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### Potentially toxic elements in urban soils

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2 **Potentially Toxic Elements in Urban Soils: Source Apportionment and**  
3 **Contamination Assessment**

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## 13 **Abstract**

14 Soils play a vital role in the quality of the urban environment and the health of its residents. City soils and street  
15 dusts accumulate various contaminants and particularly potentially toxic elements (PTEs) from a variety of human  
16 activities. This study investigates the current condition of elemental concentration in the urban soils of Hamedan, the  
17 largest and the fastest-growing city in western Iran. Thirty-four composite soil samples were collected from 0-10 cm  
18 topsoil of various land-uses in Hamedan city and were analyzed for total concentration of 63 elements by ICP-MS.  
19 The possible sources of elemental loadings were verified using multivariate statistical methods (principal component  
20 analysis and cluster analysis) and geochemical indices. The spatial variability of the main PTEs were mapped using  
21 geographic information system (GIS) technique. The results revealed a concentration for As, Co, Cr, Mn, Mo, Ni  
22 and V in the soil samples comparable to the background values as well as a range of associations among these  
23 elements in a single component suggesting geogenic sources related to geological and pedogenic processes. Whilst,  
24 the soils mostly presented a moderate to considerable enrichment/contamination of Cd, Zn, Pb, and Sb and moderate  
25 enrichment/contamination of Cu, Zn and Mo. It was found that anthropogenic factors, vehicular traffic in particular,  
26 control the concentration of a spectrum of elements that are typical of human activities, i.e. Cd, Cu, Hg, Pb, Sb and  
27 Zn. Lead and Sb were both the most enriched elements in soils with no correlation with land use highlighting  
28 general urban emissions over time and the impact of transport networks directly on soil quality. The highest  
29 concentrations of As was recorded in the southern part of the city reflecting the influence of metamorphic rocks. The  
30 effect of the geological substrate on the Co and Ni contents was confirmed by their maximum concentrations in the  
31 city's marginal areas. However, high spatial variability of urban elements' contents displayed the contribution of  
32 various human activities. In particular, the increased concentration of Cd, Sb and Pb was found to be consistent with  
33 the areas where vehicular traffic is heaviest.

34 **Keywords:** *Urban geochemistry; Soil Contamination; Environmental Geochemistry; Multivariate Statistics;*  
35 *Enrichment Factor; Contamination Factor.*

## 36 **1. Introduction**

37 Urban areas are the most densely-populated areas with the geographical focus of contamination discharging from  
38 various anthropogenic sources (Acosta et al. 2009; Pickett et al. 2011; Tume et al. 2018). These sources can include

39 one or more of: transport sources (motor exhausts, brake pads, tire wear); commercial and industrial emissions  
40 (energy production, metallurgical industry, electronics, chemical plant, fuel combustion, incinerators, etc.); domestic  
41 activities (construction and demolition, waste disposal, wastewater); and agricultural operations (application of  
42 fertilizers, pesticides, wastewater irrigation) (Wei and Yang 2010; Patinha et al. 2015; Rate 2018; Argyraki and  
43 Kelepertzis 2014; Hu et al. 2013; Li et al. 2017). Emission of harmful substances, in particular Potentially Toxic  
44 Elements (PTEs) has become a worldwide environmental concern in urban areas as a result of rapid industrialization  
45 and urbanization (Cheng et al. 2014; Johnson and Ander 2008; Manta et al. 2002; Su 2014; Yuan et al. 2014).

46 Although some elements are essential micronutrients and are considered beneficial for human and plant health  
47 and growth, their enrichment may reach levels which become a potential health risk (Fordyce and Ander 2003). In  
48 contrast to organic contaminants, PTEs are persistent in the environment and their concentrations remain stable or  
49 may accumulate over time (Lee et al. 2006). The prolonged presence of PTEs represents a significant challenge for  
50 the health of the urban population (Woszczyk et al. 2018; Micó et al. 2006; Wuana and Okieimen 2011; Guney et al.  
51 2017; Lu et al. 2014; Tang et al. 2013). Direct inhalation, ingestion, dermal contact, drinking of contaminated water  
52 and food chain are the principal pathways of human exposure to PTE contaminants in urban environments  
53 (Abrahams 2002; McLaughlin et al. 2000; Poggio et al. 2009).

54 As an essential compartment of the urban ecosystem and sink for PTEs, soils contribute directly or indirectly to  
55 the general citizens' quality of life (Biasioli et al. 2006; Christoforidis and Stamatis 2009). Potentially toxic  
56 elements from local geogenic sources and from atmospheric deposition of dusts and suspended particles may also be  
57 incorporated into urban soil compartment (Norra 2009; Xia et al. 2011). Many researchers have focused on the  
58 necessity for a better understanding of urban soil and dust pollution (Hu et al. 2013; Li et al. 2017; Manta et al.  
59 2002). Urban soils are known to have distinctive features such as heterogeneity, high spatial variability of chemical,  
60 physical, and biological properties, unpredictable layering, rapid change in land use, poor structure, fragmented  
61 distribution and high content of trace elements (Ajmone-Marsan et al. 2010; Kabata-Pendias and Mukherjee 2007;  
62 Manta et al. 2002; Xia et al. 2011). For this reason, the traditional approach in environmental survey, used in intact  
63 natural environment may not be appropriate in city-wide assessments (Wong et al. 2006). In addition, population,  
64 time, location, urban sprawl, intensity of human activities and micro-environmental parameters such as topography,  
65 wind direction, and urban runoff may give rise to micro-environmental variation (Amato et al. 2009; Chen et al.  
66 2005).

67 The characterization of soil and dusts for metal contamination assessment is an effective scientific tool which  
68 provides an insight into the source(s) of contamination and enables policy-makers to more effectively manage urban  
69 sites in order to protect public and ecosystem health.

70 This study investigates the geochemistry of urban soils in Hamedan city of Iran where is believed to have an  
71 active and increasing pollution burden on its basic infrastructure due to increasing population and industrial growth  
72 in previous two decades. The main objectives of this study are: 1) to determine the total concentration of potentially  
73 toxic elements (focusing on those with environmental implications) in urban soil under different land uses from  
74 Hamedan city; 2) to assess the degree of Hamedan soil pollution in comparison with uncontaminated sub-urban soils  
75 and soils from other cities throughout the world as well as applying contamination factor (CF) and enrichment factor  
76 (EF); 3) to identify the possible sources (natural and/or anthropogenic) of PTEs in soils and spatial distribution of  
77 the accumulated elements.

## 78 **2. Materials and methods**

### 79 **2.1 Study Area**

80 Hamedan city, in west of Iran (34°48' N, 48°31' E), is the official and political center of Hamedan province of Iran.  
81 Hamedan is an ancient city with a history of over 3000 years and one of the oldest capitals in the world. Hamedan  
82 was the capital city of Median Empire which was conquered in 550 B.C by Cyrus the Great (Jabarivasal 2012). The  
83 municipality spreads over an area of about 60 km<sup>2</sup> with a population of about 600,000 according to a national census  
84 in 2016. Considering the relative density of population, Hamedan ranks sixth in the country and it is known as a  
85 metropolis in February 2010 (Shojaeimehr and Zakerhaghighi, 2013). Hamedan is an important center of economy,  
86 transportation and manufacturing. Industrial zones of the city are particularly located at a distance of at least 10km  
87 eastward from the city border mainly consisting of small-scale downstream metal industries such as slabs, electrics,  
88 car spares, stone polishing etc. Hamedan has experienced a significant urbanization rate during the past 20 years.  
89 Considering the ratio of families having cars in the country, it is estimated that Hamedan contains approximately  
90 85000 private vehicles. According to Hamedan news agencies, the local vehicular fleet has increased to more than  
91 4000 public vehicles of which about 390 are public buses and remaining are taxis.

92 Geographically, Hamedan is located in the northern foothills of the Mt. Alvand at an altitude of 1813 meters  
93 above sea level (Shojaeimehr and Zakerhaghighi, 2013). The climate of Hamedan is cold and semi-arid with an

94 average annual rainfall of about 330 mm and a mean temperature of 11°C. The prevailing wind direction is from  
95 southeast to northwest.

96 From the geological point of view, Hamedan is located in the Sanandaj-Sirjan structural zone (SSZ) of the  
97 Zagros Mountain Ranges. This area is best characterized by Alvand intrusive complex composed of granite to  
98 granodiorite bodies (Fig. 1) outcropped at the surface toward the southwestern side of the city, where Ganjnameh  
99 and Abbas-Abad valleys are on view. Metamorphic processes related to Alvand magmatism has produced various  
100 facies of slate, phyllite, schist and hornfels rocks which are exposed in the southern part of the city. Hamedan is  
101 underlain by the Quaternary alluvial deposits and alluvial fans derived from weathering of the Alvand granitic and  
102 metamorphic rocks (Fig. 1).

## 103 **2.2 Sample Collection and Analytical Methods**

104 Topsoil samples (0–10 cm depth) were randomly collected from all open, unrestricted lands in Hamedan. Samples  
105 were taken at 31 locations from residential (8 samples), green spaces (11 samples), agricultural lands (6 samples),  
106 parks (4 samples), and playgrounds (2 samples). Four street dust samples were collected from pavements with small  
107 plastic brush and pan. In addition, three samples were taken from suburb far from any pollution sources to represent  
108 the natural background concentrations. The location of sampling points is shown in Fig. 1. The uppermost topsoil  
109 layer is of particular interest in urban geochemistry studies because of the likelihood of atmospheric aerosol  
110 deposition from anthropogenic sources. Composite samples were obtained at each sampling site by thoroughly  
111 mixing five sub-samples collected at corners and center of a 2×2 m square by using a stainless steel shovel to have a  
112 representative sample with a weight of 2kgs. Vegetation debris and coarse-grained particles were manually removed  
113 before packing the samples. Soil samples were stored in polyethylene zip-lock bags and transported to laboratory.  
114 Soils were dried at room temperature and were then disaggregated to pass through 2 mm nylon sieve mesh for  
115 analysis.

116 The values of pH, EC and TDS were measured using a calibrated instrument in an aqueous suspension of 10g  
117 soil and 25ml distilled water according to BS 1377: Part 3:9.0 (1990b) in Zamin Kavan Jonoub Geotechnical Lab,  
118 Tehran, Iran.

119 The organic matter content was measured by Walkley-Black titration method based on the oxidation of organic  
120 matter by  $K_2Cr_2O_7$  (Sims and Wolf 1995).

121 The grain size of soil samples was determined by dry sieve analysis based on the particle size distribution  
122 procedure provided by BS 1377: Part 2: 9.4 (1990).

123 The concentration of major and trace elements in soil samples was measured using aqua regia extractions. A  
124 0.5g sample was digested at 90°C in a microprocessor controlled digestion block for 2h. Digested samples were  
125 diluted and analyzed for 63 elements by Perkin Elmer Sciex ELAN ICP/MS in ActLabs analytical laboratory,  
126 Canada. For quality control and quality assurance purposes, three duplicate and one blank samples were analyzed.  
127 The analytical data represents reasonable and good precision mostly less than 8% and never higher than 10%.

### 128 **2.3 Statistical Methods**

129 The geochemical results were analyzed for descriptive and multivariate statistics using R3.3.1 and SPSS 23.0  
130 software. First of all, the distribution of data was tested with the Shapiro-Wilk's test ( $p < 0.05$ ). Due to the non-  
131 normal distribution of the data, nonparametric statistics was used. Nonparametric kruskal-wallis test was conducted  
132 to determine the differences of PTEs concentration among the five different land uses. The degree of correlation  
133 between the measured elements was determined with Spearman correlation matrix ( $p < 0.05$ ,  $p < 0.01$ ). Additionally,  
134 principal component analysis (PCA) was employed to elucidate the possible sources of PTEs in the Hamedan  
135 surface soils. In the PCA, different groups of elements were categorized based on the concept of communality for  
136 each element. PCA is a powerful tool to differentiate pollution. The varimax rotation method was used in this  
137 analysis to improve the value of factor matrix. Hierarchical cluster analysis (CA) was applied for the same variables  
138 to differentiate the geochemical groups using the Ward's linkage method and the results were presented in a  
139 dendrogram with Squared Euclidean distances.

### 140 **2.4 Geochemical Indices**

141 Enrichment factor (EF) is widely used to identify the contribution of anthropogenic sources in soils (Li et al. 2017).  
142 EF of individual elements in soils is calculated as:

$$143 \quad EF = [C_i/C_{Sc}]_{\text{sample}} / [C_i/C_{Sc}]_{\text{background}}$$

144 in which:

145  $C_i$  and  $C_{Sc}$  are concentrations of the target and reference element in soil sample and in the background sample. The  
146 most commonly used reference elements are Al, Fe, Me, Mn, Sc, Ti (Reimann and Caritat 2000; Yongming et al.



147 2006). Scandium was preferred to Al and Fe and was selected as the reference element in this study since it has no  
148 industrial and/or geogenic origin.

149 Five levels of enrichment can be categorized on the basis of EF (Qingjie et al. 2008):

- 150 -  $EF < 2$  deficiency or minimal enrichment,
- 151 -  $2 < EF < 5$  moderate enrichment,
- 152 -  $5 < EF < 20$  significant enrichment,
- 153 -  $20 < EF < 40$  very high enrichment,
- 154 -  $EF > 40$  extremely high enrichment.

155 Concentration factor (CF) is the quotient of concentration of each element in soil sample ( $C_n$ ) and the  
156 concentration of the same element in reference soil ( $B_n$ ) (Dung et al. 2013).

$$157 \quad CF = C_n / B_n$$

158 Reference soil can be either the world's mean concentration or determined locally from an unpolluted site. The  
159 pollution status of elements is classified into four levels from unpolluted to very polluted as below (Abraham and  
160 Parker 2008):

- 161 -  $CF < 1$  low contamination;
- 162 -  $1 \leq CF < 3$  moderate contamination;
- 163 -  $3 < CF < 6$  considerable contamination;
- 164 -  $CF > 6$  very high contamination

165 Since the composition of soil samples is varied from site to site, in this study local background values were  
166 used to calculate the corresponding degree of EF and CF.

167 The spatial distribution patterns (geochemical maps) showing the hot spots of elevated concentrations were  
168 produced using ArcGIS 10.5 software.

### 169 **3. Results and Discussion**

#### 170 **3.1 Physico-Chemical Parameters**

171 The physico-chemical parameters were determined for Hamedan urban soils. The pH values range from 6 to 7.25  
172 with a mean value of 6.87, which suggest circum-neutral acidity for all the topsoils. Despite the fact that soils of Iran

173 are generally alkaline, the pH of urban soils of Hamedan indicates the influence of the Alvand granite complex. The  
174 urban soils of Hamedan have a pH similar to the background with low variation between different land uses.

175 The electrical conductivity (EC) ranges broadly with a median of 2650 $\mu$ S/cm. The largest EC was measured in  
176 residential soils (67300), decreasing in green spaces ( $EC_{Ave}=5076$ ), parks ( $EC_{Ave}=2143$ ) and agricultural lands  
177 ( $EC_{Ave}=1938$ ). Playgrounds showed the lowest EC values ( $EC_{Ave}=1429$ ). The high EC values of soils in residential  
178 areas are related to the high calcium content in cement and concrete and gypsum which are commonly found in  
179 demolition and construction wastes. Organic matter contents vary from 0.4% to 12.9% with a median of 2.8%. The  
180 maximum and the minimum values belong to parks and residential lands, respectively, reflecting active use of soil as  
181 a growing medium. Sand is the predominant fraction in 78% of the urban soil samples, showing a silty-sand texture.  
182 The rest 22% of the samples show a sandy-silt texture. The soil samples contain 9.89 to 29.9% clay size fraction.  
183 Particle size distribution of Hamedan urban soils follows the land use classes of the city.

### 184 **3.2 PTEs Concentrations**

185 Sixty-three elements were analyzed in all soil samples (Appendix 1); of these, 13 elements were selected for further  
186 analysis based on their known significance in the urban environment ( Charlesworth et al. 2011; Chen et al. 2005;  
187 Giusti 2011; Ljung et al. 2006; Wong et al. 2006; Yesilonis et al. 2008). The mean concentrations of As, Ba, Co, Cr,  
188 Mn, Mo, Ni, V and Zn in the soil samples were 18.9, 124, 13.1, 56.4, 683, 0.77, 54.9, 61.1 and 115.2 mg kg<sup>-1</sup>,  
189 respectively. These values were compared to the background values of the elements in soils from remote suburb of  
190 Hamedan as well as the mean values of the elements from studies in different cities around the world, as shown in  
191 Table 1. It is universally admitted that comparing concentrations of elements in urban soils with values measured in  
192 other cities is an advantageous practice to better estimate the status of contamination (Duzgoren-Aydin, 2007).

193 When compared with the background concentration of the PTEs in the suburban soil of Hamedan, As, showed  
194 mean concentrations comparable to the background values, suggesting a geogenic source for this element. Mean  
195 concentrations of As in urban and suburban soils of Hamedan are 9 times greater than those in the uncontaminated  
196 soils worldwide reported by Kabata-Pendias and Mukherjee (2007). Moreover, it is observed that the content of As  
197 measured in urban and background soil samples of Hamedan is above the mean values when compared to 11 other  
198 cities around the world. This can be attributed to the natural enrichment of arsenic in Sanandaj-Sirjan plutono-  
199 metamorphic belt. Concentrations of Co, Cr, Ni and V in the soils of Hamedan city are below the observed values in  
200 suburban areas indicating a geogenic source for these elements. On the other hand, the elements with higher

201 concentration in the urban soil samples compared to the background (e.g. Cd, Cu, Hg, Pb, Sb and Zn) can be  
202 possibly connected to certain anthropogenic activities in addition to the original content from the parent soils.

203 In comparison to the background soil value ( $0.07 \text{ mg kg}^{-1}$ ), Cd shows 2 fold rise in urban soils ( $0.14 \text{ mg kg}^{-1}$ ),  
204 though, this is still below the worldwide values for Cd ( $0.53 \text{ mg kg}^{-1}$ ). In a recent study, Solgi et al. (2016) reported a  
205 concentration of  $0.23$  to  $2.30 \text{ mg kg}^{-1}$  for Cd in urban park soils of Hamedan. The average content of Cu in Hamedan  
206 soils, both city ( $39 \text{ mg kg}^{-1}$ ) and background ( $36.5 \text{ mg kg}^{-1}$ ), are greater than those in most of the reported values in  
207 other cities. This indicates that in addition to geogenic sources, extra origin(s) from human activities added copper to  
208 the urban soils. Similarly, slight increase is observed for the amount of Zn in Hamedan city soils ( $115 \text{ mg kg}^{-1}$ ) in  
209 comparison to the background ( $90.6 \text{ mg kg}^{-1}$ ) and uncontaminated soils ( $100 \text{ mg kg}^{-1}$ ) values, suggesting possible  
210 anthropogenic sources of Zn in the soils. As can be seen in Table 1, mean concentration of Hg in urban soils is about  
211 11 times higher than the local background levels, representing a significant anthropogenic source for Hg in  
212 Hamedan city. Pb and Sb are similarly enriched up to 3 times in the urban soil samples.

213 The four street dust samples revealed higher concentrations of some PTEs, so that the highest concentration of  
214 Cd ( $0.35 \text{ mg kg}^{-1}$ ) and Hg ( $1.340 \text{ mg kg}^{-1}$ ) were found in SD17 and the highest content of Mo ( $1.15 \text{ mg kg}^{-1}$ ) and Pb  
215 ( $289 \text{ mg kg}^{-1}$ ) were measured in SD21 dust samples.

216 As can be noted from the mean values listed in Table 2, variation in land use showed little effect on  
217 distribution of elements in urban soils of Hamedan, confirmed statistically (kruskal-wallis H) that there is no  
218 significant difference in concentration of PTEs in various land use types ( $p\text{-value} > 0.05$ ). However, it is observed  
219 that agricultural land contains high contents of As, Co, Cr, Cu and Ni. Pb and Sb are slightly more concentrated in  
220 green space soils. Zn and V are dominant elements in parks and residential areas, respectively.

221

### 222 **3.3 Evaluation of the Strength of Soil Pollution**

223 Enrichment factors for PTEs in urban soils of Hamedan are calculated and illustrated in the boxplots Fig. 2.

224 Almost all of the EF values for As, Co, Cr, Mn, Ni and V in Hamedan soils are below 2 confirming the  
225 deficiency or minimal enrichment of these elements and the influence of the local geology. Cadmium has  
226 moderately enriched in 32% of the soil samples ( $2.22 < \text{EF} < 4.84$ ), while 19% of the samples are significantly  
227 enriched in Cd ( $5.23 < \text{EF} < 11.26$ ). The mean EF value for Cd is 3.23. Seven of the 31 analyzed soils fall in the  
228 category of “moderate enrichment” for Cu, with the EF values ranging from 2.14 to 3.95. However, the mean value

229 of EF for Cu (1.75) shows “minimal enrichment”. Similar results are shown for Mo with 10 moderately enriched  
230 soil samples (32%) and the mean EF value of 1.81. Lead appeared to be the most serious enriched element in soils of  
231 Hamedan city with the EF mean value of 6.82. More than half of the soil samples are moderately enriched and 26%  
232 are significantly enriched in Pb ( $2.59 < EF < 4.83$  and  $5.34 < EF < 14.44$ , respectively). The enrichment of Pb and Cd in  
233 Hamedan urban soils has already been identified in previous papers (Solgi et al. 2016; Yeganeh et al. 2012).

234 Almost all of the analyzed soils (97%), present various levels of enrichment in antimony. 51% of the samples  
235 fall into the category of moderate Sb enrichment with the minimum and the maximum observed EF values of 2.04  
236 and 4.62, respectively. Significant enrichment in Sb is observed in 45% of the samples including the EF values  
237 ranging from between 5-13.48. One of the samples was very highly Sb enriched, showing the EF value of 22. In  
238 average, the enrichment factor of Hamedan soils for Sb is 6.15. Zinc is enriched in 42% of the samples (13 soil  
239 samples). Among these, 31% (11 samples) show moderate and the rest show significant enrichments.

240 Dust street samples including one collected from downtown Shir-Sangi square of Hamedan show the highest  
241 EF levels, so that it was extremely enriched showing the EF value of 54.31 for Pb.

242 The assessment of contamination factor for PTEs of Hamedan urban soils is depicted in Fig. 3. Similar to the  
243 results of enrichment factor analysis, the geogenic elements of As, Co, Cr, Mn, Ni and V group together and show  
244 the least contamination with the average contamination factor of less than 1. Contamination factor for Cd in about  
245 42% of the samples ranges from 1.2 to 2.9 which indicate moderate contamination for this element. Five of the 31  
246 soil samples with CF values between 3.07 and 3.87 are considerably contaminated by cadmium. For Cu, a moderate  
247 contamination is observed in 45% of the samples where the CF ranges between 1 and 2.17. More than half of the  
248 samples are moderately contaminated by Mo showing the minimum and maximum CF values of 1.01 and 1.63. The  
249 highest contamination factor is observed for Pb and Sb with the same average CF of 3.7. About 58 and 55% of the  
250 samples fall in the category of “moderate contamination” for Pb and Sb, respectively. Pb in 26% and Sb in 29% of  
251 the analyzed samples are considerably high by showing the respective CF values of 3.15-5.85 and 3.26-4.36. Very  
252 high contamination of Pb ( $5.49 < CF < 21.09$ ) and Sb ( $6.13 < CF < 13.64$ ) is observed in five and four of the analyzed  
253 soil samples, respectively. With respect to Zn, the majority of samples (67%) are within the category of “moderate  
254 contamination” and the remaining are low.

255 The elements with some degrees of enrichment or contamination with respect to the background level probably  
256 suggest the influence of human interventions.

## 257 **3.4 Interrelationship of PTEs**

### 258 **3.4.1. Bivariate statistics**

259 The correlation between the elements can provide some information on their origin in a metropolitan area like  
260 Hamedan. Prior to correlation tests, normal distribution of elements was checked by shapiro-wilk test, as correlation  
261 coefficient depends on the linear combinations of the variables. The result of Spearman's correlation matrix of the  
262 PTEs for the surface soil of Hamedan city is shown in Table 3. As it is indicated, the correlation coefficient between  
263 Co and Cr is 0.880, which represents a strong, positive, linear correlation at the 0.01 significance level which shows  
264 their close association in most soil samples. In addition, Co shows strong positive correlation with both Ni (0.893)  
265 and V (0.717). Cr-Ni and Cr-V form two other highly correlated pairs with a correlation coefficient of 0.836 and  
266 0.766, respectively. In addition, moderately positive correlations are shown between As and Co (0.566), Cr (0.473),  
267 Ni (0.526) and V (0.492). As it is mentioned before, As, Co, Cr, Ni and V occur naturally at abundant levels in  
268 suburban soils of Hamedan, thus the association of these elements can be a reflection of their common source. Cu-  
269 Pb and Pb-Zn show the same considerable positive correlation of 0.825. A significant correlation between Cu with  
270 Zn (0.724) was observed due to the coexistence of these elements as a result of human activities in Hamedan city.  
271 The element pairs Cd-Zn (0.652), Cu-Hg (0.671), Hg-Pb (0.649), Hg-Sb (0.531), Hg-Zn (0.475) and Ni-V (0.532)  
272 had high to moderate positive linear correlation at 0.01 significance level, indicating the similar influential factor. Pb  
273 and Mo (0.433) and Cu and Sb (0.426) were moderately correlated at 0.05 significance level.

274

### 275 **3.4.2. Multivariate statistics**

276 In addition to the correlation coefficient analysis, multivariate statistics was used by principal component analysis  
277 method for assessment of the sources of PTEs in Hamedan city. Varimax rotation with Kaiser Normalization was  
278 applied. Five principal components were extracted from the available dataset accounting for over 80% of the total  
279 variance and considering the eigenvalues greater than 1. The results of the factor loading and communalities are  
280 shown in Table 4. Factor loadings bigger than 0.71 are regarded as excellent, and those smaller than 0.32 are  
281 considered as very poor. The KMO (Kaiser–Meyer–Olkin) test showed a reliable value (0.615) indicating that PTEs  
282 concentration data of Hamedan soils are suitable for principal component analysis.

283 The first factor (F1) explains 28.17% of the total variance and shows positive association between As, Co, Cr,  
284 Ni and V with the factor loadings of 0.635, 0.862, 0.814, 0.895, and 0.664, respectively. This factor can be an

285 indication of the influence of lithogenic inputs into the urban soils as the dominant elements are typical lithophile  
286 elements according to the Goldschmidt's classification and mineralogical components of rocks in the area. Cr and Ni  
287 derived from pedogenic materials are reported from other cities in the world (Zheng et al. 2008; Argyraki and  
288 kelepertzis 2014). Association of the major elements of Al (0.844), Fe (0.698), K (0.545), Mg (0.783) confirms a  
289 geogenic control and reflects a reasonable grouping based on the similarities in the geochemical behavior of these  
290 elements. The basement of Hamedan is composed of pre-Jurassic rocks consisting of schist, hornfels and phyllite  
291 (Baharifar et al. 2004; Sepahi 2008). Association of As which is a chalcophile metalloid in F1 group elements, is  
292 referred to the Sanandaj-Sirjan plutono -metamorphic belt. This zone of the Zagros Orogen is well-known for As  
293 enrichment due to the strong relationship of arsenic with gold mineralization in this particular tectonic settings. This  
294 has been reflected in elevated amounts of As in background as well as in the urban soils of Hamedan. Khaleghian  
295 and Modabberi, (2014) and Yeganeh et al. (2012) reported the high concentration of As in agricultural soils and  
296 potatoes, wheats and Maize grown in agricultural lands around the city. Similar result obtained from urban study of  
297 Estarreja, north-western Portuguese coast where high concentration of As in the city soil were attributed to the  
298 presence of pyrite in the mineralogical suite of the region (Cachada et al. 2012). Vanadium (0.627) and Fe (0.489)  
299 are also partially presented in the second factor (F2, 12.83% of total variance) along with Mn (0.884) and Ti (0.804).  
300 The influence of parent material and natural processes is deduced for association of these elements. The third factor  
301 (F3) explaining 11.83% of the total variance is dominated by Ba, Cu, Mo and Pb with the factor loading values of  
302 0.712, 0.515, 0.503, 0.831, respectively. The F3 elements, according to many previous studies on urban soil quality,  
303 are known as urban elements and are indicators of traffic-related contamination (Adachi and Tainosho 2004; Hays et  
304 al. 2011; Rodríguez-Seijo et al. 2017; Saeedi et al. 2012; Zechmeister et al. 2005). These elements contribute in the  
305 fabrication of automobiles or as additive for engine operation or fuel or resulting from corrosion and deterioration of  
306 vehicle metal parts (Kuang et al. 2004; Dresel 2007). The concentration of Ba, for example, can be related to brake  
307 linings in cars and its emission occurs as a result of frictional processes (Fernández-Espinosa and Ternero-  
308 Rodríguez 2004). Copper compounds serve as anti-wear additive and friction-reduction agent in lubricants (Okorie  
309 et al. 2012). Even though lead used to be a significant component applying as anti-knock agent in petrol (Callender  
310 and Rice 2000), it has been phased out from gasoline in 1990s in Iran. Considering the long residence time of Pb and  
311 non-biodegradability and cumulative tendency of this element (Mielke et al. 2010), it is believed that enrichment of  
312 Pb in current urban soils represents footprints of prevalent use of tetraethyl lead in the past (Carrero et al. 2013;

313 Cicchella et al. 2008; Dean et al. 2017; Francek 1992; Galušková et al. 2014; Lau and Othman et al. 1997; Lin et al.  
314 1998; MacKinnon et al. 2011; Poňavič et al. 2018; Sutherland et al. 2000; Wong 1982) and its reworking through  
315 circulation of urban dusts by local winds. The fourth factor (F4), which accounts for 9.79% of the total variance, is  
316 dominated by Cd (0.899), Hg (0.468) and Zn (0.817). The association of these elements can be mainly attributed to  
317 transportation means. Vehicle tires are main source for cadmium and zinc which may lead to contamination of urban  
318 soils (Davis et al. 2001; Mitchell et al. 2014; Smolders and Degryse 2002; Adachi and Tainosho 2004; Turner and  
319 Rice 2010; van Beers and Graedel 2007; van Bohemen and van De Laak 2003; Zheng et al. 2008). Zinc can also be  
320 derived from wearable parts on vehicle brakes (e.g. disc pads). Moreover, cadmium is typically an anthropogenic  
321 element derived from a wide range of sources in cities including tire wear, paints, pigments, electroplating, plastic  
322 stabilizer, solid wastes and wastewaters and phosphate fertilizers (Kisku et al. 2000; Romic and Romic 2003). The  
323 association of volatile element of Hg in this PC fits with a model of wider anthropogenic sources in urban  
324 environments. Yeganeh et al. (2012) has reported high concentration of Hg in Hamedan soils, water and food crops  
325 which has caused significant potential risk for the city population. The exact source of Hg in Hamedan soils is  
326 unknown to the authors. Even though copper presented in factor 3, its highest factor loading (0.702) appeared in  
327 factor 5 (F5) along with Sb with the factor loading of 0.772. Partial representation of Cu in another factor implies an  
328 ambiguous behavior and probably the presence of different anthropogenic inputs. The mean ratio of Cu:Sb which is  
329 commonly used to identify the source of antimony, differs significantly in Hamedan soils with the reported  
330 diagnostic criteria (Sternbeck et al. 2002) for brake wear particles ( $4.6 \pm 2.3$ ). Therefore, attribution of Sb together  
331 with Cu in brake linings is unexpected. Although the particular source of antimony in Hamedan city soils is still not  
332 clear, its significant concentration in urban soils compared to the background together with elevated EF and CF  
333 values confirm an anthropogenic source for this element. An extra source might be horticulture. As according to  
334 Pietrzak and McPhail (2004), this contributes plant macronutrients such as phosphorus in addition to certain metals  
335 like copper, as emerged in F5. Factor 6 (F6) explain 9.64% of the total variance and accounts considerable  
336 concentration of Mo (0.648). As mentioned before, molybdenum is also weakly presented in F3 displaying its  
337 diffuse origin due to the contribution of a wide range of natural and urban parameters (Peltola and Åström 2003).

338 To illustrate the interrelationship of the elements, the first three factors are plotted in three-dimensional space  
339 in Fig. 4, where the associations between elements can be seen.

340 Cluster analysis was used to visualize the classification of PTEs according to their plausible origin. The  
341 dendrograms (Fig. 5) confirm the attributions explained by PCA analysis. Two distinct clusters were identified for  
342 the potentially toxic elements in Hamedan urban soils indicating two main sources:

343 i) Natural: the cluster of geogenic origin which is divided in two subcategories; the upper sub-cluster is made up of  
344 V, Ti, K and Mn displaying the geochemical contribution of underlying Alvand batholith. Whilst, the other sub-  
345 cluster includes the elements (e.g. Al, Fe, Mg, As, Co, Cr, Ni) which are mainly associated with the metamorphic  
346 formations surrounding the Alvand Batholith.

347 ii) Mixed: in addition to the influence of the local geology in supplying a fraction of trace elements in soil samples,  
348 the other extra non-natural sources have loaded certain elements in the studied urban soils of Hamedan. Two sub-  
349 clusters were identified with typical anthropogenic elements including Cd, Pb, Zn, Cu, Sb and Hg. As it is found  
350 from the bivariate statistical analysis, the concentration of each element presented in the mixed cluster is positively  
351 and significantly correlated with the other elements belonging to the same cluster. This fact can be an indication of a  
352 common source. The divided components containing Hg-Cd-Zn, Sb-Cu and Ba-Pb-Mo in the PCA analysis is  
353 confirmed with the distinct sub-cluster are shown in the CA (Fig. 5). Moreover, as it is explained, anthropogenic  
354 elements reveal higher mean concentrations in urban soils compared to the background soils in Hamedan. These  
355 evidence along with the calculated elevated values for the enrichment and contamination factors, highlight the input  
356 of PTEs from human activities in Hamedan. This group of elements has previously been interpreted as  
357 anthropogenic by many scholars (Rodríguez-Seijo et al. 2017; Costa and Jesus-Rydin 2001; Rate 2018).

358

### 359 **3.5 Spatial Distribution**

360 The spatial distributions of concentrations of a number of elements in Hamedan city are visualized by a set of  
361 geochemical maps (Fig. 6) prepared by ArcGIS. The segment division displayed in the geochemical maps are  
362 according to concentrations of 5%, 25%, 75%, 95% and 100%.

363 In agreement to Spearman, PCA and CA results, the spatial distribution analysis suggests that the concentration  
364 of As, Co, Cr, Ni and V is most tightly controlled by soil parent materials. As it is mentioned before, Hamedan is  
365 built upon the old alluvial fans and young terraces which are derived from weathering of the metamorphic rocks  
366 from short distances in south and southwest of the city. The piedmont alluvial deposits occur along the valley  
367 margins toward the Hamedan plain and form the foothills bordered by Alvand metamorphic and plutonic highlands.



368 In the north, the cultivated land, consists of clay alluvial soils probably originated from metamorphic bedrocks. The  
369 development and thickness of sediments increase toward the north.

370 Concentration of arsenic accords with the metamorphic rock units with the highest values in the southern part  
371 of Hamedan city (Fig.6). Toward the north, due to the less influence of metamorphic rocks and continuous leaching  
372 process the content of As decreases.

373 As seen from the maps (Fig. 6), variations in the levels of Co and Ni demonstrate similar pattern where the  
374 influence of parent materials has been involved. The total content of Co in the study area is lower compared to Ni,  
375 though both elements show hotspots in the city's marginal areas. Despite the fact that Cr displays a spatial  
376 distribution different to Co and Ni, the strong statistical correlation among these elements can be attributed to their  
377 common natural source.

378 Two critical regions for Cd are recognized (Fig. 6): the high-value distribution area in north of the city may be  
379 related to the agricultural lands and the influence of fertilizers in addition to the impacts of the nearby highway.  
380 While, the hotspots in central and southwestern of the urban areas may indicate the direct influence of vehicular  
381 traffic. Ganjnameh and Abbas-Abad are roads to recreational and touristic areas in the southwest of the city with  
382 significant traffic density. The latter may be the contributing factor in higher concentration of Sb, as a traffic-  
383 generated element, appearing in the vicinity of Ganjnameh road. The valley may funneled the wind and prevented  
384 dissipation of traffic-related contaminants in the plain. As it is illustrated in the map (Fig. 6), lead is characterized by  
385 higher concentrations along the outer ring road of the city which serves both city and regional traffic with constant  
386 congestion. This is correlated with traffic volume and association of some infrastructures (garages, auto-truck  
387 service and repair shops) which are generally located around the main entrances of the city.

388 High spatial variability of Cu, Hg, Mo and Zn even in the short range indicates the spatial heterogeneity caused  
389 by various human activities (Liu et al. 2014). This is due in part to the natural background soil but, mainly the result  
390 of long-term complex anthropogenic processes.

#### 391 **4. Conclusion**

392 Geochemical study of surface soil in Hamedan city of Iran revealed that the concentration of As, Co, Cr, Ni and V  
393 are close to the regional background values, so they may have been originated from the natural parent materials.  
394 This result is reinforced by correlation coefficients, PCA and CA analyses identifying geochemical association of

395 these elements which were also spatially related. Moreover, the information obtained from this study showed that Pb  
396 followed by Sb and Cd are the most enriched elements in Hamedan city soils. These elements along with Cu, Hg,  
397 Mo and Zn showed anthropogenic influence mainly related to vehicular traffic and automobile exhaust. It is deduced  
398 that the control of industrial activity is minor probably due to the remote location of Hamedan industrial zones (Bou-  
399 Ali Industrial Town) in the north of the city at a distance of about 10 km downwind. Land use showed to have little  
400 or no effect on the enrichment of PTEs in Hamedan surface soils. Spatial distribution maps displayed the  
401 contribution of metamorphic parent rocks in accumulation of arsenic in both natural and city soils. An identical  
402 pattern of special distribution was observed for Co, Ni revealing the influence of geogenic factor. In contrast, the  
403 urban elements display large variability throughout the city which indicates the interruption caused by human  
404 activities. Lead concentration, however, accords with the main highway network of the city inherited from past  
405 usage of Pb in gasoline which has been preserved in soils. Due to the traffic density in Hamedan roadways and  
406 dense network of roads the potential for ongoing inputs of PTEs exists. The study of bioavailability of concerned  
407 elements and their risk assessment is recommended for further research.

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638

639 **Table Captions**

640 **Table 1.** PTEs concentrations ( $\text{mg kg}^{-1}$ ) in surface soils of Hamedan city in comparison to Hamedan background  
641 soils, uncontaminated soils and the average values in different cities of the world.

642 **Table 2.** The result of kruskal-wallis H test and mean values of PTEs ( $\text{mg kg}^{-1}$ ) in 31 soil and street dust samples  
643 from various land uses of Hamedan city

644 **Table 3.** Spearman's correlation matrix for PTEs in the surface soils and street dusts of Hamedan city

645 **Table 4.** The rotated component matrix of PTEs in urban soils from Hamedan



646 **Figure captions**

647 **Fig. 1.** Geological map of the Hamedan city in West of Iran and the sampling locations (Redrawn from Hamedan  
648 1:100000 scale geological map, Geological Survey of Iran)

649 **Fig. 2.** Box plots of PTE enrichment factor (EF) in urban soils of Hamedan; the band near the middle of each box  
650 represents the median. The bottom and top of the box are the first and third quartiles, respectively. Whiskers (the  
651 vertical lines) are the 1.5 interquartile ranges of the lower and upper quartiles.

652 **Fig. 3.** Box plots of PTE contamination factor (CF) in urban soils of Hamedan; the band near the middle of each box  
653 represents the median. The bottom and top of the box are the first and third quartiles, respectively. Whiskers (the  
654 vertical lines) are the 1.5 interquartile ranges of the lower and upper quartiles.

655 **Fig. 4.** Principal component analysis results in the three-dimensional space: plot of loading of the first three factors

656 **Fig.5.** Dendrogram of the cluster analysis (CA) of the urban topsoils of Hamedan based on the PTEs concentrations

657 **Fig. 6.** Geochemical maps showing the spatial distribution of certain geogenic (As, Co, Ni) and anthropogenic (Cd,  
658 Pb, Sb) elements in the urban soils of Hamedan city. The map legends are as per Fig. 1. The diameters of circles are  
659 proportional to the concentration of given elements.

**Table 1**

		As	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Sb	V	Zn
Hamedan Urban soils	Min	11.1	0.01	9.1	42	22.7	0.01	0.48	36.7	17.7	0.57	39	67
	Max	27	0.35	17.1	76	79.3	1.34	1.15	70.6	289	5.25	79	322
	Mean	18.94	0.14	13.08	56.42	39.05	0.15	0.77	54.86	51.77	1.47	61.13	115.16
	Median	18.8	0.11	13.1	58	35.4	0.09	0.72	54	37.9	1.12	62	101
	SD	3.94	0.1	1.97	7.23	13.27	0.23	0.18	9.02	50.43	1.03	10.41	47.21
	Skewness	-.07	.53	-.02	.19	1.65	4.85	.613	.056	3.7	2.41	-.29	3.0
	Kurtosis	-.55	-.82	-.34	.70	2.98	25.46	-.454	-.881	16.8	6.12	-.39	12.0
Hamedan Background soils (mg kg <sup>-1</sup> )		21.9	0.075	18.2	72.5	36.5	0.012	0.7	62.4	13.7	0.39	105	90.6
<sup>1</sup> Uncontaminated soil		2.5	0.53	12	83	24	0.07	1.5	34	44	0.3	67	100
<sup>2</sup> Galway (Ireland)		8		6	35	27			22	58			85
<sup>3</sup> Napoli (Italy)		11.9	0.37	6.3	11.2	74			8.9	141	2		158
<sup>4</sup> Trondheim (Norway)		3.3	0.12		58	32			43	32			80
<sup>5</sup> Annaba (Algeria)			0.3		28.3	23.8				42.3			64.7
<sup>6</sup> Ibadan (Nigeria)		3	0.15		55.5	32			16.5	47			93.5
<sup>7</sup> Murcia (Spain)					16.3	8.9			11.1	21.9			16.6
<sup>8</sup> Baltimore (USA)			0.89		38.3	35.2			18.4	89.3			80.7
<sup>9</sup> Chicago (USA)		13.2		11	65	59			31	198			235
<sup>10</sup> Shanghai (China)			0.52		107.9	59.25			31.14	70.69			301.4
<sup>11</sup> Turku (Finland)			0.2		37	19.15			12.45	20			72.5

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<sup>1</sup>Kabata-Pendias (2010), <sup>2</sup>Zhang (2006), <sup>3</sup>Cicchella et al. (2008), <sup>4</sup>Andersson et al. (2010), <sup>5</sup>Maas et al. (2010), <sup>6</sup>Odeyemi and Abimbola (2008), <sup>7</sup>Acosta et al. (2011), <sup>8</sup>Yesilonis et al. (2008), <sup>9</sup>Cannon and Horton (2009), <sup>10</sup>Shi et al. (2008), <sup>11</sup>Salonen and Korkka-Niemi (2007)

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665

**Table 2**

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<b>Land use</b>	<b>As</b>	<b>Cd</b>	<b>Co</b>	<b>Cr</b>	<b>Cu</b>	<b>Hg</b>	<b>Mn</b>	<b>Mo</b>	<b>Ni</b>	<b>Pb</b>	<b>Sb</b>	<b>V</b>	<b>Zn</b>
AG	21.3	0.1	14.1	62.0	43.1	0.1	663.7	0.7	63.1	49.0	1.6	63.8	107.4
GS	17.3	0.2	12.0	52.5	40.1	0.2	666.0	0.8	49.3	61.5	1.9	57.7	114.6
PK	17.1	0.2	13.5	57.0	38.5	0.1	719.3	0.9	55.0	58.2	1.1	60.8	170.0
PG	17.7	0.1	12.6	54.0	27.4	0.0	610.5	0.6	56.7	25.2	1.4	54.5	88.9
RS	20.8	0.1	13.8	58.0	37.8	0.1	723.8	0.8	55.8	44.0	1.0	65.6	101.0
chi-squared	6.42	6.62	6.19	6.62	3.32	2.54	4.65	7.45	9.77	2.71	3.51	3.00	4.62
df	4	4	4	4	4	4	4	4	4	4	4	4	4
p-value	0.17	0.16	0.19	0.16	0.51	0.64	0.32	0.11	0.04	0.61	0.48	0.56	0.33

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*Abbreviations: agricultural land (AG), green space (GS), park (PK), playground (PG) and residential (RS)*

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**Table 3**

	As	Cd	Co	Cr	Cu	Hg	Mn	Mo	Ni	Pb	Sb	V	Zn
As	1												
Cd	-0.257	1											
Co	<b>.566**</b>	0.088	1										
Cr	<b>.473**</b>	-0.035	<b>.880**</b>	1									
Cu	-0.211	0.3	-0.018	0.201	1								
Hg	-0.003	<b>.386*</b>	-0.016	0.102	<b>.671**</b>	1							
Mn	-0.076	-0.072	.388*	.397*	0.056	0.127	1						
Mo	-0.276	0.006	-.463**	-0.294	.361*	0.261	0.017	1					
Ni	<b>.526**</b>	0.198	<b>.893**</b>	<b>.836**</b>	0.112	0.061	0.115	-.484**	1				
Pb	-0.283	.466**	-0.184	-0.07	<b>.825**</b>	<b>.649**</b>	0.021	<b>.433*</b>	-0.069	1			
Sb	0.127	0.254	-0.016	-0.001	.426*	<b>.531**</b>	0.046	-0.058	0.058	.426*	1		
V	<b>.492**</b>	-0.118	<b>.717**</b>	<b>.766**</b>	-0.078	0.095	<b>.468**</b>	-0.209	<b>.532**</b>	-0.331	-0.105	1	
Zn	-.450*	<b>.652**</b>	-0.127	-0.087	<b>.724**</b>	<b>.475**</b>	-0.073	0.324	-0.026	<b>.825**</b>	.382*	-0.34	1

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

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

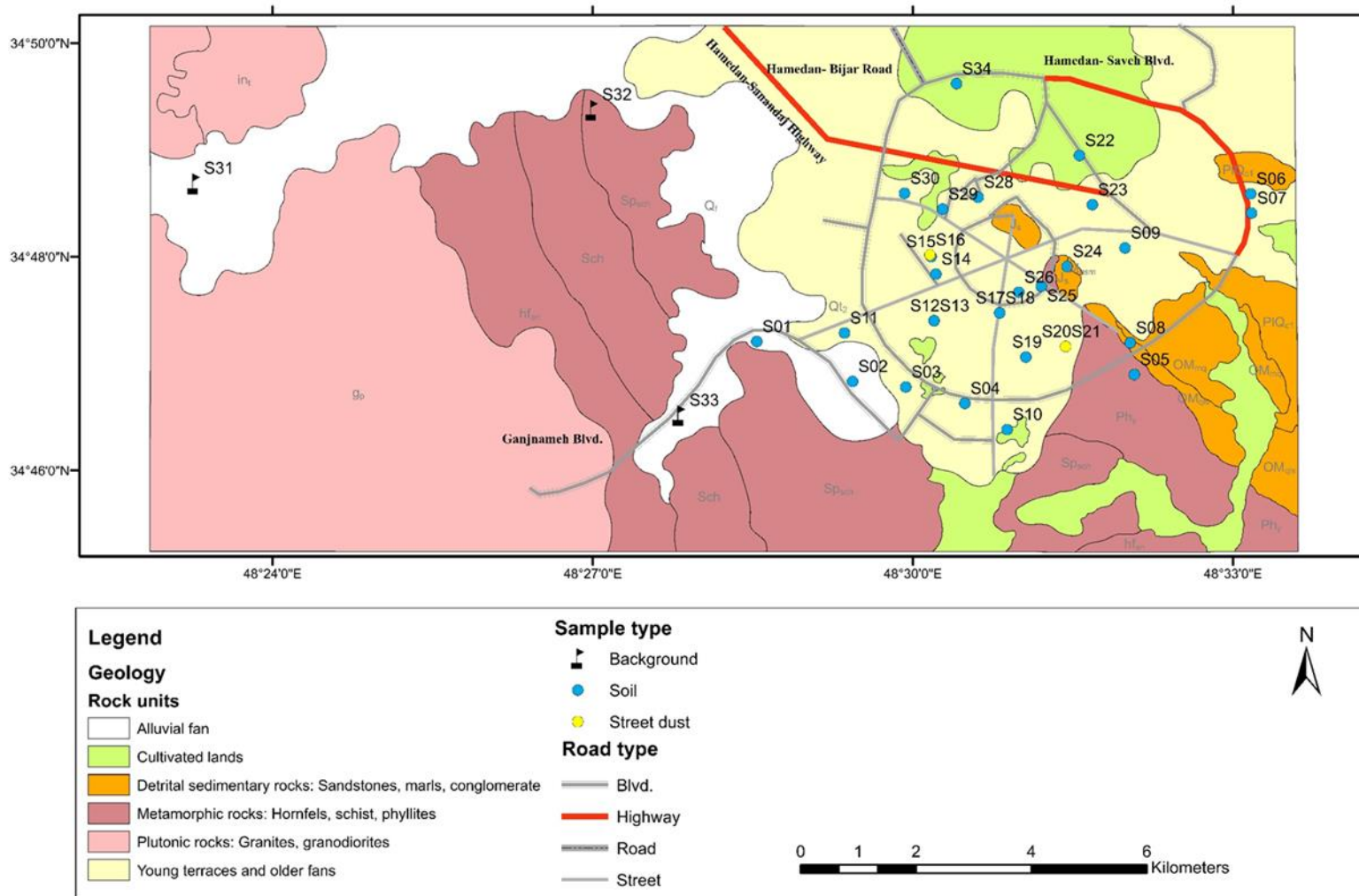
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**Table 4**

Elements	Rotated Component Matrix					
	F1	F2	F3	F4	F5	F6
As	<b>0.635</b>	-0.042	-0.359	-0.306	-0.009	0.245
Ba	-0.234	-0.075	<b>0.712</b>	-0.067	-0.272	-0.171
Cd	-0.065	-0.068	-0.093	<b>0.899</b>	0.057	-0.087
Co	<b>0.862</b>	0.327	-0.143	0.044	-0.109	-0.234
Cr	<b>0.814</b>	0.413	0.194	-0.005	0.073	-0.079
Cu	0.042	0.013	<b>0.515</b>	0.169	<b>0.702</b>	0.113
Hg	-0.502	0.184	-0.314	<b>0.468</b>	0.309	0.066
Mn	0.128	<b>0.884</b>	0.087	-0.028	0.023	-0.172
Mo	-0.326	0.032	<b>0.503</b>	0.215	0.058	<b>0.648</b>
Ni	<b>0.895</b>	0.063	-0.132	0.196	-0.003	-0.238
Pb	-0.318	-0.013	<b>0.831</b>	0.117	0.171	0.065
Sb	-0.086	0.057	-0.107	-0.007	<b>0.772</b>	-0.409
V	<b>0.664</b>	<b>0.627</b>	-0.225	-0.115	-0.046	0.123
Zn	0.058	-0.089	0.34	<b>0.817</b>	0.119	0.051
Al	<b>0.844</b>	0.298	-0.221	-0.208	0.008	-0.156
Fe	<b>0.698</b>	0.489	-0.175	-0.049	-0.179	-0.312
K	<b>0.545</b>	0.447	-0.271	-0.181	0.309	0.376
Mg	<b>0.783</b>	0.051	-0.276	-0.015	0.053	0.055
Na	-0.154	-0.025	-0.147	-0.118	0.022	<b>0.831</b>
P	0.008	-0.055	-0.116	0.166	<b>0.77</b>	0.395
Ti	0.429	<b>0.804</b>	-0.088	-0.04	0.022	0.205
<b>Eigenvalue</b>	7.811	2.680	2.241	1.897	1.340	1.263
<b>% variance explained</b>	28.172	12.836	11.834	9.793	9.776	9.644
<b>Cumulative % variance</b>	28.172	41.009	52.843	62.636	72.411	82.055

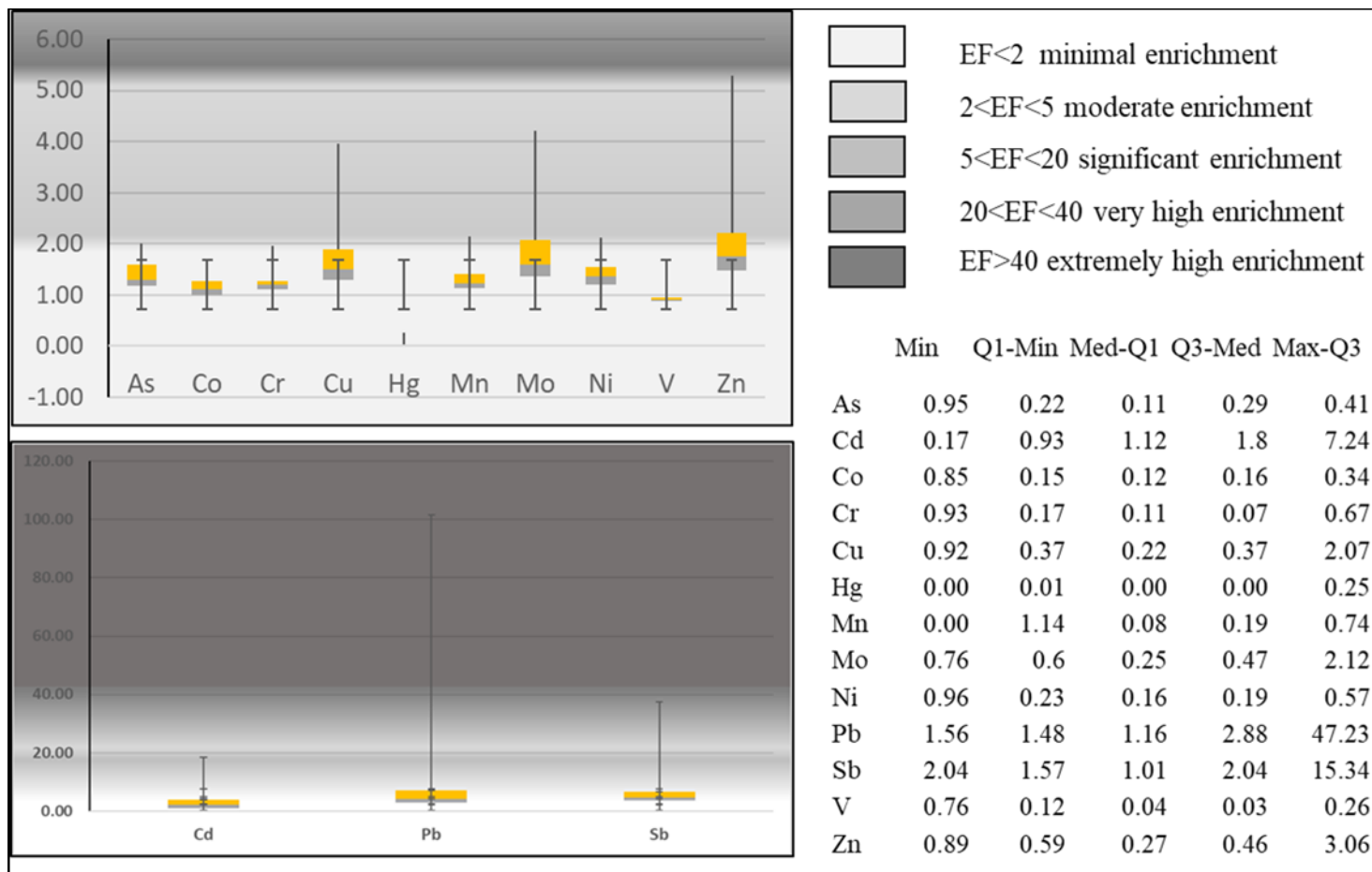
*Extraction Method: Principal Component Analysis.*  
*Rotation Method: Varimax with Kaiser Normalization.*  
*Rotation converged in 9 iterations.*

Figure 1.



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Figure 2.

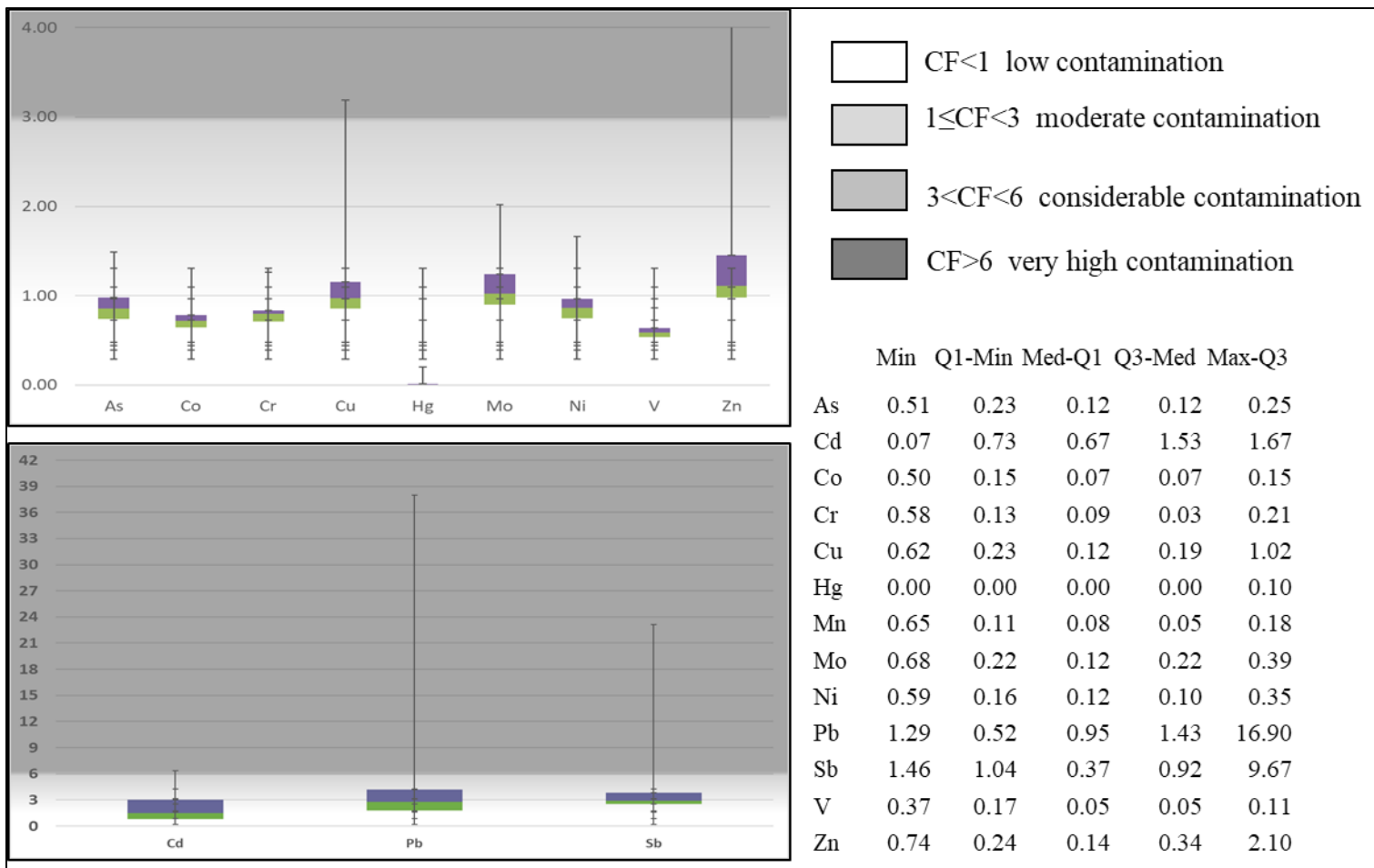


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Figure 3.



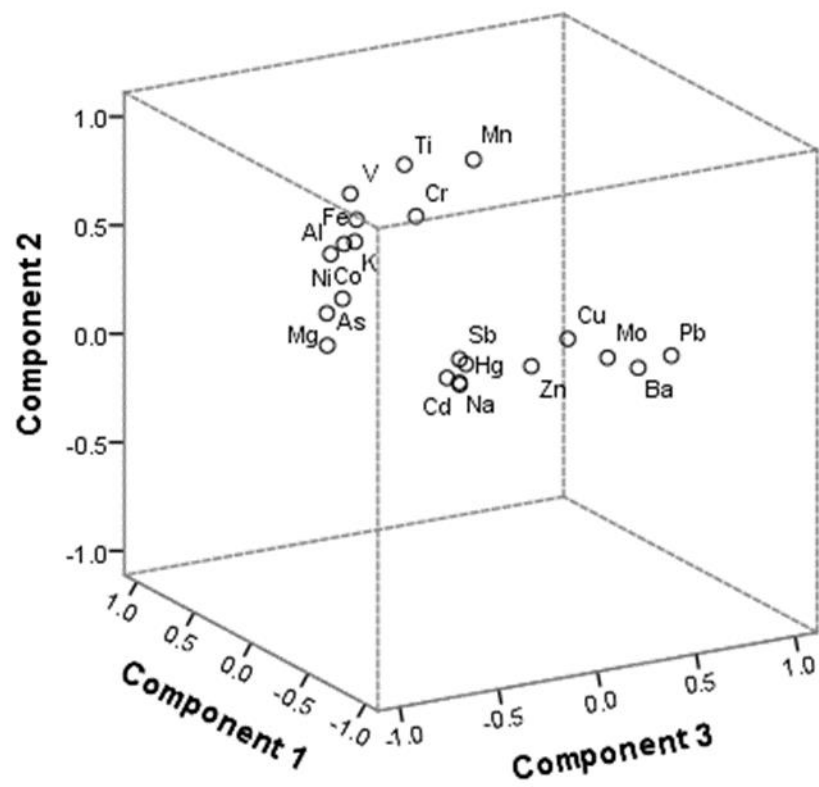
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Figure 4.

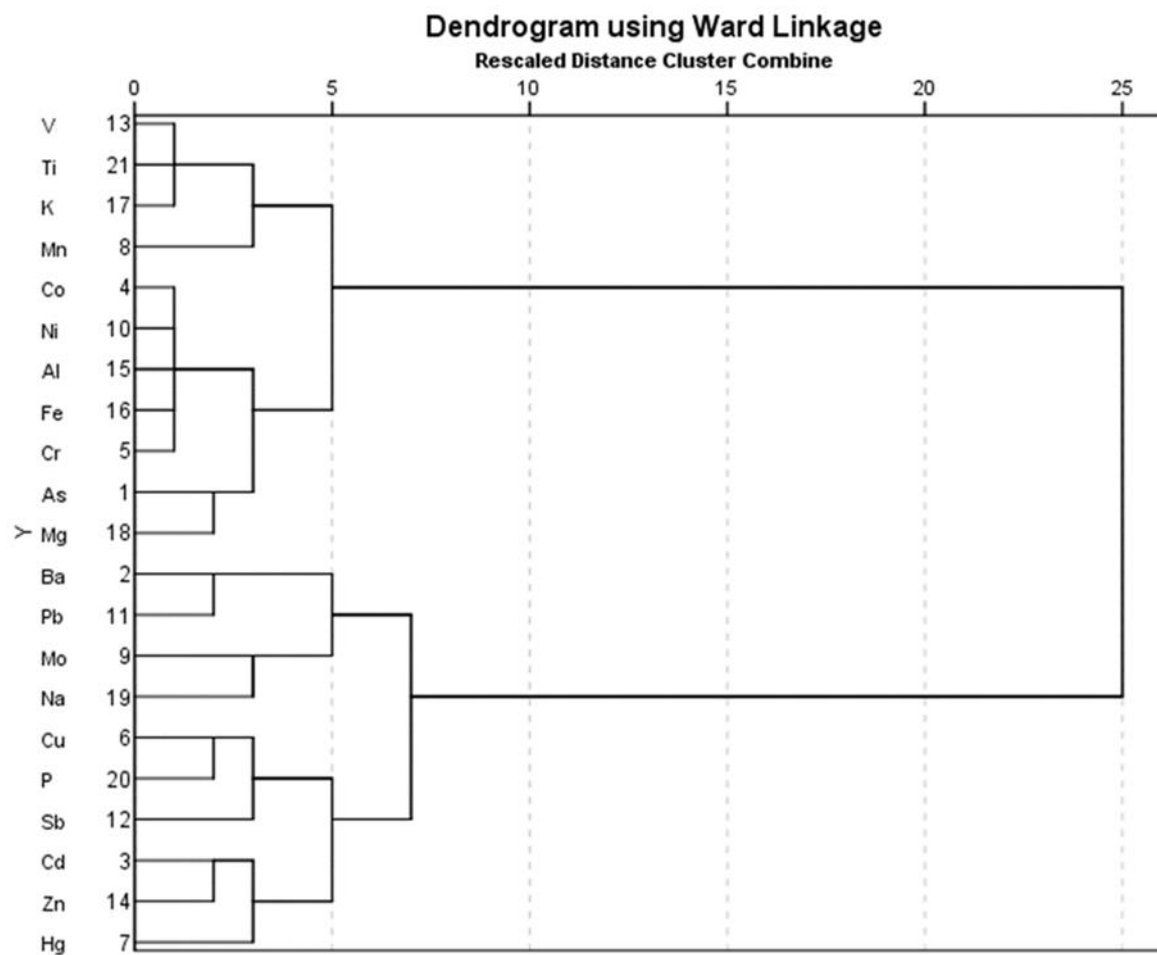


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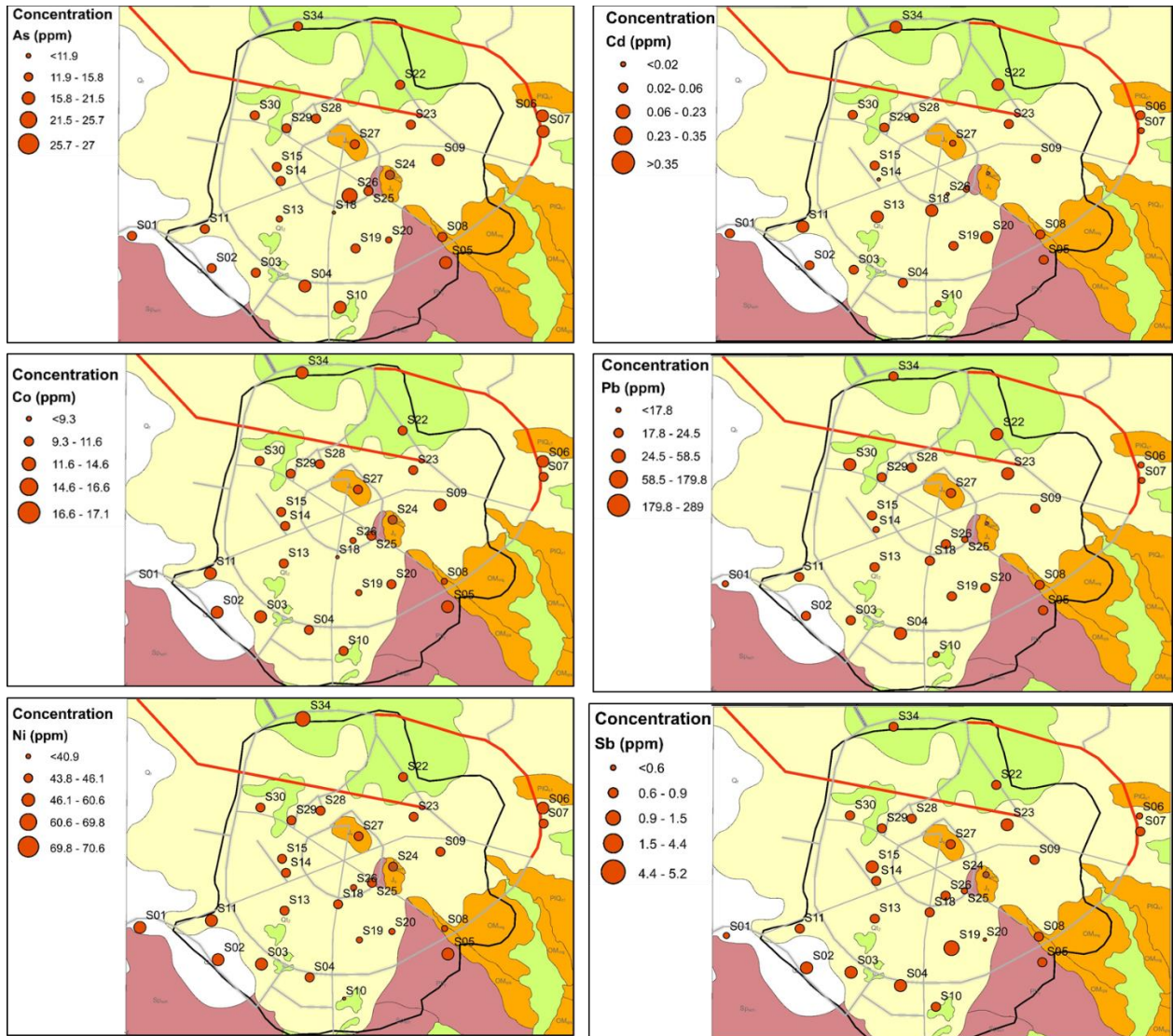
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Figure 5.



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708 **Figure 6.**



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711 **Supplementary Material**

712 The results of Sixty-three elements analyzed in urban topsoils of Hamedan

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	Unit	DI	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15	S16	S17	S18	S19	S20	S21	S22	S23	S24	S25	S26	S27	S28	S29	S30	S31	S32	S33	S34
Ti	%	0.001	0.197	0.162	0.123	0.141	0.09	0.088	0.083	0.068	0.122	0.125	0.141	0.1	0.111	0.171	0.113	0.019	0.083	0.074	0.118	0.134	0.071	0.111	0.129	0.179	0.17	0.133	0.129	0.142	0.143	0.134	0.18	0.22	0.331	0.166
S	%	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
P	%	0.001	0.114	0.215	0.213	0.329	0.18	0.119	0.129	0.12	0.177	0.118	0.176	0.155	0.248	0.135	0.168	0.086	0.236	0.273	0.232	0.126	0.147	0.135	0.19	0.105	0.115	0.273	0.319	0.176	0.161	0.277	0.132	0.109	0.076	0.289
Li	ppm	0.1	45.7	43.6	38.4	39.8	43.9	38.8	35.5	32.7	41.5	41.4	37.8	31.2	36.2	52.4	35.6	40.4	27.5	28.7	40.5	41.3	24.1	30.7	37.6	55.5	50.1	39.6	36.7	41	34.2	35.9	41.6	44.6	55.8	44.8
Be	ppm	0.1	1.1	1.1	1.1	1.2	1	1.2	1	0.9	1.1	1	1	0.8	1.2	1.2	1	0.9	0.7	0.8	1.3	1	0.9	0.9	0.8	1.3	1.1	1.2	1	1.1	1	0.9	1.6	1	1	1.1
B	ppm	1	16	19	22	20	22	21	23	19	20	14	21	24	27	14	25	10	16	27	18	22	15	16	20	14	14	20	22	22	18	22	10	14	7	21
Na	%	0.001	0.059	0.052	0.049	0.078	0.062	0.058	0.064	0.066	0.084	0.071	0.069	0.137	0.135	0.065	0.066	0.086	0.094	0.092	0.067	0.094	0.078	0.078	0.166	0.07	0.142	0.363	0.128	0.106	0.082	0.075	0.096	0.055	0.057	0.077
Mg	%	0.01	0.94	0.86	0.93	0.93	0.95	0.99	0.83	0.69	0.91	0.68	0.9	0.83	0.92	0.86	0.91	0.71	0.65	0.75	0.77	0.84	0.59	0.77	0.93	0.85	0.85	0.78	0.91	0.87	0.85	0.81	0.72	1.11	1.09	1.1
Al	%	0.01	2.75	2.51	2.4	2.48	2.36	2.49	1.97	1.73	2.25	1.91	2.37	1.73	2.08	2.46	2.14	2.33	1.46	1.55	2.09	1.88	1.41	1.91	2.2	2.29	2.25	2	2.21	2.18	2.08	2.16	2.4	2.92	3.08	2.87
K	%	0.01	1	1.07	0.87	1.04	0.78	0.69	0.65	0.61	0.83	0.77	0.95	0.64	0.89	1.07	0.91	0.58	0.56	0.7	0.85	0.73	0.52	0.69	0.82	0.93	0.87	1.09	1.03	1.16	0.76	0.88	0.77	1.14	1.42	1.23
Bi	ppm	0.02	0.29	0.35	0.34	0.33	0.29	0.24	0.29	0.19	0.28	0.28	0.45	0.23	0.27	0.28	0.24	0.21	0.22	0.26	0.28	0.41	0.23	0.28	0.25	0.25	0.25	0.21	0.25	0.28	0.28	0.42	0.13	0.31	0.39	0.39
Ca	%	0.01	2.41	1.65	5.81	2.59	4.63	6.12	5.53	6.68	5.9	2.27	2.26	4.76	5.7	2.1	4.15	2.92	4.19	4.31	3.24	5.67	4.89	5.35	5.2	4.31	3.04	4.07	4.99	4.32	3.21	3.84	0.91	1.2	0.32	3.69
Sc	ppm	0.1	10.5	9.6	9.2	9.6	7.1	7.5	6.2	5.3	8	7.2	8.5	6.3	7.1	10.9	8	4.9	5.5	4.3	7.4	8	4.7	6.9	7.7	10	9.6	7.9	8.7	8.6	8.1	8.1	9.4	10.3	13.9	10.4
V	ppm	1	79	75	66	67	57	59	53	48	64	61	70	50	57	72	64	45	43	45	57	62	39	56	61	77	69	66	62	67	66	60	71	82	128	78
Cr	ppm	1	67	60	64	63	59	61	50	44	59	48	65	48	58	61	58	50	42	45	54	51	55	53	57	61	55	52	58	60	57	58	50	73	72	76
Mn	ppm	1	883	778	714	765	672	538	625	539	688	603	653	753	691	798	628	593	717	563	662	548	694	699	705	836	789	551	710	681	780	650	661	817	849	690
Fe	%	0.01	4.2	3.82	3.57	3.42	3.54	3.29	3.41	2.81	3.59	3.22	3.66	3.11	3.39	3.77	3.25	3.56	2.84	2.66	3.16	2.98	2.64	3.28	3.37	3.57	3.47	2.91	3.19	3.34	3.3	3.03	3.88	4.12	4.36	3.78
Co	ppm	0.1	17.1	16.2	14.8	13.9	16	14.6	12.8	10.7	14.6	12	14.8	12.6	13.6	14	13.6	11.5	9.5	10.5	11.1	11.6	9.1	12.1	13.6	13.7	12.8	10.6	12.8	13.8	13.1	12.3	14.1	17.7	18.7	16.1
Ni	ppm	0.1	67.3	62.2	68.5	60.6	64.7	69.3	54.8	46.1	60	43.8	67.6	44.2	58.5	54	60.3	53.1	44	47	45.1	45.3	36.7	52.5	59.4	53.7	49.4	44.3	54	59.2	49.6	55	36.9	70.8	54	70.6
Cu	ppm	0.01	31.6	34.8	34.4	40.3	40	29.5	29.4	22.7	35.4	25	46.8	33	40.7	32.4	30.8	24	35.5	38.8	75.5	33.3	56	55.4	52	27.8	27.7	36.4	43.8	39.2	33.3	79.3	25.2	30.2	42.8	45.9
Zn	ppm	0.1	93.4	101	88.3	103	111	87.6	95.3	88.2	106	89	322	134	129	83.5	97.2	80.6	165	170	120	111	146	167	101	67	76.8	69.9	100	102	95.1	134	88.9	85.6	95.6	136
Ga	ppm	0.02	11.1	10.1	9.59	9.93	9.05	8.99	7.66	6.34	8.98	7.98	9.85	6.91	8.05	9.95	8.9	8.01	6.21	6.3	8.62	7.95	5.39	7.53	8.38	9.59	9.4	8.46	8.73	8.88	8.47	8.98	13.5	11.3	13.8	11.4
Ge	ppm	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
As	ppm	0.1	20.7	21.2	21.5	24.9	23.2	24.5	22.4	18.1	22.8	23.5	21.4	13.9	15.4	18.8	20.9	14.4	12.8	12.4	15.8	15.1	11.1	17.1	19.4	20.7	17.9	27	18.5	19.7	17.5	16.5	7.8	22.1	21.7	18
Rb	ppm	0.1	68.1	67.7	56.1	62.5	49	45.7	39.4	38.8	52.1	75.9	62	45.6	50.4	72.9	60	26.6	34.2	35.5	62.5	66.2	32.6	41.6	47.2	71.1	65.7	65.9	54	58.2	52.9	57.6	62.2	73	116	74.8
Sr	ppm	0.5	58.1	57	109	80.8	134	175	184	158	135	58.3	75.1	164	156	75.3	117	82.7	141	155	108	145	124	138	158	117	96.5	193	159	124	99.7	112	43.9	35.9	23	121
Y	ppm	0.01	11.9	10.1	9.02	10.2	12.1	10.7	10.2	10.2	11.1	9.35	8.49	12	8.09	10.9	7.79	6.52	10.2	7.2	10.6	7.63	8.98	9.27	10.7	8.52	10.3	7.43	9.26	9.11	10.1	8.48	14.8	9.61	8.13	9.14
Zr	ppm	0.1	2.4	1.4	1.4	1.2	1	1.2	0.8	0.9	1.2	0.9	1.5	0.9	1.1	1.7	1.2	1.7	0.6	1.1	0.7	1.1	0.7	1.1	1.7	2	2	1.3	1.8	1.1	1.5	1.1	2	2.4	2.3	1.4
Nb	ppm	0.1	3.1	2.9	2.5	2.6	1.9	1.7	2.2	1.8	1.9	3	3.6	2.9	3.3	2.2	2.4	0.8	2.5	2.7	3.1	3.9	2.1	1.9	2.1	2.1	2.1	3.2	2.7	3.2	3.4	2.8	2.9	2.8	2.8	3.3
Mo	ppm	0.01	0.7	0.55	0.64	0.57	0.58	0.58	0.66	0.64	0.74	0.87	0.97	0.88	0.86	0.48	0.63	0.55	0.82	0.87	0.67	0.68	1.15	1.12	0.72	0.9	0.76	1.12	0.89	0.71	0.81	1.06	0.48	0.93	0.48	0.58
Ag	ppm	0.002	0.284	0.397	0.484	0.781	0.43	0.289	0.338	0.234	0.651	0.392	0.581	0.323	0.424	0.418	0.46	0.177	1.04	0.543	0.729	0.409	0.328	0.545	0.514	0.282	0.259	0.607	0.749	0.554	0.62	0.892	0.236	0.247	0.144	0.724
In	ppm	0.02	0.05	0.04	0.04	0.04	0.02	0.03	0.03	0.03	0.03	0.04	0.03	0.03	0.04	0.03	0.03	0.03	0.03	0.02	0.03	0.03	0.02	0.03	0.03	0.04	0.04	0.03	0.03	0.03	0.04	0.04	0.05	0.04	0.07	0.04
Sn	ppm	0.05	3.51	5.58	4.87	4.97	16.5	3.18	3.16	2.33	5.29	3.6	7.99	4.18	5.68	4.33	3.29	1.49	4.98	5.58	5.88	5.9	>200	9.46	5.25	3.56	3.65	6.24	6.37	5.21	4.45	17.6	3.43	2.54	3.62	6.47
Sb	ppm	0.02	0.79	3.62	3.79	1.7	1.27	0.65																												

Tb	ppm	0.1	0.5	0.4	0.4	0.4	0.5	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.3	0.4	0.3	0.3	0.3	0.3	0.4	0.3	0.4	0.3	0.3	0.4	0.4	0.3	0.6	0.5	0.5	0.4					
Dy	ppm	0.1	2.3	2	1.7	2	2.2	1.9	1.8	1.8	2	1.9	1.6	2	1.5	2	1.5	1.3	1.6	1.2	1.9	1.4	1.5	1.6	1.9	1.6	1.9	1.4	1.7	1.7	1.8	1.6	2.8	2	2	1.8		
Ho	ppm	0.1	0.5	0.4	0.4	0.4	0.5	0.4	0.4	0.4	0.5	0.4	0.4	0.5	0.3	0.5	0.3	0.3	0.4	0.3	0.4	0.3	0.3	0.4	0.4	0.4	0.4	0.3	0.4	0.4	0.3	0.6	0.4	0.4	0.4			
Er	ppm	0.1	1.2	1	0.9	1.1	1.3	1.1	1.1	1.1	1.2	1	0.9	1.3	0.8	1.1	0.8	0.7	1	0.7	1.1	0.8	1	1	1.2	0.9	1.1	0.8	1	0.9	1	0.8	1.4	1	0.8	0.9		
Tm	ppm	0.1	0.2	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.2	0.1	0.1	0.2	0.1	0.1	0.1	<0.1	0.1	<0.1	0.2	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.1	<0.1	0.1	
Yb	ppm	0.1	1	0.8	0.8	0.9	1	0.9	0.9	0.9	1	0.8	0.7	1.2	0.7	0.9	0.7	0.5	0.9	0.6	1	0.6	0.9	0.9	1	0.8	1	0.7	0.8	0.8	0.9	0.7	1.1	0.8	0.5	0.7		
Lu	ppm	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	<0.1	0.1	0.1	<0.1	0.1	<0.1	0.1	<0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	<0.1	0.1	0.1	<0.1	0.1	
Hf	ppm	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	
Ta	ppm	0.05	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<
W	ppm	0.1	0.2	0.3	0.2	0.5	0.2	0.1	0.2	0.2	0.2	0.3	0.3	12.9	0.4	0.3	0.2	<0.1	0.3	0.3	0.3	0.4	0.4	0.7	0.4	0.4	0.4	0.4	0.4	0.3	0.3	0.7	0.3	0.1	0.4	0.2		
Re	ppm	0.001	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<	<
Au	ppb	0.5	<0.5	7	1.7	9.2	22	<0.5	<0.5	<0.5	<0.5	3.9	19.9	4.6	13.9	2.5	7.7	<0.5	203	10	17.3	9.5	8.7	17	16.3	<0.5	<0.5	9.8	24.7	8.1	5.8	127	<0.5	<0.5	<0.5	30.8		
Tl	ppm	0.02	0.39	0.39	0.31	0.33	0.29	0.29	0.24	0.22	0.27	0.33	0.35	0.22	0.29	0.4	0.33	0.15	0.19	0.21	0.34	0.32	0.18	0.24	0.26	0.38	0.35	0.27	0.27	0.33	0.28	0.28	0.29	0.45	0.6	0.37		
Pb	ppm	0.01	23.5	29.7	30.4	80.2	56.5	22	22.1	25.2	37.5	24.5	58.5	103	42.9	21.1	32.5	17.9	75.2	43.1	40.5	29.9	289	107	62.1	17.7	21.1	37.9	47	39.6	28.2	89.1	10.7	14.7	12.7	50.1		
Th	ppm	0.1	11.3	10	6.5	8.8	8	7	7	6	8	9.3	5.8	4.7	4.5	11	5.4	7.8	4.5	1.9	7.9	5.5	3.3	6.5	7.4	7.3	9.9	6	7.4	7	7.2	7.3	16	11.4	15	8.2		
U	ppm	0.1	1.4	1.6	1	1.4	1	1.1	1.3	1	1.1	1.3	1.2	1.2	1.1	1.2	1	0.8	1	0.9	1.3	1.1	0.9	1	1.1	1	1.2	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.6	1.4	1.9	1.4
Hg	ppb	10	70	150	150	220	90	20	30	50	80	70	150	100	90	60	80	10	1340	150	150	70	70	80	110	60	50	310	250	110	90	200	20	20	<10	140		

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