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EVALUATION OF THE BEHAVIOR AND DISTRIBUTION OF MERCURY AND ASSOCIATED HEAVY METALS IN CONTAMINATED SOILS FROM AN ABANDONED MERCURY COMPLEX IN THE AZZABA REGION (NORTHEAST ALGERIA)

This research is about the mercury and toxic metals pollution caused by the mining processes of cinnabar deposits at Ismail abandoned mercury complex in Algeria. This complex has caused many health and environmental problems in Azzaba area. The effect has continued to date with the presence of toxic elements even after almost 20 years since the site closed. Planning for remediation was never considered. However, this study aims to characterize the soil, by mercury and associated metals concentrations and physicochemical parameters. Also, to evaluate the behavior and distribution of toxic elements in samples based on the physicochemical parameters of the environment. The results show that all samples have a high level of toxic metals (Hg, Zn, Pb, As, Cr, Cu, and Sb) with averages in ppm, respectively (1526, 8421, 4372, 238, 134, 389, 124), these concentrations exceed standards, which increase the environmental risks. The statistical results show a correlation between pH–(Zn, Pb, Cr), Ec–(Pb, Cr and Cu), CEC–(Zn, Cu and As), OM–Zn and CaCO₃–(Zn, Pb, Cr, Cu and Sb) indicate that physicochemical parameters can affect the behavior and the mobility of metals. Except for Hg, which behaves in a particular way. In addition, according to ANOVA tests, Hg and As are evenly distributed throughout the study area. Unlike other metals, Pb, Cu and Sb to move to the surrounding soil or accumulate at a distance of 150 m while Zn and Cr accumulate in the upper part of the waste dump. This research investigates how toxic elements disperse or accumulate, make an assumption about their geochemical origin, and analyses their interactions with different soil characteristics. In addition, it contributes to the assessment of environmental risks and provides a relevant scientific support for planning appropriate decontamination and site restoration strategies.

Keywords: mercury district, toxic elements, physicochemical properties, soil, mobility, accumulation.

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1. Introduction

The mining industry is the most important industrial sector for the economies of most countries worldwide and classing as the second oldest sector after agriculture [1]. Despite mining is the main source of metals and materials of construction, but it affects human health and the environment by its processes. The effects on flora and fauna increase during mining operations [2]. Different studies indicate that mining operations are the main factors of environmental pollution due to the enormous quantities of waste produced which contain heavy metals, that affect water, soil quality and even human health. The potential of pollution depends on the type of natural resource extracted and processed. The soil close to the source is more polluted, and the effect gets less significant with distance from the source [3].

The most important aspect of mining pollution is the dispersion and distribution of toxic metals such as mercury, which affect soil, water, and air quality [1].

The abandoned mines of cinnabar are sources of Hg contamination of the environment [4]. Mercury is very toxic pollutant that can cause damage to human health [5]. The effects of mercury can include neurological disorders, kidney damage and risks to fetal development, so strict monitoring is required to reduce exposure. Mercury accumulates in the environment through the air, water and even biological organisms via the food chain [6].

In light of this, the mercury district in northeastern Algeria is considered as a critical concern. The exploitation and treatment of cinnabar deposit caused significant environmental problems and affect human health especially local residents and workers [7]. All previous studies confirm that, since the initiation of the cinnabar deposit processing and treatment project in the Azzaba region, both human health and environmental conditions have been adversely affected by mercury contamination. These studies have identified the region as a critical pollution hotspot. However, since the closure of the plant in 2005, no remediation or restoration efforts have been undertaken.

The contamination by the inorganic mercury vapors in the exploitation of cinnabar deposits was important [8]. The health of workers and residents in the town of Azzaba was targeted, with cases of abortions, stillbirths, premature births and hypertension between 1989 and 1995 [9].

Tremors, bad results in handwriting tests and finger-nose test, these symptoms of mercury contamination manifested themselves among the students and workers at the factory [10].

A sanitary study on 88 factory workers, 354 schoolchildren from the Azzaba region, and 124 children from Annaba, located far from the contaminated area. This research aims to analyze mercury levels in urine to confirm the symptoms observed previously. The results approve a mercury concentration of approximately 650 $\mu\text{g/g}$ of creatinine in workers, 2.49 $\mu\text{g/g}$ of creatinine in schoolchildren from Azzaba and 0.45 $\mu\text{g/g}$ in control children, which is the lower mercury concentration in urine [9]. A study on average blood mercury levels was conducted among workers (from the processing plant, support staff and logistics staff), residents of Azzaba and those of Constantine, a city far from Azzaba. The recommended exposure standard is 15 $\mu\text{g Hg/l}$ of blood. The average blood mercury concentration was 53.9 $\mu\text{g/l}$ among workers at the processing plant (with calciners being the most exposed, with an average of 89.7 $\mu\text{g/l}$) and 14.18 $\mu\text{g/l}$ among residents of Azzaba, while the concentration observed among residents of Constantine was significantly lower at 2.92 $\mu\text{g/L}$, thus remaining below the permissible limit [11].

Another study was carried out to measure mercury concentrations in the cord blood of newborns at Azzaba. The results were compared to those of a control group in Constantine. The results showed a high mean mercury concentration ten times more in Azzaba's newborns than in the control blood [12].

Based on the results of previous studies carried out on soils during the production phase, the closure period and ten years after the cessation of its activity [8], the soil is strongly affected and constitutes an essential indicator of environmental pollution related to the exploitation and treatment of cinnabar deposits. In addition, these studies indicate a spatial dispersion of mercury, and concentrations decrease beyond one kilometer from the site. Generally, the most significant impact is observed in soils located near the source of contamination, and decreases as the distance from the source increases [3].

The effects of past mining activities in the soil are shown in the high concentration of mercury and other toxic elements resulting from the alteration of waste, the atmospheric dispersion of fine particles, and emissions from the heat treatment of cinnabar [13].

Thus, *the object of this research* is the mercury and toxic metals pollution caused by the mining processes of cinnabar deposits at Ismail abandoned mercury complex in northeastern Algeria.

The aim of this research is to evaluate and take an idea about the behavior and the distribution of mercury – the essential pollutant – and the associated toxic elements in contaminated soil in the mercury complex according to physicochemical parameters. This step is important to investigate the current environmental impact of past mining activities. The results facilitate the assessment of the feasibility of remediating this polluted site, or at least to minimize the environmental risks particularly through phytoremediation – an economical and eco-friendly method – consequently to design a remediation plan adapted to the geochemical characteristics of the soil.

Tasks used to achieve the research aim:

1. To characterize the soil of the treatment waste and the surrounding soil at different distances – mercury and associated metals concentrations and physicochemical analysis.

2. To statistically analyze results – correlation and ANOVA tests – and interpret these results in order to draw a general conclusion about the current behavior of toxic elements in the polluted area.

2. Materials and Methods

2.1. The study area

Azzaba is the largest town in the city of Skikda. This depression is a slightly gullied plain with 8 km wide, with topography composed of hills and plains, located in the mercurial North Numidian, Northeast of Algeria (Fig. 1). It is located about 500 km to the east of Algiers, 80 km to the northeast of Constantine, 70 km to the southwest of Annaba and 32 km to the southeast of Skikda [9]. Mediterranean town in Algeria, characterized by climate hot and dry in summer and cool and humid in winter. Winds come from the northwest direction.

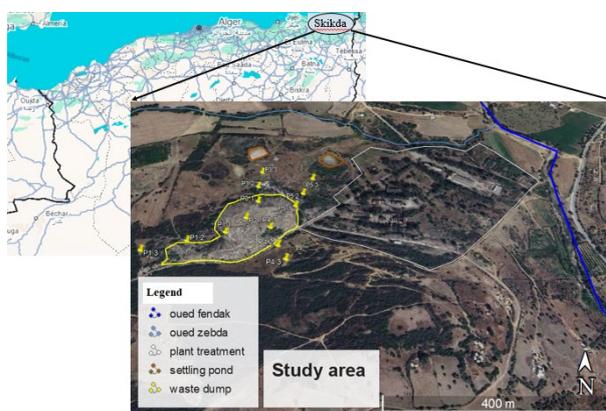


Fig. 1. The study area and its main components (Google earth 2025)

The mineralization at Azzaba is composed mainly of impermeable rocks from the Paleozoic and Lutetian-Priabonian periods. This layer lies between two aquifers; the Oligocene aquifer and Paleocene Eocene aquifer [14]. The mineralization contains cinnabar (HgS), is hosted by a formation characterized by carbonate microbreccias, limestones and clays [10, 15]. The Azzaba mercury district comprises three abandoned mines (Ismail, Mra Sma, and Guenicha) as well as a 46 ha of mercury complex that includes a processing plant, waste dump (calcine), and two settling ponds (Fig. 1). It is found in a mountain range of limestone in the northern Numidian Belt, which has metal deposits such as mercury, arsenic, antimony, lead, and zinc. Mining activities in the Azzaba region were the extraction of cinnabar from three mines and the treatment of cinnabar to obtain metallic mercury [16].

The Ismail mercury complex was established in 1971 after the discovery of a mercury deposit in southwest of Azzaba. The exploitation of the Ismail, Mra Sma, and Guenicha deposits successively has made the processing unit profitable.

The mercury deposits in the study area are located on the northern flank of the limestone belt south of Azzaba. These deposits are classified as polymetallic deposits containing lead, zinc and copper, where mercury is present in trace amounts, as well as mercury-rich polymetallic deposits containing mercury, lead, zinc and copper, where mercury is the main metal [14]. The mineralization is hydrothermal and dates from the Miocene to Quaternary period [7].

2.2. Sampling and preparation

2.2.1. Soil Sampling

Soil sampling has been carried out in April 2023, in the dry season period, with a circular strategy – radial form – from a central point by taking a distance of 50 m between samples. The point of sample represents a grid of 10×10 m, which is representative of three sub-samples taken randomly after removing the top layer of the soil. A total of 13 soil samples were collected. Two different zones were sampled: from the waste dump -top and bottom-, and from the soil between the waste dump and the settling ponds (Fig. 2). The soils of the study area

are brown clays. Each three sub-sample was dried in the air, mixed using quartering to form a representative sample, crushed by a mortar to form a homogeneous texture, and sieved to 2 mm to obtain the fine soil fraction.

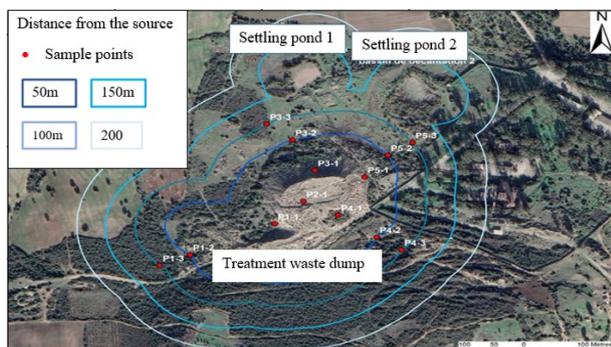


Fig. 2. Sample points with distances from pollution source

It was obtained the following groups of samples (Fig. 2):

- Group A (P1.1, P2.1, P3.1, P4.1, P5.1): samples taking from the top of the waste dump;
- Group B (P1.2, P3.2, P4.2, P5.2): sample from bottom – the lower part – of the waste dumps;
- Group C (P1.3, P3.3, P4.3, P5.3): soil samples near the waste dump, the treatment plant and the two settling ponds – the soil adjacent.

2.2.2. Analytical methods

Physicochemical analyses:

- pH: using a pH meter (HANNA) according to ISO 10390, preparing 10 g of soil with 25 ml of distilled water. After mixing and decantation, the measurement can read directly.
- Electrical conductivity (EC) measurement (HANNA) using the procedure described in ISO 11265. The same suspension prepared for pH is used for direct conductivity measurement using a conductivity meter.
- Organic matter (OM) determination through the Walkley Black method for organic carbon content [17]. The organic matter content was determined by the oxidation of organic carbon by dichromate and titration.
- Cation exchange capacity (CEC): was assessed using the ammonium oxalate method according to NF X31-130.
- Carbonate content (CaCO₃): using calcimeter of Bernard according to ISO 10693 by preparing 1 g of soil with HCl in the calcimeter, after measuring the volume of CO₂ produced [18].

Chemical analysis: was conducted by the Energy Dispersive X-ray Fluorescence Spectrometer (EDXRF-Shimadzu EDX 7000 PTB ASSY) (Fig. 3, a). The prepared soil was placed in a cuvette (Fig. 3, b) and read the results directly in the instrument.



Fig. 3. The energy dispersive X-ray fluorescence spectrometer with prepared samples: a – the energy dispersive X-ray fluorescence spectrometer; b – sampled prepared

The detection limits of elements of this instrument is very low. The results obtained will be compared to the limits presented in the tables (Tables 1–3).

Table 1

Regulatory limits in soil in ppm (AFNOR U44-041)

Toxic element	Regulatory limit in soil ppm French regulatory limits according to AFNOR U44-041
Hg	1
Zn	300
Pb	100
As	25
Cr	150
Cu	100
Sb	30

Table 2

Limits of physicochemical parameters (pH and EC)

pH [19]		EC (µS/cm) [20]	
< 3.5	Ultra Acid	< 500	Non-Saline
3.5–4.4	Extremely Acid	500–1000	Slightly Saline
4.5–5.0	Very Strongly Acid	1000–2000	Saline
5.1–5.5	Strongly Acid	2000–4000	very Saline
5.6–6.0	Moderately Acid	> 4000	very strongly saline
6.1–6.5	Slightly Acid		
6.6–7.3	Neutral		
7.4–7.8	Slightly Alkaline		
7.9–8.4	Moderately Alkaline		
8.5–9.0	Strongly Alkaline		

Table 3

Limits of physicochemical parameters (OM, CEC and CaCO₃)

OM% [20]		CEC (meq/100g)		CaCO ₃ %	
<0.7	Very poor	<5	Very low	<2	Trace
0.7–1.5	Poor	5–10	Low	2–10	Low
1.5–3	Moderately poor	10–20	Medium	10–25	Medium
3–6	Rich	20–30	High	25–55	High
>6	Very rich	>30	Very high	>55	Very high

2.2.3. Statistical method

The statistical analysis was carried out using Excel 2013 to organize preliminary data, Origin software (Origin 2025b) to create diagrams and SPSS statistical software (IBM.SPSS.statistics.v22) for the statistical calculations of correlation between the parameters and ANOVA and post hoc tests.

3. Results and Discussion

3.1. Characterization of soil quality

3.1.1. Physicochemical results

pH: Soil pH control the solubility and mobility of heavy metals, so indicator of pollution [21, 22]. In this study, the pH values were between 8.65 and 7.32. This shows that the pH is changing from very alkaline to neutral (Table 2). The interval of the standard pH for the growth of plants range between 6 and 7.5 according to FAO [23]. The pH values change as the distance increases, go down as the distance goes up (Fig. 4, a).

EC: reflects the soil's capacity to conduct electrical current. The EC values in this study range from 1011 µS/cm to 3350 µS/cm, which shows a change from saline to very saline conditions (Table 2). Similarly, for pH values, the results regarding electrical conductivity demonstrate a decrease with increasing distance (Fig. 4, b).

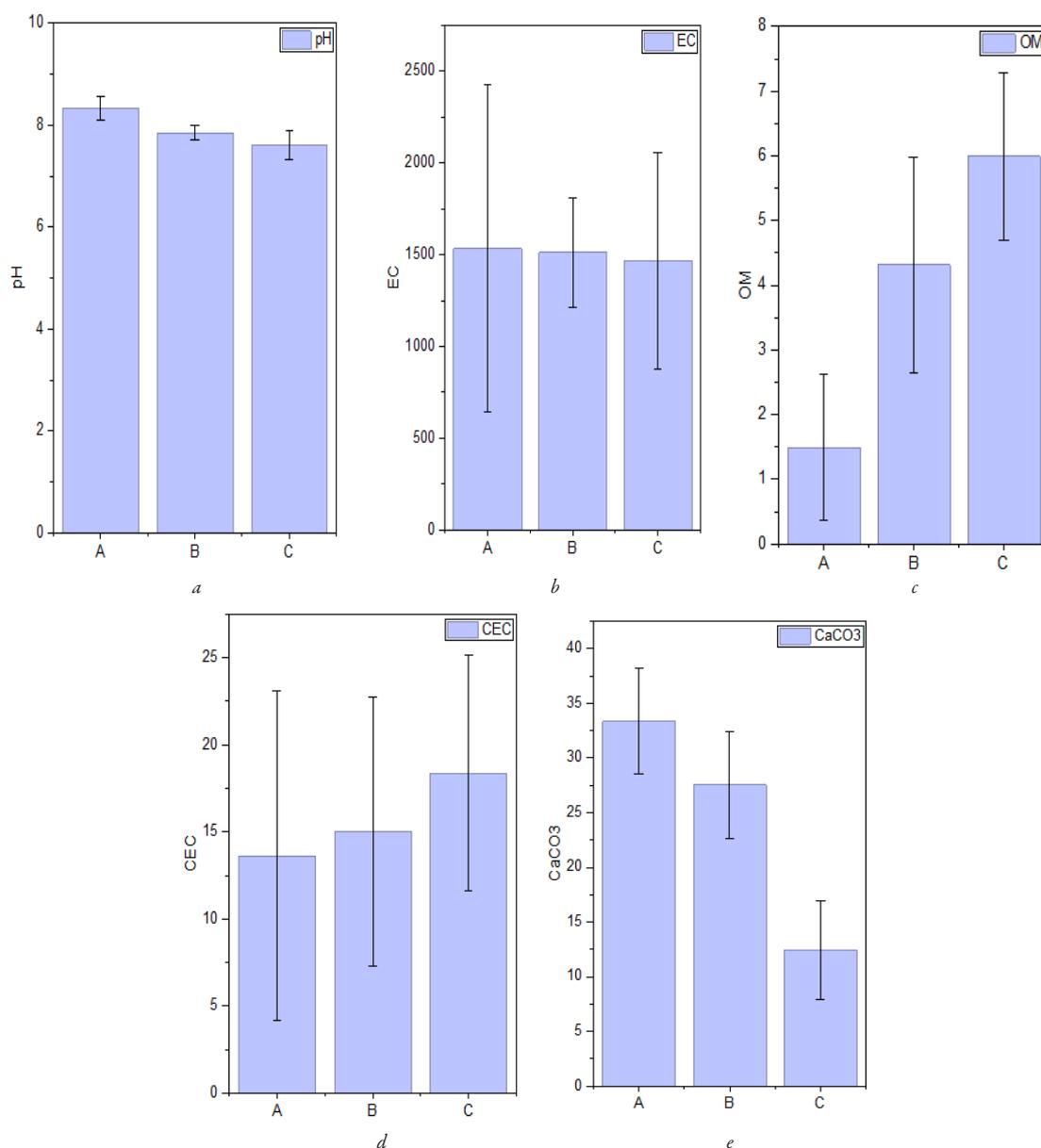


Fig. 4. Results of physicochemical variations according to soil type at different distances A, B, C: *a* – pH variations; *b* – EC variations; *c* – OM variations; *d* – CEC variations; *e* – CaCO₃ variations

OM: the values range from 0.28 to 7.93%; these indicate a transition from soil very poor in organic matter to very rich in organic matter (Table 3). Contrary to pH and electrical conductivity, the OM value increase with the increasing of distance (Fig. 4, *c*).

CEC: indicates the soil's ability to absorb or release cations. The CEC values range from 1.5 to 29.25 meq/100 g, which means that the cation's exchange capacity goes from very low to very high (Table 3). CEC increase with the increasing of distance (Fig. 4, *d*).

CaCO₃: For the CaCO₃, the values range from 8.05% to 40.83%, which suggest a variation from slightly calcareous to highly calcareous (Table 3) depending on the samples and their sampling sites. CaCO₃ decrease with the distance (Fig. 4, *e*).

These results give an idea about the soil quality and the variation of its physicochemical characteristics by changing the distance. Knowing that the sampling is conducted in the same more or less enclosed area.

3.1.2. Chemical results

The results shown in (Table 4) indicate that the concentrations of toxic elements in the soil of the study area exceed regulatory

limits (Table 1) with the exception of Cr, which is almost within the limit. The means of metal concentrations in ppm are 1526, 8421, 4372, 238, 134, 389 and 124 for respectively Hg, Zn, Pb, As, Cr, Cu and Sb. For mercury, the concentration is very high in all samples, and exceed the limit 1 ppm.

The highest value is 4051.23 ppm, observed at the top of the waste dump. This concentration decreases to 246.11 ppm in the soil adjacent to the residue.

For zinc, the soil surrounding the residue have the highest value, 13689 ppm, while the soil adjacent to the waste have the lowest, 647 ppm. The maximum concentration of lead is 10685, in the soil far from the pollution source and the minimum is 988.03 ppm in the top of the treatment residue.

The Pb concentration increases as the slope decreases. For arsenic, both the minimum and maximum concentrations (79 and 1932 ppm) are found in the waste heap. Regarding chromium, concentrations range from 149 ppm to 376 ppm. For copper, concentrations range from 262 ppm at the top of deposit and 658 ppm in the far soil, with an average of 389 ppm.

Table 4

Concentrations of toxic elements with means (ppm)

Samples	Hg	Zn	Pb	As	Cr	Cu	Sb
P1.1	4051	8665	988	79	289	262	<DL
P1.2	309	11215	4156	1932	<DL	324	<DL
P1.3	246	11361	4304	1080	<DL	326	<DL
P2	2752	10360	3779	<DL	<DL	366	<DL
P3.1	587	13689	2273	<DL	308	258	<DL
P3.2	1197	5593	5716	<DL	<DL	462	<DL
P3.3	331	2559	8593	<DL	<DL	510	762
P4.1	718	9837	3479	<DL	376	374	<DL
P4.2	1447	7176	2797	<DL	336	361	<DL
P4.3	1363	647	547	<DL	149	265	<DL
P5.1	832	10086	2552	<DL	285	338	<DL
P5.2	2577	8322	6966	<DL	<DL	552	<DL
P5.3	3432	9961	10685	<DL	<DL	658	854
Means	1526	8421	4372	238	134	389	124

Table 5

Spearman's correlation of the physicochemical parameters

Parameters	pH	EC	CEC	OM	CaCO ₃
pH	1	-	-	-	-
EC	-0.529**	1	-	-	-
CEC	-0.185	-0.02	1	-	-
OM	-0.873**	0.334*	0.363*	1	-
CaCO ₃	0.794**	-0.444*	-0.275	-0.831**	1

Note: ** The correlation is significant at the 0.01 level (two-tailed), *the correlation is significant at the 0.05 level (two-tailed)

3.2.2. Correlation between heavy metals and physicochemical parameters

The study of the correlation (Table 6) revealed a link between heavy metals and physicochemical parameters. This means that zinc is mostly found in alkaline, calcareous soils that have low cation exchange capacity, and poor on organic matter. Zn and Cu are negatively correlated, which could mean that they have different chemical behaviors or come from different sources. Lead is found in acidic soils and positive correlative with EC. Pb and Cr an inverse relation, and they may come from the same source as Cu. Cr can precipitates and remains available in basic, carbonate rich soils with low EC. Cu is found in non-carbonated soils with high EC. In addition, soils with high CEC retain copper better, which is favorable for the retention of metal cations. As is more common in soils with low CEC, while antimony is more prevalent in soils that do not contain carbonates.

The correlation analysis shows that mercury, which is the focus of this study, has no significant correlation with the physicochemical soil parameters. Probably, because its special behavior is not controlled by the properties of the soil, but it can be related to the specific mineral phases, this is due to mining activities. Regarding interactions with other heavy metals, Hg does not have a correlation with all metals except As, which is negative, which probably means that these two elements come from different sources or have different geochemical dynamics. This suggests that it has a different geochemical behavior, which may be due to its presence in certain mineral forms (cinnabar and metacinnabar), volatility or to the fact that it has a low mobility under current soil conditions. These results support the idea that mercury spreads differently in the study area than other toxic elements.

Table 6

Spearman's correlation of physicochemical parameters and heavy metal concentrations

-	pH	EC	CEC	OM	CaCO ₃	Hg	Zn	Pb	Cr	Cu	As	Sb
pH	1	-	-	-	-	-	-	-	-	-	-	-
EC	-0.53**	1	-	-	-	-	-	-	-	-	-	-
CEC	-0.19	-0.02	1	-	-	-	-	-	-	-	-	-
OM	-0.87**	0.33*	0.36*	1	-	-	-	-	-	-	-	-
CaCO ₃	0.79**	-0.44**	-0.28	-0.83**	1	-	-	-	-	-	-	-
Hg	0.31	-0.1	0.3	-0.25	0.19	1	-	-	-	-	-	-
Zn	0.41*	-0.1	-0.37*	-0.56**	0.34*	-0.31	1	-	-	-	-	-
Pb	-0.34*	0.41*	0.01	0.29	-0.37*	-0.1	-0.04	1	-	-	-	-
Cr	0.53**	-0.38*	0.04	-0.25	0.35*	0.07	-0.01	-0.73**	1	-	-	-
Cu	-0.2	0.37*	0.4*	0.29	-0.32*	0.23	-0.35*	0.84**	-0.45**	1	-	-
As	-0.15	0.03	-0.59**	-0.13	0.17	-0.32*	0.42**	-0.05	-0.21	-0.47**	1	-
Sb	-0.16	0.03	0.07	0.21	-0.39*	0.1	-0.2	0.63**	-0.37*	0.58**	-0.23	1

Note: ** - the correlation is significant at the 0.01 level (two-tailed); * - the correlation is significant at the 0.05 level (two-tailed)

3.2.3. ANOVA

The ANOVA and post hoc tests shown in Table 7 indicate important remarks:

There is no significant difference between groups A, B, and C for mercury. This means that Hg is homogeneously distributed the study area, without any effect of distance.

For Zinc There is a significant difference between groups, and the concentration decreases with distance from the center of the heap. This suggests that there is a probable source linked to mining waste, and it is slowly dispersing in the surrounding soil.

The lead shows a difference between the groups. However, the concentrations of group A and B are similar but that of group C is the highest. This can be explained by the existence of natural accumulation zones due to the topography of the area, as well as by the low mobility of Pb, which results in the accumulation of Pb in low-lying areas.

There were big differences in the amounts of chromium between the groups and the group A had the highest concentration. This means that Cr is directly related to the source of pollution and its concentration decreases with distance.

There is no difference between the groups B and C in terms of the concentration of copper, which were similar, but group A had lower amounts. However, Cu levels went up in soils that were farther away from the main source of pollution. This could be because the topography and precipitation made the Cu move more easily, or because the treatment plant and the settling ponds was close to group C.

Arsenic showed no significant differences between groups, which had a distributed pattern that was probably controlled by local geochemical factors.

The levels of antimony were much higher in group C than in groups A and B. The Sb amount near the treatment waste areas is absent, but it accumulated in soils far away from the waste dump. This is likely because of its slow mobility and accumulates in low-lying areas.

Results of ANOVA test and post hoc test (Games-Howel)

Metals	Groupe A \pm SD	Groupe B \pm SD	Groupe C \pm SD
Hg	1788.13 \pm 1430.76 (a)	1382.41 \pm 845.13 (a)	1342.91 \pm 1340.61 (a)
Zn	10527.23 \pm 1742.17 (a)	8076.35 \pm 2146.43 (ab)	6132.18 \pm 4810.77 (b)
Pb	2614.38 \pm 1021.53 (a)	4908.71 \pm 1643.68 (a)	6032.08 \pm 4088.05 (b)
Cr	251.55 \pm 134.50 (a)	84.08 \pm 152.10 (b)	37.16 \pm 67.22 (b)
Cu	319.77 \pm 51.93 (b)	424.79 \pm 93.15 (a)	439.79 \pm 161.81 (a)
As	15.75 \pm 32.61 (a)	483.02 \pm 873.82 (a)	270.12 \pm 488.67 (a)
Sb	DL/2 (a)	DL/2 (a)	403.82 \pm 423.14 (b)

Note: the letters *a*, *b*, and *ab* assigned to the means indicate statistically different groups

3.3. Discussion

The mercury concentrations obtained in the mercury complex and in the zone close to the plant treatment, are high and ranges between 331 and 4051 ppm with mean of 1526 ppm. This result is close to Seklaoui results [7] who obtained a mean of mercury in the mercury complex 1812 ppm. The study area remains contaminated even 20 years after the plant closure and the impact of this pollution is always present. Antimony and lead were found in high concentrations in the soil next to the calcine waste deposit, which is different from what Seklaoui [7] indicated. This is due to the topography of the area characterized by slopes and the effects of precipitation. The concentrations of heavy metals decrease with increasing distance from the industrial area. Hg levels decrease and reach values close to the geochemical background (approximately 1.5 mg/kg) at a distance greater than 1 km [7, 24].

The physicochemical results highlight different indications about the study area conditions: pH results suggest a slow or minimal mobility and bioavailability of metals in the soil [22]. EC results indicate

that the soil samples contain different amounts of dissolved salts, with concentrations varying depending on the sampling location [25]. OM results indicate a variation in the organic matter content in samples. The low values of organic matter can result an acceleration in the process of soil erosion, while high concentrations of organic matter affect the soil pH by reducing it [25]. CEC highlights the differences between soils in the capacity to retain cations, consequently, nutrients [26]. The calcareous content varies from one sample to another.

Calcareous and alkaline soils promote the immobilization of heavy metals, leading to their precipitation and adsorption and, in the long term, their accumulation [27, 28]. In addition, the positive correlation between OM and CEC can be explained by the complex, which can be made by metal cations and organic matter, which makes it harder for toxic elements to move through the soil [29].

The correlation between physicochemical parameters confirms that alkaline soil contains limited organic matter and soluble salts. These conditions can make toxic elements less mobile and less bioavailable. This reduces the risk to the environment. But, these substances can accumulate in the soil over time and, in the case of a change in the characteristics of the soil with the climate change, the behavior of these substances also changes, which can increase pollution and make the environment more dangerous. So, in the remediation plan, neutralization or even alkalization of the site is very important. In addition, the monitoring and the control of the physicochemical parameters are essential, as any variation can influence the distribution of metal elements.

The results of correlation that classified metals in two groups: (Pb, Cu, and Sb) and (Zn and As), knowing that the metals of each group are positively correlated with each other. The metals of each group can be from the same mineralogical source. However, Hg acts alone, which could be explained by its mineralogy and volatility.

The ANOVA demonstrate that the mining waste dump and surrounding soil exhibit significantly higher levels of several contaminants.

Table 7

It also allowed to statistically distinguishing the groups of samples according to their level of contamination. Metal concentrations decrease or vary significantly with distance from the source, with some elements showing peripheral accumulation. Hg and As present almost similar levels of contamination; therefore, a similar distribution throughout the study area in the distances 50 m, 100 m and 150 m, and the other associated metals present a heterogeneous distribution in the same distances.

Our study area is very contaminated with mercury and other toxic elements, and all values exceed the regulatory limits, especially for mercury, which is more than 1000 times the limits, which is 1 ppm in soil according to WHO and AFNOR U44-041. So, the site can be classified as an extremely contaminated site.

Under the uncontrolled natural effects external to our study – runoff, leaching, erosion, precipitation and atmospheric dispersion – the distribution of metals and physicochemical parameters can be affected. In addition, the presence of the enormous quantity of metals requires the permanent closure of the mercury complex with its compartments: the treatment plant, the calcination waste dumps and the settling ponds that are close to the heap to prevent human access and further disturbance. Therefore, it is possible to suggest that the calcination waste dump represents the actual main source of toxic element dispersion. So, it must be buried, under the ground followed by the installation of an impermeable sealing layer and a clay-rich cover. The clay layer would contribute to reducing metal mobility by enhancing adsorption processes and stabilizing the system, even in the case of changes in soil physicochemical conditions.

The limitations of this work are that the research is conducted in an area that is relatively small in comparison to the regional scale. Therefore, the research is only being conducted at the local level, which is the Ismail mercury complex, the most polluted area.

In addition, this research requires mineralogical analysis to identify other parameters (mineralogical conditions) that may influence the distribution and availability of mercury and other toxic elements. If it is possible, the analysis of mercury speciation to determine the different forms of mercury present in the area. It provides a plus for future studies.

The developments in the future for this research include mainly the study of actual spatial dispersion of pollutants to limit the polluted area and the regular monitoring of the mercurial complex. Also, the bioaccumulation study, which will identify hyperaccumulator plants. In addition, the establishment of a vegetated buffer zone the contaminated area, using identified hyperaccumulator plant species capable of accumulating mercury, by using phytoremediation processes (phytostabilization or phytoextraction) to limit atmospheric dispersion of Hg and stabilizing the soil contamination.

4. Conclusions

1. The chemical analyses in this research show a very high amount of Hg and other toxic elements in the soil samples that exceed the regulatory limits. The principal pollutant, Hg had a mean of 1526 ppm, which is more than 1000 times the limit of 1 ppm. These results are similar to previous studies even after twenty years since the closure of the mercury complex. Therefore, the mining impact is steel present today. In addition, the physicochemical parameters indicate that soil properties change with the different distances. Knowing that there are three different types of samples characterize the groups: the first is the top of the waste dump (calcine), the second is the soil near from the dump, and the third is the soil far from the central point of the waste with a distance of 150 m. Thus, each group of samples is different from each other, and the physicochemical results was confirmed this. pH, EC, and CaCO₃ decrease as moving away from the center of the waste dump, while OM and CEC increase at 150 m from the center point. In this section, it was only studied the variation in physicochemical parameters in relation to distance and not toxic elements. In addition, the main purpose of this research was not to study spatial variation, but exactly how the parameters change in different soil types in the polluted area and even to evaluate in a general way the behavior of heavy metals as they move away from a central point of the heap on a local scale.

2. The statistical analysis indicate different results:

- The correlation between physicochemical parameters analyses and the correlation results indicate that there is a correlation between the parameters: pH is negatively correlated with Ec and OM and positively correlated with CaCO₃, while CEC is positively correlated with OM. Therefore, in alkaline soil the soil is calcareous, the OM is reduced, a change in cation exchange capacity, which affects metal retention and a redistribution of soluble salts.
- The correlation between physicochemical parameters and the concentrations of toxic elements shows a correlation between pH and (Zn, Pb and Cr), Ec and (Pb, Cr and Cu), CEC and (Zn, Cu and As), OM and Zn and CaCO₃ and (Zn, Pb, Cr, Cu and Sb). So, the physicochemical analysis can affect the distribution, mobility, bioavailability, and retention of metal elements in the soil of the studied area by influencing spatial distribution and potential environmental risk in long term. Except for mercury, which has a different behavior that may be caused by its mineralogical characteristics and volatilization.
- The ANOVA and Games Howell tests show that Hg is evenly distributed throughout the study area, and its distribution is homogeneous. Its accumulation is not influenced by soil quality or even distance, and the same is true for As. Unlike other metals, Pb, Cu, and Sb accumulate at a distance of 150 m, while Zn and Cr accumulate in the upper part of the waste dump. This confirmed that

the groups located at the mining waste dump and surrounding soil of mercury complex exhibit significantly higher levels of several contaminants. This test also allowed to statistically distinguishing the groups of samples according to their level of contamination. Metal concentrations decrease or vary significantly with distance from the source, with some elements showing peripheral accumulation. Mercury present in all groups with the same level. However, these results also depend on the specific characteristics of soil when samples are collected at short distances from each other within nearly the same area.

The results of this research can facilitate the management of a monitoring plan at the mercury complex level, by taking into account the behavior of toxic elements present in the soil without neglecting the physicochemical characteristics of the soil. By closing off the contaminated area, burying the heap of waste, covering it with a layer of clay for neutralization, and adding an impermeable insulating layer to seal it.

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Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, including financial, personal, authorship or other, which could affect the research and its results presented in this article.

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Data availability

There is no data associated with the manuscript.

Use of artificial intelligence

The authors affirm that no artificial intelligence technologies were employed in this work.

Authors' contributions

Rania Sbaghdi: Conceptualization, Methodology, Software, Formal analysis, Investigation, Writing – original draft, Visualization; **Abdellali Bouzenzana:** Supervision, Conceptualization, Methodology, Writing – review and editing; **Hani Bouyahmed:** Conceptualization, Methodology, Investigation, Data curation, Writing – review and editing; **Abdelfettah Gherib:** Supervision, Conceptualization; **Samir Chekchaki:** Software, Investigation; **Iness Braham:** Resources.

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