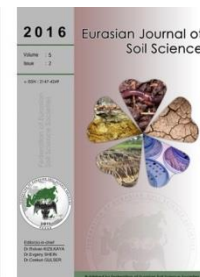




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Heavy metal pollution affected by human activities and different land-use in urban topsoil: A case study in Rafsanjan city, Kerman province, Iran

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Abstract

The excessive input of trace elements into urban soil has become one of the most important concerns in industrial and crowded cities all over the world. The contamination of urban soils can affect the health of people living in urban areas, and the surrounding ecosystems. Current study was conducted to assess the effects of human activities as well as different land-use on accumulation of trace elements in urban topsoil and also identify the potential risks to human health in Rafsanjan (Iran). A total of 100 topsoil samples were taken from different localities of Rafsanjan City and analyzed for Zn, Pb, Cu and Cr using the atomic absorption spectrophotometric method. Pollution index (PI) was calculated for each trace element to identify the rate of trace element accumulation with respect to the background values. Land-use map and geochemical maps were also created for evaluating of spatial distribution of pollution index and trace elements concentration in the studied area. Overlapping the concentrations map and land-use map revealed that the highest values of pollution index and trace elements concentration were located in central part of the city and highways with a great vehicle traffic load and also in the vicinity of industrial factories that increased potential health hazards to the local community. On the other hand, lowest values of trace elements were located in green-lands with strict vehicle traffic laws. These results indicated that different land-use and human activities have affected quality of urban topsoil of Rafsanjan resulting in great apprehensions regarding public health in crowded parts of the city.

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Introduction

Trace elements are ubiquitous in our environment, as a result of natural and anthropogenic activities, and humans are exposed to them through various pathways such as inhalation of dust (Christoforidis and Stamatis, 2009; Narouzi and Khademi, 2015), food chain (Harmanescu et al., 2011), etc. Some trace elements such as Zn and Cu are necessary due to their role as metalloenzymes (Harmanescu et al., 2011). According to Food and Drug Administration (FDA) these metals are known as cofactors of a number of enzymes (FDA,

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2001); however, recommended dietary allowances (RDA) of Zn and Cu for adults are 8–11 and 0.9 mg day⁻¹, respectively, and beyond this range deficiency and toxic effects are observed (FDA 2001; Singh and Garg, 2006). Cu surplus had been associated with liver damage (FDA, 2001). Furthermore, metal fumes cause fever with flu-like symptoms; also, hair and skin discoloration may be caused by fumes of this trace element, although dermatitis has not been reported. Systematically as well, copper dust and fumes may cause irritation of the upper respiratory tract, a metallic taste in the nausea and mouth (Broyer et al., 1972).

The clinical signs of zinc toxicities have been reported as vomiting, diarrhea, bloody urine, icterus, liver failure, kidney failure and anemia (Fosmire, 1990). Also, Zn reduces immune function and the levels of high density lipoproteins (FDA, 2001). Lead is considered to be the most important toxin of trace elements which can be absorbed through ingestion by food and water, and inhalation (Duruibe et al., 2007). Lead poisoning may cause inhibition of the synthesis of hemoglobin; joints and reproductive systems, dysfunctions in the kidneys, cardiovascular system and acute and chronic damage to the central nervous system as well as peripheral nervous system (Ogwuegbu and Muhanga, 2005). Based on the previous reports lead poisoning is also associated with damage to the gastrointestinal tract and urinary tract which result in bloody urine, neurological disorder and can cause severe and permanent brain damage (INECAR, 2000). Poor development of the grey matter of the children's brain is caused by lead thereby resulting in poor intelligence quotient (IQ) (Udedi, 2003). Acute and chronic effects of lead result in psychosis (Duruibe et al., 2007).

Chromium is also one of the known environmental toxic pollutants in the world. Despite a lot of research on the role of chromium in biological systems, it is still a controversial issue and no significant conclusions can be arrived with the available data. Chromium (VI) enters into the cells readily and is reduced to form stable chromium (III) complexes which react slowly and were considered non-toxic. Nevertheless, recent studies suggest that chromium (III) in fact damages cellular organelles, DNA and proteins and can be lethal to organisms and their offspring (Natesan and Balachandran Unni, 2008). Chromium exposure can cause skin rashes, respiratory problems, kidney and liver damage, upset stomach, ulcers, alteration of genetic material, weakened immune systems, lung cancer and ultimately death (McGrath and Smith, 1990; Kabata-Pendias and Pendias, 2011).

In spite of our comprehensive knowledge of pernicious and detrimental effects of trace elements on human health, during the last decades, contamination of urban soils by trace elements has gradually become one of the most significant concerns in metropolitan areas (Giannis et al., 2010; Minkina et al., 2014) and also impose a long-term burden on the biogeochemical cycles in the urban ecosystem (Papa et al., 2010). Extensive use of sewage sludge and waste water for irrigation, pesticide, vehicle exhausts' emissions, mining and rapid development of industries without effectual control has led to a large accumulation of trace elements in soil (Shi et al., 2009).

Street dusts and top roadside soils in urban areas considered as a sign of trace element pollution from atmospheric deposition (Christoforidis and Stamatis, 2009). Although leaded gasoline is the main source of Pb, other trace elements such as Cu, Zn and Cd are coming from car components, tire abrasion, lubricants, industrial and incinerator emissions (Markus and McBratney, 1996; Wilcke et al., 1998). It is proved that source of Cr in the street dust is corrosion of cars (Ferguson and Kim, 1991; Akhter and Madany, 1993) and plating of some motor vehicle parts (Al-Shayep and Seaward, 2001), respectively.

Comparing the trace element concentration with guideline or quantifying of an accumulation factor (pollution index, PI) with respect to the background concentration issued to evaluate the degree of contamination in the urban areas (Jung, 2001). Despite the presence of numerous industrial factories as well as rapid growth of population in Rafsanjan, a few studies associated with trace elements contamination in urban topsoil have been carried out. Urban topsoil, as well as agricultural soils, is being threatened by trace elements as a result of rapid industrialization and urbanization during the last two decades. The current study, however, is focused on soil pollution by trace elements in Rafsanjan, which is attributed to vehicle emissions, domestic heating and other anthropogenic activities. The aim of the present study is to assess the effects of different land-use as well as human activities on topsoil trace element pollution and also identify the potential risk to human health in Rafsanjan.

Material and Methods

Study site

The study site is located in the urban area of Rafsanjan City in Kerman province relatively situated at the southeast of Iran (Figure 1) which is an important social economic southeast of Iran. The soil of Rafsanjan is calcareous and saline its mean annual temperature and average annual precipitation are 14.5 °C and 140 mm, respectively, with a population of approximately 0.4 million.

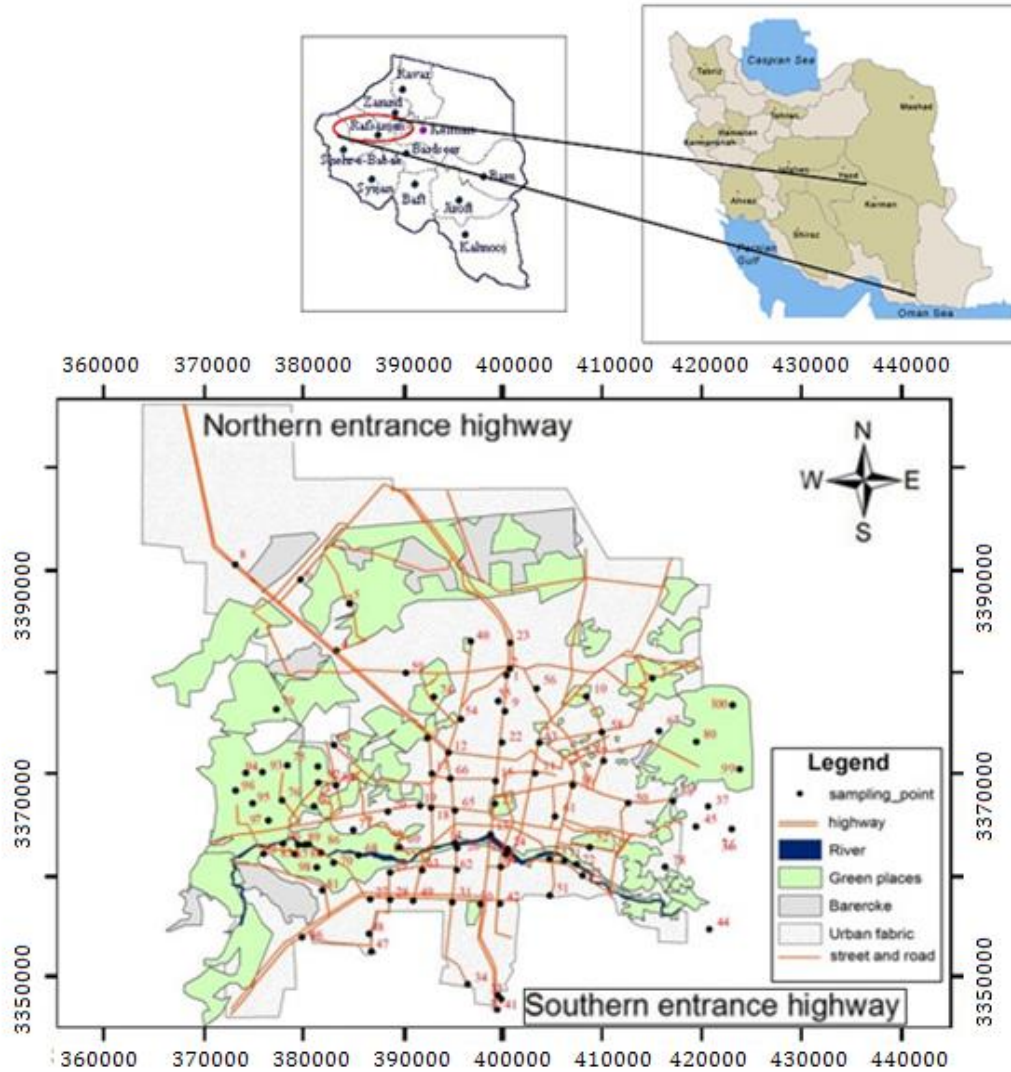


Figure 1. Studied area, sampling points and land-use map of Rafsanjan

Sampling

Sampling points were chosen from different parts of Rafsanjan extending from longitude 55° 59' 30"E and latitude 31° 13"N. For this topsoil investigation, uppermost layer of the soil profile (0–1 cm), where industrial dust and emissions from vehicles are deposited, was collected. This indicates that these topsoil textures are characterized by the predominance of finest particle size. Also the background soil samples were collected from 60cm depth (Morton-Bermea et al., 2009). Sampling points were selected from different land-use to cover the different zones such as parks, green-lands, road side, crowded places and industrial areas of the city in order to specify and clarify the effects of green spaces or urbanized points on polluting the surface and comparing several points with different usage.

A total of 100 samples were collected in summer 2013, the top 1 cm layer of the soil profile was taken with a plastic trowel, stored in a plastic bag and transferred to laboratory immediately. The coordinates of the sample locations were recorded with a GPS, and the sampling points locations are given in Figure 1.

Laboratory analysis

Samples were air-dried. About 25 g portions were ground until fine particles (sieved by 200 μm nylon mesh) were obtained (Morton-Bermea et al., 2009). In order to measure the trace elements' concentrations (Pb, Zn, Cu, Cr), 2.5 g of each sample were digested by nitric acid (4 M) in water bath at 80 $^{\circ}\text{C}$ (Sposito et al., 1982). Afterward, trace elements' concentrations were determined by atomic absorption spectrophotometer Perkin-Elmer 3030.

Statistical analysis and pollution index calculation

Descriptive statistics including the mean, standard deviation, minimum, maximum, median and range were determined and PI was defined as trace element concentration in the sample (topsoil)/background median value. Analysis of the data was done with SPSS statistical software v 16.

Geo-statistical analysis based on GIS

Spatial interpolation and GIS mapping (kriging) techniques were employed to produce spatial distribution maps for the four observed trace elements by ArcGIS v.9. (Tao, 1995; Cattle et al., 2002; Yasrebi et al., 2009). Regarded as mirror of pollution rate in surface soil compared to background, pollution index (PI) was used for depicting geochemical maps. The PI was defined as the value of the pollution index of each element, calculated by the use of the ratio of the trace element concentration in topsoil to the background concentration of the corresponding trace element as the following formulation (Lu et al., 2008; Faiz et al., 2009; Wei et al., 2009; Morton-Bermea et al., 2009).

$$PI = \frac{C_i}{B_i}$$

Where C_i is the concentration of element in topsoil, B_i is the background value.

Results and Discussion

Land-use study

As shown in Figure 1, most of the green-lands are located in west, southwest, east and also river bank, while the gigantic highways which connect the north of Iran to south are located in northwest, north and south. The northwest of the city is also considered as the greatest industrial area of Rafsanjan city. Most of the urban fabrics, traffic load and commercial centers are seen in central parts of Rafsanjan.

Statistical study

Table 1 represents minimum, maximum, median and standard deviations for each trace element and intervention guideline, dictated by Canadian Council of Ministers of the Environment (CCME, 2007).

Table 1. Minimum, maximum, median, mean, standard deviations and maximum acceptable concentration (MAC) of each analyzed trace elements in samples and background

	Median (mg kg^{-1})	Mean (mg kg^{-1})	Min ^a (mg kg^{-1})	Max ^b (mg kg^{-1})	MAC ^c (mg kg^{-1})	Range	SD ^d
Samples							
Pb	73.2	84.2	17.4	215.4	140	198	50.9
Zn	154.8	196.7	38.4	651.6	200	613.2	118.6
Cu	52	59.9	20.8	144	63	123.2	30.4
Cr	59	61.1	29.5	110	64	80.5	16.7
Background							
Pb	19.9	25.1	23.1	27.6		4.5	3.25
Zn	63.6	86.2	64.3	99.1		34.8	17.40
Cu	21.2	24.2	17.9	28.5		10.6	4.51
Cr	21.1	23.3	18.3	26.4		8.1	3.43

^a Minimum concentration (mg kg^{-1})

^b Maximum concentration (mg kg^{-1})

^c Maximum acceptable concentration (mg kg^{-1})

^d Standard deviation

Based on the obtained results, maximum values of Zn, Pb, Cu and Cr were 651.6, 215.4, 144 and 110 mg kg⁻¹, respectively, while minimums were 38.4, 17.4, 20.8 and 29.5 mg kg⁻¹. Maximum values of all studied trace elements in samples were higher than the selected standards. With respect to Zn, Pb, Cu and Cr concentrations, about 36.84, 15.79, 38.95 and 40 % of data were larger than maximum acceptable concentration (MAC). None of the means, however, was larger than MAC. Mean concentrations of the analyzed trace elements in urban soils were 196.7, 84.2, 59.9 and 61.1 mg kg⁻¹, respectively, for Zn, Pb, Cu and Cr, which exceed their background values in all sites. Concentration ranges of Zn, Pb, Cu and Cr were observed to be 613.2, 198, 123.2 and 80.5 mg kg⁻¹, respectively (Table 1). Zinc showed the highest range of concentration while the lowest range belonged to chromium. Medians as well as mean values for the all trace elements were more than background. [Wei and Yang \(2010\)](#) reported that concentration of trace elements in urban soils of all studied cities in China exceed their background values. It can be attributed to the role of human activities in increasing trace element concentrations ([Morton-Bermea et al., 2009](#)).

Pollution index and geochemical maps

Figures 2 and 3 represent the values and limitations of four evaluated trace elements in several sampling points based on the PI values and concentration of them. The PI was classified as: PI <1 low level of pollution; 1 < PI < 5 moderate level of pollution and 5 < PI high level of pollution ([Morton-Bermea et al., 2009](#)).

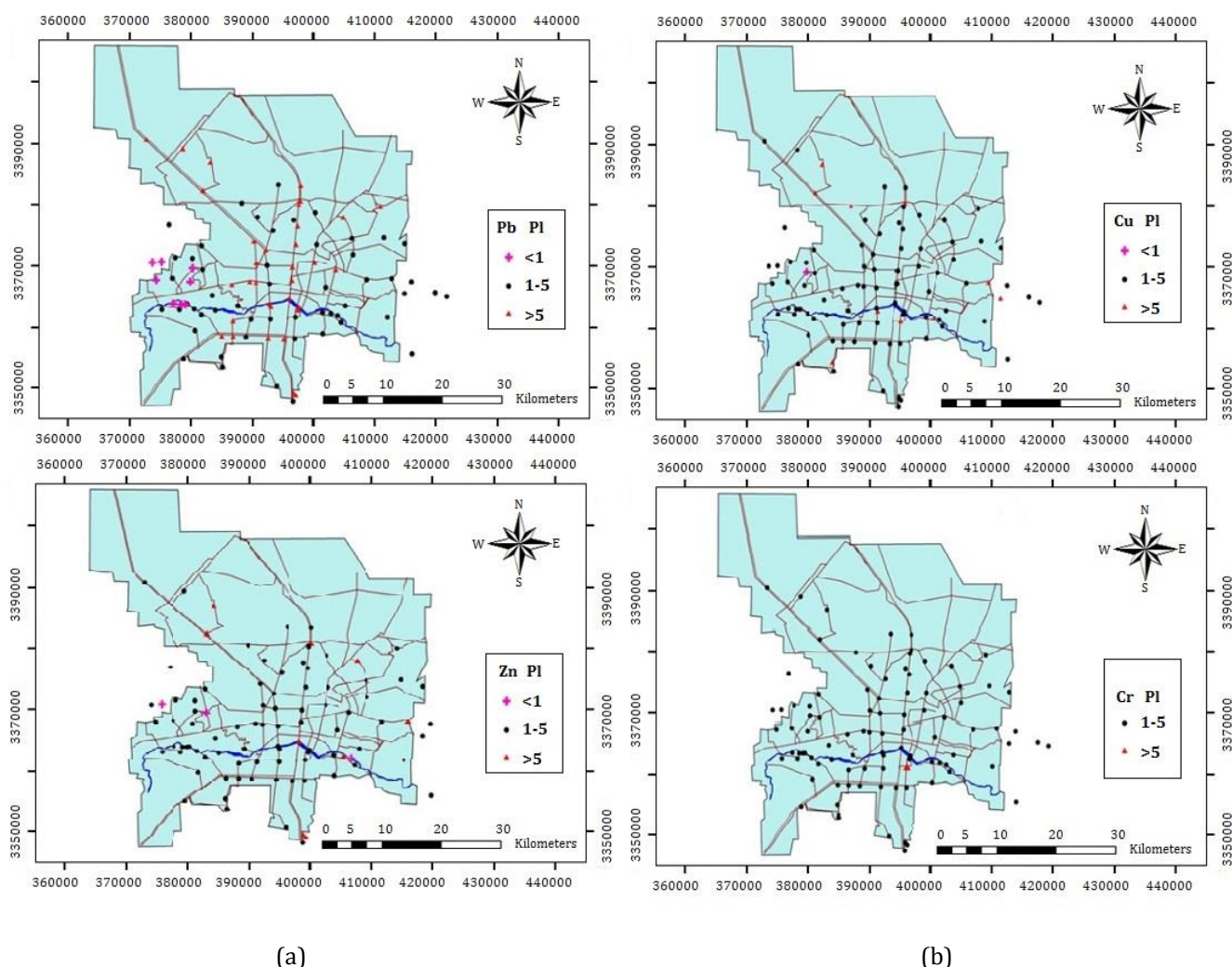


Figure 2. (a) Pollution index (PI) values for Pb and Zn in the studied zone. PI values were calculated as ratio between sample metal concentration and background median. (b) Pollution index (PI) values for Cu and Cr in the studied zone. PI values were calculated as ratio between sample metal concentration and background median

In comparison with the other trace elements, Pb allocated the largest value of PI to itself, varied from 0.9 to 10.8. All sampling points with high level of pollution (PI > 5) are located in the center, south and northwest of the city, where the highest amount of vehicle traffic load and industrial activities can be seen. Other

scientists had also reported that maximum amounts of lead were measured in central parts of cities (Hernandez-Alvarez 2001; STV Gobierno del Distrito Federal 2008; Morton-Bermea et al., 2009). Incontrovertibly, lead has been partly derived from tetraethyl lead, used as an additive to gasoline, released by vehicles into the environments so that more urban areas in the vicinity of highways have a critical lead concentration in topsoil. As shown in Figure 3, the highest concentration of Pb was also measured in northwest, north and central part of the city where human health is threatened by severe symptoms including anemia, a decrease handgrip strength, pale skin, abdominal pain, nausea and paralysis of the wrist joint, etc. On the other hand, continued exposure can lead to decreased fertility and/or increased risk of miscarriage or birth defects (Zheljzakov and Jekov, 1994).

It is obvious that minimum amounts of PI and concentration of Pb were found in the west and south west of Rafsanjan. Based on Figure 1 these parts of the city belong to green-lands and river bank with strict traffic rules. Studying some of China's urban topsoil and road dusts, Shi et al. (2008) reported that traffic contaminations are one of the major sources of trace elements in urban environment.

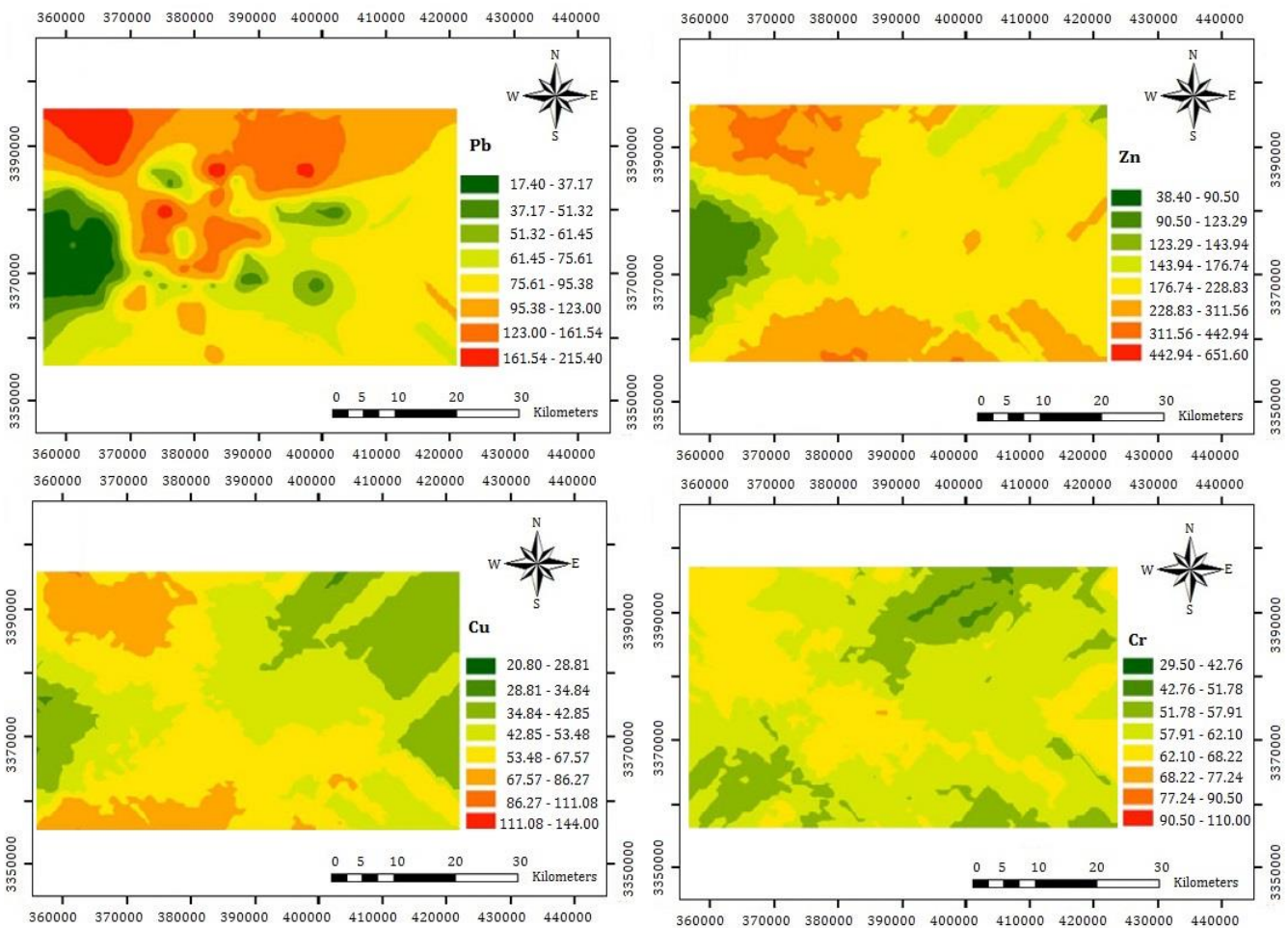


Figure 3. Spatial distribution of trace elements (mg kg⁻¹) in the studied zone

PI values for Zn in different urban topsoil varied from 0.6 to 10.2. Maximum values of PI for Zn are found to be in south, north and northwest. Although the number of PIs which is classified in a high level of pollution (PI > 5) is less than those for lead, comparison between Figures 1 and 3 revealed that the maximum concentration of Zn was measured in the vicinity of industrial factories located in north and northwest, and also the north and south entrance highways of Rafsanjan. Lower Zn concentration in center compared to the north and northwest suggests that concentration of Zn in topsoil is more relative to the industrial activity than vehicle traffic load. Nevertheless, concentrations of zinc in the central parts of Rafsanjan with high traffic load were higher than its concentration in the west and southwest (dense green-lands), which can prove the role of vehicles' emissions or abrasion to increase concentration of Zn. Despite the fact that Zn is an essential element for plants, animals and human, prolonged exposure to this metal in the contaminated part of the city may cause vomiting, icterus, bloody urine, kidney failure, anemia and liver failure, etc.

(Fosmire, 1990). Similarly to lead, lowest concentrations of Zn were also found in the west and southwest of Rafsanjan, which reminds the role of green-lands and restrictive rules of traffic. Many scientists believe that the sources of Pb, Zn, Cu and Cr in urban areas are mainly derived from industrial activities and traffic emission (Ferguson and Kim, 1991; Akhter and Madany, 1993; Markus and McBratney, 1996; Wilcke et al., 1998).

PI values obtained for Cu and Cr are more stable with the ranges of 0.9–6.8 and 1.4–5.2, respectively. In fact, most of the selected points have a moderate PI ($1 < PI < 5$) for Cu. There were just a few places in industrial and over-crowded parts of the city (north, northwest and center) that showed acute values of Cu PIs. Among the analyzed samples, only one point was found for $PI < 1$ for Cu which, as well as other trace elements, is situated in the western green-land regarded as the lung of Rafsanjan. Figure 3 indicated that the pattern of distribution of Cu in the urban topsoil of Rafsanjan was approximately similar to that of Zn, which means risk of the liver damage (FDA, 2001), hair and skin discoloration, irritation of the upper respiratory tract, etc. (Broyer et al., 1972), are higher in north and northwest, and also north and south entrance highways of Rafsanjan than in the central parts and green places.

From Figure 2 it can be found that, there is just one point with high PI for Cr in downtown, while none of the sampling points showed low PI ($PI < 1$). According to Figure 3 most of the central, north and northwest areas have a concentration between 62.10 and 68.22 mg kg⁻¹ which are near the MAC (64 mg kg⁻¹) and may cause respiratory problems, alteration of genetic material, weakened immune systems, etc., for humans (McGrath and Smith, 1990; Kabata-Pendias and Pendias, 2011). Lowest concentrations of Cr were measured in northeast, south and southwest where there are no significant vehicle traffic load and industrial activities as well.

Conclusion

Based on the obtained PIs, approximately all concentrations of the determined trace elements in the urban soils of Rafsanjan are higher than their background values and the maximum concentrations of Zn, Pb, Cu, and Cr in soil samples exceed the MAC. Finding the lowest quantities of analyzed trace elements in green-lands and parks with strict vehicle traffic rules on one hand and the highest amounts in highways, industrial areas and city center with highest traffic load on the other hand emphasizes the negative role of vehicles' traffic load and industrial activities in polluting the urban areas. In other words, the poor management of industrial development, urban construction and traffic load in Rafsanjan has seriously endangered the public health in most of the residential areas. It is suggested that effective monitoring of industrial activities and fuel quality as well as adoption of laws to reduce the traffic load may decrease the quantity of pollutants and trace elements' poisoning in studied areas.

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