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Original Article

Accumulation of Heavy Metals in Soil, Leaf and Fruit of, *Malus domestica, Elaeagnus angustifolia* and *Pyrus communis* Trees around A Zinc Factory in Zanjan, Iran

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ABSTRACT

Heavy metals cannot be analyzed in the environment easily and can cause many problems in the concentrated food chain for the environment and human being. The purpose of this research is the evaluation of *Malus domestica*, *Elaeagnus angustifolia* and *Pyrus communis* in terms of the rate of absorption in metals such as Lead, Cadmium, Nickel and chrome through the leaves of trees in the surrounding of Zanjan lead and Zinc factory and also determination of the mentioned trees health. Randomly, we gathered our samples based on the soil leave and the fruits of the mentioned trees. The digestion of the samples was done by acidic digestion and the rate of concentration was measured by the help of atomic absorption set. The results showed that the highest rate of concentration was in Pb and Cd metals and in the leaves of *Pyrus communis* and *Elaeagnus angustifolia* were (3/08 µg/gr and 64/8 µg/gr) respectively. The concentration of Ni was less that others. The highest rate of lead concentration was in *Malus domestica*(4/16 µg/gr)and the highest rate of Cr was found in *Elaeagnus angustifolia* (2/5 µg/gr), and also the concentrations of Cd and Ni were less than other metals. The results of this research showed that *Malus domestica, Eleagunus angustifolia,* and *pyrus communis* trees could absorb heavy metals in their leave more than others. Even this action has high importance because of pollution reduction in soil, the concentration of these metals in the fruits can be regarded as a danger for the health of human beings.

KEYWORDS: *Malus domestica, Elaeagnus angustifolia, Pyrus communis*, soil, phytoremediation, heavy metals.

INTRODUCTION

one of the most important environmental concerns can be related to the increase of industries, industrial pollutants and also the adjacency of industrial, urban, and agricultural centers in most of the areas. The penetration of these pollutants to soil and also because of soil pollution, the life of plants and animals will be in danger (Farahmand kia *et al*., 2002). Since soil can be considered as a natural environment for the growth of plants directly and indirectly, any change in the quality of soil and also its chemical and physical features will have a considerable effect on plants and animals. Also pollutant factors after their penetration into water will contaminate water and can pollute the air too. Thus it will pb to the contamination of food chain(kabata-Pedias *et al.*, 1992).

Phytoremediation is a new technique that strong plants are used to remove or decrease the concentration of chemical and mineral pollutants. Also the mentioned plants can decrease the effect of dangerous environmental factors (Pulford *et al*.,2003). Many studies have been conducted on the potential of trees which show the high ability of trees in the absorption of soil contamination.(Shariat, *et al*.,2010) conducted a research on the effects of Cd on Eucalyptus and found out the concentration of Cd was in leaf, root, and stem respectively. (Pierre *et.al* 2001)in their study on Populus tree, understood that the highest rate of pollution was both in the soil and leaves. (Marques2009) with his investigation on the rate of concentration of Pb, Ni, and arsenic in root, stem, and leaves concluded that *Robinia pseudoacacia* tree was able to concentrate metals in its different parts. Therefore, this tree is recommended for the purpose of phytoremediation. One of the most important factors on human health can be related to the use of healthy food. Fruits are regarded as major parts in human being diets, which are full of biological active agents and play an important role in the health of human beings. They have Antioxidant, Anti-mutagenic, and anti bacterial features (Rainbow *et al.,* 2007). Fruits can accumulate heavy metals in themselves and it is dependent on the growth place and their natural

features. Since fruits are used constantly, their health is necessary.

Due to the pollution of Zanjan pb and zinc factory in the neighborhood of Zanjan province, this research was conducted to investigate the rate of pb, and Cd, Cr and Ni concentration in the trees of *Malus domestica, Elaeagnus angustifolia , Pyrus communis*, since the mentioned samples are over 20 years old, the results can be a good reflection of the real reaction of these kinds.

MATERIAL AND METHODS

The mentioned area in the neighborhood of Zanjan Pb and zinc factory (the largest production company of Pb and zinc in the middle east), Fig.1 show the study area.

Fig. 1. The situation of the study area

to conduct the study, sampling was based on some trees of *Malus domestica, Pyrus communis, Elaeagnus angustifolia* . They were over 2 years old and our data was collected in three times in September of 2011 year randomly.

The sampling was based on the leaves enjoyed the same situation in terms of absorption of sunlight (liu et.al 2004). The leaves and fruits were washed and finally were rinsed with distilled water. The samples were then placed in a container with the temperature of 105 °C and its duration was 24 to 18 hours. After getting dried completely, 0/5 gram of each sample was measured with an exact scale and then acidic digestion function was conducted. In this research, we made use of wet digestion method for leaves and fruits digestion. For acidic digestion a mixture of nitric acid and acid percholoric with the proportion of 4 to 1 was used(Gupta,2000). the sampling of soil was based on the depth of 0-15 centimeters of soil and it was conducted randomly (sadeghi,2002). The sample were kept in the laboratory of, the natural resources faculty, Tarbiat Modares university of Iran for a week and in dry weather. Then it was sifted from mesh sifter number 2 and placed for 24 hours and with 110 °C in a container.

For the determination of concentration in heavy metals, 1 gr of sifted soil was measured and them was poured into a utensil dish and next a mixture of acid nitric, floridric, and cloridric was added 2,2, and 4 mL respectively to each of them. It was placed on the heater to get dry gradually. Then 20 mL of normal 2/5 acid chloric was added to it. It was heated to have dissolution. The digested sample was passed from Watman 42 paper. It was then added to deionized water with the volume of 25 mL(Cappuynes et.al 2007). The rate of concentration was measured by the help of atomic absorption set produced of Phillips Company, model PU9400X. About Pb, Cd, Ni and Cr the rates of concentrations were 1.83, 0.18, 0.31, and 0.43 respectively. The relative standard deviation of all the samples was under 5%.

Also bioaccumulation factor was calculated (Macfarlane et al., 2007). The more it approaches 1, the more it will have absorption power. For the investigation of this factor, the proportion of concentration in heavy metals was calculated and the results are observable on table 3.

Bcf =metal concentration in plant / metal concentration in soil

For data analysis, SPSS 17 software was used.

The method of data analysis was one side variance. The comparison of multiple average was done by the help of Dancan test.

RESULTS

in terms of concentration The metals such as Pb, Cd and Cr did not have very significant differences. The difference in the concentration of Ni was significant (95%).

In terms of concentration, the difference between Cr, Cd, and Ni was not significant (sig > %5). But there was a significant difference in terms of concentration in Pb metal (sig < %5). *Pyrus communis* had a higher rate of concentration. The rate of concentration in fruit of *Malus domestica* pb was (4.16 microgram/gram) and Cr concentration in fruit of *Elaeagnus angustifolia* was (2.5 microgram/gram). The Cd and also Ni concentration were not detected by machine. Ni metal concentration in the leaves of trees and also *Elaeagnus angustifolia* was low. In all of the species, the average rate of concentration was higher in the leaves in comparison with the fruits. Generally a significant difference was not found (Table 1).

Table 1. Mean concentrations in soil, leaf and fruit trees µg/mg

Species	sample	(Ni)	(Cr)	(Cd)	(Pb)
	soil	22/50±2/50	33/16±1/60	3/41±1/37	250±25
Malus domestica	leaf	ND	63/16±2/56	0/75±0/25	113/33±12/58
	fruit	ND	0/83±1/44	ND	4/16 ±2/88
	soil	14±1/32	30/66±2/75	2/58±0/80	283/32±125/83
Elaeagnus	leaf	ND	64/8±2/40	ND	33/66±14/10
angustifolia	fruit	ND	2/50±2/50	ND	3/33±1/44
	soil	14/16±3/8	21/86±2/88	3/41±1/75	153/33±62/91
Pyrus communis	leaf	ND	63/66±1/20	3/08±0/94	167±14/70
	fruit	ND	1/66±1/44	ND	2/50±1/22

ND: Non Detect

With the comparison of table 1 analysis and the presented standards in table 2, we should tell that the rate of Pb and Cd metal was higher than standard level with reference. To environmental protection agency criteria.

Table 2. Concentration of some heavy metals in soil and the standard view of the world average (ppm)

Standard			
USEPA	GLC	Global average	Element
10	10	20	Pb
0/06	-	0/3	Cd
100	10	80	Cr
40	20	33/7	Ni

The highest rate of transfer in Pb, Cd and Cr belonged to leaves and soil of pear tree (table 3). Bioaccumulation factor in the leaves and fruit of some trees in terms of Ni and Cd concentration was not calculated because of low concentration.

Table 3. Transfer of metals from soil to leaves and fruit

Species	Bioaccumulation factor	Ni	Cr	Cd	Pb
Malus domestica	Soil to leaf	ND	1/94	0/21	0/45
	Soil to fruit	ND	0/02	ND	0/016
Elaeagnus angustifolia	Soil to leaf	ND	2/11	ND	0/11
	Soil to fruit	ND	0/08	ND	0/01
Pyrus communis	Soil to leaf	ND	2/90	0/90	1/08
	Soil to fruit	ND	0/07	ND	0/02

DISCUSSION

Due to industrialization of societies, the rate of pollution in the industrials areas and its neighborhood has increased and this fact will Pb to soil pollution and also trees and plant pollution too.

The research showed that the average rate of metal concentration of Pb and Cd in the urban industrial areas equals 208 and 2/8 µg/kg respectively.

While in rural areas we do not have industrial pollution and equals 106 and 1/6 µg/kg respectively.(Ahmed ko *et al*,1993). The conducted study showed that the soil and plants concentration of Zanjan province is related to metal mines melting metal factories and also phosphate compost (Karimpoor *et al*,1994). The research showed that the concentration of pb and Zn in Zanjan province is higher than European industrial areas and also north America which is regarded very high for a city that has many residential areas (Farahmand kia *et el*, 2002).

The rate of Sequestration in pb in the industrial European areas (Deboudt et al,2004) and also north America (Jeffries et al,1981) is in the range of (49-175) and (32-956) µg/m^2/day respectively. Where as in Zanjan the rate of daily Sequestration is equals with (4-45) mg/gr (Farahmand kia *et el*, 2002).

The investigation of soil in terms of metal concentration has shown that the rate of pb and Cd is higher than the standards of environmental protection agency and it can be suggested that the soil of this area is contaminated to Pb and Cd. In the present study, the concentration of pb metal was higher than other metals and it is because of the activity of factories and other related industries of Pb in Zanjan province (karimipoor *et al*,1994). Whit the investigation of concentration in the leaves of the trees, it became clear that the highest rate of concentration in Cr was in leaf of *Elaeagnus angustifolia* and its average was 64/8 µg/gr and also the highest rate of pb and Cd concentrations

were in the leaves of *Pyrus communis* and they were 167 and 3/08 µg/gr respectively. While the concentration of Ni was less than normal level and we could not detect it.

In this research, the concentration difference in the metals such as Cd, Cr and Ni was not significant (sig>%5)but there was a significant difference in terms of Pb concentration. *Pyrus communis* had the potential to absorb the metal. Many studies have revealed that trees are different in terms of absorption and accumulation of metals in their stem and leaves which is related to their genetic features(Sawinalis *et a*l,2001., Kim and fergussen,1994., and Piczak *et al*,2003). Heavy metals penetrate into soil and plants via air. With the increase of metal concentration in the soil, the rate of metal concentration will be increased in the plants. Trees have different potentials in the absorption of metal. This difference is because of environmental and genetic conditions. Also some other metals can penetrate into the leaves directly through Cuticles (Kord *et al*,2010). The exposure of plants to heavy metals can emerge the feature of poisoning in the plants (Verkleij and schat,1990., MacFarlane and Burchett,2001). Table (3) shows the rate of metal transfer to plants and fruits from soil.

Based on the results, the rate of metal transfer to leaves was high and high transfer of Cr to leaves can help the plant not to lose its leaves, so the rate of Cr concentration will be decreased in the plant. The leaves of *Pyrus communis* can absorb a high rate of Pb, Cd, and Cr. Zheng *et al*(1997) study showed that unnecessary heavy metals accumulate in the leaves and then separate from the plants after leaves fall.

Lacerda *et al*(1993) measured the rate of concentration in Pb, Cd, and Ni.

Table 4. Relevant studies conducted in different locations (µg/gr)

Scholar	fruit	Cr	Cd	Ni	Pb
(Mahdavian *et al*, 2008)	Orange	32/82	1/80	ND	ND
	banana	37/87	4/64	ND	195/19
	peach	47/61	3/85	38/39	9/52
	apple	ND	6/42	97/72	19/04
(Mohamad *et al*,2000)	Grapes	28/57	3/63	57/142	57/142
	date	1/45-0/02	-	-	7/94-0/44
(Radwan *et al* 2006)	Tomatoes	-	0/01	-	-
	Apricots	0/0169-0/0162	0/22-0/19	3/66-3/41	2/50-2/36
(Ferre-Huguet *et al*, 2008)	apple	ND	ND	ND	ND
	peach	ND	Nd	0/260	0/020
	orange	0/130	ND	0/220	0/010
	Tomatoes	ND	ND	ND	ND
(Saracoglu *et al*, 2009)	Tomatoes	-	-	-	0/025
	Strawberries	-	-	-	0/017
	apple	-	-	-	0/019
	lemon	-	-	-	0/014
(Zeid *et al*,2010)	apple	-	0/414	-	0/309
	Bilberry	-	0/509	-	0/566
	Tea	-	0/913	-	0/317
(Bobrowska-grzesik *et al*,2008)	apple	3/93	0/173	0/0971	1/80
	banana	3/43	0/262	1/316	3/152
	lemon	3/97	0/292	0/975	1/961
	Mango	4/095	0/275	5/033	1/914
	Tomatoes	2/864	0/245	0/144	0/531
(Parveen *et al*,2003)	apple	-	0/14	-	0/76
	Strawberries	-	-	-	-
	Zucchini	-	0/33	-	1/06
	Cucumber	-	0/36	-	1/72

Table(4) shows the rate of metal concentration in the trees and these differences are due to the differences of concentration, and also the chemical structure of soil and its mineral materials(zahir,2009). As it is clear in the tables, it should be mentioned that different fruits accumulate different amounts of metals. With the investigation of the concentration in Cr, Ni, Pb, and Cd in different plants and vegetables such as apple, orange, peach, and tomato irrigated by Ebro river in Spain revealed that Cd concentration was insignificant and the rate of pb and Ni in peach was higher than other fruits(Ferre-huget,2008). Also the rate of pb concentration in Riyaz was different for strawberry, apple, lemon, and tomato(Savacoglue,2009). The rate of pb was in tomato and apple had a high potential to absorb pb more than lemon and strawberry. Mahdavian(2008)research on the rate of concentration of metals in Bangalore city of India showed that the rate of concentration will be increased with the increase of pollution. Pb concentration in the fruits of neighborhood factories was higher than other trees. It seems that

being in the vicinity of these factories is the main reason of soil concentration in this area. Afyoni *et al*(1998) stated that with the increase of heavy metals in soil, the rate of concentration will be increase in the plants. Bahati and Singh(2005) and Sillanpaa(1992) mentioned that there is a direct relationship between concentration increase in the plant and also soil. The soil that is near to the root is the first source that heavy metals can penetrate into the plants(Logan and Chaney,1983). The results of this research showed that the rate of metal concentration in the leaves is more than fruits which is in correspondence with other researches(Aghabarati et al,2002). Paula *et al*(2006) mentioned the reason of this event because of the differences in plant morphology.

Morphology of fruits and plants is effective on the rate of dust. There are many patterns for different rates of concentration in plants and fruits. Accumulation of heavy metals is related to the soil and the accumulation process starts from soil and then transfers to the leaves and fruits (Zahir,2009). The reason of heavy metal accumulation is related to the concentration difference and the feature of these metals (Samani Majd *et al,*2007). The other reason is related to genetic features and also their potential in pollution absorption. These trees can accumulate a high rate of metals in their different structures and this will pb to soil pollution decrease. It should be mentioned that these poisonous element are major dangers for food chain. These types of features in the fruit will pb to acute and chronic effects in human being and other creatures. Since heavy metals have dangerous effects on human beings especially children, the rate of tolerable daily intake of pb and Cd was 25 µg/kg and 7µg/kg respectively . it was passed in 61st committee of WHO and FAO. For metals such as Cr and Ni, the rates are not clear. But WHO organization has mentioned the tolerable daily intake of Ni 5µg/kg. (Mohamad AE,2000).

If the intake is higher than the mentioned amount, it will result in some side effects and dangerous problems in human beings bodies. It has been proved that if the rate of daily intake of Cd equals with 140-260 µg/day, during 10 years of usage the kidneys will stop working. (Bahemuka *et al,*1998) .

Table 5. Comparison of lead entering the body µg/kg per week with standard PTWI

fruit	PTWI for children	PTWI for adult	pb entering the body of the week	% of PTWI for children	% of PTWI for adult
Malus domestica	375	1500	416	110	27
Elaeagnus angustifolia	375	1500	331	88	22
Pyrus communis	375	1500	250	66	16/6

In the present study the rate of tolerable weekly intake of pb was determined and just in apple tree, the rate of pb concentration was dangerous for children. In the long run, the usage of them will have terrible and dangerous side effects on body. Thus it is suggested that we should be cautious about eating the grown fruits in the neighborhood of industrial areas. Since the research was 20 years old trees, the concept of phytoremediation can be discussed. The results of the study showed that *Pyrus communis* can be regarded as the accumulator of Pb, Cd and Cr and *Malus domestica* and *Elaeagnus angustifolia* trees can be used as the accumulator of Cr in polluted areas because of pollution absorption by trees, the fruits of these trees can accumulate the metals. As a result, planting the trees in contaminated soil can probably increase the presence of poisonous metals in food chain which is regarded as a serious danger.

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