Environmental Science and Pollution Research (2021) 28:44098–44110
https://doi.org/10.1007/s11356-021-13552-y

RESEARCH ARTICLE

Bioaccumulation of heavy metals in *Stachys inflata* and *Scariola orientalis* affected by particulate matters of a cement factory in central Iran

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Received: 2 December 2020 / Accepted: 16 March 2021 / Published online: 12 April 2021

Abstract

Industrial activities can affect accumulation of pollutants (e.g., heavy metals (HMs)) by plants and influence their entrance to the food chain. This research was carried out on accumulation of HMs including chromium (Cr), lead (Pb), and zinc (Zn) by two plants *Stachys inflata* and *Scariola orientalis* grown in natural grasslands in vicinity of a national park where they are influenced by dispersion of particulate matter (PM) through Sarooj Cement Factory in central Iran. The PM spatial dispersion of the factory was determined using the AERMOD model. Soil and vegetation samples were collected based on the modeled PM levels to analyze their HM contents. Bioconcentration factor (BCF) and transfer factor (TF) from root to shoot were determined in two widespread plants of the region: *Stachys inflata* and *Scariola orientalis.* The mean concentration of HMs in the soil samples was as follows: Zn (145.39 mg/kg) > Pb (78.52 mg/kg) > Cr (32.69 mg/kg) which was significantly correlated with simulated PM concentrations. This indicated the common source and distribution pattern of HMs which affected their accumulation in plants. TF and BCF values of the HMs were higher in *Scariola orientalis* than those of *Stachys inflata*, especially for Cr showing potentially higher risk to enter the food chain. The results showed that HM concentration in the soil as well as their accumulation by plants were correlated with the simulated PM deposition and not with linear distance from the factory.

Keywords AERMOD · Pollution · *Scariola orientalis* · *Stachys inflata* · Bioconcentration factor

Introduction

The environmental, ecological and health risk of heavy metal (HM) contamination is a serious growing global concern due to the toxicity of their excess levels which impairs the functioning of living organisms through bioaccumulation (Khan et al. 2015). To cope with such a concern, the first step is to determine the (mostly human-induced) sources and distribution pattern of HM contamination in every subsystem of the affected ecosystems like air, soil, and living organisms (Luo et al. 2019). This undertaking, however, has proven to be a tantalizing task. Even if emissions come from a point source, the dynamic characteristics of some intermediate subsystems, such as air and water, may obscure our understanding of the transference and distribution pattern of contamination into other parts (Wang et al. 2018; Liu et al. 2017). For instance, the concentration of particulate matter (PM)–bond HMs emitted from an industrial stack into air and their descent on soil may not necessarily diminish with increasing distance from the source, but may vary significantly depending on the characteristics of the region and the emitting source (Moreno-Silva et al. 2020; Soleimani et al. 2018; Tartakovsky et al. 2016; Gibson et al. 2013). In such a particular case, atmospheric dispersion modeling has proven a powerful means for simulating the distribution and variability of atmospheric components such as gases and aerosols from one or more emitting sources. For instance, Mousavi et al. (2014) assessed PM dispersion from a cement factory in Shahrood, Iran, using the AERMOD model, finding that the specific location of the factory in the foothills of a mountainous area resulted in a very

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uneven dispersion of PMs and targeted locations for establishing emission controlling plants. Prevailing wind is playing a key role in the dispersion of PMs to the surrounding environment from cement factories. Khaniabadi et al. (2018) stated that levels of PM concentration in downwind of a cement plant were higher than those in the upwind. The spatially uniform dispersion of air pollutants from cement stacks was also documented by other studies in this field (Seangkiatiyuth et al. 2011; Abu-Allaban and Abu-Qudais 2011; Noorpoor and Rahman 2015; Balter and Faminskaya 2017), corroborating the fact that the dispersion and, more specifically, air-to-soil transference of pollutants are complex processes of many environmental drivers, especially wind direction, topography, and the characteristics of emission source(s).

As a state-of-the-art modeling system, the AERMOD has seen a surge of popularity in modeling the dispersion of various atmospheric pollutants like SO_2 and sulfur hexafluoride (SF_6) (Thepanondh et al. 2016; Langner and Klemm 2011), NO_2 (Panek et al. 2020), PMs (Michanowicz et al. 2016), and hydrogen cyanide (HCN) (Seangkiatiyuth et al. 2011). Essentially, the AERMOD is devised to simulate atmospheric dispersions across short spatial distances not exceeding 50 km by assuming that the vertical and horizontal concentration distributions follow Gaussian distributions and plume flow is either impacting and/or following the simple topographical regime of the terrain (Cimorelli et al. 2005). The AERMOD model is a useful tool to determine the concentration level of pollutants in nearby exposed communities such as plant communities, and different land uses (Adeniran et al. 2018). Therefore, this can assist the spatial tracking and biomonitoring of the pollutants released from the stacks of the factories.

A scholarly attention has been also focused on the routes through which HMs move from soil to roots and aboveground parts (i.e., shoot) of plants. Soil acts as geochemical sinks of HMs by controlling the transport of contamination to other components of the biosphere such as water, air, and plants (Overesch et al. 2007). Plants themselves also respond differently to elevated levels of HMs, indicating that the mobility of HMs from soil to living organisms (started by vegetation) rests on physico-chemical properties of soil and characteristics of target species (Jambhulkar and Juwarkar 2009; Wisłocka et al. 2006). For instance, increasing of soil pH can reduce the uptake of some essential micronutrients such as Fe, Mn, Cu, and Zn (Adamczyk-Szabela et al. 2015; Fässler et al. 2010; Aisien et al. 2010). Moreover, the toxicity and bioavailability of HMs vary largely depending on certain characteristics of soil including organic carbon content, type and amount of clay minerals, soil solution properties (e.g., ionic strength and pH), and phosphate and lime content which may affect plant diversity (Huang et al. 2020).

Understanding the HM mobility between these components (air-soil-plant) has significant management and conservation implications to clean up the environment from toxic HMs (Oves et al. 2012). In cement manufacturing, particularly, large amounts of combusted fossil fuels and dust stemming from processing of raw material are emitted into the atmosphere where the released PM-bond HMs can be carried over large distances before descending to the soil surface. The cement manufacturing facilities have extremely high potential to pollute the environment (Isikli et al. 2003). They contribute to dispersing a wide variety of HMs depending on the type of fossil fuels used to heat raw materials (limestone and clay) up to 1200–1500 °C (Cutillas-Barreiro et al. 2016). Many environmental pollutants also come through other cement-related processes such as quarrying mine stones, grinding and transportation of raw materials, packaging, and dispatching the final product (Cutillas-Barreiro et al. 2016; Sikkema et al. 2011). The primary concern regarding cement manufacturing, however, may be related to the risk of large-scale HM contamination such as mercury (Hg), copper (Cu), chromium (Cr), cadmium (Cd), nickel (Ni), manganese (Mn), lead (Pb), iron (Fe), and chromium (Cr) associated with the released PMs.

Given the significant contribution of cement factories in HM contamination through the air-soil-plant cycle, this study employed a coupled modeling-measurement approach to track HM emissions from a cement factory in the central arid part of Iran (located in the immediate vicinity of two important protected areas) from air to soil and plants. Specifically, the spatial dispersion of PMs emitted from Sarooj Cement Factory was done using the AERMOD model (Cimorelli et al. 2005). We measured the concentration of three heavy metals including chromium (Cr), zinc (Zn), and lead (Pb) in soil and plant tissues (root and shoot) of two abundant plant species (i.e., *Scariola orientalis* and *Stachys inflate*) in the study area. Here, the correlation of soil HMs content with PMs concentration dispersed from the cement factory was evaluated to clarify the translocation of HMs to the plants in the ecosystem surrounding the potential pollution source.

Materials and methods

Study area

Sarooj Cement Factory with a total area of 1974 m^2 is located in central Iran (32° 59′ N, 50° 59′ E; 1992 m a.s.l.) and restricted to the Ghamishlo Protected Area in the west and Palang Galoon in the north (Fig. 1). This factory has been in operation since 2004 and has the capacity to produce 2000 tons clinker per day and 600,000 tons each year. The factory is established in Mehrdasht district located in Najafabad Township, Isfahan Province which has a good accessibility to the main roads of central Iran.

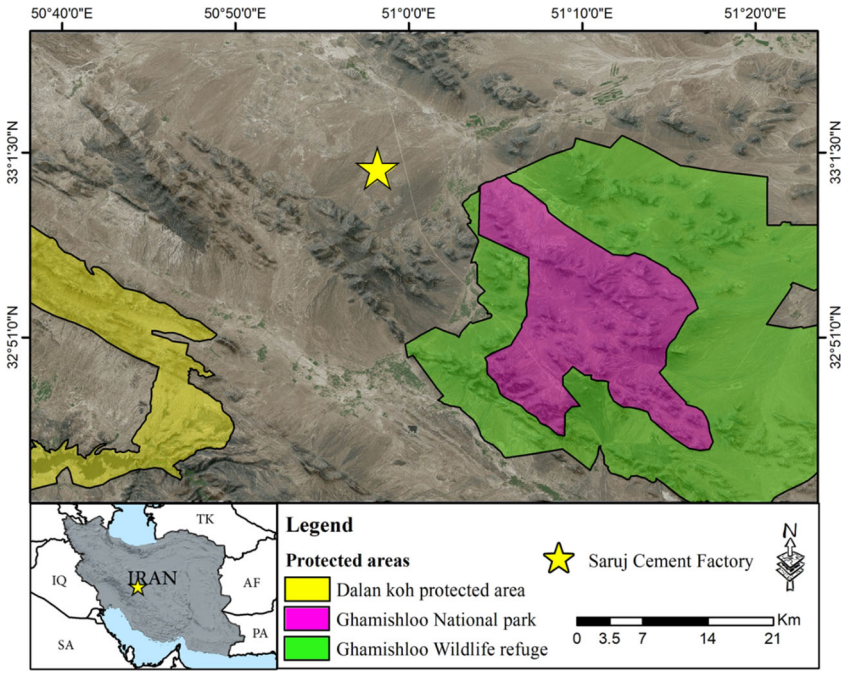

Fig. 1 Geographic location of Sarooj Cement Factory

Dispersion modeling of PMs using AERMOD

We used the American Meteorology Society-Environmental Protection Agency Regulatory Model, known as AERMOD (v. 8.1.0) (Lakes Environmental Software, Waterloo, Ontario, Canada), to simulate the spatial distribution and variability of PMs released from the cement factory. The AERMOD utilizes a meteorological (AERMET) and a terrain (AERMAP) processor to provide the AERMOD Gaussian Plume Model with appropriate input data. Three types of data were used in the process of PM dispersion using the AERMOD model as *Elevation data*, *Meteorological data*, and *Emission Source data*. In order to calculate the concentrations at receptors positioned at locations with varying elevations, the ASTER 30 m digital elevation model (DEM), downloaded freely from the USGS Earth Explorer system, was supplied to AERMAP to produce a representative terrain-influence height (also known as or hill height scale) and elevation (above mean sea level) for each receptor. To develop meteorological inputs for the AERMOD, AERMET was fed with two types of data. Hourly meteorological standard data including wind speed, wind direction (Fig. 2), temperature, air pressure, relative humidity, and cloud coverage were obtained from Isfahan Weather Forecast Organization (http://www.esfahanmet.ir) in 2017. To calculate hourly boundary layer parameters including Monin-Obukhov length, convective velocity scale, temperature scale, mixing height, and surface heat flux, we used upper air radiosonde data—Isfahan 2017 (https://ruc.noaa.gov/raobs). The source data including PM emission from two stacks as Grate Cooler and Cooling Fan (Table 1) were obtained from the Monitoring Laboratory of the cement factory. The emission source parameters of two stacks (as point sources), used in the dispersion model, were stack coordinates, stack elevation (m), stack height (m), inner diameter of the stacks (m), emission velocity (m/s), emission rate (g/s), and emission temperature of a stack (°C). Having terrain and meteorological data processed by AERMAP and AERMET and emission source data, the simulation was carried out under a complex terrain with a grid spacing of 1000 m with 94×94 receptor grids for 24 h and annual intervals.

Soil and plant sampling

In this research, we applied an innovative systematic-random sampling procedure instead of dividing the study area into strata based on linear distance and assigning a number of sample points to each stratum. As dispersion of PMs, this matter is related to various conditions such as meteorological, topographical, and emission source characteristics and not only related to the linear distance from the emission source. Therefore, we, first, simulated the PM dispersion from Sarooj Cement Factory using the AERMOD. Then, we classified the output map of the AERMOD model into 8 classes based on PM concentrations (Fig. 3). In total, 36 sampling points (a number of 4, 4, 6, 6, 9, 3, 2, and 2 points to classes 1–8) were assigned based on the area of the class through a random procedure.

Two abundant plant species including *Scariola orientalis* and *Stachys inflata* in the study area were selected which are found ubiquitously in the Iranian central arid landscapes. Both plant species and not protected, *Scariola orientalis* (Asteraceae, 15–25 cm) and *Stachys inflata* (Labiateae, 15–

Table 1 Emission source parameters of the Grate Cooler and Cooling Fan

Stack name	Stack elevation (m)	Stack height (m)	Inner diameter of stack (m)	Emission temperature (°C)	Emission velocity (m/s)	Emission rate (g/s)
Grate Cooler	1979	110	2.5	198.6	9.27	0.0034
Cooler Fan	1979	90	0.3	118.2	12.02	0.0056

40 cm) are perennial herbs (Ghahreman 2008). Previous studies stated the high potential of HM accumulation by tissues of *Scariola orientalis* (Rajabzadeh et al. 2015; Ghaderian and Ghotbi Ravandi 2012; Chehregani et al. 2009) and *Stachys inflata* (Rasti et al. 2020; Mahohi and Raiesi 2019).

However, 72 plant samples were collected (36 samples for each species) from and disturbed in the area affected by anthropogenic activities such as Sarooj Cement Factory. The sampling sites were not located in the protected area; therefore, there was no special permission needed. The formal identification of the samples has been undertaken by a colleague from the Department of Natural Resources, Isfahan University of Technology, based on a field study and using the national guideline of "Flora of Iran" (Ghahreman 2008).

Plant samples of three randomly selected individuals were collected within a 10×10 m plot placed around each point. In total, 36 soil composite samples were also collected as close to the root of the species from a 0–30-cm soil layer. The samples were transferred to a laboratory under controlled conditions (temperature <4 °C). The collected soil samples of each point were ultimately mixed to obtain the maximum homogeneity.

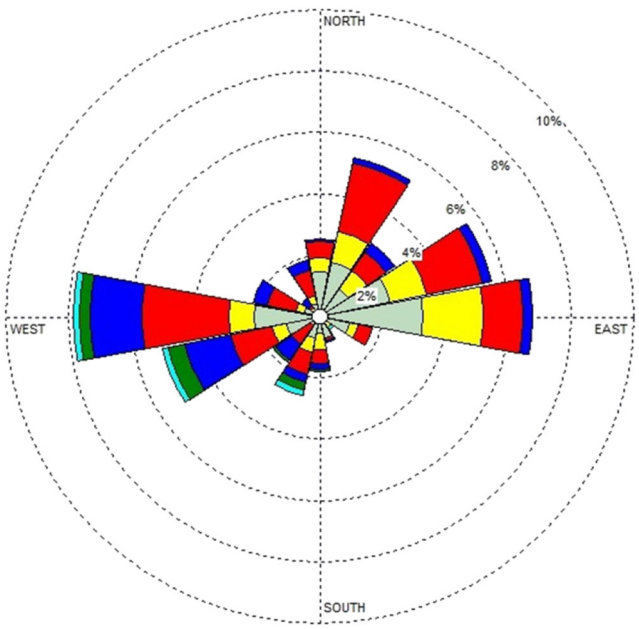

Fig. 2 The wind rose showing the annual prevailing wind in the study area in 2017

Heavy metal analysis

In the laboratory, soil and plant samples (note that root and shoot were analyzed independently) were air-dried, pounded, passed through a 2-mm sieve, and dried in an oven for 24 h at 100 °C. Subsequently, 1 g of each oven-dried sample was digested using 10 mL of aqua regia (1:3 nitric acid (65%, Merck, Germany) to hydrochloric acid (37%, Merck, Germany) at 100 °C for 3 h. After cooling down to the room temperature, samples were diluted to 25 mL with distilled water and then centrifuged at 2000 rpm for 5 min. The resulting extracts were then kept in a refrigerator prior to measuring HM concentration using the flame atomic absorption spectroscopy instrument (PerkinElmer, AAnalyst 700). As mentioned in the "Introduction" section, the type and concentration of aerosol-bound heavy metals emitted from cement factories are highly variable and depend on the type of fuel and raw materials used in the clinker manufacturing process. Hence, we first obtained a sample from dust aerosols emitted from the factory to characterize the contribution of different heavy metals in advance using the same method as above, thus, selecting which ones to focus on. Three elements including Cr, Pb, and Zn were selected for analysis of the soil and plant samples because their concentrations were found to be the highest in the dust sample (Table 2) while their concentrations were naturally low in the soils of the region as compared to those of Fe, Al, and Mg. In addition to HMs, pH and electrical conductivity (EC) of the soil samples were measured in a 1:2.5 soil-water suspension (Kim et al. 2016), organic carbon (OC) by the Walkley-Black Method (FAO 2019; Enang et al. 2018), and $CaCO_3$ content by the acid-base titration method (Pértile et al. 2017).

Bioconcentration and transfer factors

Bioconcentration factor (BCF) and transfer factor (TF) were used to account the potential HM soil-to-plant transfer as well as root-to-shoot translocation, respectively. BCF was determined by dividing HM content in plant tissues (root and shoot) to HM content of the soil. This factor is also a useful means of measuring the plant potential as bio-indicator. TF is a common coefficient used to investigate the mobility of HMs through plants and can be determined by dividing HM concentration in shoot to of root (Soleimani et al. 2010). These

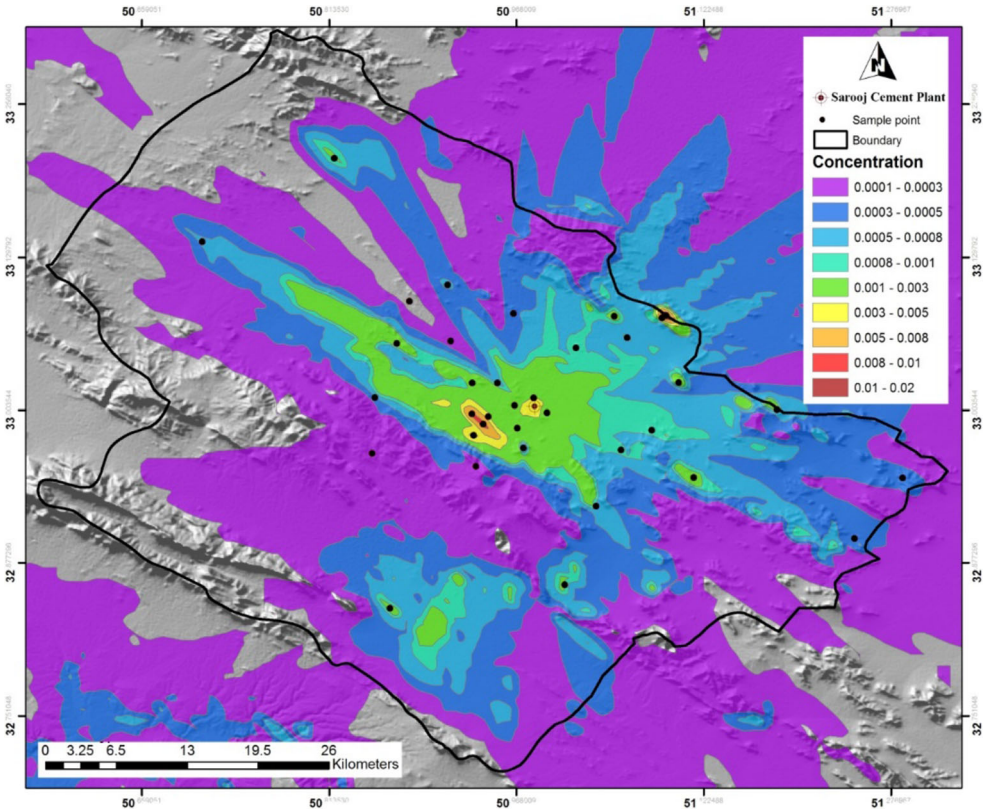

Fig. 3 Distribution and variability of PM concentration modeled using AERMOD as well as the soil and plant sampling points (black circles) in the study area. In total, 36 points were assigned to 8 classes of PM concentrations as 4, 4, 6, 6, 9, 3, 2, 2 points to classes 1–8 (from the lowest to the highest PM concentration), respectively

two indices were applied in this research to understand how metals distributed around the factory can be transferred into the plant tissues.

Statistical analysis

The central tendency index of mean and dispersion indices such as standard deviation, coefficient of variation, and measures of skewness were calculated to describe the resulting data. The normality of data distribution was tested by interpretation of skewness and kurtosis whose values should range between −2 and 2 to confirm the normal distribution of data (Tong 2012). The Pearson and Spearman correlation tests (de Winter et al. 2016) were applied on normal and non-normal data to determine the strength of the association between the modeled distribution of PMs and the concentrations of HMs at the location of the sampling points. We standardized the data prior to correlation tests by subtracting each value from the mean of the sample, then, dividing it by the standard deviation. We also included the distance from the factory to investigate whether the concentration of HMs decreases significantly with increasing the distance from the factory. The mean data were compared using Tukey test ($p<0.05$) by Minitab 16.

Results

PM dispersion surrounding the cement factory

According to the AERMOD modeling results (Fig. 3), the PM emission concentration was maximum around the factory and decreased outwards especially towards the eastern parts where topography is mostly flat. The influence of complex topographical features on PM dispersion was more evident in the southwest of the factory where long and narrow mountains block the uniform southwesterly flow of PM dispersion from the factory. Such topography created another distinct PM hotspot in the south by allowing the air and emissions to accumulate and pass through a narrow passage into a relatively plain region surrounded by mountains.

Table 2 Metal concentrations of deposited dusts of Sarooj Cement Factory

Metal	Cd	Co	Cu	Cr	Pb	Zn	Mn	Mg	Al	Fe	Ca
Concentration (mg/kg)	4.25	7.47	21.47	34.47	40.85	110.92	893.7	19927.5	30875	41825	401250

Table 3 Selected chemical characteristics of the soil samples

	pH	EC† (μS/cm)	OC†† (%)	$CaCO_3$ (%)	Cr (mg/kg)	Zn (mg/kg)	Pb (mg/kg)
Min	7.1	456	0.8	18.38	15.07	124.13	53.14
Max	8.6	1195	2.83	27.80	64.01	171.15	112.14
Mean	7.6	782.3	1.44	22.7	32.69	145.39	78.52
Std.	0.3	136.1	1.13	3.47	12.59	13.47	13.92
Skewness	1.00	0.72	0.71	0.46	0.43	−0.06	0.26
Kurtosis	1.11	2.66	0.72	−1.30	−0.68	−1.14	0.02

† Electrical conductivity

†† Organic carbon

Selected soil chemical characteristics and heavy metal concentration of soil and plants

The pH of the soil samples ranged from 7.1 to 8.6, with a mean value of 7.6. The mean (± standard deviation (SD)) EC and calcium carbonate percentage were 782.3 ± 0.17 μS/cm and (22.7 ± 0.15) %, respectively (Table 3). The mean concentrations of HMs in the soil samples were as follows: Zn (145.39 mg/kg) > Pb (78.52 mg/kg) > Cr (32.69 mg/kg) (Table 3). Cr had the widest range of change (SD of 0.39) with a minimum and maximum of 15.07 and 64.01 mg/kg, respectively, while Zn concentration ranging from 124.13 to 171.15 mg/kg was distributed in a higher concentration than that of the other ones across the region. The concentration of Pb ranged between 53.41 and 112.14 mg/kg (SD of 0.18). Figure 3 shows the spatial distribution of the concentration of HMs in the soil samples surrounding Sarooj Cement Factory. It indicated that HMs were not distributed uniformly

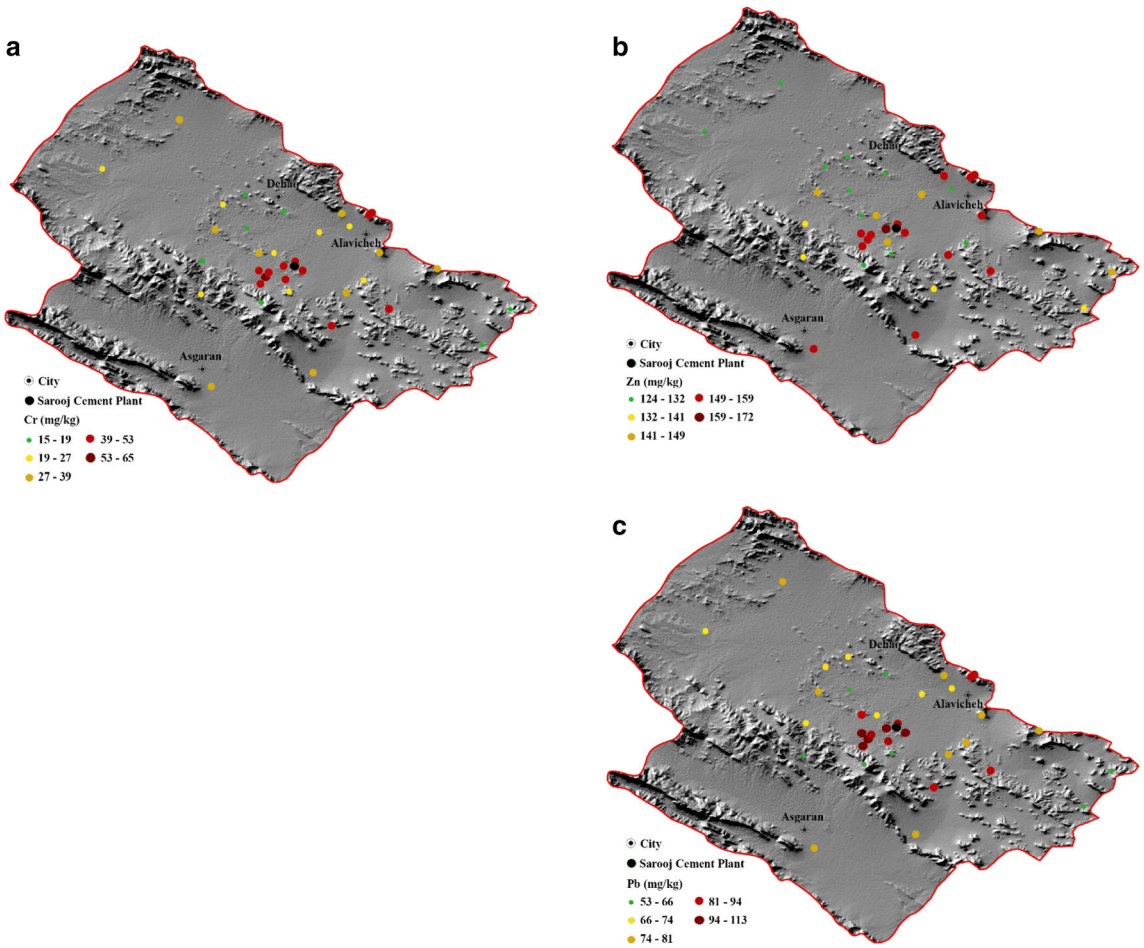

Fig. 4 Spatial distribution of the soil metal contents including Cr (**a**), Zn (**b**), and Pb (**c**) in the sampling points affected by Sarooj Cement Factory

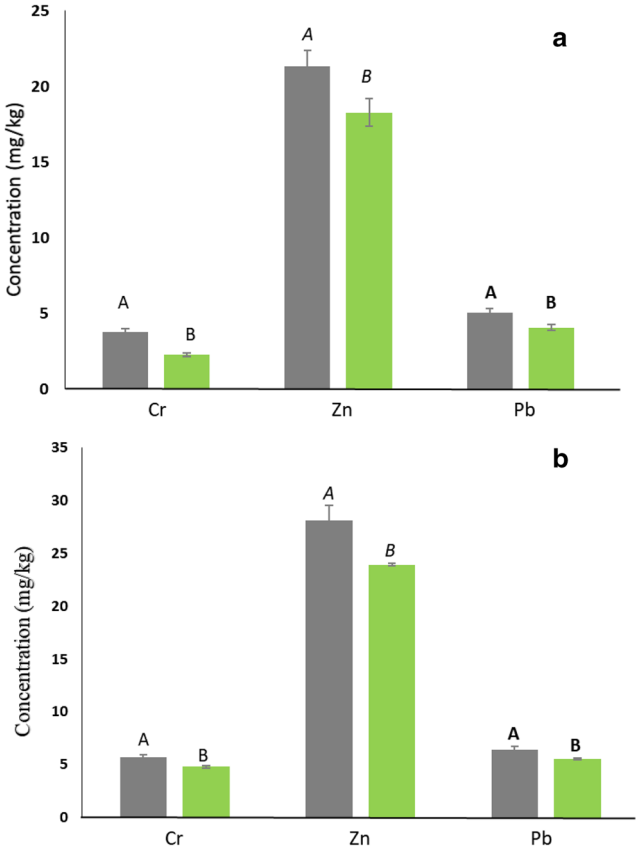

Fig. 5 Heavy metal accumulation in root (grey color) and shoot (green color) tissues of *Stachys inflate* (**a**) and *Scariola orientalis* (**b**). Different letters mean significant difference (p<0.05) for each metal

across the surrounding area. The concentration of HMs was not correlated with the distance from the factory, although those concentrations were higher in the vicinity of the factory. The results showed that the distribution pattern of the HMs in the soil was not uniform where Zn was distributed in farther distances followed by Pb. However, the spatial distribution of the HMs in the soil surrounding the factory followed the pattern of the simulated PM deposition (Figs. 3 and 4) where the concentration in vicinity of the factory was the highest.

The mean concentration of Zn was also the highest in the biomass of both plant species, followed by Pb and Cr. The reason could be the role of Zn in plant growth which is considered as an essential micronutrient; whereas, the other elements do not have such a role. All the investigated metals were accumulated in the root of both plant species (*Scariola orientalis* and *Stachys inflate*) higher than that of the shoot (Fig. 5).

The results of TF and BCF values are shown in Table 4. TF values of the three metals were higher in *Scariola orientalis* than that of *Stachys inflata*, especially for Cr levels in which the TF value of *Scariola orientalis* was nearly 30% higher than that of *Stachys inflata*. In terms of Zn, both species performed almost equally with TF values about 0.9 which were the highest in comparison to the values of the other elements. BCF values of *Scariola orientalis* were notably higher than that of *Stachys inflate, particularly for Cr and Zn elements*. Among the metals, as a plant nutrient, Zn showed the highest concentration in both plant tissues.

The results of Pearson's correlation test, which was selected based on the normal distribution of HMs concentrations, showed that the relationships in HM concentrations between plant species and the soil samples (Table 5) were all statistically significant ($p < 0.01$). Pb and Cr had the strongest correlation coefficient ($p < 0.01$) of the relationship between *Stachys inflata* and *Scariola orientalis* and the soil samples, respectively, while the weakest significant relationship was related to Zn for both *Stachys inflata* and *Scariola orientalis* ($p < 0.01$) species. The relationship between HM concentrations and the soil properties was tested using Spearman's test for EC because of its non-normal distribution and Pearson's for the remaining normally distributed soil variables (Table 5). In the soil samples, the strongest relationship was observed between pH and Cr ($p < 0.05$). In the plant species, the strongest relationship was observed between EC and Pb in *Stachys inflata* ($p < 0.05$) and between EC and Cr in *Scariola orientalis* ($p < 0.05$). Irrespective to the soil and species, the strongest relationship of HM concentrations with pH and EC was related to Pb and Cr ($p < 0.05$), respectively. The relationship of the lime percentage was the highest with Cr in the soil and with Zn in both species ($p < 0.05$) while the lowest relationships were related to Pb in the soil and *Scariola orientalis* and Cr in *Stachys inflata* ($p < 0.05$). The highest relationship of OC was with Cr in the soil ($p < 0.05$) and with *Scariola orientalis* and with Pb in *Stachys inflata* ($p < 0.05$).

Figures 6 and 7 show the spatial distribution of the HM concentration in the biomass of *Scariola orientalis* and *Stachys inflata* growing in neighboring of Sarooj Cement

Table 4 The contents of Cr, Zn, and Pb, and the values of transfer factor (TF) and bioconcentration factor (BCF) of the studied plant species. Data represent mean±SD

	Scariola orientalis			*Stachys inflata*		
	Cr	Zn	Pb	Cr	Zn	Pb
Plant content (mg/kg)	10.49±2.49	52.07±9.88	11.95±3.43	6.02±1.43	39.61±9.79	9.11±2.49
TF	0.88±0.24	0.88±0.25	0.89±0.25	0.62±0.21	0.87±0.20	0.86±0.34
BCF	0.35±0.05	0.36±0.05	0.15±0.03	0.20±0.06	0.27±0.06	0.12±0.02

Table 5 Correlation of the selected soil characteristics with heavy metal contents of the plants

		Scariola orientalis			*Stachys inflata*		
		Cr	Zn	Pb	Cr	Zn	Pb
Soil	Cr	0.76**	0.71**	0.84**	0.63**	0.74**	0.77**
	Zn	0.61**	0.59**	0.69**	0.55**	0.52**	0.65**
	Pb	0.68**	0.66**	0.80**	0.56**	0.63**	0.69**
	pH	0.70**	0.61**	0.72**	0.56**	0.65**	0.63**
	EC	0.42*	0.24^{ns}	0.44*	0.40*	0.34 ^{ns}	0.22 ^{ns}
	$CaCO_3$	0.82**	0.84**	0.69**	0.27 ^{ns}	0.63**	0.49 *
	Organic carbon	0.83**	0.74**	0.79**	0.49 *	0.65**	0.71**

*Significant at $p<0.05$

**Significant at $p<0.01$

ns: not significant

Factory, respectively. It shows that similar to the soil, HM accumulation by plants does not uniformly occur across the factory surrounding. Although the accumulation of HMs by the plants in the vicinity of the factory was higher than that of the distant points, their spatial distribution was correlated to the simulated PM deposition and not to the linear distance from the factory. The results showed that the bioaccumulation pattern of the HMs by the plants was not uniform across the area surrounding the factory. As Figs. 6 and 7 show, both plant species had higher HM accumulation in the vicinity of

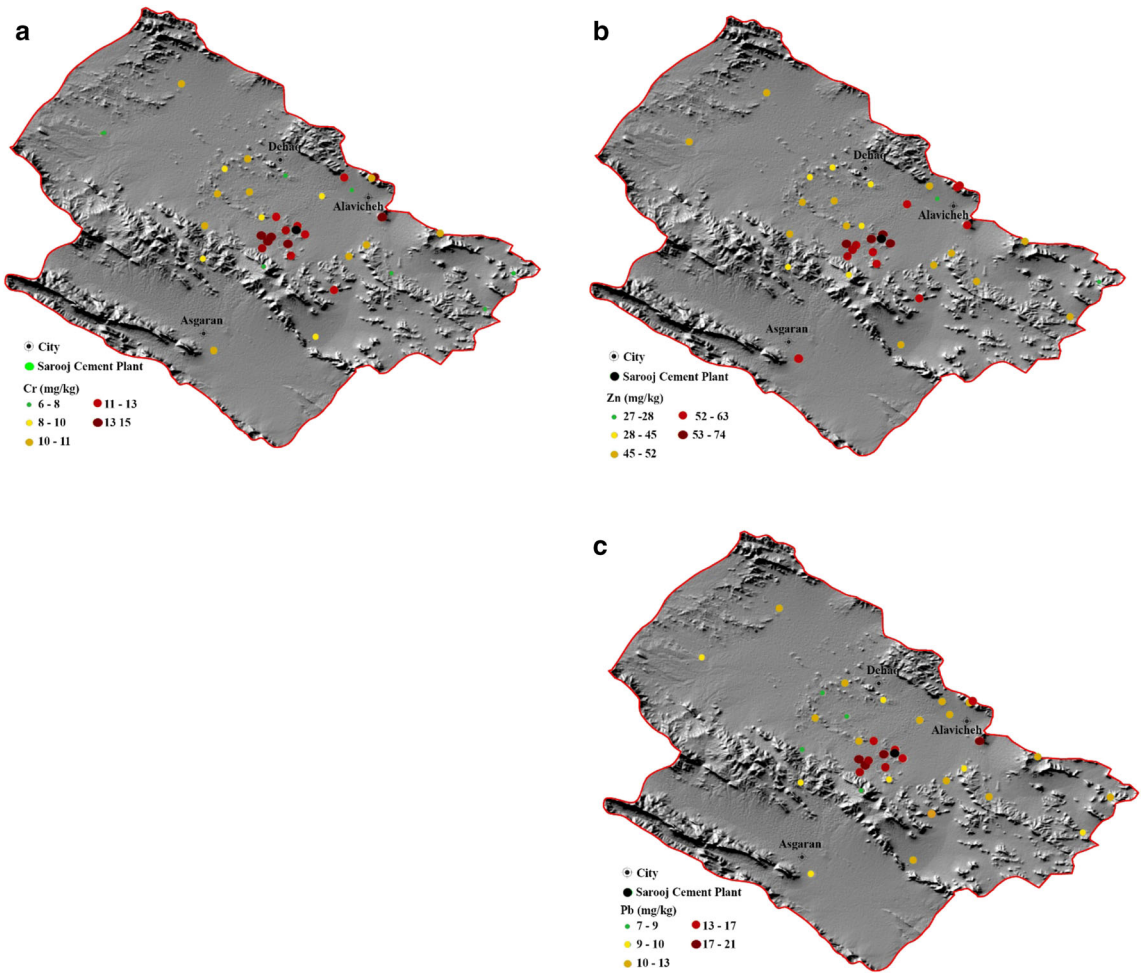

Fig. 6 Spatial distribution of the metal contents including Cr (**a**), Zn (**b**), and Pb (**c**) in biomass of *Scariola orientalis* the sampling points affected by Sarooj Cement Factory

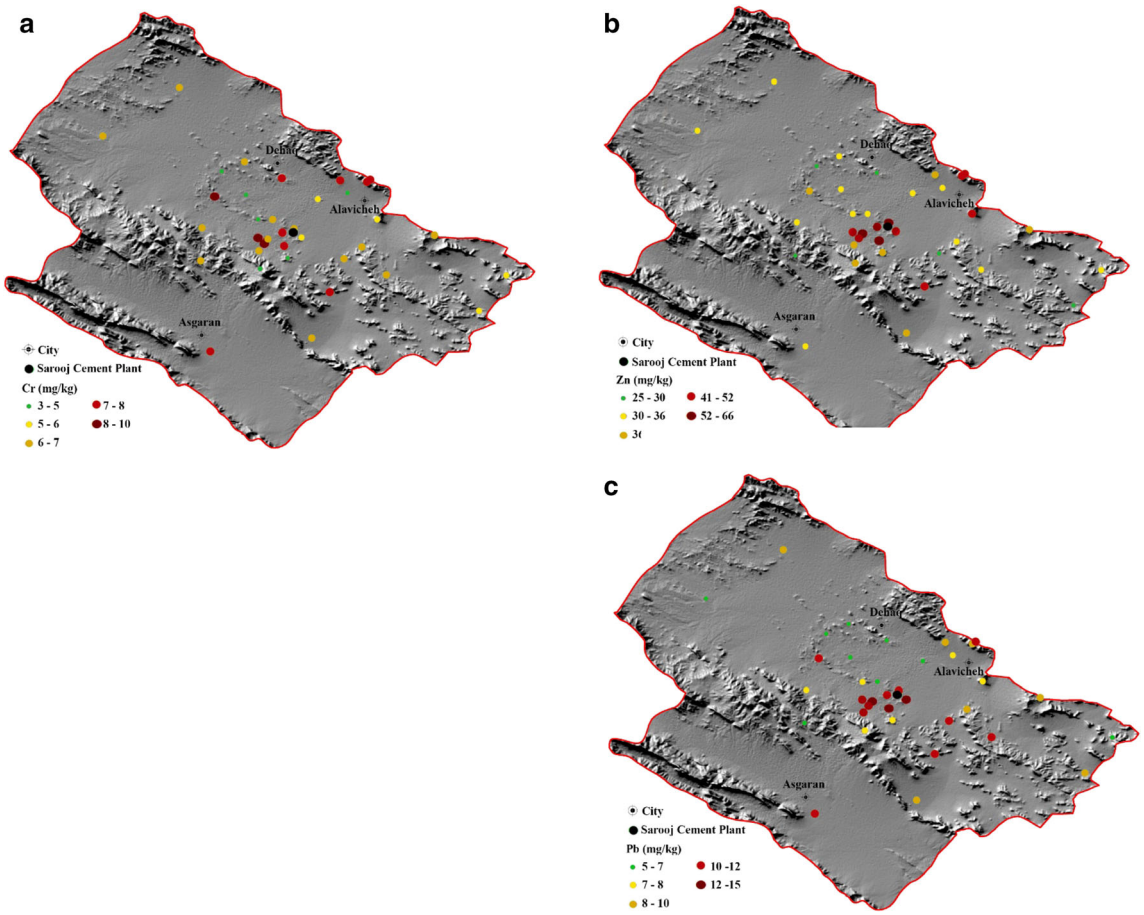

Fig. 7 Spatial distribution of the metal contents including Cr (**a**), Zn (**b**), and Pb (**c**) in biomass of *Stachys inflata* the sampling points affected by Sarooj Cement Factory

the factory; whereas, their accumulation differed across the region. Comparing the spatial distribution of the HMs in the biomass of the two species showed that *Stachys inflata* had higher accumulation of Cr than that of *Scariola orientalis* in farther sampling points.

PM dispersion and spatial distribution of heavy metals

Figure 8 shows the correlation analysis between the soil HM content and PM concentration at the sampling points. The results showed that the soil HM contents (i.e., measured) were significantly correlated ($p < 0.01$) to the simulated PM concentration (i.e., predicted), whereas, Cr (R^2=0.75) and Zn (R^2=68) had the highest and lowest correlation. The correlation analysis of the soil HM content with a linear distance from the factory (i.e., emission source) did not show any significant association.

The concentrations of HMs in both soil and plant samples were significantly different among PM classification groups (Table 6). In most cases, the trend of HM concentrations was consistent with that of PM concentrations, except for Cr in *Scariola orientalis* whose concentration in class 6 was higher than that in class 7. Using the Tukey test, the soil and plant samples were each divided into a number of groups according to the difference in their HM contents between PM classification groups (Table 6). The soil samples were only classified into three groups for Zn while they were classified into six and eight groups in terms of Cr and Pb. The concentration of Zn in *Scariola orientalis* was not significantly different among PM classes due to being grouped in only one class by Tukey's test. In the case of *Stachys inflata*, Cr was classified into three classes, and Zn and Pb were each grouped into five ones. Overall, the concentration of HMs, especially Zn, was found to be uniform in *Scariola orientalis* samples of different PM classification groups, while in the soil samples, the Zn concentration was considerably different with increasing levels of PMs.

The same letters in each column indicate insignificant differences between the classes (p>0.05)

Discussion

Knowing the spatial distribution of HMs is an important issue to capture the contamination degree of the environment,

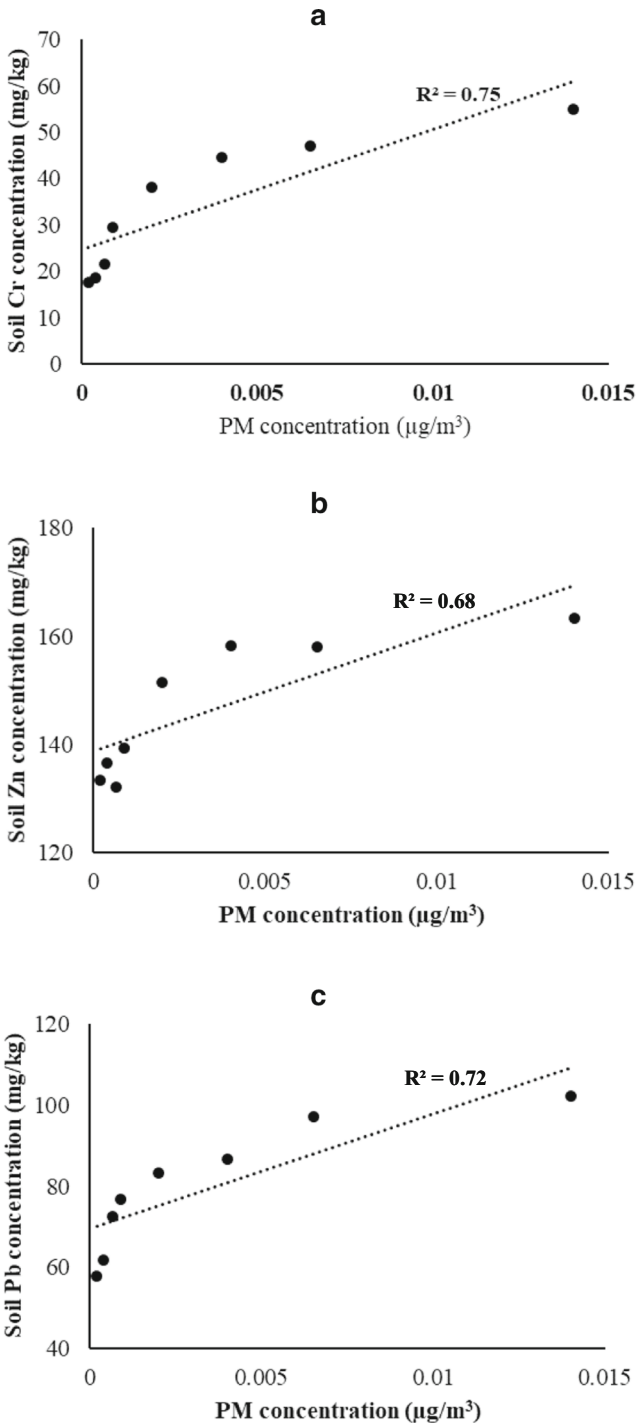

Fig. 8 Correlation analysis between the concentration of heavy metals measured in soil (**a** Cr, **b** Zn and **c** Pb) and PM deposition simulated by AERMOD model. The 8 points are representing the average of the simulated PM concentration of sampled points within the related class described in Fig. 3

particularly in cases where pollutants are distributed through air circulation. The results of this study corroborate those of Heckel and LeMasters (2011) and Bhaskar et al. (2008), indicating that the distribution of PM-bond HMs is a function of various factors ranging from terrain characteristics to meteorological conditions. As shown in Fig. 3 in directions where the terrain is flat and is aligned with prevailing wind patterns (Fig. 2), the concentration and expansion of HMs are relatively high. In accordance with our results, Heckel and LeMasters (2011) found that the spatial distribution and concentration of pollutants modeled by the AERMOD are more profound in plain areas that are exposed to prevailing winds. Thanks to atmospheric dispersion models (e.g., AERMOD), we are fully cognizant of the fact that pollutants' aerial dispersion occurs non-uniformly and may expose non-expected areas.

The systematic-random sampling procedure adopted in this research to take surface soil and plant samples allowed providing a holistic picture of HM contamination in this research. Moreover, we refined HMs into three ones (Zn, Pb, and Cr) that were more likely to document concerns according to the at-source measured concentrations. These metals have been reiterated as major pollutants of cement manufacturing. For instance, Mandal and Voutchkov (2011) found high concentrations and strong associations among the metals in soils around a cement factory in Kingston, Jamaica, that confirm their common source. Ogunkunle and Fatoba (2014) also found similar results, indicating that high Zn, Pb, and Cr enrichments in soil were attributed to cement manufacturing activities. Ogunbileje et al. (2013) analyzed the cement dusts from Nigeria and the USA which their findings revealed that concentrations of heavy metals are factory-dependent.

The results of HM content in the soil samples revealed no risk of Cr and Zn for agricultural and pastoral farming, whereas, the Pb content showed possible risk to agricultural farming and vegetation of protected areas (Canadian Council of Ministers of the Environment (CCME) 2007). According to the results, the plant species could accumulate more Zn than Pb and Cr. Since Zn is an essential element for plant growth (Medina-Velo et al. 2017), its accumulation by the plants was more than that of the other two metals. Furthermore, it seems that the HM accumulation by plants has been related to the corresponding HM content in the soil which follows the trend of Zn> Pb> Cr. The transfer factor (i.e., the metal concentrations in shoot to root) showed that all the HMs were mostly accumulated in the plant root than the shoot. Additionally, the results of BCF revealed that Pb accumulation in both plant species was less than that of Cr and Zn. It might be due to the effect of the soil chemical characteristics and reactions (e.g., bonding with carbonate) which could reduce the bioavailability of this metal and, therefore, decrease its uptake by the plants. However, it should be noticed that the mentioned processes might be also occurred for Cr and Zn but not as much as Pb. The possible entrance of metals through the deposited PMs on plant leaves should be considered. However, due to the low precipitation in the study area, the chance of metal uptake by plants might be low.

Although the BCF factor for both plants was less than the unit which is an index of bioindicators, it seems that both plant

Table 6 Mean comparison of HM concentration among PM classes in the soil, *Scariola orientalis* and *Stachys inflata*

Class	PM ($\mu g/m^3$)	Soil			*Scariola orientalis*			*Stachys inflata*		
		Cr**	Zn**	Pb**	Cr**	Zn*	Pb**	Cr**	Zn**	Pb**
8	0.008–0.02	55 ^{a}	163.4 ^{a}	102.3 ^{a}	14.6 ^{a}	62.8 ^{a}	8.18 ^{a}	8.3 ^{a}	49.6 ^{ab}	11.8 ^{a}
7	0.005–0.008	47.1 ^{ab}	158.1 ^{ab}	97.3 ^{ab}	11.6 ^{ab}	57.4 ^{a}	14.6 ^{abc}	6.7 ^{ab}	42.6 ^{abc}	11.0 ^{abcd}
6	0.003–0.005	44.5 ^{bc}	158.3 ^{ab}	86.6 ^{abc}	13.6 ^{ab}	62.0 ^{a}	15.1 ^{ab}	6.1 ^{ab}	61.7 ^{a}	12.5 ^{a}
5	0.001–0.003	38.1 ^{bc}	151.5 ^{ab}	83.2 ^{bc}	11.0 ^{ab}	56.2 ^{a}	12.4 ^{bcd}	6.4 ^{ab}	42.2 ^{bc}	10.2 ^{a}
4	0.0008–0.001	29.5 ^{de}	139.4 ^{b}	76.7 ^{c}	9.0 ^{b}	48.1 ^{a}	11.0 ^{bcd}	5.6 ^{ab}	36.1 ^{bc}	8.8 ^{abcd}
3	0.0005–0.0008	21.5 ^{de}	132.2 ^{b}	72.6 ^{cd}	9.7 ^{ab}	44.2 ^{a}	11.1 ^{bcd}	8.5 ab	33.5 ^{bc}	6.4 ^{cd}
2	0.0003–0.0005	18.5 ^{e}	136.5 ^{b}	61.9 ^{d}	8.7 ^{b}	47.2 ^{a}	8.9 ^{cd}	5.3 ^{b}	31.3 ^{c}	7.1 ^{d}
1	0.0001–0.0003	17.7 ^{de}	133.5 ^{b}	58.0 ^{d}	8.5 ^{b}	44.5 ^{a}	8.22 ^{d}	4.5 ^{b}	33.6 ^{bc}	6.1 ^{bcd}

**Significant at $p<0.01$

*Significant at $p<0.05$

species could have the bioaccumulation potential of the metals where they showed the TF up to 0.9 (Table 4). Since the pH of soil in the region was more than 7.5 (Table 3), having considerable amount of $CaCO_3$, the bioavailability of the metals in soil could be reduced. Another potential way of uptake could be from the plant leaves surface which might be a sink of associated metals with PMs. However, it needs more investigation to find the pathways of metal uptake by the plants.

The mean Zn concentration, as the highest among the analyzed HMs, was below the reference limit of 200 mg/kg (CCME 2007), but near the levels expected to be seen around mega cement factories (140 to 170 mg/kg) (Ogunkunle and Fatoba 2014). Due to the enormous supplies of fossil fuel needed in the process of cement production, all studies investigating soil HM contamination around cement factories included Pb as a potential contaminant. The mean concentration of Pb exceeded the CCME limit of 70 mg/kg while in terms of Cr, it was half as much as the CCME reference threshold (64 mg/kg).

Due to the high compatibility of *Scariola orientalis* and *Stachys inflata* with arid climatic conditions, they are widespread in central Iran (Ghahreman 2008). Although the BCF of HMs for the plants was in the range of 0.12–0.36, other studies have revealed higher potentials of metal accumulation by the plants particularly in polluted soils (Safari Sinegani and Dastjerdi 2008). Yoon et al. (2006) argued that different TF and BCF values in the same species across various landscapes might be related to different concentration of metals found in soil.

The transference path pictured in this research poses a serious threat to wildlife species of the two protected areas surrounding the cement factory. In other words, the air-soil-plant path of HMs would be continued further by the accumulation in the body of the region's important species that forage from these plants considering that the region occasionally is used for pastoral uses as well as wildlife corridor (Makki et al. 2013). Beyond the conflict arose between the economic advantages of the cement manufactured from natural resources of the region and wildlife protection, it is now important to draw a more effective border between areas that have been highly influenced by HMs and the distribution pattern of major wildlife species in this ecologically valuable region.

In order to minimize biases and achieve a more reliable picture of the region's condition, especially when comparing findings with the reference thresholds, measurements should be highly representative and capture all probable locations with varying HM concentrations. The majority of studies in this field and all those discussed above distributed their samples through a descending pattern with increasing distance from the factory to oversample the factory's adjacent areas. Sampling site selection is a fundamental issue which has to be considered in any study design of research on HMs assessment. Deciding on an efficient sampling strategy, consisting of determining the location, density, and number of samples, has always been a daunting task as it should provide a high representativeness of the region while minimizing the number of samples and resource utilization (Gregoire and Valentine 2007).

Conclusion

The results of this study revealed that soil HM distribution and transference to plant biomass from a potential pollution point source (i.e., cement factory) is a consequent of combinatorial effect of various parameters such as site topography, meteorological condition, emission characteristics, soil properties, type of plant species and heavy metals, and not merely linear distances. Consideration of the combined results of dispersion

models (e.g., AERMOD) and HM monitoring of the soil and plant samples can provide a viewpoint of an environmental effect of a point source pollution with detailed information. Since *Scariola orientalis* and *Stachys inflata* showed Pb, Cr, and Zn bioaccumulation capability, the potential risk of the HMs entrance to food chain through the plant tissues should be considered.

Acknowledgements We thank Dr. Mostafa Tarkesh Esfahani for his assistance in statistical analysis. We thank also Dr. Mohammad Shafiezadeh and Dr. Ali Asgarian for their assistance in preparing the maps and graphical abstract.

Availability of data and materials Not applicable

Author contributions Hossein Moradi: conceptualization, methodology, software, supervision, writing-review and editing; Mohammad Abbasi: software, formal analysis, validation; Mohsen Soleimani: conceptualization, methodology, supervision, writing-review and editing.

Funding Partially by Isfahan University of Technology

Declarations

Ethics approval and consent to participate Not applicable

Consent for publication Not applicable

Competing interests The authors declare no competing interests.

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