Assessment of trace metal contamination of soil in a landfill vicinity: A southern Africa case study

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\textbf{ABSTRACT}

Contamination of soils by trace elements is a worldwide concern and has negative effects on environmental sustainability. Geochemical assessment of soils using appropriate indicators and pollution indices has received much attention in recent years in efforts to rehabilitate this resource. This study quantified pollution of soils by trace elements at the Roundhill landfill, South Africa using indices and multivariate statistics. Soils were collected and assayed for trace metals using x-ray fluorescence. Pollution indices classified soil contamination levels while multivariate statistical analysis was conducted using principal component and cluster analyses. Findings showed that concentrations of all elements decreased with increasing distance from the landfill. Low to extremely high pollution was evident in all soils and Cr had the highest values compared to other elements. Negative correlation and weak clustering of Cr and Cd was associated with different wastes disposed at the landfill. Reported pollution in soils was associated with the influence of landfill leachate in the investigated area.

\begin{thebibliography}{1}

\bibitem{1} Contamination of soils by trace elements is a worldwide concern and has negative effects on environmental sustainability. Geochemical assessment of soils using appropriate indicators and pollution indices has received much attention in recent years in efforts to rehabilitate this resource. This study quantified pollution of soils by trace elements at the Roundhill landfill, South Africa using indices and multivariate statistics. Soils were collected and assayed for trace metals using x-ray fluorescence. Pollution indices classified soil contamination levels while multivariate statistical analysis was conducted using principal component and cluster analyses. Findings showed that concentrations of all elements decreased with increasing distance from the landfill. Low to extremely high pollution was evident in all soils and Cr had the highest values compared to other elements. Negative correlation and weak clustering of Cr and Cd was associated with different wastes disposed at the landfill. Reported pollution in soils was associated with the influence of landfill leachate in the investigated area.

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1. Introduction

Soils contain trace metals that are important nutrient components, but can be toxic at elevated levels. These elements are derivatives of lithologic transformations and anthropogenic pollution. Concerns on contamination of soils by trace elements are on the rise although the mechanisms of assessing the pollution levels precisely are limited.\textsuperscript{1,2} These concerns are justified by the complex nature of soils, which enhances adsorption of disposed pollutants resulting to adverse environmental effects.\textsuperscript{3} Soils in addition act as medium to transmit pollutants to water resources, plants and atmosphere through diffusive and dispersive movements, which result to bioaccumulation, phytoaccumulation and geoaccumulation.\textsuperscript{4}

In sub-Saharan Africa, trace metal pollution in soils is a common phenomenon in vicinities of hotspots such as mines, landfills, urban and industrial zones.\textsuperscript{5} In South Africa, soil pollution from
landfill leachate is widespread since many of the country’s cities generate waste equivalent to that of developed countries, most of which is disposed. However, more than 90% of the waste is landfilled unscientifically and becomes a pollution threat to soils.\textsuperscript{6} Urbanization and industrialization have worsened the state, as solid waste generation exceeds the management capacity.\textsuperscript{7} The use of pollution indices to assess contamination levels is a solution to land clean-up and pollution control.\textsuperscript{8} These indices are suitable geochemical indicators of extents, hotspots and sources of pollution. Additionally, they estimate environmental and ecological risks associated with pollution and distinguish lithologic sources from human-propagated pollution.\textsuperscript{9-10} Single indices such as geaccumulation index ($I_{geo}$), contamination factor (CF), pollution degree (PD) and pollution load index (PLI) are examples of such indices.\textsuperscript{11} They classify soils based on predetermined metal background levels and provide information on its sustainability.\textsuperscript{12} Combined with multivariate studies, pollution indices explain trace metal occurrence, processing and multidimensionality.\textsuperscript{13-14} This study aimed at analysing the contamination by trace metals in soils of Roundhill landfill vicinity in Southern Africa using pollution indices and multivariate statistics.

2. Results and Discussion

2.1 Trace Metal Content of soils

The descriptive statistics of assayed trace elements of various sampling sites are presented in Table 1. The means of all trace elements exceeded the background levels (Table 6) with exception of Co and Zn. This observation suggested that sampled soils were contaminated. Of all the assayed metals, the mean concentration of Cr was the highest compared to Pb that was the lowest. High Cr levels even in the reference site could be associated to lithologic contribution of the element. A geologic survey conducted in the area confirmed, that its rocks are ultra-mafic and have high levels of Cr.\textsuperscript{15} The values of standard deviation ($SD$) ranged from 34 to 688 mg kg\textsuperscript{-1}, which depicts great dispersion of concentrations at various sampling sites. The values of the coefficient of variation (CV) confirmed the great spread of trace element concentrations. Lower values of standard errors ($SE$) in Cd, Cu, Pb and Zn showed a high reliability of their means compared to other trace elements.

| Site\Parameter \ Site| Parameter | Cd  | Co  | Cr  | Cu  | Ni  | V   | Pb  | Zn  |
|-------------------|-----------|-----|-----|-----|-----|-----|-----|-----|-----|
| L0                |           | 154 | 365 | 1039| 293 | 500 | 600 | 110 | 246 |
| L50               |           | 102 | 378 | 955 | 240 | 345 | 502 | 49.2| 136 |
| L100              |           | 76  | 318 | 957 | 130 | 253 | 465 | 18.9| 94  |
| L250              |           | 43  | 267 | 873 | 192 | 286 | 361 | 6.5 | 133 |
| L500              |           | 12  | 544 | 1178| 170 | 468 | 615 | 71  | 94  |
| West1             |           | 111 | 209 | 1365| 81  | 281 | 308 | 48.4| 124 |
| West2             |           | 91  | 75  | 2997| 192 | 264 | 293 | 64.4| 120 |
| East1             |           | 13  | 439 | 905 | 202 | 333 | 272 | 44.2| 132 |
| Ref.              |           | 3   | 49  | 757 | 162 | 225 | 100 | 2.5 | 94  |
| Min               |           | 3   | 49  | 757 | 81  | 225 | 100 | 2.5 | 94  |
| Max               |           | 154 | 544 | 2997| 293 | 500 | 615 | 110 | 246 |
| Mean (mg kg\textsuperscript{-1}) |       | 67  | 294 | 1225| 185 | 328 | 391 | 46  | 130 |
| SD                |           | 52  | 163 | 688 | 61  | 96  | 169 | 34  | 47  |
| SE                |           | 17  | 54  | 229 | 20  | 32  | 56  | 11  | 16  |
| CV (%)            |           | 78  | 55  | 56  | 33  | 29  | 43  | 74  | 36  |
2.2 Values of Pollution Indices and Contamination Classes

Pollution indices calculated from trace metal concentrations of sampling sites (Table 1) and classification of soils at these sites are presented in Table 2. Contamination factor (CF), levels of Cr at all sampling sites were elevated compared to other trace metals. About 49% of the total calculated CF values revealed very high contamination at the sampling sites by the trace metals. There was no pollution due to Zn and contamination by Co was low in most sampling sites. The CF values of all elements in areas close to the landfill (L0, L50, L100, West 1, and West 2) were higher compared to the other sampling sites. This could arise due to high leachate concentration and its subsequent horizontal migration. In Ariyamangalan landfill of India, CF values of sampling sites decreased with increasing distance from the dumpsite due to the dispersive movement of leachate.16

Table 2. Contamination factor (CF) and geoaccumulation (Igeo) index values of trace elements at sampling sites and classification of soils

| Parameter | Cd | Co | Cr | Cu CF | Ni | V | Pb | Zn | Cd | Co | Cr | Cu | Ni | V | Pb | Zn |
|-----------|----|----|----|-------|----|---|----|----|----|----|----|----|----|----|----|----|
| L0        | 20.5 | 1.2 | 159.9 | 18.3 | 5.5 | 4.0 | 5.5 | 1.0 | 4.1 | 0.2 | 32.0 | 3.7 | 1.1 | 0.8 | 1.1 | 0.2 |
| L50       | 13.6 | 1.3 | 146.9 | 15.0 | 3.8 | 3.4 | 2.5 | 0.6 | 2.7 | 0.3 | 29.4 | 3.0 | 0.8 | 0.7 | 0.5 | 0.1 |
| L100      | 10.1 | 1.1 | 147.2 | 8.1  | 2.8 | 3.1 | 1.0 | 0.4 | 2.0 | 0.2 | 29.5 | 1.6 | 0.6 | 0.6 | 0.2 | 0.1 |
| L250      | 5.7  | 0.9 | 134.3 | 12.0 | 3.1 | 2.4 | 0.3 | 0.6 | 1.2 | 0.2 | 26.9 | 2.4 | 0.6 | 0.5 | 0.1 | 0.1 |
| L500      | 1.6  | 1.8 | 181.2 | 10.6 | 5.1 | 4.1 | 3.6 | 0.4 | 0.3 | 0.4 | 36.3 | 2.1 | 1.0 | 0.8 | 0.7 | 0.1 |
| West1     | 14.8 | 0.7 | 210.0 | 5.1  | 3.1 | 2.1 | 2.4 | 0.5 | 3.0 | 0.1 | 42.0 | 1.0 | 0.6 | 0.4 | 0.5 | 0.1 |
| West2     | 12.1 | 0.3 | 461.1 | 12.0 | 2.9 | 2.0 | 3.2 | 0.5 | 2.4 | 0.1 | 92.2 | 2.4 | 0.6 | 0.4 | 0.6 | 0.1 |
| East1     | 1.7  | 1.5 | 139.2 | 12.6 | 3.7 | 1.8 | 2.2 | 0.6 | 0.4 | 0.3 | 27.9 | 2.5 | 0.7 | 0.4 | 0.4 | 0.1 |
| Ref.      | 0.4  | 0.2 | 116.5 | 10.1 | 2.5 | 0.7 | 0.1 | 0.4 | 0.1 | 0.0 | 23.3 | 2.0 | 0.5 | 0.1 | 0.0 | 0.1 |

Geoaccumulation index (Igeo) values of various trace elements ranged from not-polluted in Zn to extremely contaminated in Cr and were all lower compared to the CF values, since the index has a constant to reduce trace element contribution from lithologic sources. The Igeo values of this study depict the influence of landfill leachate on trace elements concentrations in soils. A similar observation was in a study evaluating trace metals at Tianjin landfill, China.19 Open dumping of solid waste and generation of landfill leachate was associated with high CF and Igeo values in a study evaluating trace metals at Tianjin landfill, China.19

Pollution load index (PLI) and pollution degree (PD) levels of all sampling sites were calculated to assess soil toxicity due to the assayed contaminants and results were as shown in Table 3. The PLI values revealed the presence of pollution in soils from all trace metals with exception of Co and Zn whose levels were <1. Similarly, all elements caused very high pollution degrees in soils with exception of Co and Zn that had moderate and low contamination levels, respectively. A study of soils from a landfill near the Nile Delta, Egypt revealed very high contamination and both PLI and PD values were >1 and > 28, respectively.20

Table 3. Pollution load index (PLI) and pollution degree (PD) values of soils at different depths

| Parameter | Cd | Co | Cr | Cu | Ni | V | Pb | Zn |
|-----------|----|----|----|----|----|---|----|----|
| PLI       | 5.1 | 0.8 | 102.8 | 8.6 | 3.1 | 2.1 | 1.4 | 0.6 |
| PD        | 93.1 | 8.8 | 1696.3 | 103.9 | 32.5 | 23.4 | 20.8 | 4.9 |
2.3 Multivariate Statistics of the Heavy Metals

Inter-elemental relationships of trace elements using Pearson’s correlation coefficient were as shown in Table 4. They were calculated from the metal concentrations shown in Table 1. Co-Ni, Co-V, V-Ni, Ni-Pb and Cu-Zn had strong positive correlation, which could point to the elements having similar waste sources. Electronic, ash, plastic and paper wastes at the landfill site could have contributed to the observed correlation of Cu and Zn. A similar study established these wastes as sources of Cu and Zn from dumpsites.\textsuperscript{21} Treated health wastes, electronics and metal scrap disposed in Roundhill landfill could be common sources of Co, V, Ni and Pb. In Baotou area of China, dumping of electronic and health wastes was attributed to the accumulation of Co, V, Ni and Pb.\textsuperscript{22} Strong positive correlations of Cr, Cu, Ni, Pb and Zn were attributed to similar origin and geochemical affinities in a heavy metal assay of Chinese grassland soils.\textsuperscript{23} Industrial waste disposal in Kayseri region of Turkey was associated to strong positive correlation between Cu-Zn and Co-Ni.\textsuperscript{24}

Chromium (Cr) had a weak or negative correlation with all other elements, suggesting different origin, which could include chemical plants in the area, leather tanning, electroplating and textile wastes disposed in the landfill. Weak negative correlation of Cr with Co, Cu and Zn was attributed to agricultural and industrial sources in a trace element analysis of soils at Mersin Province of Turkey.\textsuperscript{25} Cadmium weakly correlated with other trace elements, a trend that could arise due to different sources of wastes such as pigments and plastics. A similar trend was reported in Brazilian soils, where Cd had weak correlations with Cr, Co, Cu, Fe, Mn and Zn due to different sources of the element.\textsuperscript{26}

Table 4. Pearson’s correlation between trace metal concentrations at different sampling sites

| Variables | Co  | Cr  | Cu  | Ni  | V   | Zn  | Pb  | Cd  |
|-----------|-----|-----|-----|-----|-----|-----|-----|-----|
| Co        | 1   | -0.420 | 0.283 | 0.735 | 0.752 | 0.174 | 0.398 | -0.072 |
| Cr        | -0.420 | 1   | -0.056 | -0.154 | -0.107 | -0.059 | 0.326 | 0.273 |
| Cu        | 0.283 | -0.056 | 1   | 0.601 | 0.409 | 0.737 | 0.529 | 0.299 |
| Ni        | 0.735 | -0.154 | 0.601 | 1   | 0.805 | 0.618 | 0.820 | 0.271 |
| V         | 0.752 | -0.107 | 0.409 | 0.805 | 1   | 0.408 | 0.639 | 0.426 |
| Zn        | 0.174 | -0.059 | 0.737 | 0.618 | 0.408 | 1   | 0.688 | 0.691 |
| Pb        | 0.398 | 0.326 | 0.529 | 0.820 | 0.639 | 0.688 | 1   | 0.591 |
| Cd        | -0.072 | 0.273 | 0.299 | 0.271 | 0.426 | 0.691 | 0.591 | 1   |

Values in bold are different from 0 with a significance level $$\alpha=0.95$$

Results of the transformed data of trace elements after principal component analysis (PCA) are presented in Fig. 1. The transformation resulted to eight factor loadings (F1-F8) with Eigen values of 4.1, 1.8, 1.0, 0.6, 0.3, 0.1, 0.05 and 0.005 contributing to 52, 22, 12, 8, 4, 1, 0.6 and 0.06 % of total variability in respective order. However, the study focused on the first two factor loadings that contributed to approximately 75% of total variability. The correlation of trace elements showed close linkages between Cu-Zn, Ni-V, Cu-Pb and Pb-Zn based on their narrow angles. Close elemental linkages represented with narrow angles could be because of a common pollution source as reported in a similar heavy metal correlation analysis in soils of Islamabad area of Pakistan.\textsuperscript{27} Cadmium-Co and Co-Zn axes formed right angles and were unrelated while Cr and Cd were unrelated with all other elements. Cadmium, Co, Cu, Ni, Pb, V and Zn were related to the first factor loading, while the second factor loading best represented Cr correlation. These observed weak positive and strong negative associations of trace elements were attributable to different pollution origins as established in a trace metal analysis of agricultural soils in Peloponnese, (Greece) using a similar approach.\textsuperscript{12}
These results were consistent with Pearson’s correlation. Additionally, they agreed with cluster analysis results (Fig. 2a) that showed four groups of trace elements; one with Cd, another Cr, another with Cu and Zn and a last one with Co, Ni, Pb and V. The analysed trace elements in this study had different relationships unlike a trace metal assessment at Khulna landfill (Bangladesh) vicinity, where all elements had close geochemical affinities.28 A cluster analysis of sampling sites is shown in Fig. 2b. L0 and West 2 sampling sites were unique from the others. This could be consistent with results of Table 4, whereby, L0 had high levels of Cd, Cu, Pb and Zn while the West 2 had the highest concentration of Cr. The other sampling sites had relatively the same trace metal concentration trends hence they clustered together.

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**Fig. 1.** Biplot showing the relationships between active variables and active observations

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**Fig. 2.** Dendrograms showing agglomerate hierarchical clustering results of a) trace elements and b) sampling sites
3. Conclusions

In this study, pollution indices were calculated using assayed concentrations of trace metals and their background levels to classify soils based on their contamination levels. Multivariate statistical analyses were used to correlate observed soil pollution to different solid wastes of Roundhill landfill and resultant leachate. In conclusion, leachate from the landfill had great influence on pollution of investigated soils.

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4. Materials and Methods

4.1 Study Area

Roundhill landfill is located in Buffalo city municipality of South Africa’s Eastern Cape Province (latitude 32°53’13.66”S and longitude 27°37’26.20”E), (Fig. 3). The site covers 56 hectares, has a 3.5° slope towards the north-and-south-east and was previously a natural grassland for grazing. The landfill receives approximately 500 tonnes of general (business, domestic, building and demolition wastes) and treated healthcare wastes daily. At its commissioning in 2006, the facility was covered with a geomembrane liner that has undergone extensive damage and become inadequate due to waste increments. Existing leachate management system was insufficient characterized by leakages, runoffs and no connection to a wastewater treatment plant although the area has positive water balance. In response to these inadequacies, a temporary landfill cell consisting of a protection layer, a compacted clay liner and leachate collection system have been installed and rehabilitation is underway.

Area climate is temperate and warm with a mean temperature of 21°C, evaporation and rainfall levels ranging from 160-170 mm/month and 400-1000 mm/year, respectively. Area soils have high clayey content, which was one of the factors that made the location suitable for landfill construction. These soils accumulate trace elements due to their strong adsorptive properties. Soils in the area have low
organic matter content due to high temperatures that enhanced decomposition. The study area has a minor aquifer system with a groundwater depth greater than 40 m and a low groundwater potential, as the yields of boreholes are below 1 L/s. Low vertical permeability and lateral movement of groundwater is associated to the clayey nature of area soils.

4.2 Soil Sampling and Analysis

Soils were collected from 8 sampling sites namely; L0, L50, L100, L250, L500, West 1, West 2 and East 1 and a reference site (Ref.) two kilometres from the landfill facility (Fig. 3). A convenience sampling approach, whereby only sampling points, which were accessible to the researcher was used due to the harsh terrain of the landfill vicinity that was bushy, rocky and steep. This method is suitable in studies, where locating the population is difficult and the geographic distribution of research elements is out of the researcher’s proximity. At each sampling site, soils were collected at three depths; 30, 60 and 100 cm to represent topsoil, subsoil 1 and subsoil 2, respectively. A total of twenty-seven samples were collected and transferred to polyethene bags, sealed and labelled for analysis. Prior to analysis, they were oven-dried at 105°C for 12 hours to minimize systematic bias and physical interferences on the x-ray fluorescence (XRF) signal, which result from the presence of soil moisture.

The dry soil samples were ground in an agate mortar and pestle and sieved with a 75-micron sieve to reduce matrix effects during analysis. Loss on Ignition (LOI) analysis was done by burning about 30 g of each soil sample in crucibles at 950°C for 2 hours to remove their volatile substances. Soils were further pulverized to get a representative sample before their manual pressing using a hydraulic press. Concentrations of trace elements were determined using a sequential XRF spectrometer (PW 2404, Phillips, Holand). Equipment calibration was conducted using reference materials of predetermined intensities. Each soil sample was prepared in triplicates, placed on sterile carriers and mounted in the equipment cassette for analysis. Assayed trace metals included cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), vanadium (V) and zinc (Zn).

4.3 Chemical Characteristics of Leachate

Leachate was suspected to be the pollutant source in the vicinity of Roundhill landfill. A sample was collected from an open pond next to the landfill and analysed for chemical qualities. The results were as shown in Table 5.

| Parameter                  | Unit         | value  |
|----------------------------|--------------|--------|
| pH                         | -            | 8.4*   |
| Electrical conductivity    | mS m⁻¹       | 1661   |
| Total dissolved solids     | mg/L         | 8990   |
| Chemical oxygen demand     |              | 2600   |
| Biological oxygen demand   |              | 1443   |
| Sodium                     |              | 2860   |
| Magnesium                  |              | 569    |
| Calcium                    |              | 1258   |
| Potassium                  |              | 450    |
| Ammonium                   |              | 11.26  |
| Nitrates                   | mg/L         | 160    |
| Chloride                   |              | 4.29   |
| Cd                         |              | 0.15   |
| Co                         |              | 0.25   |
| Cr                         |              | 8.77   |
| Cu                         |              | 0.75   |
| Ni                         |              | 0.46   |
| V                          |              | 0.19   |
| Pb                         |              | 5.9    |
| Zn                         |              | 48.9   |
4.4 Pollution Indices

Four indices were used to evaluate trace metal contamination in soils. The contamination factor \(\text{CF}^\text{35}\) was calculated as a ratio between a particular metal concentration and the background levels that are shown in Table 6 and provided by South Africa’s Department of Environmental Affairs\textsuperscript{36}, using Eq. (1).

\[
\text{CF} = \frac{C_{Hm}}{C_{\text{normal}}}
\]  

where, \(\text{CF}\) is the contamination factor, \(C_{Hm}\) is the mean concentration of a specific heavy metals and \(C_{\text{normal}}\) represented background values by DEA.\textsuperscript{36}

| Trace metal | Cd | Co | Cr | Cu | Ni | V | Pb | Zn |
|-------------|----|----|----|----|----|---|----|----|
| Background values (mg kg\(^{-1}\)) | 7.5 | 300 | 6.5 | 16 | 91 | 150 | 20 | 240 |

Table 7. Criteria for soil classification using pollution indices

| Index Method | Values | Class | References |
|--------------|--------|-------|------------|
| \(\text{CF}\) | <1     | Low contamination | \textsuperscript{35} |
|              | >1-3   | Moderate contamination |
|              | >3-6   | Considerably high contamination |
|              | >6     | Very high contamination |
| \(I_{\text{geo}}\) | <0     | Not polluted | \textsuperscript{37} |
|              | 0-1    | Not polluted-moderately polluted |
|              | >1-2   | Moderately polluted |
|              | >2-3   | Moderately-strongly polluted |
|              | >3-4   | Strongly polluted |
|              | >4-5   | Strongly-extremely polluted |
|              | >5     | Extremely polluted |
| \(PLI\)     | <1     | Not polluted | \textsuperscript{38} |
|              | >1     | Polluted |
| \(PD\)      | <7     | Low contamination | \textsuperscript{20} |
|              | \(7 \leq PD \leq 14\) | Moderate pollution |
|              | \(14 \leq PD < 28\) | Considerably high pollution |
|              | \(PD \geq 28\) | Very high pollution |

Geoaccumulation index \((I_{\text{geo}})\) was used to evaluate trace metals’ contamination due to anthropogenic changes by applying a constant to rectify their lithologic sources\textsuperscript{37} and was calculated as shown in Eq. (2).

\[
I_{\text{geo}} = \log_2 \frac{C_{Hm}}{1.5 \times C_{\text{normal}}}.
\]  

where;

\(I_{\text{geo}}\) is the geoaccumulation index and 1.5 is a natural constant.

Pollution load index \((PLI)\) was quantified using Eq. (3):

\[
PLI = \frac{(CF_1 \times CF_2 \times CF_3 \ldots CF_n)^{3}}{n}
\]  

\(3\)
where;

PLI is the pollution load index and $n$ represented the number of assayed trace metals

These three single indices calculated from individual concentrations of metals in soils have been used to classify soils and sediments based on their pollution extent.\(^{10-11,23,38}\)

Pollution degree (PD), an integrated contamination index was calculated as a sum of contamination factors of individual trace metals.\(^{35,38}\)

Soils were classified using these pollution indices as outlined in Table 7.

4.5 Statistical Analysis

Descriptive statistics: mean, standard error (SE), standard deviation (SD), minimum, maximum and coefficient of variation (CV) described trace metal content in the sampled soils. Pearson’s correlation coefficient, which is a measure of association strength between two variables interrelated pairs of trace elements.\(^{40}\) The method involved assessing the linearity between any two trace elements and showed a probability of common origin of these pollutants. Relationships and patterns of trace elements were assessed using two multivariate statistical approaches; principal component analysis (PCA) and cluster analysis (CA).\(^{17}\) The latter categorized metals to classes based on their correlations while the former, transformed original values of trace metal concentrations to new variables known as principal components and factor loadings. Cluster analysis was done using Euclidian distances and Ward’s method as the criteria to form clusters while PCA was displayed as factor loadings and Eigen values using a biplot.\(^{41}\) These two approaches are widely used to establish relationships in trace element contamination of soils.\(^{18,25}\) Data analysis was conducted using XLSTAT software at a $P<0.05$ significance level.

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