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Geoaccumulation and Ecological Risk Indexes in Papaya Cultivation Due to the Presence of Trace Metals

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Abstract: The aim of this research was to evaluate the impact of heavy metals on Maradol papaya cultivation soil, through the geoaccumulation index (I_{geo}) and the ecological potential risk index (RI). Soil samples from 15 locations in the Cotaxtla municipality of Veracruz, Mexico were tested for pH, soil texture, and concentrations of lead (Pb), chromium (Cr), cadmium (Cd), zinc (Zn), copper (Cu), and organic matter (MO). The pH varied between values of 5.5 ± 0.10 and 7.7 ± 0.22, while the MO varied from 1.57% ± 0.97% to 13.1% ± 1.342%. The type of soil texture represented 48% sandy loam, 40% loam, 8% clay loam, and 4% silt-loam. For heavy metals, average levels were found in the following order Cr (0.695 ± 0.018) > Zn (0.615 ± 0.016) > Pb (0.323 ± 0.012) > Cu (0.983 ± 0.011) > Cd (0.196 ± 0.011) mg kg^{-1}. The I_{geo} values from 96% of the analyzed sampling points were below zero and were considered uncontaminated. The other 4% of samples, from the Potrerillo1 (PT) site, had I_{geo} values of 1.13, where the highest concentration of Cd was found, which indicates moderate contamination levels. The RI index at the PT site was in the category of moderate contamination, and the rest of the points correspond to the category of low pollution.

Keywords: accumulation; potential risk; heavy metals

1. Introduction

Heavy metals are currently the pollutants of greatest concern because they are highly toxic at low concentrations and can bioaccumulate and enter the food chain [1,2].

The distribution dynamics followed by heavy metals in soil can reach groundwater by leaching, and by runoff reach surface waters. These chemical compounds, in addition to being retained in the soil, interact with solutions present in the environment [3]. Heavy metals have a strong ability to bind to organic molecules or can simply precipitate in the form of carbonates, phosphates, or hydroxides [4]. In the soil, metals are found in different forms of oxidation, such as inorganic compounds, metal complexes, and organometallic compounds. When these metal compounds dissolve in water, they dissociate into ions and tend to behave like cations; they become part of the exchange complex and are available for absorption in plants, by displacing the essential cations [5].

In agricultural soils, metals accumulate through various sources, such as industrial waste, wastewater, inorganic fertilizers, manure, agrochemicals, and irrigation water, among others [6]. Some chemical fertilizers carry traces of heavy metals to the ground, due to the impurities of natural materials and minerals, mainly phosphate and nitrogen compounds, which causes an increase in the concentration of these significantly over time [7–9]. The prolonged exposure of crop plants in soils with heavy metals increases their absorption and depends on factors such as pH, cation exchange capacity, organic matter content, clay content, and redox potential; these determine the soil capacity to retain or mobilize heavy metals [10]. The solubility of trace cations increases as the pH is more acidic, thus increasing its mobility in soil and availability of absorption to crop plants; it has been reported that at pH 5, it is considered a medium absorption for Cd, weak for Co and Zn, and too weak for Cu, Cr, and Pb [11].

While heavy metals with organic matter form complexes that vary according to each metal, for Cu the complexes that are formed are considered unavailable, however, for the Cd in its interchangeable form, it increases its availability to be absorbed by the plants [12].

Heavy metals in plants cause a stress factor that develops physiological reactions [13]. Metallic stress has notable effects on crop productivity and growth; different responses are triggered, ranging from biochemical reactions to impacting crop yields [14]. Heavy metals can be absorbed by plants by replacing essential elements required as nutrients, such as P, K, and Mg [15]. However, some micronutrients such as Zn, Cr, and Cu, when they exceed the limits required by the plants, can cause toxicity. The bioaccumulation of heavy metals in the edible parts of agricultural crops represents a risk to humans, since metals can pass through the trophic links [16].

To evaluate the bioaccumulation of heavy metals in agricultural soils, several studies have been carried out, in which the spatial distribution of these pollutants in impacted areas, with toxic effects on public health, is reported by the consumption of food grown in these contaminated soils [17]. Heavy metals in trace amounts can accumulate in soils of agricultural areas, due to their characteristics and buffer capacity [18,19].

The risks, the degree of toxicity, and persistence of the metals depend on the impact that the soils receive by different anthropogenic activities. The use and application of geoaccumulation indexes (I_{geo}) and the potential ecological risk index (RI) will identify the source of pollutants and the degree of bioaccumulation in soil [20]. The geoaccumulation index is applied to quantify the concentration of heavy metals in soils at the level of the earth's crust, with respect to the natural concentration, and thus the origin of the possible sources of contamination is identified [21]. On the other hand, the ecological risk index reveals the level of accumulation and toxicity of metals, to determine the degree of contamination to which the soils are exposed. In agricultural production systems, the intensive use of fertilizers provides metallic elements in trace amounts, as well as through organic amendments, use of agrochemicals, irrigation water, atmospheric depositions, and wastewater [22,23].

In Mexico, there are 1.2 million hectares dedicated to agriculture distributed in various entities; the production of fruit trees such as papaya stands out (*Carica papaya* L.), which is exported to the United States and Canada [24]. The municipality of Cotaxtla is the one with the highest papaya production in the central area of the Gulf of Mexico, representing 24% with 25,775 tons [25]. This study evaluated the concentration of heavy metals Pb, Cd, Cr, Cu, and Zn in the papaya cultivation soils of this important export zone, and its relationship with soil characteristics, such as pH, organic matter, and textural soil type. Geoaccumulation rates were evaluated (I_{geo}), as was the potential ecological risk index (RI) of metals exposed to soils with trace concentrations.

2. Materials and Methods

This research was carried out in the Sotavento region where Cotaxtla is located, the main export zone for papaya cultivation (*Carica papaya* L.) from the central area of the Gulf of Mexico. The area is located at the geographical coordinates 18°44′–18°59′ north latitude and 96°11′–96°32′ west longitude, at an altitude of 10 to 200 m above the sea level. Twenty-five hectares corresponding to production units (UP) of papaya cultivation were analyzed. Quadrant areas were selected of 100 × 100 m (1 ha) and five simple subsamples of 500 g were taken for each production unit, one collected in the central part of the area and the others directed to cardinal directions at a distance of 25 m [26]. The five subsamples were taken at 20 cm depth, using a hole digger. The 125 subsamples were grouped by production unit and homogenized to obtain composite samples of 2 kg, as shown in Figure 1 [27,28]. The samples were kept in sealed polythene bags, labeled, and transported for analysis to the Aquatic Resources Research Laboratory (LIRA) of the Technological Institute of Boca del Río.

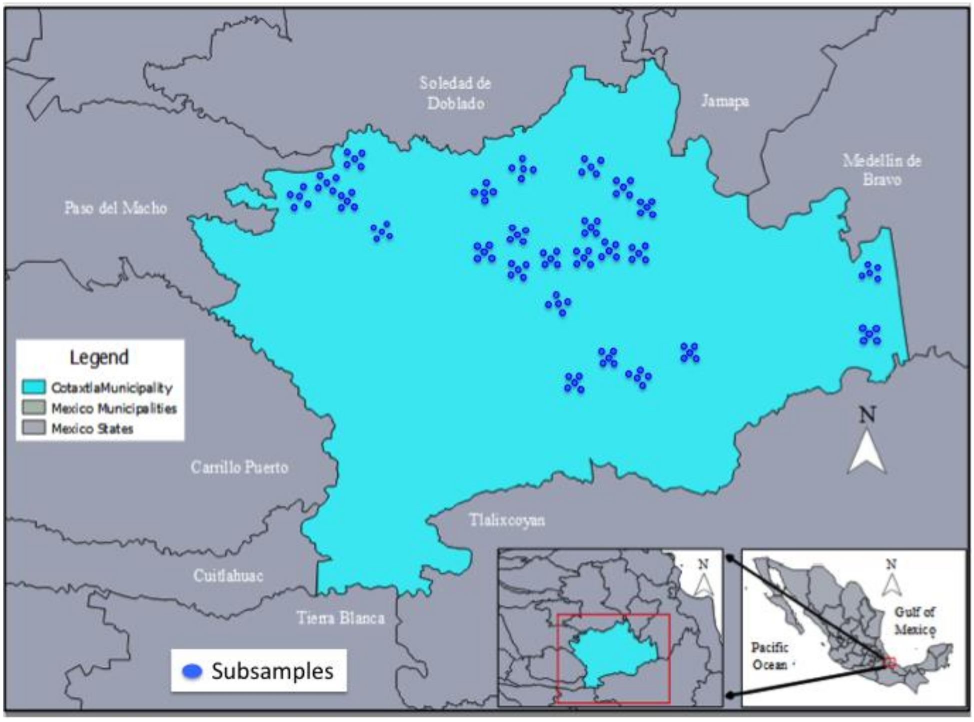

Figure 1. Location of the study area and sampling points in the municipality of Cotaxtla.

The pH measurements were made with a CONSORT Model C6010 table potentiometer in a soil/distilled water ratio of 1:2. Organic matter was analyzed by the ignition method, proposed by Schulte and Hopkins [29]. The soil texture was made by the Bouyoucos hydrometer procedure [30].

2.1. Heavy Metal Analysis

Soil samples were analyzed for heavy metals Pb, Cd, Cr, Cu, and Zn under the specifications of NOM-117-SSA1-1994 [31], by atomic absorption spectrometry. The soil was dried in trays at 35 °C, and subsequently screened to obtain the finest particles. Then, 0.5 g of these particles were weighed and 10 mL of nitric acid (HNO_3) 70% reactive grade was added (suprapuro) J.T. Baker®, for digestion in Teflon vessels, and they were introduced to the microwave CEM Mars 5 (CEM, Corporation Mathews, NC, USA). After digestion, samples were filtered using a Nalgene bottle with a Millipore model filter HAWP04700 of 0.45 µm, and a vacuum pump. The filtrate was transferred to a 25 mL volumetric flask and titrated with deionized distilled water (1 µmho·cm^{-1} at 25 °C). The samples were transferred to amber glass bottles previously labeled and kept refrigerated until analysis. The atomic absorption equipment used was the Thermo Scientific Model Ice 3500 AA System (Thermo Scientific®, China), using flame spectrophotometry. The parameters used in the atomic absorption equipment for the analysis of the samples and standards were performed in triplicate.

The calibration curve was performed using certified standards High-Purity Standards® (High-Purity Standards, Charleston, SC, USA) at the concentration of 1000 µg mL^{-1} at 2% in HNO_3. The calibration curve was performed at an adjusted range from least to greatest near the analyte to obtain a correlation coefficient greater than 0.95. In the analysis of sample readings for metals Cd and Pb, an argon gas graphite furnace was used (5.0 ultra-high purity, Praxair®, Danbury, CT, USA) at a wavelength of 228.8 and 217 nm, respectively. Meanwhile, with metals like Cr, Cu, and Zn, a flame was used with air -C_2H_2 and nitrous oxide (5.0 ultra-high purity, Praxair®). The wavelength for the Cr was 357.9 nm, for Cu 324.8 nm, and for Zn 213.9 nm.

2.2. Geoaccumulation Index (I_{geo})

In order to know the risk factors in the agricultural soils of the Sotavento region in the center of the Gulf of Mexico, the geoaccumulation index was determined (I_{geo}) proposed by Muller [32], which allows the evaluation of the degree of contamination of heavy metals in soil and sediments. This index is defined with the following equation:

$$I_{geo} = \log_2 \frac{C_n}{kB_n} \quad (1)$$

where C_n represents the metal concentration in the analyzed soils, B_n represents the background geochemical concentration of the metal in the earth's crust, the constant k (k = 1.5) is a correction coefficient that determines the influence of natural fluctuations and the influences of anthropic sources.

The values of I_{geo} are classified according to seven degrees of contamination, where Grade 1 corresponds to uncontaminated soil ($I_{geo} \leq 0$); Grade 2 refers to soil without contamination to moderately contaminated ($0 < I_{geo} \leq 1$); Grade 3 corresponds to soil with moderate pollution ($1 < I_{geo} \leq 2$); Grade 4 indicates moderate to highly contaminated soil ($2 \leq I_{geo} < 3$); Grade 5 indicates high pollution ($3 \leq I_{geo} < 4$); Grade 6 is high to extremely contaminated soil ($4 \leq I_{geo} < 5$); and Grade 7 indicates extremely contaminated soil ($I_{geo} \geq 5$) [33].

2.3. Index of Potential Ecological Risk

To assess the degree of contamination by heavy metals in soil, the potential ecological risk index (RI), presented by Hakanson, will be calculated [34] that assesses the risk in soils according to the toxicity of heavy metals and the response in the environment. Thus, it is calculated with the following equation:

$$RI = \Sigma\, E_{i,} \quad (2)$$

$$E_i = T_i \frac{C_i}{B_i}, \quad (3)$$

where RI is calculated with the sum of the risk factors for heavy metals in soil. Thus, E_i represents the potential ecological risk factor that is calculated with Equation (3), where C_i represents the concentration obtained from metals in the cultivated soils evaluated, while B_i is the background geochemical concentration [18,35]. T_i is the metallic toxic factor, which was standardized by Hakanson [34], and that is classified according to the level of toxicity of metals, so Cd > Pb = Cu > Zn; in this way, the risk factor for Cd is 30, Pb and Cu is 5, Cr with risk factor 2, and Zn 1 [36].

Sun et al. [37] reported four categories to classify the potential ecological risk index (RI); range RI ≤ 50 represents low pollution, 50 < RI ≤ 100 is moderate pollution, 100 < RI ≤ 200 refers to considered pollution, while high pollution is when RI ≥ 200.

2.4. Statistical Analysis

The heavy metal results were represented on a spatial distribution map of the study area of the Sotavento region. The ArcGIS version program used was 10.3. For the data, a one-way analysis of variance (ANOVA) was applied, and to evaluate significant differences in the concentration of metals, the physicochemical data by UP and a Tukey test in case of being significant ($p < 0.05$), was used with the program Statistic 7.0 (StatSoft, Inc. Tulsa, USA), Likewise, a Pearson linear regression analysis was performed to determine if there was a relationship between pH, organic matter (MO), and the textural characteristics regarding the concentrations of the metals analyzed in soil.

3. Results

The pH recorded in the UP, as shown in Table 1, ranges from 5.5 ± 0.01 to 7.7 ± 0.22, where it is observed that the cultivation areas LO (Lomitas1), TR (El Trapiche), TA (Los Tamarindos), and SI (Santa Inés), correspond to basic soils higher than pH 7, while LY, PT (Potrerillo1), PP (Potrerillo2), and VC (Vista Clara) are at a slightly neutral pH between 6.6 and 6.8. On the other hand, the rest of the crops that are 68% of the UP are at a pH that ranges from 5.5 to 6.5; the optimal range for plants to absorb essential nutrients. The pH showed significant differences ($p \leq 0.05$) among TA, TR, and SY (Soyolapa2), however, between TA and TR no statistical differences are shown, as well as with the sites BV (Buena Vista) and SI. However, pH is an essential factor for the mobility of heavy metals in soil, that is, at more acidic pH there is a greater availability of metals to be absorbed in crops [11].

For MO, the highest values reported among the UPs are reported for SI with 13.1% ± 1.342% and for VC with 12.8% ± 1.061%, that, according to the reference values of the NOM-021-SEMARNAT-2000 [30], corresponds to soils with high content of MO. The lowest reported value is for LA (Loma de Angosta) with 1.57%, characterized by being a very low soil in MO. Twelve percent of MO corresponds to soils with medium levels, while 32% are in low levels; also, 48% with levels are reported as very low, as established in the official standard. The content of MO is a determining factor in the absorption of heavy metals in crops, since at higher MO content, chelates are formed, which capture metal ions, causing immobility and possibility of absorption towards plants [4,38]. The MO concentration of the present study shows significant differences ($p \leq 0.05$) between the points SI, VC, PP, and LA; however, there are no significant differences between the SI and VC points. It is observed that LA does not show significant differences with respect to the points BV, LH (Loma de Hoyos1), LI (Lomitas3), LM (Lomitas2), LO, LT (Lomitas4), ML (Mata Limón), MT (Mata Tambor), SF (San Francisco), SL (Soyolapa3), SO (Soyolapa1), SP (Soyolapa4), and SY.

The texture characteristics of the analyzed soils are presented in Table 1, where 48% of the production units are made up of FA (sandy loam) soil, while 40% corresponds to F (franc) soils; on the other hand, the 8% and 4% correspond to FR (clay loam) and FL (silt loam) soils, respectively.

Figure 2 shows the spatial distribution of heavy metal concentration in the study area. Heavy metal values are reported in Table 1, which represents the mean and standard deviation by location. The highest concentrations of Pb meet at the points in VC with 0.32 ± 0.01 mg kg^{-1} and MP (Mata Espino3) with 0.31 ± 0.02 mg kg^{-1}. The minimum concentration reported for Pb was at point TR with 0.18 ± 0.01 mg kg^{-1}, as shown in Figure 3.

Regarding what was obtained for Cr, the highest concentration was in VC with 0.70 ± 0.02 mg kg^{-1} and 0.63 ± 0.02 mg kg^{-1} at point MS (Mata Espino2), while point SF shows the lowest value with 0.212 ± 0.011 mg kg^{-1}. The points VC, SI, MS, LT, SF, and TA show the greatest significant differences ($p \leq 0.05$), however, between the points LT and TA, no significant differences were observed. No differences were observed among the points BT (Bajos Tlachiconal), LO, ME (Mata Espino1), and MP, as was the same case for points BV, LA, LH, LI, LM, LT, ML, MT, and TR, which did not indicate significant differences ($p \leq 0.05$).

In relation to Cd concentrations, the values range from 0.02 to 0.03 mg kg^{-1}, however, the highest reported value was the PT point with 0.20 ± 0.01 mg kg^{-1}; this shows that there are significant differences ($p \leq 0.05$) between the PT point and the rest of the cultivation areas, however, no significant differences were observed between these sites ($p \leq 0.05$).

The highest Zn values were reported in the points ME 0.62 ± 0.02 mg kg^{-1} and MS with 0.55 ± 0.01 mg kg^{-1}, and the PP point shows the lowest value with 0.11 ± 0.01 mg kg^{-1}. Significant differences were observed ($p \leq 0.05$) among the points ME, SL, SO, BV, LI, LT, PP, SI, TA, TR, and VC, however, BV and LT did not reflect significant statistical differences, as did the SF point.

Table 1. Values of soil texture, pH, organic matter (MO), and heavy metal concentration in the study area of the Sotavento region.

UP	Textural Features (%)					pH	MO (%)	Average Concentration (± SD) (mg kg^{-1})				
	GF	A	L	AG	GT			Pb	Cr	Cd	Zn	Cu
BT	3.7	59.3	34.0	2.9	SL	6.5 ± 0.05	4.5 ± 0.26	0.26 ± 0.02	0.49 ± 0.01	0.02 ± 0.01	0.42 ± 0.01	0.18 ± 0.01
BV	3.0	47.1	38.7	11.2	L	7.5 ± 0.04	4.1 ± 0.12	0.20 ± 0.02	0.32 ± 0.03	0.02 ± 0.01	0.19 ± 0.02	0.98 ± 0.01
TR	2.1	76.1	17.0	4.8	SL	7.6 ± 0.03	5.1 ± 0.35	0.18 ± 0.01	0.34 ± 0.02	0.02 ± 0.01	0.26 ± 0.01	0.14 ± 0.01
LO	12.3	53.5	26.5	7.7	SL	5.5 ± 0.10	2.4 ± 0.25	0.22 ± 0.02	0.46 ± 0.01	0.02 ± 0.01	0.47 ± 0.02	0.16 ± 0.02
LM	6.9	53.4	36.0	3.8	SL	6.5 ± 0.26	2.0 ± 0.05	0.23 ± 0.01	0.31 ± 0.02	0.02 ± 0.01	0.43 ± 0.01	0.16 ± 0.01
LI	4.6	82.3	11.1	2.0	SL	5.8 ± 0.28	2.1 ± 0.19	0.19 ± 0.01	0.29 ± 0.02	0.02 ± 0.01	0.29 ± 0.01	0.17 ± 0.01
LT	2.9	61.1	33.8	2.2	SL	6.5 ± 0.02	4.1 ± 0.10	0.24 ± 0.02	0.28 ± 0.02	0.02 ± 0.01	0.19 ± 0.02	0.13 ± 0.01
LA	0.3	57.6	15.6	26.5	SL	5.8 ± 0.05	1.6 ± 0.97	0.26 ± 0.01	0.29 ± 0.02	0.03 ± 0.01	0.15 ± 0.01	0.16 ± 0.01
LH	1.9	22.8	62.7	12.6	LS	6.4 ± 0.04	3.2 ± 2.57	0.21 ± 0.01	0.29 ± 0.01	0.02 ± 0.01	0.52 ± 0.01	0.18 ± 0.01
LY	0.0	51.6	38.4	10.1	SL	6.6 ± 0.10	5.4 ± 0.43	0.27 ± 0.01	0.42 ± 0.01	0.03 ± 0.01	0.36 ± 0.01	0.19 ± 0.01
TA	9.7	38.9	43.0	8.4	L	7.7 ± 0.22	5.8 ± 0.34	0.24 ± 0.01	0.28 ± 0.01	0.02 ± 0.01	0.28 ± 0.01	0.18 ± 0.01
ME	6.7	19.4	37.4	36.5	L	6.3 ± 0.02	5.9 ± 0.27	0.25 ± 0.02	0.48 ± 0.02	0.02 ± 0.01	0.61 ± 0.02	0.27 ± 0.01
MS	4.4	21.3	38.3	36.0	CL	6.4 ± 0.02	5.8 ± 0.24	0.27 ± 0.03	0.63 ± 0.03	0.02 ± 0.02	0.55 ± 0.01	0.20 ± 0.01
MP	4.1	34.6	37.6	23.7	CL	6.2 ± 0.02	6.4 ± 0.77	0.31 ± 0.02	0.45 ± 0.03	0.03 ± 0.01	0.39 ± 0.01	0.20 ± 0.01
ML	9.9	56.0	25.7	8.5	L	6.2 ± 0.05	3.1 ± 1.19	0.27 ± 0.02	0.34 ± 0.02	0.03 ± 0.01	0.39 ± 0.01	0.22 ± 0.01
MT	13.6	47.5	25.9	13.0	SL	5.8 ± 0.26	3.4 ± 0.38	0.27 ± 0.02	0.33 ± 0.02	0.03 ± 0.01	0.46 ± 0.01	0.20 ± 0.01
PT	6.8	29.5	39.8	23.9	SL	6.7 ± 0.02	6.6 ± 0.33	0.24 ± 0.02	0.36 ± 0.02	0.20 ± 0.01	0.45 ± 0.01	0.13 ± 0.01
PP	1.8	62.3	32.0	3.9	L	6.8 ± 0.02	8.1 ± 2.38	0.29 ± 0.02	0.43 ± 0.02	0.03 ± 0.01	0.11 ± 0.01	0.19 ± 0.01
SF	6.8	52.5	27.8	12.9	SL	6.2 ± 0.02	3.8 ± 0.56	0.23 ± 0.01	0.21 ± 0.01	0.02 ± 0.01	0.16 ± 0.01	0.22 ± 0.01
SI	2.4	34.2	35.1	28.4	SL	7.2 ± 0.03	13.1 ± 1.34	0.29 ± 0.01	0.55 ± 0.02	0.02 ± 0.01	0.36 ± 0.01	0.12 ± 0.01
SO	0.0	50.9	36.4	12.7	L	5.8 ± 0.20	3.8 ± 0.18	0.22 ± 0.02	0.38 ± 0.02	0.02 ± 0.01	0.54 ± 0.01	0.19 ± 0.01
SY	0.0	54.1	36.8	9.0	L	5.6 ± 0.11	3.0 ± 0.24	0.27 ± 0.02	0.38 ± 0.02	0.02 ± 0.01	0.42 ± 0.01	0.22 ± 0.01
SL	1.8	50.1	36.8	11.3	L	6.3 ± 0.02	3.2 ± 0.27	0.29 ± 0.01	0.39 ± 0.01	0.03 ± 0.01	0.53 ± 0.01	0.25 ± 0.02
SP	2.3	50.2	38.1	9.4	L	6.4 ± 0.03	3.5 ± 0.87	0.28 ± 0.01	0.35 ± 0.01	0.02 ± 0.01	0.50 ± 0.01	0.26 ± 0.01
VC	2.2	77.6	18.1	2.1	L	6.8 ± 0.04	12.8 ± 1.06	0.32 ± 0.01	0.70 ± 0.02	0.02 ± 0.01	0.26 ± 0.01	0.22 ± 0.01

AG: thick clay, A: sand, GF: fine gravel, L: silt, MO: organic matter, Cd: cadmium, Cr: chromium, Cu: copper, Pb: lead, Zn: zinc, GT: textural group, UP: production units.

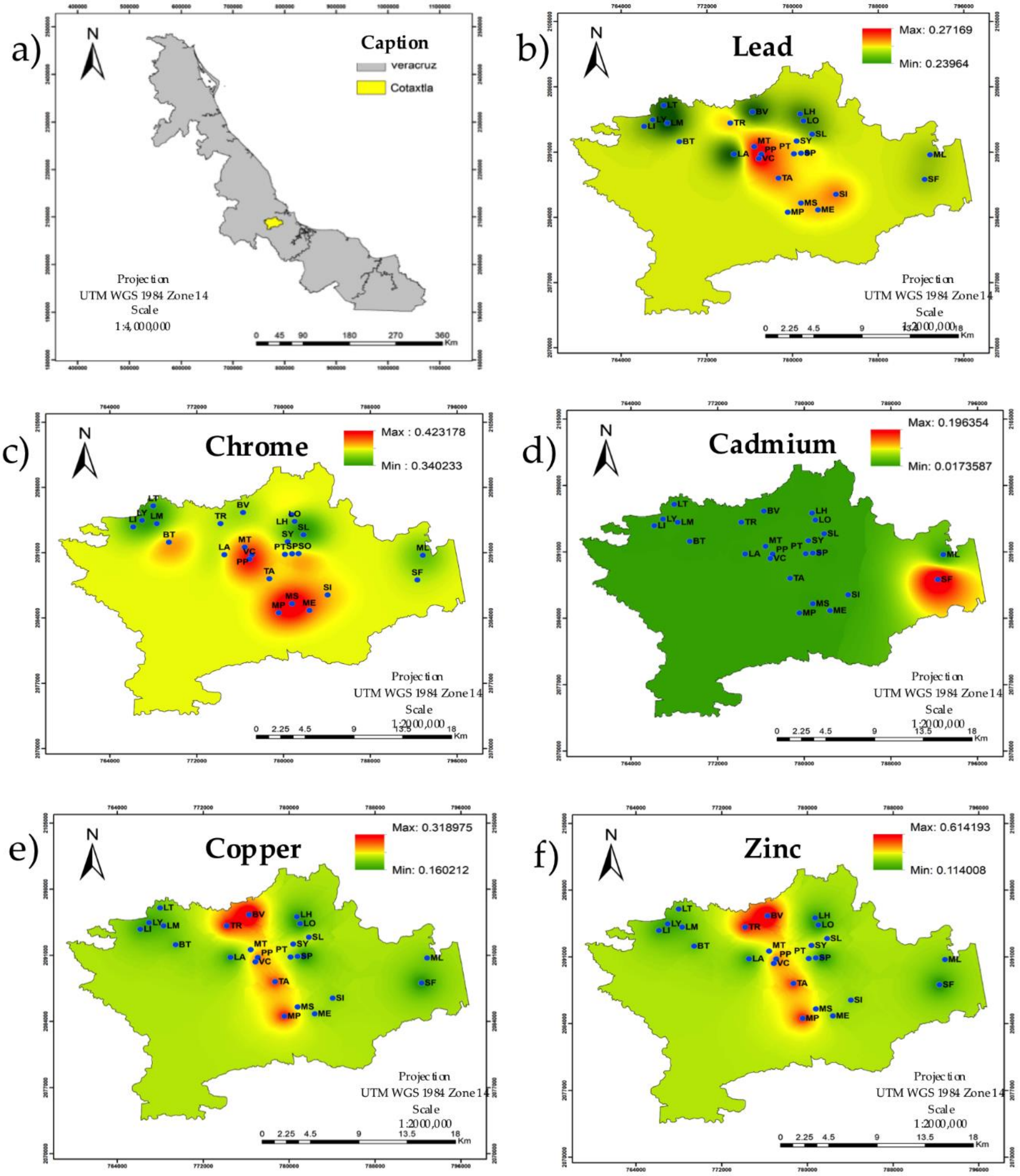

Figure 2. Special distribution of heavy metals from the study area of the Sotavento region in the central area of the Gulf of Mexico; (**a**) Cotaxtla, Veracruz, México, (**b**) lead, (**c**) chromium, (**d**) cadmium, (**e**) zinc, (**f**) chromium. Note: BT, Bajos Tlachiconal; LI, Lomitas3; TA, Los Tamarindos; MT, Mata Tambor; SO, Soyolapa1; BV, Buena Vista; LT, Lomitas4; ME, Mata Espino1; PT, Potrerillo1; SY Soyolapa2; TR, El Trapiche; LA, Loma de Angosta; MS, Mata Espino2; PP, Potrerillo2; SL, Soyolapa3; LO, Lomitas1; LH, Loma de Hoyos1; MP, Mata Espino3; SF, San Francisco; SP, Soyolapa4; LM, Lomitas2; LY Loma de Hoyos2; ML, Mata Limón; SI, Santa Inés; VC, Vista Clara.

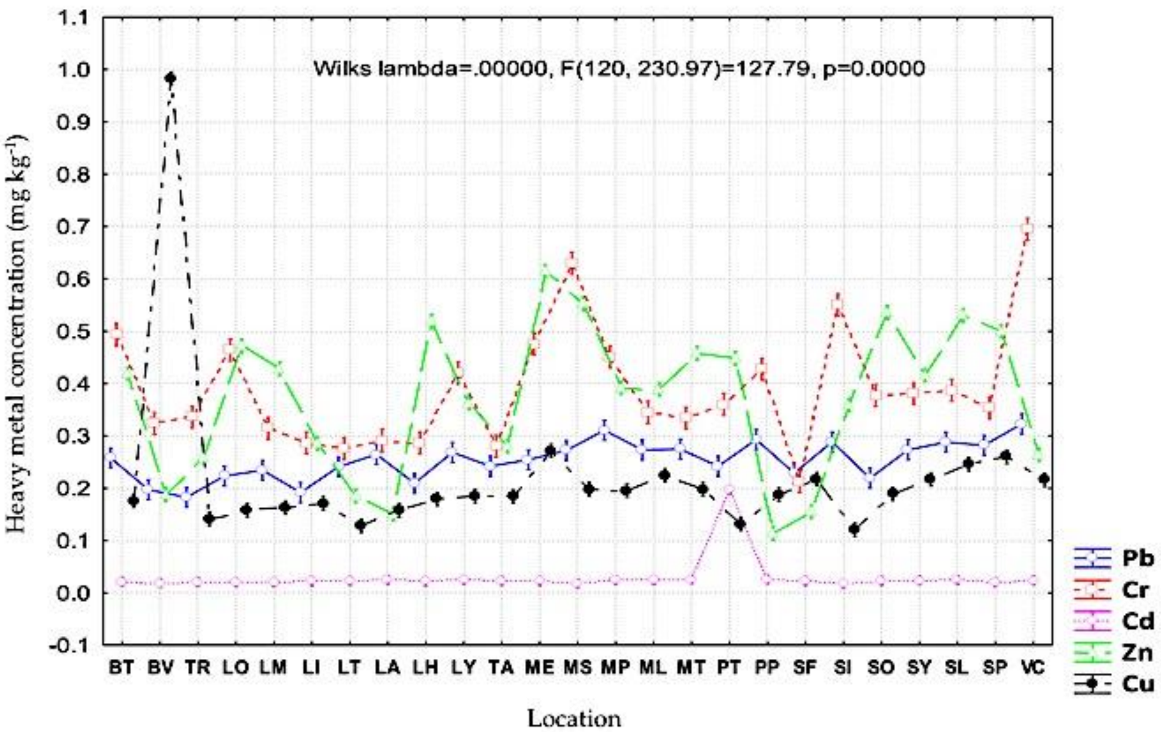

Figure 3. Heavy metal concentration in soil of the sampling sites of the study area of the Sotavento region in the central area of the Gulf of Mexico.

For Cu, the highest concentration results are shown at point BV with 0.98 ± 0.01 mg kg^{-1} and 0.26 ± 0.01 mg kg^{-1} at point SP, while the lowest concentration was reported at point SI with 0.12 ± 0.01 mg kg^{-1}. Therefore, crop areas BV, ME, and SI show significant differences ($p \leq 0.05$), however, among BT, LH, LI, LM, LO, MP, MS, MT, PP, SP, and TA, no significant statistical differences were shown ($p \leq 0.05$).

Table 2 reflects the analysis of Pearson's correlation between the variables reported in the present study. The average correlations are between Pb and Cr ($r = 0.607$, $p = 0.002$) and a negative correlation between Pb and MO ($r = -0.612$, $p = 0.001$); on the other hand, there is an average correlation between Zn and sand content ($r = 0.573$, $p = 0.003$), however, the strongest correlation was observed between MO and pH ($r = 0.749$, $p < 0.001$). Table 3 shows the reference limits for heavy metals in agricultural soils according to studies carried out in several countries, where it can be observed that for Pb, Cd, Cu, Cr, and Zn values below the reference limits were found. However, the PT point with 0.20 ± 0.01 mg kg^{-1} is above the limits established in China (0.056 mg kg^{-1}), but they are among the regulated limits for Mexico.

Table 2. Pearson correlation coefficient and P value among the variables reported in the study.

	AG	A	GF	L	pH	MO	Cd	Cr	Cu	Pb	Zn
AG	1.00										
A	−0.769 <0.001	1.00									
GF	−0.003 0.988	−0.164 0.444	1.00								
L	0.232 0.276	−0.761 <0.001	−0.9 0.677	1.00							
pH	−0.271 0.201	0.263 0.214	−0.084 0.695	−0.119 0.579	1.00						
MO	−0.141 0.511	0.156 0.466	−0.287 0.174	−0.007 0.973	0.749 <0.001	1.00					
Cd	0.206 0.335	−0.239 0.261	0.132 0.537	0.127 0.554	−0.161 0.453	−0.205 0.337	1.00				
Cr	0.306 0.146	−0.128 0.55	−0.14 0.514	−0.049 0.821	−0.324 0.122	−0.376 0.07	−0.065 0.762	1.00			
Cu	−0.012 0.956	−0.066 0.76	−0.074 0.732	0.141 0.51	−0.136 0.526	0.032 0.883	−0.131 0.541	−0.082 0.703	1.00		
Pb	0.217 0.309	−0.122 0.569	−0.024 0.912	−0.012 0.956	−0.34 0.104	−0.612 0.001	−0.044 0.838	0.607 0.002	−0.238 0.263	1.00	
Zn	0.391 0.059	−0.573 0.003	0.141 0.511	0.468 0.021	−0.174 0.416	−0.182 0.395	0.107 0.618	0.291 0.168	−0.168 0.434	0.119 0.58	1.00

AG: thick clay, A: sand, GF: fine gravel, L: silt, MO: organic matter, Cd: cadmium, Cr: chromium, Cu: copper, Pb: lead, Zn: zinc.

Table 3. Established reference limits for heavy metals for agricultural use in different countries.

Reference Limits	Heavy Metals in Agricultural Soils (mg kg^{-1})					References
	Pb	Cd	Cu	Cr	Zn	
Study Data	0.32	0.20	0.98	0.70	0.62	
Mexico *	400	37		−280	300	[39]
Mexico **	35	0.35	-	-	-	[30]
Canada	70	1.4	63	64	250	[40]
China	36	0.056	17	50.5	47.3	[41]
European Union	100–600	2–6	-	-	-	[42]
United States	100	3	100	100		[43]

* NOM-147-SEMARNAT/SSA1-2004, ** NOM-021-SEMARNAT- 2000. Own elaboration.

Accumulation and Risk Index

Table 4 shows the analyzed results of the geoaccumulation index, which according to the classification of Müller [32], all points are in Grade 1 as uncontaminated soils, however, the point PT with a I_{geo} of 1.13 is in Grade 2, identified as moderately contaminated. On the other hand, the ecological risk factor (E_i) and the potential ecological risk indexes (RI) for each of the study sites showed a sequence of the risk factors that goes in order of Cd > Pb > Cu > Cr > Zn; however, the risk index for each sampled point represents low contamination, unlike the PT point, which shows a medium degree of contamination, since it is within the range 50–100 for the risk index (RI).

Table 4. Results of the geoaccumulation index (I_{geo}), ecological risk factor (E_i), and potential ecological risk index (RI) for each study site in the Sotavento region.

Code	I_{geo}					E_i					RI	GC
	Pb	Cr	Cd	Zn	Cu	Pb	Cr	Cd	Zn	Cu		
BT	−6	−4	−2	−6	−6	0.26	0.14	10.67	0.03	0.15	11.50	L
BV	−6	−5	−2	−7	−3	0.20	0.09	9.50	0.01	0.82	10.82	L
TR	−6	−5	−2	−7	−6	0.18	0.10	10.33	0.02	0.12	10.93	L
LO	−6	−5	−2	−6	−6	0.22	0.13	10.17	0.04	0.13	10.91	L
LM	−6	−5	−2	−6	−6	0.23	0.09	10.17	0.03	0.14	10.89	L
LI	−6	−5	−2	−6	−6	0.19	0.08	10.83	0.02	0.14	11.46	L
LT	−6	−5	−2	−7	−6	0.24	0.08	11.55	0.01	0.11	12.23	L
LA	−6	−5	−2	−7	−6	0.26	0.08	12.50	0.01	0.13	13.26	L
LH	−6	−5	−2	−6	−6	0.21	0.08	10.83	0.04	0.15	11.52	L
LO	−6	−5	−2	−6	−6	0.27	0.12	12.67	0.03	0.15	13.51	L
TA	−6	−5	−2	−7	−6	0.24	0.08	11.50	0.02	0.15	12.24	L
ME	−6	−4	-2	−5	−5	0.25	0.14	11.33	0.05	0.23	12.25	L
MS	−6	−4	−2	−6	−6	0.27	0.18	9.00	0.04	0.17	9.93	L
MP	−6	−5	−2	−6	−6	0.31	0.13	12.50	0.03	0.16	13.44	L
ML	−6	−5	−2	−6	−5	0.27	0.10	12.33	0.03	0.19	13.19	L
MT	−6	−5	−2	−6	−6	0.27	0.10	13.00	0.04	0.17	13.84	L
PT	−6	−5	1.13	−6	−6	0.24	0.10	98.23	0.03	0.11	98.96	M
PP	−6	−5	−2	−8	−6	0.29	0.12	13.00	0.01	0.16	13.87	L
SF	−6	−6	−2	−7	−5	0.23	0.06	11.33	0.01	0.18	12.04	L
SI	−6	−4	−2	−6	−6	0.29	0.16	8.67	0.03	0.10	9.53	L
SO	−6	−5	−2	−6	−6	0.22	0.11	11.50	0.04	0.16	12.25	L
SY	−6	−5	−2	−6	−5	0.27	0.11	12.00	0.03	0.18	12.87	L
SL	−6	−5	−2	−6	−5	0.29	0.11	12.50	0.04	0.21	13.43	L
SP	−6	−5	−2	−6	−5	0.28	0.10	10.17	0.04	0.22	11.09	L
VC	−6	−4	−2	−7	−5	0.32	0.20	11.83	0.02	0.18	12.88	L

GC: pollution category, B: low pollution, M: moderate pollution.

4. Discussion

In papaya cultivation soils in the Sotavento region in the central area of the Gulf of Mexico, the total average concentrations of heavy metals carried a sequence Cr > Zn > Pb > Cu > Cd, with concentration values that varied from 0.18 to 0.32 mg kg^{-1} for Pb, 0.212–0.70 mg kg^{-1} for Cr, 0.02–0.20 mg kg^{-1} for Cd, 0.11–0.62 mg kg^{-1} for Zn, and 0.12–0.98 mg kg^{-1} for Cu. The Cd is similar to the one reported by Cai et al. [44] in agricultural soils in southeast China, with values of 0.10 mg kg^{-1}, but below the one reported for Cu, Zn, Cr, and Pb. Studies conducted by Hu et al. [45] report average Cd values of 0.2 mg kg^{-1} in rice cultivation areas in China, similar to the highest value of 0.2 mg kg^{-1} of this study, but in less concentration for the rest of the metals. López et al. [24] evaluated agricultural land with similar values for Cd (0.06–0.76 mg kg^{-1}), but lower than those reported for Cr (11.31–33.85 mg kg^{-1}), Cu (0.004–99.98 mg kg^{-1}), Pb (4.87–41.79 mg kg^{-1}), and Zn (21.98–109.44 mg kg^{-1}).

In papaya cultivation soils in the Sotavento region, the average concentrations of heavy metals showed a sequence Cr > Zn > Pb > Cu > Cd. Pb concentrations varied in the present studies between 0.18 and 0.32 mg kg^{-1}, less than reported by Acosta et al. [46] with 48.9 mg kg^{-1} in agricultural soils, and is attributed to the constant use of fertilizers and pesticides.

Cr values ranged from 0.212 to 0.70 mg kg^{-1}, similar to those achieved by Murtic [47] on agricultural soils in Serbia, which showed an average of 0.44 mg kg^{-1}. Regarding Cd, they revealed values between 0.02 and 0.20 mg kg^{-1}, values similar to that reported by Ke-Lin [48], Olivares et al. [49], and Bautista et al. [50], with values of 0.24, 0.25, and 0.3 mg kg^{-1}, respectively. Ebong et al. [51] assessed land near urban landfills in Uyo, Nigeria, finding high values of Cd with 9.24 mg kg^{-1}, which is related to the urban waste of Ni-Cd batteries and motor oils and insecticides.

Regarding the levels of Zn found in this study, concentrations ranged between 0.11 and 0.62 mg kg^{-1}, while the Cu was found between 0.12 and 0.98 mg kg^{-1}, values that are related to those reported by Roca et al. [52] for Zn 0.92 and Cu 1.03 mg kg^{-1}, but with values lower than those reported by López et al. [24].

Pollution levels of Zn and Cu are related by the influence of anthropogenic activities as reported in the province of Iran, where agricultural soils have levels of 23.8 mg kg^{-1} for Zn and 7.0 mg kg^{-1} for Cu [53]. Kabata [11] mentions that tolerance levels in plants should not exceed 0.5 mg kg^{-1} of Pb, 1 mg kg^{-1} of Cr, 0.2 mg kg^{-1} for Cd, 50 mg kg^{-1} for Zn, and 15 mg kg^{-1} for Cu, however, these may vary by species and soil characteristics.

In this study it should be noted that the highest values for Pb and Cr correspond to the same UP (VC), which contains a high content of organic material (12.8% ± 1.06%) and a pH of 6.8. This indicates that the metals Pb and Cr will not be easily absorbed by the crop plants, since they are not available due to the near neutral pH, as well as the high MO content, that can probably form chelating complexes that trap metal ions and does not allow passage to plants.

Furthermore, the highest concentrations found for Cd, Zn, and Cu may not be available for papaya cultivation because the soils meet a pH of 6.7, 6.3, and 6.5, respectively. However, it was observed that 24% of the UP presented acid soils between 5.5 ± 0.10 and 5.8 ± 0.28, which can pose a risk to crops as they can show greater availability for heavy metals and be easily absorbed by crop plants. However, no strong correlations were observed between metal concentrations with respect to pH, MO, and soil texture; however, the highest correlation was observed between pH and MO, which may indicate that the amendments used to increase the organic material in soils bring organic compounds that reduce the pH.

The presence of heavy metals in agricultural soils is directly related to controlled agricultural practices, which accumulate metals in the soil, either through the addition of inorganic fertilizers, organic amendments, or pesticides [54]. It also influences and depends on the irrigation water used. To increase production, inorganic fertilizers were used in an average of 600 kg ha^{-1} per year [55]. Papaya cultivation is characterized by being fast growing, with an early and continuous production, which demands high amounts of nutrients for its development [56]. The long-term use of uncontrolled quantities and the application of inorganic fertilizers can acidify the cultivation soils, which favors the mobility of heavy metals and the easy absorption by plants. That is, as the pH value in soil approaches the neutral value, the mobility of heavy metals in the soil is reduced [57].

Pearson's correlation between the evaluated variables does not show strong correlations between metals and the physicochemical characteristics of the soil. The average correlations are observed between Pb and Cr (r = 0.607) and a negative correlation between Pb and MO (r = -0.612); in the case of Zn, it showed an average correlation with respect to the sand content (r = 0.573), however, the strongest correlation was observed between MO and pH (r = 0.749). The results of the metals and the physicochemical variables do not reflect a direct correlation, nor are they related between the agricultural areas; this is because the producers in the Cotaxtla area do not use the same agricultural management in relation to the quantity and type of inorganic and agrochemical fertilizers for pest control. Thus, a relationship between the data obtained and the proximity of the cultivation areas with the urban areas was not observed, although livestock areas, poultry farms, and some quarries located in nearby municipalities are registered [58]. However, it cannot be ruled out that, if metal concentrations are lower than those established by official standards, they can be absorbed by crop plants, especially in soils that reported an acidic pH; however, it occurs in sandy soils that some metals, such as Cd, can precipitate in the form of $CdCO_3$ when there is a low content of organic matter and an alkaline pH [59].

The geoaccumulation and potential risk indexes allow the determination of the level of contamination in soils and sediments, and the present study reports a positive value for the geoaccumulation index (I_{geo}) at point PT (Potrerillo1) with a value of 1.13, corresponding to Grade 3, which indicates a moderately contaminated soil. On the other hand, most of the cultivated soils analyzed do not present pollution problems. In relation to the potential ecological risk index (RI) of the production areas evaluated, they report an RI of 98.98 at the PT site, which indicates that it is moderately contaminated, while the other cultivation areas showed a low contamination range. This is because the risk index was adopted to assess the potential toxicity of heavy metals and represents the accumulation of different metals at each crop site [60].

5. Conclusions

The management and application of agrochemicals, as currently carried out in papaya cultivation, reflected that these products influence the values of pH and organic matter found; the results obtained show differences between sampling points.

The manifest concentrations of heavy metals Pb, Cr, Cd, Cu, and Zn were reported below the national permissible limits for land use. However, the geoaccumulation indexes (I_{geo}) showed that 96% of the analyzed sampling points are in a range of uncontaminated, with only 4% corresponding to Potrerillo1 (PT), which indicates that the soil is moderately contaminated.

The RI showed that the PT point is in a moderate contamination category, and the 96% of the remaining points correspond to a low contamination category.

The scientific knowledge that was generated in this study reveals that the levels of heavy metals reported do not represent a toxicological risk that prevents further papaya cultivation in the central region of Sotavento. However, being an area of high production of Maradol papaya, the export volume of this has economic importance; therefore, it will be necessary to promote the proper management of agrochemicals to minimize the risk of accumulation in soils and absorption by the edible parts of the plant, which would reflect a threat to public health.

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References

1. Nagajyoti, P.C.; Lee, K.D.; Sreekanth, T.V.M. Heavy metals, occurrence and toxicity for plants: A review. *Environ. Chem. Lett.* **2010**, *8*, 199–216. [CrossRef]
2. Abollino, O.; Aceto, M. Heavy metals in agricultural soils from Piedmont, Italy. Distribution, speciation and chemometric data treatment. *Chemosphere* **2002**, *49*, 545–557. [CrossRef]
3. Navarro, A.J.P.; Aguilar, A.I.; López, M.J.R. Aspectos bioquímicos y genéticos de la tolerancia y acumulación de metales pesados en plantas. *Ecosistemas* **2007**, *16*, 10–25. [CrossRef]
4. Sauvé, S.; Hendershot, W.; Allen, H.E. Solid-solution partitioning of metals in contaminated soils: Dependence on pH, total metal burden, and organic matter. *Environ. Sci. Technol.* **2000**, *34*, 1125–1131. [CrossRef]
5. Facchinelli, A.; Sacchi, L.; Mallen, E. Multivariate statistical and GIS-based approach to identify heavy metal sources in soils. *Environ. Pollut.* **2001**, *114*, 313–324. [CrossRef]
6. Hu, Y.; Cheng, H. Application of stochastic models in identification and apportionment of heavy metal pollution sources in the surface soils of a large-scale region. *Environ. Sci. Technol.* **2013**, *47*, 3752–3760. [CrossRef]
7. Huang, S.W.; Jin, J.Y. Status of heavy metals in agricultural soils as affected by different patterns of land use. *Environ. Monit. Assess.* **2008**, *139*, 317–327. [CrossRef]

8. Martí, L.; Burba, J.; Cavagnaro, M. Metales pesados en fertilizantes fosfatados, nitrogenados y mixtos. *Revista de la Facultad de Ciencias Agrarias* **2002**, *34*, 43–48.
9. Wuana, R.A.; Okieimen, F.E. Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation. *ISRN Ecol.* **2011**, 1–20. [CrossRef]
10. Lokeshappa, B.; Shivpuri, K.; Tripathi, V.; Dikshit, K.A. Assessment of Toxic Metals in Agricultural Produce. *Food Public Health* **2012**, *2*, 24–29. [CrossRef]
11. Kabata, P.A.; Pendias, H. *Trace Elements in Soil and Plants*; CRC Press: Boca Raton, FL, USA, 2000.
12. Alloway, B.J. *Heavy Metals in Soils: Trace Metals and Metalloids in Soils and Their Bioavailability*; Springer Science & Business Media: Berlin/Heidelberg, Germany, 2012; Volume 22.
13. Baker, A.J.M. Metal Tolerance. *New Phytol.* **1987**, *106*, 93–111. [CrossRef]
14. Gill, M. Heavy metal stress in plants: A review. *Int. J. Adv. Res.* **2014**, *2*, 1043–1055. [CrossRef]
15. Clemens, S.; Ma, J.F. Toxic Heavy Metal and Metalloid Accumulation in Crop Plants and Foods. *Annu. Rev. Plant Biol.* **2016**, *67*, 489–512. [CrossRef] [PubMed]
16. Méndez, P.; Ramírez, G.; César, A.; Gutiérrez, R.; Alma, D.; García, P. Contaminación y fitotoxicidad en plantas por metales pesados provenientes de suelos y agua. *Trop. Subtrop. Agroecosyst.* **2009**, *10*, 29–44.
17. Wang, F.; Huang, C.; Chen, Z.; Bao, K. Distribution, Ecological Risk Assessment, and Bioavailability of Cadmium in Soil from Nansha, Pearl River Delta, China. *Int. J. Environ. Res. Public Health* **2019**, *16*, 3637. [CrossRef] [PubMed]
18. Rueda, S.G.; Rodríguez, V.J.A.; Madriñán, M.R. Metodologías para establecer valores de referencia de metales pesados en suelos agrícolas perspectivas para Colombia. *Acta Agronómica* **2011**, *60*, 203–217.
19. Valladares, G.S.; Camargo, O.A.; Carvalho, J.R.P.; Silva, A.M.C. Assessment of heavy metals in soils of a vineyard region with the use of principal component analysis. *Sci. Agric.* **2009**, *66*, 361–367. [CrossRef]
20. Trujillo, G.J.M.; Torres, M.M.A. Niveles de contaminación en tres sectores de Villavicencio, a través del índice de geo-acumulación(I-geo). *Orinoquia* **2015**, *19*, 109. [CrossRef]
21. Fadigas, F.D.S.; Do Amaral, S.N.M.B.; Mazur, N.; Dos Anjos, L.H.C.; Freixo, A.A. Proposition of reference values for natural concentration of heavy metals in Brazilian soils. *Revista Brasileira de Engenharia Agricola e Ambiental* **2006**, *10*, 699–705. [CrossRef]
22. Yadav, S.K. Heavy metals toxicity in plants: An overview on the role of glutathione and phytochelatins in heavy metal stress tolerance of plants. *South Afr. J. Bot.* **2010**, *76*, 167–179. [CrossRef]
23. Nicholson, F.A.; Smith, S.R.; Alloway, B.J.; Carlton-Smith, C.; Chambers, B.J. An inventory of heavy metals inputs to agricultural soils in England and Wales. *Sci. Total Environ.* **2003**, *311*, 205–219. [CrossRef]
24. López, P.M.E.; Del Rincón, C.M.C.; Muñoz, T.C.; Ruiz, A.G.M.; Solís, S.S.; Zanor, G.A. Evaluation of trace elements contamination in agricultural soils in southwest of Guanajuato, Mexico. *Evaluation* **2017**, *27*. [CrossRef]
25. SAGARPA. Agrícola Nacional. *Planeación Agrícola Nacional 2017–2030* **2017**, *I*, 1–14.
26. Vázquez, D.C.A.; Marchant, B.P.; Quintana, J.R.; Santiago, A.; Lafuente, A.L.; Webster, R. Spatial variation of trace elements in the peri-urban soil of Madrid. *J. Soils Sediments* **2014**, *14*, 78–88. [CrossRef]
27. Norma Mexicana NMX-AA-132-SCFI-2016: Muestreo de suelos para la identificación y la cuantificación de metales y metaloides, y manejo de la muestra. Available online: http://www.economianmx.gob.mx/normas/nmx/2010/nmx-aa-132-scfi-2016.pdf (accessed on 12 January 2019).
28. Aydinalp, C.; Marinova, S. Distribution and forms of heavy metals in some agricultural soils. *Pol. J. Environ. Stud.* **2003**, *12*, 629–633.
29. Schulte, E.E.; Hopkins, B.G. Estimation of soil organic matter by weight loss-on-ignition. *Soil organic matter: Anal. Interpret.* **1996**, *46*, 21–31. [CrossRef]
30. Diario Oficial. NOM-021-SEMARNAT-2000 Norma Oficial Mexicana, que establece las especificaciones de fertilidad, salinidad y clasificación de suelos, esudio, muestreo y análisis. Publicado el 31 de ciiciembre de 2002. Available online: http://dof.gob.mx/nota_detalle.php?codigo=717582&fecha=31/12/2002 (accessed on 11 February 2018).
31. Secretaría de Salud (SSA). Norma Oficial Mexicana NOM-117-SSA1-1994. In *Método de Prueba Para la Determinación de Cadmio, Arsénico, Plomo, Estaño, Cobre, Fierro, Zinc y Mercurio en Alimentos, Agua Potable y Agua Purificada por Espectrometría de Absorción Atómica*; Diario Oficial de la Federación; Secretaría de Salud, Estados Unidos Mexicanos: Ciudad de México, México, 1995; pp. 1–15.
32. Müller, G. Index of geoaccumulation in sediments of the Rhine River. *GeoJournal* **1995**, *2*, 108–118.

33. Ma, X.; Zuo, H.; Tian, M.; Zhang, L.; Meng, J.; Zhou, X.; Min, N.; Chang, X.; Liu, Y. Assessment of heavy metals contamination in sediments from three adjacent regions of the Yellow River using metal chemical fractions and multivariate analysis techniques. *Chemosphere* **2016**, *144*, 264–272. [CrossRef] [PubMed]
34. Hakanson, L. An ecological risk index for aquatic pollution control. A sedimentological approach. *Water Res.* **1980**, *14*, 975–1001. [CrossRef]
35. McBride, M.B. *Environmental Chemistry of Soils*; Oxford University Press: New York, NY, USA, 1994.
36. Liu, Y.; Xiao, T.; Baveye, P.C.; Zhu, J.; Ning, Z.; Li, H. Potential health risk in areas with high naturally-occurring cadmium background in southwestern China. *Ecotoxicol. Environ. Saf.* **2015**, *112*, 122–131. [CrossRef]
37. Sun, Y.; Zhou, Q.; Xie, X.; Liu, R. Spatial, sources and risk assessment of heavy metal contamination of urban soils in typical regions of Shenyang, China. *J. Hazard. Mater.* **2010**, *174*, 455–462. [CrossRef] [PubMed]
38. Perea, E.; Ojeda, D.; Hernández, A.; Ruiz, T.; Martínez, J. Utilización de quelatos en la agricultura. *Aventuras del pensamiento (Synthesis)* **2010**, 1–5.
39. Secretaría de Salud (SSA). Norma Oficial Mexicana NOM-147-SEMARNAT/SSA1-2004. In *Que establece criterios para determinar las concentraciones de remediación de suelos contaminados por arsénico, bario, berilio, cadmio, cromo hexavalente, mercurio, níquel, plata, plomo, selenio, talio y/o vanadio. Diario Oficial de la Federación; Secretaría de Salud, Estados Unidos Mexicanos: 2004*; Secretaría de Salud (SSA): Ciudad de México, México, 1995; pp. 1–68.
40. Canadiam Council of Minister of the Enviroement. (CCME). Soil Quality Guidelines for the Protection of Environmental and Human Health. Available online: http://ceqg-rcqe.ccme.ca/en/index.html (accessed on 25 January 2020).
41. China National Environmental Monitoring Centre (CNEMC). *The Background Values of Chinese Soils*; Environmental Science Press of China: Beijing, China, 1990; pp. 15–505.
42. European Union. *Heavy Metals in Wastes*; European Commission on Environment. 2002. Available online: http://ec.europa.eu/environment/waste/studies/pdf/heavymetalsreport.pdf (accessed on 8 June 2019).
43. Ahaneku, I.E.; Sadiq, B.O. Assessment of heavy metals in Nigerian agricultural soils. *Pol. J. Environ. Stud.* **2014**, *23*, 1091–1100.
44. Cai, L.; Xu, Z.; Ren, M.; Guo, Q.; Hu, X.; Hu, G.; Wan, H.; Peng, P. Source identification of eight hazardous heavy metals in agricultural soils of Huizhou, Guangdong Province, China. *Ecotoxicol. Environ. Saf.* **2012**, *78*, 2–8. [CrossRef]
45. Hu, B.; Jia, X.; Hu, J.; Xu, D.; Xia, F.; Li, Y. Assessment of heavy metal pollution and health risks in the soil-plant-human system in the Yangtze River Delta, China. *Int. J. Environ. Res. Public Health* **2017**, *14*, 1042. [CrossRef]
46. Acosta, J.A.; Faz, A.; Martínez, M.S.; Arocena, J.M. Enrichment of metals in soils subjected to different land uses in a typical Mediterranean environment (Murcia City, southeast Spain). *Appl. Geochem.* **2011**, *26*, 405–414. [CrossRef]
47. Murtic, S.; Brkovic, D.; Djuric, M.; Vujinovic, I. Heavy metal dynamics in the soil-leaf-fruit system under intensive apple cultivation. *Acta Agriculturae Serbica* **2014**, *19*, 123–132. [CrossRef]
48. Ke-Lin, H.U.; Zhang, F.R.; Hong, L.; Feng, L.; Bao-Guo, L. Spatial Patterns of Soil Heavy Metals in Urban-Rural Transition Zone of Beijing. *Pedosphere* **2006**, *16*, 690–698. [CrossRef]
49. Olivares, R.S.; García, C.D.; Lima, C.L.; Saborit, S.I.; Llizo, C.A.; Pérez, A.P. Niveles de cadmio, plomo, cobre y zinc en hortalizas cultivadas en una zona altamente urbanizada de la ciudad de la habana, Cuba. *Revista Internacional de Contaminacion Ambiental* **2013**, *29*, 285–293.
50. Bautista, C.A.; Arnaud, V.M.D.R.; Carrillo, G.R. Elementos traza en dos áreas agrícolas. *Terra Latinoamericana* **2011**, *29*, 123–131.
51. Ebong, G.A.; Akpan, M.M.; Mkpenie, V.N. Heavy metal contents of municipal and rural dumpsite soils and rate of accumulation by Carica papaya and Talinum triangulare in Uyo, Nigeria. *J. Chem.* **2008**, *5*, 281–290. [CrossRef]
52. Roca, N.; Pazos, M.S.; Bech, J. Disponibilidad de cobre, hierro, manganeso, zinc en suelos del NO Argentino. *Ciencia del suelo* **2007**, *25*, 31–42.
53. Jalali, M.; Hemati, N. Chemical fractionation of seven heavy metals (Cd, Cu, Fe, Mn, Ni, Pb, and Zn) in selected paddy soils of Iran. *Paddy Water Environ.* **2013**, *11*, 299–309. [CrossRef]
54. Martín, J.A.R.; Arias, M.L.; Corbí, J.M.G. Heavy metals contents in agricultural topsoils in the Ebro basin (Spain). Application of the multivariate geostatistical methods to study spatial variations. *Environ. Pollut.* **2006**, *144*, 1001–1012. [CrossRef]

55. Chen, T.; Liu, X.; Li, X.; Zhao, K.; Zhang, J.; Xu, J.; Shi, J.; Dahlgren, R.A. Heavy metal sources identification and sampling uncertainty analysis in a field-scale vegetable soil of Hangzhou, China. *Environ. Pollut.* **2009**, *157*, 1003–1010. [CrossRef]
56. García, J.L.E.; Veloz, C.S.; Damián, M.T.M.; Garza, Á.M.; García, P.S.; Hernández, R.M.S. Fertilización orgánica, mineral y foliar sobre el desarrollo y la producción de papaya cv. Maradol. *Terra Latinoamericana* **2003**, *21*, 157–166.
57. Ordóñez, R.; Kheraiwish, D.; Polo, M.J.; Giráldez, J.V.; González, P. Influencia del encalado sobre la movilidad de metales en un suelo contaminado en el valle del río Guadiamar (Sevilla). *Estudios de la Zona no Saturada del Suelo* **2005**, *7*, 29–32.
58. Esperanza González Hernández. Problemas ambientales y de salud en la cuenca del río Atoyac, Veracruz: Estrategias regionales y mapeo colectivo. In *Megaproyectos Urbanos y Productivos; Impactos socio-territoriales*; Universidad Autónoma del Estado de México: Toluca, México, 2017; pp. 235–244. Available online: http://ri.uaemex.mx/handle/20.500.11799/65706 (accessed on 15 October 2019).
59. Bradl, H.B. Adsorption of heavy metal ions on soils and soils constituents. *J. Colloid Interface Sci.* **2004**, *277*, 1–18. [CrossRef]
60. Luan, J.; Chai, M.; Li, R. Heavy Metal Migration and Potential Environmental Risk Assessment During the Washing Process of MSW Incineration Fly Ash and Molten Slag. *Procedia Environ. Sci.* **2016**, *31*, 351–360. [CrossRef]