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THE TOXIC LEGACY OF ARTISANAL AND INFORMAL MINING: XRF AND GIS ANALYSIS OF SOIL CONTAMINATION BY Hg, Pb AND As IN THE SECOCHA ANNEX, CAMANÁ, PERU

El legado tóxico de la minería artesanal e informal: análisis FRX y SIG de contaminación del suelo por Hg, Pb y As en el Anexo Secocha, Camaná, Perú

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Key words: Hg, Pb, As, Igeo, X-ray fluorescence.

ABSTRACT

Hg, used as the main input in the gold amalgamation process in artisanal mining, along with lead Pb and As present in the toxic waste resulting from mining activity, cause serious effects on the environment and human health, as it occurs in the Secocha annex (Camaná, Peru). The objectives of the present study were to determine the concentrations of Hg, Pb, and As in the soil of the Secocha annex, evaluate the level of contamination of the site, determine the spatial distribution of contamination and the concentrations of the evaluated elements, and determine the origin of these contaminants. To achieve these objectives, satellite imagery, field sampling, X-ray fluorescence techniques, soil quality environmental regulations, geo-accumulation indices (Igeo), and geographic information system techniques were used. The results revealed maximum concentrations of 350 and 176.6 mg/kg for Hg and Pb, respectively. Of the 72 soil samples collected, the concentrations of Hg located within the urban/industrial area, where gold recovery activities are carried out, exceeded environmental regulations to a greater extent. In turn, the calculated Igeo revealed extreme soil contamination (5 < Igeo) due to the presence of Hg in most of the study area (95%), followed by moderate to heavy contamination (2 < Igeo < 3) due to the presence of Pb and As (0.5 and 5%, respectively). To reduce contamination and the concentrations of the evaluated elements, it is recommended to carry out studies to reuse inputs, change gold processing methodologies, and/or relocate the generated waste.

Palabras clave: Hg, Pb, As, Igeo, fluorescencia de rayos X.

RESUMEN

El Hg, utilizado como insumo principal en el proceso de amalgamación del oro en la minería artesanal, junto con el Pb y el As presentes en los desechos tóxicos resultantes de la actividad minera, provocan graves efectos en el medio ambiente y en la salud humana, tal como ocurre en el anexo de Secocha (Camaná, Perú). Entre los objetivos del presente estudio se consideró determinar las concentraciones de Hg, Pb y As en el suelo del anexo de Secocha, evaluar el nivel de la contaminación del lugar, determinar la distribución espacial de la contaminación y las concentraciones de los elementos evaluados, y determinar el origen de estos contaminantes. Para alcanzar estos objetivos se utilizaron imágenes de satélite, muestreo en campo, técnicas de fluorescencia de rayos X, normativas ambientales de calidad de suelo, índices de geo-acumulación (Igeo) y técnicas de sistemas de información geográfica. Los resultados revelaron concentraciones máximas de 350 mg/kg y 176.6 mg/kg para Hg y Pb, respectivamente. De las 72 muestras de suelo recolectadas, las concentraciones de Hg ubicadas dentro del área urbano/industrial, donde se llevan a cabo actividades de recuperación de oro, fueron las que superaron en mayor medida las normativas ambientales. A su vez, los Igeo calculados mostraron una contaminación extrema del suelo (5 < Igeo) por la presencia de Hg en la mayor parte del área de estudio (95 %), seguido por una contaminación de moderada a fuerte (2 < Igeo < 3) por la presencia de Pb y As (0.5 y 5 %, respectivamente). Con la finalidad de reducir la contaminación y las concentraciones de los elementos evaluados, se recomienda llevar a cabo estudios para la reutilización de insumos, cambiar de metodologías para el procesamiento del oro y/o reubicar los desechos generados.

INTRODUCTION

Peru's Law No. 27651 (GP 2002), regulated by Supreme Decree No. 013-2002-EM, may have established formalization procedures for artisanal and small-scale mining, but in reality, the miners face a myriad of challenges. From insufficient economic, technical, and technological resources to implement environmental measures, as well as limited knowledge of administrative and legal procedures, to prior informality and a lack of access to credit and formal markets, these miners struggle to meet the regulations. The barriers are significant, and they demand attention if artisanal and small-scale mining in Peru is to thrive.

Extracting precious metals requires using chemicals and large quantities of water in the extraction wells. The substances inside the shafts, which in turn depend on the type of soil or mine, combined with the chemicals used, produce a large amount of toxic waste. Toxic wastes from tailings and waste rock mining processes include lead (Pb), cadmium (Cd), arsenic (As), and free cyanide, among others (López et al. 2003). In artisanal gold mining, the recovery of this element is traditionally carried out by amalgamation of gold with mercury (Hg) or by the cyanidation process. The amalgamation technique is widely used in this type of mining by several developing countries because it turns out to be a simple methodology that requires little capital investment (Cuentas-Alvarado and Velarde-Ochoa 2005, Güiza-Suárez and Aristizabel 2013, Saldarriaga-Isaza et al. 2013). However, this methodology has caused serious environmental and human health damages in both Latin American and African countries (Hilson 2002, Hilson and van der Vorst 2002).

The study area (the Secocha annex) is located in the Department of Arequipa, Peru. It is a wide alluvial cone resulting from the mouth of a narrow and steep valley that descends on the right bank to the Ocoña River, called Posco-Secocha valley, in the middle-upper part of which are the Miski and Posco mines (Quispe-Aquino 2020). Both margins of the Posco-Secocha valley are made up of intrusive rocks and gold-bearing veins of hydrothermal origin with mineralization of pyrite, quartz, chalcopyrite, pyrrhotite, galena, and native gold, precisely where the Miski-Posco mine is located (Quispe-Aquino 2020). Once the ore is extracted to the surface, it is manually reduced, and the highest grade is selected; then it is transported to the Secocha annex to be processed in an artisanal manner using "quimbaletes" (large mortars) and "sopletes" (flame-generating devices). According to Quispe-Aquino (2020), farmers interviewed at the site revealed that the intensive use of Hg began in 2004 and 2005 in the upper part of the Secocha annex.

Research carried out by authors such as Cuentas-Alvarado and Velarde-Ochoa (2005), Costa et al. (2009), Osores-Plenge et al. (2010), Doria-Mesquidaz et al. (2013), Olivero-Verbel et al. (2014), and Rocha-Román et al. (2018) in different locations where similar methodologies were adopted for the gold recovery process in this type of artisanal mining, uncovers that the environmental impacts generated by the use of Hg take place during the processing of the minerals in the quimbaletes to obtain the amalgam, and in the sopletes by the burning of the amalgam. Regarding the use of quimbaletes, although the sludge from the milling process contains a high concentration of Hg (Costa et al. 2009), it should be emphasized that during ore processing, Hg emissions to the environment are also generated by evaporation (Pfeiffer and de Lacerda 1988). During burning, a high percentage of Hg is released into the atmosphere, affecting the health of personnel involved in this activity and the nearby population (Cuentas-Alvarado and Velarde-Ochoa 2005, Costa et al. 2009, Rocha-Román et al. 2018). Exposure to Hg can cause various health problems, such as headache, amnesia, insomnia, nausea, emotional changes (depression and anxiety), memory loss, and neurological alterations (Casas et al. 2015). Moreover, there is evidence associating exposure to Hg compounds and cancer (UNEP 2002).

According to Kalnicky and Singhvi (2001), field portable X-ray fluorescence (FPXRF) spectrometry is a common analytical technique that allows a much faster turnaround time than conventional soil analysis methods. FPXRF technology has been widely accepted by the environmental community as a viable analytical approach for field applications due to the availability of an efficient radioisotope excitation source combined with highly sensitive detectors and their associated electronics (Kalnicky and Singhvi 2001). Complementing this technique, Geographic Information Systems (GIS) are supported by the work of numerous authors (e.g., Tao 1995, Mielke et al. 2000, Facchinelli et al. 2001, Norm et al. 2001, Romic and Romic 2003) as a method to analyze the distribution of heavy metals in soil and determine their possible origins. On the other hand, Natural Neighbors (NN) is a rather practical spatial interpolation method that requires few decision parameters and offers acceptable results for sampling points with an irregular distribution (Garzón-Barrero 2013). It consists of an alternative to linear interpolation based on the Delaunay triangulation (Sibson 1981), where the value of an interpolation point is estimated from weighted values of the nearest surrounding points in a triangulation (Bannister and Kennelly 2015). The authenticity of this technique can be verified in the work done by Garzón et al. (2012).

Given the conditions of the study area, in which workers and local people, including children, are exposed to substances harmful to health and the environment, it is considered necessary to perform the following actions:

1. Determining the concentrations of Hg and Pb in soil, since both have been classified as priority pollutants by the United States Environmental Protection Agency (Yang et al. 2018) and regulations and As, a metalloid with chemical properties and environmental behavior similar to that of heavy metals (Hu and Cheng 2013). For this purpose, the FPXRF technique will be used, and the concentrations will be compared to the environmental quality standards proposed by Peru, Canada, and Australia.
2. Determining the degree of contamination of the site using geo-accumulation indices (Igeo) proposed by Müller (1981).
3. Analyzing the spatial distribution of the evaluated elements' concentrations and determining the sources of contamination, as well as the spatial distribution of the Igeo using interpolation techniques and GIS.

The results obtained will allow competent authorities to formulate strategies, implement measures to reduce pollution in the area, and make informed decisions.

MATERIALS AND METHODS

Study area

The Secocha annex is located in the district of Mariano Nicolás Valcárcel, in the province of Camaná, between 695 086-697 609 m East and 823 2707-823 1154 m South, with an altitude between 400 and 600 masl (**Fig. 1**). The climate is of the Lomas to Desert subtype, with clear sky and high temperatures. The average annual temperature is 19.5 ºC, with February being the hottest month at 27.1 ºC and August being the coldest, with a temperature of 12.7 ºC. The average annual precipitation is 0.75 mm, with a minimum average precipitation of 0 mm in April and a maximum of 5 mm in January (Peña-Contreras and López-Tejeira 2020). According to Quispe-Aquino (2020), the Secocha annex has a population of 15 000 inhabitants, mainly concentrated in the urban/industrial zone. In addition, there is an area dedicated to agriculture in this locality, where different products such as wheat, beans, and potatoes, among others, are cultivated. However, through the analysis of satellite images, it has been identified that out of the 150 ha designated for agriculture, only 70 ha are being utilized.

Delimitation of the study area

To compare the soil concentrations of the elements evaluated with the proposed environmental quality standards (**Table I**), the study area was divided into three zones (**Fig. 2**, **Table II**); however, priority was given to the evaluation and sampling of Zone 1 (urban/industrial area) and Zone 2 (agricultural area) for the following reasons:

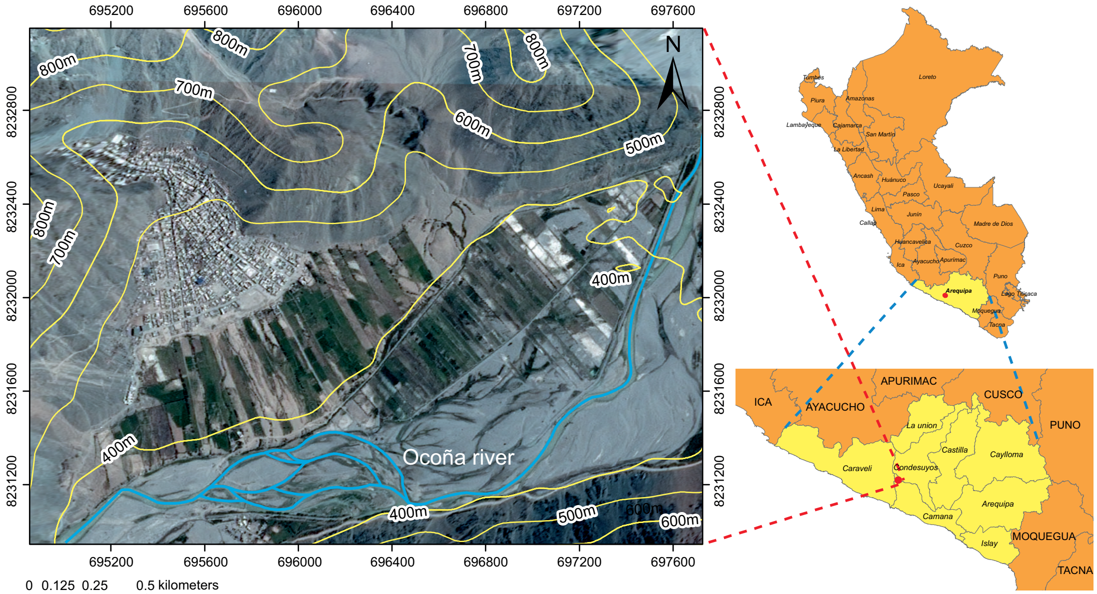

Fig. 1. Satellite image of the study area (Secocha annex), located in the province of Camaná in the Arequipa region (Peru).

TABLE I. ENVIRONMENTAL REGULATIONS FOR SOIL QUALITY.

Soil classification	Element	Soil quality standard (mg/kg)		
		ECA Peru	SQG Canada	HIL Australia
Urban/industrial	Hg	6.6	24	120
	Pb	140	140	1200
	As	50	12	500
Agricultural	Hg	6.6	6.6	-
	Pb	70	70	-
	As	50	12	-

ECA: Peruvian environmental quality standard.
SQG: Canadian soil quality guidelines for the protection of the environment and human health.
HIL: Australian health investigation levels.

Zone 1 contains the quimbaletes and sopletes, where the gold amalgamation processes with Hg are carried out, and where the amalgam is burned in the sopletes. Residual materials from these activities are stored in bags scattered to a greater or lesser extent throughout the area. Poultry is raised in the area and is used for human consumption despite being in direct contact with the soil. Zone 1 is where most of the population is concentrated, and the largest number of houses, gold sales stalls, and some sports fields are located, which are used by the local children. The soil is quite compact due to the continuous transit of trucks that transport not only workers to the different mining operations but also basic necessities. This soil characteristic is also attributed to the fact that the inhabitants discharge wastewater from inside their homes directly into the street because there is no drainage system. Zone 2 consists of productive cropland that supplies the population. Zone 3 corresponds to farmland with no agricultural production, in other words, it is in disuse.

Contamination assessment

Location of sampling points

In the urban/industrial and agricultural areas, the sampling points were distributed regularly using a 150 × 150 m grid to obtain greater detail and precise concentrations of the elements evaluated.

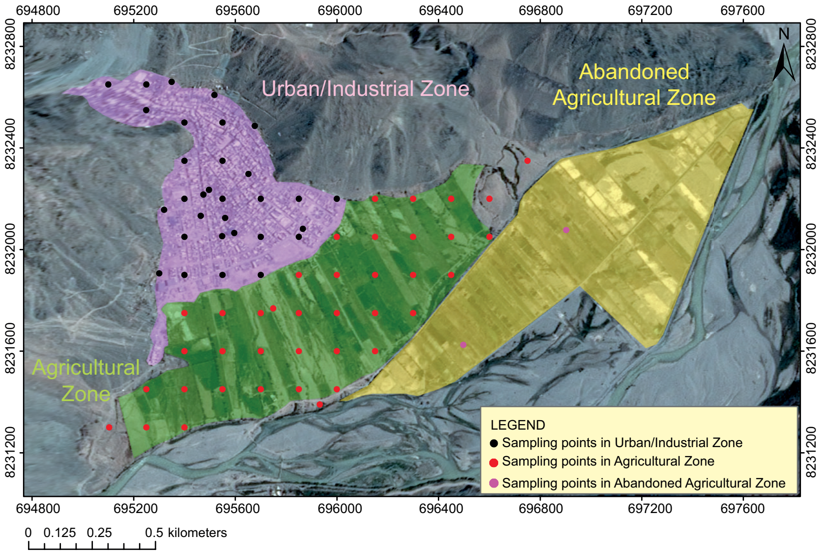

Fig. 2. Delimitation of the study area into zone 1: urban/industrial area (pink), zone 2: agricultural area (green), and zone 3: abandoned agricultural area (yellow). Black dots correspond to samples located within the urban/industrial area, red dots to samples located within the agricultural area, and pink dots to samples located within the abandoned agricultural area.

TABLE II. DESCRIPTION OF THE EVALUATED AREAS.

Evaluated Area	Description
Urban/Industrial	The majority of the population is concentrated in this sector, where gold recovery activities using sopletes and quimbaletes are carried out and gold sales stalls are abundant.
Agricultural	In this sector, agriculture is active, vegetables are harvested to supply the population, and part of this area is in contact with the Ocoña River.
Abandoned Agricultural	Agriculture was previously developed in this sector, but currently, the land is unused.

The sampling points that were not accessible due to the position of the houses were slightly displaced from their original position, registering the new coordinates with a GPS navigator (Garmin brand) that had an acceptable positioning error (less than 5 m). Additionally, certain sectors were sampled that were considered of interest due to their proximity to quimbaletes, sopletes, and gold-selling posts (**Fig. 3**, **Table III**).

Soil sample collection

At each sampling point, a small hole was dug from which the material to be analyzed was extracted. To avoid direct contact of the personnel with the collected soil sample and contamination of different specimens with each other, latex gloves were used, which were discarded and replaced by new ones at the time of each sampling. A small plastic shovel was used to remove the soil surface, which was cleaned with water each time new samples were collected. Each extracted sample was preserved in polypropylene bags with a thickness of 0.2 mm and a capacity of 750 g, labeled with their respective code (**Table IV**). A portable cooler was used to transport the samples to the laboratory, where they were sieved with 2 mm mesh sieves for subsequent analysis.

Sampling in the urban/industrial area

The sampling depth in the urban/industrial area was 0 to 10 cm. No deeper depths were dug due to soil compaction. Although in some studies, a sampling depth of 0 to 20 cm has been considered adequate for assessing the presence of heavy metals in soil (Akoto et al. 2008, Yang et al. 2018, Li et al. 2019, Wang et al. 2019), others have used a depth of 0 to 10 cm for this purpose (Ma et al. 2015, Qing et al. 2015).

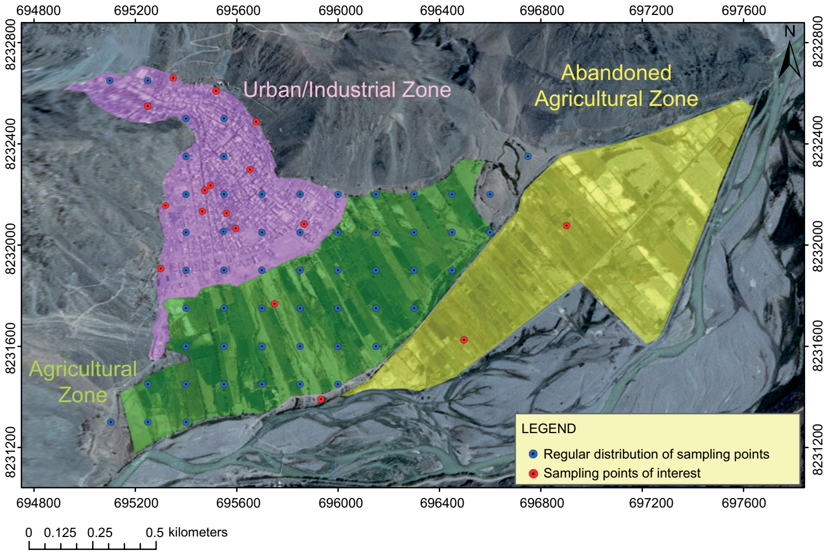

Fig. 3. Distribution and labeling of sampling points in the study area. Blue points (random points) correspond to the initial strategic grid of 150 × 150 m. Red points (points of interest) correspond to complementary samples to achieve greater detail and accurately determine the evaluated elements' concentrations.

TABLE III. CLASSIFICATION, DESCRIPTION, AND DISTRIBUTION OF SAMPLING POINTS BASED ON THE RECOMMENDATIONS OF MINAM AND ARMA.

Classification	Description	Evaluated Area		
		Urban/Industrial	Agricultural	Abandoned Agricultural
Points of Interest (n = 17)	According to Ministerio del Ambiente (MINAM) and Autoridad Regional Ambiental (ARMA) experts, 17 sampling points were considered as points of interest in specific sectors of the study area.	13	2	2
Regularly distributed points (n = 55)	Systematic statistical sampling was carried out using a regular grid pattern as the sampling scheme in order to cover the potentially contaminated site area homogeneously and obtain random sampling points. This type of sampling was chosen because the distribution of pollutants in the site was not clear.	18	37	0

TABLE IV. CLASSIFICATION OF SAMPLING POINTS ACCORDING TO THE EVALUATED AREA AND THE SAMPLE CODE.

The number of samples	Evaluated Area
31	Urban/Industrial
39	Agricultural
2	Abandoned Agricultural

sc-UIz-Nº: Secocha - Urban/Industrial zone - The number of samples.
sc-Az-Nº: Secocha - Agricultural zone - The number of samples.
sc-Aaz-Nº: Secocha - Abandoned Agricultural zone - The number of samples.

Sampling in the agricultural area

Sampling in this uncompacted soil allowed a depth of 20 cm to be reached using a hand auger. The procedure for preserving and transporting the samples was the same as for the urban/industrial area.

XRF instrumentation and elemental analysis

Given the advantages and support of the FPXRF technique (Kalnicky and Singhvi 2001), an XRF analyzer was used for the quantitative analysis of soil samples. Once the soil samples were in the laboratory, the FPXRF analyzer M series, model VANTA, Olympus brand, was placed directly on the sampling bags. The XRF analyzer was calibrated using the same thickness as the polypropylene bag to further minimize these undesirable effects. To ensure that the information obtained when using PXRF is reliable, two important aspects were considered: 1) the air was isolated from the sampling bag containing only the specimen to be evaluated, and 2) each sampling bag stored a material content equivalent to three-quarters of its capacity, which avoided masking due to the presence of the polypropylene. With the discharge capacity offered by the FPXRF analyzer, the results of the evaluated elements' concentration values were obtained in a spreadsheet, from which the statistical analyses and the calculation of the Igeo were performed and served as input data for the elaboration of the interpolation maps.

Heavy metals and international environmental regulations

Hg, Pb, and As were the evaluated elements given their chemical properties, characteristics, and health effects, as mentioned by Hu and Cheng (2013) and Yang et al. (2018). The concentrations of these elements were compared to the environmental quality standards for soils (ECAs) D.S. Nº 002-2013-MINAM (MINAM 2013), soil quality guidelines (SQG) (CCME 2007), and health investigation levels (HIL) for soil (EMA 2013) proposed by the regulations of Peru, Canada, and Australia, respectively. Peruvian ECAs regulations were considered since they are followed in the country where the study area is located. In the absence of ECA regulations for the evaluated elements, it was deemed appropriate to resort to Canadian SQG regulations, which have values similar to those of the ECAs and, like the latter, take into account human health, ecological receptors, and the environment. The Australian HIL regulation has a more human health-oriented approach, which explains the higher concentrations compared to the previous ones. Collectively, these three regulations work well when evaluating ecological receptors, the environment, and human health. Furthermore, the use of these regulations is supported by a report prepared by MINAM (2016).

Determination of soil contamination

To determine the level of soil contamination, the geo-accumulation index (Igeo) proposed by Müller (1981) was used:

$$Igeo = log_2\left[\frac{Cn}{A \times Bn}\right] \quad (1)$$

where A is a constant whose value is 1.5, Cn corresponds to the concentration of the metal or metalloid in the soil, and Bn to the geochemical background value of the same element evaluated. To determine the Igeo, Bn values proposed by Fernández-Ochoa et al. (2022) for Pb (17 mg/kg) and As (4.8 mg/kg), and the Bn value proposed by Berrow and Reaves (1984) for Hg (0.06 mg/kg) were used. Values of Igeo < 0 characterize the soil as practically uncontaminated, 0 < Igeo < 1 as uncontaminated to moderately contaminated, 1 < Igeo < 2 as moderately contaminated, 2 < Igeo < 3 as moderate to heavily contaminated, 3 < Igeo < 4 as heavily contaminated, 4 < Igeo < 5 as heavily contaminated to extremely contaminated, and 5 < Igeo as extremely contaminated (López-Pérez et al. 2018).

Concentration and Igeo mapping

Given the advantages and authenticity of the NN technique (Garzón et al. 2012, Garzón-Barrero 2013), this was the interpolation method used to generate interpolation maps for the concentrations of the evaluated elements and the Igeo. The software used to elaborate these maps was ArcMap 10.4.1.

RESULTS

PXRF study: basic statistics and comparison of environmental regulations

Table V summarizes the statistical parameters (range, mean, median, standard deviation [SD], percentiles, skewness coefficient [Skw], and kurtosis [Kur]) of Hg, Pb, and As concentrations. The soil samples with the concentrations mentioned above were taken at the end of 2018, providing insight into the state of the soil at that time. **Table VI** compares the number of samples that exceed the proposed standards under the ECA, SQG, and HIL regulations. The statistical distribution of the evaluated elements' concentrations for the urban/industrial and agricultural areas is presented in box plots (**Fig. 4**) created using JASP software v. 0.14.0.0.

Interpolation maps of concentrations and Igeo

Four maps of Hg concentrations were prepared: three for the urban/industrial area (**Fig. 5a-c**) and one for the agricultural area (**Fig. 5e**), where a single map was created for both the Peruvian (ECA) and Canadian (SQG) regulations since the two coincide. The Australian regulation, on the other hand, does not have a directive for this element. Regarding Pb, a single map was created for the urban/industrial area since the Peruvian and Canadian regulations also coincide (**Fig. 5d**). In contrast, no map was created for the Australian regulation since the collected samples did not exceed the permitted values. Similarly, a single map for the agricultural area was prepared with the ECA and SQG (**Fig. 5f**) since the Peruvian and Canadian regulations coincide; the Australian regulation does not have a guideline regulation for this element, so no map was created for it. For As, a single map was created for the entire Secocha annex (**Fig. 5g**) since concentrations evaluated with the SQG slightly exceeded the permissible threshold, which is the same for both the urban/industrial and agricultural areas. No maps were

TABLE V. BASIC STATISTICS OF Hg, Pb AND As CONCENTRATIONS IN SOIL FROM SECOCHA ANNEX (in mg/kg).

Soil type	Element	Range	Mean	Median	S.D.	Skw.	Kur.	Percentiles							
								5	10	25	50	75	90	95	98
Urban/ Industrial (n=31)	Hg	2.8 - 350.0	37.9	11.5	81.5	3.4	11.2	3.1	4.1	6.3	11.5	25.2	60.5	198.2	326.0
	Pb	15.0 - 176.6	48.4	38.7	36.0	1.9	4.4	16.0	17.4	26.1	38.7	60.9	87.8	113.6	141.5
	As	7.7 - 33.9	20.4	20.1	6.9	0.1	-0.4	9.4	11.8	15.3	20.1	24.9	26.6	33.0	33.5
Agricultural (n= 41)	Hg	0.0 - 25.0	4.4	3.6	3.7	4.5	24.4	2.2	2.2	3.0	3.6	4.3	5.2	8.6	13.2
	Pb	12.0 -93.0	23.9	17.6	17.2	2.8	8.0	14.2	14.3	15.9	17.6	20.7	40.2	65.0	80.2
	As	6.4 - 39.0	23.8	23.3	6.9	–0.2	1.2	9.7	17.6	20.2	23.3	27.8	30.4	36.8	38.6

* Standard Deviation (S.D.).
* Skewness coefficient (Skw.).
* Kurtosis (Kur.).

TABLE VI. CLASSIFICATION OF SAMPLING POINTS BASED ON ASSESSED REGULATIONS.

Soil type		Peru	Canada	Australia	Peru	Canada	Australia	Peru	Canada	Australia
		NER			CER			ER		
Urban/ industrial (n = 31)	Hg	3	23	28	6	0	1	22	8	2
	Pb	28	28	31	2	2	0	1	1	0
	As	31	1	31	0	3	0	0	27	0
Agricultural (n = 41)	Hg	26	26	-	11	11	-	4	4	-
	Pb	38	38	-	1	1	-	2	2	-
	As	41	1	-	0	0	-	0	40	-

NER: Not Exceeding the Regulation.
CER: Close Exceeding the Regulations.
ER: Exceeding the Regulation.

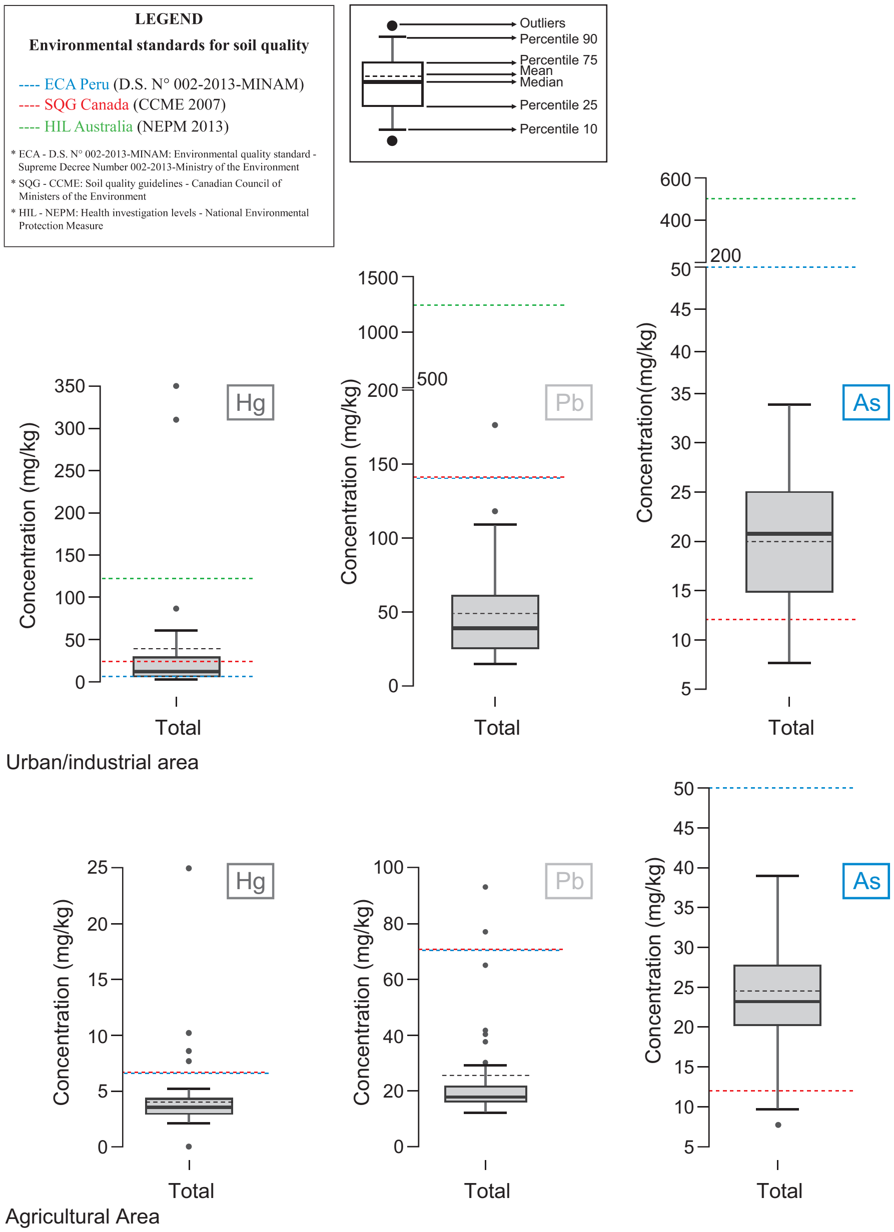

Fig. 4. Box plots showing the statistical distribution of Hg, Pb, and As concentrations in urban/industrial and agricultural soil areas of the Secocha annex, emphasizing median, quartiles, dispersion, and outlier identification.

created for the Peruvian and Australian regulations since none of the collected samples exceeded the permissible values.

Based on the calculated Igeo values, it is evident that the soil is extremely contaminated (5 < Igeo) due to the presence of Hg in most of the study area (95%), followed by heavy to extreme contamination (4 < Igeo < 5) in some sectors of the agricultural area (5%) (**Fig. 6a**). Furthermore, Igeo values for Pb (**Fig. 6b**) reveal sectors with moderate to heavy contamination (2 < Igeo < 3) that comprise up 0.5% of the total area, while moderately contaminated sectors (1 < Igeo < 2) represent 10%. Additionally, 37% of the study area is classified as uncontaminated to moderately contaminated (0 < Igeo < 1). Notably, these percentages mainly apply to the urban/industrial area; however, the practically uncontaminated category (Igeo < 0) accounts for 52% of the total study area, primarily concentrated in the agricultural area. Igeo values for As show that while most of the soil is moderately contaminated (77%), there are small sectors both within the urban/industrial area and the agricultural area where the soil is moderate to heavily contaminated (5%) (**Fig. 6c**).

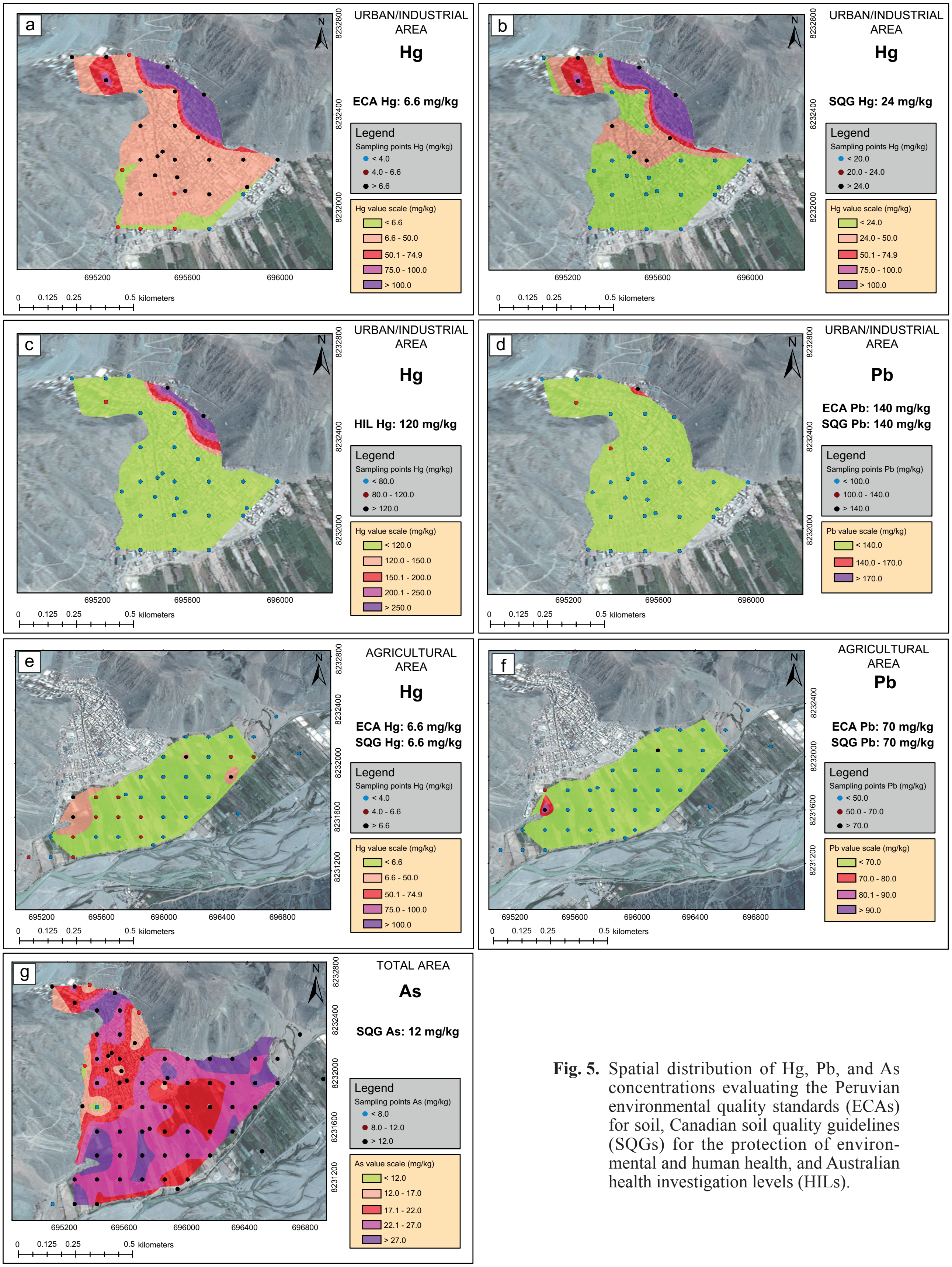

Fig. 5. Spatial distribution of Hg, Pb, and As concentrations evaluating the Peruvian environmental quality standards (ECAs) for soil, Canadian soil quality guidelines (SQGs) for the protection of environmental and human health, and Australian health investigation levels (HILs).

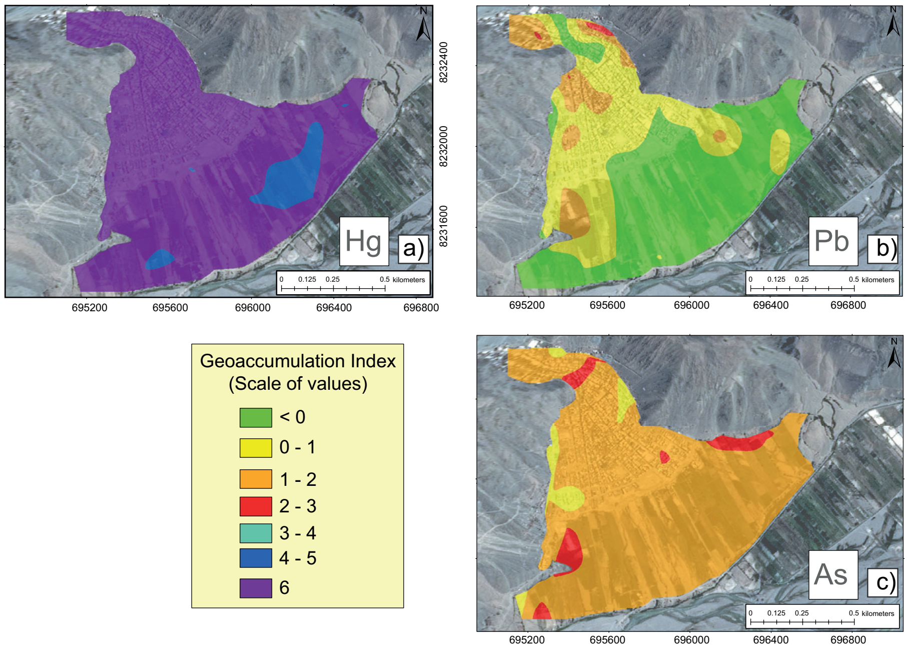

Fig. 6. Spatial distribution of geo-accumulation indices (Igeo) for Hg, Pb, and As in the Secocha annex.

DISCUSSION

Pollutants' spatial distribution patterns

The purpose of the present study was to evaluate the content of Hg, Pb, and As in the soil of the Secocha annex, and high concentrations of these elements were found, especially in the urban/industrial area, where values significantly exceeded the limits established by environmental quality standards, posing a serious risk to the health of the population, ecosystems, and the environment (CCME 2007, EMA 2013, MINAM 2013) (**Fig. 5**). In turn, the Igeo revealed severe levels of contamination (**Fig. 6**), as the maximum category corresponds to extreme contamination due to the presence of Hg. The distribution of the concentrations of each evaluated element and the pollution present in the location are described below.

Hg

The ECA of 6.6 mg/kg adopted by Peruvian regulations (**Fig. 5a**) is greatly exceeded within the urban/industrial area. The most affected zone (violet area in the figure) is due to a large number of sopletes and gold-selling stalls where amalgam burning takes place, an activity that, according to Cuentas-Alvarado and Velarde-Ochoa (2005), Costa et al. (2009) and Rocha-Román et al. (2018), releases Hg into the atmosphere. When condensed, deposited on the soil, and redistributed by vehicular traffic and human activity (Adjorlolo-Gasokpoh et al. 2012, Rocha-Román et al. 2018), Hg results in the high concentrations observed in the surrounding areas (pink and red zone). In the pink and red zones at the head of the alluvial cone, some sports fields are adjacent to a high number of quimbaletes, hence a higher amalgamation process occurs. The main input of this activity is Hg (Cuentas-Alvarado and Velarde-Ochoa 2005, Güiza-Suárez and Aristizabel 2013, Saldarriaga-Isaza et al. 2013), and scattered bags containing residual material from gold recovery, which still have a high Hg content (Costa et al. 2009), have also been observed in the area. This is a cause for concern since children use these facilities, affecting their health and capacity (UNEP 2002, Casas et al. 2015). The remaining samples that exceed this regulation (cream zone) are due to quimbaletes scattered throughout the urban/industrial area, and since their number decreases significantly in areas adjacent to agricultural land, Hg concentrations also decrease (green zone). The SQG of 24 mg/kg adopted by Canadian regulations emphasizes those areas where Hg concentrations are higher and, therefore, pose a greater risk to ecosystems and ecological receptors. Both the central part (cream zone) and the head of the alluvial cone coincide with those sectors where a higher number of quimbaletes are concentrated

(**Fig. 5b**). The HIL of 120 mg/kg, adopted by Australian regulations focuses on the area where the amalgam burning activity is carried out, located on the left flank of the alluvial cone (**Fig. 5c**), which, according to MINAM et al. (2016), poses a serious threat to human health and must be carefully evaluated.

Regarding the agricultural area (**Fig. 5e**), it has been observed that a large number of samples with concentrations close to or above the limits established by the ECA and SQG of 6.6 mg/kg are located towards the right flank and, to a lesser extent, towards the left flank of the alluvial cone's mouth. This spatial distribution is due to the deposition of residual material resulting from mining activities without any safety protocol; when interacting with the environment, this material causes the evaporation of Hg (Pfeiffer and de Lacerda 1988) and can be transported by the atmosphere due to its ability to be in a gaseous state (de la Rosa et al. 2004, Fu et al. 2010, Li and Tse 2015).

Pb

When evaluating the 140 mg/kg ECA and SQG for Pb within the urban/industrial area (**Fig. 5d**), it was determined that the highest concentration (red zone in the figure) spatially coincides with the highest concentration of Hg located in the sector where the gold sales stalls and sopletes are located. According to the ATSDR (2016), soil can be a reservoir for airborne particles with Pb residues. Additionally, Nolasco-Macollunco (2001) states that the highest Pb concentration values are found near emission sources. These two factors explain why Pb concentrations in the soil of the analyzed sector are high. The samples with Pb concentrations close to exceeding these regulatory standards coincide with concentrations of Hg samples in areas with higher amounts of quimbaletes, which can be explained based on the findings of López et al. (2003) and Figueroa-Sánchez and Hurtado-León (2011), who state that Pb concentrations are an inherent characteristic of materials extracted from the wells. The latter conducted a soil sampling in six adjacent pits near Cerro El Toro in La Libertad, where artisanal gold mining is practiced, and determined that Pb concentrations vary significantly from one pit to another, with minimum values of 9.32 mg/kg and maximums of 218.20 mg/kg.

When evaluating the 70 mg/kg ECA and SQG for Pb in the agricultural area (**Fig. 5f**), it is observed that the spatial arrangement of the highest concentrations of Pb coincides with those of Hg. The latter are localized and do not show a dissemination pattern, which is attributed to the presence of piles of residual material. The influence of wind and/or atmospheric transport is not decisive in these areas since the Pb is strongly adhered to the soil and residual material, which coincides with observations by the ATSDR (2016).

As

Coinciding with López et al. 2003, the As concentrations recorded in the Secocha annex (**Fig. 5g**) are characteristic of materials extracted from the wells for processing, whose residues release this metalloid when abandoned and exposed to environmental conditions (Filippi 2004). The dissemination of As throughout the entire study area is the result of the important role played by wind dispersion in this type of arid-semiarid environment, as mentioned by Razo et al. (2004), Navarro et al. (2008) and Romero et al. (2008), in accordance with the climatic conditions of the site described by Peña-Contreras and López-Tejeira (2020). The sectors with the highest As concentrations, such as the head of the alluvial cone and much of the agricultural zone (violet areas in the figure), coincide with the zones where the highest concentrations of Hg and especially Pb were recorded, which is related to the findings of Santos-Santos et al. (2006), who state that contaminants such as As are commonly found in areas with Pb pollution.

Geo-accumulation index (Igeo)

According to Casas et al. (2015), exposure to Hg like it occurs in the Secocha annex (**Fig. 6a**) can cause various health problems such as amnesia, headache, nausea, emotional changes, memory loss, and neurological alterations, among others. Therefore, the presence of high levels of Hg contamination in the study area suggests a possible impact on the health of residents and workers. In addition, according to UNEP (2002), there is evidence linking exposure to Hg components to cancer. Given the degree of extreme contamination by Hg, it is likely that these health effects will become even more severe over time.

On the other hand, chronic exposure to soil pollution, which is considered moderate to heavy due to the presence of Pb and As (**Fig. 6b**, **c**), can cause paresthesia, myalgia, arthralgia, general fatigue, weight loss, paralysis, encephalopathy, dark blue line on the gums, intermittent and severe colic, changes in skin color, renal failure, cardiovascular diseases, arteriosclerosis, and neurological effects. These symptoms, signs, and/or toxic effects on health have been mentioned by Singh and Ma (2006), Poma (2008), Burger and Pose-Román (2010), and

Rodríguez-Rey et al. (2016). Additionally, the World Health Organization warns that there is evidence suggesting that prolonged occupational exposure to Pb contributes to the development of cancer (IARC/WHO 2006, WHO 2019).

CONCLUSIONS

Maximum concentrations of Hg (350 mg/kg) and Pb (176.6 mg/kg) were recorded in the urban/industrial area of the Secocha annex. The spatial distribution of these concentrations is related to 1) amalgam burning activity, 2) gold amalgamation, 3) poor conservation of mining waste, and 4) wind as a dispersing agent, the latter not being determinative in the case of Pb. The spatial distribution of soil samples with concentrations of Pb that exceed or are close to exceeding the environmental quality standards of Peru and Canada coincides with samples containing concentrations of Hg that also exceed these standards and the Australian standard. The calculated Igeo values revealed extreme soil contamination (5 < Igeo) due to the presence of Hg in most of the study area (95%), followed by moderate to heavy contamination (2 < Igeo < 3) due to the presence of Pb and As (0.5% and 5%, respectively). Given the chronic exposure and the degree of contamination by Hg, it is likely that the effects on the health of the inhabitants will become even more severe over time. XRF sampling and GIS were necessary to achieve the objectives proposed in this study. A prior recognition of the study area is recommended to avoid displacing and/or relocating the sampling points in the field. Based on the results obtained and to reduce contamination and the concentrations of the evaluated elements, studies should be carried out to reuse inputs and/or change methodologies for gold processing and/or relocate the generated waste.

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