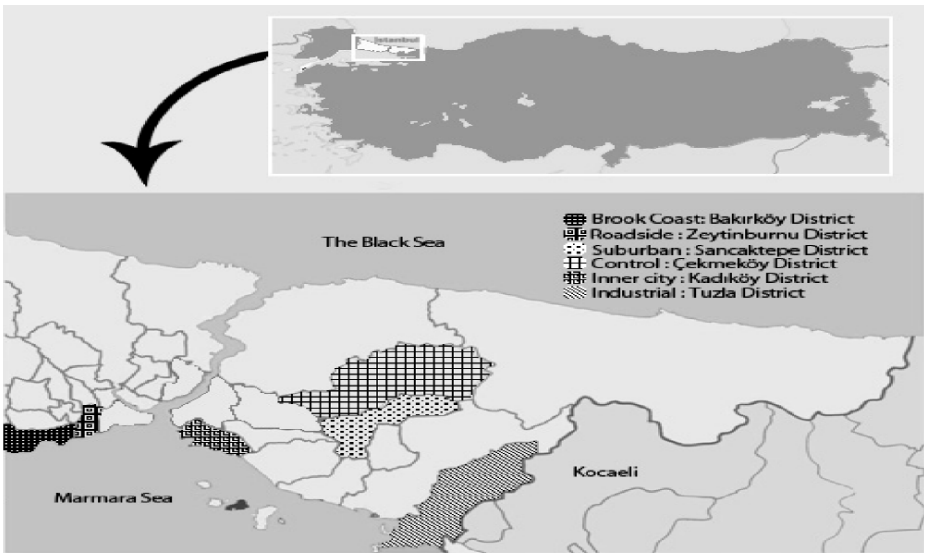

Fig. 1. Istanbul, Turkey, and the studied districts of Bakırköy, Sancaktepe, Tuzla, Kadıköy, Zeytinburnu, and Çekmeköy.

carried out using Varian Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). The stability of the device was evaluated every 10 samples by examining an internal standard. Reagent blanks also were prepared to detect any potential contamination during the digestion and analytical procedure. All chemicals used in this study were analytical reagent grade (Merck, Darmstadt, Germany). Peach leaves (NIST, SRM-1547) and CRM 039-050 were used as reference material, and all analytical procedures were performed for reference materials [1, 16]. All chemicals were analytical reagent grade. Detection limits of Cd^{2+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} are 0.3×10^{-3}, 0.3×10^{-3}, 0.5×10^{-3}, 0.8×10^{-3}, 2×10^{-3}, and 0.2×10^{-3} $\mu g\cdot ml^{-1}$, respectively.

In this study, the standard error values of the means were calculated to compare the site categories (Figs. 2 and 3). A paired *t*-test was performed to determine the significance of washing of the leaves, and comparing metal contents of washed and unwashed plant samples for each type of site and *F*-test (ANOVA) was performed to compare different localities (Figs. 2 and 3). Within this respect, it was determined that the percentage amount of metals decreased because of washing (Tables 2-4).

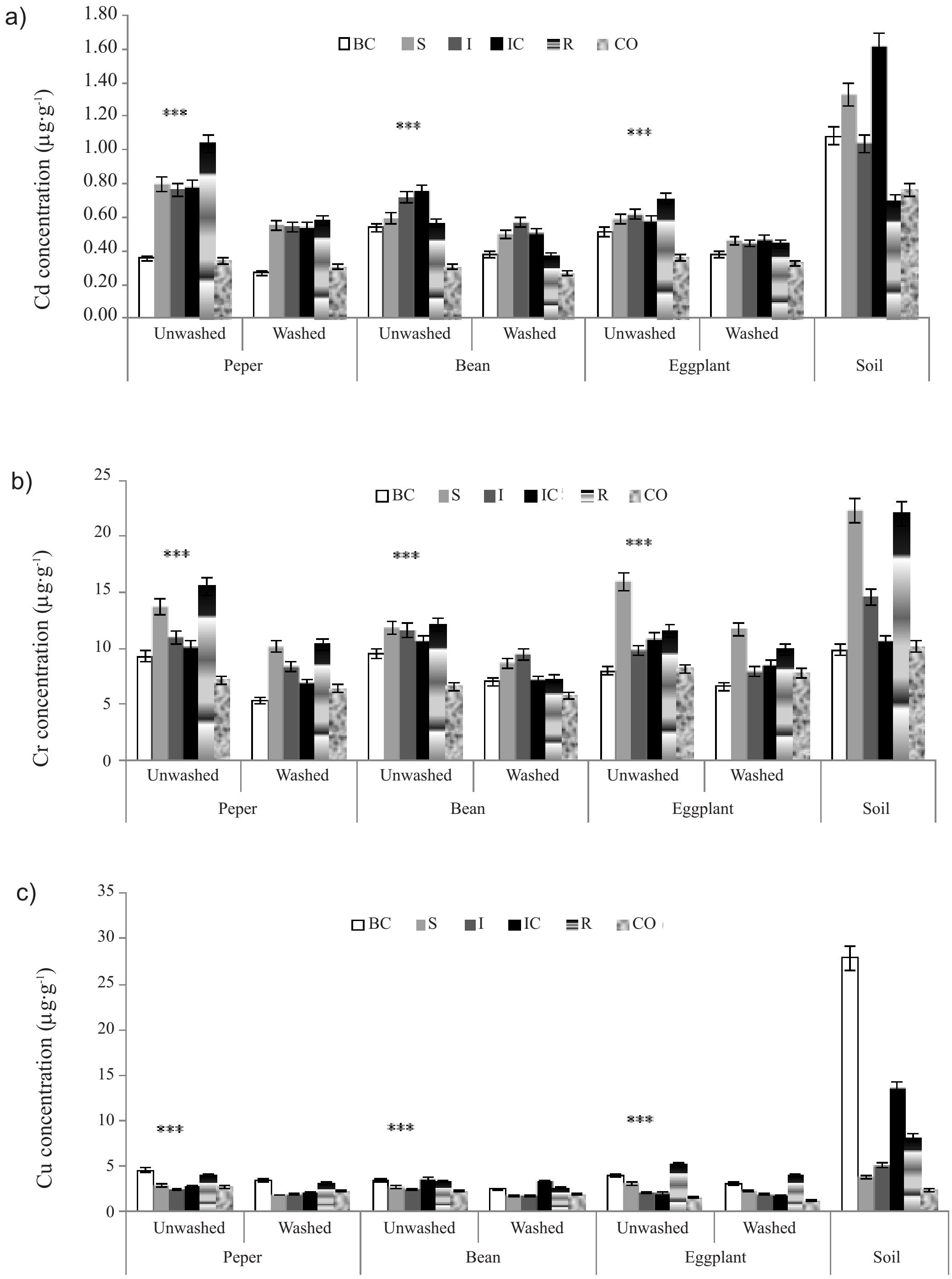

Fig. 2. Mean Cd (a), Cr (b), and Cu (c) concentrations ($\mu g\cdot g^{-1}$ dw) in washed and unwashed leaves, and soil with S.E. bars. BC – Brook Coast, S – Suburban, I – Industrial, IC – Inner City, R – Roadside, U – Urban, and CO – Rural area. Significances of differences between washed and unwashed plants, from *t*-test, are indicated above the columns (*p<0.05, **p<0.01, ***p<0.001 significant).

Results and Discussion

The mean values of Cd, Cr, Cu, Ni, Pb, and Zn concentrations found in vegetables and soil are given in Figs. 2 and 3. According to our results, the ranges of metal accumulation were between 0.70-1.61 µg/g dw for Cd, 9.84-22.30 µg/g dw for Cr, 1.5-27.85 µg/g dw for Cu, 4.03-18.60 µg/g dw for Ni, 47.12-123.97 µg/g dw for Pb, and 1.05-37.04 µg/g dw for Zn.

Our findings for Cc are parallel with those of [16-19]. There are relatively lower Cd concentrations in vegetables [20]. The washed vegetable samples had markedly lower Cd levels. The Cd removal percentage is seen higher from the samples that collected from highly polluted areas (Figs. 2 and 3).

The findings from the samples matched with the findings of the studies on the other vegetables [17, 21]. The Cr results were higher than those from our study [18].

In our study the findings from the vegetable samples agreed with the findings on the examples of fruits consumed as vegetables [17, 19, 22, 23]. In addition, the findings are higher than our study [20, 24] (Figs. 2 and 3). The findings of our study are higher than some previous studies, which show that Cu contamination was very high where our vegetable samples were collected [25, 26]. Although our Cu values are higher than some previous studies, the vegetables cultivated in Istanbul and its soil consisted of lower Cu and do not endanger human health.

The nickel findings from our study are a little bit higher than the nickel findings from studies [17, 23, 24].

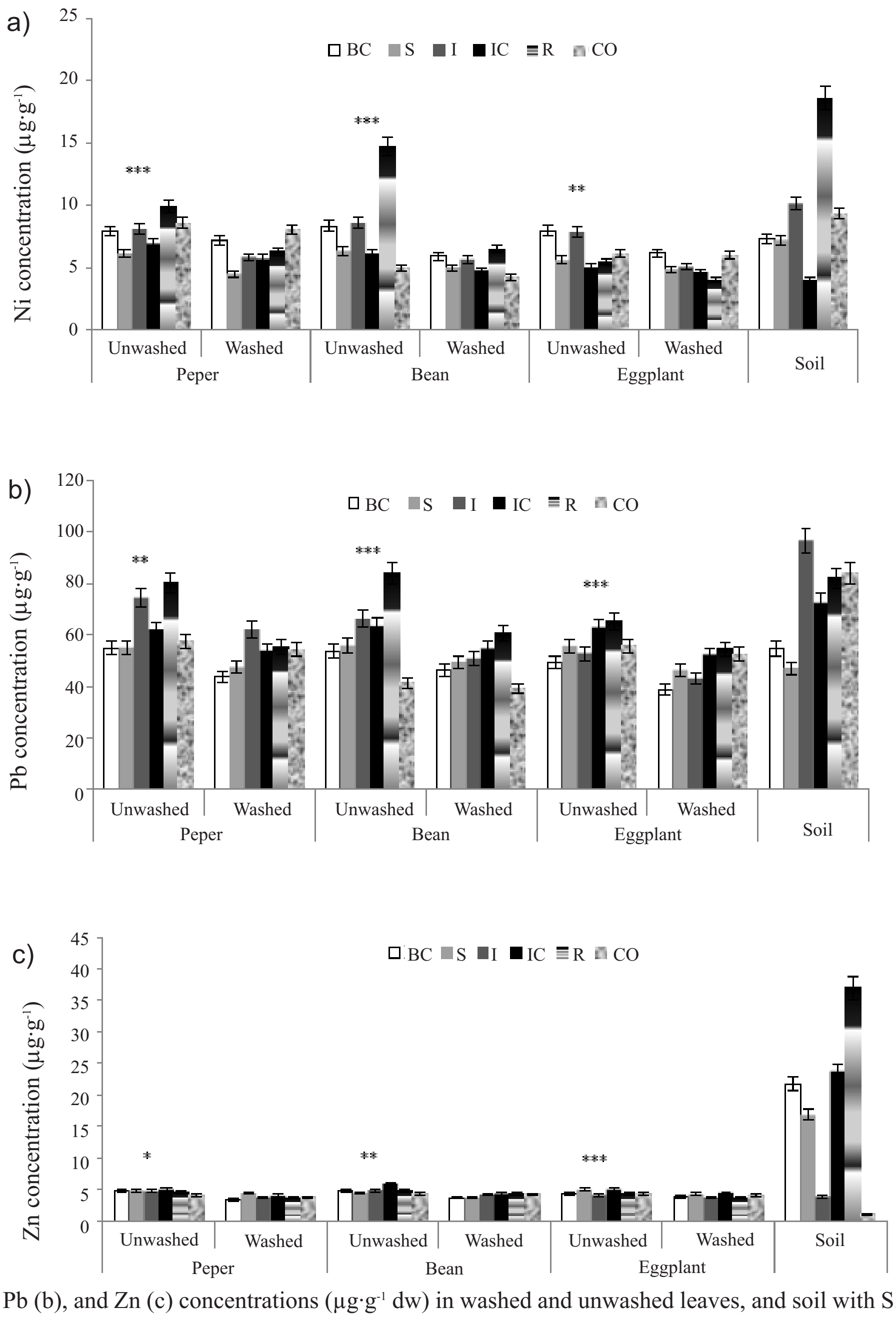

Fig. 3. Mean Ni (a), Pb (b), and Zn (c) concentrations (µg·g⁻¹ dw) in washed and unwashed leaves, and soil with S.E. bars. BC – Brook Coast, S – Suburban, I – Industrial, IC – Inner City, R – Roadside, U – Urban, and CO – Rural area. Significances of differences between washed and unwashed plants, from *t*-test, are indicated above the columns (*p<0.05, **p<0.01, ***p<0.001 significant).

Table 2. Total percentages of Cd, Cr, Cu, Ni, Pb, and Zn removed from the fruit samples of *Capsicum annum* L. through washing procedure in six different stations.

Location	Cd (%) Removal	Cr (%) Removal	Cu (%) Removal	Ni (%) Removal	Pb (%) Removal	Zn (%) Removal
Brook Coast	23.52	42.63	25.66	9.57	20.28	31.79
Suburban	30.46	26.10	36.58	26.58	13.86	8.40
Industrial	28.87	24.01	23.54	27.73	16.49	20.90
Inner City	30.65	31.71	26.51	17.36	13.30	20.29
Roadside	43.84	33.35	21.65	36.76	30.99	21.49
Ballıca Village	9.59	10.31	19.45	6.00	5.24	9.71

Table 3. Total percentages of Cd, Cr, Cu, Ni, Pb, and Zn removed from the fruit samples of *Phaseolus vulgaris* L. through washing procedure in six different stations.

Location	Cd (%) Removal	Cr (%) Removal	Cu (%) Removal	Ni (%) Removal	Pb (%) Removal	Zn (%) Removal
Brook Coast	28.94	26.32	29.46	28.73	13.69	23.97
Suburban	15.86	26.63	35.44	20.78	11.38	17.48
Industrial	20.79	18.55	29.44	34.08	23.15	14.95
Inner City	33.13	32.32	5.68	21.9	13.57	26.36
Roadside	35.46	40.44	21.14	55.86	27.86	11.41
Ballıca Village	12.83	11.90	15.44	14.48	5.55	2.92

Table 4. Total percentages of Cd, Cr, Cu, Ni, Pb, and Zn removed from the fruit samples of *Solanum melongena* L. through washing procedure in six different stations.

Location	Cd (%) Removal	Cr (%) Removal	Cu (%) Removal	Ni (%) Removal	Pb (%) Removal	Zn (%) Removal
Brook Coast	26.71	17.58	19.65	22.67	21.48	11.68
Suburban	21.78	26.38	25.71	13.13	16.91	14.57
Industrial	27.76	19.24	9.72	35.10	18.24	11.56
Inner City	18.80	21.73	10.23	7.90	16.85	11.82
Roadside	37.33	14.11	23.38	26.11	16.56	16.84
Ballıca Village	8.63	4.04	23.48	2.03	5.86	5.10

The nickel findings of other studies show parallelism with the nickel findings from our study [18, 27]. Following the washing procedure, the nickel levels of vegetables were significantly reduced. Ni removal percentage is high, especially in highly polluted sample sites (Figs. 2 and 3).

The levels of lead found in our study are higher than those from other studies in Turkey and other countries [16, 18, 20, 27]. Our data from the vegetable samples show parallelism with the zinc values of some other studies [17, 22, 26]. The Zn values reported from other studies are higher than our study [18, 19, 23, 24]. The zinc pollution in Istanbul is seen to be much lower than the results in other countries (Figs. 2 and 3).

This study showed that the contamination levels of metals in soil and vegetables were mainly related to local and regional sources. In conjunction with this, the levels of metal concentrations were found to be significantly different between the sites. The concentrations of metals in unwashed and washed vegetable samples studied here showed that the relationship and the correlation between the samples was significant (Table 5). The findings and analysis show that the amount of metals declines when getting further from pollution sources. When it is considered that the segregation of metals declines further from pollution sources, we conclude that it is very important to establish industrial plants far from the city center, or to relocate them to commuter towns. The concentrations of metals in soils were lower than those [28]. From our results, it can be said that environmental pollution is quite low in Istanbul, but it can be a threat in the following years.

Table 5. The correlation of the metals in washed and unwashed vegetables.

Vegetables	Cd	Cr	Cu	Ni	Pb	Zn
Pepper	0.96	0.94	0.92	0.84	0.63	0.27
Bean	0.89	0.82	0.82	0.85	0.94	0.57
Eggplant	0.90	0.96	0.99	0.58	0.97	0.93

Conclusions

Pesticides and manure are the two most important sources of segregated metals in foodstuffs. For this reason, the use of chemical inputs in agriculture should be reduced and biological weed controls should be introduced, as used in some western countries. Awareness should be raised among agricultural producers by arranging specific educational programs. Parallel with an increase in population and industrialization, it is easy to see that environmental pollution and its important role in metal pollution will increase in the future. Therefore, we suggest that the competent authorities should consider this case, to develop prospective plans for environmental protection. Water sources used in agriculture should be kept meticulously clean and carefully managed. Therefore, legal measures should be taken and implemented sensitively by local governments and appropriate authorities. Of the surveyed metals in our study, Pb and Cd are highly toxic for all living creatures, while Cu and Zn (in trace amounts) are essential for plants.

The accumulation of metals on plants depends on different factors, including genetic specialties in addition to characteristics of metals and distance from pollution sources, surfaces of vegetables, climatic factors such as wind direction, soil properties, and intake from soil. In addition, while vegetables are growing, the use of pesticides and the content and the quality of irrigation water are important.

The distance from pollution sources plays an important role in metal contamination of soil and vegetable samples. We suggest that the high contamination levels observed in some samples depend on wind direction and speed and the properties of local soils used for growing vegetables. Cleanliness should be ensured when vegetables are being consumed, and they should be washed properly. When it is necessary to grow vegetables within or near residential areas, artesian wells should be opened to water them.

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