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Short Communication

Determination of heavy metal pollution in water, soil and plants of vegetable gardens in Ardabil

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ABSTRACT:

Food security in a growing population with limited natural resources is one of the most important issues of the world. Accumulation of heavy metals in food and their concentrations increase and reaching to a risk limit can threaten human health. The purpose of this study, is to study the heavy metals lead and cadmium in vegetables, cultured on spinach and watercress at 10 Gardens of Ardabil. This study is cross-sectional and 81 samples in water, soil, and spinach and watercress were prepared during the months of June, July and August in 2015 and after preparation according to the standard methods and using atomic absorption spectrophotometer (Perkin Elmer) for the determination of heavy metals. SPSS software was used for data analysis. The results showed that the mean level of lead and cadmium in all samples were less than the EPA standard. Between studied orchards in terms of the amount of cadmium and lead no statistically significant different was seen. The independent t-test showed that in terms of cadmium between two species of spinach and watercress there found a significant difference at the 5% level so that the amount of cadmium in spinach was more than the watercress. Since the concentration of heavy metals in all samples at second and third stages in July and August were zero, but in the first step in June, the amount of heavy metals have been found in some samples showed that all three samples of first cut had more contamination than second and third cut. And in this case, the concentration of heavy metal pollution in hibernation at vegetable gardens Ardabil is possible. The results of spinach cadmium amount in the first cut in the three garden of *viz.,*3, 6 and 10 showed that in the garden (3), the amount of cadmium in water is higher than the standard and is concentrated in spinach and the gardens of 6 and 10 Cadmium in the soil of the gardens, is slightly higher that is condensed in spinach thus it can be considered that spinach in terms of cadmium has bioaccumulation.

Keywords:
Bioaccumulation, Cadmium, Lead, Spinach, Cress, Ardabil.

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INTRODUCTION

Heavy metals are the most important sources of non-point pollution of natural resources. Each year, thousands of these elements enter into the system on a global scale soil (Tiller *et al*., 1999). Since the contamination of crops with heavy metals, resulting in decreased quality of agricultural products on the one hand and on the other hand is a serious threat to human health, thus in terms of environmental aspects are very important. Thus the accumulation of heavy metals and increase in their concentration are reaching the danger zone can threaten human health seriously by entering to the human food chain, (Cui *et al*., 2005). Annually, about 38,000 tonnes of cadmium and nearly a million of lead will be added to the soil in which large amounts are related to dust in the atmosphere, scattering the ashes and urban waste and its low levels are related to the use of chemical fertilizers and sewage sludge (Nriagu and Pacyna 1998). Two heavy metals lead and cadmium are crucial carcinogenic elements in the development of cancer, especially gastrointestinal (Waalkes 2003; WHO, 2003). Among the heavy metals, some of which, such as zinc, copper, and cobalt values are necessary for many biological systems, including humans (Reza, *et al*., 2000; Shokrzadeh *et al*., 2011). While some other heavy metals such as cadmium, lead and arsenic are highly toxic to plants, animals and humans (Kabata-Pendias, 2011; Li *et al*., 2004). Cadmium is a known carcinogen in the development of cancer (Türkdoğan *et al*., 2003; WHO 2003). And it seems that its influential factor in the development of heart disease and blood pressure (Edmunds and Smedley, 1996). Lead also influence the blood system and kidneys, causing metabolic disorders and neuro-physical defects in children. It was also reported that if large amounts of heavy metals such as lead, into the body of pregnant mothers, babies, premature birth and severe mental retardation will be greatly increased (Zagrodzki *et al*., 2011; WHO, 2003). Removing heavy metals from the contaminated land by plants, especially agricultural products are one of the most important ways of entering elements into the food chain (Fu *et al*., 2008). Plants can collect large amounts of cadmium in themselves without damage (Alloway, 1995). Cadmium accumulation in plants can increase the absorption potential of elements by human and this will be done when the plants are a part of the diet (Kabata-Pendias 2001). To raise awareness to public opinion in Egypt to assess the crop of heavy metals, we examined analysis of several samples of crops including strawberries, cucumbers, dates and class of vegetables. Considering the two carcinogenic elements of cadmium and lead, and usefulness of zinc and copper in the efficacy in diet, four elements were measured in the products listed. The results showed that leafy vegetables such as lettuce and spinach had the highest levels of lead and cadmium, among other products, but they by estimating the daily intake of these nutrients in tested agricultural products, considered this amount less than WHO, FAO report (Radwan and Salama, 2006). A study was done on samples of rice and vegetables in Jyanksv China in 2010, average concentration of chromium, copper, zinc, cadmium, mercury and lead in rice was less than desired standard and in vegetables only Chrome has exceeded the limit (Cao *et al.,* 2010). Heavy metals because of high solubility in water, can be absorbed by living organisms. With the arrival of heavy metals in the food chain, high concentrations may be accumulated in the human body. If heavy metals with the concentrations above the permitted concentrations enters into human body, they can cause different disorder in humans (Babel and Kurniawan, 2004). Given that the consumption of contaminated vegetables and the consequent illnesses associated with the consumption of certain types specially cancer, kidney disease, nervous system and impose direct and indirect costs to any country society thus this study is intended to evaluate the lead and cadmium as dangerous heavy metals in the

products (spinach and cress) of Ardabil gardens.

MATERIALS AND METHODS

10 samples of water for irrigation and as well as 10 samples of cultivation of soil gardens and spinach and cress were sampled during the months of June, July and August in 1394 from each garden that one sample was collected of spinach and cress and the total samples were 81. Samples were prepared using the standardization method and analyzed at using atomic absorption spectrophotometer (Perkin Elmer) at the Islamic Azad University, Ardabil, to determine the amount of lead and cadmium (Brebbia, 2015). The measurement results for each month of heavy metals in any garden were compared through the EPA standard and to assess differences between products as well as the garden in the city. T-test and analysis of variance was used and to compare means and using SPSS software.

Extraction of soil samples

First, 5 g of each soil sample was weighed on scales and 10 ml of concentrated nitric acid was added until the concentrated nitrogen dioxide vapors leaving in the water bath. Then, 10 ml concentrated Perchloric acid and10 ml nitric acid was added to each sample, and to make clear solution, it was heated on a water bath. Resulted solution was filtered using 42 Whatman filter paper and Buchner funnel. Distilled water was added to the filtered extract reach to a volume of 50 ml.

Preparation of vegetables, spinach and watercress for extraction

Cress and spinach were washed after sampling and then were rinsed with distilled water. Then were air dried on clean, fabric cloth for two to three days and, put in the oven at 75 ° C for 24 hours. Then the milling and powdering was done. After milling samples, one gram of each sample was weighed and placed it an electric oven for two hours at a temperature of 550 ° C to become ashes.

Table 1. Assay results for lead and cadmium in water and soil samples of spinach and cress studied at all the three sampling time (June, July and August 2015)

Garden no.	Water Cd (ppm) June	Water Lead June ppm	Soil Cd June Ppm	Soil Pb June (ppm)	Cd June spinach ppm	Spinach lead June ppm	Cress lead June ppm	Cress Cd June ppm	Cd spinach July ppm	Spinach lead bar ppm	Cress lead July ppm	Cd Cress July ppm	Water Cd August ppm	Water Lead August ppm	Cd spinach August ppm	Spinach lead August ppm	Cd Cress August ppm	Cress lead August ppm
1	0.407	0	0.72	9.97	-	-	-	-	-	-	-	-	0	0	-	-	-	-
2	0.083	0	0.76	10.02	0	0	0	0	0	0	0	0	0	0	0	0	0	0
3	0.055	0	0	10.02	7.5	0	100.17	0	0	0	0	0	0	0	0	0	0	0
4	0	0	0.62	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
5	0	0	0.66	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
6	0	0	1.28	10.21	9.8	0	400.4	0	0	0	0	0	0	0	0	0	0	0
7	0	0	0.53	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
8	0	0	0.58	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
9	0	0	0.79	7.3	-	-	0	0	-	-	0	0	0	0	-	-	0	0
10	0	0	0.93	0	8.8	0	0	0	0	0	0	0	0	0	0	0	0	0

Table 2. The results of analysis of variance for cadmium and lead in the gardens

		Sum of squares	Freedom degree	Mean square	F	Significance level
Cadmium	Intergroup	39.843	9	4.427	0.702	0.701
	Within the group (error)	163.893	26	6.304		
	Total	203.736	35			
Lead	Intergroup	36933.648	9	4103.739	0.85	0.597
	Within the group (error)	125533.759	26	4828.221		
	Total	162467.407	35			

Table 3. The he results of analysis of variance cadmium and lead between resources (water, soil and vegetation)

		Sum of square	Freedom degree	Mean square	F	Significance level
cadmium	Inter group	15.273	2	7.637	1.337	0.276
	Within the group (error)	188.462	33	5.711		
	Total	203.736	35			
lead	Inter group	7541.942	2	3770.971	0.803	0.456
	Within the group (error)	154925.464	33	4694.711		
	Total	162467.407	35			

Extraction of lead and cadmium from plant

In this study, the dry oxidation method was used to extract the plant, one gram of ash sample was added in 10 ml of HCl 2N and the contents became then obtained. Samples were put on the heater at 95 ° C to start boiling. At this stage, the contents became yellow and white smoke is created. The content was moved into the 100 ml balloon and was reached to 100 ml by adding distilled water. After mixing, solution was filtered through Whatman filter paper 42 and poured into small plastic containers with lids that are pre-prepared and was numbered and placed it firmly closed.

RESULTS

The results showed that in the first stage of sampling at three orchards in June , gardens 1, 2 and 3 showed high levels of cadmium, and amount of soil cadmium and watercress had lead as well as in sample 6 it showed higher than standard. pH of the water gardens showed decrease amount of pH in water

Table 4. The he results of t-test to compare cadmium values measured in water with EPA standards

	Standard EPA 005/0 :					
	T-test	Freedom degree	Significance level	Mean difference	Confidence degree 95%	
					Lowest	Highest
Cadmium	1.551	9	0.155	0.099	-0.0454	0.2434

Table 5. The he results of t-test between the cadmium and lead with standards in the soil

	Standard EPA: 50					
	T-test	Freedom degree	Significance level	Mean difference	Confidence degree 95%	
					Lowest	Highest
Lead	-28.187	9	0.000	-45.248	-48.8794	-41.6166

Table 6. t-test for cadmium in the soil

	Standard EPA: 1					
	T-test	Freedom degree	Significance level	Mean difference	Confidence degree 95%	
					Lowest	Highest
Cadmium	-3.061	9	0.014	-0.313	-0.5443	-0.0817

Table 7. The results of t-test for cadmium in plant

	Standard EPA: 3					
	T-test	Freedom degree	Significance level	Mean difference	Confidence degree 95%	
					Lowest	Highest
Cadmium	-1.55	15	0.142	-1.36875	-3.251	0.5135

Table 8. T-test results for lead in the plant

	Standard EPA: 300					
	T-test	Freedom degree	Significance level	Mean difference	Confidence degree 95%	
					Lowest	Highest
Lead	-10.584	15	0.000	-268.71438	-322.8279	-214.6009

sample in the second phase compared to the first stage. Also results of the second stage (July) showed that there was no contamination of spinach and cress to lead and cadmium and the results of the third phase (August) also showed little or no contamination of spinach and cress to lead and cadmium is (Table 1).

Analysis of variance of heavy metals lead and cadmium between the gardens showed that between amount of cadmium and lead levels there was no significantly difference. (sigcd = 0.701 and sig pb = 0.579) (Table 2).

Also between the amounts of heavy metals lead and cadmium measured in terms of resources (water, soil Plants) no significant difference was observed. 0.276 sig cd = and sig pb = 0.456) (Table 3).

T-test for comparing the measured values of cadmium in irrigation water showed that between average amounts of cadmium in the study area with the EPA standard, there was no significant difference. (sig> 0.05) (Table 4).

The results of t-test showed that the amount of lead in the soil between the mean value measured of soil and the EPA standard at the level of 1% (sig = 0.00) was significant. So that the average lead-in area was less than standard (4.7 <50) (Table 5).

T-test showed the amount of cadmium mean value measured in the study area with EPA standards at the level of 5% (sig = 0.014) had significant difference as comparison showed that the mean cadmium was less than standard. (0.68 <1) (Table 6).

The results of t-test showed that the amount of cadmium measured of mean area with EPA standard had no significant difference (sig = 0.142) (Table 7).

Results of t-test comparison of the lead mean values measured with the EPA standard showed mean lead with EPA standard at 1%, by almost 99% confidence was significant (sig = 0.00), as mean comparison showed that lead levels in plants is significantly less than the EPA standard. (31.28 <300) (Table 8).

A sample t-test results showed that the amount of cadmium between spinach and cress there was significant difference at the 5% level (sig = 0.05), as the amount of cadmium in spinach was more than cress (3.26> 0). In case in terms of amount of lead between two species no significance difference was seen (sig =

Table 9. T-test results for the cd, pb between the two types of cress and spinach

	Levine test		T-test						
	F	Significance level	T	df	Significance level	Mean difference	Standard deviation	Confidence degree 95%	
								Lowest	Highest
Assuming equal cadmium	80.776	0.000	2.03	14	0.062	3.26	1.6	-0.18	6.7
Assuming unequal			2.03	7	0.082	3.26	1.6	-0.53	7.06
Assuming equal lead	1.195	0.018	-1.25	14	0.23	-62.57	49.82	-169.43	44.29
Assuming unequal			-1.25	7	0.249	-62.57	49.82	-180.39	55.25

0.230) (Table 9).

DISCUSSION

Given that the amount of lead and cadmium in all samples of water, soil, spinach and Cress was lower than the standard level, which indicates acute infection of studied gardens with heavy metals; Shahamat *et al.* (2009) examined the amount of lead and cadmium in the vegetables fields of Gorgan therefore vegetable and water samples from five northern region of Gorgan for four consecutive months in the fall of 1387 was sampled and examined. For him, the cadmium and lead in water and vegetables were below the standard limit. In the first sample during June 1394 case of gardens (1) had cadmium contamination and garden 3 and (2) had lower amount of cadmium and other gardens didn't have cadmium contamination because garden 1, 2 and 3 are located in the urban area and well water is used for the irrigation of the garden (1) especially in the urban areas. Therefore, absorption wells used for sewage in residential areas can cause pollution, but water of gardens 4 to 10 that are located in agricultural area, away from residential areas showed no cadmium pollution The study of heavy metals in vegetables cultivated around Shahrood city also showed that 150 random sample were taken during the last three months (every 50 months); the average concentration of chromium, cadmium and lead exceeding the standards provided by WHO and FAO that reported main reason access of municipal and industrial wastewater to irrigation were water used in vegetable gardens. According to independent t-test that the rate of uptake and accumulation of cadmium in spinach are more than Cress. This indicates that broader-leaved plants are more likely to have higher concentration of cadmium. The results showed that in India around the river Musi risk factor for heavy metals in vegetables, especially spinach and amaranth leaves are high. Because conductivity and transpiration rate is high in these vegetables as well as broad leaf plants, they are more susceptible to physical contamination by dust from the soil. The survey is also corresponded to the present study (Adriano, 2001). The results showed that between the first stage of sampling results in the June and second and third stages in July and August there are apparent differences so that in some cases cadmium and lead in the first stage, however, often was observed below the standard but in all samples of the second and third stages, including water, spinach and Cress cadmium and lead levels were measured zero. In the survey, different subject can be involved. Including with regard to the area of Ardebil in practice about five months is for planting and harvesting vegetables and actually well water will not be used more than six months and the amount of cadmium occur in the samples of the first stage caused by the accumulation of cadmium in the well in the gardens of No. 1, 2 and 3 that are located in urban areas adjacent to residential homes. And as a result, first cut products of spinach and Cress also show cadmium amount, but in case of water use and picked up several vegetables, virtually the accumulation of heavy metals in second and third cut is zero. Vegetable products of first cut in terms of heavy metals are more polluted than second and third cut. Results of spinach cadmium in first cut of three garden (3), 6 and 10 showed that in the garden (3), the amount of cadmium in water gardens is higher than standard that is concentrated in spinach and in the gardens of 6 and 10 Cadmium is, slightly high in the soil and is concentrated in spinach crop, so it was concluded that spinach in terms of cadmium has bioaccumulation.

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