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Isotherms of Adsorption of Heavy Metals in Soils and Sediments of the La Villa River Basin-Panamá

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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

The study was carried out within the La Villa river basin (Herrera and Los Santos provinces). In these lands, great agricultural activity is developed, highlighting the production of corn, tomatoes, melons, watermelon, beans, peppers, sugarcane, meat and milk livestock. They are subjected to intensive use of agrochemicals and influenced by discharges of by-products from some industrial and agro-industrial companies located within the basin. The objective of the study was to determine by means of Langmuir isotherms the maximum adsorption of Mn, Zn, Cu, Pb and Cd in soils and sediments of areas with intensive agricultural activity within the La Villa river basin. Five soil and sediment samples were taken from producer´s farms in the rainy season (June-November 2016) and five samples in the dry season (January-April 2017). The total concentration of the heavy metal was determined. The isotherms of the trace metals in soils and sediments were determined in the samples taken at both times of the year by applying different concentrations of the metal in a $CaCl_2$ 0.01 M solution. High levels of Cu were found in soils and Cu, Mn, Cr and As in sediments. The Mn isotherm showed low values and low adsorption force, Cu and Zn showed high adsorption values, but with low retention force. For Pb, high adsorption values were observed, but very low retention force in the dry season, contrary to Cd, which obtained low adsorption values, but with a higher force. This behavior is closely related to the texture of the soils. The Cu, Zn and Mn showed high significant correlations with the clay content in the soil, contrary to the pH and the organic matter did not obtain a good correlation with the adsorption of the metals.

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1. INTRODUCTION

For an element to be considered heavy metal (HM), it must meet two characteristic

- Have metallic characteristics
- Have a density higher than the average of the earth's crust (5; 5.5; 6 gcm^{-3}). [1].

Chromium (Cr), cadmium (Cd), mercury (Hg), lead (Pb) and arsenic (As) are considered the most toxic. Nickel (Ni), silver (Ag), tin (Sn), antimony (Sb) and molybdenum (Mo) are also toxic. Moderately toxic manganese (Mn), copper (Cu), zinc (Zn), selenium (Se) and low toxic under special circumstances iron (Fe), aluminum (Al), titanium (Ti), bismuth (Bi) [2].

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Adsorption can be non-specific, such as cation exchange capacity or specific. The latter is produced by the affinity of some metal ions for a particular adsorption site, for this reason metals are specifically adsorbed in a certain order of preference, for example, Cd <Zn <Cu <Pb [2,3]. This type of adsorption is affected by pH, the presence of oxides and hydroxides and organic matter [4].

The adsorption phenomenon is generally described by graphs called adsorption isotherms that represent the amount of HM (adsorbate) adsorbed per gram of sediment (adsorbent) as a function of the equilibrium concentration of the adsorbate at a constant temperature [5].

The usefulness of these isotherms for the prediction of HM mobility in different environments is based on the fact that they take into account ionic and binding forces, pH, redox potential, cation exchange capacity, organic matter, clay content and mechanisms of reactions in the internal and external spheres of soil colloids [6,7,8].

Fontes and Gomes [9] observed that the adsorption of the metals Cr, Ni, Cu, Zn, Cd and Pb in Oxisol, Ultisol and Alfisol conformed to the Langmuir model. Chamorro and Sánchez [10], studying the adsorption of Pb in soils of the mining region in the department of Cauca, Colombia, found that the Langmuir isotherm was the model that best suited to explain the type of phenomenon that occurred between the metal and the soil. Villarreal [11] determined by means of the Langmuir isotherm the maximum phosphorus retention capacity (P) of 46 soils belonging to the main existing soil orders in Panama. However, this work has not been done for HM such as Pb, Ni, As, Cd, Cu, Zn that represent greater danger. Arboleda [12], Insuasty et al. [13], conducted studies on adsorption and contamination of HM in Colombian agricultural soils.

The present study was carried out in areas where there is a great agricultural activity. In these lands historically the production of corn, tomatoes, melons, peppers, pastures and livestock has been developed. These are lands subjected to an intensive use of agrochemicals and influenced by discharges of by-products from some industrial companies located within the basins.

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The objective of this research was to determine by means of Langmuir isotherms the maximum absorption capacity of HM in productive soils within the La Villa-river basin Panama.

2. MATERIALS AND METHODS

The experiment consisted of a completely random monitoring of the concentration of HM in soils and sediments located in the upper, middle and lower basin of the La Villa River.

The La Villa river basin has an area of 1157.5 km^2 (645.8 km^2 in the province of Herrera and 511.7 km^2 in the province of Los Santos). It is mostly composed of alfisols and inceptisols soils according to the Soil Taxonomy Classification

System [14,15] formed in the Upper Cretaceous, initially covered by intermediate volcanic material, basic volcanic material and tuffs [16].

This basin in its upper part has an average rainfall of 2,200 mm and in its lower part of about 1,054 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 [14].

Soil samplings were carried out on productive farms within the La Villa river basin to determine the concentration of heavy metals (cadmium, nickel, copper, iron, manganese, zinc, lead, arsenic, chromium) in the rainy season (10 samples of soil and 11 sediments from June to December 2016) and in the dry season (9 soil samples and 11 sediments from February to April 2017).

To carry out the samplings, the systematic or grid method was used, 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 (Fig. 1).

The definition of the sampling methodologies was decided by the topography, type of main activity, local climate and type of soil, for which it was tried to select a preferably rectangular area of approximately 10.0 x 30.0 meters, on which the took the sub-samples (from which it is inferred that the samples were composite) with a number of 15 in each grid, with approximately 100.0 grams each, at 30.0 centimeters deep. Later they were homogenized so that said sampling offered representative results for the description of the site.

The best time for soil and sediment sampling was decided taking into account the technology used by the farmer. Agricultural use without irrigation, the sampling period corresponded to the one with the greatest accumulation of contaminants in the soil, which, in annual crops, corresponds to the harvest time, when the chemical contaminants used during the development period of the plant have accumulated. In the case of irrigated agro-export crops, it generally occurs in the dry season. Each sampled site was georeferenced using a GPS to determine its exact location.

To determine the absorption capacity of each soil, 3g of soil were equilibrated with 200 ml of the HM solution under study in variable concentrations, prepared from a standard of 2,500 mg of metal l^{-1} in calcium chloride ($CaCl_2$) 0,01M shaken for 16 hours at 3,000 rpm and centrifuged for 30 minutes [18].

In the supernatant solution the concentrations of the heavy metal at equilibrium (c) were determined. The adsorbed HM (x) was calculated as the difference between the applied HM and the HM in solution. With these values the relations were calculated:

mg of HM adsorbed g^{-1} of soil (x/m) and mg of HM in equilibrium kg^{-1}/mg of HM adsorbed g^{-1} of soil (c/x/m).

The mathematical equation to calculate the Langmuir isotherm is the following [19]:

$$C/x/m = 1/k.b * c/b$$

thus, if $Y = c/x/m$ and $X = C$; the intercept of the line is 1/k * b and the slope is 1/b

Knowing the slope 1/b, the maximum absorption capacity of the HM (b) and the retention energy constant (k) were calculated.

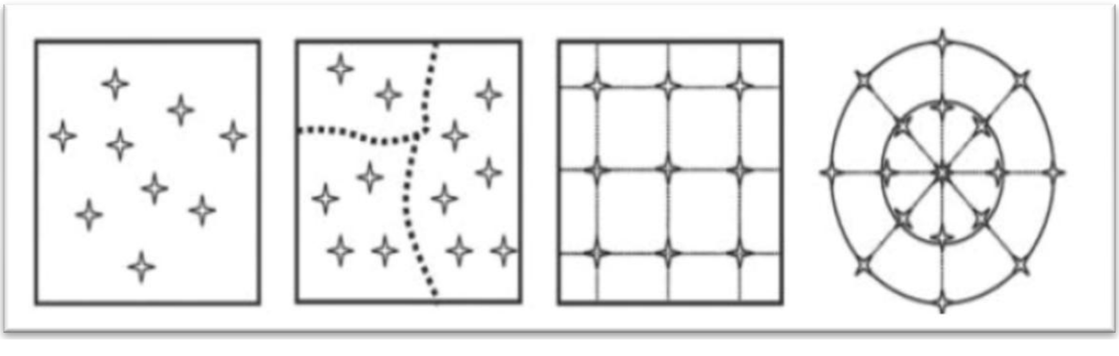

Fig. 1. Grid scheme used for systematic soil and sediment sampling [17]

This methodology provides information on the concentration of the remaining HM in the soil solution (intensity factor), which is in equilibrium with the HM of the solid phase (capacity factor).

The maximum adsorption of Cu, Zn, Mn, Pb and Cd was determined.

The location of the sites where the soil and sediment samples were taken can be observed in Villarreal et al. [20] and Villarreal et al. [21].

Pearson's correlation analysis was performed between the maximum adsorption of each metal with the content of organic matter, percentage of clay in the soil and pH, among the samples collected in the dry season as well as in the rainy season.

3. RESULTS AND DISCUSSION

The HM contents in the sampled soils and sediments during the rainy season of 2016 and the dry season of 2017 can be seen in Villarreal [20] and Villarreal et al. [21], respectively.

In soils and sediments collected in the rainy (5 samples) and dry (5 samples) seasons in the La Villa river basin, the maximum absorption capacity of each metal and the force with which it is retained was determined by means of the Langmuir isotherm.

Tables 1 to 5 show the results obtained. Cu presented high adsorption values in soil and sediments, especially in the rainy season, but with low retention force (Table 1). Zn, on the other hand, presented lower levels of adsorption, but is retained with greater force (Table 2). Mn has very low levels of adsorption (Table 3). Most of the soils of Panama are acidic (40% ultisols) and are naturally rich in Fe and Mn oxides (Villarreal et al. 2013). Pb also presented high levels of adsorption (Table 4) and with Cd very low levels of adsorption were observed, however, it is the metal that is most strongly retained (Table 5).

Cortés et al. [22], investigating the capacity and retention force of metals such as Cd, Cu, Pb and Zn in andisols and vertisols of Colombia, found the following adsorption order: Pb> Zn> Cd> Cu and the order of the attractive force was: Cd> Pb> Cu> Zn, coinciding in many aspects with this research. Chamorro and Sánchez [10], determined a Pb adsorption capacity in mining soil of the department of Cauca-Colombia of 6.42 mgg^{-1} of soil.

Figs. 2, 3, 4, 5 and 6, show the isotherms of Cu, Zn, Mn, Pb and Cd, respectively. These models represent the trend of the adsorption kinetics of a certain metal.

According to Sposito [19], differences in adsorption capacity and strength between metals are probably associated with differences in the compositions of soil solutions, the net surface charges of the ions that form complexes on the surface of the internal and external spheres and the ionic cloud of the diffuse double layer. They are also associated with the content of carboxylic (ACOOH), hydroxylic (AOH) and phenolic (aromatic ring-OH) functional groups present in humic acids in the soil [23].

The adsorption processes in the soil and sediments are highly influenced by the pH, percentage of sand and clay, amount of organic matter in the soil.

As the adsorption curve can be observed, Cd does not decay. According to Parra and Espinosa [24], Cd has a higher affinity for adsorption sites than other elements. Cd and Zn compete for adsorption sites, which may be due to the chemical similarity between these elements (electronegativity, oxidation state). Chantawong et al. [5], found that the presence of Cd produced a significant decrease in Zn adsorption but did not affect Pb adsorption.

When performing Pearson correlations between the metal adsorption capacity of the La Villa river soils and sediments with some properties such as clay content, pH and organic matter content, statistically significant high correlations were observed especially with clay content.

In the dry season (Table 6), a highly significant correlation was obtained between Cu and clay and Mn and clay, and statistically significant between Zn and clay. The pH and the content of organic matter did not show significant correlations for the adsorption of metals in these soils in the dry season. Significant high correlations were also observed between some metals such as: Zn - Cu; Mn-Zn; Pb-Cu; Pb-Mn; Cd-Pb and Cd-Mn.

In the rainy season (Table 7), coinciding with the dry season, high statistically significant correlations were observed between the adsorption of the metals Cu, Zn and Mn with the clay content. This indicates that in the soils of the La Villa river basin, the clay content of the soils and sediments is a determining factor in the adsorption capacity of metals.

Table 1. Maximum copper adsorption capacity and retention force in soils and sediments of the La Villa river basin

Rainy Season	Type of Sample	Langmuir Model	Maximum Adsorption Capacity	Retention Force (K)
Upper Basin			$mgkg^{-1}$	
Quebrada de Piedra	Soil	Y=0.038x + 0.0392 R^2= 0.63	263.16	0.1
Quebrada de Piedra	Sediment	Y=0.0037x + 0.0466 R^2= 0.74	270.27	0.08
Middle Basin				
Cocullo	Soil	Y= 0.004x + 0.0424 R^2= 0.75	250.00	0.09
Lower Basin				
El Ejido	Soil	Y=0.0035x + 0.0425 R^2= 0.69	285.71	0.01
La Villa	Soil	Y= 0.0048 + 0.0449 R^2= 0.80	208.33	0.11
Dry Season				
Upper Basin				
Río La Villa	Soil	Y=0.0077x + 0.1475 R^2= 0.48	129.87	0.05
Quebrada Chen	Sediment	Y= 0.0086+0.1596 R^2= 0.48	116.28	0.05
Middle Basin				
Río La Villa	Soil	Y= 0.1038x + 0.78 R^2= 0.74	96.34	0.13
Río La Villa	Sediment	Y=0.0111x + 0.1962 R^2= 0.47	90.09	0.06
Lower Basin				
Río La Villa	Sediment	Y=0.0115x + 0.0984 R^2= 0.73	86.96	0.12

Table 2. Maximum zinc adsorption capacity and retention force in soils and sediments of the La Villa river basin

Rainy Season	Type of Sample	Langmuir Model	Maximum Adsorption Capacity mgkg^{-1}	Retention Force (K)
Upper Basin				
Quebrada de Piedra	Soil	Y=0.0208x + 0.2089 R^2= 0.95	48.08	0.10
Quebrada de Piedra	Sediment	Y=0.006x + 0.072 R^2= 0.92	166.67	0.08
Middle Basin				
Cocullo	Soil	Y=0.0149x + 0.142 R^2= 0.97	671.14	0.11
Lower Basin				
El Ejido	Soil	Y=0.0024x + 0.0359 R^2= 0.82	416.67	0.07
La Villa	Soil	Y= 0.0074 + 0.1155 R^2= 0.80	135.14	0.06
Dry Season				
Upper Basin				
Río La Villa	Soil	Y=0.0564x + 0.2996 R^2= 0.98	17.73	0.19
Quebrada Chen	Sediment	Y= 0.0086x + 0.196 R^2= 0.95	13.04	0.22
Middle Basin				
Río La Villa	Soil	Y=0.1667x + 0.9633 R^2= 0.95	6.00	0.17
Río La Villa	Sediment	Y=0.1665x + 0.9833 R^2= 0.95	6.01	0.17
Lower Basin				
Río La Villa	Sediment	Y=0.0143x + 0.1461 R^2= 0.96	69.93	0.10

Table 3. Maximum manganese adsorption capacity and retention force in soils and sediments of the La Villa river basin

Rainy Season	Type of Sample	Langmuir Model	Maximum Adsorption Capacity mgkg^{-1}	Retention Force (K)
Upper Basin				
Quebrada de Piedra	Soil	Y=0.1631 + 3.7441 R^2= 0.80	6.13	0.04
Quebrada de Piedra	Sediment	Y=0.1461x + 7.0526 R^2= 0.57	6.84	0.02
Middle Basin				
Cocullo	Soil	Y=0.3583x + 12.773 R^2= 0.69	2.79	0.03
Cuenca Baja				
El Ejido	Soil	Y=0.1347x + 6.1093 R^2= 0.60	7.42	0.02
La Villa	Soil	Y=0.1457x + 0.5792 R^2= 0.98	6.86	0.25
Dry Season				
Upper Basin				
Río La Villa	Soil	Y=0.5131x + 35.833 R^2= 0.41	1.95	0.01
Quebrada Chen	Sediment	Y= 0.6295x+45.992 R^2= 0.36	1.59	0.01
Middle Basin				
Río La Villa	Soil	Y=0.4825x + 24.058 R^2= 0.55	2.07	0.02
Río La Villa	Sediment	Y=0.14x + 3.5925 R^2= 0.86	7.14	0.04
Lower Basin				
Río La Villa	Sediment	Y=0.1933x + 2.2424 R^2= 0.97	5.17	0.09

Table 4. Maximum lead adsorption capacity and retention force in soils and sediments of the La Villa river basin

Rainy Season	Type of Sample	Langmuir Model	Maximum Adsorption Capacity	Retention Force (K)
Upper Basin			$mgkg^{-1}$	
Quebrada de Piedra	Soil	Y=0.0047x + 0.0129 R^2= 0.88	212.77	0.36
Quebrada de Piedra	Sediment	Y=0.011x + 0.0638 R^2= 0.96	90.91	0.17
Middle Basin				
Cocullo	Soil	Y= 0.0323x - 0.3439 R^2= 0.97	30.96	0.09
Lower Basin				
El Ejido	Soil	Y=0.0046x + 0.0672 R^2= 0.99	217.39	0.07
La Villa	Soil	Y= 0.001x + 0.1019 R^2= 0.64	1000.0	0.01
Dry Season				
Upper Basin				
Río La Villa	Soil	Y=0.0107x + 0.1052 R^2= 0.98	93.46	0.1
Quebrada Chen	Sediment	Y= 0.0647x+1.9913 R^2= 0.92	15.46	0.03
Middle Basin				
Río La Villa	Soil	Y=0.3089x + 5.5316 R^2= 0.89	3.24	0.06
Río La Villa	Sediment	Y=0.0131x + 0.1248 R^2= 0.97	76.34	0.11
Lower Basin				
Río La Villa	Sediment	Y=0.008x + 0.2457 R^2= 0.95	125.00	0.03

Table 5. Maximum cadmium adsorption capacity and retention force in soils and sediments of the La Villa river basin

Rainy Season	**Type of Sample**	**Langmuir Model**	**Maximum Adsorption Capacity**	**Retention Force (K)**
Upper Basin			$mgkg^{-1}$	
Quebrada de Piedra	Soil	Y=0,5459x - 4.0043 R^2= 0.81	1.83	0.14
Quebrada de Piedra	Sediment	Y=0.6959x – 2.3743 R^2= 0.95	1.44	0.29
Middle Basin				
Cocullo	Soil	Y=0.8311x + 2.8153 R^2= 0.98	1.20	0.3
Lower Basin				
El Ejido	Soil	Y=0.6621x + 0.9963 R^2= 0.96	1.51	0.66
La Villa	Soil	Y=0.5156x – 1.739 R^2= 0.96	1.94	0.30
Dry Season				
Upper Basin				
Río La Villa	Soil	Y=0.9946x – 1.5518 R^2= 0.98	1.01	0.64
Quebrada Chen	Sediment	Y= 1.9568x-10.987 R^2= 0.99	0.51	0.18
Middle Basin				
Río La Villa	Soil	Y= 4.937x – 52.27 R^2= 0.98	0.20	0.09
Río La Villa	Sediment	Y=1.2824x + 4.2463 R^2= 0.99	0.78	0.30
Lower Basin				
Río La Villa	Sediment	Y=0.6483x – 9.757 R^2= 0.96	1.54	0.07

Table 6. Correlations between adsorption capacity of soils and sediments of the La Villa river vs soil properties in dry season

	Clay	pH	Organic Matter	Cu	Zn	Mn	Pb	Cd
Clay	1							
pH	-0.363	1						
Organic Matter	0.297	0.792**	1					
Cu	0.605**	-0.290	0.403	1				
Zn	0.451*	0.111	0.135	0.748**	1			
Mn	0.659**	-0.241	0.431	0.062	0.498*	1		
Pb	0.379	-0.014	0.153	0.618**	0.428	0.454*	1	
Cd	0.330	0.253	-0.078	0.397	0.375	0.507*	0.796**	1

Table 7. Correlations between adsorption capacity of soils and sediments of the La Villa river vs soil properties in rainy season

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Pb	0.379	-0.014	0.153	0.618**	0.428	0.454*	1	
Cd	0.330	0.253	-0.078	0.397	0.375	0.507*	0.796**	1

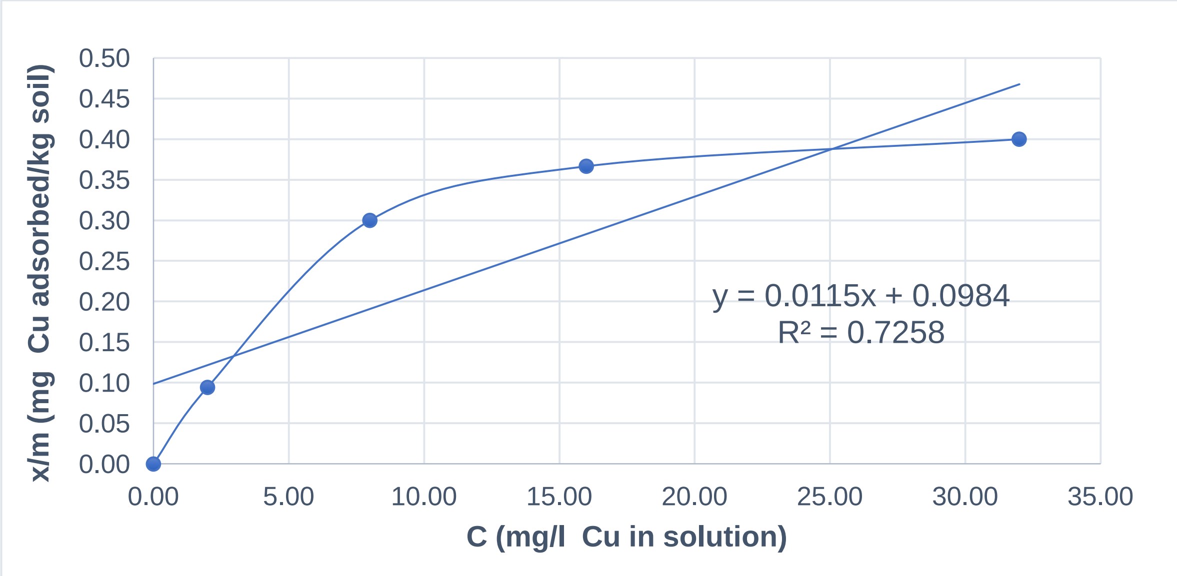

Fig. 2. Langmuir isotherm of Cu adsorption in the soil of the lower La Villa river basin. Dry season 2017

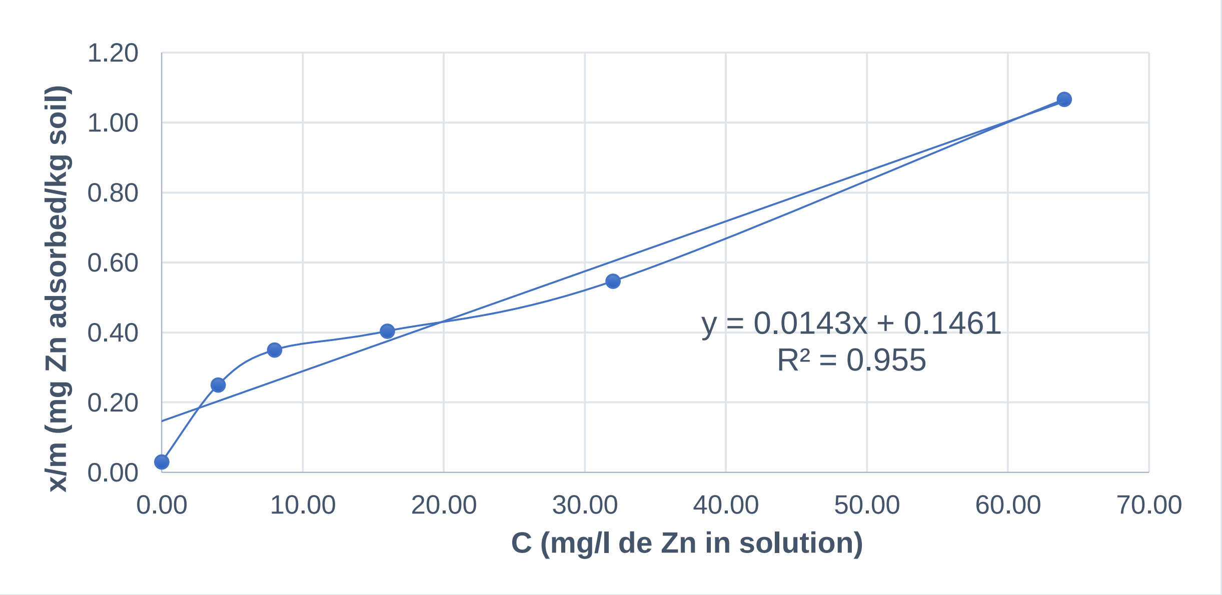

Fig. 3. Langmuir isotherm of Zn adsorption in the soil of the lower La Villa river basin. Dry season 2017

In experiments carried out by Cortés et al. [22], found a high correlation between metals and the content of organic matter and pH. Vega et al. [25], observed that the retention of Cu occurred mainly due to the formation of complexes with organic matter.

The composition of the organic matter and the mineral phase of the soil, as well as the pH, have significant effects on the adsorption of Cd; Soils with high contents of organic matter or iron oxides adsorb more Cd than those with large amounts of type 2:1 clays, however, they present high CEC (cation exchange capacity) [26]. The most stable organic fraction, at the same time more resistant to mineralization, in general can retain heavy metals, and in particular Cd, in unavailable forms. However, soil organic matter (SOM) can have opposite effects on the adsorption of this element, the soluble fraction manages to make it complex, facilitates its mobility in the soil and by mineralizing it allows greater availability [27].

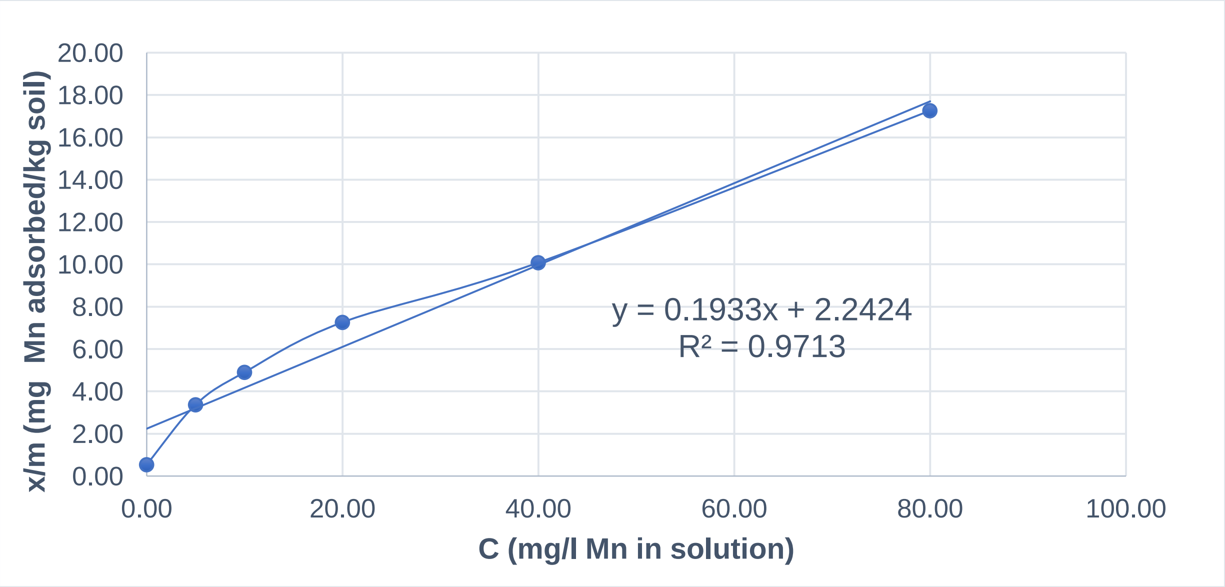

Fig. 4. Langmuir isotherm of Mn adsorption in the soil of the lower La Villa river basin. Dry season 2017

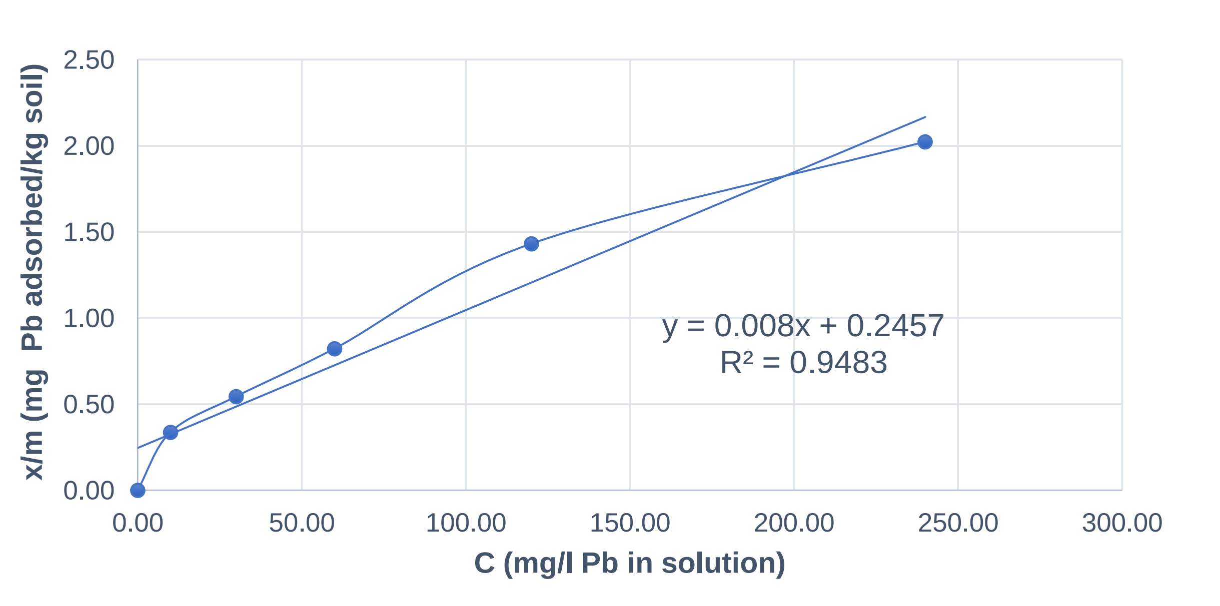

Fig. 5. Langmuir isotherm of Pb adsorption in the soil of the lower La Villa river basin. Dry season 2017

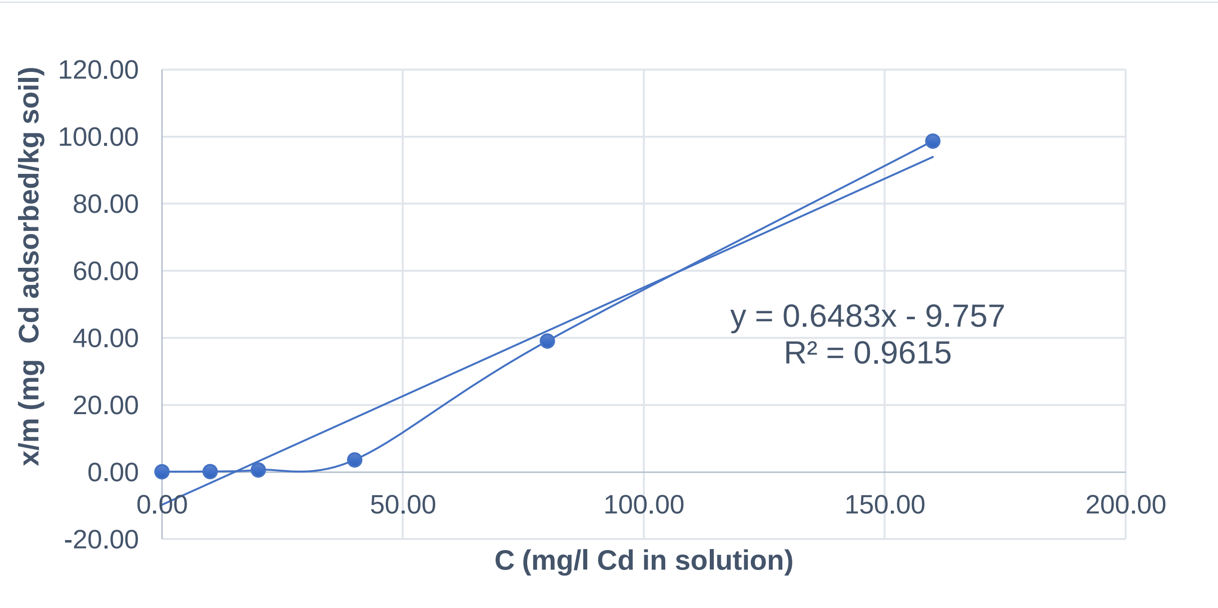

Fig. 6. Langmuir isotherm of Cd adsorption in the soil of the lower La Villa river basin. Dry season 2017

4. CONCLUSIONS

- In the rainy season the highest adsorption values were in this order: Pb> Zn> Cu> Mn> Cd. In the dry season: Cu> Pb> Zn> Mn> Cd. Lower Cu concentrations in the dry season favored a greater number of adsorption sites available, increasing the adsorption capacity of the metal by soils and sediments.
- The adsorption force for Cu and Zn was higher in the dry season, while Pb, Mn and Cd were retained with greater force in the rainy season. Being the order of retention energy in the rainy season: Pb> Cd> Zn> Cu> Mn. In dry season: Cd> Zn> Cu> Pb> Mn.
- Cu, Zn and Mn showed high correlations with clay content in soil and sediments. On

the contrary, pH and organic matter did not show to have much influence on the adsorption of heavy metals in the soils and sediments of the La Villa river basin.

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 the National Secretariat for Science, Technology and Innovation (SENACYT) and personal efforts of the authors.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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