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Environmental Impact of Potentially Toxic Elements on Tropical Soils Used for Large-Scale Crop Commodities in the Eastern Amazon, Brazil

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Citation: Braz, A.M.d.S.; Costa, M.L.d.; Ramos, S.J.; Dall'Agnol, R.; Fernandes, A.R. Environmental Impact of Potentially Toxic Elements on Tropical Soils Used for Large-Scale Crop Commodities in the Eastern Amazon, Brazil. *Minerals* **2021**, *11*, 990. https://doi.org/10.3390/min11090990

Academic Editor: Pedro Tume

Received: 23 July 2021
Accepted: 27 August 2021
Published: 10 September 2021

Abstract: The Amazon soils demand high rates of fertilizer application to express high agricultural potential, making it necessary to carry out frequent monitoring of ecological functions and biogeochemical processes in this important biome. The concentrations of As, Ba, Cd, Co, Cr, Cu, Hg, Ni, Pb and Zn and contamination indexes were studied in Oxisol and Ultisols cultivated with citrus (*Citrus sinensis* (L.) Osbeck), oil palm (*Elaeis guineensis* Jacq.) and black pepper (*Piper nigrum* L.), at 26, 10 and 5 years of implantation, respectively. The potential risk of contamination was estimated by the enrichment (EF) and bioaccumulation (BAF) factors. Moderate enrichment of Ba, Pb and Zn ($2 < EF < 5$) and significant enrichment of As and Cu ($5 < EF < 20$) were observed. In addition, the following orders of bioaccumulation were found: oil palm—Cu > Zn > Hg > Ni > Ba > Co > As > Cr > Cd ≈ Pb; black pepper—Zn > Hg > Cu > Ba > Ni > Co > Pb >> As > Cr > Cd; and citrus—Hg > Ni > Ba > Zn > Co > Cu > As > Pb >> Cr > Cd. However, all elements are in concentrations below the prevention and investigation values established by Brazilian legislation, that is, the management practices in the crops studied are not contributing with damage to soil and human health risks.

Keywords: soil chemistry; enrichment factor; soil pollution; risk assessment

1. Introduction

The Brazilian Amazon is a new agricultural frontier and a major food producing area, exporting soy and beef to global markets [1]. In this biome, there is a pressing challenge to reconcile food production and conservation of natural ecosystems [2]. The state of Pará is the second largest Brazilian state, with 1,247,955 km^2, of which approximately 57% consists of indigenous territories and protected areas, representing 29.73% of the Brazilian Amazon (4,196,943 km^2) and 14.65% of the Brazilian territory. The main economic activities in the state of Pará and in the Amazon include agriculture, mainly livestock, crop production, and mining [3,4]. In 2017, the state of Pará produced 286,768 tons of citrus, 1,634,476 tons of oil palm, and 39,577 tons of black pepper, which respectively represents 2.0, 97.0, and 50.0% of the national production [5].

The growing demand for food production and energy generation, associated with society's call against the conversion of forests into agricultural areas in the Amazon, has intensified the use of fertilizers in order to increase crop productivity. The raw materials used in the production of phosphate and micronutrient fertilizers usually contain several chemical elements, which depending on the amount and time of application, can become an environmental concern [6–10]. In addition, the disposal of waste and the application of pesticides and fertilizers can increase the concentration of potentially toxic elements (PTEs), such as Pb, Cd, Cu, Mn, Zn and Hg, in soils and groundwater, which may cause toxicity risks to the ecosystem and human health [11–17]. Although these elements occur naturally, anthropogenic sources contribute significantly to increased rates of PTE redistribution among the compartments of the environment [18,19].

In this way, environmental preservation agencies have used standardization models and techniques in order to distinguish natural and anthropogenic sources of PTEs in soils [20–24]. In addition, scientific studies have established background values (natural source), which can be used to assess the occurrence of changes associated with anthropogenic activities [25–27].

The enrichment factor (EF) obtained from the ratio between the PTE concentration in the cultivated soil and the concentration under natural conditions (background value) have been widely used to assess the effects of pedogenetic processes and other non-lithogenic factors, including the human influence on the concentration of chemical elements in the environment [24,28–35]. Alagarsamy and Zhang [36] classified the EF of an element as natural when EF = 1, enriched when EF > 1, and depleted when EF < 1. Rubio et al. [37] consider EF values between 1 and 3 as moderate, from 3 to 6 as strong, and higher than 6 as severe. EF values > 2 are strongly related to anthropic actions [38]. The ratio between the concentrations of PTEs in plant tissues and the total concentration in soils, which is called bioaccumulation factor (BAF), is one of the most important input variables in human health risk assessments [39,40].

The determination of the PTE concentrations in agricultural soils, as well as the calculation of indexes based on these levels, with a view to the evaluation of soil quality, can provide qualitative and quantitative information in environmental risk assessments. Such studies are scarce in the agricultural frontiers of the Amazon, whose agricultural areas demand high rates of inputs, especially phosphate fertilizers. Therefore, the present study aimed to (i) evaluate the PTE concentrations in soils of agroecosystems of citriculture, pipericulture and oil palm in the Amazon; (ii) determine the contamination indexes, such as the enrichment and bioaccumulation factor and; (iii) establish/discuss relations with natural values and safety standards of environmental protection agencies.

2. Material and Methods

2.1. Study Site

The study site is located in the Brazilian Amazon (Figure 1), represented by commercial plantations of citrus (*Citrus sinensis* (L.) Osbeck) with 26 years of implantation (1°48′08″ S 47°11′56″ W); oil palm (*Elaeis guineensis* Jacq.) with 10 years of implantation (2°13′18″ S 48°47′52″ W); and black pepper (*Piper nigrum* L.) with 5 years of implantation (1°47′07″ S 47°04′07″ W). The predominant soil orders correspond to Oxisols and Ultisols [41], which are usually characterized by high acidity, low availability of nutrients, and dominance of the sand fraction in the surface layer, with predominance of kaolinite in the clay fraction [42].

In the implantation of the citrus cultivation, 3 kg of chicken manure and 26.2 g of P (60 g of P_2O_5—single superphosphate) were applied per pit, as well as 60 g of N (133.3 g of urea) and 24.9 g of K (30 g of K_2O—potassium chloride) per plant. From the second to the fifth year, 200 g of N (444.4 g of urea), 39.3 g of P (90 g of P_2O_5—triple superphosphate), and 149.4 g of K (180 g of K_2O—potassium chloride) were applied per citrus plant. From the sixth year on, the production fertilization started with 80 kg ha^{-1} of N (177.8 kg of urea), 8.7 kg of P (20 kg ha^{-1} of P_2O_5—triple superphosphate), and 33.2 kg of K (40 kg ha^{-1} of K_2O—potassium chloride). In the oil palm cultivation area, 2.3 kg ha^{-1} of P (5.3 kg ha^{-1} of P_2O_5—Arad natural reactive phosphate) was applied, in addition the formulation NPK 11-07-23 + 2.5% Mg + 0.5% B, and annual applications of the formulation NPK 10-07-22. For the implantation of black pepper cultivation, 1.5 kg of chicken manure and 38.2 g of P (87.5 g of P_2O_5—thermophosphate Yoorin) were used per pit. In the first and second years, 22.5 g of N (50 g of urea), 8.1 g of P (18.45 g of P_2O_5—triple superphosphate), and 24.9 g of

K (30 g of K_2O—potassium chloride) were applied per plant. From the third year onwards, 67.5 g of N (150 g of urea), 10.7 g of P (24.6 g of P_2O_5—triple superphosphate), and 48.1 g of K (58 g of K_2O—potassium chloride) were added per plant. In addition to fertilization, the cupric fungicide known as Bordeaux mixture ($CuSO_4$ + Ca $(OH)_2$) was also applied in the cultivations of citrus and black pepper. All plantations were irrigated using water from wells located on the respective areas.

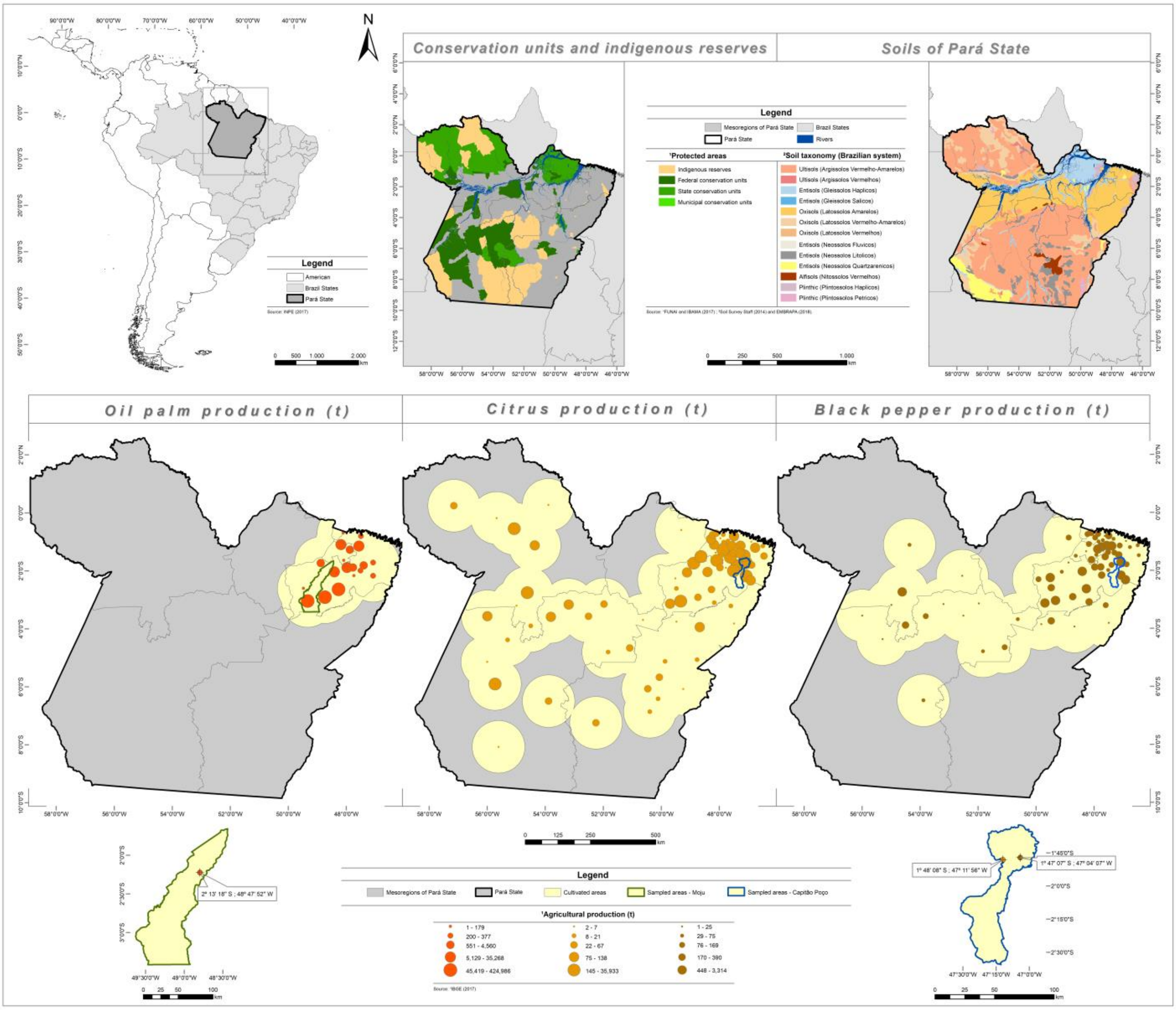

Figure 1. Study site and sampling of Oxisols and Ultisols from the state of Pará, Brazil.

2.2. Sampling and Analyzes of Soils and Plants

The soils were sampled in the 0–0.2 m layer. In each crop area, 10 subsamples were collected to form one composite sample, with three replications, making a total of 30 subsamples and 3 composed samples by cultivation area. Soil samples were also collected in areas adjacent to the plantations, composed of native or naturally recovered vegetation (regionally called *capoeiras*), which were considered as reference areas.

Plant samples were collected at the same points of soil collection, to verify the bioaccumulation potential of PTEs by cultivation. Leaf sampling in black pepper and citrus plantations consisted of collecting freshly ripe leaves, in the middle third portion of the crown per useful plant, in the order north, south, east and west [43,44]. For oil palm, from the third or fourth year of cultivation, the leaf sampling was performed on leaf No. 17 (from apex to base), considered as the best expression or the ideal physiological state for the oil palm [45].

Chemical and granulometric analyses of soil samples were carried out according to Silva [46]: pH in H_2O and 1 mol L^{-1} KCl solution (1:2.5); Ca^{2+} and Mg^{2+} in 1 mol L^{-1} KCl solution, quantified by atomic absorption spectrophotometry; K^+ extracted with 0.05 mol L^{-1} HCl solution, quantified by flame photometry; available P extracted with 0.05 mol L^{-1} HCl + 0.0125 mol L^{-1} H_2SO_4 (Mehlich-1) and determined by colorimetry; the organic carbon was determined by the Walkley & Black method (wet combustion) with potassium dichromate; the total Al_2O_3 was found by sulfuric attack; and the clay content was determined by the pipette method [47].

The concentrations of PTEs in soils from each cultivation area were extracted using acid digestion in a microwave oven (Mars Xpress, CEM Corporation, Matthews, NC, USA) [48]. For this purpose, 0.5 g soil samples (100 mesh) were weighed and placed in Teflon tubes, followed by the addition of the acid solution (HCl: HNO_3 3:1). The extracts were diluted with ultrapure water to a final volume of 50 mL and filtered (PTFE 0.45 mm).

To quantify the concentrations of PTEs in plants, the dry matter was powdered in a Willey-type knife mill and processed in a 20-mesh sieve. After that, 2 mL of HNO_3, 2 mL of H_2O_2 and 5 mL of ultrapure water were applied in 250 mg of the plant material in Teflon tubes, followed by digestion in a microwave oven (Mars Xpress, CEM Corporation, Matthews, NC, USA) [49].

The concentrations of As, Ba, Cd, Co, Cr, Cu, Hg, Ni, Pb and Zn in all samples were quantified by inductively coupled plasma mass spectrometry (ICP-MS), in triplicate, including certified reference materials for soils (ERM® CC-141) and plants (ERM® CD281) and blank samples.

2.3. Enrichment and Bioaccumulation Factors

The enrichment factor (EF) was calculated to verify the degree of contamination by PTEs in the areas used for cultivation, in relation to the area without significant anthropogenic effects (reference area—forest soil), whose concentrations of PTEs are mainly associated with the parent material. Several elements are used for geochemical normalization, such as Al, Ca, Fe, Mn, Ti and V [29]. In this study, the element used was Al_2O_3, which guarantees more robustness and reliability to the results obtained, since its concentration tends to be more uniform [36,37,50,51], following Equation (1) [29]:

$$EF = (C_n/C_r)/(B_n/B_r) \quad (1)$$

where C_n is the concentration of the PTE in sample n, C_r is the concentration of Al_2O_3 in the same sample, B_n is the concentration of the PTE in the reference area, and B_r is the concentration of Al_2O_3 in the reference area. The EF values were classified according to Sutherland [52], who divided this index into five classes: $EF < 2$, deficient to minimal enrichment; $2 \leq EF < 5$, moderate enrichment; $5 \leq EF < 20$, significant enrichment; $20 \leq EF < 40$, very high enrichment; $EF \geq 40$, extremely high enrichment.

The bioaccumulation factor (BAF) has been widely used to understand the degree of accumulation of a given contaminant in plant tissue [53–55]. In this study, BAF was obtained using Equation (2) [56].

$$BAF = [C_p/C_s] \quad (2)$$

where C_p is the concentration of PTE in plant tissue and C_s is the concentration of PTE in the soil.

2.4. Statistical Analyses

The results were submitted to descriptive statistical analysis and the Shapiro–Wilk normality test ($p < 0.05$). Data that did not follow the normal distribution were transformed.

To understand the degree of the relationship between soil attributes and PTEs in soils and plants, Pearson's correlation analysis was carried out ($p < 0.05$). All statistical analyses were performed using the software Statgraphics Centurion 18 (v. 18.1.14).

3. Results

3.1. Soil Attributes

According to the United States Soil Taxonomy [41], the soil of oil palm cultivation is classified as Typic Hapludox, while the soils of black pepper and citrus cultivation are classified as Typic Hapludult (Table 1). The soils of areas cultivated with oil palm and citrus showed values of pH H_2O equal to 4.6 and 4.7, respectively (Table 1), and the soil cultivated with black pepper presented a pH H_2O of 5.2. The ΔpH (pH KCl–pH H_2O) values of the soils in this study were −0.3, −0.5 and −0.6 for oil palm, black pepper and citrus, respectively.

Table 1. Classification, chemical attributes and granulometry of the soils studied (n = 3).

Crops	Oil Palm		Black Pepper		Citrus	
Areas	**Cultivation**	**Reference**	**Cultivation**	**Reference**	**Cultivation**	**Reference**
Soil Order	**Typic Hapludox**	**Oxisol**	**Typic Hapludult**	**Ultisol**	**Typic Hapludult**	**Ultisol**
pH (in H_2O)	4.6 ± 0.32	4 ± 0.26	5.2 ± 0.80	4.1 ± 0.06	4.7 ± 0.21	4.4 ± 0.25
pH (in KCl)	4.3 ± 0.29	3.7 ± 0.15	4.7 ± 0.62	3.7 ± 0.15	4.1 ± 0.49	3.8 ± 0.24
Ca^{2+} (mmol$_c$ kg^{-1})	9.6 ± 0.38	1.3 ± 3.01	34 ± 1.97	11.3 ± 0.42	13.7 ± 0.72	5.1 ± 1.0
Mg^{2+} (mmol$_c$ kg^{-1})	2.5 ± 0.1	1.7 ± 1.82	15 ± 0.57	10 ± 0.1	9 ± 0.17	1.2 ± 0.57
K^+ (mmol$_c$ kg^{-1})	0.9 ± 0.09	0.6 ± 0.25	4.2 ± 0.36	0.5 ± 0.02	0.5 ± 0.05	0.1 ± 0.28
P (mg kg^{-1})	5 ± 4.8	2.6 ± 2.94	234 ± 194.32	1 ± 0.0	8 ± 7	1.5 ± 0.3
Al_2O_3 (g kg^{-1})	54.1 ± 9.11	54 ± 10.82	71.7 ± 31.55	52.9 ± 36.98	53.6 ± 12.82	48.8 ± 10.31
Organic carbon (g kg^{-1})	11.6 ± 3.5	13.5 ± 2.54	16 ± 7.46	11 ± 3.05	6.9 ± 3.16	9.7 ± 2.05
Clay (g kg^{-1})	277 ± 78.11	303 ± 102.39	171 ± 76.51	168 ± 50.86	60 ± 11.55	63 ± 49.65
Sand (g kg^{-1})	590 ± 115.36	599 ± 155.88	712 ± 58.51	758 ± 60.35	919 ± 16.65	879 ± 92.86
Silt (g kg^{-1})	133 ± 40.25	98 ± 40.41	117 ± 24.68	74 ± 9.87	21 ± 6.11	58 ± 43.89

The concentration of Ca^{2+} was 9.6 mmol$_c$ kg^{-1} in the oil palm areas, while it was equal to 13.7 and 34 mmol$_c$ kg^{-1} for citrus and black pepper areas. The concentrations of Mg^{2+} were 2.5, 15 and 9 mmol$_c$ kg^{-1} in the areas of oil palm, black pepper and citrus, respectively. The level of K^+ was lower in soils cultivated with oil palm and citrus (0.9 and 0.5 mmol$_c$ kg^{-1}, respectively) when compared to the black pepper cultivation area (4.2 mmol$_c$ kg^{-1}).

The available P concentrations were 5, 234 and 8 mg kg^{-1} in oil palm, black pepper and citrus soils, respectively. The organic carbon content was lower in soils cultivated with oil palm (11.6 g kg^{-1}) and citrus (6.9 g kg^{-1}) in relation to the black pepper cultivation area (16 g kg^{-1}). The predominant particle size fraction in all studied soils was sand (Table 1).

3.2. Concentrations, Enrichment and Bioaccumulation of PTEs

The average PTE concentrations obtained for the studied soils, both in the cultivation areas and in the natural forest (reference area), are shown in Table 2. In general, the soil cultivated with oil palm exceeded the values found in the native area for As, Ba, Cr and Pb. The soil cultivated with black pepper showed concentrations of Ba, Cr, Cu, Ni, Pb and Zn, higher than the values found in the native area. In the soil cultivated with citrus, in turn, this behavior was observed only for Cu and Zn. The Cd values were similar in all sampled areas and small variations were observed for Co and Hg. In soils cultivated with oil palm and black pepper, there was enrichment by As, Ba and Pb (Figure 2). The soils cultivated with black pepper and citrus showed enrichment by Cu, and only the soil cultivated with citrus presented enrichment by Zn (Figure 2).

Table 2. Concentrations of potentially toxic elements in soils and quality guidelines.

Area	As	Ba	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn
	mg kg^{-1}									
Oil palm	1.3 ± 3.06	24.8 ± 4.04	0.4 ± 2.82	1.0 ± 0.56	50.0 ± 0.41	2.0 ± 0.82	0.05 ± 12.88	2.0 ± 0.34	7.0 ± 0.43	8.0 ± 0.98
Reference	0.1 ± 0.09	10.3 ± 4.97	0.4 ± 2.00	2.0 ± 0.06	40.0 ± 0.38	2.0 ± 0.80	0.06 ± 12.00	6.0 ± 0.86	2.0 ± 0.66	11.0 ± 1.48
Black Pepper	2.0 ± 1.53	32.3 ± 0.87	0.4 ± 3.41	2.0 ± 0.43	70.0 ± 6.02	16.0 ± 1.78	0.05 ± 12.01	4.0 ± 0.47	6.0 ± 0.18	19.0 ± 1.23
Reference	0.2 ± 1.06	10.3 ± 0.69	0.4 ± 2.89	2.0 ± 0.24	50.0 ± 8.00	2.0 ± 0.89	0.07 ± 11.98	2.0 ± 0.55	1.0 ± 0.07	8.0 ± 2.00
Citrus	0.6 ± 2.89	17.0 ± 0.25	0.4 ± 3.10	2.0 ± 0.60	40.0 ± 0.52	36.0 ± 1.70	0.05 ± 13.01	2.0 ± 1.83	4.0 ± 0.29	21.0 ± 2.65
Reference	0.9 ± 1.91	18.9 ± 0.91	0.4 ± 3.00	2.0 ± 0.10	50.0 ± 0.28	5.0 ± 1.49	0.05 ± 12.57	3.0 ± 1.38	5.0 ± 0.38	9.0 ± 2.12
QRV- Pará 75th [a]	1.4	14.3	0.4	-	24.1	9.9	0.26	1.4	4.8	7.2
QRV- Pará 90th [a]	2.6	33.4	0.9	-	35.5	18.2	0.45	6.1	7.5	21.0
QRV- Brazil [b]	3.5	75.0	<0.5	13.0	40.0	35.0	0.05	13.0	17.0	60.0
PV- Brazil [b]	15.0	150.0	1.3	25.0	75.0	60.0	0.50	30.0	72.0	300.0
RV- Brazil [b]	35.0	300.0	3.0	35.0	150.0	200.0	12.0	70.0	180.0	450.0

[a] Quality reference values established for soils from the state of Pará [25]; [b] Quality criteria established for soils of Brazil (QRV = Quality reference value; PV = Prevention value; RV = Research value) [23].

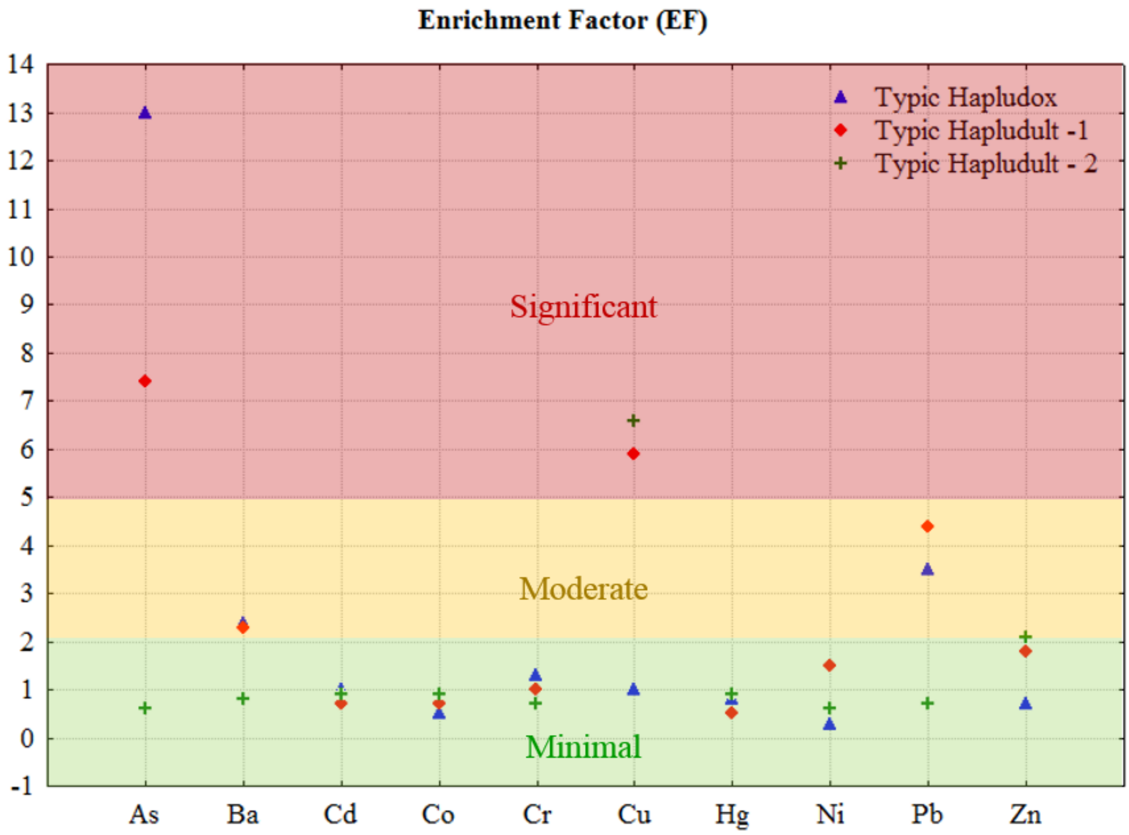

Figure 2. Enrichment factors of PTEs in areas cultivated with oil palm (Typic Hapludox), black pepper (Typic Hapludult-1) and citrus (Typic Hapludult-2).

The PTEs in plant tissues showed great variation between crops (except Cd, which remained constant) and, in general, the highest levels were observed for the citrus, with the exception of Zn, which was higher in black pepper (Table 3).

Table 3. Concentrations of potentially toxic elements in plant tissues.

Crops	As	Ba	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn
	mg kg^{-1}									
Oil palm	0.09 ± 0.00	9.00 ± 0.01	0.01 ± 0.00	0.10 ± 0.00	3.00 ± 1.73	4.10 ± 1.34	0.03 ± 0.01	1.03 ± 0.15	0.23 ± 0.06	13.33 ± 3.21
Black pepper	0.09 ± 0.00	23.33 ± 5.17	0.01 ± 0.01	0.57 ± 0.21	2.67 ± 0.57	13.50 ± 0.62	0.04 ± 0.01	2.70 ± 0.52	0.70 ± 0.35	25.00 ± 1.73
Citrus	0.16 ± 0.12	23.33 ± 5.77	0.01 ± 0.01	0.97 ± 0.64	3.33 ± 0.58	16.57 ± 0.40	0.08 ± 0.03	2.83 ± 0.93	1.03 ± 0.84	20.67 ± 1.16

High Cu and Zn bioaccumulation factors (BAF) were obtained for oil palm (Figure 3). In black pepper, a high bioaccumulation factor was obtained only for Zn. The elements Ba, Hg, and Ni showed high bioaccumulation in citrus cultivation (Figure 3). In general, the following bioaccumulation orders were obtained: BAF oil palm: Cu > Zn > Hg > Ni > Ba > Co > As > Cr > Cd ≈ Pb; BAF black pepper: Zn > Hg > Cu > Ba > Ni > Co > Pb >> As > Cr > Cd; BAF citrus: Hg > Ni > Ba > Zn > Co > Cu > As > Pb >> Cr > Cd.

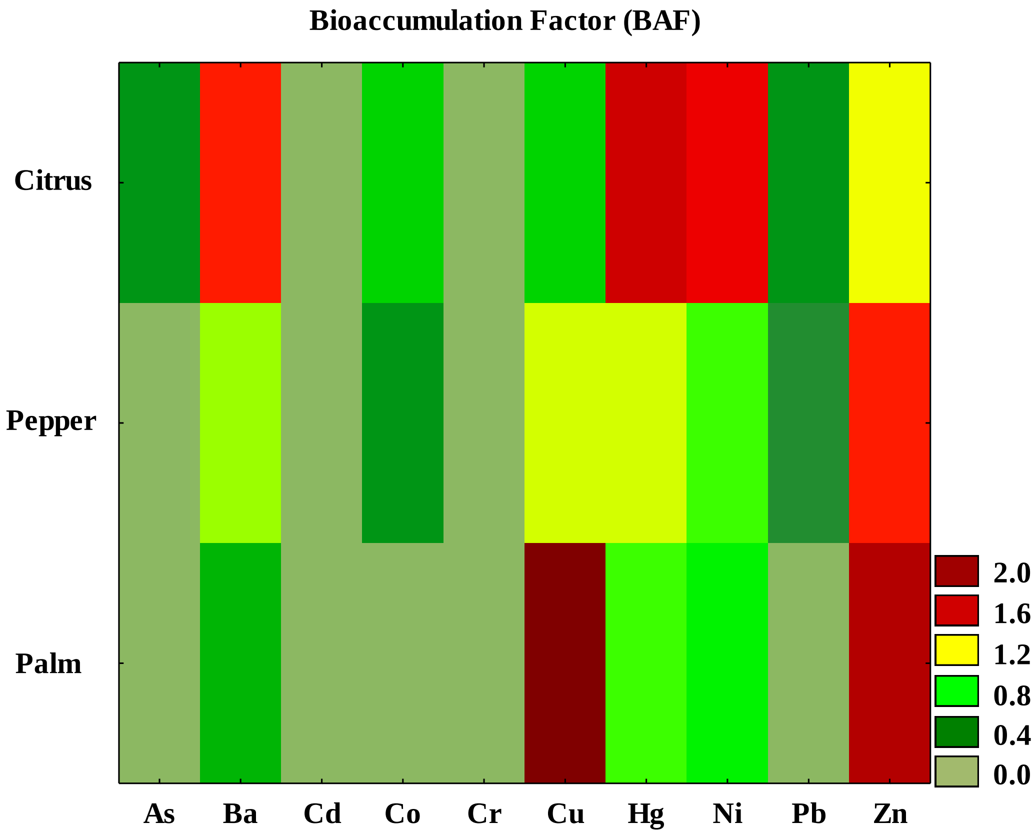

Figure 3. Bioaccumulation factors based on the average concentration of PTEs in plant tissues of the citrus, black pepper and oil palm cultivation areas.

3.3. Correlation Study

Pearson's correlation coefficients indicated that the PTEs were significantly correlated in both soils and plants (Figure 4). In plants, significant and positive correlation coefficients were observed between As–Co, As–Hg, As–Pb, Ba–Cd, Ba–Pb, Cd–Pb, Co–Pb, Co–Hg, as well as and significant and negative coefficients between Cu–Zn ($p < 0.05$). Additionally, the PTEs in the soils studied were also significantly correlated with the values of pH, Ca, K, P, Al_2O_3, OC and granulometry (Figure 4).

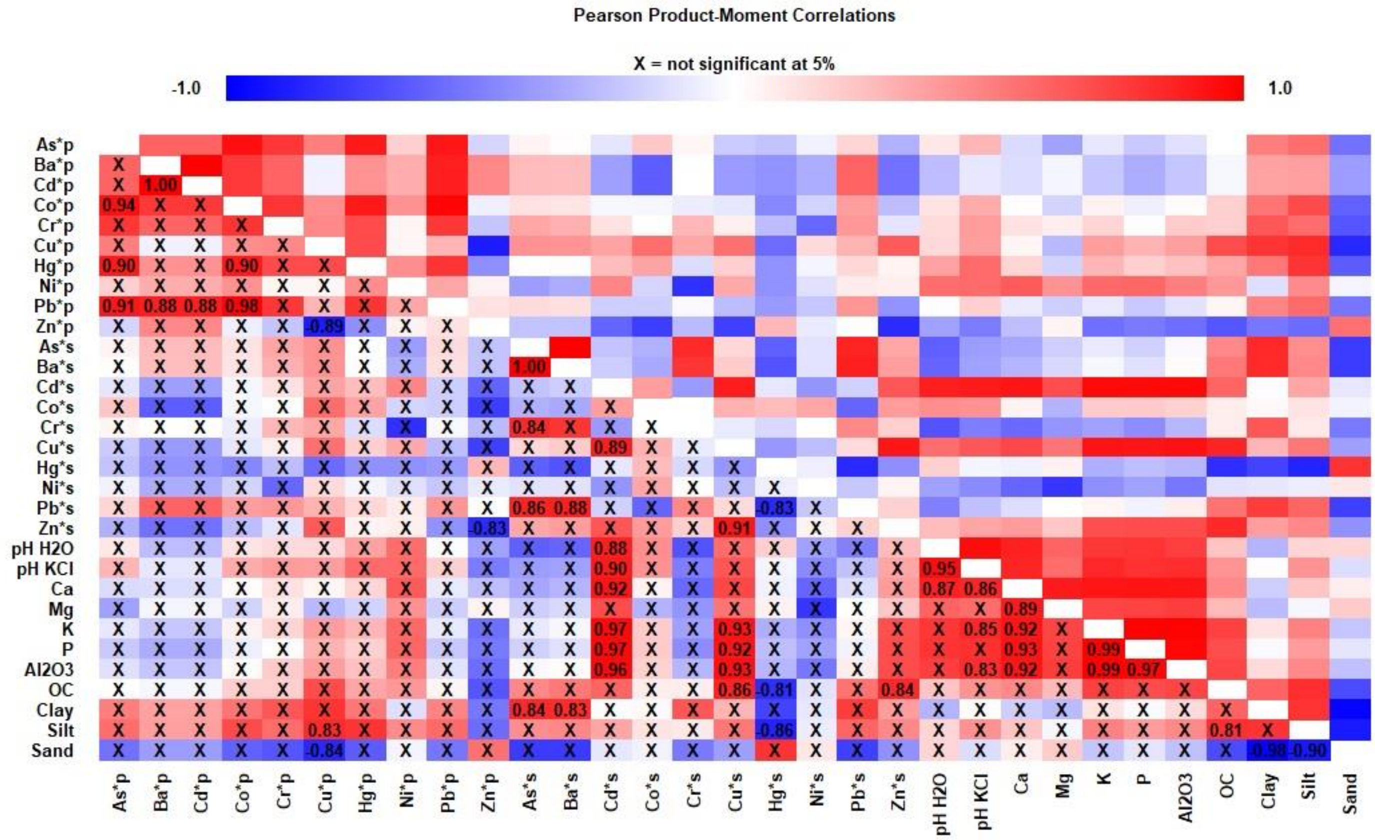

Figure 4. Heatmap of Pearson's correlation coefficients between soil attributes and potentially toxic elements in soils and plants. * *p* = plant; * s = soil.

4. Discussion

4.1. Soil Attributes

Even following the criteria and recommendations for the use of limestone and fertilizers, all the studied soils have a high acidity (pH $H_2O < 5$), with the exception of the black pepper cultivation, which presented a medium acidity [57]. In tropical regions, the climatic conditions favor the leaching of bases, increasing acidity, including areas that have received liming. A study in the Eastern Amazon showed that Oxisols and Ultisols have a high acidity [42,58]. In the Western Amazon, Moreira and Fageria [59] studied 3340 soil samples collected in primary forest, secondary forest, native forest, fallow area, polyculture and monoculture areas, and observed that more than 94% of the samples had acidity values in ranges considered high to very high, according to the classification by Venegas et al. [57].

The concentration of Ca^{2+} was considered low in the oil palm areas, while it was medium and high for citrus and black pepper areas, respectively, according to the classification by Venegas et al. [57]. The values of Mg^{2+} were classified as low in the oil palm areas, high in the black pepper area, and medium in the citrus area [57]. The concentration of K^+, in turn, was considered low in soils with oil palm and citrus, while the soil cultivated with black pepper showed a high concentration.

The available concentration of P in oil palm, black pepper and citrus soils were, respectively, very low, very high, and low, according to the classification by Venegas et al. [57]. Frazão et al. [60] evaluated oil palm plantations with 4, 8 and 25 years of implantation in Amazon soils, and observed soil P contents equal to 4.3, 3.9 and 4.2 mg kg^{-1}, respectively. The higher P content in the soil of the area cultivated with black pepper may be related to the residual effect of fertilization with thermophosphate [61].

The total organic carbon (TOC) was low in soils with oil palm and citrus when compared to black pepper cultivation, due to the longer time of implantation of these crops and the strong rainfall and high temperatures that prevail in this part of the Amazon, which contribute to the fast decomposition of organic matter [42]. In addition, in the area of black pepper cultivation, the higher contents of organic carbon may be related to the greater frequency of organic fertilization in relation to the other crops. Bayer and Mielniczuk [62] observed that the organic matter content in Ultisol was reduced from 31 g kg^{-1}, under natural conditions, to 18 g kg^{-1}, as a result of successive crops. Bowman et al. [63] observed reductions from 55 to 63% in the TOC of the soil (0–15 cm) in sixty years of cultivation. De Souza Braz et al. [64] found decrease in organic carbon of a Typic Hapludox from the Eastern Amazon, after 15 years of pasture.

The clay contents of the studied soils were within the range observed by Birani et al. [58] in Typic Hapludox (38 to 931 g kg^{-1}) and Typic Hapludult (53 to 719 g kg^{-1}), from the Eastern Amazon. The results obtained indicate the predominance of the sand fraction, which is a characteristic observed in most soils in the state of Pará [42].

4.2. Concentrations, Enrichment and Bioaccumulation

The average concentrations of PTEs, compared with the respective reference areas (control), were higher for As, Ba, Cr and Pb in the oil palm cultivation; As, Ba, Cr, Cu, Ni, Pb and Zn in the black pepper cultivation; and Cu and Zn in the citrus cultivation. The use of mineral and organic fertilizers in the studied areas may have contributed directly to increased concentrations of PTEs, since agricultural inputs are carriers of several chemical elements [65]. Soils subjected to intensive cultivation for long periods tend to have higher concentrations of PTEs [66].

However, in the soil with oil palm cultivation, Ni and Zn concentrations decreased from 6.0 to 2.0 mg kg^{-1} and from 11 to 8.0 mg kg^{-1}, respectively, indicating accumulation/exportation by the crop. The bioaccumulation of Zn by the oil palm obtained in the present study corroborates the results of Aini Azura et al. [67], who found increasing values of Zn in oil palm leaves with different implantation ages (<10, >15 and >20 years), due to phosphate fertilizer application.

The enrichment of Cu in areas cultivated with black pepper and citrus is associated with the use of fungicides, such as Bordeaux mixture ($CuSO_4$ + Ca $(OH)_2$), which is commonly applied in these crops, resulting in increased concentrations of Cu in the soils [68–70]. Increased concentrations of Cu were also observed in soils of grape cultivation, resulting from the application of fungicides [71–73].

The average concentration of Cd (0.4 mg kg^{-1}) in the studied soils was not modified by the cultivation and use of inputs. The soils showed values below 1 mg kg^{-1} of Cd, which are expected in uncontaminated soils [74]. Under natural conditions, according to Kabata-Pendias and Pendias [65], the average Cd value in soils is 0.53 mg kg^{-1}. Campos et al. [75] observed an average Cd concentration of 0.66 mg kg^{-1} in Oxisols from Brazil.

The concentration of As (0.1–2.0 mg kg^{-1}) in this study was well below the average of 5.2 mg kg^{-1} (natural conditions) observed by Campos et al. [76] for 17 Brazilian Oxisols. In Oxisol from the second largest Brazilian biome (*Cerrado*), Marques [77] obtained an average As concentration of 38 mg kg^{-1}. An average value of 10 mg kg^{-1} of As is considered normal in uncontaminated soils [78,79]. The World Health Organization considers the range from 1.0 to 40 mg kg^{-1} as natural in uncontaminated soils [80].

The Co concentrations from1.0 to 2.0 mg kg^{-1} in the soils with oil palm, citrus and black pepper cultivation are below the background average (20.3 mg kg^{-1}) observed by Dos Santos and Alleoni [81] in soils from the Southwestern Amazon. The highest concentration of Zn (21 mg kg^{-1}) observed in soil with citrus cultivation was less than the average of 22.52 mg kg^{-1}, obtained by Biondi et al. [82] in soils from the Northeastern Brazil. The low concentrations of PTEs in the studied soils may be related to the sedimentary origin of Amazon soils [42,83]. Other processes may have been preponderant for the results found in the present study, such as the low adsorption capacity of the soils, increasing leaching, followed by the absorption by plants [84,85].

Sandy soils, as those assessed in this study, have low adsorption capacity and allow greater leaching of PTEs [86]. Tume et al. [87] observed positive correlations of the clay fraction with the concentration and mobility of PTEs in soils. However, EF values show moderate enrichment of Ba, Pb and Zn ($2 < EF < 5$), and significant enrichment of As and Cu ($5 < FE < 20$), indicating anthropogenic source.

The high BAF of Hg in citrus cultivation may be related to the low organic carbon content in the soil. Yu et al. [88], studying the accumulation of Hg in plants, observed an inverse relationship between the organic carbon and the concentration of Hg in plant tissues, and the lower the organic carbon in the soil, the greater the concentration of Hg in plants. In the plant tissues of black pepper, Duressa and Leta [89] observed concentrations of As, Cd, Cr, Hg and Pb in the ranges of 0.43–0.81, 0.87–1.45, 0.55–2.25, 0.29–0.77, and 0.53–0.84 mg kg^{-1}, respectively. Sebastian and Godwin [90] evaluated the concentrations of Cd, Cu, Pb and Zn in two species of citrus and obtained average values of 0.45, 0.55, 1.34, and 6.27 mg kg^{-1} in *C. reticulata* and 0.84, 1.14, 1.75, and 4.41 mg kg^{-1} in *C. sinensis*, respectively. In the present study, results of BAF higher than 1 were found for Cu and Zn in oil palm cultivation; Ba, Hg and Ni in citrus cultivation; and Zn in black pepper cultivation. Values of BAF above 1 indicate that the plant can be used in phytoremediation programs [53].

In this study, the PTEs under agricultural conditions were in concentrations lower than the quality reference values established by the Brazilian environmental protection agency CETESB [20], with the exception of Cr in black pepper cultivation, indicating low risk of environmental contamination and hazard to human health. It is convergent with the results obtained by Fernandes et al. [25] for soils in the Eastern Amazon.

The concentrations of PTEs found in cultivated soils in this study were also lower compared to the averages mentioned in previous studies. Mirzaei [91], studying the ecological and human health risks of soil and grape heavy metals in long-term fertilized vineyards in Iran, found average values of 51.82, 71.27, 22.50, and 1.09 mg kg^{-1} for Cu, Zn, Pb, and Cd. Rehman [92] studied the occurrence and risks of PTEs in soil and water from the Chitral urban environment, in Pakistan, and observed average concentrations of Cd, Co, Fe, Mn, Ni, Pb, Zn and Mo corresponding to 1.99, 23.5, 45,791, 490, 17.8, 14.8, 86, and 16.6 mg kg^{-1}. The lower concentrations that were observed in the present study may be related to the lower capacity of most soils from the Eastern Amazon for retaining these elements, due to their high natural acidity and to the high rainfall rates in the region, which leads to the removal of elements by weathering [42].

4.3. Comprehensive Correlation of PTEs in Soil–Crop Systems

The correlation study was carried out to identify the degree of relationship between soil attributes and PTEs in soils and plants. The significant correlations observed are probably due to the multi-contamination from the frequent anthropogenic inputs [93,94]. In addition, no correlations were found for the same element in soil and plant ($p < 0.05$), which is in agreement with previous studies [95,96] and indicates that PTEs in crops are mainly from anthropogenic inputs, such as pesticides and vehicles powered by diesel or gasoline that are used in harvesting and applying pesticides. For example, As, Hg and Pb are common constituents of many pesticides (e.g., Chlorothalonil) [97]. In this study, the high correlations between Cu–Zn, Cu–OC and Zn–OC suggest that the accumulation of Cu and Zn may be associated with fertilizer application, especially organic fertilizers [98,99].

Furthermore, the correlation results suggest that Cd and Cu have a similar origin, while As and Ba are from other similar sources, since positive correlations between different PTEs imply similar origin [100]. The correlation coefficient between Pb and Hg was significantly negative, indicating that these elements are probably from different sources. In addition, the relationship between PTEs in soils and plants was varied for each element, which suggests complex correlations of PTEs in soil and crops that may be caused by competition between elements or plant selectivity, and pollution source [101,102].

5. Conclusions

The soil cultivated with black pepper has better fertility when compared to the soils cultivated with oil palm and citrus, which have higher acidity and lower concentrations of exchangeable bases. The concentrations of As, Ba, Cr and Pb are higher in soils cultivated with oil palm in relation to the respective reference area, as well as the concentrations of As, Ba Cr, Cu, Ni, Pb and Zn in the black pepper cultivation, and Cu and Zn in the citrus cultivation. Soil enrichment factors ranged from 0.3 to 13, indicating minimal to significant enrichment. Despite this, all elements are in concentrations below the prevention and investigation values established by Brazilian legislation. Bioaccumulation factors above 1 were observed only for Cu in oil palm cultivation (2.05), Zn in black pepper cultivation (1.32), and Ba, Hg and Ni in citrus cultivation (1.37, 1.53 and 1.42, respectively). Pearson's correlation study revealed that PTEs are mainly derived from anthropogenic activities, such as the use of machinery and application of pesticides. The results found in this study are pioneering and indicate that the management practices of oil palm, black pepper and citrus crops in the Eastern Amazon are not causing damage to the soil and risks to human health.

Author Contributions: Conceptualization, A.M.d.S.B. and M.L.d.C.; methodology, A.M.d.S.B. and A.R.F.; validation, A.M.d.S.B., M.L.d.C. and A.R.F.; formal analysis, A.M.d.S.B. and S.J.R.; investigation, A.M.d.S.B.; resources, A.M.d.S.B.; writing—original draft preparation, A.M.d.S.B.; writing—review and editing, M.L.d.C., A.R.F., S.J.R. and R.D.; visualization, A.M.d.S.B.; supervision, M.L.d.C.; project administration, A.M.d.S.B. and M.L.d.C.; funding acquisition, S.J.R. and R.D. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding. The APC was funded by Instituto Tecnológico Vale.

Data Availability Statement: Data is contained within the article.

Acknowledgments: The first author thanks the Pro-Rectory of Research and Technological Development (PROPED/UFRA) for Support (Prodoutoral-04/2017). The second (Grant 305015/2016-8), third (Grant 307166/2019-8) and last (Grant 305819/2018-6) authors thank the CNPq for the financial support.

Conflicts of Interest: The authors declare that they have no conflicts of interest.

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