Journal of Geochemical Exploration 147 (2014) 268–276

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/jgeoexp

Ecological risk of heavy metal hotspots in topsoils in the Province of Golestan, Iran

Rouhollah Mirzaei [a,*], Hadi Ghorbani [b], Naser Hafezi Moghaddas [c], José Antonio Rodríguez Martín [d]

[a] Department of Environment, Faculty of Natural Resources and Earth Sciences, University of Kashan, Kashan, Iran
[b] Department of Soil Sciences, Faculty of Agriculture, Shahrood University of Technology, Shahrood, Iran
[c] Department of Geology, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad, Iran
[d] Department of Environment, Instituto Nacional de Investigación y Tecnología Agraria y Alimentaria (I.N.I.A)., Carretera de A Coruña 7.5 km, 28040 Madrid, Spain

ARTICLE INFO

Article history:
Received 22 February 2014
Revised 5 June 2014
Accepted 19 June 2014
Available online 26 June 2014

Keywords:
Trace elements
Spatial variation
Surface soil
Metal pollution assessment

ABSTRACT

Human activities, such as agriculture or mining, are a continuous source of risk for heavy metal pollution that seriously disturbs the soil environment. Massive efforts are being made to identify the tools to determine indicators of soil quality condition. This study characterises and evaluates the heavy metal (Cd, Cu, Ni, Pb and Zn) contents in the Province of Golestan (northern Iran). Pollution was assessed using the pollution index (PI) and the integrated pollution index (IPI). The potential harmful effects of these heavy metals were evaluated by the Potential Ecological Risk Index (PERI) Method. Kernel density estimation (KDE) and Local Moran's I were used for the hotspot analysis of soil pollution from a set of observed hazard occurrences. In all, 346 topsoils were examined, which represent three areas, approximately including the middle-south, west and north-east areas in this region. The heavy metal concentrations in the analysed samples did not generally present high values, despite anthropic heavy metal input. However, the potential ecological risk indexes (RI) indicated that approximately 68% and 5% of the study samples had medium and high pollution levels, respectively. Multiple hotspots for the above five heavy metals were located in the middle-south and west study areas. This anthropic heavy metal input is related to mining, agricultural practices and vehicle emissions. It was concluded that a moderate and high potential ecological risk covered about 90% of this province. In contrast, the natural origin input became more marked on a long spatial scale.

1. Introduction

The natural concentration of heavy metals like Cd, Cu, Zn, Pb or Cr in soils tends to remain low to ensure an optimum ecological equilibrium. However due to human activities, the heavy metal (HM) concentration in soils frequently rises. Indeed, problems relating to the presence of HMs in agricultural soils are well-known and affect many parts of the world (Kheir, 2010), including the Middle East. Concern about increasing levels of trace elements, especially Cd and Pb, in Iranian soils has recently led the Environmental Protection Administration (EPA) of the Islamic Republic of Iran to start a collaborative research programme to establish the presence of trace elements in Iranian soils and to obtain a meaningful picture of the spatial distribution of HMs in some selected provinces, such as Golestan.

The native metal concentration depends primarily on the geological parent material composition (Alloway, 1995). Moreover, soil properties can greatly influence the availability of HMs through processes such as adsorption or complexation, which affect their ability to extract nutrients from soils (Ross, 1994). Industrial activity, power generation, mining, smelting, waste spills or fossil fuel combustion (Li and Feng, 2012; Rodriguez Martin et al., 2014a,b; Shah et al., 2010; Weber and Karczewska, 2004) are the main sources of metal input into the environment. The most apparent result is Zn, Pb, Cd or Hg soil enrichment (Adriano, 2001; Gil et al., 2004; Ramos-Miras et al., 2011; Rodríguez Martín et al., 2007, 2013b). Metal input into agricultural soils takes place mainly through agrochemicals, manures, biosolids and compost amendments (Carbonell et al., 2011; Mantovi et al., 2003; Rodríguez Martín et al., 2013a), which substantially increase Zn, Cu and Cd content in soils (Nicholson et al., 2003). Irrespectively of the origin or contamination source, HMs can accumulate in crops and reach humans through the food chain (Burger, 2008; Rodríguez Martín et al., 2013a). In the last few decades, many soil pollution surveys on trace elements have been carried out on different scales and many studies are reported in the scientific literature (Amini et al., 2005; Rodríguez Martín et al., 2009; Weber and Karczewska, 2004; Yeganeh et al., 2013). However, very few research works have been conducted in developing countries such as Iran. To date, several attempts have been made to determine the concentration of HMs in Iranian soils (e.g., Amini et al., 2005; Dankoub et al., 2012; Dayani and Mohammadi, 2010; Geranian et al., 2013; Ghaderian and Ghotbi Ravandi, 2012; Karimi et al., 2011; Nael et al., 2009; Naimi and Ayoubi, 2013; Parizanganeh et al., 2010; Qishlaqi et al.,

* Corresponding author. Tel.: +98 9125461288; fax: +98 3155913222.
E-mail address: rmirzaei@kashanu.ac.ir (R. Mirzaei).

http://dx.doi.org/10.1016/j.gexplo.2014.06.011
0375-6742/

2009; Yeganeh et al., 2013). Except for one recent study (Yeganeh et al., 2013), research works into HMs concentrations in Iranian soils on the provincial scale are lacking. The interrelations among these soil HMs exhibit complex correlations and variations in space. There are numerous reported studies that have applied geostatistical techniques to natural resource distributions (Li and Feng, 2012; Rodríguez Martín et al., 2007, 2014a). Spatial data help scientists to define the areas at high risk and can help decision makers to identify locations where remediation efforts should be focused (Mass et al., 2010). In this context, the purpose of this research was to quantify heavy metal concentrations and spatial patterns in surface soils in the Province of Golestan in Iran. The specific objectives were to (1) determine the Cd, Pb, Cu, Ni, and Zn contents in topsoils in this province; (2) assess the ecological risk of HMs in the study area and (3) identify pollution hotspots by these HMs in the topsoils in Golestan.

2. Materials and methods

2.1. Study area

The province of Golestan is located in the northeast of Iran and on the south-eastern shore of the Caspian Sea. The study area is located between 53° 51′ to 56° 21′ of eastern longitude and 36° 30′ to 38° 7′ northern longitude, which comprises a region of approximately 20,437.74 km^2 with 11 districts and a population of some 1.6 million.

The province is bounded to the south by the elevated mountains covered by dense forests (highest altitude: 3881 m), the Caspian Sea to the northwest and the alluvial plain to the north. In general, Golestan has a moderate, humid climate known as “the moderate Caspian climate”. The effective factors behind this climate are: the Alborz mountain range, the direction of the mountains, the altitude in the area, and proximity to the sea, vegetation surface, local winds, and altitude and weather fronts. As a result of these factors, three different climates exist in the region: plain moderate, mountainous, and semi-arid. Average annual rainfall and temperature in the region are 556 mm and 18.2 °C, respectively.

The area includes different land uses, which include agricultural, industrial, urban, forest, range and uncultivated lands. Agricultural, industrial and urban areas are located mainly in the central and western parts of this region. The most important manufacturing establishments in the province of Golestan are manufacturers of food products and beverages, chemicals and chemical products, rubber and plastic products, and other non-metallic mineral products and paper and paper products. The most important crop types in Golestan are wheat, barley, cotton, soya beans, rice and citrus fruits. Most of the mines that operate in Golestan, including the mining of coal and mining of ballast, are located in the central south and the northeast of this province (Fig. 1).

2.2. Sampling and chemical analyses

In all, 346 surface soil samples (0–30 cm) were collected in the study area (Fig. 1). The coordinates of sampling locations were recorded with a GPS. About 1 kg of each sample was sent to the laboratory for an element analysis. Soil samples were dried indoors at room temperature, and impurities such as stones and tree leaves were removed from them. They were passed through a 2-nm nylon sieve. Portions of soil samples (about 50 g) were finely ground manually using a pestle and mortar to be passed through a 0.149-mm sieve and stored in closed polyethylene bags for the HM concentration analysis.

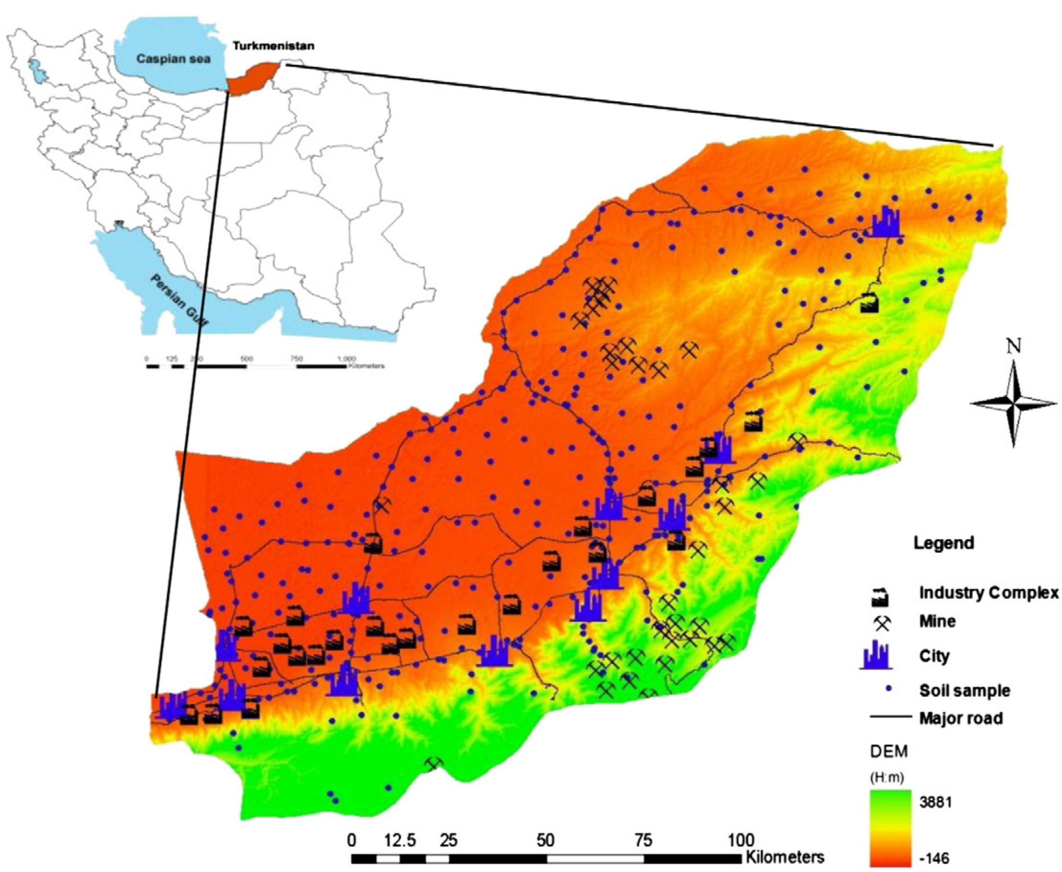

Fig. 1. The study area and the distribution of soil samples.

For the total HM concentrations of Cu, Cd, Zn, Ni and Pb, soil samples (1 g) were digested by a HCl_{O4} (5 cc)–HN_{O3} (7.5 cc)–HF (2.5 cc) mixture in a PTFE vessel at 160 °C for 6 h in an oven. Mineral residues were diluted with deionised water to 50 mL in a volumetric flask and stored in a refrigerator at 4 °C before the analysis (Bai et al., 2011). The soil Cd concentration was determined by graphite furnace atomic absorption spectroscopy (GFAAS, Shimadzu AA-670G, Japan). Cu, Ni, Pb and Zn concentrations were determined by flame atomic absorption spectroscopy (FAAS, Shimadzu AA-670, Japan). Cu, Ni and Zn concentrations were detected in all 346 samples, but the total concentrations of Cd and Pb were detected in 216 samples. An analytical quality control was carried out with standard reference material: SRM 2711 Montana II Soil (350.4 mg kg^{-1} for Zn, 41.70 mg kg^{-1} for Cd, 114 mg kg^{-1} for Cu, 1162 mg kg^{-1} for Pb and 20.6 mg $kg^{-1}$for Ni). Duplicates and reagent blanks were also used as part of the quality assurance/quality control (QA/QC) (Bai et al., 2011). The analytical precisions, as determined by the relative standard deviations of the five HMs, fell within 3 and 10, and recovery was good (81.6–98.5%).

2.3. Assessment of the soil contamination level and ecological risk

Soil pollution is often evaluated by comparing metal concentrations with the related environmental guidelines or by quantifying an accumulation factor (pollution indices, PIs) in comparison to the relevant background values. There are different indices for estimating the degree of HM pollution, such as the pollution index (PI) and the integrated pollution index (IPI) (Sun et al., 2010), the index of geoaccumulation (Igeo) (Muller, 1969), the enrichment factor (Loska et al., 2004), the contamination factor and degree of contamination (Hakanson, 1980), the individual element polluted index, the contamination factor (CF) (Rashed, 2010),the pollution load index (PLI) (Muhammad et al., 2011) and the total contamination index (Zs) (Kumpiene et al., 2011). There are also two methods to calculate the size of the polluted area from soil samples. One is the proportion of contaminated samples, and the other method calculates the polluted area from an interpolation map of soil HMs (Xie et al., 2011).

In Iran, no environmental quality standard for soils is available. Therefore in this study, both the PI and the IPI were used to assess soil pollution in accordance with the background concentration. Background concentrations were obtained from the average concentration of soil samples of untapped and unpolluted areas of the East Province. The PI and the IPI were used to assess environmental soil quality, while a PI of each metal and an IPI of the five HMs were attributed to the study area. The PI was defined as the ratio of the HM concentration in the study to the background concentration (Table 2) of the corresponding metal in Golestan. The PI of each metal was calculated and classified as low (PI < 1), middle (1 < PI < 3) or high (PI > 3). The IPI of the five HMs for the study area was defined as the mean value of the HMs' PI, and was then classified as low (IPI < 1), middle (1 < IPI < 2) or high (IPI > 2) (Sun et al., 2010).

A potential ecological risk index (RI), originally introduced by Hakanson (1980) was used to assess the degree of HM pollution in soil according to the toxicity of the HMs and the response of the environment:

$$RI = \sum E_i \tag{1}$$

$$E_i = T_i f_i \tag{2}$$

$$f_i = \frac{C_i}{B_i} \tag{3}$$

where *RI* is calculated as the sum of all four risk factors for HMs in soils, E_i is the monomial potential ecological risk factor and T_i is the metal toxic factor. Based on the standardised HM toxic factor developed by Hakanson (1980), the order of the HM toxicity level is Cd > Pb = Cu = Ni > Zn. The toxic factor for Pb, Ni and Cu is 5, 30 for Cd and 1 for Zn (Zhao et al., 2005). f_i is the metal pollution factor, C_i is the concentration of metals in soil, and B_i is a reference value for metals. *RI* represents the sensitivity of various biological communities to toxic substances and illustrates the potential ecological risk caused by HMs. Hakanson (1980) defined five E_i categories and four *RI* categories, as shown in Table 1.

2.4. Statistical analysis and geostatistic analysis

Descriptive statistics (mean, median, standard deviation, first and third quartiles, range, maximum, minimum, frequency histogram, skewness, kurtosis and the Kolmogorov–Smirnov (K–S) test) were determined by Excel 2003 (Microsoft Inc., Redmond, USA) and SPSS v.16.0 (SPSS Inc., Chicago, USA). A significance level of 0.05 was used in all the statistical tests.

The two main purposes of soil mapping are to analyse the spatial soil pollution pattern and to identify the contaminated areas, while interpolation accuracy is a relative concept; the criteria vary according to the interpolation purpose. The prediction result of the overall spatial trend of soil HMs should be as precise as possible. There is no doubt that ordinary kriging (OK) is best able to predict the overall soil pollution trend. However, for the purpose of identifying contaminated areas, the interpolation techniques are required to predict the local feature of HM input (especially local hotspots and local coldspots) more precisely. Hotspot analysis methods, such as Local Moran's I, was used, and the local maxima (hotspot) and local minima (coldspot) are reserved on the pollution map. It should be quite clear that all the interpolation results contain errors. Identifying a region as being contaminated should not be merely based on the result of the interpolation results. It has been suggested that the natural background and human activities should be considered before making a decision. The uncertainty of a pollution assessment is located mainly in the region of high local variation, so additional sampling in an uncertainty region is advised (Xie et al., 2011). The uncertainty in soil HM pollution mapping and ecological risk mapping lies mainly in the following regions: (a) the local maxima region, with a small number of isolated samples of high pollution levels surrounded by less polluted samples; (b) the local minima region, with central clean (less polluted) samples surrounded by relatively high polluted samples; and (c) the boundary of the contaminated areas. Hotspot-areas with high levels of pollution in comparison to surrounding areas need to be identified in order to provide a scientific basis for better environmental management (Zhang et al., 2008). Kernel density estimation (Lin et al., 2011) and local Moran's I (Zhang et al., 2008) are used to identify the location, spatial extent and intensity of soil pollution hotspots.

The general form of a kernel density estimator in a 2-D space, termed KDE henceforth, is given by (Xie and Yan, 2008):

$$\lambda(s) = \sum_{i=1}^{n} \frac{1}{\pi r^2} k\left(\frac{d_{is}}{r}\right) \tag{4}$$

where λ (s) is the density at location *s*, *r* is the search radius (bandwidth) of the KDE, *n* is the number of sampling points, *k* is the weight of a point *i* with distance to location *s*. *k* is usually modelled as a kernel function of the ratio between *d* and *r*. To identify soil pollution hotspots, the KDE package, based on the ArcGIS software, was used in this study.

The local Moran's I index examines the individual locations to enable hotspots to be identified based on a comparison made with neighbouring samples. Pollution hotspots can be clustered (spatial clusters) or exist individually (spatial outliers). In this study, spatial clusters of pollution would be soil samples with a high HM concentration surrounded by other samples with a high concentration. In

Table 1
Risk grades indices and grades of a potential ecological risk of heavy metal pollution.

E_i	Risk grade	RI	Risk grade
<40	Low potential ecological risk	≤50	Low potential ecological risk
40–80	Moderate potential ecological risk	50 < RI ≤ 100	Moderate potential ecological risk
80–160	Considerable potential ecological risk	100 < RI ≤ 200	High potential ecological risk
160–320	High potential ecological risk	RI > 200	Significantly high potential ecological risk
≥320	Significantly high potential ecological risk		

contrast, spatial outliers of pollution would be samples with a high HM concentration surrounded by samples with low values. They can be identified by the local Moran's I index (Anselin, 1995):

$$I_i = \frac{z_i - \bar{z}}{\sigma^2} \sum_{i=1, j \neq i}^{n} \left[w_{ij} \left(z_j - \bar{z} \right) \right] \quad (5)$$

where z_i is the value of variable z at location i; $z$bar is the average value of z with the sample number of n; z_j is the value of variable z at all the other locations (where $j \neq i$); σ^2 is the variance of variable z; and w_{ij} is a weight which can be defined as the inverse of distance d_{ij} between locations i and j. Weight w_{ij} can also be determined using a distance band: the samples within a distance band are given the same weight, while those beyond the distance band are given a weight of 0.

A high positive local Moran's I value implies that the location under study has similarly high or low values as its neighbours; thus, locations are spatial clusters. Spatial clusters include high–high clusters (high values in a high value neighbourhood) and low–low clusters (low values in a low value neighbourhood). In soil pollution, low–low clusters are "cool spots", while high–high spatial clusters can be regarded as "regional hotspots". A high negative local Moran's I value means that the location under study is a spatial outlier. Spatial outliers are values that are obviously different from the values of their surrounding locations (Lalor and Zhang, 2001). Spatial outliers include high–low (a high value in a low value neighbourhood) and low–high (a low value in a high value neighbourhood) outliers. In soil pollution, high–low spatial outliers can be regarded as isolated "individual hotspots". To identify the soil pollution hotspots, the Anselin local Moran's I package, based on the ArcGIS software, was used in this study.

3. Results and discussion

3.1. Heavy metal contents and ecological risk assessment

In general terms, the HMs concentration ranges in the province of Golestan (Table 2) do not generally present high values. It is expected that the elements with smaller coefficients of variation are dominated by natural sources, while those with larger coefficients of variation are more likely to be affected by anthropogenic sources (Manta et al., 2002). Background values were used as a basis for the threshold values for HM pollution in soil (Table 2); in Table 2, the mean HM concentration values in soil were higher than the background values, but differences were not significant, and the mean HMs concentrations, especially Cu, Pb and Ni, came close to their local background contents.

According to several works reported by Iranian studies (Amini et al. (2005) 25.6 mg kg^{-1}; Qishlaqi et al. (2009) 596.16 mg kg^{-1}; Dayani and Mohammadi (2010) 101.9 mg kg^{-1}; Parizanganeh et al. (2010) 128.51 mg kg^{-1}; Karimi et al.(2011) 44.25 mg kg^{-1}; Dankoub et al. (2012) 139.3 mg kg^{-1}; Geranian et al. (2013) 46.5 mg kg^{-1}; Naimi and Ayoubi (2013) 99.4 mg kg^{-1}), the Pb content in Golestan soils does not entail any risk. The Pb levels in these studies were higher than those described for the Golestan soils in Iran. The Zn concentrations in Golestan soils do not, in principle, pose any risk. The Zn (mean: 82.08 mg kg^{-1}) values are below the values reported by most Iranian studies done, such as Qishlaqi et al. (2009) (mean: 845.7 mg kg^{-1}); Dayani and Mohammadi (2010) (mean: 250.3 mg kg^{-1}); Parizanganeh et al.(2010) (mean: 606.2 mg kg^{-1}); Dankoub et al. (2012) (mean: 118.7 mg kg^{-1}); Geranian et al. (2013) (mean: 233.5 mg kg^{-1}) and Naimi and Ayoubi (2013) (mean: 101.1 mg kg^{-1}). Nonetheless, the levels that Darvish Bastami et al. (2012) reported for sediments from the Gorgan Bay (mean value: 42 mg kg^{-1}) and Nael et al. (2009) for forest soils (mean value: 64.95 mg kg^{-1}) are lower than those obtained for Golestan soils. According to Roca-Perez et al. (2010), a reference value for Zn in Mediterranean soil is 246 mg kg^{-1} in natural soil.

The mean value of Ni in the Golestan region (34.88 mg kg^{-1}) exhibit lower contents than Iranian literature that range from 53 to 71 mg kg^{-1} (Dankoub et al., 2012; Naimi and Ayoubi, 2013; Solgi et al., 2012; Yeganeh et al., 2013). In the Angouran region (NW Iran) Qishlaqi et al. (2009) reported a mean value of 22.59 mg kg^{-1}. Normally, soil Ni content is associated with soil parent rock control on a regional scale (Nanos and Rodríguez Martín, 2012). Consequently, this suggests a lithogenic control over Ni distribution. The Cu concentration in the study soils ranges between 9 and 93 mg kg^{-1}, which is a wide range with a coefficient of variation of 37% (Table 2). The mean Cu concentration (23.9 mg kg^{-1}) is similar to those reported by Amini et al. (2005) in various soils from Isfahan (16.74 mg kg^{-1}), by Naimi and Ayoubi (2013) in industrial soils (21.1 mg kg^{-1}), by Karimi et al. (2011) in urban soils (38.50 mg kg^{-1}) and in other studies (Dankoub et al., 2012; Darvish Bastami et al., 2012; Nael et al., 2009; Qishlaqi et al., 2009), but is significantly lower than those indicated by Qishlaqi et al. (2009) in cropland soils (1100 mg kg^{-1}). In short, Cu in Golestan soils does not reflect anthropic activity. The residual copper present in oxides and other minerals usually constitutes around 50% of total copper. Hafezi Moghaddas et al. (2013)

Table 2
Descriptive statistics of the elements in topsoils in the province of Golestan.

Variable (mg kg^{-1})	Sample number	Max	Min	Median	Mean	SD	CV (%)	Skewness	Kurtosis	Q1	Q3	BC[a]
Cd	216	0.36	0.01	0.11	0.12	0.07	58	0.62	2.54	0.05	0.175	0.07
Pb	216	44	6.8	13.6	15.42	5.81	37.6	1.52	6.5	11.65	18.5	11.8
Cu	346	93.7	9.3	21.85	23.9	9.07	37.9	2.63	15.74	18.6	26.62	18.6
Zn	346	417.4	25	78.37	82.082	30.87	37.6	4.86	47.29	65.5	92.75	64.2
Ni	346	85.35	9.5	33.85	34.88	11.59	33.22	0.79	3.95	24.92	41.8	30.3

[a] Background concentrations.

Table 3
Statistical results of the pollution index (PI) of heavy metals in Golestan topsoils and the potential ecological risk of all five heavy metals in soil and their main mean values in soil.

Element	PI			Number of samples		
	Min	Max	Mean	Low	Middle	High
Cd	0.14	5.14	1.69	90	102	24
Cu	0.52	5.03	1.29	86	257	3
Ni	0.31	3.07	1.16	124	221	1
Pb	0.57	3.72	1.30	63	151	2
Zn	0.39	6.50	1.28	80	263	3
IPI	0.66	2.76	1.34	91	236	19

Potential ecological risk of all five heavy metals in soil and their main mean values in soil

Heavy metal	Potential ecological index range	Mean value	Standard deviation
Cd	4.28–154.28	50.99	32.03
Cu	2.60–25.18	6.47	2.43
Ni	1.56–15.37	5.83	1.95
Pb	2.88–18.64	6.54	2.45
Zn	0.39–6.50	1.28	0.49
RI	39.88–125.99	69.82	14.54

found that Cu in Golestan soils is probably related to mafic rocks. However, some activities are considered to be local anomalies, and were determined by a hotspot analysis.

The Cd concentrations found in the province of Golestan (mean value 0.12 mg kg^{-1}) are similar to those reported in Spanish soils (0.16 mg kg^{-1}; Nanos and Rodríguez Martín, 2012). The Cd concentration is a relatively low concentration when compared with the mean value reported by Iranian studies in industrial soils (1.26 mg kg^{-1} reported by Solgi et al. (2012), 3.46 mg kg^{-1} reported by Parizanganeh et al. (2010)), in agricultural soils (5.3 mg kg^{-1} reported by Qishlaqi et al. (2009)), where Cd is associated with the use of phosphorus fertilisers (Hafezi Moghaddas et al., 2013; Rodríguez Martín et al., 2013a), in mining-urban soils (0.79 mg kg^{-1} by Dayani and Mohammadi (2010)), in grassland soils (1.1 mg kg^{-1} by Qishlaqi et al. (2009)), or in uncultivated soils (1.61 mg kg^{-1} reported by Amini et al. (2005)).

Table 3 shows the pollution index (P_i) calculated according to the background HM concentrations. The P_i values for all the metals are above 1.0, are classified as middle and are ranked in the following order: Cd > Pb > Cu > Zn > Ni. Nickel presents the lowest value, ranging from 0.31 to 3.07. Lead, zinc and copper obtained similar means, 1.30, 1.28 and 1.29 respectively. For Cd, the mean P_i was 1.69, ranging from 0.14 to 5.14, but 24 samples were classified as high P_i, indicating the presence problematic Cd input of soils in Golestan. Only 3, 1, 2 and 3 samples with high P_{is} for Cu, Ni, Pb and Zn, respectively, indicate the lack of problematic element pollution of Golestan soils. However for Cd, 91 samples showed a high P_{is}. Thus the soil quality of the samples has undergone a moderately impact. According to other authors (Luo et al., 2012; Mass et al., 2010), Cd contributes significantly to pollution. A high ecorisk index value for this metal might be due to the addition of such metals from anthropogenic sources. The major sources of Cd pollution are P-fertilisers (Rodríguez Martín et al., 2013a).

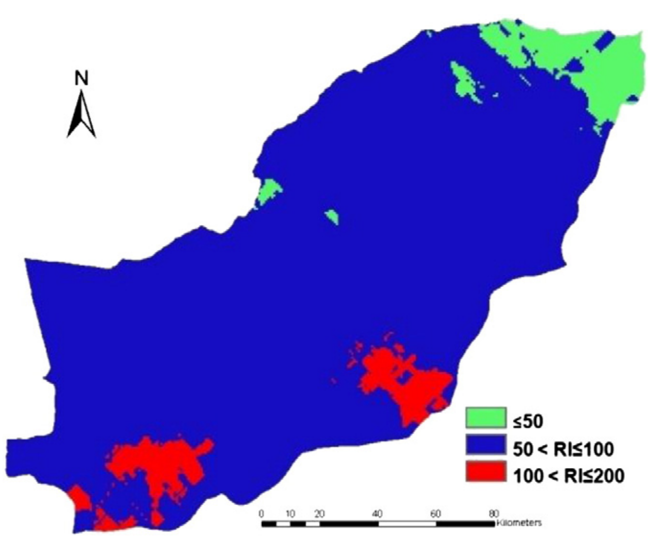

Fig. 2. Distribution of grades on the potential ecological risk of heavy metals in soil.

The results reveal that the E_i for Cu, Ni, Pb and Zn in all the study soil samples was under 40 and that these HMs also present a low potential ecological risk. Conversely, the E_i for Cd in all the study soil samples varies over a broader range in the potential ecological risk index; 47.15% of the potential ecological risk index for Cd is below 80, and for all the study soil samples. The samples with moderate and considerable potential ecological risks for Cd obtain 31.30% and 21.55%, respectively. The potential ecological risk indexes (RI) for all the study soil samples are distributed with a site-specific characteristic (Fig. 2). The soil samples showing a high potential ecological risk are distributed over the two southern parts in the study area, whereas the soil samples with a moderate potential ecological risk are distributed over the most of the study area. In the eastern part of the study area, the northeast part, some soil samples present a low potential ecological risk. Generally, the grade of potential ecological risk lowers from southwest to northeast. The polluted soils with a moderate and high potential ecological risk cover about 91.01% of all the study areas (Fig. 2).

3.2. Soil pollution hotspot maps

Kernel density estimation (KDE) transforms a dot pattern into a continuous surface, and provides a more useful representation of soil pollution distributions (Fig. 3) to allow easier detection of possible pollution hotspots (Lin et al., 2011). The results demonstrate that hotspots are often multiple, and that the spatial pattern of the five HMs are similar and notably indicate the same source of various HM hotspots. This study found that soil pollution hotspots are more clearly defined by KDE, probably because of the clustered distribution of soil pollution occurrences.

The spatial patterns also reveal Pb and Zn hotspots in the central-southern parts of the study area (Fig. 3). The areas with Cd, Cu and Ni

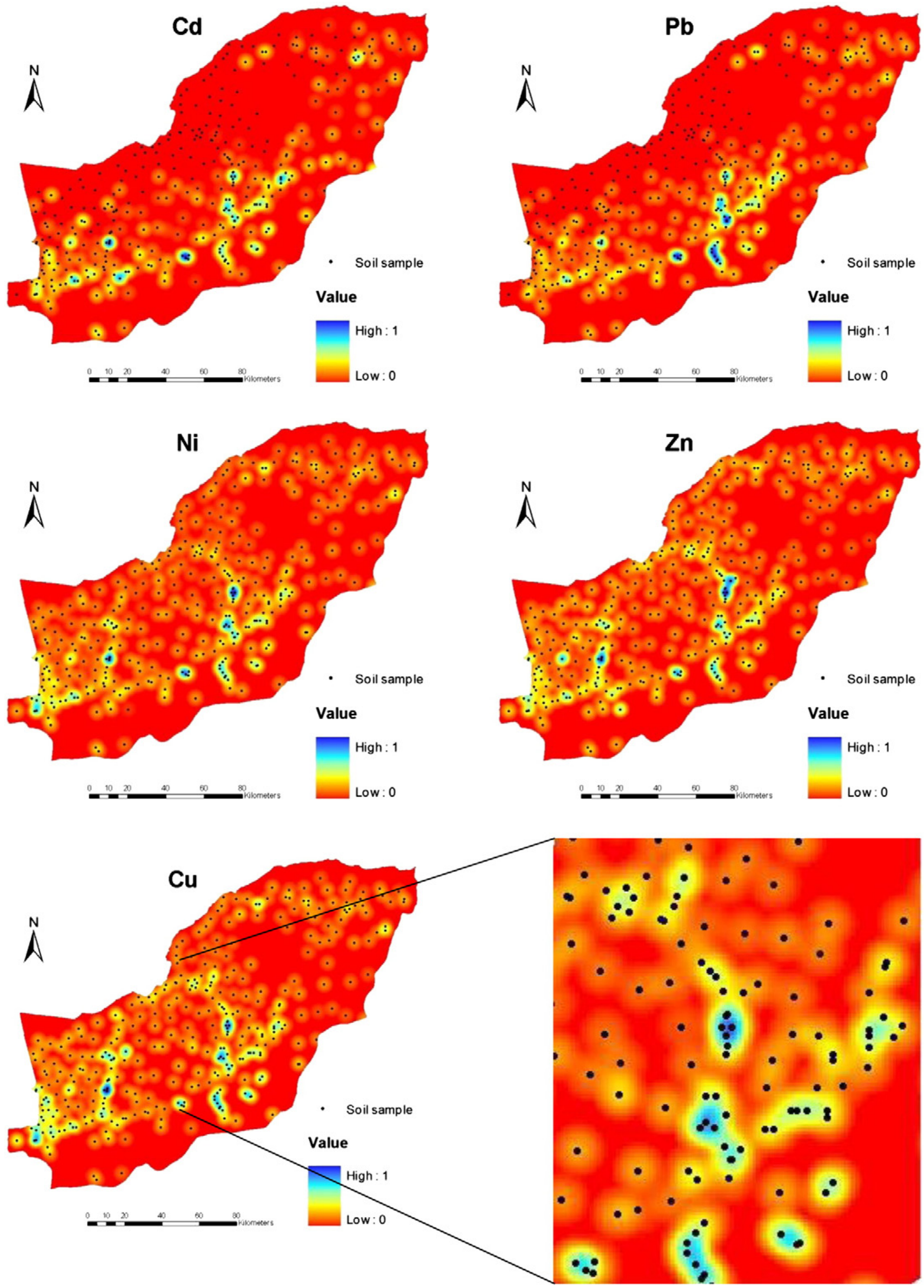

Fig. 3. The kernel density maps (stretched to a min–max range) of Pb, Cd, Cu, Ni and Zn.

Table 4
Comparison of the numbers of the significant and non-significant spatial outliers and spatial clusters.

Heavy metal	Not significant	High–high	Low–low	Low–high	High–low	Total
Cd	200	10	2	2	2	216
Cu	310	23	9	3	1	346
Ni	252	43	44	3	4	346
Pb	185	27	2	1	1	216
Zn	323	10	8	2	3	346

hotspots are particularly located in the central (middle-south) and western parts of the study area. Most of samples for all five HMs are not significant according to the local Moran's I analysis (Table 4). Generally, most samples in the eastern part of the study area are insignificant. This might be due to the lack of development in eastern parts of Golestan if compared to other parts (Fig. 1). High–high spatial clusters or hotspots of the five HMs are generally located in the south central province and in the west (Fig. 4) (this result is the same as the results in Fig. 3). There are also hotspots in northeast parts of the study area near the Iranian

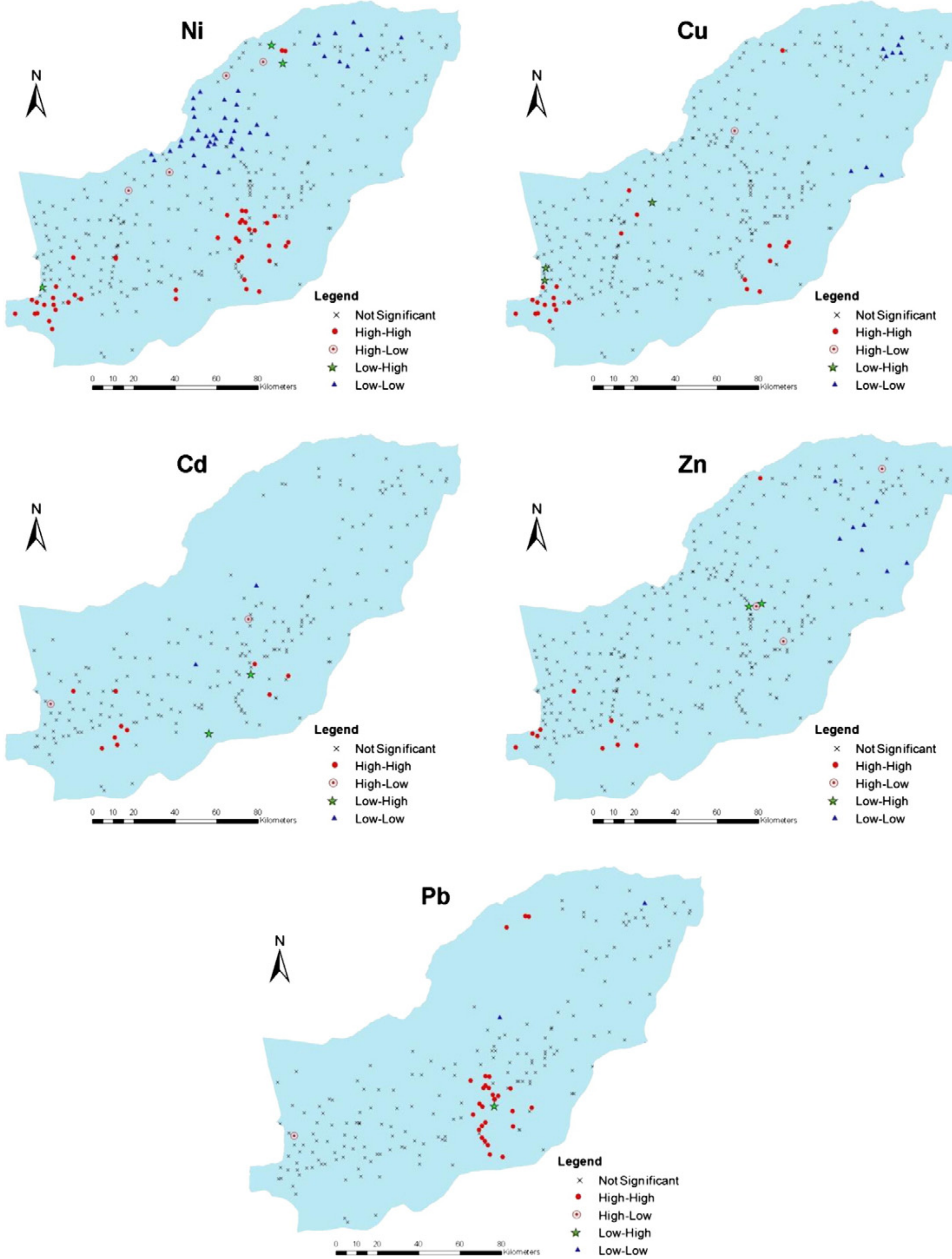

Fig. 4. Spatial distribution map of significant hotspots and cool spots for data.

boundary. In other words, there are generally three main pollution hotspot groups for the five HMs in the south-central, western and north-eastern parts of the study area, while most cool spots of the HMs are found to the east of the study area where no development has taken place. This pattern corresponds to the industrial complexes, agricultural practices, mines, cities and roads network in the study area (Fig. 1). Although it is still hard to establish a causal relationship between pollution hotspots and the influencing factors based on spatial distribution patterns, the most likely factors are pollution from the agricultural practices, industrial areas and mines in the study area. According to other authors, industrial activities are the main reasons for HM emissions in these industrial areas and for HM concentrations (Li et al., 2008). Liu and Bai (2006) and Essumang et al. (2006) have reported that roadside soils near motorways become polluted with Pb and other heavy metals by automobile exhausts. Many studies have also reported anomalously high concentrations of HMs in the surrounding areas of ore deposits and mines (Rashed, 2010; Rodríguez Martín et al., 2014b; Shah et al., 2010). There is a well-defined area of high soil Pb concentrations with a series of regional hotspot clusters distributed along the central-southern part of Golestan and in the northeast (Fig. 4), which correspond to the region of Golestan where mineral material extractions have been taken place for years (Fig. 1). Other recent studies have also indicated anomalously high Pb soil concentrations near old mines (Rodríguez Martín et al., 2014b).

One area with the most soil Cd contents or regional hotspots (high–high values) are found near Gorgan city (the largest city) in the central-western part of Golestan. Three hotspots have also been identified in the southern-central area of this province. There are also three hotspot groups of Cu in the study area located approximately in the south, west and northwest, as well as two coolspots located in the east and southeast parts of the study area. It seems that agricultural practices near the Atrak River and mining activities are the most likely sources of hotspot. Normal agricultural practices may cause HM enrichment (Mantovi et al., 2003; Nourzadeh et al., 2012). These practices are an important source of Zn, Cu, and Cd (Nicholson et al., 2003; Ramos-Miras et al., 2011) from applications of liquid and soil manures (or their derivatives, compost or sludge), or inorganic fertilisers. Intense human activities and agricultural practices seem the most likely sources of hotspots in Golestan. There are two main coolspot groups in the study area, located in the north-centre of the study area, and also in the northeast. Finally, there are four high–low outliers around the first main hotspot group.

4. Conclusions

The HM concentration ranges in the province of Golestan (Table 2) do not generally obtain high values. However based on the background values for HM pollution, this Iranian province shows contamination to a certain degree, although the contamination factors are generally moderate for all the HMs (Cd, Cu, Ni, Pb and Zn). Variation in the topsoil metal concentrations is both natural and of anthropogenic origin. There are three main pollution hotspot groups of five HMs in the southern-central, western and north-eastern parts of the study area, while most coolspots of the HMs are located to the east of the study area. Despite natural resources, this pattern corresponds to the industrial complexes, agricultural practices, mines, cities and road distribution in this area under study. However in this study, attempts have been made to determine soil contamination by HMs in Golestan topsoils. Although the contamination in the study area is not serious, several contamination hotspots have been identified in Golestan, especially in the central-southern part of the study area. Agricultural activities, mining and vehicle emissions are the most likely sources of the HM hotspots in the study area. This work also provides risk maps, based on geostatistic analysis results, thus a potential use to policymakers to decide where remediation measures are required to protect Golestan soils from HM contamination or where soil is deficient in certain HMs.

Acknowledgements

This work forms part of the comprehensive project entitled 'Soil Contamination Atlas of the province of Golestan', which is funded by the Iran Department of the Environment (3005-50). The authors are thankful for the financial support to this project. Our thanks are also due to all the people who have provided help, especially Dr. Farshid Ghorbani.

References

Adriano, D.C., 2001. Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability, and Risks of Metals. Springer, New York.
Alloway, B.J., 1995. Heavy Metals in Soils. Blackie Academic & Professional, London.
Amini, M., Afyuni, M., Fathianpour, N., Khademi, H., Fl¨uhler, H., 2005. Continuous soil pollution mapping using fuzzy logic and spatial interpolation. Geoderma 124, 223–233.
Anselin, L., 1995. Local indicators of spatial association: LISA. Geogr. Anal. 27, 93–115.
Bai, J., Xiao, R., Gong, A., Gao, H., Huang, L., 2011. Assessment of heavy metal contamination of surface soils from typical paddy terrace wetlands on the Yunnan Plateau of China. Phys. Chem. Earth 36, 447–450.
Burger, J., 2008. Assessment and management of risk to wildlife from cadmium. Sci. Total Environ. 389, 37–45.
Carbonell, G., Imperial, R.M.d, Torrijos, M., Delgado, M., Rodriguez, J.A., 2011. Effects of municipal solid waste compost and mineral fertilizer amendments on soil properties and heavy metals distribution in maize plants (Zea mays L.). Chemosphere 85, 1614–1623.
Dankoub, Z., Ayoubi, S., Khademi, H., Lu, S.G., 2012. Spatial distribution of magnetic properties and selected heavy metals in calcareous soils as affected by land use in the Isfahan region, central Iran. Pedosphere 22, 33–47.
Darvish Bastami, K., Bagheri, H., Haghparast, S., Soltani, F., Hamzehpoor, A., Darvish Bastami, M., 2012. Geochemical and geo-statistical assessment of selected heavy metals in the surface sediments of the Gorgan Bay, Iran. Mar. Pollut. Bull. 64, 2877–2884.
Dayani, M., Mohammadi, J., 2010. Geostatistical assessment of Pb, Zn and Cd contamination in near-surface soils of the urban-mining transitional region of Isfahan, Iran. Pedosphere 20, 568–577.
Essumang, D.K., Dodoo, D.K., Obiri, S., Oduro, A.K., 2006. Analysis of polycyclic aromatic hydrocarbons in street soil dust in Kumasi metropolis of Ghana. Environ. Monit. Assess. 121, 401–408.
Geranian, H., Mokhtari, A.R., Cohen, D.R., 2013. A comparison of fractal methods and probability plots in identifying and mapping soil metal contamination near an active mining area, Iran. Sci. Total Environ. 463–464, 845–854.
Ghaderian, S.M., Ghotbi Ravandi, A.A., 2012. Accumulation of copper and other heavy metals by plants growing on Sarcheshmeh copper mining area, Iran. J. Geochem. Explor. 123, 25–32.
Gil, C., Boluda, R., Ramos, J., 2004. Determination and evaluation of cadmium, lead and nickel in greenhouse soils of Almeńa (Spain). Chemosphere 55, 1027–1034.
Hafezi Moghaddas, N., Hajizadeh Namaghi, H., Ghorbani, H., Dahrazma, B., 2013. The effects of agricultural practice and land-use on the distribution and origin of some potentially toxic metals in the soils of Golestan Province, Iran. Environ. Earth Sci. 68, 487–497.
Hakanson, L., 1980. An ecological risk index for aquatic pollution control. A sedimentological approach. Water Res. 14, 975–1001.
Karimi, R., Ayoubi, S., Jalalian, A., Sheikh-Hosseini, A.R., Afyuni, M., 2011. Relationships between magnetic susceptibility and heavy metals in urban topsoils in the arid region of Isfahan, central Iran. J. Appl. Geophys. 74, 1–7.
Kheir, R.B., 2010. Spatial soil zinc content distribution from terrain parameters: a GIS-based decision-tree model in Lebanon. Environ. Pollut. 158, 520–528.
Kumpiene, J., Brännvall, E., Taraškevičius, R., Aksamitauskas, Č., Zinkutė, R., 2011. Spatial variability of topsoil contamination with trace elements in preschools in Vilnius, Lithuania. J. Geochem. Explor. 108, 15–20.
Lalor, G., Zhang, C.S., 2001. Multivariate outlier detection and remediation in geochemical databases. Sci. Total Environ. 281, 99–109.
Li, X., Feng, L., 2012. Multivariate and geostatistical analyzes of metals in urban soil of Weinan industrial areas, Northwest of China. Atmos. Environ. 47, 58–65.
Li, Z., Hou, J., Wang, J., 2008. Potential ecological risk assessment model for heavy metal contamination of agricultural soils in mining areas. Adv. Earth Sci. 23, 509–516.
Lin, Y.P., Chu, H.J., Wu, C.F., Chang, T.K., Chen, C.Y., 2011. Hotspot analysis of spatial environmental pollutants using kernel density estimation and geostatistical techniques. Int. J. Environ. Res. Publi.Health 8, 75–88.
Liu, S.G., Bai, S.Q., 2006. Study on the correlation of magnetic properties and heavy metals content in urban soils of Hangzhou City, China. J. Appl. Geophys. 60, 1–12.
Loska, K., Wiechula, D., Korus, I., 2004. Metal contamination of farming soils affected by industry. Environ. Int. 30, 159–165.
Luo, X.S., Yu, S., Zhu, Y.G., Li, X.D., 2012. Trace metal contamination in urban soils of China. Sci. Total Environ. 421–422, 17–30.
Manta, D.S., Angelone, M., Bellanca, A., Neri, R., Sprovieri, M., 2002. Heavy metals in urban soils: a case study from the city of Palermo (Sicily), Italy. Sci. Total Environ. 300, 229–243.
Mantovi, P., Bonazzi, G., Maestri, E., Marmiroli, N., 2003. Accumulation of copper and zinc from liquid manure in agricultural soils and crop plants. Plant Soil 250, 249–257.
Mass, S., Scheifler, R., Benslama, M., Crini, N., Lucot, E., Brahmia, Z., Benyacoub, S., Giraudoux, P., 2010. Spatial distribution of heavy metal concentrations in urban, suburban and agricultural soils in a Mediterranean city of Algeria. Environ. Pollut. 158, 2294–2301.
Muhammad, S., Tahir Shah, M., Sardar, K., 2011. Heavy metal concentrations in soil and wild plants growing around Pb–Zn sulphide terrain in the Kohistan region, northern Pakistan. Microchem. J. 99, 67–75.
Muller, G., 1969. Index of geoaccumulation in sediments of the Rhine River. J. Geol. 2, 108–118.
Nael, M., Khademi, H., Jalalian, A., Schulin, R., Kalbasi, M., Sotohian, F., 2009. Effect of geo-pedological conditions on the distribution and chemical speciation of selected trace elements in forest soils of western Alborz, Iran. Geoderma 152, 157–170.
Naimi, S., Ayoubi, S., 2013. Vertical and horizontal distribution of magnetic susceptibility and metal contents in an industrial district of central Iran. J. Appl. Geophys. 96, 55–66.
Nanos, N., Rodríguez Martín, J.A., 2012. Multiscale analysis of heavy metal contents in soils: spatial variability in the Duero river basin (Spain). Geoderma 189, 554–562.
Nicholson, F.A., Smith, S.R., Alloway, B.J., Carlton-Smith, C., Chambers, B.J., 2003. An inventory of heavy metals inputs to agricultural soils in England and Wales. Sci. Total Environ. 311, 205–219.
Nourzadeh, M., Hashemy, S.M., Rodriguez Martin, J.A., Bahrami, H.A., Moshashaei, S., 2012. Using fuzzy clustering algorithms to describe the distribution of trace elements in arable calcareous soils in northwest Iran. Arch. Agron. Soil Sci. 59, 435–448.
Parizanganeh, A., Hajisoltani, P., Zamani, A., 2010. Assessment of heavy metal pollution in surficial soils surrounding zinc industrial complex in Zanjan-Iran. Procedia Environ. Sci. 2, 162–166.
Qishlaqi, A., Moore, F., Forghani, G., 2009. Characterization of metal pollution in soils under two landuse patterns in the Angouran region, NW Iran; a study based on multivariate data analysis. J. Hazard. Mater. 172, 374–384.
Ramos-Miras, J., Roca-Perez, L., Guzmán-Palomino, M., Boluda, R., Gil, C., 2011. Background levels and baseline values of available heavy metals in Mediterranean greenhouse soils (Spain). J. Geochem. Explor. 110, 186–192.

Rashed, M.N., 2010. Monitoring of contaminated toxic and heavy metals, from mine tailings through age accumulation, in soil and some wild plants at Southeast Egypt. J. Hazard. Mater. 178, 739–746.

Roca-Perez, L., Gil, C., Cervera, M.L., Gonzálvez, A., Ramos-Miras, J., Pons, V., Bech, J., Boluda, R., 2010. Selenium and heavy metals content in some Mediterranean soils. J. Geochem. Explor. 107, 110–116.

Rodríguez Martín, J., Vázquez de la Cueva, A., Grau Corbí, J., López Arias, M., 2007. Factors controlling the spatial variability of copper in topsoils of the northeastern region of the Iberian Peninsula, Spain. Water Air Soil Pollut. 186, 311–321.

Rodríguez Martín, J., Vazquez de la Cueva, A., Grau Corbí, J., Martínez Alonso, C., López Arias, M., 2009. Factors controlling the spatial variability of mercury distribution in Spanish topsoil. Soil Sediment Contam. 18, 30–42.

Rodríguez Martín, J.A., Ramos-Miras, J.J., Boluda, R., Gil, C., 2013a. Spatial relations of heavy metals in arable and greenhouse soils of a Mediterranean environment region (Spain). Geoderma 200–201, 180–188.

Rodríguez Martín, J.A., Carbonell, G., Nanos, N., Gutiérrez, C., 2013b. Source identification of soil mercury in the Spanish Islands. Arch. Environ. Contam. Toxicol. 64, 171–179.

Rodriguez Martin, J., Nanos, N., Grigoratos, T., Carbonell, G., Samara, C., 2014. Local deposition of mercury in topsoils around coal-fired power plants: is it always true? Environ. Sci. Pollut. Res. http://dx.doi.org/10.1007/s11356-014-2873-0.

Rodríguez Martín, J.A., Gutiérrez, C., Escuer, M., García-González, M.T., Campos-Herrera, R., Águila, N., 2014. Effect of mine tailing on the spatial variability of soil nematodes from lead pollution in La Union (Spain). Sci. Total Environ. 473–474, 518–529.

Ross, S.M., 1994. Toxic Metals in Soil-plant Systems. John Wiley and Sons Ltd., Chichester.

Shah, M.T., Begum, S., Khan, S., 2010. Pedo and biogeochemical studies of mafic and ultramafic rocks in the Mingora and Kabal areas, Swat, Pakistan. Environ. Earth Sci. 60, 1091–1102.

Solgi, E., Esmaili-Sari, A., Riyahi-Bakhtiari, A., Hadipour, M., 2012. Soil contamination of metals in the three industrial estates, Arak, Iran. Bull. Environ. Contam. Toxicol. 88, 634–638.

Sun, Y., Zhou, Q., Xie, X., Liu, R., 2010. Spatial, sources and risk assessment of heavy metal contamination of urban soils in typical regions of Shenyang, China. J. Hazard. Mater. 174, 455–462.

Weber, J., Karczewska, A., 2004. Biogeochemical processes and cycling of elements in the environment. International Symposia on Environmental Biogeochemistry, Wroclaw, Poland. Geoderma 122, 2–4.

Xie, Z.X., Yan, J., 2008. Kernel density estimation of traffic accidents in a network space. Comput. Environ. Urban. Syst. 32, 396–406.

Xie, Y., Chen, T., Lei, M., Yang, J., Guo, Q., Song, B., Zhou, X., 2011. Spatial distribution of soil heavy metal pollution estimated by different interpolation methods: accuracy and uncertainty analysis. Chemosphere 82, 468–476.

Yeganeh, M., Afyuni, M., Khoshgoftarmanesh, A.H., Khodakarami, L., Amini, M., Soffyanian, A., Schulin, R., 2013. Mapping of human health risks arising from soil nickel and mercury contamination. J. Hazard. Mater. 244, 225–239.

Zhang, C., Luo, L., Xu, W., Ledwith, V., Poggio, L., 2008. Use of local Moran's I and GIS to identify pollution hotspots of Pb in urban soils of Galway, Ireland. Sci. Total Environ. 398, 212–221.

Zhao, Q., Xu, Q., Yang, K., 2005. Application of potential ecological risk index in soil pollution of typical polluting industries. J. East China Norm. Univ. (Nat. Sci. Ed.) 1, 110–115.