

Baseline concentration of heavy metals in agricultural soils

Línea base de concentración de metales pesados en suelos agrícolas

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ABSTRACT

The total concentrations of heavy metals in agricultural soils in the flat and piedmont zones of Valle del Cauca (Colombia) were evaluated. A simple random sampling was performed in 489 representative sampling sites. Samples were collected in the orders mollisol, inceptisol, and vertisol soils in 13 watersheds. Concentrations of Cd, Ni, Pb, Co, Cr, As, and Hg in soils do not follow a normal distribution. In some agricultural soils, concentrations of Cr, Ni, and Co exceeded typical ranges. Cr shows warning signs in the Pescador, RUT, and Tuluá watersheds. Alarm Ni concentrations were found in Guadalajara, Pescador, RUT, San Pedro, Sonso, and Tuluá. Alert Co levels were in the Jamundí and Pescador watersheds. As, Hg, Cd, and Pb showed high variability, while Cr, Ni, and Co showed moderate variability. A factorial analysis was performed using the Kaiser-Meyer-Olkin index (KMO) and Bartlett's test of sphericity. The KMO index indicated a correlation between the elements Hg, Cr, Ni, Pb, and Co. Cr, Ni, and Co have the highest contribution to the variance of component 1. In component 2, the highest variance is inversely correlated with Hg and Pb. The research provided a baseline for the levels of heavy metals in the region's agricultural soils. The concentrations of metallic elements are reported and compared with typical ranges found in agricultural soils.

Keywords: factorial analysis; soil contamination; soil taxonomy; total concentration; watershed

RESUMEN

Se evaluaron las concentraciones totales de metales pesados en suelos agrícolas en la zona plana y piedemonte del Valle del Cauca (Colombia). Se realizó un muestreo aleatorio simple en 489 sitios de muestreo representativos. Se colectaron muestras en suelos de los órdenes molisol, inceptisol y vertisol en 13 cuencas hidrográficas. Las concentraciones de Cd, Ni, Pb, Co, Cr, As y Hg en suelos no siguen una distribución normal. En algunos suelos agrícolas, las concentraciones de Cr, Ni y Co estuvieron por encima de los rangos típicos. El Cr presenta señales de alerta en las cuencas Pescador, RUT y Tuluá. Las concentraciones de Ni de alarma se encontraron en Guadalajara, Pescador, RUT, San Pedro, Sonso y Tuluá. Los niveles de Co de alerta estuvieron en las cuencas de Jamundí y Pescador. El As, Hg, Cd y Pb mostraron una alta variabilidad, mientras que Cr, Ni y Co fue moderada. Se realizó un análisis factorial mediante el índice de Kaiser-Meyer-Olkin (KMO) y la prueba de esfericidad de Bartlett. Los resultados indican que, el índice KMO en correlación entre los elementos Hg, Cr, Ni, Pb y Co. El Cr, Ni y Co tienen la mayor contribución a la varianza del componente 1. En el componente 2, la mayor varianza presenta una correlación inversa con Hg y Pb. La investigación suministró una base para metales pesados en suelos agrícolas de la región. Se reportan las concentraciones de elementos metálicos y se comparan con los rangos típicos encontrados en suelos agrícolas.

Palabras clave: Análisis factorial; contaminación de suelos; concentración total; clasificación de suelos; cuenca hidrográfica

INTRODUCTION

The protection and soil preservation require sustainable management, guaranteeing the health and quality of soil environment, provision of ecosystem services, and food security (FAO & PNUMA, 2022a). In 2021, 2.3 billion people (29.3%) worldwide faced food security problems at moderate or severe levels (FAO et al., 2022b). Soil contamination reduces the quality and quantity of crops, which affects agriculture. Furthermore, 79% of people in rural areas are living in conditions of extreme poverty (FAO & PNUMA, 2022a).

Soil contamination occurs when the concentration of a substance exceeds its assimilative capacity. The main polluting agents found in agricultural soils are associated with the presence of different metallic elements. The term 'heavy metals' refers to the group of elements whose mass is greater than 4.5 g cm⁻³, such as lead, cadmium, copper, mercury, zinc, and nickel. Low concentrations can be found naturally in the soil, but due to anthropogenic actions, their quantity can increase, with the risk of being incorporated into food chains. Due to their non-biodegradable nature, heavy metals can cause toxicity and harm human and animal health (He et al., 2015; Rodríguez-Eugenio et al., 2019). Pesticides (insecticides, herbicides, and fungicides), fertilizers (mainly phosphorus and nitrogen), and saline irrigation water are the main sources of these metallic elements in soils. Also, harmful and persistent organic complexes (Polo et al., 2002).

There is great global concern regarding soils and crops not exceeding the acceptable limits of heavy metals (Khalid et al., 2017). More than 10 million sites with contaminated soils have been reported, with more than 50% of the sites related to heavy metals or metalloids. This has a global economic impact exceeding ten billion dollars annually (He et al., 2015). In 2022, the European Environment Agency (EEA) reported that 2.8 million sites had soil contamination problems (EEA, 2022). This situation obliges countries to continuously evaluate the heavy metal content in soils. A baseline of information is essential for defining sustainable soil management policies and programs (Giri et al., 2017).

Internationally, soil quality indicators have been developed to improve their performance, protect human health, preserve environmental quality, and guarantee food security (Guzmán Morales et al., 2019). The increase in heavy metal content in agricultural soils is a major issue (Gharaibeh et al., 2020). Therefore, the quality of soils must be guaranteed to reduce environmental impacts and possible effects on human health (Doležalová Weissmannová & Pavlovský, 2017).

In the Piedmont Llanero region of Colombia, Trujillo-González et al. (2022) established a reference or baseline for some heavy metals in soils with geological characteristics that are heterogeneous, dominated by shales and sandstones in the mountainous area in the foothills by clays, mixed sediments, and conglomerates, and with a classification of soils as Oxisols, Entisols, and Inceptisols. Heavy metals were arranged in decreasing order: Cr (21.10 mg kg⁻¹), Pb (11.30 mg kg⁻¹), Ni (10.20 mg kg⁻¹), and Cd (0.30 mg kg⁻¹). The reference values serve as the maximum permissible concentrations for each element in the soil (Criado et al., 2018).

The impact of these activities on total heavy metal concentrations is unclear in the soils of the region. This research aims to evaluate the concentrations of heavy metals or metalloids in soils of the flat and piedmont areas of Valle del Cauca, Colombia. The baseline concentrations of heavy metals in soils of mollisol, inceptisol, and vertisol were determined in 13 hydrographic watersheds of the region. In the country, monitoring and follow-up of the quality of agricultural soils due to the presence of heavy metals will help guide actions that promote sustainable management of the resource.

MATERIAL AND METHODS

Study area

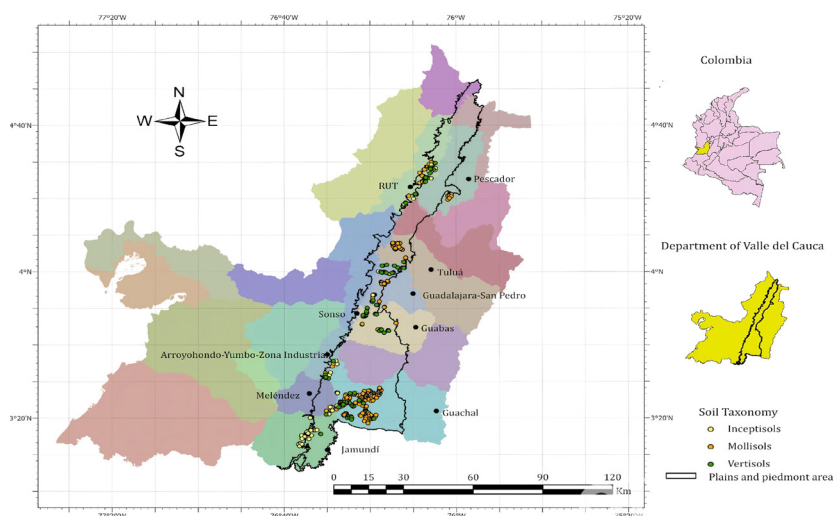
The area is located in the Flat and Piedmont Zone, in the Department of Valle del Cauca, Colombia. It has coordinates of 3° 30' and 5° 10' north latitude; 75° 42' and 77° 33' west longitude (CVC & IGAC, 2004). Precipitation has a bimodal behavior, with two rainy periods in March-May and September-November and two dry periods in December-February and June-August (Tafur Reyes et al., 2006). The average annual precipitation ranges between 1000 and 1500 mm, and the average temperature ranges between 24 and 28 °C (IDEAM, 2018). There is a typical climate that changes to very humid, humid, and dry conditions (CVC & IGAC, 2004). The geology is composed of igneous, metamorphic, and sedimentary rocks (CVC & IGAC, 2004).

The sampling sites were determined based on a cartographic analysis to determine heavy metal or metalloid levels. A total of 489 sampling sites were selected across 13 watersheds, each of which contained soils representative of crops in the flat and piedmont areas of the Department of Valle del Cauca (Figure 1). 44% of the soil samples were from sugarcane crops, while 56% were from other crops. According to Corral et al. (2015), a simple random sampling method was used. Based on the total samples, 271 correspond to mollisol soils, 128 to vertisol, and 90 to inceptisol. The soil sample was composed and disturbed, and it corresponds to a fraction of soil on one of the walls of the trunk, with a thickness of approximately 3 cm, 20 cm wide, and 30 cm deep. It was mixed into a bucket for homogenization.

Elements evaluated, methods, or techniques used for their determination

The heavy metals Cd, Ni, Pb, and Co were analyzed using the wet digestion method (HCl-HNO₃) and graphite furnace atomic absorption spectroscopy (GFAA). Detection limits were 0.02 for Cd, 1 mg kg⁻¹ for Cr and Ni, 0.75 for Pb, and 0.10 for Co, respectively. The analysis of As and Hg was conducted using Hydride generation-atomic absorption spectrometry (HGAAS). For both elements, the detection limit was 0.10 mg kg⁻¹. The analyses were conducted between the years 2017 and 2019 in a laboratory that specializes in physicochemical analysis in the agricultural and environmental domain (AGRILAB, 2022).

Figure 1. Distribution of sampling sites in the flat and piedmont areas of Valle del Cauca by soil order



Statistical Analysis

A univariate statistical analysis was performed, including measurements of position, dispersion, and shape. The distribution was made using the “Kolmogorov-Smirnov” test. Since the metallic elements do not follow a normal distribution, the Spearman correlation coefficient was used to determine the relationship between the metallic elements (Martínez Ortega et al., 2009).

The Kaiser-Meyer-Olkin index (KMO) was used to evaluate the adequacy of individual sampling of metallic elements for group consideration. The KMO index quantifies the sample fit by utilizing values that should be within a range of 0.5 to 1. Here, we apply factor analysis using Bartlett’s test of sphericity, which allows us to evaluate whether the variables are uncorrelated in a population (null hypothesis). If the value is less than 0.05, this hypothesis will be rejected, and the analysis will proceed (Marín-Pimentel et al., 2023; Montoya Suárez, 2007).

The principal component analysis was performed using the statistical programs SAS University Studio and RStudio version 4.1.3 using the readxl, corrplot, psych, and factoextra libraries (Venables & Smith, 2022). The Argis-Pro program was also used for the spatial representation of the results obtained (ESRI, 2021).

RESULTS

Statistical analysis of the normality and univariate analysis of heavy metals or metalloids

According to the Kolmogorov-Smirnov test, the seven metals studied do not have a normal distribution ($p < 0.01$). This indicates that the mean, mode, and median are different and that there is no probability symmetry about the mean or median (Tapia-Flores & Cevallos-Flores, 2021). The metallic elements maintained a non-normal distribution by soil order. It was not possible to determine Hg in the molisol and vertisol orders, and As in the vertisol order.

Univariate analysis of metals or metalloids showed differences between measures of central tendency, mean, mode, and median (Table 1). The average concentration of the elements As, Hg, Cr, Ni, Pb, and Co was below the mean concentration in the lithosphere. For Cd, it was within the range of the characteristic mean value for the Earth’s crust (Macías Vásquez et al., 2016).

Table 1. Univariate statistical analysis of metals or metalloids measured (mg kg⁻¹)

Test statistic	Element						
	As	Hg	Cd	Cr	Ni	Pb	Co
Mean	0.03	0.01	0.16	58.56	41.62	4.54	17.17
Mode	0.00*	0.00	1×10 ⁻⁶	0.00	0.001	0.00	16.00
Median	0.00	0.00	0.13	46.30	30.80	2.65	14.55
C.V	845.53	1829.63	111.14	81.32	93.17	164.41	63.41
SD	0.28	0.14	0.18	47.62	38.8	7.47	10.89
Maximum	2.92	3.01	2.77	240.00	226.00	90.00	72.60
Minimum	0.00	0.00	0.00	0.00	0.001	0.00	0.00
Kurtosis	75.44	473.85	90.07	0.63	5.91	58.08	3.32
Asymmetry	8.64	21.63	6.80	0.98	2.27	6.26	1.52
Total content in soils (Macías Vásquez et al., 2016).	0.1 - 48	0.01 - 1,8	0.01 - 3.0	40 - 200	1 - 200	3 - 189	0.05 - 300
Average concentration in lithosphere (Macías Vásquez et al., 2016).	1.5 - 2.0	0.02 - 0.05	0.1 - 0.2	100	75	16	20

SD: Standard deviation and CV: Coefficient of variation (%), *Below the detection limit.

According to Kabata-Pendias (2011), the maximum permissible concentration ranges of heavy metals (mg kg⁻¹) in soils are as follows: As of (15-20), Hg (0.5-5.0), Cd (1-5), Cr (50-200), Ni (20-60), Pb (20-300), and Co (20-50). For this study, the elements As, Hg, Cd, and Pb were within the limits reported, while Cr, Ni, and Co had higher concentrations.

At five locations situated within the watersheds of Tuluá, RUT, and Pescador, concentrations of Cr exceeding 200 mg kg⁻¹ were observed. These sites are representative of mollisol soils and different crops with pH levels > 7.0. For soil pH levels below 7.0, Cr can be toxic to plants at levels above 100 mg kg⁻¹. Furthermore, it has the potential to impact the overall growth of the plant, causing leaf chlorosis and resulting in low yields (Gonnelli & Renella, 2012).

17.2% of the sites had Ni concentrations above 60 mg kg⁻¹, with at least one site in each watershed. 70.2% of the sites evaluated corresponded to the mollisol order, 28.6 % to the vertisol order, and 1.2% to the inceptisol order. In the range of 0.05 to 10 mg kg⁻¹, Ni is an essential element for plants. In sensitive plants, the critical level of Ni occurs for values greater than 10 mg kg⁻¹ of dry matter. For plants with higher tolerance, toxicity occurs when the value is higher than 50 mg kg⁻¹. The effects of Ni on plants are correlated with delayed germination and growth retardation, yield reduction, stimulation of chlorosis and wilting of leaves, photosynthesis disorder, inhibition of CO₂ assimilation, and reduction of stomatal conductance (Gonnelli & Renella, 2012).

Concerning Co, eight sites exhibit concentrations exceeding 50 mg kg⁻¹. Five soil types are associated with the mollisol order, two with the vertisol order, and one with the inceptisol order. The toxic effects of Co on plants are evident through the appearance of white and dead edges and tips on leaves. The most notable effect is the interveinal yellowing of new leaves, which is closely related to the chlorotic effects of Fe. When Co is present in contaminated soils, it is a major cause of impairment of plant growth and functions (Kabata-Pendias, 2011).

The metals Hg, Cd, and Pb had a high variability. The levels of Cr, Ni, and Co had moderate variability (Li et al., 2013). The coefficient of variation results indicate a great heterogeneity in heavy metal concentrations in the soils of Valle del Cauca (Ramírez-Morales & Mazón-Olivo, 2018). The levels found may be affected by the agronomic practices used. It is also important to consider the nature of the parent material at the different sampling sites (Criado et al., 2018). The As level was below the maximum allowed level for agricultural soils (Kabata-Pendias, 2011).

For Hg, the Pescador watershed presented the maximum value within the proposed range without exceeding the threshold of 5 mg kg⁻¹. All values for Cd were below the recommended maximum (5 mg kg⁻¹). The concentration of Cr in some sites within the Pescador, RUT, and Tuluá watersheds exceeded the permitted limit of 200 mg kg⁻¹. The concentrations of Ni at some places exceeded 60 mg kg⁻¹, specifically in the watersheds of Guadalajara, Pescador, RUT, San Pedro, Sonso, and Tuluá. In general, Pb levels in the soils are within the permissible limits. Co exceeds the permitted limit of 50 mg kg⁻¹ in the Jamundí and Pescador watershed (Table 2). The total concentrations of As, Cd, and Hg meet the environmental quality standards for agricultural soils (Chira-Fernández, 2021). For Pb, values higher than this standard were found in some soils of the Sonso watershed. It is essential to establish a baseline for the total contents of Hg, Cd, As, and Pb, which can have a significant impact on plants and food security under certain conditions of the soil environment (Rodríguez-Eugenio et al., 2019).

Table 2. Concentration of metals or metalloids by hydrographic watershed

Watershed	Total samples (n)	Mean (mg kg ⁻¹)	Median (mg kg ⁻¹)	Maximum (mg kg ⁻¹)	Minimum (mg kg ⁻¹)
Arroyohondo	7	As:0.00* Hg:0.00 Cd:0.01 Cr: 50.31 Ni: 44.74 Pb: 5.49 Co: 22.47	As: 0.00 Hg: 0.00 Cd: 0.00 Cr: 54.50 Ni: 50.05 Pb: 4.50 Co: 25.90	As: 0.00 Hg: 0.00 Cd: 0.02 Cr: 63.30 Ni: 57.70 Pb: 11.50 Co: 29.30	As: 0.00 Hg: 0.00 Cd: 0.00 Cr: 37.83 Ni: 26.65 Pb: 0.00 Co: 11.35
Guabas	22	As: 0.00 Hg: 0.00 Cd: 0.06 Cr: 113.45 Ni: 43.14 Pb: 6.07 Co: 28.86	As: 0.00 Hg: 0.00 Cd: 0.05 Cr: 115.00 Ni: 45.00 Pb: 3.84 Co: 28.00	As: 0.00 Hg: 0.00 Cd: 0.14 Cr: 187.00 Ni: 80.00 Pb: 26.00 Co: 46.00	As: 0.00 Hg: 0.00 Cd: 0.01 Cr: 66.00 Ni: 14.00 Pb: 1.50 Co: 21.00
Guachal	159	As: 0.00 Hg: 0.00 Cd: 0.16 Cr: 26.49 Ni: 21.65 Pb: 2.14 Co: 9.54	As: 0.00 Hg: 0.00 Cd: 0.13 Cr: 21.35 Ni: 20.59 Pb: 0.67 Co: 8.73	As: 0.00 Hg: 0.00 Cd: 0.99 Cr: 98.55 Ni: 68.55 Pb: 14.27 Co: 22.44	As: 0.00 Hg: 0.00 Cd: 0.00 Cr: 0.00 Ni: 0.00 Pb: 0.00 Co: 0.41
Guadalajara	36	As: 0.00 Hg: 0.00 Cd: 0.11 Cr: 40.69 Ni: 25.79 Pb: 3.80 Co: 14.01	As: 0.00 Hg: 0.00 Cd: 0.08 Cr: 36.50 Ni: 21.00 Pb: 3.10 Co: 14.50	As: 0.00 Hg: 0.00 Cd: 0.26 Cr: 92.00 Ni: 71.00 Pb: 23.00 Co: 24.00	As: 0.00 Hg: 0.00 Cd: 0.02 Cr: 3.40 Ni: 7.60 Pb: 0.00 Co: 7.30
Jamundí	28	As: 0.00 Hg: 0.00 Cd: 0.05 Cr: 31.41 Ni: 14.49 Pb: 7.82 Co: 19.36	As: 0.00 Hg: 0.00 Cd: 0.00 Cr: 31.39 Ni: 11.35 Pb: 7.91 Co: 16.70	As: 0.00 Hg: 0.00 Cd: 0.63 Cr: 80.15 Ni: 37.00 Pb: 37.00 Co: 51.00	As: 0.00 Hg: 0.00 Cd: 0.00 Cr: 1.25 Ni: 0.00 Pb: 0.00 Co: 0.94
Meléndez	9	As: 0.0 Hg: 0.0 Cd: 0.02 Cr: 37.82 Ni: 24.88 Pb: 0.93 Co: 10.20	As: 0.00 Hg: 0.00 Cd: 0.01 Cr: 37.45 Ni: 23.45 Pb: 0.43 Co: 9.85	As: 0.00 Hg: 0.00 Cd: 0.11 Cr: 48.95 Ni: 36.05 Pb: 3.56 Co: 18.35	As: 0.00 Hg: 0.00 Cd: 0.00 Cr: 26.35 Ni: 12.10 Pb: 0.28 Co: 0.88
Pescador	41	As: 0.39 Hg: 0.09 Cd: 0.11 Cr: 98.49 Ni: 111.40 Pb: 3.61 Co: 33.81	As: 0.00 Hg: 0.00 Cd: 0.08 Cr: 97.90 Ni: 121.00 Pb: 2.72 Co: 32.50	As: 2.92 Hg: 3.01 Cd: 0.51 Cr: 232.00 Ni: 226.00 Pb: 17.00 Co: 72.60	As: 0.00 Hg: 0.00 Cd: 0.00 Cr: 6.99 Ni: 23.00 Pb: 1.08 Co: 0.00
RUT	53	As: 0.00 Hg: 0.00 Cd: 0.22 Cr: 80.00 Ni: 46.08 Pb: 7.37 Co: 18.39	As: 0.00 Hg: 0.00 Cd: 0.22 Cr: 65.10 Ni: 46.50 Pb: 8.94 Co: 18.10	As: 0.00 Hg: 0.00 Cd: 0.49 Cr: 240.00 Ni: 115.00 Pb: 25.60 Co: 31.60	As: 0.00 Hg: 0.00 Cd: 0.00 Cr: 7.46 Ni: 7.36 Pb: 0.00 Co: 9.06
San Pedro	41	As: 0.00 Hg: 0.00 Cd: 0.25 Cr: 48.18 Ni: 34.51 Pb: 7.59 Co: 15.18	As: 0.00 Hg: 0.00 Cd: 0.19 Cr: 34.00 Ni: 24.00 Pb: 3.40 Co: 13.00	As: 0.00 Hg: 0.00 Cd: 2.77 Cr: 133.00 Ni: 104.00 Pb: 77.00 Co: 35.00	As: 0.00 Hg: 0.00 Cd: 0.00 Cr: 0.70 Ni: 2.90 Pb: 1.30 Co: 5.50
Sonso	25	As: 0.00 Hg: 0.00 Cd: 0.13 Cr: 76.88 Ni: 40.72 Pb: 8.74 Co: 27.52	As: 0.00 Hg: 0.00 Cd: 0.13 Cr: 82.00 Ni: 38.00 Pb: 3.70 Co: 27.00	As: 0.00 Hg: 0.00 Cd: 0.18 Cr: 133.00 Ni: 88.00 Pb: 90.00 Co: 45.00	As: 0.00 Hg: 0.00 Cd: 0.08 Cr: 22.00 Ni: 14.00 Pb: 2.90 Co: 16.00

Watershed	Total samples (n)	Mean (mg kg ⁻¹)	Median (mg kg ⁻¹)	Maximum (mg kg ⁻¹)	Minimum (mg kg ⁻¹)
Tuluá	61	As: 0.00 Hg: 0.00 Cd: 0.29 Cr: 103.44 Ni: 70.98 Pb: 2.76 Co: 17.79	As: 0.00 Hg: 0.00 Cd: 0.27 Cr: 108.00 Ni: 57.00 Pb: 1.28 Co: 17.00	As: 0.00 Hg: 0.00 Cd: 0.87 Cr: 217.00 Ni: 202.00 Pb: 12.30 Co: 34.0	As: 0.00 Hg: 0.00 Cd: 0.00 Cr: 25.00 Ni: 16.00 Pb: 0.00 Co: 8.00
Yumbo	5	As: 0.0 Hg: 0.0 Cd: 0.02 Cr: 55.67 Ni: 46.53 Pb: 16.93 Co: 25.44	As: 0.00 Hg: 0.00 Cd: 0.02 Cr: 55.20 Ni: 45.40 Pb: 18.55 Co: 25.35	As: 0.00 Hg: 0.00 Cd: 0.02 Cr: 71.70 Ni: 58.70 Pb: 23.55 Co: 33.05	As: 0.00 Hg: 0.00 Cd: 0.01 Cr: 41.20 Ni: 29.45 Pb: 9.90 Co: 14.55
Zona Industrial	2	As: 0.00 Hg: 0.00 Cd: 0.12 Cr: 64.50 Ni: 42.50 Pb: 11.50 Co: 32.00	As: 0.00 Hg: 0.00 Cd: 0.12 Cr: 64.50 Ni: 42.50 Pb: 11.50 Co: 32.00	As: 0.00 Hg: 0.00 Cd: 0.17 Cr: 68.00 Ni: 44.00 Pb: 12.00 Co: 34.00	As: 0.00 Hg: 0.00 Cd: 0.07 Cr: 61.00 Ni: 41.00 Pb: 11.00 Co: 30.00

RUT: Roldanillo-Unión-Toro, *Below the detection limit.

DISCUSSION

Characterization of heavy metals or metalloids by soil order

According to Kabata-Pendias (2011), As concentrations did not exceed the allowable limits for any soil order. In soils of the vertisol order, As concentrations were below the detection limits (Table 3). This baseline is very important because, according to FAO, As is one of the elements with the highest risk of contamination of the food chain (Rodríguez-Eugenio et al., 2019). For the order inceptisol, global total arsenic concentrations in surface soil range from 1.3 to 27.0 mg kg⁻¹ (mean 8.40 mg kg⁻¹). For the order mollisol, 1.9 to 23.0 mg kg⁻¹ (mean 8.5 mg kg⁻¹), and no report for the order vertisol (Kabata-Pendias, 2011).

The concentrations of Hg are below the permitted limit in soils. According to the World Health Organization, Hg is one of the 10 most important pollutants (FAO & PNUMA, 2022a). This element is considered to be of low risk for human health because it is strongly bound to the soil (Rodríguez-Eugenio et al., 2019). In molisols and vertisols, the average Hg at the soil surface was 0.10 mg kg⁻¹. The concentration range for mollisol soils is between 0.02 and 0.53 mg kg⁻¹, and for Inception soils, between 0.01 and 0.50 mg kg⁻¹ (Kabata-Pendias, 2011).

The levels of Cd in soils were within the low-risk range. In soils of the Ariari region of Colombia, the measured values of Cd were below the detection limit (Mahecha-Pulido et al., 2015). The average Cd concentrations in soils of the order inceptisol are 0.45 mg kg⁻¹ (0.08 to 1.61 mg kg⁻¹). For the order mollisol, the concentration is 0.44 mg kg⁻¹ (0.18 to 0.71 mg kg⁻¹) (Kabata-Pendias, 2011). Cadmium concentrations in soils higher than 100.0 mg kg⁻¹ should be remediated (Mendoza-Escalona et al., 2021). Cd concentrations in soils of the flat and piedmont areas of Valle del Cauca do not represent an environmental risk. However, they do deserve attention because, in equatorial soils below 0.50 mg kg⁻¹ concentration, phytotoxicity was induced in the corn crop (Aguirre et al., 2022).

In some agricultural soils, Cr concentrations exceeding the permissible limits were found (Kabata-Pendias, 2011). In mollisol soils, the average Cr concentration was lower than the average values reported worldwide. For inceptisols and vertisols soils, the Cr concentrations were between 15.0 and 70.0 mg kg⁻¹, which

is typical for crops (Gómez-Puentes et al., 2020). Cr is an element with a low risk of contamination for the food chain. It is poorly soluble in soil, so it is not absorbed by plants (Rodríguez-Eugenio et al., 2019).

In the case of Ni, the maximum concentrations observed in soils were significantly higher than the permissible concentration (Kabata-Pendias, 2011). According to Rodríguez-Eugenio et al. (2019), Ni is an element that enters plant tissues easily and can cause phytotoxicity. The world average Ni concentration in mollisol soils is 25.0 mg kg⁻¹ (6.00 to 61.00 mg kg⁻¹), and for inceptisol, it is 26.0 mg kg⁻¹ (3.0 to 110.0 mg kg⁻¹) (Kabata-Pendias, 2011).

For the soil orders studied, the levels of Pb did not exceed the range observed in agricultural soils (Kabata-Pendias, 2011). These levels of Pb do not represent a potential risk to human and animal health since their bioavailability is low because they are strongly bound to soil (Rodríguez-Eugenio et al., 2019).

In both the inceptisol and vertisol orders, Co exceeds the limits allowed in agricultural soils (Kabata-Pendias, 2011). Since this element is of high risk for crops and the food chain, it is necessary to monitor and follow up on the quality of these soils (Rodríguez-Eugenio et al., 2019). There is limited information regarding the ecological risk of cobalt in soils, plants, microorganisms, and invertebrates. However, values above 40.0 mg kg⁻¹ of Co should be considered for remediation processes in soils (Ma & Hooda, 2012).

Correlation and multivariate analysis

The elements that had a KMO index greater than 0.5 were Hg (0.80), Cr (0.72), Ni (0.68), Pb (0.61), and Co (0.75). The metal elements with a communality value below 0.5 were As (0.37) and Cd (0.47). These elements were not considered for further correlation studies. Statistical significance was less than 0.05 in Bartlett's test of sphericity, indicating that there is a relationship between the variables. When As and Cd are discarded, the KMO index displays values for the metals Hg (0.83), Cr (0.72), Ni (0.71), Pb (0.62), and Co (0.76) that are equal to or greater than the initial calculated values. The Bartlett test of sphericity in this new scenario had a significance of less than 0.05 (p-value < 2.2 x 10⁻¹⁶), which confirms a strong relationship between the elements.

Table 3. Characterization of metal or metalloid concentration by soil order

Total samples (n)	Mollisol 271	Inceptisol 128	Vertisol 90
Mean (mg kg ⁻¹)	As: 0.03 Hg: 0.00 Cd: 0.17 Cr: 49.44 Ni: 37.65 Pb: 3.21 Co: 14.60	As: 0.09 Hg: 0.00 Cd: 0.12 Cr: 68.55 Ni: 53.38 Pb: 5.86 Co: 21.54	As: 0.00* Hg: 0.00 Cd: 0.18 Cr: 70.85 Ni: 41.75 Pb: 6.45 Co: 19.53
Median (mg kg ⁻¹)	As: 0.00 Hg: 0.00 Cd: 0.14 Cr: 37.20 Ni: 27.70 Pb: 1.42 Co: 12.70	As: 0.00 Hg: 0.00 Cd: 0.08 Cr: 56.45 Ni: 31.39 Pb: 3.30 Co: 17.75	As: 0.00 Hg: 0.00 Cd: 0.15 Cr: 71.55 Ni: 35.20 Pb: 3.73 Co: 17.80

	Mollisol	Inceptisol	Vertisol
Total samples (n)	271	128	90
Maximum (mg kg ⁻¹)	As: 2.92 Hg: 0.00 Cd: 0.99 Cr: 240.00 Ni: 215.00 Pb: 90.00 Co: 46.30	As: 2.34 Hg: 3.01 Cd: 0.63 Cr: 232.00 Ni: 226.00 Pb: 37.00 Co: 72.60	As: 0.00 Hg: 0.00 Cd: 2.77 Cr: 187.00 Ni: 213.00 Pb: 77.00 Co: 55.30
Minimum (mg kg ⁻¹)	As: 0.00 Hg: 0.00 Cd: 0.00 Cr: 0.00 Ni: 0.001 Pb: 0.00 Co: 3.32	As: 0.00 Hg: 0.00 Cd: 0.00 Cr: 1.25 Ni: 0.001 Pb: 0.00 Co: 0.00	As: 0.00 Hg: 0.00 Cd: 0.00 Cr: 0.00 Ni: 0.001 Pb: 0.00 Co: 0.41

*Below the detection limit.

In the principal component analysis for the metallic elements, it was found that only the first two components have an eigenvalue greater than 1 (Table 4). The first component has an eigenvalue of 2.3041 and an explained variance of 46.08 %. The elements that contribute the greatest proportion to the variance of component 1 are Cr, Ni, and Co. The first component combines elements such as Cr and Ni that represent a low risk of transfer to the food chain. However, Co could represent a high risk (Rodríguez-Eugenio et al., 2019). The possible sources of contamination in agricultural soils by Ni and Cr can be related to sewage sludge. Co can be added to the soil by applying cobalt oxides, sulfides, or arsenides (Gonnelli & Renella, 2012).

The second component has an eigenvalue of 1.012 and an explained variance of 20.24 %. In component 2, the elements Hg and Pb support the highest variance. This is due to the polymetallic association between Hg and Pb, along with As and Cd, and other elements (Chira-Fernández, 2021). Similarly, Hg and Cd are elements with low availability because they are strongly bound to the soil and pose a low risk to human health (Rodríguez-Eugenio et al., 2019). Cd is incorporated into agricultural soils by the application of phosphorus fertilizers. The presence of mercury in soil is attributed to the application of sewage sludge, trace amounts of fertilizer, lime, and manure. Furthermore, atmospheric deposition has the potential to contribute small amounts of these elements to the soil (Steinnes, 2012).

Table 4. Principal component analysis for the five heavy metals with $KMO > 0.5$.

Heavy metal	Principal components	
	C1	C2
Hg	0.2683395	0.43071428
Cr	0.5493354	-0.08666488
Ni	0.5598824	0.07518277
Pb	0.1165437	-0.89510428
Co	0.5469678	-0.01050209
Standard deviation	2.3041	1.012
Proportion of variance	46.08%	20.24%
Cumulative variance	46.08%	66.32%

Figure 2 illustrates the contribution of metals from the principal component analysis in agricultural soils of the flat and piedmont zones of Valle del Cauca. The element Pb had the greatest contribution to the two dimensions because its line was closer to the circumference and had a greater color intensity. In second place were the elements Cr, Ni, and Co, and in the final position was Hg. The elements Cr, Ni, and Mg have the greatest origins in the parent material, followed by Cu, Co, Zn, and Pb. The contributions of Hg, Cd, and As to the soil are mainly of natural origin (Galán Huertos & Romero Baena, 2008). The main sources of trace heavy metals in agricultural soils are agrochemicals, petroleum derivatives, chemical by-products used in livestock, and discharges of domestic and industrial wastewater (Rodríguez-Eugenio et al., 2019).

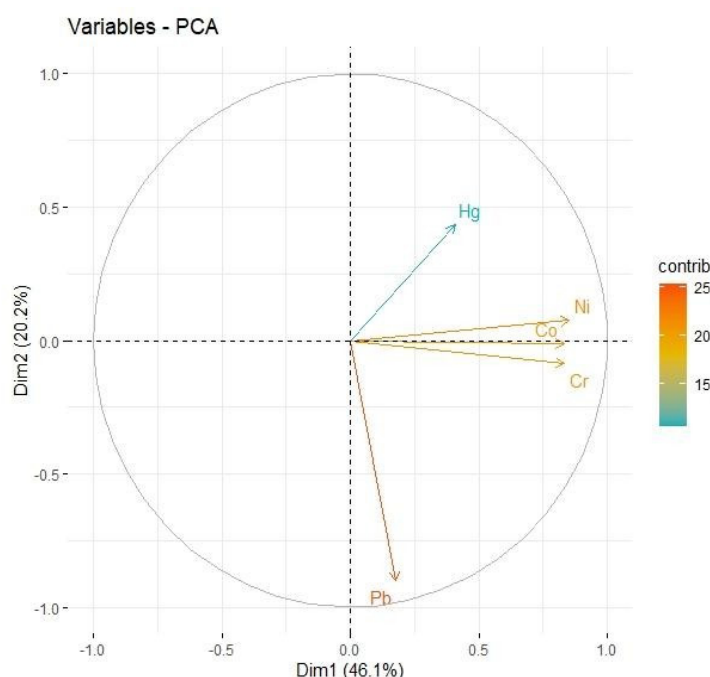


Figure 2. Contribution of metals to principal component analysis

The results of the correlation analysis are shown in Figure 3. The high color intensity indicates that there is a correlation between Cr and Ni. The concentrations of Cr and Ni in soils and sediments have increased, primarily due to the mining and smelting industries (Gonnelli & Renella, 2012). The correlation between Co and Ni and Co and Cr is categorized as moderate to strong (Martínez Ortega et al., 2009). The high content of Cr, Ni, Mn, and Cu in soils is associated with ultrabasic rocks, specifically peridotites. Low concentrations are observed in sandstones and limestones, which comprise a group of sedimentary rocks. It is also low in acidic igneous rocks (Galán Huertos & Romero Baena, 2008). The heavy metal inputs associated with the parent material play a crucial role in the levels of heavy metals in agricultural soils. For this reason, it is necessary to establish background values to assess possible contamination problems (Criado et al., 2018).

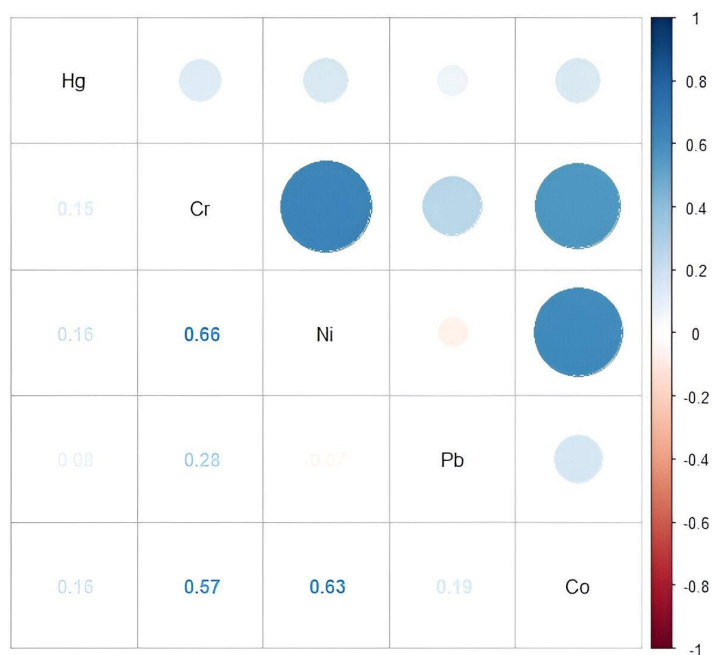


Figure 3. Spearman correlation for the 5 metals with $KMO > 0.5$.

CONCLUSIONS

The research provided a baseline for the levels of heavy metals in the region's agricultural soils. The concentrations of metallic elements are reported and compared with the typical ranges found in agricultural soils. The investigation of heavy metals in agricultural soils of the flat and piedmont zones of Valle del Cauca reveals that the total concentrations of Cr, Ni, and Co exceed the permissible limits. It is important to assess the bioavailability of elements such as As, Cd, and Co, which may pose a greater risk of contamination in the soil and transfer to plants. The total concentrations of As and Hg were very low, without an evident risk to the biocenosis of the environment due to their high toxicity.

The spatial analysis of the concentrations of metallic elements shows that there are differences based on location and soil order. These differences may be due to differences in agronomic practices and the contributions of the parent material. Accordingly, it is recommended that soil properties be monitored to see if these elements are mobile or bioavailable and if they pose a risk.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest.

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