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Surface dispersal, emission source and human health risk assessment of heavy metal(loid)s in an active gas field, Southern Iran

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Abstract:

The presence of heavy metal(loid)s in soils from anthropogenic sources such as activities related to fossil fuel processing area could pose serious threat to the ecosystem and human health. However, risk factors depend on the source, distribution and human interaction with these contaminants and therefore case specific study is needed. In this study, using a geological information system (GIS) and 63 surface soil samples, we fully assessed 190 km^2 area of a developing gas region in southern Iran. Mean concentration of manganese (Mn), zinc (Zn), copper (Cu), lead (Pb), total chromium (Cr), cobalt (Co), arsenic (As) and Cadmium (Cd) was 341.24, 129.40, 32.90, 26.85, 16.56, 7.52, 0.67 and 0.63 mg kg^{-1}, respectively, while As, Pb, Zn and Cd surpassed the local background level. Moreover, soil pollution was also assessed by the contamination factor (CF), geoaccumulation index (I_{geo}) and ecological risk factor (Er). Accordingly, these soils were classified as moderate to heavily polluted with As and Cd and un-polluted to slightly polluted by Cu, Zn, Pb, Mn, Cr and Co. The GIS and soil collection point tracing showed that the natural gas processing and residential activities were both significant pollution sources where ingestion was the main contributor to heavy metal(loid)s uptake. Overall, the hazardous index for noncarcinogenic health impact was < 1 indicating no risk; however, children were at greater risk than the adult. Total carcinogenic risk (TCR) index from As exceeded the maximum tolerable level (1.0E-04) for children and adults. Chromium Co, Cd and Pb exposure were within the acceptable limit in the adult group (TCR < 1.0E-06), but the Pb and Cr health-hazardous indices were higher than guideline value indicating the potential of cancer risk in children. Therefore, remedial actions are required to eliminate or reduce the toxicity of As, Cr and Pb attributed to the impacted soil.

Keywords: Developing zone; Heavy metal(loid)s; Pollution indices; Ecological and health risk, Source apportionment

1. Introduction

Extensive release of contaminants into the environment in process of rapid industrial development as well as urbanization is getting worse in recent years and leads to growing public concerns (Mamat et al., 2014; Zhuo et al., 2020). Heavy metal(loid)s (metals and metalloid having densities greater than 5 g/cm^3) are typical trace contaminants, which are discharged to the environment through a vast variety of processes (Alloway, 2013; Zheng et al., 2010). Generally, heavy metal(loid)s originate from natural (e.g., weathering of the parent materials) and anthropogenic activities (Faramawy et al., 2016). Industrial activities, such as smelter or gasworks play a major role in their emissions via fossil-fuel combustion, transportation sectors, waste disposals and many other industrial activities (Adimalla, 2020; Chen et al., 2015; Sun et al., 2010). Once heavy metal(loid)s reach the soil through different pathways, it may persist for a long time due to their specific inherent nature including, non-biodegradability and high resistance to decomposition (Alloway, 2013). Accumulation of heavy metal(loid)s in soil has negative effects on soil stability and quality, resulting in economic and social consequences (Chen et al., 2015; Zhuo et al., 2020). The process of heavy metal(loid)s accumulation may change with environmental conditions, thus polluted soil can act as a reservoir of pollutants and release heavy metal(loid)s to the environmental receptors such as water bodies and sediments (Ljung et al., 2006). Consequently, water and sediment become another sink and source of metal(loid)s, resulting in yet an increased rate of exposure (Pandey and Singh, 2017). High levels of heavy metal(loid) exposure not only have an adverse effect on plants and animals but also pose a chronic detrimental impact on human health via the food chain (Li et al., 2020; Yi et al., 2011). For instance, As exposure may cause skin lesions (e.g., hyperkeratosis and hyperpigmentation), respiratory symptoms, skin cancer and peripheral vascular disease (Cui et al., 2013; Kapaj et al., 2006). Kidney and bone were recognized as susceptible to the impacts of Cd with the risk of progressed osteoporosis and kidney dysfunction (Järup and Åkesson, 2009; Nawrot et al., 2010). Therefore, knowing the concentration and distribution of heavy metal(loid)s in potentially exposed contaminated soil is critical in controlling and preventing possible adverse health burden.

Currently, soil contamination research is extensively focused on determination, distribution, sources and health risks associated with contaminants mostly in the areas with high-expected concentrations of heavy metal(loid)s, such as mine site, petrochemical yards and transportation premises of oil and coal (Chen et al., 2005; Li et al., 2014; Liu et al., 2020; Wang et al., 2020). There are no studies yet to focus on a developing zone with natural gas as the main industry. Gas resource is considered environmentally friendly and clean in comparison with other fossil fuels. However, extraction, processing and combustion of natural gas are usually associated with the emission of compounds and particulates that have negative impacts on human health and the ecosystem (Faramawy et al., 2016). While gas and oil industries contribute to fast urban expansion with economic growth and job opportunities, every activity in such developing zones can accelerate the release of contaminants into the environment, including soil, which needs much attention.

Considering the urge of assessing details of potential heavy metal(loid)s pollution in a developing gas field, we studied a 190 km^2 extended gas work zone in Iran - one of the world's largest gas extraction and processing enterprises. The area included two towns and five villages with over 37,000 population. After 40 years of industrial development, it is necessary to examine the soil status as an important environmental indicator in sustainable development and health status. To the best of our knowledge, this study is the first comprehensive assessment of the soil heavy metal(loid) distribution, sources and potential human health risk in the studied area. This study aims to understand the possible contamination characteristics of soil with heavy metal(loid)s potentially linked to natural gas production and processing. This aim was elaborated with the following objectives: (1) to determine heavy metal(loid)s (Mn, Zn, Cu, Pb, Cr, Co, As and Cd) concentration and distribution, (2) to delineate the degree of soil contamination with pollution indices, including geo-accumulation index (I_{geo}), contamination factor (CF) and potential ecological risk indices (PERI), (3) assessment of the potential non-carcinogenic and carcinogenic health risks on human health (adults and children) through different pathways, and (4) identification of the main sources of soil heavy metal(loid)s in the area.

2. Materials and methods

2.1. Study area and sampling

The study area was located between 51°48′E to 52°25′E (longitude) and 27°44′N to 28°14′N (latitude) in the south of Bushehr province, Iran (Fig. 1). The study site is semiarid with an annual average temperature of 30.4 °C and relative humidity of 34 – 51% during the summer season. The area is 700 m above sea level. The examined prevailing wind direction of the area is northeast to southwest direction, as measured by the Jam Meteorological Office, June 2018. The age of geological formations in the study area varies from Cretaceous to Quaternary but the study area is mainly covered with a unit of the quaternary alluvial plain. The gas-related industry spread in a different part of the region with the focus on Jam Gas Refinery in the middle of the studied area. Because of the growing economy, almost 1500 vehicles pass daily through the main road from upstream to downstream of the refinery.

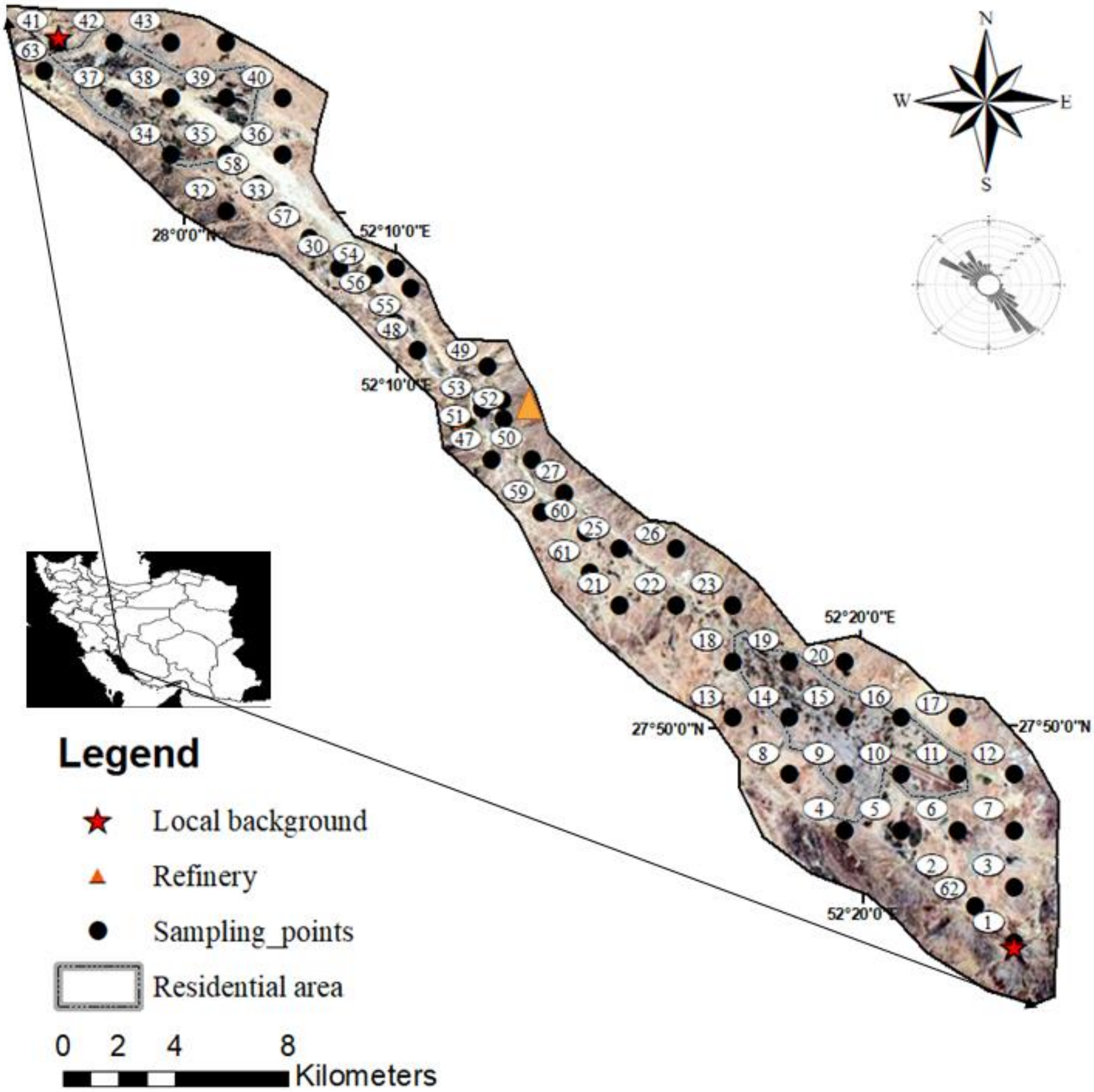

Figure. 1. Location map of the research area with sampling stations

During the summer of 2018, 65 samples consisted of 63 topsoils (0 – 20 cm) and two local backgrounds (60 – 80 cm) were collected. Using ArcGIS 9.4 (ESRI Inc.), a grid sampling method (2 km x 2 km plot) was developed while the spatial distribution of sampling points was balanced (Figure. 1). At each point, five random replications of the sample were collected using a stainless drill. These sub-samples were mixed to make a composite of replicates and stored in a single polyethylene bag at ambient conditions until further analysis. Ambient air-dried soil samples were passed through 2 mm mesh for soil properties determination and 63 μm for heavy metal(loid)s analyses.

2.2. Research methods

2.2.1. Physicochemical analysis and quality control

Soil samples were analyzed for physicochemical properties. Using a pH meter (S220, Mettler Toledo, Switzerland), pH measurement was performed after mixing soil-to-water in a ratio of 1 to 5. Total organic carbon (TOC) was analyzed using a TOC analyzer (630 - 400 - 200, LECO Corp., USA). Soil cation exchange capacity (CEC) was determined following the ammonium acetate method (pH 7.0) based on 9081 method of USEPA SW-846 (Yan et al., 2019). A modified pipette method was applied to classify soil texture where relative contents of clay, sand and silt were measured (Miller and Miller, 1987). The mineral phases were identified using X-ray diffraction (XRD) for the clay fractions. The patterns were determined on a Philips X-ray diffractometer (a = 1.54 A, 40 kV, 30 mA, calibrated with Si-standard).

Total heavy metal(loid)s content of Mn, Cd, Co, As, Pb, Cu, Zn and Cr in soils were analyzed after digestion using Aqua Regia extracts (1 HCl (37%): 3 HNO3 (69%)) in the microwave (MARS 6, CEM) according to U.S. EPA method 3051 (Hassan et al., 2007). The obtained solution was diluted up to 50 mL with Milli-Q water (resistivity 18.2 MΩ.cm) and was measured using inductively coupled Plasma Mass Spectrometry (ICP-MS) (Model 7900, Agilent Technologies, Tokyo, Japan). Standard reference soil (Montana soil, Sigma-Aldrich) was analyzed for the same alongside the studied soil samples for quality control. Following these procedures, the recovery of all heavy metal(loid)s were 87.1 – 108.2%. All labware was washed with distilled water following alternative soaking in a deacon solution followed by 2% HNO_3 and Milli-Q water to avoid contamination. To avoid any cross contaminant, blank samples (only Milli-Q water) was kept and carried out simultaneously with the same conditions as other samples.

2.2.2. Pollution Indices

This study quantitatively evaluated the pollution status of studied sites caused by heavy metal(loid)s following several indicators such as an index of Geoaccumulation (I_{geo}), contamination factor (CF), pollution load index (PLI), ecological risk factor (Er) and potential ecological risk index (Adimalla and Wang, 2018; Chen et al., 2015; Kowalska et al., 2018). In these cases, the mean of local background values was used. All the indices with related information and descriptions are listed in Supplementary Table 1.

2.2.3. Human health exposure risk

To assess the health risk of heavy metal(loid)s exposure through different pathways, including dermal absorption, inhalation of resuspended soil particles and direct oral ingestion in both children and adults were calculated as follows (Chabukdhara and Nema, 2013; Jiang et al., 2017; USEPA, 2011; Zazouli et al., 2020):

$$ADD_{inges} = \frac{\mathrm{C\ soil} \times \mathrm{IR_{ing}} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}} \times CF$$

$$ADD_{inh} = \frac{Csoil \times IR_{inh} \times EF \times ED}{PEF \times BW \times AT}$$

$$ADD_{dermal} = \frac{Csoil \times SA \times CF \times AF \times ABS \times EF \times ED}{BW \times AT} \times CF$$

ADD refers to average daily dose; all abbreviations used in the equation are elaborated in the supplementary Table 2. Then, the carcinogenic and non-carcinogenic risk posed by heavy metal(loid)s to humans, characterize quantitatively via common models including hazard quotient (HQ) and carcinogenic risk (CR).

$$\text{Non-Carcinogenic risk } (HQ) = \frac{ADD}{RFD}$$

$$\text{Carcinogenic risk } (CR) = \text{ADD} \times \text{SF}$$

Following, interactive effects of heavy metal(loid)s mixtures evaluated as a hazard (Adimalla and Wang, 2018; USEPA, 2011) and total carcinogenic risk (TCR) via three exposure pathways for a single element.

$$\text{HI} = \Sigma\,(\text{HQinges} + \text{HQinhal} + \text{HQdermal})$$

$$\text{TCR} = \Sigma\,(\text{CRinges} + \text{CRinhal} + \text{CRdermal})$$

The detailed probabilistic values of parameters for human health risk assessment of heavy metal(loid)s in soils have been collected and presented in supplementary Table 2.

2.2.4. Statistical analysis and GIS

To identify the relationship among heavy metal(loid)s in soils, multivariate statistical analyses such as Pearson's correlation coefficient analysis and Principal component analysis (PCA) were used (Zhang et al., 2018). Pearson's correlation is used to evaluate the degree of association/homology and the nature of the relationship between the variables (Sun et al., 2010). PCA is the most common multivariate statistical method utilized to identify similar variances between variables (Hotelling, 1933; Huang et al., 2015). In this case, dimension reduction with varimax rotation was used in the PCA to identify heavy metal(loid)s with natural or anthropogenic enrichment in the study area (Zhiyuan et al., 2011). Descriptive statistics of the data, the relationship between the variables and their potential sources were analyzed using IBM SPSS Statistics 22. To investigate the spatial distribution of heavy metal(loid)s in the studied area, Inverse Distance Weighting (IDW) method was also applied using the Spatial Analyst module of Arc GIS (version 10.3) (Chen et al., 2018b). IDW interpolation is widely used in soil heavy metal(loid)s study which can predict unknown data (Gu and Gao, 2019). Interpolation assumes that if there is less distance between two objects, they have stronger similarities, and weak similarities for the farther distance (Carr et al., 2008). In this study, interpolation was run with a weighting power of 2.0 and 12 neighboring samples.

3. Results and discussion

3.1. Soil properties

Physical inspection of soils reveals that foreign parts in different sizes and shapes, including clothes, textiles, plastic, tearing tyre pieces, etc. were available in most of the soils, which are remnants of urban and industrial activities. This shows that the region is affected by industrial and urban development and can have a negative effect on soil chemical, biological and physical stability.

Characteristics of soils in the study region are outlined in Table 1. pH of the study area ranges from 6.1 to 9.81, with a mean of 7.5, suggesting the neutral to weak alkaline. The distribution pattern of pH was even, and soils from only several sampling sites were slightly acidic. Natural and anthropogenic emission of SO_2 and NO as well as fertilizer applications have been documented as the main acidification causes of soils (Chien et al., 2008). Although the gas refinery industries located in the region are prone to emitting sulfur and nitrogen compounds in additional conventional agricultural inputs, soil pH in the studied samples only changed slightly toward acidic compared to the local background. The importance of other soil properties might have prevented intense acidification of the studied zone. Indeed, several other factors, including initial pH, carbon and nitrogen content, precipitation, and temperature can have a compensating effect on soil acidification (Barak et al., 1997). pH was found to be one of the major factors in heavy metal availability in soil system where acidic condition increases solubility and leachability of heavy metal(loid)s in soil (Chuan et al., 1996).

In this study, soil texture was classified according to the United States Department of Agriculture USDA (Barman and Choudhury, 2020), and most soils were loam and clay loam (Supplementary Fig. 1). Clay as an important fraction that tends to retain elements ranges from 1.6% to 52.60%, with a mean value of 29.31%. A mineralogical investigation of clay fraction in soil samples obtain with X-ray diffraction and proved the presence of both clay and non-clay minerals. In general, most of the clay minerals were low activity clay such as kaolinite. Calcite was identified to be the frequent non-clay mineral. CEC ranged from 2.11 to 29.17 cmol kg^{-1} with a mean value of 15.73 cmol kg^{-1}, which is reported as moderate, therefore, metal retention capacity might be average (Sridhara Chary et al., 2008) (Table. 1). CEC can be related to several factors, such as clays, TOC and pH of the soils. The moderate CEC of soil further represents the presence of kaolinite over the much great CEC originating montmorillonite fractions in soil (Puntervold et al., 2018). The TOC content of investigated soils ranges from 0.02 to 3.2% with a mean of 1.3%, where the background level was recorded as 0.52%. This means that the TOC was slightly high in some samples, probably due to the contribution of organic carbon from natural gas and crude oil (Iwegbue et al., 2006). In this study, the CEC of soil samples was also weakly positively correlated with TOC ($r = 0.26$, $p < 0.05$) and pH ($r = 0.43$, $p < 0.05$). TOC content influences the heavy metal distribution as they have a high affinity toward organic matter through adsorption or forming complexes with them (Sun et al., 2019).

3.2. Concentrations and spatial distribution of heavy metal(loid)s

Mean concentration of heavy metal(loid)s present in Jam area soils ranked as follows with the high to low value Mn > Zn > Cu > Pb > Cr > Co > Cd > As (Table. 1). Although Mn was the most abundant (341.24 ± 130.1 mg kg^{-1}) and Cd ranked the lowest (0.63 ± 0.76 mg kg^{-1}), comparing these mean values with the local background can give a better view of possible enrichment.

Mean values were compared with local background and several international guidelines (Table. 1). The As, Cd and Zn exceeded the local background values by 67, 10.5 and 2.05 times, respectively, while Pb was slightly enriched from its background level (1.77 times). This indicated that the anthropogenic activities exerted more of these heavy metal(loid)s compared to the background. In contrast, the concentration of Mn, Co, Cu, and total Cr was less than the local background. Comparison with guidelines of different countries often is challenging because soil quality guidelines are not uniform among countries and each country has its particular guidelines due to specific geographical, ethnological and political decisions. Accordingly, in some countries, the soil is classified based on types of land use such as agricultural, residential, recreational, industrial use, while others emphasize soil properties and soil types for the same. There are also considerable differences between guidelines value as some considered only fewer exposure routes and some countries consider soil, groundwater, consumption of fish and crustaceans exposure routes as well (Chen et al., 2018a; Provoost et al., 2006). However, the soils of the studied area are mixed in nature (industrial as a major, residential, etc.) and the threshold related to the example guidelines should therefore be cautiously stated. As the area has a high population and the refinery itself has 2500 employees, who are potentially exposed to these pollutants daily, the applied guidelines could be chosen to a more cautionary threshold, such as that for residential soils to have a better human health risk estimation. Similarly, the data compared with the residential soil guidelines of the United States and Switzerland is representative of the highest guidelines values, Norway, and Sweden with the lowest values along with Canada and Australia.

Table. 1. Statistical summary of heavy metal(loid) concentrations (unit in mg/kg) in topsoil

	Mean	Min.	Max.	Median	SD	CV	LB	ISQG	U.S.ASQG	SSQG	SWSQG	NSQG	ASQG	CSQG
As	0.67	<0.01	4.03	0.30	0.88	1.31	<0.01	18	22	NA	15	2	20	12
Pb	26.85	2.23	226.23	18.99	40.28	1.50	15.12	80	400	1000	80	60	100	140
Zn	129.40	12.65	358.42	118.0	105.4	0.81	63.01	200	23000	NA	350	100	200	200
Cu	32.90	5.88	95.84	25.51	23.30	0.71	39.83	100	3100	1000	100	100	100	63
Cr (III)	16.56	9.43	32.43	15.73	4.83	0.29	19.48	100	100000	64^{T}	120	25	50^{T}	64
Mn	341.24	111.76	698.35	341.9	130.1	0.38	450.8	NA	NA	NA	NA	NA	NA	NA
Co	7.52	0.12	18.32	6.6	5.35	0.68	12.49	40	NA	NA	NA	NA	NA	NA
Cd	0.63	<0.01	3.13	0.29	0.76	1.21	0.06	2	37	20	0.4	3	2	10
TOC%	1.35	0.02	3.2	1.4	0.82	0.6	0.52							
CEC	15.73	2.11	29.17	13.96	8.01	0.58	15.15							
Clay%	29.31	1.6	52.60	33.71	14.21	0.48	34.2							
pH	7.53	6.1	9.81	7.53	0.78	0.10	8.32							

Min. = Minimum, Max = Maximum, SD = Standard deviation, CV = Coefficient of variation**,** LB=Local background, ISQG =Iranian soil quality guideline (Keshavarzi et al., 2019), U.S.A soil quality guideline (Provoost et al., 2006), Switzerland soil quality guideline (Provoost et al., 2006), Sweden soil quality guideline (Chen et al., 2018a), Norway soil quality guidelines (Provoost et al., 2006), Australian soil quality guideline (Zarcinas et al., 2004), CSQG= Canadian soil quality guidelines (Hejami et al., 2020). ND: not applicable, T: total Chromium, *the land use/soil types for guidelines values are 'residential soil'

In comparing the study area with the mentioned soil guidelines, we observed that mean concentrations of heavy metal(loid)s in the Jam area do not reveal any specific accumulation except for Zn and Cd in comparison with Norway and Sweden soil quality guidelines, respectively. For example, the mean concentration of Pb in the study area is 26.85, which is lower than the United States, Switzerland, Norway, Sweden, Canada and Australia. Other heavy metal(loid)s showed a similar comparison (Table. 1). On the other hand, several of the studied heavy metal(loid)s had high variations (SD and CV, Table. 1) where the values in the upper range of concentrations could exceed the guidelines values, including those for industrial and residential soils. For example, Pb in station No 9 and 46 was exceeded Iran, Norway, Australia and Sweden residential soil guidelines. The maximum observed value of Pb (226.23 mg/kg) also exceeded the Canadian soil guidelines value recommended for residential soil (140 mg/kg) (Hejami et al., 2020). Several sampling points shown Zn concentration higher than international guidelines, the most prominent of these points is sample number 46, which is higher than almost all guidelines. Despite the high CV of arsenic and higher concentrations compared with the local background, it does not exceed most of the guidelines except Norway's residential soil guideline specifically at points No 11 (4.03mg/kg) and 53 (3.72mg/kg). Cd as the other important metal in pollution study with high CV in the studied area showed some sampling point with the maximum observed value of Cd (3.13 mg/kg), which is exceeded the Iran, Australia, Norway and Sweden residential soil guidelines.

The spatial variation was discussed with the value obtained by the coefficient of variation (CV) which has been classified in three range as follows: CV ≤ 0.1 indicates weak variability, $0.1 < \text{CV} < 1$ considered moderate variability and CV > 1 indicates strong variability. In this study, CV ranged from 0.29 – 1.50, which represents moderate to strong variability. The very large CV for Cd, As and Pb (CV > 1) showed extensive variability with heterogeneous distribution in the study area which can be a significant result of anthropogenic impact by local point industrial or rural settlement sources (Zhuo et al., 2020). The Co, Cr, Mn, Zn and Cu concentrations with low CVs can be an indicator of less influence of extrinsic factors on soils heavy metal(loid)s (He et al., 2019).

Figures 2 and 3 demonstrate the distribution of heavy metal(loid)s in soils of the studied area where the color gradient of black to white indicates the concentration of higher to lower values. As it is visually apparent, the studied elements represented both distributed and concentrated pattern. This pattern is a result of different activities in the area that might influence those trends. Spatial distribution clearly illustrated that refinery as well as urban activities are responsible for the discharge of heavy metal(loid)s to the soil.

Based on maps, As was found to be distributed alongside the urban area upstream and downstream where cities were developing (Fig. 2). Concentrated value of As in some points might have been affected by different specific sources, including agricultural activities (fertilizer application) and refinery activity. The highest As value was detected in sampling points No - 53 and 11, which was near to a wastewater pond of refinery and locally cultivated land, respectively. Research shows that the As can be found in different forms and concentrations in the process of gas formation, therefore evaluated concentration at point 53 may be attributed to natural gas (Faramawy et al., 2016). Sampling point number 10, 16, 33, 39 and 46 also exhibited a high value of As compare with local background and the surrounding features recorded in the sampling points shows that these points were precinct of rural cultivated land and might have been affected by these activities (Fig. 1 and 2).

The spatial distributions of Pb elevated in two distinct regions in residential areas, close to cities and around the refinery. A decreasing trend can be recognized by distance from these two regions. The results obtained for the distribution of the Cd showed highlighted contents around the residential and refinery areas as well. Some points with increased concentration may be related to agricultural activity, such as the overuse of fertilizers and pesticides, which are important Cd sources of soil pollution (Bloemen et al., 1995; Tembo et al., 2006). On the other hand, although Cr is one of the most priority in the toxicity list, the detected concentration was lower than the local background for most of the sampling site while an elevated black region toward the northern part of the refinery was recorded. This phenomenon may be due to fossil fuel consumption by the industrial sector (Cheng et al., 2014; Guertin et al., 2004).

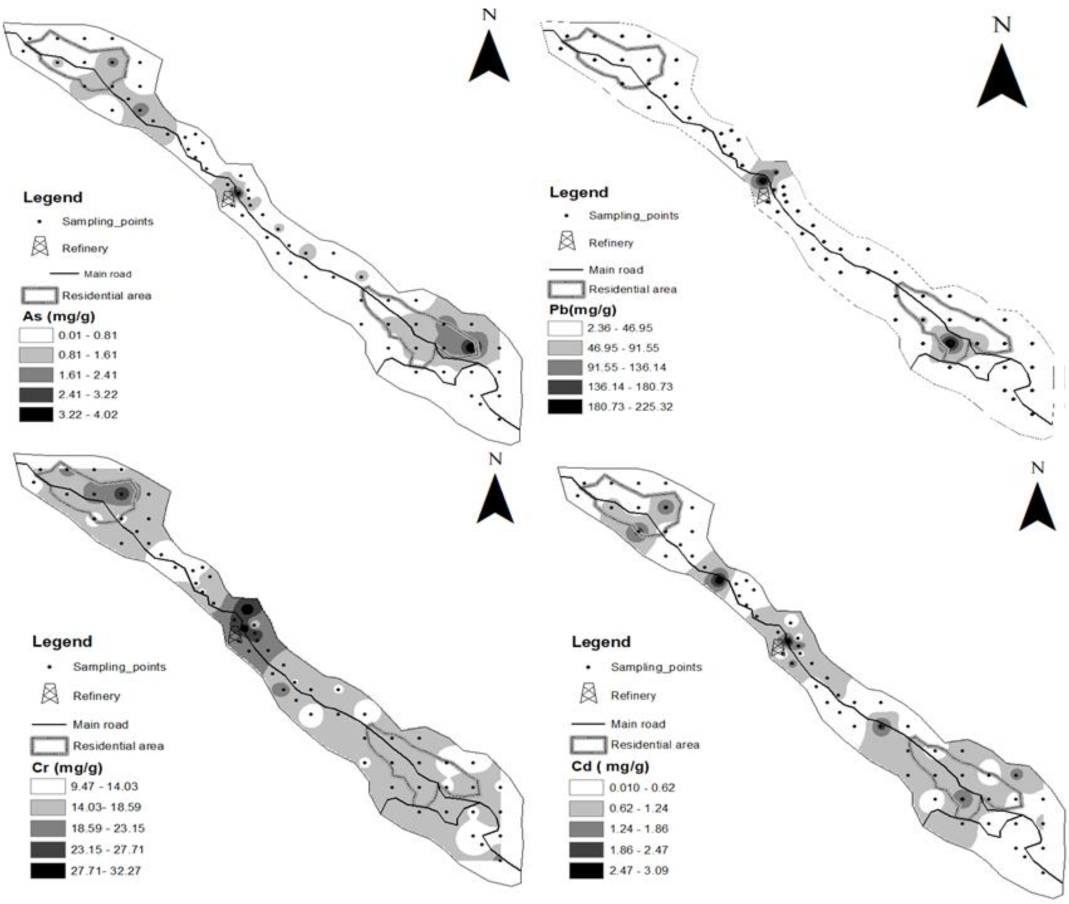

Figure. 2. Spatial distribution of As, Pb, Cd and Cr in Jam area

Along with priority pollutants (e.g., As, Pb, Cd, Cr), the spatial distributions of Cu, Zn, Mn and Co were also recorded. Concentrations of Cu and Zn were remarkably similar over the studied area. They showed high concentrations around the refinery, which might be due to industrial and traffic emissions attributed to the industrial development across the area. The distribution pattern of Mn and Co also showed similar behavior with an elevated concentration in some points (Fig. 3). The concentration of Co and Mn was not significantly higher than the local background in most of the soil samples, implying that the industrial and urban activities might have a very low contribution to their occurrence. However, some elevated amounts of Mn can occur from some anthropogenic sources, such as industrial wastewater and sewage effluent in urbanized and industrialized areas (Hou et al., 2020) or from fuel additives of petroleum products (Pellizzari et al., 1999). Indeed, in the present study, sample points 49, 53, and 54 were linked to one or many of these potential sources (Fig. 3, Fig. 1). On the other hand, the spatial distribution pattern of the Co in the studied area showed more heterogeneity than that of Mn, indicating it's both natural and anthropogenic origin (Poznanović Spahić et al., 2019).

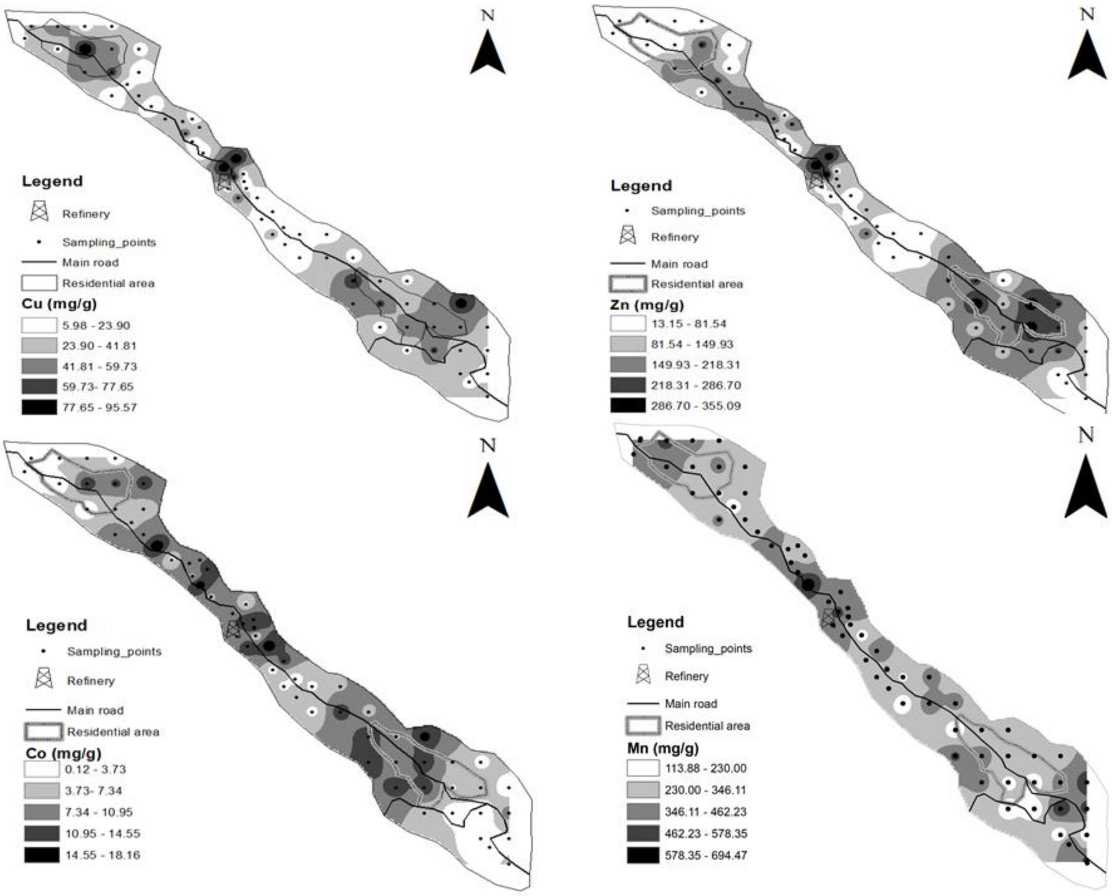

Figure. 3. Spatial distribution of Cu, Zn, Co and Mn in the Jam area

It is generally suggested that the different trends of the spatial distribution of studied heavy metal(loid)s in soil could be a representation of the combination of several points and nonpoint sources. Anthropogenic activities could be a direct link to the occurrence of a high concentration of heavy metal(loid)s (Zhang et al., 2019). Xu et al. (2020) reported that transportation activities should not be overlooked in assessing the source of trace elements, especially Pb, Zn and Cu. Indeed, in this study as well, the rapid industrial growth in the Jam region has led to more transportation activities, which could be a very important source of heavy metal(loid)s. Wind direction has been studied by many researchers to investigate the effect of wind on the distribution of elements from the different industrial facilities (Ding et al., 2017; Li et al., 2017). Considering the refinery as a potentially major source of contamination and the NE and SW as a dominant wind direction, such direction had no significant effect on the distribution pattern of heavy metal(loid)s (Fig. 1-3).

3.3. Assessment of heavy metal Pollution and ecological risk

The computed I_{geo} and CF based on local background concentration in soils are illustrated in Fig 4 a and b. The mean values of I_{geo} followed the order of As (3.72) > Cd (1.3) > Zn (-0.05) > Pb (-0.64) > Cr (-0.85) > Mn (-1.08) > Cu (-1.23) > Co (-1.92). This result suggests that the most sample sites fall between unpolluted to moderately polluted by Co, Cu, Mn, Cr, Pb, Zn with the value $0 < Igeo < 1$ (Ntekim et al., 1993). However, moderate and heavy pollution to extreme pollution was observed for Cd and As, respectively. Specifically, As had the highest Igeo value ($3 < I_{geo} < 4$) with severe to extreme levels of pollution in some soil samples that were collected in the industrial and residential domain of the studied area (Fig. 4a). The mean CF value for As (CF = 67.23) and Cd (CF = 10) indicated very high and moderate contamination, respectively (Fig. 4b). The rest of the elements showed a low contamination factor in all samples (CF = 0.03 – 1.47) (Hakanson, 1980). Pollution load index - calculated as a sum of all the heavy metal(loid)s contamination factor (CF) (Kumar et al., 2019) - showed that the soil near the refinery and residential area was more contaminated than the rest of the area. Within the study area, sampling sites 53, 46, 9 and 39 (PLI > 4) were the most polluted, as these sites showed the highest PLI within the study area and the rest of the area is low to moderately polluted (Fig. 4c). The ecological risk factor results are shown in Fig 4d. For Pb, Zn, Cr and Cu, the potential low Er indices (< 40) indicated low risk, while Cd could pose a high ecological risk (Er = 300) and As with Er ≥ 320 could be a very high risk for ecological receptors (Hakanson, 1980). The risk index of the heavy metal(loid)s in soil samples shows decreasing trend as follows: As (42360.72) > Cd (18912.89) > Pb (233.84) > Cu (164.72) > Zn (93.02) > Cr (47.32). It should be noted that the RI values more than 600, as found for the As and Cd, posed a very high risk to the ecosystem (Hakanson, 1980) (Supplementary Table. 1). The results of I_{geo}, CF, PLI and RI method showed consistency with some minor differences which may be attributed to the different toxicity of elements as well as the nature of each index.

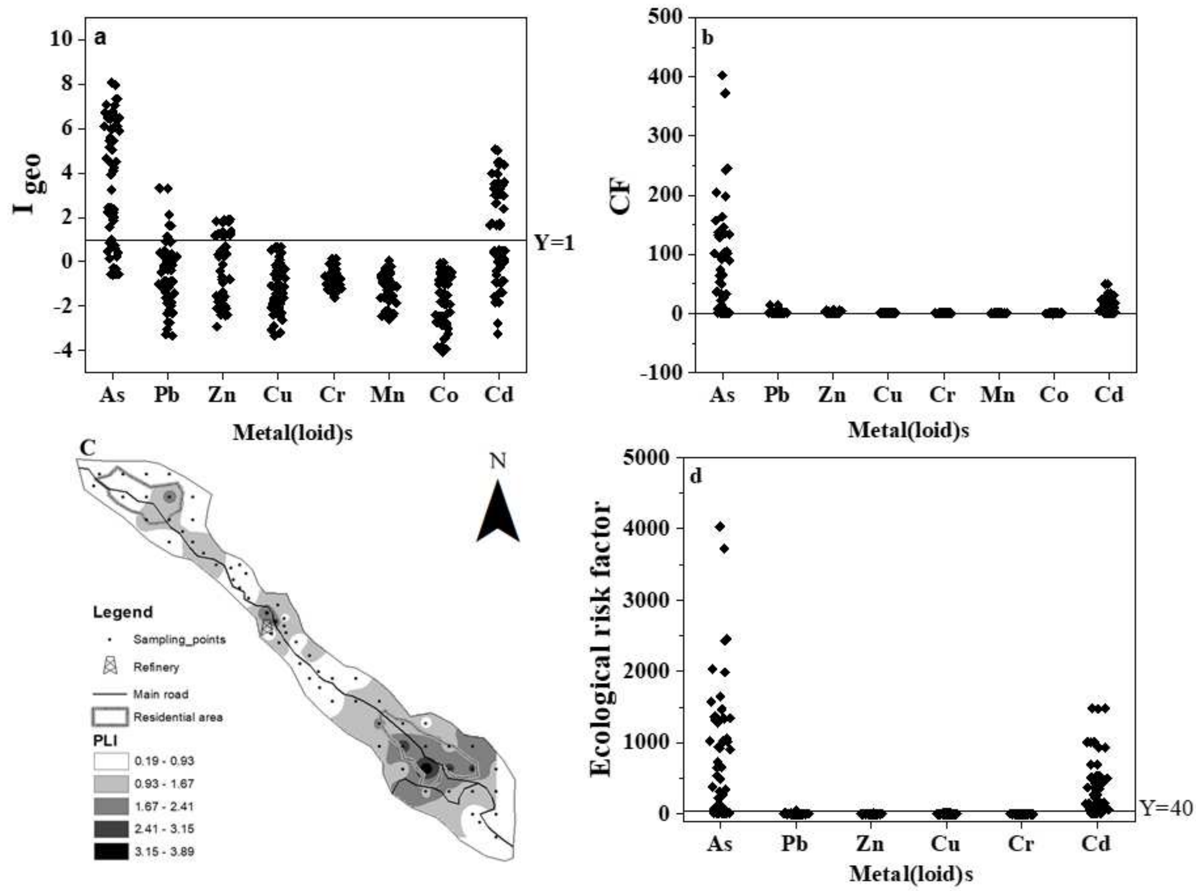

Figure. 4. Values (a) geo-accumulation index, (b) contamination factors index, pollution load index (C) and ecological risk (d) of studied heavy metal(loid)s

3.3.1. Human health risk assessment

The health risk to the human body (both adult and child) through different exposure pathways (inhalation, ingestion and dermal contact) of contaminant were assessed using various indices like hazard quotient (HQ) and carcinogenic risk (CR). It is evident that the risk factors largely depend on (i) route of exposure (ii) age of a person, and (iii) contamination species (Table. 2).

In general, HQ (non-cancer risk) values of the heavy metal(loid)s in the ingestion route of adults were greater than the dermal contact and inhalation (Table. 2). A similar trend, dominant $HQ_{ingestion}$, followed by HQ_{dermal} and $HQ_{inhalation}$, was also observed for children. However, compared to adults, the higher HQ values for children were mostly due to their behavior and hand or finger sucking during their outdoor play activities, which made them more susceptible to exposure to soil and dust (Qing et al., 2015). On the other hand, inhalation of soil is insignificant with a negligible consequence of exposure (Ihedioha et al., 2017). The highest HQ for ingestion attributed to As and the lowest level for Mn, with As > Pb > Cd > Cr > Co > Cu > Zn > Mn order for both subpopulations, while HQ of dermal and inhalation showed slightly different trends (Table. 2).

Table. 2. Non-carcinogenic hazard quotient and carcinogenic risk values of heavy metal(loid)s for adult and children through ingestion, inhalation, and dermal pathways

		HQ				**CR**			
		Ingestion	**Inhalation**	**Dermal**	**HI**	**Ingestion**	**Inhalation**	**Dermal**	**TCR**
As	**Child**	8.05E-01	1.94E-04	6.37E-03	8.12E-01	8.12E-03	1.58E-09	2.87E-05	8.15E-03
	Adult	1.69E-02	2.63E-04	1.06E-03	1.71E-01	7.62E-04	2.14E-09	4.79E-06	7.66E-04
Pb	**Child**	6.18E-01	1.82E-04	6.28E-05	6.18E-01	3.24E-04	1.43E-05	4.70E-05	3.86E-04
	Adult	5.79E-02	2.46E-04	9.95E-03	6.81E-02	3.04E-05	1.94E-05	7.83E-06	5.76E-05
Zn	**Child**	3.47E-02	1.53E-05	2.51E-03	3.73E-02				
	Adult	3.26E-03	2.08E-06	4.19E-05	3.30E-03				
Cu	**Child**	7.38E-02	3.00E-06	3.29E-04	7.41E-02				
	Adult	6.92E-03	4.06E-05	5.49E-04	7.51E-03				
Cr	**Child**	4.47E-01	2.06E-03	3.22E-02	4.81E-01	6.67E-04	2.47E-06		6.70E-04
	Adult	4.17E-02	2.79E-03	5.37E-03	4.98E-02	6.25E-05	3.35E-06		6.59E-05
Mn	**Child**	2.27E-02	4.18E-07	1.35E-03	2.41E-02				
	Adult	1.05E-04	6.62E-05	1.10E-05	1.82E-04				
Co	**Child**	3.17E-01	4.89E-02	5.73E-04	3.66E-01		2.74E-06		2.74E-06
	Adult	2.97E-02	6.63E-02	9.56E-05	9.61E-02		3.71E-06		3.71E-06
Cd	**Child**	5.08E-01	1.32E-03	7.35E-02	5.83E-01	8.32E-05	1.41E-07	4.48E-06	8.79E-05
	Adult	4.76E-02	1.78E-03	1.23E-02	6.17E-02	7.80E-06	1.91E-07	7.48E-07	8.74E-06

HQ > 1 represents a likely adverse health effect caused by concern contaminants (Cocârţă et al., 2016). The HQ values relative to an element of interest in the study region are lower than 1 for all sampling sites, indicating that any non-carcinogenic risk for these elements is eliminated for adults and children. However, it should be cautiously noted that the tendency of high HQ values for children could pose more non-carcinogenic risk caused by heavy metal(loid) exposure in the Jam area than adults (Ihedioha et al., 2017). In addition, this could greatly vary for elemental types. For example, the HI was found to be in the order of As > Pb > Cd > Cr > Co > Cu > Zn > Mn for children, and As > Pb > Cd > Co > Cr > Cu > Zn >Mn for adult (Table. 2). In general, the HI values for adults were much lower than the safe level, indicating that the exposed adults were unlikely to suffer from obvious detrimental health effects (Adimalla, 2020). Compared with adults, HI values of As, Cd, Cr and Pb was less than 1 but greater, demonstrating to have a higher probability to experience non-carcinogenic effects than adults in this area for children (Jia et al., 2018; Jiang et al., 2017).

In addition to non-carcinogenic risk, the carcinogenic health risk (CR) and TCR (total carcinogenic risk) of As, Pb, Cd, Cr and Co were estimated. Carcinogenic slope factors (SFs) are not accessible for all the studied heavy metals; therefore, only for As, Pb and Cd all three pathways were contained for the risk assessment of carcinogenesis while for the other metals only one or two pathway(s) were included in the carcinogenic risk estimation (Table. 2). According to the US Environmental Protection Agency (USEPA), CR of 1.00E-06 to 1.00E-04 is a tolerable carcinogenic/cancer risk level (USEPA, 2011). Based on the obtained data, ingestion has been identified as a major route of exposure to carcinogenic heavy metal(loid)s compare with inhalation and dermal contact (Table. 2). Inhalation and dermal contact were found to have no carcinogenic health risk in the sampling area. The estimation of carcinogenic risk through the ingestion of heavy metal(loid) in soils was 8.1E-03 (As) > 6.6E-04 (Cr) > 3.24E-04 (Pb) > 8.32E-05 (Cd) in the case of children. The same trend was recorded for adults.

However, the carcinogenic risks of As, Pb, Cr and Cd in soils for adults were lower than those for children were (Table. 2). It was found that CR values of Cd, Pb and Cr were below the threshold of 1.0E-04 established by USEPA for adults, indicating no significant carcinogenic effect attributed to the exposed soil in the Jam area . The CR values of As, Cr, and Pb for children, and As for both children and adults exceeded the maximum tolerable or acceptable risk, indicating significant health effects (Table. 2). It is also noticeable that the TCR values for children followed the order As > Cr > Pb which exceeded the acceptable limit (1.0E-04) (Zhuo et al., 2020).

From the health risk discussion, the child's sensitivity to the potential health issues regardless of the carcinogenic or non – carcinogenic risk was evident. A similar trend of results was reported by various studies conducted in various such soil sites across the globe. (Jia et al., 2018). It should be noted that a limited number of key factors were considered in risk assessment while additional factors might also be important but were not incorporated in this study. Hence risk estimation may be overestimated or underestimated. Therefore, in the current study, an overall estimation is made to protect public health. In future studies, the health risk of any given element should be assessed considering additional factors, including a potential toxicological variation with the elemental speciation, bioavailability, or bioaccessibility.

3.4. Geochemical associations and source analysis of heavy metal(loid)s

The potential origins and pathways of heavy metal(loid)s can be determined through inter-element relationships among them (Hou et al., 2020; Mohammadi et al., 2020; Zhuo et al., 2020). Therefore, Pearson's correlation coefficient shows a very significant correlation between As and Pb (r = 0.37), As and Zn (r = 0.66), As and Cu (r = 0.41), As and Cd (r = 0.54), Pb and Zn (r = 0.47), Pb and Cu (r = 0.41), Zn and Cd (r = 0.37), Zn and Cu (0.48) and Co and Mn (r = 0.34) at 0.01 level (Table. 4). Correlations among these elements may reveal their similar sources, mutual dependence and common geochemical behavior in the studied soils (Lu et al., 2010). In contrast, a negative correlation between Mn and As, Pb and Mn, or Co and As reflects the opposite (Huang et al., 2019; Li et al., 2013; Sun et al., 2010).

Table. 3. Pearson's correlations matrix among heavy metal(loid)s (n=63)

	As	**Pb**	**Zn**	**Cu**	**Cr**	**Mn**	**Co**	**Cd**
As	1							
Pb	**0.37****	1						
Zn	**0.66****	**0.47****	1					
Cu	**0.41****	**0.41****	**0.48****	1				
Cr	0.10	0.20	0.03	0.18	1			
Mn	-0.09	-0.13	-0.07	0.17	0.06	1		
Co	-0.01	0.08	0.02	0.05	0.16	**0.32****	1	
Cd	**0.52****	0.02	**0.37****	0.24	0.16	0.00	0.09	1

**. Correlation is significant at the 0.01 level

To identify sources of contaminants in Jam soils, principal component analysis (PCA) was used. Kaiser-Meyer-Olkin (KMO) and Bartlett's tests of sphericity were performed on data to determine the suitability for conducting PCA (Nour, 2019). The KMO value was 0.75 whereas a value of more than 0.6 is considered satisfactory. According to the Bartlett ball test, soil data were qualified for PCA as the test result was less than the significant level of 0.05, which can reject the null hypothesis of the Bartlett sphericity test (Ma et al., 2016). After extracting the number of significant factors, they were subjected to varimax rotation and the factor loadings are explained in the Rotated component matrix (Table. 4). It derived two eigenvalues higher than one that explains 53.78% of the total variance in the data (Table. 4).

Table. 4. The explained results of the total variance (extraction method: principal component analysis)

Component	Initial Eigenvalues			Sums of Squared Loadings		
	Eigenvalues	**Variance**	**Cumulative%**	**Eigenvalues**	**Variance**	**Cumulative%**
1	2.99	37.33	37.33	2.9862	37.3272	37.3272
2	1.32	16.45	53.78	1.3164	16.4549	53.7821
3	0.97	12.08	65.86			
4	0.85	10.67	76.54			
5	0.56	7.05	83.59			
6	0.52	6.52	90.11			
7	0.47	5.93	96.04			
8	0.32	3.96	100.00			

Extraction Method: Principal Component Analysis.

Component Matrix			Rotated Component Matrix		
Heavy metal(loid)s	**PC1**	**PC2**	**Heavy metal(loid)s**	**PC1**	**PC2**
As	0.710	-0.119	**As**	0.712	0.106
Pb	0.744	-0.208	**Pb**	0.772	0.031
Zn	0.793	-0.296	**Zn**	0.846	-0.037
Cu	0.743	-0.206	**Cu**	0.771	0.033
Cr	0.542	0.401	**Cr**	0.392	0.548
Mn	0.053	0.614	**Mn**	-0.139	0.601
Co	0.201	0.668	**Co**	-0.015	0.698
Cd	0.641	0.380	**Cd**	0.492	0.559

Component 1 explained 37.33% of the total variance that was heavily weighted primarily by As, Pb, Zn, Cu, Cd and moderately by Cr. This indicates that the six elements share a degree of homology and could have a similar origin. This result was consistent with

Pearson's correlation analysis result (Table. 4). These heavy metal(loid)s were intervened by industrial and urban activities, such as natural gas processing facilities, agricultural and transportation activities in the area, resulting in their emission into the soil environments. Studies have found that Pb-containing gasoline combustion can increase the soil content of Pb (Sun et al., 2010; Zhang et al., 2018). Similarly, the combustion of crude oil can also release trace amounts of Cd that were present in the crude oil mixture (Manno et al., 2006; Zhang et al., 2016). Zinc may have been derived from refinery and petrochemical units as well as lubricating oils, tires, mechanical abrasion of vehicles (Zhuo et al., 2020). On the other hand, brake dust is often recognized as a significant carrier of Cu since Cu is a key element used for heat transfer of the brake system (Benhaddya et al., 2016; Rastmanesh et al., 2017). Agricultural activities, including usage of fertilizers and pesticides, often contribute to the source of Zn, Cd and Pb; among them, Cd is often traced as a marker metal for these agriculture-driven sources of contaminant (Straffelini et al., 2015). Industrial activities such as industrial discharge and sewage sludge have been reported to be As emission sources (Zhang et al., 2018). Therefore, industrial and urban sources were attributed to the first principal component.

Component 2 is dominated by Mn (0.61%), Co (0.66%) and moderately by Cr (0.40%) in the same group of origin. These were slightly higher or approximately equal content to the local background values (Table. 1). Therefore, the results of the descriptive analysis, distribution pattern and pollution indices of these elements indicate that they were mainly may be originated from a natural source (local soil). Furthermore, Pearson's correlation shows a strong correlation between Mn and Co. Based on the analysis, natural sources were considered to be the source of the second principal component (Cai et al., 2015; Garelick et al., 2008).

4. Conclusions

The concentration, surface dispersal and emission source of heavy metal(loid)s, including As, Zn, Pb, Cr, Cu, Mn, Co, and Cd in soil samples collected from Jam, South of Iran have been investigated in this study. The mean concentration of Co, Mn, Cr, Cu and Zn were less than the local background value while As, Cd and Pb were higher. The soils were moderate to heavily polluted by Cd and As and the level of Cu, Zn, Pb, Co, Mn and Zn detected in the studied soils did not pose any pollution risk. Human health risk assessment suggests that ingestion may constitute the most important exposures over all pathways in the studied area. The non-carcinogenic risk in both population group (children and adult) was low (HI < 1); however, the comparison suggests that the child's vulnerability toward pollutant attributed health issues are greater than that for adults. Although cobalt and cadmium TCR values were in the safe range and did not pose a cancer threat in both groups. Cd, Cr and Pb showed cancer risk to children population, while As exceeded the limit in the case of ingestion as the medium of exposure to adults and children. Although natural gas is known as a clean fossil fuel, the accumulation properties of heavy metals may cause overburden of heavy metal(loid)s overtime in such environments. One of the most important factors involved can be continuous development in various urban and industrial sectors depends on this industry. Therefore, the surface dispersal of heavy metal(loid)s corresponds well to the industrial and urban areas. According to correlation coefficient analysis coupled with PCA, As, Zn, Pb, Cu, Cd and Cr might originate from the refinery industry, urban, cultivation and traffic activities. The complexity of the studied environment made difficulties in discussing and judging soil quality. However, the good representative samples of 190 km^2 area could help understand the soil quality as well as the contamination status and potential management strategies. Overall, the results of this study will help prepare an appropriate scientific framework and a foundation for further studies. It can also provide a valuable resource for areas with similar conditions beyond regional aspects. Furthermore, according to the characteristics of the region, it is important to undertake research on organic pollutants as well as other priority elements such as mercury in such gas field areas.

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Author Contributions

The manuscript was written through contributions of NK and BB. The investigation, data curation conceptualization, data generation, formal analysis, methodology, writing - original draft were conducted by NK. BB involved in supervision, investigation, review & editing of this project. All other authors reviewed and edited the manuscript.

Supporting Information

All indices with relevant information and descriptions with the detailed probabilistic values of parameters for human health risk assessment of heavy metal(loid)s in soils have been collected and presented as supplementary information.

Conflicts of interest

There are no conflicts to declare.

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Figures

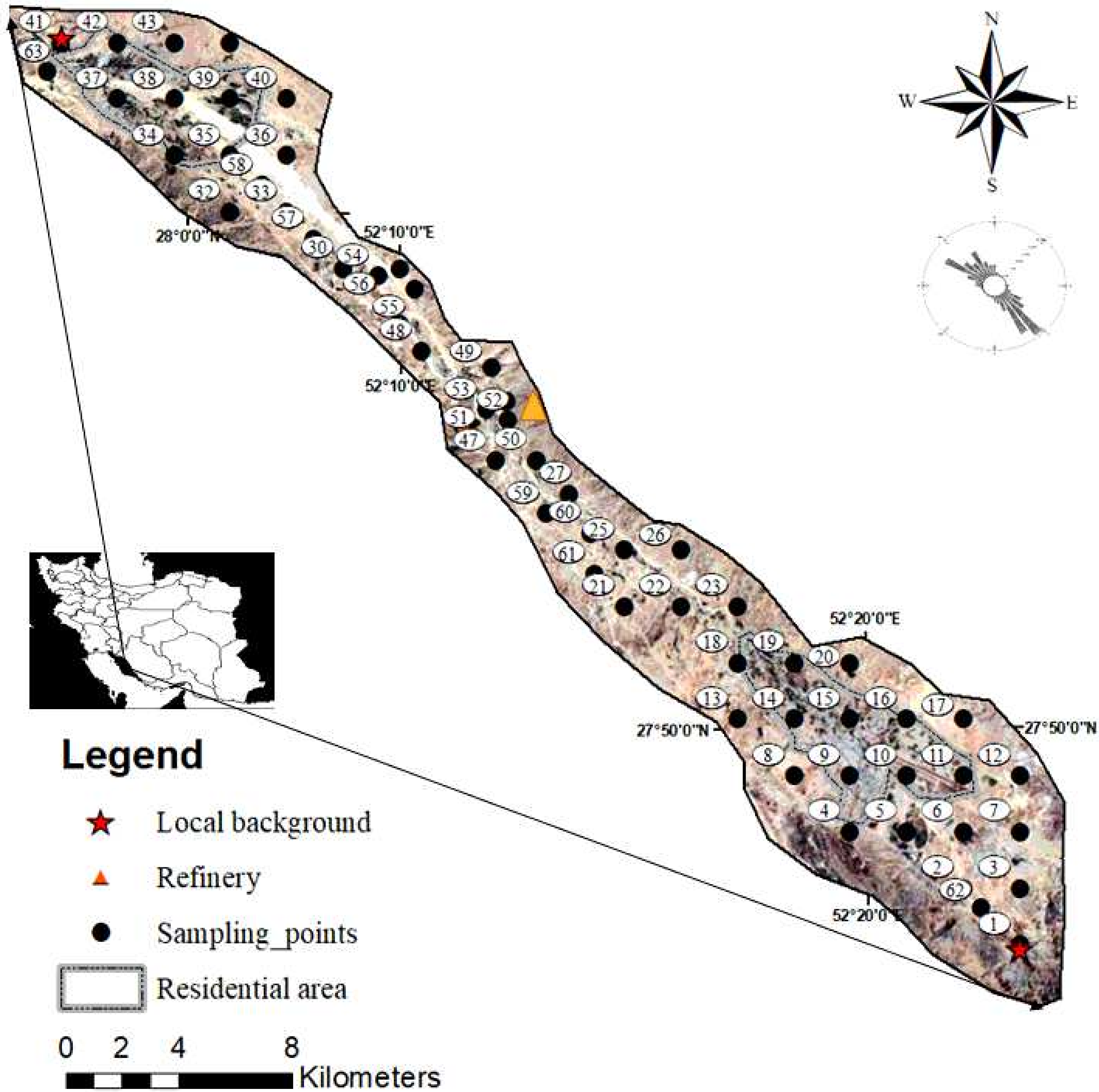

Figure 1

Location map of the research area with sampling stations

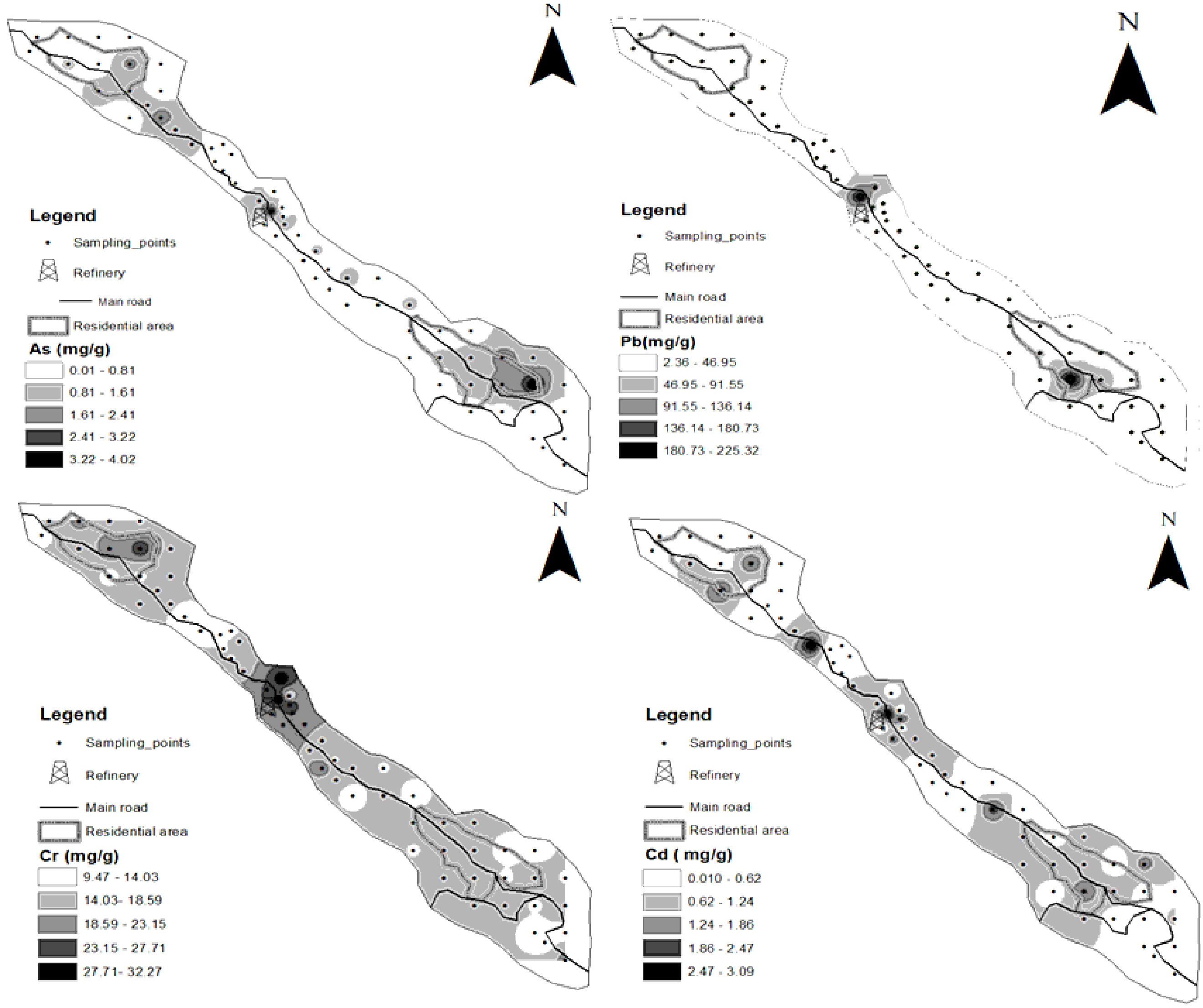

Figure 2

Spatial distribution of As, Pb, Cd and Cr in Jam area

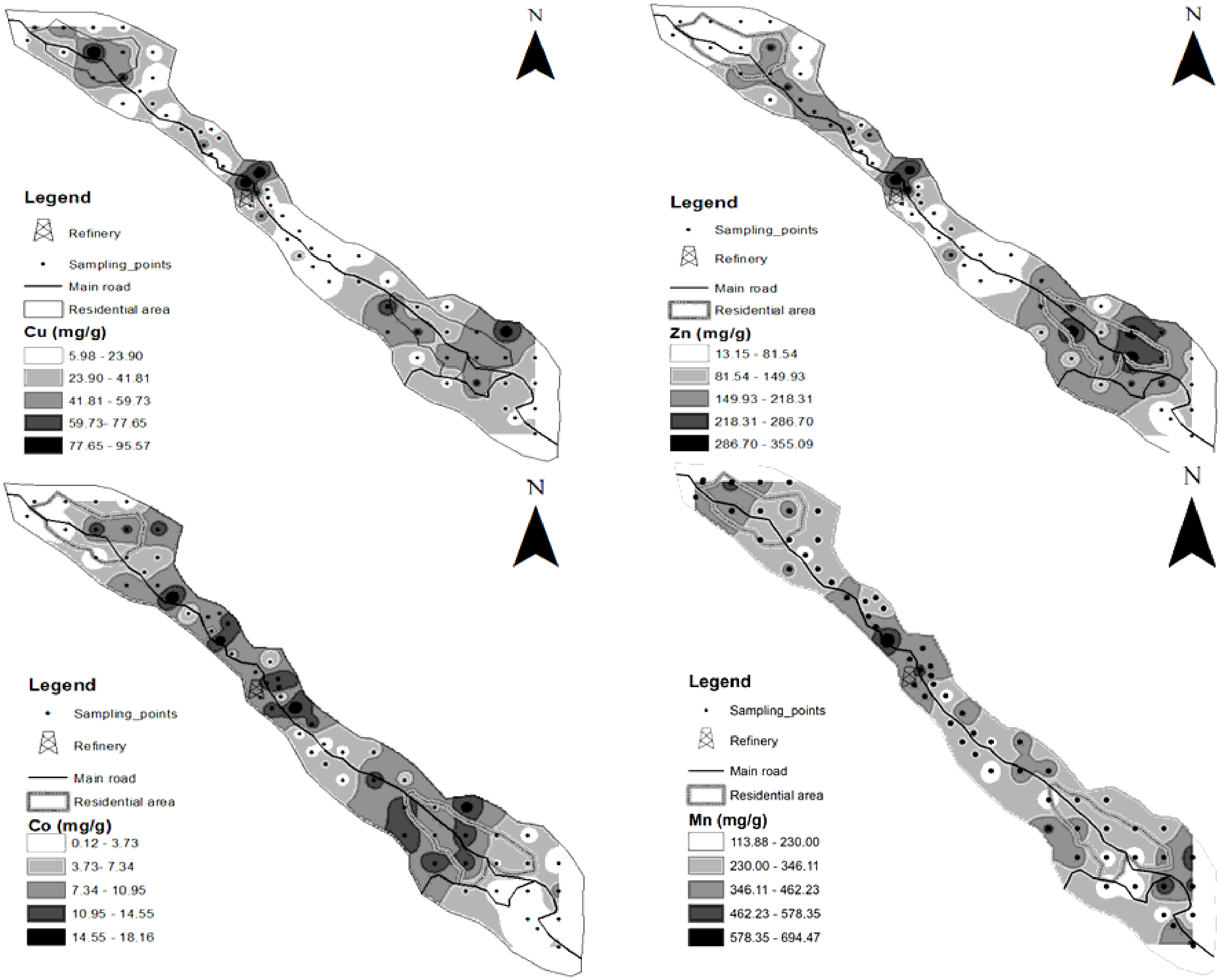

Figure 3

Spatial distribution of Cu, Zn, Co and Mn in the Jam area

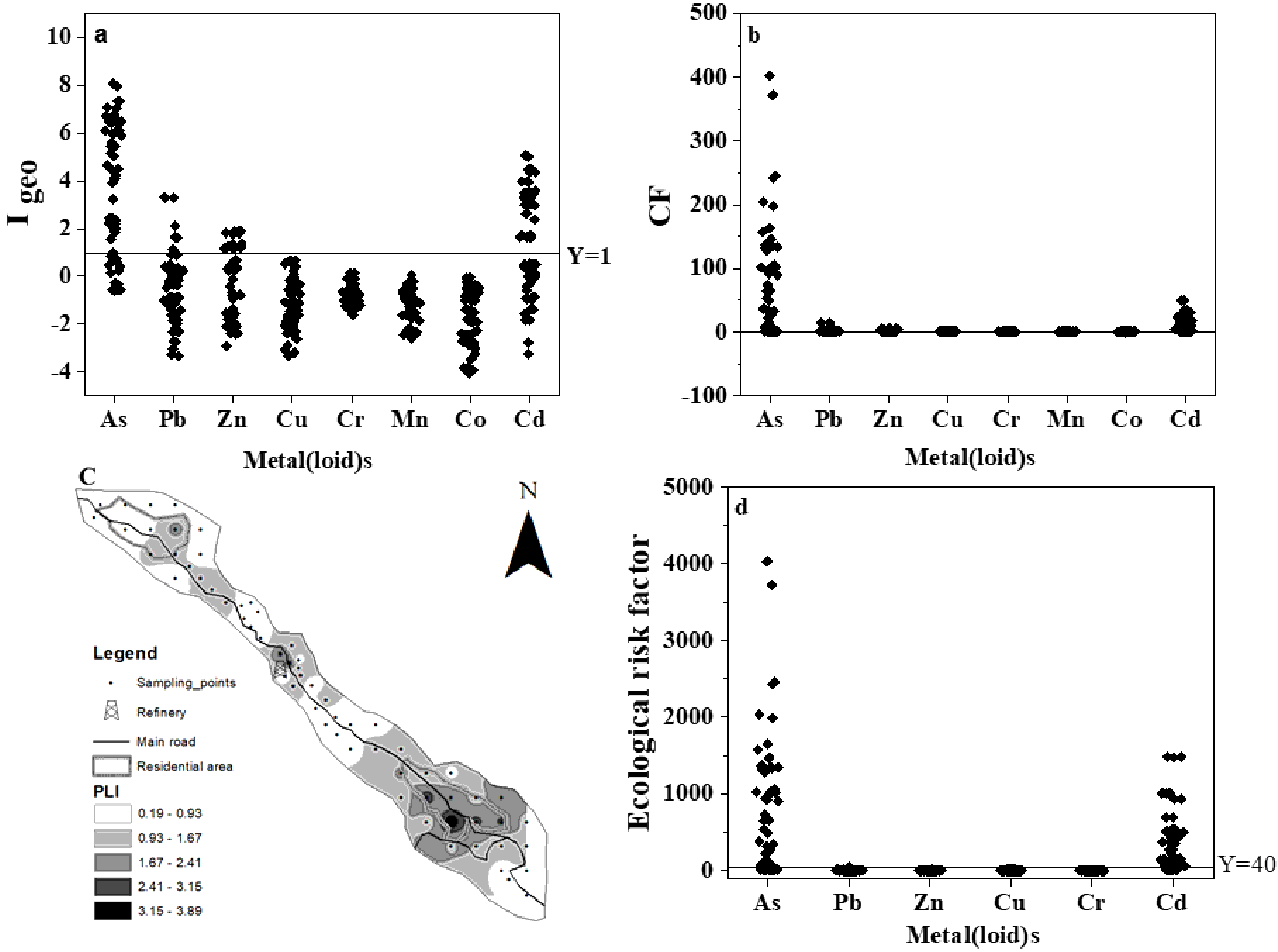

Figure 4

Values (a) geo-accumulation index, (b) contamination factors index, pollution load index (C) and ecological risk (d) of studied heavy metal(loid)s

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