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Metal concentrations and metal mobility in Ait Ammar Moroccan mining site

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Abstract

To aid in evaluating the environmental impacts of a mining activities in the Oued Zem region, Morocco, pedological characteristics of mining site were examined to assess the risks of metals mobility. After appropriate preparation, the concentrations of metals (Cd, Cr, Cu, Fe, Pb and Zn) and P in 21 soil samples collected around a former iron mine in the Oued Zem region were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). The results showed very high levels: Fe (43.55 104 mg Kg-1), P (0.92 104 mg Kg-1), Cr (222.16 mg Kg-1) and Zn (153.3 mg Kg-1), a relatively high pH (pH_{KCl} = 6.13, pH_{water} = 7.41), high organic carbon content (2.93 %), a low nitrogen level (0.06 %) and, thus, a high C/N ratio. According to principal components analysis (PCA), three distinct factors explaining 71.267% of the variance were showed. A first factor including metals (Zn, Cr, Fe and Cu) and P with a positive loading, total kjeldahl nitrogen, organic matter and soil pH combined for the second component and the third factor characterizing Cd with a positive loading and Pb with a negative loading.

Keywords: iron mine, metals, bioavailable, PCA, Morocco.

Introduction

Mining is an essential activity that provides the raw materials for society. However, unless adequate precautions are taken, mining can be accompanied by serious negative impacts on the environment and on human health. There may be changes in landscapes, destruction of habitats, air and water pollution, changes in river regime and ecology, permanent degradation of land and land instability [1].

Iron (Fe) ore has been exploited from the deposit located in Ait Ammar area in Oued Zem region, for about 27 years and closed in 1964 (Figure 1). Morocco, mainly the southern region, has a large number of metalliferous sites. Some of them which are being exploited while others have been abandoned [2]. These sites are concentrated in the region of Marrakech, Ouarzazate and in the North of the Anti-Atlas Mountains [3].

In Morocco several iron deposits are known but the main ones are First Kettara who had been operated for pyrrhotite (for production of sulfuric acid), then the Ouixane district in Nador region and finally the numerous deposits Tafilalet (including n'Tourza Imi) and Ait Ammar [3]. Morét [4] reported that the Moroccan iron is hematite form or oolitic ore, that is to say sedimentary ore; iron is quite common in older sediments of Morocco. Iron oxides are among the best reservoirs of metals [5] they have control over the concentration and availability of trace elements in soil solution [6].

The most important mechanism that justifies the fixation of trace elements by iron oxides is the specific adsorption, which depends strongly on pH and ionic strength. Heavy metals can bind to the outer surface of iron oxides and then migrate to the internal sites or adsorbed directly to internal sites of iron oxide [6]. When attached to the outer surface of iron oxides, they are easily mobilized by strong acids and complexing agents or by acidification of the medium [7-8].

Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. Mining is one of the most important sources of heavy metals in the environment. Mining and milling operation together with grinding, concentrating ores and disposal of tailings, along with mine and mill waste water, provide obvious sources of contamination [8]. Heavy metal contamination has been one of serious problems in the vicinity of abandoned mine sites. These heavy metals have a potential to contaminate soil and water. They can be dispersed and accumulated in plants and animals, and taken in by human beings as consumer. Human health risk assessment has been used to determine if exposure to a chemical, at any dose, could cause an increase in the incidence of adverse effect to human health [9].

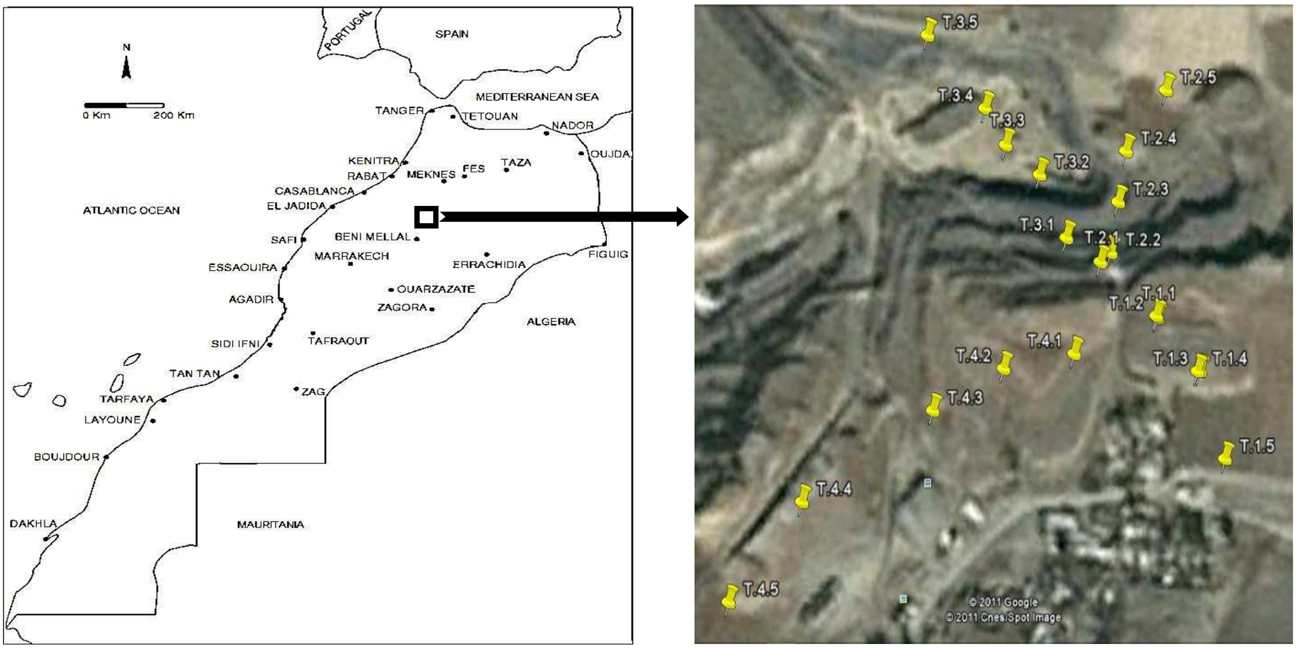

Figure 1: Location of the study area, Ait Ammar, Oued Zem region, Morocco

Assessment of soil contamination with heavy metals can be determined by estimating the bioavailable fraction of toxic metals. Metal mobility in soils has generally been assessed using a chemical approach based up on selective extractions [10-11].

Knowledge of the soil properties and interactions between other metals is important to assess the bioavailability of same metals and uptake by plants in order to reduce potential food chain contamination [12]. Thus, the main objectives of this study were (a) to determine total concentrations of P, Fe and other associated metals (Cd, Cr, Cu, Pb, and Zn) in soils from the contaminated area at Ait Ammar; (b) to investigate the relationship between soil properties (pH, organic matter (OM) and total kjeldahl nitrogen (TKN)) and these metals; and (c) to examine the mobility of these seven metals.

2. Materials and methods

2.1. Site Description

The studied area is located in northwestern of Oued Zem city (about 25 km) and 170 of Casablanca, in the Khouribga Province, central Morocco (Figure 1). The region's climate is Mediterranean, arid to semi-arid continental character with a dry season from April to October and a rainy season from November to March. The average annual rainfall is 350 mm with a large variation in time and space. The averages annual evaporation is about 1800 mm. Temperatures are experiencing very significant seasonal variations: a peak in August of 40 °C in January and a minimum of 3 °C [13]. In 19th of July 2010, 21 topsoil samples were collected (4 transepts with 5 points each + a reference site) (Figure 1). Geographic coordinates of each site sample location were determined with a Trimble Navigator global positioning system (GPS). The coordinates of each site were showed in table1.

2.2. Soil characterization

Topsoil (< 20 cm depth) from a metal-contaminated site in Ait Ammar mining area was collected in 19 July 2010. A soil subsample was a passed through a 2-mm sieve and subjected to chemical characterizations.

Soil pH values were measured in a 1/5, sample/1 M KCl, extract after shaking for 15 minutes and left to settle for 30 minutes. Total organic carbon (TOC) was analyzed by dichromate oxidation and titration with ferrous ammonium sulphate [14]. TKN was determined by the Kjeldahl procedure. Soil pH (H_2O) and conductivity were measured in a soil-water suspension (1:5, w/v extraction ratio) according to the method described by Pereira et al. [15]. Soil moisture was determined by oven drying at 105 °C for 24 hours.

Table 1: Description of the study site in the Oued Zem region of center Morocco

Sample Code	**UMT Coordinates**
T.1.1	29 S 720066 3661172
T.1.2	29 S 720065 3661173
T.1.3	29 S 720105 3661134
T.1.4	29 S 720103 3661134
T.1.5	29 S 720129 3661071
T.2.1	29 S 720014 3661211
T.2.2	29 S 720023 3661218
T.2.3	29 S 720029 3661255
T.2.4	29 S 720035 3661292
T.2.5	29 S 720070 3661337
T.3.1	29 S 719983 3661228
T.3.2	29 S 719958 3661273
T.3.3	29 S 719927 3661294
T.3.4	29 S 719908 3661320
T.3.5	29 S 719855 3661372
T.4.1	29 S 719992 3661144
T.4.2	29 S 719929 3661132
T.4.3	29 S 719866 3661100
T.4.4	29 S 719750 3661031
T.4.5	29 S 719686 3660957
Ref	29 S 727740 3634697

2.3. Total and bioavailable metal concentrations

Concentrations of totals metals were determined by inductively coupled plasma atomic emission spectrometry ICP-AES after digestion of samples. 2 mL of concentrated HNO_3 were added to 150 mg of soil samples, and mixed. The samples were then heated at 100 °C until dryness. After this, 3 mL of concentrated HF were added to the Teflon vessels and heated at 140 °C for 15 hours at the minimum (vessels closed). After cooling the vessels were opened and heated until dryness at 110 °C. 2 mL of concentrated HNO_3 were added and heated (110 °C) until dryness, this step was repeated, the fifth time of dryness was got with (2 mL of concentrated HCl and 120 °C) (The objective of these repeated occasions of HNO_3 and HCl, is to ensure as complete as possible evacuation of excess HF: Indeed, traces of HF in the sample solution would quickly deteriorate the nebulization system). 25 mL of HCl (2 M) were added and heated for 2 hours at 100 °C and the vessels were closed. After cooling and filtration, all samples were analyzed for Cd, Cr, Cu, Pb, Zn, Fe and P as well as seven major elements by ICP-AES using a (Jobin Yvon ULTIMA 2) apparatus.

Soil 0.01 M $CaCl_2$- soluble trace element concentrations were determined in 1/10 soil sample (≤ 2 mm)/0.01 M $CaCl_2$ extracts [16-17]. After shaking for 2 h on a tabletop shaker, extracts were decanted and 60 mL were centrifuged (2000 xg), and metal concentrations were measured by ICP-AES (The National Centre for Scientific and Technical Research, Rabat, Morocco).

2.4. Statistical treatment of data

To evaluate the analytical data, Principal component analysis (PCA) and Correlation analysis were performed to determine the relationship between the values of the different trace elements in soil. The significance level reported ($P \leq 0.05$) is based on Pearson's coefficients. Statistical analysis was carried out using SPSS 17.0 for Windows.

3. Results and discussion

3.1. The physicochemical parameters

The chemical characteristics of the soil 21 samples in studied mine are presented in Table 2. Analysis demonstrates a wide range of physicochemical properties with pH_{KCl}, pH_{Water}, conductivity, OM content, water content, TOC, TKN and C/N ratio ranging from 3.99 to 7.14, 4.64 to 7.97, 32.40 to 1656.67 µS cm^{-1}, 0.11 to 5.05%, 0.64 to 8.49%, 0.0647 to 2.929%, 0.007 to 0.1884% and from 2.36 to 132.94, respectively.

The pH values for the samples were slight acid or slight alkaline except the sample T.3.2 who was strong acid (4.64). Accordingly with Slattery et al. [18], our results were between ranges in pH common for humid and arid region. At the same time, values of mining soil pH_{KCl} (Potential acidity) are, generally, below of those of pH_{Water} in different types of soil [19-20]. For OM, two samples of the studied soils have an organic matter contents > 3% which indicated that the soils in this area are relatively fertile. The measures of two sites of long-term experiment belonging to the National Institute of Agronomic Research of Settat, Morocco, were showed an average 0.7% organic carbon (OM = 1.20 %) [21], while total TKN was, in most soils, uniformly very low (0.07-0.1884%), resulting in high C/N ratios (2.40-132.94).

Table 2: Characterization of soils of Ait Ammar mining site

Samples	**pH_{KCl}**	**pH_{Eau}**	**Conductivity**	**OM (%)**	**Water (%)**	**TOC (%)**	**TKN (%)**	**C/N Ratio**
T.1.1	6.13 ± 0.06	7.20 ± 0.10	151.77 ± 6.2	2.69	2.11	1.5593	0.0908 ± 0.0003	17.17
T.1.2	5.10 ± 0.04	7.38 ± 0.14	59.07 ± 1.9	0.85	2.83	0.4951	0.0840 ± 0.0000	5.89
T.1.3	5.29 ± 0.04	6.88 ± 0.02	82.33 ± 2.0	1.96	2.12	1.1353	0.0593 ± 0.0050	19.15
T.1.4	5.74 ± 0.02	6.99 ± 0.10	53.50 ± 1.0	0.82	1.79	0.4766	0.0105 ± 0.0049	45.39
T.1.5	5.77 ± 0.01	6.87 ± 0.20	103.17 ± 2.2	3.72	1.55	2.1579	0.0489 ± 0.0001	44.13
T.2.1	5.60 ± 0.05	6.94 ± 0.14	75.57 ± 4.4	2.68	1.51	1.5565	0.0489 ± 0.0000	31.83
T.2.2	4.89 ± 0.01	7.13 ± 0.06	40.27 ± 5.6	0.71	2.71	0.4117	0.0139 ± 0.0000	29.62
T.2.3	5.83 ± 0.01	6.90 ± 0.03	217.83 ± 3.4	2.22	1.56	1.2889	0.0175 ± 0.0050	73.65
T.2.4	6.21 ± 0.05	7.06 ± 0.10	100.17 ± 4.5	1.60	1.10	0.9306	0.0070 ± 0.0000	132.94
T.2.5	6.01 ± 0.03	7.41 ± 0.07	100.50 ± 5.1	0.88	6.02	0.5128	0.0839 ± 0.0001	6.11
T.3.1	5.44 ± 0.01	7.11 ± 0.06	55.37 ± 2.3	1.07	1.75	0.6216	0.0138 ± 0.0002	45.04
T.3.2	3.99 ± 0.03	4.64 ± 0.02	201.73 ± 6.8	1.28	0.64	0.7425	0.0417 ± 0.0001	17.81
T.3.3	5.72 ± 0.01	6.28 ± 0.09	1656.67 ± 31.5	5.05	1.51	2.929	0.1396 ± 0.0098	20.98
T.3.4	5.80 ± 0.12	6.68 ± 0.05	124.10 ± 14.8	2.21	1.67	1.2822	0.1249 ± 0.0008	10.27
T.3.5	6.33 ± 0.05	7.14 ± 0.06	200.23 ± 9.5	1.90	0.98	1.1038	0.0227 ± 0.0024	48.63
T.4.1	5.06 ± 0.06	6.84 ± 0.09	70.10 ± 2.0	0.77	2.18	0.4447	0.0140 ± 0.0000	31.76
T.4.2	4.39 ± 0.02	6.47 ± 0.03	78.13 ± 1.8	0.11	2.24	0.0647	0.0274 ± 0.0006	2.36
T.4.3	4.39 ± 0.01	6.63 ± 0.02	32.40 ± 0.2	0.99	3.12	0.5722	0.0208 ± 0.0097	27.51
T.4.4	5.79 ± 0.06	6.72 ± 0.07	95.77 ± 2.9	0.43	2.61	0.2511	0.1045 ± 0.0006	2.40
T.4.5	5.63 ± 0.01	6.54 ± 0.04	367.00 ± 8.2	2.13	5.50	1.238	0.0479 ± 0.0188	25.85
Ref	7.14 ± 0.02	7.97 ± 0.13	161.17 ± 7.1	2.55	8.49	1.4798	0.1884 ± 0.0203	7.85

3.2. Total metal concentrations in soil samples

The total concentrations (mg kg^{-1}) of seven elements of interest (Cd, Cu, Cr, Fe, P, Pb and Zn) obtained of 21 soil samples are reported in Table 3. The most obvious feature of this soil was the presence of relatively high levels of heavy metals, as compared with reference soil, such as cadmium (>7 up to 398%), chromium (>30.5 up to 134%), copper (>32 up to 223%), zinc (>14 up to 99%), lead (>67.5 up to 3770%), iron (>24 up to 725%) and, to a lesser difference, phosphate (>2 up to 84%). These metal concentrations confirming a very important polymetallic pollution.

3.3. Statistical analysis

3.3.1. Principal Component Analysis (PCA)

The total metal concentrations (Cd, Cr, Cu, Zn, Pb and Fe), P and chemical characteristics (pH_{KCl}, OM and TKN) were used for statistical analysis to determine their interrelationships following PCA. The total variance shows the significant factors and the percent of variance explained by each of variables before undergoing rotation which accounted for 71.26% of the total variance (Table 4). Loading values suggest a correlation between certain elements and soil characteristics of analyzed data. PCA allows the visualization of the information derived from the experimental data set into three principal components, retaining the maximum possible variability within that set (Table 5). A component plot in rotated space is given in Figure 2. The agglomerative hierarchical clustering procedure was used to evaluate similarities among samples and which illustrates the three groups. The three Principal Components (PCs) were extracted according to the Kaiser criteria in which only components with eigenvalues >1 were included in the analysis**.**

Table 3: Total metal concentrations in the soils of Ait Ammar mining site (mg.Kg^{-1})

Samples	Cd	Cr	Cu	Zn	Pb	Fe	P
T.1.1	1.370	108.376	28.776	76.237	12.457	228030.0	5530.0
T.1.2	0.972	142.368	59.522	153.300	28.668	435490.0	7910.0
T.1.3	0.370	222.162	42.717	98.394	8.945	317640.0	4530.0
T.1.4	1.325	81.210	23.130	62.360	2.853	182050.0	2840.0
T.1.5	1.179	88.018	27.702	85.071	0.982	75210.0	1150.0
T.2.1	0.911	119.737	36.194	65.559	0.911	199330.0	1540.0
T.2.2	1.533	89.042	26.054	63.755	17.471	179910.0	3430.0
T.2.3	1.655	113.335	31.022	115.610	26.679	214240.0	2660.0
T.2.4	0.556	50.956	14.352	22.251	12.350	14620.0	270.0
T.2.5	1.341	136.758	26.592	77.988	0.894	50490.0	450.0
T.3.1	3.057	136.966	51.974	145.323	0.815	373790.0	8240.0
T.3.2	1.927	192.272	28.905	152.876	1.071	296450.0	3710.0
T.3.3	0.711	139.099	22.561	29.490	1.421	49900.0	570.0
T.3.4	0.777	83.149	19.116	29.219	0.622	26220.0	390.0
T.3.5	0.808	113.314	20.691	35.077	13.740	31950.0	680.0
T.4.1	0.547	156.498	62.672	129.899	14.757	313080.0	6180.0
T.4.2	0.976	195.685	37.887	135.534	34.567	358810.0	9200.0
T.4.3	0.979	202.884	99.607	123.835	0.979	309560.0	5460.0
T.4.4	1.089	151.876	17.601	120.666	0.726	333280.0	3310.0
T.4.5	20.399	167.954	21.929	92.987	1.700	282780.0	2840.0
Ref	5.136	166.017	44.760	155.377	0.917	59780.0	11020.0

Table 4: Total variance and factor loading from Principal Component Analysis (PCA) extraction method

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total
1	4.217	42.173	42.173	4.217	42.173	42.173	3.601
2	1.815	18.151	60.324	1.815	18.151	60.324	2.251
3	1.094	10.943	71.267	1.094	10.943	71.267	1.275
4	0.957	9.575	80.842				
5	0.606	6.061	86.902				
6	0.520	5.196	92.099				
7	0.294	2.938	95.037				
8	0.199	1.994	97.031				
9	0.173	1.731	98.762				
10	0.124	1.238	100.000				

Table 5: Component matrix divided variables into 3 groups by Principal Component Analysis (PCA)

	Component		
	1	2	3
Zn	**0.909**	-0.141	0.005
P	**0.887**	0.048	-0.199
Cr	**0.796**	-0.112	0.289
Fe	**0.727**	-0.541	0.035
Cu	**0.713**	-0.189	-0.119
TKN	0.198	**0.888**	0.098
pH_{KCl}	-0.361	**0.744**	-0.016
OM	-0.329	**0.643**	0.227
Cd	0.095	-0.028	**0.824**
Pb	0.175	-0.364	**-0.630**

The PCA analysis results (Table 4) show that the first component (PC1) has the highest factor loading (3.601) followed by PC2 and PC3 with factor loadings of 2.251 and 1.275, respectively. Table 5 shows component matrix obtained from PCA extraction and variables included in each component. The first component (PC1), accounts for the most important associations, and is strongly correlated with Zn, P, Cr, Fe and Cu as illustrated by the high factor loading in PC1. Variables that are correlated with one another are combined into factors which are thought to be representative of the underlying correlations [22]. Iron is one of the most common elements present in the soil [23-24]. Sainger et al. [25] found that Fe, Zn, Cr and Cu were highly correlated with r = 0.96. Cao et al. [26] reported that P has a high affinity for Pb, Cu and Zn and desorption of Cu and Zn was sensitive to pH change, increasing with pH decline, whereas Pb desorption was decreased with a strongly acidic; this pH change may explain the absence of Pb in this group. The results also imply that Zn, P, Cr, Fe and Cu originate from the same geogenic source hence the strong correlations and interrelationships.

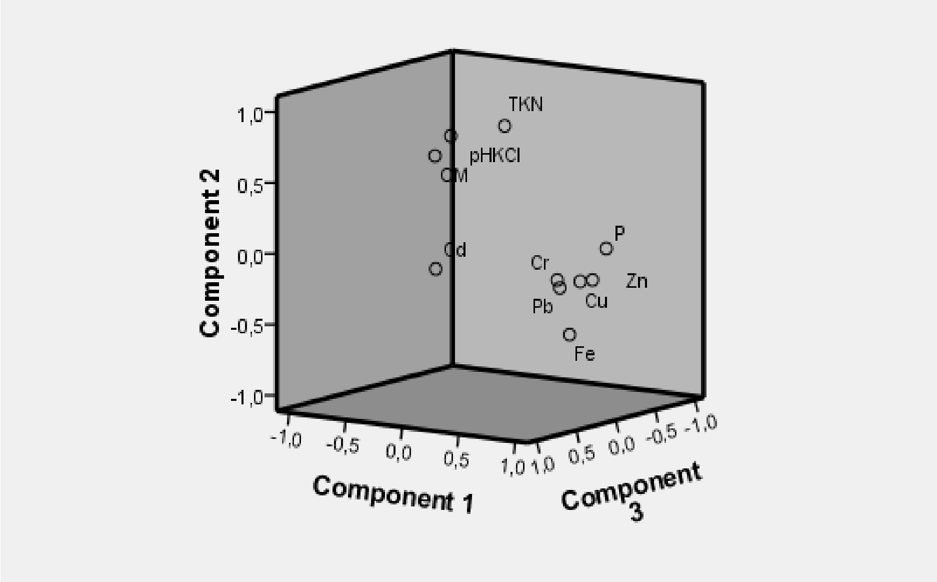

Figure 2: Component plot in rotated space OM, pH_{KCl}, TKN, Cr, Cu, Cd, Pb, Zn, Fe and P of iron mining soil.

The second component (PC2) is mostly dependent upon NTK, pH_{KCl} and OM which has a factor loading of 2.251. Melero et al. [27] and Akkajit and Tongcumpou [28] reported that OM is highly correlated with TKN and with soil pH respectively. Alvarenga et al. [29] concluded that pH is positively correlated with soil OM and soil total nitrogen (r = 0.87 and r = 0.73 respectively). Additionally significative and positive correlations between soil pH and organic C and total nitrogen were observed by Vásquez-Murrieta et al. [30] and Li et al. [31]. Basta and Sloan [32] reported that the application of organic residues can promote an increase in soil pH.

Alternatively, the third component (PC3) comprised only the Cd and Pb. Alloway [33] reported that Pb is considered to have a synergistic effect on Cd uptake due to its being preferentially absorbed, thus leaving more Cd in soil solutions. Several studies have found relationships most commonly observed between Cd–Pb [23, 34-35].

3.3.2. Correlations between chemical properties

In order to investigate the relationship between chemical properties, correlation analysis was performed between the different properties (Table 6). The strength of the associations was interpreted according to the Hopkins's correlation classification [36]: insubstantial (0.0–0.1), low (0.1–0.3), moderate (0.3–0.5), high (0.5–0.7), very high (0.7–0.9) and nearly perfect (0.9–1.0). Results show weak positive relationships in all cases between Cd-pH, Cd-OM and Cd-NTK (r = 0.114, 0.079 and 0.051, respectively). This suggests that a correlation has not been found between Cd-pH, Cd-OM and Cd-NTK. Burgos et al. [37] found weak positive correlation Cd-OM (r = 0.148) and weak negative correlation Cd-pH (r = -0.090).

A high correlation ($p < 0.01$) is observed between total concentration metals except Cd and Pb. Zn was the metal most highly correlated with P and Fe and correlated with Cr and the same between Fe and P. The iron was significantly and negatively correlated ($p < 0.01$) with OM and pH. These variables (OM and pH) are negatively correlated with total concentrations of Cr, Cu, Zn, Pb, Fe and P, conversely they were insubstantial or low positively correlated with Cd. Alvarenga et al. [29] concluded that the organic amendments were also effective in the in situ immobilization of metals, as shown by the negative Pearson's correlation coefficients obtained.

Table 6: Correlation coefficients between pH_{KCl}, OM, TKN, total concentration metals (Cd, Cr, Cu, Zn, Pb and Fe) and P

	pH_{KCl}	**OM**	**TKN**	**Cd**	**Cr**	**Cu**	**Zn**	**Pb**	**Fe**	**P**
pH_{KCl}	1.000									
OM	0.429*	1.000								
TKN	0.477*	0.452*	1.000							
Cd	0.114	0.079	0.051	1.000						
Cr	-0.481*	-0.206	0.124	0.183	1.000					
Cu	-0.430*	-0.265	-0.146	-0.126	0.538**	1.000				
Zn	-0.381*	-0.426*	0.024	0.114	0.659**	0.580**	1.000			
Pb	-0.244	-0.338	-0.321	-0.202	0.015	0.090	0.193	1.000		
Fe	-0.642**	-0.531**	-0.294	0.114	0.595**	0.527**	0.735**	0.332	1.000	
P	-0.176	-0.362	0.137	0.065	0.523**	0.576**	0.807**	0.326	0.602**	1.000

*Correlation is significant at the 0.05 level.
**Correlation is significant at the 0.01 level.

3.4. 0.01 M $CaCl_2$-extractable trace element concentrations

Ranges values of 0.01 M $CaCl_2$-extractable element concentrations were within the 0.13–0.15 mg kg^{-1} for Cd, 0.04–3.70 mg kg^{-1} for Cu, 0.02-0.56 mg kg^{-1} for Fe, 0.37-1.05 mg kg^{-1} for Zn and 0.02-2.48 mg kg^{-1} for P (table 7). 0.01 M $CaCl_2$-extractable concentrations of Cr and Pb in almost all samplings were below the detection limits (0.02 mg L^{-1} for Cr and 0.04 mg L^{-1} for Pb).

Table 7: Available metal concentrations in the soils of Ait Ammar mining site

Samples	**Available Cd**	**Available Cr**	**Available Cu**	**Available Fe**	**Available Pb**	**Available Zn**	**Available P**
T.1.1	0.14	-	0.43	0.20	-	0.38	0.78
T.1.2	0.15	-	0.11	0.11	-	0.79	1.47
T.1.3	0.14	-	0.15	0.07	-	0.57	0.33
T.1.4	0.14	-	0.15	0.04	-	0.58	0.31
T.1.5	0.14	-	0.15	0.16	-	0.71	2.48
T.2.1	0.14	-	0.23	0.08	0.09	0.70	0.12
T.2.2	0.14	-	0.18	0.05	-	0.80	0.20
T.2.3	0.13	-	0.41	0.05	-	0.37	0.46
T.2.4	0.14	-	0.22	0.04	-	0.63	0.04
T.2.5	0.13	-	0.41	0.02	-	0.38	0.40
T.3.1	0.13	-	0.41	0.03	-	0.37	0.60
T.3.2	0.15	0.02	0.18	0.56	-	1.05	1.09
T.3.3	0.15	-	0.22	0.07	-	0.79	0.30
T.3.4	0.14	-	0.21	0.11	-	0.63	0.19
T.3.5	0.13	-	0.42	0.05	-	0.38	0.32
T.4.1	0.14	-	0.26	0.03	-	0.49	0.09
T.4.2	0.14	-	0.04	0.35	-	0.55	0.05
T.4.3	0.14	-	0.24	0.05	-	0.47	0.05
T.4.4	0.14	-	0.23	0.06	-	0.45	0.06
T.4.5	0.14	-	3.70	0.07	-	0.50	0.02
Ref	0.14	-	-	0.11	-	0.54	2.08

-, below detection limit (Cr: 0.002 mg/L, Cu: 0.002 mg/L and Pb: 0.004 mg/L)

Adriano [8] reported that determination of bioavailable trace element concentrations might be more useful for environmental protection and ecological risk assessment: the total analysis may give information concerning possible enrichment of soil with trace elements, but it is not sufficient for estimating their mobility and availability for ecological processes. To extract bioavailable trace elements Kabata-Pendias [38] has proposed 0.01 M $CaCl_2$. In the soil samplings, Cu, Fe, Zn and P concentrations were, in general, significantly different between soil samples. In the Cd available case, no significant differences between samples were observed (Table 6). Pérez-de-Mora [39] reported that available Pb in all samplings was below the detection limit. In addition to reducing metal solubility, rock phosphate amendments are also effective in reducing phytoavailability of Pb and other metals [40-44]. Takeuchi and Arai [45] suggested that Pb immobilization resulted from the formation of a more stable lead phosphate, such as $Ca(10-x)Pbx(PO_4)_6(OH)_2$ via an ion exchange mechanism where aqueous Pb replaces Ca on the hydroxyapatite lattice. Ma et al. [46], on the other hand, proposed the dissolution of rock phosphate and subsequent precipitation of a pyromorphite-like mineral ($Pb_{10}(PO_4)_6X_2$, X = OH^-, Cl^-, F^-, etc.) as the primary mechanism. Cao et al. [26] concluded that fluoropyromorphite ($Pb_{10}(PO_4)_6F_2$) is primarily responsible for Pb immobilization by phosphate. Al-Oud and Helal [47] reported that iron had a high efficiency in immobilizing Pb. Iron greatly decrease Cr (VI) into Cr (III) [48] and precipitate of hydroxides of trivalent Cr and Fe [49-50] and this product can be used as an efficient adsorbent material for Cd(II) [51]. Economou-Eliopoulos et al. [52] reported that Cr in soil is mostly hosted in chromite, Fe-chromite, Cr-bearing goethite.

According to Figure 3 we observed that the element iron is the least available except for samples T.3.2 and T.4.2 it increases a little and this may be due to the pH_{KCl} (3.99, 4.39 respectively). In contrast, acidification of the soil would lead to a significantly increased ecotoxicological hazard potential following the increasing of solubilisation of metals [53-54]. Akkajit and Tongcumpou [28] concluded that the mobility of iron is the lowest between Cd, Mn, Zn, Pb and Cu. It was also observed that, generally, if the available P increase the available Cu decreases and vice versa. Phosphate rock has a high affinity for Cu (114 mmol/Kg) [26].

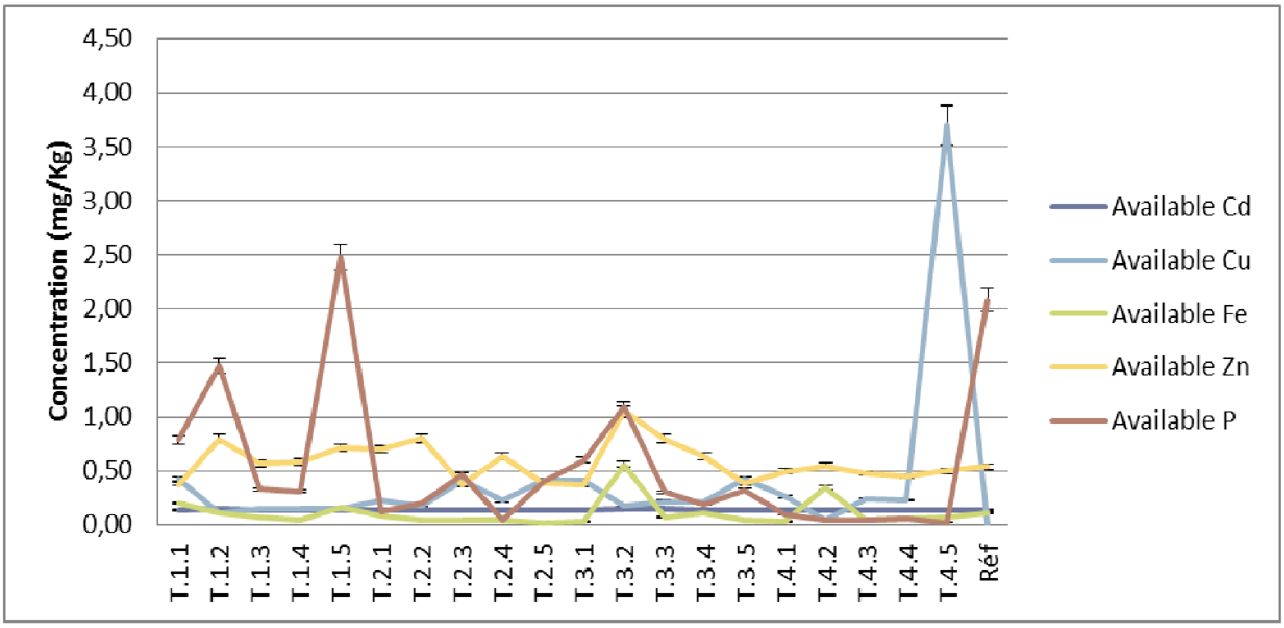

Figure 3: Available metal concentrations of iron mining area (Ait Ammar)

Conclusion

The soil samples collected from the abandoned iron mining of Ait Ammar in Oued Zem region, Morocco, show high concentrations of metals, especially Fe, P, Cd, Cu and Cr which may cause serious environmental impacts.

Total and available metal concentrations in these soils give interesting information on their mobility, bioavailability and toxicity. Furthermore, botanical and microbial toxicity tests give adequate information about metal bioavailability and toxicity (underway results).

Principal Component Analysis (PCA) together with correlation analysis has been conducted in order to demonstrate relationships between pH, OM, TKN and the presence of six metals (Cd, Cr, Cu, Zn, Pb and Fe) and P. The results showed mutually supportive outcomes that Fe in soil was correlated with Zn, P, Cr and Cu, implying that some interactions and/or relations existed between these metals. Knowledge of the level of Cd, Cr and Cu and the effects of soil properties and the presence of other metals is essential to provide an accurate basis for further protection, remediation and reduction of the adverse impacts of these metal contaminations.

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