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Heavy Metals Accumulation in Some Vegetables and Soils in Istanbul

Etem OSMA[1]*, Memduh SERIN[2], Zeliha LEBLEBICI[3], Ahmet AKSOY[4]

[1]Erzincan University, Faculty of Arts and Sciences, Department of Biology 24100, Erzincan- TURKEY

[2]Marmara University, Faculty of Arts and Sciences, Department of Biology 34722, Istanbul- TURKEY

[3]Nevşehir University, Faculty of Arts and Sciences, Department of Biology 50300, Nevsehir- TURKEY

[4]Erciyes University, Faculty of Arts and Sciences, Department of Biology 38039, Kayseri- TURKEY

*Corresponding author: etemosma@hotmail.com

Abstract
This work was designed to assess the concentration of six toxic metals in the soil and in unwashed and washed samples of different vegetable species (*Petroselinum crispum*, *Brassica oleraceae* var. *acephala*, *Beta vulgaris* var. *cicla* collected from six different sites (stream side, inner city, industrial, suburban, roadside, and rural) in Istanbul in 2007. Concentrations of Cd, Cr, Cu, Ni, Pb, and Zn were determined by using ICP-OES. It was found that the average highest values of metal accumulations were detected in unwashed samples. The correlation was significant between metal accumulations and the sites, where the vegetables were grown, in the industrial areas and along the roadsides. The highest and lowest average values in the vegetables varied between 0.24-0.89 μg/g dw for Cd, 3.73-14.04 μg/g dw for Cr, 1.47-5.19 μg/g dw for Cu, 3.13-13.65 μg/g dw for Ni, 29.28-87.00 μg/g dw for Pb, and 3.48-5.74 μg/g dw for Zn. The pattern of total metal contrations in the vegetables followed Pb>Cr>Ni>Zn>Cu>Cd.
Keywords: Heavy metal, Istanbul, pollution, vegetable.

İstanbul'da Bazı Sebzeler ve Topraklarda Ağır Metal Birikimi

Özet
Bu çalışmada, 2007 yılında, dere kıyısı, şehir içi, sanayi bölgesi, kenar semt, yol kenarı ve kontrol bölgesi olmak üzere İstanbul'un toplam altı lokasyonundan, *Petroselinum crispum*, *Brassica oleracea* var. *acephala*, *Beta vulgaris* var. *cicla*'ya ait yıkanmış ve yıkanmamış sebze örnekleri ile yetiştikleri toprak örnekleri toplanarak altı toksik metalin miktarı tespit edilmiştir. Toplanılan örneklerde Cd, Cr, Cu, Ni, Pb ve Zn miktarları, ICP-OES kullanılarak tayin edilmiştir. Yıkanmamış örneklerde metal birikiminin en fazla olduğu bulunmuştur. Endüstriyel ve yol kenarlarında yetişen bitkilerde ise metal birikiminin daha fazla olduğuna ilişkin bağlantı tespit edilmiştir. Elde edilen sonuçlara göre bitkilerde ağır metallerin en yüksek ve en düşük değerleri Cd için 0,28-0,89 μg/g kuru ağırlık, Cr için 5,33-14,04 μg/g kuru ağırlık, Cu için 1,47-5,19 μg/g kuru ağırlık, Ni için 3,06-13,65 μg/g kuru ağırlık, Pb için 29,28-86,20 μg/g kuru ağırlık ve Zn için 3,70-5,74 μg/g kuru ağırlık arasında değişim göstermektedir. Bitkilerde toplam metal konsantrasyonlarının sıralanışı Pb>Cr>Ni >Zn>Cu>Cd şeklindedir.
Anahtar Kelimeler: Ağır metal, İstanbul, kirlilik, sebze.

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INTRODUCTION

Pollution and contamination of the soil, water, and air has become inevitable as a result of anthropogenic activities. Environmental pollution by toxic metals has increased steadily since the industrial revolution, thereby causing serious ecological problems (Akguc et al. 2008, Huseyinova et al. 2009). Significant amounts of heavy metals and other chemicals are introduced into the environment particularly by industries, mining, agriculture, combustion of fossil fuels and traffic (Yılmaz et al. 2006, Ozturk et. al. 2008, Yasar et al. 2010). Their impact is clearly on the manifested on terrestrial and aquatic flora and fauna (Okafor and Opuene 2007, Mahvi 2008, Akinci and Caliskan 2010, Demirayak et al. 2011).

Exposure to heavy metals continues and is even increasing. Consequently, elevated levels of heavy metals affect food quality and human health all over the world (Dogan 2003, Kachenko et al. 2006). Since the beginning of the 20th century, the mobilization of heavy metals in the biosphere by human activity has become an important issue (Nriagu 1979) and during the last twenty years, environmental problems have started to be a part of daily life in several countries (Yasar et al. 2010).

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Living organisms require varying amounts of trace metals, although they can be toxic if ingested in excess quantities. Trace elements can occur in high concentrations in plants growing in polluted areas and these plants could pose a risk for human health (Demir and Aydın 2000, Sharma et al. 2004, Dogan and Colak 2009). Plants growing in contaminated areas can accumulate high concentrations of heavy metals without visible changes in their appearance or yield but exceed animal and human tolerance (Kovalchuk et al. 2001, Prasad and Freitas 2003). Both endurable and deadly doses of toxic compounds for different plants have been set up for years and in some situations, the alteration of the chemical composition of the plants which are under the action of pollutants has been observed (Kabata-Pendias and Pendias 2001, Nameni et al. 2008). However, heavy metal exposure may result in toxic effects on humans by the consumption of contaminated plants as food (Okoye et al. 2011).

Istanbul is Turkey's most congested city with a population of over 15 million. The population is increaseing at a fast rate, making it one of the largest metropolitan areas in the world (Kaya and Curran 2006). The city and its boundaries cover am area of 5.712 and 1.831 square kilometers, respectively. The city enjoys a temperate climate, located within a climatic transition zone between, the oceanic and mediterranean climates. Summer is generally hot and humid, average temperature between July and August being 28°C. Winter is cold, wet and often snowy, with temperature dropping to on average of 5°C. Spring and autumn are usually mild and wet and the weather can be chilly to warm, though the nights are chilly (Altay et al. 2010).

The quality of air, water and soil has been affected as a result of increased human activities; such as, building, traffic, and active industry (Yılmaz et al. 2006, Altay et al. 2010).

The aims of this study is to identify the contaminant factors in the areas where vegetables are grown, to determine the pollution levels of different heavy metals and their distribution in vegetables, correlate the pollution levels with distance of sampling areas to the contaminants, and to determine the ways of contamination.

MATERIAL AND METHODS

A total of 18 samples of three different vegetables (chard, parsley and cabbage) were collected Istanbul (Table 1). The samples were collected from different fields during August–September 2007 (Fig. 1).

Samples collected from stream side were from the Ayamama brook, situated in the Bakirkoy district on the European side of Istanbul (Anonymous 2011a). The suburban vegetable samples were collected from the Sancaktepe district, on the Asian side of Istanbul (Anonymous 2011e). The samples from the industrial area were collected from the Tuzla district, also on the Asian side of Istanbul (Anonymous 2011f, Anonymous 2011c). The inner station samples were collected from Goztepe in the Kadikoy district and the roadside samples were collected from Prof. Dr. Muammer Aksoy Street in the Zeytinburnu district (Anonymous 2011d, Anonymous 2011g). The last station, where the control samples were collected, was a village (Ballica village) in the Cekmekoy district (Anonymous 2011b).

Vegetables were hand picked using vinyl gloves and carefully packed into polyethylene bags (Alam et al. 2003). Only the edible parts of each vegetable were used for analysis. In addition, soil samples were collected from the sites form where the vegetables were taken. Vegetable samples were divided into two sub-samples; one sub-sample was thoroughly washed several times with tap water followed by distilled water to remove dust particles and the second sub-sample was left untreated. All vegetable samples were oven dried at 80°C for 24 h. So as to protect the plant material from microbial decomposition and ensuring a constant reference value by determining dry weight in contrast to fresh weight, which is difficult to quantify (Markert 1993, Aksoy et al. 2005). To ensure the uniform distribution of metals in the sample, all materials were milled in a micro-hammer cutter and sieved through a 1.5-mm sieve and kept in clean polyethylene bottles. The soil samples were collected with a stainless steel crab, air dried and passed through a 2-mm sieve. After homogenization, soil samples were placed in clear paper bags and stored for analysis (Demirezen and Aksoy 2006).

Analysis was done according to the method given by Aksoy and Oztürk (1996), Heavy metals were studied using a Varian Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). The stability of the device was evaluated at every ten samples by examining an internal standard. Reagent blanks were also prepared to detect any potential

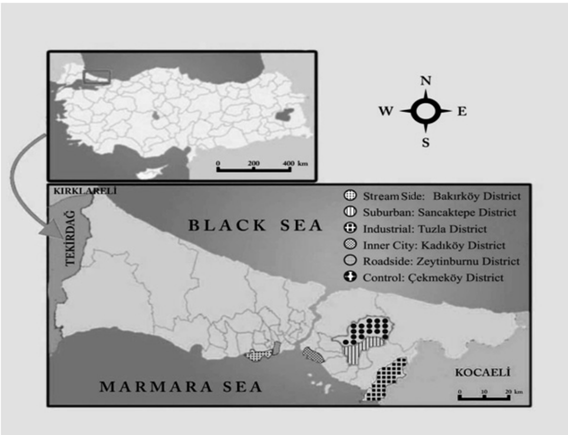

Fig. 1. Map of Istanbul showing study sites of Bakırköy, Sancaktepe, Tuzla, Kadıköy, Zeytinburnu and Çekmeköy.

Table 1. The English, Turkish, and scientific (Latin) names of the vegetables used.

English	Local name (Turkish)	Scientific name (Latin)
Parsley	Maydanoz	*Petroselinum crispum* (Miller) A.W. Hill
Cabbage	Kara lahana	*Brassica oleracea* L. var. acephala DC.
Chard	Pazı	*Beta vulgaris* L. var. cicla (L) Moq

contamination during the digestion and analytical procedure. All chemicals used in this study were analytical reagent grade (Merck, Darmstadt, Germany).

A Statistical Package was used for the calculation of standard deviation. The standard error values of the means were calculated to compare the site categories. A paired t-test was performed to determine the significance of the washing of samples, comparing heavy metal contents of plant samples for each site, and F-test (ANOVA) was performed to compare different localities.

RESULTS

The mean values of Cd, Cr, Cu, Ni, Pb and Zn concentrations in the vegetables and soils studied are given in Figure 2. The concentrations of heavy metals in these samples were quite varied such as, 0.24-0.89 μg/g dw for Cd, 3.73-14.04 μg/g dw for Cr, 1.47-5.19 μg/g dw for Cu, 3.13-13.65 μg/g dw for Ni, 29.28-87.00 μg/g dw for Pb, and 3.48-5.74 μg/g dw for Zn. The order of the levels of heavy metals obtained from different kinds of vegetables was (washed and unwashed samples) comparatively evaluated according to different contamination areas. According to our results, the highest and lowest values of heavy metal accumulation varied 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 dwfor Ni, 47.12-123.97 μg/g dw for Pb, and 1.05-37.04 μg/g dw for Zn.

The result of present study showed that cabbage (0.84 μg/g dw), parsley, (0.80 μg/g dw) and chard (0.89 μg/g dw) from vicinities of stream side and the industrial areas exhibited the highest Cd levels respectively (Fig. 2a). The Cd concentration was higher in the unwashed samples than the washed ones. At the control station, the amount of the Cd concentration was the lowest and the pollution rate was also very low. The percentages of Cd removal values varied from 10.03 to 33.87 percent for parsley, from 14.38 to 47.36 percent for cabbage and from 9.43 to 25.62 percent for chard, dependent upon area type (Tables 3-5).

The higher Cr concentrations were found in cabbage (14.04 μg/g dw), parsley (14.01 μg/g dw), and chard (12.38 μg/g dw) in the vicinity of the roadside and suburban areas (Fig. 2b). Cr contamination was higher in the soil than the vegetable samples. The percentages of Cr removal values varied from 16.85 to 21.95 percent for parsley, 7.01 to 26.67 percent for cabbage, and from 9.15 to 29.67 percent for chard depending upon area type (Tables 3-5).

The highest concentrations of copper in the industrial environment and the roadside were recorded in cabbage (3.18 μg/g dw), parsley (3.53 μg/g dw), and chard (5.19 μg/g dw), respectively (Fig. 2c).

The concentrations of nickel was found to follow a similar general trend as Cd, with the highest values in cabbage (13.65 μg/g dw), chard (10.07 μg/g dw), and parsley (10.70 μg/g dw), found in the roadside samples and the industrial site (10.70 μg/g dw), respectively (Fig. 2d). In addition, the percentages of Ni removal values varied from 8.84 to 31.56 percent for parsley, 6.72 to 41.87 percent for cabbage, and from 4.06 to 21.33 percent for chard dependent upon area type (Tables 3-5). Our data revealed that nickel accumulation in soils and vegetables was within the acceptable ranges for human health.

In our study, the highest concentrations of lead in cabbage (72.48 μg/g dw), parsley (79.89 μg/g dw), and chard (87.00 μg/g dw) was found near the roadside (Fig. 2e). The percentages of Pb removal values varied from 5.96 to 17.61 percent for parsley, 6.47 to 26.92 percent for cabbage and 4.97 to 22.71 percent for chard depending upon the area type

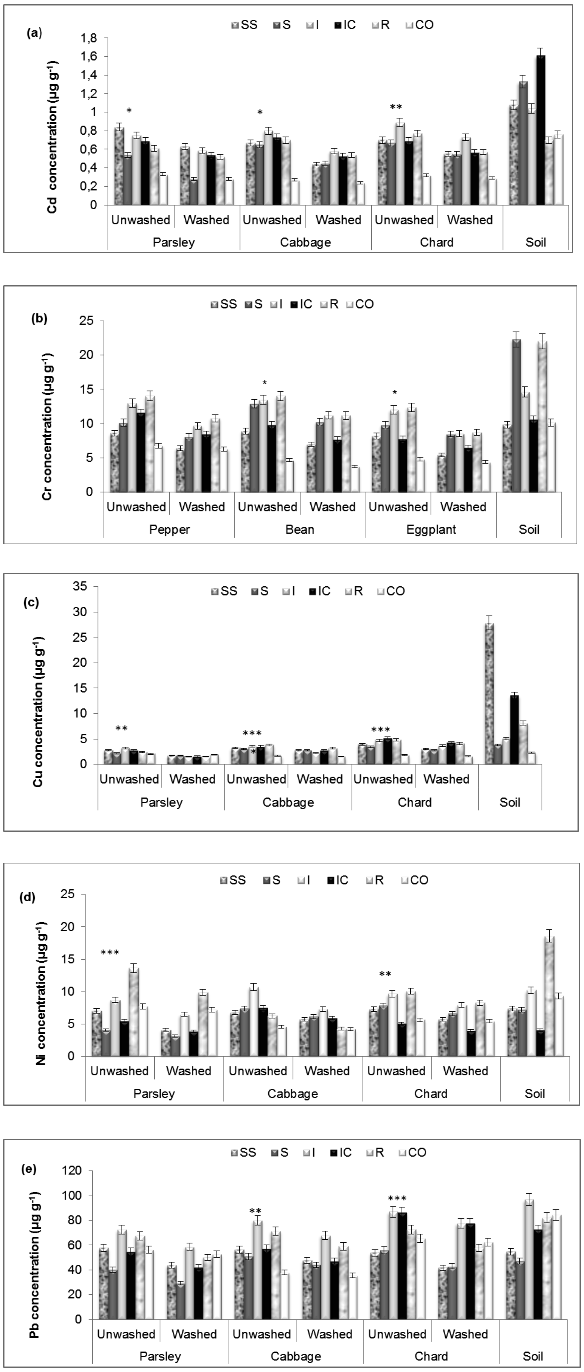

Fig. 2. Mean, Cd (a), Cr (b) Cu (c) Ni (d), Pb (e), and Zn (f) concentrations (µg/g dw) in washed, unwashed leaves and soil with Standart Error.
Bars, SS: Stream side, S: Suburban, I: Industrial, IC: Inner City, R: Roadside, CO: Control area. Significances of differences between washed and unwashed plants from t-test, are indicated above the columns (* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$ significant).

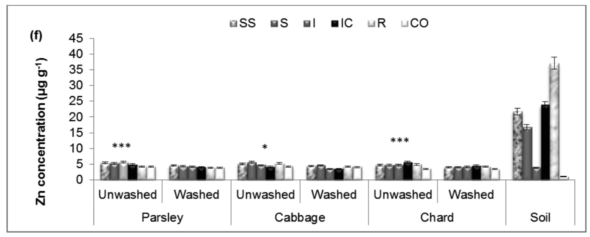

Fig. 2. Continue

(Tables 3-5).

The average highest values of zinc accumulation in cabbage (5.57 µg/g dw), parsley (5.74 µg/g dw), and chard (5.57 µg/g dw) was found in the samples collected near the inner-city and the suburban areas, respectively (Fig. 2f). It was also observed that the average lead concentration was high near the roadside, as well. The zinc accumulation levels in the soil and the vegetables in Istanbul were in small amounts.

DISCUSSION

In this study, it was observed that the concentrations of heavy metals (Cd, Cr, Cu, Ni, Pb, and Zn) in vegetable samples were higher near the roadside and industrial areas in comparison with the other areas and the control station. The distinguishing ability between air-borne and soil-borne contamination was assessed by washing the samples with deionized distilled water. The results indicated that there was no significant difference between the unwashed and washed samples. The soil samples for heavy metal analyses were collected from six selected sites namely, stream side, inner city, industrial, suburban, roadside, and rural areas. Concentrations of Cd, Cr, Cu, Ni, Pb, and Zn were estimated. According to our results, concentrations of Ni and Zn were higher in the roadside areas. For Cd, Cr, Cu, and Pb, the high concentrations were recorded in the inner city, suburban, stream side, and industrial areas respectively.

Our results agree with those reported by Demirezen and Aksoy (2006), Kachenko and Singh (2006), Prabu (2009) and Akan (2009). Previous studies carried out by other researchers (Eslami et al. 2007, Yargholi et al. 2008, Lacatusu et al. 2008, Kumar et al. 2009, Rosborg et al. 2009) show that Cd were found higher than our results. Cd is accepted as a first-degree carcinogenic material. The levels of Cd in the soil and vegetable samples at the selected sites in Istanbul were recorded as being within the limits defined by Anonymous (1992) for

Table 2. Relationships between heavy metal concentration in unwashed and the washed leaves of vegatables.

Vegetables	Cd	Cr	Cu	Ni	Pb	Zn
Cabbage	0.90	0.94	-0.51	0.95	0.91	0.91
Parsley	0.95	0.99	0.87	0.93	0.99	0.80
Chard	0.99	0.93	0.97	0.97	0.97	0.97

Table 3. Total percentage of Cd, Cr, Cu, Ni, Pb and Zn removed from the samples of *Petroselinum crispum*, through washing procedure in six different stations.

Location	Cd (%)	Cr (%)	Cu (%)	Ni (%)	Pb (%)	Zn (%)
	Removal	Removal	Removal	Removal	Removal	Removal
Stream Side	33.886	21.949	14.831	15.993	15.713	14.750
Suburban	30.125	20.496	8.553	16.273	13.425	19.620
Industrial	28.114	16.851	37.110	31.593	14.941	24.690
Inner City	27.828	21.713	20.962	20.725	17.609	15.654
Roadside	22.313	20.159	16.957	31.039	17.236	19.311
Ballıca Village	10.037	19.624	10.364	8.841	5.955	3.037

Table 4. Total percentage of Cd, Cr, Cu, Ni, Pb and Zn removed from the samples of *Brassica oleraceae* var. *acephala*, through washing procedure in six different stations.

Location	Cd (%)	Cr (%)	Cu (%)	Ni (%)	Pb (%)	Zn (%)
	Removal	Removal	Removal	Removal	Removal	Removal
Stream Side	24.620	25.454	37.707	41.868	23.984	15.767
Suburban	47.359	20.216	19.816	23.069	26.916	17.686
Industrial	20.420	25.412	53.196	25.646	18.943	24.659
Inner City	21.944	26.666	42.998	28.148	22.967	16.275
Roadside	14.384	23.168	40.216	27.558	25.771	10.149
Ballıca Village	14.648	7.018	10.756	6.727	6.471	7.642

Table 5. Total percentage of Cd, Cr, Cu, Ni, Pb and Zn removed from the samples of *Beta vulgaris* var. *cicla* through washing procedure in six different stations.

Location	Cd (%)	Cr (%)	Cu (%)	Ni (%)	Pb (%)	Zn (%)
	Removal	Removal	Removal	Removal	Removal	Removal
Stream Side	20.913	33.933	24.046	21.325	22.709	14.507
Suburban	17.594	13.358	20.181	15.895	14.189	13.595
Industrial	17.911	29.066	23.179	17.584	10.689	11.573
Inner City	17.717	16.049	17.604	20.785	10.010	18.728
Roadside	25.624	29.666	14.050	17.654	20.659	12.960
Ballıca Village	9.434	9.149	11.483	4.064	4.970	2.290

human health.

Our results for Cr are consistent with those reported by Akan (2009) but a little higher than those reported by Prabu (2009). The study showed that the contamination levels of Cr in the vegetable samples was mainly related to regional sources. The accumulation levels of Cr in the vegetable species collected from various areas in this study were lower and within acceptable limits.

In the present study, the concentration of Cu in leaves was the same as reported by (Kachenko and Singh 2006, Akan et al. 2009 and Rosborg et al. 2009). The studies performed by (Raza 2005, Lacatusu et al. 2008, Cheraghi et al. 2009, Prabu 2009) show that concentrations of Cu were higher than the values obtained in this study. Cu concentrations in this study were quite low in the soil samples and pose no danger to human health.

Similar studies with some other vegetable species were carried out by Rosborg et al. (2009) and Hussain (2006) and they obtaned similar results for Ni, but other studies carried out in Turkey and other countries showed disagreement with the current study for Ni, they have reported lower values than ours for Ni, Demirezen and Aksoy (2006), Raza (2005), Chao et al. (2007), Akan (2009). Kumar et al. (2009) studied different vegetable species, their findings had a broad agreement with the results obtained by us for Ni. Studies undertaken by other workers for Ni reveal much lower values than those reported here (Demirezen and Aksoy 2006, Kachenko and Singh 2006, Eslami et al. 2007, Chao et al. 2007, Rosborg et al. 2009 Akan 2009).

Pb contents in the soil and vegetables were lower than the results obtained in our study in Istanbul (Demirezen and Aksoy 2006, Chao et al. 2007, Eslami et al. 2007, Kumar et al. 2009). The highest value of Pb was detected near the roadside.

Zinc levels were quite low in the soil and vegetable samples in Istanbul. Results for Zn are higher than our results asper the data published by Demirezen and Aksoy (2006), Chao et al. (2007), Eslami et al. (2007), Prabu (2009).

Present results indicate that anthropic inputs (industrial, inner city, and traffic etc.) in Istanbul have elevated the levels of heavy metals in the soil, water, and air and in conjunction with this, the concentrations of heavy metals in test vegetable species and soil were recorded as being near the background. In general, the concentrations of heavy metals were better correlated with the pollution level in the soil and test vegetables used in this study (depending on distance between industrial facilities, traffic density, climatic factors, structure of topography, surface of the vegetable species, pesticides, and all the sampling sites). The concentrations of Ni, Pb and Cd were higher than the other heavy metals such as Cu, Zn, and Cr in the soil and test vegetables at all the sampling sites. Necessary precautions should be taken by the authorities to keep the levels of these heavy metals low. Also, agricultural practices should not be performed close to such sites in Istanbul because of the contamination risk.

Air-borne and soil-borne contaminations can be assessed by washing the test vegetables with de-ionized distilled water. A comparison of results obtained in this study revealed that the lowest heavy metal accumulations were detected near the control area whereas higher contaminations were detected near other areas.

This study also showed that contamination levels of heavy metals in the soil and test vegetables were mainly related to local and regional sources. The levels of heavy metal concentrations were found to be significantly different between the sites. The positive correlation for pollution rate between the control and the sampling sites were confirmed by using t and f tests (Table 2). It was found that the levels of Cu and Zn concentrations were in small quantities. In order to protect human health, the sources of pollutants in aquatic and terrestrial environments must be identified and then, necessary precautions taken to contain them. The concentrations of heavy metals in unwashed and washed vegetable samples studied here showed that the relationship and the correlation between the samples was significant. All values are below the Anonymous (1993) permissible levels. The concentrations of heavy metals obtained from the soil measurements in this study were lower than those reported by Ross (1994). It can be concluded that the environmental pollution level is low in Istanbul but it will be good to adopt protective measures before it is too late.

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