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Assessment of soil contamination around an abandoned mine in a semi-arid environment using geochemistry and geostatistics: Pre-work of geochemical process modeling with numerical models

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ABSTRACT

One of the most serious environmental issues related to mining industry in Morocco and elsewhere around the world, is the pollution from abandoned mine sites. Mine wastes cause obvious sources of soils contaminations. Climatic effects such as heavy rainfall engender metals dispersion in semi-arid areas, since soils are typically and scarcely vegetated. In this study, extension and magnitude of soils contaminations with toxic elements from abandoned Kettara mine, in Morocco, are assessed using geochemical analysis and geostatistics for mapping. Soils and mine wastes are sampled and analyzed for 41 chemical elements (Mo, Cu, Pb, Zn, Ag, Ni, Co, Mn, Fe, As, U, Au, Th, Sr, Cd, Sb, Bi, V, Ca, P, La, Cr, Mg, Ba, Ti, Al, Na, K, W, Zr, Ce, Sn, Y, Nb, Ta, Be, Sc, Li, S, Rb and Hf). Based on enrichment factor (EF), only five elements of interest (Cu, Pb, Zn, As, and Fe) were selected in this research. Geochemical background is determined with exploratory data analysis and geochemical maps were elaborated using geostatistics in Geographic Information System (GIS) environment.

The obtained results show that Kettara soils are contaminated with metals and metalloid that exceed the established geochemical background values ($\text{Cu} \approx 43.8 \text{ mg/kg}$, $\text{Pb} \approx 21.8 \text{ mg/kg}$, $\text{Zn} \approx 102.6 \text{ mg/kg}$, $\text{As} \approx 13.9 \text{ mg/kg}$ and $\text{Fe} \approx 56978 \text{ mg/kg}$). Geochemical maps show that the deposited mine wastes are responsible for soils contaminations with released metals and metalloid that have been dispersed downstream from the mine waste mainly, through water after rainfall. For sustainable development and environmental planning, the current study is expected to serve as a reference for politicians, managers, and decision makers to assess soils contaminations in abandoned mine sites in Morocco.

Keywords: Geochemical mapping, soil contamination, geochemical background, Kettara abandoned mine, GIS, simple kriging.

1. Introduction

Acid Mine Drainage (AMD) from mine waste and contaminations of soils and water with metals are considered as major environment problems in mining areas ([U.S Bureau of Mines, 1994](#)). This environment phenomena is produced with oxidation of sulfide minerals e.g. pyrite and pyrrhotite ([Hakkou et al., 2008a](#); [Bussiere, 2009](#)). Consequently, acidification would increase the dissolution of toxic metals from tailings, waste rock piles, and open pits. Therefore, soil and water ecosystem will be contaminated ([Sams et al., 2000](#); [Bell et al., 2006](#)). Certainly, as rainfall water infiltrates into the underground soil/rock, it can cause pore-water flow in the pore space of the soil/rock. The resulting pore-water flow can be advective or convective ([Zhao et al., 2004, 2008a](#)) depending on geological conditions of the mine site. When the pore-water becomes in contact with the soil/rock, it can react chemically with the mine waste dissolving heavy metals at the mine site. Since the dissolved heavy metals can be transported in the soil/rock through pore-water advection, convection and solute diffusion/dispersion ([Zhao et al., 2007](#)), they can contaminate both the land and the groundwater at the mine site. In addition, as demonstrated theoretically, the dissolved metal front may become unstable when it propagates in the soil/rock at the mine site ([Zhao et al., 2008b, 2010a](#)). This is the scientific problem, known as the mine site contamination, which is the focus of this study.

1 With the stimulus of exploring giant ore deposits in the deep earth, extensive and
2 systematic work has been conducted to develop advanced computational methods and
3 algorithms for simulating physical and chemical processes associated with ore body formation
4 and mineralization within the Earth's crust (Zhao et al., 2009, 2010b). As a result, a new
5 emerging discipline, known as the computational geosciences (Zhao et al., 2009), has been
6 established. Due to mathematical similarity, the advanced computational methods and
7 algorithms (Zhao et al., 2006, 2009) can be also used to solve mine site contamination
8 problems if the geological and the geochemical data are available at the mine site. From this
9 point of view, the scientific significance of this study can be described as follows. First,
10 detailed geochemical data produced in this study can be used as an example to extend the
11 advanced computational methods and algorithms to the computational simulation of mine site
12 contamination problems. This will answer how and why the mine site is contaminated in a
13 scientific manner. Second, advanced computational methods and algorithms are then used to
14 develop techniques to remove heavy metals from the contaminated mine site, which is known
15 as the mine site remediation problem (Zhao et al., 2012) and has great practical significance in
16 the current world.

17
18 Furthermore, knowledge of soil geochemistry is fundamental when we attempt to
19 determine the effects stemming from an anthropogenic activity and its impact on the geo-
20 ecosystems as a result of its toxicities (Guillén et al., 2011). In this respect, it is essential to
21 establish geochemical maps for chemical elements associated with different lithologies in
22 order to distinguish if their source is geogenic or anthropogenic (Plant et al., 2001). In
23 addition of the scientific or mining standpoint, geochemical maps constitute an effective tool
24 for environmental planning (Ferguson and Kasamas, 1999; Li et al., 2004). They reveal
25 information about source, distribution, and dynamics of chemical elements. Geochemical
26 maps include both the geogenic concentration or geochemical background (GB) value, and
27 the concentration that is the result of anthropogenic activity (Guillén et al., 2011). This
28 explains why GB defined by Hawkes et al. (1962) as "*the normal abundance of a chemical*
29 *element in barren earth material*" has become crucial in environmental studies. It was
30 introduced to differentiate between normal and abnormal element concentration (Martínez et
31 al., 2007). Exploratory Data Analysis (EDA) has been recommended as an effective tool to
32 determine the GB (Zhou et al., 2010). According to the literature, this method was tested and
33 proved by numerous authors (Bouessah et al., 2003; Reimann et al., 2005b).

Finally, GIS based on geostatistical analysis is one of the most important tools for studying environmental geochemistry problems (Acosta et al., 2011). It provides an effective means for researching the spatial variability of pollutants (Sun et al., 2012). Geostatistics is an advanced methodology that facilitates quantification of the spatial features of soil parameters and enables spatial interpolation (Zhang et al., 2000; Carlon et al., 2001). According to the literature, numerous authors have used kriging analysis in GIS environment to elaborate geochemical maps to quantify both extension and magnitude of contamination with toxic elements (Li et al., 2004; Li and Feng 2011; Nakayama et al., 2011; García-Lorenzo et al., 2012).

The abandoned Kettara mine site (Morocco) was selected to analyze the impact of mining activity on the surrounding soils. The objectives of this study were as follows: 1) geochemical characterization of Kettara soils and tailings; 2) determination of GB values of selected chemical elements in Kettara soils; and 3) elaboration of geochemical maps regarding the selected toxic elements and their comparison with the elaborated GB to reveal the degree of pollution of the Kettara mine site surrounding soils and to examine possible health risks.

2. Materials and Methods

2.1. Study site

The abandoned Kettara mine is located approximately 35 km northwest of Marrakech city in the core of the central Jebilet Mountains (Figure 1). According to the latest governmental census (2004), the population of Kettara village is approximately 2000 people. The climate of this region is classified as semi-arid environment with average maximum and minimum temperature ranging from 12 °C in January to 29 °C in July, respectively. The average annual rainfall is 250 mm. The potential evapotranspiration rate surpasses 2500 mm/year. NE-SW wind flow is prevailing in the study site (ONEM, 1997). Perennial streams do not exist and surface water consists of ephemeral watercourses that are operational only during rainfall events.

1 The Kettara mine had undergone three mine exploitation phases. The first phase, between
2 1938 and 1962, the iron oxide was extracted from the iron hat “gossans” to produce red oxide
3 (50 to 58 % of Fe) for paint industry. The second phase, between 1955 and 1966, the zone of
4 cementation was exploited for pyrite (180000 tons with 38 wt % of Sulfide) (Huvelin, 1977).
5 During these two phases the ores were delivered in their raw state without any mineralogical
6 concentration, and the mine wastes were about 1 million ton (Mt) of coarse waste rocks. The
7 third and final phase, between 1964 and 1981, the mine produced more than 5.2 Mt of
8 pyrrhotite concentrate containing an average of 29% wt sulfide. The pyrrhotite was extracted
9 from the ore by gravimetric separation (jigs). This ore enrichment process generated a wide
10 range of particle size fractions in the mine wastes (jigs refuse materials). These latter can be
11 divided into two broad classes of material: coarse mine wastes (fine gravel) and fine mine
12 wastes (silt). Throughout this period, more than 3 Mt of mine wastes were stockpiled over an
13 area of about 30 ha (Figure 2). The Kettara wastes contain 1.6 to 14.5 wt % sulfur, mainly
14 sulfide minerals (e.g., pyrrhotite, pyrite, chalcopyrite, galena, and sphalerite) (Hakkou et al.,
15 2008a). The Kettara mine wastes have produced significant amounts of AMD. Previous
16 researches (Hakkou et al., 2008b) have shown that effluent water samples had low pH (2.9 to
17 4.2), and high concentrations of sulphate (from 47 to 5000 mg/L) and iron (from 1 to 1200
18 mg/L). Furthermore, the Cu and Zn concentrations had reached 58 and 45 mg/L, respectively.
19 At the Kettara mine site, several secondary minerals have been observed at the surface (e.g.,
20 goethite, jarosite, alunite, gypsum). The presence of these minerals in large quantities shows
21 that AMD generation is very active at Kettara (Hakkou et al., 2008a).

22
23 The Kettara sulfide deposit is a typical example of metamorphosed deposits hosted by
24 Visean volcano-sedimentary formations. The mineralized body consists of major and minor
25 lenses of massive pyrrhotite, with small amounts of sphalerite, galena, chalcopyrite, pyrite,
26 arsenopyrite and glaucodot. The structure resulted from an intra-Westphalian tectono-
27 metamorphic phase of the Hercynian orogeny (Hibti et al., 1999). The substrate of Kettara is
28 composed of fractured and altered shale, which facilitates AMD infiltration. Furthermore, the
29 principal groundwater table is located in this formation and has a depth of between 10 m and
30 20 m. According to Lghoul et al. (2012), groundwater sampled at Kettara mine site from wells
31 located downstream the mine wastes is contaminated by the AMD, mainly by sulphates
32 (>1200 mg/L) and presents high conductivity values, 3000 to 3680 μ S/cm.

2.2. Sampling and samples preparation

Special consideration was given to the used criteria to select sampling points' locations. After a review of topographic and geologic maps, and according to previous studies on the abandoned Kettara mine (Hakkou et al., 2008a; Khalil et al., 2011), soil sampling was established in 3 different areas based on the location of the mine wastes. The sampling design was made to compare concentration gradient and possible chemical elements mobilization. The distance between sampling points varies from 150 to 350 m. Four groups of soil samples have been collected: 1) samples located upstream of the mine waste (13 samples); 2) samples located nearby the mine waste (27 samples); 3) samples located downstream of the mine site (22 samples); and 4) mine waste samples from the Kettara mine tailings (12 samples). Finally, 62 soil samples (from S1 to S62) and 12 mine waste samples (from R1 to R12) were collected within the study site, approximately 6 km² (Figure 2). Geographic coordinates of sampling points were measured using a Global Positioning System (GPS) within ± 5 m accuracy, with the "Lambert North Morocco" map projection.

Samples were taken within the first 20 cm of soil using a stainless steel shovel. To minimize sampling errors, each sample underwent a quartering operation, photographed with a digital camera, and then stored in a polyethylene bag. After this step, each sample was dried in an oven at 100 °C in the laboratory and then sieved through a 2 mm mesh. The total sample under 2 mm was ground in agate mortar until a fraction smaller than 63 μ m for subsequent chemical analysis.

2.3. Chemical analysis

Chemical analyses were carried out at Acme Analytical Laboratories Ltd. (Vancouver, Canada), accredited under ISO 9002. The considered analyzed elements are Mo, Cu, Pb, Zn, Ag, Ni, Co, Mn, Fe, As, U, Au, Th, Sr, Cd, Sb, Bi, V, Ca, P, La, Cr, Mg, Ba, Ti, Al, Na, K, W, Zr, Ce, Sn, Y, Nb, Ta, Be, Sc, Li, S, Rb and Hf. Soil samples were digested using a strong multi-acid method that dissolves most minerals. Then, 0.25 g split was heated in HNO₃-HClO₄-HF to fuming and taken to dryness. The residue was further dissolved in HCl. Then, solutions were analyzed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

The data quality was assessed using duplicates samples analyses, blanks, and concentration measurements accuracy estimation. This latest was achieved based on repeated analyses of multi-element soil standard “OREAS 45c” prepared from a 50:50 blend of barren soil, and soil characterized by anomalous levels of precious and base metals. The anomalous sample was obtained from soil developed over a Ni-Cu-PGE mineralized contact between gabbro and pyroxenite from the Southern Murchison region of Western Australia. While, the barren sample was taken from an *in situ* layer of mature soil developed over early tertiary olivine basalt in outer eastern Melbourne, Victoria, Australia. According to data quality results assessment, the concentration measurement accuracy was estimated at $\pm 5\%$ for all the considered elements. Finally, analytical results of blank solutions showed that all the elements of interest are below the detection limits.

2.4. Statistical analysis

2.4.1. Descriptive statistics

The following statistical parameters were determined for the 41 elements considered and analyzed: minimum, maximum, mean and median for the central tendency measurement, standard deviation and variation coefficient for the data dispersion measurement; while the data distribution was tested for normality using Kolmogorov-smirnov (K-S) test, kurtosis and skewness (Tables 1 and 2). These parameters will be helpful for comparing datasets, therefore summarizing the obtained results and facilitating its subsequent interpretation (Burgos et al., 2005; Martínez et al., 2007; Cai et al., 2012).

2.4.2. Enrichment factors

In order to select chemical elements that have been enriched in Kettara soils, enrichment factor (EF) was calculated (Martínez et al., 2007; Bourennane et al., 2010; Li and Feng, 2011). The concept of EF was developed in the early seventies to derive the origin of elements in the atmosphere, precipitation or seawater, and was progressively applied to other environmental materials such as soils, lake sediments or peat (Reimann et al., 2005b; Bourennane et al., 2010). It was widely employed to identify the anthropogenic source of

metallic elements (Li et al., 2011). Based on EF, five contamination categories were recognized: 1) $EF < 2$ states deficiency to minimal enrichment; 2) $2 \leq EF < 5$ moderate enrichment; 3) $5 \leq EF < 20$ significant enrichment; 4) $20 \leq EF \leq 40$ very high enrichment, and; 5) $EF > 40$ extremely high enrichment (Han et al., 2006; Lu et al., 2009a, b). The EF was calculated for the chemical elements using the following generalized equation according to Chester and Stoner (1973) and Zoller et al. (1974):

$$EF_{El} = \frac{[El]_{\text{sample}}/[X]_{\text{sample}}}{[El]_{\text{crust}}/[X]_{\text{crust}}}$$

Where “*El*” is the element under consideration, the square brackets indicate concentration (usually in mass/mass units, such as mg/kg), “*X*” is the chosen reference element (see below) and the subscripts “sample” or “crust” indicate which medium concentration refers to. Crust refers to Clarke of Earth’s crust, most often continental or Upper Continental Crust (UCC). The Clarke values corresponding to mean concentration of chemical elements in the UCC were given by McLennan (2001). In this study, Aluminum was selected to be the reference value. Indeed, Al is the most common reference value used to calculate the EF (Buat-Menard and Chesselet, 1978; Lu et al., 2009a; Bourennane et al., 2010).

Table 1 summarizes EFs values which indicate how many times measured concentrations exceed the Clarke values.

2.4.3. Exploratory data analysis (EDA)

In addition to the statistical and EF analyzes, the EDA technique was assessed because it is an appropriate technique for identifying anthropogenic influences (Zhou et al., 2010). EDA was applied to determine the GB of soil. This latter will serve as a reference to assess the soil contamination by toxic elements. EDA consists of elaborating graphs such as histograms with the distribution curves, box plots also called a box-and-whiskers plot, in which six parameters are described (lower limit, first quartile, median, third quartile, upper limit and extreme values), and normal Quantile-Quantile plots (Q-Q plots) which were applied to look for different intervals of toxic elements concentrations which imply likely presence of different

processes or multiple population (Zhou et al., 2010). In addition, the EDA will provide a better observation of the shape of the distribution values (Martínez et al., 2007).

2.5. Geochemical mapping and multi-criteria analysis using GIS

The coordinate's locations of sampling soils and the concentration values of selected chemical elements were intergraded in a GIS database. Spatial interpolation and mapping were carried out for the target elements using geostatistics. This consisted of complex semi-variograms for each considered elements (Cu, Pb, Zn, As and Fe). Both ordinary and simple kriging were tested considering different mathematical models for adjustment. According to Li et al. (2001), the optimized model should minimize standard mean (close to 0), and the standard roots mean square error (RMSE) should be closest to 1. Iterative testing concluded that exponential model provided the best adjustment with excellent RMSE values. In addition, similar accuracies were obtained with ordinary and simple kriging. Consequently, only the latest was selected in this study. The theoretical semi-variograms model values and errors estimation are summarized in Table 3.

Multi-Criteria Analysis (MCA) using GIS was applied on derived geochemical maps in order to elaborate a risk map of soil contamination. This map was established using spatial analyst of Arc GIS software conducting queries on the geochemical map of each considering elements (ESRI, 2012). Each query extract only the areas characterized with highly anomalous content of toxic elements (hot spots). Areas where metallic and metalloid content exceeds 300 mg/kg for Cu, 100 mg/kg for Pb, 300 mg/kg for Zn, 50 mg/kg for As and 100000 mg/kg for Fe were extracted. Finally, those areas were overlaid to establish the risk map of contaminated soils which will be so informative for politician and decision maker (Komnitsas and Modis, 2006).

3. Results and discussion

3.1. Statistical analysis

The EFs analysis shows five different classes. The first class considers the elements with minimal enrichment and it includes the following elements: Mo, Ni, Co, Mn, U, Th, Sr, V, Ca, P, La, Cr, Mg, Ba, Ti, Al, Na, K, W, Zr, Ce, Sn, Y, Nb, Ta, Be, Sc, Rb, and Hf. The second class considers elements with moderate enrichment and it includes the following elements: Pb, Zn, Ag, Fe, Cd and Li. The third class considers elements with significant enrichment and it includes Sb and Cu. The fourth class considers elements with high enrichment and it includes As and Bi. Finally, the fifth class, which corresponds to elements with extremely high enrichment, includes only Au (Table 1). Although the following elements: Ag, Cd, Bi, Sb, Li, and Au have an EF ranging from 2.93 to 70.09, their concentrations in the Kettara soils are extremely low. Their mean concentrations are 0.13 mg/kg, 0.32 mg/kg, 2.52 mg/kg, 1.57 mg/kg, 42.45 mg/kg, and 0.11 mg/kg, for Ag, Cd, Bi, Sb, Li, and Au, respectively (Table 1). These low concentrations would not have any adverse effects on humans or animals in Kettara area. However, the elements Cu, Pb, Zn As, and Fe have an EF ranging from 2.17 to 25.17 and their concentrations in Kettara soils are high with a mean concentration of 203.38 mg/kg, 41.44 mg/kg, 135.95 mg/kg, 33.31 mg/kg, 769.74 mg/kg, for Cu, Pb, Zn As, and Fe, respectively (Table 1). The Cu, Pb, Zn As, and Fe were selected as elements with important interest because they are related to mineral paragenesis and therefore, to mining and mineralogical activities in Kettara. Furthermore, they are known to be toxic and hazardous at high concentrations (Lockitch, 1993; Chowdhury et al., 2000; Gurzau et al., 2003; Peplow and Edmonds, 2005; Davies et Mundalamo, 2010).

The Cu, Pb, Zn, As, and Fe concentration levels ranged from 20.6 to 1687 mg/kg, 7.6 to 207.8 mg/kg, 62 to 449 mg/kg, 6 to 124 mg/kg and 43300 to 374900 mg/kg, respectively. The mean concentrations are 203.38 mg/kg, 41.44 mg/kg, 135.95 mg/kg, 33.31 mg/kg and 76974 mg/kg, for Cu, Pb, Zn, As, and Fe respectively (Table 1). These concentrations disclose that metallic and metalloid content in the Kettara soil is high. In order to reveal if the origin of this content is weather geogenic or anthropogenic and for a better observation of the values distribution shape, Figures 3, 4 and 5 illustrate graphs (histograms, box plots and Q-Q plots for the selected elements) obtained from EDA. Figures 3a to 3e shows that all histograms are asymmetric and right-skewed. Skewness characterizes the distribution asymmetry degree around its mean (Zhou et al., 2010). The skewness feature of Cu, Pb, Zn, As, and Fe concentrations suggests that the majority of the samples are located in the lowest intervals of concentration. Figures 4a to 4e shows that all the boxes are displaced towards the minimum concentration values. This confirms the fact that the concentrations distribution of selected

elements is skewed. Numerous outliers (anomalous values above the upper limit of the box plots) of Cu, Pb, Zn, As, and Fe are shown in the box plots (Figures 4a to 5e). Outliers are indicators of unusual processes. They usually exist in mineralized region or in contaminated sites (Zhou et al., 2010). According to the Figures 2 and 4, the outliers of selected elements are located nearby and downstream the mine wastes which, are the likely source of the anomalous metallic and metalloid content. Figure 5 shows the Q-Q plots of selected elements. The measured values are plotted on the X axis and the expected values under a normal distribution are plotted on the Y axis. Q-Q plots provide a powerful visualization of the data which shows inflection points that imply the likely presence of different processes (Zhang et al., 2008; Zhou et al., 2010). The plots of selected elements (Figures 5a to 5e) undergo inflection points and they are far from the theoretical normal slop. This implies that the selected elements concentrations distribution is asymmetric. Furthermore, the large standard deviation, variation coefficient, skewness, and kurtosis calculated for each selected elements (Table 1) imply that these elements have asymmetric distributions with a long tail to the right which suggest the presence of high extreme values and, consequently, high degree of pollution. Asymmetries are also reflected by the numerical test of normality Kolmogorov-smirnov (K-S test) that gives values of zero for all the selected elements which indicates that the concentration values are not normally distributed (Martínez, 2002; Chen et al., 2011). According to the EDA results and the calculated statistical parameters, the Kettara soil involves different intervals of concentrations, which imply the existence of multiple populations resulting from geogenic and anthropogenic enrichment.

High concentration levels were found also for selected elements in the Kettara mine wastes (Table 2). The Concentrations ranged between 879 and 6971 mg/kg for Cu, 7 and 778 mg/kg for Pb, 79 and 361 mg/kg for Zn, 13 and 715 mg/kg for As and 90200 and 413600 mg/kg for Fe. The mean concentrations are: Cu (2428 mg/kg), Pb (156 mg/kg), Zn (176 mg/kg), As (200 mg/kg), and Fe (294825 mg/kg). These concentrations exceed widely the Clarke values given by McLennan (2001) indicating that Kettara mine wastes are extremely enriched in toxic elements. Consequently, it is plausible that the mine wastes are the main source of the soil contamination in Kettara region.

3.2. Determination of the soil geochemical background and anomalous values

The soils GB was defined based on the normality curves which provided a detailed visualization of experimental data distribution (Zhou et al., 2010). The plot curves of Cu, Pb, Zn, As, and Fe undergo an inflection point (Figures 5a to 5e). The plot curves of Zn and Fe (Figures 5c and 5e) shows the existence of two populations of concentration. However, they show the existence of three populations of concentration for the other selected elements (Figures 5a, 5b, and 5d). The inflection point allows distinguishing between natural or geogenic concentration values (the first population with low values) and anthropogenically influenced samples (second and third population with high values). The second and the third population are interpreted as one population because they are representing the result of mining activity (Martínez et al., 2007). After deducting these two populations, the next step was to determine the GB values and the anomalous values for Kettara soils. From the studied variable, the values of the mean and medians for each population were derived. The mean values obtained for the first and for the second populations correspond, respectively, to the GB and to the anomalous values. Net anomalous values can be deduced by subtracting the GB values from the anomalous values.

Soil GB values, anomalous values and net anomalous values are reported in Table 4. Unfortunately, in Morocco no environmental guidelines exist to regulate maximum permissible metals and metalloid concentrations in soils or to give reference values above which action should be taken to mitigate environmental risk. Therefore, the obtained values in this study will be compared with guidelines adopted by Canada and European community (Kabata-Pendias and Pendias, 1992; CCME, 2006). These guidelines were used in El-Khalil et al. (2008) research which were undertaken to assess the metal contamination from mining sites in the south of Morocco. The results indicate that GB values of Cu (43.8 mg/kg), Pb (21.8 mg/kg), Zn (102.6 mg/kg), and As (13.9 mg/kg) are below the used reference values (Table 4), whereas the GB of As exceed slightly the Canadian guideline for As (12 mg/kg). According to these results, the geogenic concentrations of Cu, Pb, Zn, and As in Kettara soils will not have any adverse health effects. However, calculated anomalous values of Cu (397.2 mg/kg), Pb (55.6 mg/kg), Zn (196.5 mg/kg), As (42.6 mg/kg), and Fe (152346 mg/kg) reveal the contribution of anthropogenic activity in contaminating Kettara soils. The calculated anomalous values of Cu and As are above the used reference values (Table 4). The origin of anthropogenic activity and dispersion mechanism of contaminants will be discussed in the following section.

3.3. Geochemical mapping and multi-criteria analysis

The spatial distribution of metals and metalloid in the Kettara soils was analyzed using GIS mapping technique based on geostatistics (simple kriging). The obtained geochemical maps were then overlaid with other thematic maps such as stream networks and mine wastes maps. According to the geochemical maps (Figure 6), higher concentrations of Cu, Pb, Zn, As, and Fe were observed around and especially downstream the mine wastes. These concentrations decreased with increasing distances from the mine waste sites. Generally, areas located downstream of the mine wastes contained higher concentrations than those located upstream.

The studied Kettara soils are characterized by very high concentration levels of Cu ranging from 20 to 1687 mg/kg (Figure 6a). Normal values are located essentially upstream the mine wastes. The highest values which exceed widely the established GB (43.8 mg/kg) are located downstream the mine wastes. Intermediate values are located far from the mine wastes downstream these letters. The geochemical map of Cu (Figure 6a) showed that this element was derived essentially from the mine wastes located in the northern side of the study area and that were related to the second and third phase of the mining exploitation (mine wastes from the exploitation of pyrite and pyrrhotite). Those mine wastes are very rich in Cu (Table. 2). The origin of Cu in the mine wastes was chalcopyrite (Hakkou et al., 2008a) which was present in the mineral paragenesis of Kettara (Hibti et al., 1999). This element was derived from the mine wastes by AMD action and subsequently dispersed with ephemeral water courses and surface runoff during the rainy season. It should be mentioned that the effect of the main flows direction of surface water follows slopes which enhances the pollution spread. Mechanical dispersion by wind action may play part especially if we know that prevailing wind flow has relatively the same direction of metallic dispersion.

Furthermore, Pb is characterized by moderate concentration values ranging from 7.6 to 207.8 mg/kg (Figure 6b). Uncontaminated areas are located upstream Kettara mine wastes. Contaminated areas where concentrations exceed the established GB (21.8 mg/kg) occur only in the vicinity of mine wastes located in northern side of the study site. However, intermediate Pb concentrations are located in areas downstream the mine wastes deposited in southern side. After a review of Pb concentrations in mine wastes samples, it was found that mine wastes

located in southern part of the study site which were related to the first phase of mining exploitation (wastes from exploitation of iron oxide) contain lower Pb concentrations than those located in northern part. This explains the location of the formed hot-spots of Pb. This element was leached from the galena contained in the mine wastes by AMD action. Galena was left in mine wastes during the mining exploitation in Kettara mine (Hakkou et al., 2008a). The derived geochemical map (Figure 6b) shows that Pb was mainly dispersed with surface water through the ephemeral water courses and surface runoff and by mechanical dispersion through the wind.

The Figure 6c illustrates that Zn concentrations were ranging from 60 to 450 mg/kg. This map shows a big contrast in concentrations between areas located upstream of mine wastes, where Zn concentrations are normal and inferior to the established GB (102.6 mg/kg) and those located downstream, where high soils contaminations occurred. The contaminated areas are represented by two hot-spots where concentration levels reach 450 mg/kg. Intermediate concentration levels are also observed in the vicinity of mine wastes. Zn is a relatively mobile element which can easily be released from mine wastes which contain Zn bearing minerals (e.g. sphalerite) by AMD action. Likewise, Cu, Pb, and Zn had the same dispersion mechanism that prevailed in the study area.

For As element, Figure 6d shows relatively similar distribution pattern as Cu. As concentration levels are ranging from 6 to 124 mg/kg. For this element, low concentrations which are inferior to the established GB (13.9 mg/kg) are observed upstream mine wastes. However, high concentration levels of As are observed in the contaminated areas located downstream mine wastes. The concentrations in these areas exceed widely the established GB. The spatial distribution of As in the Kettara soil explains its anthropogenic origin that is the deposited mine wastes. These latter contain high concentration levels of As especially in mines wastes located in southern part of the study area where the concentration can reach 715 mg/kg (Table 2). As was leached from mine wastes by AMD as result of weathering process, and then it was spread in study area mainly by surface water and wind flow.

Comparatively to the other selected elements, Fe has the highest concentration levels in the study area (Table 1). These concentrations are ranging from 43300 to 371400 mg/kg (Figure 6e). This is not only because Fe is a major element and it's quite abundant in earth crust, but also because it was one of the main elements exploited in Kettara mine. Figure 6e shows that

Fe has, relatively, similar spatial distribution pattern as Cu and As. Uncontaminated areas are located upstream the mine wastes. However, heavily contaminated areas where concentrations exceed widely the established GB (56978 mg/kg) are located just downstream the mine wastes. Generally, geochemical map shows that concentrations decrease with distance from the mine wastes. These latter are extremely rich in Fe with concentrations ranging from 90200 to 413600 mg/kg with an average of 294825 mg/kg (Table 2). These results corroborate Hakkou et al., (2008a) research in the same study region where they used X-Ray Diffraction analysis which revealed that many Fe bearing minerals (e.g. pyrrhotite, pyrite, goethite, magnetite and jarosite) are contained with different proportions in the Kettara mine wastes. Likewise the previous elements, Fe was leached from mine wastes with AMD and afterwards, dissipated in the study area by dispersion mechanism based mainly on surface water during rainy season followed by wind flow action.

The final risk map of soil contamination of Kettara (Figure 7) was derived from the elaborated geochemical maps using the spatial analyst of Arc GIS software. Heavily contaminated areas were extracted from each considered geochemical maps (Cu, Pb, Zn, As and Fe), then they were overlaid with other thematic maps of the study area (stream networks, mine wastes and geological maps). The risk map of contaminated soils highlights areas which must be remediated.

Figure 7 showed clearly that areas located downstream the mine wastes contain very high concentration levels of Cu (>300 mg/kg), Pb (>100 mg/kg), Zn (>300 mg/kg), As (>50 mg/kg), and Fe (>100000 mg/kg). However, areas located upstream the mine wastes are unaffected with anthropogenic activity. According to our final results (Figure 7) and to the ground truth, heavily contaminated areas occurred in the core of Kettara village where the majority of population is living. The concentration levels of metals and metalloid in contaminated soils exceed the soil quality guidelines values adopted by Canada and the European community (Kabata-Pendias and Pendias, 1992; CCME, 2006). Therefore, adverse effect on human health might be expected, especially on young children health that has a higher absorption rate of metals and metalloids because of their active digestion systems. Past studies have revealed that human exposure to high concentrations of As cause severe skin cancer and hyperkeratosis (Chowdhury et al., 2000). They revealed also that Cu accumulation in the human tissues may lead to the Wilson's disease which causes liver disease and multiple organ dysfunctions (Peplow and Edmonds, 2005). Furthermore, Pb toxicity can cause

hematological, gastrointestinal, and neurological diseases, and nephropathy, abortion, stillbirth, and neonatal death (Lockitch, 1993). Finally, the inhalation and the overload of iron may lead to pulmonary siderosis and tissue damage as result of oxidation stress damage (Gurzau et al., 2003; Edison et al., 2008).

4. Conclusions

The aim of this study was the assessment of extension and intensity of soils contaminations with toxic elements from abandoned Kettara mine. Soils and mine wastes around the abandoned site were sampled and analyzed for 41 chemical elements (Mo, Cu, Pb, Zn, Ag, Ni, Co, Mn, Fe, As, U, Au, Th, Sr, Cd, Sb, Bi, V, Ca, P, La, Cr, Mg, Ba, Ti, Al, Na, K, W, Zr, Ce, Sn, Y, Nb, Ta, Be, Sc, Li, S, Rb and Hf). The soils contaminations were evaluated for the selected metals and metalloid elements (Cu, Pb, Zn, As and Fe) based on enrichment factor computing, geochemical background determining using exploratory data analysis, and geochemical mapping based on GIS and geostatistics.

The obtained results show that statistical techniques applied for processing geochemical data are very useful for identifying geochemical background values, and for discriminating between geogenic and anthropogenic concentrations in Kettara soils. Moreover, they show that GIS and geostatistics are valuable tools in elaborating geochemical maps and quantifying both intensity and extension of contaminants and therefore monitoring soils contaminations. Finally, elaboration of ultimate risk map of soil contamination, which identifies hot-spots of contaminants using spatial analysis, might be very useful in the remediation of Kettara soils.

The concentration levels of Cu, As and Fe present in Kettara soils exceed the established geochemical background and the Canadian and European soils quality guidelines. Therefore, frequent adverse health effects might be expected. The derived geochemical maps show that: 1) most of areas located downstream mine wastes are characterized by a very high concentration levels of contaminants; 2) Kettara mine wastes are responsible for soils contaminations with metals and metalloid which were released by Acid Mine Drainage action; and 3) hydric dispersion pattern during a rainfall events are qualified as the main mechanism of contaminants spreading in the study area.

1 In order to assess soils pollution resulting from anthropogenic activity, the current study
2 was undertaken in a limited and controlled area. This requires much time and high investment
3 cost. In order to overcome this problem, in the second part of this research, we'll develop a
4 new methodology integrating field spectroradiometric measurements, soils laboratory
5 analyses, semi-empirical modeling, and remote sensing image processing in order to assess
6 soils pollution and contaminations over a large territory with less time and investment.

7 The conducted work in this study can be served as the pre-work basis of establishing
8 numerical models that could be used to simulate the realistic geochemical processes of the
9 considered mine site in the future research.

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Tables and figures

Table 1: Descriptive statistics, Clarke values (a), and enrichment factors of chemical elements of examined kettara soils.

Table 2: Descriptive statistics of chemical elements of examined Kettara mine wastes.

Table 3: Theoretical semi-variogram model values and errors estimation.

Table 4: Geochemical background values, anomalous and net anomalous values obtained for Kettara soils.

Figure 1: Geographical location of study site.

Figure 2: Geological map of study site and sampling point locations.

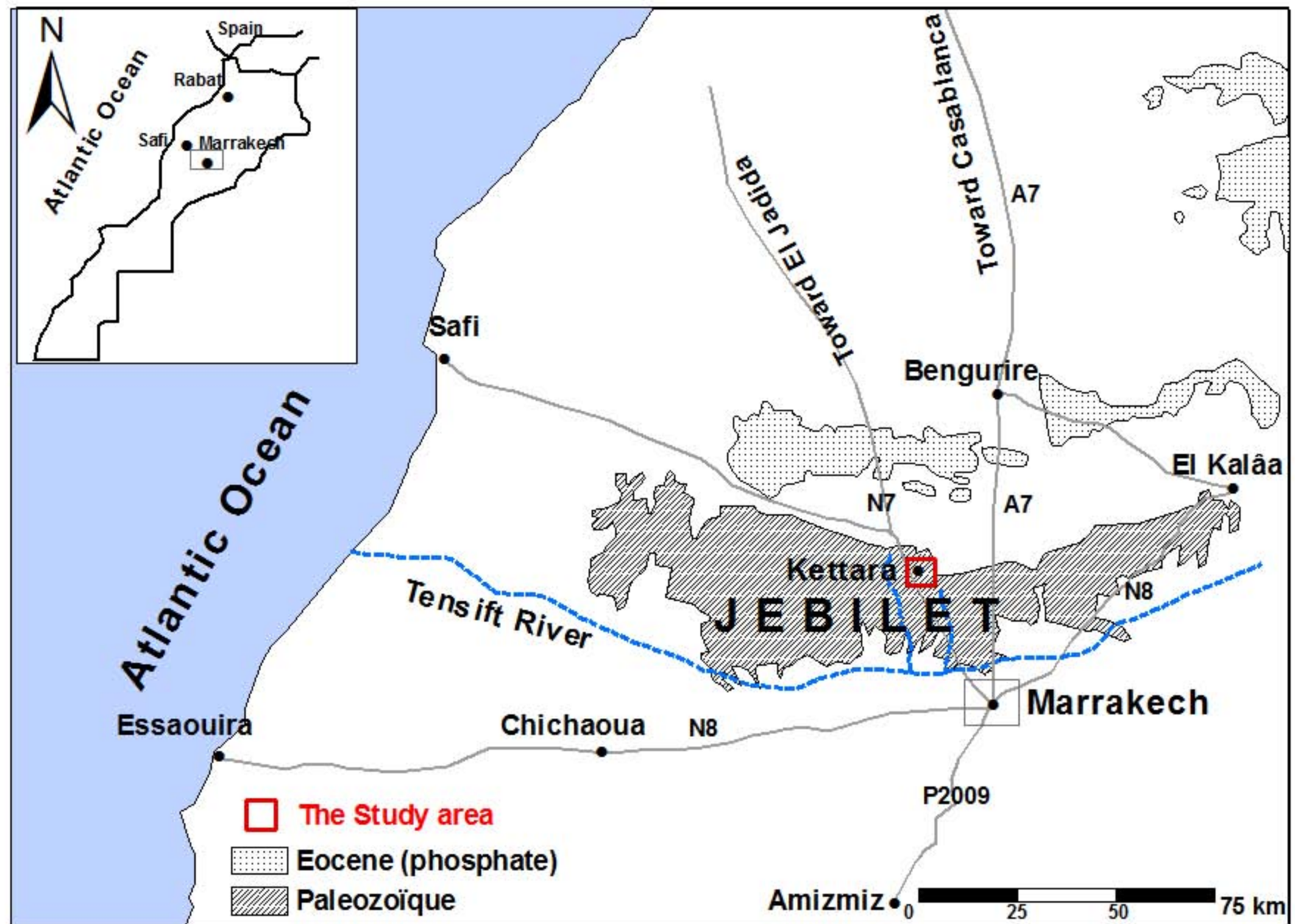
Figure 3: Histograms and cumulative frequency curves for the selected elements in soil (concentrations are in mg/kg).

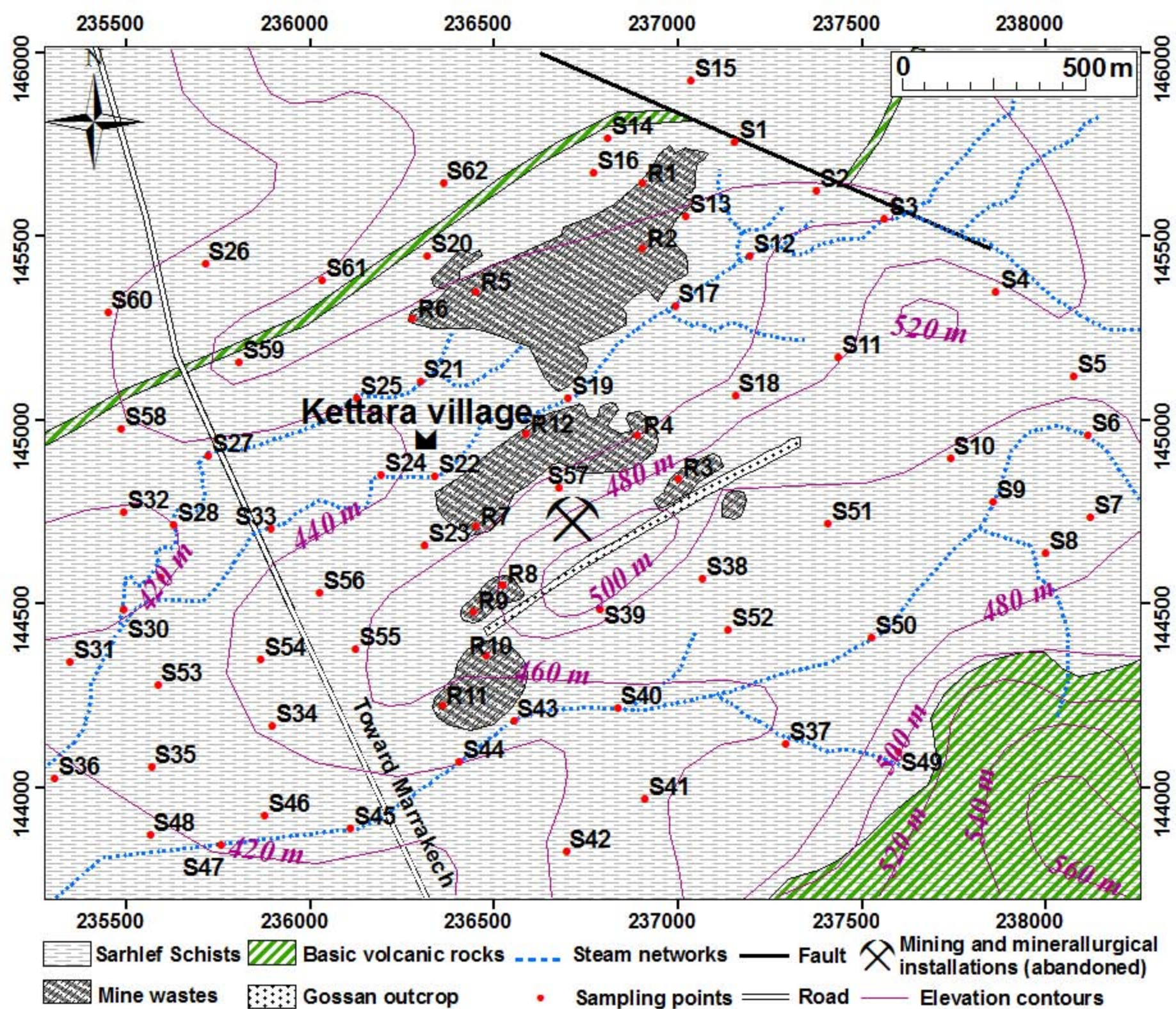
Figure 4: Box plots for the concentration of selected elements in soil (concentrations are in mg/kg).

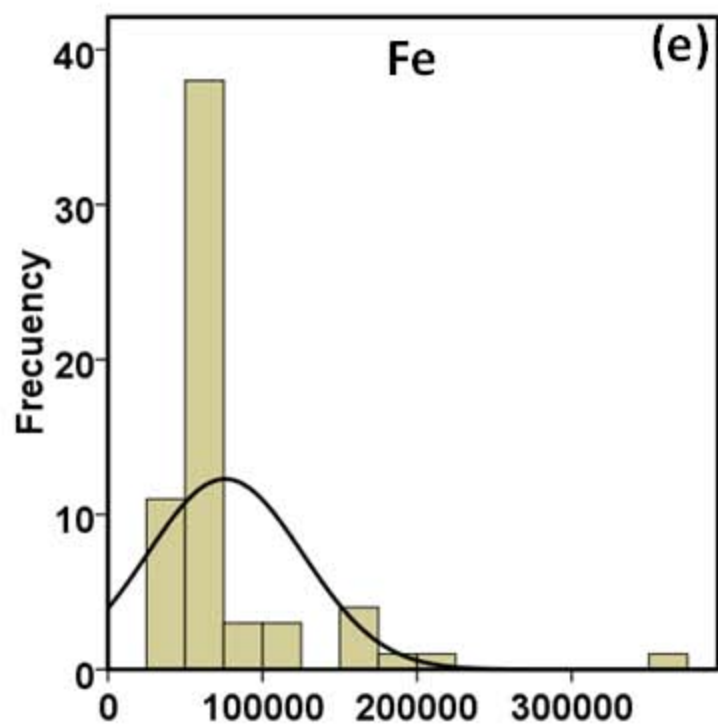
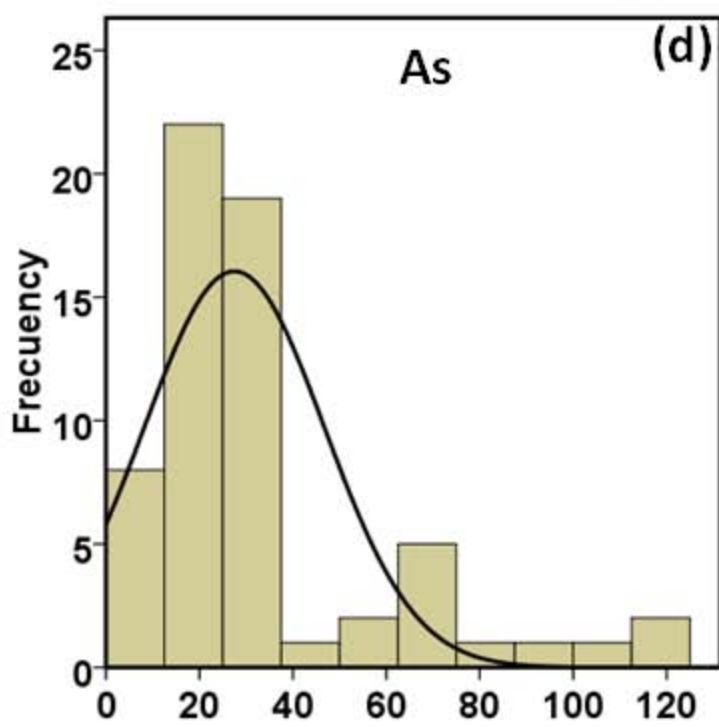
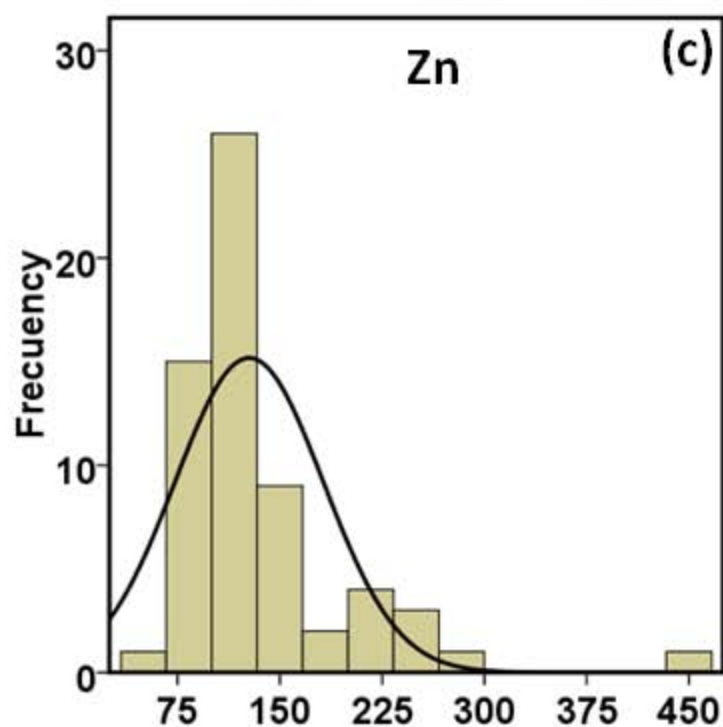
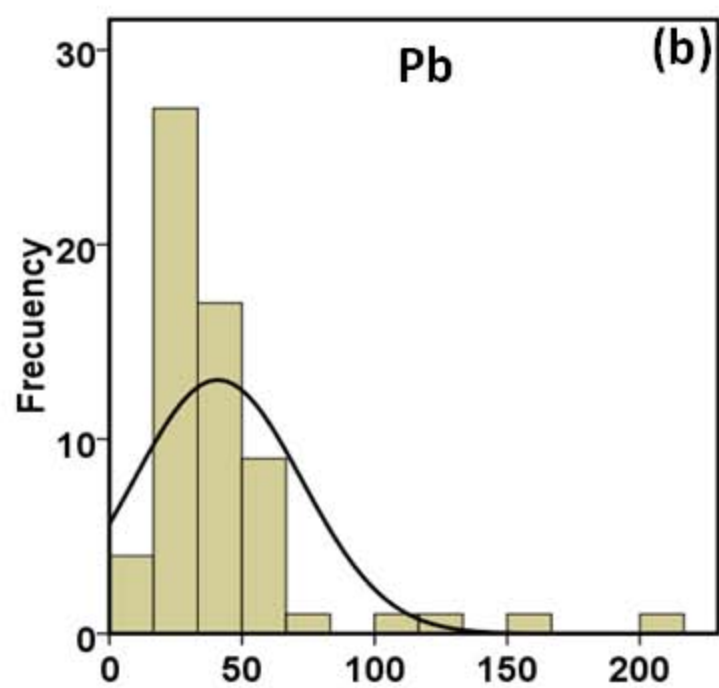
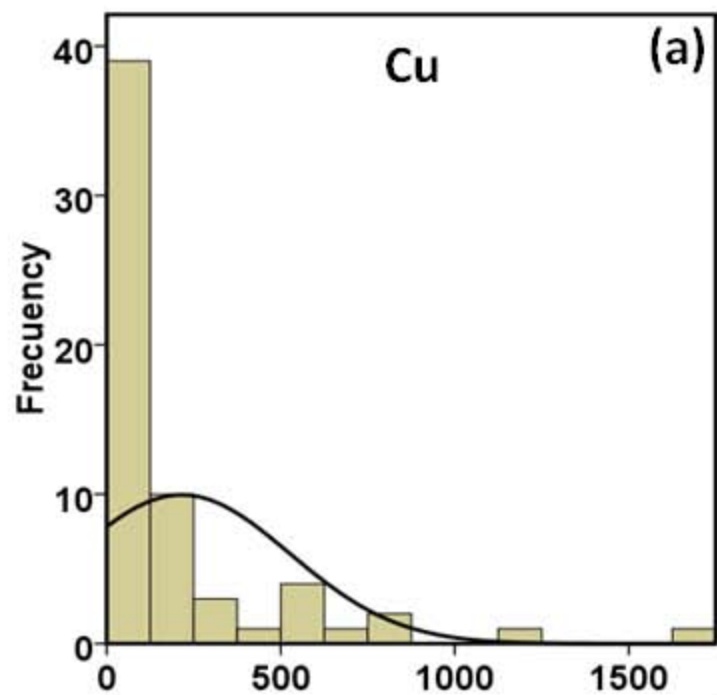
Figure 5: Normal Q-Q plots for selected elements (arrow a: inflection point).

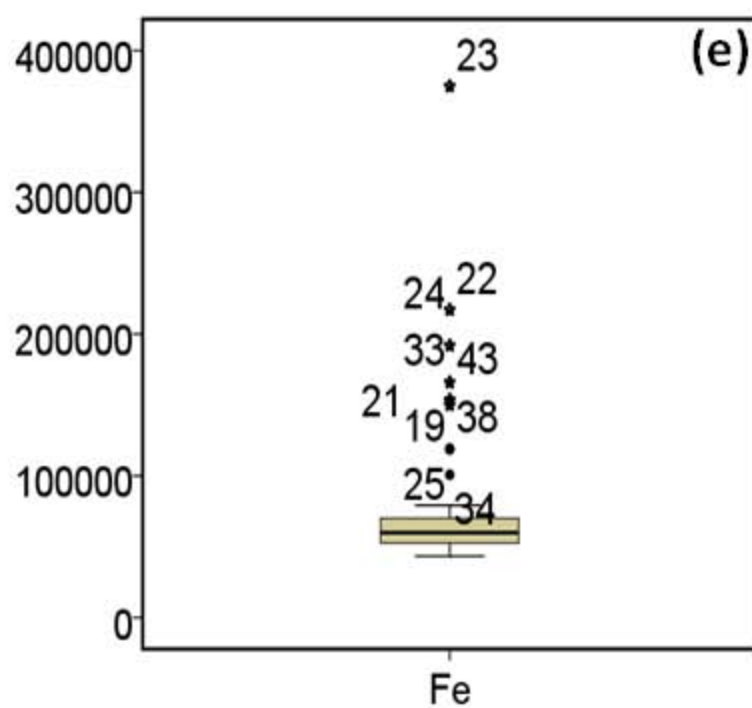
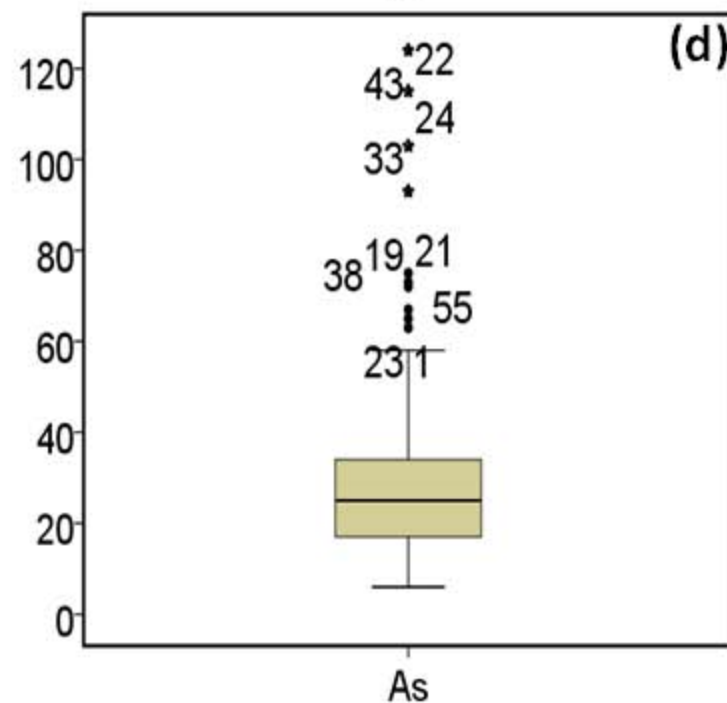
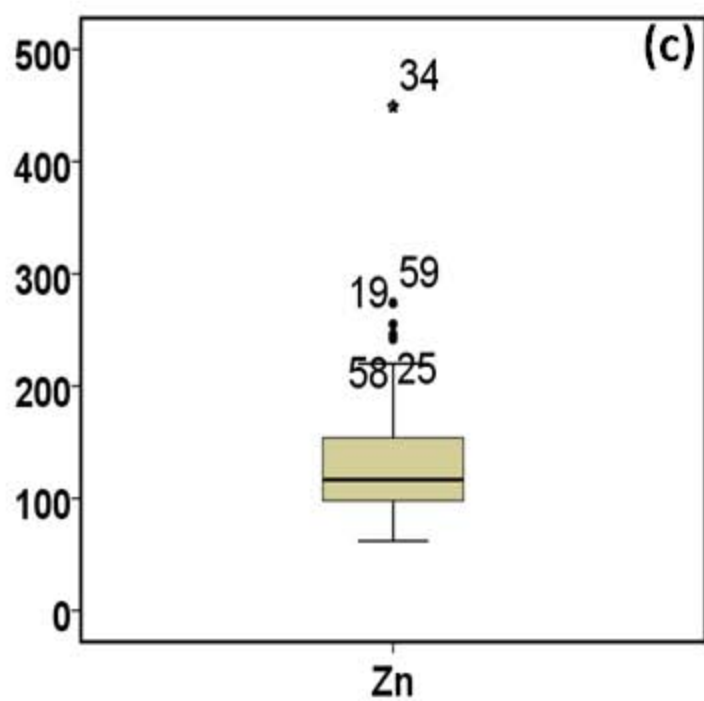
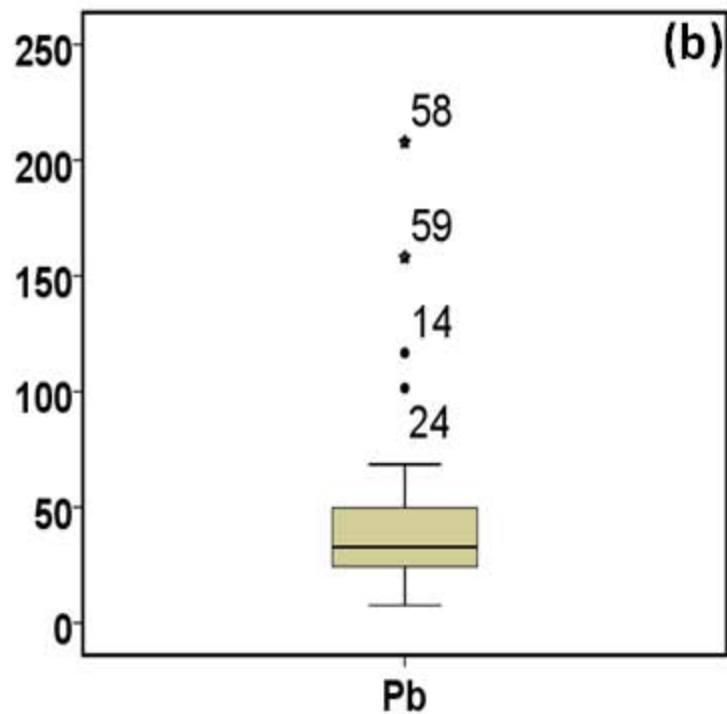
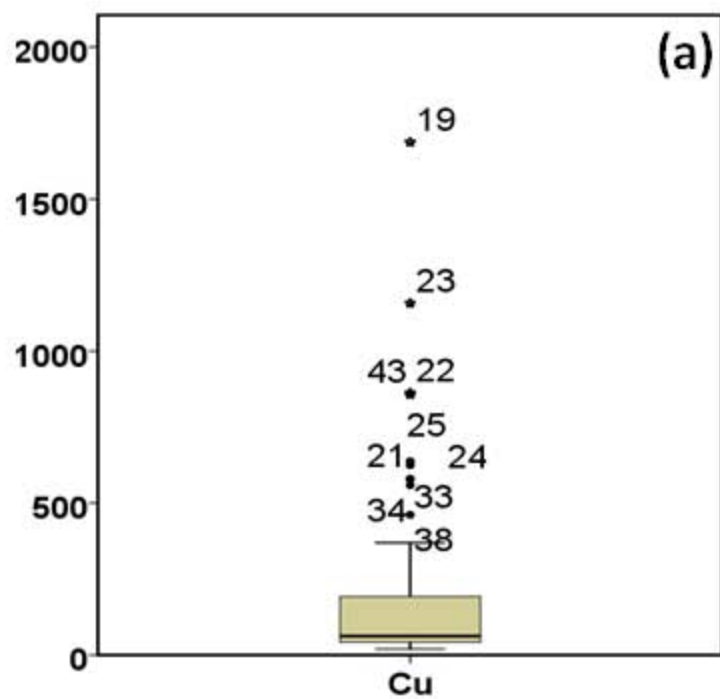
Figure 6: Geochemical maps of selected elements.

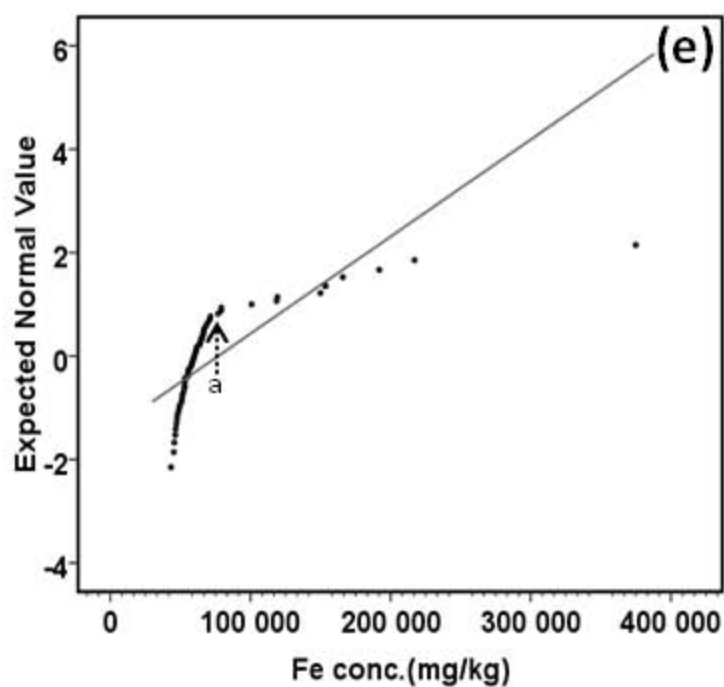
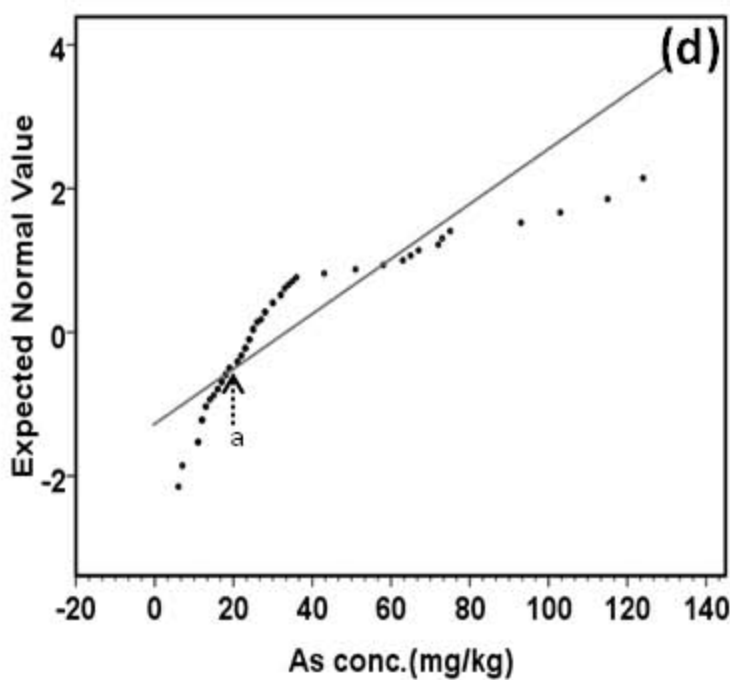
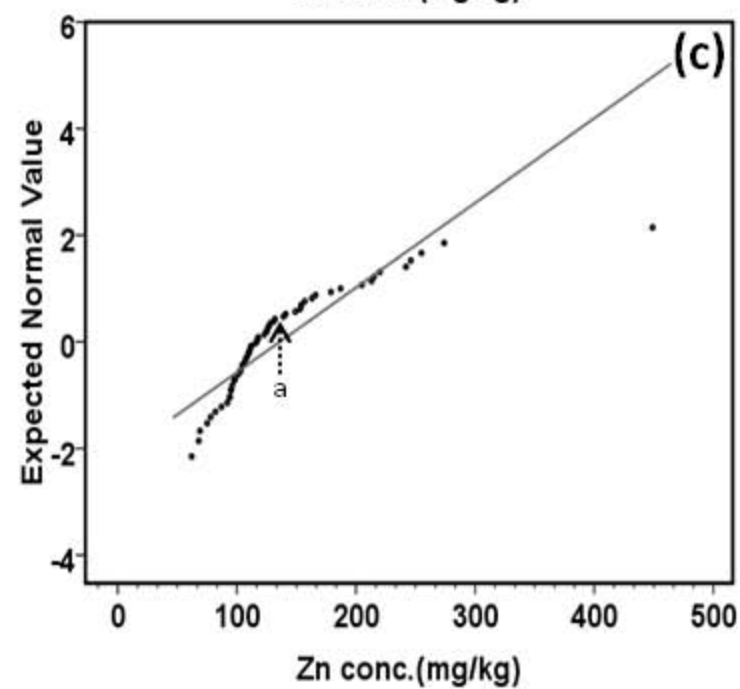
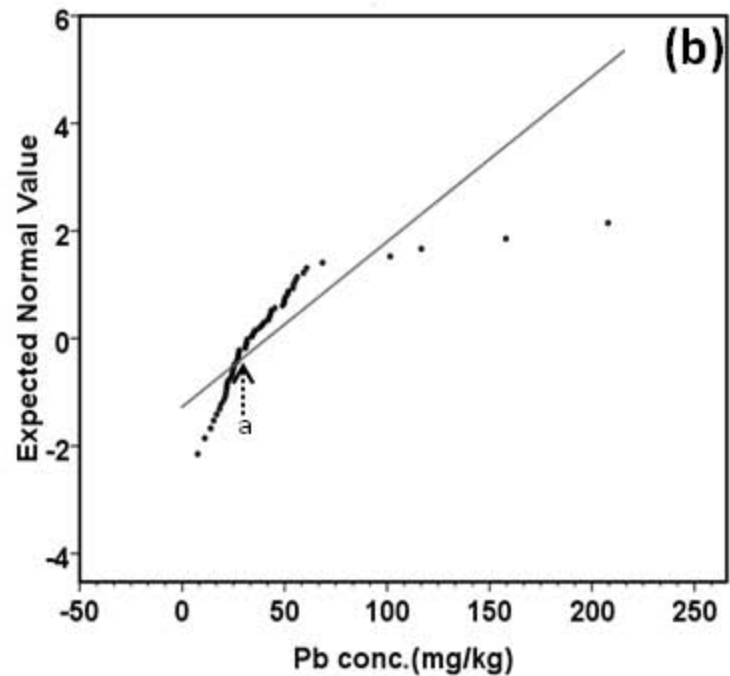
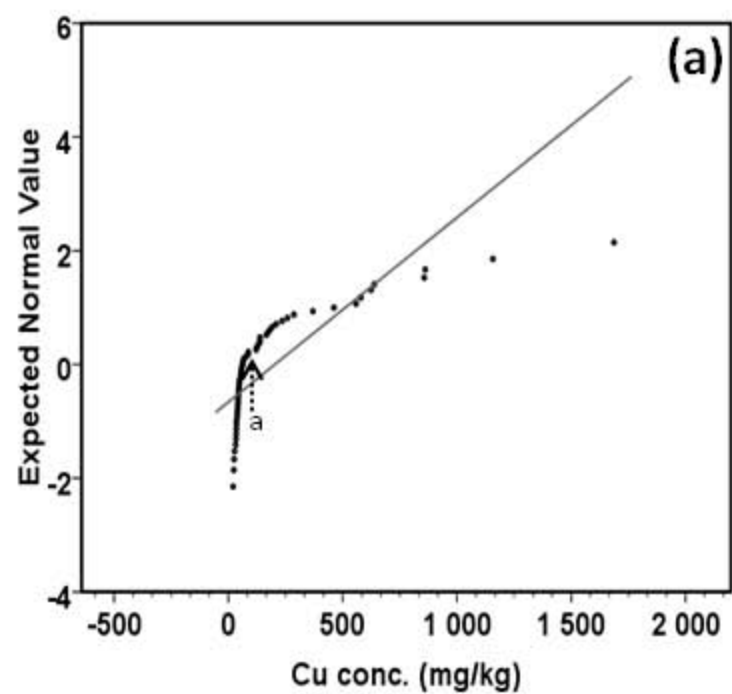
Figure 7: Risk map of soils contamination with Cu, Pb, Zn, As, and Fe.

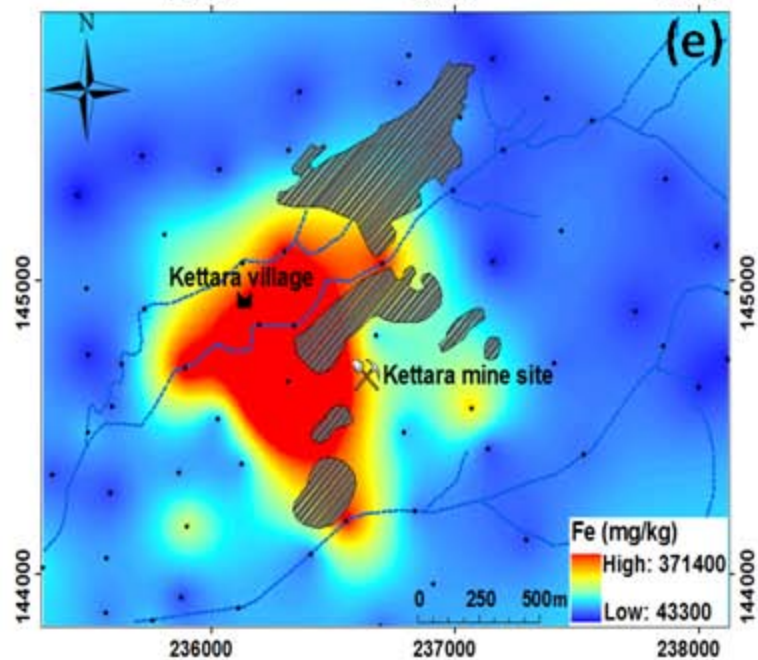
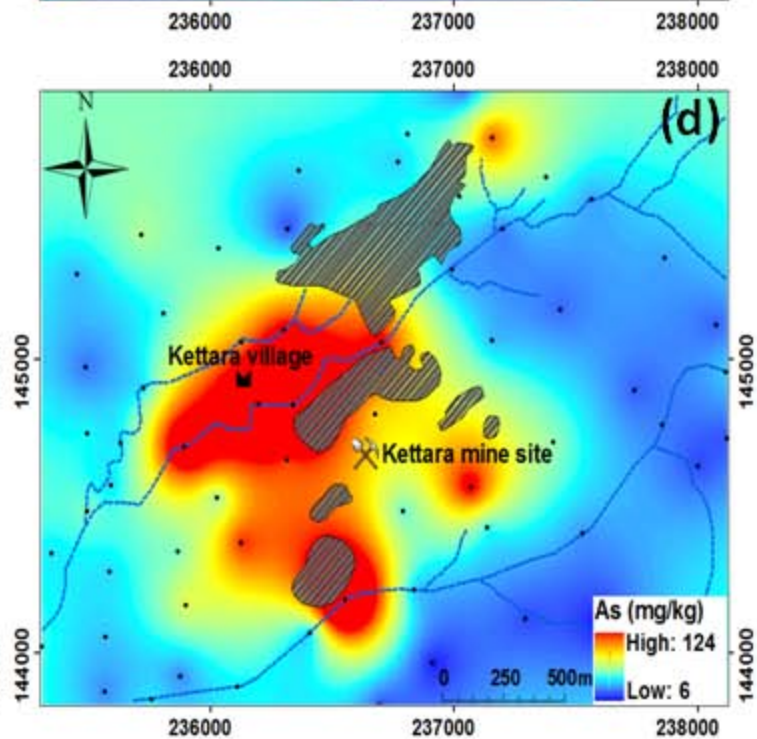
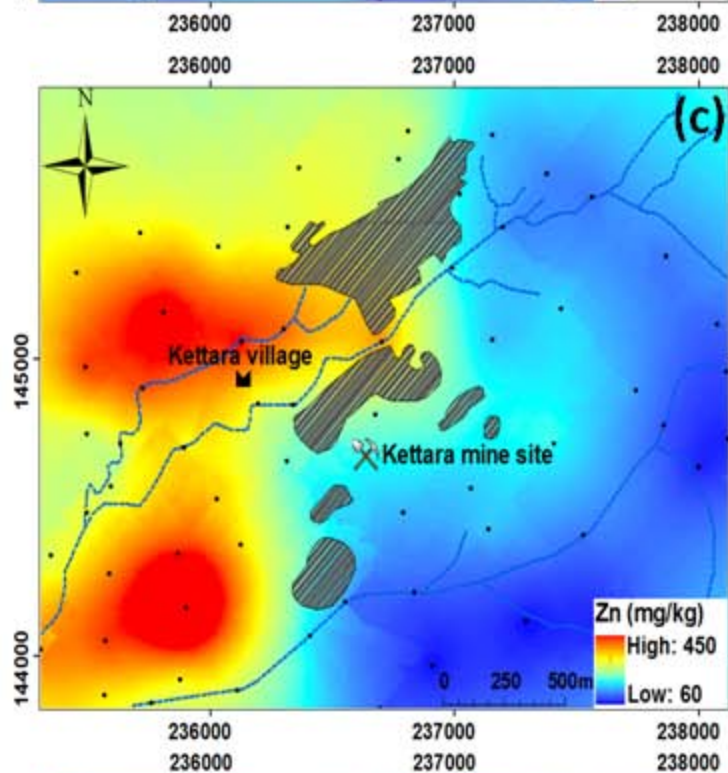
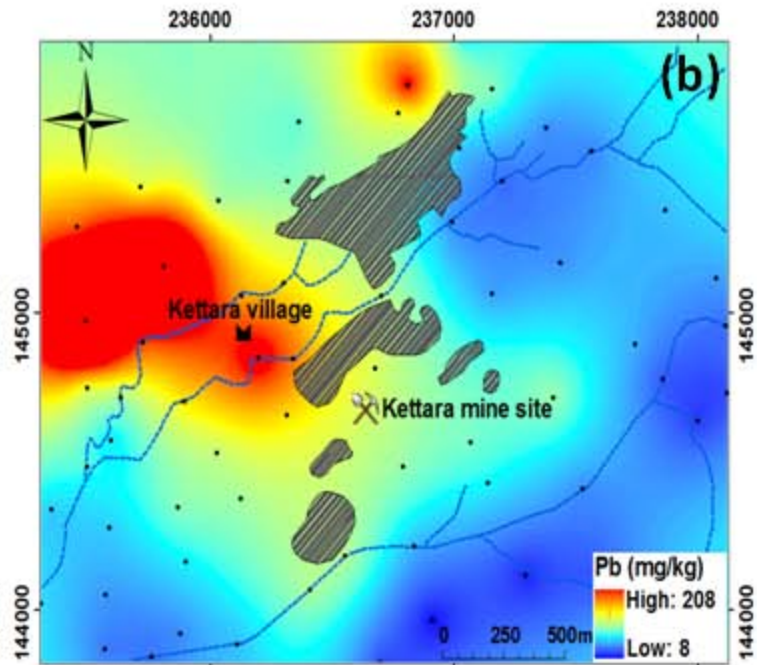
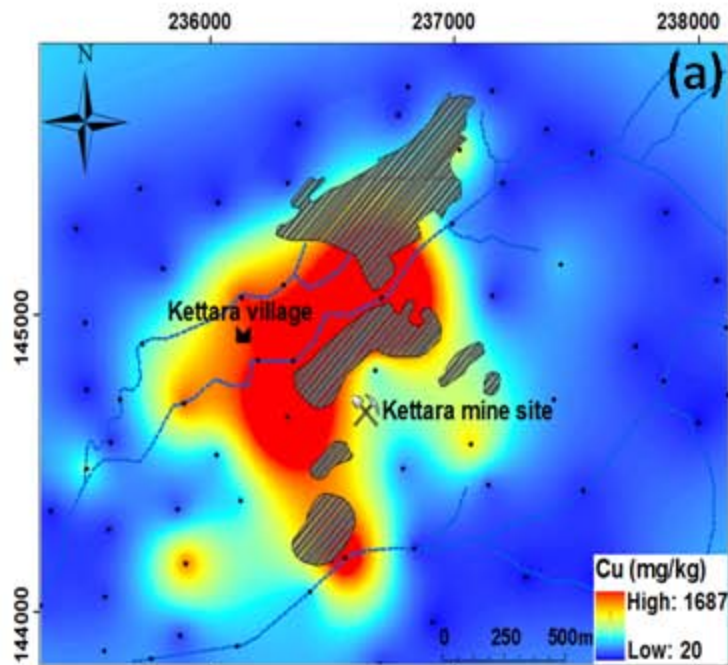






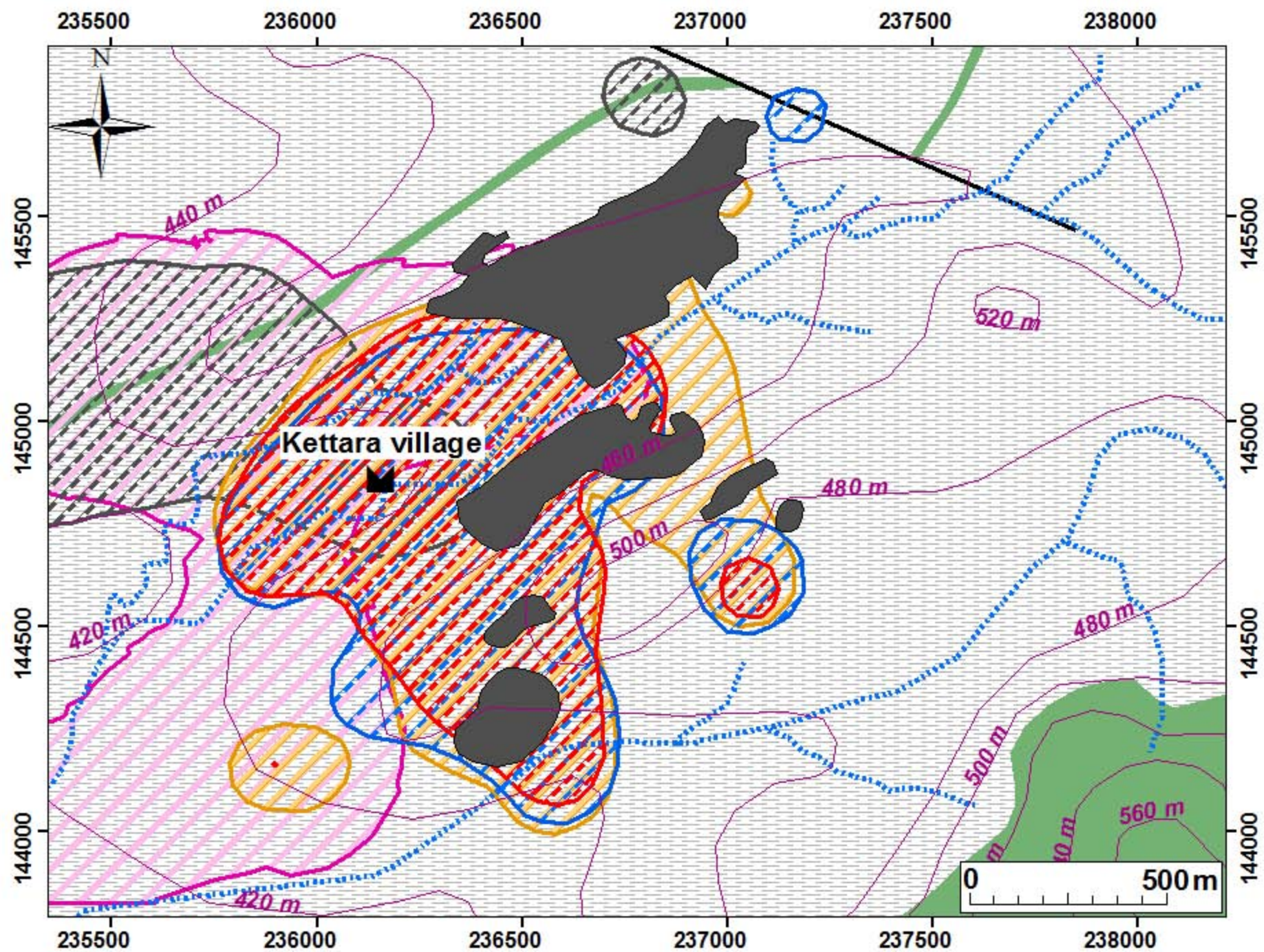






LEGEND

- Stream networks
- Soil sampling location
- Mine wastes



- | | | | |
|---------------------------|--------------------------|------------------------------|--------------------|
| Anomaly of Zn (>300mg/kg) | Anomaly of As (>50mg/kg) | Steam networks | Elevation contours |
| Anomaly of Cu (>300mg/kg) | Sarhlef Schists | Mine wastes | Fault |
| Anomaly of Pb (>100mg/kg) | Basic volcanic rocks | Anomaly of Fe (>100000mg/kg) | |

Table 1

Descriptive statistics, Clarke values (a) and enrichment factors of the chemical elements of examined Kettara soils.

Elements	Minimum	Maximum	Mean	Median	SD	VC	Skewness	Kurtosis	K-S test	Upper Continental Crust Clarke values ^a	Enrichment factor (Upper Continental Crust)
Mo	0.3	4.7	1.13	0.8	0.86	0.76	2.31	5.81	0.000	1.50	0.86
Cu	20.6	1687	203.38	62.3	308.32	1.52	2.82	9.25	0.000	25	9.22
Pb	7.6	207.8	41.44	32.9	32.57	0.79	3.25	12.97	0.000	17	2.76
Zn	62	449	135.95	116.5	62.96	0.46	2.51	9.22	0.000	71	2.17
Ag	0.1	0.9	0.13	0.1	0.14	1.06	3.46	16.40	0.000	0.05	2.93
Ni	4	246.3	56.23	46.2	36.19	0.64	3.13	12.85	0.000	44	1.45
Co	13.6	64.2	27.47	24.2	9.80	0.36	1.80	4.54	0.003	17	1.83
Mn	134	2170	911.90	886	338	0.37	0.76	2.18	0.200	600	1.72
Fe	43300	374900	76974	59800	53268	0.69	3.62	16.21	0.000	35000	2.49
As	6	124	33.31	25	26.13	0.78	1.87	3.19	0.000	1.5	25.17
U	0.5	2.3	1.53	1.6	0.37	0.24	-0.35	0.21	0.029	2.8	0.62
Au	0.1	0.6	0.11	0.1	0.07	0.67	6.60	46.62	0.000	0.0018	70.09
Th	2.2	15.8	10.86	11.4	2.99	0.28	-1.00	0.83	0.035	10.70	1.15
Sr	8	156	79.15	76.0	23.29	0.29	0.27	1.81	0.200	350	0.26
Cd	0.1	0.8	0.32	0.3	0.13	0.40	1.13	2.93	0.000	0.10	3.66
Sb	0.5	5.3	1.57	1.1	1.13	0.72	1.74	2.45	0.000	0.20	8.92
Bi	0.05	30.4	2.58	0.5	5.41	2.10	3.48	13.52	0.000	0.13	23.06
V	44	281	140.40	135.5	34.71	0.25	1.34	4.94	0.002	107	1.49
Ca	1300	73700	13813	10300	13295	0.96	2.23	6.41	0.000	30000	0.52
P	220	1450	752.58	725	207.77	0.28	0.69	2.06	0.017	700	1.22
La	8	48.4	33.82	35.7	8.27	0.24	-0.80	0.80	0.069	30	1.28
Cr	25	1081	134.97	91.0	145.19	1.08	5.09	30.66	0.000	83	1.84
Mg	2800	43800	15944	13300	7857	0.49	1.94	4.09	0.000	13300	1.36
Ba	65	652	407.55	436.0	116.22	0.29	-0.89	0.92	0.000	550	0.84
Ti	610	18340	5512	4920	2403	0.44	2.53	12.57	0.001	4100	1.52
Al	11600	89900	70923	72850	10617	0.15	-3.10	15.48	0.000	80400	1.00
Na	530	14140	5725	5505	2153	0.38	1.75	6.12	0.000	28900	0.22
K	2800	24700	18140	19450	4899	0.27	-1.10	0.85	0.003	28000	0.73
W	0.4	2.7	1.44	1.4	0.45	0.31	0.79	1.10	0.000	2	0.82
Zr	22.4	108.5	87.32	92.6	16.17	0.19	-1.39	2.95	0.003	190	0.52
Ce	17	102	72.52	76.5	18.11	0.25	-0.78	0.53	0.067	64	1.28
Sn	1.5	6.6	3.10	2.9	0.75	0.24	1.98	7.23	0.000	6	0.64
Y	2.8	49.1	20.26	19.6	6.74	0.33	1.05	4.74	0.200	22	1.04
Nb	2.4	21.8	12.64	13.4	3.62	0.29	-0.46	0.16	0.200	12	1.19
Ta	0.1	1.5	0.85	0.9	0.25	0.30	-0.42	0.36	0.004	1	0.96
Be	1	3	1.98	2.0	0.68	0.34	-0.35	0.11	0.000	3	0.74
Sc	3	30	15.76	15.0	4.44	0.28	0.92	2.56	0.000	14	1.31
Li	4.7	66.9	42.45	41.1	10.08	0.24	-0.30	2.77	0.070	20	2.41
S	1000	53000	4073	1000	9742	2.39	3.50	13.07	0.000	*	*
Rb	13.9	118.4	80.94	85.7	23.36	0.29	-0.73	-0.12	0.017	112	0.82
Hf	0.7	3.6	2.58	2.7	0.50	0.20	-1.06	1.99	0.000	5.80	0.50

^a Clarke values = mean concentrations of the chemical elements in the upper continental crust (UCC) given by McLennan (2001); Geochemical data are expressed in mg/kg; VC = variation coefficient; SD = standard deviation.

Table 2

Descriptive statistics of chemical elements of examined Kettara mine wastes.

Elements	Minimum	Maximum	Mean	Median	SD	VC	Skewness	Kurtosis
Mo	1	13.70	4.14	2.80	3.52	0.85	2.24	5.05
Cu	879	6971	2428	1508	1974	0.81	1.76	2.02
Pb	7	778	156	81	217	1.39	2.53	6.79
Zn	79	361	176	153	83	0.47	1.22	1.11
Ag	0.10	13.10	1.67	0.65	3.62	2.16	3.40	11.70
Ni	2.50	48.90	14.32	9.30	14.53	1.01	1.50	1.78
Co	14	313	67	36	85	1.27	2.63	7.41
Mn	132	879	377	282	255	0.68	0.99	-0.33
Fe	90200	413600	294825	307650	91925	0.31	-0.98	1.00
As	13	715	200	109	212	1.06	1.78	2.47
U	0.60	4.70	2	1.35	1.47	0.72	1.00	-0.69
Au	0.10	0.70	0.24	0.20	0.17	0.71	1.72	4.55
Th	0.60	17.80	7.18	6.45	5.65	0.79	0.89	-0.05
Sr	1.00	468.00	73.42	23.00	132.62	1.81	2.84	8.42
Cd	0.10	1.10	0.30	0.20	0.30	1.02	1.98	4.39
Sb	0.40	24.30	5.43	1.65	8.47	1.56	1.95	2.42
Bi	3.20	104.60	33	22.40	34.02	1.03	1.82	2.14
V	18.00	147	83	85.50	46.05	0.55	0.00	-1.36
Ca	700	21000	3333	1550	5635	1.69	3.31	11.21
P	50	1280	470.83	395	351.14	0.75	1.21	1.51
La	2.60	60.60	19.57	16	14.74	0.75	2.13	5.81
Cr	4.00	153.00	57.25	51	42.00	0.73	1.02	1.12
Mg	1200	28900	11500	10450	9718	0.85	0.55	-0.97
Ba	6	382	109	95	106	0.97	1.80	3.49
Ti	140	3340	1593	1570	981	0.62	0.35	-0.82
Al	2300	85300	35617	35550	27911	0.78	0.43	-1.02
Na	80	3150	1051	725	902	0.86	1.45	1.62
K	200	18500	3383	1700	4934	1.46	3.05	9.92
W	0.40	6.60	4.23	4.95	2.15	0.51	-0.66	-1.13
Zr	4.90	110.40	59.33	52.30	37.33	0.63	0.06	-1.50
Ce	5	118	41	36	28.84	0.71	1.85	4.70
Sn	0.80	7.60	4.29	4.55	1.99	0.46	-0.16	-0.38
Y	1	8.60	5	4.70	2.47	0.49	0.04	-1.18
Nb	0.50	11.60	5.13	5.35	3.03	0.59	0.51	0.66
Ta	0.05	0.80	0.35	0.40	0.21	0.60	0.35	0.43
Be	1.00	1.00	1.00	1.00	0.00	0.00		
Sc	0.50	13.00	6.96	7.50	4.69	0.67	-0.03	-1.84
Li	4.10	44	17.18	11.40	13.03	0.76	0.90	-0.15
S	2000	96000	41167	30000	29905	0.73	0.52	-0.50
Rb	0.70	43.90	11.13	7.35	11.89	1.07	2.08	5.32
Hf	0.10	3.30	1.67	1.45	1.08	0.65	0.31	-1.13

VC = variation coefficient; SD = standard deviation (Geochemical data are expressed in mg/kg).

Table 3

Theoretical semi-variogram model values and errors estimation.

Element	Nugget	Number of Lag	Root-mean-Square	Average-standardized Errors	Mean Standardized	RMSE
Cu	0	12	271.80	265.80	0.03056	0.9958
Pb	418.56	12	29.28	29.48	0.02168	0.9951
Zn	2648.70	12	59.18	59.48	0.02974	0.9990
As	0	12	21.72	23.04	0.04592	0.9485
Fe	0	12	40550	50690	0.02712	0.7984

Table 4

Geochemical background values, anomalous and net anomalous values obtained for Kettara soils.

Elements	Kettara soils (Saghlef Schists)			Geochemical background of Kettara soils (First population)			Anomalous content of Kettara soils (second and third population)			Net anomalous values	Canadian soils quality guidelines ^c	world ranges in non-polluted soils ^d
	N	Mean	Median	N	Mean (a)	Median	N	Mean (b)	Median	(b-a)		
Cu	62	203.4	62.3	34	43.8	43.05	28	397.2	222.2	353.4	63	6–60
Pb	62	41.4	32.9	26	21.8	22.45	36	55.6	44.4	33.8	70	10–70
Zn	62	136.0	116.5	40	102.6	105	22	196.5	172.5	93.9	200	17–125
As	62	33.3	25	20	13.9	13.5	42	42.6	30	28.7	12	1–15
Fe	62	76974	59800	49	56978	55800	13	152346	150000	95368	–	–

N is number of samples (all concentrations are expressed in mg/kg).

^c Canadian soils quality guidelines (CCME, 2006).^d Kabata-Pendias and Pendias (1992).