Revista Brasileira de Ciência do Solo

Division - Soil Use and Management | Commission - Soil Pollution, Remediation and Reclamation of Degraded Areas

Heavy metals and pesticides in soils under different land-use patterns in neotropical high Andean *Páramos*

Lizeth Manuela Avellaneda-Torres[(1)*], Andrea Patricia Pinilla Núñez[(2)], Laura Daniela Jerez Pérez[(2)] and Baudilio Acevedo Buitrago[(3)]

[(1)] Universidad Libre, Facultad de Ingeniería, Instituto de Posgrados, Programa de Ingeniería Ambiental, Grupo de Investigación Tecnoambiental, Bogotá, Colombia.
[(2)] Universidad Libre, Facultad de Ingeniería, Programa de Ingeniería Ambiental, Bogotá, Colombia.
[(3)] Universidad Nacional de Colombia, Facultad de Ciencias, Bogotá, Colombia.

*** Corresponding author:**
E-mail: lizethm.avellanedat@unilibre.edu.co

Received: October 04, 2021

Approved: March 04, 2022

How to cite: Avellaneda-Torres LM, Núñez APP, Pérez LDJ, Buitrago BA. Heavy metals and pesticides in soils under different land use patterns in neotropical high Andean *Páramos*. Rev Bras Cienc Solo. 2022;46:e0210135. https://doi.org/10.36783/18069657rbcs20210135

Editors: José Miguel Reichert and Leônidas Azevedo Carrijo Melo.

ABSTRACT: *Páramos* are unique strategic ecosystems in the neotropical region, above the upper limit of closed forest and below the lower limit of perpetual snow in the tropical mountains of Central and South America. Their soils are of particular importance for water regulation and carbon storage; however, thousands of peasants develop agricultural activities such as potato cultivation and livestock farming in these areas. This research aimed to evaluate the possible heavy metals contents (arsenic, cadmium, mercury, and lead) and pesticide residues (348 in total) associated with potato cultivation and livestock farming activities in soils of *Páramo* ecosystems (Cruz Verde and El Verjón) in Cundinamarca, Colombia. Soil samples are from areas in the *Páramo* under potato crops and livestock farming, at two different altitudes: 3300 m a.s.l. (meters above sea level) and 2900 m a.s.l.; and then, the physical-chemical properties, heavy metals, and pesticide content were determined in each sample. The results showed that none of the soils evaluated exceeded the concentrations of heavy metals permitted by the normativity that was analyzed. On the other hand, we found the presence of the fungicide dimethomorph (0.27 mg kg^{-1}) in soils under potato crops at altitudes 1 and 2, fungicide metalaxyl (0.013 mg kg^{-1}) in soils under potato crops at altitude 1, and insecticide thiamethoxam (0.048 mg kg^{-1}) in soils under potato crops at altitude 2. Anyhow, the statistical analysis did not show significant heavy metals contents or pesticide residues in the *Páramo* soils associated with potato cultivation and livestock farming; nonetheless, there are significant impacts on five of the physicochemical properties of the soils under study (moisture, bulk density, organic carbon, cation exchange capacity, and phosphorus). Although soil physicochemical parameters properties were modified by soil potato crop and cattle raising, these land land-use types did not cause relevant impacts heavy metals and pesticides, which could be due to the specific agricultural practices adopted in the area (Potato-pasture rotation system, with fallow periods of between 7 and 10 years). Finally, this study represents the first report on heavy metals and pesticide residues in *Páramo* soils.

Keywords: soil contamination, soil quality, environmental pollution, arsenic, cadmium.

INTRODUCTION

Páramos are unique strategic ecosystems that are located in the neotropical region above the upper limit of the closed forest and below the lower limit of perpetual snow in the tropical mountains of Central and South America. They are rich in endemic flora and fauna, with particular ecological functions related to hydrological supply, drinking water generation, hydrogeological regulation, and carbon storage (Díaz-Granados et al., 2005; Hofstede, 1997; Luteyn and Balslev, 1992).

Páramos are located in Colombia, along the three branches of the Andes mountain range, with the greatest extension of this ecosystem in the departments of Boyacá and Cundinamarca. Although the *Páramos* share similar biological, environmental, and climatic characteristics, the soils, vegetation, and anthropic intervention are different in each region, generating particular conditions in these biomes (Bernal-Cuesta, 2017).

Agricultural and livestock farming activities in the *Páramo* ecosystems have generated different impacts. Several studies have reported on the impacts of potato cultivation and livestock farming on the physicochemical properties, enzymatic activities, and microorganisms of the soils in the *Páramo* (Cañon-Cortazar et al., 2012); however, up to date and despite the permanent agricultural activities in these ecosystems, there are no studies on heavy metals and pesticides in the soils of *Páramo* ecosystems under potato cultivation and livestock. *Páramo* is of utmost importance given the consequences on the health of the ecosystems, human beings (as final consumers), and the biological processes of the soils.

Different studies have evaluated the concentration and bioaccumulation of heavy metals and pesticide residues generated due to agricultural activities, given the excessive or inadequate use of fertilizers or pesticides (Alves et al., 2016). Heavy metals can be leached and are not degradable in the environment (Martley et al., 2004; Alloway, 2013; Sidhu, 2016; Ashraf et al., 2019). Crops contaminated with heavy metals, either in the soil or irrigation water, can cause cancer and chronic diseases in the respiratory tract, heart, brain, and kidney (Ashraf et al., 2019).

In the case of pesticides, these are compounds that, depending on their nature, are stable to hydrolysis and photolysis, may be soluble and cause leaching into groundwater, may be resistant to microorganisms, and may also be able to persist for long periods not only in the soil, but also in water and air (FAO and WHO, 2007; Gondar et al., 2013; Bonmatin et al., 2015; Mohapatra et al., 2019; Simon-Delso et al., 2015). Their effects on human health are varied since they travel through the respiratory tract when inhaled in contaminated atmospheres; or through the ingestion of contaminated food either once or repeatedly, or even by contact with the skin, leading the individual to present both acute and chronic toxicity, and causing neurological and reproductive problems, and cancer, among others (del Puerto-Rodriguez et al., 2014). Thus, soil contamination by pesticides in agricultural areas around the world is well documented, such as the case of the study carried out by Silva et al. (2019), which reveals that the presence of mixtures of pesticide residues in soils are the rule rather than the exception, indicating that environmental risk assessment procedures should be adapted accordingly to minimize related risks to soil life and beyond.

The presence of heavy metals in the soil of the *Páramos* is of particular concern, possibly because of the traces that can be found in chemically synthesized fertilizers, which, due to their prolonged use on potato crops, can lead to an increase in their contents. Another concern is the residual nature of pesticides, mainly associated with conventional phytosanitary management with commercial pesticides of different toxicological categories, which are used on potato crops in the *Páramo* areas. On the other hand, and although in the *Páramo* livestock systems, livestock feeding is mainly done with the area's pastures, it is important to mention that there are studies on what has been determined, for example, the contents of heavy metal (Cu, Zn, As, Cr, Cd and Pb) in animal feeds and manures, finding that Animal manure is an important source of heavy metals to the environment in Northeast China (Zhang et al., 2012).

This study aimed to evaluate if there is a significant impact on the increase in the content of heavy metals and pesticide residues in the soils of the *Páramo* that have been intervened with potato cultivation and livestock farming. Additionally, we sought to evaluate if these impacts have any variation when analyzed at two different altitudes. The research hypothesis is that there is a significant increase in the heavy metals contents and pesticide residues in the soils of the *Páramo* due to the potato cultivation and livestock farming activities developed in the area. The present document can be taken as the first report that has been released on the presence of heavy metals and pesticide residues in the soils of the *Páramo*.

MATERIALS AND METHODS

Study area

This study was developed in the area between *Páramo* Cruz Verde and *Páramo* El Verjón, located in the department of Cundinamarca, Colombia (Figure 1). The average temperature in the area is 8 °C, and the main economic activities are potato (Solanum tuberosum), tomato (Solanum lycopersicum) and bean (Phaseolus vulgaris) cultivation, livestock farming, mining, and tourism (Alcaldía Municipal Choachi Cundinamarca, 2008). The agricultural practices developed in the area combine peasant knowledge together with the implementation of Green Revolution technologies. In this way, seeds are planted for a maximum of two consecutive years, followed by rest or fallow cycles of 7 to 10 years, implementing crop rotation systems with livestock, thus avoiding permanent grazing in the same area. However, conventional applications of chemically synthesized pesticides are carried out; namely, carbofuran(Furadan), parathion (Parathion), methamidophos (Monitor), Chlorpyrifos (Lorsban), profenofos (Curacron), mancozeb (Manzate), propínab + cymoxanil (Fitoraz), metalaxyl (Ridomil), hexaconzole (Anvil), and N:P:K-type fertilizers (Avellaneda-Torres et al., 2014).

Type of sampling

To identify the concentration of heavy metals and pesticide residues in *Páramo* soils, soil samples were collected from soils that had been used for potato cultivation, livestock

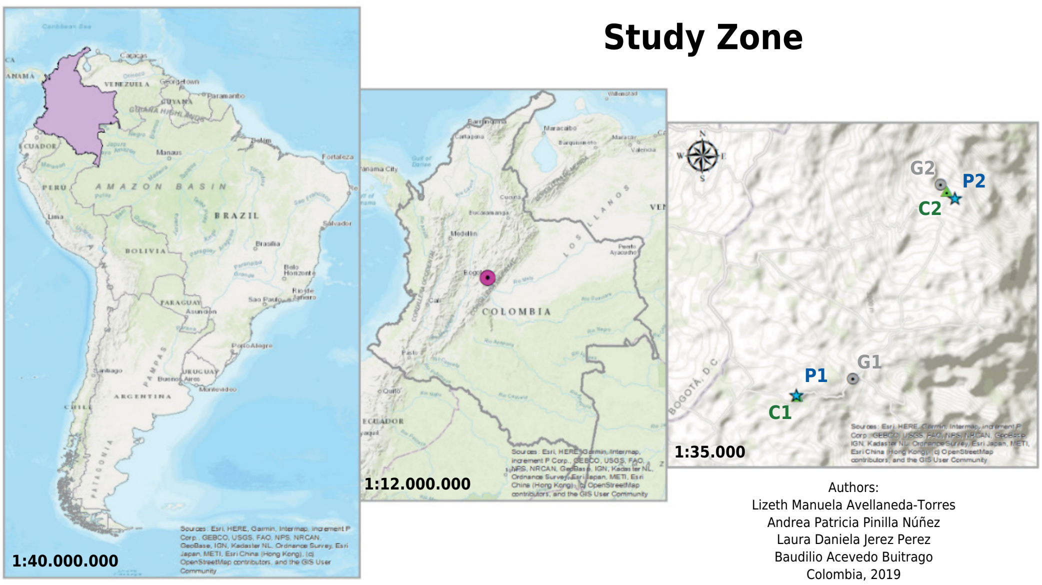

Figure 1. Map presenting where the study area is located.

farming, and *Páramo*-conservation (areas with the least possible anthropic intervention), in two altitudinal ranges, in the area between *Páramo* Cruz Verde and *Páramo* El Verjón, Colombia. Soil samples were taken after the potato crop was harvested in July 2018. Samples under the first altitudinal range were designated as C1, G1, and P1, corresponding to potato crop (3307 MASL), livestock (3246 MASL), and *Páramo* (3310 MASL), respectively. Samples from the second altitudinal range were designated C2, G2, and P2, corresponding to potato crop (2954 MASL), livestock (2938 MASL), and *Páramo* (2972 MASL), respectively.

The coordinates of the different study zones were: P1 (N 04° 35' 41.5"- W 073° 59' 09.2"), P2 (N 04° 37' 08.1"- W 073° 57' 59.3"), C1 (N 04° 35' 40.8"- W 073° 59' 08.8"), C2 (N 04° 37' 11.1"- W 073° 58' 02.7"), G1 (N 04° 35' 48.6"- W 073° 58' 44.3"), and G2 (N 04° 37' 14.1"- W 073° 58' 05.6"). After removing the vegetal layer covering the soil, the soil samples were collected in the layer of 0.00-0.20 m. For each land use and altitude, three 10 × 10 m observation quadrants were evaluated, and each quadrant consisted of 10 sub-samples collected in a zig-zag pattern, which were homogenized to obtain a composite sample, completing a total of three samples for each combination of land use and altitude. The collected samples were placed in properly labeled plastic bags and stored at -4 °C for physicochemical analysis and determination of heavy metals and pesticides; all analyses were performed in triplicate in the laboratory. In the case of pesticides, the samples were processed less than a week after their collection.

Physicochemical analysis

Physicochemical parameters of the soil were determined according to the procedures established by the IGAC (2006), using the following methods: moisture according to the gravimetric method, bulk density according to the paraffin-coated clod method, plasticity according to the Atterberg method, texture according to the Bouyoucus method, pH in water using the potentiometric method in soil-water ratio 1:1, percentage of organic carbon according to the Walkley Black method, boron by hot water extraction according to Berger and Truog (1939), and assimilable phosphorus by the Bray II method, cation exchange capacity, calcium, magnesium, potassium, and sodium chloride by extraction with ammonium acetate 1 mol L^{-1}, and exchangeable acidity by extraction with potassium chloride 1 mol L^{-1} (Avellaneda-Torres et al., 2018).

Determination of heavy metals

Determination of heavy metals (arsenic, cadmium, mercury, and lead) was performed by inductively coupled plasma emission spectrometry prior extraction by closed digestion with a mixture of nitric acid: hydrochloric acid in a 7:1 ratio, respectively. The quantification was achieved by the external standard method. Final concentration spiked calibration curves were prepared between 5.0 and 50 μg kg^{-1}. The adjustment parameters in the equipment were: stabilization pump speed 100 rpm, analysis pump speed 50 rpm, stabilization time 5 s, nebulizer gas flow 0.5 L min^{-1}, and stabilization time for sample reading 30 s to control the analysis and the results generated, the analysis of calibration standards and linearity verification ($r>0.995$), method blank, duplicate calibration curve checkpoint (% RPD <30 %), analysis of a CRM (% recovery between 75 and 125 %), and a wash white (Julshamn et al., 2013; Mao et al., 2017).

Determination of organophosphorus-organonitrogen pesticides

On a sample of 10 g of soil, the researchers performed an extraction after adding salt and then ethyl acetate, stirring with ultraturrax for 1 min, and completing the process with ultrasonic extraction for 1 h. Subsequently, the sample was taken to a centrifuge at 5000 rpm for 5 min and after decantation, the supernatant was collected and the filtration with anhydrous residue grade sodium sulfate was carried out. The concentration process was performed in a rotary evaporator, quantitatively transferred to a 1 mL volumetric balloon, and subsequently placed in a vial for injection in the gas chromatograph.

Determination of organophosphorus and organonitrogen pesticides was carried out using an HP 6890 plus chromatograph connected to a capillary column (DB-5, 30 × 0.25 mm id × 0.25 µm), with shunt for parallel connection to micro-capture electronic detectors (µECD) and selective nitrogen-phosphorus detection (NPD). Previously, an ultrasound extraction with ethyl acetate was performed. An HP 7683B autosampler and a 15-meter guard column (Retention Gap) connected from the injector to the chromatographic column were used. The quantification of pesticides (cymoxanil, dimethoate, chlorothalonil, m-parathion, malathion, folpet, profenofos, oxadixyl, l-cyhalothrin, difenoconazole, cyproconazole, propiconazole, deltamethrin, methamidophos, monocrotophos, metalaxyl, dimethomorph, azoxystrobin, tebuconazole) was conducted through the external standard method. As a control of results, the standards of the calibration curve were analyzed, and their linearity was verified, a duplicate analysis of the sample was performed (maximum CV% allowed 20 %), the analysis of the fortified matrix was carried out (recovery percentages between 75 and 93 %), as well as an analysis of a white soil sample that had the same extraction treatment as the analysis sample to verify interferences and cross-contamination. Given the negative result, no confirmatory tests were performed.

Determination of multi-residue pesticides

Determination of multiple residues (328 pesticides) was carried out using liquid chromatography with Tamden Mass Spectrometry (LC-MS/MS), with electrospray ionization detection, sim-mode acquisition, using two target ions and their relative abundance ratio. The extraction process was performed at low temperature (dry ice) and under the procedure guidelines given by the directives of the health and safety commission of the European Union (SANTE/11945/2015 E10), and the quantification by the standard addition method. The pesticides determined were selected based on pesticide use patterns in the area, conducting a search for their active ingredients and/or similar or associated chemical groups. The procedure was carried out at low temperature (dry ice), with solvents of different polarity; ethanol and acetonitrile in different proportions to avoid pesticide losses, and the binding of extracts after preconcentration. The quantification was conducted by the standard addition method, to compensate for the matrix effect and low recovery percentages of some pesticides. As a control of the results, the standards of the calibration curve for 10 % of the pesticides representative of the analysis were analyzed and their linearity was verified, a duplicate analysis of the sample (maximum CV% allowed 20 %) and the analysis of the fortified matrix (recovery percentages between 60 and 140 %) were performed, and an analysis of a white soil sample that had the same extraction treatment as the analysis sample was carried out to verify interferences and cross-contamination. Given the negative result, no confirmatory tests were performed.

Statistical analysis

Univariate analysis of data in which the variance was evaluated using the non-parametric Friedman method was performed, followed by a comparison of means using the Wilcoxon Test. A multivariate analysis of the data was also carried out using the principal component analysis, where possible interactions and relationships between variables were identified. Statistical analyzes were performed with a level of significance of $p \leq 0.05$, and using the R-Project program, version 3.4.2.

RESULTS

Physicochemical parameters

Gravimetric moisture results obtained categorize soils under *Páramo* and livestock farming as with very high moisture, and soils under cultivation as with high mositure

(Figure 2) (Sociedad Colombiana de la Ciencia del Suelo, 1991). Regarding the plasticity index, all samples showed low plasticity (Sociedad Colombiana de la Ciencia del Suelo, 1991). On the other hand, the bulk density of all the soils under study is low (IGAC, 2006). Likewise, significant differences ($p \leq 0.05$) were found between the uses given to the soil in all the evaluated physical properties, finding that the moisture was significantly higher in the soils under *Páramo*, with respect to those used for potato cultivation and livestock farming, presenting the trend *Páramo* > livestock farming > potato crops. Likewise, the bulk density was significantly higher in soils under potato crops and livestock farming with respect to soils under *Páramo*, presenting the trend potato crops > livestock farming > *Páramo.* The only significant differences ($p \leq 0.05$) were found between the altitudes that were evaluated in the parameters of plasticity and bulk density, without finding a unique trend in terms of altitude.

Soils under *Páramo* showed significantly higher organic carbon content than the intervened soils, showing the following significant trend *Páramo* > livestock farming > potato crop (Figure 3). In the case of cation exchange capacity, the same trend was observed. In the case of phosphorus, there is a significant increase in soils under potato cultivation compared to the other two uses. According to the evaluated factors, the other parameters did not show statistically significant differences or any trend. There were no significant differences ($p \leq 0.05$) for any of the variables by altitude.

Heavy metal

According to the results shown in table 1, no significant differences ($p \leq 0.05$) were found in the arsenic contents related to land use or altitude. In Colombia, there is no legislation establishing permissible values for heavy metals in soils, so the results obtained were compared with the permissible limits of other countries with similar biogeographic conditions (Peru and Ecuador) and a third reference country (Spain). According to the Ministerio de Ambiente del Perú [Peruvian Ministry of Environment] (2012), of the Ministerio del Ambiente de Ecuador [Ministry of Environment of Ecuador] (2003), and the Consejería de Medio Ambiente de la Junta de Andalucía - España [Regional Ministry for Environment, Government of Andalusia – Spain] (1999), in the case of arsenic, the soils do not exceed the maximum values that are allowed according to the regulations consulted.

In the case of cadmium, no significant differences related to land-use or altitude were found ($p \leq 0.05$). The concentration of cadmium in test C2 is higher compared to the others. In this case, according to the Ministerio de Ambiente del Perú [Peruvian Ministry of Environment] (2012), the quality standard value in agricultural land is 1.4 mg kg^{-1}. According to the Ministerio del Ambiente de Ecuador [Ministry of Environment of Ecuador]

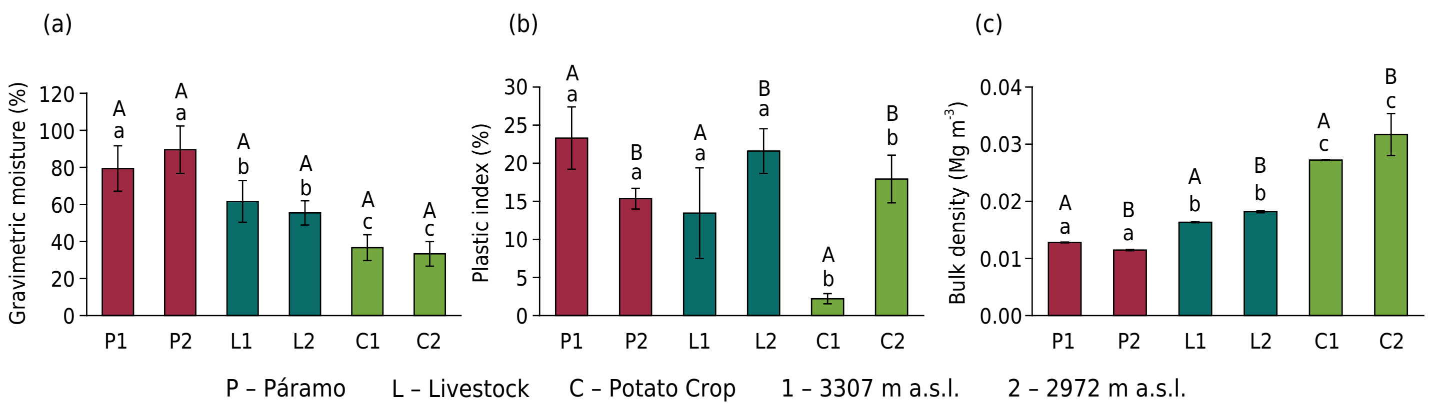

Figure 2. Physical properties of *Páramo* soils, potato cultivation, and cattle farming: (a) gravimetric moisture; (b) plasticity Index; and (c) bulk density. * Different lowercase letters on the bars represent statistically significant differences between land uses ($p \leq 0.05$). ** Different uppercase letters on the bars represent statistically significant differences between heights ($p \leq 0.05$).

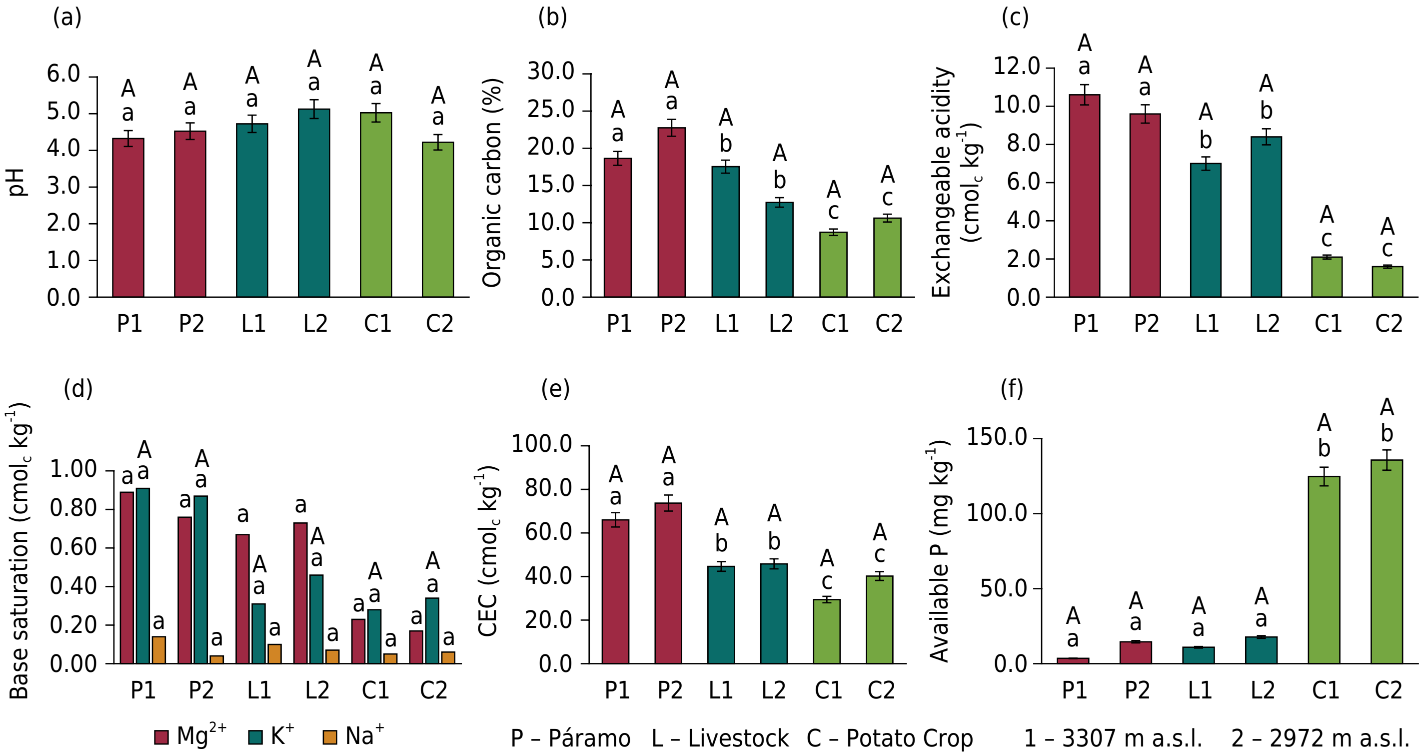

Figure 3. Chemical properties of *Páramo* soils, potato cultivation, and cattle farming: (a) pH; (b) organic carbon; (c) exchangeable acidity; (d) base saturation; (e) cation exchange capacity; and (f) available phosphorus. * Different lowercase letters on the bars represent statistically significant differences between land uses (p≤0.05). ** Different uppercase letters on the bars represent statistically significant differences between heights (p≤0.05).

Table 1. Analysis of heavy metals (As, Cd, Hg, and Pb), in the soils of *Páramo*, potato cultivation, and cattle farming

ICP MS	C1	C2	G1	G2	P1	P2	Perú	Ecuador	Spain
	mg kg^{-1}								
As	0.99Aa+0.05	0.67Aa+0.03	0.62Aa+0.03	1.08Aa+0.05	0.95Aa+0.05	0.84Aa+0.04	50	12	20
Cd	0.08Aa+0.004	0.21Aa+0.01	0.10Aa+0.005	0.10Aa+0.005	0.07Aa+0.004	0.10Aa+0.005	1.4	2.0	2.0-3.0
Hg	ND	ND	ND	ND	ND	ND	--	--	--
Pb	12.00Aa+0.6	16.63Aa+0.8	8.67Aa+0.4	13.20Aa+0.7	15.17Aa+0.8	10.21Aa+0.5	70	100	100-200

P: *Páramo*, G: cattle farming, C: Potato cultivation, 1: Height at 3307 m a.s.l., 2: Height at 2972 m a.s.l. * Different lowercase letters on the bars represent statistically significant differences between land uses (p≤0.05). ** Different uppercase letters on the bars represent statistically significant differences between heights (p≤0.05). ND: Not detected. *** As of the date of this study, Colombia does not have approved regulations on this. The values found in the title columns Peru, Ecuador and Spain correspond to the limits established in the respective countries, Ministerio de Ambiente del Peru (2012), Ministerio del Ambiente de Ecuador, the Consejería de Medio Ambiente de la Junta de Andalucía - España (1999), respectively.

(2003), the maximum value for cadmium in agricultural land is 2 mg kg^{-1}. In the case of the Consejería de Medio Ambiente de la Junta de Andalucía - España [Regional Ministry for Environment, Government of Andalusia – Spain] (1999), they establish that the limit values for agricultural soils are 2 mg kg^{-1} in acidic soils and 3 mg kg^{-1} in neutral and basic soils, within the reference level. Therefore, according to the regulations consulted in the case of cadmium, the maximum permitted values are not exceeded.

No presence of mercury was found above the detection level of the method (0.20 mg kg^{-1}) in any of the soils under study, so the regulatory requirements were not exceeded in any of the cases. Finally, on the subject of lead, no significant differences were detected (p≤0.05) in terms of the use or altitude of the evaluated soils. In the case of Ministerio de Ambiente del Perú [Peruvian Ministry of Environment] (2012), they consider a concentration of 70 mg kg^{-1} as the standard value for Pb. According to the Ministerio del Ambiente de Ecuador [Ministry of Environment of Ecuador] (2003), the maximum content allowable for Pb in agricultural soils is 100 mg kg^{-1}. According to the Consejería de Medio Ambiente de la Junta de Andalucía - España [Regional Ministry for Environment, Government of Andalusia – Spain] (1999), for agricultural soils, they determine a limit value of 100 mg kg^{-1} in acid soils and 200 mg kg^{-1} in neutral and alkaline soils, within the reference level. Thus, the results did not exceed the maximum values allowed according to the regulations consulted in the case of Pb.

Pesticides

From the 348 pesticides evaluated in the soil under study, only the compounds dimethomorph (sum of isomers), metalaxyl and thiametoxam (listed in Table 2) were reported in the amounts indicated. Soils P1 and P2 of the *Páramo* show no residue of any pesticides found in the other land uses (Table 2); this also occurs in the livestock farming soil, G1. On the other hand, the potato crop soils have the same dimethomorph content at both altitudes. Additionally, traces of this same compound are observed in the livestock farming soil, G2, but in smaller amounts. To a lesser extent, metalaxyl was found in the soils under potato crops at altitude 1, and thiamethoxam in soils under potato crops at altitude 2.

PCA

According to figure 4a, there is a correlation among the thiamethoxam, dimethomorf, cadmium, and lead, with soils under potato crops at altitude 2. Likewise, it is observed that soils under potato crops at altitude 1 have a correlation with metalaxyl content.

Table 2. Pesticides identified by LC-MS / MS in soils under *Páramo*, potato cultivation, and cattle farming

LC-MS/MS	C1	C2	G1	G2	P1	P2
	mg kg^{-1}					
Dimethomorph (sum of isomers)	0.27Aa+0.01	0.27Aa+0.01	ND	0.037Aa+0.002	ND	ND
Metalaxyl	0.013Aa+0.0007	ND	ND	ND	ND	ND
Thiamethoxam *(A)*	ND	0.048Aa+0.002	ND	ND	ND	ND

P: *Páramo*, G: cattle farming, C: Potato cultivation, 1: Height at 3307 m a.s.l, 2: Height at 2972 m a.s.l. * The different lowercase letters on the bars represent statistically significant differences between land uses with (p≤ 0.05). ** The different uppercase letters on the bars represent statistically significant differences between heights (p≤0.05). ND: not detected.

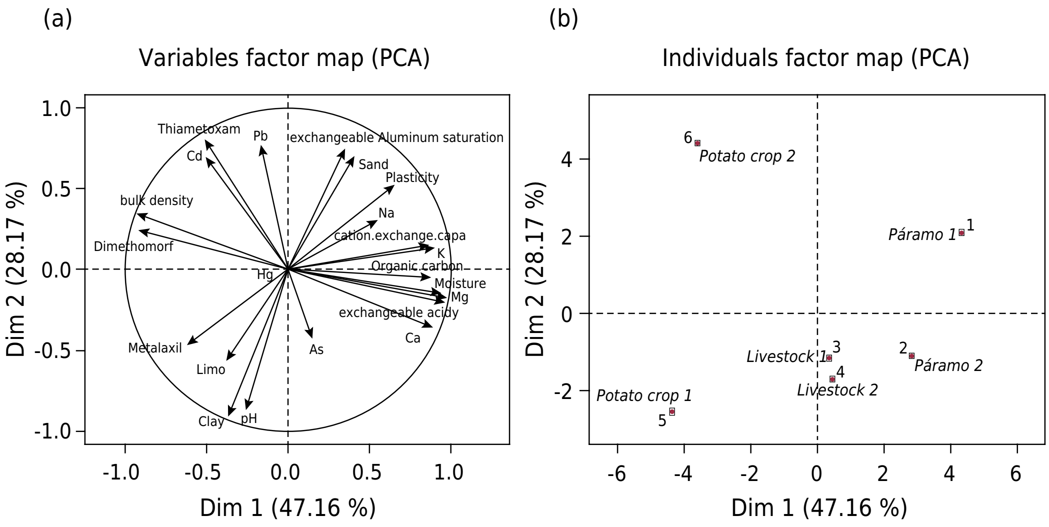

Figure 4. Analysis of principal components relating the physicochemical variables, heavy metals, and pesticides of soils under the *Páramo*, potato cultivation, and cattle farming (a); and individual map of the uses of the soils under *Páramo*, potato cultivation, and cattle farming (b).

It is observed that *Páramo* soils have the highest correlation with high organic matter contents, plasticity index, and good cation exchange capacity.

DISCUSSION

According to the regulations analyzed, none of the soils under study exceeded the permitted contents of heavy metals. Likewise, no significant differences were found between the different land uses and altitudes evaluated in relation to heavy metal content. Thus, the initial hypothesis that potato crops and livestock farming were generating significant increase in the content of heavy metals was not validated for the case study.

Regarding the residuality of pesticides in soils under potato crops at altitudes 1 and 2, we found fungicide dimethomorph (0.27 mg kg^{-1}); in potato crops at altitude 1, we found fungicide metalaxyl (0.013 mg kg^{-1}); and in potato crops at altitude 2, the insecticide thiamethoxam (0.048 mg kg^{-1}). These results contrast with the behavior of the soils under *Páramo*, where no residual of any of the pesticides evaluated was found. However, no statistically significant differences were found in pesticide content in relation to land use and the altitudes evaluated. Likewise, it is important to mention that according to the values the degradation of those pesticides on soil (DT50 typical aerobic in IUPAC Pesticide Properties Database http://sitem.herts.ac.uk/aeru/ppdb/en/search.htm) the detection seems compatible with the moment of soil collection (after potato cultivation), reporting 72.5 days for dimethomorph, 36 days for methalaxyl and, 50 days for thiamethoxam.

Similar to the present study, Liang et al. (2011) reported residues of the fungicide dimethomorph in soils under bell pepper crops, finding concentrations between 0.05-0.94 and 0.29-1.05 mg kg^{-1} for the years 2008 and 2009, respectively. The results obtained in this investigation are within these same ranges (0.27 mg kg^{-1}). According to the study developed by Kailani et al. (2019) on pesticide residuality in soils in Jordan, they found contents of metalaxyl fungicide between 1.44 and 2.66 mg kg^{-1}, which compared to this research is higher than the results obtained in soils under potato crops (0.013 mg kg^{-1}). Finally, as reported by He et al. (2016), soils under corn cultivation in China show concentrations of thiamethozam insecticide between 0.01 and 0.44 mg kg^{-1}; values that represent higher concentrations compared to those obtained in soils under potato crops in the present study (0.048 mg kg^{-1}).

Within the study of pesticide residuals, it should be noted that to date, no guidelines have been found for monitoring pesticide residues in Latin American soils or in the European Union (Hofstede et al., 2003; Silva et al., 2019). Additionally, Colombian researchers evaluated the concentration and distribution of heavy metals (Cr, Ni, Pb, Cd, Hg, and Zn) and pesticides (organochlorine and organophosphorus) of agricultural soils in an Irrigation District (Martínez-Mera et al., 2019). In the study of Martínez-Mera et al. (2019), the presence of pesticides in the soils was not reported. In contrast, the content of heavy metals in the soils varied as follows Zn > Cr > Ni > Pb > Hg > Cd (Martínez-Mera et al., 2019). Another study in Colombia obtained leaching risk maps of the pesticides imidacloprid, lambda-cyhalothrin, and chlorpyrifos in agricultural soil under an onion (Allium cepa L.) crop in Tibasosa, Boyacá. Which found that lambda-cyhalothrin and chlorpyrifos have lower movement risks, thus reducing their risk of affecting groundwater and surface water. However, imidacloprid does present a greater risk of contamination of the aquifers and mobility, becoming a potential pollutant (Navarro et al., 2021). Despite, these studies have not been carried out on *Páramo* soils.

Furthermore, these results indicate that none of the pesticides found in the soils of the area exceed the toxicity levels reported by IUPAC for mammals for acute oral levels (Mammals - Acute oral LD_{50} - mg kg^{-1}), which are: 3900 for dimethomorph; 375 for metalaxyl; and 1563 for thiamethoxam (http://sitem.herts.ac.uk/aeru/ppdb/en/search.htm). However, new results on pesticide residues in the soils of the *Páramo* are invited or awaited, as at the date of this publication, this document constitutes the first report. According to these results and although there are pesticide residues in soils under potato crops, the hypothesis that agricultural activities in the area generate significant pesticide residues was not validated, so the differences between land-uses and altitudes that were evaluated were not statistically significant. Therefore, it can be analyzed that (despite the soil samples being taken after the potato crop was harvested) there is no evidence of significant impact in the content of heavy metals or pesticide residues associated with potato cultivation and livestock farming in the area. This can be explained by the fact that current agriculture and livestock farming practices in the area under study have specific land use patterns and local agricultural practices developed mainly in the *Páramo*, in contrast to other country areas where potato crops and livestock farming activities are developed.

These patterns or local uses of the land are a combination of practices inherited from the Green Revolution (mass application of agrochemicals) but also from traditional agricultural wisdom, such as the implementation of a potato-pasture rotation system, with long periods of fallow, in which the potato crop is planted for up to two cropping periods on the same soil and then rested on a cattle pasture system for seven years or more, which allows crop rotation periods that mitigate potential impacts. Likewise, these specific agricultural practices of the area present a low intensity in relation to the number of cattle per hectare of land, finding a low density of cattle heads (0.24–0.36) per hectare of land (Avellaneda-Torres et al., 2018). Additionally, these livestock systems do not receive industrial or commercial food or feed; their feeding is fundamentally based on the consumption of grasses in the area, which do not receive a chemical fertilization process for their growth. These practices correspond to patterns of peasant family agriculture or subsistence agriculture, which present behaviors different from those of commercial agriculture developed at lower altitudes in relation to those of the *Páramo*, in which there are no rest periods, but rather an intensive use of the soil and if processes of chemical fertilization of pastures can be presented, as well as feeding of livestock with external commercial products.

Moreover, these practices correspond to patterns of peasant family agriculture or subsistence agriculture, which present different behaviors from those of commercial agriculture in the potato-grazing systems developed at lower altitudes in relation to those of the *Páramo*

Five of the physicochemical parameters of the soils evaluated (gravimetric moisture, bulk density, organic carbon, cation exchange capacity, and phosphorus) showed significant differences due to the activities of potato cultivation and livestock farming. In the case of gravimetric moisture, organic carbon, and cation exchange capacity, they were higher in *Páramo* soils, which demonstrates the conservation of this ecosystem by maintaining the natural vegetation that protects moisture, as well as the maintenance of organic matter and cation exchange capacity. On the other hand, soil bulk density increased under potato crops and livestock farming, which is explained by the trampling activities of cattle and mechanical work in the sowing of the crop that increase soil compaction. Likewise, the phosphorus content is higher in soils under potato crops, which corresponds to the application of phosphorus fertilizers that modify the natural content of phosphorus in the soil (Hofstede, 1997; Martínez et al., 2008; Llambí et al., 2012).

These results are partially consistent with those reported by Avellaneda-Torres et al. (2018), who indicated that organic carbon, cation exchange capacity, calcium, potassium, and NH4 were modified by potato cultivation and livestock farming activities in the *Páramo* areas of Los Nevados National Natural Park. We agree with arguments that gravimetric moisture, organic carbon, and cation exchange capacity reflect the advantages of *Páramo* soils that still retain their native vegetation, thus conserving moisture. In contrast, cultivated soils showed lower moisture because they were more exposed to sunlight and air. Similarly, there is greater soil compaction in the cultivated areas due to cattle trampling and potato cultivation activities, in a potato-pasture rotation system.

CONCLUSIONS

No significant content of heavy metals or significant residual pesticides was found in *Páramo* soils associated with potato cultivation and livestock farming in the area under study. This behavior is attributed to the specific practices developed in the area in which, although there is an application of chemically synthesized agricultural supplies, there is also the implementation of a potato-pasture rotation system, with long periods of fallow. In this system the potato crop is planted for up to two cropping periods on the same soil and then rested on a cattle pasture system for seven years or more. This system also presents a low intensity in relation to the number of cattle per hectare of land, and the pastures (main cattle feed) do not present chemical fertilization Finally, this study represents the first report on heavy metals and pesticide residues in *Páramo* soils.

SUPPLEMENTARY DATA

Supplementary data to this article can be found online at https://www.rbcsjournal.org/wp-content/uploads/articles_xml/1806-9657-rbcs-46-e0210135/1806-9657-rbcs-46-e0210135-suppl01.pdf.

ACKNOWLEDGMENT

This research was funded by Universidad Libre (Project Code 11030107). Special thanks to the farmers in the area for allowing the development and completion of this study.

AUTHOR CONTRIBUTIONS

Conceptualization: Baudilio Acevedo Buitrago (equal) and Lizeth Manuela Avellaneda-Torres (equal).

Data curation: Baudilio Acevedo Buitrago (equal), Laura Daniela Jerez Pérez (equal) and Lizeth Manuela Avellaneda-Torres (equal).

Formal analysis: Andrea Patricia Pinilla Núñez (equal), Baudilio Acevedo Buitrago (equal), Laura Daniela Jerez Pérez (equal) and Lizeth Manuela Avellaneda-Torres (equal).

Funding acquisition: Baudilio Acevedo Buitrago (equal) and Lizeth Manuela Avellaneda-Torres (equal).

Investigation: Baudilio Acevedo Buitrago (equal) and Lizeth Manuela Avellaneda-Torres (equal).

Methodology: Baudilio Acevedo Buitrago (equal) and Lizeth Manuela Avellaneda-Torres (equal).

Project administration: Baudilio Acevedo Buitrago (equal) and Lizeth Manuela Avellaneda-Torres (equal).

Supervision: Lizeth Manuela Avellaneda-Torres (lead).

Writing – original draft: Andrea Patricia Pinilla Núñez (equal), Baudilio Acevedo Buitrago (equal), Laura Daniela Jerez Pérez (equal) and Lizeth Manuela Avellaneda-Torres (equal).

Writing – review & editing: Andrea Patricia Pinilla Núñez (equal), Baudilio Acevedo Buitrago (equal), Laura Daniela Jerez Pérez (equal) and Lizeth Manuela Avellaneda-Torres (equal).

REFERENCES

Alcaldia Municipal Choachí Cundinamarca. Esquema de Ordenamiento Choachí Cundinamarca 2008 - 2011. Choachí: Alcaldía de Choachí; 2008.

Alloway BJ. Sources of heavy metals and metalloids in soils. In: Alloway BJ, editor. Heavy metals in soils: Trace metals and metalloids in soils and their bioavailability. 3rd ed. Dordrecht: Springer; 2013. p. 11-50. (Environmental Pollution 22).

Alves LR, Reis AR, Gratao PL. Heavy metals in agricultural soils: From plants to our daily life (a review). Científica. 2016;44:346-61. https://doi.org/10.15361/1984-5529.2016v44n3p346-361

Ashraf S, Ali Q, Zahir ZA, Ashraf S, Asghar HN. Phytoremediation: Environmentally sustainable way for reclamation of heavy metal polluted soils. Ecotox Environ Safe. 2019;174:714-27. https://doi.org/10.1016/j.ecoenv.2019.02.068

Avellaneda-Torres LM, Sicard TEL, Rojas ET. Impact of potato cultivation and cattle farming on physicochemical parameters and enzymatic activities of Neotropical high Andean *Páramo* ecosystem soils. Sci Total Environ. 2018;631-632:1600-10. https://doi.org/10.1016/j.scitotenv.2018.03.137

Avellaneda-Torres LM, Torres E, León-Sicard TE. Agricultura y vida en el *Páramo*: Una mirada desde la vereda El Bosque (Parque Nacional Natural de Los Nevados). Cuad Desarro Rural. 2014;11:105-28. https://doi.org/10.11144/Javeriana.CDR11-73.avpm

Berger KC, Truog E. Boron determination in soils and plants. Ind Eng Chem Anal Ed. 1939;11:540-5. https://doi.org/10.1021/ac50138a007

Bernal-Cuesta IM. Conflictos socioambientales en el *Páramo* de guacheneque y estrategias de conservación para el ordenamiento ambiental regional [dissertation]. Bogotá: Universidad Nacional de Colombia; 2017.

Bonmatin J-M, Giorio C, Girolami V, Goulson D, Kreutzweiser DP, Krupke C, Liess M, Long E, Marzaro M, Mitchell EAD, Noome DA, Simon-Delso N, Tapparo A. Environmental fate and exposure; neonicotinoids and fipronil. Environ Sci Pollut Res. 2015;22:35-67. https://doi.org/10.1007/s11356-014-3332-7

Cañon-Cortazar RG, Avellaneda-Torres LM, Torres-Rojas E. Microorganismos asociados al ciclo del nitrógeno en suelos bajo tres sistemas de uso: Cultivo de papa, ganadería y *Páramo*, en el Parque Los Nevados, Colombia. Acta Agron. 2012;61:371-9.

Consejería de Medio Ambiente de la Junta de Andalucía. Los criterios y estándares para declarar un suelo contaminado en Andalucía y la metodología y técnicas de toma de muestra y análisis para su investigación. España: Consejería de Medio Ambiente de la Junta de Andalucía y las Universidades de Granada, Huelva y Sevilla; 1999. Available from: http://www.ugr.es/~fjmartin/INFORMES/Criterios%20y%20estandares.pdf.

del Puerto-Rodriguez AM, Tamayo SS, Estrada DEP. Efectos de los plaguicidas sobre el ambiente y la salud. Rev Cubana Hig Epidemiol. 2014;52:372-87.

Díaz-Granados MA, González JDN, López TS. *Páramos*: Hidrosistemas sensibles. Rev Ing. 2005;22:64-75. https://doi.org/10.16924/revinge.22.8

Food and Agriculture Organization of the United Nations, World Health Organization - FAO, WHO. Pesticide residues in food 2007. Joint FAO/WHO Meeting on Pesticide Residues. Rome: FAO, WHO; 2007. Available from: https://www.fao.org/3/a1556e/a1556e00.pdf.

Gondar D, Lopez R, Antelo J, Fiol S, Arce F. Effect of organic matter and pH on the adsorption of metalaxyl and penconazole by soils. J Hazard Mater. 2013;260:627-33. https://doi.org/10.1016/j.jhazmat.2013.06.018

He M, Song D, Jia HC, Zheng Y. Concentration and dissipation of chlorantraniliprole and thiamethoxam residues in maize straw, maize, and soil. J Environ Sci Heal B. 2016;51:594-601. https://doi.org/10.1080/03601234.2016.1181903

Hofstede R. La importancia hídrica del *Páramo* y aspectos de su manejo. In: Estrategias para la Conservación y Desarrollo Sostenible de Páramos y Punas en la Ecorregión Andina: Experiencias y perspectivas; CDCPP, del 15 de agosto al 3 de octubre de 1997. Ecuador: CDCPP; 1997.

Hofstede RGM, Segarra P, Mena P. Los *Páramos* del Mundo. Quito: Global Peatland Initiative/NC-IUCN/EcoCiencia; 2003.

Instituto Geográfico Agustín Codazzi - IGAC. Métodos analiticos del laboratorio de suelos. 6th ed. Bogotá: IGAC; 2006.

Julshamn K, Maage A, Norli HS, Grobecker KH, Jorhem L, Fecher P, Dowell D. Determination of arsenic, cadmium, mercury, and lead in foods by pressure digestion and inductively coupled plasma/mass spectrometry: First action 2013.06. J AOAC Int. 2013;96:1101-2. https://doi.org/10.5740/jaoacint.13-143

Kailani MH, Al-Antary TM, Alawi MA. Monitoring of pesticides residues in soil samples from the southern districts of Jordan in 2016/2017. Toxin Rev. 2021;40:198-214. https://doi.org/10.1080/15569543.2019.1580747

Liang H, Li L, Li W, Wu Y, Zhou Z, Liu F. Dissipation and residue of dimethomorph in pepper and soil under field conditions. Ecotox Environ Safe. 2011;74:1331-5. https://doi.org/10.1016/j.ecoenv.2011.02.009

Llambí LD, Soto-W A, Célleri R, De Bievre B, Ochoa B, Borja P. Los suelos del *Páramo*. In: Borja P, editor. *Páramos* Andinos: Ecología, hidrología y suelos de *Páramos*. Ecuador: Condesan; 2012.

Luteyn J, Balslev H. Paramos: Why study them? In: Luteyn J, Balslev H, editors. Paramo: An andean ecosystem under human influence. United Kingdom: Academic Press; 1992. p. 1-14.

Mao J, Liu XY, Chen B, Lu FM, Wu XJ, Jiang DH, Luo LG. Determination of heavy metals in soil by inductively coupled plasma mass spectrometry (ICP-MS) with internal standard method. Electron Sci Technol Appl. 2017;4:23-31. https://doi.org/10.18686/esta.v4i1.36.

Martínez H, Fuentes JP, Acevedo E. Carbono orgánico y propiedades del suelo. R C Suelo Nutr Veg. 2008;8:68-96. https://doi.org/10.4067/S0718-27912008000100006

Martínez-Mera EA, Torregroza-Espinosa AC, Crissien-Borrero TJ, Marrugo-Negrete JL, González-Márquez LC. Evaluation of contaminants in agricultural soils in an Irrigation District in Colombia. Heliyon. 2019;5:e02217. https://doi.org/10.1016/j.heliyon.2019.e02217

Martley E, Gulson BL, Pfeifer HR. Metal concentrations in soils around the copper smelter and surrounding industrial complex of Port Kembla, NSW, Australia. Sci Total Environ. 2004;325:113-27 https://doi.org/10.1016/j.scitotenv.2003.11.012

Ministerio de Ambiente del Perú. Resolución Ministerial No. 307-2012-Minam. Republica del Peru: Minam; 2012.

Ministerio del Ambiente de Ecuador. Decreto Nº 3.516 - Norma de Calidad Ambiental del recurso suelo y criterios de remediación para suelos contaminados (Anexo II, Libro VI: De la Calidad Ambiental, del Texto Unificado de la Legislación Secundaria del Ministerio del Ambiente). Ecuador: Ministerio del Ambiente; 2003.

Mohapatra S, Siddamallaiah L, Matadha NY, Udupi VR, Raj DP, Gadigeppa S. Dissipation of neonicotinoid insecticides imidacloprid, indoxacarb andthiamethoxam on pomegranate (*Punica granatum* L.). Ecotox Environ Safe. 2019;171:130-7. https://doi.org/10.1016/j.ecoenv.2018.12.070

Navarro L, Camacho R, López J, Saldarriaga J. Assessment of the potential risk of leaching pesticides in agricultural soils: Study case Tibasosa, Boyacá, Colombia. Heliyon. 2021;7:e08301. https://doi.org/10.1016/j.heliyon.2021.e08301

Sidhu G. Heavy metal toxicity in soils: Sources, remediation technologies and challenges. Adv Plants Agric Res. 2016;5:00166. https://doi.org/10.15406/apar.2016.05.00166

Silva V, Mol H, Zomer P, Tienstra M, Ritsema C, Geissen V. Pesticide residues in European agricultural soils – A hidden reality unfolded. Sci Total Environ. 2019;653:1532-45. https://doi.org/10.1016/j.scitotenv.2018.10.441

Simon-Delso N, Amaral-Rogers V, Belzunces LP, Bonmatin JM, Chagnon M, Downs C, Furlan L, Gibbons DW, Giorio C, Girolami V, Goulson D, Kreutzweiser DP, Krupke CH, Liess M, Long E, McField M, Mineau P, Mitchell EAD, Morrissey CA, Noome DA, Pisa L, Settele J, Stark JD, Tapparo A, Van Dyck H, Van Praagh J, Van der Sluijs JP, Whitehorn PR, Wiemers M. Systemic insecticides (neonicotinoids and fipronil): trends, uses, mode of action and metabolites. Environ Sci Pollut Res. 2015;22:5-34. https://doi.org/10.1007/s11356-014-3470-y

Sociedad Colombiana de la Ciencia del Suelo. Fundamentos para la interpretación de análisis de suelos, plantas y aguas para riego. Santafé de Bogotá : Santafé de Bogotá: Sociedad Colombiana de la Ciencia del Suelo; 1991.

Zhang F, Li Y, Yang M, Li W. Content of heavy metals in animal feeds and manures from farms of different scales in northeast China. Int J Environ Res Public Health. 2012;9:2658-68. https://doi.org/10.3390/ijerph9082658