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soils of the Isfahan industrial zone, Iran
A geochemical survey of heavy metals in agricultural and background

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abstract

There is a growing public concern about the potential accumulation of heavy metals in agricultural soils of Iran. This is mainly the result of rapid urban, mining and industrial discordant development over the last several decades, which has jeopardized the ecology, food safety, human health, and sustainable development of agriculture. To investigate the soil pollution, a total of 105 agricultural soil samples and 40 background soil samples were collected from the Isfahan industrial zone. Accordingly, total concentrations of 7 heavy metals (including Cu, Pb, Zn, Cd, Ni, Co and Cr), associated with Al, Fe, Mn and some physicochemical properties of soils were determined. The geochemical background and threshold was predicted using the Median Absolute Deviation (MAD) method. The median concentrations of heavy metals in agricultural soil were nearly similar to those of background soil, with some outlier data in the vicinity of the industrial and mining areas. Based on correlation coefficient and factor analyses, the primary source of Ni, Co, Cr, Fe and Al was determined to be geogenic, whereas the source of Pb, Zn and Cd is substantially controlled by anthropic activity. Our observations proved that in the Isfahan industrial zone, both human and natural sources affect the concentrations of Cu and Mn. Maps of heavy metal pollution indices in agricultural soils reveal high level of pollution in the vicinity of Bama$_{\text{Pb-Zn}}$ mining area along with Esfahan and Mobarakeh Iron-Steel plants.

1. Introduction

Soil serves many vital functions in the ecosystem and is a fundamental resource for human survival and development (Li et al., 2008; Wong et al., 2002). Therefore, it is critical to protect it from pollution and ensure its sustainability (Alloway, 1995; Nriagu, 1988). In the recent years, soil pollution has been accepted as an important environmental issue both in developed, and developing countries, mainly because of the effects of soil pollution on changes in the land use patterns (Andreu and Boluda, 1995; Chen et al., 2009). Among numerous soil pollutants, heavy metals (HMs) are especially dangerous due to their high toxicity and persistence in the environment. Two primary sources have been identified for HMs pollution; natural or geological inputs including rock weathering and thermal springs, and anthropogenic sources including metalliferous mining and associated industries, vehicle exhaust emissions and agronomic practices (Gallego et al., 2002; Micó et al., 2006; Rodríguez Martín et al., 2007; Zhang et al., 1999). A large proportion of toxic concentrations of HMs is introduced from farming practices, such as organic and mineral fertilization, application of pesticides, and irrigation water. (Rodríguez Martín et al., 2007; Romic and Romic, 2003). Heavy metals can be transferred from the soil to other ecosystem compartments such as groundwater and crops. Hence, they can affect human health by polluting water supply and food chain (De Temmerman et al., 2003; Sa´nchez-Camazano et al., 1998). The study of the Concentration, spatial distribution and source identification of HMs in agricultural soils is very important in order to identify the areas of pollution and assess the potential sources of pollutants (Li and Feng, 2012). Usually, the identification of pollutant sources is conducted with the aid of multivariate statistical analyses, such as correlation analysis, Factor analysis etc. (Einax et al., 1997; Han et al., 2006; Li and Feng, 2012; Luo et al., 2007; Tahri et al., 2005). On the other hand, many environmental pollution indices are typically used to assess enrichment of HMs and to describe soil quality in the environment (Abrahim and Parker, 2008; Din, 1992; Hakanson, 1980;

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Jung, 2001; Muller, 1969; Nishida et al., 1982; Praveena et al., 2007; Shin and Lam, 2001; Tomlinson et al., 1980). Pollution indices are also powerful tools to distinguish the source or origin of heavy metal contaminations (Caiero et al., 2005).

The study area with a surface of approximately 7850 km^2 is located in the center of Iran (Fig. 1). In the last two decades, this region has undergone a rapid transition from a traditionally agriculture-based economy, to an increasingly industrial/mining-based economy. Industrial and mining operations accompanied by expansion of the population along with pollutant emission have considerably increased waste and wastewater discharges in the study area. Once heavy metals enter and accumulate in agricultural soil through irrigation and atmospheric deposition, the risk of contamination of the food chain is dramatically enhanced. The aims of this research are: (1) to evaluate heavy metal contents of agricultural and background soils in the study area; (2) establish geochemical background levels for heavy metals; (3) to assess the degree of heavy metal contamination and their geochemical association in the soils; and (4) to investigate potential sources of heavy metal contamination in the region.

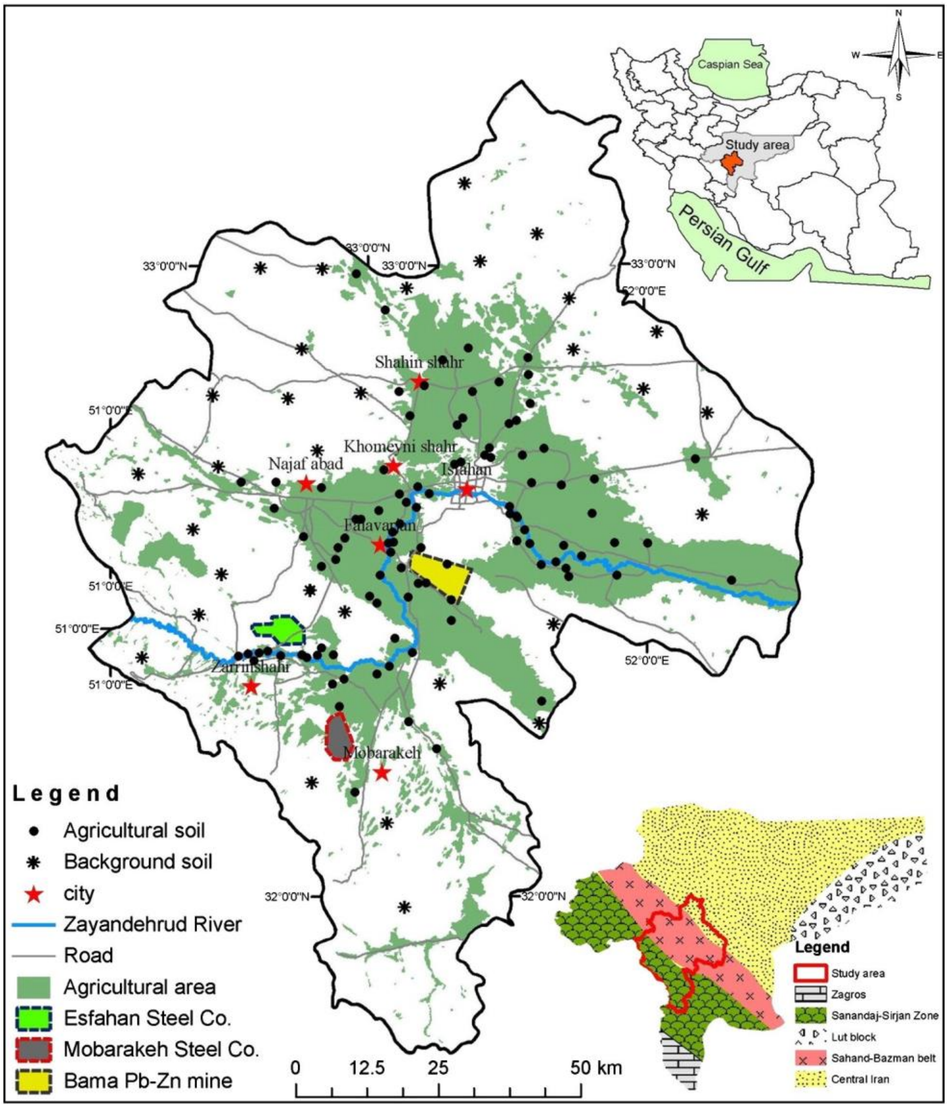

Fig. 1. Location of agricultural soils and sampling sites.

2. Materials and methods

2.1. Study area

The study are is located between 51° 8′ and 52° 12′ E longitude and 32° 11′ and 33° 6′ N latitude, with a total surface area of 7850 km^2 (including 9 counties) and mean altitude of 1643 m.a.s.l. west of Isfahan province (Fig. 1). According to the Isfahan meteorological office internal reports, the climate of the study area is arid to semi-arid. The mean monthly temperature reaches its maximum (28.8 °C) during July–August and its minimum (3.3 °C) in January. Mean annual temperature is 10.8 °C. Also, rainfall is seasonal and 80% of rainfall occurs between January and April. The mean annual rainfall is about 70 mm. The study area is a part of Zayandehrud River basin, an important agricultural area (still with traditional agricultural practices) in central Iran (200000 ha of intensively cultivated land). Cereals comprise the largest proportion of this cultivated area (60 %). Fruit production (7%) is also locally important. The area, with an approximate population of 3.6 million, is also intensively industrialized. Nearly 4000 small factories are active in the region. These factories are mostly small metallic and non-metallic (75%), textile (8.5%), chemical (7.5%), food (5%), electronic (3%) and pharmaceutical (1%) plants. Large scale industry including petrochemical and oil refinery industries, chemical industry, cement industry, power generation plants, iron and steel industry are mainly concentrated on the banks of Zayandehrud River (Fig. 1). Sewage discharge and emission of exhaust gas, as well as industrial emissions and mining dusts can have negative repercussions on soils, and negative effects on the quality of agricultural products (Gil et al., 2010; Rodríguez et al., 2009). Geologically, the study area includes parts of three sedimentary-structural zones introduced by Nabavi (1976), namely Sahand-Bazman volcano-magmatic belt, Sanandaj-Sirjan metamorphic belt, and Central Iran zone. The Quaternary unconsolidated alluvial sediments are widely distributed in the study area (Fig. 1). Lithologically, the main exposed rocks are Mesozoic sedimentary rocks (limestone, dolomite, shale and sandstone) intruded by granodioritic intrusions (e.g., Kolahghazi Mountain). The Irankuh Pb-Zn deposit is a famous non-ferrous ore deposit in the area. Major soil types are calcaric regosols, calcaric cambisols, and sodic solonchask.

2.2. Sampling and analyses

In this study, a total of 105 agricultural soil samples (AS) were collected from 0 to 30 cm depth. Also, 40 background soil samples (BS) were taken to determine geochemical background in the period April to August, 2012. The background soils are non-arable whereas, conventional agricultural practices are commonly carried out on AS. In order to obtain bulk composite samples, four individual sub-samples were collected using a stainless steel spade, within a radius of 5 meters of a central point. Soil samples were mixed thoroughly and approximately 1.0 kg of fresh samples were collected and kept in plastic bags. Coordinates of sampling points were recorded by GPS. In the laboratory, the soil samples were air-dried at room temperature, then after removing pebbles and other debris, were passed through 63 μm and 2 mm sieves.

Soil pH was measured in a 1:2.5 soil-water suspension (measured by a glass electrode Eutech model Cyberscan pH620). Electrical conductivity was determined in the saturation paste extract (1:5 soil-water suspension; Rayment and Higginson, 1992) using a conductivity cell. Soil organic matter (SOM) was measured using the Walkely-Black method (Jackson, 1958). Cation Exchange Capacity (CEC) was determined by saturating soil samples with sodium acetate solution, replacement of the absorbed sodium with ammonium, and determination of displaced sodium by flame photometry. Carbonate concentration was analyzed by a manometric measurement of the CO_2 released following acid (HCl) dissolution (Houba et al., 1995). Granulometric analysis was carried out using the hydrometer method (ASTM D422-63, 2008). Metal contents (Cr, Ni, Pb, Cu, Zn, Co, Fe, Al, Mn and Cd) were extracted by 4 acids digestion (HF-HCl-HNO_3-$HClO_4$) of the 63 μm soil fraction in accordance with EPA standard method (EPA-3052, 1996). Total metal contents in soil extracts were determined using inductively coupled plasma – mass spectrometry (ICP-MS) in ACME lab, Canada (1 T-MS group, multi-acid digestion). Detection limits were 0.02% for Al and Fe, 0.02 mg kg^{-1} for Cu, Pb and Cd, 0.2 mg kg^{-1} for Zn and Co, 0.1 mg kg^{-1} for Ni, 1 mg kg^{-1} for Cr and 2 mg kg^{-1} for Mn. The accuracy of the method was verified by analyzing certified standard reference materials (STD OREA 45C and STD OREA 24C). The analytical recovery was between 90 and 110% for all elements, except for Cd (77%). All reagents used were of analytical grade and were checked for possible trace metal pollution. Nine replicate samples were analyzed to check the precision of the results. Standard deviation percentage calculated on 9 replicates ranged between 2% and 9% for all tested elements.

2.3. Data processing

Prior to data interpretation, values below the detection limit (DL) were adjusted to one-half of the detection limit for purposes of statistical calculation. The descriptive analysis and other statistical tests were performed using SPSS version 20 for windows and R statistical software. The Kolmogorov-Smirnov test (K–S) was applied to investigate normal distribution for both datasets. The K–S test confirmed that heavy metal contents in background samples are normally distributed ($P > 0.05$). The values of K–S test for agricultural soils showed that, Cu, Pb, Zn and Cd concentrations are not normally distributed ($P < 0.05$), as also inferred by the high skewness values. The non-normal distribution is due to the presence of outliers, which correspond to samples with increased concentrations. Therefore, the concentrations of Cu, Pb, Zn and Cd were transformed to natural logarithms in order to stabilize their variance for subsequent statistical analyses. After log-transformation, the distributions of Cu, Pb, Zn and Cd were found to be still nonnormal. The relationships between soil properties and metal contents were investigated by using two-paired correlation analysis and factor analysis (FA). Inter-element relationships can provide interesting information on heavy metal sources and pathways (Dragovic et al., 2008; Goovaerts, 2001; Manta et al., 2002). Factor analysis was used to reduce the high dimensionality of variable space and to better understand the relationships among elements and also to identify the origin of HMs in agricultural and background soils. In this regard, varimax with KaiserMeyer-Olkin (KMO) Normalization was used as the rotation method and factors extracted with an eigenvalue >1.

2.4. Calculation method for geochemical background

In geochemistry, the term *geochemical background* is defined as the normal distribution of an element in barren earth material, and it is more realistic to see the background as a range rather than an absolute value (Hawkes and Webb, 1962). Both geochemical (direct) and statistical (indirect) methods are used for assessing background concentration of HMs in the environment (Matschullat et al., 2000; Teng et al., 2010). However, statistical methods are more popular than geochemical methods, as they are used not only for assessing background contents and the separation of geochemical anomalies from geochemical background, but also have low laboratory work and cost (Gałuszka, 2007). The calculation of mean ±2std in order to estimate a threshold value and the range of background concentration has been used for almost 50 years. However, this method depends on normality of dataset (Reimann et al., 2005). Most datasets in environmental geochemistry are skewed. Therefore, this method is not sufficiently robust. The median ±2MAD ($MAD = median_i\,(|X_i - median_j(X_j)|)$) is better suited for the estimation of threshold values and the range of background data (Reimann et al., 2005; Teng et al., 2010). It is a non-parametric method and not dependent on the distribution of the dataset (Hoaglin et al., 2000). The results of K–S test indicate that HMs, Al, Fe, Mn and other edaphic parameters data distributions are nearly normal (except for EC and SOM), with small differences between the mean and median values and the skewness values close to 0 (Table 1). The MAD and median + 2MAD (upper limit) in background soils of the study area are presented in Table 1.

2.5. Calculation of pollution index methods

In this study, three indices of the P_i, P_n and PLI are applied to qualify the observed degree of heavy metal enrichment and to evaluate anthropogenic influences in the AS. In order to identify the type of metals responsible for pollution, P_i and P_n (Li et al., 2003) were used, while the cumulative effect of all contaminants were manifested using the PLI indices (Tomlinson et al., 1980). Accordingly, three pollution indices are calculated using the following equations:

$$PI_i = C_i / S_i \tag{1}$$

$$P_n = \sqrt{\frac{\left(\frac{1}{n}\sum_{i=1}^{n} PI_i\right)^2 + (Max\ PI)^2}{2}} \tag{2}$$

$$PLI = \sqrt[n]{PI_1 \, PI_2 \, \ldots \, PI_n} \qquad (3)$$

where, C_i is the measured value of element i at each sampling point, and S_i is the regional background value of the heavy metal i; PI_i is the single pollution index, P_n is the comprehensive pollution index (Nemero index), max (PI) is the maximum value of the pollution indices of the heavy metal, and n is number of heavy metals.

3. Results and discussion

3.1. Soil properties

The descriptive statistics for AS and BS samples are presented in Table 1. Statistical calculations on datasets provided information about the frequency distribution of concentration of Al, Fe and Mn, as well as some edaphic properties such as pH, EC, SOM, CEC, sand, silt and clay fractions in soils. In agriculture soils pH ranged from 7.39 to 8.62, with a mean value of 8.02. AS is predominately basic (pH of 50% of the samples is >8), due to the high carbonate content of the parent rock. Average pH in BS samples is 8.18. Mobility and retention of heavy metals are also strongly affected by soil pH.

Table 1
Statistical summary of some soil properties and metal concentrations in agricultural and background soils (in mg kg^{-1}for Cu, Pb, Zn, Cd, Ni, Cr, Co, Mn and % for Al and Fe).

Agricultural soils (n = 105)

	Mean	S.D.	Skewness	C.V.	Median	MAD	Min	Max	ESCo (n = 30)	MECo (n = 7)	BM$_{Pb-Zn}$(n = 7)
pH	8.02	0.27	−0.03	3.37	8.03	0.25	7.39	8.62	7.9	8.3	7.6
E.C.	2.17	2.25	3.85	103.00	1.60	0.96	0.26	13.89	1.13	1.17	7.62
S.O.M.	2.8	1.1	1.2	39.0	2.7	0.8	1.0	6.6	1.0	1.8	0.7
CaCO3	34.6	5.2	−0.1	15.2	35.3	4.4	21.5	45.4	34.8	33.4	37.4
Sand (%)	31.0	17.5	0.7	56.6	27.1	19.9	3.7	79.6			
Clay (%)	25.7	9.1	0.0	35.7	26.8	9.8	5.2	51.8			
Silt (%)	43.4	12.0	−0.5	27.6	45.2	12.2	15.2	62.7			
CEC	17.8	6.6	−0.9	37.3	20.5	4.0	1.6	34.3			
Al	5.3	0.6	0.7	12.1	5.2	0.7	3.8	6.9	4.4	3.8	2.5
Fe	2.8	0.6	4.3	21.8	2.8	0.3	1.2	7.7	5.9	17.4	3.0
Mn	649.9	177.3	4.1	27.0	640.0	83.0	328.0	1866.0	1156.0	1420.0	2255.0
Cu	35.7	10.3	2.1	28.8	33.2	4.7	15.4	84.0	45.9	64.5	78.6
Pb	34.6	44.9	4.9	130.0	23.2	5.4	7.2	319.3	73.4	58.3	2244.0
Zn	111.5	143.3	9.2	129.0	90.1	16.2	50.2	1510.3	221.1	562.3	2469.1
Ni	66.2	10.0	0.4	15.1	64.6	8.2	35.6	94.8	79.3	88.6	54.2
Co	14.7	2.5	1.1	17.0	14.7	1.9	7.0	27.9	18.4	19.3	17.7
Cd	0.43	0.83	9.66	193.00	0.31	0.07	0.11	8.68	0.74	1.60	10.48
Cr	85.9	9.7	0.3	11.3	86.0	10.4	67.0	116.0	91.5	106.0	49.0

Background soils (n = 40)

	Mean	S.D.	Skewness	C.V.	Median	MAD	Min	Max	Median + 2MAD	MSW*	UCC**
pH	8.18	0.20	−0.15	2.40	8.20	0.26	7.88	8.45	8.72		
E.C.	0.86	0.20	3.69	89.80	0.44	0.10	0.29	2.62	0.63		
S.O.M.	1.1	0.7	1.4	68.6	0.9	0.3	0.6	3.5	1.4		
CaCO3	32.6	9.2	−0.9	28.3	34.7	4.0	13.1	45.5	42.7		
Sand (%)	30.5	15.1	0.7	49.0	28.0	17.5	10.3	63.7	63.0		
Clay (%)	26.2	6.3	0.0	24.0	26.8	5.0	13.4	39.3	36.9		
Silt (%)	43.3	11.1	−0.2	25.0	44.5	11.1	22.9	61.1	66.7		
CEC	17.6	4.6	−0.6	26.1	20.1	1.6	10.6	24.0	23.3		
Al	5.5	0.4	−0.1	7.6	5.4	0.7	4.9	6.1	6.8		
Fe	2.6	0.2	−0.2	9.4	2.7	0.3	2.2	3.0	3.2	3.5	3.0
Mn	641.2	139.4	−0.3	21.7	643.0	74.1	299.0	934.0	791.2	530.0	527.0
Cu	25.7	4.9	−0.8	18.9	25.1	2.6	13.4	32.7	30.3	25.0	25.0
Pb	28.1	10.3	0.2	36.7	27.5	5.0	7.3	49.2	37.5	17.0	14.8
Zn	79.6	21.7	−0.2	27.2	80.0	20.0	34.8	119.8	120.0	70.0	65.0
Ni	59.3	11.9	−0.7	20.0	61.4	10.8	31.1	80.2	83.0	20.0	56.0
Co	13.3	2.2	−1.8	16.4	13.7	2.1	6.9	15.6	17.9	10.0	24.0
Cd	0.26	0.09	−0.53	34.30	0.27	0.07	0.07	0.43	0.42	0.30	0.10
Cr	90.9	8.0	0.2	8.8	88.0	8.9	79.0	102.0	105.8	80.0	126.0

E.C.: Soil electrical conductivity, S.O.M: Soil organic matter (%), CaCO3: Carbonates (%). (dS/m), S.D: Standard deviation, C.V: Coefficient of variation, MAD: Median absolute deviation, ESCo: Esfahan steel company, MECo: Mobarakeh steel company, BM$_{Pb-Zn}$: Bama Pb-Zn mine, MSW: median soil worldwide, UCC: Upper continental crust, *Reimann and de Caritat, 1998, **Wedepohl, 1995.

Cationic elements tend to be more mobile in low pH (Kashem and Singh, 2001; Martinez and Motto, 2000; Rodríguez Martín et al., 2007; Rodrı´guez Marti´n et al., 2013). The soil in the study area is predominately agricultural with low to medium organic matter content. The mean SOM in agricultural soils is 2.8%, with values ranging between 1% and 6.6% (Table 1). Soil organic matter (SOM) influences heavy metal absorption in soil. This effect is probably due to the cation exchange capacity of organic materials (Martin and Kaplan, 1998). In AS, calcium carbonate ranges from 21 to 45 % (mean = 34.6%) being strongly to extremely calcareous according to Avery classification (Avery, 1980). The mean value of carbonate is higher than the mean value reported by Jalali and Hemati (2013), for paddy soils (25%) of Felavarjan, Fooladshahr and Zarrinshahr counties in Isfahan province. The moderately alkaline pH, High $CaCO_3$ content, and low to medium SOM are three typical characteristics of soils in Central Iran (Dayani and Mohammadi, 2010; Jalali and Hemati, 2013; Karimi et al., 2011). Also, 36% of AS and 16% of BS are saline with an electrical conductivity in the saturation paste extract above 2 dS m^{-1}. The result is believed to reflect the use of poor quality groundwater and municipal wastewater, along with the presence of evaporite sediments, especially east and north of the study area. Although soil EC does not directly affect plant growth, it has been used as an indirect indicator of the amount of nutrients available for plant uptake and salinity levels (Smith and Doran, 1996). CEC values range between 1.36–34.2 cmol^{+}kg^{-1}, averaging 17.76 cmol^{+}kg^{-1}, indicating moderate cation exchange capacity (Table 1), similar to those found for paddy soils in Central Iran (Jalali and Hemati, 2013). Soil granulometric fractions are also related to metals content in soil, particularly clay content, which tend to retain metals (Rodríguez et al., 2008). Clay fraction percentage in AS and BS ranges from 5.2 to 51.8% (mean, 25.7%) and 13.4 to 39.3% (means, 26.2%), respectively. Regarding soil texture, most samples fall in the silty clayey loam (25%), clayey loam (22%), and loam (18%) categories. The other soil textural classes are sandy loam, silty loam, sandy clayey loam, silty clay and loamy sand (Fig. 1). The main differences of edaphic parameters between AS and BS lie in EC and SOM. Mean electrical conductivity in AS (2.17 dS/m), doubles that of BS (0.86 dS/m), and soil organic matter content in AS (mean, 2.8 %) is 2.5 times higher than that of BS (mean 1.1 %), justified by the amount of organic fertilizers used on arable lands and also irrigation with low quality (saline) waters. Major element (Al, Fe and Mn) concentrations in AS and BS are similar. Mean Al, Fe and Mn concentration in two soil categories range from 5.3– 5.5%, 2.6–2.8% and 641–649 mg kg^{-1}, respectively. Fe and Mn mean concentration is higher than the mean values reported by Jalali and Hemati (2013) for paddy soils of Isfahan region (Fe: 1240 mg kg^{-1}; Mn: 95.7 mg kg^{-1}).

3.2. Heavy metal content

Heavy metal contents in agricultural soils of Iran are reported by many authors (Amini et al., 2005; Dayani and Mohammadi, 2010; Hani and Pazira, 2011; Jalali and Hemati, 2013; Jalali and Khanlari, 2008a; Rahmanipoura et al., 2014). The statistical summary of the measured HMs content in the study area soils is presented in Table 1. The concentration (mg kg^{-1}) of HMs in agricultural soil samples ranges as follows: Cu 15.4–84 (Mean:35.7), Pb 7.2–319 (Mean:34.6), Zn 50.2–1510 (Mean:111), Ni 35.6–94.8 (Mean:66.2), Co 7–27.9 (Mean:14.7), Cd 0.11–8.68 (Mean:0.43) and Cr 67–116 (Mean:85.9) mg kg^{-1}. The ranges reflect high variability with moderate to high coefficient variations for Cd, Zn, Pb and Cu, demonstrating higher contents of the measured heavy metals in AS with statistically significant differences. Distributions of Zn, Pb, Cd and Cu are strongly positively skewed (Table 1), showing high metal concentration suggestive of heterogeneous spatial distribution of HMs in AS. High concentrations (above background values) coupled with a high coefficient of variation indicate anthropogenic inputs for HMs. Average Pb and Cd contents in AS samples are lower than those in paddy soils of central Iran reported by Jalali and Hemati (2013), and mean Pb and Cd in agricultural soil of Fooladshahr, Zarrinshahr and Falavarjan reported by Amini et al. (2005). According to Jalali and Hemati (2013), the mean Cu and Zn contents in paddy soils of Isfahan region are 7 and 23.8 mg kg^{-1}, respectively which is lower than corresponding concentrations in AS samples in the study area. Cr, Ni and Co concentrations in AS samples exhibit low coefficient of variation, close to those in BS samples. Moreover, these metals display homogeneous distributions, thus suggesting a major natural lithologic source. The mean value of Ni is higher than the mean reported by Jalali and Hemati (2013) in paddy soil of Isfahan Province (13.4 mg kg^{-1}). Average contents of Ni, Cr and Co in AS are higher than those in agricultural soils of west (Jalali M. and Khanlari, 2008b), north (Hani and Pazira, 2011) and northwest of Iran. According to Table 1, total content of HMs decreases in the order: Zn N Cr N Ni N Cu N Pb N Co N Cd in AS, while the order in BS is: Cr N Zn N Ni N Pb N Cu N Co N Cd. It can be seen that except for Pb and Cr, the order of HMs abundance is similar. Nonetheless, these concentrations are higher than those described for Mediterranean agricultural soils in Spain (Rodrı´guez Marti´n et al., 2013), Duero River basin soils (Nanos and Rodríguez Martín, 2012), Northern Belgium (Temmerman et al., 2003) and even those reported for more intensive farming areas (Andreu and Boluda, 1995) and also median soil worldwide (Kabata-Pendias and Mukherjee, 2007; Reimann and de Caritat, 1998).

Table 2
Descriptive statistics of the soil contamination indices.

In the study area, potential industrial pollution sources mainly come from mining and Steel plant smelters. The median HMs contents (along with Fe, Al and Mn) are illustrated in Table 1. The median contents of HMs (mg kg^{-1}) in $\text{Bama}_{\text{Pb-Zn}}$ mining area are: Cu 78.6, Pb 2244, Zn 2469, Ni 54.2, Co 17.7, Cr 49 and Cd 10.48. In $\text{Bama}_{\text{Pb-Zn}}$ mining area, the pollution sources include mine dumps, tailing dam and extraction dust. Therefore, HMs are released into agricultural soils through dry deposition, and also by leaching of mine dumps and tailing dam. According to Dayani and Mohammadi (2010), HMs concentrations showed that the soils in the vicinity of mining sites, particularly the old Bama mining site, are severely polluted by mining activity. Esfahan (ESCo) and Mobarakeh (MSCo) Iron and Steel plants also generate a large amount of atmospheric dust with high Fe, Zn, Cu, Pb and Cd content. Median values for Fe, Zn, Cu, Pb and Cd (mg kg^{-1} with the exception of Fe) in ESCo and MSCo industrial areas are: 5.9 and 14.4%, 221 and 562, 46 and 64, 73 and 58, 0.74 and 1.6, respectively.

3.3. Geochemical background of HMs

The upper limit (UL) of regional background (median + 2MAD) in the study area was compared with median soil worldwide (Reimann and de Caritat, 1998) and mean upper continental crust (Wedepohl, 1995). The background values of HMs are higher than both references (with the exception of Cr and Co of UCC). Chinese recommended values for HMs (mg kg^{-1}) are: Cu 24, Pb 26, Zn 74, Co 12.7, Ni 29 and Cr 61 (CNEMC, 1999; CNEPA, 2004), all being lower than UL of background in the study area. The UL of background in the study area is also higher than background of HMs in Belgium arable soils reported by VLAREBO (1996) and De Temmerman et al. (2003), except for Pb (43 mg kg^{-1}). According to Adriano (2001), mean Pb in European soils is 39 mg kg^{-1} which is slightly higher than calculated background (37 mg kg^{-1}) in the study area. Based on analytical results, 15% of AS samples were above regional background. Some authors (e.g., Alloway, 1995) suggest that atmospheric deposition of Pb could occur in agricultural soils close to roads with heavy traffic, resulting from solid particles and motorvehicle exhaust fumes. Other authors (e.g., Biasioli et al., 2012; Gowda et al., 2010; Liua et al., 2005; Nikolaidis et al., 2010; Soriano et al., 2012) believe that industrial and mining dust deposition are the main sources of Pb in agricultural soils, especially in densely industrial and mining areas. In the study area, both sources could contribute in the observed increased Pb levels in AS. Reference values of Mediterranean natural soils for Cu and Zn are 46 mg kg^{-1} and 246 mg kg^{-1}, respectively. These values are higher than upper limit of background in the study area (Cu 30 mg kg^{-1} and Zn 120 mg kg^{-1}). According to several unpublished reports, Cu and Zn are depleted in Isfahan soils. However, in 88% of AS samples Cu concentration is higher than regional background. The most important activity, which produces high concentration of Cu in AS, is the use of fungicidal sprays (copper oxychloride; $Cl_2Cu_4H_6O_6$), that reach the soil surface directly and indirectly as crops. Similar results have been reported by Micó et al. (2006). The mean Zn concentration in AS (111 mg kg^{-1}) is higher than those found in BS samples (79.6 mg kg^{-1}). The high Zn concentrations found in AS are usually related to agrochemical treatments (e.g., inorganic fertilizer use and pesticides), where Zn is present in most soil amendments employed in agriculture (Nziguheba and Smolders, 2008; Rodrı´guez Marti´n et al., 2013). However, the significant increase in Zn content in AS samples in the study area are believed to be related to the Pb-Zn mining dust deposition, and also urban environment as a consequence of vehicle tyre and brake abrasions, and exhaust emissions. In Mediterranean soils, a mean value of 42 mg kg^{-1} Cr and 26 mg kg^{-1} Ni was reported by Roca-Perez et al. (2010). In this study, background values for Cr and Ni are measured as 105 mg kg^{-1} and 83 mg kg^{-1}, respectively. Concentration of Ni, Cr and Co is lower than their levels in regional background, indicating the elements are appreciably enriched by human activity. According to Facchinelli et al. (2001) and Rodríguez Martín et al.

Heavy metal	PI-Mean	PI-Max	PI-CV%	PI classes (% of total samples)				Pn
				A	B	Moderate^C	High^D	
No								Low
Cu	1.18	2.77	24	20	74	6		Moderate (2.12)
Pb	0.92	8.51	119	85	8.5	3	3.5	High (6.05)
Zn	0.93	12.59	138	87	10	2	1	High (8.92)
Ni	0.80	1.14	13	93	7			No (0.98)
Co	0.82	1.56	12	94	6			Low (1.24)
Cd	1.02	20.67	208	79	18	1.5	1.5	High (14.63)
Cr	0.65	1.10	11	96	4			No (0.9)

PLI (7 heavy metals)

Mean PLI	Min PLI	Max PLI	0 b PLI b 1	1 b PLI b 2	PLI N 2
0.85	0.35	2.93	88%	10%	2%

A: *Pn* ≤1, B: 1 b *Pn* ≤2, C: 2 b *Pn* ≤3, D: *Pn* N3.

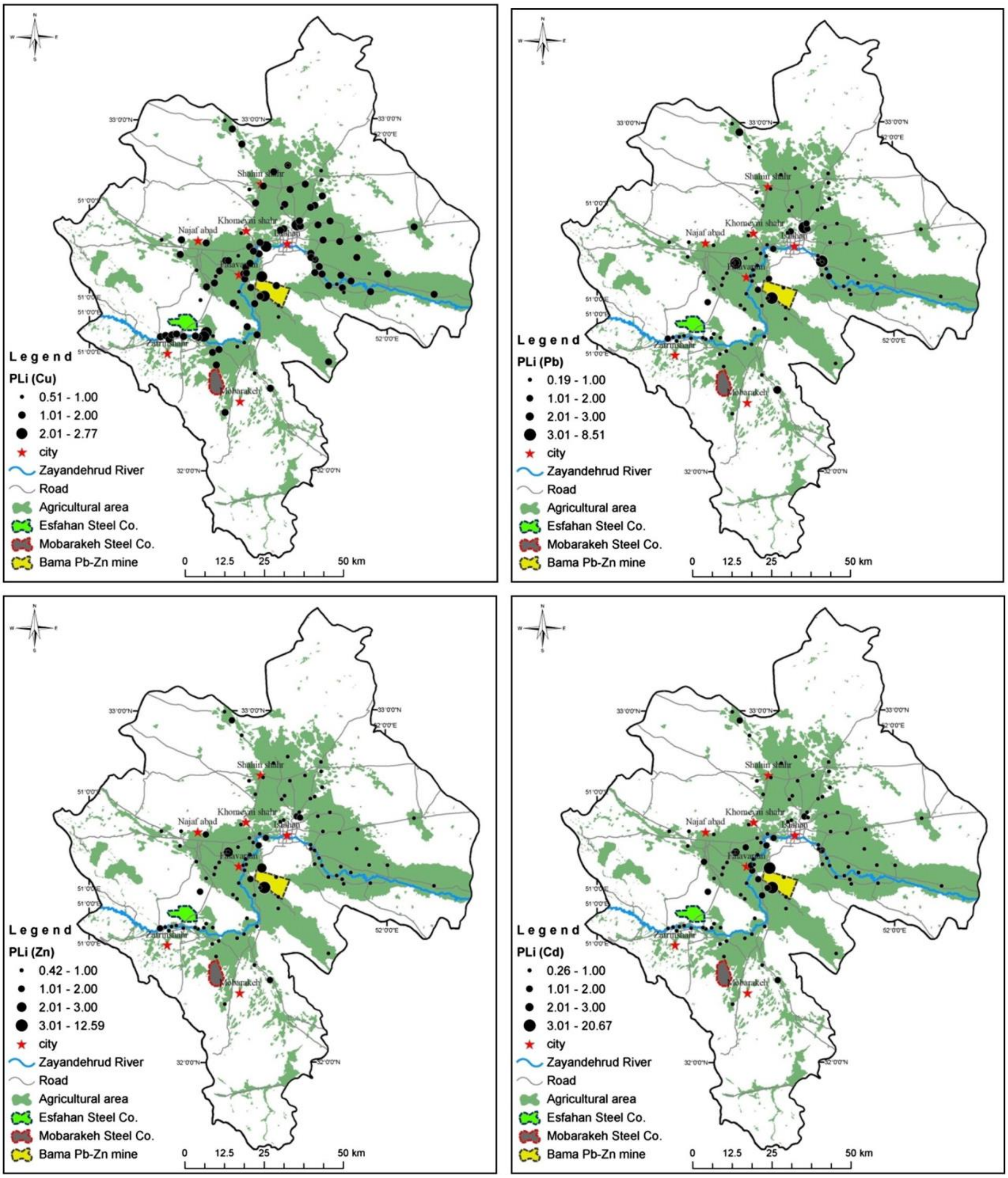

Fig. 2. Dot plot maps of heavy metal pollution index in agricultural soils.

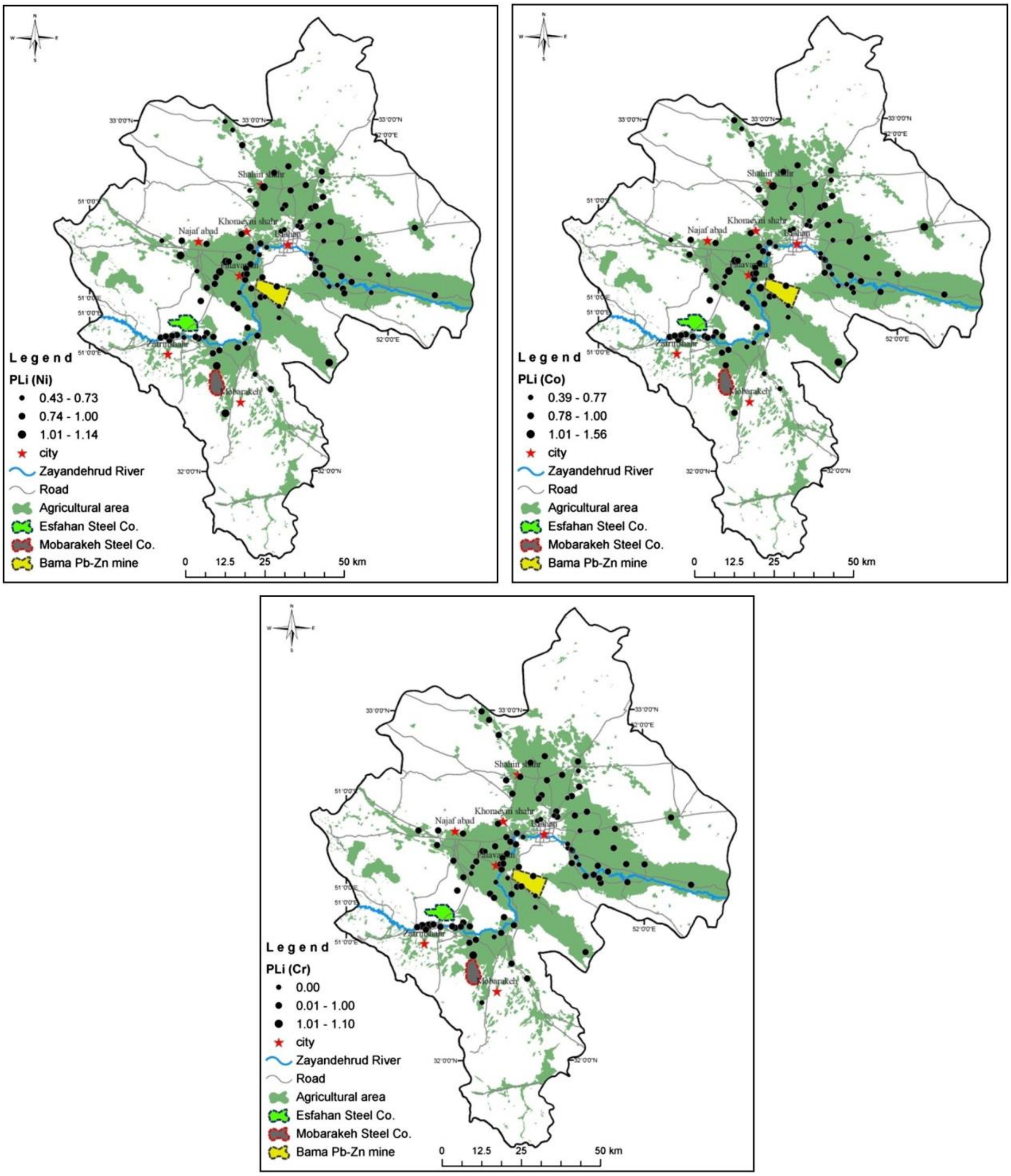

Fig. 2 (*continued*).

(2006), anthropic inputs of Cr, Ni and Co in fertilizers, limestone and manure are lower than the concentration already present in the soils. Consequently, this suggests a lithogenic control over the distribution of Cr, Ni and Co. Cd concentration in natural soils normally oscillates between values below 1 mg kg^{-1} and 3 mg kg^{-1} (Adriano, 2001; Rodríguez Martín et al., 2005). The upper limit of background in the study area (0.42 mg kg^{-1}) is higher than mean Cd content in Spain (0.23 mg kg $^{-1}$), reported by Rodríguez Martín et al. (2013). The concentration of Cd in 16% of AS samples exceeds the UL of regional background value. Some fertilizers and pesticides are known to contain various levels of Cd (Kabata-Pendias and Pendias, 1992). Nonetheless, the AS samples with high Cd content are located near Bama Pb-Zn mine and urban areas.

3.4. Pollution indices

Table 3
Correlation matrix of heavy metals and soil properties in the agricultural soils (n = 105).

	pH	SOM	CEC	CaCO3	Sand	Clay	Silt	Cu	Pb	Zn	Cd	Ni	Co	Cr	Mn	Fe
SOM	-0.346^{**}															
CEC	-0.413^{**}	0.426^{**}														
CaCO3	0.358^{**}	-0.277^{*}	−0.18													
Sand	0.19	-0.291^{*}	-0.450^{**}	0.07												
Clay	-0.357^{**}	0.530^{**}	0.662^{**}	−0.12	-0.771^{**}											
Silt	0.00	0.01	0.13	0.00	-0.874^{**}	0.365^{**}										
Cu	−0.20	0.329^{**}	0.317^{**}	−0.16	−0.20	0.472^{**}	−0.07									
Pb	-0.233^{*}	0.338^{**}	0.388^{**}	0.07	-0.286^{*}	0.482^{**}	0.05	0.350^{**}								
Zn	-0.249^{*}	0.333^{**}	0.354^{**}	0.00	-0.233^{*}	0.425^{**}	0.02	0.448^{**}	0.687^{**}							
Cd	-0.240^{*}	0.300^{**}	0.305^{**}	0.03	−0.20	0.368^{**}	0.01	0.376^{**}	0.671^{**}	0.988^{**}						
Ni	0.04	0.19	0.12	-0.289^{*}	−0.17	0.255^{*}	0.05	0.08	−0.17	−0.10	−0.12					
Co	−0.16	0.17	0.17	-0.559^{**}	−0.18	0.259^{*}	0.06	0.06	−0.11	−0.02	−0.03	0.690^{**}				
Cr	−0.11	0.251^{*}	0.02	-0.515^{**}	0.04	0.01	−0.07	0.18	−0.12	−0.03	−0.03	0.511^{**}	0.473^{**}			
Mn	−0.13	0.254^{*}	0.427^{**}	−0.09	-0.341^{**}	0.543^{**}	0.08	0.257^{**}	0.423^{**}	0.488^{**}	0.439^{**}	0.232^{*}	0.230^{*}	−0.09		
Fe	−0.17	0.330^{**}	0.293^{*}	-0.588^{**}	−0.21	0.366^{**}	0.02	0.05	0.11	0.07	0.02	0.541^{**}	0.531^{**}	0.431^{**}	0.701^{**}	
Al	-0.230^{*}	0.324^{**}	0.294^{*}	-0.608^{**}	−0.22	0.371^{**}	0.04	0.12	−0.16	−0.10	−0.14	0.604^{**}	0.773^{**}	0.280^{*}	0.258^{*}	0.913^{**}

** Correlation is significant at the 0.01 level (2-tailed).
* Correlation is significant at the 0.05 level (2-tailed).

According to Eqs. (1), (2) and (3), the values of single factor index, comprehensive pollution index and pollution load index were calculated using HM concentration in agricultural soil. Classification of AS samples based on PI, P_n and PLI are shown in Table 2. The order of mean PI decrease is Cu N Cd NN Zn N Pb N Co N Ni N Cr. considering regional background values, most heavy metals except for Cd and Cu have class A PI mean indicating no contamination. It is notable that of the total agricultural soil samples 6%, 6.5%, 3% and 3% are moderately to highly contaminate by Cu, Pb, Zn and Cd, respectively. The Nemero's soil pollution index (P_n) for all sampling points was calculated to show the relative magnitudes of elemental soil pollution. The obtained P_n values for Pb, Zn and Cd were 6.05, 8.92 and 14.63, respectively. The results revealed that the pollution degree falls in class D, indicative of heavily contaminated area. P_n calculation for other heavy metals, fall into class A for Ni and Cr, class B for Co and class C for Cu showing no to moderate contamination in agricultural soils. The pollution load index of all stations was calculated from PI of each constituent samples. As shown in table 2, the mean PLI is 0.85, indicating no pollutant or deterioration of soil quality. The highest PLI (2.93) was observed in an AS sample located near the $\text{Bama}_{\text{Pb-Zn}}$ mining area. All these approaches are compared to derive realistic estimate of the degree of HM contamination in the agricultural soils. It seems that PLI is an effective tool for differentiating natural and anthropogenic sources in the study area. A pollution index map is presented in Fig. 2.

3.5. Correlation coefficient

Pearson correlation coefficient results between HMs and other soil characteristics are presented in Table 3. A study of correlation matrix among analyzed variables shows considerable degree of interrelationship. Clay fractions and SOM content in AS samples display significant positive correlation with cation exchange capacity in P b 0.01. Grain size and SOM content are found to be important factors affecting metal distribution. Sand fraction is found to be negatively correlated with HM concentrations, whereas positive correlation exists between HMs with SOM and clay fractions. This indicates that HMs are mainly distributed over clay minerals and SOM. Heavy metal contents are higher for clayey soils than in silty or sandy soils, especially in contaminated soils. Similar results are reported from other parts of the world (Chen et al., 2007; Du Laing et al., 2009; Sevinc et al., 2007; Swarnalatha et al., 2012). The high correlation between metals (Cu, Zn, Fe and Mn) and organic fraction shows high affinity of these metals for organic compounds suggesting possible strong complex formations (Marchand et al., 2011). Moreover, the results show that Pb, Zn and Cd positively correlate at P b 0.01 (r = 0.67–0.98). The good correlation among these elements may reflect similarity in their occurrences or geochemical processes that contribute/control their behavior in AS. Pb, Zn and Cd also show significant correlation with Mn and Cu (r = 0.25– 0.48) at $P \leq 0.01$, probably indicating common influential factors on concentration of these heavy metals. Meanwhile, Co and Ni show strong positive correlation with Al (r= 0.60–0.77) and Fe (r = 0.74–0.85), suggesting strong association with alumino-silicate phases and Fe-oxides as important products of parent rock weathering. Cr also significantly correlates with Ni, Co, and Fe at P b 0.01 and with Al at P b 0.05. The significant correlation between Cr, Co, Ni, Al and Fe, is likely due to degradation of parent rocks, suggesting their geogenic association. In addition, relatively poor correlation is also found between Cu, Pb, Zn, Cd and Mn with Ni, Co, Cr, Al and Fe. This could be attributed to anthropogenic inputs of these HMs (Cu, Pb, Zn, Cd and Mn). All heavy metals in agricultural soils display significant correlation with pH, probably reflecting the low variability of pH (3.3%) in agricultural soils.

3.6. Factor analysis

The results of FA for HMs, Al, Fe, Mn, Clay, CEC and SOM in agricultural soils are presented in Table 4. According to the results of initial eigenvalues (N1), three principal components are considered, accounting for over 74% of the total variance. The factor loading plot (Fig. 3) shows the grouping of HMs and other soil properties in agricultural soils. The first component (PC1), explaining 35.7% of total variance, strongly and positively relates to Cd, Pb, Zn (0.89–0.94), and partly to Cu (0.66) and Mn (0.60). According to several studies, the association of these heavy metals can be interpreted by an anthropogenic or a geogenic origin (Cai et al., 2010; Davis et al., 2009; Nanos and Rodríguez Martín, 2012; Rodríguez Martín et al., 2006; Romic and Romic, 2003). PC1 can be defined as an anthropogenic component since Cd, Pb and Zn in some

Table 4
Total variance explained and component matrix (3 factors selected) for agricultural soils.*.

T component	Initial eigenvalues					Extraction sums of squared loadings				Rotation sums of squared loadings			
Total			% of Variance		Cumulative %	Total		% of Variance	Cumulative %	Total		% of Variance	Cumulative %
1	4.642	35.709	35.709	4.642	35.709	35.709	3.764	28.955	28.955 2	4.010	30.850	66.558	4.010
	30.850	66.558	3.651	28.082	57.037								
3		1.087	8.358	74.916	1.087	8.358	74.916	2.324	17.879	74.916			
4		0.938	7.219	82.135									
5		0.641	4.931	87.067									

Component matrix

Parameters	Component matrix			Rotated component matrix		
	1	2	3	1	2	3
SOM	0.592	0.128	−0.211	0.307	0.194	0.529
Clay	0.788	0.118	−0.373	0.388	0.177	0.769
CEC	0.663	0.079	−0.505	0.247	0.061	0.798
Cu	0.660	−0.143	0.195	0.664	0.123	0.196
Pb	0.770	−0.560	0.123	0.894	−0.245	0.249
Zn	0.797	−0.502	0.242	0.945	−0.142	0.178
Ni	0.211	0.831	0.197	−0.101	0.868	0.099
Co	0.302	0.861	0.168	−0.056	0.908	0.179
Mn	0.763	−0.039	−0.006	0.606	0.168	0.434
Fe	0.386	0.867	−0.006	−0.075	0.871	0.368
Cd	0.754	−0.514	0.281	0.935	−0.150	0.119
Cr	0.162	0.523	0.600	0.179	0.731	−0.304
Al	0.327	0.817	−0.175	−0.177	0.749	0.462

* Extraction method: principal component analysis, rotation method: Varimax with Kaiser normalization, rotation converged after 25 iterations.

agricultural soils have the highest loading on PC1. As previously indicated, the concentration of these elements in agricultural soils is typically influenced by human activity, especially by Bama$_{Pb\text{-}Zn}$ mine. Soil copper content is often affected by several anthropic and geogenic influences on a local scale (Rodríguez Martín et al., 2007). This result reflects either industrial activity or direct use of pesticides on crops. It seems that Cu content in AS is mainly related to the use fungicides. However, it must be pointed out that Cu concentration in AS, lies between 15.4 and 84 mg kg^{-1}, which according to several studies is considered normal in natural soils (Alloway, 1995; Roca-Perez et al., 2010). The second component (PC2) including Cr, Ni, Co, Al and Fe can be defined as a geogenic component, as the variability of the elements seems to be controlled by parent rocks. The geogenic component explains 30.8% of the total variance. According to previous studies, it is well-known that Ni, Co and Cr concentrations in soils is highly dependent on their contents in lithological units, and also in basic and ultrabasic rocks (Facchinelli et al., 2001) where the contents of both metals are high. The lithogenic nature of Cr and Ni in PCA has been clearly demonstrated by Rodríguez Martín et al. (2006) and Rodríguez et al. (2008), where Cr and Ni are also grouped in the same component. On the other hand, the anthropic Cr and Ni inputs are as low as their concentrations in soil (Facchinelli et al., 2001; Rodrı´guez Marti´n et al., 2013). This is corroborated not only by the low coefficient of variation for Ni, Co and Cr in AS, but they also come very close to regional background values. The third component (PC3), which explains 8.35% of total variance, shows high positive factor loadings on Clay, CEC and SOM (Fig. 3).

4. Conclusion

No significant differences were found in the main physicochemical soil parameters between AS and BS (except SOM and EC). However, the concentration of some HMs in AS is higher than those in BS. Calculation of regional geochemical background and threshold value of heavy metals shows Cu, Pb, Zn and Cd enrichment in agricultural soils. The pollution indices highlighted Cu, Pb, Zn and Cd significant role in metal enrichment in some parts of Isfahan industrial zone (Bama$_{Pb\text{-}Zn}$ mining area, and ESCo and MSCo areas), indicating considerable contribution of anthropogenic sources, while Cr, Ni and Co do not exceed background ranges in the entire study area. In general, the studied elements display similar spatial patterns, indicating that geogenic source exert the main control on the distribution of the analyzed elements in AS. A fact also confirmed by strong correlation of HMs in multivariate statistical analysis. The results are important for the development of proper management strategies in order to decrease the number of point sources of pollution by various remediation practices in the study area.

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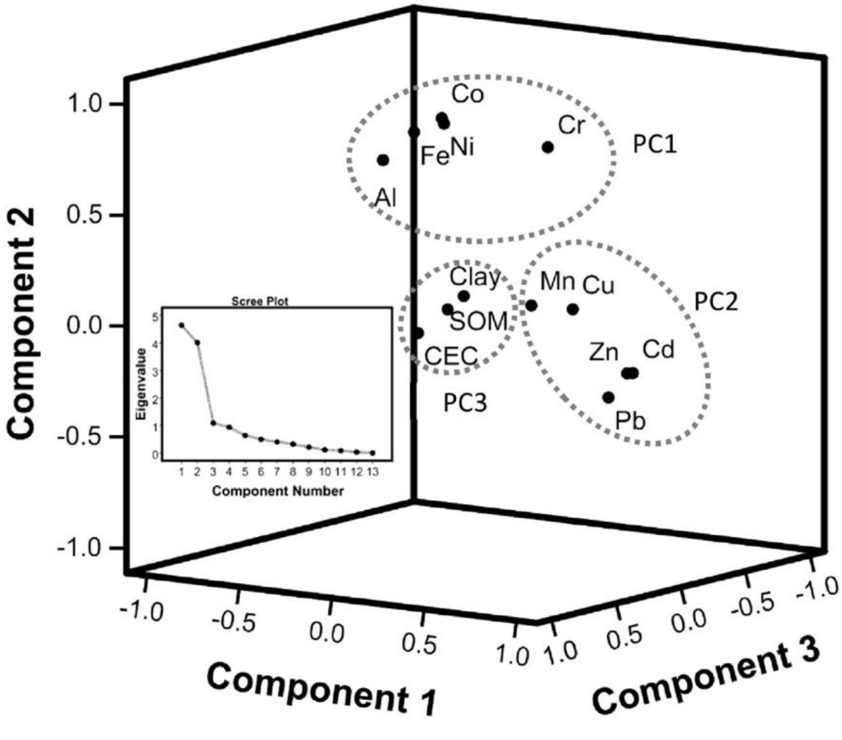

Fig. 3. Factor analysis loading plots for the two rotated components.

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