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COMPARATIVE ANALYSIS FOR POLLUTED AGRICULTURAL SOILS WITH ARSENIC, LEAD AND MERCURY IN MEXICO

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BACKGROUND

The use of mercury in Mexico has been mainly associated with the ancient mining activity in the Country. The mining industry in Zacatecas, a state whose productive activities were characterized by gold and silver mining during the Colonial times, used a lot of mercury in the mineral extraction processes, giving as a side result that residual mercury was deposited in the tailing ditches, or even in the large plain zones of the Zacatecan valley, a fact that gives a potential health and environmental risk due to its persistence, toxicity and bio-accumulative behavior.

INTRODUCTION

The Commission for Environmental Cooperation of North America (CEC), as part of its North American Regional Action Plan (NARAP) for mercury, instrumented a regional study to evaluate mercury contamination in the mining zone of the state of Zacatecas-Mexico in coordination with the National Institute of Ecology of Mexico in order to make a heavy metal comparative analysis of polluted soil samples to enforce the analytical capabilities in Mexico. The study involved a Canadian private laboratory and the

laboratory of the Environmental Management Unit of the National Autonomous University of Mexico (UNAM).

The site for this study was located in the flooding zone of the Valley of Zacatecas, which comprises from San Joaquin to Tacoaleche (from south to north) and from Guadalupe to the mountains of Veta Grande and Zacatecas (from west to east) and covers an area of 600 km^2 approximately. (Figure 1).

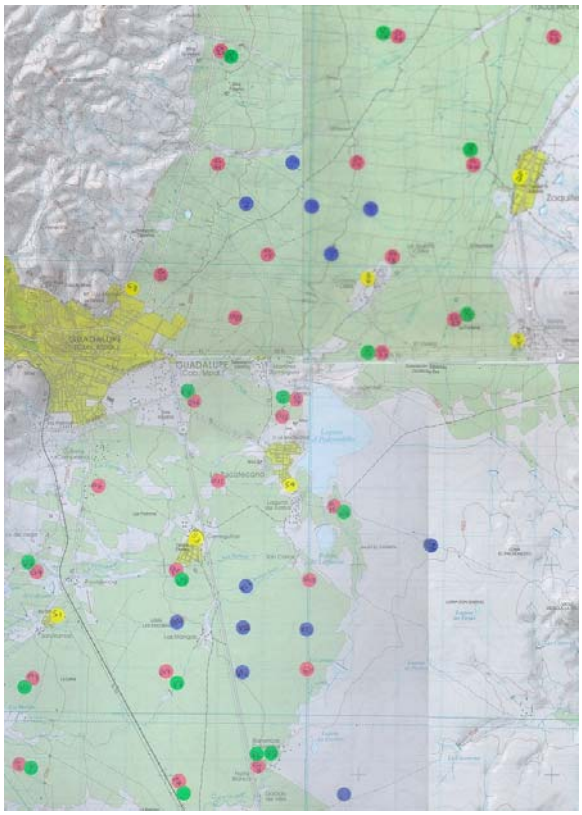

Figure 1. Sampling of contaminated agricultural soil in Guadalupe, Zacatecas

The polluted soil sample analysis included quantification of arsenic, lead and total mercury. These heavy metals represent the highest risk for the communities nearby and most of the metal content in the soil of the Zacatecan region.

OBJECTIVE

The main goal of this work is to identify the contamination in agricultural soils polluted with tailings from the mining activity in the state of Zacatecas, Mexico, as part of the NARAP for mercury of the Commission of Environmental Cooperation of North America as well as to improve the analytical capabilities through comparative analysis between laboratories.

METHODOLOGY

The experimental part of the project comprises the following stages:

Soil sampling

Because of the fact that there are few analytical studies in the zone for supporting the sampling program, it was proposed a sampling screen of 2 × 3 km from San Jerónimo, in the south, until Tacoaleche, in the north, covering a distance of 20 km approximately. In the west-east direction the grid goes from the Veta Grande and Zacatecas mountains. 20 sampling sites were selected in the grid and were identified sequentially as G-1 to G-20.

One of the main goals of this research was to identify the surface pollution profile in terms of atmospheric re-emission and local deterioration because of air transported dust. For this, the 20 soil samples were taken at a 0-15 cm depth.

The sampling activities consisted of the following:

1. A topographic map was used to navigate as close as possible to all sampling sites previously identified in the grid pattern shown in Figure 1;
2. Sampling preference was given to areas under active agricultural cultivation;
3. In cases where cultivated fields were not located in the vicinity of the sampling site, the area showing the least amount of visual disturbance was selected for sample collection;
4. A GPS instrument was used to record longitude and latitude coordinates in degrees, minutes and seconds of the site as well as height in meters above sea level;
5. A 15 cm depth hole was excavated for sampling;
6. A stainless steel hand trowel was used to remove any soil that may have come in contact with the pick or shovel and to prepare a vertical side-wall for sampling;
7. Sections of soil from the 0-15 cm depth from each hole were placed in a stainless steel bowl and gently dis-aggregated to ensure that a representative sample was collected from the sampling point;
8. Soil from the stainless steel bowl was placed directly into pre-labeled 500 mL PET bottles and securely capped and labeled;
9. On completion of sampling, all sampling equipment was thoroughly scrubbed with bottled water and sprayed with methanol to remove any particles that may have escaped the water cleaning process;
10. At the end of each day, the sample containers were double wrapped and sealed in new plastic bags and additional ice was added for transport to analysis;

Sampling data (localization, soil description, site characteristics and use of the land) is shown in Table 1.

Table 1. Description of sampling sites and sort of soil samples for analysis in Zacatecas

Site	Latitude, longitude & altitude	Soil Description	Site Description
G-1	N22-42-36.96, W102-31-21.24, A.S.E. 2268.7m	Brown, humid, mud, gravel	Farmed field 2002 beans
G-2	N22-43-32.96, W102-30-49.06 A.S.E. 2257.8m	Brown, dry, mud, gravel	Undergrowth
G-3	N22-44-26.15, W102-29-36.04 A.S.E. 2237m	Reddish, hydrated, mud	Farmed field 2002 corn
G-4	N22-43-07.01, W102-29-59.79 A.S.E. 2235.8m	Reddish, dry, mud, sand	Farmed field 2002 corn
G-5	N22-43-38.74, W102-29-29.58 A.S.E. 2219.5m	Dry, mud Brown stony, rock at 15 cm	Undergrowth (virgin area)
G-6	N22-42-51.62, W102-28-10.16 A.S.E. 2201.9m	Humid, gray mud, some clay	Farmed field 2002 corn
G-7	N22-42-13.40, W102-27-46.98 A.S.E. 2215.6m	Brown Reddish, mud	Farmed field 2002 beans
G-8	N22-44-36.94, W102-28-18.04 A.S.E. 2194.0m	Brown dark, dry, little clay	Farmed field 2002 corn
G-9	N22-44-14.22, W102-28-27.84 A.S.E. 2190.3m	Brown dark, humid, clayish	Field ready for farming
G-10	N22-44-47.27, W102-25-23.13 A.S.E. 2184.6m	Brown Reddish, dry, mud, some gravel	Farmed field 2002 beans
G-11	N22-44-40.92, W102-26-58.50 A.S.E. 2185.6m	Brown Reddish, stony	Farmed field 2002 beans
G-12	N22-46-03.28, W102-27-27.20 A.S.E. 2175.3m	Brown Reddish, dry, mud, some clay, thick	Farmed field 2002 beans
G-13	N22-46-16.05, W102-28-32.97 A.S.E. 2213.4m	Brown Reddish, dry, mud, some clay	Farmed field 2002 beans
G-14	N22-46-03.86, W102-29-53.47 A.S.E. 2253.45m	Brown, mud, some clay, thick	Grass & Undergrowth
G-15	N22-47-19.60, W102-29-15.85 A.S.E. 2252.24m	Brown Reddish, mud, thick	Farmed field 2002 beans
G-16	N22-47-24.72, W102-25-58.56 A.S.E. 2154.9m	Brown Reddish dark, humid, mud, some clay	Farmed field 2002 corn

Site	Latitude, longitude & altitude	Soil Description	Site Description
G-17	N22-47-22.45, W102-27-37.41 A.S.E. 2197.4m	Brown Reddish, dry, mud, little gravel	Farmed field 2002 beans
G-18	N22-45-42.13, W102-26-05.33 A.S.E. 2159.95m	Brown, humus, mud organic	Farmed field 2002 corn
G-19	N22-45-06.43, W102-27-09.86 A.S.E. 2174.6m	Brown dark, dry, humus, mud, some clay	Farmed field 2002 oats
G-20	N22-46-16.05, W102-28-32.97 A.S.E. 2213.4m	Brown Reddish, dry, mud, some clay	Farmed field 2002 beans

Quantitative Analysis

The analytical methodology used in this project by both the Canadian and the UNAM laboratories was:

- Arsenic and lead – EPA SW 846: 3050B/6010B
- Total mercury – EPA SW 846: 7471A

Soil samples were dried on air for 48 hours or more if necessary. Samples were crushed in a mortar and then passed through a 2 mm mesh.

RESULTS

Analytical results for both the Canadian and the UNAM laboratories are shown in Table 2:

Table 2. Comparative analysis for arsenic, lead and mercury in soil samples collected in Zacatecas

Sample	Arsenic		Mercury		Lead	
	UNAM (ppm)	CANADA (ppm)	UNAM (ppm)	CANADA (ppm)	UNAM (ppm)	CANADA (ppm)
G-1 (0-15)	9.82	9.50	0.25	0.12	17.29	11.00
G-2 (0-15)	8.64	7.60	0.70	0.24	22.51	15.00
G-3 (0-15)	12.21	9.40	0.76	0.99	27.00	38.00
G-4 (0-15)	9.28	3.60	0.25	0.18	17.35	12.00
G-5 (0-15)	11.00	4.60	0.31	0.34	22.14	19.00
G-6 (0-15)	8.62	7.90	0.86	0.40	18.41	18.00
G-7 (0-15)	7.00	3.00	0.59	0.09	14.04	10.00
G-8 (0-15)	182.41	89.00	36.41	32.00	511.97	620.00
G-9 (0-15)	107.65	87.00	32.11	52.00	432.90	650.00
G-10 (0-15)	10.49	5.40	0.20	0.15	15.58	13.00

Sample	Arsenic		Mercury		Lead	
	UNAM (ppm)	CANADA (ppm)	UNAM (ppm)	CANADA (ppm)	UNAM (ppm)	CANADA (ppm)
G-11 (0-15)	17.08	13.00	3.41	3.50	51.17	53.00
G-12 (0-15)	11.22	6.20	0.64	0.00	23.78	29.00
G-13 (0-15)	12.25	5.50	0.49	0.48	29.44	26.00
G-14 (0-15)	7.24	5.60	0.54	0.52	21.77	26.00
G-15 (0-15)	23.26	8.30	0.74	0.83	36.72	33.00
G-16 (0-15)	23.03	5.60	0.75	0.65	21.61	21.00
G-17 (0-15)	7.79	6.70	0.86	0.78	38.94	31.00
G-18 (0-15)	80.32	68.00	198.35	290.00	868.13	1300.00
G-19 (0-15)	120.73	54.00	90.78	110.00	586.23	720.00
G-20 (0-15)	8.97	7.00	1.77	0.61	34.59	30.00

** Results shown are an average for three sample analysis at each site*

RESULT ANALYSIS

According to the soil analysis from both laboratories, samples G-8, G-9, G-18 and G-19 have the highest concentration for the three metals analyzed. These samples are close to the communities of Santa Teresa, La Zacatecana, la Purísima and El Vivero respectively. These sites are used for corn, beans and oat farming, which are part of the basic diet of the local population.

It is important to say that it is necessary for a further speciation of the heavy metals in order to find if the metals could be bio-available and as a consequence could have potential for human and environmental risk.

The soil analysis for the three metals was consistent in both laboratories. And the difference shown could be attributed to the management of the samples or differences in the equipment resolution.

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