



# Application of Geochemical Indices in Evaluating Potentially Harmful Element Contamination at Mining Centres in the Sanyati Catchment, Zimbabwe

Daina Mudimbu<sup>1\*</sup>, Theophilus C. Davies<sup>2</sup>, Dexter Tagwireyi<sup>3</sup> and Maideyi L. Meck<sup>1</sup>

<sup>1</sup>Department of Chemistry and Earth Sciences, University of Zimbabwe, Harare, Zimbabwe, <sup>2</sup>Faculty of Natural Sciences, Mangosuthu University of Technology, Durban, South Africa, <sup>3</sup>Department of Pharmacy and Pharmaceutical Sciences, University of Zimbabwe, Harare, Zimbabwe

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### \*Correspondence:

Daina Mudimbu  
deemudimbu@gmail.com

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The release of potentially harmful elements (PHEs) into the environment in mineralised and mining areas has been associated with a variety of health-related disorders, especially non-communicable diseases such as cancer, heart and kidney failure and mental and cardiovascular disorders. The present study sought to evaluate the application of geochemical indices in assessing the degree of contamination at two sites, Kadoma and Hurungwe, both within the Sanyati Catchment, an important mining and agricultural hub in Zimbabwe. This evaluation was conducted by determining the concentration levels of 16 PHEs in 58 top-soil and stream sediment sample locations. The samples were collected during the period 2015–2017 and analysed for total PHE content using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). To assess the degree of contamination of the soils and stream sediments, contamination indices were computed and the potential ecological risk to the area was evaluated. A correlation analysis revealed PHE associations as strongly influenced by lithology and Au mineralisation in the Kadoma setting. Assessment of multi-element contamination using the pollution load index revealed significant contamination in 52% of the soil sample sites and 38% of the sediment sample sites in Kadoma. The results indicate that As, Cr, Mo, and Sb are the main contaminant PHEs in the Kadoma site. Potential ecological risk ranged from moderate to very high at 71% of soil sample locations and 53% of sediment locations and the key contributors were Sb, As, and Hg. At the Hurungwe site, Cr and Mo were found to be key contaminants with a low potential ecological risk for all samples. This study demonstrates the successful application of geochemical indices in evaluating the degree of single and multi-element contamination as the first step toward a human health risk assessment in mining environments. It is expected that these results would assist municipal authorities in their effort to formulate credible mitigative measures to protect the health of nearby residents and surrounding ecosystems and make an informed decision regarding land use planning and post-mining rehabilitation of contaminated land at mining centres.

**Keywords:** potentially harmful elements, spatial analysis, potential ecological risk, Zimbabwe, geochemical indices

## 1 INTRODUCTION

Geochemical mapping is useful in identifying regions of unusually high concentrations of chemical elements on or below the Earth's surface and is applied in both mineral exploration and environmental studies. Anomalous levels of an element can signify a potential mineral deposit or the impact of anthropogenic contamination (Salomão et al., 2021). Some of these chemical elements can be found at potentially toxic levels, raising concerns for human health. The potentially harmful elements (PHEs) are derived from rocks, soils, natural waters and the atmosphere; these are environmental media, where their content varies depending on natural biogeochemical processes and anthropogenic perturbations in which they are involved throughout their environmental cycling. Soils, especially those found at or near the metalliferous mines and metal smelters, are often found to be highly contaminated with PHEs such as As, Cd, Cr, Cu, Pb, Ni, and Zn (Boularbah et al., 2006; Qu et al., 2012; Weissmannová et al., 2019). Over the years surface soils and stream sediments become contaminated through the effect of improper disposal of mining and other industrial wastes. The net result of such large-scale pollution is a heavy toll on human health as PHEs are transferrable through various pathways into the human food chain (Davies, 2013; Finkelman et al., 2018). It is thus becoming increasingly necessary for studies to be conducted to evaluate the level of pollution by PHEs from both geogenic and anthropogenic sources and to quantify the risk they pose to human health.

The mining areas in Zimbabwe are no exception to the accumulation of PHEs. A study on the challenges posed by the widely distributed mine tailings within the Zimbabwe mining landscape revealed that Sb, Cu, Co, Zn, Ni, As, and Pb may be high pollutants in most areas in the vicinity of these mine wastes (Meck, 2013). Other studies in Zimbabwe have charted the dispersion of PHEs due to mining and reiterated the negative impacts this has on the environment (Ashton et al., 2001; Lupankwa et al., 2004; Tunhuma et al., 2004; Ravengai et al., 2005). However, there is a paucity of studies in Zimbabwe that have used geochemical indices or conducted evaluations of the potential ecological risk posed by anomalous concentrations of PHEs in soils or stream sediments. Examples of studies that have investigated human health impacts associated with geogenic or mining-related PHEs in Zimbabwe include those on the impact on local communities of anomalous levels of fluoride in drinking water leading to dental fluorosis (Mamuse and Watkins, 2016); the health impacts of the continued use of mercury (Hg) in gold (Au) processing by artisanal miners in Zimbabwe (Steckling et al., 2014; Becker et al., 2020; Bose-O'Reilly et al., 2020; Mambrey et al., 2020) and investigation of the impacts of As on human health at Cam and Motor mine (Mosso, 1989). Other studies conducted focused on the health risk of PHEs concerning human exposure through dietary intake (e.g., fish, animal products, crops or vegetables) (Muchuweti et al., 2006; Nharingo et al., 2015; Kanda et al., 2020). However, none of these studies have included an evaluation of geochemical signatures of the study areas nor the individual or combined potential ecological risk

posed by the PHEs in the soils and stream sediments. The link between geology, soil and biota (humans included) is an important one as rocks and minerals sourced from the Earth's crust are the basic "building blocks" of all life forms providing the major, minor and trace elements that are needed for health in humans and animals (Dissanayake, 2005; Finkelman and Centeno, 2020). PHE contaminants can affect human health through a variety of ways such as primary consumption (e.g., drinking water), or elemental biomagnification through the food chain, or through direct skin contact, inhalation (of dust and aerosols), or intended (geophagy), or unintended (ingestion of dirt or soil by children). Despite the challenges associated with identifying the aetiology, there are diseases and conditions such as tooth decay, dental and skeletal fluorosis, goitre and other iodine deficiency disorders, keratosis, Keshan disease, asbestosis, pneumoconiosis, silicosis, cardio-vascular diseases, renal failure, mesothelioma and a variety of other cancers that have been linked to either high levels of potentially toxic elements or non-optimal levels of certain essential elements and minerals that are found naturally occurring in the geological environment (Centeno et al., 2016; Finkelman et al., 2018). The current study aims to provide a model on how to fill this void in evaluating gold mining environments, which Zimbabwe is well endowed with and whose exploration and mining have been the country's key economic drivers for centuries.

Geochemical indices are ratios of elements in an environment of concern and background reference concentrations, and have been used to evaluate soil physical and chemical development over geologic time (Mikkonen et al., 2016; Heidari et al., 2022). In environmental studies, the most commonly used soil contamination assessment methods can be assigned to two groups, namely quantitative and qualitative (Wu et al., 2014). The quantitative methods involve the evaluation of each PHE concentration in the site under investigation against a reference value. This reference value is also known as a geochemical background, baseline, or "normal" value and has been determined through investigations on the composition of the Earth's crust (e.g., Turekian and Wedepohl, 1961; Taylor and McLennan, 1985; Rudnick and Gao, 2003) or by using various analytical and or statistical techniques at regional and national scales (Ander et al., 2013; Zhao et al., 2013; Hao et al., 2014; Kicińska and Turek, 2017). Examples of quantitative methods include geo-accumulation index ( $I_{geo}$ ) and contamination factor (CF) which are singles indices. Complex indices can also be derived from them to assess the overall degree of contamination of the soil at a site. The quantitative contamination indices allow the comparative evaluation of contamination within study sites and against studies conducted by other researchers. However, due to the variations in the reference levels used, to determine credible thresholds for the different contamination categories it is often prudent to use the indices in combination to get a balanced interpretation of the extent and degree of contamination (Wu et al., 2014; Niu et al., 2021). Other methods involve multivariate analyses that employ various assumptions on the data distribution (normal or non-normal)



of the variables under study and these include amongst others principal component analysis (PCA), correlation analysis and cluster analysis (Wu et al., 2014). Though these methods have been referred to as qualitative methods Wu et al. (2014) due to the generation of descriptive groupings, they still depend on quantitative data and are often used to investigate the correlations among contaminants and contaminant sources (Weissmannová et al., 2019; Rinklebe et al., 2019; Niu et al., 2021).

The analysis of PHE concentrations in soils can be used in generating an ecological risk index which is a quantitative measure of the ecological risk of a contaminant in a given system, thus, it constitutes a useful tool in pollution control (Hakanson, 1980; US EPA, 2002; Kumar et al., 2020). The behaviour of PHEs that enter the body (whether toxic or beneficial) is determined by several geochemical and biochemical factors engendering their (PHEs) transfer right from the source (e.g., soil particle size distribution, pH and organic matter content) *via* various migration pathways (mobility characteristics) into the body (e.g., chemical form and bioavailability), where they (PHEs) are involved in various metabolic processes (Antoniadis et al., 2019; Rinklebe et al., 2019). Tracking the fate of PHEs from their release, movement through the environment and their uptake and measurement as well as monitoring their levels in plants and other organisms is a mammoth task. Soil contamination indices have therefore been used successfully in evaluating the degree of contamination of a site, forming the basis for human health risk assessments associated with soil exposure (Liu et al., 2017; Proshad et al., 2018; Weissmannová et al., 2019; Rinklebe et al., 2019; Yu et al., 2021).

The main aim of this study was to evaluate the usefulness of geochemical indices in assessing the extent of single and multi-element contamination by PHEs at mining centres in the Sanyati Catchment and to ascertain if the overall degree of contamination by computing a Pollution Load Index (PLI). Through determination of an ecological risk index the study site was also assessed for PHEs that pose a threat to environmental and public health and correlation analysis used to identify potential PHE sources.

## 2 METHODOLOGY

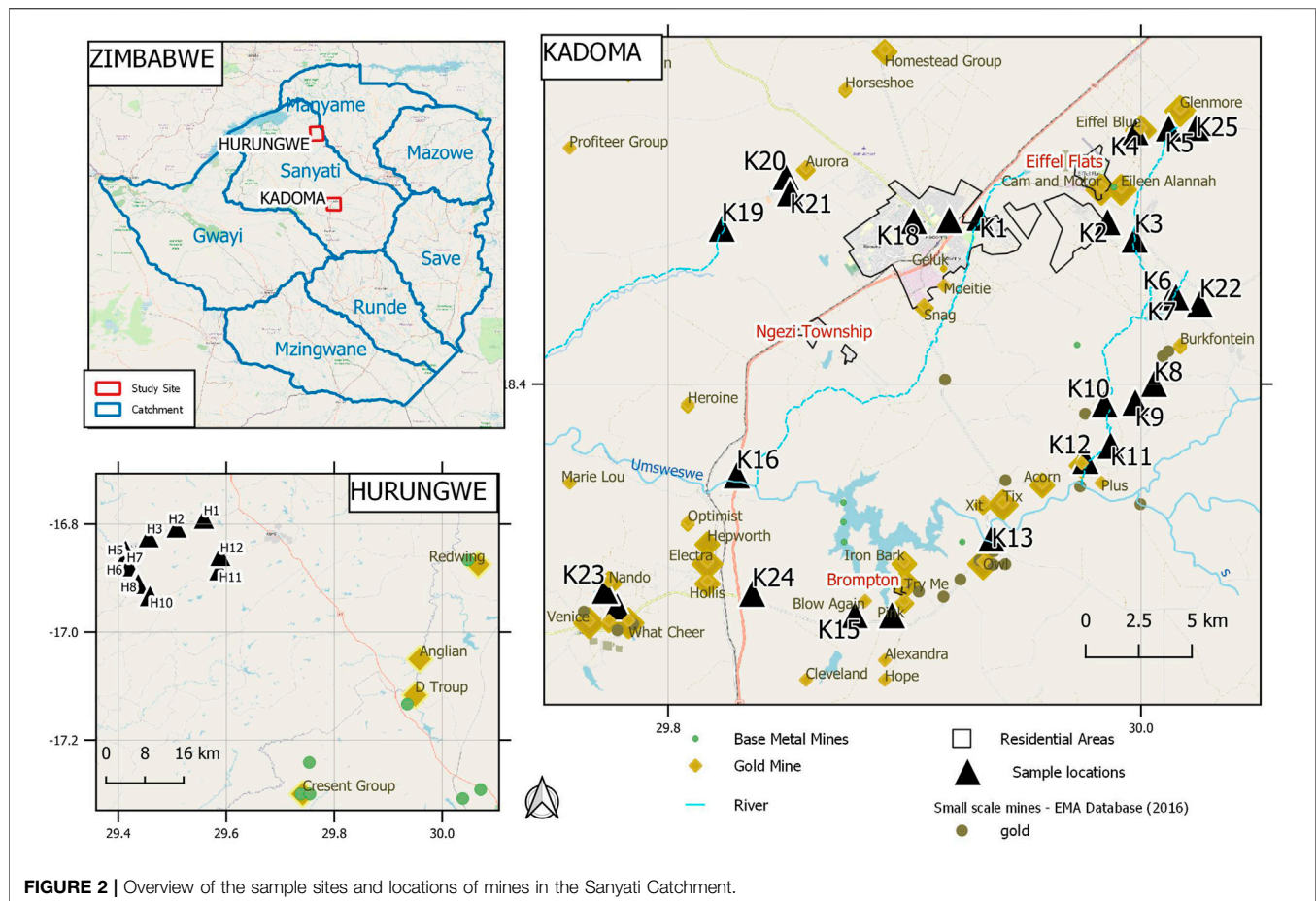
### 2.1 Study Sites

The Sanyati Catchment is one of the seven river catchments in Zimbabwe covering an area of approximately 7,300 km<sup>2</sup> and administratively straddles three provinces, Mashonaland West, Midlands and Mashonaland East. The catchment is host to some of the largest, richest and most productive gold mines hosted in the oldest historic Archaean greenstone belts, i.e., key gold mining zones of the country (Ashton et al., 2001; Ravengai et al., 2005). The term “greenstone belt” as used here describes deformed and metamorphosed exceptionally thick volcano-sedimentary successions, generally enveloped by granitic and gneissic rocks, and confined to the Archaean, which ranges in

age from the Eoarchaeon (>3,600 Ma) to the Neoarchaeon (ca. 2,500 Ma) (Anhaeusser, 2014) (**Figure 1**). Greenstone belts are known to be extremely varied in their lithological composition, including a diverse range of volcanic, plutonic and sedimentary units that are structurally complex having undergone multiple phases of deformation, metamorphism and metasomatic alteration as well as successive intrusions (Anhaeusser, 2014). These ultra-mafic to mafic and volcanic lithological units are associated with varied mineralisation that includes the occurrences of Cr, Ni/Cu, chrysotile asbestos, Au/Ag, ores of Fe, magnesite, talc and barite, Cu-Zn (+/- Cu, Sb, Hg, Ag, As, W), as well as lesser amounts of pyrite—pyrrhotite and corundum. The large Cam and Motor mine in Kadoma was historically both a Au and Sb mine and other Sb deposits are found within the Kadoma area. The sedimentary units also found here, host Fe ore, barite, Au, and limestone while the granites are associated with pegmatites and may host Sn, corundum, emeralds, beryl, mica, bismuth, Mo and Ta-Nb (Anhaeusser, 2014).

The catchment comprises 10 sub-catchments and is classified as semi-arid receiving approximately 635 mm of rainfall per annum over a wet summer season that runs from November to April and is characterized by annual mean maximum and minimum temperatures of approximate 28–33°C and 19–9°C in November and June respectively (Davis et al., 2014; Mashizha et al., 2017; Chanza and Gundu-Jakarasi, 2020). The key economic activities within the catchment include mining, mineral processing and agriculture. The Major rivers that drain into Sanyati River are Munyati, Muzveze, Sebakwe, Kwekwe and Mupfure. The major towns within this catchment are Kwekwe, Kadoma, Chegutu, Gokwe, Chivhu and Mvuma. The two study sites selected for sampling are within two districts of Hurungwe and Kadoma (**Figure 2**).

All the mining activities at the Kadoma site (KAD) are situated within commercial and resettlement agricultural areas which have a tradition of being the leading producers of cotton and significant quantities of maize (Shoko and Veiga, 2004). Thriving small and medium scale horticultural activities are also hosted within these mining areas making use of the highly fertile soils and floodplains. The second site examined in this study is in the Hurungwe (HUR) District whose geological location is within the Proterozoic Magondi Belt and lies southeast of the town of Karoi. This site spans an area of approximately 24 km by 18 km, is characterised by granitic-gneiss lithology (**Figure 1**), and has been minimally impacted by large-scale mining and related activities since it is virtually bereft of economically viable sulphide gold ore deposits as found in KAD. The granites of HUR have been identified as hosts of pegmatites and much like those of greenstone belts and as such some beryl deposits have been identified in HUR. The closest gold and base metal mines at the HUR site are located beyond a 40 km radius from the study site making it a suitable control for this study concerning the absence of ore rock mining-related activities. There is however informal alluvial gold mining in HUR, with key informal gold



**FIGURE 2** | Overview of the sample sites and locations of mines in the Sanyati Catchment.

panning sites along the Sanyati River as it passes through the town of Magunje (Manjengwa et al., 2012).

## 2.2 Study Design, Sample Collection and Chemical Analysis

The evaluation of the degree of soil contamination by the PHEs (As, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, V, and Zn) was done by: 1) systematically collecting soil and sediment samples and analysing their PHE content, 2) calculating soil contamination (geochemical) indices, 3) spatially assessing the pollution load index 4) computing an ecological risk index of the study area and 5) evaluating the possible sources of the PHEs through a correlation analysis.

Stream catchments were selected at each of the sites, HUR and KAD using geological and topographic maps in QGIS to ensure representation of the diversity of lithological units of the sites. Actual sample locations were confirmed using a handheld Garmin e-Trex 10 GPS. Sample sites are displayed in **Figure 2**. Soil samples were taken using a hand auger (2.5 cm in diameter), each composite (approximately 1 kg) per sample location comprised of only the upper soil horizons (A and B; from a depth of 0 to approximately 25 cm) representing the root zone, and therefore the uptake zone for nutrients and PHEs by plants. Material from the organic-rich layers, where present, was

excluded. Stream sediment samples were collected from areas of active sedimentation along the river channel at a distance from the edge to minimise contamination and bulked to one composite sample (approximately 1 kg). The soil and stream sediment samples were disaggregated and wet sieved (2 mm) at the Geochemical Laboratory of the Geology Department at the University of Zimbabwe. The soil samples were then air-dried and sent to the Performance Laboratories at Ruwa, Zimbabwe, where they were pulverised into a fine powder. The samples were then packed into small 10–15 g packets before sending for analysis. Sampling campaigns were conducted during the period November 2015 to March 2017 ensuring repeat samples were collected at each site and gathering a total of 174 soil and stream sediment samples from 58 locations in KAD and HUR. Multiple sampling campaigns were considered a necessity for monitoring the spatial and temporal (seasonal) variation of the pollution plumes, as such knowledge would aid in the formulation of mitigative measures.

Further processing and analyses of samples took place at the Bureau Veritas Minerals (BVM) Laboratories in Canada. The prepared samples were digested with a modified Aqua Regia solution of equal parts concentrated hydrochloric acid (HCl), nitric acid (HNO<sub>3</sub>) and deionized water (DI H<sub>2</sub>O) for 1 hour on a heating block or hot water bath. Each sample was made up to volume with dilute HCl and analysed for 53 elements by the

ICP-MS method for soils and stream sediments. The detection limits for the elements considered in this paper were: 1% for Fe; 0.01% for Al; 1 ppm for Mn; 2 ppm for V; 0.5 ppm for Ba and Cr; 0.1 ppm for As, Be, Co, Ni, and Zn; 0.02 ppm for Sb; 0.01 ppm for Cd, Cu, Mo, Pb; and 5 ppb for Hg. For quality control purposes and provision of an effective framework for interpreting the ensuing geochemical datasets, duplicate samples were randomly inserted in the laboratory and blind duplicate samples were also included with each batch sent. Method blanks and certified reference materials, STD DS10 and STD OREAS45EA (for soils and stream sediments), were determined intermittently during the analyses of the samples to monitor background or reagent contamination and interferences. The relative standard deviation (RSD) for a combination of lab duplicates and blind duplicates in the soil and sediment samples varied from 0.3% to 10% for all PHEs analysed with Cd recording a RSD of 20%–23%. The standard errors for the measurements in the soil samples were in the range of 0.01–5.

## 2.3 Data Processing and Statistical Analysis

Data cleaning was conducted in Microsoft Excel and analysis was performed in R (RStudio Team, 2021). Initial data cleaning involved handling data falling below the limit of detection (LOD) or left-censored data (See, e.g., Canales et al., 2018). Left-censored values were replaced using the simple method of substituting with LOD/2, a well-established method in geochemical studies (See: de Caritat and Mann, 2018). Standard statistical procedures followed in this study involved the calculation of several descriptive statistical parameters, arithmetic mean, standard deviation (SD), minimum (Min), median (Med) and maximum (Max), construction of graphs (box plots, scatter plots and quantile-quantile (Q-Q) plots). The data for this study were evaluated for normality and were found not to follow normal distribution owing to a large number of outliers. As the outliers were deemed important to this study they were not removed from the data for the bulk of the analysis and instead robust non-parametric statistical techniques were utilised (Schober and Schwarte, 2018; Statistics Solutions, 2019; Sorensen et al., 2021). To assess the significance of the differences in PHE levels in the two geological terranes, the results also were subjected to the Mann-Whitney-Wilcoxon Test. The degree of association between PHE levels within each site was evaluated with the Spearman's rank correlation test.

## 2.4 Soil Contamination Assessment Methods

Evaluation of the contamination of the soils and stream sediments was performed using a select set of geochemical indices, namely:  $I_{geo}$ , CF and the Tomlinson Pollution Load Index (PLI) (Tomlinson et al., 1980; Mortazavi et al., 2017; Tchounwou et al., 2019; Niu et al., 2021). In this study upper continental crust values as determined by Rudnick and Gao (2003) were used as the geochemical background values and in mg/kg these are: As: 4.80; Ba: 628, Be: 2.1; Cd: 0.09, Co: 17.3, Cr: 92, Cu: 28, Fe: 50,400, Hg: 0.05, Mn: 1,000, Mo: 1.1, Ni: 47, Pb:

17, Sb: 0.4, V: 97, and Zn: 67. For comparison, the results of the low-density regional geochemical survey as determined by Zhao et al. (2013) were also used in the computation of CF as background reference values for Zimbabwe. These in mg/kg are As: 4.22; Ba: 533, Be: 0.99; Cd: 0.07, Co: 10.48, Cr: 529, Cu: 16.82, Fe: 27,500, Hg: 0.02, Mn: 392.7, Mo: 0.41, Ni: 41.52, Pb: 17.94, Sb: 0.52, V: 62.1, and Zn: 26.1.

The  $I_{geo}$  was proposed by Müller (1969) to determine metal contamination in sediments by comparing current concentrations with pre-industrial levels and has since been used in several environmental pollution studies (Zhang et al., 2013; Meng et al., 2020; Niu et al., 2021). In the absence of pre-industrial values for the current study, continental crust values were utilized in  $I_{geo}$  calculation (Rahman et al., 2012). The  $I_{geo}$  was calculated as in Eq. 1 for which Müller (1969) distinguished seven classes of  $I_{geo}$  (0–6), as provided in Table 1.

The CF (Eq. 2) represents element input from anthropogenic sources. It relates the contamination of elements in the soil and sediment with geochemical background values (Balkhair, 2016; Kicińska and Turek, 2017; Rinklebe et al., 2019; Kumar et al., 2020).

$$I_{geo} = \log_2 \frac{C_n}{1.5 * B_n} \quad (1)$$

$$CF = C_n / B_n \quad (2)$$

For the Eqs 1, 2  $C_n$  is the concentration of an element in the sample ( $n$ );  $B_n$  is the concentration of the same element in the background and a correction factor of 1.5 accounts for the variability of the background value in calculating  $I_{geo}$  (Kicińska and Turek, 2017).

The Tomlinson Pollution Load Index (PLI) is one overall contamination index of a sample and has been used often to assess the quality of soil in terms of contamination (Kicińska and Turek, 2017; Proshad et al., 2018; Rinklebe et al., 2019). The PLI is the  $n$ th root (depending on the number of potential contaminants taken into consideration) of the product of CF (calculated using Eq. 4). If  $PLI > 1$ , samples are considered significantly contaminated (Rinklebe et al., 2019).

$$PLI = (CF_{s,1} \times CF_{s,2} \times \dots \times CF_{s,n})^{1/n} \quad (3)$$

Where  $CF_{s,1} \times CF_{s,2}, CF_{s,n}$  are the CF of the elements 1, 2 .... $n$  (Rinklebe et al., 2019). A PLI value equal to zero indicates non-polluted; a value of 1 indicates the presence of only a baseline level of pollutants and values above 1 indicate progressive deterioration due to trace element contamination (Rashed, 2010 as cited in Proshad et al., 2018). In this study, PLI was used in generating an interpolated map in QGIS to allow spatial interpretation of the impacts of the multi-element contamination.

The contamination indices computed were used to evaluate the degree of contamination in the study sites and to compare the present study results with those of other national and international investigations. For ease of comparison of the level of enrichment or degree of contamination computed through each index, the values were categorized into five classes (Table 1) as proposed in Wu et al. (2014) with some adaptations using other classifications (Barbieri, 2016).

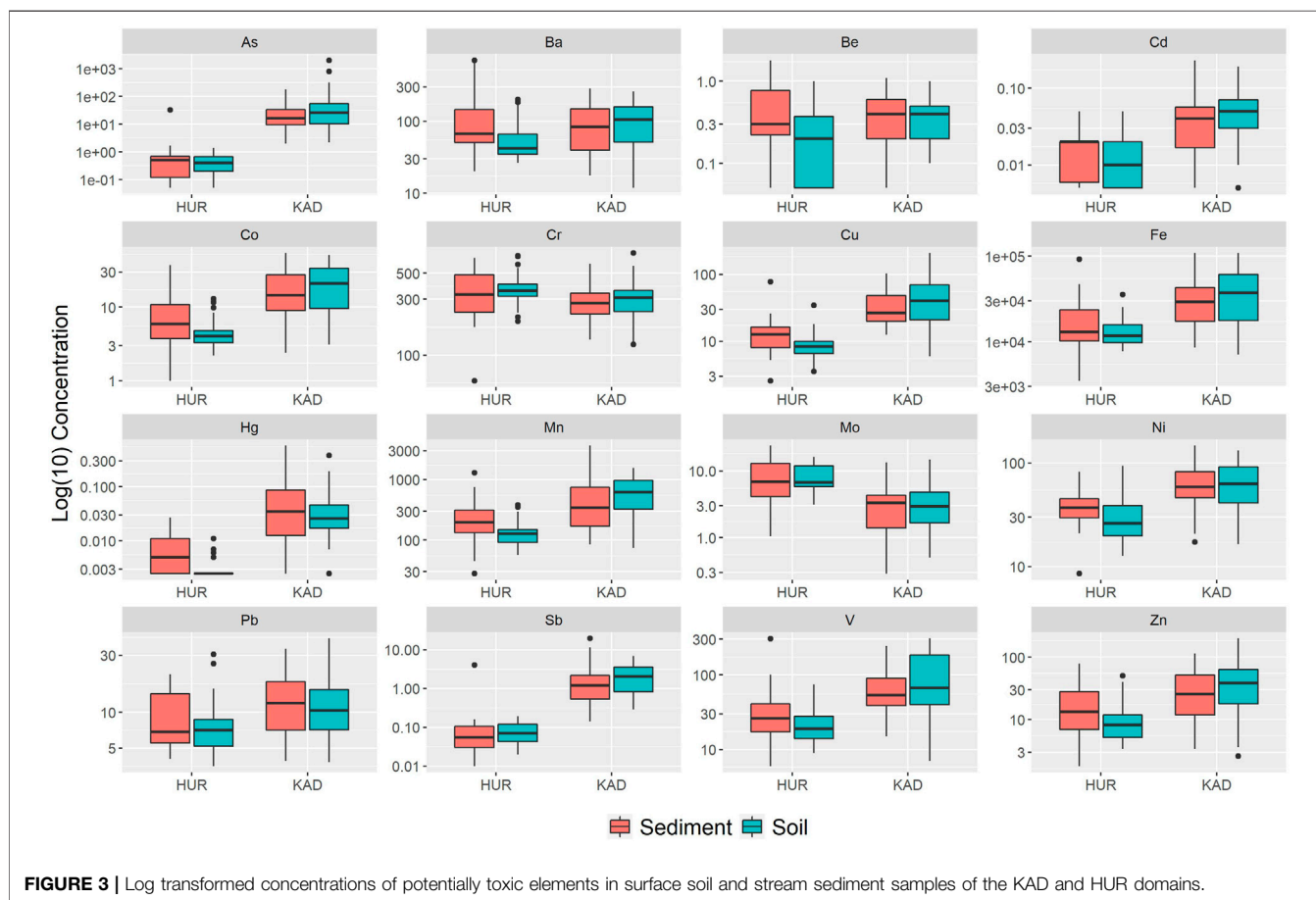
**TABLE 1 |** Classification of contamination levels based on calculated geochemical indices [Adapted from Barbieri (2016), Wu et al. (2014)].

Index class	$I_{geo}$	CF	Contamination/enrichment level
1	$<0$	$<1$	Uncontaminated/deficient to minimal enrichment
2	$0 \leq I_{geo} < 1$	$1 \leq CF < 3$	Moderately contaminated/moderate enrichment
3	$1 \leq I_{geo} < 3$	$3 \geq CF < 6$	Considerably contaminated/significant enrichment
4	$3 \leq I_{geo} < 5$	$CF \geq 6$	Highly contaminated/very high enrichment
5	$5 \leq I_{geo}$	$12 < CF$	Extremely contaminated/Extremely high enrichment

Müller (1969), Barbieri (2016), Rinkebe et al. (2019).

**TABLE 2 |** Terminology for the interpretation of Ecological risk factor ( $E_r^i$ ) and potential risk index (RI) values (Zhou et al., 2020).

Ecological risk factor	Potential ecological risk index
$E_r^i < 40$ —low potential ecological risk	RI < 150—low ecological risk
$40 \leq E_r^i < 80$ —moderate potential ecological risk	$150 \leq RI < 300$ —moderate ecological risk
$80 \leq E_r^i < 160$ —considerable potential ecological risk	$300 \leq RI < 600$ —considerable ecological risk
$160 \leq E_r^i < 320$ —high potential ecological risk	RI > 600—very high ecological risk
$E_r^i \geq 320$ —very high potential ecological risk	



**FIGURE 3 |** Log transformed concentrations of potentially toxic elements in surface soil and stream sediment samples of the KAD and HUR domains.

Classification thresholds indicated on the boxplots are the upper boundaries of the “Uncontaminated”, “Considerably contaminated” and “Extremely contaminated” classes.

### 2.4.1 Potential Ecological Risk Evaluation

The quantitative expression of the potential ecological risk posed by an individual element in a sample, defined by Hakanson

**TABLE 3 |** Descriptive statistics for PHE concentrations (mg/kg) in stream sediments and soil samples from the two domains of Hurungwe (HUR) and Kadoma (KAD) compared against Zimbabwe Levels (Zhao et al., 2013) Screening Levels for Residential Soil (SL) and Freshwater sediments Toxicity Reference Values (TRV) (US EPA, 1999).

Sediment								Soil								Zim (2013)	US EPA (2021)	
Site	Element	n	Min	Max	Median	Mean	SD	Site	Element	n	Min	Max	Median	Mean	SD	Mean	Res SL	TRV (Seds)
HUR	As	34	0.05	32.40	0.50	1.42	5.49	HUR	As	46	0.05	1.40	0.40	0.49	0.36	4.22	0.68	6.0
KAD	As	40	2.00	178.40	16.30	35.65	45.83	KAD	As	53	2.20	2000.90	26.30	91.67	291.80			
HUR	Ba	34	20.20	705.10	67.20	127.72	158.60	HUR	Ba	46	26.30	199.90	42.00	60.31	43.30	533	1,500	20
KAD	Ba	40	17.70	287.80	84.80	98.62	67.78	KAD	Ba	53	11.80	259.60	105.10	110.71	63.71			
HUR	Be	34	0.05	1.80	0.30	0.58	0.50	HUR	Be	46	0.05	1.00	0.20	0.26	0.23	0.99	16	—
KAD	Be	40	0.05	1.10	0.40	0.43	0.26	KAD	Be	53	0.10	1.00	0.40	0.41	0.20			
HUR	Cd	34	0.01	0.05	0.02	0.02	0.01	HUR	Cd	46	0.01	0.05	0.01	0.02	0.01	0.07	7.1	0.6
KAD	Cd	40	0.01	0.23	0.04	0.06	0.06	KAD	Cd	53	0.01	0.19	0.05	0.06	0.04			
HUR	Co	34	1.00	37.20	5.90	7.90	6.92	HUR	Co	46	2.20	13.00	4.05	4.72	2.52	10.48	2.3	—
KAD	Co	40	2.40	54.50	14.60	19.25	13.53	KAD	Co	53	3.10	51.10	20.90	22.40	13.33			
HUR	Cr	34	60.50	676.90	327.65	364.29	169.62	HUR	Cr	46	194.60	705.40	354.60	378.97	109.63	529	—	26
KAD	Cr	40	135.70	601.30	276.40	296.32	108.53	KAD	Cr	53	123.20	744.20	308.50	319.17	126.64			
HUR	Cu	34	2.57	77.84	12.66	14.51	12.38	HUR	Cu	46	3.52	34.58	8.32	9.22	5.09	16.82	310	16
KAD	Cu	40	12.48	102.94	26.33	37.73	25.66	KAD	Cu	53	5.95	208.56	40.39	50.45	37.33			
HUR	Hg	34	ND	0.03	0.01	0.01	0.01	HUR	Hg	46	0.00	0.01	0.00	0.00	0.00	0.02	1.1	0.2 <sup>a</sup>
KAD	Hg	40	ND	0.57	0.04	0.10	0.15	KAD	Hg	53	0.00	0.38	0.03	0.05	0.07			
HUR	Mn	34	28.00	1302.00	197.50	266.26	249.39	HUR	Mn	46	57.00	380.00	128.00	148.76	87.20	392.7	180	—
KAD	Mn	40	85.00	3645.00	344.50	577.80	666.40	KAD	Mn	53	74.00	1571.00	621.00	656.94	399.57			
HUR	Mo	34	1.05	23.93	6.92	8.24	5.35	HUR	Mo	46	3.12	16.39	6.76	8.25	3.89	0.41	39	—
KAD	Mo	40	0.29	13.49	3.33	3.83	3.14	KAD	Mo	53	0.50	14.83	2.93	3.89	3.07			
HUR	Ni	34	8.60	82.20	37.00	41.57	19.00	HUR	Ni	46	12.70	93.80	26.15	32.31	17.73	41.52	0.76	16
KAD	Ni	40	17.20	146.50	58.85	64.97	28.84	KAD	Ni	53	16.50	131.50	62.90	65.62	29.03			
HUR	Pb	34	4.05	20.76	6.83	9.44	5.09	HUR	Pb	46	3.54	30.54	7.05	8.23	5.08	17.94		31
KAD	Pb	40	3.91	34.04	11.93	13.93	8.66	KAD	Pb	53	3.82	41.46	10.37	12.09	6.85			
HUR	Sb	34	0.01	4.00	0.06	0.18	0.68	HUR	Sb	46	0.02	0.19	0.07	0.08	0.04	0.52	3.1	64.0
KAD	Sb	40	0.14	19.49	1.20	2.69	3.95	KAD	Sb	53	0.29	6.90	2.02	2.36	1.64			
HUR	V	34	6.00	304.00	26.00	39.29	50.99	HUR	V	46	9.00	74.00	19.00	24.52	15.66	62.1	39	—
KAD	V	40	15.00	244.00	53.50	78.20	59.12	KAD	V	53	7.00	307.00	67.00	110.36	90.98			
HUR	Zn	34	1.80	78.20	13.65	22.27	22.44	HUR	Zn	46	3.40	50.50	8.20	11.05	9.19	26.1	2,300	110
KAD	Zn	40	3.40	113.30	25.55	34.04	27.69	KAD	Zn	53	2.60	199.40	38.40	42.57	33.34			

<sup>a</sup>Values used are for methyl mercury. ND = below the detection limit.



**TABLE 4** | Summary of the *p*-values obtained from Mann-Whitney-Wilcoxon (MWW) Test used to verify the similarities in the distribution of the PHEs in HUR and KAD.

Sediment						Soil					
Element	W	<i>p</i>	Element	W	<i>p</i>	Element	W	<i>p</i>	Element	W	<i>p</i>
As	3	<0.001	Hg	22.5	0.003	As	0	0.000	Hg	0	<0.001
Ba	92	0.434	Mn	63	0.467	Ba	87	0.152	Mn	14	<0.001
Be	102	0.179	Mo	125	0.008	Be	70	0.038	Mo	226	<0.001
Cd	51	0.162	Ni	45	0.085	Cd	40	0.001	Ni	39	0.001
Co	35.5	0.025	Pb	52	0.183	Co	13	<0.001	Pb	81	0.096
Cr	114	0.044	Sb	6.5	<0.001	Cr	192	0.013	Sb	0	<0.001
Cu	18	0.001	V	33	0.017	Cu	13	<0.001	V	29	<0.001
Fe	44	0.075	Zn	61	0.403	Fe	26	<0.001	Zn	47	0.002

Null Hypothesis: "No significant difference between Samples from HUR and KAD." The *p*-values below 0.05 imply rejecting the null hypothesis.

(1980) as an ecological risk factor (ER also expressed in the equation as  $E_r^i$  being the ecological risk factor for each PHE). The ER calculated from the CF and an overall potential ecological risk index (RI) of an area is the sum of the ER values as shown in the Eqs 4, 5 (Hakanson, 1980; Kumar et al., 2020; Monged et al., 2020).

$$E_r^i = T_r^i \times CF^i \quad (4)$$

$$RI = \sum_{i=1}^n T_r^i \times CF^i \quad (5)$$

In these Eq. 4 and Eq. 5,  $T_r^i$  represents the toxic response factor of a given substance and CF its contamination factor. Hakanson (1980), developed the toxic response factor on the basis that the potential toxicological effect of a substance is proportional to the abundance of the said element in nature, and by integrating mutual interactions, toxicity, sedimentation character and sensitivity of aquatic systems more complex information is gleaned about potential transport of toxic elements to humans and the aquatic system (Sany et al., 2012). The proposed exposure pathway in this model is from the contamination of water—sediment—biota—fish—man (Sany et al., 2012). In the current study the ER and RI were calculated for those PHEs for which toxic response factors have been established in previous studies on freshwater river basins and these are: Hg = 40, Cd = 30, As = 10, Pb = 5, Co = 5, Cu = 5, Ni = 5, Cr = 2, V = 2, Zn = 1, Mo = 1, and Mn = 1 (Li et al., 2018; Monged et al., 2020; Wang et al., 2020; Zhou et al., 2020; Song et al., 2021). The classification terminology for interpretation is given in Table 2.

### 3 RESULTS

#### 3.1 Potentially Harmful Element Distribution in Kadoma and Hurungwe Soils and Stream Sediments

Statistical summaries and concentration levels of the PHEs considered in this study and of concern regarding human health are presented in Figure 3. The median values for total element concentrations were higher for all PHEs assessed on both KAD stream sediment and soil samples than in HUR except for Cr and Mo. Total element concentration was highest

for As in KAD soils—reaching a maximum of 2,000.9 mg/kg, (Table 3). In the KAD sediments As reached a maximum of 178.4 mg/kg. In the KAD sediments, the highest total concentration was obtained for Mn at 3,645 mg/kg. The Mann-Whitney-Wilcoxon test showed that there is no significant difference between the two sites of KAD and HUR for the elements Ba, Be, Cd, Cr, Fe, Mn, Ni, Pb, and Zn in stream sediments ( $p > 0.05$ ), while for the soils it was only Ba and Pb levels that were not significantly different (Table 4). The local geochemical signatures which characterise the KAD soils were markedly influenced by the diverse lithology and mineralisation of the greenstone belt described earlier and therefore could be considered as deriving from distinctly different terranes when compared to the granitic-gneiss lithology of HUR. Contaminant transport through river channels, erosion and dispersion or translocation of surface material through the river networks were evidenced by the greater similarities of PHE content resulting in 56% of the sediment samples in KAD and HUR not showing significant differences in their PHE levels, compared to 12.5% of soil samples.

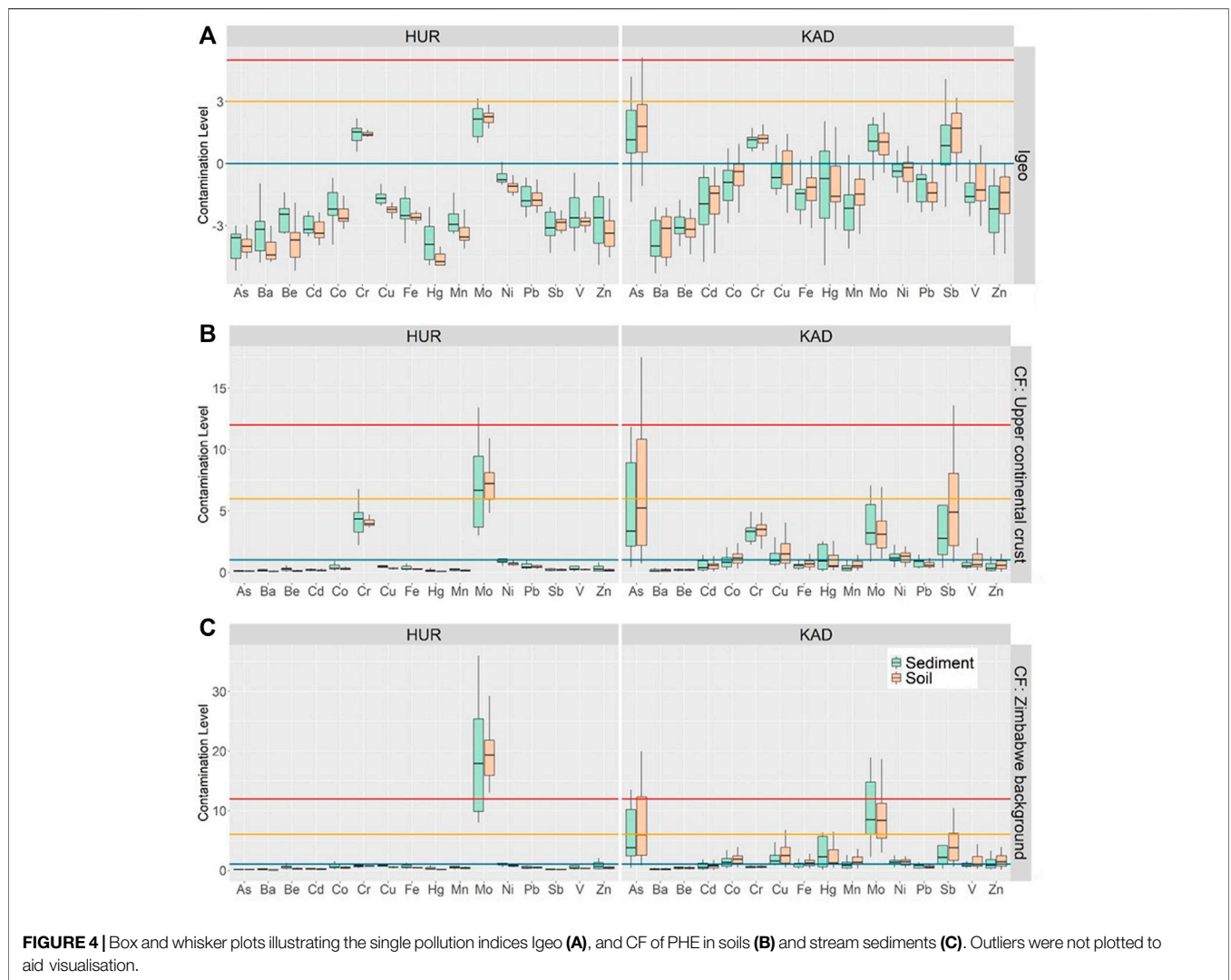
#### 3.2 Evaluation of Potentially Harmful Elements Concentration Against National Averages and Regional Screening Levels

The average PHE concentrations in soils and sediments were evaluated against results from an earlier national geochemical study (Zhao et al., 2013). The current results show a similar pattern to those of the national geochemical mapping of Zimbabwe where high average concentration values in KAD are observed for those PHEs that are ore-forming elements, i.e., Cr, Ni, and Cu as well as those having potential for ore-formation, such as Pb, Zn, Hg, Sb, and Mo. The sediment samples gave values for the elements Mo, As, Sb, Hg, Cu, Co, Ni, and Mn that were above the national geochemical averages. In the HUR soil and sediment samples, only Mo exceeded the national average levels (by at least 20 times), while all other PHEs fell below the means.

The PHE levels in soil samples were also evaluated against the USEPA Regional Screening Levels (SL) using the Target Hazard Quotient (THQ) of 0.1 (US EPA, 2021) provided in Table 3. Results show that average As, Ni, Co, Mn, and V exceeded the screening levels (SLs) by 13,300%, 874%, 265%,

**TABLE 5** | Comparison of average CF and  $I_{geo}$  values.

	Index	As	Ba	Be	Cd	Co	Cr	Cu	Fe	Hg	Mn	Mo	Ni	Pb	Sb	V	Zn
KAD sed	CF	6.47	0.14	0.19	0.52	0.96	3.25	1.20	1.16	1.59	0.48	3.58	1.26	0.75	6.15	0.72	0.44
	$I_{geo}$	1.13	-3.8	-3.23	-2.26	-1	1.07	-0.57	-1.17	-1.11	-2.32	0.99	-0.39	-1.19	1.07	-1.32	-2.29
	Max $I_{geo}$	4.2	-2.1	-1.75	-0.08	0.74	1.72	0.91	0.18	2.05	0.42	2.24	0.65	-0.07	4.08	0.5	-0.23
KAD soil	CF	17.34	0.17	0.18	0.58	1.23	3.44	1.63	1.52	0.99	0.62	3.57	1.31	0.68	5.36	1.05	0.59
	$I_{geo}$	1.87	-3.42	-3.16	-1.8	-0.58	1.12	-0.24	-1.14	-1.17	-1.56	1	-0.34	-1.3	1.45	-0.98	-1.84
	Max $I_{geo}$	7.05	-2.14	-2.17	-0.17	0.95	1.89	1.43	0.36	1.77	-0.07	2.47	0.86	0.21	3.18	0.9	0
HUR sed	CF	0.26	0.21	0.27	0.19	0.42	4.34	0.51	0.65	0.14	0.26	6.94	0.97	0.52	0.41	0.36	0.32
	$I_{geo}$	-3.78	-3.3	-2.76	-3.18	-2.08	1.45	-1.68	-2.25	-3.76	-2.83	2.04	-0.69	-1.65	-2.8	-2.4	-2.76
	Max $I_{geo}$	0.28	-0.96	-1.39	-2.3	-0.69	2.18	-0.48	-1.09	-2.10	-1.4	3.16	0.08	-0.68	0.76	-0.45	-0.89
HUR soil	CF	0.10	0.10	0.14	0.17	0.28	4.11	0.33	0.52	0.07	0.16	7.42	0.69	0.5	0.21	0.26	0.18
	$I_{geo}$	-3.99	-4.07	-3.76	-3.21	-2.49	1.45	-2.21	-2.48	-4.56	-3.37	2.26	-1.15	-1.68	-2.91	-2.66	-3.32
	Max $I_{geo}$	-2.96	-2.38	-1.89	-2.36	-1.54	1.81	-1.49	-1.54	-3.42	-2.21	2.86	-0.55	-0.77	-2.26	-1.24	-1.7



8,500%, and 183%, respectively for the KAD soil samples. An inspection of the maximum concentrations for these PHEs indicates a much higher exceedance of the SL in some localities. In HUR no soil samples exceeded the SL. For the

sediment samples, a comparison was made with the Freshwater Sediment Toxicity Reference Values (TRV) developed as a guideline for assessing sediment contamination (US EPA, 1999). The following elements

exceeded the TRV in KAD: Cr, As, Ni, and Cu by 1,038%, 494%, 306%, and 136%. In HUR Ba, Cr, and Ni levels exceeded the TRV by 535%, 1,300%, and 156%. Concentrations above SLs and TRV are an indication of levels that warrant further site-specific investigations for human health risks (US EPA, 2021).

### 3.3 Evaluation of Soil and Sediment Contamination

#### 3.3.1 Evaluation of the Geo-Accumulation Index

The results of the average and maximum  $I_{geo}$  computations presented in **Table 5** show distinct variations in the accumulation of PHEs in the two study sites. The  $I_{geo}$  values for the KAD soil and sediment samples reveal contamination levels of  $I_{geo} > 0$  for a bulk of the samples for As, Sb, Cr, and Mo, as well as a varying proportion of samples (the upper 25%–50%) for Cu and Hg. The high anomalous  $I_{geo}$  values for As and Sb in soils and sediments at certain locations were classified as highly to extremely contaminated. The PHEs Ba, Be, Cd, Co, Fe, Mn, Ni, Pb, V, and Zn were classified as uncontaminated (negative  $I_{geo}$ ) in the bulk of the KAD sediment and soil samples.

Average  $I_{geo}$  values at HUR revealed Mo and Cr as contaminants in the soil and sediment samples at moderately to considerably contaminated levels ranging from 0.57 to 3.16. The  $I_{geo}$  for the HUR sediments, however, show outlier values of Sb, As, and Ni at 0.76, 0.28, and 0.08 respectively, falling in the moderately contaminated group. The occurrence of outlier sediment samples with  $I_{geo} > 0$  values of Sb, As, and Ni that are not reflected in the soil samples suggests PHE translocation through the river system from upper portions of the HUR catchment. The translocation of PHEs from source has been reported in other studies to be in the order of hundreds of kilometres in rivers with high discharge flow rates, with changes in water chemistry aiding dissolution and precipitation and flooding events determining their eventual distribution in floodplains (Du Laing, 2009 as cited in Rinklebe et al., 2019).

#### 3.3.2 Evaluation of Contamination Factor

The KAD results (**Figure 4**) show CF values for As and Sb that range from considerably to extremely contaminated in both the soil and sediment samples when evaluated against the upper continental crust reference values (Rudnick and Gao, 2003). Moderate to considerable contamination of a large proportion of samples is also observed for Cr, Cu, Hg, Mo, Ni, and V. A small proportion (about 25%) of the samples also show moderate contamination of Cd, Fe, Mn, Pb, and Zn. The samples were classified as uncontaminated for the rest of the PHEs. A comparison was made of the CF values obtained using the geochemical background values as determined for Zimbabwe (Zhao et al., 2013). These local background values were deemed more representative of the local geochemical background levels. The CF values for the KAD samples for As were similar to those computed earlier with the Rudnick and Gao (2003) references, while Sb classification fell slightly below the “moderate to considerable contamination” group and extreme contamination was observed

for Mo in both soils and sediments. The CF value for Cr in all samples was in the uncontaminated class. This impact on CF values can be attributed to Zimbabwe’s vast mineralised regions particularly the auriferous geochemical domains and the Great Dyke with huge deposits of Cr and platinum group metals influencing the geochemical background values.

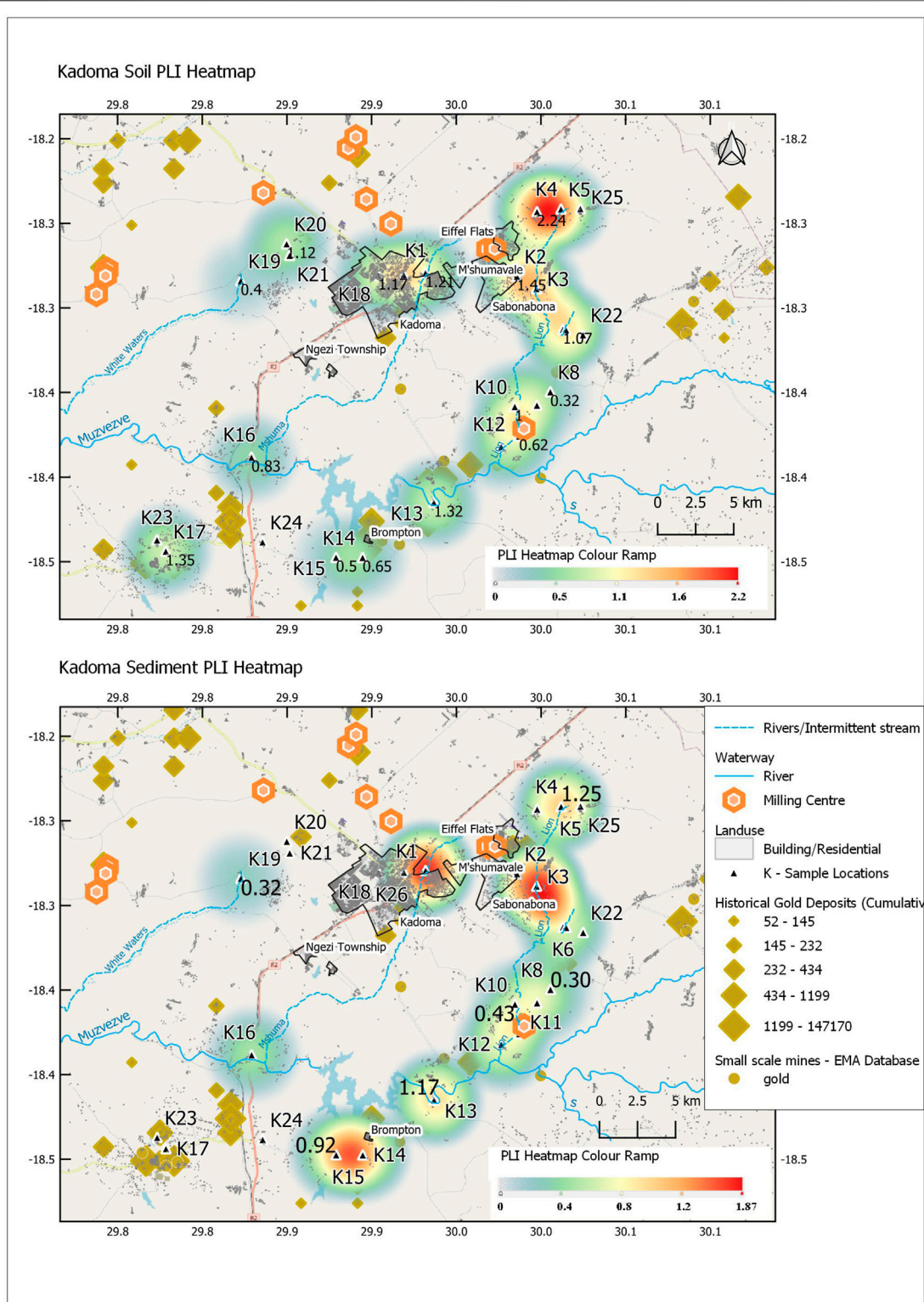
For the HUR area, only 2 PHEs Mo and Cr showed CF values above 1 with the upper continental crust value and the rest did not indicate any contamination in this site. Further inspection of the data on CF reveals that at certain sample locations in the sediment outlier values of As, Cu, Ni, Sb, and V also had  $CF > 1$  values while in soils, Ni was the only other PHE showing the same.

The categories of the degree of contamination that emerged through the computation of CF were mostly comparable with those of the  $I_{geo}$  revealing similar categories for the contamination levels of As, Cr, Mo, and Sb. The difference, however, was that of Cr and Mo classification when CF was computed from the national geochemical background values of Zhao et al. (2013).

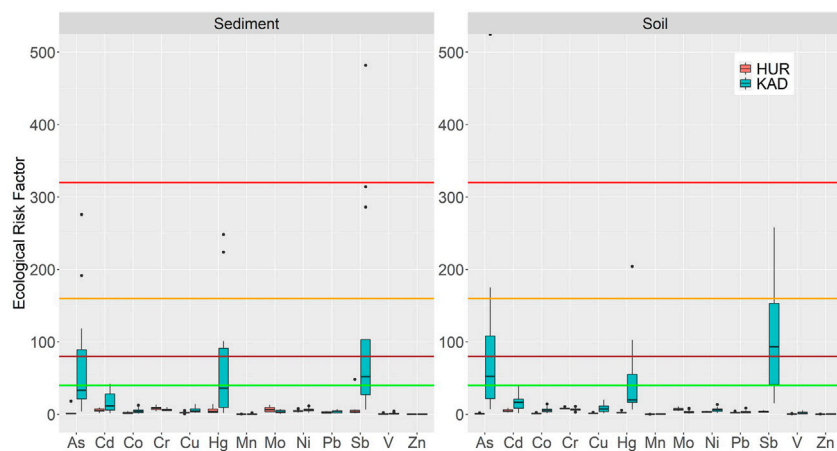
#### 3.3.3 Evaluation of Pollution Load Index

Results of PLI at several sample locations in KAD were  $>1$  (See **Figure 5**) indicating significant contamination in 52% (11 out of 21) of the soil sample sites and 38% of the sediment samples sites ( $n = 13$ ). The heatmap for the soil PLI values shows that the effect of multi-element contamination was highest at the location K4 (2.24) followed by K5 (1.64), both these locations being within 500 m of active gold mining operations. Other locations with  $PLI > 1$  that show clear associations with active gold mining, mine waste dumps and milling operations, and potential point pollution sources, were: K1, K2, K3, K6, K10, K13, K17, and K20. An inspection of the CF values for each contributing PHE shows Cr and Mo to be consistently large contributors to all PLI values in both study sites. In the KAD sediments As and Sb were the next largest contributors of high PLI values for the soil samples of which they contributed approximately 50%. Location K18 falls within a residential area without a mining operation in its vicinity, though it exhibited a  $PLI > 1$ . A more equitable contribution of other PHEs was also observed (especially  $Cr > Se > Mo > Ni > Cu > Co > Cd > Zn$ ) with As and Sb now only contributing 32% towards the PLI. The PLI value at sample location K20 was also not dominated by As and Sb for which their CF contributed only 15% to the total. An inspection of the CF values for each contributing PHE shows As and Sb as consistent and the largest contributors of high PLI values for the soil samples in which they contributed approximately 50%.

The heatmap for the sediments (**Figure 5**) revealed a different pattern with fewer locations having  $PLI > 1$ . The highest values of PLI are at K1 (1.87), K3 (1.86), and K5 (1.24) all of which are located downstream of the key mining and mineral processing operations in the area known as Eiffel Flats in which one of the country’s largest historically mined gold deposit is hosted (Cam and Motor Mine). At the locations in the southern part of the KAD area, K13 and K14  $PLI > 1$  are also attained. However, at these locations, As and Sb did not dominate in their contributions to PLI, only contributing 17% and 31% combined, while other elements particularly Hg show more prominence contributing



**FIGURE 5 |** Heat map of the PLI values for the total PHEs in soil (above) and sediment (bottom) samples at the KAD site. The red colour ramp was used to indicate the intensity of the PLI and the PLI levels at each location are highlighted in yellow. K\* represents the sample location ID.



**FIGURE 6** | Potential ecological risk factors for PHEs analysed in KAD and HUR sediments and soils. Intercepts are placed at 60, 80, 160, and 320 upper boundaries for low, moderate, considerable and high risk. Y-axis has been modified to max 500 so higher outliers in soil are omitted.

33% (K13) and 31% (K14), respectively. Spatial analysis of the satellite image indicates that locations K13 and 14 are downstream of gold mines where unrecovered slimes dams can still be seen, and are also popular informal small scale mining areas where the use of Hg in extracting gold is very common. The PLI values in the HUR site did not show any results above unity for any locations.

The maximum PLI value reached in the KAD site was 2.24 in soil samples, a relatively high value which is evidence of significant multi-element contamination, a phenomenon commonly associated with historically heavily industrialised sites (Rinklebe et al., 2019). This PLI value was compared to those obtained in other studies. In a study conducted on agricultural floodplain soils across the Central Elbe River in Germany (amongst the most highly PHE-polluted rivers in Europe due to a history of intensive industrial activity), the median topsoil PLI was 1.73 and a maximum of 3.20 (Rinklebe et al., 2019). The max KAD PLI value fell between this range signifying the comparatively high degree of contamination. An investigation of the degree of contamination of sediments in a stretch of the Subarnarekha River, India, passing through an important industrial hub, Jamshedpur city, found PLI values ranging from 0.436 to 6.92 in winter and summer respectively (Banerjee and Kumar, 2016). Previous studies of Subarnarekha River confirmed contamination and bioaccumulation problems in phytoplankton, molluscs and fish associated with this level of contamination (Banerjee et al., 2015).

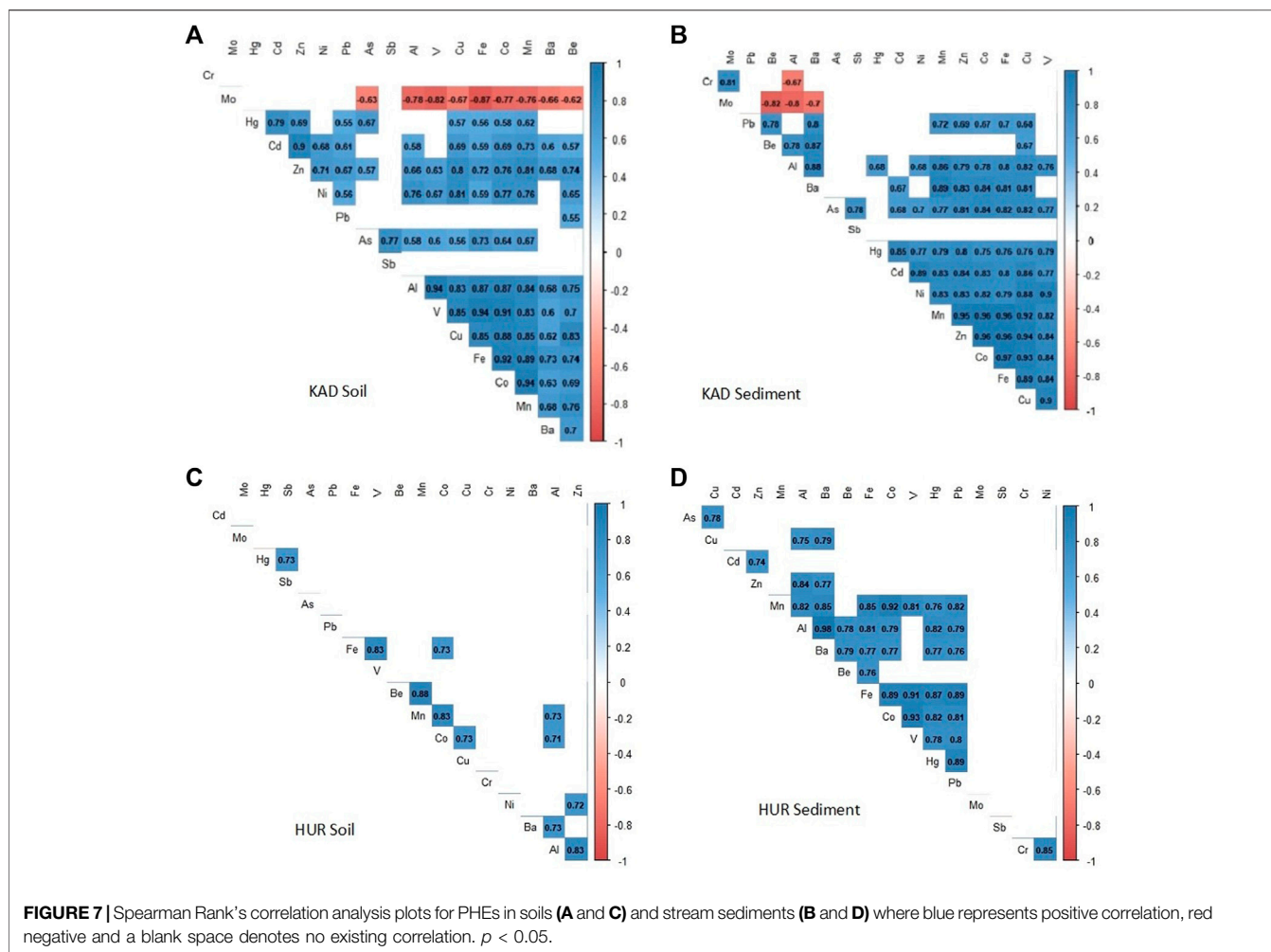
### 3.4 Evaluation of the Potential Ecological Risk

The ER values generated in the assessment of the sediment and soil samples for the 13 PHEs for which toxic risk factors were available, show that for both sediments and soil samples Sb, As, and Hg, in the KAD sediment and soil samples surpass low-risk levels, Cd levels in both KAD and HUR closely

approach the upper boundary of the low potential ecological risk category, while the rest of the elements studied fall below this level (Figure 6). Potential ecological risk for Sb at some locations, such as K3 and K15 in sediments, were between considerable to high risk, while in sample K1 a value in the very high-risk category was reached (See Supplementary Tables S1, S2 for the potential ecological risk factor and risk index at each sample location). Results of the potential ecological RI in both soils and sediments in KAD indicate considerable risk and those of HUR showed low risk. The results indicate that 71% of the KAD sediment and 53% of the soil sample locations show between low and considerable risk. Sediment samples from locations K1 and K3, both located along tributaries within 5 km downstream of the large Cam and Motor Mine and the Empress Nickel refinery, indicated very high RI values made up from mostly As and Sb contributions. Locations K15, K14, K13, K5, are at considerable risk, where Hg is the largest or significant contributor to risk. K12 shows moderate risk while the rest of the KAD sediments show low risk. In the KAD soils, RI at locations K4 and K5, indicates very high-risk levels, both influenced by anomalously high ER values for As. All the sediment and soil locations in HUR are in the low RI category.

### 3.5 Correlation Analysis

A Spearman Rank correlation analysis was applied to reveal the strength of associations of PHEs in the soils and stream sediments of the study sites and to evaluate the possible similarity of origins. The correlation coefficient ( $r$ ) can be divided into four correlation classes as  $r \leq 0.1$  low,  $r$  in the range of 0.1–0.3 medium,  $r$  in the range of 0.3–0.5 high and  $r \geq 0.5$  very strong interrelationships among PHEs (Weissmannová et al., 2019). In interpreting the correlation observed strong positive correlation among the PHEs were attributed to similar types of sources for their origin and negative correlations to related geochemical behaviours



**FIGURE 7** | Spearman Rank's correlation analysis plots for PHEs in soils (**A** and **C**) and stream sediments (**B** and **D**) where blue represents positive correlation, red negative and a blank space denotes no existing correlation.  $p < 0.05$ .

(Kumar et al., 2020). The results of the correlation analyses for the study sites with statistical significance at  $p < 0.05$  are presented as correlation plots (Figure 7).

Strong positive correlations are associated with similarity in the source of the PHE as well the method by which they reach or remain in the soil or sediments (Radomirović et al., 2020). In the KAD soils, many strong positive correlations between the PHEs were noted with coefficient values ranging from  $r = 0.55$  to  $0.94$  (Figure 7A). The very strong associations among Al, V, Cu, Fe, Co, Mn, ( $r = 0.84$ – $0.94$ ) as well as with As, Ni, Ba, and Be also showing high correlations coefficients  $>0.6$ – $0.83$  indicating a common source. These PHEs associated with the lithological units of the mineralised KAD area with ores of Au/Ag, Ni-Cu-Zn, Fe, barite and beryl (Anhaeusser, 2014). The positive associations in the soils observed for Cd, Zn, Ni, and Pb with Hg positively correlated with Cd, Zn, and Pb in that association, are common anthropogenic contaminants associated with industrial activities, sewage and automobile as well car exhausts (Lee et al., 2021). Hg in particular is commonly used in the KAD area by informal small-scale miners as part of the Au extraction technique. A combination of mining, urbanization and industrialisation

are possible sources of the anthropogenic contaminants within the KAD setting.

The KAD sediments (Figure 7B) showed a strong positive correlation between Hg, Cd, Ni, Mn, Zn, Co, Fe, and Cu with all interrelationships with  $r$  values ranging from  $0.75$  to  $0.97$ . Arsenic was also positively correlated with the PHEs in this group except for Hg. Sb showed a strong positive correlation with only As and no correlation with any of the other PHEs. Pb in sediments showed positive correlations with Be, Ba, Mn, Zn, Co, Fe, and Cu, this may result from the occurrence of galena (PbS), a lead sulphide ore within the greenstone belts together with other sulphide minerals (Ravengai et al., 2005). Cr in sediment had a strong positive correlation with Mo ( $0.81$ ) and a strong negative correlation with Al ( $-0.67$ ). Mo in sediments was strongly negatively correlated with Be ( $-0.82$ ) Al ( $-0.8$ ) and Ba ( $-0.7$ ) and had no other correlations with the other PHEs. The KAD soils and sediments showed similar signatures due to the similarities of the bulk of PHE concentrations influenced by the natural background variation.

The HUR soils showed very few significant positive correlations (Figure 7C) mostly related to the signature imparted by the granitic-gneiss lithology of the area. The

correlations in the HUR sediments (**Figure 7D**) are distinctly different from the soils at the site yet show similarities with those of the KAD sediments corroborating the suggestion of the significance of PHE dispersion within catchments and through the river system. In this assessment, Cr was only positively correlated with Mo suggesting similarity of source and showed negative correlations with Al, Fe, Co, and Hg.

## 4 DISCUSSION

### 4.1 Geochemistry and the Potential Ecological Risk

The KAD site shows significant and very similar contamination in both soils and sediments. The large contribution of As and Sb to the overall contamination in the KAD area can be attributed to their close geochemical relationship. Arsenic and Sb have been described in other studies as metalloids that show similar chemical behaviour and lithogenic occurrence (Antoniadis et al., 2019). In Zimbabwe's highly mineralised greenstone belt areas, Au is generally found bound in sulphides such as arsenopyrite (FeAsS), pyrite (FeS<sub>2</sub>), galena (PbS) and stibnite (Sb<sub>2</sub>S<sub>3</sub>) and therefore the mining and processing of its ore are linked to the release of As, Sb, Pb, Zn, and Fe (Ravengai et al., 2005). The CF values for Hg showed that the element contributes substantially to the overall PLI in the sample points associated with areas of increased informal mining activities, confirming the environmental impact of Hg use in the extraction of gold in the KAD area that has been reported by previous studies (Shoko and Veiga, 2004; Steckling et al., 2014).

The ecological risk to the freshwater ecosystem in the KAD area appears to be most affected by the processes associated with gold mining activities as evidenced by the key contributions of As, Sb, and Hg to the RI and other PHEs not showing much prominence. That said As and Hg are PHEs that have also been identified as agricultural (pesticides and fertilisers) and other non-mining (urbanization) industry contaminants Sharma et al. (2007), Wei and Yang (2010) and therefore the contribution of such activities cannot be ruled out in this setting. The influence of the natural geochemical background and mining operations in the KAD setting however outweigh the agricultural impact as observed in the land use pattern observable in satellite imagery. The contribution of Cd to the RI, though not major, may also indicate the contribution of other anthropogenic activities other than mining. Though the Empress Nickel processing plant is present in the KAD sub-catchment the results do not show Ni as a key contributor to the ecological risk as it is not a contaminant in the wastes of the roasting plant. Ore of Ni are usually low-grade high sulphide ores and the typical contaminants associated with extraction in the Ni roasting plants are gaseous emissions of sulphur dioxide that can lead to sulphuric acid production (Ekosse, 2008).

This study revealed much higher results of potential ecological risk indices for the KAD area when compared to similar studies in Zimbabwe's gold mining areas. In the town of Shamva, which is located in similar greenstone belt settings, the PHEs: As, Cr, Cu, Fe, and Pb were all reported to be posing a low potential

ecological risk with a low RI for the study site (Kanda et al., 2017). The exclusion of the Sb and other key PHEs that have been associated with contamination in mineralised and gold mining areas (Ravengai et al., 2005; Meck, 2013; Meck et al., 2020) may have had an impact on lowering the result of the ecological risk assessment in that study. When compared to other international studies, such as the review by Kumar et al. (2020) on the contamination of sediments in major Indian rivers, a far higher average RI is observed with Cd as a major contaminant attributed to industrialization, mining and urbanization. The current study however indicated a higher ER for As, Hg, and Sb which are also key contributors to contamination in the KAD area, though not assessed in the Indian study. The Sb mining activities in Hunan province in China show Sb, together with the associated Cd and Hg as the key contaminants contributing to the very high RI (Zhou et al., 2020) much higher than in KAD. The high contribution of Sb to the enhanced RI in KAD is not surprising, given the extent of Au and Sb mining activities in KAD.

### 4.2 Evaluation of Possible Contaminant Sources

The key PHE assemblages identified in the KAD area by the positive PHE correlations can be mainly attributed to the predominant lithological diversity and mineralisation of the site. The geochemical provinces of Au, Ni, Co, Cr, Pt, Pd, As, and Sb characterise the greenstone belt and the Great Dyke in the central Zimbabwe craton (Zhao et al. 2013) as well the multiple mineral assemblages of the greenstone belt lithologies, as described earlier, can be identified as the influence for the geochemical signatures and therefore correlations identified in both the KAD soil and sediment samples. The geochemically similar behaviour of PHEs such as that of As-Sb in the KAD setting does not follow for all elements as some will behave differently during secondary dispersion processes in the surficial media. This often results in only a partial agreement in their association once dispersed as compared to that determined from ore rock samples, making source identification a challenging process (Wang and Zuo, 2020).

Low or negative correlation of PHEs in soils can also refer to natural background variation or sources relating to natural processes Weissmannová et al. (2019), further it can also be attributed to several sources or a zone of high enrichment such as an ore deposit. This explanation can be used for the lack of positive associations or observed for Cr, Mo, and Sb. Cr is already known to occur in a major deposit, the Great Dyke that cuts across part of the Sanyati Catchment. Although economic deposits of Mo have not been discovered, anomalously high concentrations of this element were also identified through the National Geochemical Survey by Zhao et al. (2013) as worthy of further investigation and are known to be associated with granitic rocks. Antimony was once mined in KAD at the large Cam and Motor Mine. Both Cr and Mo are also common elements in agricultural fertilisers as well as key inputs in metal alloys and their correlation in the sediments only and not soils

may point towards an anthropogenic influence associated with agricultural and industrial activities. As a nexus of mining, industrialization, farming and urbanization, source identification of the typical PHE associated with these anthropogenic activities, i.e., As, Cd, Cu, Zn, Ni, and Pb is compounded by the fact that these are also common ore forming elements in the KAD setting.

### 4.3 Potentially Harmful Elements Contamination and the Potential Human Health Risks

Arsenic and its compounds are known human carcinogens and several studies have indicated an association between As exposure and increased mortality due to cancer (Tchounwou et al., 2012; Smith et al., 2018). Other studies have also linked As consumption in drinking water with two non-carcinogenic health conditions of concern, i.e., hypertension and diabetes (WHO, 2018) and cardiovascular disease (Phung et al., 2017). Sb is an element of environmental concern due to its genotoxicity (Mao et al., 2019) and in epidemiological studies, exposure to Cr (VI) by the inhalation route has been associated with lung cancer (Kotas and Stasicka 2000) and the IARC has classified Cr (VI) in Group 1 human carcinogen and Cr (III) in Group 3 (IARC, 2012). Mo is an essential element for human health and only rare cases of toxicity in humans have been reported, it is however known to be very toxic to some animals, especially ruminants (Novotny and Peterson, 2018).

The present study was preceded by an evaluation of the uptake of PHEs by vegetables grown within the same study sites and an assessment of the potential risk posed by their bioaccumulation in the edible parts (Meck et al., 2020). That study identified Pb, As, and Cd levels well above safe limits for human health in common vegetables grown in from the study site. The city of Kadoma and its residential suburbs that include, Eiffel Flats, Sabonabona, Ngezi, and Rimuka all fall within the KAD study site together with several residential sites some of which were former mine staff compounds that have continued to grow into informal settlements. Small and medium scale horticultural plots produce vegetables that are sold to the city and beyond with some active livestock farming producing meat and milk products. Fish from rivers and the main dam Claw Dam also form part of the dietary intake and comparison with other studies have shown PHE concentrations PLI values obtained in KAD to be of levels of concern for biomagnification. Fish consumption is a main entry for aquatic pollutants such as toxic metals (e.g., Hg and Cd) whose bioaccumulation and biomagnification are known to occur along the food chain, and can result in a whole array of systemic illnesses (See, e.g., Isangedighi and Samuel David, 2019). Subsistence farming is very common and many families rely on food crops grown in this setting for their daily consumption.

In the light of the evaluation of the degree of contamination by PHEs in this study, there is a risk of exposure through both dietary and non-dietary intake which would warrant further investigation by government authorities and environmental agencies.

## 5 CONCLUSION

This study has evaluated the degree of contamination in soils and sediments using geochemical indices at two sites within the Sanyati Catchment, KAD being an auriferous site from which gold has been extracted for over a century and HUR bereft of economic metal or mineral deposits. It was deduced that though As, Sb, Cr, and Mo are the main contaminant PHEs in the KAD site, potential ecological risk resulted from Sb, Hg, and As, posing between moderate and very high ecological risk in 71% of soil and 53% of the sediment samples. The HUR site results showed a low RI for all soils and sediment samples.

The geochemical distribution of PHEs in soils over the KAD and HUR terranes has shown varying trends, reflecting the influence of differences in the lithological composition of the two sites attributed to their geological setting. The PHE distribution levels in sediments of the sites were, however, markedly similar, indicating the predominant role of the PHE dispersion process wrought by sediment transport through sub-catchments from upper reaches.

The correlation analysis showed the influence of lithology and mineralisation on the natural background variation and hence the geochemical signatures of soils and sediments. Any remediation plans would need to be carefully targeted at specific points in the catchment where higher concentrations may be found, however, total removal would not be possible. Land use planning would need to be well informed by the geochemistry of each locality.

The study showed the importance of the application of a variety of geochemical indices in the evaluation of the degree of PHE contamination in soils and sediments of an area particularly during the hazard identification phase of the risk assessment as well as for environmental management and monitoring. The importance of separately evaluating the different surficial media of soils and sediments was also evidenced particularly in the variations noted in soil and sediment contamination at the HUR site especially when the practices of the use of floodplains in the growing of crops. The study also revealed how including toxicological risk factors in evaluating health risks within the system aids potential risk evaluation, as contamination may not denote pollution. It is hoped that the results from this study may be used as a model by environmental practitioners and in the design of experiments to elucidate the role of parameters such as chemical form and bioavailability that engender the transfer of PHEs into the food chain and their subsequent metabolic reactivity that produces toxicity and disease.

## DATA AVAILABILITY STATEMENT

The raw data from the chemical analysis and all field measurements supporting the conclusions of this article will become available from the corresponding author once all research has work been completed and published.



## AUTHOR CONTRIBUTIONS

Conceptualisation: DM, MM, TD, and DT; Methodology: DM, MM, and TD; Data Collection and Analysis: DM and MM; Formal Analysis: DM; Writing-Original Draft: DM; Writing-Review and Editing: DM, MM, TD, and DT; Supervision: MM, TD, and DT.

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## SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fenvs.2022.829900/full#supplementary-material>

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