



Trace Metals Distribution and Fractionation in Soils Around the Abandoned “Ichmoul” Pb-Zn Mill-Mine, North-East of Algeria

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ABSTRACT

In order to assess the environmental impact of soil polluted with trace metals, representative soils were collected surrounding the abandoned Pb–Zn mine mill (SM soils), and the new temporary ore storage site (SS soils), which are located in the vicinity of Medina (Aures), North-east of Algeria. Total digestion has been used to determine the total content of Zinc, Copper, Lead, Cadmium, and Arsenic, then it was analysed by inductively coupled plasma atomic emission spectrometry (ICP-AES). The sequential extraction Tessier scheme was also used to extract the chemical forms of Zn, Cu, and Pb, and their concentrations in each fraction were analyzed by atomic absorption spectrometry. Lead was the most abundant trace metals, its concentration in $\text{mg}\cdot\text{kg}^{-1}$ ranged between (67.20 – 46000), followed by Zinc (26 - 1853), Copper (32 – 495), Arsenic (8 – 116), and Cadmium (0.3 - 7.30). Sequential extraction shows that Zinc was mainly associated with reducible and residual fractions. Copper was bound predominantly with the minerals in the residual fraction, followed by the organic matter. Lead was bound mainly with carbonate fraction in SM soils, while Pb in the SM soils was mainly associated with the reducible fraction. The Pb, Zn, Cu mobility factor was significantly higher in SM soils than in SS soils. These results indicate that anthropic activities related to ore concentration and mining process lead to increased concentration of trace metals in surrounding soils, hence their mobility and bioavailability, this consists a potential risk to the environment and biota.

KEYWORDS Mobility, Bioavailability, Trace Metal, soil pollution, Ichmoul

INTRODUCTION

The environmental problems associated with abandoned mines and concentration process of metal ore are serious and global (Dybowska et al. 2006). As these sites are considered severely polluted by trace metals (Cheng et al. 2018; Liu et al. 2005; Maiz et al. 1997; Nriagu 1996; Razo et al. 2004; Rodriguez et al. 2009; Seklaoui et al. 2016). Moreover, areas affected by former mining operations can be still heavily contaminated up to present, even though the remains of such operations are not really visible (Álvarez-Ayuso et al. 2012). To assess the potential risk of

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pollution, accurate measurements of the TMs content of the neighbouring soil are needed (Maiz et al. 1997). However, the determination of the total concentration of trace metals (TMs) in soils does not provide sufficient information on the environmental risks (Adamo et al. 2002; Alomary and Belhadj 2007; Doelsch et al. 2008; Dybowska et al. 2006; Jena and Franciskovic-bilinski 2013; Maiz et al. 1997; Rauret 1998; Sungur et al. 2015). Trace metals are distributed in the various components of the soil and associated with them in different chemical forms (Hickey and Kittrick 1984; Ahumada et al. 1999; Rodriguez et al. 2009). In environmental studies, mobility and bioavailability of TMs in the soil are determined by their chemical forms, since their conduct in the environmental system depends on their chemical speciation (Adamo et al. 2002; Li and Thornton 2001; Ma and Rao 1997; Rodriguez et al. 2009). So, it is necessary to quantify these potentially bioavailable forms, which are able to accumulate in living organisms and influence their development (Hooda 2010). Two first extractions (Water-soluble and exchangeable) are considered bioavailable; carbonate, reducible, and oxidizable fractions may be possibly bioavailable; while the residual form is essentially not available to both plants or microorganisms (Ahumada et al. 1999; Ma and Rao 1997; Rodriguez et al. 2009). To identify and evaluate the availability of trace metals in soils, both the single extraction (Chaudhary et al. 2016; Hosseiwwnpur and Motaghian 2015; Zhang et al. 2010) as well as the sequential extraction have been used (Ahmadipour et al. 2014; Ahumada et al. 1999; Alomary and Belhadj 2007; Bendicho 1999; Hickey and Kittrick 1984; Howard and Sova 1993; Jordão and Nickless 1989; Kotoky et al. 2003; Lee 2006; Li et al. 1995; Li and Thornton 2001; Lim and Kiu 1995; Ma and Rao 1997; Maiz et al. 1997; Muntau et al. 1993; Murray et al. 1999; Narwal et al. 2008; Nyamangara 1998; Ogundiran and Osibanjo 2009; Qasim and Motelica-Heino 2013; Ramos et al. 1994; Rodriguez et al. 2009; Sarapulova et al. 2017; Schuwirth et al. 2007; Sungur et al. 2015; Tessier et al. 1979; Ullrich et al. 1999; Ure et al. 1993; Vega and Andrade-couce 2016; Xian 1989). Exhaustive information on the origin, speciation, mobility and bioavailability of trace metals under different environmental conditions is given by the sequential extraction method (Nyamangara 1998). The several sequential extraction schemes were proposed, which are primarily different in the nature of the reagents used and the time needed for optimum extraction to identify and determine the availability of soil trace metals. In this study we have adopted sequential extraction proposed by Tessier et al. (1979).

The objectives of this research were (i) to identify the total concentration of trace metals (Pb, Zn, As, Cu and Cd) in polluted soils surrounding the abandoned Pb–Zn mill-mine (SM), and the new temporary ore storage (SS), both located in Ichmoul area (Medina) north-eastern Algeria, (ii) to determine the chemical fractionation of Pb, Zn, and Cu using the Tessier's scheme sequential extraction procedure and (iii) to carry out a preliminary assessment of the environmental risk associated with Trace Metals pollution in soils from the studied area.

MATERIALS AND METHODS

Soil samples were taken in the surroundings of the ‘‘Ichmoul’’ Pb–Zn abandoned mill-mine, located in the vicinity of Medina, in East Batna province, North-Eastern Algeria (Fig. 1). The mineralization is composed mainly of barite, galena, locally accompanied by grey copper, sphalerite, chalcopyrite, pyrite and various oxidation products (Hadouche et al. 2010). It is an old abandoned mine that was exploited from 1932 until 1954, using room and pillar technique. It was considered only as a Pb mine, during its exploitation period, of about 116,000 tons of ore (6% Pb) were extracted (Daoud 1974). Both the mining process and the ore concentration were interrupted in 1954. After 1962, the population of Medina exploited the remains of the old mine for the extraction of lead sold in the souks as K'hol for eye

makeup. As a result, over than 9000 tons of rock waste have been produced and more than 8000 tons of tailings rich in barite and lead have been stored at the mine site (Daoud 1974). In 2013, the national company ENOF resumed the exploitation of Ichmoul mine. After the ore extraction, the company temporarily stores it nearby farmland near next to the road to facilitate its carriage later. Storing the ore in the non-original natural conditions in which it was found, may release large amounts of trace metals such as Lead, Zinc, Cadmium and Copper that can set a potential risk to the environment.

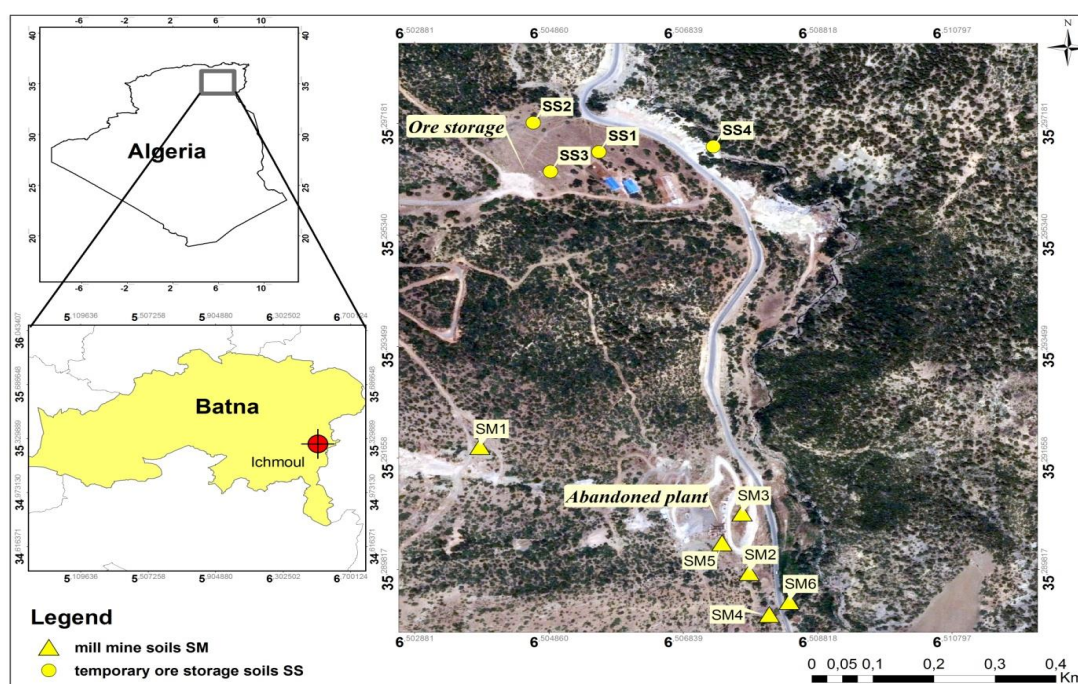


Figure 1. Study area and soil sampling locations

For this research, two sites were selected; the first is next to the old mill-mine, selected points designated as SM1, SM2, SM3, SM4, SM5, and SM6. From 1932 to 1954, this area was occupied by a concentration of Zn and Pb ore for over 20 years. The site was overflowing with milling residue, remains of settling basin, and mining wastes. Several metal-bearing (Pb, Zn, Cu, As, and Cd) mineral species were identified such as Barite, Galena, Chalcopyrite, Cerussite, Smithsonite, Dolomites, Oxides, and silicates (Larachi, 2019). For the second site, the soil samples were collected surrounding the new temporary ore storage site SS1, SS2, SS3, and SS4. Sampling, which took place in 2017, was from the topsoil (0–10 cm), it was stored in transparent plastic bags, and sent to the laboratory. The collected soil samples were air-dried, manually homogenized and sieved using a 2 mm mesh sieve, to remove total plant matter. All samples were stored in plastic jars at room temperature before analysis. A part of the samples was used for the determination of the soil physicochemical properties measurements (pH, organic matter content OM, electrical conductivity EC, and granulometry), while the other part was crushed with a ceramic slurry and sifted by a 250 μm sieve (Mathieu and Pieltain 2003), to be used for both sequential extraction and total acid digestion.

Chemical analyzes were performed with the double deionised water $18.2 \text{ M}\Omega\text{cm}^{-1}$ obtained with (Milli-Q® Advantage A10 System), in preparing both solutions and dilutions. All laboratory glassware were rinsed three times with double deionised water after being placed for 24 h in HNO_3 (10%, v / v).

The principal physicochemical properties (<2 mm fraction) of the soil samples were defined by the following methods: the pH of samples was measured using pH meter (Multi 3430 WTW) in the extracted distilled water (1:2.5 w/v) (NF ISO 10390 2005). To measure soil electrical conductivity EC, an EC-meter (HI 2315 Conductivity Meter HANNA) was used from the extracted suspension (1:5 w/v) according to (NF ISO 11265 1995). The measurement of particle size was carried out using the pipette method (NF X31-107 2003). The organic matter OM concentrations were determined according to (NF ISO 14235 1998). Total carbonate (CaCO₃) was determined according to (NF ISO 10693 2014). Analysis of total concentration of Pb, Zn, Cd and Cu in the soil samples, were determined with multi-acid (HClO₄-HF-NHO₃-HCl) digestion, using GE ICP40B method that provides concentrations for 33 elements trace elements with analysis by inductively coupled plasma atomic emission spectrometry (ICP–AES) according to (DIN EN ISO 11885 2009).

To evaluate TMs fractionation in samples (<250 μm fraction), we applied Tessier's sequential extraction procedure. The five-step sequential extraction method is described in details in (Tessier et al. 1979). Table 1 summarizes the chemical fractions obtained in five steps of the Tessier's scheme. The concentrations of Pb, Zn, and Cu in each fraction were measured using PerkinElmer atomic absorption spectrometry (AAS-PinAAcle 900T). All extraction steps were performed in triplicates and their averages were recorded. Moreover, as a measure of quality control, the concentrations of TMs obtained in the five steps of sequential extraction were summed and compared to their total concentration (Ahmadipour et al. 2014; Qasim and Motelica-heino 2014; Sungur et al. 2015), the recovery for sequential extraction can be obtained as follows:

$$\text{Recovery} = \frac{\text{fractions obtained by the sequential procedure}}{\text{single digestion with strong acids}} \times 100$$

Table 1. Extraction conditions of the Tessier's scheme

Fraction	Extractants and conditions
Exchangeable (F1)	1 M MgCl ₂ (pH=7), 8 ml, 1 h.
Bound to carbonate (F2)	1 M NaOAc (pH=5), 8 ml, 5 h.
Bound to Fe-Mn oxides or Reducible (F3)	0.04 M NH ₂ OH·HCl in 25% HOAc (v/v), 20 ml, 95 °C, 6 h.
Bound to organic matter or Oxidizable (F4)	30 % H ₂ O ₂ , 5 ml and 0.02 M HNO ₃ , 3 ml, 2 h, 85°C, 30 % H ₂ O ₂ , 3 ml and 3.2 M NH ₄ OAc, 5 ml, 85 °C, 3 h.
Residual (F5)	HF, HClO ₄ , HNO ₃

RESULTS AND DISCUSSION

The physiochemical properties of the studied soil samples are summarized in Table 2. The pH was neutral, slightly alkaline at an average 7.75 and 8.12 for the temporary ore storage soils SS, and mill mine soils SM, respectively. Neutral pHs for SS soils could be due to the low amount of carbonate (an average of 1%) and alkaline pHs for SM soils could be attributed to the significant amount of carbonate that ranged between 2,87-22,68%. The average soil electric conductivity was 0.29 mS.m⁻¹, which indicates low salinity for all the studied samples. Organic matter ranged from 4.44 to 17.12 %, the presence of forest vegetation in the mill-mine area and the farmland surrounding the temporary ore storage site might explain the high OM content values which can be considered in the usual range for these types of forest soils. Calcium carbonate content was very low in SS soils samples and ranged from (3,89 - 22.68%) for SM soils samples.

Total metal contents of all soils samples (mg.kg⁻¹, dry matter), concentrations Cd (0.3–7.3 mg.kg⁻¹, median 0.85), Cu (32–495 mg.kg⁻¹, median 46), Pb (67.2–46000 mg.kg⁻¹ median 672)

Zn (153–1853 mg.kg⁻¹, median 240), and, As (8–116 mg.kg⁻¹, median 19.25). The TMs concentrations for most soils samples were higher than: the World Health Organization (WHO) recommendations and Zn 90 mg.kg⁻¹, Pb <35 mg.kg⁻¹, Cu 30 mg.kg⁻¹, Cd 0.35 mg.kg⁻¹ (Tembo et al. 2006). Where Pb showed the highest concentration levels among trace metals, followed by Zn> Cu>Cd>As.

The enrichment factor (EF) and geo-accumulation index have been used widely by several researchers to estimate and quantify the degree of metal pollution in soil, and differentiate between the anthropogenic and natural source of metals pollution. The global average concentration of TMs in shale, soil, or crust has been used to determine background levels (A. Ghrefat et al. 2011; Binta et al. 2013; Çevik et al. 2009; Dragovic and Mihailovic 2009; Karbassi et al. 2016; Loska et al. 2007; Nowrouzi and Pourkhabbaz 2014; Pekey 2006). The world average shale (As 13, Pb 20, Cd 0.3, Cu 45, Zn 95, Fe 47 200 mg.kg⁻¹) obtained from Turekian and Wedepohl (1961) are used in this study.

Table 2. Physicochemical characteristics of the soils, elements total concentrations, and statistical descriptive

	As	Pb	Cd	Cu	Zn	Fe	pH	CaCO ₃	OM	EC	Clay
SS1	20	246	0,6	37	153	39780	7,67	0,55	12,64	0,29	28
SS2	28	740	2,6	45	1199	37120	7,8	0,21	7,64	0,25	38
SS3	19,5	604	0,7	61	207	32130	7,49	0,19	17,12	0,38	24
SS4	19	152,1	0,3	32	108	47600	8,07	3,04	3,95	0,19	16
SM1	116	4095	1,6	495	436	23554	8,13	3,89	4,84	0,23	29
SM2	14	3020	1	47	273	27140	8,11	14,44	5,4	0,37	19
SM3	12,6	6786	1,2	40	425	29640	8,03	22,68	4,44	0,23	13
SM4	8	67,2	0,4	45	26	24255	8,48	2,87	2,56	0,22	6
SM5	22	46000	7,3	121	1853	24000	7,97	13,48	3,78	0,22	8
SM6	10,4	273,6	0,3	67	63	19040	8,02	9,55	2,12	0,18	7
Min	8	67,2	0,3	32	26	19040	7,49	0,19	2,12	0,18	6
Max	116	46000	7,3	495	1853	47600	8,48	22,68	17,12	0,38	38
Median	19,25	672	0,85	46	240	28390	8,03	3,46	4,64	0,23	17.5
mean	26,95	6198	1,6	99	474,3	30425,9	7,98	7,09	6,45	0,26	18.80

CaCO₃ (%), OM (%), clay (%), elements (mg.kg⁻¹), EC (mS.cm⁻¹)

The Enrichment Factor (EF) in soil was calculated as follow:

$$FE = \frac{(C_x / C_{Fe})_{sample}}{(C_x / C_{Fe})_{shale}}$$

Where (C_x/C_{Fe}) sample is the ratio of the concentration of the concerned element (C_x) to the Fe concentration (C_{Fe}) in the soil sample, and (C_x/C_{Fe}) shale is the ratio of the same element to Fe in average shale. Where, EF< 1.5 indicates no enrichment, 1.5 <Ef < 3 minor enrichment, 3<EF<5 moderate enrichment, 5<EF<10 high-moderate enrichment, 10<EF<25 high enrichment, 25<EF<50 very high enrichment and EF > 50 extremely high enrichment (Chen et al. 2007).

To estimate the metal pollution intensity in this study, we have calculated the geo-accumulation index (*I_{geo}*) as follow:

$$I_{geo} = \text{Log}_2 \left[C_n / (1.5 * B_n) \right]$$

Where C_n is the concentration of concern TMs in soil, and B_n is the concentration of the same elements in the shale (Muller 1979). The geo-accumulation index (*I_{geo}*) divides the degree of metal pollution into seven classes as follow: *I_{geo}* < 0 indicates uncontaminated, 0

$<I_{geo} < 1$ uncontaminated to moderately contaminated, $1 < I_{geo} < 2$ moderately contaminated, $2 < I_{geo} < 3$ moderately to heavily contaminated, $3 < I_{geo} < 4$ heavily contaminated, $4 < I_{geo} < 5$ heavily to extremely contaminated, $I_{geo} \geq 5$ extremely contaminated.

The enrichment factor and geo-accumulation index were calculated, the results are shown in Table 3.

For enrichment factor, Lead shows very high to extremely high enrichment except for samples SS4 and SM4 which Pb appears high-moderate enrichment, indicating mainly anthropogenic origin. Whereas, Zinc and Cadmium are high to very high enriched in soils samples in vicinity of the pollution source (SS2, SM1, SM2, SM3, SM5); and no enriched or moderate enriched away from the source of pollution (SS1, SS4, SM4, SM6). Arsenic and copper show much lower values of the enrichment factor, either no enriched or little to moderate enriched in all studied soil samples except for the sample SM1, which was highly enriched by As and Cu due to its nearness to mine tailing and the ore heap.

Table 3. Enrichment factor and Geo-accumulation index (I_{geo}) value of soil sample

Sample	As	Pb	Cd	Cu	Zn
EF					
SS1	1,83	14,59	2,37	0,98	1,91
SS2	2,74	47,05	11,02	1,27	16,05
SS3	2,20	44,36	3,43	1,99	3,20
SS4	1,45	7,54	0,99	0,71	1,13
SM1	17,88	410,30	10,69	22,04	9,20
SM2	1,87	262,61	5,80	1,82	5,00
SM3	1,54	540,32	6,37	1,42	7,12
SM4	1,20	6,54	2,59	1,95	0,53
SM5	3,33	4523,33	47,86	5,29	38,36
SM6	1,98	33,91	2,48	3,69	1,64
I_{geo}					
SS1	3,98	7,60	-1,08	4,87	6,92
SS2	4,57	9,29	1,14	5,25	9,99
SS3	4,26	9,21	-0,54	5,90	7,66
SS4	3,65	6,65	-2,33	4,40	6,16
SM1	7,28	12,42	1,10	9,37	9,19
SM2	4,02	11,77	0,21	5,77	8,31
SM3	3,74	12,81	0,35	5,41	8,82
SM4	3,38	6,45	-0,95	5,87	5,08
SM5	4,85	15,88	3,26	7,31	11,25
SM6	4,10	8,82	-1,01	6,79	6,70

The results of I_{geo} show all soil sample extremely contaminated by Lead and Zinc. This is due to the activity associated with the processes of extraction and storage of the ore, and the concentration of these two metals in this area. The values of I_{geo} for Arsenic and Copper demonstrate heavy or extremely heavy contamination. Whereas, the soil samples were uncontaminated or moderately contaminated by Cadmium, except for SM5 which showed heavy Cd contamination.

We selected Zn, Cu, and Pb to examine their chemical distribution in the soil fractions. The results of the sequential extraction and recovery test are summarized in Table 4, and Fig 2.

Zinc Zn recovery was between 98.74 and 108.62 % for both SS soils and SM soils which can be considered as acceptable compared to the studies of (Li and Thornton 2001; Qasim and Motelica-Heino 2013; Sungur et al. 2015). Zn fractionation is dominated by the reducible fraction F3 (ranging between 33.64-47.82% and 38.34-61.42% of total Zn concentrations for the SS soils and SM soils, respectively), and the residual fraction F5 (ranging between 39.88-

49.18% and 17.07-37.49% for the SS soils and SM soils, respectively). Zinc in oxidizable fraction F4 was also appreciable constitute between 10.74 and 15.13% of the total Zn for all studied samples, this indicates that these three solid phases are of a major importance as they are Zn carriers in this study. Carbonate fraction contributed by 7.59 to 14.83% for SM soils and 0.48-1.14% for the SS soils, while the exchangeable fraction of the Zn was of a minor amount ranging 0.09 to 0.42%. Xian 1989 found that the exchangeable and carbonate forms strongly controlled Zn absorption by cabbage plants (*Brassica oleracea*) more than the total content of TMs in the soil. In this study, the zinc present in non-residual fractions was significant from the standpoint of zinc mobility and bioavailability, this is consistent with what was indicated (Sungur et al. 2015), since Zn concentration in the grains were similar to that of the acido-soluble (F1+F2) and the reducible fractions of soil samples. Therefore, they concluded that high levels of the TMs in these fractions can easily transfer to the food chain.

Data in Fig 2 indicate that general distribution of Zn into the various fractions for SM soils and SS soils followed the order: F3~F5>F4>F2>F1. The fractionation of zinc in our study is consistent with studies (Hickey and Kittrick 1984; Jordão and Nickless 1989; Kotoky et al. 2003; Li et al. 2000; Ma and Rao 1997; Maiz et al. 1997; Ogundiran and Osibanjo 2009; Ramos et al. 1994).

Table 4. Fractionation of Zn, Cu, and Pb in SS temporary ore storage soils and SM mill-mine soils obtained by Tessier's scheme (concentration in mg.kg⁻¹ ± standard deviation, and in brackets, percentage of the total)

Samples and trace metals	F1	F2	F3	F4	F5	Σ5 fractions	Recovery %	
Zn	SS1	0,68 ± 0,24 (0,42)	2,66 ± 0,48 (1,63)	54,76 ± 4,29 (33,64)	24,63 ± 4,42 (15,13)	80,07 ± 11,18 (49,18)	162,8	106,4
	SS2	1,12 ± 0,36 (0,09)	17,44 ± 1,14 (1,47)	566,13 ± 27,26 (47,82)	127,11 ± 20,35 (10,74)	472,10 ± 43,93 (39,88)	1183,9	98,74
	SS3	0,72 ± 0,21 (0,33)	6,83 ± 0,82 (3,15)	87,39 ± 7,46 (40,28)	29,32 ± 3,35 (13,51)	92,70 ± 9,38 (42,73)	216,96	104,81
	SM1	1,64 ± 0,94 (0,35)	35,94 ± 3,90 (7,59)	290,87 ± 20,80 (61,42)	64,28 ± 7,64 (13,57)	80,83 ± 5,13 (17,07)	473,57	108,62
	SM2	0,91 ± 0,20 (0,30)	4,06 ± 3,22 (14,83)	127,36 ± 21,61 (42,87)	42,60 ± 2,96 (14,34)	82,14 ± 8,50 (27,65)	297,07	108,82
	SM3	0,84 ± 0,19 (0,20)	45,92 ± 5,91 (10,71)	164,35 ± 16,57 (38,34)	56,81 ± 11,31 (13,25)	160,71 ± 37,47 (37,49)	428,63	100,85
Cu	SS1	1,00 ± 0,52 (2,51)	1,19 ± 0,42 (2,99)	1,45 ± 0,39 (3,63)	4,90 ± 1,80 (12,31)	31,28 ± 2,32 (78,56)	39,81	107,59
	SS2	0,99 ± 0,21(2,00)	1,62 ± 0,48 (3,28)	5,75 ± 2,34 (11,59)	16,86 ± 3,36 (34,01)	24,35 ± 2,94 (49,12)	49,57	110,16
	SS3	1,26 ± 0,26 (1,88)	1,42 ± 0,13(2,11)	3,33 ± 0,95 (4,95)	16,78 ± 3,32 (24,90)	44,60 ± 6,36 (66,17)	67,4	110,49
	SM1	2,02 ± 0,55 (0,37)	76,40 ± 12,22 (13,97)	327,39 ± 22,04 (59,88)	81,13 ± 10,70 (14,84)	59,81 ± 9,54 (10,94)	546,76	110,46
	SM2	1,18 ± 0,41 (2,32)	2,95 ± 0,24(5,78)	5,89 ± 1,62 (11,54)	8,70 ± 3,47 (17,05)	32,29 ± 2,23 (63,31)	51	108,52
	SM3	0,92 ± 0,09 (2,11)	2,70 ± 0,98 (6,19)	1,93 ± 0,29 (4,42)	6,71 ± 2,10 (15,39)	31,35 ± 2,38 (71,90)	43,61	109,02
Pb	SS1	0,87 ± 0,38 (0,38)	17,63 ± 3,82 (7,79)	120,42 ± 14,82(53,17)	52,62 ± 8,88 (23,23)	34,94 ± 1,23 (15,43)	226,49	92,07
	SS2	2,11 ± 0,28 (0,32)	93,56 ± 10,78 (13,99)	378,42 ± 13,33 (56,59)	127,03 ± 13,25 (19,00)	67,61 ± 5,07 (10,11)	668,72	90,37
	SS3	2,77 ± 0,50 (0,44)	84,72 ± 9,65 (13,53)	284,27 ± 20,78 (45,41)	173,16 ± 12,58 (27,66)	81,08 ± 2,52 (12,95)	625,99	103,64
	SM1	41,29 ± 9,12 (1,10)	1652,16 ± 221,99 (43,91)	1671,18 ± 108,40 (44,42)	319,27 ± 83,32 (8,49)	78,54 ± 5,32 (2,09)	3762,44	91,88
	SM2	34,18 ± 1,29 (1,22)	1579,16 ± 137,63 (56,23)	951,52 ± 21,02(33,88)	163,43 ± 26,83 (5,82)	80,02 ± 10,07 (2,85)	2808,3	92,99
	SM3	101,81 ± 15,05 (1,66)	3200,50 ± 190,60 (52,20)	2272,91 ± 68,61 (37,07)	460,23 ± 21,71 (7,51)	95,99 ± (1,57)	6131,43	90,35

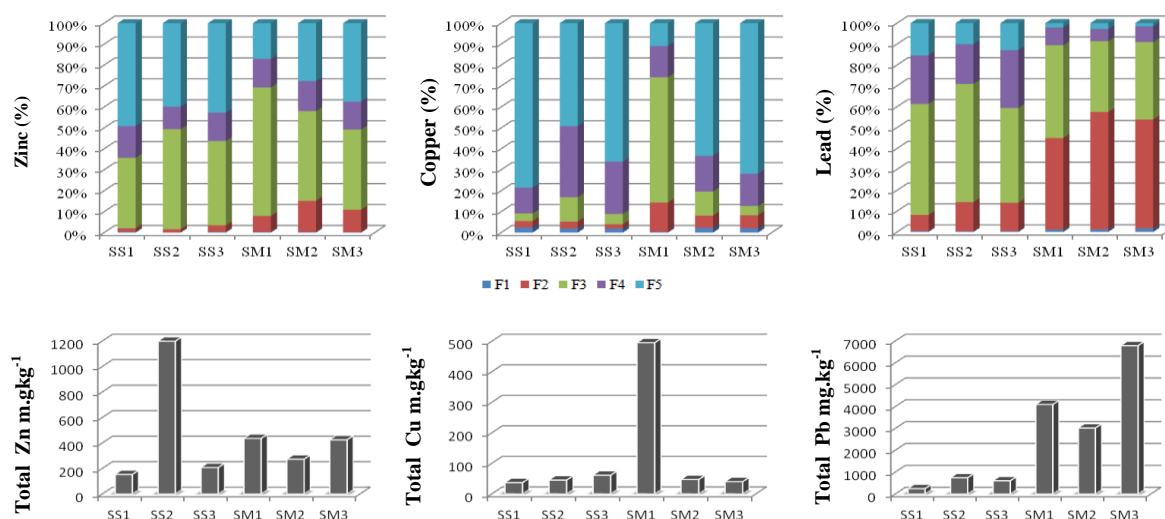


Figure 2. Total and Fractionation of Zn, Cu, and Pb in temporary ore storage soils (SS soils), and mill-mine soils (SM soil). Tessier's scheme: F1 (exchangeable fraction), F2 (bound to carbonate), F3 (reducible), F4 (oxidizable), F5 (residual).

Table 5. Pearson's correlation (r) between trace metals TMs concentrations in different fractions of soils and physicochemical characteristics of the soils

	Variables	Total	Clay	pH	CaCO ₃	OM
Zn	Exchangeable	0,386	0,386	0,601	-0,122	-0,57
	Bound to Carbonate	0,037	-0,570	**0,915	*0,842	*-0,877
	Bound to Fe-Mn oxyde	**0,975	0,685	0,187	-0,241	-0,382
	Bound to Organic matter	**0,991	0,593	0,215	-0,12	-0,433
	Residual	**0,966	0,599	-0,096	-0,2	-0,164
Cu	Exchangeable	**0,960	0,189	0,365	-0,248	-0,186
	Bound to Carbonate	**0,999	0,201	0,504	-0,14	-0,384
	Bound to Fe-Mn oxyde	**0,999	0,222	0,489	-0,162	-0,371
	Bound to Organic matter	**0,990	0,306	0,407	-0,249	-0,301
	Residual	*0,876	-0,004	0,182	-0,204	0,019
Pb	Exchangeable	**0,983	-0,746	0,67	*0,912	-0,675
	Bound to Carbonate	**0,992	-0,745	0,761	**0,921	-0,745
	Bound to Fe-Mn oxyde	**0,989	-0,595	0,762	0,792	-0,754
	Bound to Organic matter	**0,943	-0,594	0,562	0,726	-0,573
	Residual	0,718	-0,544	0,433	0,636	-0,411

**Correlation is significant at the level <0.01

* Correlation is significant at the level <0.05

The analysis of statistical data showed that the distribution of Zinc in last three chemical fractions is directly related to the total Zn content, where a statistically positive correlation at the level of $P < 0.01$ was detected between Zn total concentration and reducible F3, oxidizable F4, and residual F5 fractions (Table 5), this shows that zinc distributions in these three chemical forms are influenced by the total zinc content of the soils. A positive correlation was observed between the clay contents of samples and residual fraction F5 ($r = 0.701$), carbonate fraction (F2) shows a positive correlation with CaCO₃ content ($r = 0.842$) and pH value ($r = 0.915$); calcium carbonate is a powerful absorbent to produce complexes with Zn as double salts (CaCO₃.ZnCO₃) (Li et al. 2000); also that pH value was a factor in soluble Zn. These results agree with study of McLean and Bledsoe 1992; where they explained that Zinc is readily adsorbed by clay minerals, carbonates, or hydrous oxides, since Zinc hydrolysis at $pH > 7.7$ and the hydrolyzed Zn is strongly adsorbed to soil surfaces, therefore control the zinc

mobility. This can be observed in SS soils, where the sample SS2 has the largest total zinc concentration (1199 mg.kg^{-1}), although it is relatively far from the ore storage site compared to SS1 and SS3. This can be due to the relatively low topographic locations in the direction of water flow, and the high clay containment ratio (38%), these factors enable zinc to accumulate in this site. The negative correlation between the carbonate fraction F2 and the organic matter ($r = -0.877$) can be explained by the increase of the amount of the organic matter that is negatively affected by carbonate content, and thus the amount of zinc associated with carbonate F2 will be affected.

Copper Cu recovery ranged between 107.59 and 110.49 % for all studied samples; this recovery rate was satisfactory compared to the study of (Ma and Rao 1997; Sungur et al. 2015). Cu was primarily bound to the residual fraction ranging from 49.12 and 78.56% of the total Cu concentrations for all the studied samples (Fig. 2). This was observed in several studies (Lee 2006; Ma and Rao 1997; Ramos et al. 1994), except for SM1 which the reducible fraction F3 had the greatest amount of Cu 59.88%, such it could be due to the nature of this soil sample formed by mine tailing. Also, a significant amount of Copper was associated with organic fraction, ranging from 12.31 and 34.01% of total Cu concentrations, this applies to the results of Hickey and Kittrick 1984 which showed that copper has an important association with the organic matter fraction. The next most considerable fraction was the reducible fraction ranging from 3.63 and 11.59%. The accumulation of copper in the Fe-Mn oxide fraction may be due make it bioavailable, as Sungur et al. 2015, found that the Cu concentrations of corn grains were very similar to the Fe-Mn oxide fraction of soil samples. The role of the carbonate fraction (F2) fraction was significant, ranging from 2.11 to 13.97 % for the total content of Cu, while the exchangeable fraction (F1) represented the lowest amount ranged between 0.37 and 2.51% of total content of Cu (Table 4). The fractionation of copper in each fraction followed the order: $F3 > F4 > F2 > F5 > F1$, for the SM1, while it followed the order: $F5 > F4 > F3 > F2 > F1$ for SM samples (Fig. 2). Results from this study correspond with other data in the literature (Hickey and Kittrick 1984; Jordão and Nickless 1989; Ma and Rao 1997; Ramos et al. 1994).

Moreover, Pearson's correlation showed a positive correlation statistically at the level of ($P < 0.01$), between total Cu concentration and different chemical fractions (Table 5); this shows that copper distributions in various chemical forms are related directly to the total copper content in the soils, this relationship is also mentioned in the study of (Ogundiran and Osibanjo 2009). The distribution of copper in the various parts of the soil did not show any significant correlation to calcium carbonate, organic matter content, or pH. This can be explained the largest amount of Cu that was bound to the primary minerals in the residual fraction, or to Fe-Mn oxides.

Lead (Pb) recovery was ranged between 90.35% and 103.64% that could be acceptable compared to the study of (Li et al. 1995; Qasim and Motelica-heino 2014; Sungur et al. 2015). Pb fractionation differed in both SS soils and SM soils (Fig 2 and table 4). In SS soils, Lead was mainly associated with a reducible fraction F3 that contains ranged from (45.41-56.59%); as Pb has a high stability to be concentrated in this fraction (Ramos et al. 1994), where the Fe-Mn oxide is significant metal scavengers, especially at a high pH level (Tipping et al. 1986). However, it should be noted that the oxide association with trace metals does not guarantee its immobilization in the soil, thus the metals attached to the Fe-Mn oxides remain labile and can easily be released when the oxides are decomposed under reduced conditions (Chlopecka 1996). This association of Pb with Fe-Mn oxides has been reported previously (Jena and Franciskovic-bilinski 2013; Maiz et al. 1997; Rodriguez et al. 2009). The next most abundant fraction of Pb in these soils is the oxidizable fraction ranged from 19.00 to 27.66%, while the carbonate and residual fraction which ranged between (7.79-13.99%), and (10.11-15.43%)

respectively. A very minor amount of lead is in the exchangeable phase (<1.0%). While at SM soils are shown that Pb was mostly associated with carbonate ranged from 43.91-56.23% of Pb total. This is consistent with the thermodynamic prediction that Cerussite (PbCO_3) would be the prevailing lead mineral under the eh-pH conditions of mine tailing areas (Brookins 1988). Larachi's results (2019) showed that the Cerussite is a secondary mineral phase which is found in the waste rocks in Ichmoul. The high amount of carbonate fraction F2 can indicate environmental problems as carbonates can dissolve readily with soil characteristics changing. These results agree with the study Nasrabadi et al (2010) that lead is mainly present in the acid-soluble part (F1+ F2) of the Haraz River sediments. The next most abundant fraction was a reducible fraction ranging between 33.88 and 44.42% of total Pb content, these results similar to studies (Howard and Sova 1993; Li and Thornton 2001; Qasim and Motelica-heino 2014). The oxidizable fraction was also important and comprised between 5.82-8.49% of the total Pb content. As a small amount of Pb was associated with the residual fraction ranged from 1.57-2.85%; since the galena is usually the main source of Pb in the Lead ores, where the oxidative dissolution of galena dominates at pH 6 and 8 to form anglesite (PbSO_4) (Heidel and Tichomirowa 2011; Issaad et al. 2019). In addition, the dominant forms of Pb in the air particles surrounding of lead mining and smelting areas are in the form of PbSO_4 , PbO, and PbS, (Clevenger et al. 1991), this can be explain the small Pb amount in the residual fraction in the all studied samples especially in SM soils. The exchangeable fraction forms the rest of the Pb content, ranged from 1.10-1.66%. Although this ratio can appears low (<2%), the concentration of Pb in this fraction is considerable (34.18 to 101.81 mg.kg^{-1}), this can pose a great risk to the environment and living organisms, where it was reported that increased plant Pb uptake is related to increased exchangeable Pb in the soil. Thus, the bioavailability of lead in soil can be valued using the Pb in the exchangeable fraction (Li and Thornton 2001). The observed results of Pb in the exchangeable fractions and carbonates in the surrounding SM and SS soils are evidence of high contamination of the environment with mobile and bioavailable Pb resulting from the abandoned mill-mine activity and the new temporary storage ore, consequently, it is reasonable to foretell plant Pb uptake, and leaching into the groundwater. Distribution of Pb among various fractions in SS soils followed the order $F3 > F4 > F5 > F2 > F1$, and it was as follows $F2 > F3 > F4 > F5 > F1$ in SM soils.

Pearson correlation shows that there were positive correlations at the level of ($P < 0.01$) of total Pb, with exchangeable F1 (*0.983), carbonate F2 (*0.992), reducible F3 (**0.989), and oxidizable fraction F4 (**0.943); this may show that Lead tends to accumulate in the mobile fractions under physicochemical conditions of mining areas, which can become available after changes in soil environmental conditions. In addition, the carbonate content shows a significant positive correlation at the level of $p < 0.01$ with exchangeable Pb ($r = *0.912$), carbonate fraction ($r = **0.921$), and the total Pb concentration ($r = *0.872$). It may be attributed that calcium carbonates can react as a potent absorbent for Lead and it can compose a PbCO_3 with increased pH value and carbonate. Thus the carbonate content can increase mobility and bioavailability of Pb due to a positive correlation with Pb in an exchangeable fraction F1 (Table 5).

The mobility factor MF is known as the potential movement of TMs out of the contaminated environment, is based on the relative content of elements that are weakly bound to soil components. The relative index of trace metals mobility was estimated as (Kabala and Singh 2001; Khorasanipour and Aftabi 2011; Ogundiran and Osibanjo 2009; Qasim and Motelica-heino 2014) on the basis of the following equation:

$$MF = \frac{F1 + F2}{F1 + F2 + F3 + F4 + F5} \times 100$$

The elevated MF values are considered as indications of high mobility and bioavailability of trace metals in soils (Ma and Rao 1997). The mobility factor of TMs was calculated and the results are shown in Table 6 and Fig 3. The results indicate that the mobility factors of Zn, Cu, and Pb were higher in the SM soils, than in the SS soils. The MF in SS soils was an average of 2.37%, 4.91%, and 12.15% for Zn, Cu, and Pb, respectively; while in the SM soils the MF for Pb was very high, with an average of 52.11%, and it was significant for Zn, and Cu with an average 11.33%, 10.25%, respectively.

Table 6. Mobility factor of trace metals in SS and SM soil samples

Sample	Zn%	Cu%	Pb%
SS1	2,05	5,5	8,17
SS2	1,57	5,27	14,31
SS3	3,48	3,98	13,98
SM1	7,94	14,34	45,01
SM2	15,14	8,1	57,45
SM3	10,91	8,3	53,86
Mean SS \pm SD	2,37 \pm 0,99	4,91 \pm 0,82	12,15 \pm 3,45
Mean SM \pm SD	11,33 \pm 3,62	10,25 \pm 3,55	52,11 \pm 6,40

SD Standard deviation

Furthermore, Pb shows a significant high total content (Fig. 2), and high mobility factor (Fig. 3), especially in SM soils compared to SS soils. That corroborates the mobile nature of lead in the soil surrounding the former mining activities.

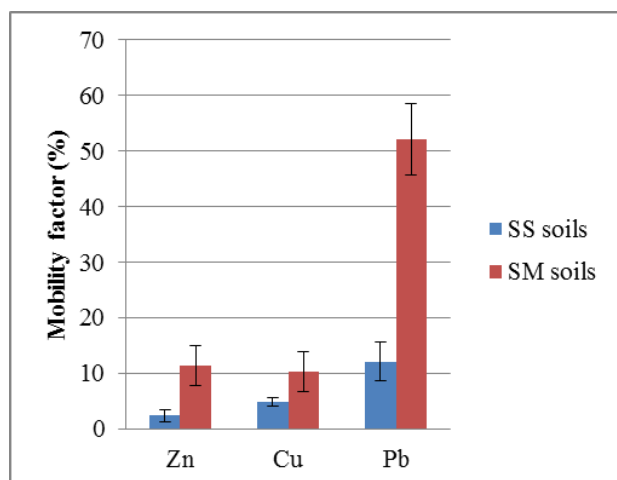


Figure 3. Mobility factor of trace metals from the SS and SM soils

CONCLUSION

The results of this study showed a high concentration of trace metals in the surrounding soil of the abandoned Ichmoul Pb-Zn mill-mine especially the SM soils compared to SS soils. The total trace metals were high for Pb, Zn and Cu than for As and Cd suggesting the order of concentration of metals is Pb>Zn>Cu>As>Cd. The results of the geo-accumulation index (*I_{geo}*) and enrichment factor (EF) proved high TMs pollution especially Pb and Zn in the studied area. Fractionation of TMs obtained by Tessier's scheme shows that Zn was mainly associated with Fe-Mn oxide and residual fractions. Copper was found mainly in the residual fraction, while Lead was mostly associated with carbonate fraction in SM soils and was

principally associated with the reducible fraction in the SS soils. The stability of trace metals increases according to the increase in the extraction step according to the following; exchangeable < carbonate-bound < Fe-Mn oxide-bound < organic matter-bound < residual; Thus, the lead shows high mobility due to a large amount of Pb in exchangeable and carbonate fractions, followed by Zn, while Cu was shown high stability. The results of our study concluded that there is high contamination with trace metals in the soil surrounding the abandoned Ichmoul mill-mine especially lead and zinc, which are potentially bioavailable and have a significant environmental risk in this area.

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CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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