Environ Geochem Health (2020) 42:3529–3542
https://doi.org/10.1007/s10653-020-00595-2

ORIGINAL PAPER

Biogeochemical assessment of the impact of Zn mining activity in the area of the Jebal Trozza mine, Central Tunisia

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Received: 21 June 2019 / Accepted: 1 May 2020 / Published online: 12 May 2020

Abstract Soil pollution associated with potentially toxic elements (PTEs) from mining residues is a significant problem worldwide. The decommissioned Jebal Trozza mine, located in central Tunisia, may pose a serious problem because of the possible high concentrations of PTEs present in its wastes. This mine is a potential source of contamination for agriculture in this area due to both direct causes (pollution of agricultural soils) and indirect causes (pollution of sediments that accumulate in a dam used for irrigation). The aim of the study reported here was to assess the effects of local mining activity in two respects: (1) in terms of soil quality, as determined by soil edaphological parameters and PTEs contents in the mining wastes and local soils; and (2) in terms of biological quality, as evaluated by quantification of enzymatic activity as an indicator of bacterial activity in soils and wastes. The mine tailings contained high levels of Pb (1.83–5.95%), Zn (7.59–12.48%) and Cd (85.95–123.25 mg kg^{-1}). The adjacent soils were also highly contaminated with these elements, with average concentrations of Pb, Zn and Cd that exceeded the European standard values for agricultural soils (3, 300 and 300 mg kg^{-1} for Cd, Pb and Zn, respectively). Enzymatic dehydrogenase showed zero activity in waste piles and very low activity in PTE-contaminated soils, but this activity returned to normal values as the pollution decreased, thus demonstrating the effect that the contamination load had on the health of the studied soils. A Statistical Factor Analysis clearly distinguished three groups of samples, and these are related to the influence that mining on the soils and sediments had on the PTE concentrations and their effects on the biological quality of the soil. An environmental assessment based on the enrichment factor criteria indicated risk levels that varied from strongly to severely polluted. The risk appears to be greater close to the mine, where the highest PTE levels were determined.

Keywords Contamination · Enzymatic activity · Heavy metals · Potentially toxic elements · Mobility · Soil mining

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Introduction

Mining waste management is currently a major environmental concern, since mine wastes represent potential sources of contamination (Levy et al. 1997; Sheoran and Sheoran 2006; Babbou-Abdelmalek et al. 2011) due to their composition. These wastes usually contain high concentrations of potentially toxic elements (PTEs: Pb, Zn and Cd, among others), and such elements may become available in the environment unless appropriate reclamation is carried out on the corresponding piles, which is often not the case. Furthermore, in areas affected by mining activity, the metal load may be a greater concern than acidity in terms of environmental damage (Kuyucak 2002). Large quantities of host rock, nonmarketable ores and mine tailings have accumulated in the proximity of decommissioned mining sites, and these materials still remain in areas that are often unsuitable for storage in the absence of management, including monitoring and rehabilitation (Razo et al. 2004; Dold 2008). This situation makes the waste more responsive and leads to a serious risk of metal contamination, which in turn threatens the environment and human health. Numerous factors have an influence on the composition and related reactivity of the residues, and these include the composition of the ore and gangue, together with the mineralogical processes applied to the ore (Lottermoser 2007).

Metallic contaminants can migrate from mine sites to various environmental compartments, i.e., water, air and soil, via several physicochemical transfer mechanisms such as transport in solution after chemical alteration, transport in suspension by water and air and transport by different anthropogenic activities (Querol et al. 2000; Moreno et al. 2007; Higueras et al. 2016; Sun et al. 2018). The presence of toxic elements in soils has a considerable impact on the environment by causing damage to microflora, flora and fauna, thus restricting soil use (Adriano 1986; Higueras et al. 2016). Besides, mining sites, whether they are active or not, represent important sources of such contamination involving potentially toxic metallic elements (Higueras et al. 2016, 2019). Furthermore, such mining-related contamination may persist for centuries after mine closure (Hudson-Edwards et al. 1999a, b, c; Coulthard and Macklin 2003) and may become chronic depending on the contaminant and the nature of the receiving environment (persistence). This situation is the norm in mining sites as these contaminants are associated with elements that are difficult to remove by natural processes.

There is now an awareness in North Africa of the risks associated with former mining activities (El Adnani et al. 2007; Barkouch and Pineau 2016 in Morocco; Mlayah et al. 2009; Boussen et al. 2013; Ayari and Charef 2016; and Khelifi et al. 2019 in Tunisia; Ali et al. 2016 in Northern Egypt). This awareness is already widespread in the world, and numerous environmental studies have been carried out to assess contamination related to mining activities, the dynamics of trace elements in the short and long terms (mobility and bioavailability) and the risks of release and dissemination of PTE, which may favor their incorporation into food chains (Rodríguez et al. 2009; Rocha et al. 2011; Martínez-Sánchez et al. 2014; Reimann et al. 2015; Antoniadis et al. 2017, among others). The work described here concerns the potential impact of PTEs on soils affected by mining activity, and the results provide new insights into the role of these contaminants in microbiological activity. The study was carried out at the former mining site of Jebel Trozza (the Kairouan region, Central Tunisia). This old Pb/Zn mine is located in a rural district surrounded by agricultural land (olive trees), and it provides significant amounts of sediments to a local dam that is used for irrigation. Despite the huge amount of mining waste and its potential risks, studies have not previously been carried out on the impact of mining activities in the area. Thus, it is necessary to characterize the source of contamination and to identify metal contaminants and their impact on the quality of the surrounding soils. In addition, an assessment of soil health, as outlined by USDA (2018), was carried out based on the determination of dehydrogenase enzyme activity, which, as a main hypothesis of this work, provides important information about the biological characteristics necessary to maintain soil fertility and soil health. The results obtained provide an insight into the relationship between mining-induced changes and microbiological activity.

Materials and methods

Description of the site

The old Pb/Zn mine of Jebel Trozza is located approximately 15 km to the South-West of Haffouz, in central northern Tunisia, approximately 150 km SSW from Tunis (Fig. 1). The tailings present in the area are a result of mining activity carried out between the years 1907 and 1937 (Sainfeld 1952). The buildings, excavations and tailings have been totally abandoned since the mining activity ceased and recovery measures have not been carried out.

The physiography of the area is hilly with significant altitudinal variations. The mine is crossed by an unnamed stream that runs from West to East and is a tributary of the Ben Zitoun stream. The outflow of the mine stream to the Ben Zitoun stream occurs at the so-called El Houareb dam, which was originally built to provide drinking water for the Sahel region but is now used for irrigation. Google Earth images show a significant accumulation of sediments in the dam, most of which very probably come from the mine area (Fig. 2).

The meteorology of the area is characterized by a semiarid climate. Meteorological data between 2003 and 2013 (INM, Institut National de Météorologie 2015) indicate that the average annual rainfall varies between 201.8 and 385 mm. The highest monthly average precipitation is in September (49.48 mm) and the driest month of the year is July, with an average of 5.46 mm. The lowest temperature is recorded in February (12.82 °C), while the month of July shows the highest average temperatures, which reach 31.26 °C. The prevailing wind blows from the north and northwest sector in winter and from the south and southwest sector in summer.

The Jebel Trozza deposit is located along the northern margin of the so-called Hajeb El Ayoun basin. The mineralization corresponds to vein filling, hosted in dolomites of Late Albian age. The mineralogy of the ore, as described by Bouhlel and Fortuné (1985), includes galena (PbS), cerussite ($PbCO_3$) and hemimorphite ($Zn_4(Si_2O_7)(OH)_2 \cdot H_2O$). The latter is usually a secondary mineral of Zn that is formed due to weathering of sphalerite (ZnS), which has not been described in this mine area. The total mine production reached 91,476 tons of lead concentrate and 5398 tons of zinc concentrate. The contents recorded for the concentrates were 55% and 30% for Pb and Zn, respectively. The latter was produced exclusively by zinc oxide mineralization, and the production of zinc

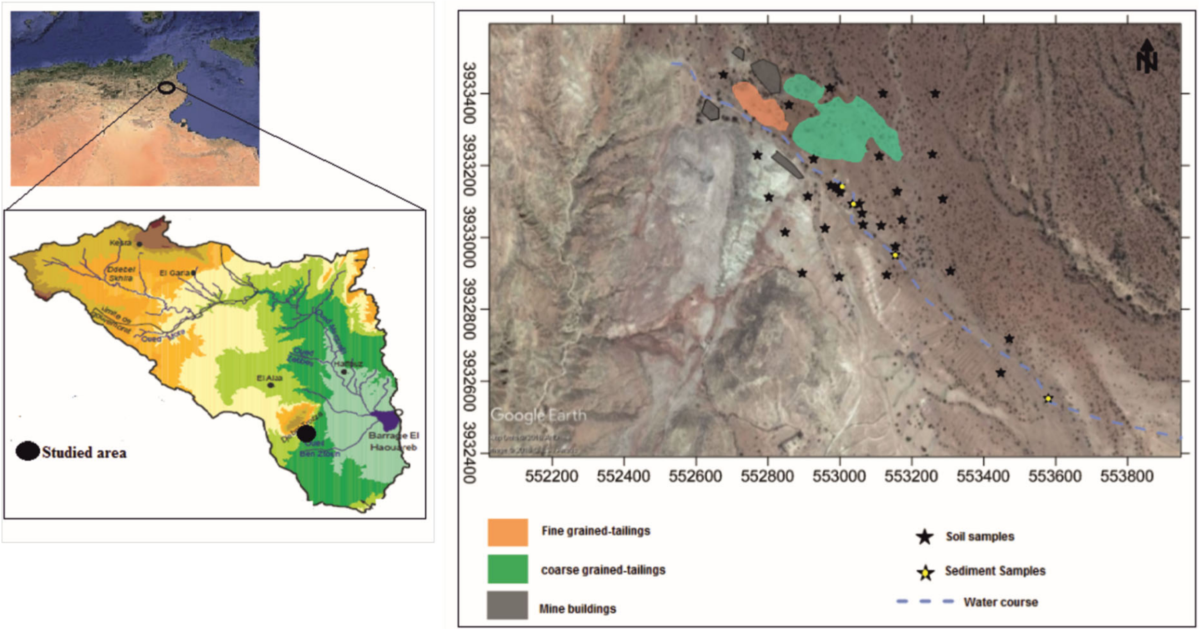

Fig. 1 Location of the mining area in North-Central Tunisia (left) and Google Earth image of the area (right) showing the locations of sampling sites and mine wastes

Fig. 2 Satellite image of the area showing the mining sediments flooding the El Houareb dam

sulfides was not reported at this mine. Due to the low efficiency of the process for the concentration of hemimorphite, the tailings contain substantial zinc concentrations, which are estimated to be more than 10% (ONM 2005).

Sample collection

Mine waste and soil sampling

Two major types of mine waste were clearly separated in the decommissioned mine area, namely fine-grained residues (most probably corresponding to residues from the mineral concentrating process) and coarse-grained residues (probably corresponding to mine sterile, which still contains minor quantities of ore). The distributions of these two types of residues are shown in Fig. 1.

Two sampling surveys were conducted, and these included sampling of tailings and soils from the Jebel Trozza mine site. The location from which each sample was taken (Fig. 1) was recorded using GPS (Global Positioning System) technology.

Waste sampling was carried out from two types of tailing residues: Four samples were taken from the fine fraction tailings (DF) (from the top and the base of the tailings), and five samples were taken from the coarse-fraction tailings (DG) (Fig. 1). In order to evaluate the regional effects of the abandoned mine residues and to estimate the lateral dispersion, a total of 35 sediment and soil samples were collected considering the mineral extraction location and the most representative areas. In the first stage, 12 soil samples and four sediment samples were taken randomly in the immediate proximity of the mining area. The additional samples (19 samples) were collected in the second stage using a regular grid that included samples located far from the mine area. A baseline sample (T_0) was also collected outside the mining area. All samples were collected after removing the first layer of surface soil (2 cm), and they correspond to the top 20 cm, according to the criteria of Spaargaren and Nachtergaele (1998). These authors considered that the most important part of the soil profile for the control of degradation is the topsoil and that this is also the best way to evaluate the incorporation of trace elements in soil profiles.

Sample preparation and analysis

In the laboratory, samples were air-dried, transferred to clean polyethylene bags and subsequently sieved to < 2 mm to remove the gravel. The sieved samples were used to determine the edaphological parameters, including reactivity (pH), electrical conductivity (EC) (which is considered to be an expression of salts content), carbonates content, grain size analysis, enzymatic activity and geochemical concentrations.

The reactivity (pH) of the soil was measured on samples with a solid/solution ratio of 1:2.5 with distilled water (Thomas 1996) using an INOLAB WTW720 pH meter. The determination of carbonates was carried out according to the Bernard Calcimeter procedure (Porta 1986), which is based on the measurement of the volume of CO_2 released upon treatment of the sample with hydrochloric acid. Particle size determination was carried out on soil samples, mine tailings and sediments sieved to 2 mm according to the standardized method (NFX31.107) (Christophe et al. 2017).

According to Wolinska and Stepniewska (2012), dehydrogenase activity (DHA) is one of the most suitable, important and sensitive bio-indicators related to soil PTEs pollution. DHA was assayed by colorimetric determination methods and was determined by the reduction of triphenyl tetrazolium chloride (TTC) to triphenylformazone (TPF), with results expressed as mg TPF g^{-1} soil day^{-1} according to Jin et al. (2009) and Zhang et al. (2011). The analysis was performed on a UNICAM Helios 3 spectrophotometer. Calibration with triphenyl tetrazolium chloride solutions, blanks and batch analysis were performed to ensure the quality and reproducibility of the results. Geochemical analysis (trace elements and major elements) of the samples was carried out by X-ray fluorescence. This technique provides reliable information about the geochemical composition of solid, ground and homogenized samples without the need for prior chemical treatment. X-ray fluorescence is also fast, simple, economical and is reliable for this type of survey (Higueras et al. 2012; Suh et al. 2016; Turner et al. 2018). The analytical instrument used was a Panalytical Epsilon 1 energy-dispersive X-ray fluorescence spectrometer capable of performing quantitative analysis from Na to Am with a thin-window Ag anode 50 kW X-ray tube. This is a very sensitive technique for PTEs, with detection limits in the mg kg^{-1} range, which makes it a very useful tool to characterize the dispersion of trace elements in soils and sediments (Gilfrich 1990; Török et al. 1998; Dos Anjos et al. 2000).

All analyses were performed in acid-washed pre-cleaned centrifuge tubes. Quality control in the laboratory was achieved by analyzing replicate samples to evaluate precision. Blank extractions were also carried out.

X-ray diffraction of samples hand-ground to < 100 µm was performed using a Philips X´Pert MPD diffractometer with Cu-Kα radiation, a programmable divergency slit, graphite monochromator and seal detector with Xe gas.

Determination of enrichment factor (EF)

According to Soubrand-Colin (2004), calculation of the enrichment factor is of interest to determine whether an element has a natural or anthropogenic origin and to identify the horizons in which PTEs tend to accumulate or mobilize. Mathematically, EF is defined by the following equation:

$$\mathrm{EF} = (C_m/C_r)_{\mathrm{Soil}}/(C_m/C_\mathrm{r})_{\mathrm{Background}}$$

where C_m is the concentration of the element m in the sample and C_r is the concentration of the reference element.

In order to minimize the influence of grain size and mineral composition on elemental concentrations and to identify possibly anomalous metal concentrations, PTEs concentrations were generally normalized by conservative elements such as Al, Fe and Sc (Aloupi and Angelidis 2001; Amin et al. 2009; Naifar et al. 2018). Sutherland (2000) used five EF categories to identify the degree of trace metal pollution: $\mathrm{EF} < 2$ indicates depletion to minimal contamination; EF = 2–5, moderate contamination; EF = 5–20, significant pollution; EF = 20–40, very strong pollution; and $\mathrm{EF} > 40$, extreme pollution.

Statistical analysis and mapping

Statistical analysis was carried out in this study. Pearson's correlation matrix and factor analysis (FA) were performed to establish the relationship between metals and to identify their sources in the surface soils. Data were analyzed using Minitab 15® statistical software.

Mapping of the distribution of metallic elements and other edaphological parameters in the studied area was carried out using SURFER 8.1 software.

Results and discussion

General characteristics

The physicochemical parameters and geochemical compositions of the studied samples (soils, sediments and mine wastes) are shown in Table 1. Soils and sediments mainly consist of carbonates and silicates, in accordance with the geological character of the rocks that host the mineral deposit. The formation of the ore deposit should have produced, as one would expect in this type of carbonate-hosted deposit, the silicification, dolomitization and ankeritization of the original host rocks (Garnit et al. 2018). However, in the mine waste, the Fe-rich minerals are much more abundant as a consequence of the presence of pyrite and related sulfides in the ore paragenesis (Bouhlel and Fortuné 1985; Hamed et al. 2017). Clay minerals have been researched in the area by XRD, but their presence has not been confirmed. However, there is a clear correlation between the concentrations of Al_2O_3 and K_2O with the finer granulometric fractions ($r = 0.474$ $p < 0.05$, $r = 0.578$ $p < 0.05$, respectively) for soils and sediments; this relationship is absent for the waste samples, which is common in certain ore deposits (Daldoul et al. 2015).

The physicochemical parameters of the mine waste accumulations include alkaline reactivity (high pH) due to the higher carbonates/sulfates content when compared to soils and sediments. This property allows the acidity generated by the hydrolysis of sulfides to be buffered by the carbonates present in the waste. This interpretation was confirmed with samples taken from soils near the mine, which had pH values between 7.6 and 8.6, thus indicating the low acidification potential of the exploited mineralization and its wastes.

Trace elements in mine tailings, soils and sediments

The concentrations of different trace elements analyzed in the different environmental matrices are shown in Table 2. The concentrations of Mn, Rb and Sb in the three environmental matrices were quite similar. These elements were therefore attributed to a geogenic origin related to the regional geology. For the rest of the analyzed elements, the highest

Table 1 Physicochemical parameters and major element contents in soils, sediments and mine waste samples (% weight)

	Sand	Mud[a]	pH	$CaCO_3$	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	SO_3
Mine tailings										
Min	12.00	21.00	8.05	10.57	16.06	2.74	25.29	2.47	0.12	0.55
Max	79.00	88.00	8.80	26.02	20.97	5.47	42.56	10.49	0.34	3.42
Average	47.89	52.11	8.43	17.63	18.48	3.73	30.59	6.73	0.21	1.31
Median	68.00	32.00	8.45	17.01	18.10	3.61	29.91	6.98	0.20	0.92
Soils										
Min	37.00	28.00	7.60	2.54	23.23	3.86	2.22	1.37	0.38	0.11
Max	72.00	63.00	8.60	26.01	61.90	14.30	11.54	3.61	2.12	21.01
Average	59.48	40.52	7.93	17.87	37.49	8.58	5.25	2.39	1.30	4.94
Median	60.00	40.00	7.90	19.60	37.08	7.83	5.07	2.42	1.22	0.32
Sediments										
Min	73.00	9.00	7.67	18.96	26.27	3.57	7.57	2.92	0.33	0.43
Max	91.00	27.00	7.80	25.68	40.09	8.32	10.02	4.06	1.17	7.34
Average	84.50	15.50	7.73	21.78	32.66	5.25	9.22	3.57	0.60	4.07
Median	87.00	13.00	7.73	21.24	32.14	4.55	9.63	3.64	0.45	4.25
T_0										
Average	ND	ND	8.80	4.63	57.44	6.98	2.07	1.04	1.32	0.11

ND not determined

[a] Silt + clay fractions

Table 2 Trace element contents in soils, sediments and mine waste samples (mg kg^{-1})

	Ba	Cd	Cl	Cr	Cu	Mn	Pb	Rb	Sb	Sn	Sr	Te	Ti	Zn	Zr
Mine tailings															
Min	518.0	86.0	<DL	NQ	NQ	376.5	1830.0	<DL	26.0	139.0	335.0	87.8	633.3	7592.5	22.6
Max	2054.5	123.3	5280.0	NQ	NQ	605.0	5950.5	81.3	48.5	226.0	2339.5	129.8	1530.0	12,488.5	410.9
Average	1103.4	107.5	4782.5	NQ	NQ	450.7	3459.2	31.5	35.2	174.1	1190.1	105.7	921.2	10,217.0	131.5
Median	1049.0	109.7	4782.5	NQ	NQ	433.5	2998.5	22.4	33.8	169.2	894.0	102.3	896.1	10,468.0	89.6
Soils															
Min	16.5	0.5	15.7	14.5	9.0	333.9	18.5	1.5	13.8	61.9	16.0	39.1	101.5	44.0	78.7
Max	4660.0	38.6	201.1	171.2	55.9	1570.0	1210.0	64.9	28.8	130.7	759.5	79.2	403.0	4361.5	349.7
Average	747.7	10.1	56.9	51.4	30.9	927.2	266.3	31.4	19.6	85.8	202.3	55.1	243.6	793.3	187.7
Median	252.0	4.1	35.0	46.0	32.3	971.0	82.0	28.7	18.6	82.9	149.5	53.0	231.0	218.5	181.3
Sediments															
Min	129.5	16.8	35.0	12.9	6.0	1365.0	496.0	1.5	22.6	103.0	167.0	60.4	100.0	1102.5	69.4
Max	456.5	39.0	66.2	35.2	53.8	1620.0	958.0	24.7	28.0	126.3	815.5	74.8	827.4	4028.0	168.6
Average	279.8	30.6	48.3	20.9	25.1	1522.5	724.8	8.2	25.6	114.9	488.3	68.3	318.8	2946.0	104.2
Median	266.5	33.4	46.0	17.7	20.4	1552.5	722.5	3.2	25.9	115.1	485.3	69.1	174.0	3326.8	89.3
T_0															
Average	139.5	0.5	2000	57.2	14.7	259.1	25.2	30.2	16.2	63.1	70.5	42.4	1995.0	67.3	293.1

NQ not quantified, < *DL* below detection limit concentrations were detected in the mining waste and their origin was attributed to the mining process. In this group of elements associated with mining, it is worth highlighting the potential toxicity and the contents detected in the mining tailings for Pb (average: 34.59 mg kg^{-1}), Zn (average: 102.17 mg kg^{-1}) and Cd (average: 107.46 mg kg^{-1}). In particular, the coarser wastes contained the highest concentrations of Zn, whereas waste with a smaller grain size showed higher Pb concentrations, with Cd concentrations similar in both waste types.

Soils and sediments also contained very high concentrations of Zn, Pb and Cd, which clearly exceeded the local baseline levels (sample T_0). The geographic distribution of these elements in the studied area (Fig. 3) indicates that both types of samples contain higher metal concentrations when they are located close to the waste piles (S2, E2, E3, E6, E7, E8, E12 and E17). This finding supports the assumption that mining activity is the main local source of Zn, Pb and Cd.

The anomalous concentrations of the elements of concern extend in the SE direction, following the orography of the valley in which the mine is located (Fig. 3). Wind and water as erosive and transporting agents are the main drivers for the dispersion of these contaminants, even in semiarid environments (Sánchez-Donoso et al. 2019). It is noteworthy that the concentrations of the three contaminants considered here in the sediments located downstream from the tailings piles are higher than those found in the surrounding soils, which suggests that—despite the semiarid regional conditions—water-driven erosion plays a greater role than wind-driven erosion in the dissemination of the contaminants away from the source. However, a strong correlation exists between the three elements Zn, Cd and Pb, with correlation coefficients of 0.939, 0.833 and 0.909, respectively. These significant correlations, together with their strong correlation with Fe ($R > 0.82$), support the common origin of the elements from the mining ore. In contrast, the correlation between these elements and S is practically null ($R < 0.1$) and this demonstrates that the ores do not correspond to metal sulfides, as indicated by Bouhlel and Fortuné (1985).

The enrichment of PTEs in the soils close to mining sites can be found in similar studies in relation to carbonate. For example, Elouaer et al. (2016) reported heavy metal contents of Zn, Pb and Cd that reached 42.368, 12.825 and 230 mg kg^{-1}, respectively, in northern Tunisia (ebel Ressas mine). Likewise, in carbonate-rich Mediterranean soils from the Jalta Pb–Zn mine, Northern Tunisia, Boussen et al. (2013) reported concentrations of Zn, Pb and Cd of 17.229, 4.813 and 42 mg kg^{-1}, respectively.

The PTE contents of the soil samples closest to the mine area are clearly higher than Tunisian standards in agricultural areas (100 mg kg^{-1} for Pb, 300 mg kg^{-1} for Zn and 3 mg kg^{-1} for Cd) (Baize 1997) by factors of 37, 39 and 4, respectively. In addition, it is worth noting the low PTE contents in the baseline soil, with values of 25.25, 67.3 and 0.55 mg kg^{-1} for Pb, Zn and Cd, respectively, when compared to the aforementioned Tunisian standards.

Dehydrogenase activity (DHA)

The activity of the enzyme dehydrogenase (DHA) reflects the total range of oxidative activity of soil microflora (Järvan et al. 2014), and this activity has

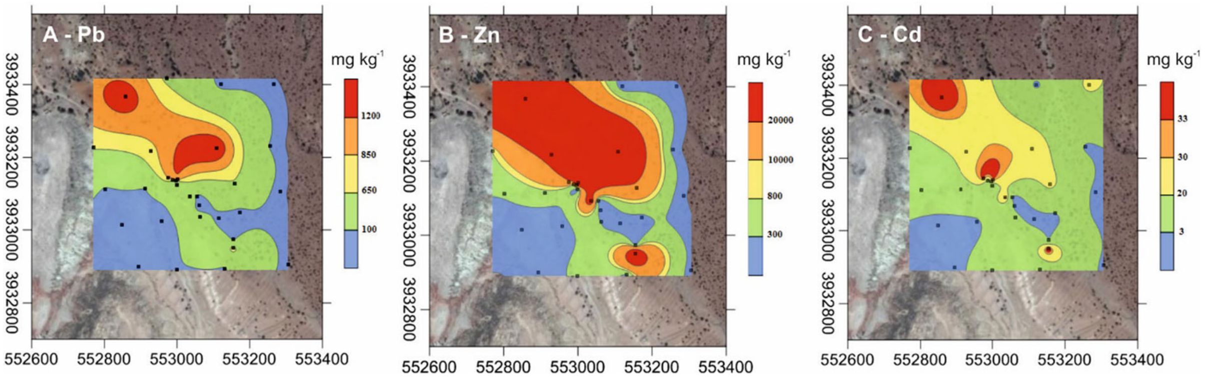

Fig. 3 Distribution maps of potentially toxic elments concentrations at the surface

been highlighted as a general comparative index for the microbiological activity of soils (Dotaniya et al. 2019). Several biotic and abiotic factors affect soil dehydrogenase activity, and these include the incubation time and temperature, soil aeration status and soil moisture content. The activity values in soils are also often used as a measure of disruption caused by the presence of pesticides, trace elements or management activities (Kumar et al. 2013). In this study, the DHA values (Table 3) were lower than the detection limit (< 0.9 mg TPF g^{-1} day^{-1}) for all tailing samples, which are also the samples with the highest PTE contents and materials with a low degree of evolution in terms of pedogenesis. In contrast, DHA values above the detection limit tend to increase with decreasing concentrations of PTE and they reached values that can be considered as normal for an area with a semiarid climate and low agronomic productivity, as in the surroundings of the mine area, where a blank sample gave a value of 7.97 mg TPF g^{-1} day^{-1}. The average DHA value measured in the soils of this area is 26.4 mg TPF g^{-1} day^{-1}, with a maximum value of 141.4 mg TPF g^{-1} day^{-1} (Table 3). This maximum value is lower than that measured at a mercury mining and metallurgy site in Almadén (Spain) (484 mg TPF g^{-1} day^{-1} by Campos et al. (2018) and is also lower than most values measured in different polluted contexts: 110 mg TPF g^{-1} day^{-1} measured by Meier et al. (2017) in contaminated soils; 140–580 mg TPF g^{-1} day^{-1} described by Mukhopadhyay and Maiti (2010) for restored soils from mine sites; and comparable to those measured by Hinojosa et al. (2004) for heavily polluted soils from the Aznalcollar (Seville) area, which was affected by a significant spill of sulfides (see Grimalt et al. (1999) for details of this accident). In contrast, other factors associated with potential bacterial toxicity, such as soil acidity or high salt contents, do not appear to be of importance for the activity of this enzyme.

Table 3 Statistics for dehydrogenase activity (DHA) measured in the different types of samples collected

	Soils	Sediments	Mine tailings
DHA (mg TPF g^{-1} day^{-1})			
Min	0.90	0.90	< DL
Max	141.39	29.31	< DL
Average	26.39	8.26	< DL
Median	18.49	1.42	< DL

DL detection limit

The distribution of DHA values in the studied area is presented in Fig. 4. The similarities in the results are clear, in inverse terms, between this map and that for the distribution of PTEs (Fig. 3), particularly in the case of Pb (Fig. 3a). This finding again shows the negative effects that the presence of these pollutants has on the bacterial activity of the soils.

The status of environmental contamination in soils and sediments

In order to study the relationships between elements in the area, a factor analysis was performed, followed by varimax rotation and extraction of four factors (Principal Components Analysis, PCA). These four factors account for 84.2% of the total variance. It can be seen from the results in Table 4 that Factor 1 explains 34.7% of the total variance, with a grouping of the elements directly related to ores and waste materials. This factor can therefore be considered as a 'contaminant factor.' The second factor accounts for 22.2% of the total variance, and the clustered variables are related to the silt and clay grain-size fractions and the biological conditions. Factor 3 appears to be related to the physicochemical conditions of the soils and sediments, and it explains 13.6% of the total variance. The fourth factor only accounted for 11.9% of the total variance, and this was a geologic factor related to the

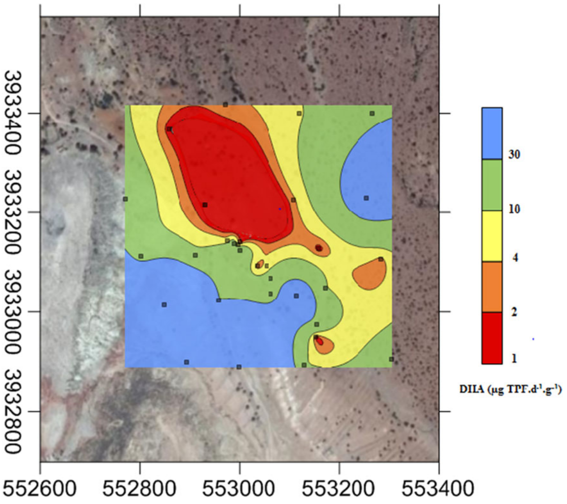

Fig. 4 Distribution of DHA in the studied area

Table 4 Total explained variance and component matrix for the analyzed dataset: factor analysis with varimax rotation

Variable	Factor 1	Factor 2	Factor 3	Factor 4
pH	– 0.233	– 0.027	**0.800**	0.015
CE	0.105	– 0.491	– **0.794**	0.184
MO	– 0.040	**0.736**	0.075	– 0.035
$CaCO_3$	0.009	– 0.075	0.040	**0.961**
DHA	– 0.165	**0.683**	0.044	– 0.222
MgO	**0.698**	0.138	0.009	0.590
Al_2O_3	– 0.370	**0.849**	0.247	– 0.155
SiO_2	– 0.202	0.331	0.590	– **0.629**
P_2O_5	– 0.176	**0.676**	0.598	– 0.064
SO_3	– 0.259	– 0.404	– **0.798**	0.169
Cl	0.116	– **0.531**	0.372	– 0.410
K_2O	– 0.552	**0.723**	0.317	– 0.164
CaO	0.173	– 0.322	– 0.403	**0.815**
Ti	0.087	**0.626**	0.165	0.063
Fe_2O_3	**0.979**	0.031	– 0.051	– 0.021
Mn	**0.823**	0.368	0.083	– 0.154
Zn	**0.924**	– 0.306	– 0.153	0.035
Rb	– 0.532	**0.780**	0.215	– 0.148
Sr	**0.722**	– 0.343	–0.355	0.252
Cu	**0.865**	–0.296	– 0.124	– 0.046
Zr	– 0.363	**0.650**	0.349	– 0.379
Cd	**0.833**	– 0.328	– 0.266	0.043
Sn	**0.930**	– 0.114	– 0.086	0.248
Sb	**0.873**	– 0.212	0.076	0.237
Te	**0.920**	– 0.114	– 0.066	0.191
Ba	**0.647**	– 0.272	– 0.020	– 0.131
Pb	**0.889**	– 0.345	– 0.031	– 0.003
% Total variance	34.7%	22.2%	13.6%	11.9%

Figures in bold correspond to loadings > 0.5 or < -0.5

The significance of KMO and Bartlett's sphericity test is < 0.001

carbonated matrix in which the mineral deposits are embedded.

Samples fall into three categories based on the factor analysis results shown in Fig. 5: (1) clean or natural samples (area G-III in Fig. 5) characterized by a low metal load, a significant presence of silt and clay fractions and significant biological activity, (2) moderately impacted samples (area G-II in Fig. 5) with a moderate metal load, moderate presence of silt and clay fractions and moderate-to-low biological activity and (3) contaminated samples (area G-I in Fig. 5) characterized by a high metal load, a low-to-zero biological activity and the presence of mud fractions. These categories, in addition to clearly distinguishing the different sample types in the area, highlight the relevance of the dependence of the metal load on the biological activity. The highest presence of metals in the soil matrix produces a decrease in the biological activity, thus suggesting that a significant proportion of the metals present in the area is biologically available.

Together with the relationships between elements, the contamination present in the study area was evaluated and the enrichment factor (EF) was chosen for this purpose. This index was calculated by selecting the element concentrations in the baseline sample (T_0) as reference values and taking aluminum as the grain-size normalizing factor. Likewise, the EF was calculated for the potentially harmful elements that form Factor 1 (Cd, Cu, Cr, Sb, Pb and Zn) because these elements can be considered as contaminants from mine activities in the area (Table 5).

The calculated EF values for the soils at the mine range from 6.1 to 1164.4 for Zn, from 4.6 to 864.9 for Pb and from 0.95 to 126.73 for Cd. According to the EF classification (Sutherland 2000), the average EF values for Zn (166.6) and Pb (136.3) correspond to an extremely polluted environment, while for Cd the average EF (23.26) corresponds to a very strongly polluted environment. Within the samples, the highest EF values were found for samples close to the pollution source and samples close to the stream that crosses the mining area. These results are consistent with the spatial distribution maps (Fig. 3), where samples that surround the tailing areas and samples close to and throughout the stream crossing the mining site were considered to be the most polluted. In contrast, the average EF values for the other trace elements Cu, Cr and Sb were 1.8, 0.7 and 1.17, respectively. These values (EF < 2) indicate depletion of these metals to minimal contamination in the soils of the mining area, which are frequently associated with Zn–Pb ore deposits. For sediment samples, the average EF values for Zn (716), Pb (440) and Cd (87.6) correspond to an extremely polluted environment.

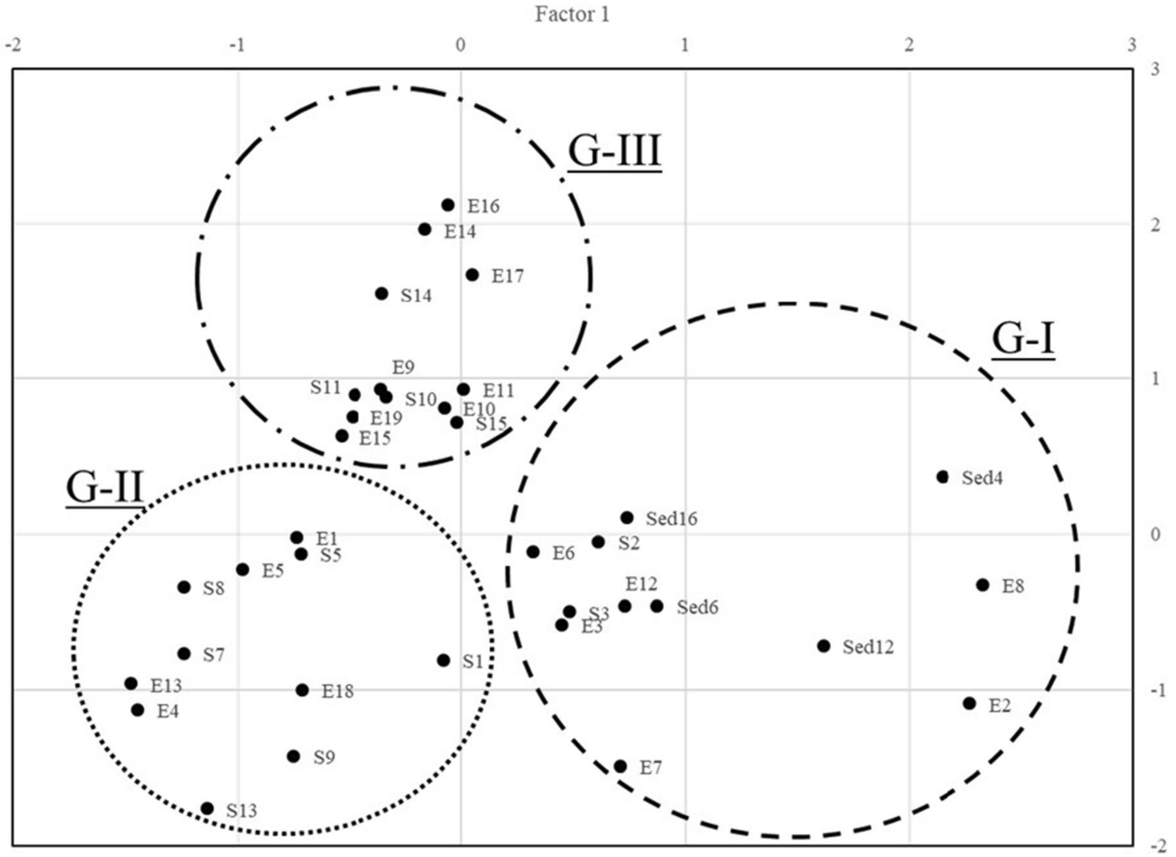

Fig. 5 Graphical results of the FA applied to samples based on the element concentrations, physicochemical parameters and grain-size fractions of sediments

Table 5 EF values for soil and sediment samples

	Pb	Zn	Cd	Cu	Cr	Sb
Soil samples						
Min	4..6	6.1	0.95	0.557	0.3127	0.469
Max	864.9	1164.4	126.73	5.576	1.845	3.204
Average	136.3	166.6	23.26	1.796	0.6924	1.179
Sediments						
Min	245	137	25.5	0.56	0.3127	1.288
Max	750	1171	121.1	6.14	0.5943	3.239
Average	440	716	87.6	2.35	0.4882	2.352

Conclusions

The Jebel Trozza mine site is an area that is highly polluted with Cd, Pb and Zn. These pollutants could have negative effects on the environment and human health by affecting local waters and agricultural soils through the accumulation of contaminated sediments in a dam used for irrigation. The decommissioned mine site is the main hot spot in the area, but the spatial distribution determined suggests significant dispersion of the PTE, which can be exported to other areas and thus extend the problem to zones far from the main source. The relationships between PTE concentrations and DHA activity demonstrate the significant impact that these contaminants have on the soil health status. These relationships also highlight areas with high metal loads, where enzymatic activity disappears—probably as a consequence of the harmful effect that these contaminants have on soil biota populations. Furthermore, the behavior of DHA with respect to the metal load suggests that this enzymatic parameter could be of interest as a rapid test to assess the impact of metal load on soil quality status.

Further studies are required to determine the risks highlighted in this study and to identify a basis for the appropriate recovery of the area through remediation activity.

Acknowledgments This research was carried out with the support for IE from the *Laboratoire Génie Environnement et Ecotechnologie*, ENIS, Sfax University (Tunisia), for her stay in IGeA-UCLM. Projects CGL2015-67644-R (Spanish *Plan Nacional de I+D+i, Ministerio de Economía y Competitividad*) and 2019-GRIN-27011 (*Ayudas a Grupos de Investigación UCLM*) partly funded the laboratory work in Almadén, IGeA-UCLM. Neil Thompson, Ph.D. CChem MRSC, revised the English style.

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