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GIS-Based Spatial Distribution and Evaluation of Selected Heavy Metals Contamination in Topsoil around Ecton Mining Area, Derbyshire, UK

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Abstract**—**The study area (Ecton mining area) is located in the southern part of the Peak District in Derbyshire, England. It is bounded by the River Manifold from the west. This area has been mined for a long period. As a result, huge amounts of potentially toxic metals were released into the surrounding area and are most likely to be a significant source of heavy metal contamination to the local soil, water and vegetation. In order to appraise the potential heavy metal pollution in this area, 37 topsoil samples (5-20 cm depth) were collected and analysed for their total content of Cu, Pb, Zn, Mn, Cr, Ni and V using ICP (Inductively Coupled Plasma) optical emission spectroscopy. Multivariate Geospatial analyses using the GIS technique were utilised to draw geochemical maps of the metals of interest over the study area. A few hotspot points, areas of elevated concentrations of metals, were specified, which are presumed to be the results of anthropogenic activities. In addition, the soil's environmental quality was evaluated by calculating the Mullers' Geoaccumulation index (I geo), which suggests that the degree of contamination of the investigated heavy metals has the following trend: Pb > Zn > Cu > Mn > Ni = Cr = V. Furthermore, the potential ecological risk, using the enrichment factor (EF), was also specified. On the basis of the calculated amount or the EF, the levels of pollution for the studied metals in the study area have the following order: Pb>Zn>Cu>Cr>V>Ni>Mn.

Keywords**—**Heavy metals, GIS, multivariate analysis, geoaccumulation index, enrichment factor.

I. Introduction

THERE are many anthropogenic causes of environmental pollution by heavy metals. However, different industrial operations and urban improvements are considered to be the significant drivers for environmental contamination [48], [55]. As a result, nowadays environmental pollution by potentially toxic metals and their consequences for human health and organisms on the whole have become a key concern for many researchers worldwide.

Since heavy metals, unlike organic compounds, are non-biodegradable, they seem to accumulate in human and living organisms and cause various diseases, for instance damage to the liver and nervous system, digestive disorders and kidney problems [19], [33]. Heavy metals can discharge into the environment via both natural and anthropogenic sources. Natural sources include the weathering and breaking down of parent rocks, while anthropogenic sources include various human activities such as industrial processes, mining waste, agricultural application of fertilizers and sewage [14], [47].

To deal with heavy metal contamination, some techniques are needed such as Geographic Information System (GIS). GIS is a computerised data system that has the ability to display, simulate and measure problems related to environmental components (i.e. soil, air and water) [34]. In addition, this technique enables researchers to identify the relationship between pollutants, e.g. rare earth elements, and environmental constituents such as soil by analysing multilayers of these pollutants with different type of soils [6]. According to [50], GIS-based maps are very important for studies related with environmental investigations due to their ability to visualize the relationship between different lands features and environmental datasets. Moreover, GIS is a powerful tool for soil contamination research [32]. For example, [59] used the spatial distribution of heavy metals using GIS to indicate areas of soil polluted with heavy metals (i.e. hotspots, areas of high heavy metal concentration surrounded by areas of relatively low concentration). Therefore the GIS technique can help the investigator gain more insight into the present pollution as it gives a map with different colours making it easy to distinguish between polluted and unpolluted areas. Furthermore, using the geostatistical methods for pollution assessment enables researchers to use different spatial interpolation techniques, with a special focus on kriging and its different forms [5]. In addition, [3] highlighted that spatial distribution and the display of contaminated metals in an area of interest are very important as they give a better understanding with respect to the source of the pollutants, the pathway of exposure and the expected risk. Therefore, the spatial distribution of potentially toxic metals via the GIS approach has been widely used in estuarine environments [26] to evaluate the ecotoxicological influences of trace elements on organisms in the area of interest. For reasons mentioned above, in the current study the inverse distance weighted (IDW) method of the GIS software was used to identify areas contaminated with heavy metals. Heavy metal pollution has become a problem of great concern worldwide. These chemical materials have been introduced

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into the environment from different sources and their emission levels depend on the physicochemical properties [17]. As a result, evaluation of such pollution is very important in order to identify the extent to which a particular area has been polluted, as this will help in putting a suitable plan for remediation into the action. To achieve this task, many methods have been used by different researchers, and in the present study, Muller method of the geoaccumulation index has been applied to assess the contamination of the soil in the study area. This approach is a well-known method in the field of contamination assessment and has been used by many researchers [2], [29], [38].

Since the current study area has been used by grazing cattle, heavy metals are more likely to access the human body via the soil-animal-human pathway. Therefore, the assessment of the ecological risk for the aforementioned metals is very important as it provides valuable data to assess and predict the risk that the soil contaminants may pose to human health, flora and fauna [53]. Regarding the potential ecological risk assessment, many approaches have been used to perform this task. For instance, the EF is mentioned in [39], the contamination factor (Cf) is proposed by [16], and the integrated pollution index (IPI) is mentioned by [56]. In this study the EF method was used to estimate the potential ecological risk of the investigated soil pollutants in the study area. To apply this method, concentrations of the metals of interest have to first be normalised by using reference elements (i.e. Fe, Sc, Ti, Al, Ca, and Mn) [56]. However, in the current study Mn was used as a reference element for the standardization of our dataset because this element has been commonly used for the estimation of the EF [35].

The main objectives of the current work were: 1) The determination, firstly, of the total concentration of some selected heavy metals in topsoils and then of their spatial variability using the GIS approach over the study area of Ecton, UK, and thus points of anomalous concentration; and 2) the assessment of the studied metals contamination limits via geoaccumulation indexes and EFs. This will enable us to identify the adverse effects that these metals could pose to the surrounding environment since the area is currently used for livestock rearing.

II. Materials and Methods

A. Study Area

The study area, Ecton mining area, is located in the southern part of the Peak District, Derbyshire, England. It is bounded by the River Manifold from the west (Fig. 1). This area has been mined for a long period. From the time of the Roman Empire the focus was on the production of Pb, and from the period from the 16th century until the mid-19th century, the production of Zn was very important [42]. Zn and Pb, and more recently fluorspar (calcium fluoride), on the Carboniferous Limestone, have been extracted extensively for a long time, from linear outcrops at the surface, which are known locally as “rakes” [13]. As a result, huge amounts of heavy metals have been released into the surrounding area and are most likely to be a significant source of heavy metal contamination to the local soil, water and vegetation. In addition, as the area is principally used for pasture for cattle and sheep, it is likely that contaminant metals could access the human body via the soil-animal-human pathway, thereby posing a potential risk to human health.

B. Geological Setting of Study Area

The geology of the area has been described by [17], who pointed out that from the Devonian to the Tertiary period, the majority of England and Wales was covered by the following sedimentation units:

1. During the period (Permian-Triassic) the lithology was Sandstone and the majority was red sandstone. During the Cretaceous and Tertiary, the main lithology was Greensand and Bagshot respectively.
2. In the Carboniferous and Jurassic periods, the common lithology was shales
3. Finally, the Limestone lithology was predominant in the Carboniferous and Jurassic periods.

However, according to [7], the study area is characterised by its bedrocks, which consist of Carboniferous Limestone (Dinantian) (Fig. 2), which affects both the topography and hydrogeology of the area and from borehole data, the minimum thickness of the Dinantian rocks is about (600 m) around Buxton

C. Sample Collection and Preparation for Analysis

During the period 4th-9th August, 2015, 37 soil samples (5-20 cm in depth) were collected from the study area (Fig. 1). The geographical coordinates (Northing and Easting) for all of the collected samples were recorded at the time of sample collection using a Global Positioning System (GPS) tool, as this will help to plot the sample locations when using the GIS software for mapping and the spatial distribution of the studied heavy metals across the study area. The following procedure was adopted to prepare the samples for analysis, as mentioned by other researchers, for instance [30], [57].

1. Once the sample bags had been brought to the lab, all of the contents were distributed on a stainless steel tray. This was followed by the disaggregation of large pieces and pieces of wood and plant roots were removed. Then all of the containers were labelled clearly.
2. In the lab all of the trays were placed in an open space on the allocated bench at normal temperature for about seven days. The samples were turned over and mixed once every day until all of the samples were completely dry.
3. When the samples had dried, they were sieved using a 2 mm sieve.
4. Again large pieces of sample that were left on the sieve were broken down using porcelain pestle and mortar and passed through the sieve. After that, all of the samples were kept in polyethylene sealable bags with suitable labelling (i.e. sample name and sieved grain size) in a cupboard until the necessary analyses had been done.

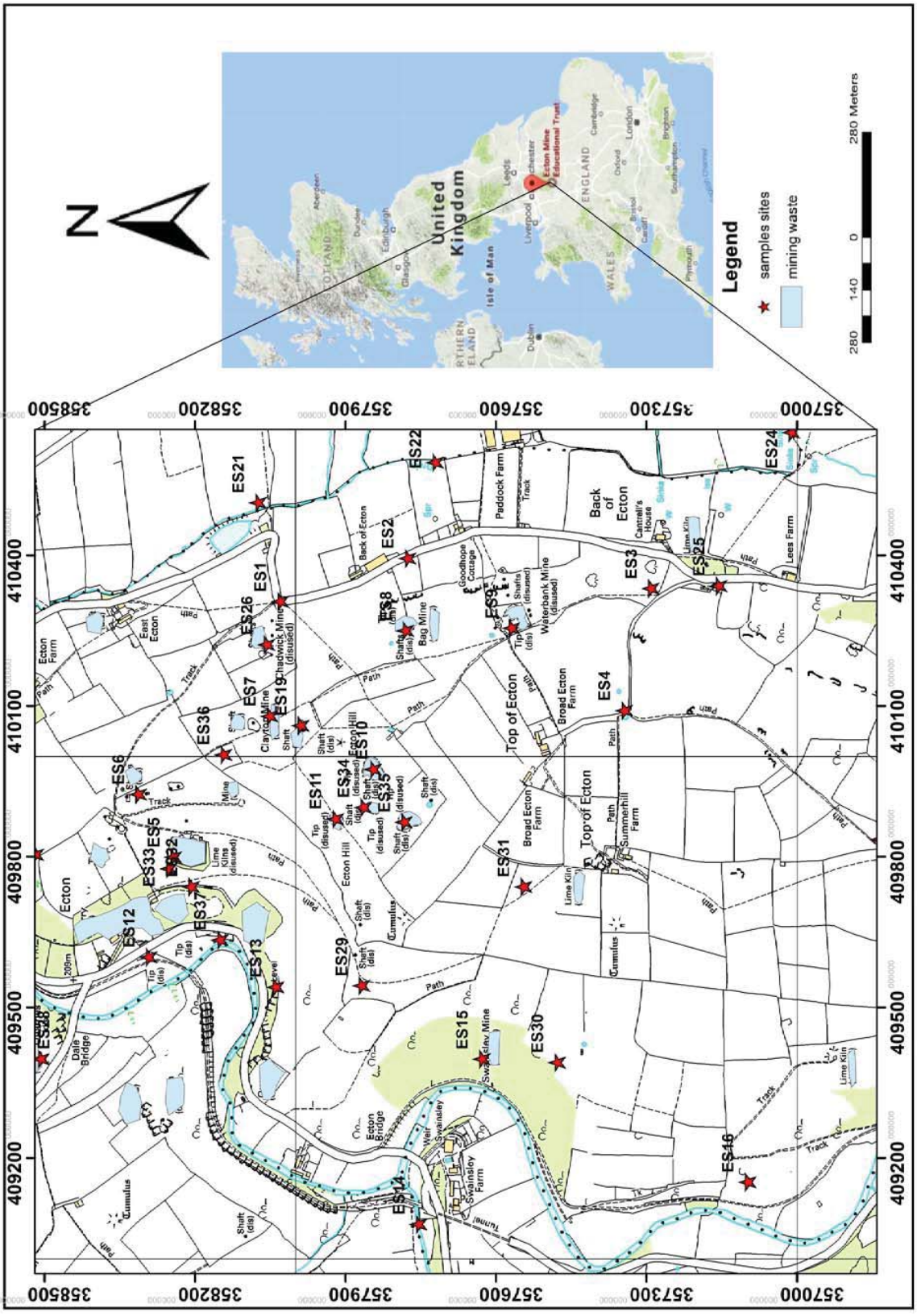


Fig. 1 Study area map showing sample locations

D. Chemical Analysis

The total concentrations of heavy metals were determined using the ICP-OES facility at the University of Wolverhampton. Although the best way of determining the total concentration of heavy metals is by digesting samples with strong concentrated acids, for instance hydrofluoric acid (HF) or nitric acids HNO_3/perchloric acid HClO4 [45], [46], these acids were ruled out due to safety reasons while working in the lab. Consequently, instead, the samples were digested using a mixture of nitric acid and hydrogen peroxide H_2O_2. 0.5 g of fine grind of each sample was digested with 5 ml of nitric acid and 1ml of hydrogen peroxide in a Milestone Ethos 900 Microwave digester using a four stage programme. The programme was set to run at different settings (250 W, 400 W, and 650 W) for about one hour. After digestion, the digester vessels were left to cool down, and then the samples were filtered into 50 ml volumetric flasks and made up to 50ml. Finally, the supernatants were transferred into a small bottle and labelled to be analysed later using the ICP-OES facility. The results were given in the units ppm. To convert this unit to mg/kg, the following equation was used:

$$\text{Concentration in (mg/kg)} = V/M \times C$$

where V is the volume that the extraction was made up to (i.e. 50 ml), C is the concentration of the element in the filtered solution (supernatant), M is the mass of the sample used (i.e. 0.5 g).

E. Statistical Analysis

Using the SPSS software package (Windows version 20) descriptive statistical parameters (Max, Min, Average, and Standard D.) were calculated to be used later for the determination of the geoaccumulation indexes and evaluation of the ecological risk that the metals could pose to the environment. In addition, spatial variation maps of the studied metals over the study area were performed via the method of IDW using the geostatistical analysis function of the Arc-GIS 10.1 software. Finally, all of the data were normalized geochemically using a conservative element (Mn in this study) prior to being used in the calculation of the EF. According to [8], [10], [11], [31], [40], [44], [54], conservative elements such as Al, Fe, Li, TOC, etc. are well known in the procedure of normalization because the ratios of the studied heavy metals to the conservative elements are to some extent stationary in the Earth's crust.

III. Results And Discussion

A. Geochemical Maps for Selected Heavy Metals Using GIS Mapping Approach

The spatial differences in the concentrations of the selected heavy metals (i.e. Cu, Pb, Zn, Mn, Ni, Cr, and V) over the study area were investigated using the inverse IDW method of the GIS software, as this approach has been considered to be an efficient way to display contaminant amounts spatially in environmental pollution studies and has been used by many researchers such as [15], [28], [41], [51], [58]. Spatial distribution maps for each element mentioned above are mentioned below, as this may help to distinguish areas contaminated with heavy metal from anthropogenic activities such as mining and the agricultural application of fertilizers.

1. Copper

The average concentration and spatial distribution of copper over the study area are shown in Table II and Fig. 3 respectively. It can be seen that the Cu content in the studied soil samples ranged from 11.8 mg/kg to 5126 mg/kg (Table I). Depending on the concentrations of the studied heavy metals in the Earth's Crust (Table III), it is obvious that all of the Cu concentrations in the study area were above the limits of the Earth's Crust (i.e. 55 mg/kg) especially samples located in the northern part of the area (Fig. 2, dark brown colour). The reason for such an elevated concentration is most likely to be the proximity of these samples to the locations of mining waste (Fig. 1). In addition, as the area has a long mining history and ore metals were extracted during the 19th and at the beginning of the 20th century from the area, the mining waste produced has left a high concentration of contaminant metals because of poor ore separation during the extraction process [1]. Furthermore, the majority of mining areas in the UK during the mining operations were not controlled by specific laws regarding, for instance, how to discharge industrial effluent, and mining waste [9]. As a consequence, high concentrations of heavy metals around mining areas were found in both the horizontal and vertical direction within the soils [21].

2. Lead

The lead concentrations for the analyzed soil samples ranged from 28.8 mg/kg to 36644.3 mg/kg (Table II).

The concentration levels of Pb for all of the collected samples are above the Earth's crust values (i.e. 12.5 mg) (Table III). The spatial distribution of Pb across the study area is shown in Fig. 3. It can be observed from Fig. 3 that the highest levels of Pb (dark brown colour) were recorded approximately on the eastern side of the study area. The majority of these samples are located next to mining sites (Fig. 1).

The best interpretation for such high levels is that anthropogenic activities (past mining operations) are responsible for these high levels. In addition, the contribution of heavy metals from agricultural application of fertilisers cannot be ruled out. For example, [1] has pointed out that the continuous use of chemicals such as fertilisers and pesticides in agriculture plays a significant role in increasing levels of heavy metals in soils. Furthermore, many studies have illustrated that high concentrations of lead can be found in soils around industrial sites due to the atmospheric emissions from exhausted gases and burning fossil fuels, which are then deposited in the soil causing the concentrations of Pb to be elevated [21], [25].

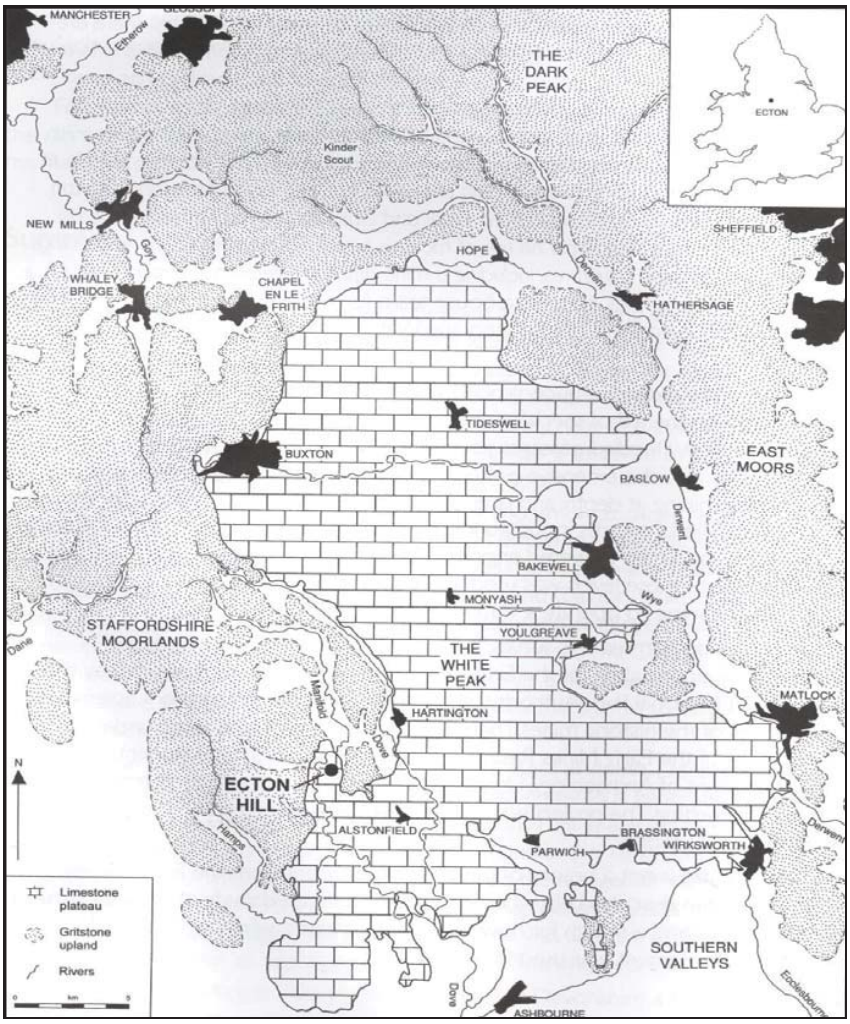


Fig. 2 Map of Peak District showing the lithology of study area which is mainly covered by Carboniferous Limestone (adopted from [3])

3. Zinc

The concentrations of zinc in the studied soil samples ranged from 68 mg/kg to 14378.3 mg/kg (Table II). All of the soil sample amounts of Zn were above the Earth's Crust limits (i.e. 70 mg/kg) (Table II) except the sample ES17, which is slightly under the limit (68 mg/kg). The spatial distribution map of zinc over the study area is given in Fig. 3.

It can be seen that samples with elevated amounts of Zn are located in the northern part of the study area (dark brown colour in Fig. 3) and these samples are situated next to mining waste locations (Fig. 1). This suggests that such high levels of Zn are most likely to have been introduced into the soils due to mining operations, which, as mentioned before, introduce large amounts of contaminants into the surrounding environment especially areas around mining waste heaps, as shown in Fig. 1. In addition, as highlighted by [1], a possible key factor that played a significant role in dispersing contaminant heavy metals into soils during the mining period in the 18th and early 20th centuries in the UK was the poor separation of ore minerals. Furthermore, the author mentions that the application of chemicals in agriculture, for instance fertilizers, is considered to be another possible source of heavy metals in soils, as these chemicals contain trace amounts of heavy metals such as Zn and Cu to enhance the plant growth

4. Manganese

In the current study, the maximum and minimum concentrations of Mn were 3478.8 mg/kg and 127.5 mg/kg respectively (Table II). The majority of the collected soil samples have Mn concentrations above the Earth's Crust value of 950 mg/kg (Table III).

The spatial distribution map of Manganese is shown in Fig. 3. It can be observed that the highest levels of Mn were found in the samples from the northern and southeastern parts of the study area (dark brown colour in Fig. 3). The majority of the sites with elevated levels are located close to locations of mining waste in the area (Fig. 1).

Like the case of Cu, Pb and Zn, past mining operations in the area are most likely to be the source of such elevated concentrations. Because burning fossil fuels, as mentioned by many researchers such as [28], is a significant anthropogenic

source of heavy metals including Mn, the high levels of Mn in the present study are likely to have come from burning coal, as this source was used to supply the required energy for mining operations during the mining period in the past [3].

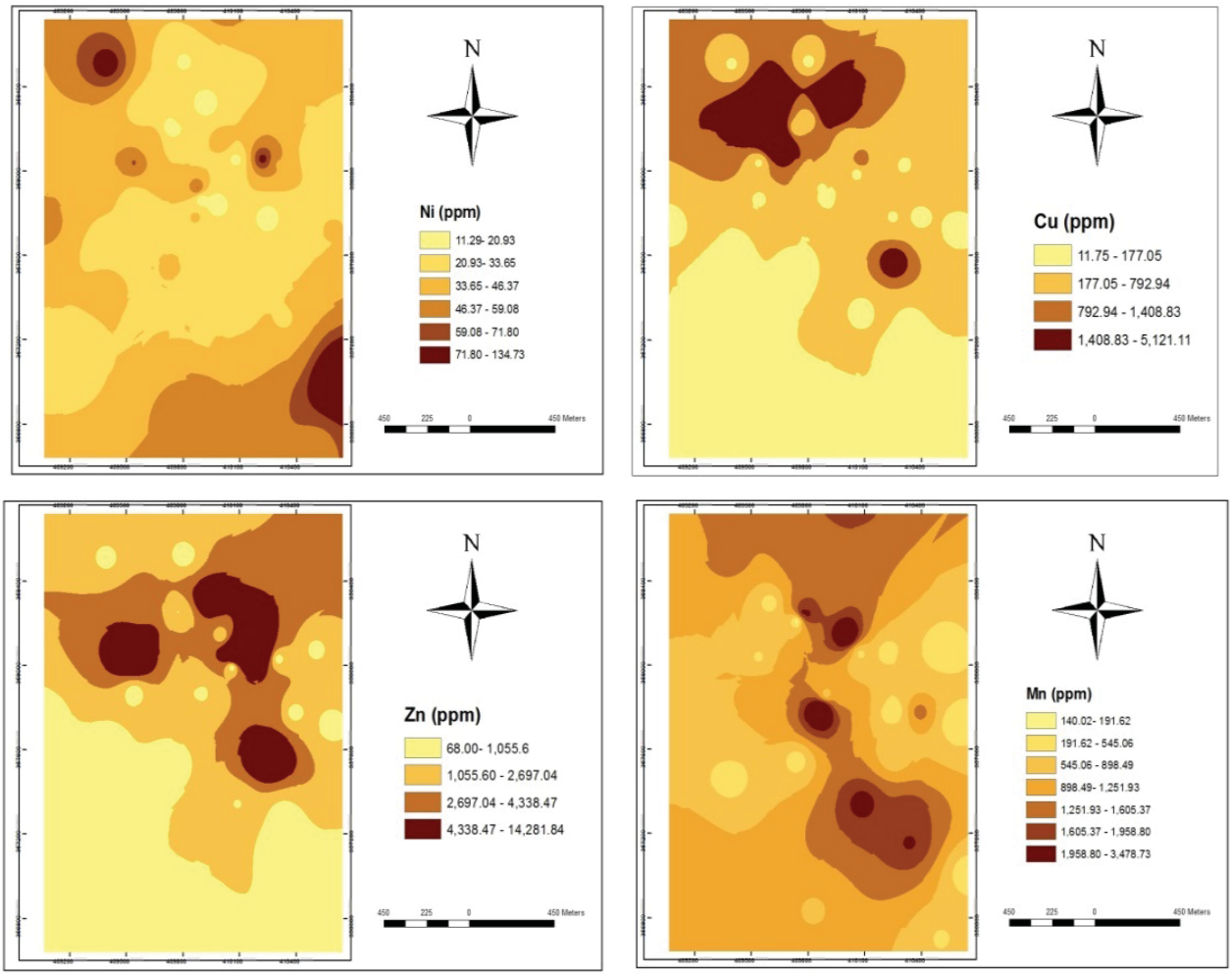
5. Chromium

The Cr concentrations for the collected soil samples ranged from 1 mg/kg to 99 mg/kg (Table II). All of the analyzed samples were found to be under the Earth's Crust value of 100 mg/kg for Cr. The spatial distribution map for Cr over the study area is shown in Fig. 3.

Although all of the samples were found to have a concentration less than the Earth's Crust, there are some spots with a dark brown colour (Fig. 3) at which high levels of Cr were recorded. The distribution mode of such elevated areas is similar to that of Zn (Fig. 3). This may suggest that Cr and Zn are related and have the same anthropogenic source, which seems to be past mining operations in the area. Similarly, for example, [49] found high concentrations of Cu, Pb, Z, and Cr in floodplain soils affected by mining activities in the Yorkshire, UK.

6. Nickel

The current study shows that Ni has a concentration ranging from 11.3 mg/kg to 134.8 mg/kg (Table II). The concentration levels of Ni for all of the collected samples were under the Earth's Crust level of 75 mg/kg for Ni except for samples ES24, ES26 and ES28 (Fig. 1), in which the concentrations of Ni were 143.75 mg/kg, 76.25 mg/kg and 80.75 mg/kg respectively.



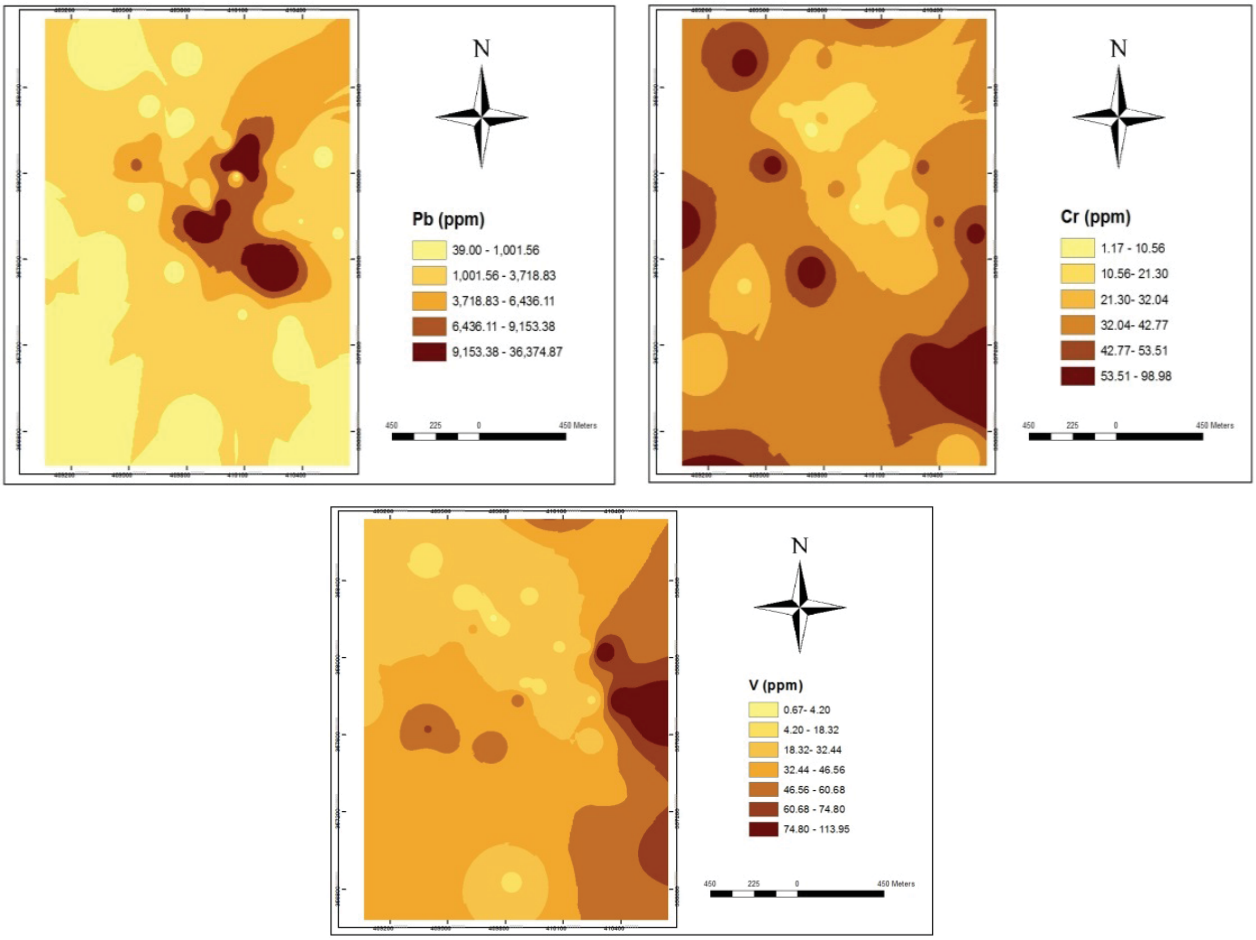


Fig. 3 Spatial distribution of metals being studied over the study area

The spatial distribution map of Ni for the collected soil samples over the study area is shown in Fig. 3. It can be seen that there are three spots with a dark brown colour (Fig. 3) where high concentration levels of Ni were found.

The possible source for such elevated levels does not seem to be from ore mining operations because other samples in the same area did not show high elevations although their locations are next to mining waste sites (Fig. 1). Therefore, natural sources (e.g. weathering of parent rocks) are the most likely explanation for such levels, although anthropogenic sources (e.g. the combustion of fuel and coal) cannot be ruled out, as it has been pointed out by other researchers such as [36] that one of the most significant sources of Ni is burning fossil fuels because coal was used to supply energy during the mining period and for a long time [3].

TABLE I
MULLER'S GEOACCUMULATION INDEX AND DIFFERENT CONTAMINATION CLASSES [12]

I_{geo}	I_{geo}	Contamination degree
0	<0	Uncontaminated
1	0-1	Uncontaminated/moderately
2	1-2	Moderately contaminated
3	2-3	Moderately contaminated/
4	3-4	Strongly contaminated
5	4-5	Strongly
6	>5	Extremely contaminated

7. Vanadium

In the present study, the concentrations of V were found to be in the range of 0.5 mg/kg to 114 mg/kg (Table II). All of the collected soil samples were found to have concentration levels of V less than the amount in the Earth's Crust, except for the sample ES22, in which the concentration of V was 114 mg/kg, which is a slightly more than the Earth's Crust value. The spatial distribution map of V over the study area is shown in Fig. 3. From Fig. 3, it can be seen that the highest concentrations of V are located in the eastern side of the study area (dark brown colour). As in the case of Ni, the possible source of such levels is most likely to be natural, i.e. from weathering of parent rocks. In addition, similar results for V concentrations were recorded elsewhere by other researchers, for example [43].

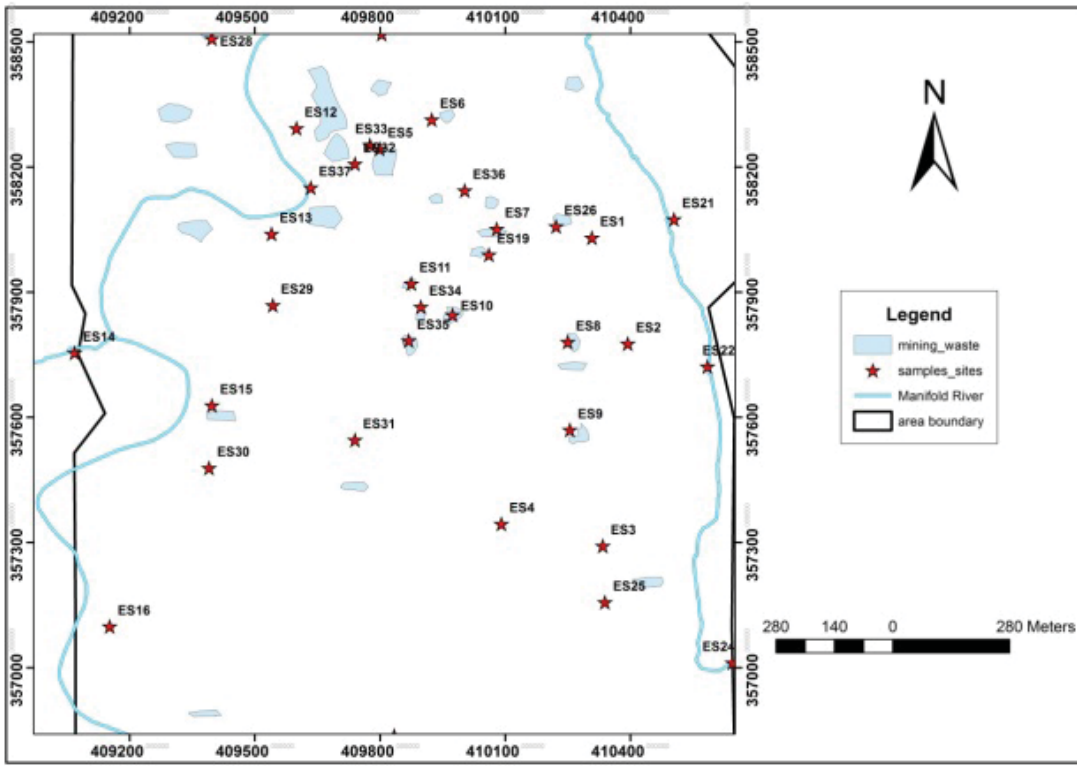


Fig. 4 Locations of collected soil samples and mining waste sites at the study area

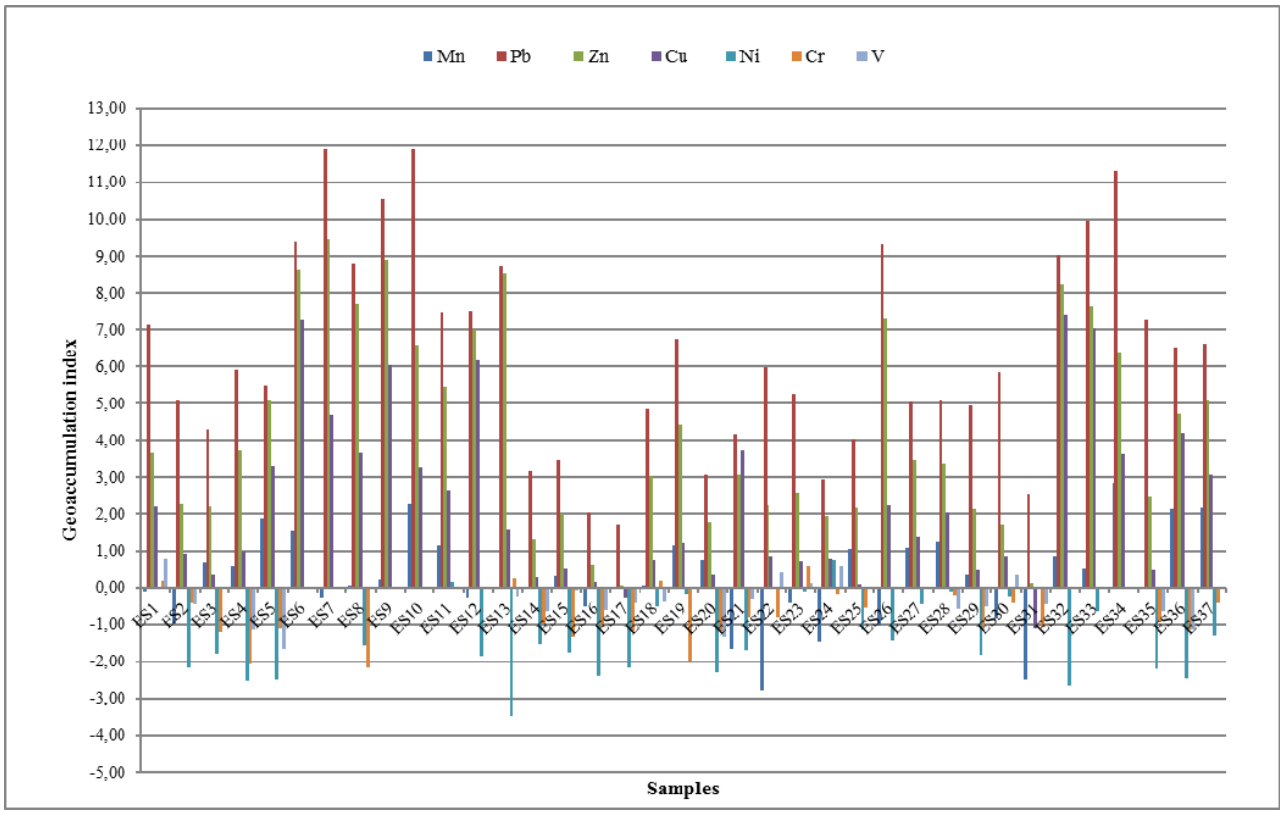


Fig. 5 Muller geoaccumulation indexes of heavy metal contamination in soil samples at the study area

Overall, from the spatial distribution maps for all of the heavy metals studied (i.e. Cu, Pb, Zn, Mn, Cr, Ni, and V), it can be observed that the mode of spatial distribution for the elevated concentration sites for Cu, Pb, and Zn are similar and they are located close to mining waste sites (Fig. 1). With regard to pollution sources, all of the studied elements were found to have concentration levels over that of the Earth's Crust with possible sources being anthropogenic activities (i.e. past mining operations) except Ni and V, of which the majority of samples had heavy metal levels under that of the Earth's Crust values, suggesting a natural source of these metals.

B. Heavy Metal Contamination Assessment in the Ecton Mining Area

Nowadays, heavy metal pollution has become a problem of great concern worldwide. These chemical materials have been introduced into the environment from different sources and their emission levels depend on the physicochemical properties [18]. As a result, the evaluation of such pollution is very important in order to identify the extent to which a particular area has been polluted, as this will help to put a suitable plan for remediation into action. To achieve this task, many methods have been used by different researchers, and in the current study the following approaches are applied to assess the contamination of soil in the study area.

1. Heavy Metal Contamination Assessment Using Muller's Geoaccumulation Index (Igeo)

This approach is a well-known method in the field of contamination assessment and has been used by many researchers (e.g. [2], [29], [38]). In the present study this method has been utilised. It shows the degree of metal contamination by dividing the current concentration of the metal of interest by its background using (1) [12]:

$$Igeo = \log2 (Pi/1.5*Piback) \quad (1)$$

where pi is the measured concentration of the studied heavy metal, and piback is the background amount of the heavy metal. The constant number (i.e. 1.5) is a factor of background correction because of lithology effects. According to the authors mentioned above, the geoaccumulation index (Igeo) has been classified into seven classes (Table I), starting from class 0 (uncontaminated), and ending with class 6 (extremely contaminated). First, geoaccumulation indexes (Igeo) for all of the collected soil samples were calculated using the Muller equation, as shown in Fig. 5.

Finally, the total evaluation of heavy metal contamination was carried out for all of the soil samples using the average amount of (Igeo) for all of the metals so that the different (Igeo) classes of pollution for all of the soil samples (Table IV) were indicated. It can be seen that among all of the studied metals, lead has the highest amount of contamination.

The results show that Pb is at a level of extreme contamination (i.e. class 6) in the studied samples (Fig. 5 and Table IV). In addition, depending on the amount of the geoaccumulation index (Igeo), lead is most likely to be the harmful element as it has the peak Igeo value of about 12 in samples ES7 and ES10 (Fig. 5). Regarding the level of contamination with Cu, the degree of contamination with this metal is indicated to be class 3 (i.e. moderately/strongly contaminated) in Table IV, and reached the highest value of approximately (7.5) in sample ES32 (Fig. 5). However, the geoaccumulation index values (Igeo) for Zn illustrate a contamination level of strongly contaminated/extremely contaminated (i.e. class 5) in the soil samples with a peak value of almost (9.5) in sample ES7 (Fig. 5).

Finally, all of the other investigated elements (i.e. Ni, Mn, Cr, and V), based on the calculated geoaccumulation index (Igeo), have a contamination level of class 0 (i.e. uncontaminated) in all of the soil types except for Mn, for which the soil samples are classified as uncontaminated/ moderately contaminated (i.e. class 1) (Fig. 5) and (Table II). Overall, depending on the calculated average geoaccumulation index classes, the degree of contamination of the collected soil samples with the studied heavy metals is in the following order: Pb>Zn>Cu>Mn>Ni=Cr=V.

It can be suggested that the elevated concentrations of Cu, Pb and Zn in the studied samples are more likely to be due to mining processes, as this area (Ecton area) was mined for a long time for the production of copper, lead and zinc. As a result, the concentrations of these metals have been elevated in the area due to the disposal of mining waste into the surrounding environment [5], [14], [18], [38].

2. Assessment of the Potential Ecological Risk

Evaluation of the potential ecological risk for the area of interest is very important as it gives valuable data to investigate and predict the risk that soil contaminants could pose to human health and the surrounding media [53]. To this end, as has been mentioned before, many approaches have been used to evaluate the potential ecological risk, and thus in this study the EF method was used to estimate the potential ecological risk of the investigated soil pollutants in the study area. To apply this method, the concentrations of the metals of interest have to first be normalized using reference elements (i.e. Fe, Sc, Ti, Al, Ca, and Mn) [56]. In the current study Mn was used as a reference element for standardization because this element has commonly been used for the estimation of the EF [35]. The amount of the EF for the studied metals was calculated using (2):

$$EF= [Cn (sample)/(Cref (sample)]/[Bn (background)/(Bref (background)] \quad (2)$$

where: Cn is the measured concentration of the element in the sample, Cref is the concentration of the reference element (i.e. Mn) in the sample, Bn and Bref are the concentrations of the element and reference metal in the upper crust and Earth's crust respectively [54]. According to [45], based on this method the calculated EF amounts can be categorised into five groups of enrichment (Table V).

To find out the potential environmental risk for the studied metals, the EF method was calculated and the average

amounts in the soil of the study area are shown in Table VI and illustrated in Fig. 6. Based on the calculated EF, it can be seen that the average amount of the EF of lead in all of the studied soil samples is the highest among the studied metals followed by zinc and copper (Fig. 6). However, the potential environmental risk of Pb, Cu and Zn is almost the same and is considered to be at the level of extremely high enrichment in all of the studied soil samples (Table VII). In addition, all of the other investigated metals (i.e. V, Cr, Mn, and Ni) are classified as group 1 (deficiency to minimal enrichment) in all of the samples. It can be seen from the calculated amount of the EF that the level of metal pollution in the study area is in the following order: Pb>Zn>Cu>Cr>V>Ni>Mn. Overall, the high levels of EF (contamination) in the studied samples were found mainly in the case of Pb, Cu and Zn (Table VII) and the possible source of such levels is more likely to be anthropogenic as this area has been used for mining and for a long period to extract the aforementioned metals, as mentioned by many other researchers such as [5], [23], [24], [38].

Finally, since in the current study two methods (i.e. geoaccumulation index (Igeo) and EF have been utilised to assess the level of contamination in the study area, it would be worth knowing the extent to which the results of these two methods are correlated. The average values for the Igeo and EF indexes are shown in Table VIII. The results show that there is a strong correlation between the calculated Igeo index and EF (Fig. 7) with a correlation coefficient of (R2= 0.9065) suggesting an acceptable result for both methods and similar environmental data in terms of the ecological assessment. Similar findings were found by other researchers elsewhere, such as [39], who investigated the pollution coming from some selected heavy metals similar to those of our study in an area affected by mining activities in Chile.

IV. Conclusions

On the basis of the Earth's Crust amounts, the results show that the concentrations of Cu, Pb and Zn exceeded the Earth's Crust values. However, lower concentrations were found for Mn, Cr, Ni and V. It can be seen from the GIS-based spatial variation maps that a few hotspots, areas of elevated concentrations, were indicated over the study area. These points were found to be around mining waste piles, suggesting an anthropogenic source for such high concentrations, as the area has been used for Cu, Pb, and Zn extraction for a long time. The calculated geoaccumulation indexes show that the degree of contamination by the studied metals has the following order: Pb>Zn>Cu>Mn>Ni=Cr=V. The EF approach was applied to assess the potential ecological risk of the selected metals. The enrichment degree of Mn, Cr, Ni and V was classified as deficient to minimal, whereas the enrichment limits for Cu, Pb and Zn were indicated to be extremely high.

As a result, these metals can pose a risk to human health and living organisms. Finally, a strong and positive correlation was observed between the geoaccumulation indexes and the EFs, suggesting an acceptable result for both methods when assessing the environmental pollution caused by heavy metals.

TABLE II
Descriptive Statistics of Total Heavy Metal Concentration at Study Area

TABLE II	Cu	Pb	Zn	Mn	Cr	Ni	V
Mean	593.9	3176.9	2314.7	1074.5	35.8	38.3	39.3
Max	5126.0	36644.3	14378.3	3478.8	99.0	134.8	114.0
Min	11.8	28.8	68.0	127.5	1.0	11.3	0.5
SD	1326.8	7306.0	3601.7	812.6	20.9	24.0	25.9

TABLE III
Heavy Metal Abundance in the Earth's Crust [27]

Metals	Cu	Pb	Zn	Mn	Cr	Ni	V
Concentration limits	55	12.5	70	950	100	75	101

TABLE IV
Geoaccumulation Index Classes for Studied Metals at the Study Area

Metals	V	Cr	Mn	Ni	Cu	Zn	Pb
Soil samples	Class 0	Class 0	Class 1	Class 0	Class 3	Class 5	Class 6

TABLE V
Ecological Risk Assessment Groups Using EF

Enrichment groups	EF	Enrichment degree
1	EF < 2	Deficiency to minimal enrichment
2	2 ≤ EF < 5	Moderate of enrichment
3	5 ≤ EF < 20	Significant enrichment
4	20≤EF< 40	Very high enrichment
5	EF≥40	Extremely high enrichment

TABLE VI
Average Amount of EF for Studied Heavy Metals

Metals	V	Cr	Mn	Ni	Cu	Zn	Pb
Soil samples	1.85	1.96	1.36	1.68	42.50	81.87	181.77

TABLE VII
Potential Ecological Risk Assessment Using the EF Approach for Studied Heavy Metals in the Study Area

Studied metals	V	Cr	Mn	Ni	Cu	Zn	Pb
Enrichment groups measured	1	1	1	1	5	5	5

TABLE VIII
Mean Values for Calculated Geoaccumulation Index and EF for Study Area

Studied elements	V	Cr	Mn	Ni	Cu	Zn	Pb
Geoaccumulation Index (Igeo)	-	-	0.28	-	2.27	4.25	6.36
EF	1.85	1.96	1.36	1.68	42.50	81.87	181.77

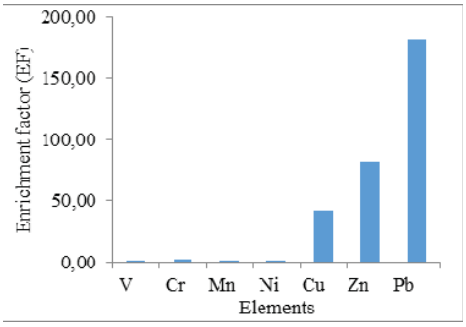


Fig. 6 Calculated average **EF** for collected soil sample from the study area

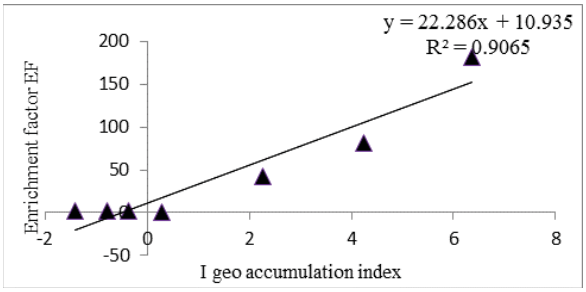


Fig. 7 Correlation between geoaccumulation index and **EF**

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