Sources and pollution assessment of trace elements in soils of some selected mining areas of southwestern Ghana

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ABSTRACT

This study presents a detailed assessment of the soil quality of the Prestea-Huni Valley and Wassa areas which host a significant portion of Ghana's mining industries. A total of 300 soil samples were collected across the districts. Zn (71%), Ni (54%), Mn (5%), Fe (46%), and Cr (50%) exceeded their respective guidelines. Similarly, 50%, 100%, 43%, and 98% of the soil samples were beyond acceptable limits for Co, Cu, As, and Ba respectively. Soils within the study areas had elevated concentrations of V, Cr, As, Ag, and Pb whereas Mn, Cu, Ni, Zn, Sr, and Co were in bearable concentrations. High levels of As and Pb could be attributed to the long-practiced mining activities and the application of inorganic fertilizers. Disparities were shown in the computed pollution indices due to various factors that affect their importance. Pollution indices may not be readily comparable. The factor analysis showed significant loadings of Ag, Ba, Cr, Cu, Fe, Ni, Pb, V, and Zn as they showed higher signals of the data and predominantly impacted the quality and variability of the soils. The Friedman rank-sum test showed significance: $\chi^2(4) = 958.66$, $p < .001$ for As, Pb, Zn, Cu, and Cr, $\chi^2(4) = 1046.73$, $p < .001$ for Ni, Mn, Fe, Co, and Ba, and $\chi^2(2) = 448.62$, $p < .001$ for V, Sr and Ag using an alpha value of 0.05. Elemental variations in the soils indicate that the factors influencing the accumulation of heavy metal(loid)s were by a range of factors.

1. Introduction

Mining is a major activity that affects the chemical and physical characteristics of soil resulting from the disposal of mining waste including tailings and polluted wastewater into the natural environment (Azevedo-Silva et al., 2016). To address the global challenge of soil pollution and the associated ecological and public health implications, Reyes et al. (2019) indicated that mapping tools and geostatistical computations have been adopted in the identification and differentiation of the origin, patterns, distributions, concentrations and possible impacts of elements/heavy metals with anthropogenic and geo-natural provenances for proper assessment.

Ghana is endowed with large gold deposits particularly to the southwestern part of the country; where the Wassa and Prestea-Huni Valley districts are located. This area constitutes a significant proportion of the active mines of Ghana. One of the predominant industrial activities that contribute to metal pollution in Ghana is wastes and leachate from mining

activities. Mining and processing of the ore have contributed immensely to environmental degradation and pollution in the area. The fine sands and silts in the wastes are dispersed into the surrounding environments by surface runoff and by wind-suspended particles (Bempah and Ewusi, 2016; Dang et al., 2019). The impacts of mining activities have been well-established. For instance, in a study by Nguyen et al. (2021) in eight types of mining sites in Vietnam, Cu, Cd, Zn, As, Hg and Pb levels reached 120.46, 2.91, 71.70, 8.87, 6.69, and 21.70 (mg/kg) were reported. Recently, Mensah et al. (2015), Petelka et al. (2019), Amuah et al. (2021), and Kazapoe et al. (2021a,b) have reported above-threshold concentrations of heavy metals and metalloids in the soils of some gold mining areas in Ghana. The ingestion and accumulation of these elements may pose debilitating impacts on public health through oral and dermal routes and may also affect ecological systems. These negative implications make monitoring and assessment of soils in the study areas important to safeguard, protect, and manage public health and environmental resources from the deleterious effects of mining activities.

Even though recognized indices such as the single pollution index, geo-accumulation index, and enrichment factors have been widely adopted in the quantification of elemental contaminations in environmental mediums, these indices are not scale-invariant since modifications of the units for measurement alter the results of the analysis (Petrik et al., 2018). Recent studies conducted within mining areas in Ghana including Zango et al. (2013), Bempah and Ewusi (2016), and Darko et al. (2019) employed degree of contamination, enrichment factors, geo-accumulation index, pollution load index, and contamination factor. However, in this study, other indices; modified contamination degree (mCd), potential contamination index, and factor analysis coupled with widely used indices were used to determine the controls in elemental quality and the contractional availability in the soils. The study is essential because recently, there has been an accelerated rate of mining in Ghana using more sophisticated mining machinery which could pose more deleterious health and environmental implications. Though vanadium and strontium pose adverse health complications including nausea, diarrhea, and impair the growth of bones, earlier studies conducted did not consider these elements. Also, no categorical study using modified contamination degree, potential contamination index potential ecological risk, the Friedman rank-sum test and k-means cluster analysis has been conducted in the areas. Therefore, this study forms a foundational investigation on the soil chemistry, the potential sources, levels, and the distribution of heavy metal(loid)s and PTEs in the Prestea-Huni Valley and Wassa areas of southwestern Ghana for source control and remediation processes to maintain environmental quality and to protect public health.

2. Materials and methods

2.1. Description of the study areas

The Prestea-Huni Valley and the Wassa East, Central, and West districts which fall within southwestern Ghana (Figs. 1 and 2) house a majority of Ghana's mining activities (Ghana Chamber of Mines, 2015). These areas experience bimodal rainfall with maximum temperatures reaching 29 °C (Ghana Statistical Service (GSS), 2014). These conditions make them some of the wettest and agriculturally viable districts in Ghana. The geology is of the Prestea-Huni Valley is characterized by Birimian and Tarkwaian gold-bearing rock types. It is fragmented as litho-structural assemblies that are fault-bounded and dipping steeply westward (Kesse, 1985). Quansah and Amankwah (2011) have indicated that the area is naturally composed of arsenic and sulfur in the Birimian and chlorites, sericites, quartz, chloritoids, limonites, and calcites in the Tarkwaian. These rock types of geological formations are related to hydrothermal veins and quartz, which contain high concentrations of sulfide and gold formations. However, the findings of Dzigbodi-Adjimah (1993) reveal that the Birimian rocks in Ghana are embedded with both essential and toxic elements.

2.2. Soil sampling and soil preparation procedures

Using a soil auger, 300 soil samples at a depth of 0–20 cm were taken from both non-mining and mining areas in the Prestea-Huni Valley and Wassa areas. This study considered mining and non-mining communities within the major mining zone (Fig. 1) which was divided into ten grids using ArcGIS 9.3ⓒ. From each grid, 300 soil samples were randomly collected. Sampling and handling procedures were carried out following the USEPA (2004) guidelines and protocols. The samples were contained in high-density polyethylenes which were preconditioned under washing with HNO_3 4 mol/L and ultra-pure water and dried in the sun. The soil samples were also air-dried and sieved through a 2-mm nylon sieve to remove large debris. Cross and gross contaminations were prevented by sealing the samples in polythene bags. The geographical locations of the sampling points were taken using a Global Positioning System (GPS). Other lithological processes and anthropogenic activities that can have impacts on soil chemistry; weathering, geopedological and geomorphic processes, fertilizer application were also observed.

2.3. Analytical techniques and quality assurance and control

This study entailed thirteen (13) soil quality analytical parameters. These included lead, chromium, zinc, copper, silver, barium, cobalt, iron, manganese, nickel, vanadium, strontium and arsenic which were analyzed using a ThermoARL model 9800XP simultaneous/sequential XRF. Instrument parameters used are; 50 kV, 50 mA with a 30-s counting time/element. The analytical method employed used press pellet analysis of all elements with an 11.7 g sample mixed with a 1.3 g
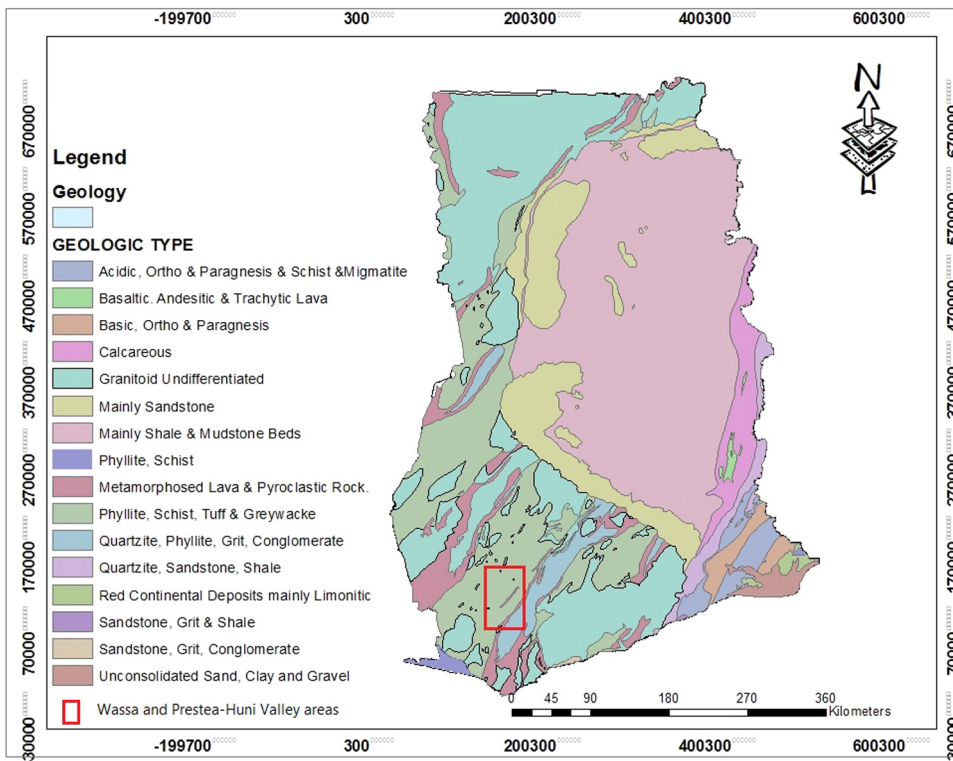
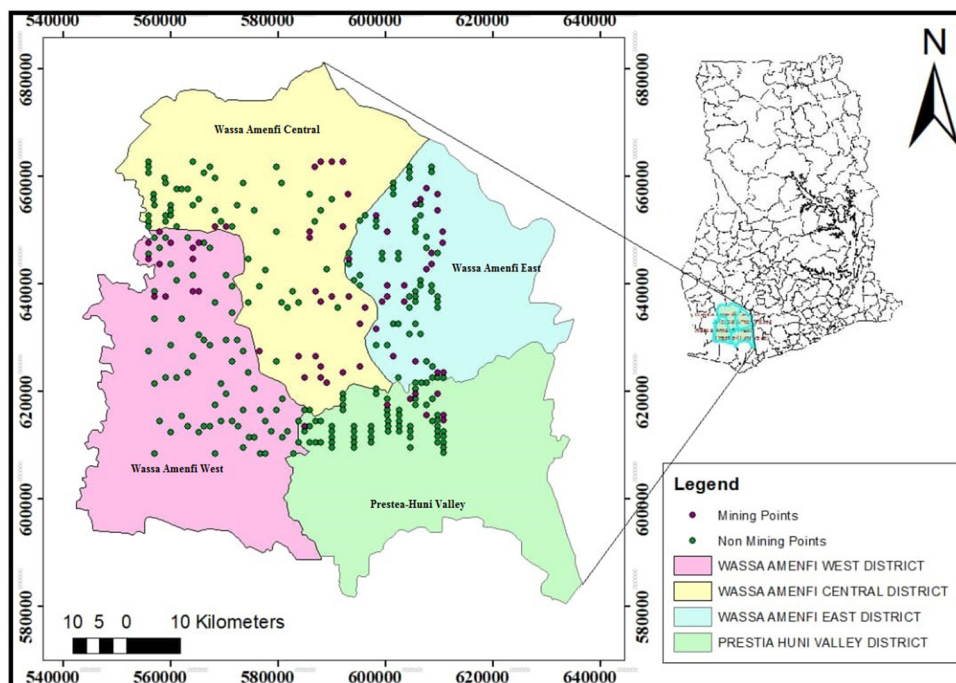**Fig. 1.** Geological description of the areas.

Fig. 2. Location and sampling points.

wax binder. ICP-MS-Sample powders were digested in Aqua Regia on a hotplate at 80 °C. This was then diluted and analyzed on a Perkin Elmer Elan 6000 ICP-MS using the TotalQuant program. Indium was used as an internal standard.

To guarantee analytical precision and quality control, a duplicate sample of each was included per every 19nth and 29nth samples respectively. The precision of the data was computed as Relative Percentage Difference (RPD) using the formula following Reyes et al. (2019).

$$\%RPD = \left[\frac{(S_v - D_s)}{\frac{S_v + D_v}{2}}\right] X\,100 \tag{1}$$

S_V = original sample value and D_s = duplicate sample value. The %RPD computations are presented in Supplementary Table 1.

2.4. Geostatistical and geochemical computations

2.4.1. Index of geo-accumulation (Igeo)
The Igeo of the soil samples were examined to assess the level of soil pollution. Igeo was calculated using Muller's formula:

$$Igeo = log2\left[\frac{Ci}{1.5\,(C_r)}\right] \tag{2}$$

Ci = concentration of the elements and Cr = background value of the elements. An adapted format of Muller's classification (1969) by Kazapoe et al. (2019) was used (Supplementary Table 2).

2.4.2. Enrichment factors
The EF was calculated using the formula proposed by Sinex and Helz (1981) and Kazapoe et al. (2019) presented in Eq. (3). This was to assess the magnitude of contaminants in the area.

$$EF = \frac{C_c/C_{ref}}{B_c/B_{ref}} \tag{3}$$

C_c = elemental concentration, C_{ref} = concentration of the reference element, B_c = crustal value of the studied element, and B_{ref} = crustal value of the reference element. Information presented in Supplementary Table 2 was used to classify the enrichment levels of the samples. Fe was used as the reference element following Sinex and Wright (1988).

2.4.3. Contamination factor and degree of contamination
The presence and concentration of elements in the sampled soils were determined using the contamination factor (C_f^i) and degree of contamination (C_d). C_f^i is a sum of all contamination factors for all the examined elements, whiles C_d is the sum of C_f^i elements; a single elemental index. The C_f^i calculation was presented as:

$$C_f^i = \left[\frac{C_o^i}{C_n^i}\right] \tag{4}$$

C_n^i = pre-industrial concentration of the individual is elements, whereas C_o^i = mean elemental concentration of the samples. The grade of the calculated C_f^i was determined following Rahman et al. (2012) (Supplementary Table 2). The degree of contamination (Eq. (5)) was used to examine the overall contamination in the soil. Classification is shown in Supplementary Table 2.

$$C_{d=}\sum_{i=1}^{n} C_f^i \tag{5}$$

This study adopted the suggested grading by Hakanson (1980) for the analysis and classification of C_d.

2.4.4. Modified contamination degree (mCd) and potential contamination index (C_p)
The mCd and C_p were determined using the formulas presented by Hakanson (1980) and Dauvalter and Rognerud (2001) which are respectively presented as:

$$mCd = \left[\frac{\sum_n^i CF}{n}\right] \tag{6}$$

$$Cp = \left[\frac{C_{sample}}{C_{background}}\right] \tag{7}$$

CF = contamination factor, and n = number of samples, and C_{sample} = sample concentration, and $C_{background}$ = background concentration. C_p is classified as < 1 (low contamination), > 1 - < 3 (moderate contamination) and > 3 (severe contamination) and the description of mCd are in Supplementary Table 2.

Table 1
Statistical summary of results.

	Ba	Cr	As	Ag	Co	Cu	Zn	Fe	V	Ni	Sr	Pb	Mn
Min	4.00	17.00	2.00	4.00	4.00	4.00	9.00	0.44	8.00	2.00	4.00	5.00	80.00
Max	1005.00	331.00	246.00	17.00	65.00	75.00	123.00	13.00	519.00	71.00	362.00	71.00	2500.00
Med	218.00	80.00	14.00	4.00	6.00	11.00	24.00	2.86	85.00	9.00	83.00	6.00	156.50
Avg	213.10	86.25	18.37	4.58	7.60	12.56	27.86	3.09	92.06	11.24	99.77	7.85	212.40
SD	113.68	38.97	20.63	1.88	5.26	8.53	13.30	1.72	51.83	9.65	70.59	5.58	202.14
Skew	1.26	2.02	6.57	4.35	5.13	2.90	2.57	1.88	3.68	2.97	1.06	6.02	6.60
Kurt	7.25	8.64	60.62	20.42	48.26	14.33	10.93	6.42	22.17	12.31	0.96	57.52	61.04
CV (%)	53.35	45.18	112.34	41.09	69.23	67.90	47.74	55.62	56.29	85.90	70.75	71.09	95.17
SE_M	6.56	2.25	1.19	0.11	0.30	0.49	0.77	0.10	2.99	0.56	4.08	0.32	11.67
WHO (1996)								35					
Crommentuijn et al. (2000)	9.0	3.8	4.5		24	3.5	16		1.1	2.6		55	
McLaughlin et al. (2000)		100	20			100			200			150	500
Arhin et al. (2016)			15.00			0.40	20.00						
Kazapoe and Arhin (2019)		80.74	13.29		6.44					8.67		6.69	

2.4.5. Pollution load index (PLI)

To estimate the overall pollution status of the samples, the pollution load index (PLI) of the metal contaminants was calculated using Eq. (8) recommended by Tomlinson et al. (1980).

$$PLI = [CF1 \times CF2 \times CF3 \times \cdots \times CFn]^{\frac{1}{n}} \tag{8}$$

CF = contamination factor of metal and n represents the number of HM measured. Where PLI ≥ 1 (unpolluted), PLI = 1–3 (moderately polluted), PLI = 3–5 (highly polluted), and PLI ≤ 5 (very highly polluted)

2.4.6. Ecological risk factor (Erf)

Erf quantitatively determines the potential ecological risk of elements through anthropogenic activities (Hakanson, 1980). This was computed using the expression:

$$Erf = \left[Tr \times C_f^i \right] \tag{9}$$

Tr = toxic response factor and C_f^i = contamination factor. The description of the Erf is shown in Supplementary Table 2. The Tr of the elements are presented as Mn = 1, Zn = 1, Ni = 5, Pb = 5, Cu = 5, Co = 5, As = 10, and Cr = 2) (Sinex and Helz, 1981).

2.5. Statistical analysis of data

The R software (3.6.2 version) and Microsoft Excel (2016 version) were employed to compute the descriptive statistics were determined using the log-transformed data that were then back-transformed to describe the central tendency and variability of the concentration of the studied elements. Factor analysis (FA) was done to explain the correlation structure of the variables through a smaller number of factors. The dataset was subjected to a Centered Log Ratio (CLR) transformation using the formula suggested by Kazapoe et al. (2021a). This is presented as:

$$CLR_{Fe} = log_{10} \left[\frac{MC_{Fe}}{\sqrt[n]{C_1 C_2 C_3 \ldots C_n}} \right] \tag{10}$$

MC_{Fe} = concentration of Fe in soil (an immobile element) and $C_1 C_2 C_3 \ldots C_n$ = the concentrations at individual points.

3. Results and discussion

3.1. Soil quality

Table 1 presents the statistical summary of the soil quality. As is a high-impact toxicant. The measured As ranged from 2.00 to 246.00 ppm (avg. 18.37 ppm). About 43% of the obtained As values were above the baseline value of 15 ppm recommended by Arhin et al. (2016) in the Wassa area. Compared to Mensah et al. (2015) where the level of As fell between 0.90 ppm and 5.40 ppm in Damang-Abosso, the results of this study were higher. However, the findings of the study corroborated with Darko et al. (2019) where As levels were 3.50–862.50 ppm in a mining community in Gbani, northern Ghana. Ag concentrations fell within 4.00–17.00 ppm. All the soil samples exceeded the average crustal value of 0.07 ppm indicated by Taylor (1964). This was dissimilar with the findings of Mensah et al. (2015) where Ag ranging between 0.10 ppm to 0.60 ppm was recorded in Damang-Abosso in the southwestern part of Ghana.

The concentration of Fe and Pb respectively ranged from 0.44 ppm and 13.00 ppm (avg. 3.09 ppm) and 5.00 ppm and 71.00 ppm (avg. 7.85 ppm). The study showed that though all the samples were within the threshold of 35 ppm

suggested by WHO (1996) for Fe, 46% of the samples exceeded the 6.69 ppm guideline presented by Kazapoe and Arhin (2019) for Pb. This was similar to the findings of Darko et al. (2019) where Pb levels were 3.6–63.20 ppm. Sr and V had centered results of 99.77 ppm and 92.06 ppm respectively. The concentrations ranged between 4.00-362 ppm (CV% of 71%) for Sr and 8–519 ppm (CV% of 52%) for V. The study showed that though all the samples were below the average crustal value of 375 ppm stipulated by Taylor (1964) for Sr, 47% were beyond the average crustal value for V (135 ppm). The extremely high V values relate to the findings of Kesse (1985) which described the underlying geology of the area to compose granitic intrusions which are alkaline-based.

Barium (Ba) and Cobalt (Co) respectively ranged from 4.00–1005.00 ppm and 4.00–65.00 ppm. Also, 98% and 50% of these elements respectively exceeded the recommendation by Crommentuijn et al. (2000) (9.00 ppm) for Ba and Kazapoe and Arhin (2019) (6.44 ppm) for Co. The deviations shown in Table 1 revealed the distribution of Barium was dispersed and ununiformed whereas the concentrations of Co varied largely. This could be attributed to mining activities within the areas as discussed by the Agency for Toxic Substances and Disease Registry (ATSDR) (2004). The results (Table 1) of Cr ranged from 17.00–331.00 ppm (avg. 86.25 ppm). Furthermore, 50% of the samples exceeded the threshold of 80.74 ppm suggested by Kazapoe and Arhin (2019) whereas Cu ranged from 4.00–75.00 ppm (Avg. 12.56 ppm) with 100% of the samples exceeding the threshold levels of 0.40 ppm by Arhin et al. (2016). These findings were similar to Darko et al. (2019) where the concentrations of Cr and Cu ranged between 17.8 ppm and 178.3 ppm, and 9.70 ppm and 140.10 ppm in northern Ghana.

The concentration of Ni was 2.00–71.00 ppm. The study showed that 54% of the samples exceeded the 8.67 ppm recommendation suggested by Kazapoe and Arhin (2019) for Ni. Mn levels fell between 80.00 ppm and 2500.00 ppm (avg. 212.40 ppm). However, about 5% of the samples exceeded the 500 ppm recommended by McLaughlin et al. (2000). The kurtosis (61.04) and CV% (95%) indicated that the distribution of Mn was highly dispersed. The results of Zn were ununiformed and dispersed (CV% of 48%), ranging between 9.00–123.00 ppm (Avg. 27.86 ppm). The Zn concentration exceeded the 20.00 ppm guideline discussed by Arhin et al. (2016). About 71% of the samples exceeded this guideline.

3.2. Assessing soil quality: pollution indicators

3.2.1. Index of geo-accumulation (Igeo) and enrichment factor (EF)

Assessing the level of enrichment in soil aids in the quantification of heavy metal pollution via anthropogenic activities and, geogenic and lithogenic sources (ur Rehman et al., 2018). The results presented in Table 1 show that the centered geo-accumulation indices and enrichment factors of the assessed elements ranged between 0.030–13.120 and 0.305–146.684 respectively. The Igeo computations showed that except for Ag which had all the samples described as extremely polluted and As were 22%, 43%, and 20% of the samples were unpolluted to moderately polluted, moderately polluted, and moderately to strongly polluted, and 5.67% (strongly polluted), 3.33% (strongly to extremely polluted), and 18% (extremely polluted), the other elements considered were unpolluted to moderately polluted. Similar to the computed Igeos, all the samples recorded Ag enrichment > 40 (extremely high enrichment) (Fig. 3a). The EF showed that 1% and 5.33, 97% and 3%, 95% and 5%, 69.3% and 29.3%, 99.7% and 0.3%, 98.7% and 1.3%, 84% and 14.7%, 98.7% and 1.3%, 92% and 7%, and 98% and 1.3% of the samples evaluated for As, Ba, Co, Cr, Cu, Mn, Pb, Sr, V and Zn respectively showed deficient to minimal enrichment, and moderate enrichment. However, 55.3%, 0.3%, 1.3%, 0.3% 1%, 0.3% and 0.7% of the soils respectively showed significant enrichment for As, Ba, Cr, Ni, Pb, V, and Zn. Also, 32.3% of the samples indicated very high enrichment for As, whereas 18.6% and 0.3% posed extremely high enrichment for As and Pb. The centered Igeo results could be categorized as Ag > As > Cr > V > Pb > Fe > Ba > Zn > Co > Sr > Cu > Mn > Ni in the scale of accumulation, whereas EF was presented as Ag > As > Cr > Pb > V > Ba > Fe > Zn > Co > Sr > Mn > Cu > Ni in order of enrichment (Fig. 3b). This study indicated that the soils were significantly polluted with Ag, As, Cr, Pb, and V, whiles Ni, Cu, Mn, Sr, Co, and Zn were barely presented (Fig. 3a–b). The exceedance of the average EF suggests that Ag, As and Pb were driven by anthropogenic factors. The accumulation and enrichment of Ag and As could be attributed to the underlying gold-bearing geology of the areas, and the use of arsenic in the extraction and processing of minerals as described by Hogarh et al. (2016). Similarly, Atafar et al. (2010) in a study in Mahidasht, Iran attributed elevated As and Pb concentrations to the application of inorganic fertilizers. The variation in the Igeo and EF levels of the assessed elements across the areas suggests that the processes impacting elemental accumulation and enrichment were influenced by varied processes.

3.2.2. CF, mCd, and C_d indices

Contamination factor (CF) is employed in the evaluation of heavy metal contamination as a ratio of the elemental concentration of the sampled soils and the pre-industrial concentrations of the studied elements, whereas the modified contamination degree is the mean of the CF and C_d is a sedimentological process which is the sum of the CF. CF and mCd are effective tools for assessing soil over time. The study showed that apart from Ag and As that recorded 100% CF levels below < 1 (low contamination), none of the samples for Cu, Ni, and Sr were below the low contamination level. However, 14.33%, 43.67% and 42%, 5.67%, 23% and 71.33%, and 30.67%, 32% and 37.33% of the samples showed moderate, considerable and high contamination respectively for Cu, Ni and Sr. Considering the PTEs, Cr, Pb and Zn respectively had 26.33%, 10% and 2% (low contamination), 71.67%, 89.67% and 50.67% (moderate contamination), 2%, 0%, 46.33% (considerable contamination) and as Zn showed 1% high contamination, Cr and Pb showed no high contamination for CF. Meanwhile, the average CF values for Ba (5.096), Co (4.225), Fe (2.423), Mn (5.776), and V (1.862) depict that V and Fe were "low
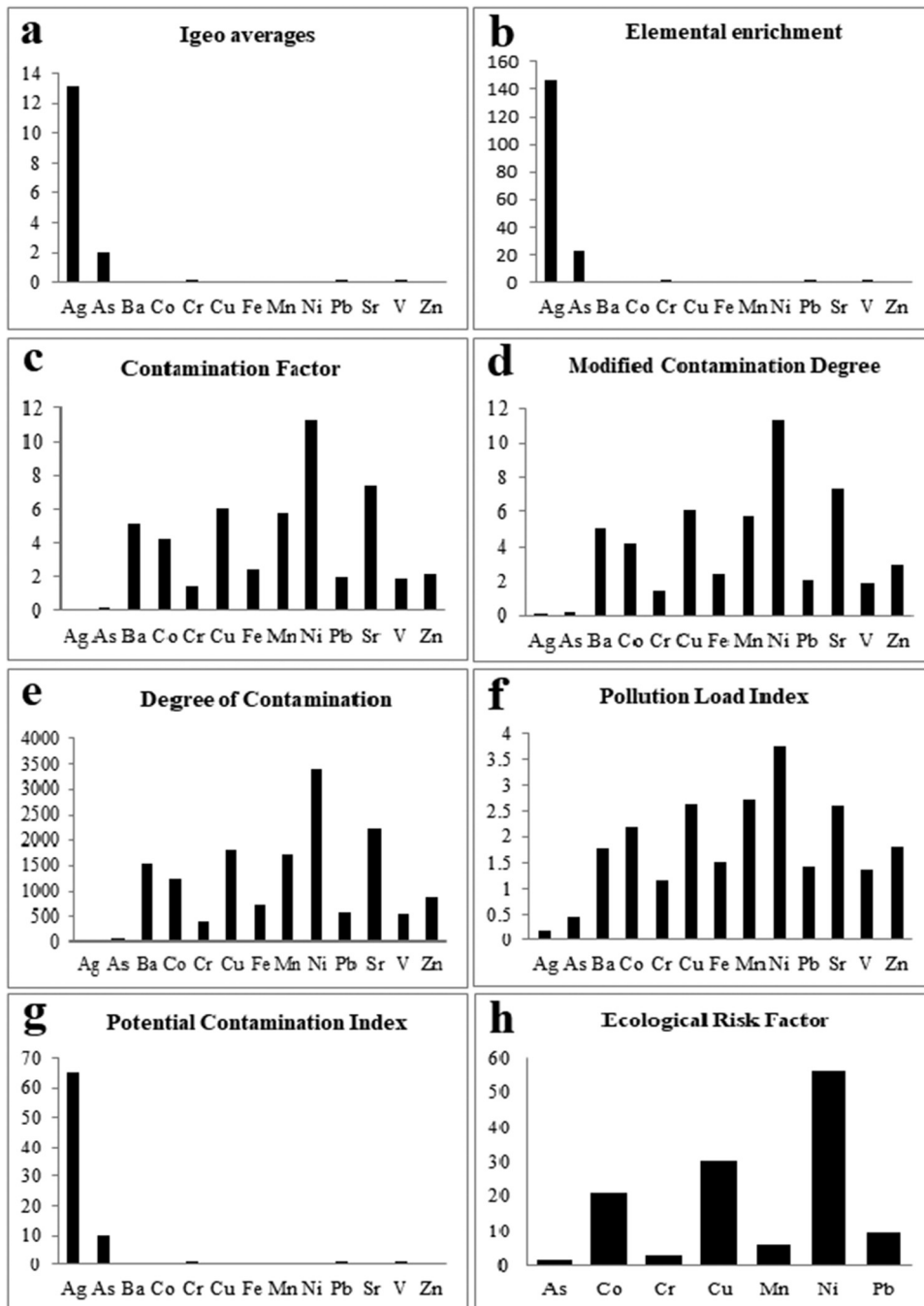
Fig. 3. Description: (a) Igeo (b) EF (c) CF(d) mCd (e) C_d (f) PLI (g) C_p (h) Erf.

contaminated" whereas Ba, Co, and Mn were "considerably contaminated" (Fig. 3c). Similar to the CF results, the mCd computation rated Ni as "very high contamination" with an average of 11.317 (Fig. 3d). However, Table 1 showed that Ag (avg. 0.016), As (avg. 0.168), and Cr (avg. 1.398) ranged between "no to very low contamination", whereas V (avg. 1.862) and Pb (avg. 1.936), and Fe (avg. 2.423) and Zn (avg. 2.928) fell within the low and moderate contamination ranges respectively. High contamination elements based on the mCd analysis were Co (avg. 4.225), Ba (avg. 5.096), Mn (avg. 5.796), Cu (avg. 6.101), and Sr (avg. 7.371). The C_d calculations presented in Table 1 indicates that, apart from Ag (avg. 4.917) which fell within the low contamination class (< 8), As (avg. 50.411), Ba (avg. 1528.674), Co (avg. 1267.629), Cr (avg. 419.529), Cu (1830.266), Fe (avg. 726.856), Mn (avg. 1738.782), Pb (avg. 580.818), Sr (avg. 2211.317), V (avg. 558.669 and

Zn (avg. 878.497) were considerably contaminated ($12 \leq C_d < 24$) (Supplementary Table 2). The CF, mCd and C_d centered results could be described as Ni > Sr > Cu > Mn > Ba > Co > Zn > Fe > Pb > V > Cr > As > Ag (Fig. 3e). According to the results (CF, mCd, and C_d) presented Ni, Sr and Cu were the most contaminated element in the soils. The level of Ni and Cu could be due to the unearthing of ores through mining activities that have been studied to contain traces of Cu and Ni which further harden the subsurface and hinder the seepage of these elements, which is attributable to elemental accumulation.

3.2.3. Pollution load index (PLI) and potential contamination index (C_p)

The PLI and Cp give information about the total degree of metal contamination in each respective sample location. Similar to the CF, mCd, and C_p results, the PLI computation showed that Ag and As were unpolluted. Except for Cr, Cu, Mn, Ni, Sr, and V which had no samples within the unpolluted limits, 3% and 97%, 2% and 83%, 3.33% and 96.67%, 8.33%, and 91.67%, and 92.67% and 7.33% of samples analyzed for Ba, Co, Fe, Pb, and Zn were respectively unpolluted and moderately polluted. However, 15% for Co, 31.33% for Cu, 32.33% for Mn, 24.67% for Ni, and 36% for Sr were within the range of highly polluted soils, whereas 5%, 10.67%, 29%, and 3% of the soils representing Cu, Mn, Ni, and Sr were very highly polluted. Dissimilar with the ranking of elements based on the computed CF, mCd and C_d, the mean PLI analysis showed Ni > Mn > Sr > Cu > Co > Ba > Fe > V > Pb > Cr > As > Zn > Ag. The C_p analysis presented in Fig. 3f could be presented as Ag > As > Cr > V > Pb > Fe > Ba > Zn > Co > Sr > Cu > Mn > Ni. This showed similarity with the computed Igeo. Unlike with the CF, mCd, C_d, and PLI, all the samples were severely contaminated with Ag whereas the majority (91%) were for As. Meanwhile, all the samples assessed for Ni and Sr were within the low contamination range (< 1) (Fig. 3g). A majority of the soils analyzed for Ba (98%), Co (99%), Cr (74%), Cu (99%), Mn (99%), Pb (90%) and Zn (98%) were within the low contamination range, whereas 93% and 91%, respectively for Fe and V were moderately contaminated.

3.2.4. Ecological risk factor (Erf)

The Erf is an index that determines the degree of the possible ecological risk posed by an element in an environmental medium. Elements with available toxic response factors were considered in this study (As, Co, Cr, Cu, Mn, Ni, Pb, and Zn). The results presented in Table 1 indicated that except for Cu and Ni, all the other elements showed low ecological risk (Erf < 40). The mean results were 1.680 (As), 21.127 (Co), 2.797 (Cr), 30.504 (Cu), 5.796 (Mn), 56.586 (Ni) and 9.680 (Zn). Nonetheless, a majority of the samples showed low Erf for Cu (82%) and Ni (47%), whereas 18% and 34% in the same order posed moderate risk factors. The study showed that 12% and 6% of the samples were respectively within the considerable and high-risk factor ranges for Ni. The Erf computations could be presented as Ni > Cu > Co > Pb > Mn > Cr > As (Fig. 3h). The high ecological risk of Ni above the unpolluted range of < 40 could be related to the unearthing of rock materials via mining activities. This may require attention due to its ability to bio-accumulate, be persistent in the environment, and pose several health implications.

3.2.5. Possible factors of trends in pollution indices

The simultaneous use of several indices has been identified as more accurate in the assessment of heavy metal pollution in soil (Kowalska et al., 2018). Several studies have indicated that the selection of a pollution index depends on different factors including contamination levels, the origin of the heavy metal, the potential ecological risk, and the purpose and application of the index (Kowalska et al., 2018). Some previous studies have indicated that pollution indices may not be readily comparable (Kowalska et al., 2018). In this study, there were disparities in the computed pollution indices as Igeo, EF and C_p amplified Ag and As (Fig. 3a–b and g) whereas Fig. 3c–e) (mCd, CF and C_d) indicated Ni > Sr > Cu > Mn > Ba > Co > Zn > Fe > Pb > V > Cr > As > Ag, PLI showed Ni > Mn > Sr > Cu > Co > Ba > Fe > V > Pb > Cr > As > Zn > Ag (Fig. 3c–e) and Erf presented Ni > Cu > Co > Pb > Mn > Cr > As (Fig. 3h). This relates to the claim of Petrik et al. (2018) that pollution indices are not scale-invariant and may show different outputs. Similar results shown by Igeo and C_p could be related to the formulas which are very similar except for the constant 1.5 in Igeo (Eq. (2)). Also, EF does not vary much from Igeo and C_p except for the introduction of the concentration obtained for a reference element; Fe, Mn, Sc, Ca, Ti or Al (which may not show significant variations in EF results if the concentrations obtained per sample are very close) and background value of the same reference element (which is a constant). The introduction of the constant in Igeo and reference element may not introduce any significant scale variance between these indices. Also, mCd and C_d are respectively computed by dividing the sum of C_f^i (contamination factor) by the number of samples (300) (which does not change) and summing the C_f^i. PLI presents a similar pattern with mCd, C_f^i, and C_d because no external constant such as average crustal value/background vale is introduced except for n (number of samples) which does not change. Considering Erf, since it is computed by multiplying Tr (toxic response factor) and C_f^i, it is expected that it may share a similar trend with mCd, PLI, and C_d. However, the varying toxic response factors ascribed to the various elements may result in a slight variation between Erf, and mCd, PLI, and C_d (Compare Fig. 3c–e, f and h). Therefore, it is likely that these indices 'Igeo, EF, and C_p', 'mCd, C_f^i and C_d', and 'Erf' will show similar trends.

Table 2
Summary of factor analysis.

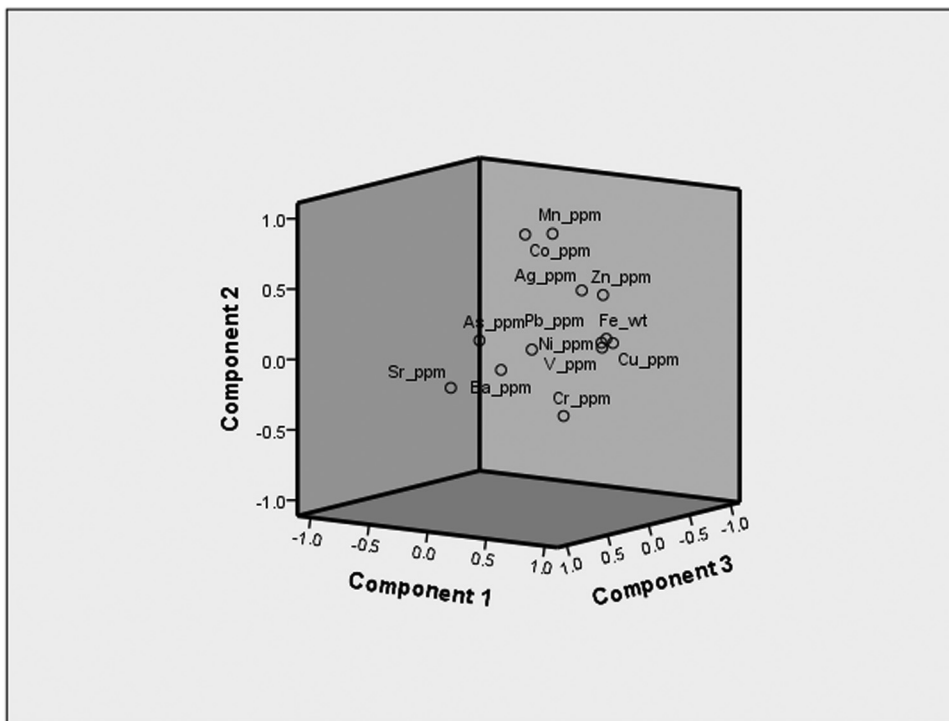|	Factor 1	Factor 2	Factor 3
Ni	**.850**	−.082	−.254
Fe	**.862**	.070	−.157
Ba	**.649**	.421	.109
Co	.285	−.421	.448
Sr	.263	**.691**	.305
V	**.867**	.178	−.011
Zn	**.732**	−.465	−.162
Ag	**.586**	−.285	.239
Cr	**.625**	.460	−.390
Cu	**.861**	−.030	−.130
Mn	.439	−.688	.082
Pb	**.503**	−.139	.194
As	.471	.292	**.600**
Variance	**42.1%**	**15.1%**	**8.1%**

Fig. 4. Factor analysis loading plot.

3.3. Factor analysis

Factor analysis results are presented in Table 2 and Fig. 4. It aimed at identifying the basic factors significantly influencing the sources and factors affecting the quality of soils in the areas. In this study, three (3) factors were presented. These explained 65.3% of the total variance (3). Factor 1 which presented a variance of 42.1% was characterized by Ag, Ba, Cr, Cu, Fe, V, Ni, Pb, and Zn (Fig. 4). This suggests that these elements predominantly influenced the quality, characteristics, and variability of the soils. Sr and As respectively described factors 2 and 3 with respective variances of 15.1% and 8.1%. The quality of the soils was significantly influenced by PTEs and heavy metals which could be attributed to geo-natural and human-induced factors. Dominant activities such as mining and agricultural activities, and geomorphic, geopedological, and weathering processes can contribute to the availability, deposition, accumulation, and distribution of these elements.

3.4. covariance–variance analysis

The Pearson correlation analysis as presented in Table 3 and Supplementary Fig. 1 was done to determine the relationship between the assessed elements in the soil samples. Mugheri et al. (2019) describe the covariance–variance

Table 3

Variance–covariance matrix.

	Ag	As	Ba	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sr	V	Zn
Ag	1.00												
As	0.29	1.00											
Ba	0.23	0.08	1.00										
Co	0.40	0.48	0.10	1.00									
Cr	0.12	0.17	**0.53**	**−0.06**	1.00								
Cu	**0.54**	0.18	0.40	0.26	0.43	1.00							
Fe	**0.65**	0.30	0.47	0.23	0.45	**0.76**	1.00						
Mn	0.44	0.10	0.08	**0.69**	**−0.05**	0.33	0.32	1.00					
Ni	0.45	0.24	0.36	0.30	**0.56**	**0.72**	**0.60**	0.37	1.00				
Pb	0.17	0.41	0.19	0.09	0.18	0.32	0.21	0.16	**0.54**	1.00			
Sr	−0.02	0.23	**0.54**	−0.04	0.28	**0.61**	0.09	**−0.17**	0.01	0.05	1.00		
V	**0.63**	0.31	0.40	0.20	0.40	**0.78**	**0.80**	0.23	**0.56**	0.18	0.12	1.00	
Zn	0.47	0.13	0.24	0.34	0.21	**0.56**	**0.58**	**0.59**	**0.54**	0.30	**−0.19**	0.43	1.00

matrix as a measure of closeness of dissimilar variables. In this study, positive (direct) and negative (inverse) relationships were highlighted. Table 3 shows that Ag was influenced by Cu, Fe, V, and Sr as it established direct relationships with Cu (r = 0.54), Fe (r = 0.65), and V (r = 0.63), and an indirect correlation Sr (r = −0.02). Ba was directly associated with Cr (r = 0.53) and Sr (r = 0.54), whereas Sr was negatively related to Zn (r = −0.19) and Cr showed direct associations with Ni (r = 0.56) and inversely with Mn (r = −0.05). Similar to the findings presented in Table 3, Darko et al. (2019) in a study in Gbani, Upper East Region of Ghana showed that As did not show any relationship with Cr (r = 0.17), Cu (r = 0.18), Mn (r = 0.10), Ni (r = 0.24) and Pb (r = 0.41). The inverse relationship between Cr and Mn is supported by the CF and mCd results where Mn is seen as a significant pollutant whereas Cr showed low pollution and the C_p computation where a reverse of this order was established. Similarly, the Co and Cr inverse correlation (r = −0.06), Co and Sr (r = −0.04) and the positive association of Co and Mn (r = 0.69) and Cu and Fe (r = 0.76) relate with the C_p (Ag > As > Cr > V > Pb > Fe > Ba > Zn > Co > Sr > Cu > Mn > Ni) ranking of elements based on their levels of contamination. Cu, Fe, Pb, V and Zn were directly related with Ni (r = 0.72, 0.60, 0.54, 0.56 and 0.54) respectively. This could be attributed to Ni dominance in the environment as described by the PLI and C_d analyzes. The study further showed that the levels of V, Sr and Zn were impacted by Cu and Fe as they established positive correlations of r = 0.78 (Cu and V), r = 0.61 (Cu and Sr), r = 0.56 (Cu and Zn), r = 0.80 (Fe and V), and r = 0.58 (Fe and Zn). Mn also presented a negative association with Sr (r = −0.17). Dissimilar to Darko et al. (2019) where Mn and Zn showed an inverse relationship (r = −0.422), this study presented a positive relationship (r = 0.59).

3.5. Friedman rank sum test

A Friedman rank-sum test was conducted to determine the quality of their medians. This was to understand how their distributions differ. The results of the Friedman test were significant based on an alpha value of 0.05, $\chi^2(4) = 958.66$, $p < .001$ for As, Pb, Zn, Cu, and Cr, $\chi^2(4) = 1046.73$, $p < .001$ for Ni, Mn, Fe, Co, and Ba, and $\chi^2(2) = 448.62$, $p < .001$ for V, Sr and Ag. These indicate significant differences in their medians. Pairwise comparisons were examined between each combination of variables. The results of the multiple comparisons indicated significant differences, based on an alpha value of 0.05, between the following variable pairs: As–Pb, As–Zn, As–Cu, As–Cr, Pb–Zn, Pb–Cu, Pb–Cr, Zn–Cu, Zn–Cr, Cu–Cr, Ni–Mn, Ni–Fe, Ni–Ba, Mn–Fe, Mn–Co, Fe–Co, Fe–Ba, Co–Ba, V–Ag and Sr–Ag (Fig. 5).

3.6. K-means cluster analysis

A k-means cluster analysis was conducted to find similar groupings among the data. First, the number of clusters, k, was chosen through graphical assessment. The k-means cluster analysis was conducted and assessed through descriptive statistics and linear discriminant analysis (LDA). The optimal number of clusters was chosen by plotting the total within-cluster sum of squares as a function of the number of clusters (Larson et al., 2005). The optimal number of clusters is the point where the curve appears to flatten, indicating that additional clusters would have little effect on the total within-cluster sum of squares. For this analysis, 4 clusters were chosen.

For Ag, clusters 1, 2, 3 and 4 had means of 5.63 ± 2.28, 13.86 ± 2.85, 4.04 ± 0.29, and 4.32 ± 0.99. Fe presented means of 4.69 ± 1.59, 9.53 ± 2.20, 2.04 ± 0.82, and 3.47 ± 0.95 for clusters 1–4 whereas Co had 9.09 ± 5.14, 21.41 ± 20.83, 6.82 ± 3.55, and 7.22 ± 3.52 in the same order. Pb showed 13.86 ± 5.43 and 6.34 ± 2.93 as the highest and lowest means while Zn and As had means ranging from 23.22 ± 8.23 to 64 ± 16.04 and 11.75 ± 6.35 to 52.86 ± 32.96. The means Ba, Cr, Cu, and Mn ranged between 135.94 ± 71.89 and 287.07 ± 91.47, 64.27 ± 22.40 and 123.97 ± 61.65, 7.79 ± 3.26 and 41.0 ± 21.07, and 170.65 ± 87.93 and 747.57 ± 893.41 were respectively obtained. Ni and Sr respectively presented averages of 25.03 ± 14.50 and 78.55 ± 56.77 (cluster 1), 34.57 ± 16.52 and 51.43 ± 56.34 (cluster 2), 6.48 ± 3.70 and 62.49 ± 39.23 (cluster 3), and 11.13 ± 4.50 and 156.74 ± 69.24 (cluster 4) whereas V showed cluster 1 = 128.55 ± 57.50, cluster 2 = 295.14 ± 126.96, cluster 3 = 62.54 ± 18.99, and cluster 4 = 104.31 ± 21.80.
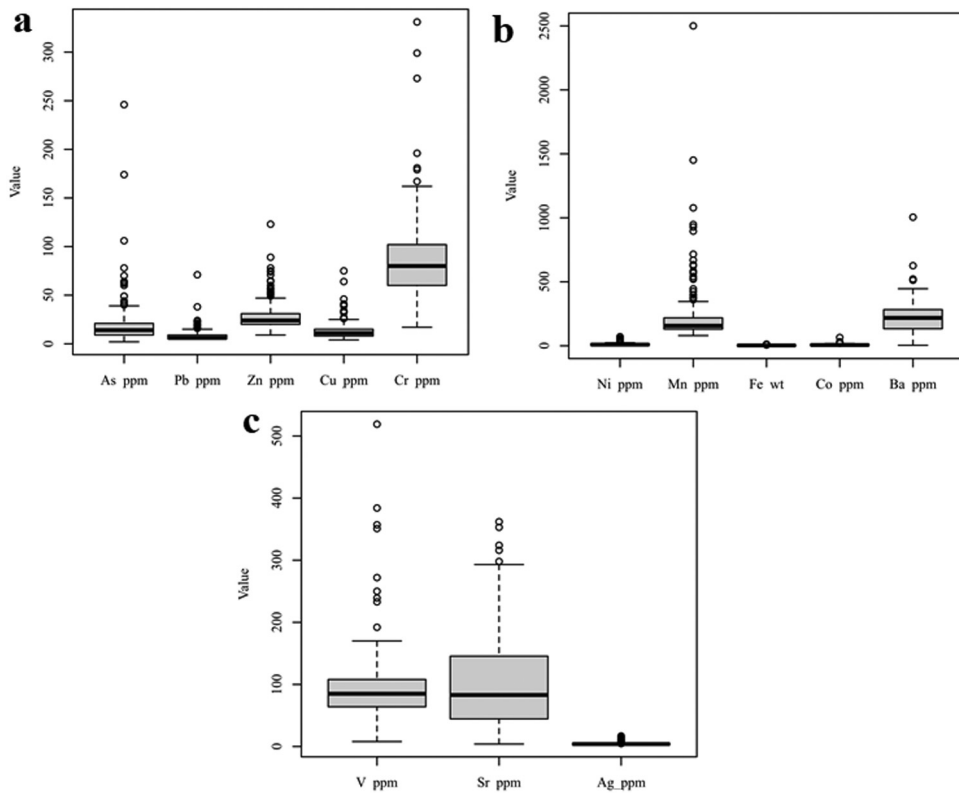
Fig. 5. Boxplots from Friedman rank-sum test (a) As, Pb, Zn, Cu, and Cr (b) Ni, Mn, Fe, Co, and Ba (c) V, Sr and Ag.

The Linear Discriminant Analysis (LDA) components by clusters was done to understand if the clusters show separation in the data. It identifies the percentage of total separation in each component of the analysis. For component 1 (LD1), means of -2.76, -11.62, 1.22, and 0.11 were shown for clusters 1, 2, 3, and 4. For LD2, clusters 1, 2, 3, and 4 had averages of 0.27, -2.31, -1.01, and 1.33 whereas LD3 had -1.63, 2.21, 0.03, and 0.38 in the same order (Fig. 6). Correlations were also calculated to determine which variables had a large ($r \geq .50$ or $r \leq .50$) or moderate ($r \geq .30$ or $r \leq .30$) contribution to the LDA components. Considering LD1, Ag ($r = -0.85$), Fe ($r = -0.85$), Zn ($r = -0.72$), Cu ($r = -0.81$), Mn ($r = -0.54$), Ni ($r = -0.72$), and V ($r = -0.81$) had a strong contribution and Co ($r = -0.45$), Pb ($r = -0.40$), As ($r = -0.33$), Ba ($r = -0.32$), and Cr ($r = -0.33$) had a moderate influence on the component. In LD2, Ba ($r = 0.76$), Cr ($r = 0.58$), and Sr ($r = 0.80$) had a strong contribution and no variables had a moderate influence for the component. Meanwhile for LD3, no variables had a strong contribution and Pb ($r = -0.38$), Zn ($r = -0.44$), Cr ($r = -0.37$), Ni ($r = -0.43$), and Sr ($r = 0.33$) had a moderate influence on the component. The variables that have large correlations for components that exhibit a significant percentage of trace contribute the most in separating the clusters.

3.7. Possible pathways of potentially toxic elements in crops

A previous study by Zango et al. (2013) assessed heavy metals (Cd, Cu, Ni, Pb, and Zn) in crops including plantain (*Musa paradisiacal*) and cassava (*Manihot esculenta Crantz*) in the Wassa area. The study showed that the elemental levels in the crops exceeded the observed concentrations in the soil samples. The results obtained respectively ranged between 19.45 mg/kg and 142.39 mg/kg, 27.01 mg/kg and 76.21 mg/kg, 19.63 mg/kg and 53.93 mg/kg, 99.42 mg/kg and 357.15 mg/kg, and 1.42 mg/kg and 5.84 mg/kg for Cu, Pb, Ni, Zn, and Cd. The contents of Cd, Cu, Pb and Zn in the plantain samples exceeded FAO/WHO standards whereas Cd, Pb, and Zn were high in the cassava samples. A similar study by Bortey-Sam et al. (2015) in the Tarkwa area showed that about 30% of cassava samples collected, contained higher concentrations of Pb. Amonoo-Neizer et al. (1996) and Golow and Adzei (2002) have also shown high levels of As and Zn in the Obuasi and Dunkwa-on-Offin areas. Similarly, Amasa (1975) reported levels of As in plantain (2.29 mg/kg^{-1}) and cassava (2.65 mg/kg^{-1}) in Obuasi and its environs. Hayford et al. (2009) also revealed that the maximum elemental-levels of metals in cassava and plantain were Cr = 0.72 μg/g and 3.42 μg/g, Cu = 66.39 μg/g and 8.74 μg/g, Hg = 0.25 μg/g and 0.52 μg/g, As = 0.7 μg/g and 0.25 μg/g, Sb = 0.03 μg/g and 0.03 μg/g, V = 0.8 μg/g and 0.76 μg/g, and Zn = 38.42 μg/g and 24.92 μg/g respectively in the Tarkwa-Prestea area. The computed daily in the selected crops from the Wassa area (Zango
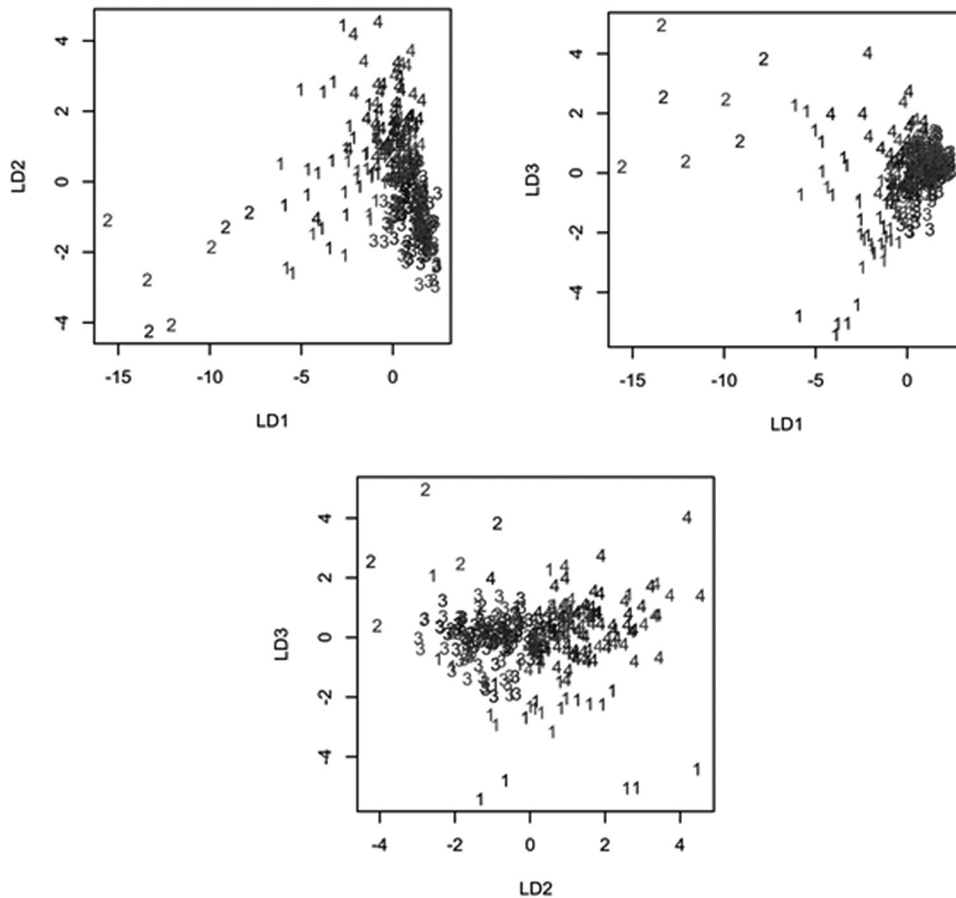
Fig. 6. Plot of LD components by cluster groups.

et al., 2013) showed that the intake of metals (DIM) and health index (HRI) of both cassava and plantain revealed that consumers of these commodities produced from these areas are prone to deleterious dietary and health impacts associated with Cd, Cu, Ni, Pb and Zn.

4. Conclusion and recommendations

Southwestern Ghana hosts a significant portion of Ghana's legal and illegal, large and artisanal mining companies. Mining is one of the predominant anthropogenic activities that pose serious deleterious impacts on soil quality; the chemical and physical characteristics of the soil. The concentrations of most of the studied elements were not uniformly distributed. The findings of the study showed that the studied elements were moderately-highly presents in soils as As (43%), Ag (100%), Pb (46%), V (47%), Ba (98%), Co (50%), Cr (50%), Cu (100%), Mn (5%), Ni (54%) and Zn (71%) exceeded either the recommended threshold or the average crustal values. Generally, the soil samples had elevated concentrations of V, Cr, As, Ag, and Pb whereas Mn, Cu, Ni, Zn, Sr, and Co were in bearable concentrations. Though the pollution indices showed an inconsistent level of pollution, Ag, Ni, Cu, Sr, and Mn were more dominant in the soils. This could be due to the scale-invariant nature of pollution indices. Also, location-specific geochemical backgrounds are required and should be based on soil- and site-specific criteria as well as the purpose and scale of the heavy metal assessment process. The availability and distribution of these elements could be attributed to mining and agricultural activities, and geopedological, weathering, and geomorphic factors and processes. It is therefore recommended that there is the need for:

- strengthening existing environmental policies geared towards regulating mining activities
- considering regular monitoring of mining activities within these areas
- remediation application to reclaim polluted areas
- reducing the application of agrochemicals
- checking illegal and unregulated mining
- assessing the levels of HM(loid)s in crops grown in the area

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.eti.2022.102329.

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