An Investigation on As, Cd, Mo and Cu Contents of Soils Surrounding the Meyduk Tailings Dam

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ABSTRACT: The contents of As, Cd, Cu and Mo were determined in soil surrounding Meyduk tailings dam based on 21 surface soil samples. Assessment of toxic element pollution in studied soil samples needs knowledge of pre-anthropogenic metal concentration to act as a reference against which measured values could be compared. Estimating the background values was executed by sampling rocks adjacent to soil sampling stations. Various indices including enrichment factor (EF), pollution load index (PLI), modified contamination degree (mCd) and geoaccumulation index (Igeo) were used for determining the contamination level of soil in the vicinity of tailings impoundment under the effect of the tailings dust. Anthropogenic pollution was diagnosed from natural one by sequential extraction done by Tessier et al. method and calculating pollution intensity index (IPOLL). The results indicate a significant upward enrichment in northeastern and southwestern surface soil around the tailings dam for Cd and Cu. The dominant wind direction demonstrated that only the contamination of southwestern soil around the tailings dam would be attributed to tailings dust while the dispersive dusts scattered after the mine explosions generally affected the northeastern part.

Key words: Enrichment factor, Geoaccumulation index, Pollution intensity, Tailings dust

INTRODUCTION

Soil is a thin part of the earth surface system interacting between nature and man. Consequently, it is seen as a subtle ecosystem with mineral and chemical contents reflecting natural or anthropogenic influences (Peh et al. 2010). There is an increasing awareness that heavy metals presented in soil may have negative effects on human health and on the environment (Abrahams, 2002; Mielke et al., 2005; Selinus et al., 2005; Lee and Mohamed, 2009; Al-Juboury, 2009; Uba et al., 2009; Dauwalter et al., 2009; Venugopal et al., 2009). One of the most crucial properties of metals is that they are not biodegradable in the environment (Nuremberg, 1984; Harte et al., 1991; Schuurmann and Market, 1998; Ahmed et al., 2010; Sundararajan and Natesan, 2010; Adjei-Boateng et al., 2010; Taghnia Hejabi et al., 2010). Assessing soil pollution with toxic elements has to be done in comparison to baseline concentrations in soil. Pollution, in this case, will be measured as the amount (or the ratio) of the sample metal enrichment above the concentrations present in the background value (Abraham and Parker, 2008; Rafiei et al., 2010; Razos and Christides, 2010; Nasrabadi et al., 2010a). In order for assessing the impact of toxic metal pollution on different environments by using various enrichment calculation methods, several works have been done (Abraham and Parker, 2008; Adomako et al., 2008; Aikpokpodion et al., 2010; Ghrefat, 2010, Liu et al., 2005; Loska et al., 1995; Nasrabadi et al., 2010b). Some indicators of contamination in soil and sediment most often applied in these studies are enrichment factor, pollution load index, modified contamination degree and geoaccumulation index. The environmental pollution with metals in the vicinity of Meyduk tailings dam has not been previously investigated. Such investigations are required if the environmental impacts in the region of the dam are to be understood quantitatively and qualitatively. The main objective of the current study is to assess the extent and degree of metals, and the

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origin of these metals in surface soil using the enrichment factor, pollution load index, modified contamination degree, geoaccumulation index and sequential extraction procedure. The metals considered of concern in the investigation are As, Cd, Cu and Mo.

MATERIALS & METHODS

The study was held in Meyduk copper complex located 42km northeast of Shahr-e-Babak city and 132km northwest of Sarcheshmeh copper mine in Kerman province, Iran. It’s situated between 30° 25’N and 55° 10’E (Fig.1). This complex consists of mining units, concentrator (processing) plant, and tailings retentive structures (tailings and water dams). The copper complex commenced its activity in 1999 while the tailings dam began its work in 2005. The dominant direction of the wind in this region in most times of the year is toward southwestern part of the area. Twenty-one surface soil samples were collected from top 5-10 cm of soil in four directions. For every station, the composite sample was made from subsamples. Sample transferring to the laboratory was done by polyethylene bags for preventing sample oxidation. Before chemical analysis, the samples were dried in oven at the temperature of 60 oC for 4 hours (the average duration after which the weight of the samples would not be changed any more). They were fine-crushed then sieved to less than 2mm and pulverized to minus 75 µm. Next, the prepared samples were transformed to LabWest Laboratory (Australia) for inductively coupled plasma mass spectrometry (ICP-MS) analysis. For preparing the sample for this kind of analysis, four steps performed at LabWest Laboratory. These four stages were weighing samples (0.2 gr would be adequate), adding acids (a mixture of hydrofluoric, hydrochloric and nitric acids) then running through microwave process under the temperature of 170 oC and the pressure of 16 Bar, adding boric acid solution to complex free fluoride and re-dissolve precipitates and finally making to volume, mixing and reading solution using ICP-MS. For checking the accuracy of the analysis, a number of CRMs (International Certified Standard Reference Materials such as Chinese Geochemical Standards or GSDs) were analyzed, and then the measured data were compared with the published data. Acceptable results were the ones which had a z-score between -2 and +2, i.e. the 95% confidence interval. If a result was >|3| then it would be considered a rejected outlier and it would be reanalyzed. Checking the precision of the analysis was also done by analyzing some duplicate samples for the aimed elements. The comparison of the results with original samples was done by computing RSD value which stands for Relative Standard Deviation. For estimating background values, the rock samples from the same stations of soil samples were collected (the weather of the studied site is arid, so the rainfall effect can be approximately ignored in soil erosion or rock displacement in Meyduk area (as precipitation figures collected from Meyduk meteorological station also confirmed). In other words, we can consider Meyduk soil as an in-situ type of soil which is dominantly formed from its underneath bed-rock of which the rock sample collected from every station (as total, 21 rock samples were collected) can be representative. On the other hand, the geological map of the area does not show high variety of rocks in the studied region). A number of calculation methods have been suggested for quantifying the degree of metal enrichment. Different ranges have been proposed in various studies to convert the calculated numerical results into broad descriptive bands of pollution with low to high intensity (Abrahim and Parker, 2008). In this study, four methods have been discussed as follows:

The enrichment factor (EF) is calculated by comparing the concentration of a tested element with that of a reference element (Liu et al., 2005). The value of the enrichment factor was calculated using the following modified formula based on the equation suggested by Buat-Menard and Chesselet (1979):

\[
EF = \frac{C_n(sampling)}{C_{ref}(sampling)} \times \frac{B_{n}(background)}{B_{ref}(background)}
\]

Where:

- \(C_n(sampling)\): the content of the examined element in the examined environment
- \(C_{ref}(sampling)\): the content of the reference element in the examined environment
- \(B_n(background)\): the content of the examined element in the reference environment
- \(B_{ref}(background)\): the content of the reference element in the reference environment

The reference element is assumed to have little variability of occurrence and is present in trace concentration in the examined environment. It is also possible to use a geochemically characteristic element which is present in the environment in high concentration, but is characterized by none of these effects i.e. synergism or antagonism towards the examined element (Loska et al., 1995). The most common reference elements are Sc, Mn, Ti, Al and Fe.
(Buat-Menard and Chesselet, 1979; Martin and Meybeck, 1979; Li, 1981; Reimann et al., 2000; Schiff and Weisberg, 1999; Sutherland, 2000; Tomza et al., 1982; Pacyna and Winchester, 1990; Quevauviller et al., 1989). In this study, Sc and the rock samples were regarded orderly as reference element and reference environment. Five contamination categories are recognized on the basis of the enrichment factor as follows:

<table>
<thead>
<tr>
<th>EF value</th>
<th>Designation of quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>EF&lt;2</td>
<td>Deficiency to mineral</td>
</tr>
<tr>
<td>EF=2-5</td>
<td>Moderate enrichment</td>
</tr>
<tr>
<td>EF=5-20</td>
<td>Significant enrichment</td>
</tr>
<tr>
<td>EF=20-40</td>
<td>Very high enrichment</td>
</tr>
<tr>
<td>EF&gt;40</td>
<td>Extremely high enrichment</td>
</tr>
</tbody>
</table>

The contamination factor (CF) which gives an indication of the level of contamination, proposed by Hakanson (1980), was computed for soil samples using the measured concentrations of the toxic elements and their corresponding values in rock samples.

\[
CF = \frac{M_x}{M_b}
\]

where \(M_x\) and \(M_b\) respectively refer to the mean concentration of a pollutant in the contaminated soil samples and the baseline concentration in reference environment like rock in this study. The pollution level was computed by following procedure of Pollution Load Index (PLI) of Tomlinson et al. (1980):

\[
PLI = \sqrt[n]{(CF_1 \times CF_2 \times CF_3 \times CF_4 \ldots \times CF_n)}
\]

In this formula, \(CF_1\) to \(CF_n\) indicate the contamination factors calculated for the first soil sample to the \(n^{th}\) one. A PLI value close to one indicates heavy metal loads near the background level, while values above one indicate soil pollution (Cabrera et al., 1999; Liu et al., 2005). A modified and generalized form of Hakanson (1980) equation for the calculation of the overall degree of contamination was defined as the sum of all contamination factors \((C_f)\) for a given set of pollutants divided by the number of analyzed pollutants just as bellow (Abrahim, 2005):

\[
mC_d = \sum_{i=1}^{i=n} \frac{C'_f}{n}
\]

Where:

- \(n\) = number of analyzed elements
- \(i\) = \(i^{th}\) element

\(C'_f = \) contamination factor

For the descriptive classification of the modified contamination degree \((mC_d)\), the following gradations are proposed:

<table>
<thead>
<tr>
<th>(mC_d) value</th>
<th>Designation of quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>(mC_d&lt;1.5)</td>
<td>Nil to very low degree of</td>
</tr>
<tr>
<td></td>
<td>contamination</td>
</tr>
<tr>
<td>(1.5 \leq mC_d &lt; 2)</td>
<td>Low degree of contamination</td>
</tr>
<tr>
<td>(2 \leq mC_d &lt; 4)</td>
<td>Moderate degree of contamination</td>
</tr>
<tr>
<td>(4 \leq mC_d &lt; 8)</td>
<td>High degree of contamination</td>
</tr>
<tr>
<td>(8 \leq mC_d &lt; 16)</td>
<td>Very high degree of contamination</td>
</tr>
<tr>
<td>(16 \leq mC_d &lt; 32)</td>
<td>Extremely high degree of</td>
</tr>
<tr>
<td>(mC_d \geq 32)</td>
<td>Ultra high degree of contamination</td>
</tr>
</tbody>
</table>

Index of geoaccumulation \((I_{geo})\) proposed by Müller (1979) has also been widely used to evaluate the degree of metal contamination in terrestrial, aquatic as well as marine environments in comparison to background contents (Sutherland, 2000; Sahu and Bhosale, 1991; Singh et al., 1997). Concentrations of geochemical background are multiplied each time by the constant 1.5 in order to allow content fluctuations of a given substance in the environment as well as very small anthropogenic influences (Loska et al., 1995). Values of the geoaccumulation index can be defined as follows:

\[
I_{geo} = \log 2^{\frac{C_n}{B_n}}
\]

Where:

- \(C_n\) = concentration of the examined element in the examined environment
- \(B_n\) = geochemical background of a given element in reference environment

Müller (1981) has distinguished six classes of the geoaccumulation index:

Chemical fractionation differentiates metals of natural origin from those derived from anthropogenic sources (Passos et al., 2010). The applied method for sequential extraction was the recommended 5-step procedure by Tessier et al. (1979) as mentioned below.

1-Exchangeable fraction: Samples were extracted with 8 mL of 1M MgCl₂ (pH = 7.0) and continually shaken for a period of 1 hour (at 20°C).

2-Fraction bound to carbonates: The residue left after fraction 1 was extracted with 8 mL of 1M NaOAc (pH = 5.0) and continually shaken for a period of 5 hours (at 20°C).
Metal Contents of Soils Around Tailing Dam

<table>
<thead>
<tr>
<th>Igeo class</th>
<th>Igeo value</th>
<th>Designation of quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$I_{geo}$ = 0</td>
<td>unpolluted</td>
</tr>
<tr>
<td>1</td>
<td>$0 &lt; I_{geo} &lt; 1$</td>
<td>unpolluted to moderately polluted</td>
</tr>
<tr>
<td>2</td>
<td>$1 &lt; I_{geo} &lt; 2$</td>
<td>moderately polluted</td>
</tr>
<tr>
<td>3</td>
<td>$2 &lt; I_{geo} &lt; 3$</td>
<td>moderately to strongly polluted</td>
</tr>
<tr>
<td>4</td>
<td>$3 &lt; I_{geo} &lt; 4$</td>
<td>strongly polluted</td>
</tr>
<tr>
<td>5</td>
<td>$4 &lt; I_{geo} &lt; 5$</td>
<td>strongly to extremely polluted</td>
</tr>
<tr>
<td>6</td>
<td>$5 &lt; I_{geo}$</td>
<td>extremely polluted</td>
</tr>
</tbody>
</table>

3-Fraction bound to Fe and Mn oxides and hydroxides: The residue left after fraction 2 was extracted with 20 mL of 0.04M NH$_2$OH.HCl in 25% acetic acid (HOAc) and occasionally shaken for a period of 6 hours (at 96 ± 3°C).

4-Fraction bound to sulfides and to organic matter: 3 mL of 0.02M HNO$_3$ and 5 mL of 30% H$_2$O$_2$ were added to the residue left after fraction 3. A pH of 2.0 was achieved using HNO$_3$. This mixture was kept at 85 ± 2°C for a period of 5 hours and occasionally was shaken. 5 mL of 30% H$_2$O$_2$ were added after 1.5 and 3 hours. 5 mL of 3.2M NH$_4$OAc in 20% HNO$_3$ was added into the cooled mixture.

5-Residual fraction: 10 mL of HF and 2 mL of HClO$_4$ were added to the residue left after fraction 4 and the sample was evaporated. The residue left was dissolved in 50 mL of 2% HCl.

Extraction efficiency of the Sequential extraction procedure expressed as percentage of the total contents estimated by the following equation:

$$E(\%) = \frac{\sum C_{Fi}}{Tc} \times 100$$

where $E(\%)$ represents the extraction efficiency of the studied metals, $C_{Fi}$ is the average concentration of each fraction and $Tc$ is the total content of each studied metal in soil (Lei et al., 2009).

2.6. Pollution Intensity Index

Assigning the pollution intensity of the studied elements according to chemical partitioning results can be done as follows (Karbassi et al., 2008):

$$I_{POLL} = \log \frac{Bc}{L_p}$$

Where $I_{POLL}$, Bc and Lp are indicative of pollution intensity, bulk concentration and lithogenous portion, respectively. In this study, the residual fraction of the chemical partitioning was assumed as the lithogenous portion while the calculation of this index was applied for recognizing the intensity of anthropogenic pollution.

RESULTS & DISCUSSION

The computed mean values of RSD for studied elements in original and duplicate samples were as follows: As (1.81%), Cd (6.25%), Mo (2.57%) and Cu (1.97%). The calculated accuracy results are referred in Table 1. Descriptive statistics of studied element concentrations in surface soil samples are presented in Table 2. According to this table, the mean values of studied metal contents arranged in the following decreasing order: Cu > As > Mo > Cd, among which Cu, As and Cd show the coefficient of variation (C.V) higher than 1 that can be attributed to an anthropogenic source for these elements. For testing this assumption, computing the aimed pollution indices and applying sequential extraction procedure for contaminated surface soil samples would be essential. Table 3 summarizes the concentration of 4 studied elements analyzed in surface soil samples, the pollution load index, and the modified contamination degree. Fig.1 and Fig.2 also depict the severity of pollution in the soil in the vicinity of the tailings dam. Box plots (Fig.3 and Fig.4), Table 4, and Table 5 exhibit EF and Igeo ranges of variation for the studied elements. According to Table 3 (as it can be seen in Fig.1 and Fig.2), S10, S9, S3 and S1 are the four highest polluted sample sites. Two other computed indices (EF and Igeo) also indicate high values for these sample sites. For identifying the natural and anthropogenic source for the contamination of the selected soil samples, sequential extraction was applied. Because of the low distance between S9 and S10, only S10 was selected for sequential extraction in addition to S1 and S3. The results of the extraction by Tessier et al. method (1979) are shown in Table 6. The mean percentage of extraction efficiency was 93% for As, 125% for Cd, 101% for Cu and 138% for Mo.

None of the studied elements shows the predominant presentation in the exchangeable or bound to carbonate fraction. The results represent the dominant percentage of Cd in the fraction bound to Fe and Mn oxides and hydroxides by the amount of approximately 69%. Association with hydroxides of
Table 1. The calculated z-scores for checking the accuracy of the analysis (mean concentrations by µg/kg)

<table>
<thead>
<tr>
<th>CRMs and calculated parameters</th>
<th>Type</th>
<th>Mo</th>
<th>Cu</th>
<th>As</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>GSD-10</td>
<td>Original</td>
<td>14.9</td>
<td>20.4</td>
<td>24.6</td>
<td>1.05</td>
</tr>
<tr>
<td>Mean GSD-10</td>
<td>Measured</td>
<td>14.78</td>
<td>23.26</td>
<td>24.24</td>
<td>1.04</td>
</tr>
<tr>
<td>Std Dev</td>
<td></td>
<td>0.52</td>
<td>2.05</td>
<td>0.91</td>
<td>0.39</td>
</tr>
<tr>
<td>z-score</td>
<td></td>
<td>0.2</td>
<td>-1.4</td>
<td>0.4</td>
<td>0.0</td>
</tr>
<tr>
<td>GSD-12</td>
<td>Original</td>
<td>8.6</td>
<td>1227</td>
<td>114</td>
<td>3.62</td>
</tr>
<tr>
<td>Mean GSD-12</td>
<td>Measured</td>
<td>8.1</td>
<td>1221</td>
<td>116</td>
<td>3.75</td>
</tr>
<tr>
<td>Std Dev</td>
<td></td>
<td>1.3</td>
<td>52.3</td>
<td>3</td>
<td>0.15</td>
</tr>
<tr>
<td>z-score</td>
<td></td>
<td>0.4</td>
<td>-0.1</td>
<td>-0.5</td>
<td>-0.9</td>
</tr>
<tr>
<td>GSD-4</td>
<td>Original</td>
<td>18.3</td>
<td>35.5</td>
<td>20</td>
<td>0.2</td>
</tr>
<tr>
<td>Mean GSD-4</td>
<td>Measured</td>
<td>18.5</td>
<td>35.7</td>
<td>21</td>
<td>0.21</td>
</tr>
<tr>
<td>Std Dev</td>
<td></td>
<td>0.94</td>
<td>3.2</td>
<td>1</td>
<td>0.02</td>
</tr>
<tr>
<td>z-score</td>
<td></td>
<td>-0.2</td>
<td>-0.1</td>
<td>-0.5</td>
<td>-0.5</td>
</tr>
<tr>
<td>GSD-6</td>
<td>Original</td>
<td>24.2</td>
<td>380.4</td>
<td>13</td>
<td>0.4</td>
</tr>
<tr>
<td>Mean GSD-6</td>
<td>Measured</td>
<td>24.47</td>
<td>378.09</td>
<td>14</td>
<td>0.41</td>
</tr>
<tr>
<td>Std Dev</td>
<td></td>
<td>0.8</td>
<td>25.7</td>
<td>0.68</td>
<td>0.02</td>
</tr>
<tr>
<td>z-score</td>
<td></td>
<td>-0.3</td>
<td>0.1</td>
<td>-1.5</td>
<td>-0.6</td>
</tr>
<tr>
<td>GSD-8</td>
<td>Original</td>
<td>3.5</td>
<td>5.6</td>
<td>2.7</td>
<td>0.07</td>
</tr>
<tr>
<td>Mean GSD-8</td>
<td>Measured</td>
<td>3.27</td>
<td>5.30</td>
<td>2.6</td>
<td>0.06</td>
</tr>
<tr>
<td>Std Dev</td>
<td></td>
<td>0.46</td>
<td>0.25</td>
<td>0.24</td>
<td>0.01</td>
</tr>
<tr>
<td>z-score</td>
<td></td>
<td>0.5</td>
<td>1.2</td>
<td>0.4</td>
<td>0.8</td>
</tr>
<tr>
<td>GSD-9</td>
<td>Original</td>
<td>14.4</td>
<td>34.9</td>
<td>8.9</td>
<td>0.23</td>
</tr>
<tr>
<td>Mean GSD-9</td>
<td>Measured</td>
<td>14.72</td>
<td>32.46</td>
<td>8.9</td>
<td>0.26</td>
</tr>
<tr>
<td>Std Dev</td>
<td></td>
<td>0.89</td>
<td>3.54</td>
<td>0.37</td>
<td>0.02</td>
</tr>
<tr>
<td>z-score</td>
<td></td>
<td>-0.4</td>
<td>0.7</td>
<td>0.0</td>
<td>-1.4</td>
</tr>
</tbody>
</table>

Table 2. Descriptive statistics of studied elements in surface soil samples

<table>
<thead>
<tr>
<th>Element</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Mean</th>
<th>Std. Deviation</th>
<th>C.V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>0.48</td>
<td>2.4</td>
<td>0.91</td>
<td>0.44</td>
<td>0.48</td>
</tr>
<tr>
<td>Cu</td>
<td>26.74</td>
<td>725.46</td>
<td>112.30</td>
<td>153.80</td>
<td>1.37</td>
</tr>
<tr>
<td>As</td>
<td>3.93</td>
<td>117.60</td>
<td>18.40</td>
<td>24.50</td>
<td>1.33</td>
</tr>
<tr>
<td>Cd</td>
<td>0.07</td>
<td>2.14</td>
<td>0.50</td>
<td>0.52</td>
<td>1.02</td>
</tr>
</tbody>
</table>

Fe and Mn acts to dissipate trace metals, due to large adsorption surface areas. According to Table 5, Cu was the metal with the largest proportion in the fraction bound to organic matter (around 48% of the total). Association of the metals with organic matter can be explained by the high affinity of the elements for the humic substances or sulfides. Anthropogenic metals are predominantly found in the most labile soil extraction fractions (soluble in acid including exchangeable and bound to carbonate fraction, associated with Fe and Mn oxides, and associated with organic matter and sulfides) which are vulnerable to small changes in environmental conditions, such as those caused by human activity (Pempkowiak et al., 1999). The results of the sequential extraction exhibit that there are anthropogenic sources for Cd and Cu as they have shown their predominant portion in a non-residual fraction and have bound to Fe-Mn oxides-hydroxides and organic matter which confirmed their C.V value higher than 1.

In the residual fraction, where the metals are bound to silicates and are therefore unavailable to the aquatic system (Tüzen, 2003), As and Mo show the greatest
Table 3. Mean concentrations (ìg/kg), pollution load index and modified contamination degree of elements in soils from the sampling points

<table>
<thead>
<tr>
<th>Code</th>
<th>Mo</th>
<th>Cu</th>
<th>As</th>
<th>Cd</th>
<th>PLI</th>
<th>mCd</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.93</td>
<td>130.95</td>
<td>5.67</td>
<td>0.61</td>
<td>3.58</td>
<td>4.62</td>
</tr>
<tr>
<td>S2</td>
<td>0.86</td>
<td>68.94</td>
<td>15.03</td>
<td>2.14</td>
<td>1.43</td>
<td>1.72</td>
</tr>
<tr>
<td>S3</td>
<td>0.93</td>
<td>60.66</td>
<td>20.50</td>
<td>1.16</td>
<td>4.19</td>
<td>5.28</td>
</tr>
<tr>
<td>S4</td>
<td>0.63</td>
<td>26.74</td>
<td>117.60</td>
<td>0.38</td>
<td>2.36</td>
<td>4.75</td>
</tr>
<tr>
<td>S5</td>
<td>0.61</td>
<td>76.98</td>
<td>12.23</td>
<td>0.32</td>
<td>2.56</td>
<td>2.99</td>
</tr>
<tr>
<td>S6</td>
<td>0.77</td>
<td>44.10</td>
<td>12.23</td>
<td>0.28</td>
<td>1.88</td>
<td>2.12</td>
</tr>
<tr>
<td>S7</td>
<td>1.34</td>
<td>316.37</td>
<td>21.37</td>
<td>0.48</td>
<td>1.83</td>
<td>3.93</td>
</tr>
<tr>
<td>S8</td>
<td>0.95</td>
<td>93.21</td>
<td>9.73</td>
<td>0.41</td>
<td>2.04</td>
<td>2.76</td>
</tr>
<tr>
<td>S9</td>
<td>2.40</td>
<td>144.39</td>
<td>28.67</td>
<td>1.17</td>
<td>4.82</td>
<td>5.01</td>
</tr>
<tr>
<td>S10</td>
<td>1.49</td>
<td>725.46</td>
<td>42.27</td>
<td>1.30</td>
<td>6.49</td>
<td>9.12</td>
</tr>
<tr>
<td>S11</td>
<td>0.48</td>
<td>79.47</td>
<td>6.37</td>
<td>0.20</td>
<td>1.07</td>
<td>1.21</td>
</tr>
<tr>
<td>S12</td>
<td>0.63</td>
<td>31.92</td>
<td>4.37</td>
<td>0.10</td>
<td>1.11</td>
<td>1.14</td>
</tr>
<tr>
<td>S13</td>
<td>0.66</td>
<td>36.82</td>
<td>8.27</td>
<td>0.18</td>
<td>0.97</td>
<td>1.02</td>
</tr>
<tr>
<td>S14</td>
<td>0.64</td>
<td>54.98</td>
<td>12.00</td>
<td>0.17</td>
<td>0.89</td>
<td>1.23</td>
</tr>
<tr>
<td>S15</td>
<td>0.84</td>
<td>45.32</td>
<td>5.13</td>
<td>0.47</td>
<td>0.98</td>
<td>1.55</td>
</tr>
<tr>
<td>S16</td>
<td>0.52</td>
<td>54.84</td>
<td>6.17</td>
<td>0.13</td>
<td>0.55</td>
<td>0.68</td>
</tr>
<tr>
<td>S17</td>
<td>1.41</td>
<td>95.66</td>
<td>18.27</td>
<td>0.31</td>
<td>1.78</td>
<td>1.91</td>
</tr>
<tr>
<td>S18</td>
<td>0.80</td>
<td>117.18</td>
<td>9.50</td>
<td>0.19</td>
<td>1.32</td>
<td>1.35</td>
</tr>
<tr>
<td>S19</td>
<td>0.75</td>
<td>48.49</td>
<td>15.90</td>
<td>0.11</td>
<td>0.68</td>
<td>0.75</td>
</tr>
<tr>
<td>S20</td>
<td>0.99</td>
<td>40.91</td>
<td>3.93</td>
<td>0.07</td>
<td>0.63</td>
<td>0.71</td>
</tr>
<tr>
<td>SNP</td>
<td>0.63</td>
<td>64.93</td>
<td>11.20</td>
<td>0.48</td>
<td>1.24</td>
<td>1.34</td>
</tr>
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</table>

Table 4. EF values for measured studied elements in sampling points

<table>
<thead>
<tr>
<th>EF</th>
<th>As</th>
<th>Cd</th>
<th>Cu</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>5.79</td>
<td>18.79</td>
<td>31.53</td>
<td>6.25</td>
</tr>
<tr>
<td>S2</td>
<td>1.30</td>
<td>5.28</td>
<td>2.55</td>
<td>1.25</td>
</tr>
<tr>
<td>S3</td>
<td>7.60</td>
<td>11.24</td>
<td>8.45</td>
<td>1.46</td>
</tr>
<tr>
<td>S4</td>
<td>18.91</td>
<td>3.62</td>
<td>3.89</td>
<td>0.48</td>
</tr>
<tr>
<td>S5</td>
<td>7.21</td>
<td>4.44</td>
<td>18.23</td>
<td>6.08</td>
</tr>
<tr>
<td>S6</td>
<td>6.60</td>
<td>8.59</td>
<td>11.16</td>
<td>2.72</td>
</tr>
<tr>
<td>S7</td>
<td>1.47</td>
<td>0.33</td>
<td>10.84</td>
<td>1.32</td>
</tr>
<tr>
<td>S8</td>
<td>6.55</td>
<td>3.30</td>
<td>6.77</td>
<td>0.72</td>
</tr>
<tr>
<td>S9</td>
<td>22.03</td>
<td>14.13</td>
<td>27.12</td>
<td>14.76</td>
</tr>
<tr>
<td>S10</td>
<td>19.44</td>
<td>13.64</td>
<td>42.32</td>
<td>3.46</td>
</tr>
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<td>0.75</td>
<td>1.06</td>
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<td>12.80</td>
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<td>12.77</td>
<td>7.68</td>
</tr>
<tr>
<td>S13</td>
<td>1.41</td>
<td>3.22</td>
<td>2.20</td>
<td>3.23</td>
</tr>
<tr>
<td>S14</td>
<td>0.12</td>
<td>0.80</td>
<td>1.46</td>
<td>0.54</td>
</tr>
<tr>
<td>S15</td>
<td>1.33</td>
<td>10.39</td>
<td>1.28</td>
<td>1.56</td>
</tr>
<tr>
<td>S16</td>
<td>0.23</td>
<td>1.36</td>
<td>1.53</td>
<td>0.80</td>
</tr>
<tr>
<td>S17</td>
<td>4.29</td>
<td>7.24</td>
<td>2.53</td>
<td>3.80</td>
</tr>
<tr>
<td>S18</td>
<td>2.29</td>
<td>3.16</td>
<td>3.70</td>
<td>2.07</td>
</tr>
<tr>
<td>S19</td>
<td>0.74</td>
<td>1.34</td>
<td>1.48</td>
<td>0.49</td>
</tr>
<tr>
<td>S20</td>
<td>1.14</td>
<td>0.77</td>
<td>1.22</td>
<td>0.35</td>
</tr>
<tr>
<td>SNP</td>
<td>1.35</td>
<td>3.10</td>
<td>2.07</td>
<td>1.12</td>
</tr>
</tbody>
</table>
Fig. 1. Location of the study area and the samples taken from water in Meyduk

Fig. 2. Pollution Load Index (PLI) of the soil in the vicinity of Meyduk tailings dam
Metal Contents of Soils Around Tailing Dam

Table 5. Igeo values for measured studied elements in sampling points

<table>
<thead>
<tr>
<th>Igeo values</th>
<th>As</th>
<th>Cd</th>
<th>Cu</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.20</td>
<td>1.89</td>
<td>2.64</td>
<td>0.31</td>
</tr>
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<td>S2</td>
<td>-0.80</td>
<td>1.23</td>
<td>0.17</td>
<td>-0.86</td>
</tr>
<tr>
<td>S3</td>
<td>1.90</td>
<td>2.46</td>
<td>2.05</td>
<td>-0.48</td>
</tr>
<tr>
<td>S4</td>
<td>3.16</td>
<td>0.77</td>
<td>0.87</td>
<td>-2.16</td>
</tr>
<tr>
<td>S5</td>
<td>0.68</td>
<td>-0.02</td>
<td>2.01</td>
<td>0.43</td>
</tr>
<tr>
<td>S6</td>
<td>0.36</td>
<td>0.75</td>
<td>1.12</td>
<td>-0.91</td>
</tr>
<tr>
<td>S7</td>
<td>0.14</td>
<td>-2.01</td>
<td>3.03</td>
<td>-0.01</td>
</tr>
<tr>
<td>S8</td>
<td>1.48</td>
<td>0.49</td>
<td>1.52</td>
<td>-1.71</td>
</tr>
<tr>
<td>S9</td>
<td>1.92</td>
<td>1.27</td>
<td>2.21</td>
<td>1.34</td>
</tr>
<tr>
<td>S10</td>
<td>2.58</td>
<td>2.07</td>
<td>3.71</td>
<td>0.09</td>
</tr>
<tr>
<td>S11</td>
<td>-0.57</td>
<td>-0.07</td>
<td>0.36</td>
<td>-1.63</td>
</tr>
<tr>
<td>S12</td>
<td>-0.08</td>
<td>-0.77</td>
<td>-0.08</td>
<td>-0.81</td>
</tr>
<tr>
<td>S13</td>
<td>-1.39</td>
<td>-0.20</td>
<td>-0.75</td>
<td>-0.19</td>
</tr>
<tr>
<td>S14</td>
<td>-2.84</td>
<td>-0.16</td>
<td>0.71</td>
<td>-0.71</td>
</tr>
<tr>
<td>S15</td>
<td>-1.40</td>
<td>1.56</td>
<td>-1.45</td>
<td>-1.17</td>
</tr>
<tr>
<td>S16</td>
<td>-3.21</td>
<td>-0.66</td>
<td>-0.49</td>
<td>-1.43</td>
</tr>
<tr>
<td>S17</td>
<td>0.29</td>
<td>1.05</td>
<td>-0.47</td>
<td>0.12</td>
</tr>
<tr>
<td>S18</td>
<td>-0.44</td>
<td>0.03</td>
<td>0.25</td>
<td>-0.58</td>
</tr>
<tr>
<td>S19</td>
<td>-1.44</td>
<td>-0.58</td>
<td>-0.44</td>
<td>-2.04</td>
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<tr>
<td>S20</td>
<td>-0.69</td>
<td>-1.25</td>
<td>-0.60</td>
<td>-2.41</td>
</tr>
<tr>
<td>SNP</td>
<td>-0.66</td>
<td>0.54</td>
<td>-0.04</td>
<td>-0.93</td>
</tr>
</tbody>
</table>

Table 6. Sequential extraction results (µg/g) for S1, S3 and S10 in 5 steps

<table>
<thead>
<tr>
<th>Element</th>
<th>As</th>
<th>Cd</th>
<th>Cu</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-1- EX</td>
<td>0.01</td>
<td>0.04</td>
<td>0.65</td>
<td>0.03</td>
</tr>
<tr>
<td>S-1- CAR</td>
<td>0.09</td>
<td>0.10</td>
<td>9.52</td>
<td>0.01</td>
</tr>
<tr>
<td>S-1- Fe/Mn</td>
<td>3.47</td>
<td>0.52</td>
<td>10.95</td>
<td>0.56</td>
</tr>
<tr>
<td>S-1- ORG</td>
<td>0.22</td>
<td>0.03</td>
<td>41.47</td>
<td>0.01</td>
</tr>
<tr>
<td>S-1- RES</td>
<td>4.45</td>
<td>0.06</td>
<td>21.19</td>
<td>0.77</td>
</tr>
<tr>
<td>S-3- EX</td>
<td>0.01</td>
<td>0.12</td>
<td>1.15</td>
<td>0.06</td>
</tr>
<tr>
<td>S-3- CAR</td>
<td>0.24</td>
<td>0.35</td>
<td>4.44</td>
<td>0.01</td>
</tr>
<tr>
<td>S-3- Fe/Mn</td>
<td>4.68</td>
<td>0.76</td>
<td>14.46</td>
<td>0.37</td>
</tr>
<tr>
<td>S-3- ORG</td>
<td>0.39</td>
<td>0.04</td>
<td>30.05</td>
<td>0.01</td>
</tr>
<tr>
<td>S-3- RES</td>
<td>8.63</td>
<td>0.04</td>
<td>10.75</td>
<td>0.66</td>
</tr>
<tr>
<td>S-10- EX</td>
<td>0.01</td>
<td>0.10</td>
<td>1.87</td>
<td>0.08</td>
</tr>
<tr>
<td>S-10- CAR</td>
<td>1.14</td>
<td>0.17</td>
<td>100.82</td>
<td>0.01</td>
</tr>
<tr>
<td>S-10- Fe/Mn</td>
<td>9.31</td>
<td>1.44</td>
<td>376.36</td>
<td>0.52</td>
</tr>
<tr>
<td>S-10- ORG</td>
<td>0.23</td>
<td>0.01</td>
<td>477.92</td>
<td>0.42</td>
</tr>
<tr>
<td>S-10- RES</td>
<td>17.65</td>
<td>0.09</td>
<td>62.54</td>
<td>1.04</td>
</tr>
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</table>

Table 7. Comparison of various pollution indices for extracted samples in the studied area

<table>
<thead>
<tr>
<th>Element</th>
<th>Mean concentration (µg/kg)</th>
<th>EF</th>
<th>Igeo</th>
<th>IPOLL</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>22.81</td>
<td>10.94</td>
<td>1.56</td>
<td>1.15</td>
</tr>
<tr>
<td>Cd</td>
<td>1.02</td>
<td>14.56</td>
<td>2.14</td>
<td>4.01</td>
</tr>
<tr>
<td>Cu</td>
<td>305.69</td>
<td>27.43</td>
<td>2.8</td>
<td>3.28</td>
</tr>
<tr>
<td>Mo</td>
<td>1.12</td>
<td>3.72</td>
<td>-0.03</td>
<td>0.44</td>
</tr>
</tbody>
</table>
content, with average percentage 58% and 55% respectively. Elevated concentrations of metals in the residual fraction indicate that soils are relatively unpolluted, and that the elements derive mainly from lithogenic origins (Chandra Sekhar et al., 2003). Meanwhile, different relative behaviors of the metals in the different phases (exchangeable, carbonates, Fe and Mn oxides, organic matter and sulfides, and aluminosilicates) are probably reflective of different origins of pollution. Regions where the metals are weakly associated with soils have experienced more recent pollution. Locations where metals are significantly associated with the oxidizable or reducible soil fractions are influenced by pollution that is less recent (Passos et al., 2010). As also indicated the same condition for its C.V value as Cu and Cd, but it was released dominantly in the last fraction of the sequential extraction. This can be interpreted by
assuming an old anthropogenic source for As such as the mine explosion dust.

The conclusions obtained from C.V values and the contribution of every studied element in 5 extracted fractions can be confirmed by the pollution intensity index \( I_{\text{poll}} \) values, depicted in Table 7. As it can be seen in Table 7, the order of recent anthropogenic effect (tailings dust) on originating pollution is exhibited as follows: Cd>Cu>As>Mo. This kind of the sequence is as the same as the bioavailability order of the studied elements in tailings dust extracts determined in recent studies in Meyduk area (Kargar 2010). Except for \( I_{\text{poll}} \), this verification was not observed in other calculated pollution indices (EF and Igeo) as shown in Table 7.

For two metals (Cd and Cu) with dominant presentation in non-residual fractions of the surface soil extract, two anthropogenic source of pollution was supposed comprising tailings dust and mining explosion dust. Recognizing the main pollutant source could be possible by considering the frequent wind direction in the region. The data collected during recent 10 years in Bon-Yakeh meteorological station indicate the southwest as the frequent direction of the wind. In this way, the severity of pollution in S1 and S3 can be almost justified. However, the main reason of the pollution for S10 that is located in northeast of the tailings catchment can be attributed to mine explosions caused its dusts to be dispersed during some seasons especially summer in the vicinity. Although northeast is not the predominant direction of the wind, it seems that the large expansion of mining activities has extremely influenced on the surface soil located in the northeastern bank of the tailings dam. Considering the high values of computed indices in S9 and S10 proves this fact. This effect was more sensible in comparison to tailings dust impact. One of its reasons can be related to the new discharges of the tailings produced by concentrator plant added into the previous tailings impoundment. This led the tailings reservoir not to be dried completely, therefore it cannot be scattered so much by the power of the wind.

CONCLUSION

Recognizing the severity of soil pollution can be understood by computing some common pollution indices such as EF, PLI, \( m_e \) and \( I_{\text{geo}} \). In Meyduk surface soil surrounding the tailings catchment, the highest values of the calculated indices, considering As, Cd, Cu and Mo content, were observed in northeastern and southwestern parts of the studied region. Near Meyduk tailings impoundment, two kinds of anthropogenic source can affect on surface soil pollution. These sources include in mine explosion and tailings dusts. The dominant wind direction shows that the southwestern soil around the tailings reservoir is frequently under the effect of the tailings dust while the northeastern part is influenced by the mine explosions. The results of the sequential extraction exhibit that there are anthropogenic sources for Cd and Cu as they have shown their predominant portion in a non-residual fraction and have bound to Fe-Mn oxides-hydroxides and organic matter which confirmed their C.V higher than 1. As also indicated the same condition for its C.V value, but it released dominantly in the last fraction of the sequential extraction. This can be interpreted by assuming an old anthropogenic source for As such as the mine explosions dust. For Mo, by C.V value lower than 1 and frequent release in bound to aluminosilicate fraction, a lithogenic source was proposed. The \( I_{\text{poll}} \) values also indicated the more recent anthropogenic sources for Cd and Cu in comparison with As and Mo.

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