Distribution of Heavy Metals around the Dashkasan Au Mine

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ABSTRACT: The aim of the study is to determine the major source and extent of metal pollution in the vicinity of Dashkasan gold mine. Dashkasan mine has resulted in extensive contamination of soils by Arsenic (As) and potentially toxic ore-related elements including Mercury (Hg), Antimony (Sb) and Cadmium (Cd). Soils samples were collected and analyzed for As, Cd, Hg, Pb and Sb. The concentration of each heavy metal is controlled by different parameters (soil pH, iron and aluminum oxide content, clay content, organic matter and cation exchange capacity). The maximum content in the soils were 485, 3.2, 100, 2710 and 640 mg/kg for As, Cd, Hg, Pb and Sb, respectively. In particular, the extracted concentration of As, Cd, Hg and Sb are in excess of the tolerable levels. Positive correlation with organic matter and clay content but not with pH has been observed for most of elements analyzed in this study. Enrichment factor (EF) analysis and cluster analysis (CA) highlighted the lithogenic origin of heavy metals. It also revealed the need for detailed geochemical surveys in the future in order to decrease the uncertainty of discrimination between lithogenic and anthropogenic origin of metals of interest.

Key words: Arsenic, Heavy metals, Contamination, Dashkasan, Gold mine

INTRODUCTION

The problem of soil pollution by heavy metal has been receiving an increasing attention in the last few decades (Hasan et al., 2010; Mumba et al., 2008; Kashulin et al., 2008; Mensi et al., 2008; Venugopal et al., 2009; Dixit and Tiwari, 2008; Biati et al., 2010; Nouri et al., 2010; Abdul Aziz et al., 2010; Gaur and Dhanikhar, 2009; Akoto et al., 2008; Dauwalter et al., 2009; Uba et al., 2009; Ahmad et al., 2010). Soils can act as a scavenger agent for heavy metal and an adsorptive sink in contaminated environments (Priju & Narayana, 2007; Ahmed and Al-Hajri, 2009; Oygard and Gjengedal, 2009) It is therefore considered to be an appropriate indicator of heavy metal pollution. Metals accumulate in soil from both natural and anthropogenic sources occur in the same manner, and this makes it difficult to identify and determine the origin of heavy metal present in soil. Contaminated soils from various sources, however, contain significant levels of the elements. Average concentrations of As, Cd, Hg, Pb and Sb in the Earth’s crust are 1.5, 0.2, 0.08, 13 and 0.2 mg/kg1 respectively (Mason & Moore, 1982). Because pollution of the soil environment may affect human health directly and indirectly (Deckers et al., 2000; Opene and Agbozu, 2008; Nabi Bidhendi et al., 2007; Resmi et al., 2010), a proper estimation of the potential hazard of polluted area is essential. Many studies have examined relationships among elements and between elemental concentrations and other soil properties (clay content, cation exchange capacity, pH, soil texture, carbonate content) in non-contaminated soils (Navas & Machin, 2002; Burt et al., 2003; Vega et al., 2004; Covelo et al., 2007; Dragovic et al., 2008; Praveena et al., 2008). Methods of multivariate analysis have been widely used in these investigations to identify pollution sources and to apportion natural vs. anthropogenic contribution (Facchinelli et al., 2001; Slavkoviæ et al., 2004; Micó et al., 2006; Luo et al., 2007; Shetty and Rajkumar, 2009; Murugesan et al., 2008; Vinodhini and Narayanan, 2009; Abdullahi et al., 2009; Uba et al., 2009; Rahmani et al., 2009).

The present study was carried out as a preliminary survey on soil contamination of Dashkasan area. There are only a few studies on level of soil pollution in this area (Sayyareh et al., 2005). The aims of this study are: (i) to determine concentrations of five heavy metals (As, Cd, Hg, Pb and Sb) in soils of investigated area as a basis for future geochemical surveys; (ii) to reveal their relationships with physico-chemical characteristics of the soil; (iii) to analyze their intra-relationships and (iv) to highlight their lithogenic or anthropogenic origin by both enrichment factor analysis and cluster analysis (CA).
MATERIALS & METHODS

Dashkasan antimony-Arsenic-gold mine is located in west of Iran, 42 km NE of Qorveh, Kordestan Province, Iran (Fig. 1). The area is a part of Sanandaj-Sirjan magmatic-metamorphic zone (Stocklin, 1968). Based on geological observations, the oldest rock units in the area belong to the Jurassic series and are slates, phyllites and quartzites. The youngest units are Neogene volcano-clastic conglomerates, basaltic flows, block lavas and Quaternary agglomerates. The plutonic rocks in the area consist of a Neogene, calc-alkaline microgranite-microgranodiorite intrusive with microgranular porphyritic textures. Dashkasan mine is considered as a vein-type deposit in which its related mineralization is controlled by tectonic structures. The deposit is hosted by dacite, rhyodacite and microgranodiorite subvolcanic rocks which are mainly associated with silicic, argillic and pyritic alterations. The ore parageneses in the veins includes quartz, stibnite, pyrite, realgar, orpiment, pyrotite, chalcopyrite, bornite, galena, boulangerite, aurostibite, gold, stibiconite, kermesite and iron-hydroxides (Rastad et al., 2000). Thirty eight soil samples were collected from the around the Dashkasan mine in June and July 2007 (Fig. 1). Each sample was taken within a depth of 0-20 cm from the surface. Approximately 10 g of the samples were taken in 50 ml distilled water and agitated for 10 minutes. The solutions were left undisturbed for 1h with occasional shaking before measuring the pH (Segura et al. 2006). A combined glass electrode connected to a pH-meter (744&! metrohm) was used for pH measurements. Organic matter in the soil was determined by ignition at 450 °C in a muffle furnace. The percentage of loss of ignition (LOI) was considered as total organic matter (TOM) and the cation exchange capacity (CEC) was calculated by the equation (Malakouti & Homaie, 1994):

\[ \text{CEC} = (2.5 \times \text{LOI}) + (0.57 \times \text{Clay \%}) \]

The hydrometry method and sieve analysis were used for particle size analysis (Bowles, 1978). Once the organic matter had been removed, the remaining mineral sample was weighted and subjected to particle size analysis in order to determine the following fractions: sand (2-0.0625 mm), silt (0.0625-0.002 mm) and clay (<0.002 mm). The samples were dried for two days at 60 °C. The dry soil were disaggregated, sieved on a 10 mesh (2 mm) screen, then quartered, pulverized and passed through a 120 mesh (<125 µm) sieve. Total element concentrations were determined in all the soil samples. The term total is used as the amount of metals dissolved according to the four acid (HCl, HF, HNO₃, HClO₄) dissolution method. The measurements were carried out by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry) and acid mixture digestion by Australian Laboratory Services (ALS) in Canada. To determine relative degree of metal contamination, comparisons were made to background concentrations in the Earth’s crust using Fe as reference element following the assumption that its content in the crust has not been disturbed by anthropogenic activity. The EF, were calculated according to the equation generalized from Zoller et al. (1974):

\[ \text{EF} = \frac{([M]/[Fe])_{\text{soil}}}{([M]/[Fe])_{\text{crust}}} \]
where \([M]\) is the concentration of any element, \([\text{Fe}]\) is the concentration of \(\text{Fe}\), and the subscripts “soil” and “crust” indicate which medium the concentration refers to. Multivariate analysis was performed using SPSS 16 software for windows. An agglomerative hierarchical cluster analysis (CA) based on between-groups linkage method and correlation matrix was performed. Results are shown in a dendrogram where steps in the hierarchical clustering solution and values of the distance between clusters (Pearson correlation) are represented. Details on cluster analysis can be found in standard chemometric textbooks (Brereton, 2003).

RESULTS & DISCUSSION

Descriptive statistics for heavy metal contents, physico-chemical soil characteristics of analyzed soil are summarized in Table 1. Soil texture estimated to be sandy mud according to soil textural triangle (Folk, 1980) (Fig. 2). Most soils were brown in color. The pH did not vary much and was slightly basic (7.15–7.75), which suggests neutral to sub-alkaline conditions for all the soil samples. At low pH (ca. 6.5), the mobility and leaching of toxic metals increase, and their mobility and availability decrease as the pH approaches neutral or rises above seven. Organic matter content in the soils ranged from 3.4% to 8%. Cation exchange capacity (CEC) shows broad variation ranging from 18.08 to 43.81 meq/100g. The correlation between heavy metal content and soil physico-chemical characteristics is shown in Table 2. Soil pH was not correlated with heavy metal content of analyzed soils. Organic matter was correlated positively (\(p < 0.01\)) with As. The cation exchange capacity exhibited a significant relationship with As and Sb (\(r = 0.649, r = 0.533, p < 0.01\)) and with Cd, Hg and Pb (\(p < 0.05\)). Strong positive correlation were found between clay content and As and Sb concentration (\(p < 0.01\)). Inter element relationships provide information on heavy metal sources and pathways. According to the values of Pearson correlation coefficient (Table 2) all metals are highly correlated (\(p < 0.01\)). Arsenic showed strong positive correlation with Sb (\(r = 0.851, p < 0.01\)). Basic statistics for total concentrations of heavy metals in surface soil samples are shown in Table 1. The maximum concentrations of heavy metals in surface soils were 485, 3.2, 100, 2710 and 640 mg/kg for As, Cd, Hg, Pb

<table>
<thead>
<tr>
<th>Table 1. Basic statistics for heavy metal contents, physico-chemical soil characteristic of the around Dashkasan mine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
</tr>
<tr>
<td>As (mg/kg)</td>
</tr>
<tr>
<td>Cd (mg/kg)</td>
</tr>
<tr>
<td>Hg (mg/kg)</td>
</tr>
<tr>
<td>Pb (mg/kg)</td>
</tr>
<tr>
<td>Sb (mg/kg)</td>
</tr>
<tr>
<td>Org.M (%)</td>
</tr>
<tr>
<td>CEC (meq/100g)</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Clay (%)</td>
</tr>
<tr>
<td>Silt (%)</td>
</tr>
<tr>
<td>Sand (%)</td>
</tr>
</tbody>
</table>

Fig. 2. Ternary diagram of the mine soil texture (After Folk, 1980)
S: Sand, Sc: Clayey Sand, Sm: Mudy Sand, Sz: Silty Sand, Cs: Sandy Clay, Ms: Sandy Mud, Zs: Sandy Silt, C: Clay, M: Mud, Z: Silt
Table 2. Correlation between elements, organic matter, cation exchange capacity, pH and grain size distributions in the studied soils

<table>
<thead>
<tr>
<th></th>
<th>As</th>
<th>Cd</th>
<th>Hg</th>
<th>Pb</th>
<th>Sb</th>
<th>Org.M</th>
<th>pH</th>
<th>CEC</th>
<th>Clay</th>
<th>Silt</th>
<th>Sand</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>0.689**</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>0.585**</td>
<td>0.794**</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.517**</td>
<td>0.835**</td>
<td>0.716**</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>0.851**</td>
<td>0.600**</td>
<td>0.635**</td>
<td>0.334**</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Org.M</td>
<td>0.331*</td>
<td>0.220</td>
<td>0.213</td>
<td>0.294</td>
<td>0.232</td>
<td></td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>0.127</td>
<td>0.191</td>
<td>0.042</td>
<td>0.282</td>
<td>0.032</td>
<td>-0.059</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CEC</td>
<td>0.649**</td>
<td>0.409*</td>
<td>0.362*</td>
<td>0.337*</td>
<td>0.533**</td>
<td>0.135**</td>
<td>0.170</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clay</td>
<td>0.588**</td>
<td>0.307</td>
<td>0.302</td>
<td>0.209</td>
<td>0.553**</td>
<td>0.024</td>
<td>0.038</td>
<td>0.878**</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silt</td>
<td>-0.232</td>
<td>0.111</td>
<td>0.205</td>
<td>0.171</td>
<td>-0.111</td>
<td>-0.023*</td>
<td>-0.162</td>
<td>-0.0931</td>
<td>0.102</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Sand</td>
<td>0.131</td>
<td>-0.033</td>
<td>-0.069</td>
<td>-0.165</td>
<td>0.169</td>
<td>0.189</td>
<td>0.071</td>
<td>-0.319</td>
<td>-0.368*</td>
<td>-0.454**</td>
<td>1</td>
</tr>
</tbody>
</table>

* Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

and Sb, respectively. These values were significantly higher than those in natural soil (Bowen, 1979), and also higher than the tolerable levels, which are considered as phytotoxicity excessive, 20 mg/kg of As, 200 mg/kg of Pb, 3 mg/kg of Cd (Ross, 1994; Singh & Steinnes, 1994), 3 mg/kg of Hg and 5 mg/kg of Sb (Kabata-Pendias & Pendias, 1992). A very wide range between minimum and maximum values was observed. This could be due to either a marker variation in the mineralogical composition of the different soils in the studied area and/or different amounts of heavy metals that have been released to the various soils from various sources (Idris et al., 2007). Distribution maps for As, Cd, Hg and Sb concentrations in surface soil samples are shown in Fig. 3.

Significant concentrations of As and Sb were found in the sites around mine due to mineralization associated with those metalloids, with the average values of 106.5 and 65.6 mg/kg, respectively. Most As in the soils of Dashkasan area is relatively immobile, bound to iron and manganese oxhydroxides, organic matter and carbonates or found in the residual mineral fraction, i.e. in refractory minerals. The concentrations of the metals however, were relatively low in a nearby control area with the same geology as the mine. However, it can be expected that soils in the study area are highly contaminated. Therefore large area in the vicinity of the mine would not be useful for agricultural activities due to the due to contamination of As.

Basic statistics for EFs of all analyzed metals is shown in Table 3. The values of EFs were calculated taking into account the following values of concentrations of metals in upper continental crust, 0.102 mg/kg for Cd, 17 mg/kg for Pb, 2 mg/kg for As, 0.056 mg/kg for Hg and 0.31 mg/kg for Sb (Wedepohl, 1995). The EF values show the enrichment for As and Sb. There is no accepted pollution ranking system or categorization of degree of pollution on the EF analysis. It cannot provide a reliable assessment of the degree of human interference with the global environment (Reimann and Caritat 2005) but only indicate lithogenic or anthropogenic origin of the contaminations. The results obtained by cluster analysis are presented by dendrogram where the distance axis represents the degree of association between-groups of variable, i.e. the lower the value on the axis, the more significant the association (Fig. 4). As can be seen Cd, Pb and Hg are grouped into one branch, while As and Sb are into other branch. In the study area soils, two distinct clusters can be identified. Cluster I: contained CEC, clay content, organic matter content and silt. Cluster II: contained studied heavy metals as well as pH and sand content. Comparison of the average values of heavy metal concentrations obtained in this study (Table 1) with the values available from literature indicate that As and Sb are higher than the mean values established for uncultivated area worldwide. The higher content of As and Sb are probably due to parent material, i.e. dacite, rhyodacite and microgranodiorite subvolcanic rocks common in Dashkasan area which are mainly associated with silicic, argillic and pyretic alterations. No significant correlation between soil pH and heavy metal content was observed for analyzed soils (Table 2). These
Fig. 3. Distribution maps of As, Cd, Hg, Pb and Sb (mg/kg) in the soils of around Dashkasan mine.
Table 3. Descriptive statistics of the EFs of heavy metals in analyzed soils

<table>
<thead>
<tr>
<th>Element</th>
<th>Mean</th>
<th>Median</th>
<th>Skewness</th>
<th>Kurtosis</th>
<th>Range</th>
<th>Min</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>70.5790</td>
<td>52.4128</td>
<td>4.058</td>
<td>20.019</td>
<td>511.49</td>
<td>11.14</td>
<td>522.63</td>
</tr>
<tr>
<td>Cd</td>
<td>10.5156</td>
<td>6.1354</td>
<td>3.537</td>
<td>12.565</td>
<td>59.15</td>
<td>4.23</td>
<td>63.39</td>
</tr>
<tr>
<td>Hg</td>
<td>256.9369</td>
<td>8.6853</td>
<td>3.668</td>
<td>12.987</td>
<td>3848.29</td>
<td>0.23</td>
<td>3848.52</td>
</tr>
<tr>
<td>Pb</td>
<td>22.3245</td>
<td>7.1266</td>
<td>4.410</td>
<td>21.093</td>
<td>290.14</td>
<td>1.83</td>
<td>291.96</td>
</tr>
<tr>
<td>Sb</td>
<td>299.6757</td>
<td>99.1560</td>
<td>5.149</td>
<td>28.852</td>
<td>4435.46</td>
<td>13.93</td>
<td>4449.39</td>
</tr>
</tbody>
</table>

Fig. 4. Dendrogram derived from the hierarchical cluster analysis of heavy metals content and physico-chemical characteristics in analyzed soils

results are consistent with those obtained by Tume et al., (2006) for natural surface soils of Catalonia, Spain, and by Manta et al., (2002) for non-stratified soils from Sicily and also by Dragove et al. (2008) for soils of Zlatibor. The correlations between heavy metal concentrations and soil organic matter content obtained in this study (Table 2) indicated that soil organic matter content played a fundamental role in the control of As sorption by soils. Results of correlation analysis between heavy metal contents and particle size distribution confirmed the results obtained in studies conducted world-wide which have been shown that the fine-grained soil fraction exhibit higher tendency for heavy metal adsorption than coarse-grained soils since it contains soil particles with large surface area such as clay mineral, iron and manganese oxy-hydroxides, humic acids (Bradl, 2004). Positive correlations were observed between As and Sb and clay fraction of the soil. The high concentration of these elements could be attributed to incorporation of such elements in the lattice of the clay minerals (Al-Juboury, 2009). Correlation analysis (Table 2) showed that all heavy metals are highly correlated (p ≤ 0.01). This may indicate same origin and controlling factors of all heavy metals in analyzed soils. Enrichment factors were used to speculate on lithogenic or anthropogenic origin of analyzed heavy metals (Table 3). These factors alone cannot precisely distinguish sources of these elements in soils but may be useful as indicators for the role of weathering and other pedogenic processes on their distribution. Cluster analysis performed on elemental concentrations and physico-chemical characteristics of the soils shows two distinct clusters (Fig. 4). Cluster I includes CEC, clay content, organic matter content and silt. There is a close relationship between CEC and clay content. Cluster II consists of heavy metals. These elements may originate from the natural parent materials of the soils. Real-world examples of regional geochemical surveys demonstrate that EFs are influenced by a number of factors of which contamination is but one (Reimann & Caritat, 2005). Application of cluster analysis showed the attribution of metals in one source. All heavy metals in studied area have lithogenic origin. Results obtained by applying this multivariate method are consistent with those obtained by correlation analysis of heavy metal contents with soil physico-chemical characteristics.

CONCLUSIONS

The concentrations of heavy metal As, Cd, Hg, Pb and Sb and their relationships with physico-chemical characteristics of the soils around the Dashkasan mine,
west of Iran have been studied. The concentration of As, Cd, Hg, Pb and Sb in mine soils ranges from 18 to 485, 0.5 to 3.2, 0.01 to 100, 26 to 2710 and 5 to 640 mg/kg, with an arithmetic mean of 106.53, 0.80, 9.03, 255.03 and 65.63 mg/kg, respectively. The highest concentrations of the heavy metals were recorded in topsoil near the mine. There is a progressive decrease of heavy element concentrations with increasing distance from the mine. The application of EF analysis and CA pointed out lithogenic origin of all heavy metals in soils around Dashkasan mine. The mean EF that is more than 5 is clearly indicative of metals enrichment in soils of area of study. This study also highlighted the further need for research including detailed geochemical surveys in this area. The preliminary compilation of As distribution in soils shows the role of geology as the main governing factor.

REFERENCES


