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Research article

Appraisal of pollution of potentially toxic elements in different soils collected around the industrial area

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ABSTRACT

It is imperative to understand the pollution of potentially toxic elements (PTEs) in different soils in order to determine the sustainable management approaches for soils. Potentially toxic elements (Fe, Mn, As, Pb, Zn, Ni, Cu, Cr, Co and Cd) were determined in agricultural, non-agricultural and industrial soils of Punjab, India. The concentration of PTEs at industrial soils were highest followed by non-agricultural and agricultural soils. The percentage change recorded from agricultural to non-agricultural soils for PTEs were 3.19% for Fe, 25.3% for Mn, 63.8% for Cu, 13.5% for Cr, 49.8% for Pb, 79.6% for Ni, 35.8% for Co and 32% for Cd. From non-agricultural to industrial soils, the percentage change observed for PTEs were 89% for Zn, 2.03% for Fe, 21.9% for Mn, 68.2% Cu, 9.2% for Cr, 35.8% for Pb, 18.4% for Co, 30.4% for Cd and 43.4% for As. The results of contamination factor, enrichment factor, geo-accumulation index, pollution and modified pollution indices also resulted severe contamination of Cd and As in all soil types. Ecological risk assessment results revealed that Cd exhibited very high risk in different soil types. The outcomes of this study will aid in forming approaches to decline the perils allied with PTEs in soils, and produce guidelines to save the environment from long term accrual of PTEs.

1. Introduction

Soil is considered as one of the most substantive non-renewable natural resource that supports plethora of flora as well as fauna (Jansson and Hofmockel, 2019). Unfortunately, unsustainable development models are degrading agricultural soils at an alarming rate (Kopittke et al., 2019). Soil receives a lot of pollutants from diverse sources related to agriculture and other industries (Naveedullah et al., 2013; Kumar et al., 2019a). The rapid and incessant usage of inorganic pesticides, herbicides etc., has led to degradation of major agricultural edaphic system. Automobiles and other transportation systems also polluted the nearby fields (Kumar et al., 2019b). Amid other unwanted contaminants, heavy metals (HMs) form major pollutants having the starkest impact on plants. Industrial effluents rich in different kinds of heavy metals also reach soil either through water used for irrigation purposes or other anthropogenic activities.

HMs have high atomic density with atomic number more than 20. Being non-degradable, they persist in soil for very long duration of time (Mahey et al., 2020). Present global agricultural requirement pressurises producers to increase yield that induces involvement of unsustainable methods like HM based mineral phosphate fertilizers. Other HMs pollution sources are run-off water from minning area, sewage disposal, smelting, and cement manufacturing etc (Walter et al., 2006; Ogunkunle and Fatoba, 2013). These HMs are taken up by crop plants and reach humans in biomagnified levels which pose a great risk to humans as is evident from increased number of pathological issues related with kidneys, liver, bone, pancreas etc (Kawatra and Bakhetia, 2008). Piling up of HMs in soil is a major hurdle in achieving global food safety. Most of the

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developing cities, due to fast development, are unable to curb this menace and face major edaphic degradation due to accumulation of HMs.

The district Ludhiana of Punjab is known as industrial hub and also called Manchester of India (Sikka and Nayyar, 2016). The town is famous for electroplating, machine tools, bicycle, woollen and dying work. The above said industries generate vast amount of sludge and industrial waste which directly discharged into Buddha Nullah tributary of Satluj river (Sikka et al., 2009). The waste reaching soil keeps on accumulating as HMs cannot be degraded or destroyed. Both essential and non-essential HMs are considered toxic for terrestrial and aquatic organisms. There abundance more than threshold level cause ecological imbalance.

The present work was conducted first to appraise the potentially toxic elements (Cr, Cu, Co, Fe, Cd, Ni, Mn, As, Pb, Zn and Cd) in industrial, agricultural and non-agricultural soils of Ludhiana, Punjab (India). Secondly, Principal component analysis (PCA) and correlation analysis were performed to measure the relation of potential toxic elements (PTEs) with each type of soil. At last, the level of pollution and appraisal of risk were determined by using various pollution indices and ecological risk assessment indices. This work will reveal the contamination of potentially harmful elements in various type of soils, as well as how the amount of PTEs varies with soil type.

2. Material and methods

2.1. Study area

The present study was carried out at different sites (Supplementary Table S1) in Ludhiana district of Punjab, India (Figure 1) during May 2017 to October 2019. The mean temperature and humidity during collection was 35–42 °C and 58.1% respectively (Kumar et al., 2010). According to the koppen climatic classification, the climatic conditions in the Ludhiana district are humid subtropical (Yeotikar et al., 2019) with 758 mm per year average annual rainfall (Hadda et al., 2020). The soil of Ludhiana has a loamy texture. According to 2011-12 census, the total area of Ludhiana was 3, 57, 800 ha and total population was 34, 98, 739.

2.2. Collection of samples

The soil was sampled in triplicates from each sampling sites which were air dried and powdered to study the content of PTEs. The samples were properly coded and stored till further analysis.

2.3. Analysis of soils for potentially toxic elements

Heavy metal estimation was done using Varian 20 model of atomic absorption spectrophotometer (AAS) after open digestion of soil samples with perchloric acid and nitric acid (1:4 ratio respectively) (APHA, 1998). The different chemicals used in the analysis of heavy metal were of analytical grade. The reference solutions for heavy metal analysis were likewise obtained from Agilent technologies and different solutions of varied concentrations were made by dilution with double distilled water. The reference solutions were also run as a sample after every ten sample readings to ensure proper working of the instrument.

2.4. Computation of pollution indices

Various pollution indices have been presented by various researchers to determine the contamination level of PTEs in soil. The various indices calculated for the present study is as follows:

2.4.1. Contamination factor (CF)

CF factor is used to calculate the anthropogenic input into the soil. It was calculated by dividing the PTEs level in soil samples by the reference environment value (Hakanson 1980).

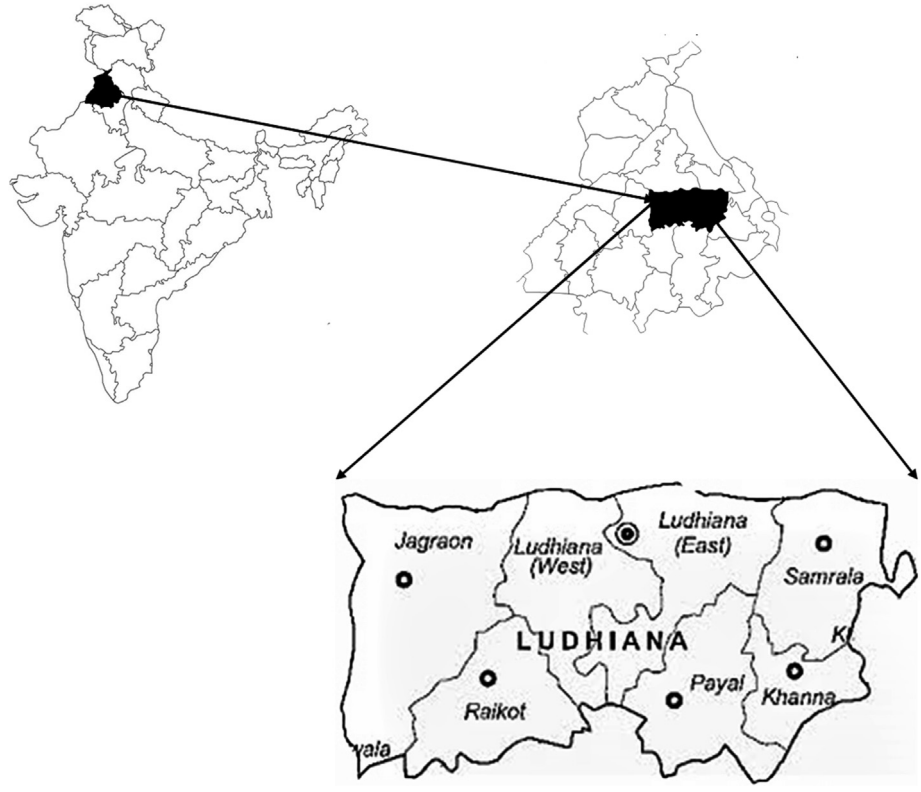

Figure 1. Location of study area along with different sampling sites.

$$CF = \frac{\text{Concentartion of each PTE}}{\text{Background value of each PTE}} \quad \text{Eq (1)}$$

2.4.2. Enrichment factor (EF)

EF depicts the natural and human influences on PTE concentrations (Delgado et al., 2010). Taylor and McLennan (1995) provided the PTE reference values, and the scores used to categorise the pollution level on CF and EF values are provided in supplementary Table S2.

$$EF = \frac{\text{Concentartion of PTE in samples/Fe concentration in the samples}}{\text{Background values of PTE/Background value of Fe}} \quad \text{Eq (2)}$$

2.4.3. Geoaccumulation index (Igeo)

The pollution of PTEs in soils is determined by Igeo index and calculated by Eq. (3) (Muller 1981). The reference values for PTEs were used as per Taylor and McLennan (1995). The constant value 1.5 denotes changes in the content of heavy metal in the surrounding environment (Tian et al., 2017).

$$Igeo = \log_2 \frac{\textit{Heavy metal concentration in soil samples}}{1.5 \times \textit{heavy metal concentration in background environment}} \quad \text{Eq (3)}$$

2.4.4. Pollution index (PI) and modified pollution index (MPI)

The Pollution index was calculated by taking the average and maximum value of contamination factor (CF) for each PTE in the soil, whereas the modified pollution index (MPI) takes the maximum and mean value of enrichment factor (EF) for each PTE in the soil. The PI and MPI were computed as per method of Nemerow (1991) as in Eq. 4 and Eq 5 respectively.

$$PI = \sqrt{\frac{(CF_{average})^2 + (CF_{maximum})^2}{2}} \quad \text{Eq. (4)}$$

$$MPI = \sqrt{\frac{(EF_{average})^2 + (EF_{maximum})^2}{2}} \quad \text{Eq (5)}$$

Supplementary Table S3 shows the grades used to categorise pollution levels.

2.4.5. Ecological risk indices (RI and MRI)

The ecological risk indices were calculated by using potential and modified ecological risk indices as in Eq 6 and Eq 7 respectively.

$$RI = \sum CF \times Tr \quad \text{Eq (6)}$$

$$MRI = \sum EF \times Tr \quad \text{Eq (7)}$$

where Tr denotes the toxic reaction factor of each PTE derived from Heidari et al., (2019). Table S4 lists the ratings used to categorise the ecological hazard.

2.5. Statistical analysis

All the statistical analysis was performed on triplicates and data was presented as mean ± std. error. Pearson's correlation analysis was performed to determine correlation among PTEs in different soils. The principal component analysis (PCA) using Varimax rotation with Kaiser Normalization was used to examine the order of major PTEs in the soil and how they changed with change in soil type using loading plot. All statistical analyses were performed using the Past (version 4.02) software programme.

3. Results and discussion

3.1. Analysis of potentially toxic elements in different soils and their comparison with soil guidelines

The comparative analysis of PTEs (Fe, Cu, Mn, Zn, Ni, Cd, Cr, Co, Pb and As) in industrial, non-agricultural and agricultural soils were represented in Table 1. PTE contents were considerably lowest in agricultural soils, average in non-agricultural soils and highest in industrial soils (Table 1). Gowd et al. (2010) compared the possible harmful elements of agricultural soils to background soil in India and found that 42.5 %, 47.5 %, 82.5 %, 97.5 %, and 100 % sample sites exceeded their concentrations for Co, Ni, Mn, Zn, and Pb, respectively. Similarly, when PTEs in non-agricultural soils were compared to Indian background levels, 100 % of the sampling sites exceeded baseline values for Pb, Mn, Zn, Co, As and Ni (Gowd et al., 2010). In comparison to Indian baseline values, PTEs in industrial soils exceeded 60 % for Cd, 80 % for Cu and 100 % for Co, Pb, As, Mn, Ni and Zn (Gowd et al., 2010). The percentage increase observed from agricultural to non-agricultural soils for different PTEs were 63.8% for Cu, 13.5% for Cr, 3.19% for Fe, 49.8% for Pb, 25.3% for Mn, 79.6% for Ni, 32% for Cd, 35.8% for Co, whereas 2.02 and 2.99 times increase was found for Zn and As respectively. The percentage change from non-agricultural to industrial soils for different PTEs were 9.2% for Cr, 18.4% for Co, 35.8% for Pb, 89% for Zn, 21.9% for Mn, 2.03% for Fe, 68.2% Cu, 30.4% for Cd and 43.4% for As, and 4.21 times increase in Ni. From agricultural to industrial soils the percentage change were 5.2% for Fe, 52.8% for Mn, 24% for Cr, 60.8% for Co and 72.2% for Cd, while 3.8, 2.7, 2.03, 7.5 and 4.2 times increase were found for Zn, Cu, Pb, Ni and As respectively.

3.2. Principal component analysis of potentially toxic elements in soils

The order of PTEs was determined using principal component analysis (PCA) on the PTEs data. The four components of PCA with eigen values were found above one, accounts 72.9% of the variation. The loadings values for the PCA are tabulated in Table 2. The Liu et al. (2003) method was used to categorise factor loadings as strong, moderate, or weak based on absolute loading values more than 0.75, 0.75–0.50, or 0.50–0.30, respectively. The PC1 contributed 32.22% variance which was due to strong positive loadings of Co, Cd and moderate positive loadings of Ni and As. The PC2 resulted into 15.46% of total variance which was due to moderate positive loading of Mn. In PC3, moderate positive loading of Zn contributes 13.31% of total variance while in PC4, moderate negative loading of Cu and moderate positive loading of Pb resulted into 11.99% of variance.

Table 1. Analysis of potentially toxic elements (PTEs) in soils collected from study area.

PTEs (mg/kg)	Agricultural	Non-Agricultural	Industrial
Zn	41.8 ± 1.78a	84.9 ± 6.81b	160.5 ± 41.88c
Mn	242.4 ± 6.39a	303.9 ± 2.59b	370.5 ± 14.94c
Cu	31.9 ± 1.84a	52.3 ± 0.21b	88.1 ± 21.42c
Pb	84.4 ± 3.03a	126.6 ± 2.03b	172.1 ± 17.48c
Ni	27.1 ± 1.28a	48.7 ± 2.71b	205.5 ± 49.15c
Co	14.2 ± 0.49a	19.3 ± 0.2b	22.9 ± 0.69c
Cd	2.5 ± 0.08a	3.3 ± 0.04b	4.41 ± 0.25c
As	118.3 ± 15.83a	354.1 ± 9.88b	507.8 ± 26.91c

One way Anova followed by tukey post hoc test was applied to compare the mean difference between each variable at each sampling site. The mean followed by different letters in each row shows significant difference at 5% level of significance.

Table 2. Loading values for different PTEs under each principal component.

PTEs	Principal components			
	PC1	PC2	PC3	PC4
Zn	0.227	-0.164	**0.650****	-0.398
Mn	-0.305	**0.681****	-0.319	0.184
Cu	0.381	0.098	0.186	**-0.655****
Pb	0.223	-0.100	0.562	**0.606****
Ni	**0.656****	-0.048	0.221	0.391
Co	**0.916***	0.030	0.020	-0.160
Cd	**0.907***	0.177	0.108	-0.004
As	**0.572****	0.370	-0.434	-0.059
Eigenvalue	3.22	1.54	1.33	1.19
Variance	32.22	15.46	13.31	11.99
Cumulative variance	33.22	47.6	61	72.9

Extraction method: principal component analysis.
Rotation method: Varimax with Kaiser normalization.
* and ** represents Strong and moderate loadings, respectively and shown in bold letters.

Figure 2 shows the loading plot for different loading values of principal components which demonstrated that industrial, non-agricultural and agricultural soils were vastly different from one another in terms of PTEs content. The analysis of PTEs in industrial, non-agricultural and agricultural soils also revealed that all the PTEs were significantly different in three soils with maximum content of the same at industrial soils. Industries are responsible for most of the heavy metal pollution in the present study sites. The area is dominated by bicycle, woollen and hosiery industries. Further, the town is known for preparation of machine tools, dying work and electroplating (Setia et al., 2020).

The pearson's correlation was performed on the PTEs data in order to find the inter-associations among the studied parameters at all the sampling sites (Figure 3). From the results of correlation analysis, it was reported that all PTEs were positively correlated with each other at all the sampling sites. This positive relationship of PTEs with each other in all sampling sites signifying that PTEs have same source in all soil types. The positive correlation among PTEs is accredited to similar type of sources accountable for PTEs concentration and anthropogenic activities such as industrial activities like spring industry, iron rods factory, iron industry, cycle industry etc., and agricultural practices like usage of pesticides, fertilizers and herbicides are responsible for PTEs concentration (Kumar et al., 2019c; Keshavarzi and Kumar 2019).

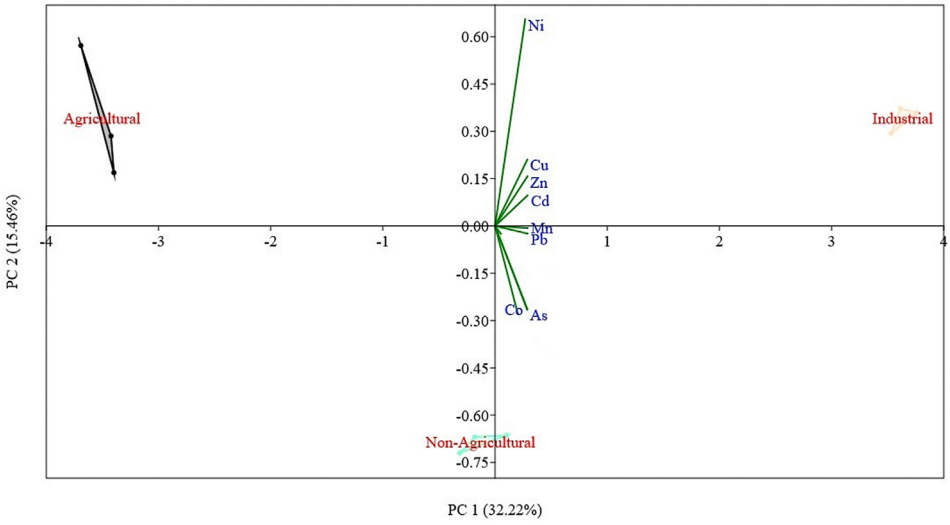

Figure 2. Loading plot of PCA showing different soil variables.

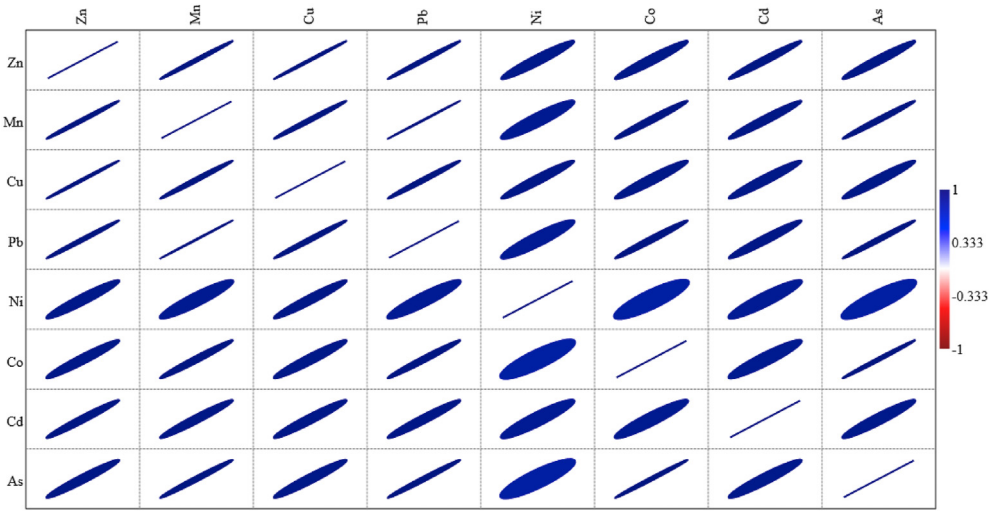

Figure 3. Pearson's correlation analysis of potentially toxic elements. All blue circle indicates the positive correlation. Moreover, small and light color circle represents less correlation, whereas large and dark color circle represents high correlation.

3.3. Appraisal of pollution level of potentially toxic elements in soils

The contamination factor (CF), enrichment factor (EF), and geo-accumulation index (Igeo) were measured to monitor the PTEs level and their pollution in diverse soils (Figure 4). The scores recommended by Hakanson (1980) were used to compare the contamination of each metal in respective soil. The CF in the agricultural soils was in the order of As > Cd > Pb > Ni > Co > Cu > Zn > Mn. Thus, As and Cd were found to be highly contaminated in agricultural soils, whereas Pb was shown to be significantly contaminated. Similarly, the CF values of As and Cd were highest in non-agricultural soils, followed by Co, Pb, Cu, Mn, Ni and Zn. Thus, like agricultural soils, non-agricultural soils have also revealed high contamination with Cd and As, while significant contamination of Pb. The Mn, Ni, Zn, Co and Cu exhibited little contamination in both non-agricultural and agricultural soils. In industrial soils, the CF value for As was maximum trailed by Cd, Ni, Pb, Cu, Co, Zn and Mn. The industrial soils exhibit huge contamination with Ni, Cd, As, and Pb, whereas considerable to modest contamination with Cu, Co, Zn and Mn. The grades recommended by Sutherland (2000) were used to categorise the level of pollution based on EF among industrial, non-agricultural and agricultural soils. The EF results of agricultural soils indicated extreme enrichment of Cd, Ni, As and Pb; high enrichment of Co and Cu, while substantial enrichment of Mn and Zn. Similarly, non-agricultural soils showed extreme enrichment of As, Cd, Co, Pb and Cu; high enrichment of Ni and Zn, while substantial enrichment of Mn. Industrial soils had the highest enrichment of all the examined PTEs, with As, Ni, Cd, Cu, Zn, Pb and Co showed extreme enrichment and Mn showing significant enrichment. On the basis of Igeo, the grades of Muller (1981) were used to classify the contamination level. According to the Igeo data, agricultural soil was very polluted with As, Ni, Cu, Cd, Co, Zn, Cu and Pb; while Mn was significantly polluted. Industrial and non-agricultural soils, on the other hand, were found to have the highest levels of contamination across all PTEs investigated.

Pollution index (PI) and modified pollution index (MPI) was also computed for different PTEs to find their pollution load (Figure 5 A and B). Nemerow (1991) proposed PI and MPI grades on the basis of the fact that in agricultural soils Ni, Pb, Zn, As and Cd revealed serious contamination, Co and Cu moderate contamination, while Mn exhibited minor pollution. On the other hand, As, Pb and Cd demonstrated serious pollution in non-agricultural soils, Cu revealed severely; Co and Ni moderately while Mn and Zn exhibited mild pollution. In the examined area, PI values of As, Pb, Cd, Ni and Cu in industrial soils indicated severe contamination, Zn and Co indicated moderate pollution, while Mn indicated little contamination. The MPI values for all PTEs investigated in industrial, non-agricultural and agricultural soils were greater than 10, indicating that these PTEs were severely polluted in the area.

3.4. Ecological risk appraisal of potentially toxic elements in soils

For various PTEs in soils, the ecological risks were classified as potential ecological risk (RI) and modified potential ecological risk (MRI) (Figure 6). The potential ecological risk (Er) value of Cd in agricultural soils indicated a high danger of Cd in the study area's agricultural soils, although high risk was exhibited by As, while Mn, Ni, Zn, Pb, Cu and Co showed a less risk. Similarly, non-agricultural soils were found to have a very high risk of Cd, a high risk of As, and a low risk of Ni, Mn, Co, Pb, Cu and Zn. Similarly, As and Cd indicated very high risk in industrial soils, while Ni showed moderate risk and Co, Mn, Pb, Cu and Zn exhibited less risk in the studied region. On the basis of the grades employed by Kumar et al. (2018) for grading of ecological risk, Zn, Mn and Co indicated low ecological threat in all the soil samples, while Cu demonstrated a less to moderate ecological danger in the area. The modified potential ecological risk (mEr) of Cd, Pb and As in agricultural soils was extremely high; Co, Ni and Cu were high; while Mn and Zn were low. Similarly, in non-agricultural soils, Pb, As, Cu and Cd presented a great risk, whereas Mn and Zn presented a less risk and Co and Ni presented a high risk in the studied region. Industrial soils were reported with very high risk of Ni, Cd, Pb and As; low risk of Mn and Zn, while high risk of Co and Cu. The findings of the ecological risk assessment suggested that Cd is the most important pollutant in the area. Our findings on ecological risk

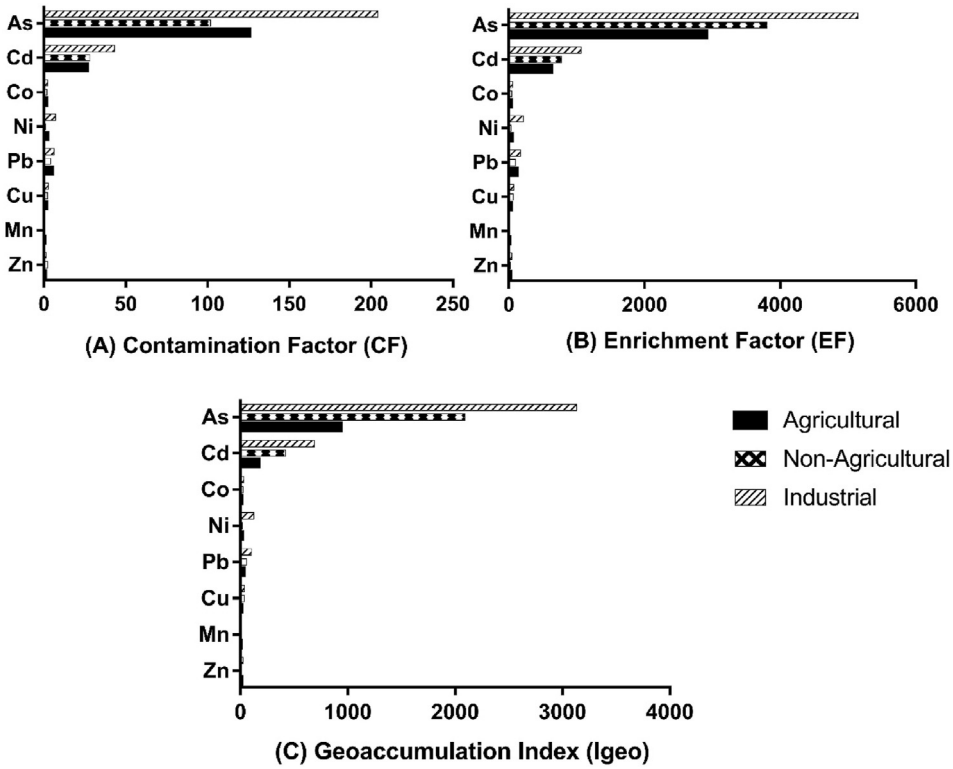

Figure 4. CF, EF and Igeo indices of potentially toxic elements.

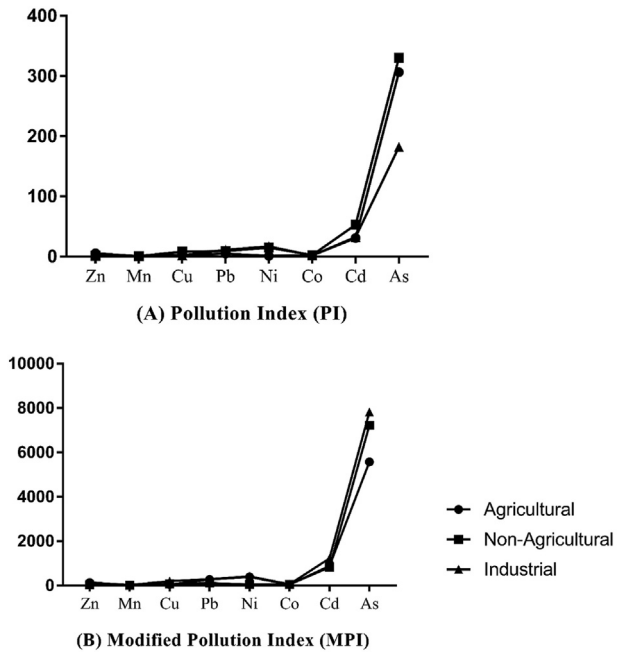

Figure 5. Pollution index (A) and modified pollution index (B) of different potentially toxic elements in soils.

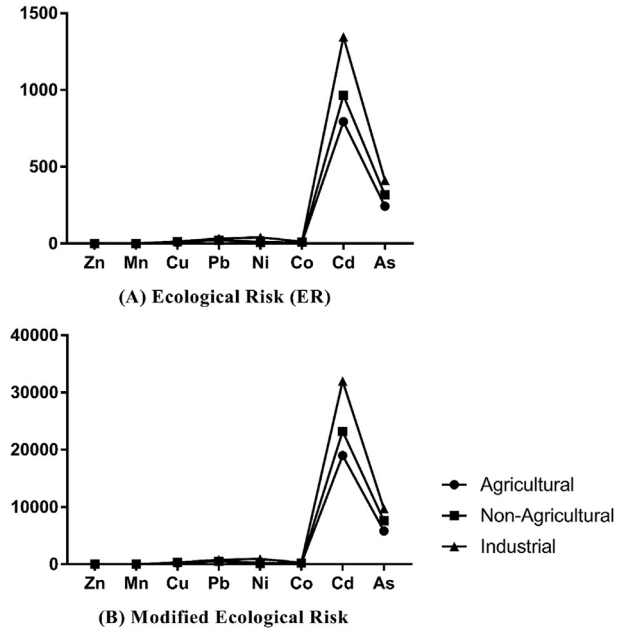

Figure 6. Ecological risk assessment of potentially toxic elements in soils collected from study area.

assessment are consistent with those of Kumar et al. (2018), Dogra et al. (2020), and Pandit et al. (2020). They also stated in their investigations that Cd is the primary pollutant which is responsible for soil pollution. The following is the pattern followed by different soils based on RI and MRI values: Non-agricultural soil > industrial soil > agricultural soil.

4. Conclusions

According to the findings of the current study, industrial soils had the highest concentrations of potentially harmful components compared to non-agricultural and agricultural soils. The comparison between industrial soils and background levels of Indian soil resulted that the value of soil samples exceeded their values for Mn, Co, Pb, As, Zn, Ni and while 80 % and 60% exceeded for Cu and Cd respectively. In comparison to their limits in agricultural soils, 42.5 %, 47.5 %, 82.5 %, 97.5 % and 100 %, and of the sampling sites exceeded their Co, Ni, Mn, Zn and Pb concentrations. In all non-agricultural sites, the values of As, Mn, Ni, Pb, Zn and Co exceeded in contrast with their limits. Pearson's correlation analysis indicated that PTEs have same source of origin and mainly industrial activities in the area contribute PTEs level in the soil. The results of RI, MRI, CF, EF, Igeo, PI and MPI showed that Cd and As are the main pollutants in the soils of study area.

Declarations

Author contribution statement

Falwinder Verma: Performed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Sharanpreet Singh: Performed the experiments; Wrote the paper.

Salwinder Singh Dhaliwal: Contributed reagents, materials, analysis tools or data.

Vinod Kumar: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Rakesh Kumar: Analyzed and interpreted the data.

Jaswinder Singh, Chander Parkash: Conceived and designed the experiments.

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Data availability statement

Data will be made available on request.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

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