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An Analysis of Heavy Metals Quantity Especially Pb, Cr and Cd in Grape and Various Leaves Types of *Vitis Vinifera* L. Harvested in Malekan Based on the Distance From the Road

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Abstract

Providing healthy food and protecting sources from pollution has been one of the concerns of human societies and decision – making centers so that protecting food from pollution, detecting sources of pollution and measuring them become important. Because of nutritive and political significance of grape in this area, extensive use of leaf and fruit of this plant, developing urban areas around grape gardens and construction of Tabriz – Miandoab road which is the most important link between East and West Azarbaijan had us to examine the impact of this road construction and urban environment pollutants such as lead chromium and cadmium on the quality of this valuable crop. Firs the samples were taken from different adjacent places and medium distances far from the road then each place located exactly by Google earth and GPS. Digestion was done through burning dry material and hydrochloric acid and their ashes were analyzed by atomic absorption and in this experiments effects of 2 factors; garden distance from the main road with levels 1: for 50meter, 2: for 120-200 meter, 3: for above 800 meter. Plant organ with levels 1: for fruit, 2:for leaves on (Pb, Cr, Cd accumulations as a variable at the end the results processed by SPSS software. In the tested area, it became clear that, from the accumulation of heavy metals perspective, there is no meaningful difference in existing distance between road and garden. There in a meaningful difference among heavy metals accumulation. In other words increase ratio of one metal to another was different that the resulted differences are shown in corresponding graphs. Interaction among elements and distance between garden and road was not meaningful.

Keywords: *Vitis vinifera* L, Phytoremediation, Heavy metals accumulation, Lead, Chromium, Cadmium

Introduction

There is an inverse relationship between lead poisoning and learning reduction. Cadmium makes clear its effect through inhibiting carbohydrates breathing. It is likely that they replace critical elements existed in respiratory enzymes. A moderate amount of chromium in animals diet cause them to live longer, because it is a necessary element for body and its main function is to maintain the normal metabolism of glucose (thanai,1388). Grape whit the scientific name of Vitis vinifral L. from the family of vitaceae is a shrub. It

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is climbing shrub with lobe and simple leaves, and its flowers are on bunches. Iran, Pakistan and Afghanistan are its main habitats (Mozaffarian, 1383). Lead is counted as a poisonous element for plants because it impedes the photosynthesis and respiration by having effect on mitochondrial respiration and electron transfer mechanisms. In vascular plants, lead resistance mechanisms have been observed which seems to be the relationship between various permeability properties of membrane and connecting cell wall Pectic acid to lead and then formation of inactive ortho phosphate-lead. One of the ways of human body chromium contamination is inhaling dust polluted with chromium and chromite that should be avoided. Also cadmium interferes in chlorophyll synthesis, hydrolysis of water, light reactions of photosynthesis, optical non-cyclic phosphorylation and carbon fixation in Calvin cycle. Pathways to enter the mammal's body are typically through polluted air, water and food. In fact, heavy metals after entering the body are not excreted. They sediment and accumulate in tissues of fats, muscles, bones and joints which cause numerous diseases and side effects. Effects of heavy metals on human are different and the major one relates to neurological disorders. Plants in order to confront the metals, use two mechanisms of avoiding and resisting against them. Various species of metal loving plants differ in terms of metal accumulation amount within themselves (Nilsen, 2004 & Thanis, 1388).

Methods and Materials

At the end of September, fruit harvest season, samples of fruits, leaves and soil were collected according to following coordinates (sampling was conducted in ten points. Five samples of leaves and fruits and also their mean were noted) (see figure & table 1)

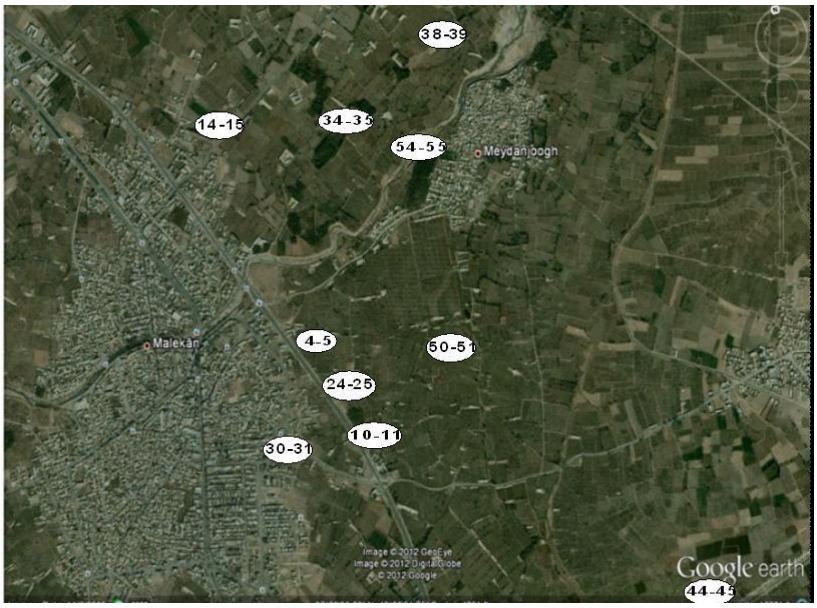

Figure 1: Coordinates of collected *Vitis vinifera* L. samples in Google earth

In order to digest dry material through burning and using hydrochloric acid, a certain amount of samples is placed in glass plates. Then they are put in the oven at 105 centigrade for 12 hours and moved to desiccator. After cooling the samples, a certain amount of them is weighted in Crucible . Samples are put in the oven at 550 centigrade for 12-16 hours until all of them are incinerated. If a sample has not been

incinerated yet, a few drops of distilled water are added and again after drying it is put in the oven until it turns to ash. The oven if turned off and having cooled the Crucibles, they are moved under hood.

Distance from the road(m)	Coordinates	Sample	Sample number
200	N: 370,08′ó,37.2" E:0460,06′,43.2"	Fruit	4
		Leaf	5
200	N: 370,08′ó,23.2" E:0460,06′,58.2"	Fruit	10
		Leaf	11
50	N: 370,09′ó,34.4" E:0460,06′,06.0"	Fruit	14
		Leaf	15
50	N: 370,08′,31.0" E:0460,06′,47.1"	Fruit	24
		Leaf	25
50	N: 370,08′,23.6" E:0460,06′,53.4"	Fruit	30
		Leaf	31
1100	N: 370,09′,13.9" E:0460,07′,35.5"	Fruit	34
		Leaf	35
2500	N: 370,07′,14.9" E:0460,08′,35.2"	Fruit	38
		Leaf	39
120	N: 370,07′,48.1" E:0460,07′,01.1"	Fruit	44
		Leaf	45
1000	N: 370,08′,29.3" E:0460,07′,07.9"	Fruit	50
		Leaf	51
800	N: 370,09′,01.0" E:0460,07′,03.3"	Fruit	54
		Leaf	55

Table 1: Geographic coordinates of *Vitis vinifera* L. sampling points in Malekan

In the next step hydrochloric acid 1.1 is added heated up to being dissolved. It is moved to 25 cc balloon through glass funnel. The metals standards are provided from the ppm 1000 mother standard, 5 solutions for each metal. After that with the use of atomic absorption machine PG 900 which is made of UK (in Jihad Research Center of Applied-science, Urmia Branch), absorption of each standard and sample is recorded. Their density are calculated and then from the samples, the quantity of each metal in treated samples with the food solution of each cation in milligram per kilogram is calculated.

Result and Discussion

Analysis and comparison of lead, chromium and cadmium quantity in *Vitis vinifera* L. fruit and leaf samples in Malekan showed that 3.54 ppm, the most lead quantity, was at sample No. 54 in fruits with 800 meters distance from the road and 1.00 ppm was the least lead quantity at sample No. 50 in fruits with 1000 meters from the road. In leaves, the most lead quantity was 19.16 ppm at sample No. 15 with 50 meters distance from the road and the least quantity was 1.41 ppm at sample No. 31 with 50 meters from the road (see; table 2,3,4) & (figure 2,3,4). Result of analysis of variance in distance and plant organ for Pb showed that between fruit and leaf Pb uptake very meaningful different. Pb uptake in leaf is the most highest to fruits. Distance and interaction between distance and plant organ is not meaningful. Result of analysis of variance in distance and plant organ for Cr showed that between fruit and leaf Pb uptake very meaningful different. Cr uptake in leaf is the most highest to fruits. Distance have not

meaningful effect on Cr uptake. Result of analysis of variance in distance and plant organ for Cd showed that between fruit and leaf Cd uptake very meaningful different. But Distance and interaction between distance and plant organ is not meaningful. It is neither meaningful interaction between this elements uptakes in fruits nor in leaves. If leaves and fruits assumes all together showed that very meaningful integration between heavy metal accumulations. It means that each of this elements cause to uptake others without considering special organs. Pb uptakes have meaningful different in distance 50meter and 200 meter. It means that Pb uptake in near the main road is highest. Bud this result is not true about other elements(see pic 6,7)&(table 5,6). According to lead accumulation in the samples and their entry to human food chain, caution in use is recommended (Arpand 2011). Lead accumulation through air pollution, has been investigated in other plants such as *Aster subulatus* (Hu Xin 2011). Lead with high toxicity and long durability in soil is considered as an unnecessary element. It causes poisoning in plants cell division and enzyme activity. Also it impairs mineral nutrition of plants and causes oxidative stress through inhibiting photosynthesis. Even in aquatic plants, heavy metal accumulation has been seen. Biological accumulation of Cr (VI), Pb (II) and Cr (III) in aqueous environment with *Caulerpa racemosa* and *Sargassum wightii* algal biomass has been studied that its results confirms our achievements (Tamilselvan, 2012). Plants in response to oxidative stress follow a set of intracellular defense mechanisms such as tolerance and detoxification in order to withstand heavy metals (Nilsen, 2004). In human beings, the lead is transmitted to the issues by red blood cells after entering the body and the values that cannot be disposed are absorbed gradually at certain positions of it. In vascular plants, lead resistance mechanisms have been observed which seem to be the relationship between various permeability properties of membrane and connecting cell wall pectic acid to lead and the formation of inactive orthophosphate-lead. Lead absorption through digestion is so difficult. At most 5-10 percent of lead is absorbed in a diet which can be increased more than 20-50 percent. Organic compounds of lead tetra-ethyl ammonium and tetra-methyl which exist in the composition of gasoline containing lead, are one of the major pollutants of environment and dangers to human health (Thanaie, 1388).

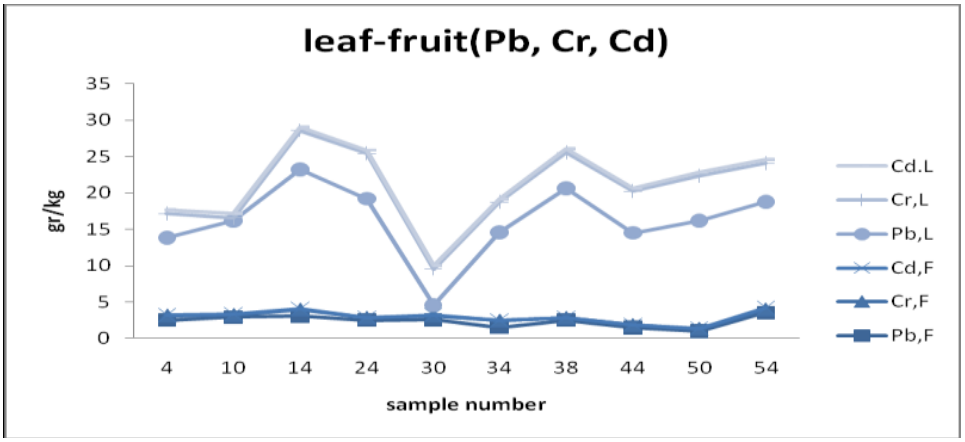

Figure 2: Amount of Pb, Cr and Cd in the ash of *Vitis Vinifera* L. leaf and fruit samples

In the research, contamination with leaf and heavy metals through air pollution has been studied. Both the pollutions from the soil and raining are absorbed by the soil that are available for the plant. Gympsum and compost are used for restoration of contaminated soil with lead (Hashimoto, 2011). Analysis and comparison of lead, chromium and cadmium quantity in *Vitis vinifera* L. fruit and leaf samples in Malekan showed that the highest amount of chromium in fruits was 0.8892 ppm in sample No. 14 with 50

meters from the road, and the lowest amount of it was 0.02841 ppm in sample No. 10 with 200 meters from the road. And also it is observed that the highest amount of chromium in leaves was 6.2053 ppm in sample No. 25 with 50 meters from the road and the lowest amount was 0.4145 ppm in sample No. 11 with 200 meters from the road. (Table 1,2,3) (Figure 2)

Table 2: Comparison of the effects of Pb and Cr accumulation in *Vitis vinifera* L. fruit and leaf

54/55	50/51	44/45	38/39	34/35	30/31	24/25	14/15	10/11	4/5	**Sample number**
3.54	1	1.51	2.51	1.52	2.53	2.52	3.05	2.92	2.52	**gr/kg (fruit sample) Pb**
14.62	14.8	12.61	17.71	12.13	1.42	16.31	19.16	12.79	10.66	**gr/kg (Leaf sample) Pb**
0.413	0.292	0.293	0.293	0.89	0.59	0.294	0.89	0.28	0.59	**gr/kg (fruit sample) Cr**
5.28	6.17	5.72	4.96	4.16	4.97	6.21	5.38	0.415	3.32	**gr/kg (Leaf sample) Cr**

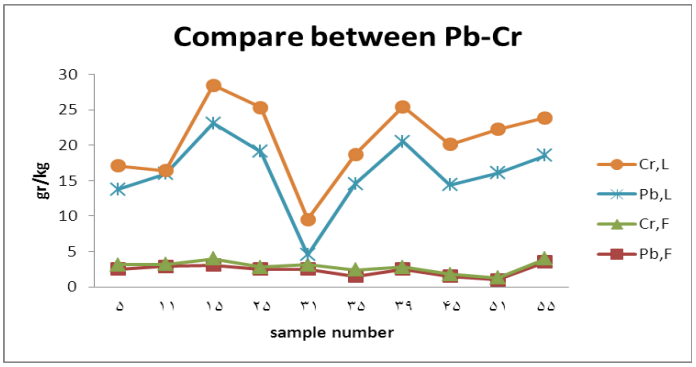

Figure 3: Comparison of the effects of Pb and Cr accumulation in *Vitis vinifera* L. fruit and leaf

This element has the capacities of Cr^{3+} and Cr^{6+} which the former one is stable and more widespread in nature. Cr^{6+} compounds form in acidic environment and low PH. Trivalent chromium generates acidic compound for being too similar to oxygen. On the other hand, as chromium is so similar to aluminum magnesium Fe^{2+} and Fe^{3+} ions, it generates complex compounds of theses metals (Tamilselvan 2012). One of the ways of human body chromium contamination is inhaling dust polluted with chromium and chromite that should be avoided. Daily chromium requirement of the human body is nearly 50 ppm. This amount of chromium is effective in digesting and metabolizing sugar and fat. Chromium is available in foods like barley, egg, meat and some fruits and vegetables (Thanie 1388). Up to now, there is no evidence of trivalent chromium which causes negative effects on workers and ordinary people in areas containing ferrochrome. Also hexavalent chromium is used in producing drugs for lung cancer and skin sensitivity. The chromium existed in chromite is trivalent chromium which is not dissolvable in water, so negative effects of chromium water are not detectable around areas with high chromite. Analysis and comparison of lead, chromium and cadmium quantity in *Vitis vinifera* L. fruit and leaf samples in Malekan showed that the maximum amount of cadmium in fruits was 0.2078 ppm in sample No. 54 with

800 meters from the road and the minimum amount of it was 0.5714 ppm in sample No. 30 with 50 meters from the road. And the highest amount of chromium in leaves was 0.6418 ppm in sample No. 11 with 200 meters from the road and the lowest amount of it was 0.40076 in sample No. 31 with 50 meters from the road. (Table 2, 3) (Figure 2, 3)

Table 3: Comparison of the effects of Pb and Cd accumulation in *Vitis vinifera* L. fruit and leaf

54/55	50/51	44/45	38/39	34/35	30/31	24/25	14/15	10/11	4/5	**Sample number**
3.54	1	1.51	2.51	1.52	2.53	2.52	3.05	2.92	2.52	**Pb gr/kg (fruit sample)**
14.62	14.8	12.61	17.71	12.13	1.42	16.31	19.16	12.79	10.66	**Pb gr/kg (Leaf sample)**
0.21	0.11	0.09	0.08	0.06	0.06	0.08	0.1	0.16	0.07	**Cd gr/kg (fruit sample)**
0.47	0.43	0.41	0.46	0.42	0.4	0.64	0.48	0.64	0.5	**Cd gr/kg (Leaf sample)**

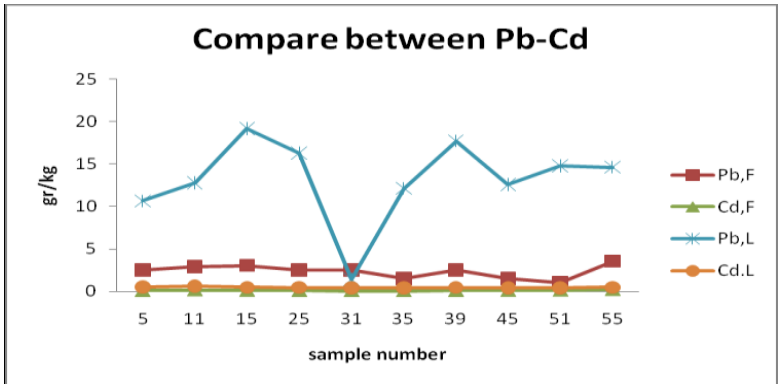

Figure 4: Comparison of the effects of Pb and Cd accumulation in *Vitis vinifera* L. fruit and leaf

Cadmium has a high affinity for binding with an iron-carrying protein and ferritin. High concentration of lead inhibits bioaccumulation of lead and cadmium. But on the whole, lead has a positive effect on cadmium absorption (Junliang 2010). Studies on laboratory animals and human beings showed that cadmium absorption through digestive tracts depends on the rate of blood ferritin and iron deficiency in a diet. Metals such as lead and cadmium are harmful to human beings more than plants that one of its reasons is the accumulation of them in nature. Extra-cellular responses in lead and cadmium accumulation at Iris pseudacorus has been examined. Cadmium, inorganic mercury compounds and lead are stored in order in tissues of liver and kidney, kidney and bone (Thanaie, 1388). 2 cultivar water spinach and their hybrids' responses to Cd and Pb showed that lead and cadmium accumulation in the shoot of pollution-safe cultivars are more less than the polluted plants. And shoot's Cd density seems to be affected by dominant genes, therefore, mating taken place in this plant may not decrease Cd accumulation rate. Interaction between Cd and Pb in soil affected by both of them shows that more Pb increases the concentration of Cd but in the cases with high concentration, Pb and Cd bioaccumulation is limited (Juanliang, 2010) that in *Vitis vinifera* L. fruits it was observed, but lead accumulation pattern in leaves was different. (Table 3,4) (Figure 2,4,5)

Table 4: Comparison of the effects of Cr and Cd accumulation in *Vitis vinifera* L. fruit and leaf

54/55	50/51	44/45	38/39	34/35	30/31	24/25	14/15	10/11	4/5	**Sample number**
0.413	0.292	0.293	0.293	0.89	0.59	0.294	0.89	0.28	0.59	**Cr gr/kg (fruit sample)**
5.28	6.17	5.72	4.96	4.16	4.97	6.21	5.38	0.415	3.32	**Cr gr/kg (Leaf sample)**
0.21	0.11	0.09	0.08	0.06	0.06	0.08	0.1	0.16	0.07	**Cd gr/kg (fruit sample)**
0.47	0.43	0.41	0.46	0.42	0.4	0.64	0.48	0.64	0.5	**Cd gr/kg (Leaf sample)**

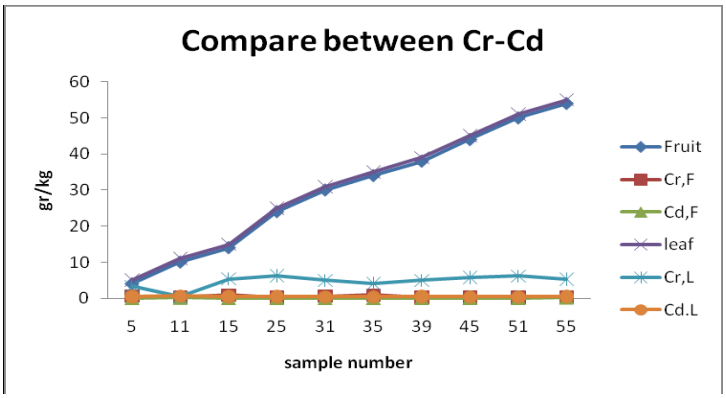

Figure 5: Comparison of the effects of Cr and Cd accumulation in *Vitis vinifera* L. fruit and leaf

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