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Heavy Metals Geochemical Baseline in Topsoil on Local Scale: A case study in Misrata, Libya

khalifa Sadeag Alatresh

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Authors affiliation
Department of Environmental Health, Faculty of Medical Technology-Misrata
khalifa903ly@gmail.com
Tel:0926511295

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ABSTRACT

In May 2022, fifty-two topsoil samples (0 to 20 cm) were collected from the Tummina agricultural area in Misrata, situated in the northwestern region of the Libyan Sahel. We analyzed the collected samples for (Fe, Al, Mn, Co, Zn, Cr, Pb, Cu, Ni, Cd, and As) through the XRF technique. Aiming to: Set the most proper normalizing element for this area, develop a local geochemical baseline (GBL) using four methods (cumulative frequency curve, iteration removal, reference metal normalization, and box-whisker plot), and compare the outcome to the upper continental crust composition and data from other continental-scale soil surveys. This investigation is the first to propose baseline values for a region in Libya. The result demonstrated that, out of two viable reference elements (Fe and Al), Al is the best reference element for the normalizing method. The mean local GBL values obtained from the four procedures of (Mn, Co, Zn, Cr, Pb, Cu, Ni, Cd, and As) were (64.12, 6.61, 8.53, 4.81, 9.5, 8.73, 5.59, 1.98, and 1.74 mg/kg), respectively. The estimated local GBL levels of (Co, Zn, Cr, Pb, Cu, Ni, and As) were significantly lower than the upper crust's (UCC) and the Earth's crust's (ECS) values for sedimentary rocks, which are often employed in screening contaminated soil. At the same time, Cd baseline levels were more significant in comparison. Hence, using the global background as a benchmark may result in underestimation or overstate of toxic elements pollution in soil, thus misrepresenting the risk heavy metals pose to human and environmental health. We propose such studies for the country's various geological regions to overcome the shortcomings of using global or world soil geochemical reference values.

خط الأساس الجيوكيميائي للمعادن الثقيلة على النطاق المحلي في التربة السطحية:
دراسة حالة في مصراتة ، ليبيا

في هذه الدراسة تم جمع 52 عينة من التربة السطحية (0 إلى 20 سم) من منطقة طمينة الزراعية في مصراتة، وتحليل العناصر (Fe، Al، Mn، Co، Zn، Cr، Pb، Cu، Ni، Cd، As). الهدف من هذا البحث هو إنشاء خط أساس جيوكيميائي محلي ومقارنته بتكوين القشرة القارية العليا وبيانات من مسوحات ترب أخرى. أشارت النتائج الى أن الألومنيوم كان أفضل عنصر مرجعي للتطبيق في منطقة الدراسة، وأن مستويات خط الأساس الجيوكيميائي المحلي (GBL) للعناصر المعنية كانت أقل بكثير من تلك في قشرة الأرض العلوية (UCC) . وأشارت الدراسة كذلك إلى أن استخدام القيم المرجعية العالمية كمعايير مرجعية لتلوث التربة قد يؤدي إلى المبالغة سلبا او ايجابا في تقييم تلوث التربة بالعناصر السامة و تأثيرها على صحة الإنسان والبيئة وتقترح دراسات مماثلة لمناطق أخرى في ليبيا.

INTRODUCTION

The Earth's surface hosts the life of people, plants, and animals and serves as the interface between the realms of the environment. Many chemical, physical, and biological activities are present in this critical zone; these processes affect energy and mass exchanges controlling diverse and vital processes, including soil formation, plant development, water storage, nutrient cycling, and transport of metals. The agricultural soil interface is under extreme production stress due to growing populations and economic expansion. Intensive human activity has resulted in global agricultural soil pollution, impeding agriculture's sustainable development (Tilman et. al., 2017). Heavy metals, a category of toxic metals, are one of the crucial causes responsible for soil pollution and environmental degradation (Burges et. al., 2015; Yuanan et. al., 2020). Several factors contribute to heavy metals' prominence as the most significant pollutants in agricultural soils, including their widespread distribution, high toxicity, and bioavailability. Moreover, they might seriously threaten the agroecosystem and public health (Hou et. al., 2020; Yang et. al., 2020). Consequently, Heavy metal contamination of agricultural soils has recently gained global attention (Yuanan et. al., 2020). Toxic elements of farm soils may reduce crops' quality and yield and lead to more pollution in terrestrial and aquatic environments. Thus, it can be reflected in human health through exposure pathways such as skin contact, inhalation, direct ingestion, and diet through the soil food chain (Rutigliano et. al., 2019; Varol et. al., 2020; J. Wang et. al., 2019). Therefore, one of contemporary society's most urgent problems is avoiding and regulating soil-borne heavy metal pollution. So, it is essential to investigate heavy metal contents in soils and evaluate the pollution level. The background and regional geochemical baseline (GBL) values are frequently used as benchmarks in assessing soil heavy metal contamination. Background value is the concentration of metals in a particular environment that reflects unaffected natural processes (Gałuszka & Migaszewski, 2011; Reimann & Garrett, 2005). Thus, it usually expresses the standard level of distinction between natural and anthropogenic element concentrations. The environmental geochemical baseline (GBL) refers to the natural abundance of an element in soil when a local data set is used as a reference. In contrast to the background value, the regional GBL value is more inclined to investigate the current ecological situation. It represents regional present-day element concentrations of background and nonpoint-source contamination (Darnley, 1997). Estimating an element's "natural background" in soils has become nearly impossible because of increasing human activities. Moreover, the natural abundance of heavy metals in the original soil varies in different regions. In such cases, the geochemical baseline (GBL) value may be used as an indicator of "ambient background" or "actual background" for measuring present levels of environmental quality and for quantifying the future changes in soil concentrations of trace elements. Another approach to assessing soil quality from pollution indices is to utilize the average composition of the upper continental crust and data from previous continental-scale soil surveys as a direct geochemical background, e.g.; (Kabata-Pendias & Pendias, 2001; Rudnick, 2003; Taylor & McLennan, 1995; Turekian & Hans, 1961). The values given are based on data from existing soil studies in various regions, often integrated with estimates of the Earth's crust geochemical composition. The empirical data in this technique are usually derived from surveys that cover minimal areas and consist of a small sample size (Kabata-Pendias & Pendias, 2001). There is disagreement about whether these values represent actual soils from wide and diverse regions, entire continents, or even all continents.

Furthermore, the samples used to generate the estimations were frequently evaluated at various times, in different laboratories, and with different analytical procedures, rendering them incomparable. Nowadays, increased attention is being focused on promoting GBL approaches use. Concerning environmental GBL determination, the methods used in the published reports mainly consist of simple and robust statistical procedures and integration combining two or more of the above (Alizadeh - Kouskuie et. al., 2020; Karim et. al., 2015; Li et. al., 2021; Tian et. al., 2017; S. Wang et. al., 2019; Zhang et. al., 2020).

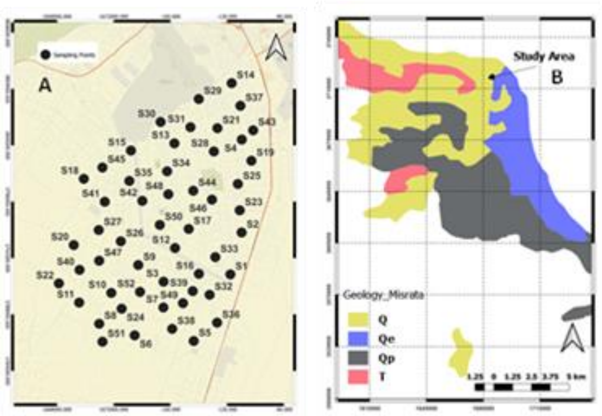

Fig. 1. (A) Location of the Tummina agricultural area and the sampling points. (B) Geological map (modified after (Persits et. al., 1997)) of the study area in Misrata and neighboring locations (Q: Quaternary; Qe: Holocene; Qp: Pleistocene; T: Tertiary) (Quaternary sediments dominate this area consist primarily of carbonate aeolian sand).

Resource depletion and environmental degradation may have occurred in the Tommina agricultural area, Misrata, Libya, as a typical agricultural area with intensive agricultural activities. Local GBLs can provide environmental management instructions for ecological management and serve as a scale for judging the feasibility of development. The topsoil is the most crucial interface of material interaction, and its geochemical baseline (GBL) level has significance for the environment. Currently, there are no studies on the local GBL in this region. As a result, this study aims to set the most proper normalizing element for this area, establish the regional geochemical baseline (GBL) of Mn, Co, Zn, Cr, Pb, Cu, Ni, Cd, and As using four widely used techniques: box-whisker plot, reference metal normalization, iterative removal, and cumulative frequency curve and compare the outcome to the upper continental crust composition and data from other continental-scale soil surveys. The findings of this study will improve our understanding of the quality of the topsoil in the Tummina agricultural area and assist in providing fundamental data support for future environmental protection policies.

MATERIALS AND METHODS

Study area

The study area lies in the northwestern region of the Libyan Sahel, southeast of Misrata city. It is popularly known as the Tummina agricultural area, located between 32°14'8.03"N and 15° 2'22.62" E (Fig. 1A). The town has a variety of commercial and industrial activities, along with semi-urban agricultural production. The study area is an essential region in Misurata city for producing vegetables, dates, olive oil, forage crops, and grapes. According to our investigation, this area is frequently irrigated due to fluctuation and low precipitation rates. Dairy or chicken manure, compound fertilizer, and urea are the main fertilizers used in this area

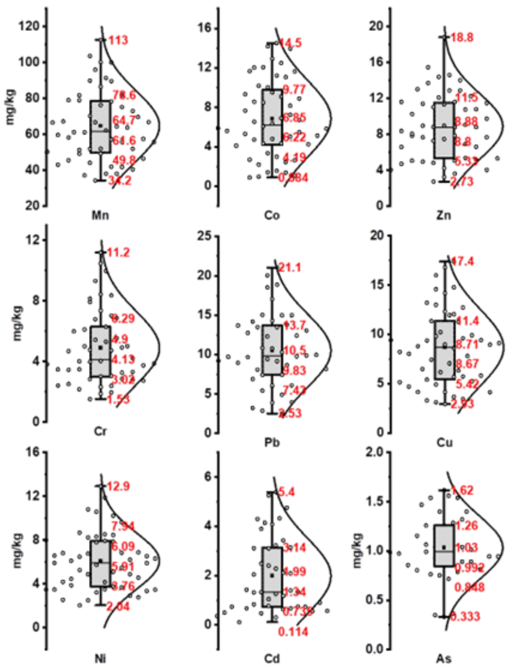

Figure 2: Geochemical baseline values derived using the box-whisker approach

Additionally, pesticides are somewhat used to control insects and diseases in vegetables and other crops. The climate is hot and dry (BWh) (Kottek et. al., 2006) with mean annual precipitation (246.9 mm/y) and temperatures ranging from 13.51°C to 28.22°C (over the period 2000-2020 recorded at Misurata Metrological Station), qualifying it as an arid region. (CADMW, 1975) reported that the basement rock of this region consists mainly of Quaternary and Tertiary sediments. The Quaternary sediments consist primarily of carbonate aeolian sand, which lies over Tertiary sediments comprised of limestone and sandstone (Fig.1B).

Soil sampling and analysis

The research area's surface layer (0–20 cm) was sampled in May 2022. The sampling sites were pre-planned at a density of around one location per 2 square kilometers. Finally, we identified 52 sampling points based on randomization to reflect the research region using a hand-held Global Positioning System (GPS) device Figure 1B. Three subsamples, weighing about 150 g each, were taken from the different sampling points using the diagonal multi-point sampling method (scale: 100 ×100 m) before being equally blended to create a homogenized sample weighing about 500 g. After air drying at room temperature (25 C°), the soil samples were crushed with agate mortar, passed through a 0.149 mm nylon sieve, and submitted to the Libyan Petroleum Institute Laboratory for total concentrations of (Fe, Al, Mn, Co, Zn, Cr, Pb, Cu, Ni, Cd, and As) using ZSX Primus II wavelength dispersive X-ray fluorescence (WDXRF).

Local geochemical baseline (GBL) defining methods

Given the absence of local information regarding background or natural concentration element values in the study area, local GCB of nine elements (Mn, Co, Zn, Cr, Pb, Cu, Ni, Cd, and As) were established using four methods. The arithmetic average was considered the final value.

Cumulative frequency distribution (CFD) method

For the relative cumulative frequency curve, the X-axis is the HM concentrations, and the Y-axis represents their corresponding cumulative frequency (Wei & Wen, 2012). This method adopts normal decimal coordinates, and there may be one or two inflection points on the curve, symbolizing outliers' lower and upper limits. We used consecutive linear fitting to find the position of inflection points. With the increase of samples of higher concentration involved in the fitting, inflection points will be found under the linear R2 > 0.95 and P < 0.05. The baseline value was calculated by all data points below the inflection point when the curve only had one bend. However, if there were two inflection points, the shape of the curve between the two bends is considered a critical factor. However, if there were two inflection points, the shape of the curve between the two bends is regarded as a vital factor. The computation data should include the part before the lower inflection point (or before the upper inflection point) in case of the middle part of the cumulative distribution curve is similar to the forepart (or the following part). The average value of computation data was considered the GBL value.

Metal normalization method

The basic idea of normalization is to take normalizing elements as the reference and establish the equation to determine the geochemical baseline according to the linear correlation between them and each metal. It can compensate for grain size and mineralogy effects on trace element concentrations. This method can be expressed as an equation established by the correlation between active and inert elements (Newman & Watling, 2007).

$$C_m = aC_n + b \quad (1)$$

C_m is the measured concentration of contaminated elements in the sample, C_n is the concentration of selected normalizing element, a and b are the regression constants. The 95% confidence interval was estimated using the OriginPro 2021, thus defining a range of data variability around each significant regression line. The scatter points outside the 95% confidence interval must be eliminated to more accurately determine the geochemical baseline. Generally accepted that the scatter points inside the 95% confidence interval are not impacted by human-caused pollution and can represent the baseline range.

Table 1 Geochemical baseline values (mg/kg) computed by various methods in the agricultural topsoil of Tummina.

Element	CFD	MN	BW	IR			The mean value of the four methods
					Lower Bound	Upper Band	
Mn	61.39	68.63	61.6	63.74	25.68	103.68	64.12
Co	6.40	6.47	6.22	6.85	-0.90	14.59	6.61
Zn	8.06	7.88	8.80	8.69	1.56	16.21	8.53
Cr	4.44	5.09	4.13	4.77	-0.53	10.97	4.81
Pb	8.36	8.33	9.83	9.84	-0.60	21.22	9.50
Cu	8.02	9.94	8.67	8.35	0.46	16.97	8.73
Ni	5.43	6.04	3.76	5.83	0.73	11.72	5.59
Cd	1.11	1.33	1.34	2.56	-1.66	7.17	1.98
As	1.29	2.35	0.99	1.62	-2.78	6.98	1.74

IR: Iteration removal method; BWP: Box-whisker; MN: Normalization method; CFD: Cumulative frequency distribution method (mean value) with $p < 0.05$ and R2 > 0.99 as a condition of the linearity of distribution;

Table 2 The correlation coefficients and regression equations of the inert and active elements.

Element	Fe	Al	Regression equation	R^2
Mn	0.006	0.311*	$y = 11.42 + 14.86 \times Al$	0.81
Co	-0.145	0.233	$y = 1.22 + 1.27 \times Al$	0.99
Zn	-0.104	0.105	$y = 1.80145 + 1.10 \times Al$	0.99
Cr	0.012	0.031	$y = 1.03 + 1.03 \times Al$	0.99
Pb	-0.171	0.196	$y = 1.88 + 1.32 \times Al$	0.97
Cu	-0.048	0.195	$y = 1.32 + 2.06 \times Al$	0.86
Ni	0.063	0.039	$y = 1.21 + 1.04 \times Al$	0.91
Cd	-0.034	0.079	$y = 0.95 + 0.09 \times Al$	0.87
As	0.031	0.294*	$y = 0.14 + 0.55 \times Al$	0.99

* and ** indicate significant correlations at P<0.05 and P<0.01 levels, respectively.

Box-whisker plot method

The box-whisker plot derived from the minimum value, first quartile, median, third quartile, and the maximum value is a valuable tool for calculating the geochemical baseline value. The calculation process is fulfilled by successively eliminating outliers outside of one and a half times the interquartile range. Finally, the remaining data median was considered the geochemical baseline value.

Iteration removal method

The iteration removal adopted double-standard deviation to quantitatively determine the geochemical baseline value (Reimann & Filzmoser, 2000). When test data showed normal distribution, outliers' upper and lower limits could be identified by calculating the average, plus or minus double-standard deviation ($\bar{x} \pm 2x$). Outliers more significant than ($\bar{x} + 2s$) and less than ($\bar{x} - 2s$) were successively removed until no outliers remained. Then, the remaining data's arithmetic average was considered the geochemical baseline value. First, test data were transformed via natural logarithm if they showed the logarithmic normal distribution and the following processing was the same as the normal distribution.

Statistical analysis

OriginLab 2021 software, Microsoft Excel for Windows, and QGIS software performed all analysis procedures and mapping. The Kolmogorov-Smirnov (K-S) test was applied to test the normal distribution of raw data.

RESULTS AND DISCUSSION

Establishing local geochemical baselines (GBL)

Table 1 shows the geochemical baseline values (mg/kg) calculated using various techniques in Tummina's agricultural topsoil. Figure 2 depicts the box-whisker plot of the nine heavy metals in the topsoil of the Tummina agricultural district. After removing outliers, the geochemical baseline values for Mn, Pb, Zn, Cu, Co, Ni, Cr, As, and Cd calculated by this method were 61.6, 6.22, 8.80, 4.13, 9.83, 8.67, 3.76, 1.34, and 0.99 mg/kg, respectively (Table 1). Using the iterative removal method, the geochemical baseline values for Mn, Pb, Zn, Cu, Co, Ni, Cr, As, and Cd were 63.74, 6.85, 8.69, 4.77, 9.84, 8.35, 5.83, 2.56, and 1.62 mg/kg, respectively (Table 1). The cumulative frequency curves for the nine heavy metals showed a single inflection point in the curves for Cd and Co (Fig. 3). The baseline values of Cd and Co were 1.11 and 6.40 mg/kg, which was calculated by all the sample points below the inflection point. In addition, two inflection points occurred in the cumulative frequency curves of (Mn, Zn, Cr, Pb, Cu, Ni, and As). Moreover, the curve shape between the two inflections was similar to that after the upper outlier. Therefore, the baseline values of these seven elements were calculated as 61.39, 8.06, 4.44, 8.36, 8.02, 5.43, and 1.29 mg/kg using the data before the upper outlier. Sample points participating in the calculation of geochemical baseline values for Mn, Co, Zn, Cr, Pb, Cu, Ni, Cd, and As accounted for 92%, 94%, 88%, 81%, 92%, 87%, 58%, and 88%, respectively. Indicating that the accumulation of the nine heavy metals in topsoil had a consistent changing trend Co > Mn > Cu > Zn > Cr > As > Pb > Ni > Cd. In the procedure of reference metal normalization, one prevalent way of normalizing geochemical data is by employing one element as a grain-size proxy to compensate for the impacts of mineralogy and grain size on trace element concentrations and to explore anomalous metal contributions (Covelli & Fontolan, 1997). The normalizing element must be an essential component of one or more of the fundamental trace metal carriers and reflect its granular variability in soils or sediments. Therefore, the elements of Al, Ti, Fe, Y, Eu, Ce, Sc, and others are commonly used as elements of standardization (Wei & Wen, 2012; Zhou et. al., 2019). Table 2 demonstrates the findings of the correlation analysis between prospective reference elements and elements of concern for selecting the most appropriate choice. Al was chosen as a proper reference element in the following normalization procedure since it positively correlates with all elements. Moreover, using the classical coefficient of variation (CV) (Guo et. al., 2012; Niu et. al., 2019) to study the elements' distribution variability and non-parametric robust coefficient of variation (CV#) (Reimann & De Caritat, 2005) to estimate the distribution variability without being affected by outliers (Table 3). In contrast to the relatively high CV values of metals impacted by anthropogenic sources, they evaluate comparatively low CV values for elements dominated by natural sources. These authors divide the degree of variability into four categories: low variability (CV < 20%), moderate variability 20% ≤ CV ≤ 50%, high variability CV > 50%, and very high variability (CV > 100%). The low variability values of Al (CV = 16%, CV# = 15%), which are less than 20% and less than the CV and CV# values of potentially dangerous elements, imply a limited anthropogenic input. Probably due to similar clay mineral combinations and consistency in the clay mineral chemistry of the study area. So, Al was considered the conservative element in this study. Despite the levels of the concentration of the metals analyzed, establishing a local baseline is vital to assess potential contamination by toxic elements and provide the means to distinguish between their natural or anthropogenic origin. The linear relationship between each element of concern and Al concentration was determined according to Equation 1 (Table 2). After iteratively eliminating the samples lying outside 95% confidence intervals, we established new linear equations for predicting the geochemical baseline value (Table 2). Finally, by substituting the average concentration of the reference element into the new equation, we calculated the geochemical baseline values as 68.63, 6.47, 7.88, 5.09, 8.33, 9.94, 6.04, 1.33, and 2.35 mg/kg for Mn, Co, Zn, Cr, Pb, Cu, Ni, Cd, and As, respectively (Table 1).

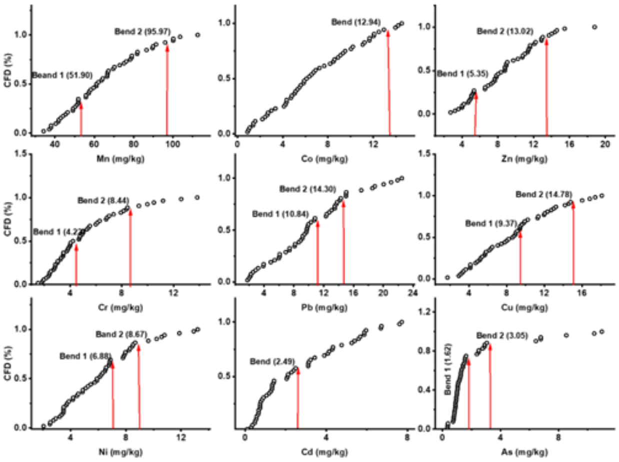

Figure 3: Geochemical baseline values computed using the cumulative frequency curve of nine elements

The average values of the geochemical baseline results obtained from the four methods were considered the final value. Consequently, the absolute geochemical baseline values for the topsoil in Tummina agricultural district were 64.12, 6.61, 8.53, 4.81, 9.50, 8.73, 5.59, 1.98, and 1.74 mg/kg for Mn, Co, Zn, Cr, Pb, Cu, Ni, Cd, and As, respectively (Table 1). Another approach to assess the soil quality from pollution indices is to use the average composition of the upper continental crust (UCC) as a direct geochemical background. Three global reference values as the average distribution of the elements in the Earth's crust for the sedimentary rocks (ECS) (Turekian & Hans, 1961) and the average compositions of the upper continental crust proposed by (Taylor & McLennan, 1995) and (Rudnick, 2003) were used to compare against the local GBL values obtained in the present study (Table 3). A first observation, the average values of the local GBL results obtained from the four methods of Co, Zn, Cr, Pb, Cu, Ni, and As were lower than their corresponding UCC and ECS values. At the same time, Cd baseline levels were more significant in comparison. Notably, the disparity between calculated local GBL values of elements and globally accepted background suggests that such studies for the country's various geological provinces are necessary to properly and effectively manage and sustain the environment against environmental degradation.

On the other hand, the geochemical background is not a constant value over time due to the natural processes taking place. Additionally, the geochemical background value is local or regional rather than global, and the value adopted affects the quality of the assessment of the local environment. The local GBL is the concentration determined at a specific time and, therefore, can include natural and human influences; further, a local GBL establishes reliable criteria for the continuous assessment and monitoring of soil quality.

Table 3. Summary of the elements' concentrations (mg/kg) in topsoil samples from the study area.

	Mean	St. Dev	CV	Minimum	Median	Maximum	MAD	CV#
Fe	3.62	0.96	26%	2.37	3.35	6.26	0.54	24%
Al	4.76	0.75	16%	3.14	4.76	6.62	0.49	15%
Mn	64.68	19.50	30%	34.22	61.62	112.54	14.08	34%
Co	6.85	3.87	57%	0.88	6.22	14.52	2.99	71%
Zn	8.88	3.66	41%	2.73	8.80	18.81	2.81	47%
Cr	5.22	2.87	55%	1.53	4.45	13.84	1.62	54%
Pb	10.31	5.46	53%	1.78	9.76	22.49	3.75	57%
Cu	8.71	4.13	47%	1.73	8.71	18.10	3.27	56%
Ni	6.22	2.75	44%	2.04	6.01	13.20	2.05	51%
Cd	2.76	2.21	80%	0.11	2.11	7.73	1.44	101%
As	2.10	2.44	116%	0.33	1.18	10.99	0.34	43%

MAD: Median Absolute Deviation

MAD = Median (xi - median (xi), where xi is the concentration of element I

CV: Coefficient of Variation

CV#: Robust Coefficient of Variation = (MAD/Median)×100,

CONCLUSION

In this study, we established the local GBL of the potentially toxic elements (Mn, Co, Zn, Cr, Pb, Cu, Ni, Cd, and As) in the topsoil of the Tummina agricultural region in Misrata, Libya. The local geochemical baseline was determined using four statistical and reference element approaches: box-whisker plot, reference metal normalization to Al as the "conservative" element, iterative removal, and cumulative frequency curve. Our study concludes that:

1- Comparatively to Fe, Al is an appropriate reference element for establishing the regional GBL for the soil of the Tummina agricultural area.

2- Estimating the "natural background" levels of the elements in the soil has become almost impossible due to increased human activity and differences in the natural abundance of these elements in the original soils in different regions. The study confirmed a significant disparity between the elements' calculated local GBL values and the globally accepted background. Thus, using the "natural background" or the global background as a benchmark may result in underestimation or overstate of toxic elements and soil contamination and therefore misrepresent the risk heavy metals pose to human and environmental health. Suggests that such studies for the country's various geological provinces are necessary to properly and effectively manage and sustain the environment against environmental degradation. Further research will combine single and integrated indices founded on the local GBL instead of natural background and global reference to investigate the ecological and health risk, distribution characteristics, and source apportionment of these elements in the Tummina agricultural area. This strategy has been widely adopted to obtain a more accurate assessment of the studied area (Li et. al., 2021; Ma et. al., 2022; Zhang et. al., 2020).

Table 4 The composition (mg/kg) of the continental upper crust (UCC) according to several authors and the average local baseline (mg/kg) from the methods used in the present work

Element	Local geochemical baseline	Turekian and Wedepohl (1961)	Taylor and McLennan (1995)	Rudnick and Gao (2003)
Mn	64.12	-	-	-
Co	6.61	19.0	20.0	17.0
Zn	8.53	95.0	71.0	67.0
Cr	4.81	90.0	35.0	69.0
Pb	9.50	20.0	20.0	17.0
Cu	8.73	45.0	25.0	39.0
Ni	5.59	68.0	20.0	55.0
Cd	1.98	0.3	0.1	0.1
As	1.74	13.0	1.5	1.6

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