INTRODUCTION

Large geochemical databases have been used to analyze the spatial distribution of natural and man-made chemicals in soils and sediments (Chiprés et al., 2009a,b). One of such databases is the North American Soil Geochemical Landscapes Project (Chiprés et al., 2009b; Smith, 2009), which encompasses the data utilized in this study. For this study, geochemical data were merged for four 1° x 2° quadrangles in northern Mexico, covering altogether more than 84,000 Km².

Spatial analysis combined with EDA has proven to produce more representative threshold values and to better represent the geochemical conditions of an area, as this method takes into consideration the fact that these data are non-normally distributed, plus the results are less affected by the presence of outliers (Carranza, 2009; Chiprés et al., 2009a; Zhang and Selinus, 1998).

1.1 Previous studies

Findings of high As content in well water within the study area prompted investigations, in soils and surface waters, seeking concentration characterization and potential As sources. Spatial distribution of As content in soils and sediments in areas of high As content in Mexico have been reported by Razo et al. (2004), Gutiérrez and Carreón (2008), Chiprés et al. (2009a), Gutiérrez et al. (2009), and Ortega-Guerrero (2009). In these studies, the presence of As has been related to weathering of As-rich rocks and redistribution of As-containing minerals. Tertiary igneous rocks (ignimbrites and rhyolites) have been pointed out as a likely As source, but the precise source and mechanisms of remobilization remain unknown. Furthermore, man-made chemicals included in fertilizers and sewage may contribute As in specific locations where these wastes are released.

1.2 Study area

The study area is within the Chihuahuan desert, which is dominated by large basins filled with alluvium typical of Basin and Range topography (Fig. 1). The surface hydrology of the area includes several closed basins, the Río Conchos basin, and a small portion of the Río Grande basin. The outcrops on the western part are primarily Tertiary volcanics (ignimbrites and rhyolites) while Paleozoic limestones and shales outcrop in addition to Tertiary volcanics in the central to eastern part of the area. At some boundaries between limestone and igneous rocks, economically important hydrothermal skarn deposits are present, comprised of silver, lead and zinc mineralization (Robertson and Megaw, 2009).

ABSTRACT: Sediment geochemical data for four 1° x 2° quadrangles in northern Mexico were merged. Exploratory data analysis (EDA) was applied to the resulting dataset (N= 2,046) in order to identify areas with arsenic (As) anomalies and their possible source. Two types of anomalies were identified. Mild As anomalies had a threshold value of 9.40 mg/kg and clustered around outcrops of volcanic rock and non-producing sulfide mineral deposits. Extreme As anomalies had a threshold value of 14.41 mg/kg and clustered near sulfide mineral deposits and towards the center of drainage basins. Spatial distribution suggests that the source of mild anomalies is enriched natural concentrations while mine tailings and/or man-made contaminants are the source of extreme anomalies.

Keywords: arsenic anomalies, Chihuahuan desert, exploratory data analysis, sediment geochemistry.
2 METHODS

Sediments of creeks were sampled by the Servicio Geológico Mexicano, and analyzed according to standard procedure (Chiprés et al., 2009b). The thresholds for anomaly values were singled out using the box diagram method (Carranza, 2009, Chiprés et al., 2009a, Reimann et al., 2005). These thresholds include the inter-quartile range (IQR = 3rd quartile – 1st quartile), lower inner fence (LIF = 1st quartile – 1.5 IQR), lower outer fence (LOF = 1st quartile – 3 IQR), upper inner fence (UIF = 1st quartile + 1.5 IQR) and upper outer fence (UOF = 1st quartile + 3 IQR). Mild anomalous concentrations are those found between LIF and LOF as well as those between UIF and UOF, while extreme “far” anomalies are concentrations lower than LOF or higher than UOF. The latter are unusually high concentrations, generally related to anthropogenic activities such as tailing piles, fertilizers, pesticide application, disposal of sewage and irrigation drain returns. Spatial distribution is obtained by plotting these concentrations in a map, utilizing ArcMap or another suitable mapping program. The conventional procedure for the spatial representation of these anomalies is small dots for non-anomalous (background) concentrations, small crosses for mild anomalies and large crosses for extreme anomalies.

3 RESULTS

Correlation analysis of selected elements (those known to be significant for this area and those commonly associated with As) produced the coefficients shown in Table 1. Elements most closely associated with As were Al, Fe and Cu, from which Fe and Cu were selected for this analysis. The boxplot calculations were conducted and the results are included in Table 2.

The anomalies of As and associated metals, Fe and Cu, were plotted individually using ArcMap GIS software. Figure 2 shows the map obtained for As. By visually superimposing anomalies for all three elements, a pattern emerges in which anomalies of all three element cluster around and directly downstream of known mineral sulfide deposits, e.g., San Antonio mine, a producing Ag, Pb and Zn. Around some minor sulfide deposits, anomalies of both Cu and As are observed, while anomalies of Fe and As pair around and directly downstream oxide mineral deposits.

![Figure 1](image)

Figure 1. The study area (shaded) corresponds to four 1° x 2° quadrangles within the state of Chihuahua, Mexico.

![Table 1](image)

### Table 1. Correlation coefficients for elements presumably associated with As (N = 2046). Coefficients > 0.3 are shown in bold for visualization purposes.

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
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<th>Ca</th>
<th>Cu</th>
<th>Fe</th>
<th>Sr</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>1</td>
<td>-0.173</td>
<td>0.144</td>
<td>0.384</td>
<td>-0.011**</td>
<td>0.108</td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>1.00</td>
<td>-0.231</td>
<td>0.303</td>
<td>0.441</td>
<td>-0.082</td>
<td>0.123</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>1.00</td>
<td>-0.145</td>
<td>-0.045*</td>
<td>0.106</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>1.00</td>
<td>-0.140</td>
<td>0.228</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>1.00</td>
<td>-0.140</td>
<td>0.228</td>
<td></td>
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<td></td>
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<td>Sr</td>
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<td>-0.110</td>
<td></td>
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<td></td>
<td></td>
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</table>

Note: The level of significance is shown by asterisks. No asterisk = significant at 99% confidence interval; * = significant at 95% confidence interval but not significant at 99%; ** = not significant at 95% confidence interval.

![Table 2](image)

### Table 2. Thresholds and number of anomalies for sediment data (N=2046). Concentrations are in ppm unless otherwise noted. All numbers of anomalies correspond to the upper fences.

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<tr>
<td>IQR</td>
<td>1.16</td>
<td>3.34</td>
<td>5.73</td>
<td>13.7</td>
<td>1.17</td>
<td>155</td>
<td>33.5</td>
</tr>
<tr>
<td>LIF</td>
<td>-0.23</td>
<td>-0.60</td>
<td>-8.03</td>
<td>-12.6</td>
<td>0.105</td>
<td>-180</td>
<td>3.53</td>
</tr>
<tr>
<td>LOF</td>
<td>-1.97</td>
<td>-5.63</td>
<td>-16.6</td>
<td>-33.2</td>
<td>-1.65</td>
<td>-413</td>
<td>-46.7</td>
</tr>
<tr>
<td>UIF</td>
<td>3.25</td>
<td>9.40</td>
<td>9.17</td>
<td>28.6</td>
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<td>UOF</td>
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<td>14.4</td>
<td>17.8</td>
<td>49.2</td>
<td>5.37</td>
<td>519</td>
<td>154</td>
</tr>
<tr>
<td>Mild anomalies</td>
<td>271</td>
<td>188</td>
<td>314</td>
<td>256</td>
<td>204</td>
<td>181</td>
<td>199</td>
</tr>
<tr>
<td>Extreme anomalies</td>
<td>11</td>
<td>92</td>
<td>7</td>
<td>125</td>
<td>33</td>
<td>88</td>
<td>41</td>
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Besides geochemistry, the data set (SGM, 2001) contains several superimposed GIS layers. Among them is a geologic map, which is convenient to identify the rock that outcrops directly above each
anomaly. Using this simple method on each of the 92 extreme As anomalies, the following rock types were recorded: tuff flow ignimbrites (47 anomalies), polymictic conglomerates of ignimbrite lithic fragments (21), rhyolite (6), rhyolitic tuff (5), ignimbrite (5), trachytic ignimbrite (2), andesite (2), trachyte (2) and sandstone-shale (2). This count supports previous assertions that the origin of the As is related to the presence of Tertiary volcanic rocks (ignimbrite, rhyolite), although it does not pinpoint any particular rock member, conditions leading to As enrichment, or concentration processes.

Interestingly, there are six clusters of As anomalies where no Fe or Cu anomalies are present (Figure 2). One of them, with As content up to 25 and 33 mg/kg in river and reservoir sediments respectively, extends along the Rio Conchos. The As presence may be explained by fertilizers and pesticides used in agriculture and/or sewage discharged to the river (Gutiérrez et al., 2009). The other five clusters are composed of mild anomalies and seem to have originated near As-rich rocks (sulfide mineral deposits nearby), whose weathered particles were transported by runoff and concentrated by evaporation.

3.1 Discussion

A statistical and exploratory analysis of sediment geochemical data was useful in determining the boundary between background and anomalous As concentrations, and in identifying the amount, concentration and distribution of two types of anomalies: mild anomalies which are related to enriched natural concentrations, and extreme anomalies which relate to the presence of mine tailings and/or anthropogenic contaminants. The thresholds for mild and extreme anomalies for this area were 9.40 and 14.4 mg/kg respectively. The association of As with other metals, obtained by correlation analysis, identified the main sources of As with either sulfide or oxide mineral deposits. Extreme As anomalies were associated with Tertiary volcanic rocks (rhyolites, ignimbrites). Clusters of As anomalies not associated with either Fe or Cu were identified as result from either natural or anthropogenic contamination based on their distribution towards the center of drainage basins, suggesting runoff transported As-rich particles.

4 REFERENCES


Chiprés JA, de la Calleja A, Tellez JI, Jimenez F, Guerrero EG, Castro J, Monroy MG Salinas JC, 2009b. Geochemistry of soils along a transect from Central Mexico to the Pacific
Coast: A pilot study for continental-scale geochemical mapping. Applied Geochemistry, 24, 1416-1428.
Arsenic anomalies of an arid region determined from sediment geochemistry

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Ma. T. Alarcón Herrera  
Environment and Energy Dept., Advanced Materials, Research Center, (CIMAV) Chihuahua, Mexico

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Mild anomalies

| Extreme anomalies |
|-------------------|--------|---|--------|---|---|---|
| 271 | 188 | 314 | 256 | 204 | 181 | 199 |

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The Water Rock Interaction Working Group of the International Association of Geochemistry and Cosmochemistry.

Otorga la presente

CONSTANCIA

a:

Ma. Teresa Alarcón Herrera

Por su participación en el XIII congreso de Water Rock Interaction, celebrado en la ciudad de Guanajuato, 16-20 de agosto del 2010.

Thomas Kretzschmar
General Secretary WRI13

Halldór Armannsson
Chairman WRI Working Group

Russell Harmon
President IAGC