Assessment of heavy metals contamination in soils around a mining site in Marrakech region, Morocco.

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Abstract
Mining sites are a permanent toxicological problem for the surrounding ecosystems and human health. In the present study we investigate the accumulation of heavy metals in agricultural soils collected from the surrounding area of a mining site of Marrakech (Morocco). The occurrence of heavy metals in field soils was, in a decreasing order, Zn > Cu > Pb and Cd. Concentrations of the heavy metals were higher in the studied soils compared to the control soil. Based on the geoaccumulation index (GeoI) and the contamination factor (CF), the contamination degree can be defined as slightly contaminated for Pb and Zn, highly contaminated for Cd and moderately contaminated for Cu. With respect to the pollution load index (PLI) the metal levels exceed local and regional background concentrations indicating contamination sufficiently high to attract attention and to pose risk to the ecosystem. Heavy metals are persistent in the environment and are subject to bioaccumulation in food chains and therefore pose substantial health risks for human and animal.

Keywords: Agricultural soils, Mining sites, Heavy metals, Contamination degree.

1. Introduction
Mining, minerals and metals have been and - in many cases - remain important to the economic and social development of a number of industrialized and some developing countries such as Morocco, which has a long mining tradition and has experienced an intense mining activity over the past centuries because of his diversified natural resources. Mining activities are one of the most important and abundant source of metal contamination of ecosystems [1]. These activities can affect small areas, but could have a significant impact on the environment [2], and they are considered to have the potential for causing heavy metal pollution and associated diseases [3,4].
The past mining activities have generated large volumes of waste rocks and concentrator tailings without any security and environmental protections and many researchers worldwide have focused on and reported assessments of heavy metal concentrations [5-7]. However, with the rising awareness that preservation of natural resources, the mining industries are increasingly concerned and influenced by public concern for the quality of the environment [8,9].
Morocco has been considered as a traditional mining region since antiquity. This country has experienced intense mining activity due to the richness and diversity of its mineral resources. Nowadays, it is estimated that there are still large reserves of iron (Fe), copper (Cu), zinc (Zn), silver (Ag) and lead (Pb) in the area and mining is still a mainstay of Morocco’s economic and social development [1,8,10]. In the region of Marrakech, mining activity represents a great danger due to the presence of high amounts of heavy metals associated with functioning or abandoned mines. Heavy metals can be toxic to living things at multiple levels. They can be dispersed and accumulated in soils, plants, groundwater, surface water, wildlife and people through the food they eat by dissemination of the particles carrying metals by wind and/or by runoff from the tailings [11-13]. They could be accumulated in the vital organs of the human body, causing numerous serious health disorders, such as decreased immunological defenses, intrauterine growth retardation, impaired psycho-social abilities, and disabilities associated with malnutrition [14,15]. Human health risk assessment may be conducted to help determine if exposure to a chemical could cause, at any dose, an increase in the incidence of adverse effects to human health [16]. On this aspect, few studies have been done to determine the heavy metal concentration around mine areas and their impact on surrounding soil [17-19]. The objective of this work was the assessment of heavy metals concentration and toxicity in soil sampled from a mining site located in the region of Marrakech. In this study, we suggested that agricultural soils are useful to assess the spread of environmental pollution in this area.

2. Materials and methods

2.1. Study area

The study was conducted in the region of Marrakech (Drâa Lesfar area), Morocco. The climate is Mediterranean with an average annual precipitation of 231 mm (10 years). The mine is located a few hundred meters from the Tensift river (Fig. 1) close to a rural community of some 2 km² whose main activity is agriculture [8]. This mine is an operating underground mine, mainly producing zinc and lead. During mining and extraction operations, the untreated mine water is pumped back out of the mine and discharged near the Tensift river. Tailings have been deposited near the mine installation and were later spread onto 0.8–1.6 ha land located at 100 m from the mine [17,19,20]. Amid the mine activities, agricultural operations, such as the planting of olive, wheat, barley and other plants, were still taking place in the affected area, which can pose a real health risk for the surrounding communities.

![Figure 1](image-url). The location of the study area (Outline et al. [20] with modifications).

2.2. Soil samples

Soils were characterized by their main physicochemical properties and by their total heavy metal contents. Soil samples were collected from selected agricultural fields. Soils were randomly sampled from the upper horizon (0-20
cm) and bulked together to form one composite sample. After transportation to the laboratory, soil was air-dried and sieved through a mesh of < 2 mm, and then sealed in paper envelopes until analysis [19].

2.3. **Digestion of soil samples**

For each sample, three powdered samples (0.5 g) were accurately weighed and placed in crucibles. The soil samples were gradually warmed to 450°C. After cooling, hydrofluoric acid (HF) and perchloric acid (HClO₄) were added to the residue, and the mixture was heated to dryness. Hydrochloric acid (HCl) was added and heated to redissolve the residue. The solution was thereafter brought to 50 ml volume with distilled water [21].

2.4. **Samples analysis**

Soil pH, electrical conductivity (EC) and organic matter (OM) content were determined following the standard analytical methods [22]. The metal analyses (Pb, Cd, Cu and Zn) of samples were carried out by using UNICAM atomic absorption spectrophotometer (AAS).

2.5. **Data analysis**

Contamination factor (CF), Geo-accumulation index (GeoI) and Pollution Load Index (PLI) are quantitative check used to describe concentration trend of metals in soils. CF is a quantifier of the degree of contamination relative to either the average crustal composition of the respective metal or to measured background values from geologically similar and uncontaminated area [23]. It is expressed as:

\[
CF = \frac{C_m}{Cr}
\]

(1)

Where \(C_m\) is the mean concentration of metal \(m\) in soil and \(Cr\) is the reference concentration (value) of metal “m”, either taken from the literature (average crustal abundance) or directly determined from a geologically similar material. The Index of Geoaccumulation (GeoI) has been widely used to evaluate the degree of heavy metal contamination in terrestrial and aquatic environments by comparing current concentrations with reference levels [24]. Geo accumulation index was computed using the equation:

\[
GeoI = \ln \left( \frac{C_m}{1.5 \times Cr} \right)
\]

(2)

Where \(C_m\) and \(Cr\) are as defined above, while 1.5 is a factor allows for possible variation in the background concentration due to lithological differences in the content of a given substance in the environment and very small anthropogenic influences [25].

Seven classes of the geochemical index have been distinguished [26]:

- GeoI< 0, practically uncontaminated;
- 0<GeoI<1, uncontaminated to slightly contaminated;
- 1<GeoI<2, moderately contaminated;
- 2<GeoI <3, moderately to highly contaminated;
- 3<GeoI <4, heavily contaminated;
- 4<GeoI <5, highly to very strongly contaminated;
- GeoI >5, very strongly contaminated.

Another commonly used index to evaluate the heavy metal pollution in soil is the Pollution Load Index (PLI). The PLI is the pollution level in trace metal [27]. The PLI represents the number of times by which the metal content in the soil exceeds the reference concentration and gives a summative indication of the overall level of heavy metal toxicity in a particular sample. The PLI is obtained as a Concentration Factor (CF) of each metal with respect to the reference value in the soil [28], by applying the following equation:
\( PLI = \frac{CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n}{n} \) \hspace{1cm} (3)

\( n \) = number of metals

Four categories of contamination factor have been distinguished [29]:
- \(<1\) = Low contamination factor indicating low contamination;
- \(1-3\) = Moderate contamination factor;
- \(3-6\) = Considerable contamination factor;
- \(>6\) = Very high contamination factor.

3. Results and Discussion

3.1. Physicochemical properties of the soil

The pH, conductivity (EC), and organic matter contents (OM) are the principal soil characteristics that determine the capacity to retain heavy metal pollutants. The average of pH in Drâa Lesfar soil is about 8.64, as a consequence of the presence of calcareous parent material, the results indicated the presence of basic soils, and this result is similar to reference samples (Table 1).

Table 1. Characteristics of Drâa Lesfar and reference soils collected from the study area.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Drâa Lesfar Soils (n=12)</th>
<th>Reference soils (n=12)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.64±0.14</td>
<td>7.20±0.08</td>
</tr>
<tr>
<td>E.C (µS/cm)</td>
<td>450±0.09</td>
<td>250±0.06</td>
</tr>
<tr>
<td>O.M (%)</td>
<td>1.16±0.08</td>
<td>1.60±0.14</td>
</tr>
<tr>
<td>Pb (µg/g)</td>
<td>127±8.28</td>
<td>37±2.27</td>
</tr>
<tr>
<td>Cd (µg/g)</td>
<td>2.41±0.65</td>
<td>0.03±0.05</td>
</tr>
<tr>
<td>Cu (µg/g)</td>
<td>203.75±28.38</td>
<td>32±3.76</td>
</tr>
<tr>
<td>Zn (µg/g)</td>
<td>414.25±13.78</td>
<td>119.75±8.89</td>
</tr>
</tbody>
</table>

E.C.: Soil electrical conductivity, O.M: organic matter (%).

The EC shows higher values (450 µS/cm) compared to the reference soil value (250 µS/cm). This increase in conductivity reflects soil salinity problems according to Mohammad and Mazahreh [30]. The relatively high content of OM (1.16%) is mainly related to the high organic matter flux to soil due to direct discharge of domestic and industrial wastewaters [31]. The high pH value measured on soils potentially limits the risk of metals mobilization [32]. The pH of the soil solution maintained at alkaline condition showed low mobility of all heavy metals, it could be attributed to the presence of carbonates at a high concentration [18]. Soil organic matter is a key for sorbing phase for metals. The dissolution of humic acid at high pH is responsible for dissolution of Cu and Pb from soil. Organic matter is important for the retention of metals by soil solids, thus decreasing mobility and bioavailability [33].

3.2. Total heavy metal levels in soil

Metal concentrations are compared with values reported for reference soils (Table 2). It was found that, in the essential heavy metals in the studied soil, Pb concentration is 127 µg/g, Cd concentration is 2.41 µg/g, Cu concentration is 203.75 µg/g and Zn concentration is 414.25 µg/g and in reference soil, Pb concentration is 37 µg/g, Cd concentration is 0.03 µg/g, Cu concentration is 32 µg/g and Zn concentration is 119.75 µg/g. This result shows that Pb, Cd, Cu and Zn concentrations in Drâa Lesfar soil are higher than those in the reference soil. The ranking order of mean values of the heavy metals in the Drâa Lesfar soils followed the sequence: Zn > Cu > Pb > Cd.
Table 2. Comparative study of these results and different works in Drâa Lesfar area (µg/g).

<table>
<thead>
<tr>
<th>Source</th>
<th>Pb</th>
<th>Cd</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>127</td>
<td>2.41</td>
<td>203.75</td>
<td>414.25</td>
</tr>
<tr>
<td>El Gharmali et al. [38]</td>
<td>1450</td>
<td>Nd</td>
<td>Nd</td>
<td>1562</td>
</tr>
<tr>
<td>Boularbah et al. [10]</td>
<td>322-2847</td>
<td>Nd</td>
<td>271-570</td>
<td>1112-4023</td>
</tr>
<tr>
<td>El Adnani et al. [8]</td>
<td>35.9-176</td>
<td>0.3-1.4</td>
<td>55.52-244</td>
<td>192.22-896.3</td>
</tr>
<tr>
<td>Barkouch et al. [37]</td>
<td>42.7</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
</tr>
<tr>
<td>El Hamiani et al. [32]</td>
<td>Nd</td>
<td>0.1-0.9</td>
<td>31.5-67.1</td>
<td>53.9-182.1</td>
</tr>
<tr>
<td>Median soil worldwide [34]</td>
<td>17</td>
<td>0.3</td>
<td>25</td>
<td>70</td>
</tr>
<tr>
<td>Upper continental crust [35]</td>
<td>17</td>
<td>0.102</td>
<td>14.3</td>
<td>52</td>
</tr>
<tr>
<td>Lower continental crust [35]</td>
<td>12.5</td>
<td>0.101</td>
<td>37.4</td>
<td>79</td>
</tr>
<tr>
<td>Kabata-Pendias &amp; Pendias [36]</td>
<td>100</td>
<td>5</td>
<td>100</td>
<td>300</td>
</tr>
</tbody>
</table>

Nd: not determined

The results in the study area was compared firstly with median soil worldwide [34] and then to the lower and upper continental crust [35,36]. All the measured heavy metals values were above the maximum values allowed in the references (with the exception of Cd reported by Kabata-Pendias, and Pendias [36]. Median soil worldwide recommended values reported by Reimann and Caritat [34] are: Pb 17, Cd 0.3, Cu 25, and Zn 70 µg/g, all being lower than mean values in the study area. Heavy metal contents in Marrakech region soils were reported by many [18,19]. Average Pb and Zn contents in Drâa Lesfar samples are lower than those reported by 11 in the same area, and average Pb is higher than those reported by many authors [8,32,37]. According to El Adnani et al. and El Hamiani et al. [8,32], the mean concentrations of Cd and Cu are 0.1-1.4 and 31.5-244 µg/g, respectively which are lower than the corresponding concentrations in samples from the study area (Table 2). Outliers are indicators of unusual processes. In the study area, potential industrial pollution sources come mainly for mining and irrigation with wastewater. It is very important to consider that those elements have high toxicity. Two reasons may be suggested to explain the contamination of soil in the mining area. Firstly, the mining residues had higher metal concentrations, particularly zinc and lead. This fact is probably due to the post processing of the mine tailings. Secondly, wind transport of dust may be another important factor influencing the spreading of pollution [19].

3.3. Contamination factor (CF), Geo-accumulation index (GeOl) and Pollution Load Index (PLI)

The contamination factor values of the heavy metals Pb, Cd, Cu, and Zn were found to be in the ranges of 3.43, 80.33, 1.45 and 0.84, respectively. The trend in the CF for heavy metals was in the ranking order of Cd > Pb > Cu > Zn indicating high contamination in the soil of Drâa Lesfar area.

Table 3. Contamination factor (CF) and geo-accumulation index (GeOl) of metals in soil from the Drâa Lesfar area.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Cm</th>
<th>Cr</th>
<th>CF</th>
<th>Geol</th>
<th>PLI</th>
<th>Overall summary of contamination level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>127</td>
<td>37</td>
<td>3.43</td>
<td>0.83</td>
<td></td>
<td>slightly contaminated</td>
</tr>
<tr>
<td>Cd</td>
<td>2.41</td>
<td>0.03</td>
<td>80.33</td>
<td>3.98</td>
<td>8.83</td>
<td>highly contaminated</td>
</tr>
<tr>
<td>Cu</td>
<td>203.75</td>
<td>32</td>
<td>6.37</td>
<td>1.45</td>
<td></td>
<td>Moderately contaminated</td>
</tr>
<tr>
<td>Zn</td>
<td>414.25</td>
<td>119.75</td>
<td>3.46</td>
<td>0.84</td>
<td></td>
<td>slightly contaminated</td>
</tr>
</tbody>
</table>

CF: contamination factor; Geol: geo-accumulation index; Cm: mean concentration of the metal in the soil; Cr: mean concentration of the metal in the reference soil.
Among the heavy metals, CF values were found to be higher for Cd, Pb and Cu, whereas relatively lower CF value was found for Zn. Calculated GeoI index for heavy metal concentrations in Drâa Lesfar is about 0.83 for Pb, 0.84 for Zn, 1.45 for Cu and 3.98 for Cd (Table 3) which shows a pronounced metallic pollution. Based on the Müller scale [26], the soil in Drâa Lesfar area is slightly contaminated by Pb and Zn, moderately contaminated by Cu and highly contaminated by Cd. The value of PLI obtained in Drâa Lesfar area is summarized in Table 3. The results indicate that the concentration levels of Pb, Cd, Cu and Zn exceeded the references values. The soil of Drâa Lesfar is contaminated overall by these metals which are a result of anthropogenic activities.

Among the calculated results, PLI value is more than 6 indicating that the soil is very highly contaminated by heavy metals which could be a problem for human life. Cd is extremely toxic and generally related to human activities, in spite of its low soil content, Cd is toxic at much lower concentrations than the other elements and can lead to a variety of adverse health effects including damage to the liver and the kidneys and cancer [39]. Pb is not an essential element for soil and is moderately toxic. According to results made by the National Institute of Occupational Safety and Health, lead causes several health effects such as neurological effects, gastrointestinal effects, anemia, and kidney disease [39]. Lead poisoning has been recognized as a major public health risk, particularly in developing countries and for children [40]. Finally, Zn and Cu are essential elements and are considered essential for living organisms [41].

4. Conclusions

Marrakech landfill leachate and water pumped back out of the Drâa Lesfar mining site may have caused heavy metals contamination of the Tensift River and the surrounding agricultural soils. High pH and high OM in soil may potentially decrease the mobility of metals. Based on the GeoI and CF, the contamination degree can be defined as slightly contaminated for Pb and Zn, highly contaminated for Cd and moderately contaminated for Cu. Furthermore, the metal pollution load has been found to exceed local and regional background concentrations indicating that the contaminations are sufficiently high to attract attention and to constitute risk to the whole ecosystem. Heavy metals are persistent in the environment and subject to bioaccumulation in foods chain and therefore constitute real dangerous health risks for human and animal. The remediation of the problem will require a much more detailed understanding of ecological and human exposure to the contaminants than currently exists.

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References