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Heavy metals in alluvial gold mine spoils in the peruvian amazon

Manuel Gabriel Velásquez Ramírez[a,*,1], Juan Antonio Guerrero Barrantes[b], Evert Thomas[c], Luis Alfredo Gamarra Miranda[d], Martin Pillaca[e], Lily Denise Tello Peramas[b], Luis Rubén Bazán Tapia[b]

[a] Instituto de Investigaciones de la Amazonía Peruana (IIAP), Proyecto Recuperación de Áreas Degradadas y Manejo Sistémico del Bosque, Jr. Ica N°1162 Puerto Maldonado, Apartado postal 17001, Peru
[b] Soil Department, Universidad Nacional Agraria, La Molina, Av. La Molina s/n, apartado postal Lima12, Lima, Peru
[c] Bioversity International, Avenida La Molina 1895, La Molina, Lima, Peru
[d] Urb. Ciudad del Pescador Bellavista Callao Mz 02 Lote 27 Calle 49, Apartado postal Callao 02, Callao, Peru
[e] Centro de Innovación Científica Amazónica (CINCIA), Jr. Cajamarca s/n, Apartado postal 17001, Madre de Dios, Peru

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ABSTRACT

Alluvial gold mining in the Peruvian Amazon has become a key driver of land degradation and deforestation. The associated release of mercury in the environment poses direct human health risks and is likely to engender cascading effects throughout local food chains. We carried out research in an alluvial gold mine concession in the Madre de Dios region to compare the degree of soil-borne pollution of heavy metals in areas where mining operations were abandoned more and less recently (1–5 and 6–8 years ago, respectively) with non-impacted old-growth forest areas. All heavy metals, were below permissible levels according to Peruvian and Canadian environmental quality standards. Mean As, Ba, Pb, Cu, Cr, Ni, V and Zn concentrations in impacted areas were 1.90 ± 1.51, 29.80 ± 22.87, 4.60 ± 2.55, 12.68 ± 8.13, 7.90 ± 3.98, 7.93 ± 3.89, 12.67 ± 6.62, and 26.65 ± 13.53 mg kg^{-1} dry matter (DM), respectively. Heavy metal concentrations were higher in non-impacted old growth forest soils than in mining spoils, and tended to increase with time since abandonment of mining operations. Hg was not detected in any of the sites. Low heavy metal concentrations in mine spoils might beexplained because of intense volatilization, reduced metal retention capacity due to the low clay and organic matter content, and leaching processes related with soil rinsing which is part of the mining operations combined with intense rainfall. Our findings suggest that heavy metal concentrations in mining spoils should not be considered to constrain forest restoration efforts or the development of similar land uses as in comparable non-impacted high forest soils.

1. Introduction

Global gold extraction has experienced a surge over recent years largely owing to booming international prices, reaching 1315.00US $ OZ TR^{-1} in 2017 (World Gold Council, 2017). Peru occupied the 4th place in the 2017 gold production, and overall mining represented 10% of the GDP. Gold extraction in the Peruvian Amazon has led to large scale deforestation and mercury pollution (Alvarez et al., 2011). In the department of Madre de Dios, also known as the "Peruvian Capital of Biodiversity", artisanal and small gold production accounts for 8% of the total annual gold production in Peru of approximately 151 metric tonnes (Ministerio de Minas y Energía, 2018). Gold mining in Madre de Dios has resulted in the deforestation of 95,750 ha (Centro de Innovación Científica Amazónica, 2018). In recent years, annual deforestation rates have fluctuated between 6000 and 11,000 ha (Asner et al., 2013) leading to an estimated topsoil loss of 1.3 t ha^{-1} year (Gomez, 2013).

Alluvial gold mining in Madre de Dios old growth forest generally involves slash and burn deforestation, sediment extraction, amalgamation of gold with mercury (Hg), burning, Hg evaporation and gold recovery (Alvarez et al., 2011; Salinas, 2007). All these stages of gold production are typically carried out on site, hence generating an

* Corresponding author.
E-mail addresses: mvelasquez@iiap.gob.pe (M.G. Velásquez Ramírez), jaguerrero.barrantes@gmail.com (J.A.G. Barrantes), E.Thomas@cgiar.org (E. Thomas), alfredogamarram@yahoo.com (L.A. Gamarra Miranda), pillacmj@wfu.edu (M. Pillaca), ltello@lamolina.edu.pe (L.D. Tello Peramas), rbt@lamolina.edu.pe (L.R. Bazán Tapia).
[1] Main researcher.

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importance source of Hg pollution in the local environment. Sediment extraction is accomplished through the use of heavy machinery or artisanal tools to bring sediment from different depths to the surface. During this process the topsoil -characterized by a fine texture- is scattered and coarse gravel, stones and boulders from deeper soil layers become to predominate at the surface (Salinas, 2007).

Hg is a potentially toxic metal which is known to accumulate in the ecosystem (Moreno-Brush et al., 2016). In spite of the adoption of the Minamata Convention which to date has been ratified by more than 100 countries worldwide, including Peru, to reduce human and environmental risk caused by Hg pollution (Ministerio del Ambiente, 2016), global annual production still amounts to 600,000 tonnes (United States Geological Survey, 2018). Hg pollution associated with gold mining has become a huge social and environmental problem in Madre de Dios (Alvarez et al., 2011). It is estimated that > 3000 tonnes of Hg have leaked in Amazonian rivers since 1980 (Webb et al., 2004). Some river fish sampled registered more than 0.3 ppm of Hg which is the maximum limit established by USEPA (United States Environmental Protection Agency, 1997). Furthermore, children hair sampled showed Hg concentrations above 2.1 ppm while the maximum permissible level according to USEPA is 1 ppm (Fernandez et al., 2013).

Recent gold mine spoils are expected to be potential loci of contamination with mercury and other heavy metals, but exposure risks are still not well understood. Here we aimed to reveal heavy metal pollution rates (As, Ba, Pb, Hg, Cu, Cr, Ni, V and Zn) in soils impacted by artisanal alluvial gold mining in the Peruvian Amazon region, Madre de Dios to provide baseline information to assess the need for pollution management strategies (Ministerio del Ambiente, 2018; Red Latinoamericana de Sitios Contaminados, 2016).

2. Materials and methods

2.1. Study area

We carried out research in the community of Fortuna, located in the Peruvian Amazon region of Madre de Dios (Fig. 1), which is one of the oldest areas were artisanal alluvial gold mining has traditionally been practiced. Annual precipitation, temperature and relative humidity in Fortuna vary between 2000–2610 mm, 18–24 °C and 87–97%, respectively (Servicios Generales y Medio Ambiente, 2006). It is located at 188 m.a.s.l. and is characterized by a warm, humid climate (Thornthwaite et al., 1949) with a climax vegetation of subtropical humid forests (Holdridge, 1967). The soil moisture content is not dry in any part for more than 90 cumulative days per year, classified as Udic soil moisture regime. The soil temperature regime is classified as hyperthermic with mean annual soil temperatures above 22 °C (Soil Survey Staff, 2014).

2.2. Soil sampling

We collected 93 top soil samples (0–20 cm depth) through stratified random sampling across 13 ha; 90 samples were collected in gold mine spoils and 3 in non–impacted forest sites. Samples were located in a broader 100 ha landscape matrix which had been subject to mining. Sampling was carried out in accordance with the Guide for Soil Sampling of Peru (Ministerio del Ambiente, 2014), Environmental Quality Standards for Soil of Peru (ECA) (Ministerio del Ambiente, 2017) and the Canadian Environmental Quality Guidelines (Canadian Council of Ministers of the Environment No. 1299; ISBN 1-896997-34-1, 2007). The sampling design was adjusted to the nature of cover vegetation and time since the last impact (Table 1). The main objective was to compare the degree of soil-borne pollution of heavy metals in soils that were abandoned more and less recently (1–5 and 6–8 years ago, respectively) with those of non-impacted old growth forest areas.

Each soil sample consisted of approximately 1 kg of topsoil. Samples were mixed, stored, air dried, and passed through a 2.0 mm sieve, after which we determined particle size distribution (sedimentation method); actual soil acidity in water extract 1:1, organic matter content (Walkley Black Method) and cation exchange capacity (CEC) (effective CEC and CEC measured with Ammonium acetate pH = 7). pH, soil organic matter, cation exchange capacity and clay particle content (%) area the most important chemical characteristic and properties that explain the heavy metal distribution in soil (Salomons, 1995). Heavy metal content (As, Ba, Pb, Hg, Cu, Cr, Ni, V and Zn in mg kg^{-1} DM) was analyzed in accordance with the EPA Method 200.7, through the use of ICP-AES. Soil characterization analyses were conducted at the Soil Chemical Analysis Laboratory, Universidad Nacional Agraria La Molina. Heavy metal analyses were conducted at a certified privet laboratory, Servicios Analiticos Generales SAC.

Additionally, we evaluated 2 soil pits in impacted areas (T1 and T2) and 3 soil pits in non – impacted areas (N1, N2 and N3) used as background. The soil pits were selected such that they were located in the same life zone, geological zone (Palacios et al., 1996) and topographical category (all at scale 1:100 000; Soil Science Division Staff 2017)). Samples from non–impacted areas were used as references to determine the impacts of alluvial gold mining on soil characteristics and heavy metal content.

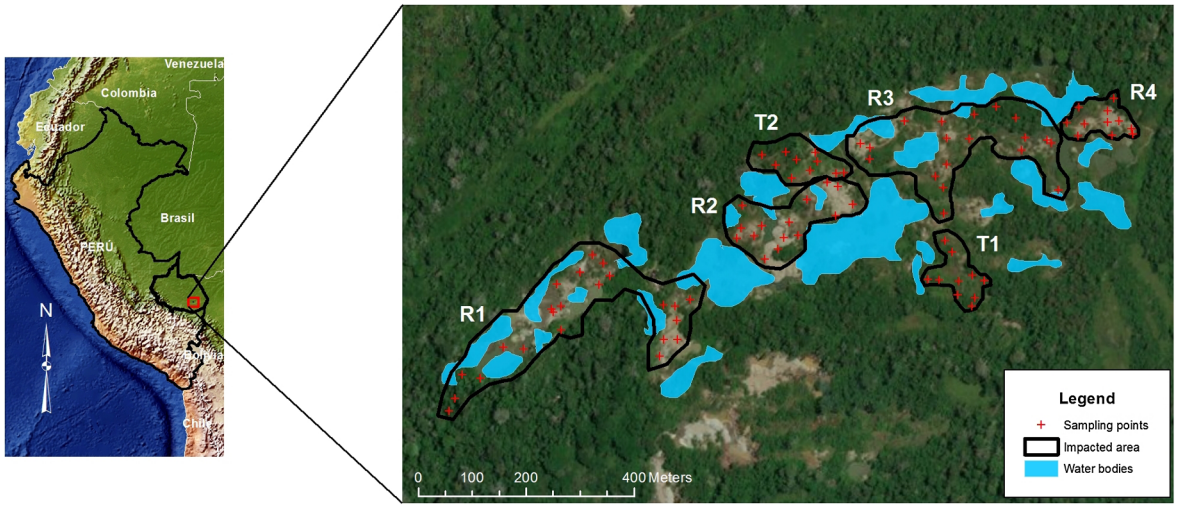

Fig. 1. Study area located at the community of Fortuna located in the Peruvian Amazon region of Madre de Dios.

Table 1
Characterization of study sites and sampling intensity.

Details of study areas		Areas				
Impact history	Vegetation cover by low shrubs	Area	Time since impact (years)	Area (ha)	Top soil samples	Soil pits
More recently impacted		R1	2.0	5	23	0*
		R2	4.0	2	15	0*
		R3	5.0	1	20	0*
		R4	1.5	3	13	0*
Less recently impacted	Secondary Forest	‘	6.0	1	10	1
		T2	8.0	1	9	1
Non-impacted	Primary forest	N	Natural or non-impacted	NA	3	3 (N1, N2 and N3)

* There were no soil pits because the site was too close to the water table.

2.3. Statistical analyses

Correlations and multiple correlations between physical and chemical soil characteristics and heavy metal content were assessed by means of Spearman correlation and dependence coefficients, respectively. Principal Components Analysis (PCA) and Cluster Analysis (CA) were used to explain the variance structure and evaluate clustering of sampling sites based on heavy metals concentrations in the soil (Facchinelli et al., 2001; Hernandez, n.d.). Geostatistical methods were applied to understand and analyze the spatial behavior of heavy metals (Montero and Larraz, 2008), based on heavy metal concentrations at different sampling locations as a function of their nearest neighbor distance h. We developed continuous soils maps through application of ordinay kriging (OK) based on a Gaussian semivariogram models (Nanos et al., 2005) in ArcGis 10.1 (ESRI Inc., USA). Experimental variogram models were generated in GeoR (v1.7-1) package for R statistical program v 3.2.2 (R Development Core Team, 2017).

3. Results and discussion

Concentrations of all heavy metals were below permissible levels in most soils samples collected from gold mine spoils according to the Peruvian Environmental Quality Standards for Soil (ECA) and Canadian Environmental Quality Guidelines (CCME) (Table 2). We did not detect Hg in any of the samples.

Soil in gold mine spoils are physically characterized by high permeability, excessive drainage, nearly level slope class (< 2%), low erosion, more than 10% rock fragments at the surface, and water table raised from its initial depth at approximately 1.50 m to close to the surface. Chemical characteristics of soils are very strongly acidity (4.77 ± 0.34 pH), low organic matter content (0.5 ± 0.62%), low cation exchange capacity (10.15 ± 6.65Cmol(+) kg^{-1}), and low clay content (6.37 ± 6.53%) (Table 2). Non–impacted soils are also characterized by very strongly acidity (4.69 ± 0.40 pH), however they have higher organic matter content (3.33 ± 0.60%), higher cation exchange capacity (35.48 ± 8.96 Cmol(+) kg^{-1}), and higher clay content (38.77 ± 4.61%). Hence, alluvial gold mining not only results in top soil loss and extreme restructuring of the soil profile (Velasquez, 2017), but it also negatively affects soil fertility and adsorption capacity.

Remarkably, all detectable concentrations of heavy metals (Table 3) in impacted areas (R1-4 and T1-2) were consistently lower than in non-impacted old-growth forest soils (N), suggesting that leaching of heavy metals may be an important side effect of mining operations. Soils worldwide receive quantities of trace metals from a wide variety of industrial wastes (Nriagu, J. Pacyna, 1988). The fact that we did not detect Hg in any of the soil samples analyzed in spite of its local (mis) use in gold production, suggests its dispersion through the environment, which is not entirely surprising given its volatile nature.

Heavy metal concentrations differed significantly between areas with different combinations of years of abandonment and vegetation cover (Table 3). There was a slight trend of higher heavy metal concentrations in gold mine spoils that had been abandoned longer ago (T1-2 compared to R1-4), which might mean that natural processes such as alluvial deposits might enhance concentrations over time. Furthermore, with increasing time since abandonment, organic soil matter increases owing to plant root exudation, litter production, animal feces and other organic sources which also increase the soil buffer capability, and consequently its heavy metal adsorption. Also, the different physical and chemical characteristics of soils as well as vegetation cover at the sampling sites are likely to have influenced heavy metal concentrations. To obtain further clarity on the influence of

Table 2
Summary statistics of heavy metal concentrations (mg kg^{-1} DM, characteristics and properties of the collected soil samples from impacted areas R and T (n = 90).

Parameters	Impacted area						
	Mean	Median	Min	Max	SD	Kurtosis (ku > 0.25)	Skewness (SKp > 0)
Heavy metal concentrations (mg kg^{-1}DM)							
As	2.07	1.90	0.30	9.10	1.51	7.67	2.43
Ba	35.86	29.80	16.60	146.50	22.87	9.61	2.98
Pb	5.21	4.60	2.46	15.00	2.55	5.26	2.29
Hg*	ND	ND	ND	ND	ND	ND	ND
Cu	13.98	12.68	2.94	43.43	8.13	3.20	1.66
Cr	9.14	7.90	3.96	22.76	3.98	4.23	2.05
Ni	8.99	7.93	4.17	22.81	3.89	3.89	1.94
V	14.10	12.04	5.80	36.54	6.62	4.15	2.05
Zn	30.55	26.65	12.20	73.20	13.53	2.25	1.58
Physico-chemical soil characteristics							
Clay particle (%)	6.37	3.40	1.44	37.40	6.56	2.99	8.93
pH	4.73	4.77	3.63	6.84	0.44	1.12	5.29
Soil organic matter (%)	0.50	0.31	0.00	3.72	0.62	2.85	9.62
CEC (Cmol (+) kg^{-1})	10.15	8.00	4.80	39.73	6.65	2.81	8.08

* ND Non detected (detection limit was 0.1 ppm).

Table 3
Average heavy metal concentrations in soil samples from impacted areas R1-4 and T1-2 (n = 90), non-impacted areas N1-3 (n = 3) and reference values according to Peruvian Environmental Quality Standards for Soil (ECA) and Canadian Environmental Quality Guidelines (CCME).

Parameters	Impacted area n = 90						Non impacted area n = 3	Soil Peruvian Environmental Quality Standards for Soil		Soil Canadian Environmental Quality Guidelines		Range heavy metal concentration in soil Kabata and Pendias (2011)
	R1	R2	R3	R4	T1	T2	N	Industrial soil	Agricultural soil	Industrial soil	Agricultural soil	
Heavy metal in soil (mg kg^{-1}DM)												
As	a 0.93 ± 0.55	ab 1.57 ± 0.60	b 2.27 ± 1.10	bc 2.17 ± 0.45	c 4.48 ± 2.65	c 2.54 ± 1.05	abc 4.60 ± 1.88	140	50	12[a]	12[a]	4.4–9.3
Ba	b 29.24 ± 0.16	B 28.19 ± 17.31	bc 36.24 + 24.10	bc 31.06 ± 5.46	c 61.20 ± 42.13	c 4 3.54 ± 21.15	abc 177.63 ± 4.69	2000	750	2000	750	175 – 520
Cd	b 1.98 ± 0.61	b 2.04 ± 1.03	bc 2.70 ± 1.16	c 2.56 ± 0.45	c 4.44 ± 2.28	c 3.05 ± 1.13	abc 6.65 ± 0.42	22	1.4	22	1.4	0.37 – 0.78
Pb	a 4.61 ± 1.33	b 4.05 ± 2.08	bc 5.03 ± 2.05	bc 4.55 ± 0.73	c 7.94 ± 4.17	c 7.04 ± 3.48	abc 13.67 ± 0.52	800[b]	70	600	70	22 – 44
Hg	ND	ND	ND	ND	ND	ND	ND	24	6.6	50[b]	6.6[b]	0.05 – 0.26
Cu	b 9.33 ± 4.84	b 12.34 ± 6.41	bc 13.36 ± 7.49	bc 13.44 ± 3.09	c 24.72 ± 11.98	c 18.85 ± 7.23	abc 34.87 ± 3.82	–	–	91	63	13 – 24
Cr	b 7.16 ± 1.89	b 7.75 ± 3.38	bc 9.38 ± 3.52	bc 8.83 ± 2.12	c 14.00 ± 6.64	c 11.04 ± 3.98	abc 21.14 ± 1.75	1000	–	87	64	12 – 83
Ni	b 7.73 ± 2.04	b 7.05 ± 3.33	bc 8.98 ± 3.57	bc 8.85 ± 1.66	c 13.57 ± 6.45	c 10.61 ± 3.96	abc 22.58 ± 1.32	–	–	89	45	12 – 34
V	b 11.42 ± 3.28	b 11.59 ± 6.01	bc 14.11 ± 5.86	bc 13.72 ± 2.59	c 21.62 ± 11.23	c 17.27 ± 6.89	abc 33.78 ± 2.40	–	–	130	130	18.00 – 115
Zn	b 0.93 ± 6.78	B 24.93 ± 10.32	bc 30.18 ± 2.40	bc 32.00 ± 9.16	c 49.51 ± 18.30	c 36.88 ± 11.72	Abc 69.30 ± 4.81	–	–	250	410	45 – 100
Characteristics and properties of soil												
Clay particle (%)	b 5.12 ± 1.98	b 5.13 ± 6.18	b 5.69 ± 4.87	bc 3.55 ± 0.55	c 14.80 ± 12.78	c 7.40 ± 6.49	abc 38.77 ± 4.61	–	–	–	–	–
pH	a 4.70 ± 0.40	a 4.61 ± 0.38	a 4.95 ± 0.60	a 4.74 ± 0.28	a 4.45 ± 0.28	a 4.70 ± 0.27	a 4.69 ± 0.40	–	–	–	–	–
Soil organic matter (%)	a 0.434 ± 0.18	abc 0.28 ± 0.47	ad 0.51 ± 0.69	abc 0.20 ± 0.12	d 1.16 ± 1.09	d 0.62 ± 0.63	abcd 3.33 ± 0.60	–	–	–	–	–
CEC (Cmol (+) kg^{-1})	a 7.75 ± 1.78	ab 11.08 ± 7.94	ab 9.28 ± 5.53	ab 8.00 ± 1.47	ab17.83 ± 12.28	ab 10.97 ± 4.70	ab 35.48 ± 8.96	–	–	–	–	–

Suggested by Canadian Environmental Quality Guidelines (CCME) as inorganic As.
Suggested by Canadian Environmental Quality Guidelines (CCME) as inorganic Hg.
ND: None detected.

Table 4
Correlations between difference heavy metal concentration in soil samples from gold mine spoils R1-4 and T1-2 (n = 90).

Parameter	As	Ba	Pb	V	Cu	Cr	Ni	Zn	CEC (Cmol (+) kg^{-1})	Clay particle (%)	OSM (%)	CEC + Clay particle + OSM
As	+1.00 a								0.40[b]	0.34[b]	0.16[b]	0.99[c]
Ba	+0.83a	+1.00a							0.54[b]	0.50[b]	0.43[b]	0.99[c]
Pb	+0.71a	+0.84a	+1.00a						0.57[b]	0.42[b]	0.37[b]	0.89[c]
V	+0.84a	+0.94a	+0.85a	+1.00a					0.57[b]	0.56[b]	0.46[b]	0.99[c]
Cu	+0.84a	+0.89a	+0.81a	+0.93a	+1.00a				0.59[b]	0.43[b]	0.39[b]	0.99[c]
Cr	+0.86a	+0.93a	+0.84a	+0.99a	+0.94a	+1.00a			0.59[b]	0.40[b]	0.37[b]	0.99[c]
Ni	+0.83a	+0.94a	+0.84a	+0.99a	+0.93a	+0.98a	+1.00a		0.58[b]	0.45[b]	0.44[b]	0.99[c]
Zn	+0.80a	+0.85a	+0.75a	+0.89a	+0.90a	+0.91a	+0.90a	+1.00a	0.56[b]	0.40[b]	0.39[b]	0.99[c]

[a]Pearson correlations between difference heavy metal concentration in soil, significance correlation at $p < 0.001$.
[b] Spearman Coefficient between soil properties and heavy metal concentration.
[c] Dependence Coefficient between soil properties and heavy metal concentration.

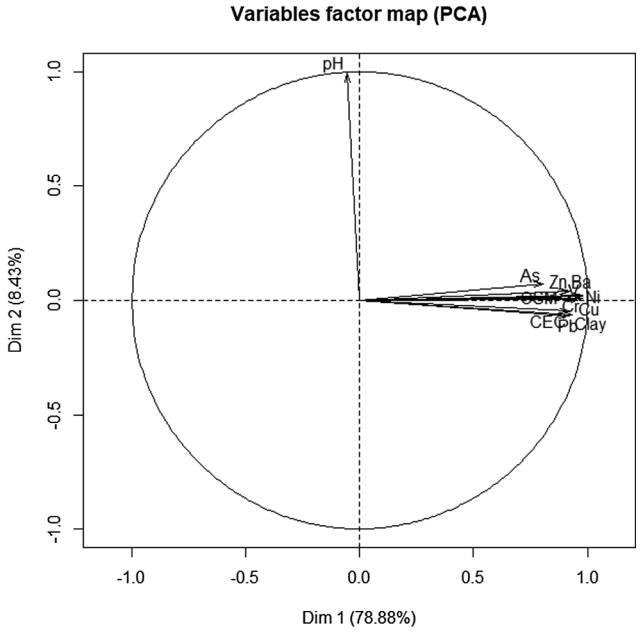

Fig. 2. PCA loading plot showing the relations between heavy metals concentrations and other soil characteristics. The first two axes explain 87% of the variance in data.

variability in soil characteristics and vegetation cover future studies might focus on more sites with more homogenous soil conditions.

In impacted areas, concentrations of the different detectable heavy metals were strongly correlated (Table 4). We applied PCA to determinate the relation between heavy metals and soil characteristic like pH, Cation Exchange Capacity (CEC), Clay content and soil organic matter (OSM), which are suggested as main factors to determinate heavy metal content in soil (Alloway, 1990; Kabata and Pendias, 2011; Salomons, 1995). The PCA diagram (Fig. 2) and the loadings of the different variables on the first two PCA axes that explain 87.30% of the cumulative variance show that concentrations of all heavy metals are strongly correlated with CEC and SOM but not pH which was independent of all other variables.

According to the PCA (Fig. 2) CEC, clay particle and organic matter (%) were the soil characteristic most closely related to heavy metal content. Pairwise correlations showed that in impacted soil samples these variables showed low to moderate correlation coefficients with heavy metal concentrations. On the other hand, the multiple correlation of these features with each concentration of heavy metal showed that at 99% of the variability of metal concentration was explained by these features (Table 4).

According to the correspondence analysis CA (Fig. 3) there was a narrow group of all metals in impacted areas and characteristics and properties of soil evaluated, except pH. The narrow grouping might be caused because of the soil alluvial origin. It would be the result of mixing and accumulation of different sediments, soils and coarse particles, causing the metals tend to accumulate and present a similar distribution.

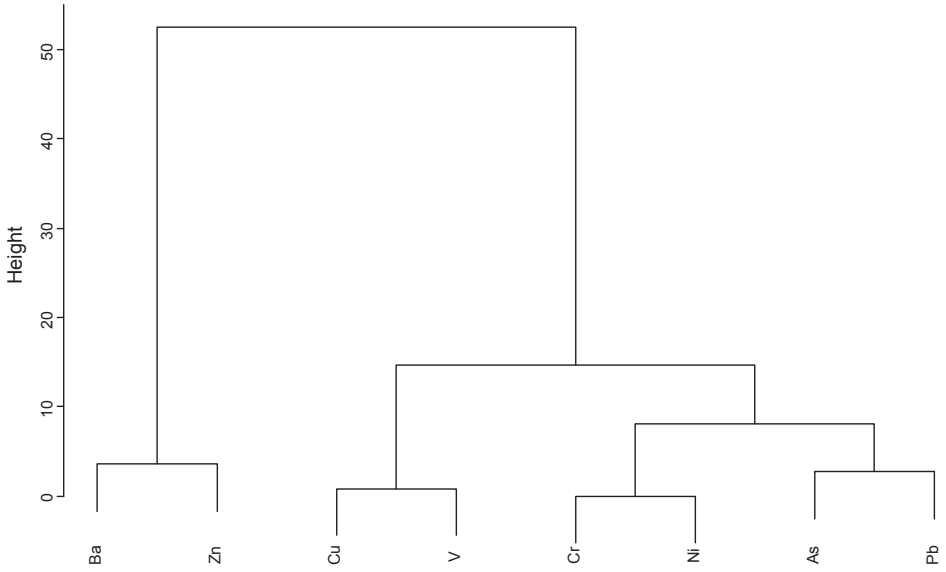

Fig. 3. Cluster diagram of heavy metals based on site characteristics.

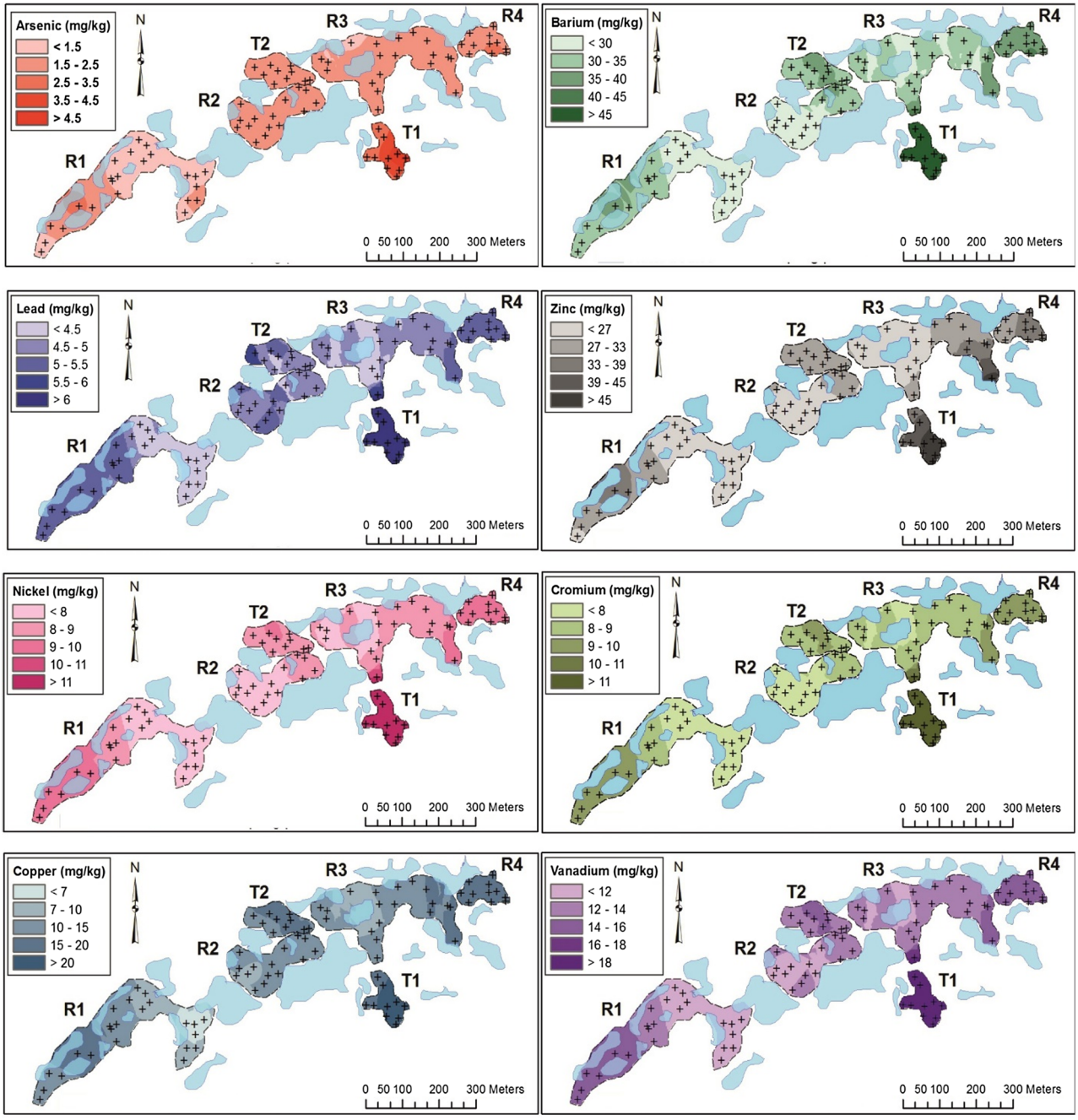

Fig. 4. Interpolation mapping of heavy metals.

Table 5
Heavy metals, chemical and properties in soil pits in impacted and non impacted areas.

Horizon	Depth (cm)	Heavy metal in soil (mg kg^{-1}DM)									Soil characteristic				
		As	Ba	Pb	Hg	Cu	Cr	Ni	V	Zn	Texture	pH	Organic soil matter (%)	Effective CEC (Cmol (+) kg^{-1})	Clay particle (%)
Non impacted area- N1															
A	0–7	4.60	250.30	13.25	ND	33.87	20.83	21.93	33.69	64.70	Silty clay	5.16	2.80	17.43	41.44
AC	7–40	3.10	265.00	14.24	ND	29.60	21.37	21.42	33.67	67.20	Silty clay	5.28	1.50	14.36	41.44
C1	40–68	3.40	73.50	11.76	ND	31.63	19.74	18.63	32.11	56.80	Loam	4.76	0.75	8.71	25.44
C2	> 68	3.10	72.30	9.81	ND	27.97	16.36	17.35	26.77	50.80	Loam	4.65	0.48	7.36	15.44
Non impacted area - N2															
A	0–10	4.70	126.30	14.26	ND	39.09	23.02	24.10	36.22	74.30	Silty clay	5.18	3.21	13.89	33.44
AC	10–21	5.20	138.90	14.65	ND	38.73	22.54	22.58	33.90	74.20	Silty clay loam	5.18	1.06	10.64	41.44
C1	21–42	2.90	142.80	14.24	ND	38.20	23.20	22.84	35.57	76.50	Silty clay	5.1	3.28	11.41	31.44
C2	42–65	3.50	138.30	13.33	ND	39.25	21.57	21.06	32.35	68.40	Silty clay loam	5.15	1.09	14.46	41.44
2C3	> 65	4.70	90.50	12.78	ND	36.95	20.90	21.18	36.09	66.10	Silty clay	5.22	0.20	9.22	23.44
Non impacted area - N3															
A	0–12	1.40	156.30	13.51	ND	31.66	19.57	21.72	31.43	68.90	Silty clay	5.6	4.01	17.81	41.44
AC	12–15	3.70	94.70	13.01	ND	34.34	22.00	20.80	34.11	71.50	Silty clay loam	4.64	1.09	7.51	27.44
C1	15–48	2.50	119.30	13.54	ND	30.02	21.15	20.62	34.02	68.50	Silty clay loam	4.7	0.85	11.26	39.44
C2	48–70	3.70	109.60	13.06	ND	34.49	21.13	21.38	34.19	66.60	Silty clay loam	5.15	0.41	9.48	31.44
C3	> 70	3.00	111.70	13.28	ND	33.94	21.29	20.31	32.74	67.40	Silty clay loam	5.21	0.61	9.89	29.44
Impacted area 6–7 years ago - T1															
A	0–10	2.00	35.60	5.14	ND	14.22	8.76	8.59	13.18	28.10	Sandy	5.13	0.17	3.31	1.44
C1	10–25	2.40	37.10	5.76	ND	9.86	10.15	10.08	15.95	29.40	Sandy	4.78	0.20	2.19	1.44
C2	25–42	1.70	26.90	3.62	ND	5.27	6.28	6.78	9.49	18.90	Sandy	5.26	0.48	3.15	1.44
2C3	> 42	2.80	52.90	6.83	ND	16.18	10.91	10.84	17.27	34.20	Sandy	4.63	0.14	2.84	1.44
Impacted area 7–8 years ago – T2															
A	0–7	2.70	67.50	8.07	ND	26.13	13.43	13.66	21.02	43.60	Sandy clay loam	4.88	2.08	8.91	21.44
C1	7–40	1.60	28.80	4.43	ND	7.72	7.40	7.72	11.31	22.60	Sandy	4.69	0.17	2.78	3.44
C2	40–48	3.20	80.80	10.36	0.27	26.71	19.93	18.07	30.37	57.00	Loamy	4.77	0.31	4.34	9.44
C3	48–77	1.90	32.40	5.15	ND	9.89	9.51	9.74	13.64	28.60	Sandy	4.36	0.17	2.16	1.44
C4	> 77	2.00	56.30	7.77	0.13	21.83	14.51	13.68	22.98	44.60	Loamy sand	4.60	0.34	3.86	3.44

ND Non detected.

3.1. Geostatistics and mapping

We constructed semi variograms for all heavy metals (Fig. 4). The nugget value below 0.05 for all heavy metals suggests some degree of spatial auto-correlation (Burgess and Webster, 1980). Points were grouped between 50 and 69 intervals (bins). Gaussian models were fitted to all variograms for interpolation and mapping purposes.

The behavior of metals in soil is influenced by clay, base saturation, Fe and Mn and pH. Heavy metals are present in the soil either as exchangeable cations with high mobility, associated with iron and manganese hydroxide with medium mobility, bound to organic substances with medium mobility, or bound to the inside of mineral particles with low mobility (Salomons, 1995). In addition, heavy metal cations are most mobile under acid conditions (Alloway, 1990), which explains why we found higher heavy metal content under acid pH.

3.2. Vertical distribution of heavy metals

Variation in soil characteristics and heavy metal concentrations across a vertical gradient in 5 soil pits (2 in impacted and 3 non-impacted areas) are presented in Table 5.

According to Velasquez (2017), alluvial gold mining management remodels the soil profile putting coarse soils (sandy, loamy sand and sandy clay loam soils) and rock fragments from deeper soil layers to the surface. After abandonment of mining operations, impacted areas are influenced by natural regeneration of vegetation which increases the organic soil matter in the surface. T1 soil profile is characterized with higher rock fragments with sand soil texture, while T2 soil profile is characterized by sand to sandy clay loam soil texture without rocks (Table 5). In contrast natural soils profile (N1-3) are characterized by silty clay to loam texture class, higher organic soil matter content from the surface to the bottom, and without any rock fragments.

In non-impacted areas (N1-3), higher heavy metal concentration were found in the top layer where also the other soil parameters reached their highest values. At deeper layers, both heavy metal concentrations and soil OSM, ECEC and clay content evaluated tended to decrease. Also, in impacted soils (T1-2) the distribution of heavy metals across soil layers showed the same patterns but with remarkable lower content of heavy metals and soil OSM, ECEC and clay content (Fig. 5).

Samples from T1 (Impacted area 6–7 years ago) contained only 1.4% of clay particles in all soil layers, while T2 (Impacted area 7–8 years ago) contained 21.44% in the top layer with decreasing values in deeper layers. The clay particle content was positively associated with organic soil matter in all layers (Fig. 5 and Table 5). The low clay and organic matter content in impacted areas is likely to result in increased leaching of heavy metals to deeper soil layers and downstream sediments, but further research is needed to confirm or refute this hypothesis.

Particularly the fact that mercury was not detected in the soil profiles of impacted areas suggests its mobility to other parts of the environment where it might cause toxic effects. Further studies are needed to evaluate the magnitude of potential heavy metal

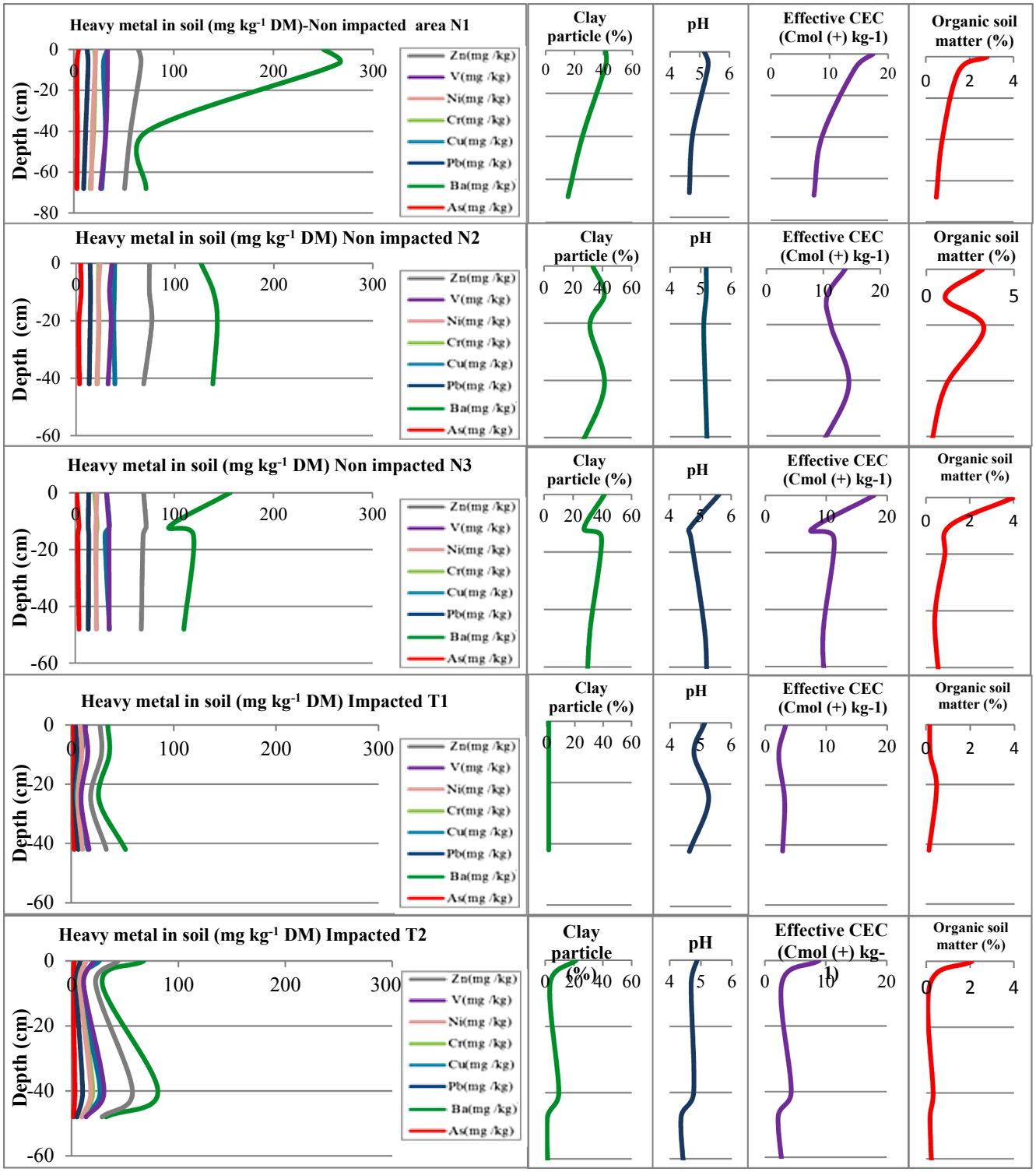

Fig. 5. Heavy metal concentrations and Physico-chemical soil properties in pits in non impacted areas (N1, N2 and N3) and impacted (T1 and T2).

accumulation downstream of mining areas in sediments which is also recommend in other artisanal and small scale gold mining experiences, like Indonesia (Reichelt-Brushett et al., 2017). Previous research found that riverine sites close to alluvial gold mining area tend to have elevated mercury concentrations in sediments (Diringer et al., 2015; Martinez et al., 2018).

More studies are needed to understand and monitor the vertical distribution of heavy metal in mining spoils with different histories of abandonment.

4. Conclusion

Our findings confirm the severe impacts caused by alluvial gold mining activities on soil structure and texture, jeopardizing the soil fertility and productivity. Concentrations in gold mine spoil soils of all heavy metals were below upper limits for agricultural use as stipulated in Peruvian and Canadian environmental quality standards. We did not detect any Hg pollution nor in non-impacted areas nor in impacted areas, suggesting its dispersion in the environment. Heavy metal

concentrations were higher in non-impacted high forest soils than in mining spoils, but concentrations tended to increase with time of abandonment of mining operations, according to the changes in soils characteristics. Our findings suggest that heavy metal concentrations in mining spoils should not be considered to constrain forest restoration activities or the development of similar land uses as in comparable non-impacted high forest soils. We hope that our research results will serve as a basis to support further integrate ecological restoration and the development of polices to promote the recovery of gold mine spoils in the Amazon.

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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.

References

Alloway, J., 1990. Heavy Metal in Soil. Wiley, New York.
Alvarez, J., Solano, V., Brack, A., Ipenza, C., 2011. Minería Aurífera en Madre de Dios y Contaminación con Mercurio. MINAM, Peru.
Asner, G.P., Llactayo, W., Tupayachi, R., Luna, E.R., 2013. Elevated rates of gold mining in the Amazon revealed through high-resolution monitoring. Proc. Natl. Acad. Sci. 110, 18454–18459. https://doi.org/10.1073/pnas.1318271110.
Canadian Council of Ministers of the Environment No. 1299; ISBN 1-896997-34-1, 2007. Canadian soil quality guidelines for the protection of environmental and human health: Summary tables.
Burgess, T., Webster, R., 1980. Optimal interpolation and isarithmic mapping of soil properties. I. The semi-variogram and punctual kriging. J. Soil Sci. 31, 315–331. https://doi.org/10.1111/ejss.12749. In press.
de Innovación, Centro, Amazónica, Científica, 2018. Tres décadas dendeforestación por minería aurífera en la amazonía suboriental peruana. Serie de resumenes de investigación.
Diringer, S.E., Feingold, B.J., Ortiz, E.J., Gallis, J.A., Araújo-Flores, J.M., Berky, A., Pan, W.K.Y., Hsu-Kim, H., 2015. River transport of mercury from artisanal and small-scale gold mining and risks for dietary mercury exposure in Madre de Dios. Peru. Environ. Sci. Process. Impacts 17, 478–487. https://doi.org/10.1039/C4EM00567H.
Facchinelli, A., Sacchi, E., Mallen, L., 2001. Multivariate statistical and GIS-based approach to identify heavy metal sources in soils. Environ. Pollut. 114, 313–324. https://doi.org/10.1016/S0269-7491(00)00243-8.
Fernandez, L., Ashe, K., Araujo, J., Field, C., 2013. Mercury in Madre de Dios: Mercury Concentrations in Fish and Humans in Puerto Maldonado. Research Brief Series No. 1. Standford.
Gomez, C., 2013. Evaluación de escenarios alternativos en sistemas sociales ecológicos afectados por la minería aluvial en Madre. de Dios. UNALM.
Hernandez, O., n.d. Temas de análisis multivariado, La univers. ed. Costa Rica.
Holdridge, L.R., 1967. Life zone ecology.Tropical Science Center. San Jose. Costa Rica.
Kabata, A., Pendias, H., 2011. Trace Elements in Soils and Plants, London 4 t. ed. London.
Martinez, G., McCord, S., Driscoll, C., Todorova, S., Wu, S., Araújo, J., Vega, C., Fernandez, L., 2018. Mercury Contamination in Riverine Sediments and Fish Associated with Artisanal and Small-Scale Gold Mining in Madre de Dios, Peru. Int. J. Environ. Res. Public Health 15, 1584. https://doi.org/10.3390/ijerph15081584.
Ministerio de Minas y Energía, 2018. Anuario Minero 2017 Anual. Colombia.
del Ambiente, Ministerio, 2018. Aprueban Criterio para la Gestión de. Sitios Contaminados.
Ministerio del Ambiente, 2017. Estándares de Calidad Ambiental para Suelos D.S 011-2017-MINAM.
Ministerio del Ambiente, 2016. Convenio de Minamata sobre Mercurio: ratificación peruan. Lima Peru.
Ministerio del Ambiente, 2014. Guía para el muestreo de suelos. R.M. 085-2014.
Montero, J., Larraz, B., 2008. Introducción a la Geoestadística, Netbiblo. ed. España.
Moreno-Brush, M., Rydberg, J., Gamboa, N., Storch, I., Biester, H., 2016. Is mercury from small-scale gold mining prevalent in the southeastern Peruvian Amazon? Environ. Pollut. 218, 150–159. https://doi.org/10.1016/j.envpol.2016.08.038.
Nanos, N., Pardo, F., Nager, J.A., Pardos, J.A., Gil, L., 2005. Using multivariate factorial kriging for multiscale ordination: a case study. Can. J. For. Res. 35, 2860–2874. https://doi.org/10.1139/x05-211.
Nriagu, J., Pacyna, J., 1988. Quantitative assessment of world-wide contamination of air, water and soils by trace metals. Nature 333, 134–139.
R Development Core Team, 2017. A language and environment for statistical computeing. R Foundation for Statistical Computing. Viena. Austria.
Red Latinoamericana de Sitios Contaminados, 2016. Concepto de sitios contaminados [WWW Document]. URL http://relasc.org/relasc2/index.php/faq-espanol/95-1-caracteristicas-generales/141-11-que-es-un-sitio-contaminado.
Palacios, O., Molina, O., Galloso, A., Reyna, C., 1996. Geología de los cuadrángulos de Puerto Luz, Colorado, Laberinto, Puerto Maldonado, Quincemial, Masuco, Atillero y Tambopata. INGEMMET, Peru In press.
Reichelt-Brushett, A.J., Stone, J., Howe, P., Thomas, B., Clark, M., Male, Y., Nanlohy, A., Butcher, P., 2017. Geochemistry and mercury contamination in receiving environments of artisanal mining wastes and identified concerns for food safety. Environ. Res. 152, 407–418. https://doi.org/10.1016/j.envres.2016.07.007.
Salinas, M., 2007. Impactos económicos y ambientales de la pequeña minería artesanal en el departamento. de Madre de. Dios. UNALM.
Salomons, W., 1995. Environmental impact of metals derived from mining activities: Processes, predictions, prevention. J. Geochemical Explor. 52, 5–23. https://doi.org/10.1016/0375-6742(94)00039-E.
Servicios Generales y Medio Ambiente, 2006. Estudio de Impacto Ambiental y Prospección Sísmica 2D, Lotes 111 y 113.
Soil Science Division Staff, 2017. Soil survey manual. Government Printing Office, Washington DC.
Soil Survey Staff, 2014. Keys to Soil Taxonomy, 12th ed. USDA-Natural Resources Conservation Service, Washington, DC.
Thornthwaite, C.., Biel, E.R., Church, P.E., Jacobs, W.C., Landsberg, H., Leighly, J.B., Hafstad, K., 1949. Report of the Committee on Climatology, 1947–1948. Transactions, American Geophysical Union, USA.
United States Environmental Protection Agency, 1997. EPA-452/R-97-003 Mercury Study Report to Congress Volume VII: Characterization of Human Health and Wildlife Risks from Mercury Exposure in the United States.
United States Geological Survey, 2018. Mineral Commodity. Summaries. United States.
Velasquez, M., 2017. Metales en suelos explotados por la pequeña minería aurífera aluvial en Madre de Dios. Perú, UNALM.
Webb, J., Mainville, N., Mergler, D., Lucotte, M., Betancourt, O., Davidson, R., Cueva, E., Quizhpe, E., 2004. Mercury in Fish-eating Communities of the Andean Amazon. Napo River Valley, Ecuador. Ecohealth 1, SU59-SU71. https://doi.org/10.1007/s10393-004-0063-0.
World Gold Council, 2017. Gold Market Primer Mine production Abril [WWW Document]. URL www.gold.org.