



Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: <http://www.elsevier.com/locate/jenvman>

Mercury in soils impacted by alluvial gold mining in the Peruvian Amazon

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ARTICLE INFO

Keywords:

Gold mining
 Mine pollution
 Mercury
 Amazon
 Peru

ABSTRACT

Gold mining is the largest source of mercury (Hg) pollution worldwide. The discharge of mercury in the environment bears direct human health risks and is likely to increase cascading effects throughout local food chains. In the Peruvian Amazon the mining process consists of slashing and burning trees, followed by extraction of gold-bearing sediment, amalgamation with Hg and gold recovery, leading each year to the degradation of 6,000–10,000 ha and the release of 180 metric tons of Hg per year to the environment. The purpose of this study was to determine soil Hg levels in soils of abandoned alluvial gold mine spoils and undisturbed forest in the Madre de Dios region, the epicenter of alluvial gold mining in Peru. We selected gold mine spoils of the two most important technologies locally applied for gold extraction, i.e., Minimally Mechanized Mining (MMM) and Highly Mechanized Mining (HMM), in the native communities of Laberinto and Kotzimba, respectively. We collected 127 and 35 soil samples (0–20cm depth) from potentially contaminated sites and undisturbed forest, respectively. Physicochemical analysis and determination of Hg levels were determined for all soil samples. None of the samples had Hg concentrations above Peruvian, Canadian and British Environmental Quality Standards for Agricultural Soil (6.6mg/kg). Hg levels in MMM and HMM were not significantly different between the two areas. The main variables explaining variation of soil Hg concentrations were the vegetation cover, soil organic matter, soil pH and clay particle content, which explained up to 80% of data set variation. Surprisingly, highest Hg concentrations were found in untouched old-growth forest bordering the mine spoils, but there was also a trend of increasing Hg concentrations with the regenerating vegetation. Our findings suggest that Hg concentrations in old mine spoils are low and shouldn't stand in the way of efforts to restore soil conditions and develop sustainable land uses. However, it is urgent to end the use of Hg in mining operation to decrease human and environmental risks.

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<https://doi.org/10.1016/j.jenvman.2021.112364>

Received 3 October 2020; Received in revised form 16 February 2021; Accepted 11 March 2021

Available online 25 March 2021

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1. Introduction

Alluvial gold mining has become a key driver of deforestation, environmental pollution and potential to harm human health in the Peruvian Amazon. Artisanal and small-scale gold mining (ASGM) in the Madre de Dios region, also known as the “Peruvian Capital of Biodiversity”. This region accounts for 10 metric tons (7%) of the total registered annual gold production in Peru of approximately 144 metric tons, and represents 71% of the Peruvian artisanal and small scale gold mining production (Ministerio de Minas y Energía, 2019). Gold mining in Madre de Dios has already resulted in the deforestation and severe degradation of 95,750 ha of old growth forests (Caballero Espejo et al., 2018). The average annual deforestation rate is above 6000 ha/yr (Asner et al., 2013) and leads to an estimated topsoil loss of 1.3 t ha⁻¹ year (Gomez, 2013) by mixing it with infertile old sediments that mining extracts. Alluvial gold mining in Madre de Dios generally involves slash and burn deforestation, followed by old sediments extraction that uses highly mechanized mining (HMM, excavators front loaders), and minimally mechanized technology (MMM, suction pumps and water cannons) that brings them from different depths to the surface (Caballero Espejo et al., 2018). During this process, the topsoil, characterized by a fine texture, is scattered and coarse gravel, stones and boulders from deeper soil layers become predominant at the surface (Salinas, 2007). Gold particles are captured through amalgamation with mercury (Hg), then recovered by burning, which evaporates Hg and sends it into the atmosphere (Alvarez et al., 2011; Salinas, 2007). All these stages are typically carried out on site, hence generating an importance source of Hg pollution in the local environment. It is estimated that between fourteen of Hg are emitted for every gram of gold produced and up to 50% of the Hg used in ASGM is released directly to the environment in spoils and when amalgam is burned (Cordy et al., 2011). In Madre de Dios was register Hg loses of 181 t every year (Arana and Montoya, 2017).

The average levels of Hg in soils of the world ranges between 0.58 and 1.8 mg kg⁻¹DM (Kabata and Pendias, 2011). The highest soil Hg concentrations are found in mine spoils. For example, in the Idrija Hg-mine (Slovenia) total Hg concentrations in contaminated soils varied between 8.4 and 415 mg kg⁻¹ (Kocman et al., 2004). The highest Hg levels in soils of mining tailings were measured in Africa amounting to 901.5 mg kg⁻¹ DM Hg in Ghana (Clifford, 2017), 1414 mg kg⁻¹ Hg DM in Tanzania (van Straaten, 2000) and 1500 mg kg⁻¹ DM in Kenya (Odumo et al., 2014).

Contamination of the ecosystem with Hg is of particular concern in the Amazon due to tropical climatic conditions under which Hg becomes extremely mobile. In equatorial regions, relatively elevated concentrations of Hg have been measured in the superficial mineral horizons of forested oxisols of, for example, French Guiana (Marc Roulet and Lucotte, 1995), the Brazilian Tocantins River Valley (Aula et al., 1994) and the Tapajós River Valley (M Roulet et al., 1996), with concentrations ranging from 0.80 to 210 mg kg⁻¹DM. Hg pollution associated with

gold mining has become a huge social and environmental problem in Madre de Dios (J Álvarez, V Solano, A Brack, 2011). It was registered Hg levels in different compartments of the Peruvian Amazon. For instance, riverine sediments near ASGM contained 0.95 mg kg⁻¹ and up to 0.29 mg kg⁻¹ in Madre de Dios and Malinowski river respectively (Diringer et al., 2015; Martinez et al., 2018). Also, it was determined a close relation between deforestation and Hg mobility in Colorado watershed near ASGM areas, where The Puquiri River and Colorado River outlets significantly higher Hg levels, 15–50 ng l⁻¹, potentially leading to bio-accumulation in fish and exposure to communities downstream. (Diringer et al., 2019). Furthermore, Hg levels in impacted soils were below 6.6 mg kg⁻¹ the Environmental Quality Standards for Soil of Peru (ECA) (MINAM, 2017) likewise Román-Dañobeytia et al. (2020), Soto-Benavente et al. (2020) and Velásquez Ramírez et al. (2020) research, getting 0.04 and less than 0.1 ng kg⁻¹. However, we can not yet omit Hg harmfulness in the environment, especially in soil.

Recent gold mine spoils are expected to be potential sites of contamination with Hg, but exposure risks are still not well understood in ASGM areas which is of concern because some mine spoils in the region are already being reforested without a clear assessment of exposure risks to Hg. The objective of this research is to determine Hg levels in soils impacted by two of the most frequently used gold mining methods employed in Madre de Dios: minimally and highly mechanized mining. We hypothesized that soil Hg levels in mine spoils depend mainly on the type of mining operations, vegetation cover and physico-chemical soil characteristics.

2. Materials and methods

2.1. Study area

We carried out the present study in soils impacted by alluvial gold mining in the Madre de Dios Region (Fig. 1). The impacted areas were selected according to the two locally most used technologies to extract sediments: Highly Mechanized Mining (HMM) and Minimally Mechanized Mining (MMM) (Fig. 2). HMM uses heavy machinery such as excavators, front loaders, and dump trucks, whereas MMM uses suction pumps and high pressure water cannons to liquefy stream-side sediments, which are transported to sluice boxes via diesel-powered water/sediment pumps (Caballero Espejo et al., 2018). The selected mines where MMM technology had been used were Santa Rita human settlement, Laberinto district, and San Jacinto Native Community. The selected mine spoils where HMM technology had been used was Villa Santiago human settlement and Kotzimba Native Community. In these areas, mercury was used to form gold-mercury amalgam in the mining spoils, then in miner's camp, it is roasted to get gold.

The study region is located between 188 and 332 m. a.s.l (meters above sea level) and characterized by a megathermal climate (tropical climate), with little or no water deficiency and possesses a saturated climate according to Thornthwaite Climate Classification (Feddema, 2005; Thornthwaite, 1948). Annual precipitation, temperature and relative humidity vary between 2000 and 2610 mm, 18–24 °C and 87–97% RH, respectively. Climax vegetation is composed of humid and very humid tropical forests according to Holdridge Life Zones System classification (Senamhi, 2017; Holdridge, 1967). The soil moisture is high throughout most of the year, classified as a Udic soil moisture regime. The soil temperature regime is classified as hyperthermic with mean annual soil temperatures above 22 °C (Soil Science Division Staff, 2017). These kind of soils in the Peruvian Amazon were classified as Entisols according to Velásquez (2017).

2.2. Soil sampling

We collected 162 surface soil samples (0–20 cm depth), 122 samples corresponded to MMM and 40 to HMM. These samples include 127 and 35 ones from impacted areas which are potentially contaminated sites

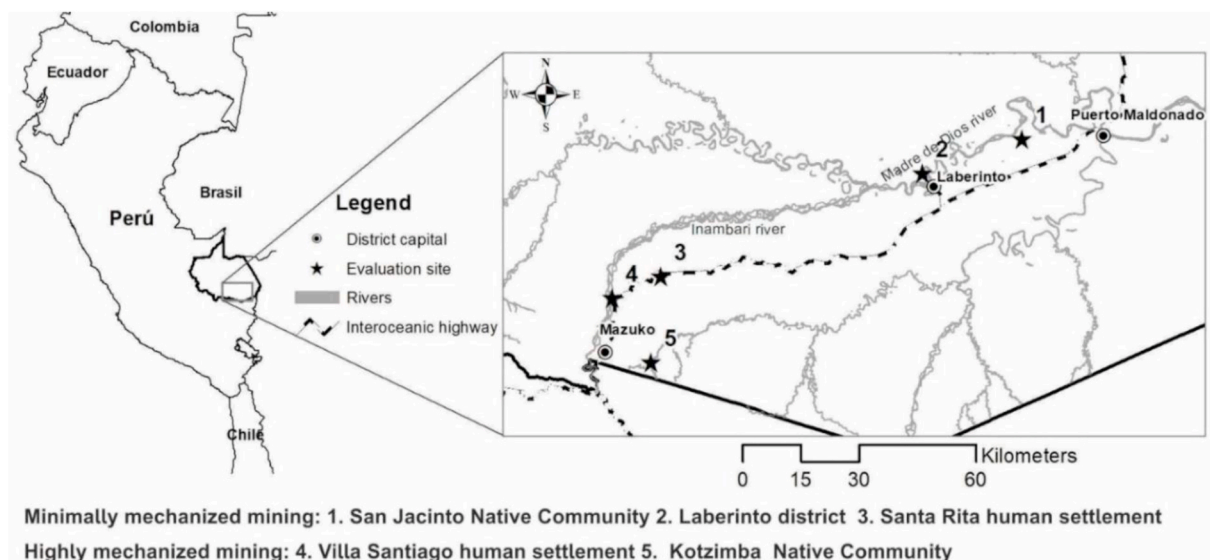


Fig. 1. Study area located at mining spoils characterized by minimally mechanized (upper right panel) and highly mechanized (lower right panel) mining technology in the Peruvian Amazon region of Madre de Dios.



Fig. 2. Technologies to extract sediments: minimally mechanized mining (left) and highly mechanized mining (right), located in Laberinto district and Kotzimba Native Community in the Peruvian Amazon, respectively.

and non impacted areas such as undisturbed forest, respectively. Grab Samples were taken through stratified random sampling across 250 ha; The sampling number depended on accessibility and study area. Sampling was carried out in accordance with the Guide for Soil Sampling of Peru (MINAM, 2014) to ensure our soil sampling plan would be suited to identify and characterize the location and expansion of the soil pollution. Soil quality was assessed in agreement with the Environmental Quality Standards for Soil of Peru (ECA) (MINAM (2017), the Canadian Environmental Quality Guidelines (CEQGs) (Canadian Council of Ministers of the Environment, 2007), and Soil Guideline Values of United Kingdom (SGVs) (Environment Agency, 2009). The sampling design was adjusted to different landscape (LUs), covering both gold mine spoils and referce forest. In the mine spoils we distinguished between LUs with (i) Uncovered Substrate (US, 52 samples), (ii) Uncovered Coarse Fragments Mounds (UCFM, 32 samples), (iii) Covered Soil (CS, 10 samples) and (iv) Covered Coarse Fragments Mounds (CCFM, 6 samples); we also included non impacted areas composed of undisturbed forest adjacent to the mine spoils, further referred to as Reference Forest (RF, 62 samples) (Table 1). Each soil sample (Table 2) consisted of approximately 0.5 kg of topsoil. Field samples were homogenized, stored in clean polyethylene containers and immediately transported on dry ice using coolers, until later freeze drying and analysis in the laboratory.

Table 1
Landscape elements considered in this study

Landscape unit (LUs)	Characteristics
Uncovered Substrate (US) ^a	Uncovered ground with predominant sand particles. Impacted area.
Uncovered Coarse Fragments Mounds (UCFM)	Uncovered ground with predominant content of clast and pebbles. Impacted area.
Covered Soil (CS)	Covered ground by natural regeneration with predominant sand particles. Impacted area.
Covered Coarse Fragments Mounds (CCFM)	Covered ground by natural regeneration with predominant content of clast and pebbles. Impacted area.

^a This is not considered soil because it lacks of the organism effect, which is part of the five soil forming factor according to Jenny (1941).

2.3. Soil and Hg analysis

Samples were mixed, stored, air dried, and passed through a 2.0 mm sieve, after which we determined particle size distribution (Bouyucos method); soil acidity in water extract 1:1 (weight of water/weight of dry soil), Soil organic matter (SOM) (Walkley Black Method) and Cation exchange capacity (CEC) (Ammonium acetate pH = 7) (ISRIC, 2002). These analyses were conducted at Soil Fertility Laboratory located in IIAF Research Center in Madre de Dios and twice replicates were

Table 2
Characterization of study areas and sampling intensity.

Technologies to extract sediments	Selected areas	Landscape units (LUs)	Area (ha)	Top soil samples (n)	
Minimally mechanized	Laberinto district	US	1.97	12	
		UCFM	0.37	12	
		CS	0.31	2	
		CCFM	0.31	2	
		RF	66.08	27	
	Santa Rita human settlement	US	46.93	16	
		RF	99.5	24	
		San Jacinto	US	4.64	12
			UCFM	1.02	7
			RF	21.15	8
Highly mechanized	Kotzimba	US	4.24	9	
		UCFM	0.26	10	
	Community	CCFM	0.47	3	
		CS	0.72	6	
		US	0.62	3	
	Villa Santiago human settlement	UCFM	0.15	3	
		CCFM	0.11	1	
		CS	0.07	2	
		RF	1.54	3	

Uncovered Substrate (US).

Covered Soil (CS).

Uncovered Coarse Fragments Mounds (UCFM).

Covered Coarse Fragments Mounds (CCFM).

Reference Forest (RF).

assessed per each sample.

Total Hg concentration in soils was determined by thermal decomposition atomic absorption with a Milestone DMA-80 mercury analyzer. The analysis was conducted according to the USEPA Method 7473. To ensure quality control, there was a strict blank control by using one blank at the beginning of every test, the DMA-80 was calibrated with liquid standard solution (1000 ppm Hg), we used of reference material TILL-2 (74 ± 13 Hg ppb) and EMC with a recovery rate above 90% and two replicates were assessed per each sample. The Hg analysis was carried out at the Mercury and Environmental Chemistry Laboratory (*Laboratorio de Mercurio y Química Ambiental -LAMQA*) in the Research Institute of the Peruvian Amazon (Instituto de Investigaciones de la Amazonía Peruana – IIAP) in Puerto Maldonado, Madre de Dios.

2.4. Data analysis

We compared Hg levels in degraded soil, using non-parametric methods, Kruskal-Wallis (p-value < 0.05) and Wilcoxon as Post-hoc test, because data were not normally distributed. First, we compared impacted (US, CS, UCFM and CCFM) versus non impacted areas (RF) (Table 3). Second, we compared between LUs (US, CS, UCFM, CCFM and RF) in Minimally Mechanized Mining Areas, and Highly Mechanized

Table 3

Summary statistics of Hg levels (mg kg⁻¹ DM), characteristics and properties of the collected soil samples from impacted areas (US, CS, UCFM and CCFM) and non impacted area (RF) (n=162).

Parameters	Impacted areas (US, CS, UCFM and CCFM) n=100					Non-impacted area (RF) n = 62				
	Mean	Median	Min	Max	SD	Mean	Median	Min	Max	SD
Hg (mg kg ⁻¹ DM)	b 0.02	0.01	0.003	0.06	0.01	a 10.10	0.09	0.005	0.28	0.06
Clay particle (%)	b 5.61	3.80	0.60	37.40	6.51	a 11.56	9.80	0.60	30.80	6.57
Sand particle (%)	a 87.36	94.20	37.40	98.80	14.82	b 60.45	59.70	16.60	97.40	16.08
Silt particle (%)	b 7.0	2.60	0.80	38.60	9.02	a 27.98	27.70	0.00	66.80	13.03
pH	a 5.22	5.27	4.16	6.25	0.44	b 4.73	4.72	3.99	5.72	0.42
Soil organic matter (%)	b 0.48	0.17	0.03	3.45	0.68	a 3.23	2.89	0.07	8.34	1.95
CEC (Cmol (+) kg ⁻¹)	b 6.06	4.80	3.20	17.60	3.15	a 15.92	14.56	4.48	28.32	5.95

mining areas (Table 4). Third, we made a comparison between each US, CS, UCFM, CCFM and RF independently from the type of mining technology, and then between Minimally Mechanized Mining Areas and Highly Mechanized mining areas (Fig. 3). Normality was assessed with Kolmogorov test.

Geostatistical methods (Montero and Larraz, 2008), and Principal Components Analysis (PCA) were used to understand the spatial behavior of Hg and the relationships among Hg levels and different explanatory variables. Experimental variogram models were generated in SGeMS beta v.2.5 b (Stanford Geostatistical Modeling Software) and statistical analyses were carried out with 'Rcmdr' (v 2.5–2), 'RcmdrMisc' (v 2.5–1) and 'RcmdrPlugin.FactoMineR' (v 1.6–0) packages for R statistical program v 3.2.2 (R Development Core Team., 2017). We developed continuous soils maps through application of ordinary kriging (OK) based on Gaussian semi-variogram models in ArcGIS 10.6 (ESRI Inc., USA).

Furthermore, we applied a generalized linear mixed model (GLMM) to assess the role of different explanatory variables in explaining Hg levels in the collected soil samples, using sampling location as the random effect variable in lme4 package for R (R Development Core Team., 2017). To reduce collinearity in the fixed-effects variables, we carried out iterative runs of the variance inflation factor (VIF) until all variables had VIF < 10. Retained variables were: the vegetation cover and mining type at each soil sample (LUs), its SOM, pH, CEC, clay and silt content. We log transformed Hg concentrations to more approximate normality and employed an information-theoretic approach in order to identify and select the best models for explaining Hg concentrations in soil. To this end, we constructed models with all possible combinations of explanatory variables described above using the MuMIn package for R program (Barton, 2018). All continuous explanatory variables were standardized by subtracting the mean value and dividing by twice the standard deviation to allow comparison of the coefficients of numeric variables with the binary variable of mining type (Gelman, 2008). Models were ranked according to the Akaike information criterion (AIC), which is commonly used for model selection and to account for potential biases due to small sample sizes. We calculated the difference in AIC value between each model and the best model (delta AIC: Δi). The best models were selected as those with Δi values < 2, and we carried out model averaging across these models to determine model coefficients (Barton, 2018). Model residuals were normally distributed and showed no specific arrangement with the fitted values or any of the explanatory variables.

3. Results

The soil samples from gold mine spoils had significantly higher pH, but significantly lower SOM, CEC and clay content than soils of reference forests (non-impacted areas) adjacent to the mines, (Table 3).

The Hg levels of all soil samples were below permitted levels according to the Peruvian Environmental Quality Standards for Soil (6.6 mg kg⁻¹; ECA), Canadian Environmental Quality Guidelines (6.6 mg

Table 4

Pairwise comparisons after Kruskal-Wallis test of average Hg levels, pH, Soil Organic Matter and Cation Exchange Capacity in soil samples. Samples correspond to Minimally Mechanized and Highly Mechanized mining areas, in Uncovered Substrate (US), Uncovered Gravel Mounds (UGM), Covered Soil (CSNR), Covered Gravel Mounds (CGMNR) and Reference Forrest (RF).

Parameters	Minimally Mechanized Mining Areas MMM (n = 114)					Highly Mechanized Mining Areas HMM (n = 48)				
	US	CS	UCFM	CCFM	RF	US	CS	UCFM	CGMNR	RF
	Hg (mg kg ⁻¹ DM)	0.01 ±0.01	0.02 ± 0.01	0.03 ± 0.02	0.04 ± 0.00	0.10 ± 0.06	0.01 ± 0.01	0.02 ± 0.01	0.01 ± 0.00	0.03 ± 0.01
Clay particles (%)	2.56 ± 2.02	6.30 ± 0.42	9.93 ± 8.38	18.80 ± 1.41	11.78 ±1 6.62	5.85 ± 10.74	5.77 ± 1.03	5.04 ± 4.81	9.64 ± 4.95	7.00 ± 3.17
Sand particles (%)	95.14 ± 3.34	80.70 ± 1.83	77.03 ± 21.83	59.20 ± 7.07	59.51 ± 15.91	90.38 ± 16.30	83.68 ± 3.39	86.56 ± 13.27	76.20 ± 15.66	78.80 ± 1.40
Silt particles (%)	2.33 ± 2.27	13.00 ± 2.26	13.03 ± 13.89	22.00 ± 5.65	28.67 ± 12.94	3.76 ± 5.97 ab	10.54 ± 3.29	8.38 ± 8.81	14.16 ± 11.39	14.20 ± 4.52
pH	5.32 ± 0.42	4.60 ± 0.09	5.34 ± 0.37	4.79 ± 0.64	4.76 ± 0.41	5.26 ± 0.36	4.86 ± 0.22	5.22 ± 0.40	4.62 ± 0.42	4.16 ± 0.10
SOM (%)	0.15 ± 0.14	1.06 ± 0.45	0.90 ± 1.11	1.93 ± 0.77	3.21 ± 1.99	0.15 ± 0.15	0.61 ± 0.32	0.42 ± 0.48	1.33 ± 0.37	3.51 ± 0.93
CEC (Cmol (+) kg ⁻¹)	4.80 ± 0.86	9.44 ± 2.48	8.52 ± 4.56 bc	12.96 ± 1.58	16.01 ± 6.08 a	5.41 ±3.43	5.46 ± 1.13	5.05 ± 2.83	7.71 ± 0.96	13.97 ±2.02

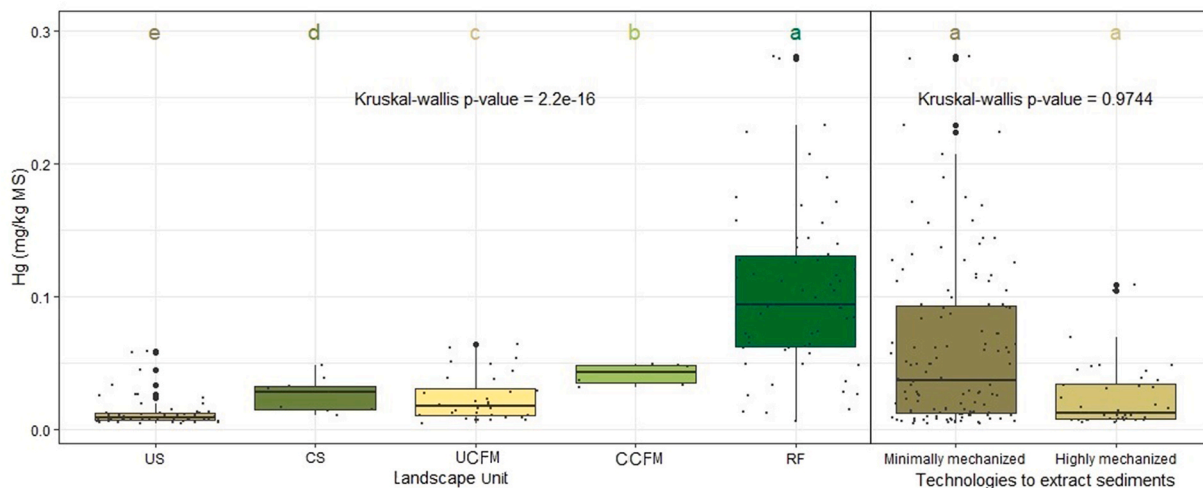


Fig. 3. Boxplots of Hg levels in soil samples from different landscape units (Kruskall Wallis text; p-value =2.2 e-16) and mining technology (p-value=0.97). Letters indicate landscape units and mining types with statistically similar Hg concentrations (Wilcoxon tests used as post-hoc tests after Kruskal-Wallis at p<0.05). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

kg⁻¹; CCME) and Soil Guideline Value of the United Kingdom (10 mg kg⁻¹); Table 4). Surprisingly, the Hg levels of soils in impacted sites were significantly lower than in non-impacted Reference Forest (p < 0.05) (Table 4). Hg in the covered sites CS (0.025 ± 0.012 mg kg⁻¹) and CCFM (0.041 ± 0.007 mg kg⁻¹) were higher than uncovered sites US (0.012 ± 0.012 mg kg⁻¹) and UCFM (0.022 ± 0.017 mg kg⁻¹), but there was no difference in Hg levels of impacted areas according to the type of mining (Kruskal-Wallis p-value: 0.945) (Fig. 3).

A plot of the first two axes of a PCA (Fig. 4) shows that Hg levels was strongly positively related with CEC and SOM and negatively with pH.

The information-theoretic modeling approach identified four models with Δi<2 that explained 80–81% of the variance in soil Hg levels (Table 5). Six different explanatory variables were present in these models, of which only vegetation cover, SOM and pH were retained by all models (Table 6).

We also mapped the spatial distribution of Hg in two mining areas (with more accessibility), one in Laberinto District (Fig. 5) and one in Kotzimba Native Community (Fig. 6) characterized by Minimally and Highly mechanized mining technology, respectively. Both Hg semi variograms showed nugget values of 0.00, ranges about 100–600 and sills 0.000053–0.0024. We fitted exponential models to both variograms for interpolation and mapping purposes (see Fig. 7).

4. Discussion

4.1. 1 Soil characteristics and Hg levels in mined landscapes

The main characteristics of mine spoils are loss of top soil and extreme soil profile remodeling caused by sand and rock fragments moved from deeper soil layers to the top, with high permeability,

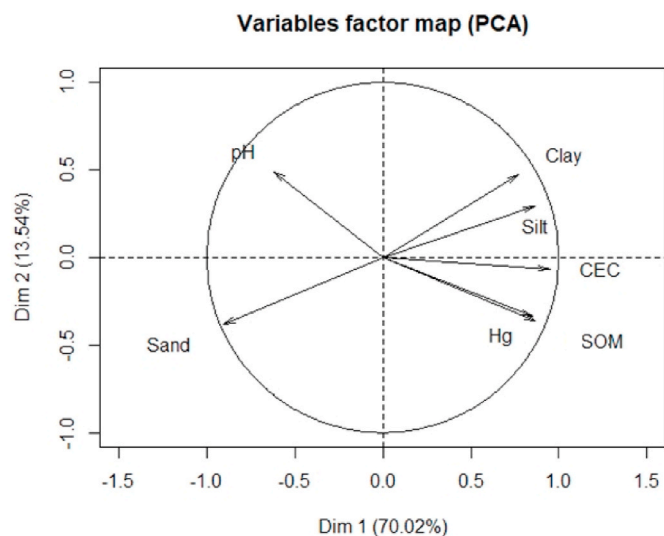


Fig. 4. PCA loading plot showing the relationship among total Hg concentrations and soil characteristics in the selected area. The first two axes explain 83.54% of the data set variability.

Table 5

The four best GLMMs with Hg concentrations in soil as response variable selected based on AICc with $\Delta i < 2$.

Models	K	logLik	AICc	Δi	wi	r^2
Vegetation + Clay + SOM + pH	10.00	-1.66	24.79	0.00	0.29	0.81
Vegetation + CEC + SOM + pH	10.00	-2.34	26.16	1.36	0.14	0.80
Vegetation + SOM + pH	9.00	-3.63	26.45	1.66	0.12	0.80
Vegetation + SOM + pH + Silt	10.00	-2.55	26.58	1.78	0.12	0.81

Log-likelihood of the overall model fit with no adjustment for the number of parameters, K the number of parameter estimates in the model, wi the Akaike weight, representing the model's relative strength compared to other best models

excessive runoff, nearly level slope class (<2%), low erosion and more than 10% rock fragments at the surface (Román et al., 2015; Velásquez Ramírez et al., 2020). Our results reveal surface soils characterized as sandy soils with low CEC and SOM, where the texture of US and UCFM are sand and sandy loam, with more than $77.03\% \pm 21.83\%$ sand particles (Table 4). Similar Brazilian artisanal gold mine spoils (Milesi et al., 2002) are predominantly composed of quartz (SiO₂) whit density close to 2.76 g cm⁻¹.

Soil Hg levels in all sampled sites were below Peruvian, Canadian and British soil quality standards, confirming similar findings reported by Velásquez Ramírez et al. (2020), Arostegui (2017), Román et al. (2015) and Mandros (2019) in soil samples collected from sites under similar conditions in Madre de Dios. Together, these results suggest lower levels of Hg contamination in local mining spoils as compared

Table 6

Effects of explanatory variables in model solutions with $\Delta i < 2$ on Hg concentrations in soil after model averaging.

Variables	Estimate	Adjusted SE	Confidence interval		z value	Pr (> z)	Relative importance
Vegetation - CS	-0.04	0.05	-0.15	0.06	0.77	0.44	1.00
Vegetation - RF	0.11	0.10	-0.09	0.30	1.08	0.28	1.00
No vegetation - UCFM	-0.16	0.08	-0.31	0.00	1.97	<0.05	1.00
No vegetation - US	-0.30	0.10	-0.49	-0.11	3.13	0.002	1.00
Soil - SOM	0.33	0.08	0.18	0.49	4.18	3E-05	1.00
Soil -pH	-0.17	0.05	-0.28	-0.07	3.30	<0.001	1.00
Soil -CEC	0.23	0.09	0.05	0.41	2.46	0.01	0.25
Soil - Clay	0.14	0.05	0.04	0.23	2.90	0.004	0.25
Soil - Silt	0.13	0.05	0.03	0.24	2.48	0.01	0.25

with findings from other studies across the Amazon. By contrast, in Brazilian and Venezuelan artisanal mining spoils, Hg soil levels were found up to 12.30 and 542.00 mg kg⁻¹ DM, respectively (Table 7).

The adsorption of Hg in soils depends on a number of factors, including the chemical form of Hg introduced, the grain size distribution of the soil, the nature and amount of inorganic and organic soil colloid, the soil pH, and the redox potential (Steinnes, 2013). Our results suggest that vegetation cover, SOM, pH and to lesser extent CEC and Clay content are the most important variables explaining variation in soil Hg levels. The strongest positive correlation was found between soil Hg and SOM ($r = 0.84$) (Fig. 4), confirming similar observations from the literature (Kabata-Pendias and Sadurski, 2004). The positive correlation between soil Hg and organic carbon content (the main component of SOM) is related with the affinity of ionic forms of Hg for functional groups and organic matter complexes (Santos-Francés et al., 2011), with maximum sorption values reported to range between 106.00 and 474.00 mg per kg of soil (Mou et al., 1999). In soils with low Hg levels, SOM allows only a very small fraction of Hg to be present in the soil solution, whereas in soils with high Hg levels, SOM causes Hg to be lost as the volatile form Hg⁰ after its reduction (Andersson, 1979). In acid soils, such as the ones we sampled, Hg²⁺ is assumed to be mainly attached to SOM (Kabata and Pendias, 2011). However, in tropical soils, the absence of a well-developed organic layer due to the rapid turnover of accumulated organic matter, might limit surficial Hg accumulation (M. Roulet et al., 1998). In line with this, sites covered with natural regeneration (CS and CCFM) had up to 47% more SOM and 97% more Hg than uncovered sites (US and UCFM) (Table 4).

Soil pH correlated negatively with Hg ($r = -0.60$, p value < 0.0001) (Fig. 4). Uncovered impacted areas (US and UCFM) had a significantly higher pH (5.30 ± 0.39) than covered areas (CS and CCFM) (4.75 ± 0.33) and RF (4.73 ± 0.42), owing to the loss of SOM. Under acidic conditions, the lower pH of soil containing H²⁺ results in greater release to soil water. In addition, when soil pH is < 6.5, adsorption of organic pollutants by soil particles can return pollutants to the soil water, enhancing Hg activity and promoting the absorption by plant roots (Yu et al., 2018). In Chinese cambisols, Yang et al. (2007) reported that under high soil pH values Hg releases to soil water. In studies of soils in Sweden, Andersson (1967) reported that Hg was adsorbed mostly on the humus fraction at low pH and on the mineral colloids at higher pH values. Accordingly, the pH decreases influenced by higher SOM at the covered areas (CS and CCFM) and RF, may explain increased Hg adsorption over time.

A positive correlation was shown between CEC and soil Hg ($r = 0.84$, p value < 0.0001) (Fig. 4), which is in line with previous findings (Kabata-Pendias and Sadurski 2004). However, less than 4% of the total Hg levels has been found to be adsorbed via electrostatic interaction (Yin et al., 1997). The positive correlation between CEC and Hg might, therefore, be due to the positive correlation between CEC and SOM ($r = 0.84$) and clay content ($r = 0.81$, p value < 0.0001). While abandoned mine sites with some vegetation cover had CEC values up to 50% higher than uncovered sites, (Table 4), higher Hg concentrations in the former might be due to higher SOM (which enhances CEC) formation in soils covered by regenerating vegetation. Similarly, in soils under the

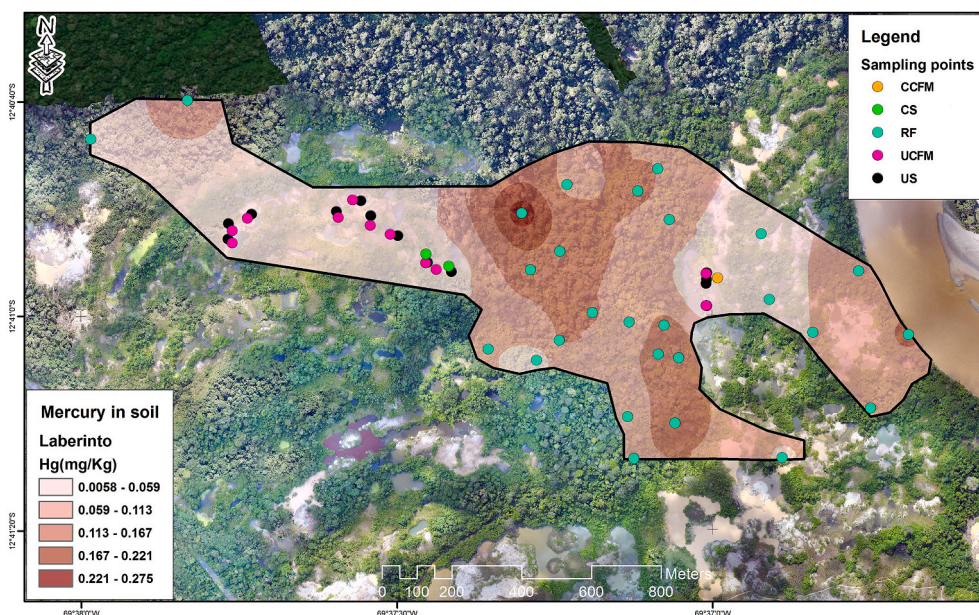


Fig. 5. Interpolation mapping of Hg level in a Minimally Mechanized Mining Area located in Laberinto district.

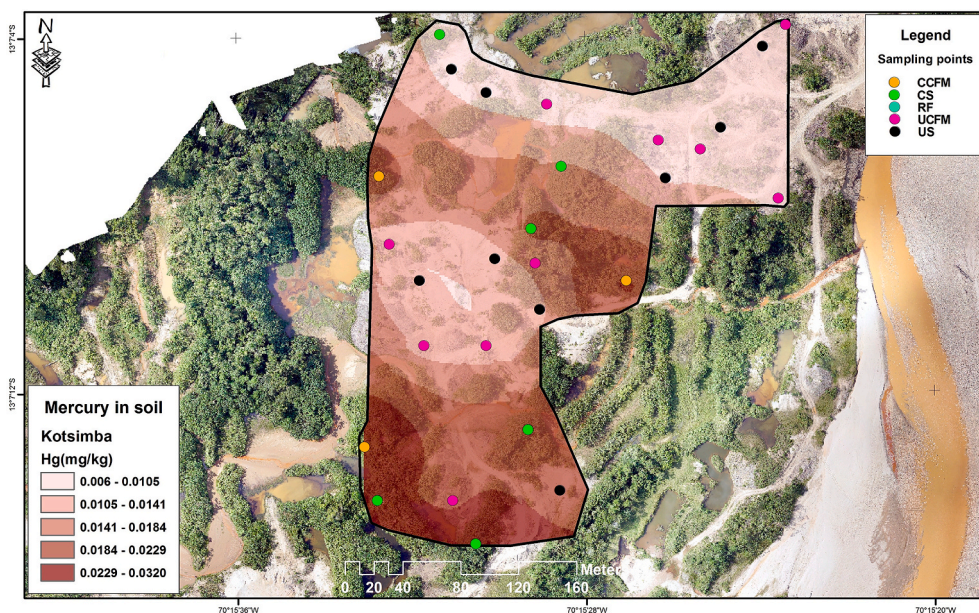
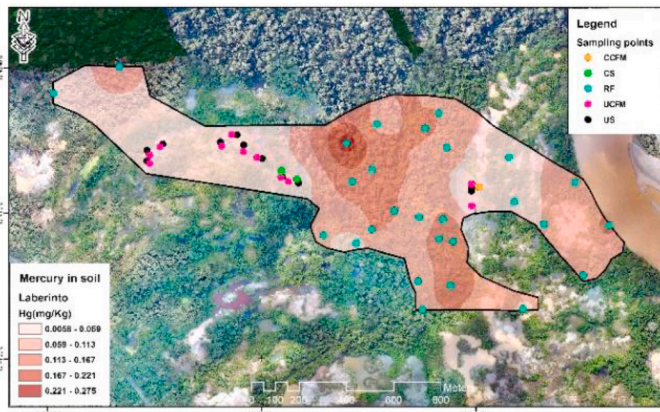


Fig. 6. Interpolation mapping of Hg level in a Highly Mechanized Mining Area located in Kotzimba Native Community.

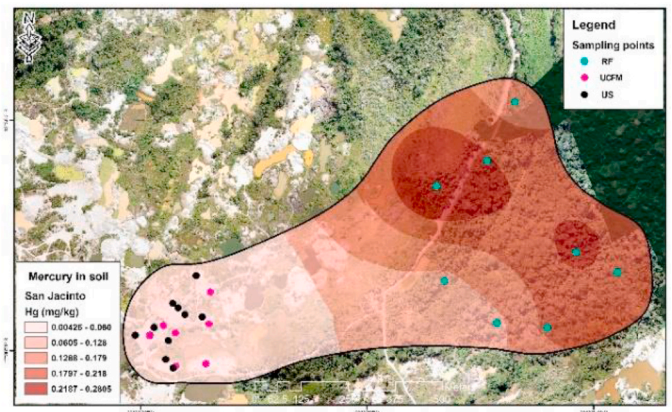
reference forest, characterized by higher CEC ($15.92 \pm 5.96 \text{ Cmol (+) kg}^{-1}$), higher Hg concentration might be due to strongly fixed Hg^{2+} by hydroxyligands of sesquioxides and various ligands of humic substances, as suggested by Steinnes (2013). Our finding that soils with higher clay content tend to contain higher Hg concentrations corroborates the results of a study of cultivated tropical soils in the Brazilian Amazon that reported higher Hg levels of clayey sites ($0.12 \text{ mg kg}^{-1} \text{ DM}$) compared to sandy areas ($0.06 \text{ mg kg}^{-1} \text{ DM}$) (Béliveau et al., 2009). In soils with lower clay and thus higher sand content, leaching of Hg might be higher, especially under the pluvial precipitation regime of the Amazon, whereby Hg is released from soils due to the displacement by polar water molecules (Engle et al., 2001).

4.2. 2 Mercury movement in mining landscapes

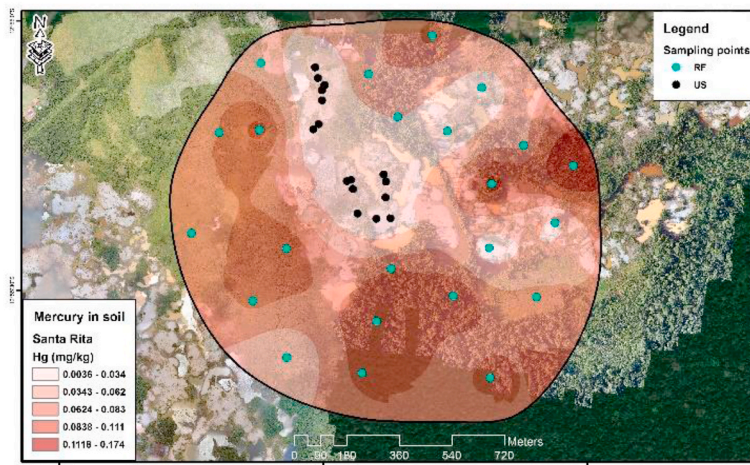
Environmental contamination by Hg can occur via multiple routes and processes. Runoff processes from mining sites increase the risk of Hg laden sediments to rivers downstream from mining areas. Hg in surface waters tends to be predominantly associated with large particles ($>0.22 \text{ mm}$) (Hurley et al., 1998; Riscassi et al., 2011). Hg levels in sediments of the Madre de Dios river were found to significantly increase downstream of mining activities (Diringer et al., 2015). In rivers, MeHg may find suitable conditions to its production such as increased temperature and decreased dissolved oxygen (Diringer et al., 2015). Elevated Hg levels was also found in sediments of rivers near ASGM areas in the Madre de Dios such as Malinowski, Tambopata and Heather rivers, with values above $19.2 \pm 3.4 \text{ g kg}^{-1}$. Hg levels in these sediments was positively correlated ($r^2 = 0.85$, $p < 0.05$) with carbon from the organic fraction



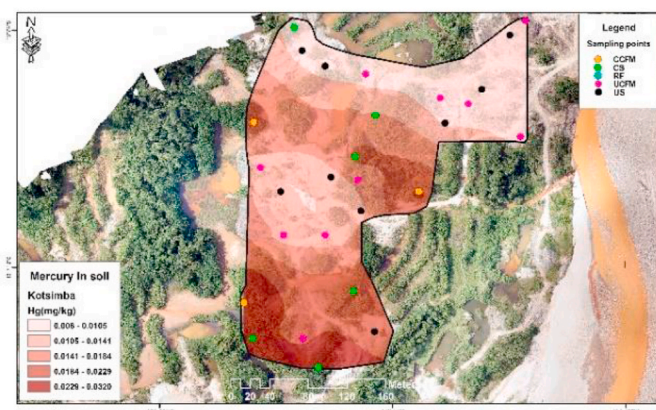
Laberinto district
Minimally Mechanized Mining



San Jacinto Native Community
Minimally Mechanized Mining



Santa Rita human settlement
Minimally Mechanized Mining



Kotzimba Native Community
Highly Mechanized Mining



Villa Santiago human settlement
Highly Mechanized Mining

Fig. 7. Interpolation mapping of Hg level in Minimally and Highly Mechanized Mining Areas.

Table 7
Hg levels (mg kg⁻¹ DM) in alluvial gold mine spoils in the Amazon.

Details	Non-impacted area or Reference Forest				Impacted areas Alluvial gold mining spoils			
	Hg in soil (mg kg ⁻¹ DM)							
Country	Peru	Brazil	French Guiana	Venezuela	Peru	Brazil	French Guiana	Venezuela
Location	Madre de Dios	Tapajós River Valley	Cayene	Cuyuní River Basin	Madre de Dios	Serra da Santa Cruz	Highlands	Cuyuní River Basin
Reference	This research	Roulet et al. (1998)	Roulet and Lucotte (1995)	Santos-Francés et al. (2011)	This research	de Andrade Lima et al. (2008)	Guedron et al. (2006)	Santos-Francés et al. (2011)
	0.01–0.28	0.90–0.21	0.08–0.12	0.02–0.40	0.003–0.06	3.10–12.30	0.04–0.05	0.16–542.00

(Martínez et al., 2018). The elevated Hg levels of these sediments could be due to the transport of Hg contaminated soil from denuded landscapes where mining occurs, or the remobilization of river sediments from turbulence associated with runoff events (Bastos et al., 2006). Hg leached from soils after deforestation has been found to be partially transferred toward water (Silveira et al., 2009).

The primary sources of mercury emissions in ASGM areas are from tailings discharge to land and water and mercury gas emissions during amalgam roasting (Esdaile and Chalker, 2018), whereas Hg stored in soil and vegetation can be volatilized during forest burning (Meléndez-Pérez et al., 2014) and deforestation (Almeida et al., 2005). Hg volatilization is also increased by higher soil temperatures (Landa, 1979), especially in areas without vegetation cover, such as our US and UCFM sites. It was registered that Hg from ASGM is not significantly deposited in nearby down-wind regions, remaining locally deposited near the mines or directly enters the global Hg pool (Beal et al., 2013). This anthropogenic Hg origin in the atmosphere was globally registered (Engstrom et al., 2014), and in Peru, Beal et al. (2013) found that modern Hg fluxes in lake cores were 3.4–6.9 $\mu\text{g m}^{-2} \text{a}^{-1}$, compared to preindustrial Hg fluxes of 0.8–2.5 $\mu\text{g m}^{-2} \text{a}^{-1}$, revealing increasing environmental risk.

In regions with high rainfall like the Amazon, freshly deposited Hg from atmospheric sources is more prone to reduction and volatilization compared to Hg stored in vegetation or in the upper soil pool (Hintelmann et al., 2002). This reactivity rapidly decreases in sites where deposited Hg binds to SOM and equilibrates fairly quickly with native Hg pools already present in the system. This likely explains why mine spoils covered by regenerating vegetation are more effective in accumulating deposited Hg through increased percentages of SOM and CEC values compared to uncovered areas that are more susceptible to leaching and volatilization processes.

The high Hg levels found in soils of undisturbed reference forest soils was likely a combination of a high capacity to fix Hg due to higher SOM percentages and lower leaching processes, and the higher effectiveness of forest canopies in trapping atmospheric Hg. The enormous leaf surface area of forest canopies allows the retention of Hg through the stomata, particularly as Hg⁰, and/or through foliar adsorption of gaseous oxidized Hg and particulate-bound Hg. As the translocation of Hg between tree roots and aboveground biomass is virtually nonexistent, Hg mass accumulated in forest canopies is believed to be largely atmospheric in origin (J. A. Ericksen et al., 2003; J. Ericksen and Gustin, 2004). Hg compounds that accumulate in plant leaves are transferred to the soil through litterfall (Fostier et al., 2015), decomposition, and via throughfall (Silva et al., 2009). Hg litterfall in Amazonian forests was found to vary between 43 ± 15 and 49 ± 14 $\text{mg m}^{-2} \text{y}^{-1}$ (Fostier et al., 2015; Silva et al., 2009; Mélières et al., 2003). Similar processes are likely to occur on abandoned mine sites with naturally regenerating vegetation (CS and CCFM); as the vegetation cover continues to develop so does its capacity to trap atmospheric Hg and accumulate it in the soil through litterfall.

5. Conclusion

Hg levels in gold mine spoil soils were below the upper limits for

agricultural and residential use as stipulated by Peruvian, Canadian and British environmental quality standards, and yielded similar values in areas under MMM and HMM mining operations. Vegetation cover, soil organic matter content, soil pH and clay particle content were the main factors explaining the variation of Hg concentrations in soils. The soil conditions of recently abandoned, uncovered mine spoils, characterized by low organic matter, low clay content, slightly acid pH, low cation exchange capacity and high sand content, in combination with intense leaching processes, results in the dispersion of Hg in the environment either through runoff or high volatilization. However, recolonization of these sites by vegetation increases soil organic matter and decreases soil pH, thus enhancing the capacity to absorb Hg. In addition, atmospheric Hg, volatilized through burning of gold/Hg amalgamation and other sources such as deforestation, is captured again by the vegetation and incorporated to the soil through litterfall and rainfall, further increasing soil Hg concentrations. Particularly troublesome is that similar processes trap atmospheric Hg and transfer it to the soil also occurs in undisturbed forest canopies with higher effectiveness, leading to uncontrollable dispersion of Hg in virgin forests and its food chains with different chemical reaction. To decrease environmental and human health risks, it is imperative to reduce Hg release into the environment by stopping Hg use for gold amalgamation and deforestation. On the other hand, the fact that recently abandoned mine sites had the lowest levels of Hg contamination suggests that these areas should be priority areas for restoration interventions and the development of sustainable land uses, as mercury concentrations in the soil will not be a problem.

Acknowledgements

This research owes special thanks to San Jacinto Native Community, Kotzimba Native Community and local miners who might use this research as a tool to manage land restoration. This study is made possible funding provided by the United States Agency for International Development (USAID) under the terms of USAID/WFU Cooperative Agreement No. AID-527-A-16-00001, Consejo Nacional de Ciencia y Tecnología (CONCYTEC) and Fondo Nacional de Desarrollo Científico y Tecnológico (FONDECYT) (Proyecto Convenio 141–2017 FONDECYT), under the terms of cooperative scientific agreement with the Peruvian Amazon Research Institute (Instituto de Investigaciones de la Amazonía Peruana). Additional funding was provided by World Wildlife Fund (Cooperative Agreement No. OT11). The contents of this article do not necessarily reflect the views of USAID or the United States Government.

Annex

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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