Determination of heavy metals in surface soils around the brick kilns in an arid region, Iran

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Abstract

There is an increasing demand for the development of brick kilns area in Iran, which emit a considerable amount of pollutants to environment. The present study aimed to investigate the extent of soil contamination by heavy metals around the brick kiln area in Aran-o-Bidgol city. The correlation coefficients, analysis of variance, principal component analysis, cluster analysis, soil contamination indices and interpolation technique were utilized to investigate the soil contamination and pinpoint the possible sources of contamination. The Results showed the average concentration of all heavy metals were greater than background values and soils were contaminated by heavy metals to some extent. Results also indicated that copper, nickel and zinc had simultaneously emanated from anthropogenic including agricultural activities and urban emissions while the sources of cadmium and lead could mostly be attributed to different anthropogenic activities including brick kilns and related transportation. The distribution maps revealed that the brick kilns emissions had only affected the concentrations of cadmium and lead to some degree.

Keywords: Brick kilns, toxic elements, multivariate analysis, topsoil, Iran

1. Introduction:

Soil contamination has been accepted as an important environmental issue in the world (Esmaeili et al, 2014; Chen et al, 2009). Soils are an important indicator of environmental quality as they act as a sinks and sources for metals and other pollutants (Karim et al, 2014; Wei and Yang, 2010). Soils polluted with metals can threaten human health, soil microbial community, water resources (surface and ground), food quality, flora and fauna. The possible sources of soil metal contamination include vehicle emissions (Yassoglou et al, 1987; Sutherland et al, 2000), various industrial activities (Schuhmacher et al, 1997; Krishna and Govil, 2005; Li et al, 2007) and atmospheric deposition of dust and aerosol (Simonson, 1995), and others (Thornton, 1991). In recent years, soils have been evaluated as a diagnostic tool of environmental conditions that influence health (Yang et al, 2011).

Among the industries, brick kiln emissions form a major source of soil contamination (Badawy et al, 2002; Ismail et al, 2012). The rapid urbanization of many cities in Asia has increased the demand for bricks, which are typically supplied from brick kilns in peri-urban areas (Ahmad et al, 2012). With rapid growth of brick production, the environmental aspects of brick making have become a serious concern that needs immediate attention (Rajaratnam et al, 2014). Brick kiln industry is an industry of poor people in Asia, where the four major countries, including China, India, Pakistan and Bangladesh produce 70–800, 140, 100 and 50 billion bricks per year respectively (Baum, 2010). There is evidence that brick kilns emit a considerable amount of pollutants. These pollutants are created due to the incomplete combustion process and the different types of fuel used in the kiln. Fuel used varies according to what is available for brick makers and includes wood, recycled motor oil, coal, fuel oil, diesel, tires, trash and plastics among others. The inefficient combustion of these furnaces favors the emission of solid particles

and greenhouse gases (Gonzalez et al, 1998). One standard traditional brick kiln may produce 86 kg of particulate matter on a 12 hours burn required to produce 10,000 bricks (Corral Avitia and De la Mora Covarrubias, 2012). When considering the different kinds of contaminants, heavy metals are especially dangerous because of their persistence and toxicity (Li et al, 2015). Heavy metals, airborne from the kiln foundries, fall on the ground in the period of few days and become distributed in soils and water sources (Martirena and Martinicurena, 2001). As time passes, enormous amounts of anthropogenic heavy metals have been started storing in the biosphere, as its removal rate is much lesser (approximately 20 times) than its loading rate and this results in continuous increase of heavy metals concentration.

Numerous studies have been reported on metals contaminations in different soils around Iran (e.g. Mirzaei et al, 2014; Karimi Nezhad et al, 2014; Yeganeh et al, 2013; Dayani and Mohammadi, 2010; Qishlaqi et al, 2009; KarimiNezhad et al, 2015). Further, several studies focused on metals contaminations in street and road dust (e.g. Soltani et al, 2015; Saeedi et al, 2012), metal smelter sites or mines (e.g. Mokhtari et al, 2015; Ghaderian and Ghotbi Ravandi, 2012), agricultural soil (e.g. Esmaeili et al, 2014) and urban parks soil (e.g. Karimi et al, 2011). However, study on metal contamination in soils surrounding a brick kiln is still not reported. In Iran, the brick kiln industry is one of the fastest-growing sectors, supporting the booming infrastructure and construction industry, with current manufacturing capacity of 50 million tons bricks a year from 7000 brick kilns surrounding all major cities of Iran. Isfahan has the highest number of brick kilns among the provinces of Iran that are mostly located in the suburbs of Aran-o-Bidgol city. There are approximately 300-350 brick kilns situated in and around Aran-o-Bidgol city and the numbers are increasing rapidly driven by increased construction activity. As a monthly average, it is estimated that a single brick kiln in this region produces about 900,000

bricks, using large amounts of rubber tires to start the fires, and burns a total of 9 tons of low-quality coal or 20 drums of used vehicle oil. The widespread existence of brick kilns in the fringes of the Aran-o-Bidgol city represents one of such important centers of anthropic activities with a potential to alter the ecology of the surrounding vegetation and soil. There is a need for a proper environmental management of natural resources and urban planning. With this background, the objectives of this research were (i) to analyze the total concentration and distribution of several heavy metals (Pb, Zn, Ni, Cu and Cd) in soils around brick kiln area in Aran-o-Bidgol, Iran, and (ii) to carry out a preliminary assessment of soil contamination associated with heavy metals in the studied area.

2. Materials and methods

2.1. Study area

Aran-o-Bidgol city ($50^{\circ} 15' - 52^{\circ} 29' \text{ E}$, $33^{\circ} 30' - 34^{\circ} 27' \text{ N}$) with at an elevation of 912 m and area of 6,051 Km^2 is situated in northeast of Kashan county in Isfahan Province, central Iran. According to the Isfahan meteorological office internal reports, the climate of the study area is arid to semi-arid. This city has cold winters and hot summers, low rainfall and a wind direction predominantly from northeast to southwest (Fig. 1B). This area was less populated a couple of decades ago at the time when these kilns were installed but now the population has gradually risen to 90 to 95 thousand people. The brick kilns in this area are traditional kilns. They are built in a circular shape by digging a 6-9 m trench that is 100-150 m long. This brick kilns uses coal, wood and furnace oil. They also used rubber in the baking process.

2.2. Soil sampling and chemical analyses

A total number of 66 surface soil (0-20 cm) samples were collected in the study area (Fig. 1A). The sampling sites were selected in such a way to cover the entire vicinity of the brick kilns. To provide a satisfactory environmental representation of the study area, concentric circles of radius 0-500 m, 500-2000 m, 2000-3500 m and 3500-5000 m were considered for surface soils. The coordinates of sampling locations were recorded with a GPS. At every sampling site, five subsamples in topsoils were mixed thoroughly to obtain a composite sample.

Fig. 1. A) A sketch map of the study area including the distribution of soil sampling points around the brick kilns in Aran-o-Bidgol city; B) Wind rose plot of the Aran-o-Bidgol city

The collected samples were air-dried in the laboratory, sieved through 2-mm plastic sieve to remove large debris, gravel-sized material and other waste materials and stored in closed plastic bags until analysis. Soil was digested with a 5:2:3 mixture of $\text{HNO}_3\text{-HClO}_4\text{-HF}$ (Li et al, 2012). Mineral residues were diluted by deionised water to 50 ml in a volumetric flask and stored in a refrigerator at 4°C before the analysis. The soil Cd concentration was determined by graphite furnace atomic absorption spectroscopy (GFAAS, Shimadzu AA-670G, Japan) whereas Pb, Ni, Zn and Cu concentrations were determined by flame atomic absorption spectroscopy (FAAS, Shimadzu AA-670G, Japan). An analytical quality control was carried out with standard reference material; SRM 2711 Montana II Soil. Duplicates and reagent blanks were also used as part of the quality assurance/quality control (QA/QC) (Bai et al, 2011). Before conducting the analysis, the FAAS was calibrated using the element calibration standards. Calibration coefficient values, limit of detection (LOD), and relative standard deviations (RSD) are presented in Table 1. Table 1 also shows the recovery rates for these heavy metals using standard reference soil (Montana Soil 2711). Recovery rates were between 88 % and 107 %, and the relative standard deviations of the five heavy metals, fell within 3.85 and 8.80, which were sufficient for environmental analysis and analytical results.

Table 1. Correlation coefficients, limit of detection (LOD), relative standard deviation (RSD), and recovery rate of each heavy metal using the standard reference soil (Montana Soil 2711) in this study.

Metal	Correlation confidents	Measured value (mg/kg)	True value (mg/kg)	Recovery rate (%)	RSD (%)
Cd	0.999	36.7	41.7	88	8.80
Pb	0.999	1138.8	1162	98	3.85
Ni	0.999	18.95	20.6	92	5.72

Zn	0.999	325.9	350.4	93	4.88
Cu	0.999	122	114	107	6.02

2.3. Estimation of soil contamination

Care needs to be taken when using the terms ‘contamination’ and ‘pollution’. Contamination is the presence of a substance where it should not be, or in levels that are above background levels. The term pollution is defined as contamination that results in adverse biological effects. In the context of soil systems, the difference between contamination and pollution is that contamination is presence of the substance in soil adversely affecting the soil, and pollution is the presence of the substance in the soil adversely affecting the usefulness of the soil (Wu et al, 2014). See the discussions provided by Wu et al (2014) and references therein. In this study, considering contamination concept, both contamination factor (CF), and geoaccumulation (Igeo), were used to assess the soil contamination in accordance with the background concentration. In this study we used the average of heavy metals concentration in soil samples which we collected from an unpolluted region in the study area as background values (Mirzaei et al, 2014). Geoaccumulation index (Igeo) is a classical assessment model for indicating heavy metal accumulation in sediments and soils, and is calculated using Eq. (1):

$$I_{geo} = \log_2 \left[\frac{C_n}{1.5 B_n} \right] \quad (1)$$

where C_n is the content of measured metal “ n ” in the samples, B_n is the crustal shale background content of the metal “ n ” (Taylor, 1964), the constant of 1.5 is introduced to minimize the variation of background values due to lithogenetic origins, and Igeo is a quantitative index of metal enrichment or contamination levels. Muller (1969) divided the geoaccumulation index into seven classes, they are: ($I_{geo} \leq 0$) practically uncontaminated; ($0 < I_{geo} < 1$), uncontaminated to moderately contaminated; ($1 < I_{geo} < 2$) moderately contaminated;

($2 < I_{geo} < 3$) moderately to heavily contaminated; ($3 < I_{geo} < 4$) heavily contaminated; ($4 < I_{geo} < 5$) heavily to extremely contaminated, and ($5 \leq I_{geo}$) extremely contaminated (Muller, 1969).

In addition, the method for calculation of contamination factor by Hakanson was utilized (Hakanson, 1980). The CF is the ratio obtained by dividing the concentration of each metal in the soil by the background value. The contamination factor is computed from the following Eq. (2):

$$CF = \frac{[C]_{\text{sample}}}{[C]_{\text{background}}} \quad (2)$$

The contamination levels may be classified based on their intensities on a scale ranging from 1 to 6: low degree ($CF < 1$), moderate degree ($1 \leq CF < 3$), considerable degree ($3 \leq CF < 6$), and very high degree ($CF \geq 6$) (Luo et al., 2007; Rashed, 2010; Islam et al., 2015).

2.4. Statistical and geostatistical analysis

At first, descriptive statistics, including maximum, minimum, mean, standard deviation (SD), coefficient of variation (CV), skewness and kurtosis, were conducted on the soil heavy metals contents. Shapiro-Wilk test was applied to investigate the normal distribution of data at a confidence level of 95%. Spearman's correlation coefficients were then calculated to identify the correlations between heavy metal concentrations. Data were processed by principal component analysis (PCA) by applying varimax rotational technique for easier interpretation. Varimax rotation maximizes the sum over the components of the variances of the squared loadings, thereby emphasizing cluster recognition. Cluster analysis (CA) was used to detect the different geochemical associations. The standardized data (by means of z-scores) were subject to Ward's method of linkage after using the squared Euclidean distance as similarity measure. These statistical methods are essential to understand the relationships among soil elements. ANOVA

was performed to determine the differences in metal concentrations among different distance intervals and different geographic directions as well. All data were analyzed using the SPSS software version 19.0. Ordinary kriging is the most commonly used interpolation method to predict the overall trend of soil contamination. However, for the purpose of identifying contaminated areas, inverse distance weighting (IDW) is more appropriate to predict local features of soil contamination, especially local hotspots and cold spots (Wu et al, 2014). Therefore, interpolation mapping was conducted using IDW within ArcGIS 10.1 software. The wind rose diagram, in a 10-year period (March 2001- March 2010) (Fig. 1B) was plotted using the WRPLOT, Lakes Environmental Software Inc (version 7.0.0).

3. Results and Discussions

3.1. Descriptive statistics

The descriptive statistics of total concentrations of heavy metals in soil samples have been given in Table 2. Considering this table, the concentrations of Cd, Pb, Ni, Zn and Cu ranges from 0.4-1.15, 1-48.53, 8.05-52.13, 25.68-165.75 and 25.68-165.75 mg/kg respectively. The average concentrations of Cd, Pb, Ni, Zn and Cu were 0.79, 12.56, 29.50, 52.23 and 14.29 mg/kg respectively which were more than their local background levels (0.15, 4.08, 8.55, 21.11 and 2.17 mg/kg respectively). Based on mean concentration, the metals in surface soils were in the following decreasing order: Zn>Ni>Cu>Pb>Cd.

The average concentrations (mg/kg) of metals in soils from different regions of the world and in the upper crust are given in Table 3 together with the appropriate references. The mean concentrations of Pb, Ni, Cu and Zn in brick kiln soils are lower than the upper crust (Rudnick and Gao, 2003). The average concentration of Pb in brick kiln soils (this work) is almost similar

to those of Turkey (Koz et al., 2012), higher than Portugal (Figueira and Ribeiro, 2005), and lower than Italy (Wahsha et al., 2012), Lead/zinc smelter of China (Li et al., 2015) and typical industrial town of China (Wu et al., 2011). Cadmium content in brick kiln soils of Aran-o-Bidgol is lower than Lead/zinc smelter of China (Li et al., 2015). In addition, the mean concentrations of Cu and Zn in brick kiln soils are much lower than those for other parts of the world. On the other hand, the mean concentration of Ni in brick kiln soils of Aran-o-Bidgol is comparable with that of in typical industrial town of China (Wu et al., 2011) and higher than other metropolitan cities except Lead/zinc smelter of China (Li et al., 2015).

It is difficult to contextualize the empirical findings of this study, as there have been few scientific studies conducted on soil contamination by heavy metals around the brick kiln area. The heavy metals concentrations were relatively high compared with the value recorded for brick kilns located in Pakistan where the total concentrations of Cd, Pb, Ni, Cu and Zn in surface soil were 0.015, 0.079, 0.059, 0.008 and 0.047 mg/kg respectively (Ishaq et al., 2010).

Considering Iranian studies, in the present study, the mean value of Cd was 0.79 mg/kg which was similar to that reported by Dayani and Mohammadi (2010) (mean 0.79 mg/kg) in mining-urban soils. When we compared the mean value reported by other Iranian studies such as Solgi et al. (2012) (mean 1.26 mg/kg) and Parizanganeh et al. (2010) (mean 3.46 mg/kg) in industrial soils —with those of our soils, we saw that our values were low. Nonetheless, the levels reported by Esmaili et al. (2014) in agricultural soils of Isfahan (mean 0.43 mg/kg) and Soffianian et al. (2014) for soils of Hamadan Province (mean 0.15 mg/kg) are lower than those obtained for brick kiln soils in this study.

Pb (mean 12.56 mg/kg) values were lower than those reported by most Iranian studies conducted in industrial areas, such as Dayani and Mohammadi (2010) (mean 101.9 mg/kg),

Parizanganeh et al. (2010) (mean 128.51 mg/kg) and Naimi and Ayoubi (2013) (mean 99.4 mg/kg).

The Cu concentration (14.29 mg/kg) was lower than that reported by Naimi and Ayoubi (2013) (21.1 mg/kg in industrial soils), but according to Jalali and Hemati (2013), the mean Cu concentration in paddy soils of Isfahan Province was 7 mg/kg which is lower than the corresponding concentrations in soil samples in the study area.

Comparing mean Ni concentration (29.50 mg/kg) in topsoil of the study area with that available from Iranian literature (e.g. Solgi et al. 2012; Naimi and Ayoubi 2013), Ni exhibited lower contents than the mean values established but obtained a greater one than that (22.59 mg/kg) reported in grassland soils by Qishlaqi et al. (2009) in the Angouran region, NW Iran.

Zn (mean 52.23 mg/kg) values were lower than those reported by most Iranian studies, such as Dayani and Mohammadi (2010) (mean 250.3 mg/kg), Parizanganeh et al. (2010) (mean 606.20 mg/kg, Naimi and Ayoubi (2013) (mean 101.1 mg/kg), Mirzaei et al. (2014) (mean 82.08 mg/kg) and Karimi Nezhad et al. (2015) (mean 1716 mg/kg).

The application of the Shapiro-Wilk test confirmed that Ni, Cu and Zn are normally distributed with the exception of Cd and Pb in the topsoil samples of the study area. For non-normal variables, logarithms of the concentration values were considered to be normally distributed. In nature, if there is no other source inputs (anthropogenic entries); the concentration of elements usually has a normal distribution (Zhao et al., 2010). It could be concluded that the natural concentration of Cd and Pb is affected by external source inputs.

The concentrations of total metals in four distance intervals were in the following decreasing order:

Cd: 500-2000 > 0-500=2000-3500 > 3500-5000; Pb: 500-2000 > 3500-5000 > 2000-3500 > 0-500; Zn: 2000-3500 > 3500-5000 > 500-2000 > 0-500; Cu: 3500-5000 > 2000-3500 > 500-2000 > 0-500; Ni: 3500-5000 > 2000-3500 > 500-2000 > 0-500. Considering this ranking, it can be concluded that with the exception of Cd, the lowest concentrations of heavy metals were found in 0-500 m interval. A visual inspection of this ranking indicated the topsoil concentrations of Ni, Cu and Zn in distance intervals are more similar than the other two heavy metals; from this, it could be said that contents of all heavy metals increase approximately as the distance from the brick kilns increase. With the exception of Pb, the results of ANOVA test found significant differences in metal concentrations among four distance intervals (Table 2) and confirmed the above-mentioned differences. These findings suggest that there are different sources of metals in the study area. This is relatively in agreement with Isaq et al. (2010) who found various differences of heavy metals contents in soil among different distance intervals and directions in brick kiln in Pakistan. To better understand the relationships between distance change and heavy metals concentration, we calculated the correlation among the heavy metal concentrations and the distance from the brick kilns; however, no significant correlations were found. In addition, we analyzed the effect of directions on heavy metal concentrations because we thought the prevailing wind direction may explain the differences as some researchers noted that heavy metal distributions around pollution sources are affected by the prevailing wind direction (Al-Shayeb and Seaward, 2001). In this field, the concentration of heavy metals in leeward area is, as expected, higher than that in windward areas (Al-Shayeb and Seaward, 2001; Wu et al, 2011). Therefore, considering prevailing wind direction, directional differences in heavy metal concentration from four different geographical directions (NE, SE, SW and NW) were investigated. Results indicated that the concentrations of Cd, Ni and Zn in the North-East, North-

West and South-East directions are significantly different from those in the South-West direction, whereas no significant difference was found for Pb and Cu in four directions. These results support the suggestion that the contents of heavy metals in brick kiln soils were closely related to prevailing wind direction (Fig. 1A). Our results are in agreement with previous research results and conclusions (Karimi Nezhad et al, 2015; Wu et al, 2011).

On the contrary, we could not find a solid relationship between heavy metals and distance from brick kilns even the relationship between heavy metal concentrations and geographic directions were not significant for Pb and Cu. The distance increase effect on heavy metal concentration was also discussed in other studies. Most studies have shown that the contents of heavy metals in topsoil decrease with increasing distance from the pollution source (e.g. Koz et al, 2012; Li et al, 2015; Wu et al, 2011). In contrast, few researches got a counterintuitive conclusion; for example Zhang et al (2015) has reported that total content of Cu in roadside soils increases with increasing distance from a highway. This result agrees with the findings reported by Zhang et al (2015) for roadside soils. However, although we thought the main reasons might be unclear, but one reason for this might be the effect of other anthropogenic sources on heavy metal concentrations which were not recognized in the area under study.

Table 2. Statistical values of total concentrations of metals (mg/kg) in the brick kiln soils of Aran-o-Bidgol (n=66)

Distance from the brick kiln	Measure	Cd	Pb	Ni	Zn	Cu
0-500 m (n=12)	Mean	0.79 ^{ab}	11.78 ^a	20.14 ^c	35.41 ^{cd}	6.75 ^{cd}
	Max	1.05	15.35	39.05	45.80	15.08
	Min	0.40	6.80	13.00	25.68	1.45
	Range	0.65	8.55	26.05	20.12	13.63
	SD	0.20	2.44	7.02	6.30	4.10
	CV (%)	25.31	20.71	34.85	17.79	60.74
	Skewness	-0.86	-0.50	1.95	0.28	0.66
	Kurtosis	-0.39	0.05	4.60	-0.48	-0.31
500-2000 m (n=6)	Mean	0.85 ^a	13.09 ^a	25.25 ^{abc}	48.26 ^{bc}	10.72 ^{bc}
	Max	1.15	25.20	49.15	133.85	29.14
	Min	0.65	2.85	9.30	27.95	2.95

	Range	0.50	22.35	39.85	105.90	26.19
	SD	0.12	5.34	15.45	27.90	8.88
	CV (%)	14.11	40.79	61.18	57.81	82.83
	Skewness	0.83	0.85	0.53	2.14	0.87
	Kurtosis	1.17	1.78	-1.75	5.37	-0.74
2000-3500 m (n=18)	Mean	0.79 ^{ab}	12.39 ^a	32.31 ^{ab}	64.72 ^a	16.34 ^b
	Max	1.10	30.55	52.13	165.75	27.43
	Min	0.40	4.20	8.05	30.50	2.25
	Range	0.70	26.35	44.08	135.25	25.18
	SD	0.16	6.86	14.71	36.01	8.01
	CV (%)	20.25	55.36	45.52	55.63	49.02
	Skewness	-0.38	1.20	-0.36	1.66	-0.72
	Kurtosis	0.95	1.50	-1.31	2.59	-0.74
3500-5000 m (n=20)	Mean	0.74 ^b	12.76 ^a	35.97 ^a	54.24 ^{ab}	19.82 ^a
	Max	1.02	48.53	48.78	135.65	35.23
	Min	0.53	1.00	17.30	28.43	12.85
	Range	0.50	47.53	31.48	107.23	22.38
	SD	0.11	10.63	9.69	28.24	5.52
	CV (%)	14.86	83.30	26.93	52.06	27.85
	Skewness	0.45	2.14	-0.58	2.01	1.38
	Kurtosis	0.48	6.10	-0.75	3.64	2.24
Total (n=66)	Mean	0.79	12.56	29.50	52.23	14.29
	Max	1.15	48.53	52.13	165.75	35.23
	Min	0.40	1.00	8.05	25.68	1.45
	Range	0.75	47.53	44.08	140.07	33.78
	SD	0.15	7.29	13.53	29.31	8.42
	CV (%)	18.98	58.04	45.86	56.11	58.92
	Skewness	-0.26	2.16	0.03	2.07	0.10
	Kurtosis	0.37	8.33	-1.53	4.22	-9.00

Note: The different superscripted letters each column indicated the difference at a significant level of $p < 0.05$ tested by a post hoc comparison of one-way ANOVA.

Table 3. Heavy metal average concentrations (mg/kg) found in different regions of Iran and world

Sampling region	Cd	Pb	Ni	Zn	Cu	Reference
Brick kiln, Aran-o-Bidgol	0.79	12.56	29.50	52.23	14.29	Present study
Upper Crust content	0.09	17	47	67	28	Rudnick and Gao (2003)
Mining area, Portugal	-	6.71	21.25	65.55	132	Figueira and Ribeiro (2005)
Typical industrial town, China	0.11	44.47	29.27	64.76	25.31	Wu et al. (2011)
Copper mining area, Turkey	-	12.02	27.04	208.4	402.84	Koz et al. (2012)
Mining area, Italy	-	122.34	22.37	1164	1851	Wahsha et al. (2012)
Lead/zinc smelter, China	12.8	712	75.0	1688	239	Li et al. (2015)
Angouran region, NW Iran	1.1	596.16	22.59	288.41	22.19	Qishlaqi et al. (2009)
Urban-mining of Isfahan, Iran	0.79	101.9	-	250.3	-	Dayani and Mohammadi (2010)
Zinc Industrial Complex Zanjan-Iran	3.46	128.50	-	606.20	-	Parizanganeh et al. (2010)
Industrial estates, Arak, Iran	1.26	60.22	-	-	-	Solgi et al. (2012)
Industrial district of central Iran	-	99.4	58.4	101.1	21.1	Naimi and Ayoubi (2013)
Paddy soils of Iran	2.8	51.6	13.4	23.8	7	Jalali and Hemati (2013)
Isfahan industrial zone, Iran	0.43	34.6	66.2	111.5	35.7	Esmaeili et al. (2014)
Hamadan Province, Iran	0.15	31.89	69.03	80	36.45	Soffianian et al. (2014)
Province of Golestan, Iran	0.12	15.42	34.88	82.08	23.9	Mirzaei et al. (2014)
Ahvaz, Iran	-	122	261	1716	157	Karimi Nezhad et al. (2015)

3.2. Correlation of heavy metals

The correlation coefficients among heavy metals are shown in Table 4. In this respect, Cu significantly correlated with Ni ($r=0.85$) and Zn ($r=0.62$). A significant correlation of Ni was also found with Zn ($r=0.65$). So, from these results and the above discussion about ranking heavy metals concentrations with respect to distance intervals, it could be shown that Ni, Cu and Zn were significantly correlated with one another. From this, it could be said that their source was almost the same, but could not be said that may be derived from the brick kiln activity.

Table 4 . Spearman's correlation matrix for heavy metals in the brick kiln soils of Aran-o-Bidgol

	Cd	Pb	Ni	Zn	Cu
Cd	1				
Pb	0.121	1			
Ni	0.200	-0.038	1		
Zn	0.214	0.184	0.651**	1	
Cu	0.002	0.182	0.859**	0.621**	1

**correlation is significant at the 0.01 level

3.3. Soil contamination assessment method

3.3.1. The geoaccumulation index

The Igeo of soil sampling points in brick kiln soils of Aran-o-Bidgol, have been presented in Fig. 2 which varied considerably across the different metals. The mean Igeo values for all heavy metals were lower than 3 (ranged from 1.11 to 2.37), suggesting that the soils were moderately or moderately to heavily contaminated (Fig. 2). The Igeo value of Pb in soils varied from 0 to 3.33 with an average of 1.11 and more than 56.06% of soil samples were moderately contaminated by Pb. The mean Igeo value for Zn was 1.14 and about 40.90% soil samples fall into class 3 of moderately polluted topsoil samples. In general, 44% of the total topsoil samples were classified into moderately to heavily contaminated with Ni (mean: Igeo 1.60). Among the

metals Cu showed the highest accumulation in topsoils. Igeo values of Cu ranged from 0 to 4 with an average of 2.35 which corresponded to class 4 of moderately to heavily polluted topsoil samples and class 5 of very heavily contaminated topsoil samples and more than 42% of soil samples were heavily contaminated by Cu. Cd (mean: Igeo 2.37) showed more accumulation in the study area as compared to Pb, Zn and Ni and about 92.42% soil samples were classified into moderately to heavily contaminated by Cd.

Fig 2 . The results of geoaccumulation index classes of heavy metals in topsoils of brick kiln area located in Aran-o-Bidgol city

3.3.2. The contamination factor index

The CF values for the heavy metals have been presented in Fig 3. The mean CFs for all heavy metals ranged from 2.49 to 6.61, which indicates that the soils were moderately to very high degree contaminated. The order for the average CF values was follows: Cu > Cd > Ni > Pb > Zn. This means that human activities had significant effects on concentrations of Cu and Cd in soils in this study area and that the soil is more contaminated by these metals. Among the sampling sites, about 50% of samples showed very high contamination for Cu. the average CF value for

Cu was 6.61, which was ranked as “high pollution”, indicating that the brick kiln soils were obviously contaminated by Cu. The average CF value for Cd was 5.31, which was ranked as “considerable pollution”, indicating that this metal might pose a potential risk to the surrounding ecosystem (Rashed, 2010; Islam et al, 2015). The average CF value for Ni was 3.46, which was ranked as “considerable pollution” level (Muhammad et al, 2011). Zn had the lowest value, ranging from 1.21 to 7.85, and most soil samples were classified as low or moderate CF. For Pb, the mean CF was 2.58, ranging from 0.20 to 10.10, but 11.85% of samples was classified as considerable CF, thus indicating the absence of problematic Pb contamination of soils in the area under study. Compared with the “geoaccumulation index”, the contaminated areas have been predicted more by the contamination factor, which could be due to the fact that geoaccumulation index predicts the contamination extent conservatively and underestimates the contamination extent because of the constant of 1.5 in its equation denominator.

Fig.3. The results of contamination factor (CF) classes of heavy metals in the topsoils of brick kiln area located in Aran-o-Bidgol city

3.4. Principal component analysis

To better understand the relationships among the heavy metals in brick kiln soils, associations of metals were determined by PCA. The appropriateness of the data for PCA was assessed based on the Kaiser–Mayer–Olkin (KMO) index; the test is recommended only if KMO is >0.70 . Because the KMO index was calculated to be 0.72 in the present research, PCA was applied to the data. The factor loadings after varimax rotations are listed in Table 5. Two main factors (F1 and F2) explained 71.59 % of the total variance, according to the initial eigenvalues (eigenvalues >1). Factor 1 had a loading from concentrations of Cu (92 %), Ni (94 %) and Zn (80 %) accounting for 49.82% of the total variance. Cd and Pb were highly loaded in Factor 2 which explained 21.77% of the total variance. Similarly, F1 and F2 can be indicated by different anthropic influences (Davies 1997; Romic and Romic 2003; Rodríguez Martín et al. 2013b), because as mentioned in assessing metal contamination, the average of all heavy metals concentrations were obviously greater than the background concentrations.

Table 5. Factor loadings for heavy metal values in in topsoil from brick kiln area located in Aran-o-Bidgol . Varimax rotation with Kaiser normalization.

	Factor 1	Factor 2
Cd	0.1	0.705
Cu	0.928	0.021
Ni	0.948	-0.07
Pb	0.031	0.773
Zn	0.802	0.266
Total variance	49.82	21.77
Cumulative percent	49.82	71.59

Significant loadings in PCA factors are shown in bold.

3.5. Hierarchical cluster analysis (HCA)

The result of CA analysis is illustrated in the dendrogram (Fig. 4); two distinct clusters can be identified. Cluster I contained Cu, Ni and Zn. Cluster II contained Cd and Pb, while the long distance between Cd and Pb may suggest that this cluster can be further divided into two sub-

clusters. The results of PCA agreed well with that of the CA. As mentioned in Section 3.1, the concentrations of all metals were obviously higher than the background values of the study area. Therefore, the distribution of all metals in soils of brick kiln area was mainly affected by anthropogenic sources.

Fig 4. Dendrogram depicting the hierarchical clustering of the heavy metals obtained by Ward's method

3.6. Spatial distribution of heavy metals

The interpolation resulting in heavy metal concentration maps have been shown in Fig. 5. In these maps, Ni, Cu and Zn showed a similar spatial pattern, with contamination hotspots located simultaneously in the soils at northeast, west and southwest regions of the study area, indicating that they were from the same sources, while the low concentration of these heavy metals located around the brick kilns, indicating no effects of brick kilns on concentration of them in surface soil samples in the study area. In contrast, the spatial pattern of Pb and Cd concentration in topsoil is also partly similar with higher concentrations in south, southwest and west regions of the study area and especially high concentration around the brick kilns. Because the entire study was located on an arid plain area without significant differences in the types of soil parent material, and the concentrations of all heavy metals were greater than background concentrations, the distribution of all heavy metals was most likely directly related to

anthropogenic sources. So, from these results and the above discussion about ranking heavy metals concentrations with respect to distance intervals and geographic directions these sources seems to be different for Cd and Pb rather than Ni, Cu and Zn. This is exactly in agreement with the results of correlation, PCA and HCA analysis. We checked all other anthropogenic sources in the study area that are likely to be the main sources of heavy metals contamination and we found that the higher concentration of Cu, Ni and Zn may originate from agricultural activities and urban emissions while Cd and Pb may originate from precipitation of aerosol particles released by traffic and brick kilns. Therefore, it can be concluded that the brick kilns could partly effect on spatial pattern of Cd and at least partially of Pb. Some of the researchers found that pollutant emissions vary according to type of kiln; fuel used and kiln operating conditions and local meteorological conditions (Rajarithnam et al, 2014). For example emissions for some pollutants were found to be higher when coal was used as the main kiln fuel rather than petroleum coke (Zemba et al., 2011), or Carrasco et al. (2002) found increased metals emissions when co-firing scrap tires, but decreased PCDD/Fs emissions. If we even assume that this hypothesis is true for our study, but we have no comparative data to examine the incremental effects (if any) of fuel used. One interesting observation in this study was that high contaminated areas were distributed in southwestern parts of study area for all heavy metals. Presence of Kashan City and the prevailing wind direction may explain this pattern. However, this is in agreement with many authors such as Luo et al (2015) who have emphasized the role of urban emissions on soil contamination by heavy metals.

Fig 5. Spatial distribution of Cd, Pb, Ni, Zn and Cu contents (mg/kg) in surface soil around the brick kilns in Aran-o-Bidgol city

As shown in this Fig. 6, the areas with high scores on component that produced high amounts of Ni, Cu, and Zn, were located in west and southwest parts of the study area where Kashan City is located far away it. Also there were some high scores in eastern regions of the area under study

where farmlands were located. As mentioned before presence of Kashan City as a larger city in southwest of the study area and agricultural activities represented by PC1 may have been the primary contributors of Ni, Cu, and Zn contamination in the soil. Thus, PC1 was mainly controlled by anthropogenic sources. Interpolated scores associated with PC2 are displayed in Fig. 6; the scores exhibit an approximately different spatial distribution than PC1 scores. High score areas were located in the west and southwest regions showed a similar pattern such as PC1, but there were some high scores in east and around the brick kilns. The high score areas located in mentioned area are associated more strongly with anthropogenic sources as well.

Fig 6. Spatial distribution map of PC scores.

4. Conclusion

In this study we aimed to determine the influence of brick kilns on surrounding topsoil contamination by heavy metals. To this end, we used several techniques such as comparing heavy metal concentrations with background values, determining of effect of increasing of distance from brick kilns and geographic directions on heavy metal concentrations, application of correlation, principal component analysis and cluster analysis in order to identify the sources of soil contamination. Application of two contamination indices to investigate the level and

extent of soil contamination by heavy metals around brick kilns and the interpolation techniques to determine the spatial distribution of heavy metals concentration in topsoils around the brick kilns were other applied techniques. At first glance, the results of different applied methods mentioned above seemed to be a bit confusing; but a deeper look into results showed some interesting conclusions. These results showed that concentrations of heavy metals in sampling soils were controlled by different anthropogenic factors. In this way, it seems that the concentrations of Cu, Ni and Zn were simultaneously controlled by agricultural activities and urban emissions and concentrations of Cd and Pb were mostly controlled by brick kilns and related transportations. Although the result of soil contamination assessment indicated that considering background concentrations, sampling soils were contaminated by heavy metals to some extent, but despite our imagination, except for Cd and for Pb to some extent, we could not find any relationship between soil contamination by heavy metals and brick kilns activity. Therefore, it can be concluded that brick kilns emissions had only affected the concentrations of Cd and Pb to some degree. Finally, we suggest determination of the concentration of metals in the stack exhaust in future researches.

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