



**HAL**  
open science

## 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

A. Khalil, L. Hanich, A Bannari, Lahcen Zouhri, O. Pourret, R. Hakkou

### ► To cite this version:

A. Khalil, L. Hanich, A Bannari, Lahcen Zouhri, O. Pourret, et al.. 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. *Journal of Geochemical Exploration*, 2013, 125, pp.117-129. 10.1016/j.gexplo.2012.11.018 . hal-02136376

**HAL Id: hal-02136376**

**<https://hal.science/hal-02136376>**

Submitted on 22 May 2019

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

4  
5 A. KHALIL <sup>a,\*</sup>, L. HANICH <sup>a</sup>, A. BANNARI <sup>b</sup>, L. ZOUHRI <sup>c</sup>, O. POURRET <sup>c</sup>, R. HAKKOU <sup>d</sup>

6  
7 <sup>a</sup> Geo-resources Laboratory, associated Unit to CNRST (URAC42), Department of Earth  
8 Sciences, Faculty of Sciences and Technology Guéliz, Cadi Ayyad University, Abdelkarim  
9 Elkhatabi Avenue, Gueliz, P.O. Box 549, Marrakech, Morocco

10 E-mail: khalil.abdessamad@gmail.com, Phone : (+212) 664 06 27 14,

11 Fax: (+212) 524 43 31 70

12 <sup>b</sup> Department of Geography, University of Ottawa, Ottawa (Ontario) K1N 6N5 Canada.

13 <sup>c</sup> HydrISE, Institut Polytechnique LaSalle Beauvais, 19 rue Pierre Waguet, F-60026 Beauvais  
14 Cedex, France

15 <sup>d</sup> LCME, Faculté des Sciences et Techniques Guéliz, Cadi Ayyad University, Abdelkarim  
16 Elkhatabi Avenue, Gueliz, P.O. Box 549, Marrakech, Morocco

17  
18 **ABSTRACT**

19  
20 One of the most serious environmental issues related to mining industry in Morocco and  
21 elsewhere around the world, is the pollution from abandoned mine sites. Mine wastes cause  
22 obvious sources of soils contaminations. Climatic effects such as heavy rainfall engender  
23 metals dispersion in semi-arid areas, since soils are typically and scarcely vegetated. In this  
24 study, extension and magnitude of soils contaminations with toxic elements from abandoned  
25 Kettara mine, in Morocco, are assessed using geochemical analysis and geostatistics for  
26 mapping. Soils and mine wastes are sampled and analyzed for 41 chemical elements (Mo, Cu,  
27 Pb, Zn, Ag, Ni, Co, Mn, Fe, As, U, Au, Th, Sr, Cd, Sb, Bi, V, Ca, P, La, Cr, Mg, Ba, Ti, Al,  
28 Na, K, W, Zr, Ce, Sn, Y, Nb, Ta, Be, Sc, Li, S, Rb and Hf). Based on enrichment factor (EF),  
29 only five elements of interest (Cu, Pb, Zn, As, and Fe) were selected in this research.  
30 Geochemical background is determined with exploratory data analysis and geochemical maps  
31 were elaborated using geostatistics in Geographic Information System (GIS) environment.

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

9  
10 *Keywords:* Geochemical mapping, soil contamination, geochemical background, Kettara  
11 abandoned mine, GIS, simple kriging.

## 12 13 **1. Introduction**

14  
15 Acid Mine Drainage (AMD) from mine waste and contaminations of soils and water with  
16 metals are considered as major environment problems in mining areas ([U.S Bureau of Mines,](#)  
17 [1994](#)). This environment phenomena is produced with oxidation of sulfide minerals e.g. pyrite  
18 and pyrrotite ([Hakkou et al., 2008a;](#) [Bussiere, 2009](#)). Consequently, acidification would  
19 increase the dissolution of toxic metals from tailings, waste rock piles, and open pits.  
20 Therefore, soil and water ecosystem will be contaminated ([Sams et al., 2000;](#) [Bell et al.,](#)  
21 [2006](#)). Certainly, as rainfall water infiltrates into the underground soil/rock, it can cause pore-  
22 water flow in the pore space of the soil/rock. The resulting pore-water flow can be advective  
23 or convective ([Zhao et al., 2004, 2008a](#)) depending on geological conditions of the mine site.  
24 When the pore-water becomes in contact with the soil/rock, it can react chemically with the  
25 mine waste dissolving heavy metals at the mine site. Since the dissolved heavy metals can be  
26 transported in the soil/rock through pore-water advection, convection and solute  
27 diffusion/dispersion ([Zhao et al., 2007](#)), they can contaminate both the land and the  
28 groundwater at the mine site. In addition, as demonstrated theoretically, the dissolved metal  
29 front may become unstable when it propagates in the soil/rock at the mine site ([Zhao et al.,](#)  
30 [2008b, 2010a](#)). This is the scientific problem, known as the mine site contamination, which is  
31 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 (Bounessah et al., 2003; Reimann et al., 2005b).

1

2 Finally, GIS based on geostatistical analysis is one of the most important tools for studying  
3 environmental geochemistry problems (Acosta et al., 2011). It provides an effective means for  
4 researching the spatial variability of pollutants (Sun et al., 2012). Geostatistics is an advanced  
5 methodology that facilitates quantification of the spatial features of soil parameters and  
6 enables spatial interpolation (Zhang et al., 2000; Carlon et al., 2001). According to the  
7 literature, numerous authors have used kriging analysis in GIS environment to elaborate  
8 geochemical maps to quantify both extension and magnitude of contamination with toxic  
9 elements (Li et al., 2004; Li and Feng 2011; Nakayama et al., 2011; García-Lorenzo et al.,  
10 2012).

11

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

18

## 19 **2. Materials and Methods**

### 20 **2.1. Study site**

21

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

31

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  $\mu\text{S}/\text{cm}$ .

33

## 1 2.2. Sampling and samples preparation

2

3 Special consideration was given to the used criteria to select sampling points' locations.  
4 After a review of topographic and geologic maps, and according to previous studies on the  
5 abandoned Kettara mine (Hakkou et al., 2008a; Khalil et al., 2011), soil sampling was  
6 established in 3 different areas based on the location of the mine wastes. The sampling design  
7 was made to compare concentration gradient and possible chemical elements mobilization.  
8 The distance between sampling points varies from 150 to 350 m. Four groups of soil samples  
9 have been collected: 1) samples located upstream of the mine waste (13 samples); 2) samples  
10 located nearby the mine waste (27 samples); 3) samples located downstream of the mine site  
11 (22 samples); and 4) mine waste samples from the Kettara mine tailings (12 samples). Finally,  
12 62 soil samples (from S1 to S62) and 12 mine waste samples (from R1 to R12) were collected  
13 within the study site, approximately 6 km<sup>2</sup> (Figure 2). Geographic coordinates of sampling  
14 points were measured using a Global Positioning System (GPS) within  $\pm 5$  m accuracy, with  
15 the "Lambert North Morocco" map projection.

16

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

23

## 24 2.3. Chemical analysis

25

26 Chemical analyses were carried out at Acme Analytical Laboratories Ltd. (Vancouver,  
27 Canada), accredited under ISO 9002. The considered analyzed elements are Mo, Cu, Pb, Zn,  
28 Ag, Ni, Co, Mn, Fe, As, U, Au, Th, Sr, Cd, Sb, Bi, V, Ca, P, La, Cr, Mg, Ba, Ti, Al, Na, K,  
29 W, Zr, Ce, Sn, Y, Nb, Ta, Be, Sc, Li, S, Rb and Hf . Soil samples were digested using a strong  
30 multi-acid method that dissolves most minerals. Then, 0.25 g split was heated in HNO<sub>3</sub>-  
31 HClO<sub>4</sub>-HF to fuming and taken to dryness. The residue was further dissolved in HCl. Then,  
32 solutions were analyzed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

1

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

13

## 14 2.4. Statistical analysis

### 15 2.4.1. Descriptive statistics

16

17 The following statistical parameters were determined for the 41 elements considered and  
18 analyzed: minimum, maximum, mean and median for the central tendency measurement,  
19 standard deviation and variation coefficient for the data dispersion measurement; while the  
20 data distribution was tested for normality using Kolmogorov-smirnov (K-S) test, kurtosis and  
21 skewness (Tables 1 and 2). These parameters will be helpful for comparing datasets, therefore  
22 summarizing the obtained results and facilitating its subsequent interpretation (Burgos et al.,  
23 2005; Martínez et al., 2007; Cai et al., 2012).

24

### 25 2.4.2. Enrichment factors

26

27 In order to select chemical elements that have been enriched in Kettara soils, enrichment  
28 factor (EF) was calculated (Martínez et al., 2007; Bourenane et al., 2010; Li and Feng,  
29 2011). The concept of EF was developed in the early seventies to derive the origin of  
30 elements in the atmosphere, precipitation or seawater, and was progressively applied to other  
31 environmental materials such as soils, lake sediments or peat (Reimann et al., 2005b;  
32 Bourenane et al., 2010). It was widely employed to identify the anthropogenic source of

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

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

7  
8  
9  
10 Where “*El*” is the element under consideration, the square brackets indicate concentration  
11 (usually in mass/mass units, such as mg/kg), “*X*” is the chosen reference element (see below)  
12 and the subscripts “sample” or “crust” indicate which medium concentration refers to. Crust  
13 refers to Clarke of Earth’s crust, most often continental or Upper Continental Crust (UCC).  
14 The Clarke values corresponding to mean concentration of chemical elements in the UCC  
15 were given by McLennan (2001). In this study, Aluminum was selected to be the reference  
16 value. Indeed, Al is the most common reference value used to calculate the EF (Buat-Menard  
17 and Chesselet, 1978; Lu et al., 2009a; Bourenane et al., 2010).

18  
19 Table 1 summarizes EFs values which indicate how many times measured concentrations  
20 exceed the Clarke values.

### 21 22 2.4.3. Exploratory data analysis (EDA)

23  
24 In addition to the statistical and EF analyzes, the EDA technique was assessed because it is an  
25 appropriate technique for identifying anthropogenic influences (Zhou et al., 2010). EDA was  
26 applied to determine the GB of soil. This latter will serve as a reference to assess the soil  
27 contamination by toxic elements. EDA consists of elaborating graphs such as histograms with  
28 the distribution curves, box plots also called a box-and-whiskers plot, in which six parameters  
29 are described (lower limit, first quartile, median, third quartile, upper limit and extreme  
30 values), and normal Quantile-Quantile plots (Q-Q plots) which were applied to look for  
31 different intervals of toxic elements concentrations which imply likely presence of different

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

3

## 4 2.5. Geochemical mapping and multi-criteria analysis using GIS

5

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

17

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

27

## 28 3. Results and discussion

### 29 3.1. Statistical analysis

30

1 The EFs analysis shows five different classes. The first class considers the elements with  
2 minimal enrichment and it includes the following elements: Mo, Ni, Co, Mn, U, Th, Sr, V,  
3 Ca, P, La, Cr, Mg, Ba, Ti, Al, Na, K, W, Zr, Ce, Sn, Y, Nb, Ta, Be, Sc, Rb, and Hf. The  
4 second class considers elements with moderate enrichment and it includes the following  
5 elements: Pb, Zn, Ag, Fe, Cd and Li. The third class considers elements with significant  
6 enrichment and it includes Sb and Cu. The fourth class considers elements with high  
7 enrichment and it includes As and Bi. Finally, the fifth class, which corresponds to elements  
8 with extremely high enrichment, includes only Au (Table 1). Although the following  
9 elements: Ag, Cd, Bi, Sb, Li, and Au have an EF ranging from 2.93 to 70.09, their  
10 concentrations in the Kettara soils are extremely low. Their mean concentrations are 0.13  
11 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,  
12 Sb, Li, and Au, respectively (Table 1). These low concentrations would not have any adverse  
13 effects on humans or animals in Kettara area. However, the elements Cu, Pb, Zn As, and Fe  
14 have an EF ranging from 2.17 to 25.17 and their concentrations in Kettara soils are high with  
15 a mean concentration of 203.38 mg/kg, 41.44 mg/kg, 135.95 mg/kg, 33.31 mg/kg, 769.74  
16 mg/kg, for Cu, Pb, Zn As, and Fe, respectively (Table 1). The Cu, Pb, Zn As, and Fe were  
17 selected as elements with important interest because they are related to mineral paragenesis  
18 and therefore, to mining and mineralogical activities in Kettara. Furthermore, they are known  
19 to be toxic and hazardous at high concentrations (Lockitch, 1993; Chowdhury et al., 2000;  
20 Gurzau et al., 2003; Peplow and Edmonds, 2005; Davies et Mundalamo, 2010).

21  
22 The Cu, Pb, Zn, As, and Fe concentration levels ranged from 20.6 to 1687 mg/kg, 7.6 to  
23 207.8 mg/kg, 62 to 449 mg/kg, 6 to 124 mg/kg and 43300 to 374900 mg/kg, respectively. The  
24 mean concentrations are 203.38 mg/kg, 41.44 mg/kg, 135.95 mg/kg, 33.31 mg/kg and 76974  
25 mg/kg, for Cu, Pb, Zn, As, and Fe respectively (Table 1). These concentrations disclose that  
26 metallic and metalloid content in the Kettara soil is high. In order to reveal if the origin of this  
27 content is weather geogenic or anthropogenic and for a better observation of the values  
28 distribution shape, Figures 3, 4 and 5 illustrate graphs (histograms, box plots and Q-Q plots  
29 for the selected elements) obtained from EDA. Figures 3a to 3e shows that all histograms are  
30 asymmetric and right-skewed. Skewness characterizes the distribution asymmetry degree  
31 around its mean (Zhou et al., 2010). The skewness feature of Cu, Pb, Zn, As, and Fe  
32 concentrations suggests that the majority of the samples are located in the lowest intervals of  
33 concentration. Figures 4a to 4e shows that all the boxes are displaced towards the minimum  
34 concentration values. This confirms the fact that the concentrations distribution of selected

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

22

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

31

32 3.2. Determination of the soil geochemical background and anomalous values

33

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

16

17 Soil GB values, anomalous values and net anomalous values are reported in Table 4.  
18 Unfortunately, in Morocco no environmental guidelines exist to regulate maximum  
19 permissible metals and metalloid concentrations in soils or to give reference values above  
20 which action should be taken to mitigate environmental risk. Therefore, the obtained values in  
21 this study will be compared with guidelines adopted by Canada and European community  
22 (Kabata-Pendias and Pendias, 1992; CCME, 2006). These guidelines were used in El-Khalil  
23 et al. (2008) research which were undertaken to assess the metal contamination from mining  
24 sites in the south of Morocco. The results indicate that GB values of Cu (43.8 mg/kg), Pb  
25 (21.8 mg/kg), Zn (102.6 mg/kg), and As (13.9 mg/kg) are bellow the used reference values  
26 (Table 4), whereas the GB of As exceed slightly the Canadian guideline for As (12 mg/kg).  
27 According to these results, the geogenic concentrations of Cu, Pb, Zn, and As in Kettara soils  
28 will not have any adverse health effects. However, calculated anomalous values of Cu (397.2  
29 mg/kg), Pb (55.6 mg/kg), Zn (196.5 mg/kg), As (42.6 mg/kg), and Fe (152346 mg/kg) reveal  
30 the contribution of anthropogenic activity in contaminating Kettara soils. The calculated  
31 anomalous values of Cu and As are above the used reference values (Table 4). The origin of  
32 anthropogenic activity and dispersion mechanism of contaminants will be discussed in the  
33 following section.

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33

### 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

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

9  
10 The Figure 6c illustrates that Zn concentrations were ranging from 60 to 450 mg/kg. This  
11 map shows a big contrast in concentrations between areas located upstream of mine wastes,  
12 where Zn concentrations are normal and inferior to the established GB (102.6 mg/kg) and  
13 those located downstream, where high soils contaminations occurred. The contaminated areas  
14 are represented by two hot-spots where concentration levels reach 450 mg/kg. Intermediate  
15 concentration levels are also observed in the vicinity of mine wastes. Zn is a relatively mobile  
16 element which can easily be released from mine wastes which contain Zn bearing minerals  
17 (e.g. sphalerite) by AMD action. Likewise, Cu, Pb, and Zn had the same dispersion  
18 mechanism that prevailed in the study area.

19  
20 For As element, Figure 6d shows relatively similar distribution pattern as Cu. As  
21 concentration levels are ranging from 6 to 124 mg/kg. For this element, low concentrations  
22 which are inferior to the established GB (13.9 mg/kg) are observed upstream mine wastes.  
23 However, high concentration levels of As are observed in the contaminated areas located  
24 downstream mine wastes. The concentrations in these areas exceed widely the established  
25 GB. The spatial distribution of As in the Kettara soil explains its anthropogenic origin that is  
26 the deposited mine wastes. These latter contain high concentration levels of As especially in  
27 mines wastes located in southern part of the study area where the concentration can reach 715  
28 mg/kg (Table 2). As was leached from mine wastes by AMD as result of weathering process,  
29 and then it was spread in study area mainly by surface water and wind flow.

30  
31 Comparatively to the other selected elements, Fe has the highest concentration levels in the  
32 study area (Table 1). These concentrations are ranging from 43300 to 371400 mg/kg (Figure  
33 6e). This is not only because Fe is a major element and it's quite abundant in earth crust, but  
34 also because it was one of the main elements exploited in Kettara mine. Figure 6e shows that

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

13

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

20

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

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

5

#### 6 **4. Conclusions**

7

8 The aim of this study was the assessment of extension and intensity of soils contaminations  
9 with toxic elements from abandoned Kettara mine. Soils and mine wastes around the  
10 abandoned site were sampled and analyzed for 41 chemical elements (Mo, Cu, Pb, Zn, Ag,  
11 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,  
12 Ce, Sn, Y, Nb, Ta, Be, Sc, Li, S, Rb and Hf). The soils contaminations were evaluated for the  
13 selected metals and metalloid elements (Cu, Pb, Zn, As and Fe) based on enrichment factor  
14 computing, geochemical background determining using exploratory data analysis, and  
15 geochemical mapping based on GIS and geostatistics.

16

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

24

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

33

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.

10

## 11 **Acknowledgments**

12 This research was supported through the International Research Chairs Initiative funded by  
13 the International Development Research Centre (IDRC), Canada, and by the Canada Research  
14 Chairs program. The authors also thank the Joint International Laboratory (TREMA) entitled  
15 "Remote sensing and water resources in the semi-arid Mediterranean area" funded by the IRD  
16 (France) and the "Comité Mixtes Interuniversitaires Franco-Marocaine (Action Intégrée  
17 Ref\_MA/09/209)" for their financial and technical support. Thanks are also extended to the  
18 the Institut Polytechnique LaSalle Beauvais, France, for funding the geochemical analysis.  
19 Finally, authors would like to thank the anonymous reviewers for their constructive  
20 comments.

21

## 22 **References**

23 Acosta, J.A., Faz, A., Martinez, M., Zornoza, R., Carmona, D.M., Kabas, S., 2011.  
24 Multivariate statistical and GIS-based approach to evaluate heavy metals behavior in mine  
25 sites for future reclamation. *Journal of Geochemical Exploration* 109, 8-17.

26

27 Bell, F.G., Donnelly, L.J., 2006. *Mining and its Impact on the Environment*. First edition,  
28 Taylor and Francis Group, Oxon.

29

1 Bounessah, M., Atkin, B.P., 2003. An application of exploratory data analysis (EDA) as a  
2 robust non-parametric technique for geochemical mapping in a semi-arid climate. Applied  
3 Geochemistry 18, 1185-1195.  
4

5 Bourennane, H., Douay, F., Sterckeman, T., Villanneau, E., Ciesielski, H., King, D., Baize,  
6 D., 2010. Mapping of anthropogenic trace elements inputs in agricultural topsoil from  
7 Northern France using enrichment factors. Geoderma 157, 165-174.  
8

9 Buat-Menard, P., Chesselet, R., 1978. Variable influence of the atmospheric flux on the trace  
10 metal chemistry of oceanic suspended matter. Earth and planetary science letters 42, 399-411.  
11

12 Burgos, P., Madejón, E., Pérez de Mora, A., Cabrera, F., 2005. Spatial variability of the  
13 chemical characteristics of a trace-element-contaminated soil before and after remediation.  
14 Geoderma 130, 157-175.  
15

16 Bussiere, B., 2009. Acid mine drainage from abandoned mine sites: problematic and  
17 reclamation approaches. Proceeding of International Symposium on Geo-environmental  
18 Engineering, ISGE2009, Septembre 8-10, Hangzhou, China 16 pages.  
19

20 Cai, L., Xu, Z., Ren, M., Guo, Q., Hu, X., Hu, G., Wan, H., Peng, P., 2012. Source  
21 identification of eight hazardous heavy metals in agricultural soils of Huizhou, Guangdong  
22 Province, China. Ecotoxicology and Environmental Safety 78, 2-8.  
23

24 Carlon, C., Critto, A., Marcomini, A., Nathanail, P., 2001. Risk based characterisation of  
25 contaminated industrial site using multivariate and geostatistical tools. Environmental  
26 Pollution 11, 417-427.  
27

28 CCME, 2006. Canadian soil quality guidelines for the protection of environment and human  
29 health. Canadian Council of Ministers of the Environment.  
30 <http://www.ccme.ca/ourwork/soil.html>. (Last accessed 2012-06-21).  
31

32 Chen, J.Q., Wang, Z.X., Wu, X., Zhu J.J., Zhou, W.B., 2011. Source and hazard identification  
33 of heavy metals in soils of Changsha based on TIN model and direct exposure method.  
34 Transactions of Nonferrous Metals Society of China 21, 642-651.

1  
2 Chester, R., Stoner, J.H., 1973. Pb in particulates from the lower atmosphere of the eastern  
3 Atlantic. *Nature* 245, 27-28.  
4  
5 Chowdhury, U.K., Biswas, B.K., Chowdhury, T.R., Samanta, G., Mandal, B.K., Basu, G.C.,  
6 Chanda, C.R., Lodh, D., Saha, K.C., Mukherjee, S.K., Roy, S., Kabir, S., Quamruzzaman, Q.,  
7 Chakraborti, D., 2000. Groundwater arsenic contamination in Bangladesh and West Bengal,  
8 India. *Environmental Health Perspectives* 108 (5), 393-397.  
9  
10 Davies, T.C., Mundalamo, H.R., 2010. Environmental health impacts of dispersed  
11 mineralisation in South Africa. *Journal of African Earth Sciences*, 58, 652-666.  
12  
13 Edison, E.S., Bajel, A., Chandy, M., 2008. Iron homeostasis: new players, newer insights.  
14 *European Journal of Haematology* 81, 411-424.  
15  
16 El-Khalil, H., El Hamiani, O., Bitton, G., Ouazzani, N., Boularbah, A., 2008. Heavy metal  
17 contamination from mining sites in South Morocco: Monitoring metal content and toxicity of  
18 soil runoff and groundwater. *Environmental Monitoring and Assessment* 136, 147-160.  
19  
20 ESRI, 2012. Environmental Systems Research Institute. <http://www.esri.com/software/arcgis>  
21 (Last accessed 2012-07-19).  
22  
23 Ferguson, C., Kasamas, H., 1999. Risk assessment for contaminated sites in Europe: Policy  
24 Framework. Vol. 2. LQM Press, Nottingham NG7 2RD.  
25  
26 García-Lorenzo, M.L., Pérez-Sirvent, C., Martínez-Sánchez, M.J., Molina-Ruiz, J., 2012.  
27 Trace element contamination in an abandoned mining site in a semiarid zone. *Journal of*  
28 *Geochemical Exploration* 113, 23-35.  
29  
30 Guillén, M.T., Delgado, J., Albanese, S., Nieto, J.M., 2011. Environmental geochemical  
31 mapping of Huelva municipality soils (SW Spain) as a tool to determine background and  
32 baseline values. *Journal of Geochemical Exploration* 109, 59-69.  
33

1 Gurzau, E.S., Neagu, C., Gurzau, A.E., 2003. Essential metals-case study on iron. Eco-  
2 toxicology and Environmental Safety 56, 190-200.  
3

4 Hakkou, R., Benzaazoua, M., Bussière, B., 2008a. Acid Mine Drainage at the Abandoned  
5 Kettara Mine (Morocco): Environmental Characterization. Mine water Environment 27, 145-  
6 159.  
7

8 Hakkou, R., Benzaazoua, M., Bussière, B., 2008b. Acid mine drainage at the abandoned  
9 Kettara mine (Morocco): 2. Mine waste geochemical behavior. Mine Water Environment 27,  
10 160-170.  
11

12 Han, Y., Du, P., Cao, J., Posmentier, E.S., 2006. Multivariate analysis of heavy metal  
13 contamination in urban dusts of Xi'an, Central China. Sciences of the Total Environment 355,  
14 176-186.  
15

16 Hawkes, H.E., Webb, J.S., 1962. Geochemistry in Mineral Exploration. Harper.  
17

18 Hibti, M., Bouabdelli, M., Mouttaqi, A., Sagon, J.P., 1999. L'effet du métamorphisme sur les  
19 minéralisations sulfurées de la province hercynienne (Meseta sud-occidentale, Maroc).  
20 Exemple des gisements sulfure's de Hajjar et de Kettara. Chronique Recherche Minière 536-  
21 537:23-37.  
22

23 Huvelin, P., 1977. Étude géologique et gîtologique du massif hercynien des Jebilettes (Maroc  
24 occidentale). Notes et Mémoires du Service Géologique du Maroc 232 bis.  
25

26 Kabata-Pendias, A., Pendias, H., 1992. Trace Elements in Soils and Plants, second edition  
27 CRC Press.  
28

29 Khalil, A., Hanich, L., Hakkou, R., 2011. Development of an Environmental Database and a  
30 Geographic Information System on The abandoned mine of Kettara (Morocco). On  
31 Proceedings of Euro-Mediterranean Scientific Congress on Engineering ISBN13 : 978-84-  
32 694-4025-4. 728-735.  
33

1 Komnitsas, K., Modis, K., 2006. Soil risk assessment of As and Zn contamination in a coal  
2 mining region using geostatistics. *Science of the Total Environment* 371, 190-196.  
3

4 Lghoul, M., Kchikach, A., Hakkou, R., Zouhri, L., Guerin, R., Bendjoudi, H., Teíxido, T.,  
5 Penã, J.A, Enriqu , L., Jaffal, M., Hanich, L., 2012.  tude g ophysique et hydrog ologique  
6 du site minier abandonn  de Kettara (r gion de Marrakech, Maroc) : contribution au projet de  
7 r habilitation. *Hydrological Sciences Journal* 57(2), 370-381.  
8

9 Li, H.B., Lin, Z.H., Liu, S.X., 2001. Application of Kriging Technique in Estimating Soil  
10 Moisture in China. *Geographical Research* 20(4), 446-452.  
11

12 Li, X., Lee, S.L., Wong, S.C., Shi, W., Thornton, I., 2004. The study of metal contamination  
13 in urban soils of Hong Kong using a GIS-based approach. *Environmental Pollution* 129, 113-  
14 124.  
15

16 Li, X., Feng, L., 2011. Multivariate and geostatistical analyzes of metals in urban soil of  
17 Weinan industrial areas, Northwest of China. *Atmospheric Environment* 8 pages (In press).  
18

19 Lockitch, G., 1993. Perspectives on lead toxicity. *Clinical Biochemistry* 26, 371-381.  
20

21 Lu, X., Loretta, Li, Y., Wang, L., Lei, K., Huang, J., Zhai, Y., 2009a. Contamination  
22 assessment of mercury and arsenic in roadway dust from Baoji, China. *Atmospheric*  
23 *Environment* 43, 2489-2496.  
24

25 Lu, X., Wang, L., Lei, K., Huang, J., Zhai, Y., 2009b. Contamination assessment of copper,  
26 lead, zinc, manganese and nickel in street dust of Baoji, NW China. *Journal of Hazardous*  
27 *Materials* 161, 1058-1062.  
28

29 Mart nez, J. 2002. Caracterizaci n geoqu mica y ambiental de los suelos en el sector minero  
30 de Linares. Ph.D. Thesis, Universidad Polit cnica de Madrid, Madrid, Spain.  
31

32 Mart nez, J., Llamas, J., De Miguel, E., Rey, J., Hidalgo, M.C., 2007. Determination of the  
33 geochemical background in a metal mining site: example of the mining district of Linares  
34 (South Spain). *Journal of Geochemical Exploration* 94, 19-29.

1  
2 McLennan, S.M., 2001. Relationships between the trace element composition of sedimentary  
3 rocks and upper continental crust. *Geochemistry Geophysics and Geosystems* vol. 2. ISSN:  
4 1525-2027.  
5  
6 Nakayama, S., M.M., Ikenaka, Y., Hamada, K., Muzandu, K., Choongo, K., Teraoka, H.,  
7 Mizuno, N., Ishizuka, M., 2011. Metal and metalloid contamination in roadside soil and wild  
8 rats around a Pb-Zn mine in Kabwe, Zambia. *Environmental Pollution* 159, 175-181.  
9  
10 ONEM (Observatoire Nationale de l'Environnement du Maroc) 1997. 'Monographie locale de  
11 l'environnement de la ville de Marrakech'. Étude réalisée pour le compte de la Wilaya de  
12 Marrakech.  
13  
14 Peplow, D., Edmonds, R., 2005. The effects of mine waste contamination at multiple levels of  
15 biological organization. *Ecological Engineering* 24, 101-119.  
16  
17 Plant, J., Smith, D., Smith, B., Williams, L., 2001. Environmental geochemistry at the global  
18 scale. *Applied Geochemistry* 16, 1291-1308.  
19  
20 Reimann, C., De Caritat, P., 2005a. Distinguishing between natural and anthropogenic  
21 sources for elements in the environment: regional geochemical surveys versus enrichment  
22 factors. *Science of the Total Environment* 337, 91-107.  
23  
24 Reimann, C., Filzmoser, P., Garrett, R.G., 2005b. Background and threshold: critical  
25 comparison of methods of determination. *Science of the Total Environment* 346, 1-16.  
26  
27 Sams, J.I., Beer, K.M., 2000. Effects of Coal-Mine Drainage on Stream Water Quality in the  
28 Allegheny and Monongahela River Basins-Sulfate Transport and Trends. *Water Resources*  
29 *Investigations Report 99-4208*, Geological Survey, Lemoyne, Pennsylvania.  
30  
31 Sun, H., Li, J., Mao, X., 2012. Heavy Metals' Spatial Distribution Characteristics in a Copper  
32 Mining Area of Zhejiang Province. *Journal of Geographic Information System* 4, 46-54.  
33

1 U.S. Bureau of Mines, 1994. Proceedings of the International Land Reclamation and Mine  
2 Drainage Conference and 3rd International Conference on the Abatement of Acidic Drainage;  
3 U.S. Bureau of Mines. Special Publication, SP 06D-94, pp 1-4.  
4

5 Zhang, C.S., Selinus, O., Wong, P., 2000. Spatial structures of cobalt, lead, and zinc contents  
6 in tills in southeastern Sweden. *GFF* (Transactions of the Geological Society in Stockholm)  
7 122, 213-217.  
8

9 Zhang, C.S., Fay, D., Grath, D.M., Grennan, E., Carton, O.T., 2008. Statistical analyses of  
10 geochemical variables in soils of Ireland. *Geoderma* 146, 378-390.  
11

12 Zhao, C., Hobbs, B.E., Ord, A., Peng, S., Mühlhaus, H.B., Liu, L., 2004. Theoretical  
13 investigation of convective instability in inclined and fluid-saturated three-dimensional fault  
14 zones. *Tectonophysics* 387, 47-64.  
15

16 Zhao, C., Hobbs, B. E., Hornby, P., Ord, A., Peng, S., 2006. Numerical modelling of fluids  
17 mixing, heat transfer and non-equilibrium redox chemical reactions in fluid-saturated porous  
18 rocks. *International Journal for Numerical Methods in Engineering* 66, 1061-1078.  
19

20 Zhao, C., Hobbs, B.E., Ord, A., Hornby, P., Peng, S., Liu, L., 2007. Mineral precipitation  
21 associated with vertical fault zones: The interaction of solute advection, diffusion and  
22 chemical kinetics. *Geofluids* 7, 3-18.  
23

24 Zhao, C., Hobbs, B.E., Ord, A., 2008a. *Convective and Adjective Heat Transfer in Geological  
25 Systems*. Springer.  
26

27 Zhao, C., Hobbs, B.E., Hornby, P., Ord, A., Peng, S., Liu, L., 2008b, Theoretical and  
28 numerical analyses of chemical-dissolution front instability in fluid-saturated porous rocks.  
29 *International Journal for Numerical and Analytical Methods in Geomechanics* 32, 1107-1130.  
30

31 Zhao, C., Hobbs, B.E., Ord, A., 2009. *Fundamentals of Computational Geoscience:  
32 Numerical Methods and Algorithms*. Springer.  
33

1 Zhao, C., Hobbs, B.E., Ord, A., 2010a. Theoretical analyses of nonaqueous-phase-liquid  
2 dissolution induced instability in two-dimensional fluid-saturated porous media. *International*  
3 *Journal for Numerical and Analytical Methods in Geomechanics* 34, 1767-1796.  
4

5 Zhao, C., Hobbs, B.E., Ord, A., 2010b. Theoretical and numerical investigation into roles of  
6 geofluid flow in ore forming systems: Integrated mass conservation and generic model  
7 approach. *Journal of Geochemical Exploration* 106, 251-260.  
8

9 Zhao, C., Hobbs, B.E., Ord, A., 2012b. Effects of domain shapes on the morphological  
10 evolution of nonaqueous-phase-liquid dissolution fronts in fluid-saturated porous media.  
11 *Journal of Contaminant Hydrology* 138-139, 123-140.  
12

13 Zhou, X., Xia, B., 2010. Defining and modeling the soil geochemical background of heavy  
14 metals from the Hengshi River watershed (southern China): Integrating EDA, stochastic  
15 simulation and magnetic parameters. *Journal of Hazardous Materials* 180, 542-551.  
16

17 Zoller, W.H., Gladney, E.S., Duce, R.A., 1974. Atmospheric concentrations and sources of  
18 trace metals at the South Pole. *Science* 183,199-201.  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29

1 **Tables and figures**

2

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

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

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

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

9 Figure 1: Geographical location of study site.

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

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

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

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

16 Figure 6: Geochemical maps of selected elements.

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

18

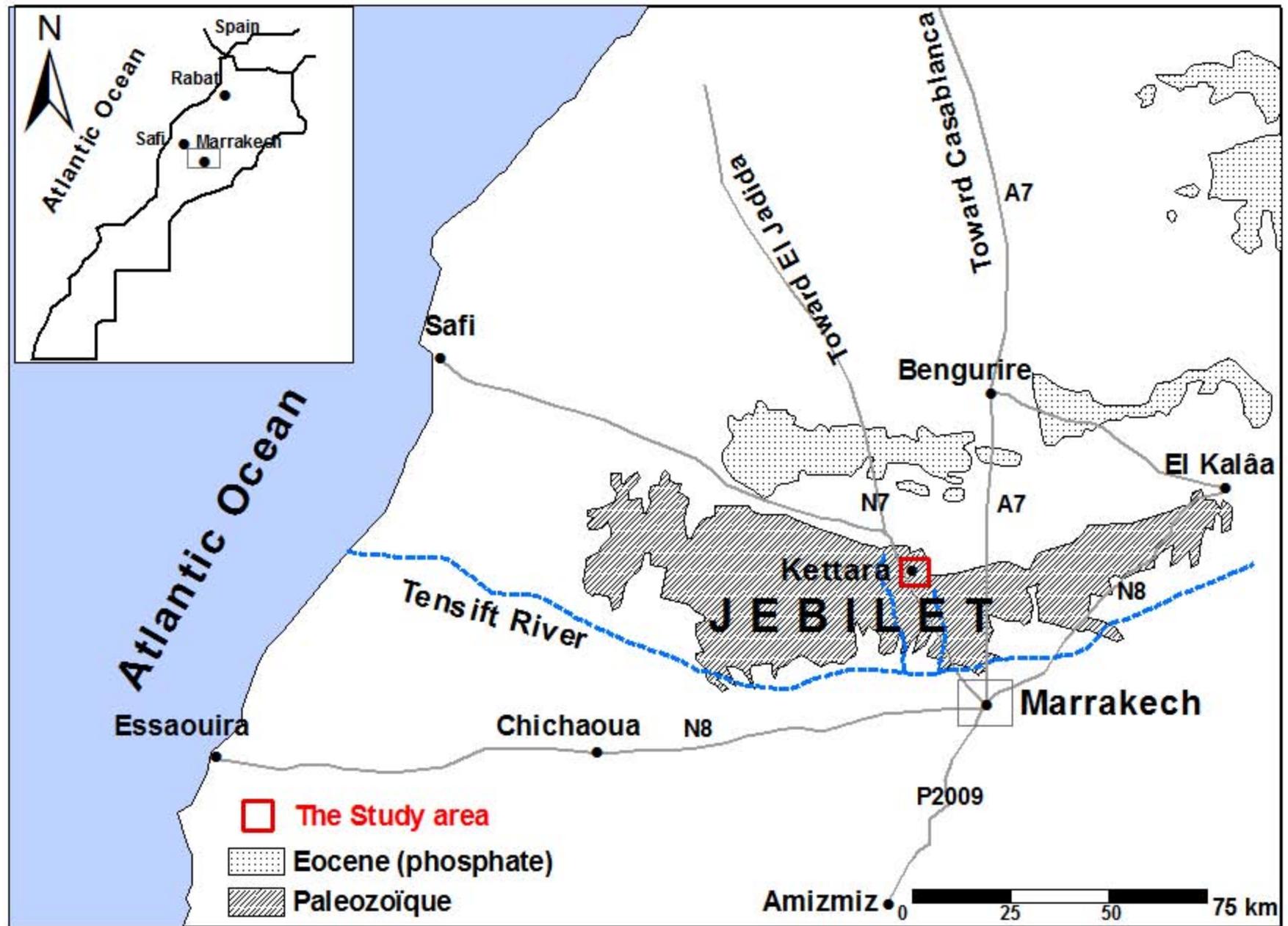
19

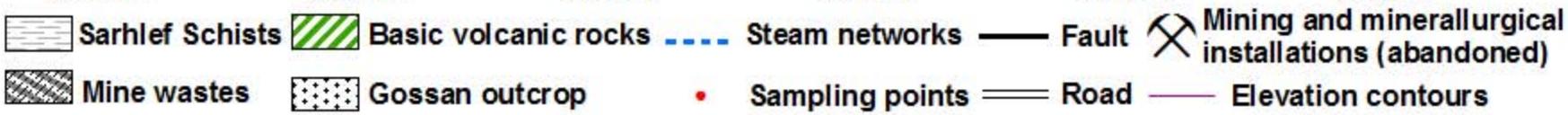
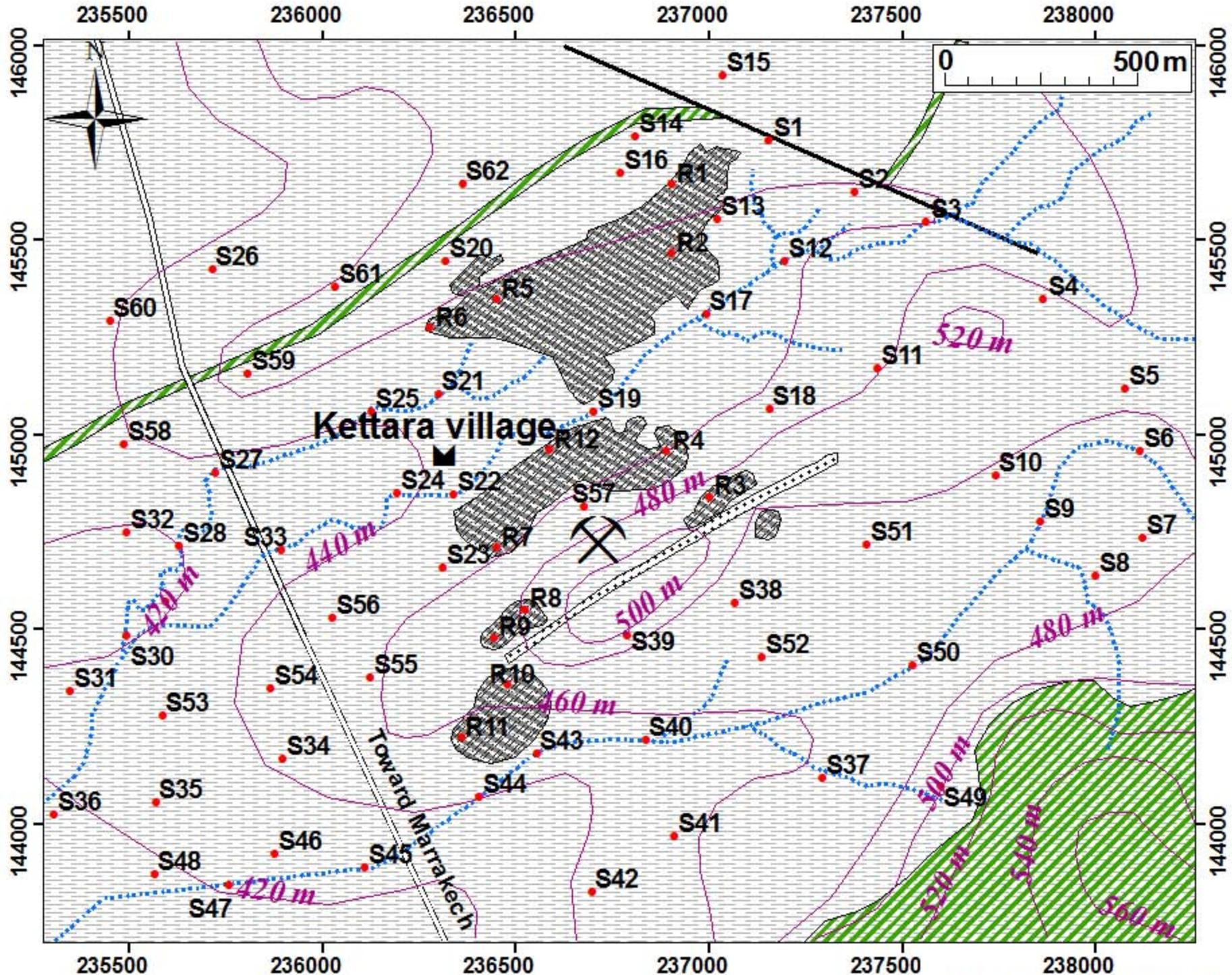
20

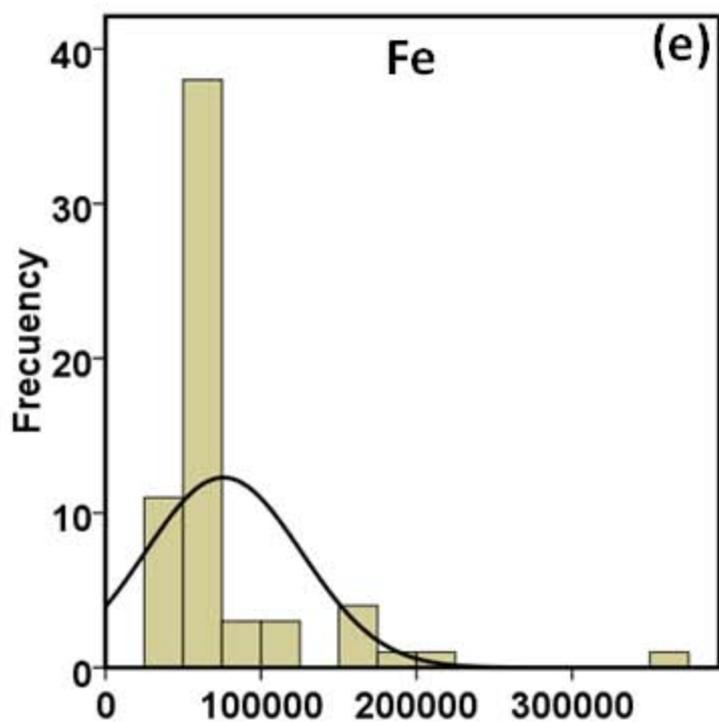
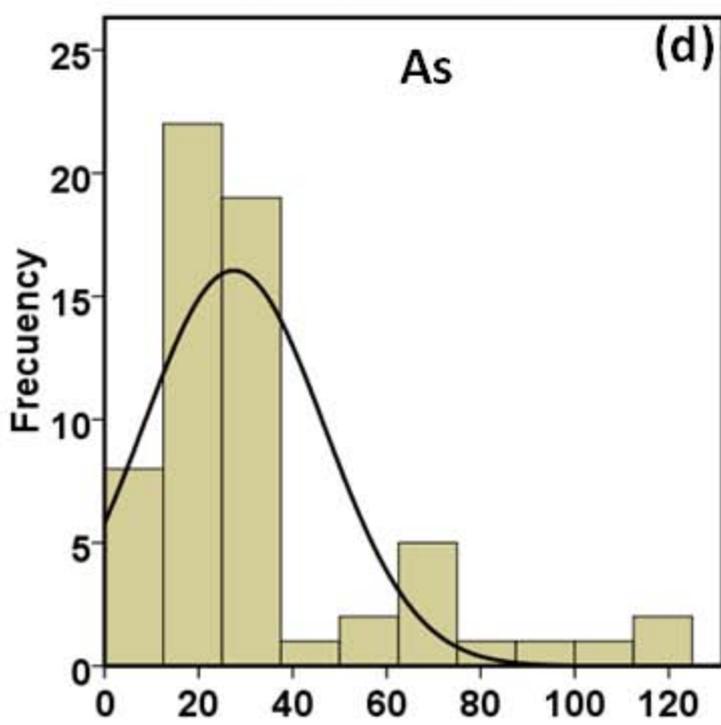
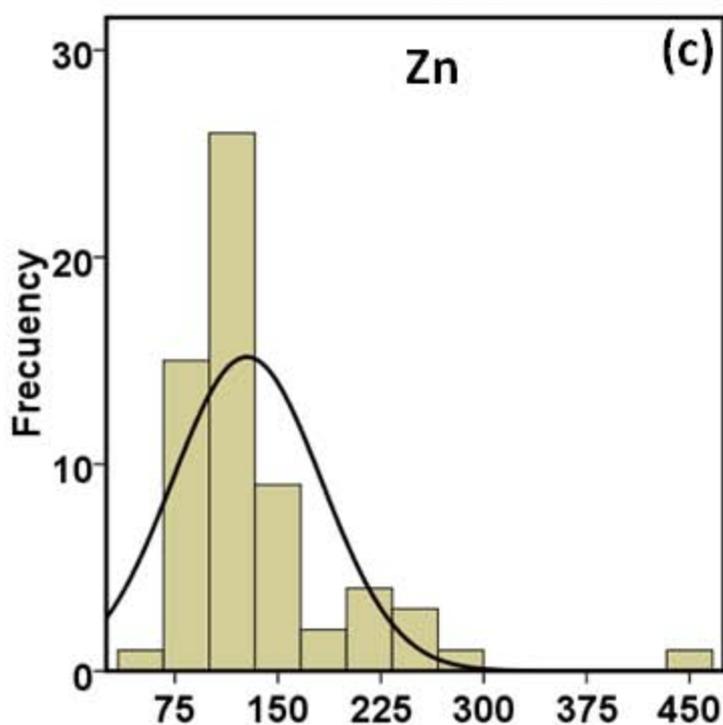
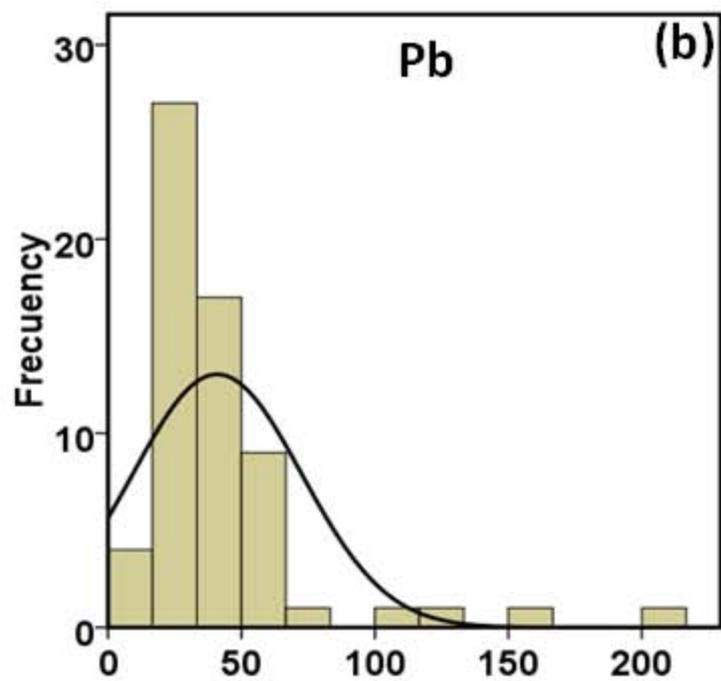
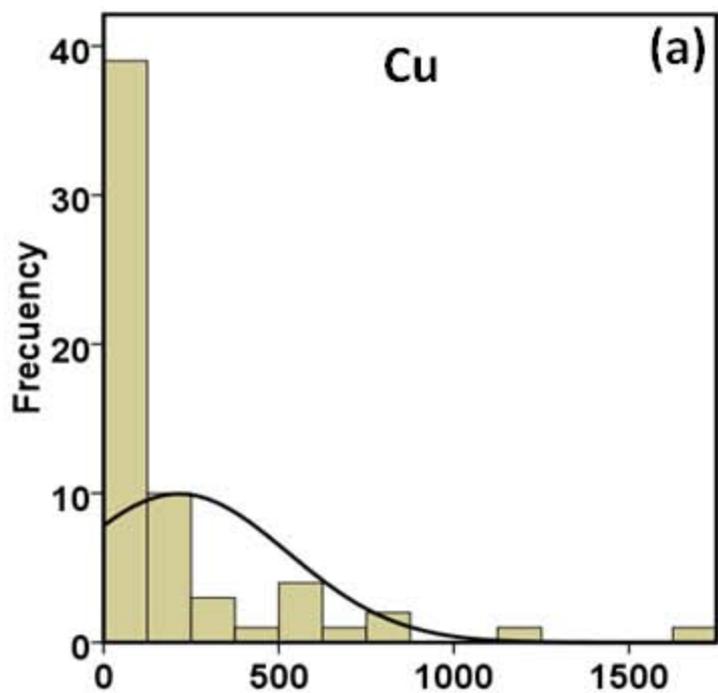
21

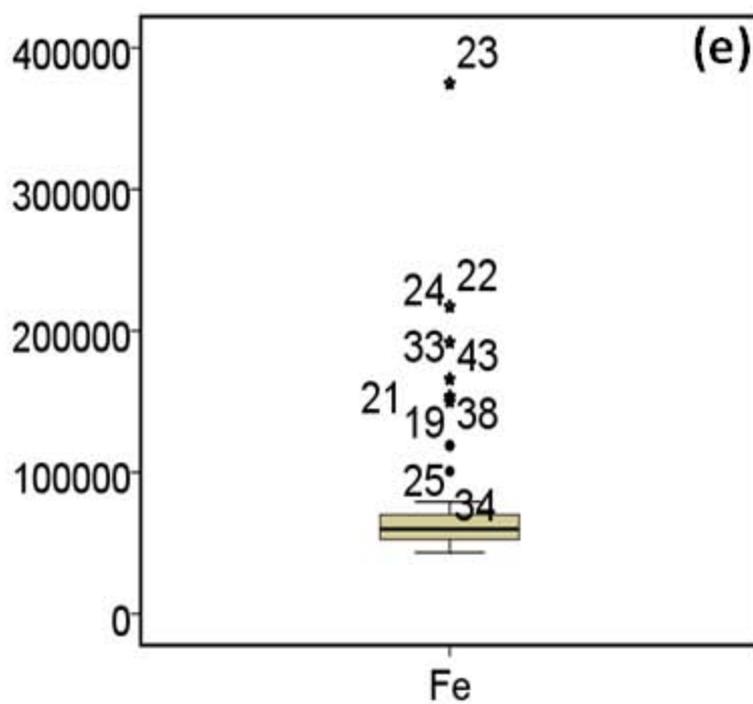
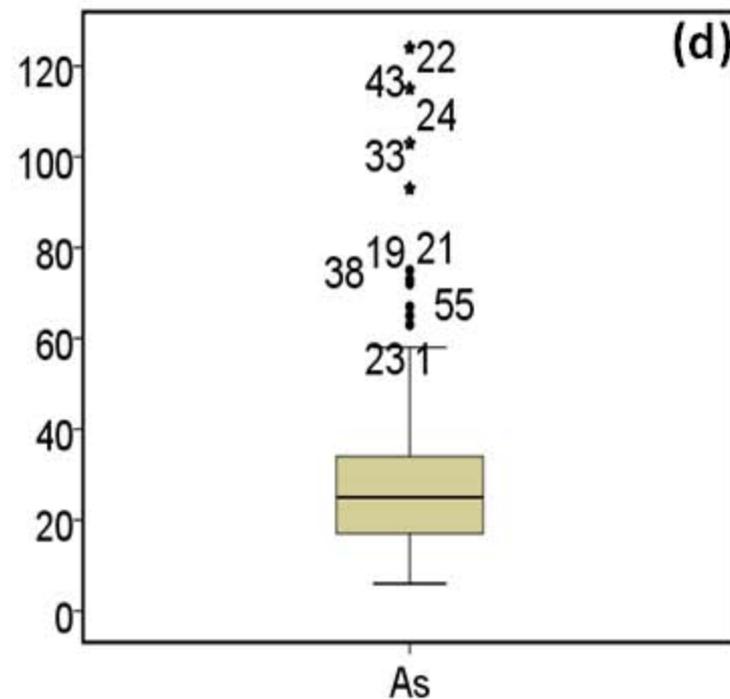
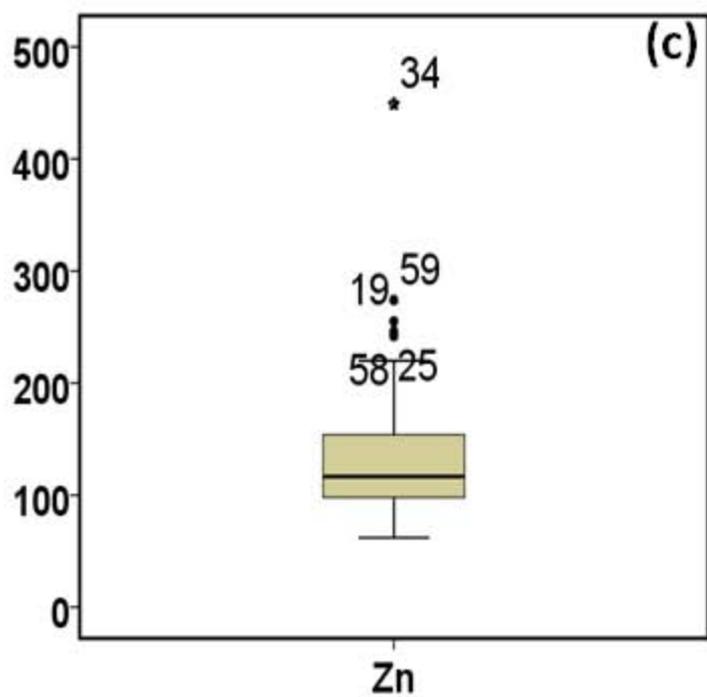
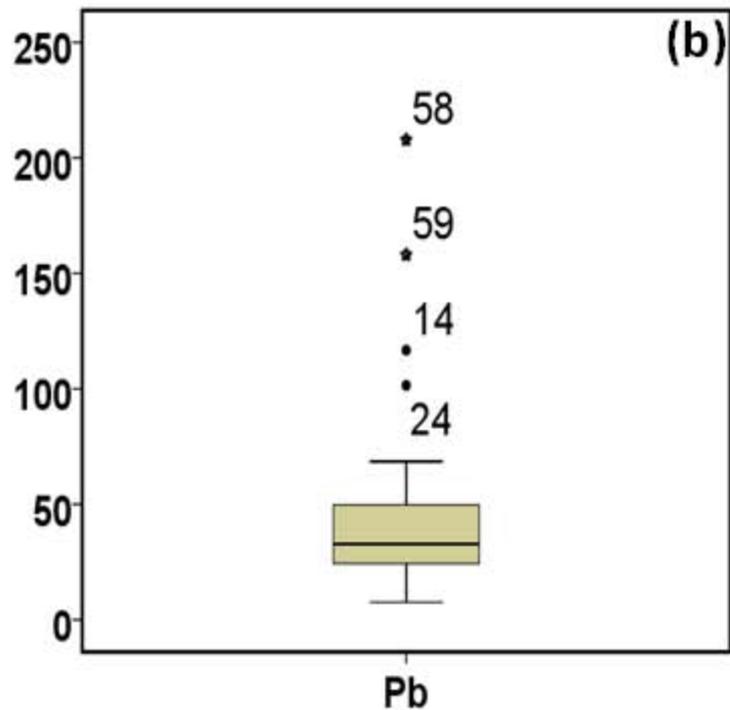
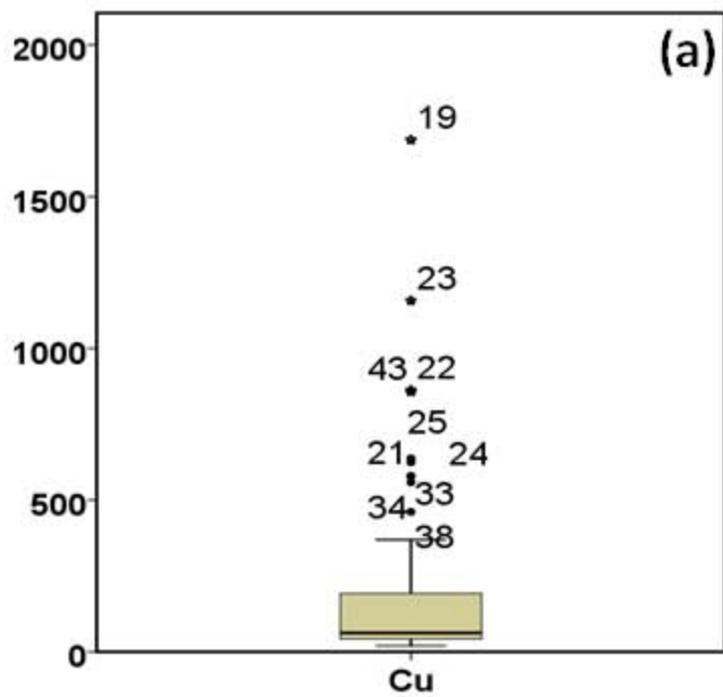
22

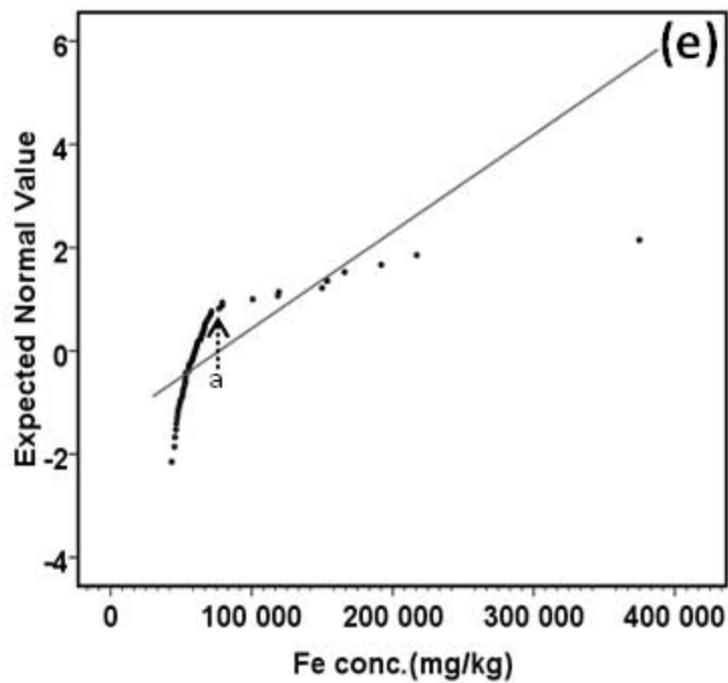
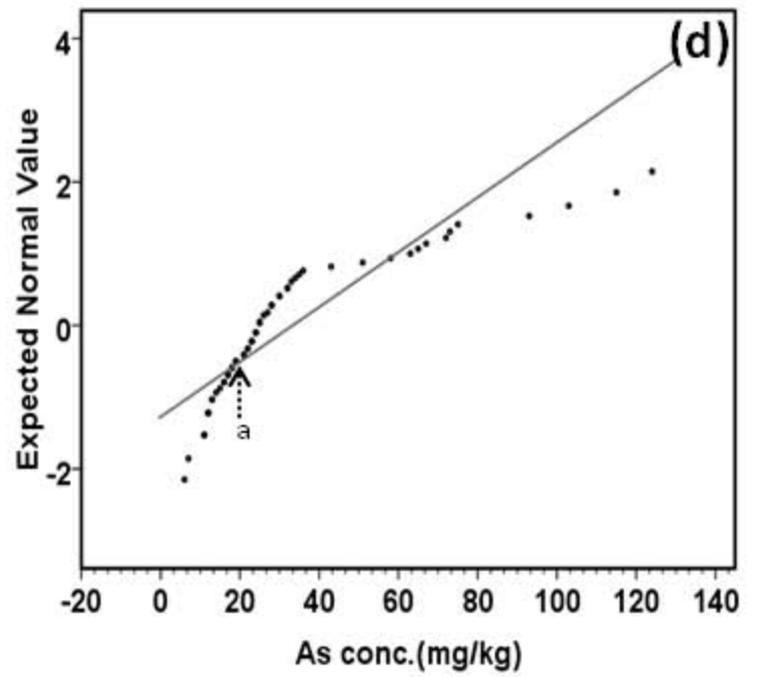
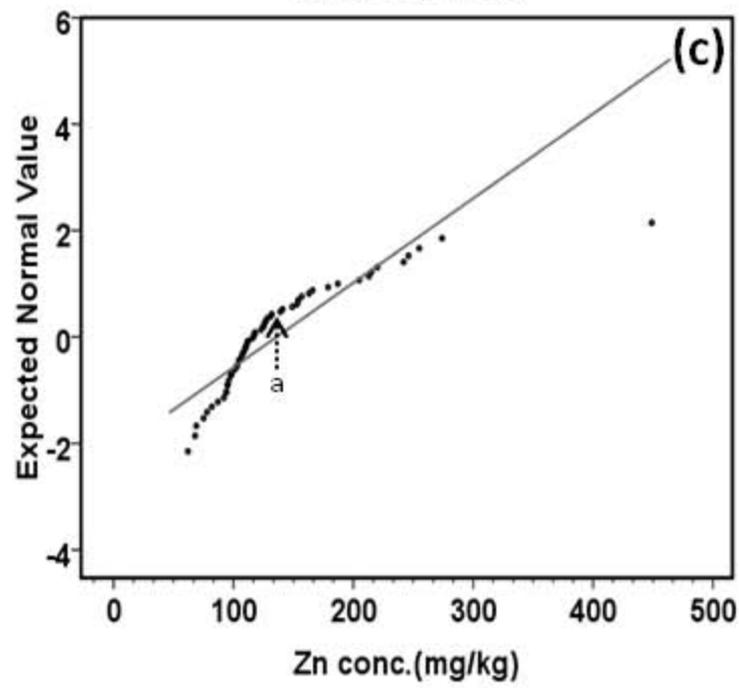
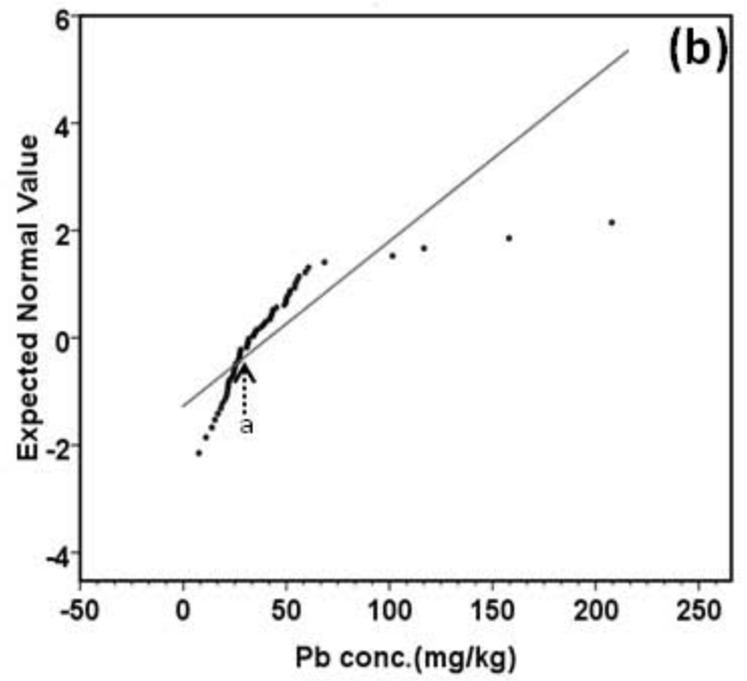
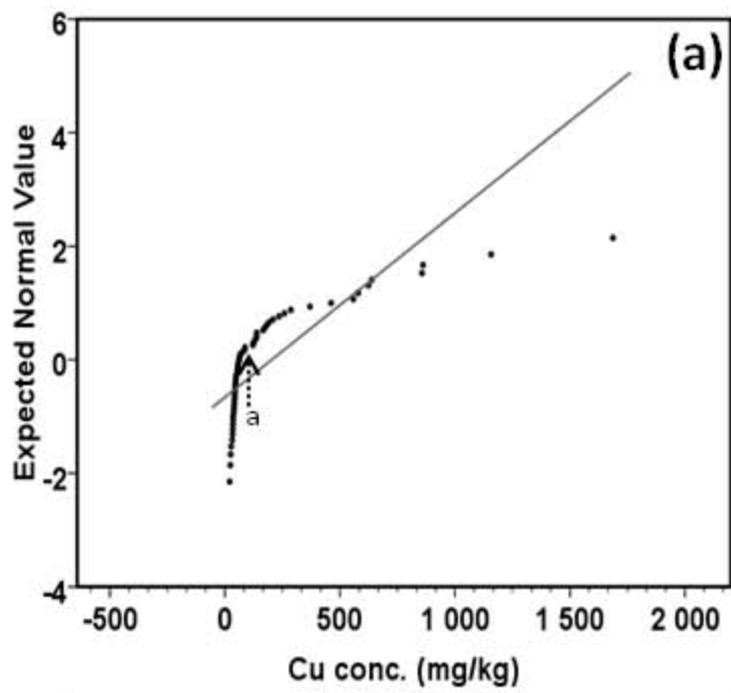
23

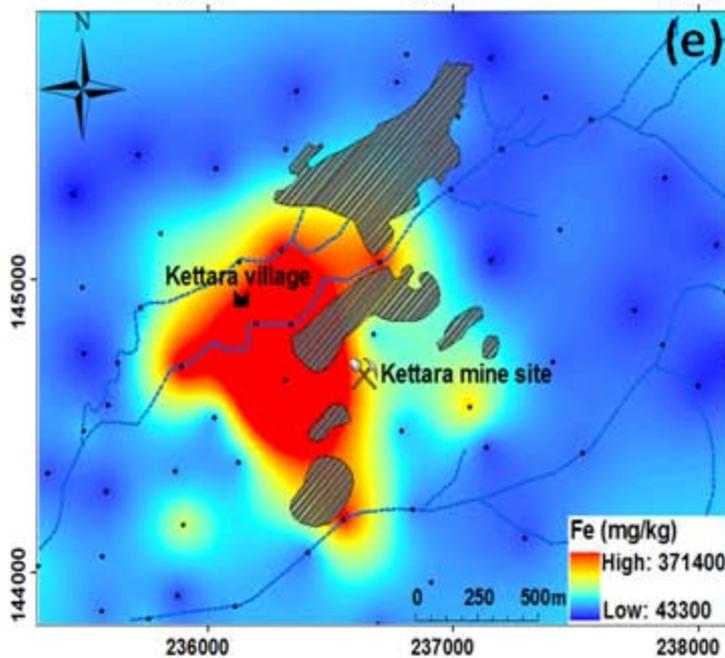
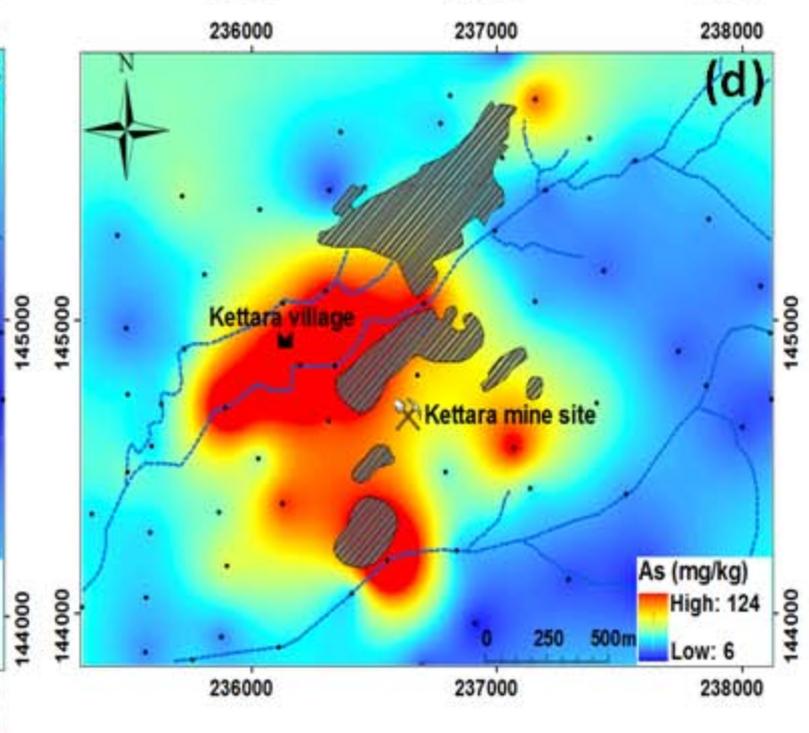
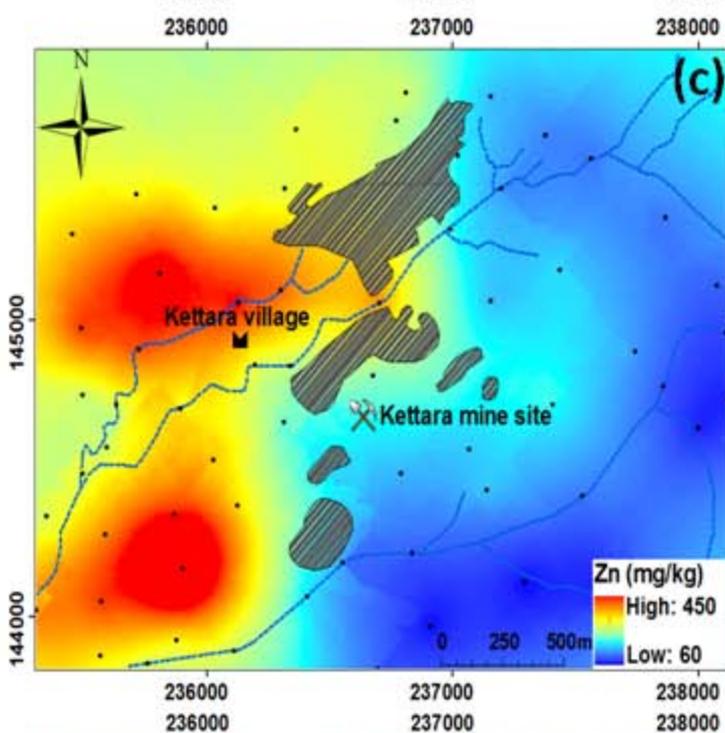
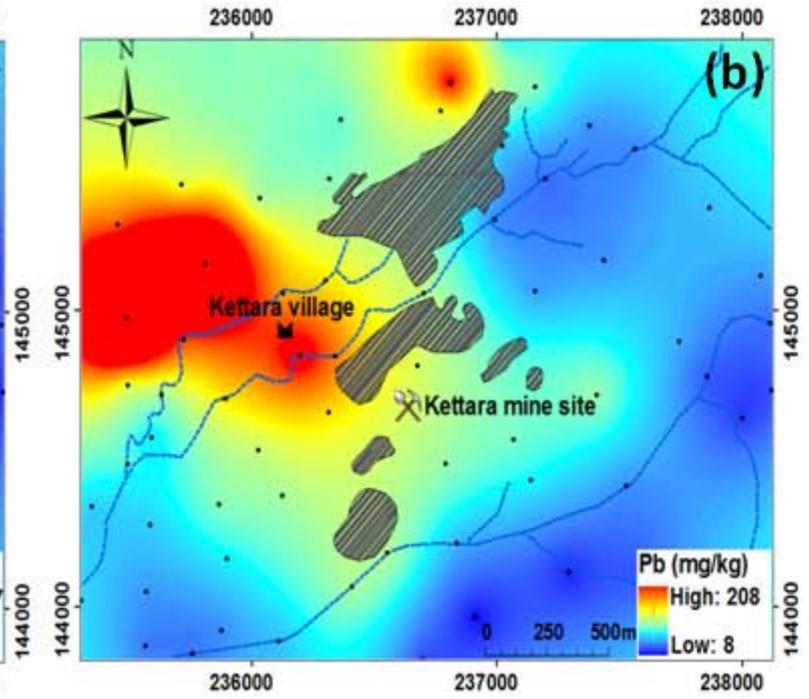
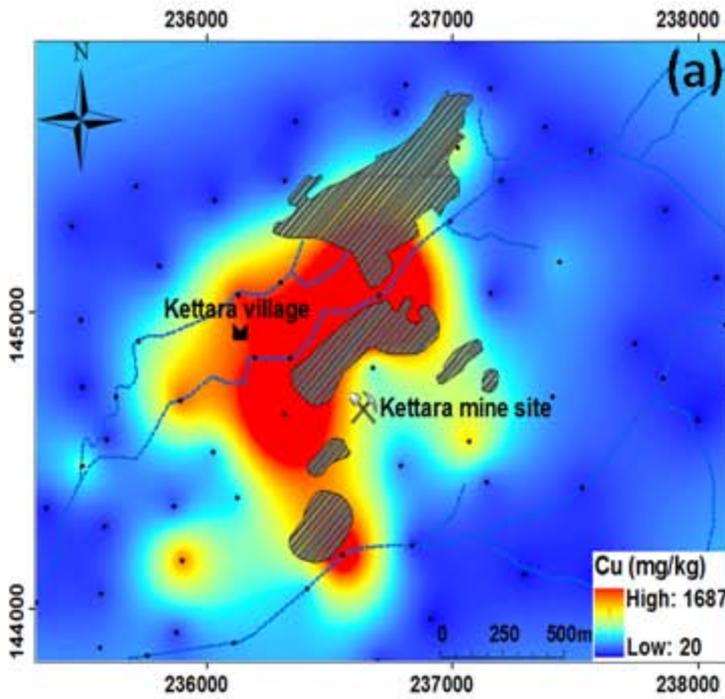






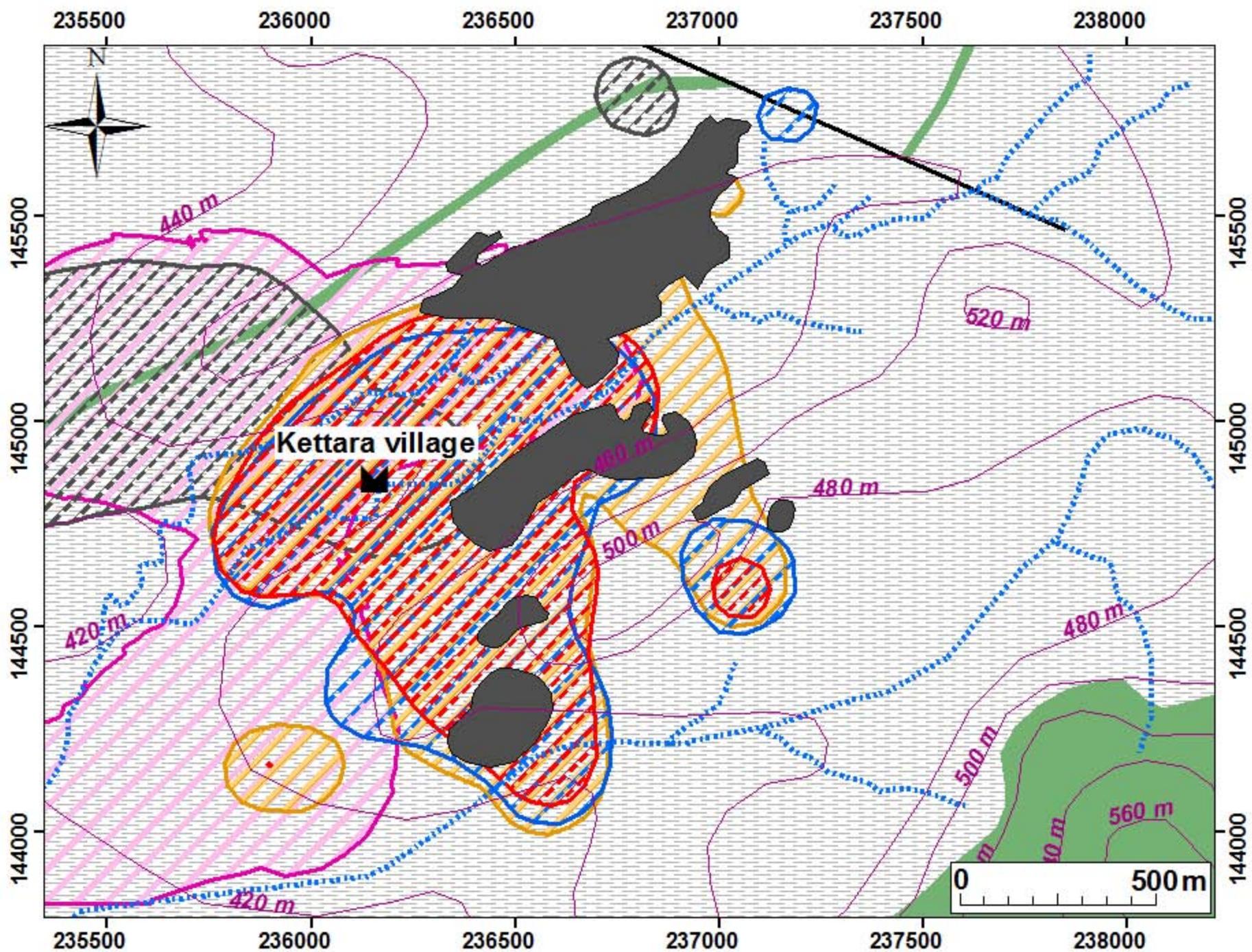






## LEGEND

- 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 <sup>a</sup>	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

<sup>a</sup> 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 <sup>c</sup>	world ranges in non-polluted soils <sup>d</sup>
	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).

<sup>c</sup> Canadian soils quality guidelines (CCME, 2006).

<sup>d</sup> Kabata-Pendias and Pendias (1992).