Arsenic anomalies of an arid region determined from sediment geochemistry

M. Gutierrez
Geography, Geology and Planning, Missouri State University, Springfield MO, USA 65897

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

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.

1 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 Km^2 (Fig. 1). Exploratory data analysis (EDA) was applied to the resulting dataset (N= 2046) in order to identify areas with arsenic (As) anomalies and their possible source.

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 Rio Conchos basin, and a small portion of the Rio 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).

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.

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

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.

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

	Al	As	Ca	Cu	Fe	Sr	Zn
Al	1	**0.415**	-0.173	0.144	**0.384**	-0.011**	0.108
As		1.00	-0.231	**0.303**	**0.441**	-0.082	0.123
Ca			1.00	-0.145	**-0.368**	**0.674**	-0.103
Cu				1.00	**0.478**	-0.045*	0.106
Fe					1.00	-0.140	0.228
Sr						1.00	-0.110

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. 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.

	Al	As	Ca %	Cu	Fe %	Sr	Zn
Median	2	5.84	1.82	12.6	2.39	111	68.8
IQR	1.16	3.34	5.73	13.7	1.17	155	33.5
LIF	-0.23	-0.60	-8.03	-12.6	0.105	-180	3.53
LOF	-1.97	-5.63	-16.6	-33.2	-1.65	-413	-46.7
UIF	3.25	9.40	9.17	28.6	3.61	286	104
UOF	4.99	14.4	17.8	49.2	5.37	519	154
Mild anomalies	271	188	314	256	204	181	199
Extreme anomalies	11	92	7	125	33	88	41

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.

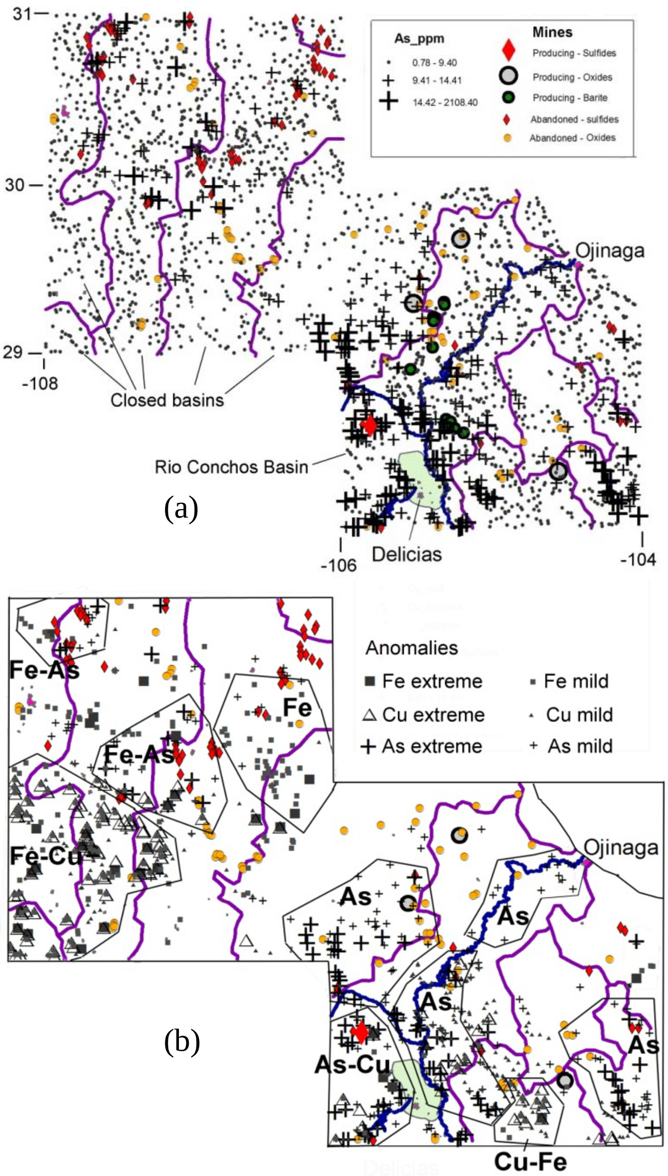

Figure 2. (a)Spatial distribution of As anomalies. Non-anomalous concentrations are depicted by points, mild anomalies with small crosses and extreme anomalies with large crosses. Mines are shown with yellow (oxide) and green (barite) circles. Large red diamonds correspond to operating mines while small diamonds are abandoned mines or prospects. Lines indicate division between basins. Eight of the ten basins shown are closed basins. (b) Fe and Cu anomalies.

4 REFERENCES

Carranza EJM, 2009. Exploratory analysis of geochemical anomalies; in Geochemical Anomaly and Mineral Prospectivity Mapping in GIS. Handbook of Exploration and Environmental Geochemistry, Vol 11 (M Hale, Editor) Elsevier BV.

Chiprés JA, Castro-Larragoitia J, Monroy MG, 2009a. Exploratory and spatial data analysis (EDA-SDA) for determining regional background levels and anomalies of potentially toxic elements in soils from Catorce-Matehuala, Mexico. Applied Geochemistry, 24, 1579-1589.

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.
Gutiérrez M, Alarcon-Herrera MT, Camacho L, 2009. Geographical distribution of arsenic in sediments within the Rio Conchos Basin, Mexico. Environmental Geology, 57, 929-935.
Gutiérrez M, Carreón E, 2008. Contenido de As, Ba, y Cu en sedimento y su asociación con depósitos minerales en el noreste de Chihuahua. Tecnociencia Chihuahua, 2, 108-117.
Ortega-Guerrero MA, 2009. Presencia, distribución, hidrogeoquimica y origen de arsénico, fluoruro y otros elementos traza disueltos en agua subterránea, a escala de cuenca hidrológica tributaria de Lerma-Chapala, México. Revista Mexicana de Ciencias Geológicas, 26, 143-161.
Razo I, Carrizales L, Castro J, Diaz-Barriga F, Moonroy M, 2004. Arsenic and heavy metal pollution of soil, water and sediments in a semi-arid climate mining area in Mexico. Water, Air and Soil Pollution, 152, 129-152.
Robertson J, Megaw P, 2009. Cinco de Mayo: A new silver, lead and zinc discovery in northern Mexico. The Leading Edge, June 2009, 730-735
Reimann C, Filzmoser P, Garrett RG, 2005. Background and threshold: critical comparison of methods of determination. Science of the Total Environment, 346, 1-16.
Smith DB, 2009. Geochemical studies of North American soils: Results from the pilot study phase of the North American Soil Geochemical Landscapes Project. Applied Geochemistry, 24, 1355-1356.
Zhang C, Selinus O, 1998. Statistics and GIS in environmental geochemistry - some problems and solutions. J of Geochemical Exploration, 64, 339-354.

Arsenic anomalies of an arid region determined from sediment geochemistry

M. Gutierrez
Geography, Geology and Planning, Missouri State University, Springfield MO, USA 65897

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

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.

1 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 Km^2 (Fig. 1). Exploratory data analysis (EDA) was applied to the resulting dataset (N= 2046) in order to identify areas with arsenic (As) anomalies and their possible source.
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 Rio Conchos basin, and a small portion of the Rio 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).

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.

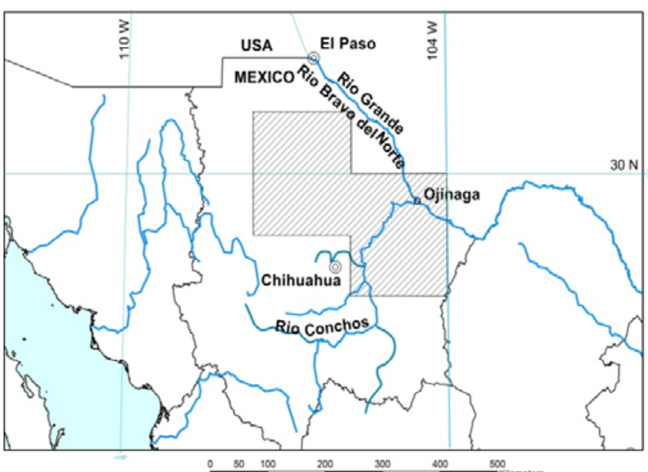

Figure 1. The study area (shaded) corresponds to four 1° x 2° quadrangles within the state of Chihuahua, Mexico.

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.

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

	Al	As	Ca	Cu	Fe	Sr	Zn
Al	1	**0.415**	-0.173	0.144	**0.384**	-0.011**	0.108
As		1.00	-0.231	**0.303**	**0.441**	-0.082	0.123
Ca			1.00	-0.145	**-0.368**	**0.674**	-0.103
Cu				1.00	**0.478**	-0.045*	0.106
Fe					1.00	-0.140	0.228
Sr						1.00	-0.110

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. 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.

	Al	As	Ca %	Cu	Fe %	Sr	Zn
Median	2	5.84	1.82	12.6	2.39	111	68.8
IQR	1.16	3.34	5.73	13.7	1.17	155	33.5
LIF	-0.23	-0.60	-8.03	-12.6	0.105	-180	3.53
LOF	-1.97	-5.63	-16.6	-33.2	-1.65	-413	-46.7
UIF	3.25	9.40	9.17	28.6	3.61	286	104
UOF	4.99	14.4	17.8	49.2	5.37	519	154
Mild anomalies	271	188	314	256	204	181	199
Extreme anomalies	11	92	7	125	33	88	41

Besides geochemistry, the data set (SGM, 2001) contains several superimposed GIS layers. Among them is a geologic map, which is convenient to idenanomaly. 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.

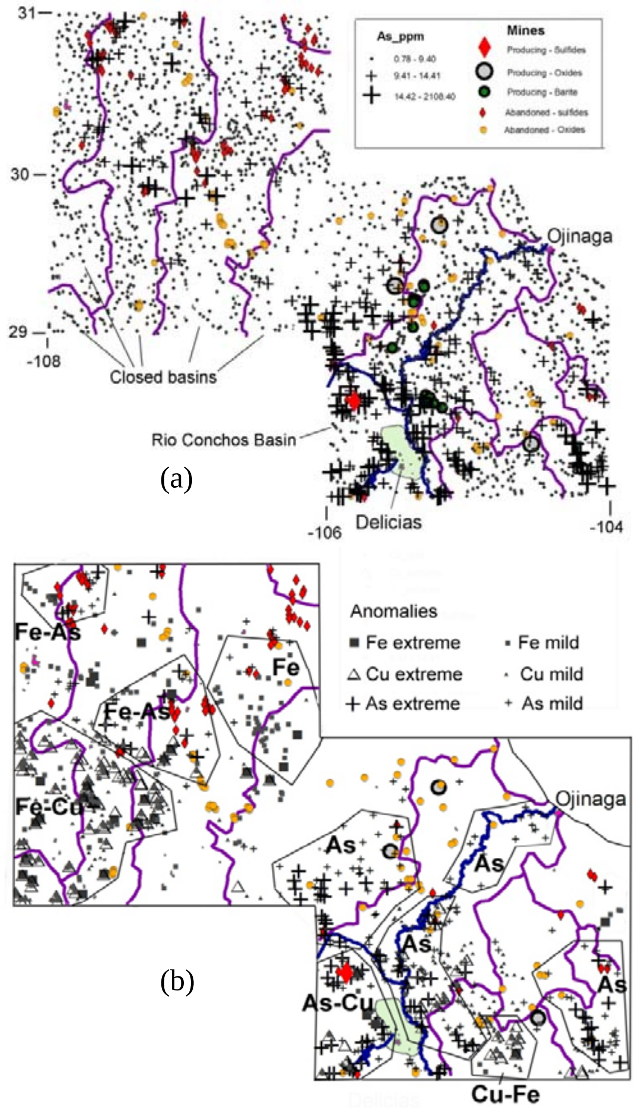

Figure 2. (a)Spatial distribution of As anomalies. Non-anomalous concentrations are depicted by points, mild anomalies with small crosses and extreme anomalies with large crosses. Mines are shown with yellow (oxide) and green (barite) circles. Large red diamonds correspond to operating mines while small diamonds are abandoned mines or prospects. Lines indicate division between basins. Eight of the ten basins shown are closed basins. (b) Fe and Cu anomalies.

4 REFERENCES

Carranza EJM, 2009. Exploratory analysis of geochemical anomalies; in Geochemical Anomaly and Mineral Prospectivity Mapping in GIS. Handbook of Exploration and Environmental Geochemistry, Vol 11 (M Hale, Editor) Elsevier BV.

Chiprés JA, Castro-Larragoitia J, Monroy MG, 2009a. Exploratory and spatial data analysis (EDA-SDA) for determining regional background levels and anomalies of potentially toxic elements in soils from Catorce-Matehuala, Mexico. Applied Geochemistry, 24, 1579-1589.

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.
Gutiérrez M, Alarcon-Herrera MT, Camacho L, 2009. Geographical distribution of arsenic in sediments within the Rio Conchos Basin, Mexico. Environmental Geology, 57, 929-935.
Gutiérrez M, Carreón E, 2008. Contenido de As, Ba, y Cu en sedimento y su asociación con depósitos minerales en el noreste de Chihuahua. Tecnociencia Chihuahua, 2, 108-117.
Ortega-Guerrero MA, 2009. Presencia, distribución, hidrogeoquimica y origen de arsénico, fluoruro y otros elementos traza disueltos en agua subterránea, a escala de cuenca hidrológica tributaria de Lerma-Chapala, México. Revista Mexicana de Ciencias Geológicas, 26, 143-161.
Razo I, Carrizales L, Castro J, Diaz-Barriga F, Moonroy M, 2004. Arsenic and heavy metal pollution of soil, water and sediments in a semi-arid climate mining area in Mexico. Water, Air and Soil Pollution, 152, 129-152.
Robertson J, Megaw P, 2009. Cinco de Mayo: A new silver, lead and zinc discovery in northern Mexico. The Leading Edge, June 2009, 730-735
Reimann C, Filzmoser P, Garrett RG, 2005. Background and threshold: critical comparison of methods of determination. Science of the Total Environment, 346, 1-16.
Smith DB, 2009. Geochemical studies of North American soils: Results from the pilot study phase of the North American Soil Geochemical Landscapes Project. Applied Geochemistry, 24, 1355-1356.
Zhang C, Selinus O, 1998. Statistics and GIS in environmental geochemistry - some problems and solutions. J of Geochemical Exploration, 64, 339-354.

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

MÉXICO 2010