

ASSESSMENT OF METALS CONTAMINATION AND ECOLOGICAL RISK IN AIT AMMAR ABANDONED IRON MINE SOIL, MOROCCO

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Abstract

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The present study is an attempt to assess the pollution intensity and corresponding ecological risk of phosphorus and metals including Cd, Cr, Cu, Zn, Pb and Fe using various indices like geo-accumulation index, enrichment factor, pollution and ecological risk index. In all, 20 surface soil samples were collected from the Ait Ammar iron mine of Oued Zem city, province of Khouribga, in central Morocco. The concentrations of heavy metals in soil samples were used to assess their potential ecological risks. According to the results of potential ecological risk index (R_p), pollution index (PI), geo-accumulation index (I_{geo}), enrichment factor (EF), potential contamination index (Cp), contaminant factor (Cf) and degree of contamination (Cd), based on the averages, considerable pollution of metals in soils of study area was observed. The consequence of the correlation matrix and principal component analysis (PCA) indicated that Fe, Cu, Zn, Cr and P mainly originated from natural sources and Cd and Pb are mostly derived from anthropogenic sources. The results showed that these metals in soil were ranked by severity of ecological risk as $Pb > Cd > Cu > Cr > Zn$, based on their single-element indexes. In view of the potential ecological risk (R_p), soils from all soil samples showed a potential ecological risk. These results will provide basic information for the improvement of soil environment management and heavy metal pollution prevention in Ait Ammar.

Key words: iron mine, soil pollution, metal, potential ecological risk.

Introduction

Heavy metal contamination of soils concern several scientists because of the potential toxicity of metals (Homa et al., 2003). Anthropogenic actions related to industrialization are central sources of heavy metals to soils (Stafilov et al., 2010). In addition, heavy metals can be transported long distances via atmospheric particulates after their liberation into the environment, which can expand the area touched by metal contamination (Wu et al., 2010); a portion of metals in the atmosphere may be transferred to soils by atmospheric deposition (Lu et al., 2010). Consequently, soils, especially those in the vicinity of industrial sites, are important sinks for heavy metals.

Soil is a dynamic natural resource for the survival of human life and due to its complex matrix is the principal receiver of the persistent contaminants such as heavy metals (Luo et al., 2007). Every soil comprises some natural quantities of heavy metals, at concentrations called backgrounds. The magnitude of a metal's background depends upon the composition of the parent rock material from which the soil was derived (Scazzola et al., 2003). Human activities that add waste material to the soils also influence its metal concentration (Pastor, Hernandez, 2012).

The results of the ecological risk assessment can reveal the possibility for soil to be contaminated, and even for the ecology to be harmed by concerned heavy metals (Fairbrother et al., 2007), so these results were usually utilized to serve as a guide for all US Environmental Protection Agency (EPA) programmes and regional offices to supplement or update the policies, practices and guidance. Consequently, such researches have got much attention from investigators over the world, and a great development has been made (Posthuma et al., 2008). Meanwhile, more and more works and practices showed that, such results from the risk assessment have little capability to reveal the real degree of their potential toxic effects totally, especially, no capability to show whether the potential toxic effect is coming into an observed harm of ecology and its degree. So, based on the results, relative strategies and methods were taken to control the risk and even their practices usually were not operated in time. Therefore, a great harm of ecology would have happened at the end. Obviously, in order to obviate an ecology system to be harmful, it is important to do an assessment of ecological risk; meanwhile, it is necessary to do primary empirical researches too.

Understanding the contamination characteristics of heavy metals in soils and identifying their environmental exposure risks not only are the basic preconditions for soil pollution prevention, but also provide important information for making decisions for remediation of contaminated soils. The objectives of this study are to identify the potential sources of phosphorus and metals and to evaluate the pollution level of soil metals in Ait Ammar iron mine area (Oued Zem, Morocco).

Material and methods

Soil samples collection and analysis

In 19 July 2010, surface soil (0 to 20 cm) was collected in the Ait Ammar iron mine (33° 04' N; 6° 38' W), which is placed in the khouribga Province, Morocco. The region's climate is arid to semi-arid (Nouri et al., 2014) and the area is rich with natural phosphate. Four transects (T1–T4) were selected along the direction of iron mine. Five soil elements from the mine were picked in each transect, forming five rounds (R) e.g. R1 contained T.1.1, T.2.1, T.3.1 and T.4.1. Points on each transect were preferred based on distance, with the most distance point being at 300 to 600 m from the corresponding first point (Fig. 1). Each sample was composed of five subsamples collected around the point and already pooled in the field. Soils at Ait Ammar are highly disturbed, varying in texture and color (brown to black). In addition, one reference site (REF) (6° 34' 2" W; 32° 49' 34" N), utilized as a fallow and located about 27 km south of the mining site, was identified. Soil from five spots at REF was mixed and treated as the transect samples, forming a total of 21 samples. The 21 samples (4 transects × 5 units + reference sample) were carried to the laboratory at 4 °C. A portion of each sample was ground to 2 mm for physico-chemical analyses.

The concentrations of phosphorus and metals (Cd, Pb, Cr, Cu, Zn, and Fe) in soil were measured after their digestion in a HNO₃, HF and HCl (Nouri et al., 2014). The concentrations of the metals were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Jobin Yvon ULTIMA 2) (The National Centre for Scientific and Technical Research (NCSTR), Rabat, Morocco).

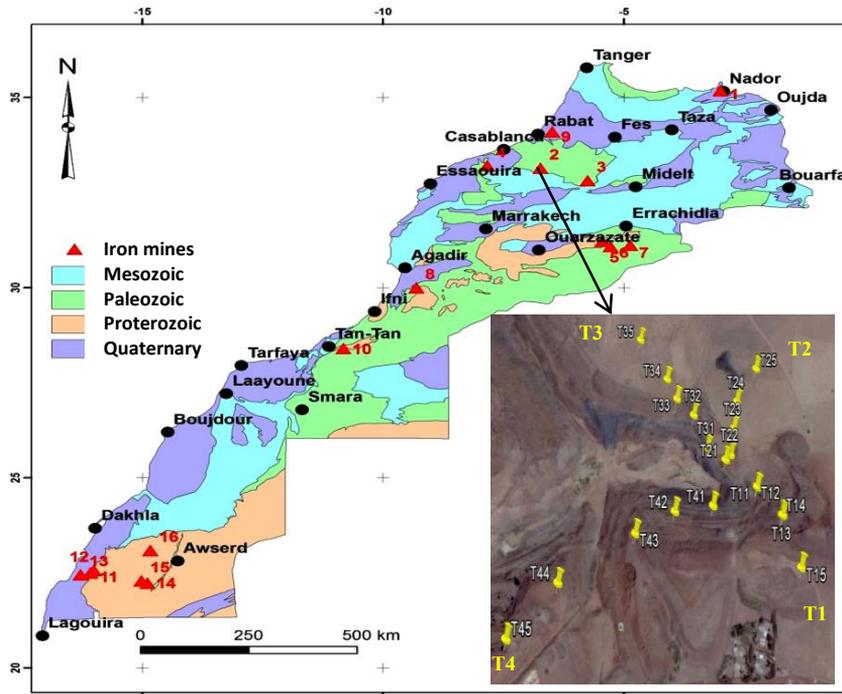


Fig. 1. The sampling map in the abandoned Ait Ammar iron mine site (Number 2).

Metal bioavailable fraction evaluated using the 0.01 M CaCl₂ extraction procedure (Houba et al., 1990; NEN, 5704 1996) and metal concentrations were measured by ICP-AES (NCSTR, Rabat, Morocco).

Soil pH was measured in a soil–water suspension (1:5, w/v extraction ratio) according to the method described in FAOUN (1970). Total organic carbon (TOC) was determined by oxidation with potassium dichromate and titration with ferrous sulphate reagent (Walkley, Black, 1934).

Assessment of soil contamination

Calculating the degree of contamination by a specified heavy metal obliges that the contaminant metal concentration be compared with a reference material (geochemical background). Such reference material should be an uncontaminated substance that is comparable with the studied samples, as reported with Maanan et al. (2014). The concentration in each point sample was used to calculate the indexes and not the mean levels of transects or rounds.

Enrichment factor

Enrichment factors (EF) were evaluated to verify heavy metals in soil originate from geogenic or anthropogenic origins. It is frequently supposed that the contents of elements in a natural medium can be justified specially by crust or geogenic origin (Jiang et al., 2013; Li et al., 2015). In this paper, the EF was determined for metals (M) by utilizing the formula:

$$EF = \frac{\left(\frac{M}{Fe}\right)_{sample}}{\left(\frac{M}{Fe}\right)_{reference}}$$

where M is the metal in consideration and Fe is a reference metal. To develop the sensitivity of the EF to the iron mine influence, the soil at a reference site was utilized as a reference. According to Zhang and Liu (2000), EF values between 0.05 and 1.5 reveal that the metal is exclusively from crustal origins or natural developments; however, EF values higher than 1.5 imply that the origins are more probable to be anthropogenic. EF can also help in revealing the contamination degree.

Potential contamination index

The potential contamination index (Cp) can be evaluated by the equation (Dauvalter, Rognerud, 2001; Maanan et al., 2014).

$$Cp = \frac{M \text{ sample max}}{M \text{ reference}}$$

where M sample max is the maximum concentration of an element in soil, and M reference is the value of the same element in a reference soil. Cp values were explained as proposed by Dauvalter and Rognerud (2001), where $Cp \leq 1$ indicates low pollution; $1 < Cp \leq 3$ is moderate pollution; and $Cp > 3$ is severe or very severe pollution.

Contaminant factor and contamination degree

Contaminant factor (Cf) is the quotient attained by division of the concentration of each metal in the soil by the reference value (Håkanson, 1980; Maanan et al., 2014).

$$Cf = \frac{M \text{ sample}}{M \text{ reference}}$$

To simplify contamination control, Håkanson (1980) suggested a method utilizing a diagnostic tool named the contamination degree (Cd). Cd was calculated as the sum of the Cf for each sample:

$$Cd = \sum_{i=1}^{i=n} Cf$$

In accordance with Håkanson (1980): $Cf \leq 1$ designates low pollution; $1 < Cf \leq 3$ is moderate pollution; $3 < Cf \leq 6$ is considerable pollution; and $Cf > 6$ is very high pollution.

Modified degree of contamination

The modified degree of contamination (mCd) was presented to approximate the complete degree of pollution using the method (Abraham, Parker, 2008; Maanan et al., 2014):

$$mCd = \frac{\sum_{i=1}^{i=n} Cf}{n}$$

where n is the number of examined elements, i is the ith pollutant and Cf is the contamination factor.

Geo-accumulation index

The geo-accumulation index (I_{geo}) was utilized to evaluate the degree of element pollution in soils by balancing the present with original concentrations; however it is hard to find original soils. The I_{geo} values of soils in research site were evaluated with the following equation:

$$I_{geo} = \log_2 (C_i / (1.5 B_i))$$

where C_i is the current elements concentration in soil samples and B_i is the geochemical reference value as defined by Taylor and McLennan (1995). The modified coefficient, constant 1.5, was utilized to characterize the effect of accumulation and geological characteristics and determine the consequence of human activities. I_{geo} can be separated into seven classes (Muller, 1969).

Pollution evaluation of heavy metals

Pollution indexes (PI) of heavy metals in soils were determined utilizing soil environment quality standards of Canadian soil quality guidelines for the protection of environmental and human health. The equation for determining PI is:

$$PI = \frac{Ci}{Si}$$

where C_i is the actual concentration of element i in soils (mg kg^{-1}), S_i is the soil quality standard or reference value of element i (mg kg^{-1}). Classifying of heavy metals PIs can be done on four groups (Wu et al., 2014). Furthermore, to present an evaluation of the general contamination class for a sample, the integrated pollution load index (PLI) and/or the Nemerow integrated pollution index (NIPI) (Nemerow, 1985) can be exercised (Tomlinson et al., 1980; Lu et al., 2014). The NIPI and PLI can be determined utilizing $[0.5 \times (I_{\text{Avg}}^2 + I_{\text{Max}}^2)]^{1/2}$ and $(PI_1 \times PI_2 \times PI_3 \times \dots \times PI_n)^{1/n}$, respectively, where I_{Avg} is the average value of all contamination indexes of the elements studied, I_{Max} is the highest value, n is the number of elements.

In accordance with Zhang et al. (2011), the PLI is separated in seven classes from none to high contamination to designate the contamination degree. Nevertheless, the grouping of NIPI can be categorized in five classes as reported by Cheng et al. (2014).

Assessment of potential ecological risk

The index was suggested by Håkanson (1980, 1988) and Maanan et al. (2014) to evaluate the heavy metal pollutants. The central function of this index is to designate the pollutant agents and where pollution investigations should be ordered. The index R_i was presented to evaluate the level of heavy metal contamination in soil, in accordance with the toxicity of heavy metals:

$$R_i = \sum E_f^i \\ E_f^i = T_r^i \times C_f$$

where R_i is determined as the summation of all risk factors for metals in soil, E_f^i is the individual potential ecological risk factor, C_f is the contamination factor, and T_r^i is the toxic response factor, characterizing the potential of metal pollution by representing the toxicity of metals. In accordance with the normalized toxic response factor suggested by Håkanson (1980), Zn, Pb, Cr, Cd and Cu have toxic response factors of 1, 5, 2, 30 and 5, respectively. The jargon utilized to define the risk factors E_f^i and R_i was proposed by Håkanson (1980).

Statistical analysis

Multivariate statistical analysis such as non-metric multidimensional scaling analysis (MDS) was used to compare the heavy metal concentrations between sampling sites. MDS was performed in PRIMER 5 (Primer-Eldt, UK). The similarity matrix was found with normalized Euclidean distance similarity of the metal concentration values converted as $\log(x+1)$. Principal component analysis (PCA) and correlation analysis were used to check for significant relationships between different heavy metals in soil samples and determine the sources of metals pollution for this research, and it is performed using Statistical Package for the Social Science software (SPSS statistics 17.0, USA). The various statistical methods were performed with a 95% confidence interval (significance $p < 0.05$). In the PCA, varimax was used as the rotation method in the analysis following standardization of the data.

Results and discussion

Soil quality

Spatial distribution of metals and phosphorus in the surface soil

Table 1 presents the total contents of metals and phosphorus in the topsoil of the research site. Generally the order of element contents in the contaminated soil was $\text{Fe} > \text{P} >>> \text{Cr} >$

Table 1. Total metals concentrations in the soils of Ait Ammar mining site (mg kg^{-1}). T: Transect; R: Round; REF: Reference.

	Cd	Cr	Cu	Zn	Pb	Fe	P
T. 1	1.04 ± 0.36	128.43 ± 51.47	36.37 ± 13.30	95.07 ± 31.39	10.78 ± 9.85	247684.00 ± 122152.62	4392.00 ± 2306.93
T. 2	1.20 ± 0.41	101.97 ± 29.75	26.84 ± 7.23	69.03 ± 29.93	11.66 ± 9.91	131718.00 ± 82478.68	1670.00 ± 1228.25
T. 3	1.46 ± 0.92	132.96 ± 35.89	28.65 ± 12.13	78.40 ± 57.82	3.53 ± 5.11	155662.00 ± 148759.25	2718.00 ± 3022.04
T. 4	4.80 ± 7.80	174.98 ± 20.65	47.94 ± 30.28	120.58 ± 14.71	10.55 ± 13.12	319502.00 ± 25391.11	5398.00 ± 2279.20
R. 1	1.47 ± 0.96	130.39 ± 18.19	44.90 ± 13.24	104.25 ± 34.01	7.24 ± 6.42	278557.50 ± 69085.20	5372.50 ± 2428.35
R. 2	1.35 ± 0.40	154.84 ± 43.46	38.09 ± 13.12	126.37 ± 36.85	20.44 ± 12.76	317665.00 ± 93544.32	6062.50 ± 2535.82
R. 3	0.93 ± 0.47	169.37 ± 44.63	48.98 ± 30.09	91.83 ± 37.15	9.51 ± 10.41	222835.00 ± 107807.24	3305.00 ± 1873.56
R. 4	0.94 ± 0.29	91.80 ± 36.96	18.55 ± 3.16	58.62 ± 38.89	4.14 ± 4.82	139042.50 ± 130180.38	1702.50 ± 1383.17
R. 5	5.93 ± 8.35	126.51 ± 29.49	24.23 ± 2.98	72.78 ± 22.41	4.33 ± 5.44	110107.50 ± 100866.83	1280.00 ± 935.33
REF	5.14	166.02	44.76	155.38	0.92	59780.00	11020.00

Zn > Cu > Pb > Cd. Fe exhibits the highest content in the topsoil, while mean contents were about $213641.50 \text{ mg kg}^{-1}$ for Fe, and below 2.12 mg kg^{-1} for Cd. The maximum values of average concentrations for heavy metals in Ait Ammar soils were distributed in T. 1 (Cr), T. 3 (Zn), T. 4 (Cd, Cu, Pb) for transects and for rounds were R. 2 (Pb), R. 3 (Cr, Cu), R. 4 (Zn) and R. 5 (Cd).

Remarkably, the metal concentrations in the reference soil did not reveal regularly lesser values than the soils from the mining area: for Cd and Cu the contents were near the mean of the mining area, for Zn and specifically for Cr the assessed contents were upper than those noted for all transects and only for Pb, the determined values were lesser than the mean. Moreover, excluding Cr and Fe, all metals were under the ranges reported by other authors (Boularbah et al., 2006; Iavazzo et al., 2012) in diverse Moroccan abandoned mines.

MDS analyses indicating that samples from mine area are clearly separated (Fig. 2). The plot of the MDS analysis of the metal concentrations does not reveal a clear relation between the soil samples (Fig. 2a, b) and the spatial distribution metals and phosphorus could be determined. This can be related to natural developments of soil and system recovery in the mining activities interrupted 51 years ago (Nouri et al., 2013). In this analysis, the stress level applied to this study evaluated by MDS is 0.08 (Fig. 2), indicating that the two-dimensional representation is valid.

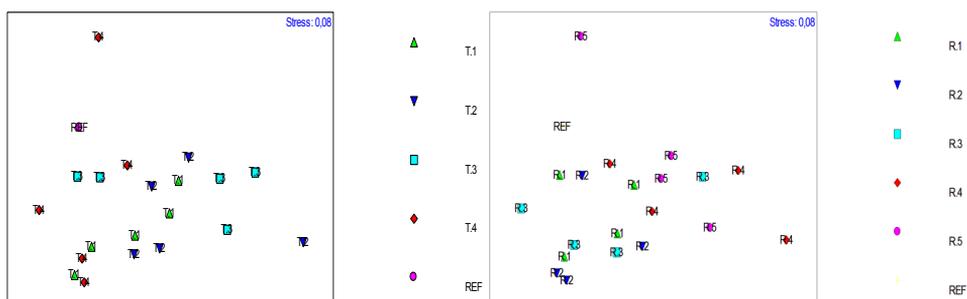


Fig. 2. Non-metric multidimensional scaling analysis of metal concentrations in the soils of Ait Ammar mining area; Analysis made: (a) by round (R), (b) by transect (T).

The chemical results of reference soils exploited over soils in unpolluted site are also expressed in Table 1 and were utilized to assess the potential enrichment of soils from Ait Ammar mine with provoked metals (Khan et al., 2008; Luo et al., 2012a). The soil contamination indices for the metals were respected and evaluated.

Bio-availability of phosphorus and metal elements in the topsoil

Due to the interactions of heavy metals with soil constituents, many soil factors can influence metal bio-accessibility (Luo et al., 2012b). Bio-availability was expressed as the element content extracted by 0.01 M CaCl₂ (Fig. 3). In this study, the elements (Zn, P and Cu) showed higher bio-availability compared to other metals. Generally, the order for mean values of bio-availability of the elements was as follows: P > Zn > Cu > Cd > Fe > Pb > Cr. Zn is known to be one of the most mobile metals, since it is highly sensitive to abiotic and biotic-induced changes (Reddy, DeLaune, 2004) and dissociates from the binding groups of the organic matter (Van Hullebusch et al., 2005).

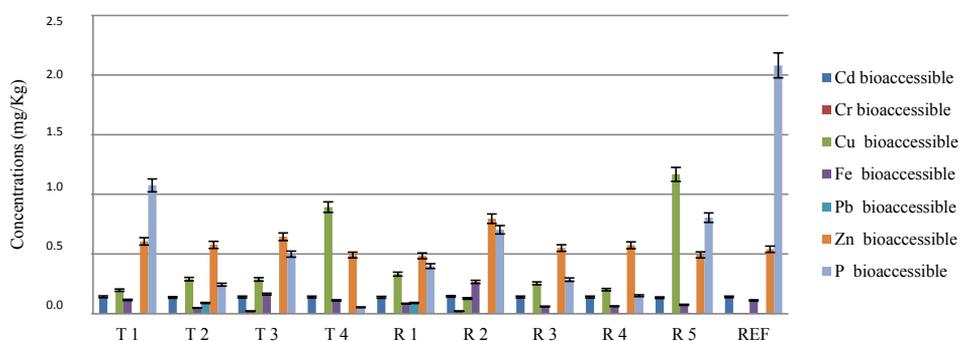


Fig. 3. Extractable metal concentrations in the soils (mg kg⁻¹); T: Transect; R: Round; REF: Reference.

The low bio-availability of these elements in the studied area might be due to the stable complexes could be formed with Fe, P (Komárek et al., 2013; Cao et al., 2004; Chen et al., 2006) and were present at high levels in the studied site with high values of chemical variables like pH and organic matter (Ma et al., 2016).

Influence parameters on metal bio-availability

The bio-availability of metals in the soils is influenced by pH, organic matter and other variables. The pH values of mining soil samples are slightly acids to neuters, ranging between 6.4 and 7.1 (Fig. 4). The pH of soil is very essential for mobility because metal accessibility is low when the pH is about 6.5 to 7 (Ma et al., 2016). The TOC levels in investigated soil samples range between 0.43 and 1.48% (Fig. 4). It is reported that contaminated mining soils are described by minimal nutrient content (Freitas et al., 2004). There is no significant spatial

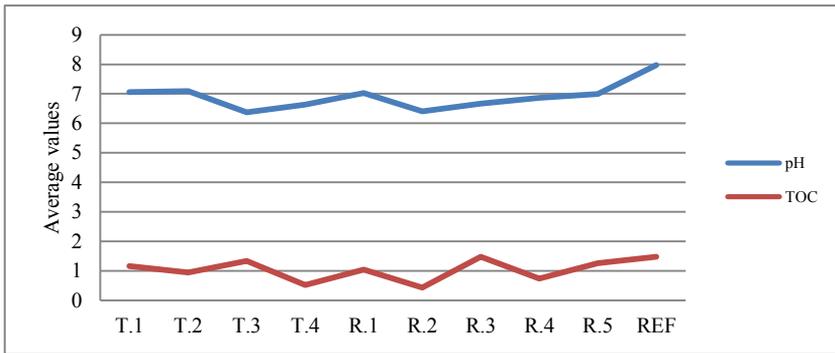


Fig. 4. Mean values of soil pH and total organic carbon (TOC, %); T: Transect; R: Round; REF: Reference.

variation in the TOC and pH values. Comparable levels were reported in soils near other abandoned Moroccan mining area (Boularbah et al., 2006; Iavazzo et al., 2012).

In conclusion, the low availability of metal due mainly to the high contents of Fe and P in the research area first and second to the pH ranging between 6.4 and 7.1, implying a relative harmless environment. For more physico-chemical parameters, see Nouri et al. (2014).

Determining geochemical relations between metals and phosphorus for soils from Ait Ammar iron mine

To assess the extent of metal pollution in the research site and determine its origins, a factor was analysed utilizing the correlation matrix levels of all the elements in the Ait Ammar soil samples. The correlation matrix utilized in the analysis deliver significant instruments for a comprehending the origin identification and the dynamics of the contaminants.

T a b l e 2. Correlation coefficient for metals and phosphorus of the raw data in mining area soils of Ait Ammar.

	Cd	Cr	Cu	Zn	Pb	Fe	P	Cd ^b	Cu ^b	Fe ^b	Zn ^b
Cd	1	0.164	-0.145	0.070	-0.180	0.160	-0.017	-0.011	0.988**	-0.046	-0.114
Cr		1	0.531*	0.652**	0.042	0.662**	0.525*	0.179	0.139	0.344	0.001
Cu			1	0.579**	0.111	0.576**	0.611**	0.045	-0.159	-0.084	-0.113
Zn				1	0.265	0.889**	0.791**	0.101	-0.009	0.380	0.000
Pb					1	0.304	0.489*	0.025	-0.187	0.131	-0.065
Fe						1	0.882**	0.211	0.085	0.237	-0.023
P							1	0.122	-0.089	0.254	-0.113
Cd ^b								1	-0.066	0.441	0.800**
Cu ^b									1	-0.121	-0.197
Fe ^b										1	0.536*
Zn ^b											1

Notes: ** - Correlation is significant at the 0.01 level (2-tailed); * - Correlation is significant at the 0.05 level (2-tailed);
^b - Bioavailable.

Correlation analysis was employed to investigate the relationships among the metals and phosphorus; the Pearson correlation coefficients between the determined chemical variables are shown in Table 2. The results reveal that there are numerous significant correlation coefficients and some are very strong. Remarkably, high correlations with a significant level at $p < 0.01$ were obtained between the elemental pairs Zn-Cr ($r = 0.652$), Fe-Cr ($r = 0.662$), Fe-Cu ($r = 0.576$), Fe-Zn ($r = 0.889$), P-Cu ($r = 0.611$), P-Zn ($r = 0.791$) and P-Fe ($r = 0.882$) revealing a common source for these elements. Cr is significantly correlated ($p < 0.05$) with Cu ($r = 0.531$) and with P ($r = 0.525$) and Pb-P ($r = 0.489$). Finally, Cd was highly associated with extractable Cu ($r = 0.988$) and inversely correlated with Cu ($r = -0.145$), Pb ($r = -0.180$) and P ($r = -0.017$) indicating the different source that delivers the soils with Cd balanced to Cu, Pb and P. Notably, negative correlations between Cd and Pb and any other elements (Cr, Cu, Fe, P and Zn) are very weak ($p > 0.05$), which implies a different source of Cd and Pb.

The results of the correlation analysis suggest that metals in soils from Ait Ammar may originate from both natural and anthropogenic sources. To identify the source of elements in soils, a principal component analysis (PCA) was performed, which has been considered to be efficient for the implementation of source identification (Anju, Banerjee, 2012).

The results of PCA for the concentrations in soils from Ait Ammar iron mine are offered in Tables 3 and 4. Two components with eigenvalues higher than 1.00 were extracted. The PCA method resulted in a reduction of the initial dimension of the dataset to two com-

Table 3. Total variance explained and rotated component matrix of PCA of elemental concentrations for soils from Ait Ammar mine.

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	3,821	54,591	54,591	3,821	54,591	54,591	3,779	53,989	53,989
2	1,262	18,027	72,618	1,262	18,027	72,618	1,304	18,629	72,618
3	0,911	13,015	85,632						
4	0,405	5,786	91,418						
5	0,378	5,394	96,812						
6	0,160	2,291	99,104						
7	0,063	0,896	100,000						

Table 4. The computed weighted values for each metal (significant loading factors are marked in bold).

Component	1	2
Fe	0.950	0.021
Zn	0.917	0.046
P	0.886	0.296
Cr	0.789	-0.248
Cu	0.719	0.153
Cd	0.154	-0.789
Pb	0.294	0.711

ponents, explaining 72.618% of the data variation. Loading plots of the components are exposed in Fig. 5. According to the rotated component matrix, PC1 and PC2 accounted for 53.99 and 18.63% of the total variance respectively. Metals Cr, Cu, Zn and Fe were discovered to be strongly associated with P in the first component (PC1) (Table 4), which mostly originated from natural sources, because Fe is mainly derived from lithogenic sources (Pejman et al., 2015)

and their mean concentrations were comparable to the corresponding reference levels, as reported by Zhang et al. (2014). PC2 includes Cd and Pb with opposite loadings, which can be identified as a tracer of anthropogenic pollution sources for Cd and Pb. It is documented that the essential origins of Cd and Pb were anthropogenic counting industrial and mining activities (Wang et al., 2015; Zhou et al., 2015; Wen et al., 2015), which was comparable with our conclusions.

PCA results are consistent with correlations matrices pointing out that most of metal variability in Ait Ammar soils can be explained by entirely natural inputs by parent materials. These results are consistent with those from next sections of contamination indices and ecological risk, which indicate that the topsoil was contaminated by Cd and Pb, whereas the Cr, Cu, Zn, and P in the topsoil originated from lithogenic sources.

Correlation matrix and PCA were utilized in this analysis to comprehend the major differences between the metals and phosphorus. A significant positive correlation is detected between Cu, Cr, Zn, Fe and P, signifying that these metals are originated from comparable origins. PCA classifies two key classes of similarities: one contained an anthropogenic origins and another a natural source.

Indices of soil contamination

Enrichment factor of heavy metals and phosphorus

To assess the degree of anthropogenic influence, the enrichment factor indices of metals and phosphorus in soils have been calculated. The enrichment factor values were listed in Table 5. The average EF values were in the following order: Pb (6.22) >> Cr (0.44) > Cu (0.38) > Zn (0.24) > Cd (0.17) > P (0.09). In general, EF values of 0.05–1.5 can be considered to be in the range of natural variability, whereas EF values greater than 1.5 suggest that the sources are more likely to have a partially anthropogenic origin (Zhang, Liu, 2000). These results further demonstrate that the topsoil was contaminated by Pb, whereas the Cr, Cu, Zn, Cd, and P in the topsoil originated from lithogenic sources.

The results showed that the average EF values of Cd, Cr, Cu, Zn, Pb and P were 0.17, 0.44, 0.38, 0.24, 6.22 and 0.09, respectively. The mean EF values of Cd, Cr, Cu, Zn and P were < 2, suggesting relatively minimal enrichment. However, the mean EF values of Pb were higher than 1.5, implying anthropogenic impact to the metal levels in iron mining

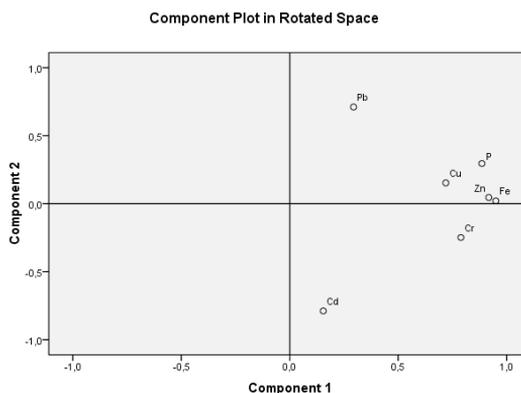


Fig. 5. Component plot in rotated space of studied area

Table 5. Assessed level of anthropogenic effect founded on the enrichment factor (EF)^b; geo-accumulation index (I_{geo})^b; pollution index (PI)^c; degree of contamination (Cd)^d; modified degree of contamination (mCd)^e and pollution load indices (PLI)^f. Metals are reported in mg kg⁻¹ ($n=20$).

	Individual Metal												Multi-Metal								
	Cd			Cr			Cu			Zn			Pb		Fe		P		PLI	mCd	
	EF	I_{geo}	PI	EF	I_{geo}	PI	EF	I_{geo}	PI	EF	I_{geo}	PI	EF	I_{geo}	PI	EF	I_{geo}				
Min	0.01	1.33	0.26	0.12	-0.04	0.80	0.07	-1.39	0.23	0.12	-2.26	0.11	0.14	-5.59	0.01	-1.84	0.04	-1.96	0.20	2.42	0.35
Max	0.84	7.12	14.57	1.28	2.08	3.47	1.31	1.41	1.58	0.59	0.53	0.77	55.07	0.20	0.49	3.05	0.14	3.13	0.86	47.62	6.80
Mean	0.17	3.03	1.52	0.44	1.27	2.10	0.38	-0.28	0.55	0.24	-0.44	0.45	6.22	-3.01	0.13	1.52	0.09	1.12	0.48	16.44	2.35
SD	0.20	1.15	3.02	0.41	0.52	0.70	0.33	0.68	0.31	0.16	0.84	0.21	12.73	2.08	0.15	1.44	0.03	1.55	0.19	12.56	1.79

^a Minimal enrichment (EF < 2), moderate enrichment (2 ≤ EF < 5), significant enrichment (5 ≤ EF < 20), very high enrichment (20 ≤ EF < 40) or extremely high enrichment (EF ≥ 40).

^b Uncontaminated ($I_{geo} \leq 0$), uncontaminated to moderately contaminated ($0 < I_{geo} \leq 1$), moderately contaminated ($1 < I_{geo} \leq 2$), moderately to heavily contaminated ($2 < I_{geo} \leq 3$), heavily contaminated ($3 < I_{geo} \leq 4$), heavily to extremely contaminated ($4 < I_{geo} \leq 5$), or extremely contaminated ($I_{geo} > 5$).

^c No pollution (PI ≤ 1), slight pollution (1 < PI ≤ 3), moderate pollution (3 < PI ≤ 5) and sever pollution (PI > 5).

^d Cd < 6 indicates a low degree of pollution; 6 < Cd < 12 is a moderate degree of pollution; 12 < Cd < 24 is a considerable degree of pollution; and Cd > 24 is a high degree of pollution indicating serious anthropogenic pollution.

^e mCd < 1.5 is nil to a very low degree of pollution; 1.5 ≤ mCd < 2 is a low degree of pollution; 2 ≤ mCd < 4 is a moderate degree of pollution; 4 ≤ mCd < 8 is a high degree of pollution; 8 ≤ mCd < 16 is a very high degree of pollution; 16 ≤ mCd < 32 is an extremely high degree of pollution; mCd ≤ 32 is an ultra-high degree of pollution.

^f Background concentration (PLI = 0), uncontaminated (0 < PLI ≤ 1), uncontaminated to moderately contaminated (1 < PLI ≤ 2), moderately contaminated (2 < PLI ≤ 3), moderately to highly contaminated (3 < PLI ≤ 4), highly contaminated (4 < PLI ≤ 5), or very highly contaminated (PLI > 5).

soils (Zhang, Liu, 2000). Table 6 shows the percentage of class distribution of pollution assessment for heavy metals in soils with enrichment factor. It can be seen from the table that the EF values of all heavy metals and phosphorus in soils were lower than 2, showing deficiency or minimal pollution. Forty per cent of the EF values for Pb surpassing 2, including 5% of samples showing extreme enrichment and other 5% samples implying very high enrichment, revealed that Pb in Ait Ammar iron mine soils corresponded to relatively serious contamination.

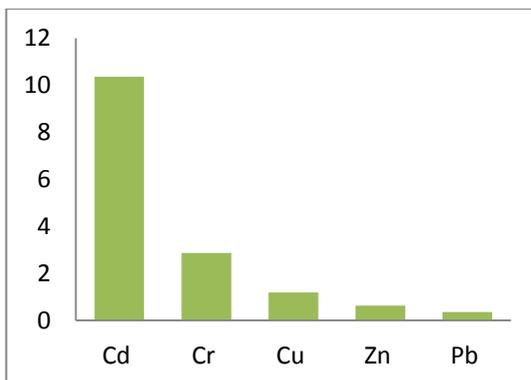


Fig. 6. Nemerow integrated pollution index of heavy metals for the Ait Ammar soil samples.

Pollution indexes of heavy metals

The pollution index can be used to provide a relative ranking of contamination levels. As shown in Table 5, the PI values of Pb, Cu and Zn are almost below 1. Chromium is the only metal with almost all the collected samples showing pollution indexes above 1 with maxima of 3.47. Cadmium for a small number of soils also demonstrates a relative enrichment with respect to the maximum background value. Interestingly, the enrichment of soil samples with Cd is severely higher in T.4.5 sample. The maximum values of pollution index for Cd are 14.57, indicating anthropogenic origin for this metal in T.4.5.

In addition, the degree of contamination of soils is low ($1 < PI \leq 3$) for all elements, and the proportion of samples, which have moderate ($3 < PI \leq 5$) and high ($PI > 5$) contamination, is 15% for Cr and 5% for Cd, respectively (Table 6). These results indicate that iron mine soils of Ait Ammar are contaminated by Cd, Cr, Cu, Pb, and Zn, but contamination is minimal for the last three metals and moderate for the two first. Furthermore, assessed to the Canadian soil quality guidelines (CCME, 1999), only Cd, Cu, Zn and Pb mean concentrations are lower than the recommended values of 22, 91, 360 and 600 mg/kg respectively whereas Cr for all transects and rounds exceeds the limit of 87 mg/kg.

Furthermore, to give a comprehensive situation of soil metals, the integrated pollution load index (PLI) for each sample was considered. The results showed that the PLI values of heavy metals in iron mine soils ranged from 0.20 to 0.86 with an average of 0.48, also indicating no pollution. Especially, the PLI values of elements in all soil samples were below than 1, showing no to low pollution according to Tomlinson et al. (1980).

In the present study, the Nemerow integrated pollution index (NIPI) of heavy metals in soils was calculated. Fig. 6 shows the NIPI values of soil metals. It can be seen from Fig. 6 that the comprehensive pollution levels varied widely among different samples. The NIPI values in soil ranged from 0.36 to 10.36. Investigations showed that the soils were slightly polluted with Cu, moderately polluted with Cr and highly polluted particularly with Cd.

Pollution assessment of soil metals using geochemical indicators

Table 5 shows the results of the geo-accumulation index (I_{geo}) values for metals and phosphorus in Ait Ammar mining soils. As shown in Table 5, the I_{geo} values of Cd vary the most, varying from the moderately contaminated level to the extremely contaminated level. In addition, the I_{geo} values of Cr vary from the unpolluted level to moderately contaminated level. However, the average I_{geo} values for Pb, Zn, and Cu were lower (negative) than other element types.

Table 6 lists the percentages of class distribution for pollution assessment of heavy metals using I_{geo} . In particular, the 40% of the I_{geo} values of Cd were higher than 3, suggesting that iron mining soils should be heavily contaminated by Cd (Muller, 1969). The result also can be drawn from Table 6 that the I_{geo} values for Cd in 5% samples are extremely contaminated level.

Table 6. Percentage of class distribution of pollution (I_{geo} , EF and PI).

	Cd	Cr	Cu	Zn	Pb	Fe	P
I_{geo}	$I_{geo} \leq 0$		5%	70%	60%	95%	25%
	$0 < I_{geo} \leq 1$		20%	25%	40%	5%	10%
	$1 < I_{geo} \leq 2$	15%	70%	5%		15%	30%
	$2 < I_{geo} \leq 3$	45%	5%			50%	30%
	$3 < I_{geo} \leq 4$	30%				5%	5%
	$4 < I_{geo} \leq 5$	5%					
	$I_{geo} > 5$	5%					
EF	$EF < 2$	100%	100%	100%	100%	60%	100%
	$2 \leq EF < 5$					15%	
	$5 \leq EF < 20$					15%	
	$20 \leq EF < 40$					5%	
	$EF \geq 40$					5%	
PI	$PI \leq 1$	75%	5%	95%	100%	100%	
	$1 < PI \leq 3$	20%	80%	5%			
	$3 < PI \leq 5$		15%				
	$PI > 5$	5%					

The I_{geo} values of Fe and P vary the most, ranging from the uncontaminated level to the heavily contaminated level. In particular, the 70% and 65% percentile I_{geo} values of Fe and P were higher than 1, respectively, suggesting that iron mining soils should be moderately contaminated by Fe and P. It is well known that different land use patterns, intensity of human activities, pollution history, and distance to emission sources may affect soil pollution to various degrees (Lee et al., 2006).

In summary, this study reveals that the surface soils in the iron mine area have been heavily contaminated with Cd, moderately contaminated with Cr, Fe and P and unpolluted with Pb, Cu and Zn, according to I_{geo} values. The average I_{geo} value indicated that the pollution degree of seven elements decreased in following sequence: Cd > Fe > Cr > P > Cu > Zn > Pb.

Potential contamination index

The C_p for seven investigated elements for Ait Ammar site is presented in Fig. 7. They demonstrate that Zn and P are at low contamination, Cr and Cu are at moderate contamination and Pb, Cd and Fe are at severe or very severe contamination levels. The highest value assigned for Pb. Pb, Cd and Fe metals at the sampling area revealed the highest degree of contamination impact focused on the C_p of the soil of Ait Ammar iron mine.

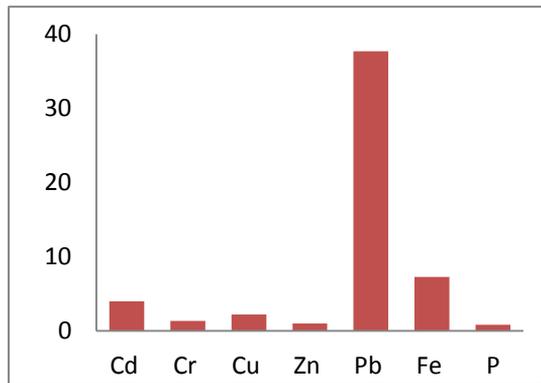


Fig. 7. Potential contamination index for studied soil samples.

Contaminant factor and contamination degree

In the current analysis, the Cd was described as the summation of all Cf for iron mine. These values are presented in Tables 7 and 5. The degree of contamination varied from 2.42 to 47.62 with a mean of 16.44, which approves that some mine soils have a great degree of pollution.

T a b l e 7. Contamination factor (Cf) for studied soil samples.

	Cd	Cr	Cu	Zn	Pb	Fe	P
Min	0.07	0.31	0.32	0.14	0.68	0.24	0.02
Max	3.97	1.34	2.23	0.99	37.70	7.28	0.83
Mean	0.41	0.81	0.78	0.58	9.96	3.57	0.32
SD	0.82	0.27	0.44	0.27	11.39	2.16	0.25

Modified degree of contamination

In the Ait Ammar iron mine, the revised Håkanson formula was utilized to determine the mCd for all the studied elements (Cd, Cr, Cu, Zn, Pb, Fe and P). The results are shown in Table 5. The values vary from 0.35 to 6.80 with an average 2.35, representing that the investigate site presents a moderate degree of pollution, with anthropogenic contamination.

Potential ecological risk

The Håkanson index delivers a measurable approach of precisely separating the level of possible hazards. Nevertheless, one disadvantage of this method is that it contains a great degree of subjectivity and ignores the weighting function or united antagonism of numerous metals. In general, the potential ecological risk index and solo metal pollution index produced diverse calculation results (Maanan et al., 2014).

The potential ecological risk factors E_i^f for each metal and the R_i for all five heavy metals combined of the research area were summarized in Table 8. The results show that the single heavy metal pollution index underlines the risk that Pb and Cd cause to the human and the environment. For other elements (Cr, Cu and Zn), the E_i^f indices were generally low. The E_i^f

Table 8. Heavy metal potential ecological risk indices of Ait Ammar mine.

	Individual metal					Multi-metal R_i^b
	Cd	Cr	E_i^{fa}	Zn	Pb	
Min	2.16	0.61	1.60	0.14	3.39	11.68
Max	119.15	2.68	11.13	0.99	188.48	995.68
Mean	12.41	1.62	3.90	0.58	49.78	273.20
SD	24.72	0.54	2.21	0.27	56.93	370.69

^a $E_i^f < 40$ indicates a low potential ecological risk; $40 < E_i^f < 80$ is a moderate ecological risk; $80 < E_i^f < 160$ is a considerable ecological risk; $160 < E_i^f < 320$ is a high ecological risk and $E_i^f > 320$ is a very high ecological risk.

^b $R_i < 95$ indicates a low potential ecological risk; $95 < R_i < 190$ is a moderate ecological risk; $190 < R_i < 380$ is a considerable ecological risk and $R_i > 380$ is a very high ecological risk.

indices for individual metals showed that the gravity of contamination of the five heavy metals diminutions in this order: Pb > Cd > Cu > Cr > Zn. Based on the R_i , the minimum, mean, and maximum potential ecological risk grades are low, considerable, and very high, respectively, which can be essentially qualified to the fact that the study site is a considerable ecological risk.

Conclusion

Different useful tools, methods and indices were employed to evaluate soil pollution and ecological risk index in Ait Ammar abandoned iron mine, Morocco. In this study, we investigated the concentrations of phosphorus and metals, including Cd, Cr, Cu, Pb and Zn and Fe in iron mine soils. The results of the correlation matrix and PCA indicated that Fe, Cu, Zn, Cr and P mainly originated from comparable sources and Cd and Pb is mostly derived from anthropogenic sources. According to the results of potential ecological risk index (R_i), pollution index (PI), geo-accumulation index (I_{geo}), enrichment factor, potential contamination index, contaminant factor and degree of contamination (Cd), based on the averages, considerable pollution of metals in soils of study area was observed. For individual metal, only Pb had high ecological risk for some site samples, without neglect the Cd impact.

The increasing of metal concentrations above the threshold is bound to have harmful effects on human. Therefore, it is necessary to design an environmental strategy not only to manage but also monitor the same with priority.

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