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Mobility of Potentially Toxic Elements (Pb, Zn, Cd, As, Sb) in Agricultural Carbonated Soils Contaminated by Mine Tailings (Northern Tunisia): A New Kinetic Leaching Approach with Organic Acids

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Abstract: The present study was carried out to show the potential of root exudates to mobilize potentially toxic elements (PTE) present in rhizospheric carbonated soils. Five different contaminated rhizospheric soils were collected from five former mining districts of northern Tunisia (Jebel Hallouf (H3), Sidi-Bouaouane (B1), Jebel Ghozlane (G7), Hammam Zriba (Z2) and Jalta (J2)). The abundant minerals in these soils are quartz, calcite and clays. These soils contain significant PTE amounts compared to the local geochemical background (LGB). The important concentrations of Pb, Zn, Cd, As and Sb are, respectively, in the order of 17,350 mg·kg^{-1} in B1, 37,000 mg·kg^{-1} in G7, 205 mg·kg^{-1} in G7, 683 mg·kg^{-1} in B1 and 145 mg·kg^{-1} in B1. Kinetic leaching tests were conducted with a mixture of low molecular weight organic acids (LMWAOs) for increasing times up to 16 h (initial pH = 2.8) to study the mobility of PTE in the rhizospheric soils. The results showed an increase in the pH of the solution (2.8) to values up to neutrality together with the increase in Ca and Mg concentrations in the leachate, resulting from the dissolution of carbonates (calcite and dolomite). Additionally, leaching tests showed important extractions of Cd and Zn (25% for Cd and 11% for Zn). Pb was also mobilized but to a lesser extent (5%). The extractability of metalloids (As and Sb) was, in contrast, relatively low, except for Jebel Hallouf and Sidi Bouaouane soils, with an extraction percentage of no more than 1% for Sb and 0.1% for As, respectively. The mobility of Zn, Pb and Cd was thought to be controlled by both the solubility of their host minerals (e.g., sphalerite, hemimorphite, cerussite and jordanite) and the high pH. In contrast, As and Sb mobility was dependent on secondary carrier phases such as iron oxyhydroxides.

Keywords: former mining; potentially toxic elements (PTE); mobility; carbonated soils; kinetic leaching; low molecular weight organic acids (LMWOAs)

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1. Introduction

In the context of ecological risk assessment of former mining sites as well as the management of their surrounding natural or agricultural environments, it is crucial to acquire knowledge about the behavior of potentially toxic elements (PTE) in different abiotic and biotic compartments of soils and to define the mechanisms which condition their transfer, their capacity to bioaccumulate and, ultimately, their toxic and ecotoxicological effects at different levels of biological integration [1,2]. Mining activities, such as ore extraction and processing, generate tailings containing mineral phases that are potentially rich in metals and metalloids. PTE can be remobilized and further transported by water or wind to the environment's various compartments (air, water, sediment and soil). Thus, these releases pose a threat to the soils surrounding the tailings and nearby plants and animals [3,4].

The determination of total PTE concentration is one of the key parameters to assess the degree and extent of soil contamination [5,6]. However, the mobility of PTE depends not only on their total concentration but also on their association with their solid carrier phase [7]. The risks of PTE uptake to vegetation should also be properly assessed. On this last point, the concept of bioavailability reflects a dynamic process [8] involving two distinct notions: (i) the stability of the thermodynamic equilibrium of PTE at the liquid/solid interface (also known as "environmental availability") and (ii) physiological processes of absorption by target organisms. Although much work has been carried out on PTE's mobility and bioavailability in former mining environments, little has been done in carbonated contexts. The majority of the Pb-Zn mining industries in northern Tunisia were still active in the last century, producing approximately 55 million tons (Mt) of Fe, 2.3 Mt of Pb, 2.0 Mt of Zn and 0.8 Mt of fluorite [9]. In this context, various leaching methods have been developed for the assessment of PTE mobility either in the mining discharges or in neighboring soils based on batch experiments (Souissi et al., 2009 [10], Souissi et al., 2013 [11], Chakroun et al., 2013 [12], simple extraction Othmani et al., 2014 [13], Souissi et al., 2015 [14]; Daldoul et al., 2015 [15], Tlil et al., 2017 [16] and Achour et al., 2019 [17]) or sequential extraction (BCR [18], Tessier et al., 1979 [19] and Maiz et al., 2000 [20]).

Souissi et al., 2015 [14], showed that for the estimation of PTE's bioavailability in Jebel Ressas soils (Northeast of Tunisia), Zn, Cd and Pb were weakly extracted or even non-mobile in demineralized water and solutions of $BaCl_2$. However, with low molecular weight organic acids analysis (LMWOAs) that simulate plant exudates in the rhizosphere, mobility was higher. Daldoul et al., 2015 [15] used several extracting agents to evaluate the mobility of Pb, Zn and Cd in Jebel Ghozlane soils. They showed that the extraction of these elements was stronger with diethylenetriaminepentaacetic acid (DTPA). The mobility order was as follows: DTPA > LMWOAs > $CaCl_2 = H_2O$.

LMWOAs have an important role in the mobilization of PTE in rhizospheric soils. They can be used to evaluate the bioavailability levels of PTE in the soil [21]. In fact, plants themselves secrete organic acids such as acetic, lactic, citric, malic and formic acids and enzymes in their rhizosphere, where physical–chemical reactions influencing PTE mobility take place [22,23].

Root exudates are made up of several types of organic acids, although the dominant types are highly dependent on the plant species and may vary over time [24,25]. In previous years, various works have been done on the mobilization of metals and metalloids by many types of organic acids [26–30]. The majority of these works have evaluated the mobility of PTE in surface soils only by individual acids or a mixture of a limited number of acids. This is insufficient for estimating the mobility of PTE in soils since it does not represent the real field conditions where a combination of several types of acid are present in the same space. In this work, a cocktail of five types of organic acid (citric, malic, fulvic, acetic, lactic acid) was used to estimate the mobility and phytoavailability of the most toxic elements: metals (Pb, Zn, Cd) and metalloids (As, Sb) in five multi-contaminated rhizospheric soils.

In fact, the objective of this work was thus to evaluate the mobility and bioavailability of PTE in soils surrounding the Pb-Zn mines of northern Tunisia (Jalta, Jebel Hallouf-Sidi Bouaouane, Jebel Ghozlane and Hammam Zriba) with kinetic leaching tests with a mixture of LMWOAs, simulating plant exudates together with mineralogical analysis of soil (X-ray diffraction) for the identification of PTE carrier minerals and geochemical approaches (bulk PTE chemical analysis, measurement of soil physical–chemical parameters).

2. Sampling and Methods

2.1. Soil Sampling

Eight rhizospheric soil samples of cultivated or wild plant species were collected around tailing piles in five mining districts of northern Tunisia (Jalta, Jebel Hallouf-Sidi

Bouaouane, Jebel Ghozlane and Hammam Zriba) (one sample per site) (Figure 1). Control samples (T) were taken from uncontaminated areas in all districts (cf. Figure 1 and Table 1).

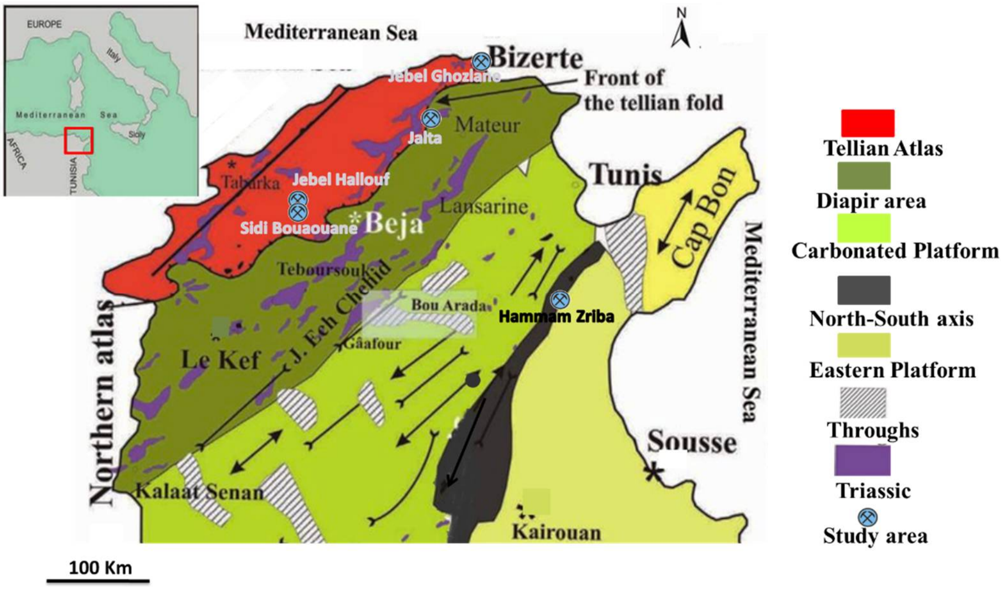

Figure 1. Location map of the study areas.

Table 1. Geographic coordinates of the collected samples.

Sample			Locality	Geographic Coordinates	
Reference	**Contaminated**	**Control**		**Latitude**	**Longitude**
H3	x		Jebel Hallouf	36°41′46.19″ N	9°0′25.15″ E
BT		x	Bouaouane	36°42′41.87″ N	9°01′15.94″ E
B1	x		Bouaouane	36°41′33.67″ N	9°0′58.97″ E
J2	x		Jalta	37°04′27.10″ N	9°31′47.76″ E
Z2	x		Zaghouan	36°20′27.46″ N	10°12′39.98″ E
ZT		x	Zaghouan	36°22′57.38″ N	10°11′01.28″ E
GT		x	Jebel Ghozlane	37°18′43.75″ N	9°46′46.61″ E
G7	x		Jebel Ghozlane	37°19′27.87″ N	9°46′16.18″ E

All soil samples were subjected to textural, mineralogical and geochemical analyses.

In the laboratory, soil samples attached to plant roots were gently removed after they were homogenized to obtain a representative sample.

They were then dried in the open air and then in an oven at 40 °C (3 d) in order to obtain very well dried samples. Soil fractions were sieved at 2 mm mesh and further crushed with an agate mortar for mineralogical and chemical analysis.

2.2. Grain Size, Physico-Chemical Analysis of the Rhizospheric Soils

Granulometric analysis of the soil samples (fraction < 2 mm) was carried out by dispersion and flocculation reagents [31].

A total of 15 mL of soil was placed in a centrifuge tube. Next, 1 mL of Texture Dispersing Reagent (5644PS) was added and then diluted with tap water to the 45 mL level, and the tube was shaken for 2 min manually. After 30 min at rest, the supernatant was poured into a second tube. After 30 min at rest, the second supernatant was transferred to another tube with the addition of 1 mL of a flocculating reagent, followed by stirring for 1 min manually. The three tubes remained at rest for 24 h for a better decantation. In the end, the level in each tube was used to calculate the percentage of each fraction.

Soil pH was measured on the bulk soil sample (soil/solution ratio = 1/2.5). According to the NF X 31-117 protocol (NF ISO 10390), 10 g of soil was mixed with 25 mL of distilled water. The solution was stirred for 15 min with a magnetic stirrer and then allowed to settle for 15 min. Measurements were made using a pH meter (Thermo Orion model 420 A+).

The conductivity (EC) of the same soil sample was measured by a conductivity meter (WTW, multi 3410, Xylem Analytics France SAS).

The estimation of the carbonate content in soil samples was performed with Bernard's calcimeter. The experiment was carried out on 250 mg of soil. Each test was repeated twice.

The determination of the cation exchange capacity (CEC) was performed with a sodium acetate solution 1 mol.L^{-1}, and 5 g of powdered soil was brought into contact with the sodium acetate solution [32]; the Na assay analysis was carried out by SAA (Analytik Jena).

2.3. Mineralogical and Chemical Characterization of the Rhizospheric Soils

Mineralogical characterization of the soils was carried out on powdered soils by X-ray diffraction (XRD) (PANalyticalX'Pert PRO MPD diffractometer) operating with Cu Kα radiation (λ = 0.15406 nm) on the basis of binocular methods. Mineralogical identification was performed by means of High Score Plus software (version 2.1, PANalytical, Almelo, the Netherlands) equipped with the ICDD PDF–2 Release 2004.

PTE total concentrations in the soil samples were determined by ICP-AES (Horiba Jobin Yvon) after mineralization of 0.25 g of powdered soil using a mixture of concentrated HF (3 mL/47–51%), HCl (1 mL/25%), HNO_3 (7 mL/67–69%) and H_2O_2 (2 mL/30%). Soil reference material (SRM 2710 of the National Institute of Standards and Technology) was mineralized and analyzed under the same conditions as the soil samples.

2.4. Kinetic Chemical Extractions

Various studies have examined the mobility of PTE in soil by several types of mixture of organic acids such as Pb by citric, oxalic and malic acids [33]; Cd by citric, malic and oxalic acids [34], malic and acetic acids [35]; and As by citric, oxalic and malic acids [36]. In our study we have used a mixture of acetic, lactic, citric, malic and formic acids according to the protocol of [22], modified by [37], and [23], also applied by [38] (Table 2). In fact, in our study, it is about kinetic chemical extractions to assess the behavior of PTE in the rhizo-spheric soils (real sample). Kinetic tests define reaction rates for both metal (loid) dissolution over time under specific conditions. In fact, the choice of this kinetic test was based on the long-term monitoring of the release of PTE by a single extractant [39]. In contrast to batch leaching tests, the sample is brought into contact with a defined volume of the extraction solution, depending on the L/S ratio, for a fixed duration (depending on the type of test) and without renewal solution [40,41].

Table 2. Extraction protocol adapted for the study of PTE behavior in rhizospheric soils.

Procedure				References
Reagent	**Temperature**	**Extraction Ratio**	**Shaking Time**	
Low molecular weight organic acids (LMWOAs) solution 0.01 mol L^{-1}, consisting of acetic, lactic, citric, malic and formic acids with a molar ratio of 4:2:1:1:1, pH 2.8	Room temperature	1/10 (4 g soil/40 mL LMWOAs)	0 min 5 min 15 min 30 min 60 min 120 min 960 min	[22] [23] [37] modified

The extraction reagents (LMWOAs) and the soil/solution ratio are shown in Table 2. The extraction was performed in acid-cleaned polystyrene centrifuge tubes by shaking at ambient temperature (20 °C) in a mechanical shaker at 20 rpm. The leachate of each cycle was subjected to pH and EC measurements after centrifugation (2000 rpm for 20 min) and filtered with a PTFE syringe filter (0.45 µm porosity). The amount of mobilized Ca, Mg and PTE (Pb, Zn, Cd, As and Sb) was determined by ICP-AES (Activa of Horiba Jobin-Yvon), and the reproducibility of the analysis was checked by running several duplicates and the accuracy by analysis of the certified standard SRM 2710. Both reproducibility and accuracy are within 5%.

All instruments were washed previously in a nitric acid bath (10% HNO_3) and then rinsed a dozen times with deionized water. All analyses have been done in the laboratories of the National Institute of Research and Physico-Chemical Analysis (INRAP).

2.5. Statistical Analysis

Statistical analyses were performed using the statistical software XLSTAT, 2022.2.1.1297; Pearson correlation coefficients were determined between total and leachate concentrations of PTE.

3. Results

3.1. Soil Characteristics

3.1.1. Soil Granulometry

Results of particle size analysis are reported in the triangular diagram of soil texture (Figure 2). They show that sand and clay are more abundant than the silt fraction (less than 25%) in all samples. All contaminated soil samples are dominated by sandy textures, going from sandy loam (Z2) to sandy clay loam (H3, J2, B1) and even to sandy clay (G7). It should be noted, however, that the textures of the control soils from Jebal Ghozlane and Bouaouane (GT, BT) are close to those of the contaminated samples from the respective mine sites (G7, B1), with the exception of soils from Bouaouane, for which the clay texture of the control sample (BT) is very different from the contaminated one (B1).

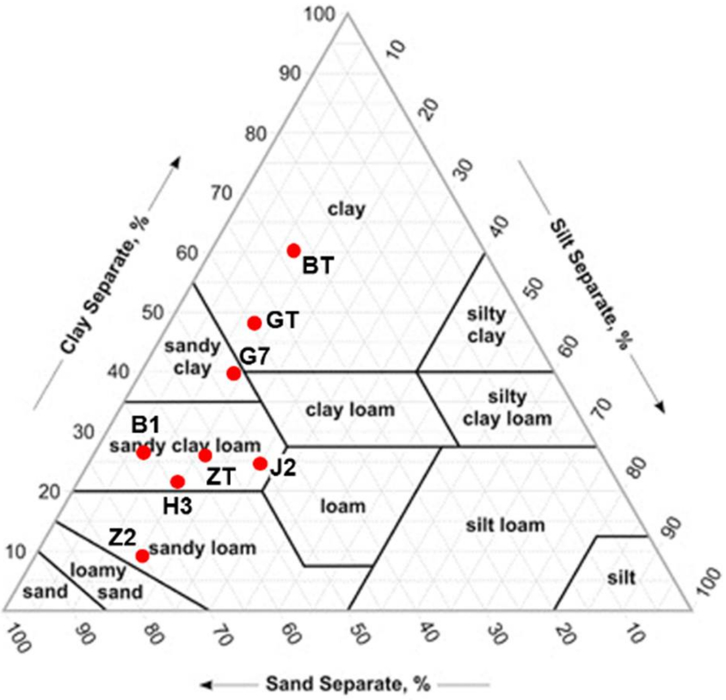

Figure 2. Triangular diagram of soil texture.

3.1.2. Physicochemical Parameters

Results for pH, EC, % $CaCO_3$ and CEC are presented in Table 3. The soil's pH values were neutral to slightly alkaline, typically varying between 7.1 and 8.3 in the different sectors.

Table 3. pH and EC values and calcium carbonate content of soil samples from the study areas.

Samples	EC ($\mu S \cdot cm^{-1}$)	pH	(% $CaCO_3$)	CEC (meq/100 g)
H3	217	8.3	75	5.5
BT	237	7.8	40	-
B1	499	7.8	46	18.4
J2	367	7.1	2	23.1
Z2	115	7.7	24	1.8
ZT	271	7.1	22	-
GT	233	8.0	50	-
G7	865	7.8	33	3.2

Note: (-): Unmeasured parameter.

The EC values of the soil samples were highly variable. EC varied between a minimum value of about 115 $\mu S \cdot cm^{-1}$ for Hammam Zriba (Z2) soil and a maximum value of about 865 $\mu S \cdot cm^{-1}$ for soil from Jebel Ghozlane (G7). The high EC values could be explained by the high content of soluble minerals in the soil [42].

CEC values varied from one sector to another. The highest values were recorded for the soils of Sidi Bouaouane (18.4 meq/100 g) and Jalta (23.1 meq/100 g) (Table 2). The lowest value was recorded for the soil of Hammam Zriba (1.8 meq/100 g).

The $CaCO_3$ content of all soil samples was always high (>20%), except for the Jalta sample (J2), which showed a very low (2%) calcium carbonate content (Table 2). High carbonates are an obvious potential for maintaining the correlative capacity of neutralization and alkalinity of the environment, resulting in overall slightly alkaline pH values ranging from 7.1 to 8.3 (Table 2, Figure 3).

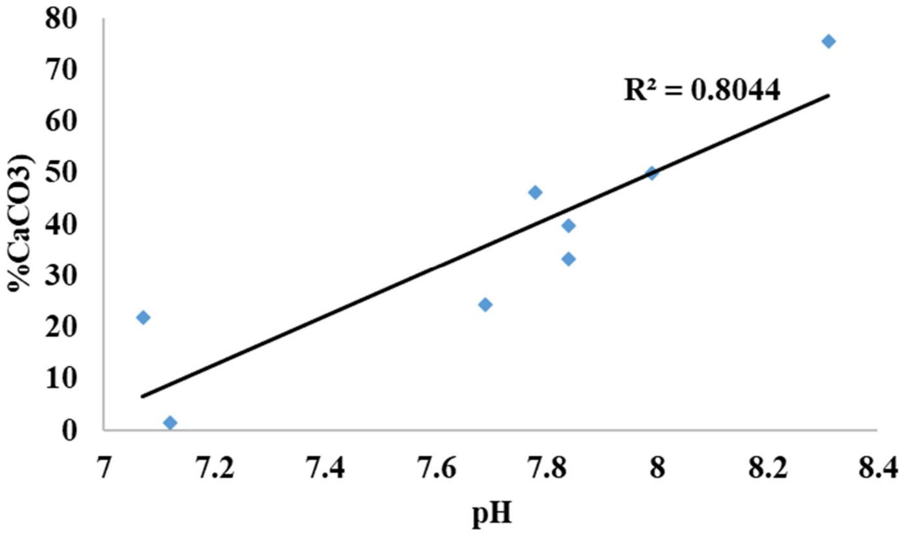

Figure 3. Relationship between soil pH and $CaCO_3$ concentrations in the studied soils.

3.1.3. Soil Mineralogy

X-ray diffractograms of the studied soils revealed a variable mineral composition (Table 3). Calcite, quartz and clays were always present, with these minerals being the more abundant mineralogical fraction in all soil samples.

The presence of high amounts of calcite reflects the general carbonated nature of bedrock in all localities. Sulphate minerals detected were barite ($BaSO_4$) and anglesite (PbSO4) in the soil of Hammam Zriba (Z2), anglesite at Jalta (J2) and gypsum at Bouaouane. Among the carbonate minerals, dolomite ($CaMg(CO_3)_2$) was present at Jebel Ghozlane and cerusite ($PbCO_3$) was present at Jebel Hallouf and Sidi Bouaouane.

Additionally, Zn-silicates (Hemimorphite ($Zn_4Si_2O_7$ $(OH)_2$•(H_2O))), Zn and Fe-sulphides ((sphalerite (ZnS), pyrite (FeS_2)), and fluorite (CaF_2) were detected at Hammam Zriba. Clay minerals, such as kaolinite, were detected in most samples, illite in samples from Jalta and Jebel Ghozlane along with sulfosalts [Jordanite: Pb_{14} $(As, Sb)_8S_{23}$] in Jalta soil (Table 4).

Table 4. Mineralogical composition of soil samples.

Sample Mineralogy	B1	BT	H3	J2	GT	G7	Z2
Quartz	+	+	+	+	+	+	+
Calcite	+	+	+	+	+	+	+
Barite	-	-	-	-	-	-	+
Hemimorphite	-	-	-	-	-	-	+
Fluorite	-	-	-	-	-	-	+
Anglesite	-	-	-	+	-	-	+
Montmorillonite	-	-	-	-	+	-	-
Dolomite	-	-	-	+	-	+	-
Illite	-	-	-	+	-	-	-
Kaolinite	+	+	+	+	+	-	-
Cerusite	+	-	+	-	-	-	-
Pyrite	-	-	-	-	-	-	+
Sphalerite	-	-	-	-	-	-	+
Jordanite	-	-	-	+	-	-	-
Gypsum	+	-	-	+	-	-	-

Note: +: Present, -: absent.

3.1.4. PTE Total Concentrations

Table 5 shows metals (Pb, Zn and Cd) and metalloids (As and Sb) total concentrations in soils. The concentrations were generally elevated and heterogeneous between the different areas, clearly exceeding the local geochemical backgrounds (LGB) and the limits of agricultural soils according to [43] (100 $mg \cdot kg^{-1}$ for Pb; 300 $mg \cdot kg^{-1}$ for Zn and 2 $mg \cdot kg^{-1}$ for Cd).

Table 5. Total PTE concentrations in the studied soils (M.C: soil reference material).

Samples		As ($mg \cdot kg^{-1}$)	Sb ($mg \cdot kg^{-1}$)	Pb ($mg \cdot kg^{-1}$)	Zn ($mg \cdot kg^{-1}$)	Cd ($mg \cdot kg^{-1}$)
B1		683	145	17,350	8620	64
BT		44	nd [a]	391	418	7
H3		669	103	10,321	7951	55
J2		110	nd [a]	3061	1240	9
G7		348	nd [a]	7943	37,000	205
GT		Nd	nd [a]	110	331	1
Z2		Nd	nd [a]	2235	12,674	35
ZT		Nd	8	91	493	Nd
M.C (SRM type 2710)	Measured	648	44	4905	6521	19
	Standard	626	384	5532	6952	218
European standards for agricultural soils		-	-	100	300	2

Note: [a]: not detected.

For the contaminated soils, Pb concentration varied from 2235 mg·kg^{-1} (H. Zriba) to 17,350 mg·kg^{-1} (Bouaouane). Zn contents varied between 1240 mg·kg^{-1} (Jalta) and 37,000 mg·kg^{-1} (J. Ghozlane). Concentrations of Cd were found between 35 mg·kg^{-1} (H. Zriba) and 205 mg·kg^{-1} (J. Ghozlane). As contents varied between 348 mg·kg^{-1} (J. Ghozlane) and 683 mg·kg^{-1} (Bouaouane). Concentrations of Sb showed only slight variations between 103 mg·kg^{-1} (J. Hallouf) and 145 mg·kg^{-1} (Bouaouane).

3.2. Kinetic Leaching Tests

Figure 4 shows the variation of the evolution of the physico-chemical parameters (pH and EC) and the concentration of metals (Ca, Mg, Zn, Cd and Pb) and metalloids (As and Sb) in the leachates with time for the leaching of rhizopheric soils with LMWOAs.

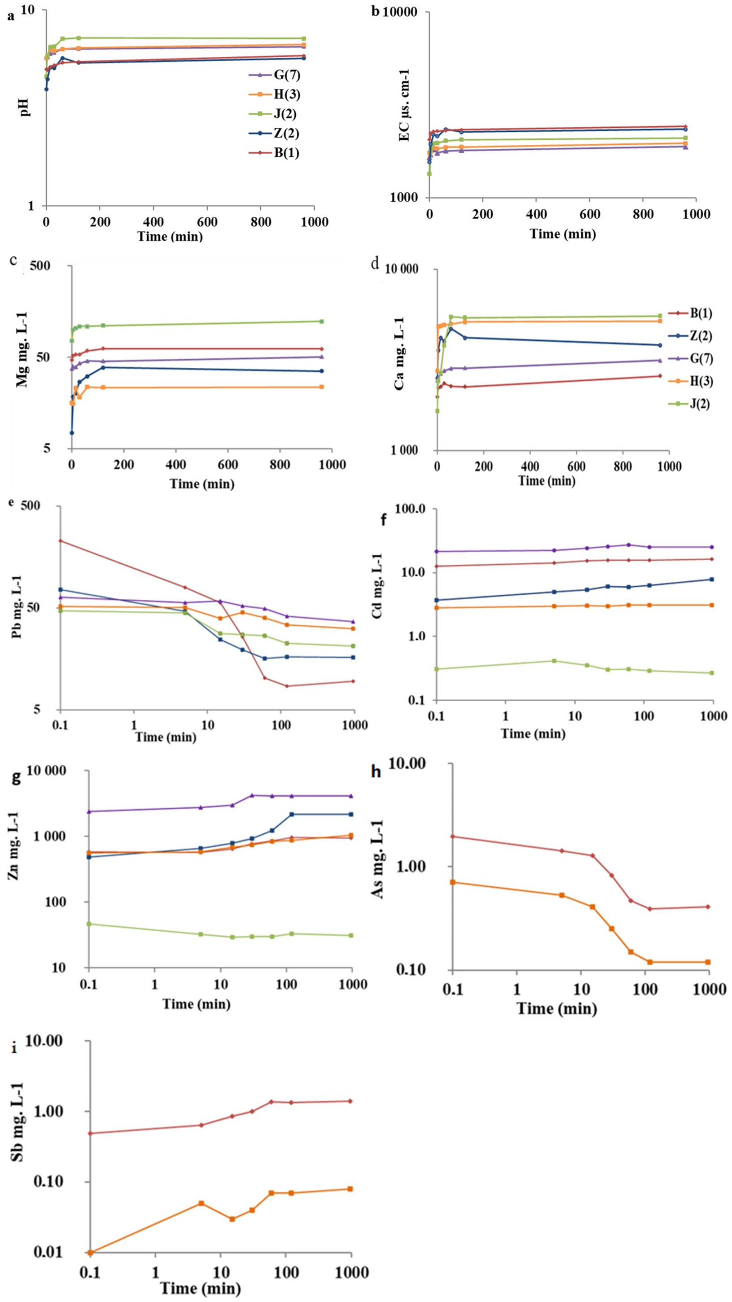

Figure 4. Variation of (**a**) pH and (**b**) EC and (**c**) Mg, (**d**) Ca, (**e**) Pb, (**f**) Cd, (**g**) Zn, (**h**) As and (**i**) Sb concentrations in the leachates during extraction with LMWOAs.

pH: The initial pH of the organic acid solution is 2.8. At the beginning of the test, the lowest pH in soil leachate was noted in Z(2) with a value of 3.9. At the end of the lixiviation experiment (16 h), the pH value varied between 5.8 and 7.2 for the different soils (Figure 4a). The lowest pH values were found in Hammam Zriba (Z2) and the highest values were observed in Jalta.

Conductivity. Leaching solutions were characterized by a rapid increase in EC during the first hour and then stabilized with a small increase until the end of the test (Figure 4b). The highest values were found for samples of Hammam Zriba and Sidi Bouaouane (2430 $\mu s \cdot cm^{-1}$ and 2340 $\mu s \cdot cm^{-1}$, respectively). The EC of these soils could be explained by the presence of relatively soluble minerals such as gypsum, calcite and dolomite.

Mg. The overall trend of the curves looks similar to those of pH in shape, showing an increase up to a maximum during the fourth cycle (after 30 min), and then stabilizing with a very small variation in concentration until the end of the test (Figure 4c). The highest concentration of Mg was found for the soil from Jalta (123 $mg \cdot L^{-1}$), resulting mainly from the dissolution of dolomite.

Ca. Ca concentrations show a rapid increase at the beginning of the test up to a maximum and then stabilize with very little variation until the end of the test (Figure 4d). This increase follows the same pattern as Mg and pH. The highest concentrations of calcium were found for samples J2 (5520 $mg \cdot L^{-1}$) and H3 (5169 $mg \cdot L^{-1}$) from Jalta and Djebel Hallouf, respectively. These concentrations reflect the soils' mineralogy, since the soil of Jebel Hallouf contains the highest amount of calcite, while the Jalta soil, although poor in calcite, contains dolomite and gypsum.

The dissolution of calcite and dolomite could explain the transition from acid to circumneutral pH of the solution. Calcite is a mineral with a high buffering capacity and was abundant in all soil samples (21% to 75% $CaCO_3$), except in the sample J2 from Jalta (2% $CaCO_3$). In this last case, the increase in pH values may be due to the neutralizing capacity of dolomite and possibly silicate (clay) minerals [44,45].

Pb. The highest concentrations of Pb in the leachates were found for all samples at the beginning of the test and the highest value (227 $mg \cdot L^{-1}$) was measured for sample B1. Then, a decrease in concentration was observed until 120 mn of stirring, and the lowest value was measured for sample B1 (9 $mg \cdot L^{-1}$). Thereafter, concentrations remained constant until the end of the test (Figure 4e).

Cd and Zn. Both elements showed similar behavior during the kinetic test for all samples (Figure 4g,h), with the exception of sample J2 (Jalta). The concentration slightly increased with respect to the initial concentration, until a maximum was reached after 30 min and 120 mn of stirring. Thereafter, concentrations remained almost constant until the end of the test, suggesting that Zn and Cd in solution are close to saturation. The highest concentrations for both elements were found for sample G7 (Djebel Ghozlane) (4158 $mg \cdot L^{-1}$ and 27.2 $mg \cdot L^{-1}$, for Zn and Cd, respectively, and then decreased towards 4105 $mg \cdot L^{-1}$ and 25.1 $mg \cdot L^{-1}$). The concentration maximum for sample J2 was reached well before other soils, showing that lesser amounts of Zn and Cd go into solutions from this sample. Moreover, the decrease in concentration before stabilization after 30 min of stirring suggests that oversaturation has been reached for both elements.

Metalloids. As and Sb were detected only in the leachates of the soils of Sidi Bouaouane (B1) and Jebel Hallouf (H3) (Figure 4e,f). The two elements behave in different ways during the test. For both samples, the highest concentrations of As were measured at the beginning of the test (2.0 $mg \cdot L^{-1}$ and 0.7 $mg \cdot L^{-1}$, respectively). Then, concentrations decreased until a minimum (0.4 $mg \cdot L^{-1}$ and 0.1 $mg \cdot L^{-1}$, respectively) of 120 min of stirring; then, they remained stable until the end of the test. Such a trend gives evidence of As extraction (precipitation/adsorption) from the solution.

The Pb and As concentration curves are similar. Leachate concentrations decreased as a function of time until stabilizing after 120 min of stirring.

Sb concentrations measured in the leachate of sample B1 were always higher than those in the leachate of sample H3. In both cases, concentrations started from a minimum (0.5 mg·L^{-1} and 0.01 mg·L^{-1}, respectively) and then increased to a maximum after 60 min of stirring (1.4 mg·L^{-1} for B1 and 0.07 mg·L^{-1} for H3), after which concentrations remained constant until the end of the test.

Figure 5 shows the variation of the extraction rate (concentration in leachate normalized to the concentration in the rhizospheric soil sample, %) of the PTE (Zn, Cd, Pb, As and Sb) by cycle. The percentages indicated towards the end of the test (after 16 h of agitation) are considered percentages of mobility.

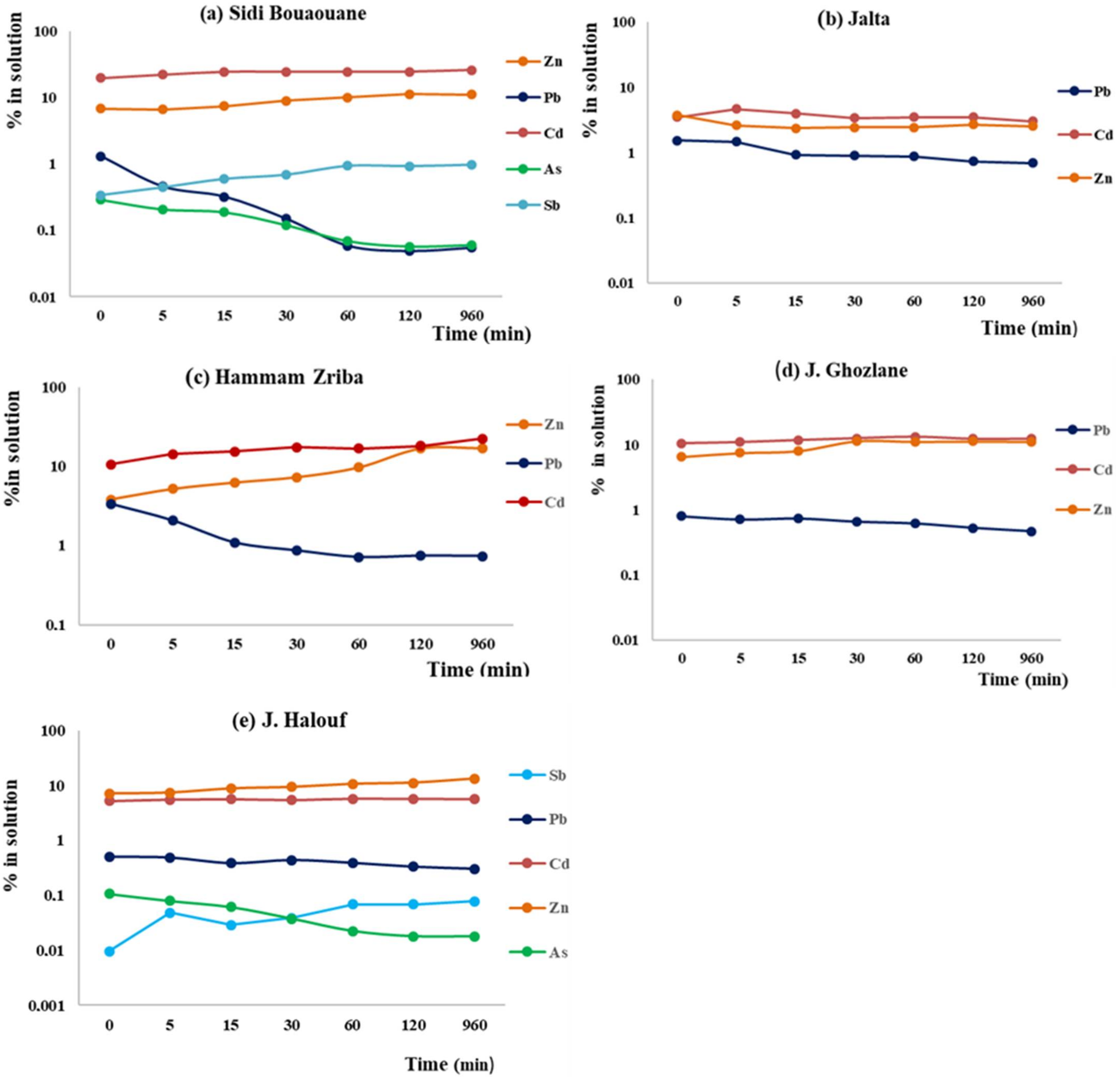

Figure 5. Evolution of the extraction rate (%) of Pb, Zn, Cd, As and Sb during the leaching test conducted on the studied soils (**a**): Sidi Bouaouane, (**b**): Jalta, (**c**): Hammam Zriba, (**d**): Ghozlane, and (**e**): J. hallouf.

Results show that during the first cycle (0 min of stirring), Zn and Cd are characterized by extraction rates higher than those of Pb. The extraction rates of metalloids (As and Sb), which are detected only for the samples from Sidi Bouaouane and J. Halouf, are below those of Zn, Cd and Pb.

During subsequent cycles, Zn and Cd extraction rates show a slight and continuous increase, with the exception of the sample from Jalta, for which the extraction rate is slightly decreasing. The highest extraction rates (25% for Cd and 11% for Zn) were recorded for the samples from Sidi Bouaouane and Jebel Ghozlane. Moreover, for all sectors, the respective curves of Zn and Cd are always similar.

On the other hand, Pb extraction rates are always decreasing for all the samples, remaining well below those of Zn and Cd. However, relatively higher extraction values of Pb are found in the sample from Hammam Zriba.

With regard to metalloids, it should be noted that extraction rates of As and Sb show opposite trends, with an increase for Sb and a decrease for As. It is worth noting that the extraction trend of As follows that of Pb.

4. Discussion

Zn, Cd and Pb are common in the mineralization of the North Tunisian metallogenic province. In the economic ores, Pb and Zn occur mainly as galena (PbS) and sphalerite (ZnS), accompanied by lesser amounts of their alteration products such as cerusite ($PbCO_3$), smithsonite ($ZnCO_3$) and hemimorphite [10]. The sectors of Sidi Bouaouane and Jebel Ghozlane showed the highest concentration levels of Cd. This element is common in northern Tunisia's mineralization in substitution for Zn in sphalerite and its oxidation mineral network [46–48].

According to [49–51], the mobility of metallic elements is not related to their total content in soil but rather to their speciation (partitioning in the carrier phase, chemical form in the soil solution, etc.). The speciation of metals in soil leachates also depends on the extractant solution's pH and chemical composition [52]. However, only soluble or exchangeable metal species in soils are bioavailable [53].

The acidic pH results in the dissolution of metal salts along with the desorption of cations and adsorption of anions [54]. As a result, the initial acid pH (2.8) of the solution of the mixture of organic acids used in the kinetic leaching test had an essential role in the extraction of PTE from rhizospheric soils.

Based on the leaching experiment results (Figure 3), we observed that metals and metalloids behave differently during the extraction test. PTE concentrations were well above the permissible limit in surface water according to [55] (As $< 0.01\ mg \cdot L^{-1}$ and Sb $< 0.02\ mg \cdot L^{-1}$ Cd $< 0.003\ mg \cdot L^{-1}$; Zn $< 3\ mg \cdot L^{-1}$) (Figure 3e–h).

Moreover, Pb mobility was low because of its low solubility [56] and an increase in the pH of the solution. Many studies have shown that Pb adsorption increases with increasing pH [57,58]. However, several authors suggested that one of the causes of Pb immobilization in the humus horizons of acid soils is the stability of the complexes formed with fulvic acids and their ability to flocculate and aggregate [59,60] and also bind to iron oxides [61].

Large quantities of extracted metals generally characterize the most contaminated samples.

Correlation analysis between total and leachate PTE concentrations (Table 6) showed that their mobilization was proportional to metal(loid)s total content, showing a greater mobility for Cd and Zn compared with other elements in the contaminated soils. Correlation analysis also indicated the presence of a positive correlation between As and Sb (R = 0.90), between Pb and Sb (R = 0.91) and between Pb and As (R = 0.92), suggesting the presence of these elements in the same mineral phase, which is Jordanite [Pb_{14} (As, Sb)$_6$, S_{23}] [16]. The highest correlation coefficient was observed between Zn and Cd (R = 0.97), which confirms that they originated from the same mineral phases, sphalerite and hemimorphite (Table 6).

Table 6. Correlation matrix (R) between total and leachate concentrations of PTE.

	[As Leachate]	**[Sb Leachate]**	**[Cd Leachate]**	**[Pb Leachate]**	**[Zn Leachate]**	**[Ca Leachate]**	**[Mg Leachate]**	**[As Total]**	**[Sb Total]**	**[Cd Total]**	**[Pb Total]**	**[Zn Total]**
[As leachate]	1.00											
[Sb leachate]	**0.97**	1.00										
[Cd leachate]	0.21	0.30	1.00									
[Pb leachate]	0.11	−0.08	−0.71	1.00								
[Zn leachate]	−0.33	−0.27	**0.81**	−0.71	1.00							
[Ca leachate]	−0.51	−0.62	−0.86	**0.76**	−0.55	1.00						
[Mg leachate]	−0.11	0.01	−0.27	**0.14**	−0.48	**0.32**	1.00					
[As Total]	**0.76**	**0.61**	0.23	**0.43**	−0.11	−0.25	−0.35	1.00				
[Sb Total]	**0.92 ***	**0.80**	0.03	**0.40**	−0.38	−0.27	−0.30	**0.90**	1.00			
[Cd Total]	−0,11	−0.08	**0.89 ***	−0.49	**0.89**	−0.55	−0.31	0.21	−0.16	1.00		
[Pb Total]	**0.92**	**0.86**	0.41	0.14	−0.08	−0.54	−0.24	**0.92 ***	**0.91 ***	0.21	1.00	
[Zn Total]	−0.27	−0.21	**0.86**	−0.63	**0.98**	−0.55	−0.36	−0.01	−0.33	**0.97 ****	0.02	1.00

Notes: * Indicates the statistical significance at probability level of $p < 0.05$. ** Indicates the statistical significance at probability level of $p < 0.01$.

Analysis of the correlations between total Cd concentration and concentration in leachates shows that Cd mobilization is proportional to total concentrations (R^2 = 0.89) (Table 6). There was also a positive correlation between Cd's mobility and that of Zn, suggesting the presence of these elements in the same mineral phase.

Zn would present greater mobility due to the complexes that could form in neutral or alkaline soils with a relative solubility [62].

The authors of [63] reported that the environmental mobility and potential phytoavailability of Pb, Zn and Cd are strongly governed by soil pH, which declines in the order Cd >> Zn > Pb; thus, only a small portion of Pb in the soil was found to be potentially available for plant uptake.

According to [64], the main parameters influencing Pb's retention in soils are pH and CEC. For a pH above 6, Pb can adsorb to the surface of clay minerals or form carbonate precipitates [65]. Several authors [66–68] have reported that Pb is mainly bound to carbonates and Fe and Mn oxyhydroxides in alkaline to neutral medium ($pH \geq 7$). In this study, calcite's neutralizing power was maintained at an alkaline pH, promoting a powerful neutralization of Pb mobility by the precipitation of cerusite ($PbCO_3$). According to [69], in a carbonated context, Pb associates with carbonates in the form of cerusite ($PbCO_3$), which strongly reduces the mobility of Pb [70], thereby confirming its decrease in leachate concentration in the leaching tests. There was no correlation between total Pb content in the soil and leachate's Pb concentration, which could be explained by the precipitation of this element during the experiment.

Dissolution kinetics showed a significant precipitation and/or adsorption of As, especially for Sidi Bouaouane (1.3% at the beginning to 0.05% at the end of the test) and Jebel Hallouf (0.1% at the beginning to 0.08% at the end of the test), suggesting that carbonates controlled its mobility in soils. These could fix As and various PTE by precipitation of secondary minerals under oxidizing conditions. Moreover, the alkaline pH controls PTE's (metals and metalloids) behavior by maintaining chemical forms such as hydroxyls, metal complexes, metal carbonates and preventing the evolution towards exchangeable ionic forms [71,72].

Different mineral phases, such as calcium carbonate, clay and sulphides, are likely to trap As and release it for any change in geochemical conditions [73–75]. In this study, several clays (illite and kaolinite) and Fe oxyhydroxides that were identified can facilitate the adsorption of As [15]. For example, according to [76], the sorption of As on calcite increases from pH 6 to 10, peaks between pH 10 and 12, and decreases beyond pH 12.

Sb was always more mobile than As and the mobility of these two elements at Sidi Bouaouane was stronger than at Jebel Hallouf. In terms of ionic size, Sb is greater than As, suggesting a higher affinity of As compared to Sb for carrier phases such as iron oxyhydroxides [77–79] and easier desorption of Sb compared to As in their carrier phases [77,80,81].

In the environment, the mobility of Sb in water varies greatly depending on its chemical form [82–84].

The good relationship between metals and metalloids' total concentrations in soils and extractable concentrations by organic acids indicates that available elements should originate from the same mineral phases. For example, Zn could result from the dissolution of hemimorphite and sphalerite at Hammam Zriba, whereas Pb is likely to result from cerusite's dissolution in the soils of Jebel Hallouf-Sidi Bouaouane and Jordanite and anglesite in the soils of Jalta and Hammam Zriba.

In addition, the dominant forms of As are the sulphide forms [Jordanite [Pb_{14} (As, Sb)$_6$S$_{23}$], realgar (As_4S_4), mimetite (Pb_5 (AsO_4) 3Cl) and arsenopyrite or mispickel (FeAsS), which were found in the tailings resulting from mining activities in the studied area [16].

Sb is commonly found in association with As in sulfosalts, such as jordanite [Pb_{14} (As, Sb)$_6$S$_{23}$] [46,77,85].

Positive correlations were also observed between Pb, As and Sb (Table 6), indicating that these elements probably come from the same mineral phases that can be represented by jordanite in the soil of Jalta.

By comparing the results of the five soil samples, it can be deduced that Zn is more mobile for sample Z2, whereas Cd is much more mobile for the other sectors (Figures 4 and 5). The authors of [15] found a similar result for the soils of Jebel Ghozlane. The mobility of Zn, Pb and Cd was controlled by their carrier phases (sphalerite, hemimorphite and cerusite) in the tailings and soils.

Overall, the order of solubility for the different samples is as follows:

- B1: Cd > Zn > Sb
- H3: Zn > Cd > Sb
- J2: Cd > Zn
- G7: Cd > Zn
- Z2: Zn > Cd

The bioavailability of PTE results from various factors related to soil properties, including the role of plant roots and microorganisms (associated microbial communities). Plant roots can reduce the bioavailability of cationic metals/metalloids either by uptake at the root surface or through complexation with biomolecules derived from roots [86]. Soil microorganisms can also influence (increase or decrease) metal/metalloid solubility. In fact, the rhizosphere corresponds to a geochemical micro-environment influenced by the plants (root exudates composed of organic acids and siderophores, respiration, etc.) and microorganisms' activities [87].

In addition, plant root exudates provide nutrition to microorganisms in the rhizosphere, increasing the rhizosphere's microbiological activity, which stimulates plant growth [88]. These exudates lead to an increase in acidity at the soil/root interface [89], which promotes minerals' solubility. On the other hand, increased dissolution of calcium carbonate was observed (Figure 3d), leading to an increase in the rhizosphere's pH, thus favoring precipitation of some metallic elements (especially Pb and As) as secondary minerals. Other metallic elements were absorbed by plants (Zn, Fe, Cd) [90]. These results were confirmed by the kinetic leaching test performed on the organic acid mixture (LMWOAs).

All organic acids (LMWOAs) secreted by plant roots and present in the rhizosphere [22,23,37,91,92] can influence the physicochemical parameters of the soil (pH, CEC, etc.) [22,93] and can thus favor, in particular, the redistribution of As between the different constituents of the soil [94] or precipitation, producing its immobilization and, consequently, decreasing its phytoavailability [95].

5. Conclusions

Soils surrounding the former Pb-Zn mines of northern Tunisia, developed on a carbonate bedrock, were characterized by a variable CEC that oscillates between 1.8 meq/100 g and 23.1 meq/100 g.

Metal (Zn, Pb, Cd) total concentrations found in soils downstream of waste rock dams were high, up to 37,000 mg·kg^{-1} for Zn and 205 mg·kg^{-1} for Cd in Jebel Ghozlane soil, 17,000 mg·kg^{-1} for Pb in the soil surrounding the old mine of Sidi Bouaouane, also in this site were important metalloid contents (As and Sb), 683 mg·kg^{-1} for As and 145 mg·kg^{-1} for Sb.

The mineralogical phases carrying these metals were sulfates (anglesite: $PbSO_4$), Zn-silicates (hemimorphite: $Zn_4Si_2O_7 (OH)_2 \bullet (H_2O)$), sulphides (sphalerite: ZnS and pyrite: FeS_2), sulfosalts (Jordanite: $(Pb_{14} (As, Sb)_6S_{13})$), carbonates (Cerusite: $PbCO_3$) and iron oxyhydroxides.

Kinetic leaching tests with LMWOAs showed that solubilization of certain mineral phases (calcite and dolomite) caused an increase in the pH of the initial solution (2.8) to neutral to slightly alkaline values and that the dissolution of the PTE varied from one soil to another and from one element to another in the leachates of the five study areas.

The highest extraction rate obtained after 960 min of agitation was recorded for Cd, reaching 25% for Sidi Bouaouane and J. Ghozlane, and 22% for Hammam Zriba. Zn is the second most mobile element, the highest value (17%) characterized the soil of Hammam Zriba.

The extraction rate of Pb was low and did not exceed 1% in the Jalta soil. The mobility of metalloids (As and Sb) was practically negligible, except at Jebel Hallouf and Sidi Bouaouane. The extraction percentage of Sb did not exceed 1% for the sample of Sidi Bouaouane and 0.1% for As.

Thus, the study of the PTE (As, Sb, Cd, Pb and Zn) by the kinetic leaching test (LMWOAs) showed that these elements behave differently under alkaline conditions. A large part of these elements (Sb, Zn and Cd) was found in soluble soil forms exceeding [96] standards in surface waters. Pb and As were the exception by their tendency to precipitate under alkaline conditions.

Consequently, these PTEs present a risk of contamination for the environment due to their mobility and are phytoavailable in carbonated soils.

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