



# Multi-geochemical background comparison and the identification of the best normalizer for the estimation of PTE contamination in agricultural soil

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**Abstract** Identifying a suitable geochemical background level (GBL) and an appropriate normalizer is imperative for ensuring soil quality, health, and security. The objective of this study was to identify the appropriate normalizer and suitable GBL for determining PTE enrichment levels in agricultural soils and investigate if there are any statistical differences due to the GBL [World Average Value (WAV) European Average Value (EAV)] used. Forty-nine topsoil samples were obtained from seven agricultural communities in the Frdek-Mstek District (Czech Republic). Portable X-ray fluorescence was used to determine the total PTEs (Cr, Ni, Cu, Y, Ba, Th, As, Pb, and Zn) concentration levels in the soil. Correlation matrix analysis was used to determine the metallic relationship between the PTEs and the normalizers (Al, Fe, Ti, Zr, Sr and Rb). Pollution indices such as contamination factor (CF), geoaccumulation index (I<sub>geo</sub>) and enrichment factor (EF) analysis were used to determine the most suitable GBL. Al, Fe, Sr, Ti and Rb strongly correlated with the CF, I<sub>geo</sub> and EF, whereas WAV performed better than the other geochemical background (EAV).

The results indicated that Rb was the suitable normalizer and WAV was the appropriate GBL for agricultural soil and provided a foundation for evaluating and surveilling soil quality and health in agricultural soil.

**Keywords** Correlation matrix · Proxy · European average value · Multivariate statistics · World average value

## Introduction

The term “geochemical background level” differentiates between natural and anthropogenic source element concentrations (Matschullat et al., 2000; Clemens Reimann, 2007). Geochemical background and normalizers are two critical approaches in estimating metal enrichment for a given area (e.g., agricultural area). However, at massive scale (continental and nationwide), researchers have reported the use of Upper Continental Crust (UCC), World Average Values (WAV), European geochemical background values for risk assessment and enrichment of PTEs in an environment (Birke et al., 2016; Oorts & Schoeters, 2014; Reimann et al., 2014; Smith et al., 2013). However, few authors have used subsoils to represent the background samples for corresponding topsoils (e.g., Facchinelli et al., 2001; Massas et al., 2009).

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While the spatial variability mapping method of potentially toxic elements (PTEs) has increasingly received relevance over the years (Plant et al., 2001), there is still a limitation on how to select appropriate geochemical background levels and corresponding normalizers for risk assessment of PTEs in any altered geogenic environment in the world. Hence, the estimation of geochemical risk potential in soils may be over or underestimated. Therefore, it is essential to note that geochemical background selection may result in significant differences while applying indices such as the enrichment factor (EF), contamination factor (CF), pollution load index (PLI), geoaccumulation index (I<sub>geo</sub>) and others in various sites. Swarnalatha et al. (2013) reported that geochemical normalization had been applied to assess the enrichment of metal pollutants, while Luoma (2018) stated that there are pre-conditions before using any normalizer. For example, aluminum (Al) is an appropriate proxy for grain size in most soil types and not a suitable normalizer in soils with variable feldspar content and metamorphic derivatives (Herut & Sandler, 2006; UNEP, 1995). Iron (Fe) and organic matter are normalizers used with no evidence of anthropogenic activities (Aloupi & Angelidis, 2001). Also, for samples enriched with T-O-T phyllosilicates [two tetrahedral (T) and one octahedral sheet (O)] sheets, Li is the most preferred normalizer relative to Al (Thi et al., 2013).

Apart from that, various elements have been used as normalizers for risk assessment in soils, for instance, cobalt (Co), manganese (Mn), titanium (Ti), silicon (Si) and zirconium (Zr) (Matthai & Birch, 2001; Liu et al., 2003; Nemr et al., 2006; Ghrefat & Yusuf, 2006; Sun et al., 2007; Zhou et al., 2007; Abraham & Parker, 2008; Çevik et al., 2009; Hu et al., 2011; Natesan & Ranga Rama Seshan, 2011; Ye et al., 2011; Kebonye & Eze, 2019). Nevertheless, the difficulties and conditions in selecting the elements mentioned above have impaired their extensive usage in risk assessment. Nonetheless, many researchers have overlooked the assumptions dictating the suitability of normalizers for assessing metals enrichment in agricultural soils dominated by the cambic horizon. According to Agyeman et al. (2021a, b), the prominence of agricultural soil stems from its use in food production, and hence a lot of emphases is dedicated to the investigation into its level of toxicity. Therefore, this study necessitated a multiple comparison approach to

select the most appropriate geochemical background level together with corresponding normalizers for agricultural soils dominated by the cambic horizon. It is hypothesized that for any productive agricultural soil, there is a need for a normalizer and geochemical background level that anthropogenic effects and activities alter sparingly and can be utilized in estimating the enrichment of PTEs and exposing the enrichment of PTEs. The local background values of the current study area are not coherent for the computation of the PTEs enrichment level in the locality. Therefore the objectives of the present study are to identify a suitable normalizer and geochemical background level appropriate for computing PTEs (Cr, Ni, Cu, Y, Ba, Th, As, Pb and Zn) enrichment in agricultural and industrial soils (predominantly cambisol within the study area) as well as to investigate further if there are statistical differences in the widely used geochemical background levels (e.g., EAV and WAV). In addition, the area of the research actively engaged in both industrial and agricultural activities, therefore the need to recognize the chemical composition of the study area based on the identification of a suitable normalizer and appropriate geochemical background levels.

## Materials and methods

### Study area

The study area is located in the Frydek Mistek District of the Moravian-Silesian Region in the Czech Republic, Europe. The community combines the previous two independent towns, specifically Silesian Frydek and the Moravian Mistek. The study area is positioned at the geographical coordinates Latitude 49° 41' 0" North and Longitude 18° 20' 0" East (See Fig. 1), at an altitude ranging from 225 and 327 m above sea level and is characterized by a cold temperate climate and a high amount of rainfall even in dry months. In Frýdek-Místek, the summers are hot and partly cloudy, and the winters are cold, dry, windy and mainly cloudy (Weather Spark, 2016). Over the year, temperatures usually range from 24 to 75° F and are rarely below 8° F or above 86° F while the average annual precipitation ranges between 685 and 752 mm (Weather Spark, 2016). The area survey of the district is projected at 1208 km<sup>2</sup>, with 39.38% of the land

allocated for agricultural activities and 49.36% for forest land. The farmland within the study area consists of the following towns Havirov, Těrlicko, Trinec, Bystřice, Jablunkov, Mosty Jablunkova and Hřčava. Trinec and Vitkovice, a part of Ostrava city where the steel industry is located, have become critical areas for assessing PTE distribution and soil quality within and around surrounding communities. The PTEs pollution in the area is caused by atmospheric deposition emitted from the steel industry nearby, vehicular emission, abrasion from tires, and agricultural activities (e.g., pesticide and insecticide applications) (Agyeman et al., 2021a, b). Nonetheless, the primary soil types in the study area are cambisols and stagnosols (Kozák, 2010). These soils dominate the Czech Republic and are found at elevation ranges of 455.1–493.5 m (Vacek et al., 2020). According to WRB (2015), cambisols soil covers about 1.5 billion hectares worldwide, and its reference soil group principally is well represented in the boreal and the temperate regions. The soils are primarily composed of colluvial, alluvial, or aeolian deposits (Fig. 1). They are characterized by a cambic diagnostic horizon with fine sandy loam texture, clay content of > 4%, with less carbonate content by a lithic discontinuity (Kozák, 2010).

### Soil sampling and analysis

A total of 49 agricultural topsoils (0–20 cm depth) were obtained across seven towns (Havirov, Těrlicko, Trinec, Bystřice, Jablunkov, Mosty Jablunkova and Hřčava) located within the district of Frydek-Místek through a regular grid design. Soils were sampled in an interval of 2 km by 2 km using a handheld GPS device (Leica Zeno 5 GPS). Samples were placed into Ziploc bags, well labeled accordingly, and transported to the laboratory. The samples were air-dried, crushed by a mechanical device (Fritsch disk mill pulverize), and then sieved (< 2 mm) to obtain a homogeneous sample. A portion of each pulverized sample was placed in the sample cup provided by the portable X-ray fluorescence (pXRF) manufacturer and with a thin polythene film underneath. A Delta Premium pXRF system (Olympus Innov-X, USA) mounted on a stand and linked to a pXRF installed computer was then used to scan each soil sample for complete element concentrations in accordance with EPA guidelines (EPA, 1998). Every soil sample was

scanned three times for PTEs, and the average result was determined for each soil sample at the very end of the soil analysis.

### Quality assurance and quality control (QA/QC)

The quality assurance and control process, the standard reference material for a portable device (i.e., pXRF 2711a NIST, the National Institute of Standards and Technology), was used in the analysis to ensure quality compliance. The reference material was occasionally measured alongside with soil samples to ensure that the analysis remained accurate until completion. The detection limits for the PTEs tested were < 10 mg/kg (Ni), < 10 mg/kg (Cu), < 5 mg/kg (Sr), < 20 mg/kg (Ba), < 5 mg/kg (Ti), < 5 mg/kg (Zn), < 5 mg/kg (As), < 5 mg/kg (Pb), < 10 mg/kg (Cr), < 5 mg/kg (Y), < 5 mg/kg (Zr), < 5 mg/kg (Th) and < 5 mg/kg (Rb). The PTEs recovery percentage were 82.3(Ni), 89.9(Cu), 86.4(Sr), 88.1(Ba), 84.7(Ti), 87.9(Fe), 81.2(Cr), 96.2(Y), 92.5(Zr), 100.9(Th) 92.1(As) 85.7(Zn) 80.4(Pb) and 98.7(Rb).

### Mathematical indices approach

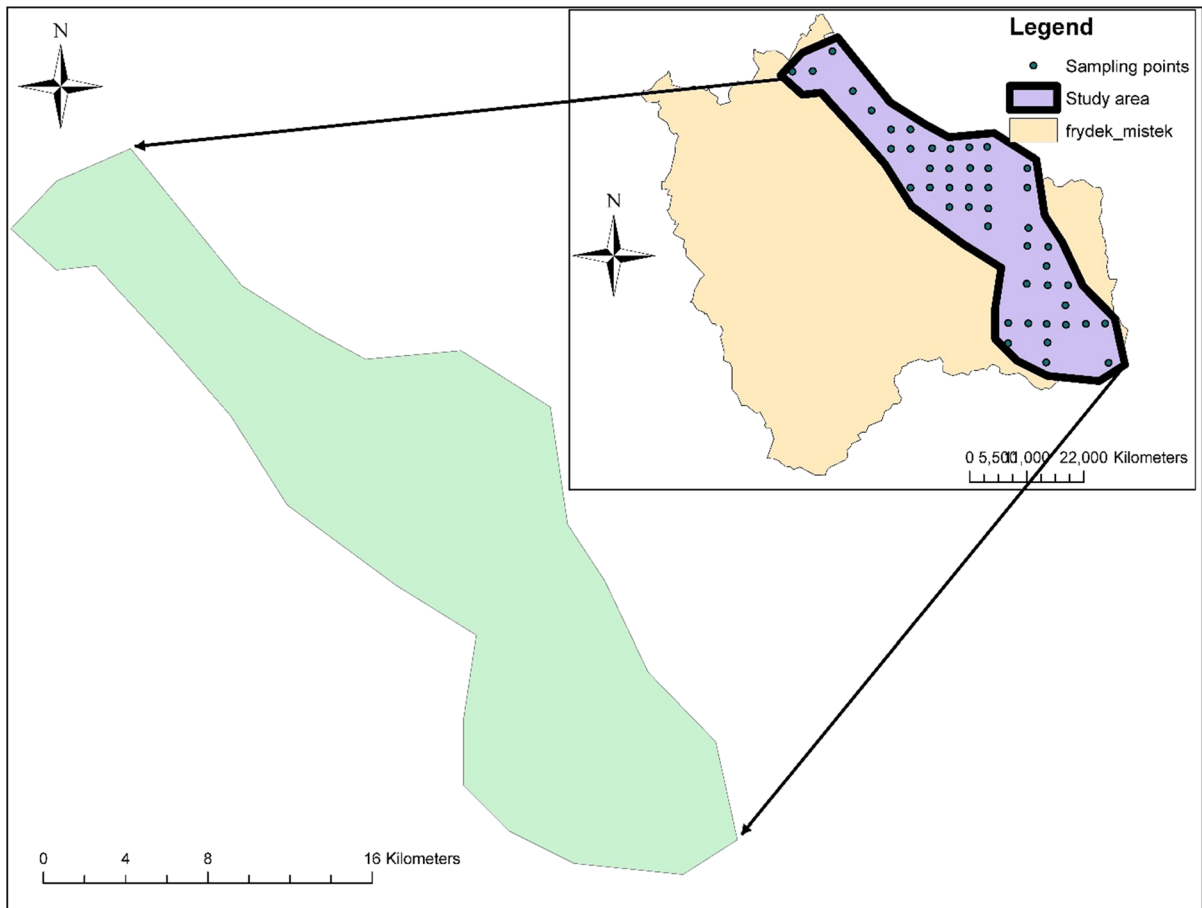
Contamination factor (CF) can be defined as a ratio between the concentrations of metal content in the sample to the background value of the metal of the same metal (Hakanson, 1980). The equation is given as

$$CF = \frac{C_{mSample}}{C_{mBackground}}, \quad (1)$$

where the  $C_m$  sample is the concentration of metal analyzed from sampled soil and  $C_m$  background is the geochemical background concentration. The baseline values used were the European average value (EAV) and World average value (WAV) (Kabata-Pendias, 2011). Hakanson (1980) categorized the contamination factor into four categories, namely  $CF < 1$ : low contamination,  $1 \leq CF < 3$ : moderate contamination,  $3 \leq CF < 6$ : considerable and  $CF \geq 6$ : very high contamination.

### Geoaccumulation index (IGEO)

This enables the assessment of contamination by comparing the current levels of PTEs concentrations



**Fig. 1** Study area map showing sampling points

to the background level of the area. The index also calculates contamination while comparing preindustrial and recent metal concentrations (Loska et al., 1997). The baseline values used were the EAV and WAV (Kabata-Pendias, 2011).

The Igeo is calculated using this equation:

$$I_{geo} = \log_2 \frac{C_{mSample}}{1.5 \times B_n}, \quad (2)$$

where  $C_m$  represents the concentration of an individual PTE,  $B_n$  is the background value (natural value of the metal in the nearby soil without human influence and is used to compensate possible variations of data due to lithogenic effects) and 1.5 constant figure that allows for an analysis of the variability of PTEs as a result of natural processes. The estimated result can be interpreted using the precise scale presented below:

Class 0 =  $I_{geo} \leq 0$  (practically uncontaminated),  
 Class 1 =  $0 < I_{geo} < 1$  (uncontaminated to

moderately contaminated), Class 2 =  $1 < I_{geo} < 2$  (moderately contaminated), Class 3 =  $2 < I_{geo} < 3$  (moderately to heavily contaminated), Class 4 =  $3 < I_{geo} < 4$  (heavily contaminated) Class 5 =  $4 < I_{geo} < 5$  (heavily to extremely contaminated) and Class 6 =  $5 \leq I_{geo} < 6$  (extremely contaminated).

Enrichment factor (EF)

This is an index that is used to calculate the concentration of PTEs in soil. The EF for each PTE was calculated to determine the concentration levels of the elements induced by anthropogenic activities. EF is mainly used to differentiate the source of PTEs, which can be natural or anthropogenic (Kowalski et al., 2018). It involves the stabilization of soil relative to reference elements. Enrichment factor computation is adopted to estimate the impact of

anthropogenic activities connected to the metal abundance in sediments or soil. Ergin et al. (1991), defined EF by the following equation:

$$EF = \frac{C_n/C_{ref}}{B_n/B_{ref}} \quad (3)$$

In which  $C_n$  represents the concentration of the examined element in the examined environment,  $C_{ref}$  denotes the concentration of the examined element in the reference environment,  $B_n$  signifies the concentration of the reference element in the examined environment,  $B_{ref}$  indicates the concentration of the reference element in the reference environment. The baseline values used were WAV and EAV (Hakanson, 1980; Kabata-Pendias, 2011). The interpretation of the estimated values is defined as follows  $EF < 2$ , denoting deficiency to minimal enrichment,  $2 < EF < 5$  representing moderate enrichment,  $5 < EF < 20$  signifying significant enrichment,  $20 < EF < 40$  suggesting Very high enrichment and  $40 >$  indicating extremely high enrichment.

#### Statistical analysis

The contamination indices (CF, EF and Igeo) and the Pearson correlation matrix were carried out using Microsoft excel. Pearson correlation matrix was also used to show the interactions between PTEs and the individual normalizers.

## Results and discussion

### Characterization of potentially toxic element concentration

The concentration of the PTEs and normalizers (Cr, Ni, Cu, Y, Ba, Th, As, Pb, Ti, Zr, Sr, Rb, Fe, Al and Zn) in the topsoil are shown in Table 1. The PTEs in the agricultural soil were within the following range, 44–112 mg/kg (Cr), 0–43 mg/kg (Ni), 9–58 mg/kg (Cu), 14–78 mg/kg (Y), 378–913 mg/kg (Ba), 5–15 mg/kg (Th), 6–26 mg/kg (As), 2–181 mg/kg (Pb), 3134–5560 mg/kg (Ti), 29–673 mg/kg (Zr), 50–128 mg/kg (Sr), 70–162 mg/kg (Rb), 7415.48–24,038.92 mg/kg (Al), 8650.32–66,459.13 mg/kg (Fe) and 53–270 mg/kg (Zn). In comparison, the mean concentrations of some

of the PTEs (Cu, Y, Ba, Th, Pb, Zr, Rb, Zn) were higher than some of the EAV's geochemical background levels (GBL) reported by Kabata-Pendias (2011). Conversely, some of the PTEs in the WAV (Ni, Cu, Ti, Sr) and upper continental crust (UCC) mean concentrations (Cr, Ni, Cu, Y, Sr) also exceeded the threshold of some of the PTEs concentration values obtained in this study (Table 1), and vice versa (Kabata-Pendias 2011). The mean concentrations of the following PTEs, Al, Fe, Cr, and Ni, were higher than the mean concentrations of PTEs obtained from this study, according to the respective PTEs mean values extracted from Hakanson (1980). The current study's Cu, As, Pb, and Zn levels, on the other hand, were found to be higher than Hakanson's reported geochemical background level. The elevation of the content of some of the PTEs such as Cu and Zn in the present study may be attributed to fertilizer application and discharge of sewage sludge. Previous studies conducted by Alloway (2013) and Romic and Romic (2003) acknowledges that agricultural activities associated with sewage sludge or fertilizers application enrich the contents of PTEs in the soil, especially Cu and Zn. According to Baize and Sterckeman (2001), PTE pollution from the geochemical background is often low in concentration, which must be considered when measuring the elemental content of a given location.

The coefficient of variability (CV%) of the PTEs was estimated, and according to Nezhad et al. (2015), the CV suggests the degree of variability within the concentration of the PTEs. If the CV is  $\leq 20\%$ , it indicates low variability; if it is  $21\% \leq CV \leq 50\%$ , it is considered as moderate variability; if it is  $50\% \leq CV \leq 100\%$  it suggests high variability and if the CV is above 100%, it is regarded as exceptionally high variability. The computed CV % indicated that Ba, Th, Ti, Sr and Rb showed a low variability with a percentage variability falling below 20% (Table 1). Other PTEs such as Cu, Cr, Y, Zr, Fe, Al, Mn and Zn showed a moderate CV, suggesting that they were more homogeneously distributed. Pb and Ni exhibited high variability, implying a non-homogenous distribution of Pb and Ni, which accounts for a probable human-related activity. The non-homogeneity of Ni and Pb foretells the presence of a local enrichment source. The average level of variability in the dataset measured using the standard deviation varies from 2.06 to 10,641.22.

**Table 1** PTEs and normalizers concentration (mg/kg)

	Al	Fe	Cr	Ni	Cu	Y	Ba	Th	As	Pb	Ti	Zr	Sr	Rb	Zn
Minimum	7415.48	8650.32	44.00	0.00	8.87	13.70	378.33	4.97	5.60	28.47	3133.67	29.43	49.67	70.47	53.17
Maximum	24,038.92	66,459.13	111.67	43.00	58.33	78.47	912.67	15.30	28.67	180.67	5560.00	673.00	127.67	161.53	270.33
Mean	14,084.82	21,602.20	62.14	16.25	21.25	28.39	490.20	11.45	9.76	50.23	4664.44	477.75	79.40	93.65	95.69
S.D	3493.47	10,641.22	14.26	10.32	9.28	8.97	87.55	2.06	4.53	25.20	516.39	145.86	14.65	14.96	37.08
Coef. var	24.80	49.26	22.95	63.47	43.68	31.60	17.86	18.01	46.40	50.17	11.07	30.53	18.45	15.98	38.75
<sup>a</sup> WAV	–	–	59.50	29.00	38.90	23.00	460.00	9.20	6.83	27.00	7038.00	267.00	175.00	68.00	70.00
<sup>b</sup> EAV	–	–	94.80	37.00	17.30	23.00	400.00	9.00	11.60	32.00	6070.00	2.10	130.00	87.00	68.10
<sup>c</sup> UCC	–	–	100.00	20.00	55.00	33.00	400.00	7.20	1.80	15.00	4400.00	165.00	375.00	90.00	70.00
<sup>d</sup> Hakanson	71,000.00	38,000.00	100.00	40.00	20.00	–	–	–	6.00	10.00	–	–	–	–	50.00

(Kabata-Pendias, 2011) <sup>a</sup>WAV World average value, <sup>b</sup>EAV European average value, <sup>c</sup>UCC Upper continental crust

<sup>d</sup>Hakanson (1980)

S.D Standard deviation

Coef. Var. Coefficient of variability

### Correlation between PTEs and normalizer

The relationship between PTEs (Cr, Ni, Cu, Y, Ba, Th, As, Pb and Zn) and the selected normalizers (Ti, Zr, Sr, Al, Fe and Rb) were computed using the Pearson correlation matrix (PCM) to determine the nexus between the PTEs and the normalizers (See Table 2). The correlation revealed positive interrelationships between the PTEs and the normalizers ranging from low ( $r = 0.01$ ) to strong ( $r = 0.92$ ), but there were also negative correlations, as shown in Table 2. Lead and Zinc [Pb and Zn (0.92)] showed a strong metallic relationship, likewise As and Pb ( $r = 0.88$ ), Ni and Sr ( $r = 0.76$ ), Cr and Ba ( $r = 0.73$ ), As and Zn ( $r = 0.75$ ). Normalizer such as strontium (Sr), zirconium (Zr) and rubidium (Rb) had a strong relationship with Ni, Th and Ba. Other PTEs correlations such Cr and Ni ( $r = 0.53$ ), Ni and Cu ( $r = 0.52$ ), Cu and Zn ( $r = 0.55$ ), Ba and Rb ( $r = 0.57$ ) as well as Th and Zr ( $r = 0.59$ ) showed moderate correlation. Rubidium and strontium exhibited a relatively strong metallic correlation with PTEs such as barium and thorium. Titanium was shown to be weakly and positively bound to yttrium, barium, and thorium, as well as weakly but negatively attracted to Cr, Cu, Ni, and As, with correlations ranging from  $r = -0.01$  to 0.16. The weak relationship between the following normalizers, Sr and Rb ( $r = 0.34$ ) and Sr and Ti ( $r = 0.21$ ), may indicate that they arise from different sources.

In contrast, the relatively strong correlation between Pb and Zn suggests an agro-anthropogenic source used as a food supplement or additive in livestock farming, such as poultry production, to induce feeding performance, stimulate growth, and ensure the development of healthy birds (Driver et al., 2006). The strong correlation between some PTEs and some normalizers may indicate mutual dependence or similarities in pollution sources (Kebonye & Eze, 2019). Conversely, the weakly correlated, as well as the negative correlation, both point to a different source of occurrence. The strongest relationship was between Pb and Zn, suggesting an anthropogenic source that might emanate from farm manure. PTEs, such as Zn and Pb, are trace elements found in the feed material, including amaranthus, which is used to feed monogastric animals (Nicholson et al., 1999). Yan et al. (2020) reported a low correlation between As and Pb (0.226) in agricultural soil in Shuozhou City, Shanxi Province, China, compared to the 0.88  $r$  value

obtained in this study. Yalcin (2020), on the other hand, reported a negative correlation for NiSr ( $-0.372$ ) and CrBa ( $-0.006$ ) as opposed to the significant connection shown in this study (Ni and Sr  $r = 0.76$ , Cr and Ba  $r = 0.73$ ). The correlation between As and Zn reported by Zhiyuan Wu et al. (2020) was 0.616, lower than the current study's  $r = 0.75$ .

### Comparison of geochemical background levels using mathematical pollution estimation indices

Pollution levels were estimated on three different levels, EF, CF, and Igeo, using two different geochemical background levels, EAV and WAV. Swarnalatha et al. (2013) and Kebonye and Eze (2019) proposed using CF and EF in establishing an appropriate normalizer, but according to Kowalska et al. (2018), Igeo and EF are relatively valuable and commonly used in pollution assessment, so we opted to use them.

EF was calculated using different normalizers (Ti, Zr, Sr, Al, Fe and Rb), as shown in Table 3. For instance, when calculating PTE enrichment levels using Zr as a normalizer in the WAV threshold level, the values obtained from using Zr as a normalizer exposed the pollution level of the PTEs better than when using the same normalizer (Zr) from a different geochemical background (that is EAV) (See Table 3). Three of the six WAV normalizers chosen to calculate PTE enrichment levels in agricultural soil (Zr, Sr, Ti) performed better than the other GBL (EAV) used to calculate PTE enrichment levels (See Table 3). It was evident that the WAV normalizers (Zr, Sr, Ti) exposed the PTEs enrichment level better, matching it with the EF interpretation precise scale. However, the estimated EFs value obtained using Al as a normalizer showed an equal strength for both GBL used. Kabata-Pendias (2011); Kelepertzis (2014), Chen et al. (2015) reported that it is problematic for agricultural soil to have a high concentration of PTEs since these soils are valuable to food production and security. Therefore, choosing a suitable GBL that can best interpret and highlight PTEs enrichment in agricultural soil is essential. According to (2018), PTE concentrations in soil that exceed allowable levels may endanger human health and negatively impact soil biota via soil microbe interaction and microbial processes.

**Table 2** Correlation matrix between PTEs

	Al	Fe	Cr	Ni	Cu	Y	Ba	Th	As	Pb	Ti	Zr	Sr	Rb	Zn
Al	1.00														
Fe	0.48**	1.00													
Cr	-0.05	-0.24	1.00												
Ni	0.26	-0.04	<b>0.53**</b>	1.00											
Cu	0.34*	0.03	0.24	<b>0.52**</b>	1.00										
Y	-0.06	-0.12	0.27	0.27	0.05	1.00									
Ba	0.11	-0.14	<b>0.73**</b>	0.47**	0.19	0.30*	1.00								
Th	-0.17	-0.18	0.07	0.21	-0.03	0.45**	0.12	1.00							
As	0.38**	0.09	0.20	0.30*	0.38**	-0.02	0.33*	0.11	1.00						
Pb	0.39**	0.14	0.20	0.29*	0.46**	-0.06	0.21	0.00	<b>0.88**</b>	1.00					
Ti	0.01	0.21	-0.01	-0.11	-0.05	0.16	0.11	0.15	-0.05	0.00	1.00				
Zr	-0.11	-0.03	-0.34*	-0.17	0.01	-0.08	-0.39**	<b>0.59**</b>	-0.11	-0.07	0.21	1.00			
Sr	0.12	-0.17	0.49**	<b>0.76**</b>	0.30*	0.37*	0.29*	0.30*	0.10	0.08	-0.13	0.01	1.00		
Rb	0.27	-0.11	0.35*	0.43**	0.05	0.11	<b>0.57**</b>	0.15	0.38**	0.10	-0.07	-0.29*	0.34*	1.00	
Zn	0.42**	0.21	0.21	0.42**	<b>0.55**</b>	-0.08	0.18	-0.08	<b>0.75**</b>	<b>0.92**</b>	-0.14	-0.16	0.19	0.10	1.00

\*\*Correlation is significant at the 0.01 level (2-tailed). \*Correlation is significant at the 0.05 level (2-tailed)



**Table 3** Pollution estimation for mean enrichment factor ( $N = 49$ )

	Cr	Ni	Cu	Y	Ba	Th	As	Pb	Zn	Normalizer
WAV	2.30	1.24	1.20	0.89	2.35	2.74	3.15	4.10	0.79	Sr
EAV	1.07	0.72	2.01	2.02	2.01	2.04	1.38	2.57	2.30	Sr
WAV	0.76	0.41	0.40	0.90	0.77	0.90	1.04	1.35	0.26	Rb
EAV	0.61	0.41	1.14	1.15	1.14	1.16	0.78	1.46	1.31	Rb
WAV	1.58	0.85	0.82	1.86	1.61	2.40	2.16	2.81	2.06	Ti
EAV	0.85	0.57	1.60	1.61	1.59	1.62	1.09	2.04	1.83	Ti
WAV	0.584	0.313	0.305	0.69	0.596	0.696	0.798	1.04	0.764	Zr
EAV	0.003	0.002	0.005	0.005	0.005	0.005	0.004	0.007	0.006	Zr
WAV	5.26	2.83	2.75	6.22	5.37	6.27	7.20	9.38	6.89	Al
EAV	3.30	2.21	6.19	6.22	6.18	6.41	4.24	7.91	7.08	Al
WAV	1.84	0.99	0.96	2.17	1.87	2.19	2.51	3.27	2.40	Fe
EAV	1.15	0.77	2.16	2.17	2.16	2.24	1.48	2.76	2.47	Fe

The relative interpretation of the estimated values of EF using diverse normalizers selected from different GBL reveals that the enrichment of agricultural soil using zirconium (Zr) exposes the PTEs enrichment level (i.e., using WAV and EAV as a GBL) from deficiency to minimal enrichment. The normalizers selected from WAV, on the other hand, reveal the enrichment level, which ranges from deficiency/minimal enrichment to moderate enrichment. Strontium and titanium, which were chosen as WAV GBL normalizers, similarly exposed the PTEs ranging from deficiency/minimal enrichment to moderate enrichment, with the exception of Rubidium and Zirconium, whose enrichment levels remained in the deficiency to minimal enrichment range (See Table 3). Most of the EFs enrichment value calculated was within the deficiency to minimal enrichment (that is below 2.0) in which according to Zhang and Liu (2002) and Peter and Adeniyi (2011), If the value of EFs ranges from 0.003 to 1.5 (See Table 3), it can be acknowledged that the content of PTEs in the agricultural soil enrichment is likely to be caused by natural processes. Nevertheless, if the concentration is beyond deficiency/minimal enrichment (that is from 2.00 upward), there is a tendency that an anthropogenic source is augmenting the natural source.

The estimation of CF and Igeo using WAV GBL was also superior to the other CF/Igeo computed using the EAV (See Table 4). This indicates that the comparative pollution indices (CF, EF, and Igeo) measured using WAV as a geochemical background level expose enrichment levels better than the other GBL (EAV) to highlight concentration levels in

agricultural soil. Among the two GBL, WAV provides knowledge of PTE concentration levels and elicits the potential risk of polluted agricultural soils, which is critical for policymakers, governments, farmers, and other stakeholders to implement countermeasures to alleviate the situation. Nonetheless, selecting the appropriate GBL for the estimation of PTEs enrichment is an essential tool in the hands of a soil scientist, environmental scientist, and pedologist to assess the spatial variability and concentration level of PTEs between areas with higher concentrations, primarily agricultural soil (Iñigo et al., 2014), as well as areas that are potentially becoming risk-prone. Computing CF and Igeo using diverse GBL relatively indicated the difference in the estimated enrichment values. WAV exposed a high level of enrichment in CF in PTEs such as Cr, Ni, Y, Th, As and Pb and likewise in Igeo PTEs such as Cr, Ni, Y, Th, As and Pb. Despite that, EAV GBL also showed enrichment in the following PTEs Cu, Ba and Zn, respectively (See Table 4). Thus, it was evident that using WAV as a geochemical background level consistently showed superiority in estimating PTEs enrichment levels in Igeo and CF.

Nonetheless, according to Matschullat et al. (2000) and Karim et al. (2015), the use of GBL such as (WAV) in the estimation of PTEs enrichment makes more sense for global or nationwide PTEs assessment. Geochemical background level, which including WAV, generally agrees to information about soil quality being assessed on an international scale and may allow for comprehensive global soil comparison beyond the local scale (Kowalska et al., 2018). The

**Table 4** Pollution estimation for contamination factor and geoaccumulation index

	Cr	Ni	Cu	Y	Ba	Th	As	Pb	Zn
WAV_CF	1.04	0.56	0.55	1.23	1.07	1.24	1.43	1.86	1.37
EAV_CF	0.66	0.44	1.23	1.23	1.23	1.24	0.84	1.57	1.41
WAV_IGEO	0.21	0.11	0.11	0.25	0.21	0.25	0.29	0.37	0.27
EAV_IGEO	0.13	0.09	0.25	0.01	0.25	0.10	0.17	0.31	0.28

tendency of polluted agricultural soil in Africa to pose a health risk to the people around such soil may have the same propensity to cause carcinogenic and non-carcinogenic related risks to someone living around polluted soil in a different continent. Furthermore, computing pollution indices using internationally accepted GBL can have an additional multi-purpose character (Kowalska et al., 2018) and help enact comprehensive policy for a sustainable international goal.

#### Correlation between estimated EF, CF and Igeo

The correlation analysis performed between the pollution indices using different normalizers (Ti, Zr, Sr, Al, Fe and Rb) selected from WAV as well as selected PTEs showed a strong, moderate, and weak correlation between each other. The strength of the correlation ranged from  $> 0.75$  as a strong correlation,  $0.5–0.75$  moderate correlation, and  $0.5$  downward indicates weak strength. In evaluating an element's suitability as a normalizer, the pollution assessment indices level (such as CF and EF) calculated by using a specific component for the selected PTEs should be positively correlated (Swarnalatha et al., 2013). The intensity of their interaction suggests that the component can be regarded as a reference element (Kebonye & Eze, 2019). The EF of metal is denoted by Me and with a corresponding normalizer as No. Conversely, the CF and Igeo of metal are represented by CFMe and IgeoMe, respectively. Table 5 displays the results of a correlation analysis performed for CF, Igeo, and a variety of prospective normalizers to determine the optimal normalizer for agricultural soil. The correlation matrix of the PTE As and the prospective normalizers (Ti, Zr, Sr, Al, Fe and Rb) showed some strong correlation between AsRb and AsSr (0.89), AsRb and AsTi (0.81), AsAl and AsFe as well as AsSr and AsTi (0.86). AsZr exhibited a weak correlation with the other normalizers ranging from  $r = 0.20$  to  $0.28$ . The CF and the Igeo correlation between the

prospective normalizer displayed the same strong metallic correlation such as CFAs and AsRb (0.91), CFAs and AsSr (0.91), as well as CFAs and AsTi (0.95). The correlation matrix witnessed with the PTE Ba showed a moderate correlation between BaRb and BaSr (0.52), BaAl and BaRb (0.55) as well as BaFe and BaRb (0.51) with a corresponding moderate correlation value for CFBa and Igeo (MeAl 0.50, MeFe 0.55, MeRb 0.59, MeSr 0.64, MeTi 0.75). The following EFs of Cr using these normalizers Al, Fe, Rb, Sr and Ti (See Table 5) showed a moderate relationship of 0.71 (MeAl/MeRb), 0.69 (MeFe/MeRb), 0.64 (MeRb/MeSr) and 0.67 (MeRb/MeTi), respectively. It similarly showed a moderate to a strong relationship with Igeo of 0.66 for CrSr, 0.79 for CrRb, 0.66 for CrAl, 0.70 for CrFe, and 0.84 for CrTi, and thus a low correlation with CFZr. The EFs of the following PTEs Cu, Ni, Pb, Y and Zn using the different normalizers displayed a strong correlation ranging from  $r = 0.77$  to  $0.91$  for MeSr/MeTi,  $r = 0.86$  to  $0.92$  for MeRb/MeTi,  $r = 0.76–0.87$  for MeTi/MeAl,  $r = 0.76$  to  $0.90$  for MeTi/MeFe,  $r =$  MeAl/MeFe for  $0.83$  to  $0.95$  and  $r = 0.86–0.93$  for MeRb/MeSr.

The normalizers also showed a strong corresponding relationship with CFMe/Igeo (Cu, Ni, Pb, Y, and Zn) and the prospective normalizers (MeTi, MeSr, MeRb, MeAl, MeFe) with coefficients ranging from  $0.93$  to  $0.96$  (Rb),  $0.89$  to  $0.94$  (Sr),  $0.92$  to  $0.95$  (Ti),  $0.75$  to  $0.89$  (Al), and  $0.75$  to  $0.89$  (Fe) respectively. The EFs for the PTEs Th showed a moderate correlation among the normalizer (MeRb/MeSr 0.65, MeRb/MeTi 0.64, MeTi/MeFe 0.60) with a corresponding moderate to high CFTh/IgeoTh (CFTh/MeRb 0.79, CFTh/MeSr 0.66 and CFTh/MeTi 0.79). Again, there was a strong correlation between PTEs and the normalizers MeAl, MeFe, MeTi, and MeRb, with consistent values of  $0.95$  (As),  $0.75$  (Ba),  $0.84$  (Cr),  $0.94$  (Y), and  $0.95$  (Cu),  $0.96$  (Ni),  $0.96$  (Pb), and  $0.93$  (Zn). Though Al, Fe, Ti and Rb demonstrated a high correlation with the PTEs and the CF/Igeo, Rb

**Table 5** Correlation matrices of enrichment factors of PTEs with different normalizer, geoaccumulation index and contamination factor

	AsRb	AsSr	AsTi	AsZr	AsAl	AsFe	CFAs	IGEOAs
AsRb	1.00							
AsSr	0.89**	1.00						
AsTi	0.81**	0.86**	1.00					
AsZr	0.20	0.24	0.28*	1.00				
AsAl	0.70**	0.73**	0.73**	0.20	1.00			
AsFe	0.68**	0.71**	0.82**	0.23	0.88**	1.00		
CFAs	0.91**	0.91**	0.95**	0.27	0.74**	0.78**	1.00	
IGEOAs	0.91**	0.91**	0.95**	0.27	0.74**	0.78**	1.00	1.00
	BaRb	BaSr	BaTi	BaZr	BaAl	BaFe	CFBa	IGEOBa
BaRb	1.00							
BaSr	0.52**	1.00						
BaTi	0.40**	0.36*	1.00					
BaZr	0.35*	0.28*	0.27	1.00				
BaAl	0.55**	0.48**	0.40**	0.25	1.00			
BaFe	0.51**	0.41**	0.61**	0.23	0.83**	1.00		
CFBa	0.59**	0.64**	0.75**	0.35*	0.50**	0.55**	1.00	
IGEOBa	0.59**	0.64**	0.75**	0.35*	0.50**	0.55**	1.00	1.00
	CrRb	CrSr	CrTi	CrZr	CrAl	CrFe	CFCr	IGEOCr
CrRb	1.00							
CrSr	0.64**	1.00						
CrTi	0.67**	0.46**	1.00					
CrZr	0.25	0.26	0.23	1.00				
CrAl	0.71**	0.61**	0.56**	0.22	1.00			
CrFe	0.69**	0.56**	0.71**	0.21	0.88**	1.00		
CFCr	0.79**	0.66**	0.84**	0.29*	0.66**	0.70**	1.00	
IGEOCr	0.79**	0.66**	0.84**	0.29*	0.66**	0.70**	1.00	1.00
	CuRb	CuSr	CuTi	CuZr	CuAl	CuFe	CFCu	IGEOCu
CuRb	1.00							
CuSr	0.92**	1.00						
CuTi	0.91**	0.84**	1.00					
CuZr	− 0.03	0.05	0.17	1.00				
CuAl	0.74**	0.65**	0.73**	0.01	1.00			
CuFe	0.76**	0.67**	0.83**	0.08	0.90**	1.00		
CFCu	0.95**	0.89**	0.94**	0.11	0.69**	0.75**	1.00	
IGEOCu	0.95**	0.89**	0.94**	0.11	0.69**	0.75**	1.00	1.00
	NiRb	NiSr	NiTi	NiZr	NiAl	NiFe	CFNi	IGEONi
NiRb	1.00							
NiSr	0.93**	1.00						
NiTi	0.92**	0.91**	1.00					
NiZr	0.37**	0.37**	0.41**	1.00				

**Table 5** continued

	NiRb	NiSr	NiTi	NiZr	NiAl	NiFe	CFNi	IGEONi
NiAl	0.88**	0.85**	0.87**	0.39**	1.00			
NiFe	0.88**	0.85**	0.90**	0.39**	0.95**	1.00		
CFNi	0.96**	0.94**	0.97**	0.41**	0.89**	0.89**	1.00	
IGEONi	0.96**	0.94**	0.97**	0.41**	0.89**	0.89**	1.00	1.00
	PbRb	PbSr	PbTi	PbZr	PbAl	PbFe	CFPb	IGEOPb
PbRb	1.00							
PbSr	0.93**	1.00						
PbTi	0.90**	0.87**	1.00					
PbZr	0.24	0.25	0.26	1.00				
PbAl	0.76**	0.75**	0.76**	0.17	1.00			
PbFe	0.73**	0.69**	0.82**	0.18	0.89**	1.00		
CFPb	0.96**	0.91**	0.95**	0.26	0.75**	0.76**	1.00	
IGEOPb	0.96**	0.91**	0.95**	0.26	0.75**	0.76**	1.00	1.00
	ThRb	ThSr	ThTi	ThZr	PbAl	PbFe	CFTh	IGEOTH
ThRb	1.00							
ThSr	0.65**	1.00						
ThTi	0.64**	0.47**	1.00					
ThZr	– 0.01	0.00	0.02	1.00				
PbAl	0.66**	0.58**	0.54**	0.05	1.00			
PbFe	0.53**	0.43**	0.60**	0.05	0.83**	1.00		
CFTh	0.79**	0.66**	0.79**	0.03	0.61**	0.52**	1.00	
IGEOTH	0.79**	0.66**	0.79**	0.03	0.61**	0.52**	1.00	1.00
	YRb	YSr	YTi	YZr	YAl	YFe	CFY	IGEYOY
YRb	1.00							
YSr	0.87**	1.00						
YTi	0.87**	0.77**	1.00					
YZr	0.81**	0.86**	0.81**	1.00				
YAl	0.82**	0.78**	0.76**	0.72**	1.00			
YFe	0.76**	0.71**	0.78**	0.70**	0.89**	1.00		
CFY	0.93**	0.86**	0.94**	0.82**	0.81**	0.77**	1.00	
IGEYOY	0.93**	0.86**	0.94**	0.82**	0.81**	0.77**	1.00	1.00
	ZnRb	ZnSr	ZnTi	ZnZr	ZnAl	ZnFe	CFZn	IGEONz
ZnRb	1.00							
ZnSr	0.89**	1.00						
ZnTi	0.86**	0.79**	1.00					
ZnZr	0.19	0.19	0.22	1.00				
ZnAl	0.69**	0.62**	0.70**	0.12	1.00			
ZnFe	0.62**	0.50**	0.76**	0.11	0.85**	1.00		
CFZn	0.93**	0.85**	0.92**	0.21	0.65**	0.64**	1.00	

**Table 5** continued

	ZnRb	ZnSr	ZnTi	ZnZr	ZnAl	ZnFe	CFZn	IGEOZn
IGEOZn	0.93**	0.85**	0.92**	0.21	0.65**	0.64**	1.00	1.00

\*\*Correlation is significant at the 0.01 level (2-tailed)

\*Correlation is significant at the 0.05 level (2-tailed)

correlated values were slightly higher than Ti, Al and Fe. PTEs such as As, Cu, Ni, Pb, Y and Zn showed a strong metallic relationship with these normalizers Sr > Ti > Rb. Zirconium exhibited a strong correlation with Yttrium’s EF but a moderate correlation with the other PTEs. The excellent relationship between the MeNo and CFMe/IgeoMe suggested that Al, Fe, Sr, Ti, and Rb specify contamination in agricultural soil. Swarnalatha et al. (2013) reported a weak correlation between NiTi/NiAl (0.67) and CrTi/CrAl (0.50) in the previous study, whereas the correlation in the current study was 0.87 and 0.56, respectively. However, the following correlation matrix between CuTi/CuAl (0.88), ZnTi/ZnAl (0.75), and PbTi/PbAl (0.81) in the previous study by Swarnalatha et al. (2013) showed a strong relationship as compared to *r* values = 0.73, 0.70, and 0.76 in this current study.

**Selection of the suitable geochemical background and normalizer**

It has been reported that the use of GBL is centered on the reliability of the characterization and quality quantification of PTEs in soil utilizing the suitable GBL to estimate the elemental content of PTEs in various soils (Gąsiorek et al., 2017; Xu et al., 2015). Ascertaining PTEs levels in agricultural soils using appropriate GBL is critical for determining the status of PTEs toxicity and alerting stakeholders to the practical steps to take to ensure human health safety. The estimated EFs confirmed that among the six normalizers (Al, Fe, Ti, Zr, Sr, and Rb) that were selected from various GBL (WAV and EAV) to compute the degree of contamination in agricultural/industrial soil, WAV was the most appropriate. Three (Sr, Ti and Zr) out of the six normalizers selected from WAV interpreted the degree of contamination of the agricultural/industrial soil at the various scale of contamination levels better than EAV (See Table 4). Furthermore, computed Igeo and CF also revealed that

selecting WAV as a geochemical background exposes contamination levels in agricultural/industrial soil better than the EAV. Geochemical background levels can facilitate the detection of PTEs in soil and play a significant role in interpreting the enrichment level of PTEs(Varol, 2011). When WAV was compared to EAV across the three pollution indices used, WAV exposed toxicity levels in the most of the PTE pollution indices computed (See Tables 3 and 4). As a result, the use of precise pollution instruments to identify and, to the maximum extent possible, ameliorate increasing soil deterioration is critical for a comprehensive assessment of the degree of contamination in agricultural soil (Qingjie et al., 2008). The agricultural field is essential because it is used for food cultivation.

In general, various normalizers such as Al, Fe, Mn, Zr, Sr, Si, and Rb were utilized to determine the degree of contamination in multiple soils (Kebonye & Eze, 2019; Swarnalatha et al., 2013). Al, Fe, Ti, Zr, Sr, and Rb were all considered and assessed to select the optimal agricultural/industrial soil normalizer. According to Carvalho et al. (2002), Al and Fe are widely used normalizers employed due to their spatial relationships with PTEs and simplicity of analysis. In addition, concentrations of Al and Fe in soils are very high and are not significantly influenced by common agricultural practices (especially Al that are occluded in the structure of phyllosilicate minerals); therefore, they are widely used as normalizers.

The Fe result obtained in the correlation matrix (See Table 3) reinforces the fact that Fe was prevalent in the study area. The pollution indexes yielded a moderate result for Al (CF and Igeo). This is due to its usage in steel and metal works and cannot be an effective normalizer for agricultural/industrial soil.

MeZr had a relatively good relationship with the PTEs as well as CFAs/IgeoAS, CFAs/IgeoBa, CFCr/IgeoCr, CFCu/IgeoCu, CFNi/IgeoNi, CFNi/IgeoNi, CFY/IgeoY, (see Table 5). Titanium alloys have

increasingly been used in aviation, aerospace, chemical, shipbuilding and other industrial sectors (Jahedi et al., 2009). Titanium alloys have a high specific strength, strong corrosion resistance, high heat resistance, simple soldering and other characteristics that have been commonly used in various fields (Cui et al., 2011). Therefore, Ti is not suitable as a normalizer in agricultural/industrial soil. Zirconium correlated poorly with CFMe/IgeoMe hence its immediate elimination as an appropriate normalizer (See Table 5). Strontium was highly correlated with CFMe/IgeoMe but was significantly enriched in the soil compared to the normal enrichment level required in the soil used. According to Kabata-Pendias (2011), Sr in phosphorites may perhaps be concentrated up to 2000 mg/kg. Consequently, it can similarly be a resident source of soil contamination owing to phosphate fertilizers. Kabata-Pendias (2011) has further stated that some amendment soil materials containing higher amounts of Sr could be a source of pollution because the average concentrations of Sr in these materials are (in mg/kg): communal sludge, 75; limestone, 610; manure, 80; P-fertilizers, 610; and industrial sludge, 270. Therefore, Sr is not suitable as a normalizer for agricultural/industrial soil.

Rubidium was suitable and the most highly correlated with CFMe/IgeoMe. MeRb demonstrated a steady correlation ranging from 0.59 to 0.96 (See Table 5). Particularly apart from it showing a moderate to high correlation with Ba, Cr and Th, it was highly correlated with the other PTEs with *r* values ranging from 0.91 to 0.96 (See Table 5). Among the prospective normalizers chosen for this study, Rb satisfies all the rigorous criteria of a normalizer and hence has no or minimal anthropogenic related effect. Since it is geochemically immobile, Rb can be well maintained in the loess-paleosol sequence after deposition and its concentration depends mainly on the properties of the winter monsoon-blown dust and the strength of the summer monsoon-induced pedogenesis (Chen et al., 2000). Literature such as Kabata-Pendias (2011) situates the behavior of Rb as mostly sedimentary plus pedogenic processes that are primarily controlled by the sorption on clay minerals. Conversely, it further states that the concentrations Rb in farmyard manure are infinitesimally small (0.06 mg/kg) and low in phosphate fertilizer with an average value of 5 mg/kg. This makes it more suitable and uninfluenced anthropogenically.

## Conclusion

In conclusion, agricultural soils require appropriate GBL and normalizers to estimate the degree of pollution in them. Identifying a suitable normalizer and the appropriate geochemical background level in assessing PTEs enrichment in soils used for crop production revealed that WAV was the most reliable GBL that evaluates the degree of contamination. Different assessment levels such as calculated EFs, CFs and Igeo using selected normalizer coupled with GBL from WAV elicited the degree of contamination better than EAV. Diverse, prospective normalizers such as Al, Fe, Ti, Zr, Sr and Rb were evaluated to expose the degree of contamination of PTEs (Cr, Ni, Cu, Y, Ba, Th, As, Pb and Zn) in cultivated soils. The correlation matrix between CFs, EFs, and Igeos was a vital parameter coupling with multiple criteria such as little or no anthropogenic influence in selecting the normalizer for cultivated soils. Therefore, Rb was chosen as the optimal and the most suitable normalizer appropriate for agricultural soils in the studied site. Even though Al, Fe, Sr and Ti demonstrated a strong metallic strength, other factors such as anthropogenic influence affected choosing any of the elements as a normalizer. Based on the findings, Rb and WAV are the suitable normalizer and GBL to evaluate the degree of contamination of PTEs in a studied agricultural field. As a result, suitable Rb and appropriate GBL (WAV) play a vital role in exposing pollution levels in this type of soil for stakeholders to take mitigating measures to ensure soil health, security, and quality. Therefore, this research work presented Rb as a suitable normalizer and WAV as appropriate GBL for the estimation of PTEs in a cultivated field.

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**Declarations**

**Conflict of interest** The authors declare that they have no known competing personal interests or relationships that could have appeared to influence the scientific work in this manuscript.

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