

Historical assessment approach of the evolution of the toxic trace element contents, transformation, distribution and redistributions, environmental risk levels and stability of Jbel Ressas tailings and agricultural soil (N-E Tunisia), to predict their management plan

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Abstract

The Jbel Ressas Pb-Zn mining wastes that had more than 600,000 m³ and their surrounding agricultural soil, that are in Northeastern Tunisia had ecological a high hazards. To suggest the wastes protection and soil remediation plan the evaluation of the historical evolution of their total and labile TTE contents, stability and distributions since their abundance (1952) and until today, which is not often possible, was a crucial step. The of Pb, Zn and Cd quantities in the initial wastes were 46640 t, 134780 t and 1150 t. the released Pb, Zn and Cd quantities in 2009 was 50% and in 2021 was 22.6%. The remained quantities are 15.6 t of Pb, 64.2 t de Zn and 0.4 t de Cd that presented a worrying environmental hazard. The pollutants speed migration was accelerated, particularly during the last 10 years. Thus, the risk of these pollutant sources is still high. Of the TTE that migrated from the tailings, only 6.1, 4.8, and 4.1% of Pb, Zn, and Cd, respectively were retained in soil. However, the soil potential ecological risk (E_{ri}) was high. From 1952 and until 2009 around 60% of the TTE tailings have been mobilized and from 2009 to 2021 around 6%. The estimation of the future evolution of redistributions and transformations of current TTE showed that the risk of Jbel Ressas residues is worrying. The whole-soil removal (U_{ts}) and relative binding intensity index (I_R) of the TEE in initial tailings sediments and soil ≈ 1 meaning that had any environmental risk. The U_{ts} and I_R evolution from 1952 and until today showed that the TTE stability and risk level increased with exposition time. Therefore, the overall historical assessment is of great interest in order to suggest solutions for polluted areas.

Introduction

The mining activities often generate large wastes volumes that were abandoned caused a widespread public concern. Although they were deposited several decades ago, they still carrying significant environmental risks. Their very high toxic trace elements (TTE) contents were often eroded towards the surrounding areas including the agricultural soils and contaminated it. Then these pollutants could be introduced into food-chain which represents a human health hazard (Zornoza et al., 2012). In order to management this of pollution sources type and contaminated soils, it is essential to make a detailed assessment. In order to carry out their global evaluations, several mineralogical, chemical, geophysical and statistical static studies and others have been developed (Navarro et al. 2008; Acosta et al. 2011; Conesa et al. 2011; Martínez-Pagán et al. 2011). However, these approaches believed incomplete to identify the appropriate remediation technique. In order to understand how to efficient manage in a sustainable manner these wastes and avoid the environmental problems associated with inaccurate risk assessment, exploring the waste history is a necessary step to the challenge. This could be done by identifying the evolution of the total pollutant content of the mine waste since its deposition and until today in order to predict its future risks. Secondly, it is necessary to evaluate the fate of the toxic elements released by the landfills towards the neighboring agricultural soils. Indeed, the evolution of TTE contents and their potential ecological risk factors (E_{ri}) (Muller 1969; Hakanson 1980; Salomons and Forstner 1984; Abraham and Parker 2007) in the agricultural soil, from ancient times to the present and probably in the future, will allow us to clarify whether or not the quantities of pollutants released by these dumps have all been trapped by the soil and their distribution.

Quantifying the total metal allows to have an idea about their abundance. However, it is insufficient to have an exact idea about their toxicity levels and their environmental and human health impacts. To assess the exact potential environmental risk of polluted site, the identification and quantification of the evolution of the TTE

bioavailability in the residues and the mobility factors (MF) from the initial waste deposition to the present day were essential (Kabata-Pendias 1993; Dean 2007; Rao et al. 2008; Camden-Smith et al. 2014).

Due to the prolonged incubation period of TTE in the mine wastes and their additions to soil (from residues) and the competition between sediment compounds and associated complex processes, changes in the redistribution and transformation of the pollutants between the different sediment fractions will have to take place. To quantitatively explore the transformation pathway(s) and kinetics of TTE, the equilibrium parameters proposed by Banin et al. (1990) were required. These are the whole soil index (U_{ts}) and the relative binding intensity index (RI). This evaluation will also allow to assess the of stability evolution degrees of the tailings and agricultural soil.

In this way, the assessment will determine the past, present and future health risk and the establishment of a short or long term management plan.

The Jebel Ressas tailings and the surrounding agricultural soils (North of Tunisia) pose serious environmental problems. In this site, more than 600,000 m³ of mining waste (3 dams: DI, DII and DIII) include high amounts of Pb, Zn and Cd (e.g. Ghorbel 2012) of which an important part has moved to the surrounding areas. To assess the pollution status of this site, physicochemical properties and total and bioavailable concentrations of TTEs of mine tailings and local agricultural soil have been performed (e.g. Ghorbel 2012; Souissi et al. 2014; Elouear et al. 2016). However, a historical assessment of the total metal contents and their labile fractions of the mine wastes and soil and their distribution is missing, which is necessary to define a management plan for the pollution sources of and soil rehabilitation.

In order that the quantitative assessment to be complete, it was also necessary to specify the evolution of the TTE mobile portions and their distribution in tailings and soil. The quantification of the of the redistribution and transformation evolutions of the TTE and their stability levels signifying their level of risk could be ensured by the calculation of the equilibrium parameters that are the whole soil (U_{ts}) and the binding intensity (reduced partition index: I_p) of the TTE (Han and Banin 1999; Fengxia and Wenbao 2010;. These parameters will make it possible to specify the quantities of total and labile TTE remaining in the waste and retained by the soil and which could present an environmental and health risk. The accuracy of the stability level and subsequent risk of these pollutants are also critical. The available information on the initial waste characteristics, which is still lacking elsewhere and the samples taken in 2009 and 2021, will be the tools for the assessment.

Therefore, the objectives of this study were to specify the assessment of (i) the past and present levels of total and available Pb, Zn and Cd (historical evolution) in tailings and soils, as well as their distributions and potential ecological risk and mobility factors, and (ii) the pathways and kinetics of transformations of Pb, Zn and Cd native to the tailings and loaded from the wastes into agricultural soils, in order to provide a management plan of the dams to limit or stop the pollutants migration and remediate the soil.

Material And Methods

Study area

The Jebel Ressas mine site is located 30 km southeast of Tunis (N-E, Tunisia) and at 36° 36' 33.02", 10°18' 56.58" (Fig. 1). The stratiform and vein mineralizations (in the form of open space \square llages) are of Pb and Zn. Both ore

types are found in the Upper Jurassic Ressas Formation (bioclastic limestones) and in contact with Triassic rocks (Sainfeld 1952). The main ores minerals are Galena (PbS), Sphalerite (ZnS) and Smithsonite (ZnCO₃).

From 1880 to 1956, the mine exploitation was in three discontinuous periods. The 70 years of activity produced huge quantities of wastes that were divided into three dumps (DI, DII and DIII) (Fig. 2). The surface and total volume of these tailings are respectively about 12 ha and 600,000 m³. From the beginning, the dumps were totally exposed and without any management. Their protection lack had greatly accelerated their alteration and erosion. But, on the dump surfaces a carbonate crust was quickly precipitated which impermeabilized them (Ghorbel 2012, Nassraoui 2021; Nassraoui et al. submitted). Thus, the wind distribution of their pollutants was made difficult if not impossible.

The Jbel Ressas wastes are surrounded by agricultural soils, mostly planted with olive trees. The average precipitation and temperature in Jbel Ressas region are around 500 mm year⁻¹, and 25°C, respectively (INM 2020). In the Ressas region, the west to North West is the main regional wind directions.

Field sampling and analytical methods

Eight cores (four in each) were taken in the DII and DIII dumps. Taking into account the wind directions, topography, slope, and texture, the same eight plots in the tailings and 32 plots in the soil were sampled in 2009, and 2021. In each plot (4 m × 4 m), eight equidistant 10 × 10 × 20 cm volumes of sediment were collected and then mixed. The composite sample was successively sieved through a 2-mm stainless steel sieve, transferred to dry polyethylene bags, freeze-dried, and stored in a cold room for further analysis.

The tailings and soil granulometric analysis was carried out using Robinson pipette method. The tailings and soil mineralogical composition was analyzed by using an X-ray diffraction (XRD) SIEMENS D-5000 type with a scanning speed of 1°/2θ min and Cu-Kα radiation (40 kV, 20 mA) from 0° to 70° (Van der Marel 1966).

The soil/water ratio 1:5 after one-hour mechanical shaking pH and electrical conductivity (EC) were measured by pH meter LPH 230 T-type and conductivity meter model ORION 150. The Ethylenediamine complex was used to determine the cation exchange capacity (CEC) (Bergaya and Vayer 1997). The calcium carbonate (CaCO₃) and total organic carbon (TOC) were determined by using the Bernard calcimeter method and the walkley-black titration method (Walkley and Black 1934), respectively. The total heavy metal concentration analysis, tailings and soil samples were processed and the obtained solution analyzed by flame atomic absorption spectrometry (AAS) equipped with a graphite furnace.

To ensure the extraction of the maximum quantities of bioavailable TTE fractions, many simple and complex procedures (sequential extraction) were tested (e.g. Tessier et al., 1979; Quevauviller 1998; Kabata-Pandias 2004; Sliti et al. 2019, Maiz et al. 2000; Favas et al. 2011). The obtained data showed that the most appropriated TTE extraction procedure is the BCR method (European Community Bureau of Reference) (Table 1) (Nassraoui et al. submitted).

The recovery percentage of sequential extraction is:

$$\% \text{ Recovery} = \frac{(F1 + F2 + F3 + F4) * 100}{(\text{total concentration})} \text{ (Eq. 1)}$$

20% of analyzed samples were replicated. To ensure the accuracy and reproducibility of each extraction step (Tessier et al. 1979; Ure et al. 1993), the use of NIST 2709a and a blank sample were often run. Each value was considered only if it was below 2%, compared to the certified value. The BCR-701 reference was also used. The non reproducible values were replicated.

All analyses were carried out respecting the quality assurance/quality control (QA/QC) protocol.

Potential ecological risk and mobility factors

The potential ecological risk factor was used to quantitatively express the potential ecological risk (RI). It was calculated as follows: $RI = \sum E_i$ and $E_i = T_i / B_i$ (Eq. 2)

Were T_i = the toxic response factor of heavy metal: $T_{Zn} = 1$; $T_{Pb} = 5$; $T_{Cd} = 30$.

C_i = the concentration of i element and B_i is the background value of the trace element i .

Hakanson (1980) proposed five levels of E_i : $E_i < 40$ low potential ecological risk; $40 < E_i < 80$ moderate potential ecological risk; $80 < E_i < 160$ considerable potential ecological risk;

$160 < E_i < 320$ high potential ecological risk; $E_i > 320$ very high ecological risk at hand for the substance in question.

The mobility factor (MF) was calculated as follows using the equation:

$$MF = ((F1 + F2 + F3) / (F1 + F2 + F3 + F4)) * 100 \text{ (Davidson et al. 1998) (Eq. 3)}$$

The ArcGis 10.6 and global mapper 21 were used to dress the hydrographic network and flow direction.

Redistribution Index and relative binding intensity of metals

U_{tf} used to describe the fractional evolution of component i in amended soil with ionic trace metal elements to the quasi-equilibrium state as in control soil. This fractional redistribution index was defined as follows:

$$U_{tf} = F_a / F_c \text{ (Banin et al. 1990) (Eq. 4)}$$

Where F_a is the fraction of the metal bound to a given component in amended soil, F_c is the fraction of the metal bound to the same component in control soil.

U_{ts} was calculated to describe the whole-soil removal of metal bound to a given component from equilibrium state to the incubated metal-amended soil (Banin et al. 1990).

$$U_{ts} = \sum_i^k (F_i \times U_{tfi}) \text{ (Eq. 5)}$$

where $i = 1$ to k sequential extraction step (1: least aggressive, $k = 4$: most aggressive),

By definition, $U_{ts} = 1$ corresponding the equilibrium state.

In the studied site, the F_c is the percentage of the total metal quantities that was bound to each sediment fraction within the initial wastes and considered control regional soil where the TTE were in quasi-equilibrium state. The F_a

was the percentage of the total amount of metal that was bound to a same sediment fraction in abandoned wastes and cultivated soils. When the environment is in a quasi-equilibrium state, U_{ff} values equals 1.

The reduced partition index (I_R) is the binding intensity of TTE to soil sediments (Banin et al. 1990). I_R was defined as follows:

$$I = \sum_{n=1}^k (F_i X(i))^n \text{ and } I_R = I / (k^n) \text{ (Eq. 6)}$$

In Jbel Ressas, F_i was the percentage of the total amount of metal that was bound to component i in abandoned wastes and active soil. n was arbitrary equal 2. $I_R = 1$ when the highest TTT amount was bound to the residual fraction (equilibrium state) and $I_R \approx 0.063$ when all pollutants transformed to soluble forms as the sequential extraction steps was four.

Results And Discussion

Tailings and soil characteristics

The four core drills carried out in DII and DIII dumps that were that were exposed long exposed (Since 195) to severe climatic conditions showed 5 and six carbonate layers with around 1 to 2.5 m thick and separated by clay layers, successively. In DII dump, sulfides (sphalerite and galena) and in DIII dump Cerusite, Smithsonite and Hydrozincite are the main minerals. Traces of gypsum are also present in DIII whose frequency increased with the frequency of the zinciferous minerals presence. The dominant grain size fraction was fine ($< 63 \mu\text{m}$). Their mean percentages in DII and DIII were 83 and 72%, respectively. The physicochemical characteristics (pH, EC, CEC, TOC, phyllosilicate) are given in Table 1. The initial wastes were mostly composed of silt (72%), clay (15%) and sand particles (13%). The pH was around the neutrality. Due to the clay proportions, the mean cation exchange capacity values were relatively high. The mean TOC concentration was 2.1% (maximum 3.28%) (Table 2). The Carbonates were the major's mineral of the actual wastes. Compared to initial wastes, a decrease tendency of pH values (from 6.7 to 7.6) and carbonate percentages (from around 60 to 55%) was observed. While an important increase of the EC values detected.

The carbonates percentage ranges were high in Jebel Ressas agricultural soil (from 7 to 100%). It characterized by wide alkaline pH ranging from 6.70 to 9.13 with a mean value 7.6. Thus, the high carbonates amount controlled the soil pH. The EC and CEC ranged from 101.7 to 5900 μscm^{-1} and from 35 to 55 $\text{meq } 100\text{g}^{-1}$, respectively. The minimum and maximum values of the soil organic matter of Jebel Ressas were from 0.34 to 2.95% (Table 3).

Tailings total trace element content and mobility

Global balance

The high pollutant concentrations of the initial residues presented a high health risk. The TTE concentrations were variable among residues to one another. The average concentrations in DII were 2.13% of Pb, 6.33% of Zn and 521 mg kg^{-1} of Cd and 2.74% of Pb, 7.56% of Zn and 683 mg kg^{-1} of Cd in DIII. Some traces of Ag, Mn and Cr were signaled.

Taking into account the initial average pollutants concentrations of the DII and DIII, the mineralogical composition and the average concentrations in 2009 of Pb, Zn and Cd within DI that were 1.27%, 5.20% and 170 mg kg⁻¹, respectively (Ghorbel 2012), the masses of Pb, Zn and Cd of the initial mine waste were 46640, 134780 and 1150 t, respectively. The content of these dumps became 22180 t of Pb, 78560 t of Zn and 508 t of Cd in 2009. In 2021, the wastes involved 10300 t of Pb, 27500 t of Zn and 291 t of Cd. Therefore, these mining wastes lost since 1952 around 70% of Pb and Cd and 79% of Zn. Thus, these dumps retained 15.6 t of Pb, 64.2 t de Zn and 0.4 t de Cd that presented a worrying environmental hazard.

As around 50% of the three trace elements left the waste over 60 years and about 22.6% over 10 years, the rate of migration of pollutants had accelerated over the last period. Thus, the risk from these pollutant sources is still high.

Toxic trace elements mobility

Following the crystallization of the impermeable carbonate crust (Ghorbel 2012, Nassraoui 2021; Nassraoui et al. submitted), the wind erosion of pollutants had significantly decreased. Thus, it was argued that only mobile fractions of the tailings TTE were likely migrated towards their surrounding areas. Therefore, evaluation of the TTE mobility evolution was imperative. The chemical behavior of toxic elements and the levels of their potential environment risk depend on the forms in which they were bounded to solid phase (Allen 1997). The sequential extraction of jbel Ressas material showed that between 83% and 99.6% of the Pb, Zn, and Cd from the two dumps were primarily bounded to the residual fraction. Thus, the sum of Pb and Zn bounded to the exchangeable, organic matter, and Mn oxides fractions represented less than 5% of the total TTE content. Cd was the most mobile element in the original TTE waste (13% in DIII). Therefore, the mobility factors (MF) of Pb, Zn, and Cd in the initial wastes were 1, 4, and 18, successively. In addition, the proportions of Pb, Zn and Cd in the residual fractions in DII became 42, 29 and 10% in 2009 and 37, 16 and 4% in 2021, respectively. Similarly, a strong decrease in the percentages of pollutants was observed in the residual fractions of DIII. Indeed, the residual fractions contained in 2009 about 13% Pb, up to 44% Zn and 42% Cd. In 2021, 9, 37.3% and 39% of Pb, Zn and Cd respectively were in mobile form (Fig. 3).

The sum of the labile pollutants of DII in 2019 and 2021 were 73 and 81%, respectively and the highest percentages were associated with organic matter.. In DIII, the sum of the mobile TTE was 67% in 2019 and 71.6 in 2021 and the majority of Cd was retained by exchangeable fraction. This evolution of TTE distributions among the different sediment fraction explained the increase of their MF. The Pb, Zn and Cd MF of DII became up to 58, 71 and 90 in 2009 and 63, 84 and 96 in 2021. In DIII, they also increased to be up 87, 62 and 58 in 2009 and up to 91, 79 and 61 in 2021 (Fig. 3). Hence, the TTE proportions bounded to exchangeable fraction, oxides fraction and organic matter increased with waste exposition time. The decreasing mobility orders of TTE in DII and DIII were Cd > Zn > Pb and Pb > Zn > Cd, respectively.

Taking these results into account, the total mass of Pb, Zn and Cd in the three landfills is 38100 t. Since the mineralogical composition of DI and DIII are comparable and about 75% of the toxic trace elements are in mobile forms, the three dumps currently contain about 28300 t of highly mobilizable TTE that present a high risk to the local environment.

Total soil toxic trace elements

Toxic trace elements and distribution

The average total concentrations of Pb, Zn, and Cd in the initial soil in 2009 and 2021 were 156.5, 19496, and 30910 mg kg⁻¹ (Table 4). The total Pb, Zn, and Cd concentrations increased approximately 125 times in 58 years (1950 to 2009) and approximately 73 times in 12 years (2009-2021). The order of change in the 3 trace elements concentrations varied with the increase period of wastes exposure. Until 2009, the increase in soil Pb content was significantly higher than that of Zn, while the soil from 2009 to 2021 was more enriched in Zn than in Pb. An increase in soil Cd content with tailings exposure time was always observed (Table 4).

The Jebel rissas MNT map shows that the highest elevation area corresponds to the tailings surfaces. The western-southwestern part of the site has the lowest elevation, while the elevations of the rest of the site are intermediate (Fig. 4). The spatial distribution of each pollutant (Table 5) and the pollutant sums showed that the site could be essentially subdivided into five zones that were distinguished by their pollution levels. The increasing order of the sums of the average concentrations of Pb, Zn and Cd in 2009 were (Table 5) Sector 3 = 37716 < Sector 5 = 17832 < Sector 1 = 15282 < Sector 2 = 13867 < Sector 4 = 12786 mgkg⁻¹. This order became in 2021: Sector 1 = 57528 > Sector 2 = 40232 > Sector 4 = 20211 > Sector 3 = 3679 > Sector 5 = 3004 mgkg⁻¹ (Fig. 4). In 2009, the sectors 4 where the altitude is the lowest had the least polluted level. However in 2021 the lowest total concentration of pollutants was in sector 5, while the soil elevation is relatively high. The sector 3 where the altitude is relatively low, it contained the highest total pollutant concentrations. Therefore, the soil altitude couldn't be considered a determining factor in pollutants distribution. However, this zonal distinction can only be virtual. Indeed, the map of hydrographic network with flow direction of Jebel Rissas showed that the low altitude zones are likely to receive the maximum amount of polluted water. However, due to the large volumes of precipitation runoff, a large part of the eroded pollutants percolated to the unsaturated zone and polluted the groundwater (Nassraoui, 2021). Thus, the only part that remained on the surface was dosed. Therefore, the surface sediment results should be viewed with caution. As reported by several authors (Boussen et al., 2013; Tembo B.D et al., 2006. Sahraoui et al., 2016), the wind pollution spreading should not be overlooked.

Global mass balance of TTE

Since all 20 cm of the soil slice was sampled and analyzed and the soil density is around 1.3g cm⁻³, the weight of the soil surface slice closest to the polluted dumps was estimated to be 0.25 km² of 20cm deep. From the total concentration per kg of sediments and weight of the surface slice sediments of this soil part, the Pb, Zn, and Cd amounts in the initial soil were 357, 356, and 32 g, respectively. The soil Pb, Zn, and Cd contents increased to approximately 70 t of Pb, 56 t of Zn, and 600 kg of Cd in 2009 and 79 t, 121 t, and 435 kg of Cadmium in 2021, respectively. Therefore, there was a progressive pollutant masses increases in the Jbel Rissas soil with the dams' exposure time. Compared to the TTE quantities released from the tailings, the soil retained only 0.2% of Pb, 1% of Zn and 0.05% of Cd. Souissi et al. (2014) reported that the average Pb, Zn and Cd concentrations of the first 2 meters of agricultural soil in the vicinity of the tailings were 0.38 and 0.87% and 6.11 mg kg⁻¹. Thus the first two meters contained around 2223 t of Pb, 5090 t of Zn and 3.5 kg of Cd. Hence, only 6.1, 4.8, and 4.1% of Pb, Zn and Cd, respectively of the quantities of TTE eroded from the tailings were lodged in the soil surrounding of Jbel Rissas dumps. Therefore probably, the pollutant quantities that migrated from the tailings reached large Jbel Rissas areas.

Ecological risk factor (Er')

Compared to the Tunisian standard where the maximum concentrations of Pb, Zn and Cd in agricultural soils are 100, 3 and 300 mg kg⁻¹, the Jbel Rissas soil was highly polluted.

Based on the background values proposed by Bowen (1979), the concentrations of Pb, Zn and Cd in the initial agricultural soil of the Jbel Ressas area were respectively 1.5, 4.5 and 2.5 times higher. In 2021, the average increase in ecological risk factors (Er^i) of Pb, Zn and Cd was about 28%, 70% and 30%, respectively, compared to the average Er^i in 2009. In 2021, the range of Er^i of Pb in the soil of Jbel Ressas is between 14 and 3200 (mean $Er^i \approx 744$). 97% of the soil area downstream of the tailings was at very high ecological risk. Only 3% of the soil that corresponds to the area away from the tailings had a low to considerable ecological risk. For Zn, 30% of the studied area had high potential ecological risk ($160 < Er^i < 320$), 47%, 11%, and 12% showed considerable, moderate, and low ecological risk, respectively. In all agricultural soils, Cd caused a very high potential ecological risk ($Er^i > 320$) (Fig. 7). The order of TTE risk was Cd > Pb > Zn. Therefore, the agricultural soil surrounding the three residues had a serious ecological risk that was mainly due to its high TTE content.

Pollutants mobility

From initial deposition to 2021, there was a gradual evolution of the waste physicochemical characteristics that should have a direct effect on the evolution of the soil TTE mobility. For example, based on the Pb mobility factors that were 24, 21, 18, 36 and 7 in sector 1 to 5, respectively; we could subdivide the Jebel Ressas soil into five sectors (Fig. 2).

In 2009, the Pb was more stable than Zn and Cd. 76, 79, 82, 64 and 94% of lead bounded in the sector 1, 2, 3, 4 and 5 to residual fractions, respectively. In all sectors, the Pb percentage ranges in the oxides fractions were from 2–18%. The Pb percentages bounded to

Exchangeable fractions did not exceed 5%. The organic fractions of sectors 1, 2, 3, 4 and 5 involved 9.3, 4, 14 and 4% of Pb, respectively (Fig. 2).

The Zn was more mobile than Pb. The decrease of labile percentages of Zn were 58 in sector 1 (F1=15, F2=18, F3=25%), 53 in sector 2 (F1=15, F2=16, F3=22%), 53 also in sector 3 (F1=14, F2=15, F3=24%), 49 in sector 4 and 43% in sector 5. However, the Zn fractions retained in the residual fraction increased from sector 1 to sector 5 (Fig. 2).

The Cd in sector 1 (55%) and 2 (58%) bounded more in labile than in residual fractions (45 in sector 1 and 42% in sector 2). In sector 3, the highest percentage of Cd bounded to residual fraction (55%). 21% of Cd associated to exchangeable fractions and 19% to oxides fraction. Just 5% of Cd fixed to organic matter fractions. In sector 4 and 5, the percentages of Cd in active forms (F1+F2+F3) were 45 and 51%, respectively and in residual fractions were 55 and 49%, respectively.

The Jebel Ressas sectorial subdivision of agricultural soil adopted in 2009 was confirmed in 2021. However, significant variations of the TTE distribution among soil fractions.

In Sector 1, the Pb percentage bounded to exchangeable fraction was low (4%). The essential Pb quantities bounded to organic matter (54%) and oxides fraction (29%). Just 14% of lead was in stable form (associated with residual fraction). 29%, 16% and 22% of Zn quantities bounded to exchangeable, organic matter and oxides fractions. Just 33% bounded to residual fraction. 5%, 31% and 36% of Cd bounded to exchangeable, organic matter and oxides fractions, respectively and only 27% to residual fraction.

In Sector 2, the highest percentage retained Pb by organic matter (39%). 26% of Pb associated with oxides fractions and only 1% bounded to exchangeable fraction. 34% bounded to residual fraction. The Zn extraction data showed that the totally Zn quantity bounded to bioavailable fractions (F1=26%, F2= 32% and F3= 41%). The maximum quantities of Cd were in active form 60% (F1=2%, F2= 17% and F3= 42%) and 40% involved in residual fraction.

In Sector 3, low percentages of Pb (4%) and Cd (10%) bounded to exchangeable fractions. 23% of Pb and 17% of Cd retained by the oxides fractions. In organic matter, the percentages of Pb and Cd were 37% and 17%, respectively. The majority of Cd (58%) and Pb (36%) fixed by residual fraction. The essential Zn quantity was bounded to exchangeable fraction (40%). In oxides and organic matter fractions the percentages of Zn were 28% and 20%, respectively and just 12% was fixed by residual fraction.

In Sector 4, a high Pb percentage was in stable form (39% associated with residual fraction), and 61% was in labile fractions (F1=1%, F2=37%, F3=23%). A high Zn percentage was in labile forms as 42% was in F1, 20% in F2, and 38% in F3. For Cd, the most percentage was in stable (57%) fraction and 43% was in active forms (F1 = 17%, F2 = 18%, F3 = 8%).

In Sector 5, the high extracted Pb (92%) and Cd (45%) portions were bounded to residual fraction. The Pb and Cd were retained by F2=F3= 3% and F2=F3= 15%, respectively. In the exchangeable fractions the percentage of Pb and Cd were 2% and 25%, respectively. 38% and 25% of Zn bounded to oxides and organic matter fractions respectively. Just 4% bounded to exchangeable fraction and 32% of the Zn fixed by residual fraction.

In 2009, the affinity orders of Pb, Zn and Cd in sectors 1, 2 and 3 (close to DIII and DII tailings) showed that the essential TTE percentages were bounded to labile fractions (F1+F2+F3). Indeed, the mobility factors (FM) in the sectors 1, 2 and 3 of the Pb were 86, 66, and 64, of the Zn 67, 99 and 88 and of the Cd 73, 60 and 42, respectively. The TTE affinity orders in the sectors 4 and 5 showed that the Pb and Cd were the more stables. The Zn in these two sectors had a high mobility that were 94 (sector 4) and 96 (sector 5). The Cd mobility factors in sector 4 and 5 were 43 and 55, respectively (Table 6). In 2021, the affinity order of Pb fraction found similar in the sectors 1, 2, 3 and 4 and essentially bounded to residual and oxide fractions. Furthermore results found that Zn was bounded essentially with residual fraction and organic matter. The data also showed that the Cd in the 5 sectors was essentially associated with residual, oxides and organic matter fractions (Table 6).

These data showed also that TTE mobility affinity orders had changed from 2009 to 2012 (Table 6) and the TTE mobility increase from 2009 to 2021. The TTE were also always more mobile close to the tailings and their lability decreased far way the contamination source, except the Zn stay elsewhere high mobile.

These summary data that included all obtained data from the studied site showed that from initial wastes deposition to 2021 an important evolution of Pb, Zn and Cd speciation's occurred (Fig. 7). Indeed, first the TTE were essentially in stable forms, particularly the Pb and Zn. After that, an important increase of the mean percentages of labile pollutant portions was observed. In 2009, the Pb, Zn and Cd percentages bounded to mobile fractions (F1+F2+F3) were 21, 51 and 51%, respectively and to residual fraction were 79, 50 and 49%, respectively (Fig. 7). In 2021, the mobile Pb, Zn and Cd fractions had increased to be 57, 84 and 55% and their stable forms declined to up 43, 16 and 45%. These data also showed that the TTE mobility order had changed from 2009 to 2012. It was Pb < Zn = Cd in 2009 and became Pb ~ Cd < Zn in 2021. This order was relatively different than in others mining contexts (e.g., Obiora et al., 2015)

Therefore, the long exposure period of the mine wastes was a determining factor as these contamination sources increased with time the Jebel Ressas soil pollution. The progressive TTE loading to the agricultural soil had progressively increased the ecological risk and the mobility factors of Pb, Zn and Cd since the deposition of the dumps and until 2021. These dumps still pose health risks. Indeed, during around 60 years of exposure, 60% of the pollutants that were initially in stable forms have been mobilized, and in the last 10 years an additional 6% of the pollutants have been transformed into labile fractions. Thus, an average of 6% of the tailings pollutants could be yearly transformed into labile forms. Since the 3 residues actually contained around 15.6 t of Pb, 64.4 t of Zn and 0.4 t of Cd, the annual mobilization of the pollutant stock will be 0.03 t of Pb, 0.1 t of Zn and 0.6 kg of Cd. By the way, the high TTE mobility of the close soil to the dumps confirmed the contribution of the mobile TTE portions to this site pollution.

Redistribution Index (U_{ts}) and relative binding intensity (I_R)

Thus, it was important to numerically assess their redistribution and transformation evolution that could be seen from changes in their "equilibrium" parameters (Banin et al. 1990; Han and Banin 1997, 1999; McGrath and Cegarra 1992)

Following the long exposition time of the mine wastes (from 1952 to 2021), the Pb, Zn and Cd incubation highly increased the whole waste values (U_{ts}) in DII and DIII to reach up to 180. During the two sampled periods (2009 and 2021), the order of the U_{ts} mean values of DII and DIII was Pb = 142 < Zn = 28 < Cd = 13. The three pollutants U_{ts} of DII in 2021 were higher than those of 2009 and with exposure time of the tailings, the three trace elements of the two mine wastes had the same decreasing trend (Fig. 8). The U_{ts} ranges of soil Pb, Zn and Cd were 13.2-0.27 in 2009 and 3.6-0.24 in 2021. The highest soil U_{ts} was of the Pb (3-13) and the less was of the Cd (0.24-0.27) and the pollutants order increase was Pb < Zn (Fig. 9).

The I_R parameter enables to quantify the relative binding intensity of TTE to the wastes and soil fractions. The relative binding intensity I_R range of the three TTE of both tailings was 0.14-0.70. The I_R of Pb in DII were higher (0.62 and 0.7) than in DIII (0.5 and 0.56). However, the Zn I_R values were higher in DIII (0.62 and 0.7) than in DII (0.44 and 0.55). For both sampling periods, the I_R increasing order of DII was Pb > Zn > Cd. However in DIII, a fluctuation of the I_R values was observed (Fig. 10). These data showed that the relative binding intensity parameter evolution of TTE in contaminated soils was different from those of the dumps. The mean I_R of the loaded Pb, Zn and Cd towards the soil were 5.87, 6.20 and 0.42. When the three TTE logged in soil they increased to be 0.9 (Pb), 0.7 (Zn) and 0.6 (Cd) in 2009. The I_R of Pb and Zn in 2021 decreased to 0.7 (Pb), 0.4 (Zn) and of Cd remained similar (0.6) (Fig. 11).

The TTE redistribution and transformation is affected by three factors that are (i) the distribution of the TTE in the native environment, (ii) the metal loading level, and (iii) the time of TTE addition (Han and Banin 1997). Hence, the TTE redistribution and transformation of whole tailings and soil (U_{ts}) and their relative binding intensity (I_R) evolution depended on the labile TTE quantities in mine wastes and on their loading level from dumps to the soil, respectively. In the initial tailings and native soil that were at quasi-equilibrate state the U_{ts} were ≈ 1 . At low and high TTE loading levels, the U_{ts} of the agricultural soil reached immediately the values around 3 and 25 (Han and Banin 1999), respectively. With time, the whole-soil should reach the equilibrium state and the U_{ts} values will decrease to be around the unity at the low TTE loading level. At the high pollutants level loading, the U_{ts} level stabilized around 3-4 indicating a return to a distribution pattern similar to the initial soil (Han and Banin 1999).

In initial tailings, the TTE were mainly bounded to residual fractions. From the first waste deposition period to 2009, the U_{ts} values were widely higher than 25 (Han and Banin 1999), particularly of Pb. These data showed that the mobile TTE quantities remained very high (far from the equilibrium state). The very high U_{ts} values increase of Pb were mainly due to the residence of a high TTE quantities in the Fe and Mn oxide and organically and sulfur fractions (Fig. 12). Compared with Pb, the found decrease of the U_{ts} (moderately low) of Zn was because this element was essentially transferred from the residual to organically and sulfur fractions (Fig. 13). However, the low Cd- U_{ts} were due to the low Cd concentrations and the differences of the TTE distribution in the dumps (Fig. 14). Therefore, the U_{ts} intensity changes were closely related to the increase of the mobile Pb, Zn and Cd quantities. As a high stable TTE percentages were transferred from 1952 to 2021 to the exchangeable and carbonate, Fe and Mn oxides and organic fractions, the tailings U_{ts} acquired larger values (from 80 to 180). These labile toxic elements moved from the tailings towards the native soil where the initial TTE were also in equilibrium state. The added quantities of the toxic elements perturbed the soil "equilibrium" parameters. Indeed, the mean U_{ts} values of Pb and Zn (major pollutants) increased from the initial values (around one) to around 3.4 in 2009 and 12 in 2021.

In DII, the Cd had the lowest bending intensity that explained by the high pollutants transfer rate to the soil. While Pb was the most toxic trace that bounded to sediments meaning that it was the most stable in the dumps. However, Pb in DIII had the lowest I_R and those of Zn and Cd were higher and comparable meaning that the Pb loading rate was higher than those of Zn and Cd. Thus, the decreasing impact health order of the two dumps pollutants was Cd > Zn > Pb. This I_R difference that depended on the transfer degree of TTE was essentially due to a difference of the mineralogical and geochemical characteristics of both dumps (Johnson et al. 2000, Singh et al. 2010; Khan et al. 2008). Indeed, the sphalerite and galena were the main minerals that contained the Pb and Zn while the Zn from DIII tailings was released from hemimorphite ($ZnCO_3$). Between 1952 and 2009, the long residence time of pollutants in the soil increased their I_R meaning that some proportions of the mobile forms of Pb, Zn and Cd bounded to residual soil fractions. After that (2009-2021), the increase of the pollutants loading level towards the soil largely decreased the soil I_R . This decline was higher for Zn (0.3) than for Pb (0.2). While the I_R of Cd remained unchanged.

Hence, the initial TTE quantities in Jbel Ressas tailings and soil had any health impact. From the 1952 to 2009, the U_{ts} increase and the I_R decrease values of tailings and soil of the TTE widely increased their potential risks. During the last 10 years, the of change rates of the U_{ts} and I_R of the Pb, Zn and Cd had further increased their health risks.

Therefore, the evaluation of the historical evolution of the tailings and soil in TTE contents, mobility's and stabilities has allowed drawing up a complete balance sheet indicating that these dykes are always a source of risk. Thus, this complete diagnosis insured the decision makers to suggest an appropriate plan for the development of the dikes and the polluted soil.

Conclusion

The overall historical assessment of the mine wastes of Jbel Ressas showed that the TTE quantities already migrated from the tailings towards the surrounding areas, remaining and retained by the soil and their distributions were evaluated. The of the TTE mobility evolution of in the whole site, the ecological indexes and the

impact of the still available TTE quantities and their danger level to the agricultural soils were also considered. The quantities of Pb, Zn and Cd in the initial wastes were 46640 t, 134780 t and 1150 t. The remained quantities in the wastes are 15.6 t of Pb, 64.2 t de Zn and 0.4 t de Cd that presented a worrying environmental hazard. During around 60 years 50% of the three traces were transferred to labile forms and during the last 10 years around 22.6%. Hence, the migration speed of pollutants was accelerated with the the dumps time exposition. Thus, the risk of these pollutant sources is still high. Of the TTE that migrated from the tailings, only 6.1, 4.8, and 4.1% of Pb, Zn, and Cd, respectively, were retained by the top two meters of soil of the investigated site where the potential ecological risk (Eri.) was high. Since 1952 and until 2009 around 60% of the tailings TTE have been mobilized and from 2009 to 2021 around 6%. The high mobility of the TTE of soil closes to the dumps and the crystallization of the impermeable carbonate crust that covered the tailings surface, confirmed the contribution of mobile soil TTE to the site pollution. Therefore, the remained TTE quantities in the tailings and their future redistribution and transformations and risks will worry.

The TTE whole-soil removal (U_{ts}) and the relative binding intensity index (I_R) that describe the evolution of the environment equilibrium state, were ≈ 1 in Jbel Ressas initial tailings and soil meanings they were stable and without any health risk. From 1952 to 2021, the U_{ts} increase and I_R decrease values of tailings and soil Pb, Zn and Cd marked the widely the increase of their instability and potential risks, particularly during the last 10 years.

Therefore, the evaluation of the historical evolution of the tailings and soil TTE contents and their motilities and stability allowed drawing up a complete balance sheet. as these source pollutions continued to be a of serious health risk, the suggestion of an appropriate management plan by decision makers urgent.

Declarations

Conflicts of interest

The authors declare no conflicts of interest

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Tables

Table 1 Used extraction procedures

Fractions	Methods	References
F1: Exchangeable and carbonate bound Fraction	0.11 mol L ⁻¹ of AcOH	Davidson et al. (1994); Ure et al. (1993)
F2: Fe and Mn oxide bound Fraction	NH ₂ OH-HCl (0.1 mol L ⁻¹ , pH 2)	
F3 (Organically and sulfur bound Fraction.)	H ₂ O ₂ (8.8 mol L ⁻¹ , pH 3.2) and AcONH ₄ (1 mol L ⁻¹ , pH 2)	
F4: Residual Fraction)	Digestion (HCl-HNO ₃) + HF (150 °C-2 h)	

Table 2 Physicochemical properties of actual tailing wastes

	pH	EC (mScm ⁻¹)	CEC (meq100g ⁻¹)	TOC (gkg ⁻¹)	Phy. (%)
Mean	7.6	2.3	16.7	2.1	15
SD	0.2	2.7	3.2	0.45	2
Min	7.3	0.2	12.3	1.2	14
Max	7.9	17.5	21.7	3.28	16
N	102	109	76	109	121

Phy.: Phyllosilicate ; N: samples number, Max: maximum; Min: minimum; SD: standard deviation; TOC: total organic carbon.

Table 3 Physicochemical properties of the agricultural soils in 2009 and 2021

	PH	EC ($\mu\text{S cm}^{-1}$)	CEC ($\text{meq } 100\text{g}^{-1}$)	OM (%)	CaCO ₃ (%)	Sand (%)	Silt (%)
Min	6.70	101.7	35.0	0.3	55.0	23.0	15.0
Max	9.13	5900.0	55.0	2.9	100.0	80.9	66.4
Mean	7.52	1647.9	42.2	1.6	49.0	51.3	37.0
SD	0.73	1538.4	6.1	0.7	26.9	15.5	13.9

Table 4 The evolution of the statistic Pb, Zn, Cd concentrations of the soil

Year		Pb (mgkg^{-1})	Zn (mgkg^{-1})	Cd (mgkg^{-1})	Total TTE
Initial*	min	27	55	0.3	
	max	85	121	1.1	
	Mean	55	101	0.5	156.5
	SD	10	23	0.3	
2009	min	181	659	9	
	max	52396	31229	139	
	Mean	10798	8600	98	19496
	SD	1299	1054	21	
2021	min	3130	12140	24	
	max	28470	28600	170	
	Mean	12128	18715	67	30910
	SD	9837	8120	62	

*: Background, TTE: toxic trace elements.

Table 5 The evolution of the average toxic trace elements concentrations of the different sectors of the agricultural soil in 2009 and 2021

	2009			2021		
	Pb	Zn	Cd	Pb	Zn	Cd
Sector 1	2148	13053	81	3130	28600	42
Sector 2	6757	6997	113	7554	13520	82
Sector 3	25054	12495	167	28470	26513	152
Sector 4	7604	5111	71	8074	12140	36
Sector 5	12427	5347	58	13414	12800	24

Table 6 The affinity orders of Pb, Zn and Cd of the different sectors in 2009 and 2021

	2009			2021		
	Pb	Zn	Cd	Pb	Zn	Cd
Sector1	F4>F2>F3>F1	F4>F3>F2>F1	F4>F2>F3>F1	F3>F2>F4>F1	F4>F1>F3>F2	F3>F2>F4>F1
Sector2	F4>F2>F3>F1	F4>F3>F2>F1	F3>F2>F1>F3	F3>F4>F2>F1	F3>F2>F1>F4	F3>F4>F2>F1
Sector3	F4>F2>F3>F1	F4>F3>F2>F1	F4>F1>F2>F3	F4>F3>F2>F1	F1>F2>F3>F4	F4>F3>F2>F1
Sector4	F4>F2>F3>F1	F4>F3>F2>F1	F4>F2>F3>F1	F4>F2>F3>F1	F1>F3>F2>F4	F4>F2>F1>F3
Sector5	F4>F3>F2>F1	F4>F3>F2>F1	F4>F3>F1>F2	F4>F2>F3>F1	F2>F4>F3>F1	F4>F2>F3>F1

Figures

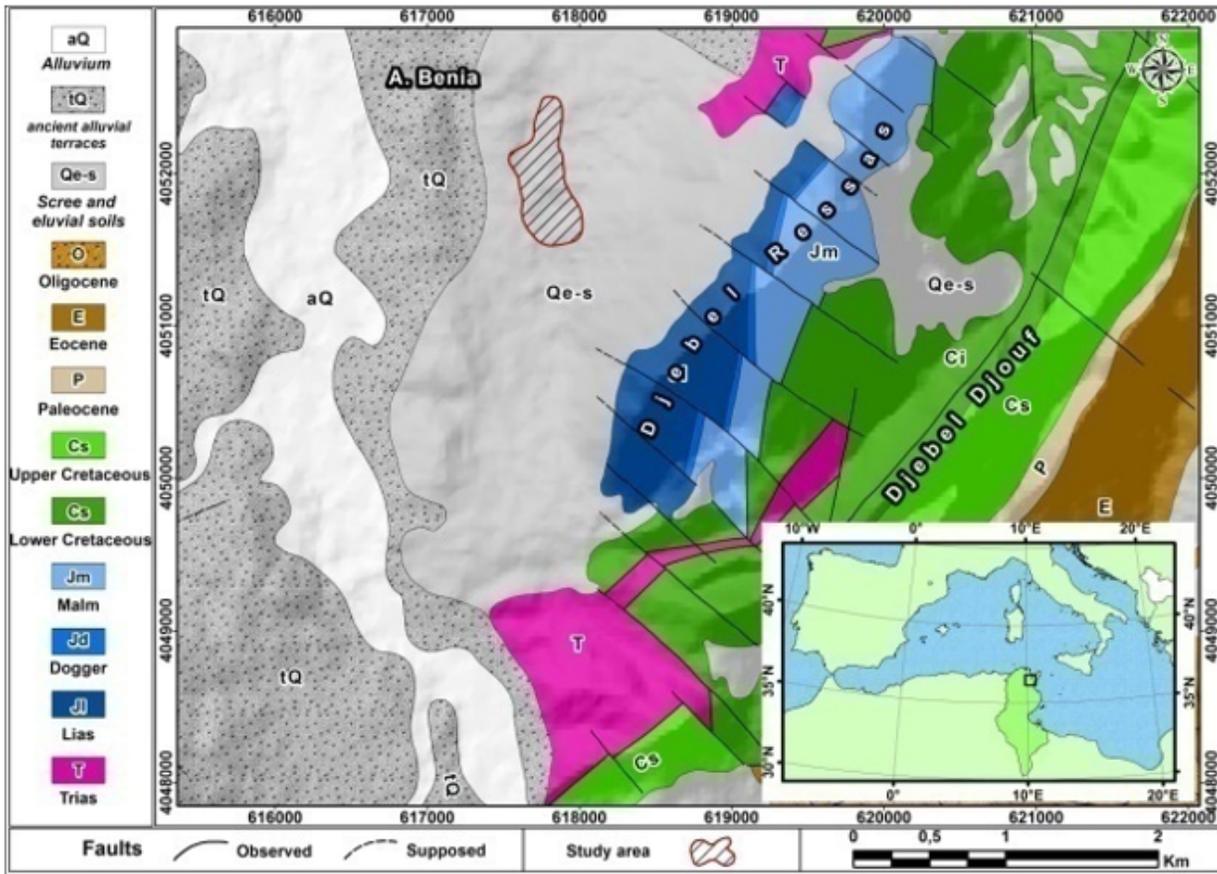


Figure 1

Geological map of the Jebel Ressas area and location of studied area

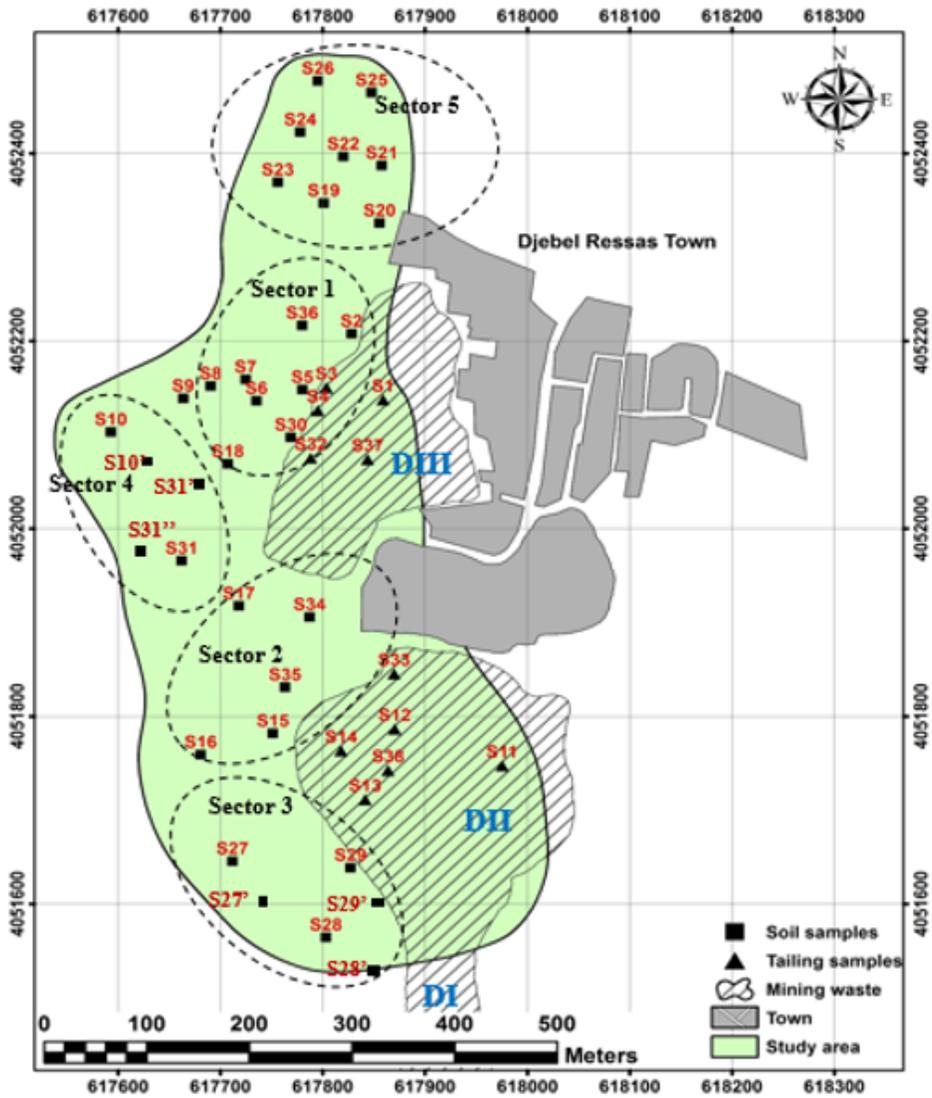


Figure 2

Jbel Ressas agricultural soil map with tailings (DI, DII and DIII) and sampled plots localizations

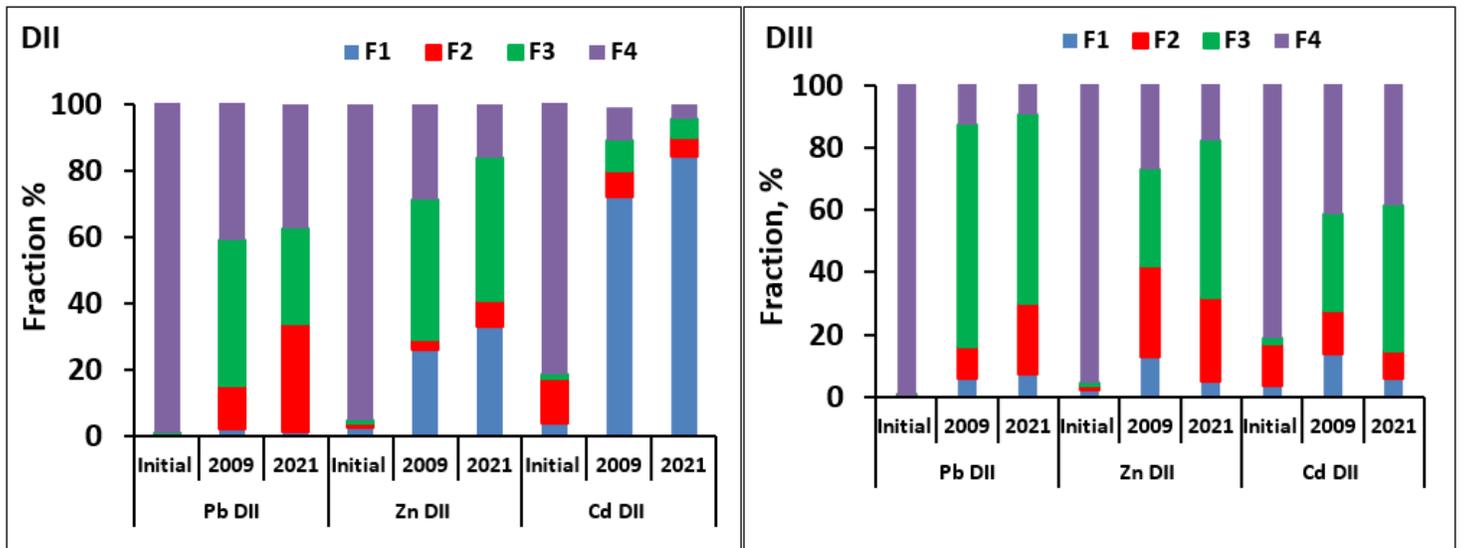


Figure 3

Evolution of toxic trace elements bounded to the Exchangeable (F1), oxides (F2), organic matter (F3) and residual (F4) fractions of DII and DIII sediments

F1: Exchangeable; F2: reductible; F3: oxidizable; F4: residual; TTE: toxic trace elements

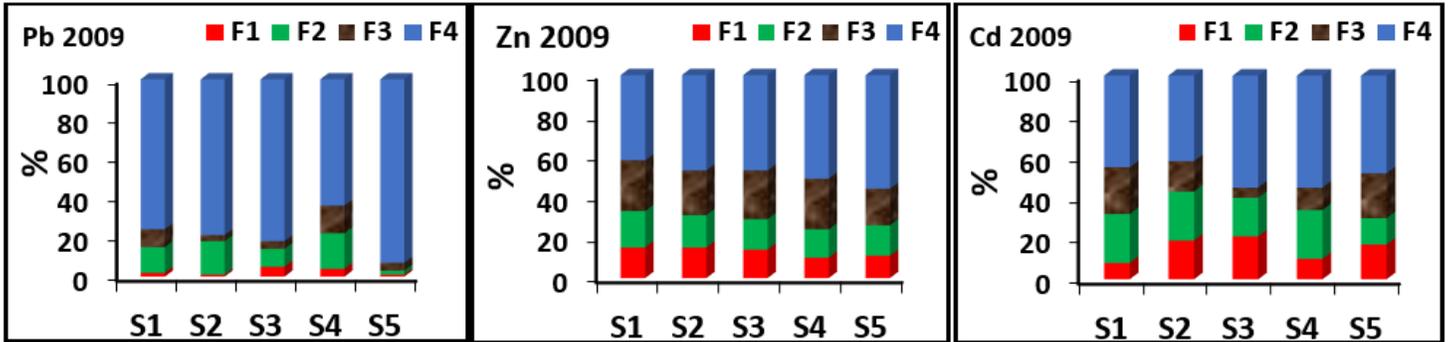


Figure 4

Percentages of the Pb, Zn and Cd in the five soil sectors that bounded to the for soil fractions in 2009

F1: Exchangeable; F2: reductible; F3: oxidizable; F4: residual; TTE: toxic trace elements

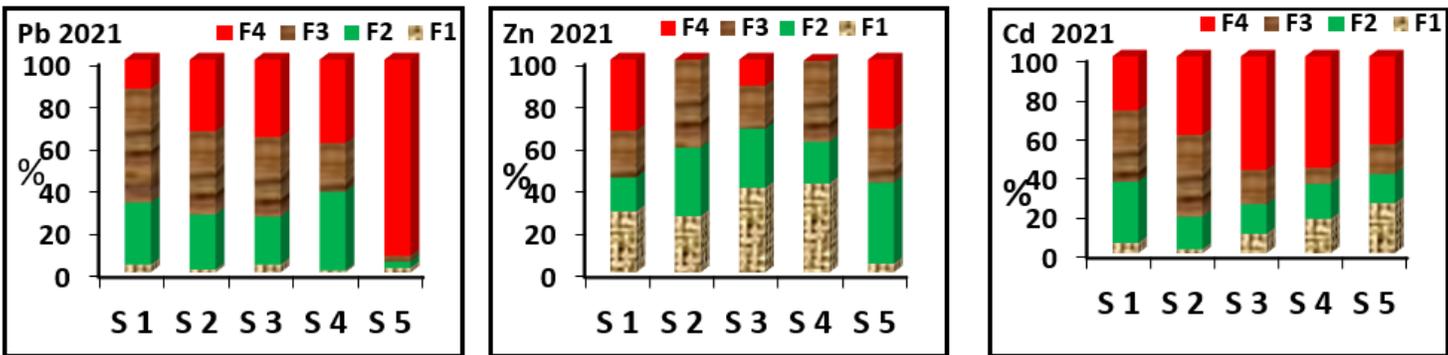


Figure 5

Percentages of Pb, Zn and Cd in the five soil sectors bounded to the for soil fractions in 2021

F1: Exchangeable; F2: reductible; F3: oxidizable; F4: residual; TTE: toxic trace elements

Figure 6

Evolution of the toxic trace elements mobility in 2009 and 2021

F1: Exchangeable; F2: reductibe; F3: oxidizable; F4: residual; TTE: toxic trace elements

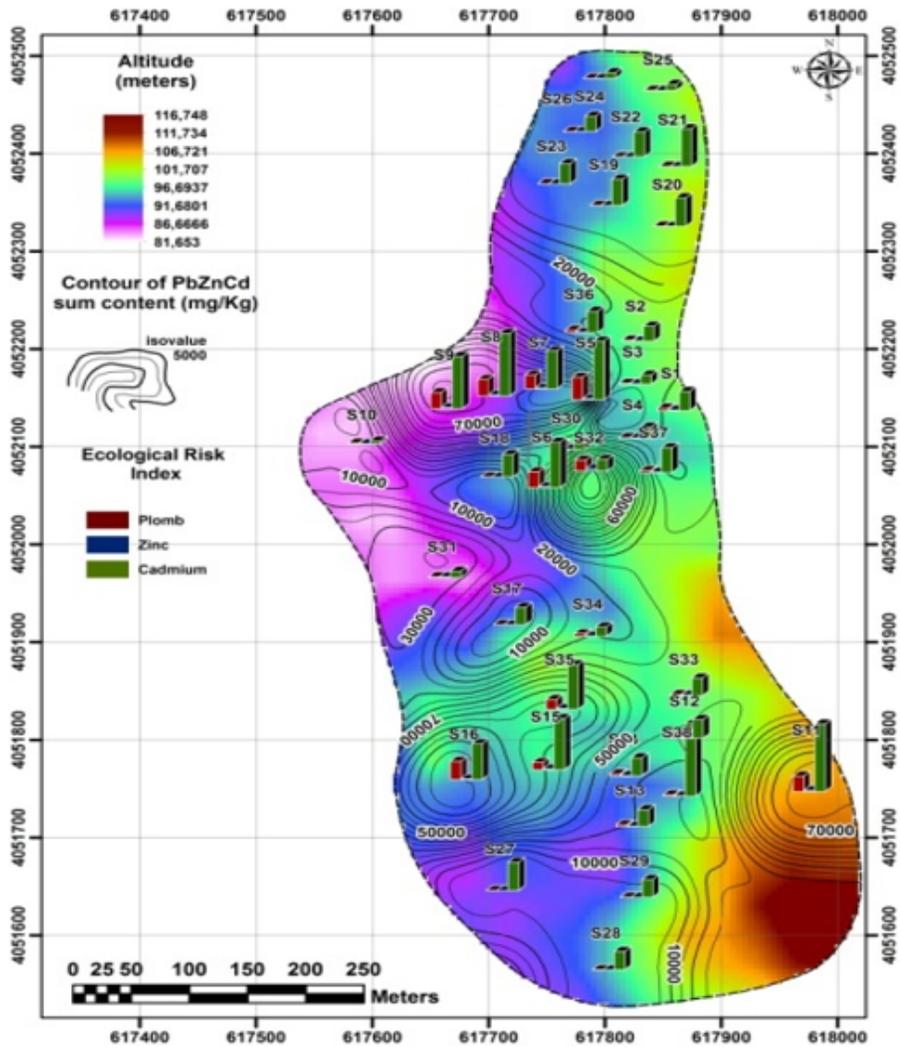


Figure 7

Distribution map of Ecological risk factor (Er^i) in agricultural soil of Jebel Ressay

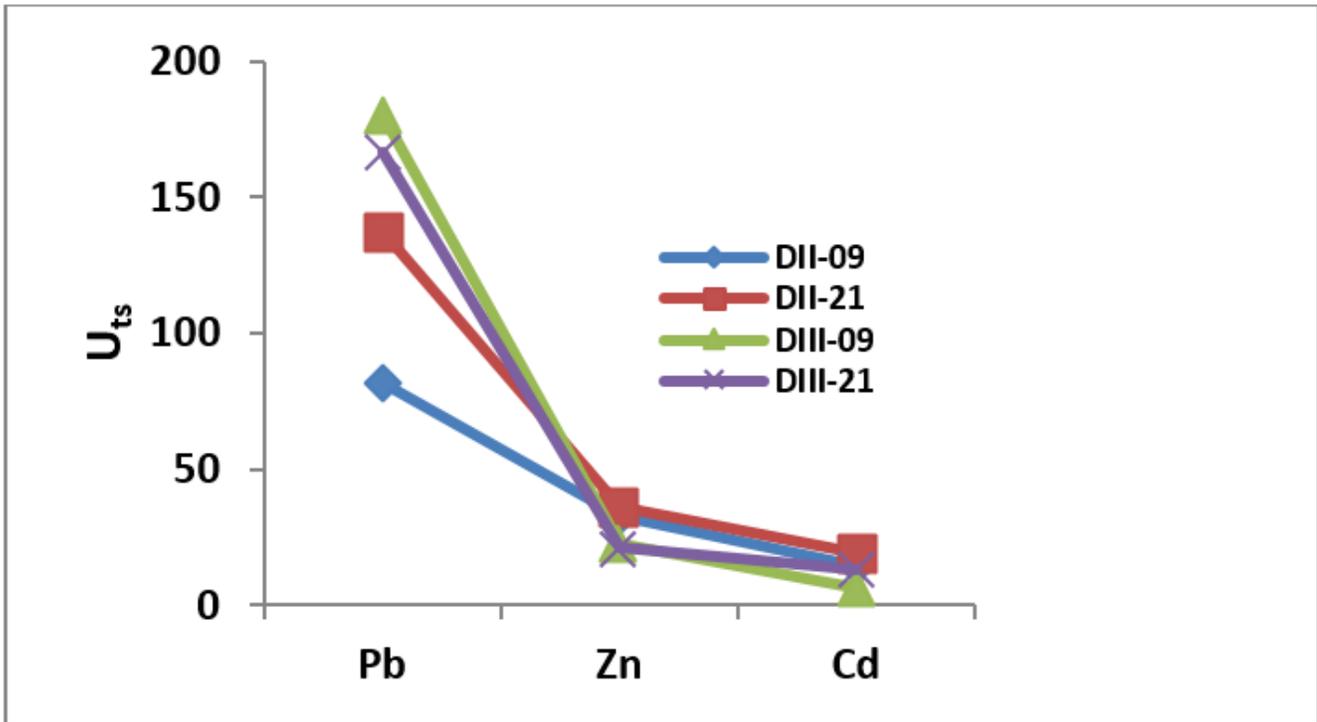


Figure 8

The long-term evolution of equilibrium parameter (U_{ts}) of the Pb, Zn and Cd in the whole dumps

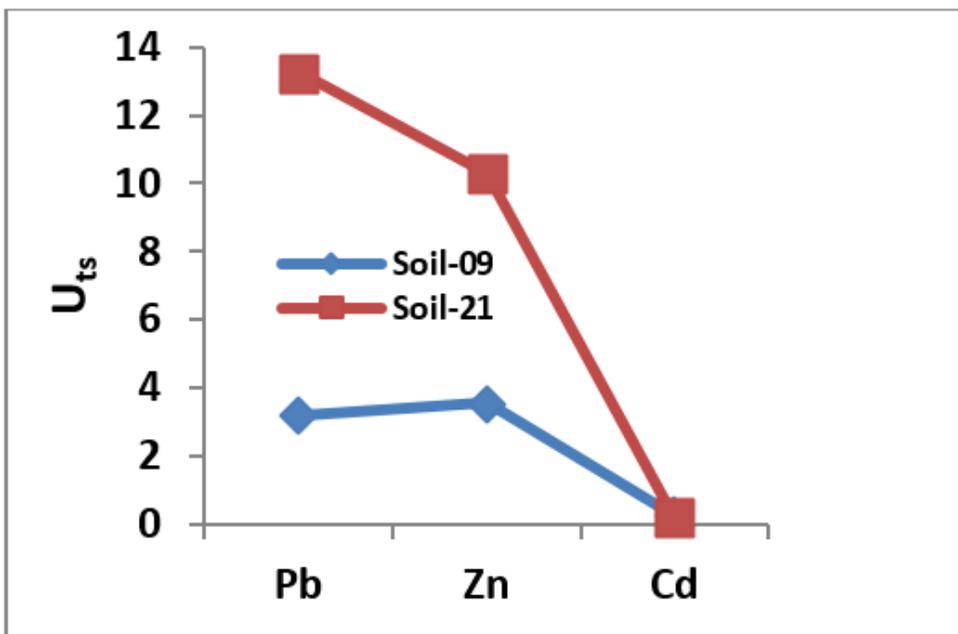


Figure 9

The long-term evolution of equilibrium parameter (U_{ts}) of the Pb, Zn and Cd in the whole soil

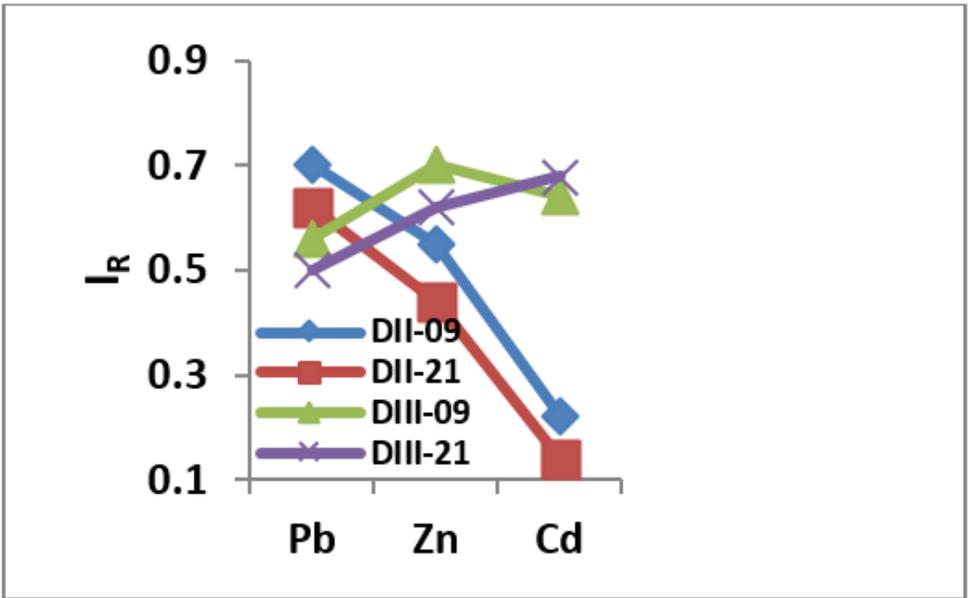


Figure 10

The Pb, Zn and Cd reduced partition index, I_R , evolution of the two dumps

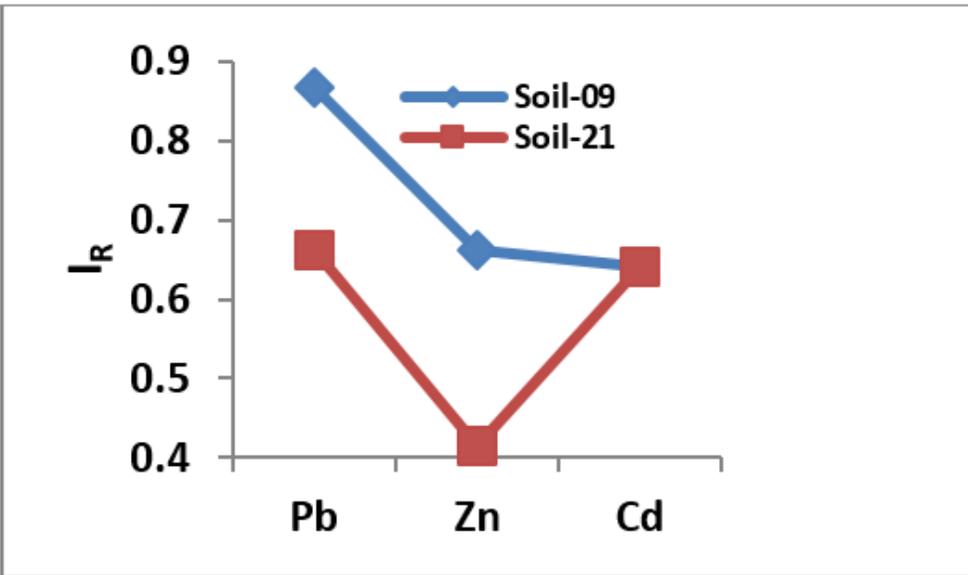


Figure 11

The Pb, Zn and Cd reduced partition index, I_R , evolution of agricultural soil

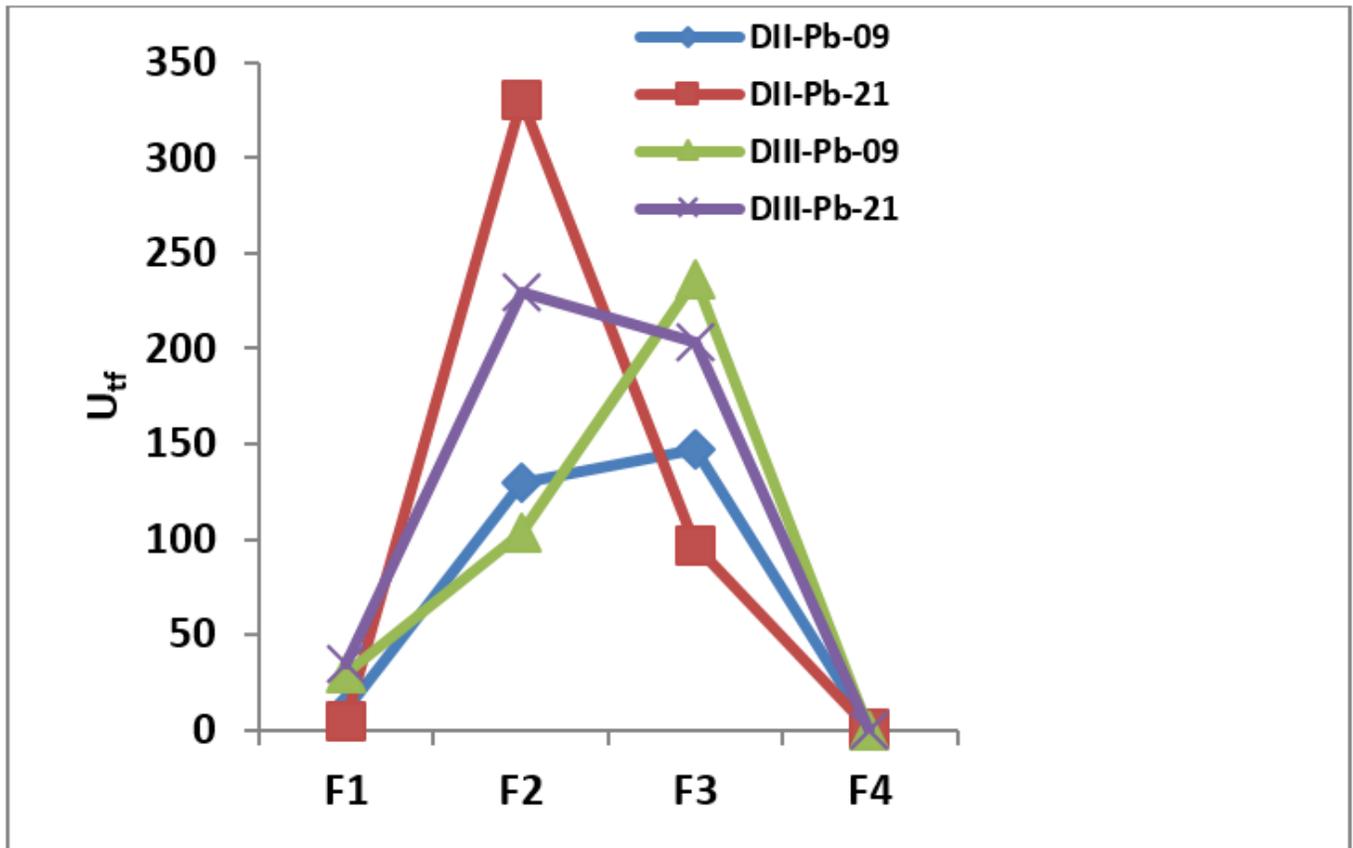


Figure 12

The long-term evolution of the Pb transformations-distribution (fractional contents U_{tf}) in the two dumps

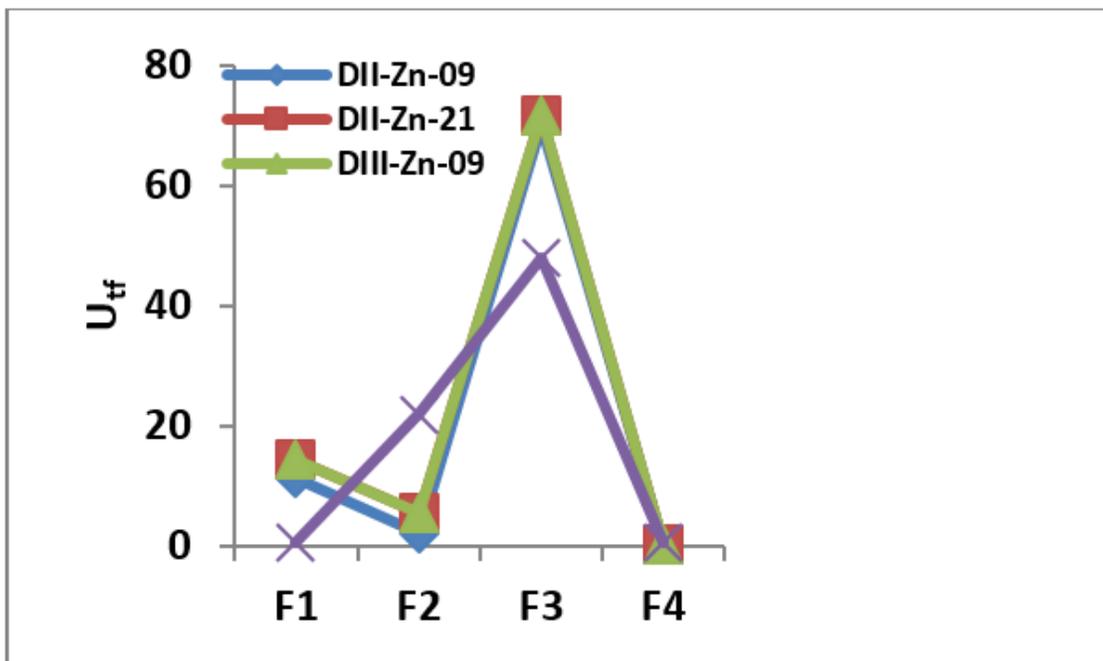


Figure 13

The long-term evolution of the Zn transformations-distribution (fractional contents U_{tf}) in the two dumps

Figure 14

The long-term evolution of "equilibrium Parameter" (U_{tf}) of the Pb in the whole dumps

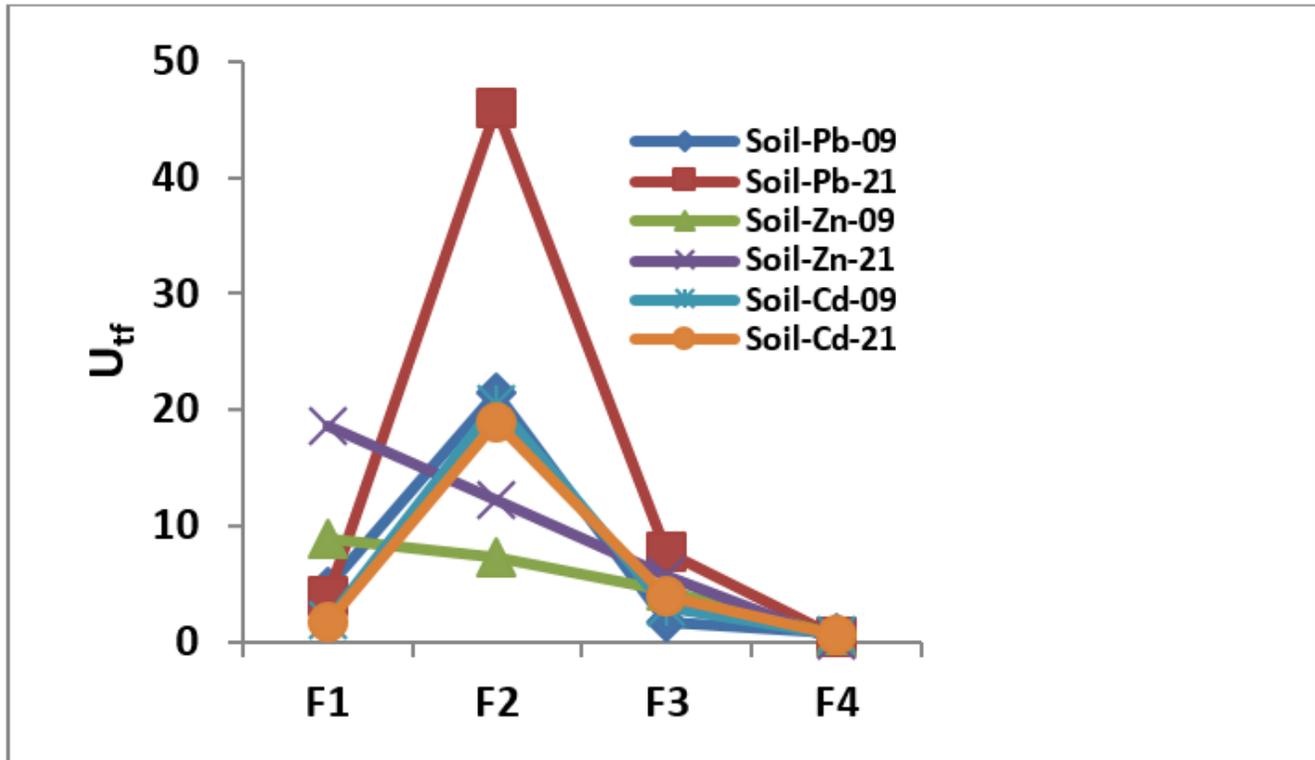


Figure 15

The long-term evolution of the Pb, Zn and Cd transformations-distribution (fractional contents U_{tf}) in soil