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## Study and Measurement of Heavy Metals in Soil and Irrigated Vegetables by Urban Wastewater: Khash city, Sistan and Baluchestan province, Iran

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#### Abstract

Soil and plant contamination by heavy metals have been studied and evaluated extensively in various countries of the world. These metals are first absorbed in the soil and then enter the plant, animal, and human bodies. The purpose of this study was to investigate the number of heavy metals (Cu, Cd, Pb, Mn) in soil and irrigated vegetables by urban wastewater: Khash, Sistan and Baluchestan.

The edible vegetables like garden cress (Lepidiumsativum) and parsley (Petroselinum crispum) and also soil for their plantation in villages around Khash city were sampled and examined a totally of 36 vegetable samples and 36 soil samples. The vegetable samples were dried in an oven at 105°C after transferring to the laboratory. Amount of heavy metal was read through two techniques of calibration and standard increase by flame atomic absorption device after acid digestion using standard solutions.

The mean concentration of lead, cadmium, manganese, and copper were obtained at 0.4654, 0.3715, 2.992, and 0.2590 in garden cress and 0.4333, 0.3123, 3.075, and 0.2655 (mg/kg of dry weight) in parsley, respectively. In addition, the mean concentration of lead, cadmium, manganese, and copper in garden cress soil were obtained at 0.4303, 0.5527, 15.78, and 0.6235 (mg/kg of dry weight), respectively and in parsley, the soil was obtained 0.3951, 0.5321, 11.000 and 0.55, respectively.

According to the findings of this study, heavy metals amounts (Cu, Cd, Pb, Mn) in the irrigated vegetable tissues by wastewater were higher than the standard level in this region.

Key words: Wastewater, Vegetables, Heavy metals, Environment.

#### Introduction

The quick growth of urban has increased wastewater production in cities at the same rate (1). The lack of proper urban infrastructures makes the great amounts of wastewaters penetrate uncontrolled and raw into water systems and pollute them (2). Population increase and following that needs an increase in the pure water attributed to most of the pure water resources to supply drinking waters. Meanwhile supplying water for agriculture faces a problem. This matter has made many regions use wastewater to irrigate their gardens (3). Although using wastewater for agriculture can be effective in the reduction of water consumption, nutrients recycling (NPK), and chemical fertilizers (4), there is always concern about gardens pollution and accumulation of hazardous pollutants such as cadmium, copper, iron, manganese, and zinc in edible plants and vegetables (3).

Heavy metals are significantly important for toxic properties and accumulation and are also long-lasting in alive organisms' bodies. Noncontrolling industries' wastes, releasing urban wastewaters, removal of hazardous wastes, and non-recycling them enter the great amounts of heavy metals into an aqueous environment in

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developing countries annually. This increase depends on the type and the characteristics of the used wastewater. The accumulation of heavy metals in the irrigated soils by wastewaters not only pollutes soil but also influences the safety and food quality of humans (5). When soil capacity reduces to hold heavy metals (for its increase in soil), heavy metal penetrates the underground waters or is released and defused as usable solutions for plant absorbance (6).

Soil and agricultural products pollution by heavy metals and their effect on human and plant health have been extensively studied and evaluated in various countries of the world. Meanwhile, elements of cadmium, lead. manganese, and copper are heavy metals that have been mentioned more. The effect of these metals on human health has been mentioned in many studies. A higher amount of copper irritates the nose and throat. If this metal enters the body as food, it brings nausea, vomiting, diarrhea, liver and kidney damage, and death (7). Cadmium and lead are also highly effective metals with defects in human health. The undesirable defects of cadmium include abdominal pain and severe vomiting, bone fracture, infertility, damage to the central nervous system, damage to the immune system and DNA, and psychological anomalies. Lead also makes disorders in the biosynthesis of hemoglobin and anemia, increased blood pressure, kidney damage, abortion, nervous system disorders, brain damage, male infertility, decreased learning ability, and behavioral disorders in children (8).

Fruits and vegetables after the grain are the most important element of the human nutritional diet. One important and effective factor to diagnose the health of vegetables is the concentrations of heavy metals in them. The pollution of vegetables by heavy metals can result from irrigation with wastewaters (9). Alyousef et al (2000) knew the increase of copper concentration in the soil as the main reason for getting thin, small, treating the roots, and wilting of buds in legumes, cereals, spinach, citrus, and lily (10). Fiddan et al (2007) noticed in their study that there is a strong relationship between elements movement in plants and their chemical properties. Manganese and cadmium are motive

and easily move through roots to aerial parts of plants, while copper and lead stay in roots (11).

The vast country of Iran face low water level like the other located countries in the earth dry ring, and big cities in Iran move toward using urban and industrial wastewaters to compensate for the great part of their need for water consumption. The long-term usage of these wastewaters enters heavy metals into the soil and transfers them to the plants higher than the limited standard level (12). Khash city with a 400-hectare vegetable cultivation area and 11 villages of the mentioned products are significantly important production and supplement of this product in the province. Lack of wastewater collection network in this city and using adsorbing well to collect wastewater and also the related problems to preparing the chemical and animal fertilizers and discharging domestic wastewater after drainage of wells and using the wastewater of these regions as fertilizer. This research was to evaluate the heavy metals in soil and irrigated vegetables of Khash city.

# Materials and Methods area of study

Khash city is one city of Sistan and Baluchestan that is limited to Zahedan from the north, Iranshahr city from the west and southwest, Saravan city from the south, and Pakistan from the east. This city is one of the oldest one in this province and has specific characteristics for its geographical situations of the central Baluchestan, Saravan city, and the capital of the province. The mean altitude of this city is 1410m and the mean annual rain is 153mm, the mean coldest month (January) is -6°C, and the mean warmest month (August) is 32°C.

## Sampling

Sampling was conducted from the agricultural lands of Abbasabad, Akbarabad, and Esmaeilabad villages with 35 out of 60, 45 out of 85, and 85 out of 120 hectares, respectively from March 2016 to April 2017 which were under the cultivation of vegetables. Generally, sampling was conducted on a vast 165hectare land. Based on the geographical situation of the mentioned villages, the agricultural lands of vegetables in each village were divided into two irrigated lands with well water and wastewater. In this region, 6 gardens were selected and samples of garden cress, parsley, and soil of the cultivation lands were selected as samples and put in the Polyethylene bags with specifications (sample type, sampling date, irrigation type, and sampling site) all samples were kept in 0-4 °C to arrive at the laboratory. The depth of soil sampling in the irrigated regions by well water and wastewater was 20-40 and 0-20 cm. generally, the put samples from all the studied regions were obtained 18 for 3 parts (soil, garden cress, and parsley) from each region (irrigated by well water and wastewater) that samples were combined and 9 samples from each one were taken for the high number of samples from each part.

Preparation and analysis of vegetable samples

The edible parts of the studied vegetables (parsley and garden cress) were separated, washed, and rinsed with distilled water in the oven at 105 C for 48 h. after drying samples, they were ground and passed through a 2 mm sieve.

For acid digestion of these samples, 5ml nitric acid and 3ml of 35% peroxide hydrogen were added per 0.5 g sample. Chemical materials were bought from German Merck Co. Samples were tittered with 50 mm deionized water after being put in a microwave for 30 min at 160 °C. Finally, the tittered samples were injected into the flame atomic absorption device (model: Nov AA 400 P) of Merck Co. to read heavy metals (cadmium, lead, copper, and manganese) by two techniques of calibration and standard increase.

Preparation and analysis of soil samples

Finally, sampling was generally obtained from 9 combined samples from the soil of each irrigated region by well water and wastewater. In the next step, the taken samples were dried in free air for 24 h (13). Then, samples were passed through 2 mm sieves to separate impurities. Then, 2 g of the tested samples were transferred inside the glass, and 15ml of 4n nitric acid was added to it. After a full mixture of samples in the glass, it was put in bath bain-marie in 80 °C for 12 h. after 12 h exposure to bain-marie, samples were passed through What man filter paper (42  $\mu$ ) and finally reached to volume and injected to flame atomic absorbance device (model: Nov AA 400 P) made in German by two calibration and standard increase techniques to read and measure heavy metals (cadmium, lead, manganese, copper). SPSS 16 and Smirnov-Kolmogorov, Duncan, variance, and Pearson analyses were used to analyze data.

#### **Results and Discussion**

The soil of the irrigated garden cress by wellwater has attributed the maximum mean heavy metals of cadmium, manganese, and copper, while the maximum mean lead was observed in garden cress treatment which was irrigated by well-water (Table 1). Later, Kolmogorov-Smirnov (KS) test was used in 0.05 sig. level to determine the normality of data. Results of this test showed that none of the measured parameters had a significant difference and the population distribution is normal (Table 2).

A significant difference was observed in lead concentration between the irrigated treatments by well water and wastewater, while a middle state was observed between the irrigated garden cress treatment by wastewater and well water and the irrigated parsley treatment by well-water from other treatments. No significant difference was observed between the irrigated garden cress soil treatment by wastewater and irrigated parsley by well water and wastewater (Fig 1a).

Cadmium bioaccumulation was observed between irrigated garden cress by well water and wastewater (Fig 1b). More explicitly, cadmium in garden cress tissue by wastewater was more than the irrigated one by well-water, but it was more in parsley in the irrigated treatments by wellwater. Statistics about the cultivation soil of these vegetables showed a significant difference between parsley and garden cress. In other words, the accumulated cadmium for both vegetables was less in the irrigated soil by wastewater than in well-water.

Comparing the mean manganese concentration among the test treatments showed that the accumulated concentration of manganese in the irrigated garden cress by well water and wastewater didn't have a statistical difference. On the other hand, a significant difference in manganese concentration was observed between the irrigated methods by well water and wastewater for parsley. Moreover, results about the cultivation soil of parsley showed that this element was higher in the irrigated treatment by well-water despite the significant difference between the irrigated soil by well and wastewater (Fig 1c). The accumulated copper concentration in the irrigated garden cress by well water and wastewater has a significant difference. This concentration was higher in the irrigated treatment soil by well-water than wastewater. Similar results were repeated for parsley vegetables and their cultivation soil (Fig 1d).

In this figure, numbers 1, 2, 3, and 4 represent cress irrigated with treated wastewater, cress irrigated with well water, cress soil irrigated with well water, and cress soil irrigated with treated wastewater), respectively. Also, numbers 5, 6, 7e, and 8 represent parsley irrigated with well water, parsley irrigated with treated wastewater, parsley soil irrigated with well water, and parsley soil irrigated with treated wastewater, respectively.

Table 1. The number of heavy metals in the vegetables and soil irrigated by well water and treated wastewater (mg/kg)

Experimental	Heavy metals (mean $\pm$ standard deviation) in mg/kg					
treatments	Pb (mg/kg)	Cd (mg/kg)	Mn (mg/kg)	Cu(mg/kg)		
*Cress	$0.002 \pm 0.47$	$0.37 {\pm} 0.007$	$2.99 \pm 0.29$	$0.26 \pm 0.011$		
**Cress	$0.021 \pm 0.46$	$0.39{\pm}0.21$	$2.67 \pm 0.26$	$0.245 \pm 0.12$		
*Cress soil	$0.44 \pm 0.01$	$0.58 {\pm} 0.002$	12.2±0.3	$0.66 \pm 0.15$		
**Cress soil	$0.43 \pm 0.01$	$0.55 \pm 0.05$	$15.7 \pm 0.85$	$0.62 \pm 0.02$		
*Parsley	$0.44{\pm}0.01$	$0.35 \pm 0.01$	$1.72 \pm 0.17$	$0.32 \pm 0.09$		
**Parsley	$0.43 \pm 0.01$	$0.31 \pm 0.01$	3.1±0.04	$0.26 \pm 0.02$		
*Parsley soil	$0.44{\pm}0.008$	$0.58 \pm 0.01$	$11.5\pm0.12$	$0.63 \pm 0.01$		
**Parsley soil	$0.39 \pm 0.008$	$0.53 \pm 0.03$	$11.1\pm0.55$	$0.55 \pm 0.06$		
Average	$0.44 \pm 0.02$	$0.46{\pm}0.1$	7.6±1.3	$0.44{\pm}0.2$		
* Irrigated with well water		** Irrigated with treated wastewater				

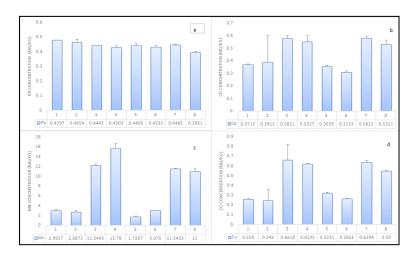


Fig 1. The concentration of studied heavy metals (lead, cadmium, manganese, copper) in each treatment

The obtained results from this research showed that the maximum mean amounts of heavy metals like cadmium, manganese, and copper were related to the irrigated garden cress soil by well-water, while the maximum mean amounts of lead were observed in the irrigated garden cress by well-water. Therefore, although the accumulation and bioaccumulation of lead and copper were more in irrigation by well-water than wastewater based on health (consumer), and environment (agricultural soil), the mentioned dangers for human and the environment necessitates the need to study the use of wastewater in agriculture of the studied region.

The present research showed that generally, the most important results danger by irrigation the vegetables and their cultivation soil by wastewater of Khash city than common water (well water) are as follows:

A) Bioaccumulation of cadmium in the vegetable plant of parsley B) Condensation of the manganese element in the vegetable soil of garden cress, C) bioaccumulation of manganese element in the vegetable tissue of parsley

This research was in agreement with the research of Koua et al. (2010) and confirmed the accumulation of heavy metals such as cadmium in the plant tissues, particularly their aerial organs. Cheraghi and Ghobadi (2013) in their research evaluated the health danger of heavy metals (cadmium, nickel, lead, and zinc) in cultivated parsley in gardens of Hamedan city. They showed in their research that the cultivated parsley in this region was polluted by cadmium. They claimed that cadmium metal transfer from soil to parsley is very simple and using this plant is not healthy for human daily consumption (14).

Cadmium absorption by plants and following that its entrance to the food chain depends on their adsorption in soil and factors such as pH, salinity, CEC, mineralogy, and organic materials (15). Plants can accumulate and store great amounts of cadmium in themselves without any problem. Cadmium accumulation in plants can increase the absorption potential of this element by a human, while these plants are a part of the human diet. Plants' ability to absorb, accumulate, store and bear cadmium is different (16). Davis et al. stated indexes of heavy metal pollution in their research as a product that lettuce, cress, and cabbage tend to store a great amount of cadmium, while potato, corn, bean, and pea store a little amount of it (17). It means cadmium absorption in leaf vegetables is relatively more than in root and tuber vegetables.

In addition, the obtained results for cadmium in this research were particularly similar to the obtained results from Borcett and Ferrousd (2003) (18); Van Lear (1998) (19), and Sergidara (2010) (20). The cadmium concentrations were higher than the standard level (WHO and EPA standards) in the vegetable's edible parts in the mentioned studies.

The obtained results from Runivasi et al. (2016) on heavy metals in various parts of some edible vegetables of Karaj city showed that manganese metal in leaves of spinach, lettuce, cabbage, and onions was more in their root and stem (21). Moreover, Akan et al. (2013) concluded in their research about metals of chrome, manganese, iron, lead, cadmium, and copper in the samples vegetables of Nigeria that leaves of cabbage, lettuce, onion, and spinach had higher than standard level (22). These results show the absorption and transfer of manganese metal on the aerial parts of this part. The obtained results from this research also refer to the high concentration of manganese metal in the edible parts (leaves) of this plant.

heavy metals		Pb	Cd	Mn	Cu
Parameters	Samples	36	36	36	36
Mean $\pm$ S.D	$0.44 \pm 0.02$		$0.46 \pm 0.11$	7.63±1.3	$0.44\pm0.2$
KS	0.73		1.01	0.13	0.14
Maximum	absolute	0.15	0.21	0.29	0.23
threshold	positive	0.15	0.18	0.29	0.23
Difference	negative	-0.108	-0.21	-0.21	-0.21
Sig.(2-tailed)		0.652	0.269	0.133	0.144

Table 2. Normality state of measured heavy metals

#### Conclusion

The irrigated garden cress by well-water and treated wastewater had the maximum and minimum lead amounts of 0.4797 and 0.3951 among the other treatments, respectively. Moreover, the maximum amounts for the other elements including cadmium, manganese, and copper in test groups of the irrigated parsley soil were recorded at 0.5822 mg/kg by well-water, 12.224 mg/kg for parsley by well-water, and 0.6618 mg/kg for the irrigated garden cress by well-water. This research showed that heavy metals amounts (cadmium, lead, manganese, and copper) in the irrigated vegetable tissues by wastewater are higher than the standard level in this region.

According to the WHO standard for cadmium and manganese heavy metals, their concentration in the irrigated garden cress and parsley by wastewater was more than the standard level, and it is suggested to prevent using wastewater in gardens. In addition, based on EPA standards for heavy metals of cadmium and manganese, the irrigated soil by wastewater showed higher than the permitted level of heavy metals of cadmium and manganese.

According to lead accumulation in the irrigated soil by wastewater, this element has no problem in agricultural soil and doesn't make an environmental problem for its accumulation as the last group has the minimum mean amount of this element and has a significant difference from other groups.

Finally, it can be claimed that no permission should be the sign to use wastewater before full pre-treatment of heavy metals by techniques of ultra-filtration because of the risk of accumulation of cadmium and manganese elements in agricultural soils of this region, and also the environmental risk of manganese accumulation in agricultural soils of this reign.

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