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Heavy Metals in Water, Soils and Sediments of La Villa River Basin- Panama

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

Determine the concentration of heavy metals in water, sediments, and crops within the La Villa river basin, Herrera and Los Santos provinces, republic of Panama. La Villa river Basin, south central of Panama, in the rainy season of 2016 (May to November) and in the dry season of 2017 (December to April). Twenty two sediments and water samples were taken using the systematic method which consists of selecting sampling points at uniform distances and crops in upper, middle and lower basin. The selected sampling was confined to a preferably rectangular area of 10.0 m x 30.0 m, on which the sub-samples were taken with a number of 15 on each grid, at 0.20m depth. For collecting the water samples, a rod with a clean plastic bottle was introduced against the current of the river. The digestion of sediments and crops to determine the concentration of heavy metals (As, Pb, Cr, Ni, Cu, Mn, Zn and Cd) was carried out according to USEPA (25) method (3051A) (SW-846). In the sediments, in the rainy season, Cu (upper and lower basin) and Mn (all levels) values were found above the USEPA Standards. In the dry season, high values of Mn were found in the middle and lower basin, Cr in the upper and lower basin and As in all areas of the basin. In the rainy and dry seasons, high levels of Mn, Zn, Cr, Cd and Pb were found in the waters of the rivers that make up the basin. The main crops at each height of the basin were analyzed, determining high levels of As and Cr in the upper basin, in the middle and lower basin Cr and Cd. It is necessary to monitor the

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concentration of heavy metals in sediments of La Villa river basin because 90% of the agrochemicals that enter the country is destined for agriculture. Each Panamanian consumes (does not ingest) 3 kg of agrochemicals annually, exceeding six times the amount used in Central America. Due to their geological origin, these soils are rich in copper, manganese and arsenic, latter being associated with iron oxides and sulfides but there is also great influence of anthropogenic activities, agriculture and industries. Some metals such as lead and arsenic showed low solubility in water but showed high concentration in sediments. Chromium and cadmium present in crops come from water.

Keywords: cadmium; arsenic; chromium; lead; trace elements.

1. INTRODUCTION

Heavy metals are generally found as natural components of the earth's crust, in the form of minerals, salts, or other compounds. They cannot be easily degraded or destroyed in a natural or biological way since they do not have specific metabolic functions for living beings [1]. Heavy metals of anthropogenic origin derive from hazardous waste, coming from industrial activities, mining, agricultural activities (irrigation, inorganic fertilizers, pesticides, manure, limestone amendments and, above all, the use of urban sewage sludge).

In Panama, some studies have been carried out for the determination of heavy metals in soils, for example [2], determined the concentration of cupric residues and heavy metals in agricultural soils of Barú associated with banana production, finding copper (Cu) levels higher than 1000 mg/kg, greatly limiting the planting of vegetables and grains in these soils. Likewise, Espinosa [3], during the development of his doctoral thesis on soils dedicated to the cultivation of bananas and oil palm in Barú, found high total values of zinc (Zn), manganese (Mn), copper (Cu), in the soil , associating it with the use of fungicides. Also high concentration of lead (Pb), coming from gasoline and especially high levels of nickel (Ni).

The National Environmental Authority [4], through the National Environmental Program, prepared the preliminary draft of environmental quality standards for soils for various uses, being the first attempt to establish adequate levels of heavy metals and other pollutants in the soil of Panama.

Villarreal et al. [5,6] working in acidic soils of Paty do Alferes, high region of the State of Rio de Janeiro, Brazil, where intensive agriculture is practiced, found that a large amount of heavy metals (also called trace metals) present in the soil came from anthropogenic applications to the soil by means of agrochemicals, phosphate fertilizers and organic fertilizers from animal husbandry. Likewise, they determined that the loss of the fertile soil layer, due to their poor preparation in favor of the slope, could serve as a means to disseminate the high levels of dissolved metals in aqueous phases, contaminating surface waters and the soils of the lower parts with the sediments from polluted highlands.

It is considered that a soil can be considered contaminated when at least 90% of present values, for a certain element, higher than the soil under [7].

It is also necessary to know what concentration of heavy metals the producers used for soil fertilization and the management of pests and diseases contain, as well as the water used for irrigation.

The problem of heavy metals such as lead, nickel, cadmium and manganese, present in water used for irrigation, lies mainly in the fact that they can be accumulated in agricultural soils. They are dangerous due to their non-biodegradable nature, the toxicity they exert on different crops and their bioavailability [8,9,10]. Additionally they might include: mercury, arsenic and chromium [11].

Mancilla-Villa et al. [12] carried out a study in the rivers, reservoirs and springs of Puebla and Veracruz to determine the content of heavy metals where mercury exceeded the maximum permissible limit indicated by NOM-001-ECOL-1996 for urban use. According to the USEPA [13] criterion, it was found that 1, 30, 15 and 20% of the analyzed samples exceed the permissible limit for As, Pb, Cd and Hg, respectively. The area under study presents similar characteristics, these differences in concentrations is due to the intense agricultural, industrial and urbanization activities, in the different sampling sites.

Gaete et al. [14], in samples from the Aconcagua River in Chile, they found high levels of copper and molybdenum, associated with mining activity in the area.

Contreras et al. [15], studied the waters and sediments of the Haina River in the Dominican Republic, finding high levels of heavy metals in the sediments but not in the waters, concluding that this is explained by the low solubility of these metals in the water and their natural tendency to precipitate and accumulate in sediments.

The present study was carried out in agroecosystems where a large agricultural activity takes place. In these lands, the production of corn, tomatoes, melons, watermelons, peppers, sugarcane, pastures and dual-purpose livestock (milk and meat) has historically been developed. They are soils subjected to intensive use of agrochemicals and influenced by discharges of by-products from some industrial companies located within the basin.

When conducting a study in Cerro Punta, Chiriquí province, Carranza [16], found that, of the 105 chemical substances used in agricultural practices, 42 were fungicides, 41 insecticides, 12 herbicides, 6 nematicides, 4 bactericides, including among these, 8 of the 12 restricted products in the agreement of the Meeting of the Health Sector of Central America and the Dominican Republic (Resscad).

The agrochemical trade in Panama exceeds 40 million dollars, of which 90% of the agrochemicals that enter the country is destined for agriculture. Each Panamanian consumes (does not ingest) 3 kg of agrochemicals annually, exceeding six times the amount used in Central America. [17].

Observing the problem, it was necessary to carry out a diagnosis, which serves as a baseline at the level of this important productive area to check, in detail, in what state is the degree of contamination of the water and sediments in these areas for the benefit of the population consumer nationwide. This will result in making better decisions about land use, bioremediation of highly polluted areas, and use of healthier products to fertilize soils and the general health of the population.

The objective of this study was to determine the concentration of heavy metals in water, sediments and crops within the La Villa river basin, Herrera and Los Santos provinces, republic of Panama.

2. MATERIALS AND METHODS

The La Villa river basin (Fig. 1) has a surface area of 1,157.5 km^2 (645.8 km^2 in Herrera province and 511.7 km^2 in Los Santos province). Coordinates: 543576 E and 858101 N. It is mostly composed of Alfisols (middle and lower basin) and Inceptisols (upper basin) according to USDA Soil Taxonomy [18,4,19] formed in the upper cretaceous, initially covered by intermediate volcanic material, basic volcanic material and tuffs [20]. This basin in its upper part has an average rainfall of 2200 mm and in its lower part of about 1054 mm per year, the latter is part of the so-called Dry Arch of Panama. Its average annual temperature ranges from 27 ° to 28°C [18].

The samplings was carried out in the rainy season of 2016 (May to November) and in the dry season of 2017 (December to April). Twenty two [7] sediments and water samples were taken using the systematic or grid method which consists of selecting sampling points at uniform distances (zig zag, diagonal or grid), depending on the area being studied. In general, this is the method used in monitoring programs, since it allows the collection of more representative samples [22] (Fig. 2).

To sample the sediments, it was treated to select a preferably rectangular area of approximately 10.0 m x 30.0 m, on which the sub-samples were taken (from which it is inferred that the samples were composite) with a number of 15 on each grid, with approximately 100.0 g each, at 0.20m deep. Later they were homogenized so that said sampling offered representative results for the description of the site. Each sampled site was georeferenced using GPS to determine its exact location (Figs. 3 and 4).

For the water samples, a rod with a clean plastic bottle was introduced against the current of the river [22] (Fig. 5).

Samples of the main crops were taken in the two seasons of the year mentioned and in the different heights of the basin.

The digestion of sediments and crops to determine the concentration of heavy metals (As, Pb, Cr, Ni, Cu, Mn, Zn and Cd) was carried out according to USEPA method 3051A [23]. The concentration of the metals was determined in a flame atomic absorption spectrometer with a continuous Xenon source.

The levels found were compared with those allowed by USEPA Standards [24]; Economical European Commission: Council Directive 126/1986, EEC [25]; Council Directive 2003/2003, CEE [26].

Fig. 1. La Villa river basin-Panama

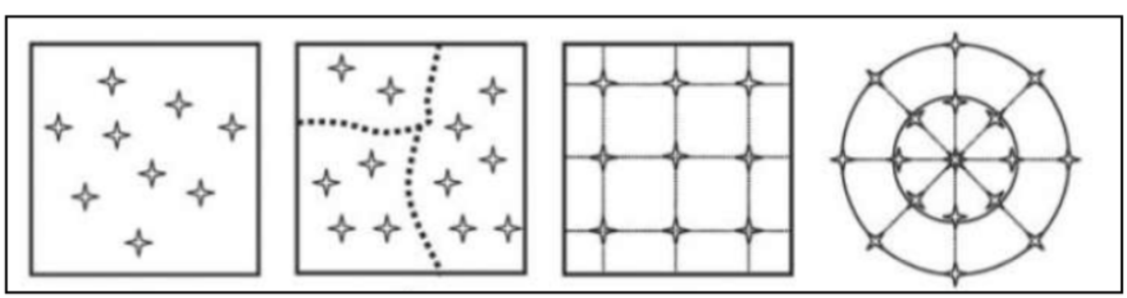

Fig. 2. Grid scheme used for systematic sediment sampling

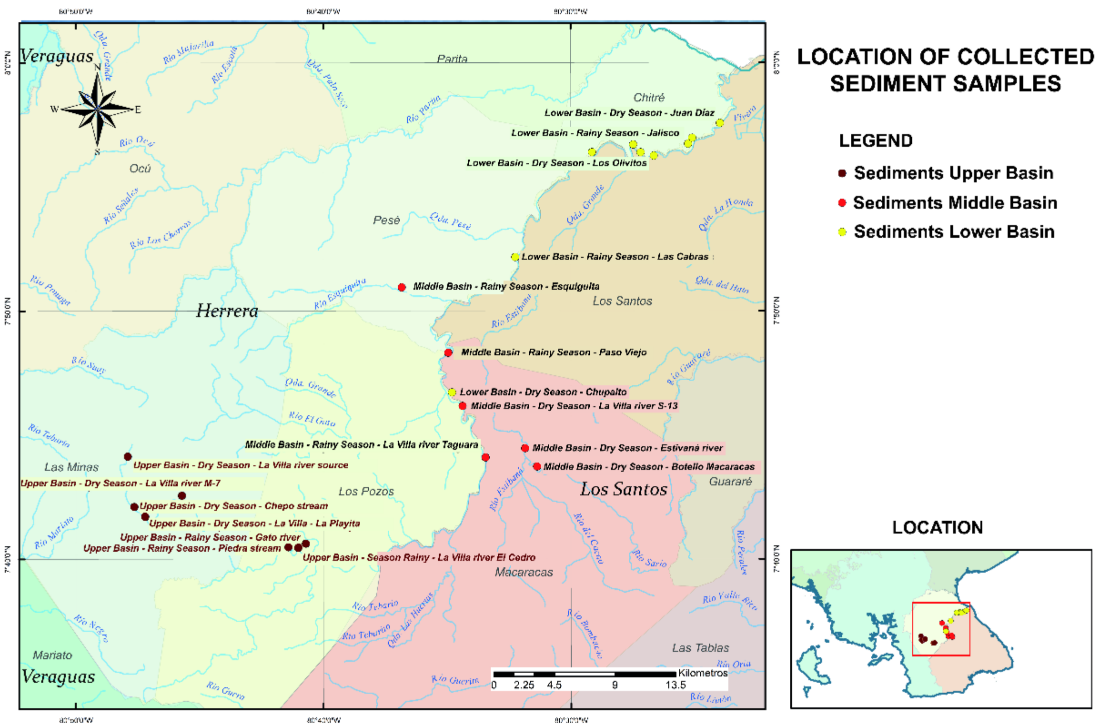

Fig. 3. Location of the points where the sediments were sampled. La Villa river basin-Panama

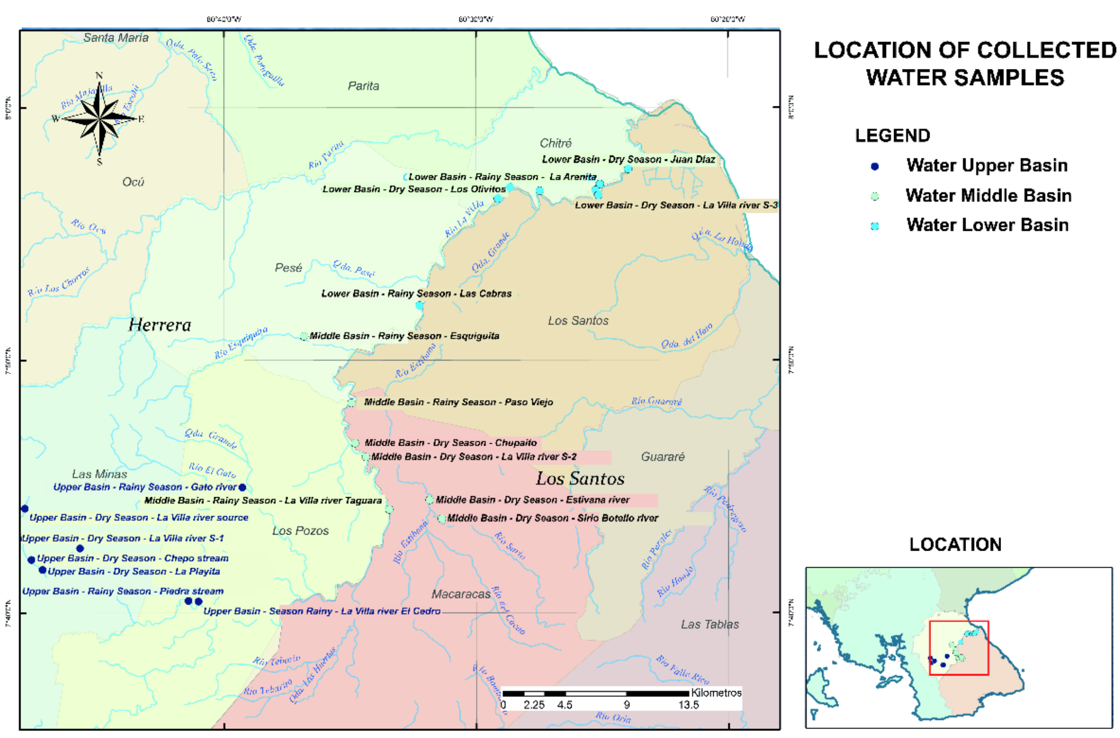

Fig. 4. Location of the points where the waters were sampled. La Villa river basin-Panama

Fig. 5. Sediment and water sampling in the La Villa river-Panama

3. RESULTS AND DISCUSSION

3.1 Heavy Metals in Sediments

The content of heavy metals in soil samples from the La Villa river basin remained within the standards established by the European Union and the United States [27].

In the sediments, in the rainy season, Cu (upper and lower basin) and Mn (all levels) values were found above the USEPA Standards [24], attributable to the excessive use of fungicides, especially in the middle and lower basin where the greatest agricultural activity is concentrated (Table 1). In the upper basin, the high concentrations of Cu are related to the mining of gold and copper in the area and that of Mn is of geological origin attributable to the high levels of Mn and Fe oxides in the soils of Panama, in addition to the common pH of the zone is around 5.5 which helps a greater bioavailability of metals. Another reason for the enrichment in the lower areas of the basin is the high degree of erosion existing in the basin as a result of deforestation and poor land use in the region.

In the dry season, when the flow of the La Villa river decreases more than 40%, high values of Mn were found in the middle and lower basin, Cr in the upper and lower basin and As in all areas of the basin (Table 2).

Cr may be due to the existence of many pig farms in the upper and middle basin of La Villa river and this is part of some nutritional supplements and the arsenic in the upper basin is of geological origin since where there is gold mining this element is associated with FeS forming complexes [28], in addition to the use of medicines and vitamin supplements used in animal husbandry (Arsenical ^{TM}).

Villarreal et al. [27], made correlations between the concentrations of heavy metals in soil and sediments with soil properties such as pH, clay content, organic matter, finding that in the rainy season Mn had a high correlation with clay content and Cr showed a high dependence on pH. In the dry season, Cu and Mn showed affinity with clay soils. The soils of the basin present a clay loam texture in the middle and clay loam with a low content of sandy organic matter in its upper parts, an acidic pH of around 5.5 and a low content of organic matter (2.2%).

3.2 Heavy Metals in Water

Tables 3 and 4 show the concentrations of heavy metals found in the waters of the La Villa river basin, in the rainy and dry season, respectively.

Table 1. Average total concentration of heavy metals in sediments of the upper, middle and lower La Villa river basin, in the rainy season, 2016

Metal	Upper Basin	Middle Basin	Lower Basin	USEPA 1993 Reference
---------------------mgkg^{-1}--------------------				
Cu	72.27	45.90	61.30	<50
Zn	92.51	74.13	90.79	
Mn	573.03	701.47	995.38	<500
Cr	67.31	52.24	64.24	<75
Cd	0.41	0.47	0.50	<6
Ni	5.56	5.64	8.61	<50
Pb	1.59	1.73	2.60	
As	7.07	3.29	5.01	<8

Table 2. Average total concentration of heavy metals in sediments of the upper, middle and lower La Villa river basin, in the dry season, 2017

Metal	Upper Basin	Middle Basin	Lower Basin	USEPA 1993 Reference
---------------------mgkg^{-1}--------------------				
Cu	46.4	38.0	16.60	<50
Zn	59.8	84.4	78.90	
Mn	460.1	814.7	925.90	<500
Cr	78.5	63.5	117.00	<75
Cd	0.34	0.39	0.45	<6
Ni	2.44	9.20	5.21	<50
Pb	1.78	2.71	0.95	
As	8.01	13.20	16.40	<8

Both in the rainy and dry seasons, high levels of Mn, Zn, Cr, Cd and Pb were found in the waters of the rivers that make up the basin. It is noted that high concentrations of Pb in the upper basin are related to the clandestine mining of gold in the area. The concentrations of Cr, Cd, Zn, Mn are closely related to the metals found in agrochemicals and synthetic fertilizers commonly used by farmers within the basin [27].

It is interesting to note that high levels of Cr, Cd and Pb were found in the IDAAN water intake (drinking water purification plant), although no analysis was carried out on the water after it was purified by IDAAN.

Although the sediments presented high levels of Cu and As, these metals apparently are not very soluble in water since their levels are minimal.

3.3 Heavy Metals in Crops

The main crops at each height of the basin were analyzed (Table 5), determining high levels of As and Cr in the upper basin, mainly, closely related to aspects of geological origin and the mining of gold and copper in the area. The high Cu values in crops such as banana, pumpkin, melon, watermelon, tomato, are related to the indiscriminate use of fungicides to combat fungi and diseases in crops.

Towards the middle and lower basin, it is observed that most of the crops show concentrations of Cd and Cr that exceed the levels recommended by Kabata-Pendias and Pendias [29].

In general, plants are more tolerant of increases in the concentration of essential elements. Different is the case of a non-essential element, where the damage increases as the element increases [30].

According to Hettiarachchi and Pierzynski [31], in soils contaminated with Pb, it is commonly associated with Cd and Zn.

In tomato plants, high Cd values were found, but according to Moral et al. [32], the Cd is partially translocated to the aerial parts, however, in the fruits it is found at undetectable levels.

The most toxic metals for higher plants as well as for certain microorganisms are: Hg, Cu, Ni, Pb, Co, and Cd [30].

Table 3. Total concentration of heavy metals in water. La Villa river basin. Rainy season. 2016

Basin	Tributary river	Cu	Mn	Zn	Cr	Cd	Pb	Ni	As
					$mgkg^{-1}$				
Upper	Piedra Stream	0.001	21.65	2.83	6.35	0.170	0.055	0.001	0.001
	La Llana y el Jobo	0.001	14.60	5.64	16.10	0.185	0.001	0.001	0.001
	El Gato	0.001	18.75	1.11	9.83	0.185	0.001	0.001	0.001
Middle	Taguara	0.001	38.00	9.93	15.17	0.190	0.001	0.001	0.001
	Paso Viejo	0.001	28.30	13.48	11.09	0.225	0.425	0.001	0.001
	Esquiguita	0.001	15.80	19.61	2.89	0.165	0.001	0.001	0.001
Lower	La Peñita	0.001	52.55	18.87	2.24	0.175	0.35	0.001	0.001
	Jalisco	0.001	18.30	9.38	1.15	0.160	0.001	0.001	0.001
	IDAAN water intake	0.001	15.85	12.50	1.15	0.155	0.615	0.001	0.001
	Las Cabras	0.001	19.55	15.44	1.11	0.220	0.17	0.001	0.001
	La Arenita	0.001	27.10	5.64	23.35	0.160	0.91	0.001	0.001
Reference	EPA 1986 (natural waters)	1.5			0.1	0.01	0.0015	0.632	0.05
	COPANIT 24-99	0.02	0.2	2	0.1	0.01	5	0.2	0.1

Table 4. Total concentration of heavy metals in water. La Villa river basin. Dry season. 2017

Basin	Tributary River	Cu	Mn	Zn	Cr	Cd	Pb	Ni	As
				$mgkg^{-1}$					
Upper	River source	0.001	8.60	8.95	1.98	0.190	0.001	0.001	0.001
	Chepo stream	0.001	19.55	3.93	1.57	0.160	0.9	0.001	0.001
	La Playita	0.001	17.15	5.34	1.41	0.195	0.001	0.001	0.001
	La Villa river	0.001	8.65	42.76	2.07	0.205	2.71	0.001	0.001
Middle	Sario river	0.001	13.85	4.42	8.28	0.145	0.345	0.001	0.001
	Estivana river	0.001	15.70	3.93	16.57	0.190	1.15	0.001	0.001
	La Villa river	0.001	17.80	8.46	7.95	0.160	0.575	0.001	0.001
	Ernesto Domínguez	0.001	16.40	5.40	0.99	0.175	0.265	0.001	0.001
Lower	Los Olivitos	0.001	13.85	17.03	2.09	0.510	0.001	0.001	0.001
	IDIAP-La Villa	0.001	16.30	7.60	1.74	0.165	0.001	0.001	0.001
	Juan Díaz Hill	0.001	15.95	4.66	1.11	0.170	1.455	0.001	0.001
Reference	EPA 1986 (natural waters)	1.5			0.1	0.01	0.0015	0.632	0.05
	COPANIT 24-99	0.02	0.2	2	0.1	0.01	5	0.2	0.1

Table 5. Total concentration of heavy metals in the main crops of the La Villa river basin. 2016-2017

Basin	Crop	Cu	Mn	Zn	Cr	Cd	Pb	Ni	As
					$mgkg^{-1}$				
Upper	Corn	5.70	0.001	10.4	9.0	0.62	2.48	5.71	103.2
	Sugar cane	7.48	1.06	10.1	35.6	0.72	4.19	5.94	162.5
	Red Bean	101.8	88.2	209.4	5.2	0.65	5.74	6.96	0.001
	Coffe	15.4	8.1	38.4	3.8	0.79	4.29	6.54	143.8
	Banana	77.2	306.7	130.7	2.5	0.60	6.54	5.35	95.70
	Rice	9.6	9.58	28.9	13.6	0.64	4.4	6.13	0.001
Middle	Corn	39.5	36.4	77.7	4.6	0.57	4.69	6.04	0.001
	Watermelon	71.4	131.7	161.4	2.6	0.75	6.51	6.81	6.10
	Cucumber	17.1	104.9	43.3	16.1	0.74	3.81	7.61	0.001
	Pumpkin	57.8	71.1	141.4	3.0	0.68	6.50	7.38	0.001
	Tomato	84.8	57.2	178.4	3.3	0.84	7.66	6.57	0.001
Lower	Watermelon	16.4	23.1	39.2	3.5	0.87	5.07	8.36	79.10
	Tomato	16.8	59.8	58.6	7.6	0.85	6.69	8.40	0.001
	Corn	23.0	37.2	25.3	4.9	0.75	4.33	8.26	0.001
	Alice grass	6.5	0.001	10.3	22.3	0.67	3.34	5.83	132.85
	Melon	43.7	16.9	67.9	10.8	0.81	5.93	10.78	0.001
	Chili pepper	26.8	19.1	19.2	4.4	0.71	5.07	8.13	101.80
Kabata-Pendias y Pendias (2001)		5-20	300	50-100	2-3	0.05-0.7	0.5-10	1-10	0.1-1.0

4. CONCLUSIONS

- The study showed that it is necessary to monitor the concentration of heavy metals in sediments, water and crops within the La Villa river basin, Herrera and Los Santos provinces, Panama.
- In the sediments, high concentrations of copper, manganese, chromium and arsenic were observed, a product of the great agricultural activity, anthropogenic contamination (fungicides, herbicides, wastewater from pig farming, agro-industry). However, due to their geological origin, these soils are rich in copper, manganese and arsenic, latter being associated with iron oxides and sulfides.
- Some metals such as lead and arsenic showed low solubility in water but showed high concentration in sediments.
- Crops such as melon, watermelon, tomatoes, pumpkin and banana showed high concentrations of Cu Cr, Cd, especially in the middle and lower basins, the source of Cr and Cd is most probably from polluted water which means that anthropogenic activities are influencing a lot on the contamination values found.

5. RECOMMENDATIONS

- It is recommended to analyze the water after being treated by the water treatment plant of the National Aqueducts and Sewers Institute (IDAAN) to check its quality, especially the levels of heavy metals in order to compare them with the levels found in natural waters. from the La Villa river.

DISCLAIMER

The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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