Soil pollution related to mercury-mining activities in the proximity of Usagre (Badajoz, SW Spain)

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Usagre (Badajoz, SW Spain) mercury mine was active for an undetermined time until its closure in 1971. The ore exploited in this mine was cinnabar (red HgS), and metallurgy was also performed locally by means of primitive furnaces of the Bustamante type. Since the closure of the mine, reclamation measures have not been carried out at the site, and actual passives include a mine shaft, an accessible descending gallery and a mine dump adjacent to the descending gallery. In the work described here, data from two soil geochemistry surveys were combined and analysed. The surveys were separated by a period of 32 years. Measurements of total gaseous mercury (TGM) in the underground mine and its surroundings were also considered. The soil geochemistry included mercury, lead, zinc and copper. The results indicate that soil pollution is mostly related to the trace mineralisations on the surface and they can therefore be interpreted as natural geochemical anomalies. TGM concentrations are extremely high inside the mine but are of very low concern outside the mine.

Keywords: mercury mining; atmospheric mercury; soils; kriging; soil-plant transfer

1. Introduction

Usagre is a small community in the Badajoz Province (Extremadura region, SW Spain) (Figure 1(A)). From a geological point of view, Usagre is located in the Hesperian Iberian Massif, specifically in the so-called Ossa-Morena Zone (Figure 1(A)) [1–5]. Despite its relative proximity to the giant Almadén Hg deposit (some 125 km to the ESE), the Usagre mercury mine is located in a very different geological context, being hosted by Cambrian carbonate rocks of this zone, whereas Almadén is hosted in Ordovician-Silurian quartzitic rocks of the Central Iberian Zone [6,7]. These Cambrian carbonate formations are common hosts of barite ($BaSO_4$) mineral deposits, which contain variable amounts of sulphides such as pyrite (FeS_2), galena (PbS), sphalerite (ZnS), chalcopyrite ($FeCuS_2$) and cinnabar; these mineralisations are similar in some aspects to the case studied by Subías et al. [8].

The mercury mine is located some 2 km to the west of Usagre (coordinates for the Sultana shaft in UTM WGS84 29S: N4249131; E745914), and the date when activity began is unknown (possibly from the mid-nineteenth Century). The mine closed in 1971, when most of the Hg mines worldwide were shut down due to the fall in Hg prices caused by environmental concerns arising from the Minamata poisoning incident
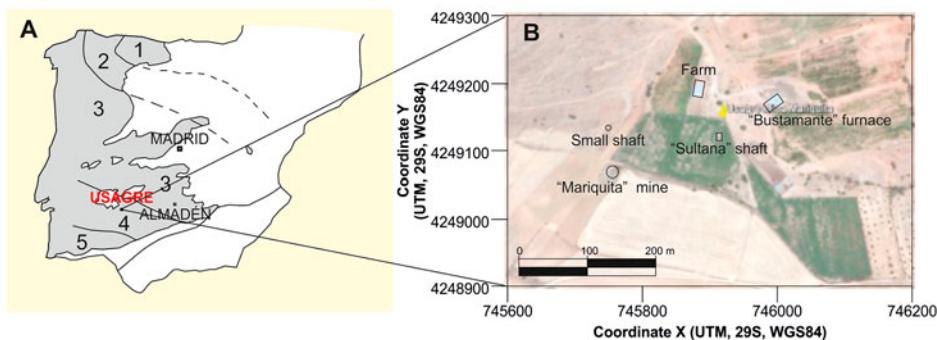
Figure 1. (A) Location of Usagre with respect to Almadén, both hosted by rocks of the Hesperian Iberian Massif (grey shaded area). (1) Cantabrian zone; (2) Asturoccidental-Leonese zone; (3) Central Iberian zone; (4) Ossa-Morena zone; (5) Southern Portuguese zone. (B) Main locations of Usagre mine.

with methylmercury [9] and a different type of poisoning caused by mercury compounds in Iraq [10].

The mine area is now abandoned, with some passives remaining as sources of pollution: in particular, the Sultana shaft is open and is operated by the land owner for irrigation purposes, and the Mariquita descending gallery is easily accessible and houses a 'sterile rock' dump with a volume of some 1000 m^3. Remediation works has not been carried out at this site. A metallurgical installation, which contains two furnaces of the 'aludeles' or 'Bustamante' type [11,12], is also present at the mining site. A schematic representation of the area is shown in Figure 1(B), and this indicates the location of the mine passives discussed above. A cross section of the area and the plant of the Mariquita mine are shown in Figure 2, based on Hernandez [13]. A previous publication by García-Sánchez et al. also concerned mercury contents in five soil samples from the area, including total, elemental and exchangeable Hg, as well as Hg contents in several local wild plant species [14]. These authors also described the local climate as being typically semicontinental Mediterranean, with wet and cold winters and dry and warm summers. The annual total precipitation is between 500 and 700 mm. Land use in the surroundings of the mine area includes agriculture (alfalfa grown besides the Sultana shaft and irrigated with water from the mine shaft) and sheep farming (a small flock is kept by local residents on wild pastures and the annually cultivated alfalfa fields).

In the work described here, we reviewed data from two soil geochemical surveys carried out in the area in question: the first survey was carried out in 1987 for mining exploration reasons and the second survey was carried out during the period December 2011–March 2012 as part of a study carried out for the Junta de Extremadura regional government with the aim of assessing local risks related to the presence of this Hg pollution source [15,16]. Data are also presented from an atmospheric mercury survey aimed at characterising total gaseous mercury (TGM) concentrations in the area. This latter survey was carried out during the second soil survey sampling.

2. Methodology

2.1. *Soils surveys*

Soil samples from the first survey (1987) were taken from the C horizon of the local soils (10–25 cm depth), in a regular grid, and included 861 samples. The samples were
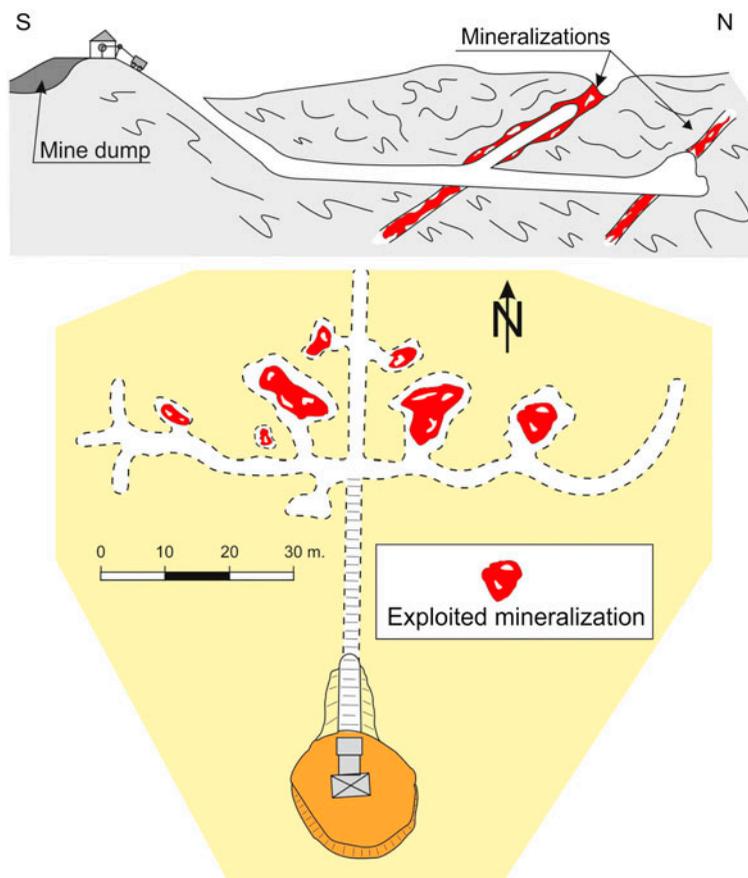
Figure 2.   Cross section and plant of the Mariquita mine.

analysed by atomic absorption spectrometry at the laboratories of the mining company 'Minas de Almadén y Arrayanes S.A.' (MAYASA), then owner of the mining rights for the area. The survey was carried out under the supervision of the first author of this paper (PH), who was then a project geologist at the aforementioned mining company [17]. Analyses included determinations of Hg as well as Pb, Zn and Cu, since the area was a prospective site for the presence of these elements. The detection limit for Hg in these samples was 1 mg kg^{-1} (ppm), and 53.5% of samples were below this detection limit; in order to obtain the maximum amount of information from these results, we assigned a value of 0.5 mg kg^{-1} to these samples for statistical calculations. Analytical quality control was carried out by analysis of 10% of the samples, which were duplicated and numbered differently before being sent to the laboratory for analysis.

The second survey was carried out during the period December 2011–March 2012, and it included 26 samples, also from the C horizon of the soil (10–25 cm depth, taken with a peak and spade). Sample preparation included drying at room temperature, sieving to remove the fraction >2 mm, and splitting and milling in an agate mortar to a grain size of <100 μm. Aliquots of these samples were analysed by Zeeman effect atomic absorption spectrometry using a LUMEX RA-915+ device in conjunction with

the RP-91C attachment for pyrolysis and also for multielements, using a portable Oxford X-MET 3000 TX XRF analyser; this technique has proven to be very effective and is sufficiently reliable for geochemical surveys for numerous heavy metals [18–23]. Quality control included the analysis of duplicate samples to check the precision with certified reference materials (NIST 2710 and NIST 2711) to achieve accuracy for both techniques (in %): Hg (98.6), Pb (89.8), Zn (99.9) and Cu (96.7). Pedological parameters for these samples were also measured (<2 mm fraction): pH was determined using a CRISON GLP-22 pH metre, and conductivity was measured using a CRISON GPL-32 conductivimeter. Samples were suspended in ultrapure water with a solid/liquid ratio of 1:2.5 and were placed on a shaker bath at 95 rpm for 120 min. Measurements were made 30 min after this procedure was complete.

2.2.   *Atmospheric Hg survey*

A TGM survey was also carried out in 2012, in parallel to the second soil survey, and included roads and walking tracks in the area and its close surroundings. The survey was performed with a LUMEX RA-915M device, which analysed TGM continuously, with measurements taken every second and continuous GPS positioning obtained for each analytical data point using a Garmin GPSmap 60CSx device. The survey included both surface data and underground data since the Mariquita mine was accessible during the survey. Technical information about the analytical device used and the type of survey undertaken can be found in a number of previous papers published by this and other teams [24–32]. The measurement range was between 2 and 25,000 ng m^{-3}, and the precision and accuracy were appropriate for this type of survey.

Statistical treatment of the data was performed using MINITAB 15.0 software, and contour maps were created using SURFER 11 software.

3.   **Results and discussion**

3.1.   *Soils*

The main basic statistics for the soil surveys are shown in Table 1. All of the analysed elements were present at concentrations that are well above normal ones for non-contaminated areas [33]. The results of the second survey show concentrations that were on average higher than those found in the first survey. This discrepancy is probably due to the fact that samples from the second survey are more centred in the contaminated area.

The correlation matrix between the four elements analysed, for the 861 data points from the first survey and for the 26 samples from the second survey, is given in Table 2. The pairs Pb–Zn and Hg–Zn are the most significantly correlated in the first survey, while the only pair without a significant correlation in the second survey is Pb–Hg.

In order to analyse the results and separate background and anomalous values, a geostatistical approach (kriging) [34] was applied using the software SURFER 11. The first step involved obtaining the experimental semivariograms corresponding to the four heavy metals analysed in the first soil survey. Semivariograms are used to enter length scale, data repeatability and anisotropy into the kriging algorithm. In our case, the semivariograms were very similar for Hg, Pb and Zn. The semivariograms were well structured and correspond to the spherical model (Figure 3(A)–(C)) with a notable nugget effect (564.7; 24,100 and 7780 mg kg^{-1} for Hg, Pb and Zn, respectively) and

Table 1. Main statistics for the analysed data. N: number of determinations; AM: arithmetic mean; GM: geometric mean; SD: standard deviation; BL: background levels [33]. All values in mg kg^{-1}.

Element	N	AM	GM	SD	Range	BL
First survey (1987)						
Pb	861	179.01	139.07	185.35	20–3400	30
Zn	861	133.38	101.10	101.04	5–2400	66
Cu	861	47.97	37.75	50.45	10–761	22
Hg	861	4706	1.31	27,337	BDL–611	
Second survey (2011–2012)						
Pb	26	370.30	261.25	362.65	71–1552	30
Zn	26	205.30	172.08	134.82	67–620	66
Cu	26	58.37	44.63	45.99	8–179	22
Hg	26	41.05	4.91	86.31	0.2–311	

Table 2. Correlation matrix between the four elements analysed, for the 861 data from the first survey and 26 samples from the second survey. All significant correlations have $p < 0.001$.

	Pb	Zn	Cu
First survey (1987)			
Zn	0.760		
Pb	0.273	0.259	
Hg	0.503	0.728	0.317
Second survey (2011–2012)			
Zn	0.795		
Pb	0.807	0.866	
Hg	0.265	0.629	0.548

variable ranges were obtained (1030; 439,000 and 13,130 mg kg^{-1} for Hg, Pb and Zn, respectively) at similar distances (close to 500 m). However, the semivariogram for copper (Figure 3(D)) is completely different compared to those of the other elements, and it corresponds to a linear model. A spherical model, such as those obtained for Hg, Pb and Zn, implies that a correlation exists between values observed in the corresponding sampling points and that these decrease with distance. However, after a certain distance (length scale is in the order of 500 m from our experimental semivariograms), the correlation disappears.

Data from the first survey were also used to calculate reference levels (RL = GM + 2SD, where GM is the geometric mean and SD the standard deviation) for the analysed elements, according to the Spanish legislation on contaminated soils [35]. The calculated RLs correspond to 510, 300, 140 and 56 mg kg^{-1} for Pb, Zn, Cu and Hg, respectively. These values were used in conjunction with others employed to enhance the visual representation of the maps. The maps obtained are shown in Figure 4 and these correspond to GM, GM + SD and GM + 3SD. It can be seen from these maps that the orange colour engulfs the area that should be considered as contaminated soils according to the aforementioned Spanish legislation [35].
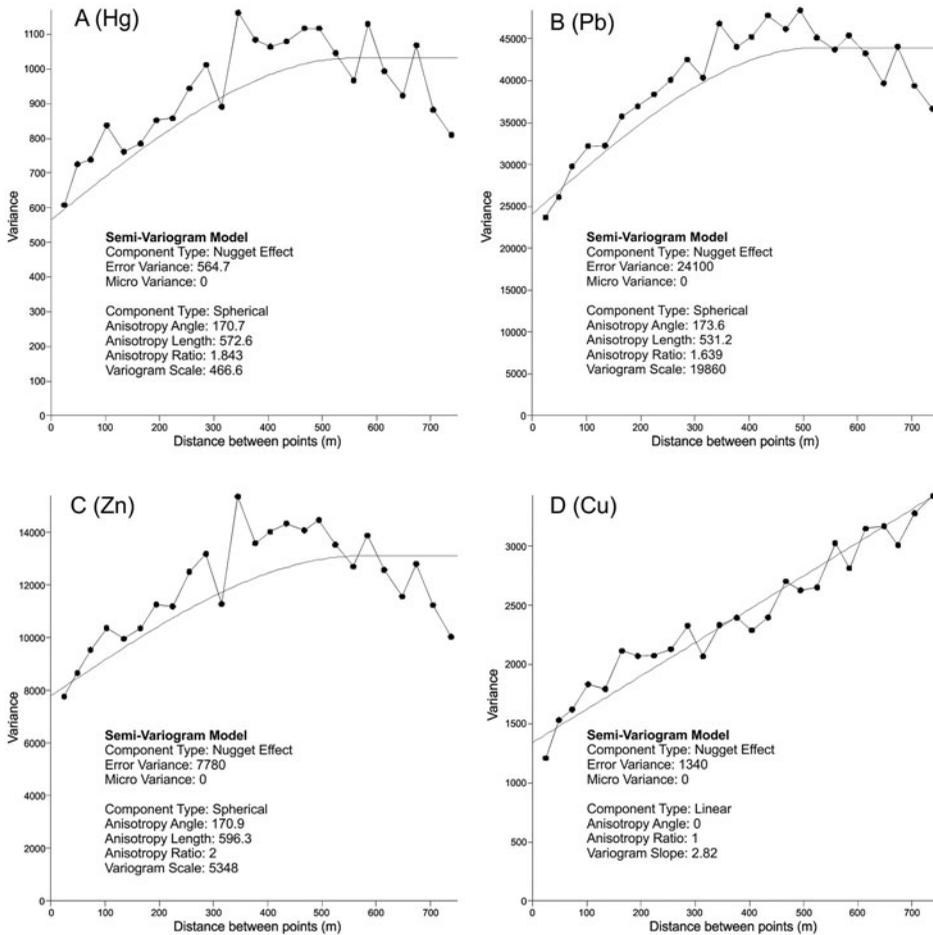
Figure 3.   Experimental variograms for Hg, Pb, Zn and Cu data and best fitting models.

The maps do not show a correspondence between the most polluted areas and the Hg mining subareas, but rather with the area in which the original geochemical anomaly caused by the exploited mineralisation should be, in particular for Hg, Pb and Zn (Figure 4(A)–(C)). The area polluted by Cu (Figure 4(D)) corresponds to an area located some 500 m to the north of the mining area and this possibly continues to the north away from the surveyed area; coincidentally, this anomalous Cu-polluted area also has relatively high Hg concentrations (Figure 4(A)), and the cause of these high values is unclear.

From a toxicological point of view, these values, which correspond to total contents of these elements, do not provide good toxicological indications of risk for the local population – including cattle and local biota. A previous study in this area [14] provided concentration data for total, elemental and exchangeable Hg, as well as for soil–plant transfer for different local species, including pastures. The values obtained by these authors are shown in Table 3, in which we have also included a calculation of the % of total Hg that represents the elemental mercury measured, the
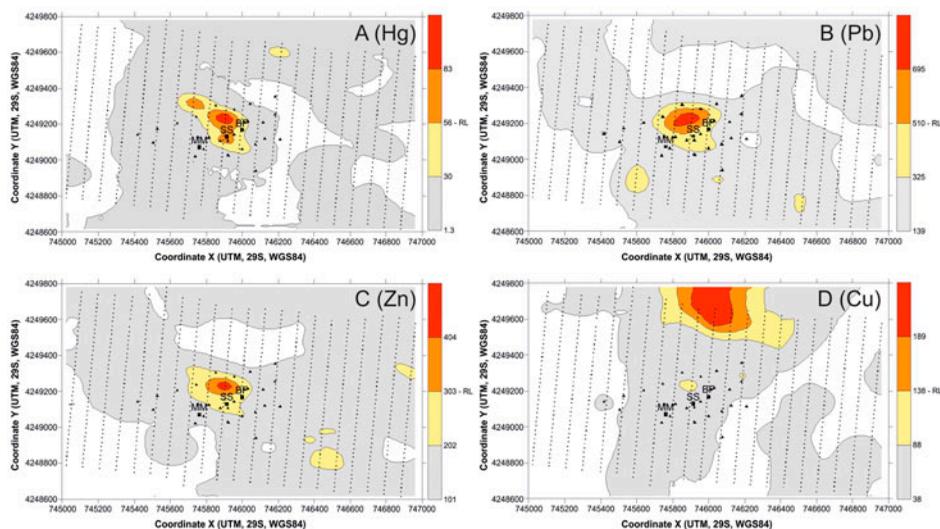
Figure 4. Contour maps of Hg, Pb, Zn and Cu concentration data in the studied area. MM: Mariquita mine; SS: Sultana shaft; BF: Bustamante furnaces.

‰ of total Hg that represents the exchangeable Hg measured and the average Hg contents in the analysed plant species for each of the five sampling sites. Correlations were also calculated between all of these parameters and the highest values were found between total mercury in the soil and calculated average Hg concentration in the plants ($r = 0.968$, $\rho = 0.007$); the equation that correlates the two values is: $HgP = 0.0152 HgT$, where HgP is the average Hg concentration in the plants analysed in each site and HgT is the total Hg content in the corresponding soils. This equation allowed the estimation of the average Hg contents expected in plants for the 1987 survey grid. These results were used to build the contour map shown in Figure 5, which corresponds to the calculated concentrations and uses the tolerable level [36] for agronomic crops as the main mapping level. In the map, the orange colour engulfs the areas where the calculated average concentration for plants surpasses this tolerable level. There are two such areas and they correspond to the surroundings of the mine area and to the northern Cu–Hg anomaly. It is worth noting

Table 3. Values from García Sánchez et al. [13] for mercury in soils (total mercury (THg); elemental mercury (EHg); and exchangeable mercury (ExHg) and in plants (HgP): calculated average Hg concentrations for all the provided plant species from each site). EHg (%): calculated percentage of elemental mercury with respect to total mercury; ExHg (‰): Calculated per thousand of exchangeable mercury with respect to total Hg. THg, EHg, ExHg and HgP in mg kg^{-1}.

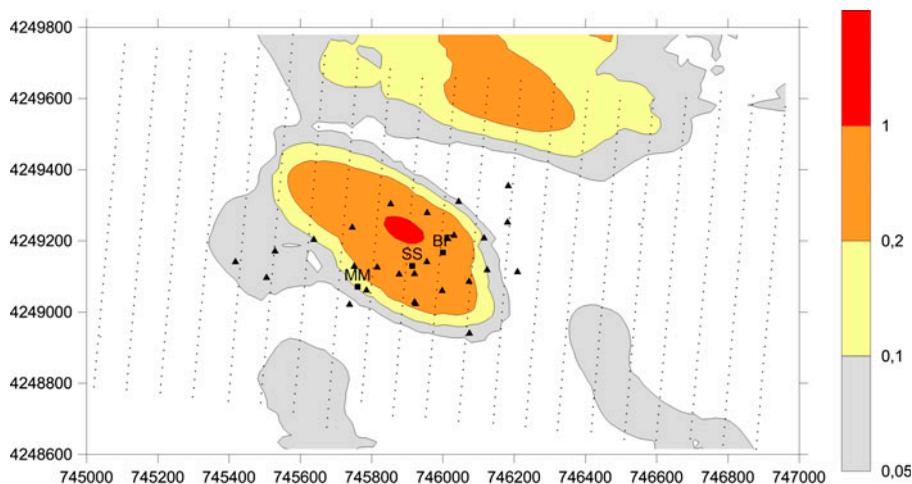| Sample	THg	EHg	EHg (%)	ExHg	ExHg (‰)	HgP
U-1	190	4	2.1	0.009	5.3	1.6
U-2	286	8	2.8	0.004	3.5	2.7
U-3	778	7	0.9	0.015	1.3	13.5
U-4	5	0.4	8.0	0.010	200.0	0.1
U-5	202	3	1.5	0.008	4.9	0.1

Figure 5.   Contour map for mercury contents in plants calculated for all the samples from the 1987 soil surveys, using the Hg contents in soils and the equation obtained between total mercury in the soil and calculated average Hg concentration in the plants. Orange and red areas surpass the tolerable level for agronomic crops [36]. All values in mg kg^{-1}. For abbreviations, see Figure 4.

that these areas are much more extensive than the areas that should be considered as contaminated soils according to the Spanish legislation, a finding that demonstrates that this legislation is not appropriate for the delimitation of polluted soil.

3.2.   *Air*

The TGM concentrations in the area are shown in Table 4, in which surface data are separated from underground data (inside the Mariquita mine). It can be seen that the values are markedly different; at the surface, the concentrations are relatively low, i.e. comparable with background values from polluted sites [28] but much lower than reference levels {air quality guideline (1 μg m^{-3}) [37] and reference level for air concentration (0.3 μg m^{-3}) [38]}. Indeed, only a few maximum values from the proximity to the old mining sites exceed the USEPA RL. In contrast, inside the mine the concentrations are well above these international standards, but they do not reach levels such as the NIOSH ceiling values, which are 'levels of exposure that should not be exceeded at any time' (0.1 mg m^{-3}) [39].

Table 4.   Main statistics for TGM concentrations from the study area. *N*: number of determinations; AM: arithmetic mean; GM: geometric mean; Max: maxima values measured. Concentration values in ng m^{-3}.

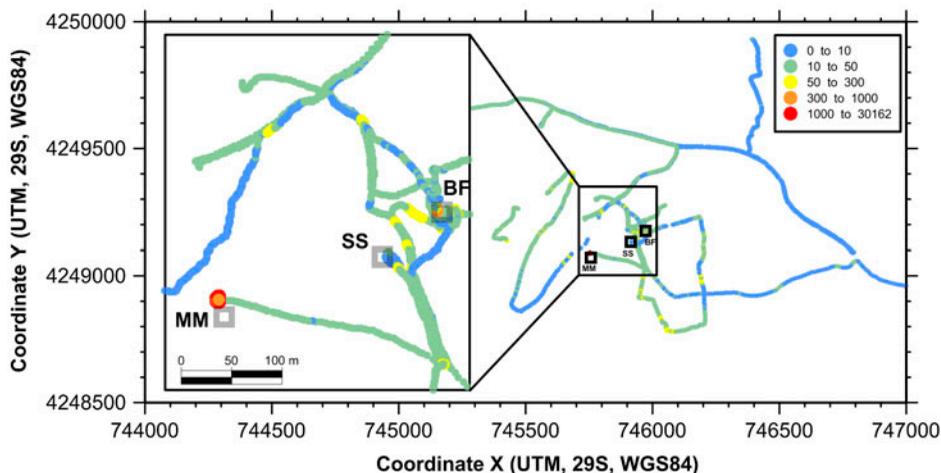| Site	*N*	AM	GM	Max
Outside the mine	8352	19	14	359
Inside the mine	2503	7804	3524	30,163

Figure 6. Plot of TGM concentrations at the surface in the studied area. Values in ng m^{-3}. For abbreviations, see Figure 4.

The contour map for the concentrations of TGM outside the mine is shown in Figure 6. It is worth noting the lack of clear correspondence between the maximum concentrations measured and the mine passives, in particular for the Mariquita descending gallery and the dump located nearby. In fact, the maximum concentrations appear to be scattered in the area, indicating that they are not real 'anomalous' concentrations but fluctuations in the general values, most probably caused by variations in wind direction and intensity during the survey.

Low TGM concentrations are normal in areas that are heavily polluted with Hg (but with long-term undisturbed soils) such as mining areas (e.g. Potosí [40,41] and Venezuela [30]). The causes of these low emissions have been interpreted as being due to oxidation of metallic Hg droplets present in the soil [30] and to the formation of stable, non-emitting Hg compounds in the soil, such as metacinnabar (isometric, black HgS) [40] and calomel (Hg_2Cl_2) [41]. The surroundings of the Usagre Hg mine correspond to pastures with a very low level of agricultural activity, so any of these mechanisms could explain the low TGM emissions from these relatively undisturbed soils.

4. Conclusions

The main conclusions that can be drawn from this study are as follows:

- The soils analysed in the proximity of the Usagre mercury mine contain concentrations of heavy metals, in particular in Pb, Zn and Hg, which are well above the international thresholds for contaminated areas.
- The maximum values for all the analysed elements appear to be related to geochemical anomalies and not directly linked with the contamination caused by the mining activity.
- Calculated metal contents in plants, on the basis of previous soil–plant transfer studies, indicate the possibility that contents exceed plant toxicity levels. The results of this part of the study demonstrate the need to use the soil-to-plant

transfer rates as reliable indicators for risks assessments, which is a much better approach than the use of reference levels calculated on the basis of statistical analysis of local or regional geochemical populations.

- TGM values measured in the atmosphere are very low for the general area, but are extremely high inside the mine. As a consequence, there is a clear need to regulate human access to the mine.

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