Contamination of barberry with heavy metals in the vicinity of Qayen Cement Company, Khorasan, Iran, in 2014: A Case study

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Abstract

Background: Soil pollution and accumulation of heavy metals in crops in industrial areas is one of the most important environmental issues threatening the life of plants, animals, and humans. The aim of this study was to determine the concentration of Cr and Cd in the soil and barberry plants in farms surrounding the Qayen Cement Company, South Khorasan Province, Iran.

Materials and Methods: In this study, 8 soil samples were collected from a depth of 0-30 cm and 30-60 cm and 4 samples of barberry plant containing fruits and leaves in summer 2014. The concentrations of Cr and Cd in the samples were determined using atomic absorption spectrometry.

Results: The maximum concentration of Cr and Cd was observed in the soil sample collected from a depth of 0-30 cm (95.10 and 1.32 mg/kg of soil, respectively). The concentration of Cr and Cd was higher in the fruits of barberry than the leaves; 18.58 mg/kg and 59.45 µg/kg, respectively, which are higher than the standard values. Transfer factor was calculated as less than 1 for all stations.

Conclusions: According to obtained results, Qayen Cement Company has the greatest impact on plants in this region. The barberry fruit is the strategic product in Qayen; therefore, attention to and management of the impact of the cement factory on agricultural products is necessary.

Keywords: Heavy Metals, Transfer Factor, Cement, Barberry

Introduction

Contamination of the environment by heavy metals is a major concern because of their toxicity and threat to human life and the environment (1-4). Cement factories have been reported as a major source of heavy metals emission into the environment with several reports showing higher concentrations of heavy metals in the vicinity of cement factories (5-9).

Contamination of the environment with many pollutants is one of the most significant problems in this century. Some metals such as Zn, Ni, and Fe are essential for metabolism in trace amounts. However, other nonessentials, such as As and Hg, have no biological role and are potentially toxic to living systems and they can be carried through soil–plant–animal–human cycles (10-12).

Generally, if the concentration of heavy metals in the soil increases, the amount available for the plants also increases (13). Some factors of importance in the determination of the amount of heavy metals uptake by plants include the chemical form of the element, heavy metal concentration, soil pH, and plant species (14).

The maximum amount of heavy metals are released into the soil via the use of sewage sludge in agricultural soils and human industrial

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activities such as paint, cement, rubber, soil phosphate fertilizer, fuel, and metal smelting industries (15).

Kabata and Pendias believe that a very small amount of heavy metals are absorbed from the soil by most crops (16). The uptake of heavy metals from polluted lands by plants, and especially agricultural products, is the most important issues in the food chain (16, 17).

A study conducted in Turkey showed that the concentration of Cr was higher in plants, soil, and blood of humans in areas surrounding the cement plant than others, showing the toxic effects of Cr (18).

Thus, the aim of this study was to determine the concentrations of toxic metals of Cr and Cd in the soil and the barberry plant farms around Qayen Cement Company, South Khorasan Province, Iran.

Material and Methods

Study area: Qayen city is located in the north of South Khorasan Province, with an area of 17,722 Km^2. Qayen is located within latitude of 33˚.43" and longitude of 59˚.11" and it is 1440 meters above sea level. The weather is strongly affected by mountains which surround this city. This area is a cold region in the Köppen climate classification and its dominant winds blow from the eastern region. The Qayen Cement Company is located 10 km from Qayen, on the road from Qayen to Birjand. The operation of the Qayen Cement Company began in January 1995. The products of this company include Portland cement type 1-325, type 1-425, type 2, type 5, and Pozzolanic Portland cement. Figure 1 shows the study area and the location of sampling stations.

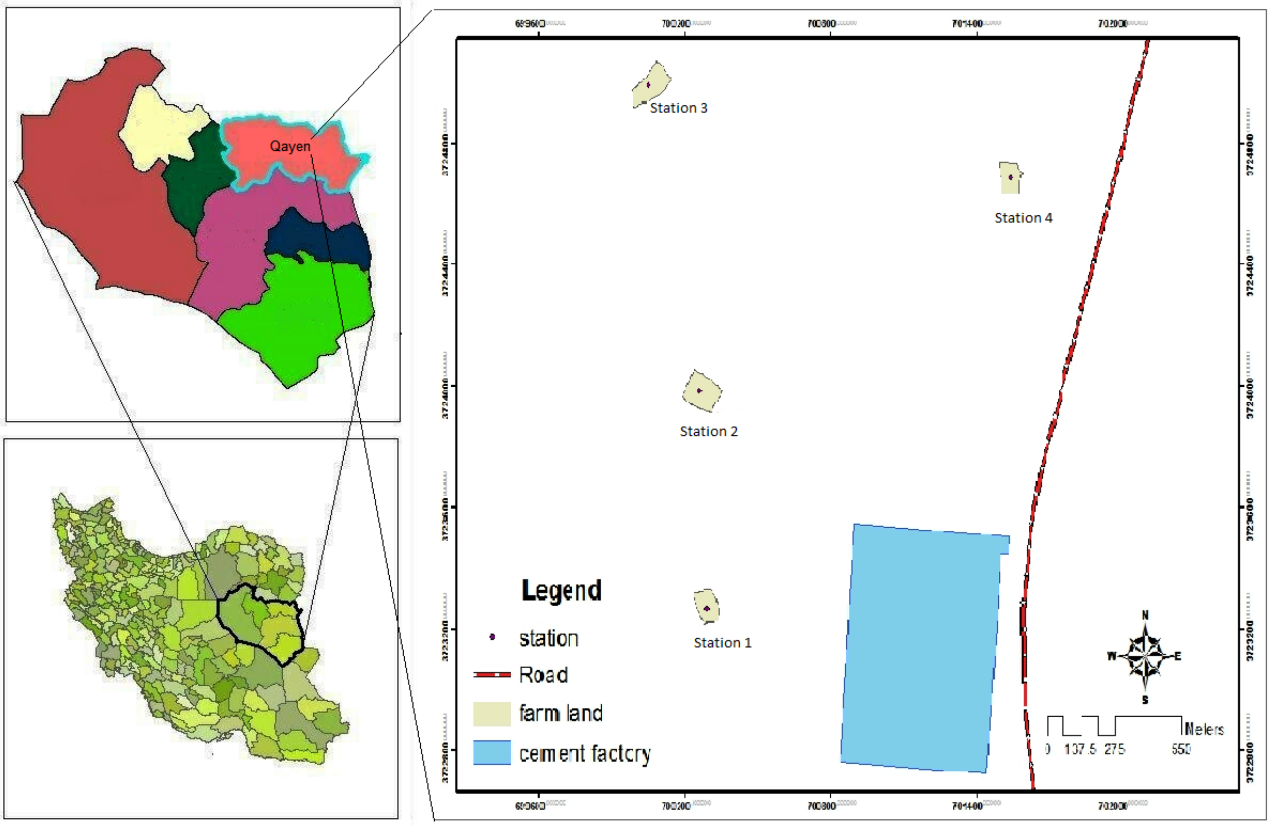

Figure 1: Map of the study area and sampling stations

Sampling: To check the status of heavy metals in 12 samples, a distance range of 500–800 meters around a cement plant was monitored in 2014. Thus, 8 soil samples were collected from around the Qayen Cement Company at two depths of 0-30 cm and 30-60 cm and 4 plant samples containing barberry fruits and leaves. Then, the samples were transported to the laboratory for further analysis. Containers and sampling equipment, sampling techniques, and maintenance, consolidation, and transmission of samples to laboratories were based on standard methods. The concentrations of heavy metals of Cr and Cd through chemical digestion were measured using atomic absorption spectrometry.

Plant analysis: Plant samples were washed thoroughly with deionized water to remove surface dust and soil, and further separated into roots, shoots, and leaves. The samples were then air-dried, chopped, and further dried for 24 hours in an oven at 70 ºC, and weighed using a balance with an accuracy of up to 0.001 g. The dried plant samples were finely ground, mixed thoroughly, and 1 g of the samples was digested in a borosilicate conical glass flask with 5:1 mixture of HNO_3 and $HClO_4$ (20) at 70–80 ºC on a hot plate. After digestion, the samples were placed in ambient air to cool. The samples were filtered using Whatman filter paper 0.45 µm and placed inside the box (19).

Soil analysis: Soil samples were prepared by air-drying, and then, passing samples through a 63 µm mesh (equivalent to a No. 230 sieve, ASTM E-11). About 0.5 g of the sample was placed in a beaker containing 5 ml of 3:1 HNO3 to HCl and covered with a watch glass. Subsequently, samples were heated until most of the liquid had evaporated, and allowed to cool before 3 ml of $HClO_4$ was added. The covers were replaced and the samples heated again until evaporation of most of the liquid. Finally, samples were cooled to room temperature before being filtered (20).

Transfer factor: The transfer factor (TF) is the motion of a heavy metal from the leaves to the fruit, which was assessed using the subsequent formula (21):

$$TF = [\text{Element of fruit (mg/kg)}/\text{Element of leaves (mg/kg)}] \times 100$$

A TF of less than 1 indicates that the metals are stored in the roots of the plant, and TF of higher than 1 shows translocation of metals to the shoots of the plant.

Statistical analysis: All the data were statistically analyzed using Excel and SPSS software (version 16, SPSS Inc., Chicago, IL, USA). Results were analyzed using descriptive and analytical statistics by box plot, and the Pearson coefficient was used to determine correlations between data.

Results

Descriptive statistics of total metal contents of the soil and plant samples are presented in tables 1 and 2. The presented results show that the highest mean concentration of Cr and also the maximum amount of Cr (95.10 mg/kg) was in the depth of 0-30 cm. In addition, the highest mean concentration of Cd and maximum amount of this metal (1.32 mg/kg) was at the depth of 0-30.

Table 1: Descriptive statistics of total metal contents of the soil of the study area

Depth (cm)	Cr (mg/kg)			Cd (mg/kg)		
	Maximum	Minimum	Mean ± SD	Maximum	Minimum	Mean± SD
0-30	95.10	52.10	72.48 ± 17.94	1.32	1.16	1.21 ± 0.07
30-60	68.75	22.29	35.56 ± 22.18	1.27	0.03	0.65 ± 0.58

Typically, the concentration range of Cd is 7-0.01 mg/kg and its limit of toxicity in the soil has been reported as 3 mg/kg (22). The results showed that with increasing of depth of soil, the concentration of Cd decreased, indicating non-leaching of Cd in the soil layer. The leaching of heavy metals was not possible in sub-soil layers due to presence of more than 40% limestone ($CaCO_3$) and alkalinity of soil. The maximum concentration of Cd in the depth of 30-60 cm was 1.27 that is less than the surface layer of the soil.

Table 2: Descriptive statistics of total metal contents of the plants of the study area

Plant	Cr (mg/kg)			Cd (µg/kg)		
	Maximum	Minimum	Mean ± SD	Maximum	Minimum	Mean ± SD
Barberry fruit	18.58	15.53	17.38 ± 1.31	59.45	30.44	41.87 ± 14.00
Barberry leaf	15.35	11.04	13.15 ± 2.13	30.49	21.46	26.29 ± 3.77

In the presented study, the transfer factor of Cr and Cd was measured at 4 stations. The results showed that the metals are stored in the fruit of barberry and the highest transfer factor was observed at the first station (Table 3).

Table 3: Transfer factor values for the measured heavy metals in plants in the study area

Station	Transfer factor (TF) Barberry leaf to fruit	
	Cr	Cd
1	0.87	0.84
2	0.61	0.51
3	0.74	0.69
4	0.78	0.58

The Pearson correlation coefficient can be used to measure the degree of correlation between the logarithms of the data on heavy metals (26). The correlation coefficient is presented in table 4. The results show a significant positive correlation between Cr and Cd in the fruit (P = 0.05) (r = 0.627). Furthermore, a significant negative correlation was observed between Cr and Cd in leaves (P = 0.01) (r = -0.699). Cd in the soil at depth of 0-30 cm had a significant positive correlation with Cr in the soil at depth of 0-30 cm and Cr in the soil at depth 30-60 cm (P = 0.05) (r = 0.955, r = 0.967). A significant negative correlation was observed between Cd in the soil (depth of 30-60 cm) and Cd in the fruit (P = 0.05) (r = -0.968).

Table 4: Pearson correlation coefficients of parameters under study

Metal	Cr in the fruit	Cr in the leaf	Cd in the fruit	Cd in the leaf	Cr in the soil at depth of 0-30 cm	Cr in the soil at depth of 30-60 cm	Cd in the soil at depth of 0-30 cm	Cd in the soil at depth of 30-60 cm
Cr in the fruit	1							
Cr in the leaf	0.129	1						
Cd in the fruit	0.627*	0.473	1					
Cd in the leaf	0.456	-0.699**	-0.186	1				
Cr in the soil at depth of 0-30 cm	0.489	0.575	-0.004	0.459	1			
Cr in the soil at depth of 30-60 cm	0.108	0.716	-0.498	-0.037	0.869	1		
Cd in the soil at depth of 0-30 cm	0.227	0.598	-0.284	0.181	0.955*	0.967*	1	
Cd in the soil at depth of 30-60 cm	-0.619	0.420	-0.968*	-0.775	0.204	0.654	0.481	1

* Correlation is significant at P = 0.05 (2-tail)

** Correlation is significant at P = 0.01 (2-tail)

Discussion

Cd has been reported to be released into the environment a result of raw material used in cement production (23), but generally at low concentrations (6).

In a previous study, the emission of heavy metals into the soil samples from the area surrounding the cement plant in the South of Jordan was demonstrated. The results showed that the mean concentration of Cr and Cd in 0-10 cm was 22.18 and 5 mg/kg, and at a depth of 10-20 cm was 6 and 2.18 mg/kg, respectively (24). Moreover, a research surveyed the pollution of soils by heavy metals in the area surrounding a cement plant and showed that the mean concentration of Cr and Cd was 83.2 and 0.9 mg/kg, respectively (24).

The amount of Cd in barberry fruit and leaf was higher than Cr. In addition, the accumulation of Cr and Cd was greater in barberry fruit than its leaves. The maximum concentration of Cd in the fruit of barberry was 59.45 μg/kg and the leaf of barberry was 30.49 μg/kg. The maximum concentration of Cr in the fruit of barberry was 18.58 mg/kg and its concentration in the leaves was 15.35 mg/kg. An investigation of the concentration of Cr in the soil and plants surrounding cement factories in Ardebil demonstrated that Cr concentration in grasses and shrubs was 7.21 and 12.08 mg/kg, respectively (25). As tables 1 and 2 show, the highest concentration of Cd was observed in the barberry fruit.The concentration of Cd was greater in the depth of 0-30 cm than the depth of 30-60 cm. The concentration of Cr was higher in the barberry fruit than barberry leaves and showed less changes compared to the amount of Cr in the soil. Cr changes range was uniform in the depth of 0-30 cm, but there was a greater range of change at the depth of 30-60 cm. Figure 2 shows more changes in Cd concentration in the fruit and leaves of barberry and soil at depth of 30-60 cm. Nevertheless, drastic changes were not observed in the soil at the depth of 0-30 cm in the stations. In the second station, the maximum concentration of Cd in barberry fruit and leaf was 59.45 and 30.49 μg/kg, respectively. In the first station, the concentration of Cd was lower in the soil; the maximum concentration of Cd in the depths of 0-30 and 30-60 cm was 1.32 and 1.27 mg/kg, respectively.

The maximum concentration of Cr in the barberry fruit was 17.97 mg/kg in the second station and in the barberry leaf was 15.35 mg/kg in the first station. In the first station, the maximum concentration of Cr was 95.10 and 68.75 mg/ kg in the soil samples from a depth of 0-30 and 30-60 cm, respectively. In the third station, the minimum concentration of Cr was 52.10 and 22.29 mg/kg in soil samples from depths of 0-30 and 30-60 cm, respectively (Figure 3).

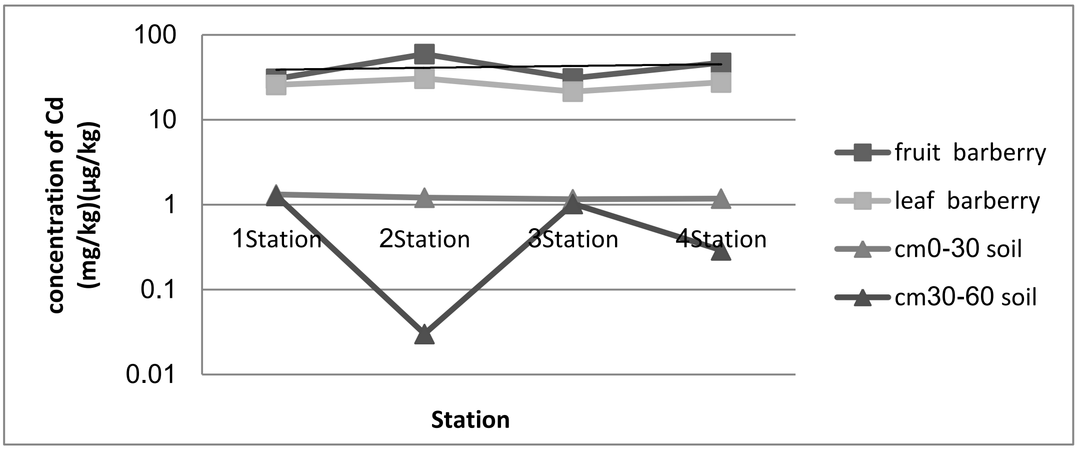

Figure 2: Comparison of Cd concentrations in plants and soil at different stations

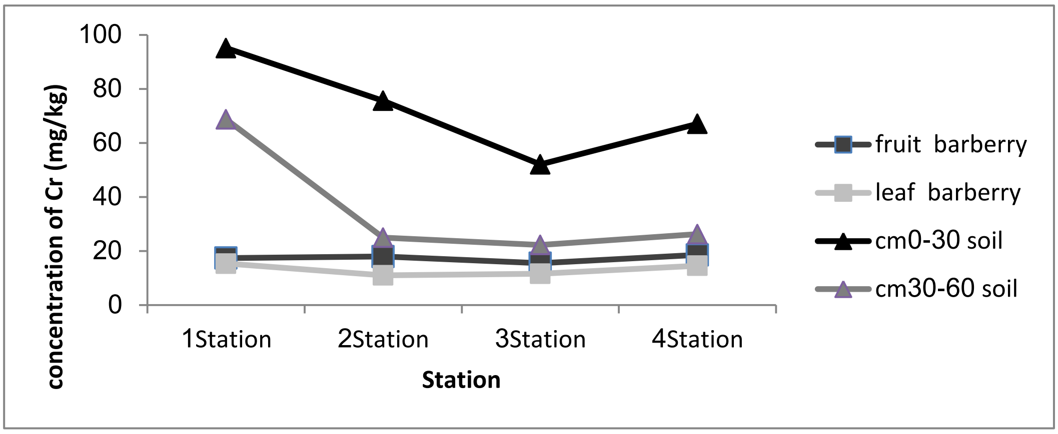

Figure 3: Comparison of Cr concentrations in plants and soil at different stations

In the present study, the lowest rate of absorption and accumulation of heavy metals belonged to Cd and the highest to Cr. Thus, the trend of the concentration change was relatively normal and predictable. The concentration of unhealthy elements such as Cd is generally lower in the environment, while the concentration of Cr is pronounced in the Earth's crust and it enters the environment and its concentration is increased through mining and cement production at different levels. The average concentrations of Cr and Cd were higher in the depths of 0-10 cm than 10-20 cm (26). The concentrations of Zn, Cr, and Pb were 132, 57, and 32 mg/kg, respectively, in soil samples collected from the area surrounding a cement plant (9). The reported concentrations are relatively high (9).

Mosavi at al., by calculating the correlation coefficient, showed that a significant correlation exists between heavy metals in all the sampling points, such as the Cr-Ni, Cu-Ni, Zn-Co, Cd-Cu, and Ni-Co correlations (27).

In the present study, a significant negative correlation ($P = 0.05$) ($r = 0.383$) was found between Cr and Cd in the soil samples from the area surrounding the mega cement plant by studying the correlation between different metals. Furthermore, the presence of Cd in the soil to some extent can the emissions from cement production and a significant correlation with Pb and Cu (28). The results of a study on heavy metal pollution in soil and plants in the vicinity of the cement plant in Volta Region, Ghana, showed a positive correlation between soil and plant samples (excluding Zn and Ni) through analysis of heavy metals in soil and plants. However, in the present study, a negative correlation was observed between the soil and plant samples (29).

Conclusion

The results obtained in this study illustrate that the concentration of Cd and Cr in barberry fruit of was higher than barberry leaves and their concentration was higher in 0-30 cm. Transfer factor for all stations was less than one. The concentration of Cd and Cr in the barberry plant was higher than standard levels, but their concentration in the soil was in the standard range. Thus, heavy metal pollution caused by Qayen Cement Company has the greatest impact on plants of the region, and since the barberry plant is a strategic product, necessary measures should be taken to reduce this pollution.

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Conflict of interest: None declared

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