1. Introduction

The current demand for food has increased the use of agricultural inputs, which can lead to accumulation of emerging contaminants (ECs). This group of contaminants is not usually included in routine monitoring programs and their adverse effects on the environment and human health are not well understood [1]. Recently, concern about the environmental risks associated with these contaminants has increased, especially rare earth elements [2], represented by La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, which comprise the lanthanides, in addition to Sc and Y, which present similar chemical and physical properties [2–5]. Such metals are typically classified into light (LREEs) and heavy (HREEs) rare earth elements according to their atomic number and mass [6].

The main way of entry of REEs and Y (REY) in agricultural soils is the application of fertilizers [7–9], especially the sources of P [10]. These inputs can present a high variability regarding the REEs and their respective concentrations, which is related to the differences in the materials used as sources, as well as the processes used to obtain the final products [10–12]. In
Brazil, it is estimated that between 10,500 and 13,000 tons of REY are added annually to soils with the large-scale application of phosphate fertilizers [11,13], which may represent a potential risk to agricultural and environmental sustainability, since these metals can bioaccumulate after being transferred from the soil to living organisms and water bodies [10]. After absorption by plants, REY can cause several negative effects, such as decreased photosynthetic rate and chlorophyll content, which can lead to cell death and reduced plant growth [14–20]. Occupational poisoning and human diseases have also been linked to contamination by REY [21].

Vanadium (V) is considered a re-emerging risk to the environment and human health, due to the high persistence in the environment [22]. It is the fifth most abundant transition element in Earth’s crust [23] and its main anthropogenic sources are mining, smelting, fossil fuel combustion, crude oil spills, and use of phosphate fertilizers containing V (such as superphosphates), which have resulted in a high abundance of this element in the biosphere [24,25]. In soils, the concentration of V ranges from 2 to 310 mg kg⁻¹, with a mean of 90 mg kg⁻¹ [26], occurring in several oxidation states, of which the most common in natural soils are the tetravalent (+IV) and pentavalent (+V) forms [27]. Among these forms, the pentavalent V is the most toxic, which may cause genotoxic effects on plants [28,29].

The bioavailability of V in soil may promote the accumulation and translocation of the element in plants, leading to serious ecological risks and significant threats to human health [29–31]. For example, death of plants was observed under high levels of V [32], as well as neurological disturbances and death of heifers [33]. Moreover, intake of high concentrations of V by humans induces diarrhea, green tongue, and hematological changes [34]. Therefore, more attention should be paid to the potential risks of V in soils, especially due to the enrichment resulting from anthropogenic activities, including agriculture.

Brazilian Amazon is a major food producing area, exporting soy and beef for large consuming countries [35]. In this region, it is extremely important to associate food production systems with the conservation of natural resources [36]. The state of Pará, in the Eastern Amazon, is the second largest state in Brazil, with a total area of 1,247,950.003 km². In 2019, this state produced 2,543,814 tons of oil palm, 35,524 tons of black pepper, and 324,422 tons of citrus (orange). With these values, the state of Pará was the first, second, and seventh largest producer of these crops in the national ranking, respectively, representing 98.5%, 32.5%, and 1.9% of the Brazilian agricultural production [37].

The impacts of anthropogenic activities on the levels of ECs may be studied using the enrichment factor (EF) [38], which considers the ratio between the concentration of the assessed element in anthropized soil and the natural concentration or background content [39,40]. Other index commonly used for this purpose is the bioaccumulation factor (BAF), which relates the levels of elements in plant tissues and the total content in the soil [38]. It is one of the most important indices in human health risk assessments [41], considering the potential that some crops and vegetables have to absorb and bioaccumulate contaminants, even at low concentrations in the soil [42].

The present study is pioneering in the assessment of concentrations, enrichment and bioaccumulation of ECs (REY and V) in agricultural systems in the Brazilian Amazon, with the following objectives: (i) to evaluate the levels of REY and V in areas cultivated with citrus, oil palm, and black pepper, after application of P fertilizers for 26, 10 and 5 years, respectively; (ii) to establish the relationship between concentrations of ECs and soil attributes; and (iii) to calculate the enrichment and bioaccumulation factors in the agricultural areas in order to discuss the potential food safety risks.

2. Materials and methods

2.1. Samples collection

The samples were collected in areas cultivated with: i) black pepper (Piper nigrum L.) for 5 years, with 13 ha, under the geographic coordinates 1°47’ 07″ S 47° 04’ 07″ W; ii) oil palm (Elaeis guineensis Jacq.) for 10 years, with 10 ha, under the geographic coordinates 2°13’ 18” S 48° 47’ 52” W; and iii) citrus (Citrus sinensis (L.) Osbeck) for 26 years, with 10.5 ha, under the geographic coordinates 1°48’ 08” S 47° 11’ 56” W, in the Eastern Amazon (Figure 1). The predominant soil orders in this region are Oxisols and Ultisols [43], characterized by high acidity, low availability of nutrients, and sandy character in the surface [44]. The general soil characterization is summarized in Table S1.

Soil collection was performed with a stainless-steel Dutch auger, to avoid contamination of the samples. In each area, 10 subsamples of soil were collected (0–0.2 m deep) to generate a composite sample, with 3 replications, totaling 30 subsamples and 3 composite samples by area. In addition, using the same method adopted in the collection in the anthropized areas, soil samples were collected in native or naturally recovered vegetation areas (without significant anthropic influence) near the plantations, aiming at studying the pollution degree in the plantations. All soil samples were collected in the rhizosphere of the studied plants, aiming to have a better response of REY and V uptake by the crops.
Plant samples were collected at the same points where soils were sampled, to assess the REY and V bioaccumulation capacity of each crop. In the black pepper and citrus areas, freshly ripe leaves were collected in the middle third portion of the crown per usef ul plant, in the way to the North, South, East and West [45,46]. In the oil palm area, leaves were collected from the third or fourth cultivation year, on leaf No. 17 (from apex to base), which represents the best expression or the ideal physiological state for the crop [47].

### 2.2. Tillage systems

At the time of planting the citrus cultivation, 3 kg of chicken manure and 60 g of P₂O₅ were added per pit, as well as 60 g of N and 30 g of K₂O per plant. From the second to the fifth cultivation year, 200 g of N, 90 g of P₂O₅, and 180 g of K₂O were applied per plant. From the sixth cultivation year, the production fertilization consisted of the application of 80 kg ha⁻¹ of N, 20 kg ha⁻¹ of P₂O₅, and 40 kg ha⁻¹ of K₂O. In the area of oil palm plantation, 5.3 kg ha⁻¹ of P₂O₅ were used, as well as NPK 11–07–23 + 2.5% Mg + 0.5% B, and annual additions of NPK 10–07–22. In the implantation of the black pepper cultivation, 1.5 kg of chicken manure and 87.5 g of P₂O₅ were applied per pit. In the first and second years, 22.5 g of N, 18.45 g of P₂O₅, and 30 g of K₂O were added per plant. From the third cultivation year, 67.5 g of N, 24.6 g of P₂O₅, and 58 g of K₂O were applied per plant. Also, the Bordeaux mixture (CuSO₄ + Ca (OH)₂), which is a widely known cupric fungicide, was used in the citrus and black pepper areas. Irrigation was carried out using water from wells situated on the same areas in all plantations.

### 2.3. Samples analyses

The concentrations of REY were determined according to Ramos et al. [11]. Samples of soils and plants were air-dried and ground (150-mesh sieve). All samples were digested by an alkaline fusion method, in duplicate. For this purpose, an aliquot of 0.1 g from each sample was fused with 1.4 g of lithium metaborate, in platinum crucibles at 1000°C in a fusion machine (Fluxer BIS, Claisse). After cooling, the resulting bead was dissolved in beakers containing 50 mL of a 2.5% solution of tartaric acid and 10% HNO₃. Each beaker was transferred to a hot plate at 120 ± 20°C with magnetic stirring for complete solubilization. After that, the samples were transferred to 100 mL polypropylene flasks and the volume was completed with a 2.5% solution of tartaric acid and 10% HNO₃. Blank samples and certified reference materials (OREAS-45c, GRE-3 and OREAS 146) were included. Contents of REY were quantified using inductively coupled plasma-mass spectrometry (Perkin Elmer, Model NexION 300D). Recovery rates varied between 90% and 110%. The total concentrations (ΣREY) were obtained as the
sum of the concentrations of each REE and Y. At the same time, to eliminate the zigzag distribution (known as the Oddo-Harkins rule), the chondrite normalization was applied [48].

The concentrations of V in soils from each cultivation area were extracted using acid digestion in a microwave oven (Mars Xpress, CEM Corporation) [49]. 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 V in plants, the dry matter was powdered in a Willey type knife mill and processed in a 20-mesh sieve. After that, 2 mL HNO$_3$, 2 mL H$_2$O$_2$ and 5 mL ultrapure water were applied in 250 mg of the plant material in Teflon tubes, followed by digestion in a microwave oven (CEM Corporation, Mars Xpress) [50]. The concentrations of V were found by inductively coupled plasma mass spectrometry (ICP-MS), in triplicate, with certified reference materials for soils (SRM® 2711a) and plants (SRM® 1570a) and blank samples.

2.4. Risk assessment – enrichment and bioaccumulation factors

The enrichment factor (EF) was obtained to study the degree of contamination associated with the REY and V in the soils assessed. The EF enables to understand the contamination in a cultivated area in relation to a reference area (native or naturally recovered vegetation), considering a reference element. Elements such as Al, Ca, Fe, Mn, Ti, and V are commonly used as a reference [40]. In the present study, the element adopted was Al$_2$O$_3$ [51], due to the fact that its behavior tends to be more uniform [52-54]. The EF was found using Eq. 1 [40].

$$EF = \frac{(C_n/C_r)}{(B_n/B_r)}$$

where \(C_n\) is the level of REY and V in sample \(n\), \(C_r\) is the level of Al$_2$O$_3$ in the same sample, \(B_n\) is the level of REY and V in the reference area, and \(B_r\) is the level of Al$_2$O$_3$ in the reference area. The results were classified according to Sutherland [55], where EF < 2 indicates deficient to minimal enrichment; 2 ≤ EF < 5 indicates moderate enrichment; 5 ≤ EF < 20 indicates significant enrichment; 20 ≤ EF < 40 indicates very high enrichment; and EF ≥ 40 indicates extremely high enrichment.

The bioaccumulation factor (BAF) has been frequently adopted to assess the degree of accumulation of a contaminant in the plant tissue [56-58]. This index is found according to Eq. 2 [41].

$$BAF = \frac{(C_p/C_t)}$$

where \(C_p\) is the level of REY and V in the plant tissue (dry weight) and \(C_t\) is the level of REY and V in the soil (100 mesh sieve).

2.5. Data analyses

The descriptive statistical analysis, Pearson’s correlation coefficients, response surface graphics and all statistical analyses were performed using the software Statistica 10.0 (Tucka, USA) [59].

3. Results

3.1. Concentrations, enrichment and bioaccumulation in soil–crop systems

3.1.1. Rare earth elements and yttrium (REY)

The concentrations of REY in soils cultivated with black pepper and oil palm were higher than those found in the reference area (Table 1). On the other hand, the citrus soil had concentrations of REY lower than the control area (Table 1). Concentrations of REEs in the soils and plants generally decreased from light to heavy elements (Figure 2). The LREE represented about 77% of the elements in the soils and 91% in plant tissues. All soils and crops showed similar distribution patterns, with a clear enrichment of REEs in relation to chondrite (Figure 3). The concentrations of REY in plant tissues are at least one order of magnitude lower than for soils, but vary over several orders of magnitude as a function of plant species and soil concentrations (Table 1).

The enrichment factors for all HREE were less than 2, considered as minimal, and the soil cultivated with citrus (Typic Hapludult-2) showed low EF (< 2) for LREE and HREE (Figure 4a). The soil cultivated with oil palm (Typic Hapludox) showed EF moderate (EF > 2) for Ce and Sm, while the black pepper cultivation (Typic Hapludult-1) showed EF > 2 for La, Ce, Pr and Sm (Figure 4a). The bioaccumulation factors generally followed the order: Black Pepper > Citrus > Oil Palm, and the bioaccumulation of Eu was the most significant (Figure 4b).

The contents of LREE were positively correlated with pH, K and P (strongly and significantly) in the cultivated soils (Figure 5). On the other hand, there was a relatively poor correlation between concentrations of HREE with soil properties. The REEs were positively and significantly correlated with the soil pH (Figure 6).

3.1.2. Vanadium

The concentrations of V (mg kg$^{-1}$) followed the order: (i) black pepper, cultivated (72 ± 5.33) and reference (18 ± 1.10); (ii) oil palm, cultivated (50 ± 2.35) and reference (18 ± 0.57); and (iii) citrus, cultivated (33 ± 3.10) and
Table 1. Concentrations of rare earth elements and yttrium in soils and plants (*n* = 3) and agricultural inputs applied to soils.

| REY (mg kg⁻¹) | Soils | Crops | Soil inputs in Brazil |
|---------------|-------|-------|-----------------------|
|               | Oil palm | Black pepper | Citrus | Oil palm | Black pepper | Citrus | Single superphosphate | Triple superphosphate | Gypsum | Limestones |
| Y             | 13.80 | 10.50 | 20.70 | 14.10 | 23.70 | 0.13 | 0.60 | 0.33 | 3.5–123.7 | 4.2–35.6 | 0.2–1.0 | 0.6–3.1 |
| La            | 11.20 | 5.60 | 15.80 | 6.80 | 9.10 | 0.40 | 1.77 | 0.77 | 8.1–604.6 | 6.2–10.4 | 0.4–2.1 | 1.2–5.9 |
| Ce            | 21.80 | 9.60 | 29.20 | 10.60 | 12.80 | 0.67 | 4.00 | 1.47 | 6.3–1098.5 | 4.7–11.0 | 0.2–3.3 | 1.3–9.7 |
| Pr            | 2.03 | 1.02 | 2.84 | 0.98 | 1.25 | 0.06 | 0.34 | 0.14 | 1.2–135.3 | 1.3–2.6 | 0.3–0.8 | 1.1–2.1 |
| Nd            | 5.90 | 3.10 | 8.80 | 3.30 | 3.90 | 0.23 | 1.33 | 0.43 | 3.4–442.9 | 2.2–3.5 | <0.007–0.5 | <0.007–6.7 |
| Sm            | 1.37 | 0.61 | 1.85 | 0.54 | 0.73 | 1.01 | 0.08 | 0.23 | 0.05 | 0.7–61.0 | 0.9–25.3 | 0.5–1.2 | 1.8–3.1 |
| Eu            | 0.28 | 0.17 | 0.34 | 0.17 | 0.19 | 0.24 | 0.03 | 0.09 | 0.04 | 0.2–14.6 | 0.1–0.3 | <0.006 | <0.006–0.2 |
| Gd            | 1.48 | 1.03 | 2.17 | 1.04 | 1.33 | 1.86 | 0.06 | 0.20 | 0.11 | 1.2–45.2 | 3.6–20.3 | 0.2–0.9 | 3.0–16.3 |
| Tb            | 0.28 | 0.22 | 0.37 | 0.17 | 0.25 | 0.40 | 0.01 | 0.02 | 0.02 | 0.1–6.6 | 1.3–1.6 | 0.5–0.8 | 0.9–2.0 |
| Dy            | 1.92 | 1.48 | 2.86 | 1.57 | 1.86 | 3.07 | 0.06 | 0.20 | 0.09 | 1.0–31.0 | 1.1–1.9 | 0.1–0.4 | 0.1–1.8 |
| Ho            | 0.49 | 0.39 | 0.78 | 0.42 | 0.52 | 0.83 | 0.01 | 0.02 | 0.02 | 0.1–4.7 | 0.3–0.5 | 0.1–0.2 | 0.2–0.3 |
| Er            | 1.59 | 1.20 | 2.53 | 1.37 | 1.76 | 2.72 | 0.03 | 0.06 | 0.03 | 0.3–7.7 | 0.1–1.5 | <0.013 | <0.019–0.4 |
| Tm            | 0.29 | 0.21 | 0.48 | 0.26 | 0.30 | 0.49 | 0.03 | 0.02 | 0.03 | (0.5–3.5)³ | (0.5–1.5)³ | - | - |
| Yb            | 2.32 | 1.76 | 3.48 | 2.00 | 2.50 | 4.09 | <0.03 | 0.09 | 0.04 | 0.4–5.7 | 0.4–2.2 | <0.009–0.1 | 0.1–0.3 |
| Lu            | 0.37 | 0.27 | 0.59 | 0.29 | 0.40 | 0.59 | 0.01 | 0.02 | 0.02 | 0.1–0.9 | 0.1–0.4 | <0.005 | <0.005 |

¹Silva et al. [13]; ³Ramos et al. [10].
In general, the cultivated soils showed higher concentrations of V than those found in the natural environment (reference areas) (Figure 7). The EF values showed moderate enrichment of V in the soils cultivated with black pepper and oil palm (2 ≤ EF < 5), and minimal enrichment (EF < 2) in the soil cultivated with citrus (Figure 8). The EF followed the order: black pepper (2.95) > oil palm (2.77) ≫ citrus (0.57). The average levels of V in plant tissues were 3.0 mg kg⁻¹ for citrus (orange), 1.7 mg kg⁻¹ for black pepper, and 0.9 mg kg⁻¹ for oil palm. The bioaccumulation factor (BAF) followed the order: citrus (0.091) > black pepper (0.023) > oil palm (0.018) (Figure 8).

Significant and positive correlation coefficients were observed between V–Fe₂O₃, V–pH and V–K₂O, as well as significant and negative coefficient between reference (53 ± 0.94).
V–SiO$_2$ ($p < 0.05$) (Figure 5). The soils presented very strong and positive linear correlations involving the V content with Fe and K oxides (Figure 9).

4. Discussion

4.1. REY in agricultural soils and plants

In the areas where Oxisols and Ultisols are formed, with strong rainfall and high temperature, associated with heavy weathering-leaching, cation losses are common and lead to a pH decrease, removal of weatherable minerals, and accumulation of oxides and kaolinite [44]. It may explain the lower concentrations of REY in topsoil due to weathering-leaching [60]. In this study, the anthropogenic activities may also justify the lower and higher levels of REY in agricultural soils when compared with the non-agricultural areas (reference areas). Phosphate fertilizers constitute the main anthropogenic source of REY and usually lead to increased concentrations of these elements in soils [10,11]. In Brazilian tropical soils and agroecosystems, the average annual rate of phosphate fertilizer applied to crops is 25 kg P ha$^{-1}$ y$^{-1}$ [61]. The frequent addition of high levels of P fertilizers and soil correctives to these soils represent 13,000 tons of REY that are applied per year [13]. However, in the citrus cultivation of the present study, the sandy soil and the longer period of soil use possibly contributed to the low concentrations of REY found, due the losses by leaching. Sandy and peaty soils tend to present lower REY contents than clayey soils, which is related to the lower retention potential of soils with a predominance of larger particles [62]. The pH decrease in soils causes leaching of REY [63].

In this study, the LREEs were usually more abundant than HREEs, which is in accordance with the findings observed in topsoil studied by Wiche et al. [64]. In the black pepper and oil palm cultivation, the enrichment factors (EF $> 2.0$) suggest an anthropogenic contribution of La, Ce, Pr and Sm. Wang and Liang [65] proposed values of EF $> 1.5$ as significant enrichment caused by anthropogenic sources. The EF values that ranged from 1.1 (La) to 2.1 (Gd) were considered low in the natural wetland soil of China[66]. Plants can solubilize LREEs from soil, absorb
and transport to leaves, and carboxylate groups in plant tissues can bind with LREE ions easier than HREEs [67,68]. REY are generally found in trivalent oxidation states, except europium and cerium, which may also occur respectively as Eu³⁺ and Ce⁴⁺ [69]. In the plant tissues of the present study, the highest bioaccumulation factor was found for Eu, with the following order: black pepper, citrus, and oil palm. This higher bioaccumulation could be due to the interchangeability of Eu with Ca in physiological processes of plant growth occurring in soil or to protein binding in photosystem II [70,71]. Europium is considered an indicator of biogeochemical processes, due to the modification of its valence state as a function of different conditions and also for the similarity to chemical characteristics of Ca [72].

The bioaccumulation of REY, also referred as transfer factors, varied from 0.02 to 0.26 in the present study. In contrast, Turra et al. [73] observed transfer factors of La ranging from 0.62 to 1.09 in citrus plants, which is mentioned among species with a good ability to accumulate REY. In a recent study by the same author, the highest transfer factor of REY was observed for La (0.0047) in Rangpur lime (Citrus limonia Osbeck) plants [74]. These differences can be attributed to soil

Figure 6. Response surface of concentrations of rare earth elements in the cultivated soils. (a) available P and pH, (b) K and pH.

Figure 7. Concentrations of vanadium in the cultivated (crops) and reference (natural) areas. Number of samples (n) = 3 for each crop and soil.
properties, soil management, planting age and cultivation environments \cite{68,75,76}. In another study, Cheng et al. \cite{77} observed that low pH in different soils from a typical Chinese field of citrus planting induced higher absorption of REY by plants. The uptake of REY tends to be higher at a low pH \cite{78}. A significant linear correlation between the content of REY from sandy soil to palm trees has been observed \cite{79}. Moreover, REY can accelerate the growth of plant tissues \cite{80}. The positive effects of La on the bell pepper quality by enhancing some growth parameters and biomolecule concentrations were found \cite{81}.

In the present study, for Amazonian tillage conditions, the pH, K and available P were the main factors influencing the contents of REEs in soils. Other study indicate that the organic acids, redox potential, and soil pH are

\begin{equation}
V = -13.3 + 14.8 \times X + 403.4 \times Y
\end{equation}

**Figure 8.** Enrichment and bioaccumulation factors of vanadium in the cultivated soils and crops. Number of samples (n) = 3 for each crop and soil.

**Figure 9.** Response surface for vanadium contents versus Fe and K oxide concentrations in soils. Number of samples (n) = 3 for each crop and soil.
4.2. Vanadium in agricultural soils and plants

The average concentrations of V in soils cultivated with black pepper and oil palm were higher than those found in the reference area, while the citrus cultivation showed concentrations lower than the reference area. The lower concentration of V in the soil cultivated with citrus may be related to the more accentuated sandy character of this soil, which promoted plant uptake and/or higher leaching losses [87,88]. The highest concentration of V in the soil cultivated with black pepper (72 mg kg\(^{-1}\)) was possibly related to use of phosphate fertilizers. Afloog and Hassan [89] studied the concentration of V in Iraq soils and attributed the higher levels in agricultural (49 mg kg\(^{-1}\)), residential (47.4 mg kg\(^{-1}\)) and industrial areas (40.2 mg kg\(^{-1}\)) to the use of chemical fertilizers. Fertilizers with a high P content and the pure phosphates (ordinary and triple superphosphate) may contain concentrations of V from 34 mg kg\(^{-1}\) to 143 mg kg\(^{-1}\) [90]. It is important to mention that crops have different demands for P, which directly reflects on the amount of fertilizer to be applied and, consequently, on the content of V (as well as REY) incorporated into the soil.

The soil cultivated with black pepper, which showed a V concentration of 72 mg kg\(^{-1}\), exceeded the average of 64 mg kg\(^{-1}\) in agricultural soils around the V mine in the municipality of Maracás, state of Bahia (Northeastern Brazil) [91]. Moreover, there is still no ordinance or legislation by government agencies about the V concentration in soils of the Brazilian Amazon. However, other countries determined environmental standards of V for soil, invertebrates and plants, such as Netherlands (42 mg kg\(^{-1}\)), Slovenia (120 mg kg\(^{-1}\)), and Czech Republic (180 mg kg\(^{-1}\)) [92]. The USA (U.S. Environmental Protection Agency, Regions 4 and 6) determined a stricter standard of 2 mg kg\(^{-1}\) of V in soils from native vegetation [93]. Canada adopted the quality reference value of 130 mg kg\(^{-1}\) of V in soils [94]. The same value (130 mg kg\(^{-1}\)) was established by the Environmental Quality Standard in China for agricultural soils [42].

The EF values showed moderate enrichment of V in soils cultivated with black pepper and oil palm (2 \< EF \< 5), and minimal enrichment (EF \< 2) in the soil cultivated with citrus. In the present study, it was observed that the levels of enrichment in agricultural soils reflect on the gradually increasing values of some soil properties (such as pH, OC, Fe\(_2\)O\(_3\), P\(_2\)O\(_5\), and K\(_2\)O). Several studies have been conducted and revealed that many soil properties, such as pH, Fe oxides, and organic carbon affect V content [95–97]. In addition, sandy soils as those assessed in this study have low EF values and allow greater leaching of V. The V content is strongly influenced by soil texture, gradually increasing with increasing clay contents from 35 ppm in coarse-textured materials to 138 ppm in fine textured soils [98]. In contrast, Moghtaderi et al. [99] observed minimal enrichment of V in agricultural soils with loam and silt loam texture from the Bandar Abbas County (South Iran). In the present study, the EF values obtained in black pepper and oil palm areas may indicate anthropogenic source.

The bioaccumulation factor (BAF) is also called as biological absorption coefficient (BAC), which can be classified into five groups: very weak absorption (0.001–0.01); weak absorption (0.01–0.1); intermediate absorption (0.1–1); strong absorption (1–10); and intensive absorption (10–100) [100]. The BAF of V for the three species studied belong to weak absorption group. Teng et al. [101], studying 36 plant samples from Panzhihua, Southwestern China, found a range from weak (0.009) to intermediate (0.371) absorption of V. In present study, the longer period of citrus cultivation, when compared to the other crops, may be related to highest V content in the leaves, and/or the preferential plant uptake due to antagonism with K, since this element is strongly important for crop fertilization. These relationships were also supported by Garcia-Jiménez et al. [102], who found a decrease of the K concentration with increasing levels of V in pepper leaves. An experiment conducted in pots under glasshouse conditions by Akoumanaki-loannidou et al. [103] showed an antagonistic effect between V and the accumulation of Fe and Pb in leaves of sweet basil. Additionally, in most cultivated plants, the internal V concentration is about 10 times lower than that in the rhizosphere [104]. The accumulation of V in plant tissue also depends on plant species and soil V content [105].

In this study, the relationship between soil properties and V concentrations, showed significant and positive correlation coefficients with Fe\(_2\)O\(_3\), pH and K\(_2\)O, as well as significant and negative coefficient to SiO\(_2\). The pH is strongly correlated with the availability of V, and in terms of ecotoxicity, it is of crucial importance in dictating the environmental risks of V, rather than its original oxidation state or total concentration [106]. The pH can be expected to control V sorption, given the strong dependence of V speciation on pH. For example, at a higher pH, pentavalent V occurs as conjugate acids of VO\(_3^−\)– that can be expected to adsorb to positively charged oxide mineral surfaces by ligand exchange, analogous to the sorption behavior of phosphate [107]. Negative correlation of silicon dioxide (SiO\(_2\)) with the V concentrations in soils, in turn, has also been supported by studies carried out in soils of Germany and Egypt by Shaheen and Rinklebe [108], who observed significant and negative correlations between total V with sand content in all soils. This is consistent
5. Conclusions

It is essential to understand the accumulation of emerging contaminants, especially in highly weathered soils, such as those soils examined in the present study. Our study is a pioneer regarding REY and V uptake by Amazonian crops with great importance for global markets. The results indicate that the concentrations of emerging contaminants are extremely influenced by soil pH under field conditions, especially in tropical areas. In addition, Eu was the most bioaccumulated element among the REY in all studied crops. The longer period of soil use with citrus cultivation in relation to the other crops was not decisive to promote cause/effect relations with the REY concentrations. On the other hand, the levels of V indicated minimal to moderate enrichment and weak bioaccumulation in these soil-crop systems. The results of this study may be useful in monitoring emerging contaminants in soils with anthropic influence. Moreover, it is suggested to carry out further studies evaluating different crops grown in the Amazon, especially under field conditions, considering that phosphate fertilization is performed frequently and on a large scale in the soils of the region, which can lead to the accumulation and bioaccumulation of emerging contaminants such as REY and V.

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Disclosure statement

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