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Soil Amendments, Physicochemical Properties, and Metal Accumulation in Soils and Vegetables of Volcanic and Non-Volcanic Regions in Ecuador

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Abstract: Heavy metal contamination in agricultural soils threatens food security and public health, especially in volcanic regions where ash alters soil properties. This study evaluates the effects of soil amendments on physicochemical properties, nutrient availability, and heavy metal accumulation in ash-affected (Mocha) and non-affected (Puyo) soils in Ecuador. A field experiment tested compost, poultry manure, inorganic fertilizer, and a control on onion (*Allium fistulosum*) and parsley (*Petroselinum crispum*). Soil analyses assessed the bulk density, texture, pH, electrical conductivity, organic matter, nutrients, metals, and metalloid concentrations of the soils and crops. Mocha soils exhibited volcanic Andisol characteristics, while Puyo soils resembled eastern Ecuadorian soils, both showing high nitrogen but deficiencies in phosphorus, potassium, and calcium. Arsenic (As), lead (Pb), and chromium (Cr) levels in soils varied between regions but not among treatments. In Mocha, As bioavailability decreased with poultry manure and compost, while other metals remained stable except in fertilized soils. In Puyo, organic amendments reduced Hg, Pb, Ni, and Cr but increased them in fertilized soils. All treatments met Ecuadorian limits for As, Cd, Pb, and Ni but exceeded those for Hg and Cr. Organic amendments improved soil quality, reduced metal mobility, and supported sustainable agriculture, with Mocha soils appearing more suitable for cultivation.

Keywords: *Allium fistulosum*; *Petroselinum crispum*; cultivated soils; heavy metals; volcanic ash

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1. Introduction

Volcanic activity is widespread throughout the Andean region of the Americas [1], producing ash nanoparticles that can affect human health, the environment, and even the climate [2]. Volcanic ash can transport metals and metalloids, including arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), and mercury (Hg)—hereafter collectively referred to as metal(loid)s [3]. These metal(loid)s can influence agricultural production [1] and may enter the food chain, leading to bioaccumulation and biomagnification [4–6].

Among the many active volcanoes in the Andean region, Tungurahua Volcano (5023 m), located in the Eastern Cordillera of the Ecuadorian Andes (Lat. 01°28′ S; Lon. 78°27′ W), stands out due to its relatively recent activity. Its last eruptive period, from September 1999 to March 2016, significantly affected environmental quality in several areas of the Tungurahua (Mocha, Cevallos, and Pelileo) and Chimborazo (Penipe) provinces—regions characterized by intensive agriculture. Tungurahua Province plays a key role in both local and national food production. In 2018, approximately 153,780 ha were used for agriculture, increasing to 155,486 ha in 2019, before contracting by 1.27% in 2020 [7].

Soil is fundamental to food production and provides essential ecosystem services, including nutrient cycling, water filtration, and the detoxification of harmful compounds [8]. Its natural buffering capacity enables it to filter, decompose, store, and neutralize toxic substances. However, soil fertility and health are highly dependent on management practices, particularly the use of organic and inorganic amendments. Organic amendments such as chicken manure—rich in nitrogen (N), phosphorus (P), and potassium (K)—can improve soil's physical and chemical properties, thereby enhancing fertility and productivity [9,10]. Compost may also play a crucial role in soil remediation by immobilizing heavy metals through natural chemical reactions, aiding the recovery of contaminated soils [11,12]. In addition, compost can increase the availability of macro- and micronutrients compared to conventional mineral fertilizers [13], while recycling agricultural and livestock waste, reducing environmental pollution, and promoting sustainable agriculture within a circular economy framework [14,15].

In contrast, mineral fertilizers can increase total microbial biomass but often cause soil acidification, lowering pH values below 5. Although urea and ammonia may temporarily raise pH and osmotic potential, they can also inhibit microbial communities, ultimately degrading soil health [16].

Ecuador is highly dependent on imported N, P, and K fertilizers. In response to rising global prices in 2008–2009, the government introduced subsidies for agrochemicals and urea to support agricultural production, particularly among resource-limited populations [17,18]. However, these subsidies have contributed to excessive fertilizer use, potentially leading to environmentally harmful agricultural practices [19].

Despite the agricultural importance of the Andean region, few studies have assessed the combined effects of organic and inorganic fertilizers on crops in this context. Previous research in Mocha [20,21] and Puyo [22,23] has primarily focused on soil properties, often without evaluating crop response or considering multiple cropping cycles. To address this gap, this study evaluates the effects of soil management treatments on physicochemical properties, macro- and micronutrient levels, and metal(loid) concentrations of soils affected by ash deposition from the Tungurahua volcano, as well as the accumulation of these elements in vegetables. An experimental design was implemented using three types of soil amendments and an untreated control, applied to both ash-affected soils (Mocha Canton) and unaffected soils (Puyo Canton), where parsley and spring onion were cultivated.

2. Materials and Methods

2.1. Experimental Design and Sampling

The experimental process was conducted in two geographically distinct areas from November 2020 to April 2022. The first study site or area was located in Mocha Canton, Tungurahua Province, west of the Tungurahua volcano (78°41′19″ W, 1°24′35″ S), a region that experienced prolonged ash deposition from the volcano. The plot, situated on land managed by the San Juan Bautista Foundation, was made accessible for research purposes. The second study site was the Pastaza Experimental Station, located east of the Tungurahua volcano in Puyo Canton, Pastaza Province (76°40′35″ W, 1°10′32″ S). This location was selected as the control site due to its position outside the volcanic ash fall zone. The station, owned by the Polytechnic School of Chimborazo, has no history of agricultural activity, ensuring minimal anthropogenic disturbance to the soil (Figure S1).

The study began with the georeferencing and environmental characterization of the experimental units in both cantons. Subsequently, soil preparation was conducted, including preliminary agronomic practices such as weed removal and surface clearing. Initial soil samples (S0) were then collected following a zigzag sampling pattern at a depth of 30–40 cm, with approximately 3 kg of soil per sample, in accordance with established protocols [24]. The S0, or baseline sampling, consisted of three soil samples from Mocha Canton and three from Puyo Canton.

For the experimental design, two crops were selected: spring onion (*Allium fistulosum* L.), chosen for its underground edible part, and parsley (*Petroselinum crispum* (Mill.) Fuss), a leafy vegetable widely consumed in the region. Three soil amendment treatments and a control (untreated soil) were applied, each with three replicates. The first treatment, soil + chicken manure (chicken manure), consisted of raw chicken manure—a commonly used organic amendment in the region—applied directly to the soil without composting, after being collected from poultry farms. The second treatment, soil + inorganic fertilizer (fertilizer), involved the use of inorganic fertilizers that are widely applied in the area and subsidized by the Ecuadorian government. Specifically, it included 10-30-10 (representing 10% N, 30% P_2O_5, and 10% K_2O) along with 46% urea, both supplied by Agroinsumos Fertisa, Guayas, Ecuador. The third treatment, soil + compost (compost), used compost produced from guinea pig manure, horticultural waste, and sawdust to enhance C input, in line with circular economy principles.

The study plots were established in Mocha and Puyo and divided into 24 subplots, each measuring 2 m in length and 3 m in width. To facilitate irrigation and weeding, the layout included three 1 m wide aisles along the land and a central aisle measuring 2 m in width. Within each plot, three ridges were prepared in a horizontal direction, with 50 cm spacing between them. Each ridge contained 12 seedlings, comprising 36 seedlings per subplot or treatment and 864 seedlings of *Allium fistulosum* and *Petroselinum crispum* across the entire experimental area in both cantons. The implementation of the two crops under the four treatments followed an experimental design based on the random allocation of subunits.

Following the incorporation of soil amendments, initial post-treatment soil samples (S1) were collected. Seedlings of *Allium fistulosum* and *Petroselinum crispum* were then transplanted into planting ridges within each subplot. At the end of the first crop cycle, the plants were harvested (roots, stems, and leaves), and soil samples (S2) were collected. In the second cycle, new seedlings were transplanted following the same design, but without additional amendments. At harvest, the vegetables and final soil samples (S3) were collected. While whole plants were harvested in both cycles, only the edible parts (onion bulbs and parsley leaves) were analyzed in this study. A total of 144 soil samples were collected—6 per treatment per site across three sampling points or cycles (S1, S2, and S3). For vegetables, 96 samples were analyzed—6 per treatment per site for each crop. Additionally, six supplemental samples were analyzed: two each of chicken manure, compost, and volcanic ash.

2.2. Preparation and Analysis of Soils, Vegetables, and Starting Materials

Soil samples S0, S1, S2, and S3 were initially dried at room temperature for 15 days, then placed in an oven at 105 °C for 24 h. Afterward, they were sifted through a 2 mm sieve [25] and subsequently analyzed. Volcanic ash samples collected from the slopes of the Tungurahua volcano, along with chicken manure and compost, underwent the same treatments prior to analysis.

In each cultivation cycle, vegetables were harvested, and onion bulbs and parsley leaves were sampled. Samples were first washed with deionized water, followed by ultrapure water. Excess moisture was removed prior to drying in an oven at 50 °C for 48 h, until a constant weight was reached. The dried material was then ground [24] and sieved to a particle size of ≤5 mm. The resulting material was used for subsequent physicochemical analysis.

The physical properties of the soils were determined using a previously established methodology [26]. Real density (measured using a volumetric flask) and apparent density (measured using the test tube method) were assessed. Texture was determined by the Bouyoucos method at a p/v ratio of 1:10. The pH was measured using the potentiometric method in an aqueous extract (1:10). Electrical conductivity (EC) was determined in the filtered extract with an extraction ratio of 1:50 (m/V). The percentage of organic matter (OM) was determined by calcination at 430 °C for 24 h.

Nitrogen and carbon (C) levels were determined using a EUROVECTOR EA3000 Direct Combustion Elemental Analyzer (EuroVector Srl, Redavalle, Italy). Calcium (Ca), copper (Cu), iron (Fe), magnesium (Mg), manganese (Mn), zinc (Zn), K, sodium (Na), and P were analyzed following acid digestion with concentrated sulfuric acid (H_2SO_4; Merck KGaA, Darmstadt, Germany). Phosphorus was subsequently quantified by ultraviolet–visible (UV-VIS) spectrophotometry, while the concentrations of the remaining elements (Ca, Cu, Fe, Mg, Mn, Zn, K, and Na) were determined by flame photometry.

The determination of metal(loid)s in soils, vegetables, amendments, and volcanic ash began with acid digestion using nitric acid (HNO_3, 65%; Merck KGaA, Darmstadt, Germany) at a 1:20 w/v ratio. The mixture was then heated in a microwave oven MARS 6 at 200 °C for 20 min under 800 PSI pressure and 950 W power. Concentrations of As, Cd, Hg, Pb, nickel (Ni), and Cr were subsequently measured in the digested samples using a Varian SpectrAA 220 Atomic Absorption Spectrophotometer (Varian, Palo Alto, CA, USA), following standard protocols described in previous studies [27]. Quality control was ensured by including blank samples, replicates, and spiked samples in each analytical batch, with recoveries close to 100%. The limit of detection (LOD) was calculated as the mean blank concentration plus three times the standard deviation of the blank concentration, multiplied by the dilution factor. The LODs for the micronutrients (Co, Cu, Fe, Mn, Se, Zn, and Ni) were 2, 3, 6, 2, 0.3, 1, 1 mg/kg, respectively, while the LODs for the heavy metals (As, Cd, Cr, Hg, and Pb) were 0.2, 2, 6, 1, and 1 µg/kg, respectively.

2.3. Nutrient Content of the Amendments

As part of the study, the amendments applied to the different plots were also chemically characterized, especially those that might exhibit greater variability due to their specific characteristics (i.e., chicken manure and compost) compared to the commercial inorganic fertilizer. The concentrations of C and N are shown in Table S1, with higher values in chicken manure. The C/N ratio was 41.83 for compost and 14.06 for chicken manure.

The concentrations of K, Ca, Cu, Mn, Na, and Zn were higher in chicken manure samples compared to compost samples, while compost had a higher Fe content, as shown in Table S2. The concentrations of Cu and Zn do not exceed the reference values regarding heavy metals and other contaminants and impurities [28]. The technical data sheet for the inorganic fertilizer, provided by the supplier, was used as a reference for macro- and micronutrient content. For example, the fertilizer contained 10% N, 30% P, and 10% K, with no reported levels of Mg or Zn. In the case of urea, 43% N was reported, with negligible concentrations of the other measured nutrients.

The analysis showed that compost contained higher concentrations of As, Pb, Cr, Co, and Ni compared to chicken manure, whereas Selenium (Se) levels were higher in chicken manure. These values are presented in Tables S2 and S3. Cd and Hg concentrations were below LOD, corresponding to the detection limit of the equipment. Additionally, the concentrations of As, Cd, Hg, Pb, Cr, and Ni were below the limit of referenced values [28].

2.4. Metal(loid) Concentrations of the Ash of the Tungurahua Volcano

Metal(loid) concentrations were determined in volcanic ash collected from the slopes of the Tungurahua volcano, and the results were compared with the reference values for soils [29], as no specific reference values exist for ash. The analysis showed that Se, Hg, and Cr exceeded the reference values for agricultural soil (1 mg/kg, 0.1 mg/kg, and 54 mg/kg, respectively). These results are presented in greater detail in Table S4.

2.5. Statistical Analysis

The analysis of physicochemical parameters, macronutrients, micronutrients, and heavy metals in soil, vegetables, amendment, and volcanic ash samples was first conducted using descriptive statistics. Analysis of variance (ANOVA) was then performed, followed by a post hoc Tukey test for multiple comparisons among treatments. A significance threshold of $\alpha = 0.05$ was used to determine statistically significant associations.

The $LOD/\sqrt{2}$ value was imputed at concentrations <LOD for statistical analysis [30]. Statistical analyses were conducted using IBM SPSS Statistics for Windows, version 22.0, developed by IBM Corporation in Armonk, New York, United States, and R software, version 4.0.3, developed by the R Foundation for Statistical Computing in Vienna, Austria [31].

3. Results and Discussion

3.1. Physicochemical Parameters in Soil Samples

The results of the physicochemical analyses of the soil samples from the Mocha and Puyo cantons are presented in Table 1. Mocha soils exhibited typical characteristics of Andisols of volcanic origin, with values consistent with those reported in previous studies [21,32–34]. In contrast, Puyo soils showed properties typical of Ecuadorian Amazon soils, with minor differences from previous observations [23,35–37].

Significant differences in EC were observed after treatment application in both cantons. The values exceeded the 200 µS/cm threshold established by [29] and were classified as "moderately saline" according to [38], indicating increased salt concentrations following the application of soil amendments. The highest average EC value, 406.09 µS/cm, was recorded in Puyo Canton.

Organic matter content differed significantly between the soils of Mocha and Puyo. Puyo soils had the highest average OM content at 51.50%, classified as "very high", a characteristic typical of Amazonian soils [23,39]. In contrast, Mocha soils had a "very low" average OM content of 0.69%, according to [38]. Among the amendments, the highest average OM content was found in chicken manure applied in Mocha (0.78%) and in fertilizer used in Puyo (51.50%).

Table 1. Physicochemical analysis of soil samples by study area and treatment.

Area	Treatment	pH	EC (uS/cm)	OM (%)	Real Density (g/mL)	Apparent Density (g/mL)	Texture
Mocha	Baseline	7.13 (7.0–7.32) [a]; 3	186.23 (181.57–191.94) [b]; 3	0.95 (0.945–0.96) [a]; 3	1.25 (1.17–1.33) [a]; 3	1.18 (1.18 1.20) [b]; 3	Loamy
Puyo	Baseline	5.17 (5.1–5.20) [b]; 3	97.82 (97.01–98.54) [a]; 3	10.00 (9.00–11.00) [b]; 3	1.48 (1.43–1.56) [a]; 3	0.70 (0.70–0.71) [a]; 3	Sandy
		<0.001	<0.001	<0.01	0.123	<0.001	
Mocha	Control	7.1 (7.1–7.3) [a]; 18	185.23 (175.84–196.63) [a]; 18	0.69 (0.46–0.83) [a]; 18	2.44 (2.38–2.5) [a]; 18	1.28 (1.26–1.31) [a]; 18	Loamy
	Chicken manure	7.2 (7.1–7.3) [a]; 18	309.89 (190.22–323.3) [ab]; 18	0.78 (0.41–0.91) [a]; 18	2.44 (2.34–2.52) [a]; 18	1.27 (1.26–1.28) [a]; 18	Loamy
	Fertilizer	7.2 (7.0–7.3) [a]; 18	281.19 (175.80–266) [ab]; 18	0.69 (0.50–0.88) [a]; 18	2.4 (2.31–2.49) [a]; 18	1.29 (1.27–1.31) [a]; 18	Loamy
	Compost	7.1 (7.0–7.2) [a]; 18	293.75 (204.50–349.55) [ab]; 18	0.71 (0.46–0.98) [a]; 18	2.34 (2.25–2.4) [a]; 18	1.29 (1.27–1.31) [a]; 18	Loamy
Puyo	Control	5.1 (4.9–5.3) [b]; 18	200.10 (100.12–239.92) [a]; 18	50.19 (39.90–60.94) [b]; 18	1.14 (0.61–1.58) [b]; 18	0.71 (0.69–0.75) [b]; 18	Sandy
	Chicken manure	5.3 (5.0–5.8) [bc]; 18	396.25 (261.99–495.58) [b]; 18	49.09 (38.83–58.38) [b]; 18	1.06 (0.61–1.31) [b]; 18	0.71 (0.68–0.73) [b]; 18	Sandy
	Fertilizer	5.1 (4.9–5.9) [bc]; 18	406.09 (237.42–614.29) [b]; 18	51.50 (40.00–61.79) [b]; 18	1.07 (0.61–1.4) [b]; 18	0.75 (0.71–0.78) [b]; 18	Sandy
	Compost	5.2 (5.1–6.0) [c]; 18	391.16 (267.67–499.13) [b]; 18	49.89 (39.20–60.23) [b]; 18	1.03 (0.61–1.42) [b]; 18	0.71 (0.67–0.72) [b]; 18	Sandy
		<0.001	<0.001	<0.001	<0.001	<0.001	

Values are presented as mean (interquartile range, IQR); sample size (*n*). pH refers to hydrogen potential, EC to electrical conductivity, and OM to organic matter. ANOVA was performed, followed by post hoc Tukey test for multiple comparisons. Mean values with same superscript ([a, b, c]) do not differ significantly between substrate groups ($p < 0.05$).

Both real and apparent density values differed between the soils from the two cantons, with Mocha soils showing the highest averages: 2.44 g/mL for real density and 1.29 g/mL for apparent density.

3.2. Macro- and Micronutrient Content of Soils

The analysis of macro- and micronutrients is presented in Figure 1 and Table S5. The contents of C and N showed significant differences between Mocha and Puyo, with a general decrease observed during the experimental phase, particularly in treatments where compost and chicken manure were applied. This reduction suggests effective assimilation by the plants. The decline is likely related to the close interaction between N and C metabolism, where N provides the C skeletons required for plant growth [40]. Additionally, it is well established that N accumulation in plants can induce changes in soil acidity [41]. The C/N ratio remained below 10, indicating adequate N availability for both plants and soil microorganisms [23].

The concentrations of Ca, Cu, Fe, Mg, Na, and P showed significant differences between the same treatments applied in Mocha and Puyo, whereas the K, Mn, and Zn concentrations remained relatively stable.

In Mocha, higher concentrations of Ca, Mg, and Na were observed, while in Puyo, the highest concentrations were found for N, C, Cu, Fe, Zn, and P.

During the experimental phase, an increase in Ca, Cu, Fe, K, Mg, Mn, Na, Zn, and P concentrations was observed in the soils of Puyo, particularly in treatments with compost and chicken manure. This increase is likely due to the high nutrient content of the applied amendments, as shown in Table S2. It may also be influenced by climatic conditions, soil origin and formation, and physicochemical properties such as pH and high OM content, which facilitate the mobility of elements between soil horizons [42].

The increase in the Fe concentrations of fertilizer-treated plots in both Mocha and Puyo is likely related to the application of inorganic fertilizers. Elevated Fe levels can also influence soil acidity [37].

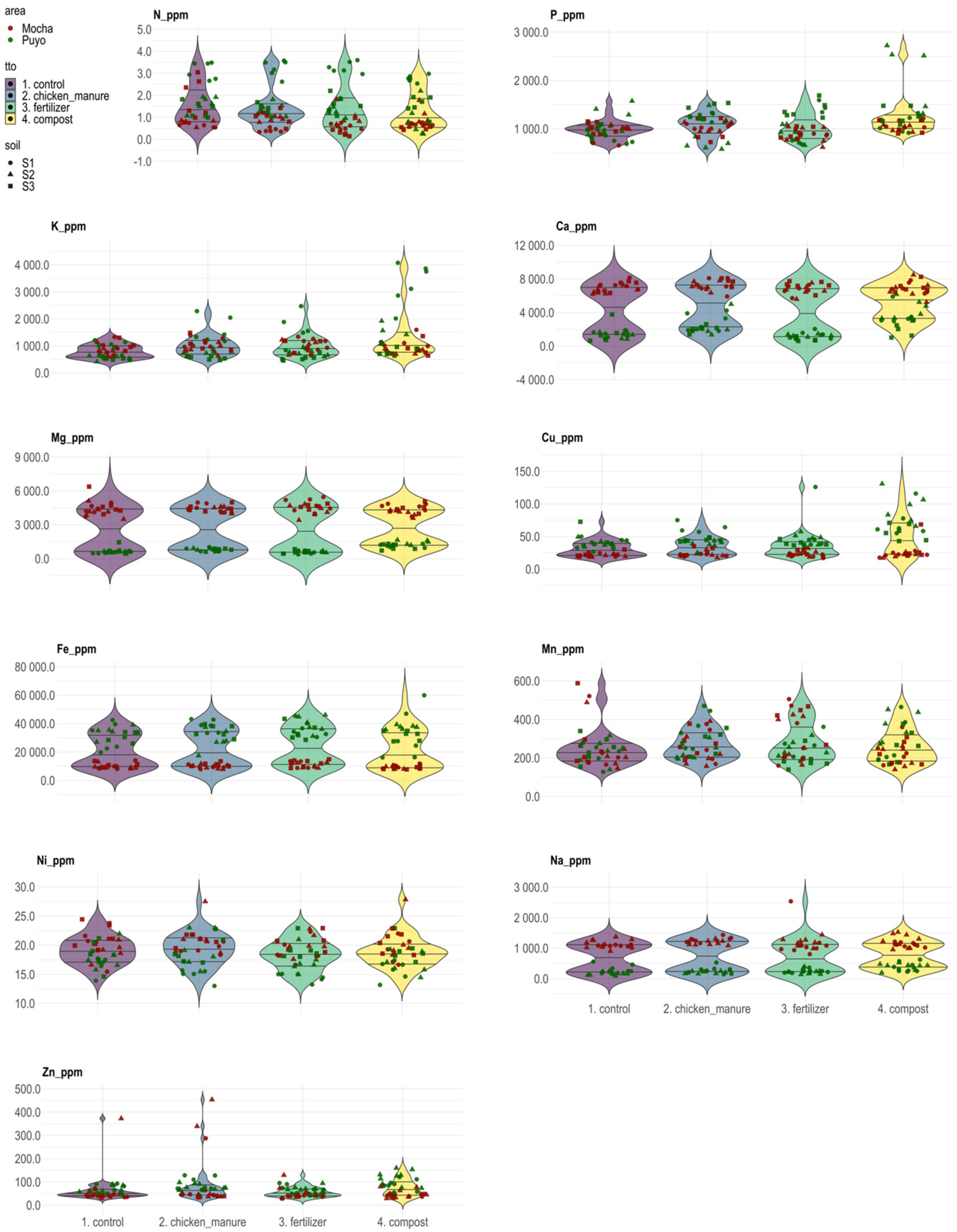

Figure 1. The macro- and micronutrient concentrations of the soils. The unit ppm corresponds to mg/kg. The width of the violins indicates the kernel density estimate of the data; wider sections indicate higher data density and narrower sections indicate lower data density. The horizontal lines within the violins provide a summary of the central tendency and dispersion of the data. Treatment (tto) refers to

untreated soil (1. Control), soil + chicken manure (2. Chicken_manure), soil + inorganic fertilizer (3. Fertilizer), and soil + compost (4. Compost). Each cultivation cycle (S1, S2, and S3) involved collecting 6 soil samples per treatment per site/area, resulting in 144 samples (6 soil samples × 3 cycles × 2 sites × 4 treatments).

Nickel levels in Mocha surpassed the reference value of 19 mg/kg, while in Puyo, they remained below this threshold [43]. Concentrations of Ni were higher in Mocha, possibly due to volcanic ash deposition from the Tungurahua volcano. The compost and chicken manure amendments contributed similar levels of Ni, as indicated in Table S2. Concentrations of Ni increased in Mocha under the compost and chicken manure treatments, and in Puyo under the chicken manure treatment. This increase may be attributed to the Ni content of the added amendments.

3.3. Metal(loid) Concentrations of Soil Samples

The concentrations of heavy metals in the soils of Mocha and Puyo are presented in Figure 2 and Table S6. The reference soils showed significant differences in the concentrations of As, Hg, Pb, Cr, and Se between the two cantons, while Cd did not differ significantly.

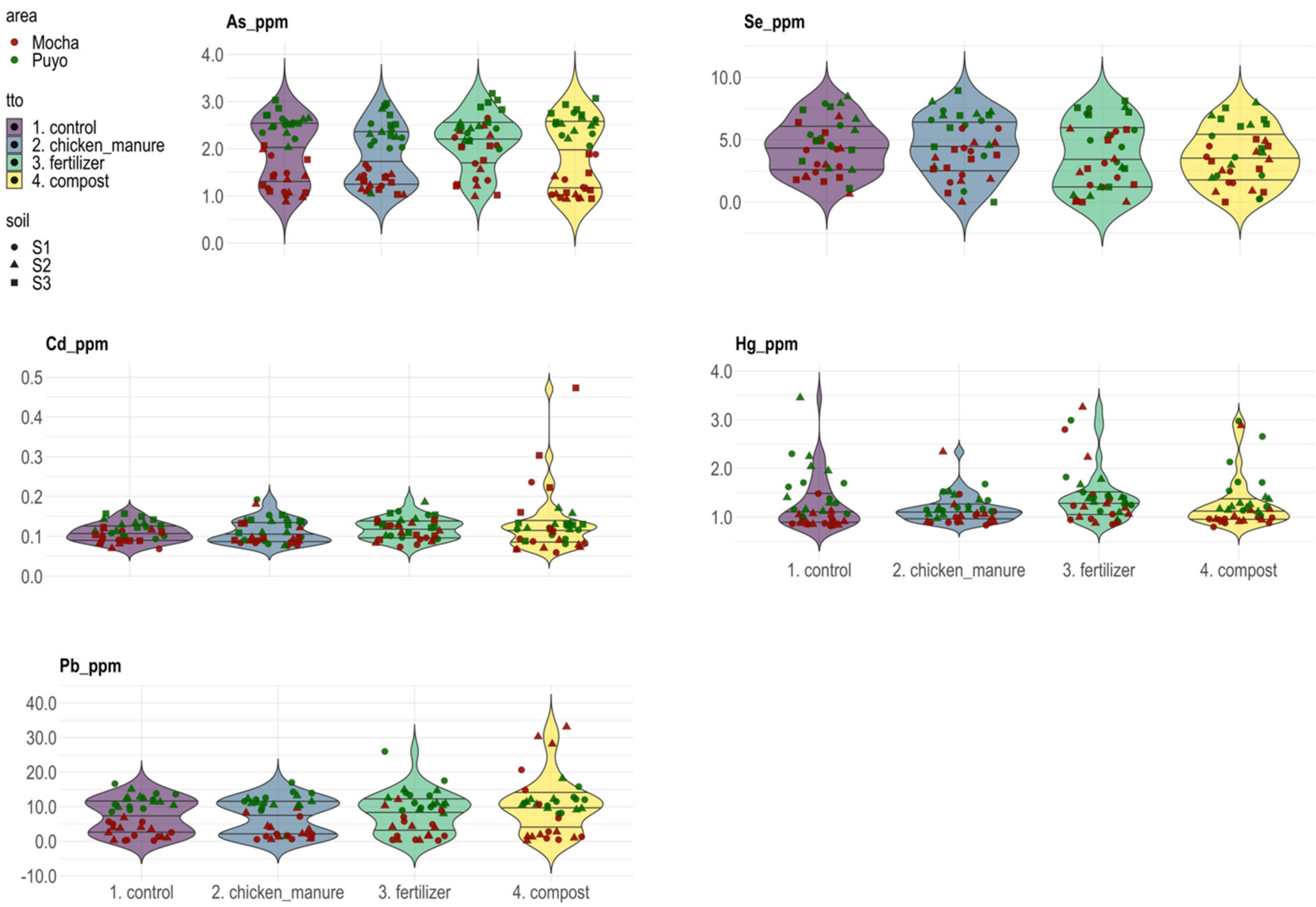

Figure 2. The metal(loid) concentrations of the soils. The unit ppm corresponds to mg/kg. The width of the violins indicates the kernel density estimate of the data; wider sections indicate higher data density and narrower sections indicate lower data density. The horizontal lines within the violins provide a summary of the central tendency and dispersion of the data. Treatment (tto) refers to untreated soil (1. Control), soil + chicken manure (2. Chicken_manure), soil + inorganic fertilizer (3. Fertilizer), and soil + compost (4. Compost). Each cultivation cycle (S1, S2, and S3) involved collecting 6 soil samples per treatment per site/area, resulting in 144 samples (6 soil samples × 3 cycles × 2 sites × 4 treatments).

In both cantons, the concentrations of As, Cd, and Pb were below the current national Ecuadorian reference values of 12 mg/kg, 0.5 mg/kg, and 19 mg/kg, respectively [29]. In contrast, Hg, Cr, and Se exceeded their corresponding limits of 0.1 mg/kg, 54 mg/kg, and 1 mg/kg [29]. According to FAO (2011) guidelines [43], concentrations of As, Pb, Se, and Cd in both cantons were within the acceptable limits of 20 mg/kg, 100 mg/kg, 10 mg/kg, and 3 mg/kg, respectively. However, Cr concentrations exceeded the FAO threshold of 100 mg/kg [43].

Heavy metal concentrations (As, Cd, Hg, Pb, Cr, and Se) were higher in Puyo soils than in Mocha. This difference may be attributed to the physicochemical properties of the soil in Puyo, where acidic pH, lower bulk densities, and high OM content can enhance the mobility of heavy metals across soil horizons [42].

The addition of organic amendments (chicken manure and, primarily, compost) contributed to a reduction in the concentrations of As, Hg, Pb, Cr, and Se in Mocha, with an even more pronounced effect observed in Puyo. An exception was the elevated Pb levels in compost-treated soils in Mocha, likely due to localized contamination at the sampling site. These findings suggest that compost and chicken manure can effectively reduce the bioavailability of heavy metals in agricultural soils.

Concentrations of As varied significantly across treatments between the cantons of Mocha and Puyo. In Mocha soils, concentrations decreased under the chicken manure and compost treatments. In Puyo soils, a decrease was observed with chicken manure, while compost resulted in a slight increase—likely due to the metal content of the amendment and local soil conditions. In both cantons, As concentrations increased under the fertilizer treatment.

The Cd content remained unchanged across all treatments in Puyo soils, whereas in Mocha soils, it showed a slight increase, possibly due to the volcanic ash origin of the soil, as shown in Table S4.

Concentrations of Hg in Mocha soils showed a slight increase during the experimental process, with the highest levels observed under the fertilizer treatment. In contrast, Puyo soils exhibited a decrease, primarily in the chicken manure treatments. These results suggest that OM influences the Hg concentrations of soils.

In Mocha soils, Pb concentrations increased across treated plots, with the highest levels observed in the compost treatment, possibly due to the combined effects of volcanic ash content and the added compost. In Puyo soils, an increase was observed only in the fertilizer treatment, likely due to the presence of Pb in the fertilizer itself.

A decrease in Cr concentrations was observed in Puyo soils under the compost and chicken manure treatments, and in Mocha soils under the compost treatment.

3.4. Metal(loid) Concentrations of Vegetable Samples

The concentrations of heavy metals in parsley leaves and onion bulb samples are presented in Figure 3 and Table S7. In general, concentrations of As, Cd, Hg, and Pb were higher in samples from Puyo than in those from Mocha.

Concentrations of As showed no significant differences between cantons or among treatments for either crop type, except in the compost treatment of onion bulbs in Puyo. Across all treatments, concentrations exceeded the most recent typical value of 0.1 mg/kg for vegetables [44], with the highest levels observed in the compost-treated samples.

Concentrations of Cd varied by area and treatment, relative to the maximum limits of 0.05 mg/kg for crops and 0.2 mg/kg for leafy vegetables [44]. In Mocha, parsley foliage remained below the limit across all treatments, while onion tubers slightly exceeded 0.05 mg/kg under the compost and fertilizer treatments. In Puyo, parsley foliage frequently exceeded the 0.2 mg/kg threshold, especially under the fertilizer and compost treatments, and onion tubers showed Cd concentrations far above the 0.05 mg/kg limit in most treatments. Compost application consistently resulted in the highest Cd levels.

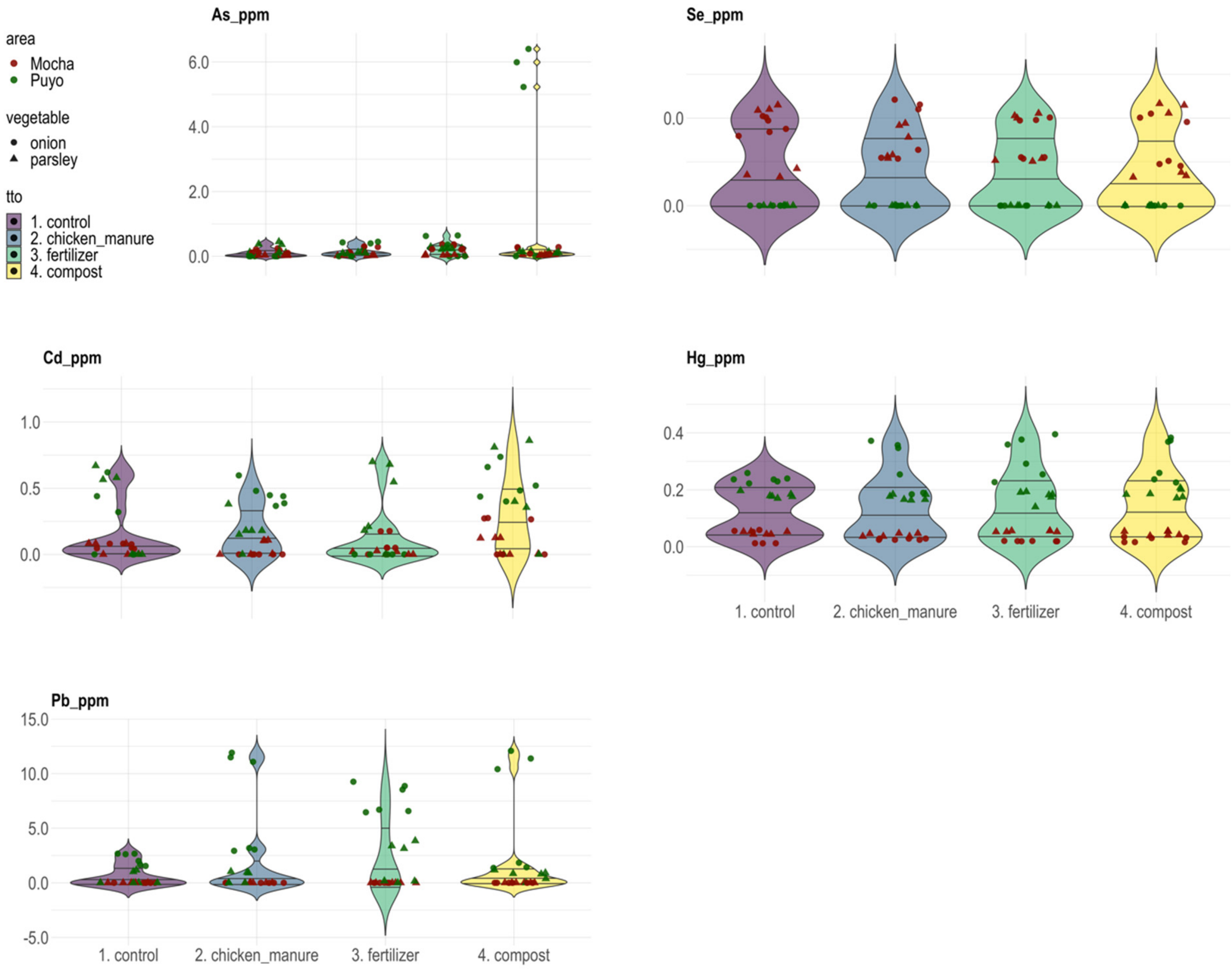

Figure 3. The metal(oid) concentrations of the edible vegetables. The unit ppm corresponds to mg/kg. The width of the violins indicates the kernel density estimate of the data; wider sections indicate higher data density and narrower sections indicate lower data density. The horizontal lines within the violins provide a summary of the central tendency and dispersion of the data. Treatment (tto) refers to untreated soil (1. Control), soil + chicken manure (2. Chicken_manure), soil + inorganic fertilizer (3. Fertilizer), and soil + compost (4. Compost). A total of 6 vegetables samples were collected per treatment per site/area for both onion bulbs and parsley leaves, resulting in 96 samples (6 vegetable samples × 2 sites × 4 treatments × 2 vegetable crops).

Concentrations of Hg showed no significant differences between crop types; however, significant differences were observed between the cantons, with higher levels detected in Puyo crops. In Mocha, values remained below the food-grade reference limit of 0.1 mg/kg for both crop types under all treatments [44]. In contrast, all treatments in Puyo exceeded this threshold for both crops.

Concentrations of Pb in Mocha were at the LOD of the equipment used. The values obtained in this study were lower than those previously reported [34] and remained below the CODEX reference limits for tubers (0.1 mg/kg) and leafy vegetables (0.3 mg/kg) [44].

In general, the metal(loid) concentrations of the cultivated vegetables were significantly lower than those of the soils, indicating minimal bioaccumulation and translocation. This may be attributed to interactions between the soil and the applied amendments. In Mocha, the concentrations of Hg, Cd, and Pb complied with the reference values (0.1 mg/kg, 0.1 mg/kg, and 0.3 mg/kg, respectively) [43], whereas in Puyo, they exceeded these thresholds. Additionally, in both Mocha and Puyo, As concentrations surpassed the FAO limit of 0.1 mg/kg [44].

3.5. Limitations of the Study

The study was conducted in two experimental units: one in Mocha, an area affected by volcanic ashfall from Tungurahua between 1999 and 2016, and another in Puyo, outside the volcano's influence zone. Site selection was based on accessibility. Although the two locations provided contrasting conditions, differences in baseline soil characteristics made direct comparisons challenging. These inherent differences influenced nutrient dynamics and metal(loid) mobility, requiring careful consideration during data interpretation. Additionally, external environmental factors unique to each site—such as relatively warmer temperatures, increased humidity, and greater precipitation in Puyo compared to Mocha during the study period—may have introduced variability beyond the controlled treatments. Despite these challenges, the study design accounted for site-specific conditions, ensuring consistency in methodology and treatment application across both locations. In addition, it is important to note that the carbon/nitrogen profile and macro-/micronutrient content of the inorganic fertilizer were based on the technical data sheet provided by the supplier, available on its website. As a commercial product, the fertilizer's composition is expected to be consistent and compliant with regulatory standards. In contrast, materials such as chicken manure and compost are more prone to compositional variability; therefore, their composition was measured prior to the start of the study.

4. Conclusions

The experimental units in Mocha and Puyo exhibited significant differences in soil physicochemical properties, primarily attributed to their distinct origin and formation processes. Mocha soils demonstrated the typical characteristics of Andisols developed from volcanic ash, while Puyo soils reflected features common to those of the Ecuadorian Amazon. Macronutrient analysis revealed higher concentrations of C, N, Cu, Fe, and P in Puyo soils, whereas Mocha soils had higher levels of Na, Ca, and Mg. Potassium, Mn, and Zn concentrations were relatively similar across both regions. Ni concentrations were within acceptable limits in Puyo but slightly exceeded the reference value in Mocha.

Regarding metal(loid)s, concentrations of As, Cd, and Pb in both Mocha and Puyo remained below the regulatory limits established by Ecuadorian standards, while Cr and Hg exceeded these thresholds in both locations. The application of organic amendments, particularly chicken manure and compost, contributed to a reduction in the bioavailability of metal(loid)s such as As, Hg, Pb, and Cr, thereby enhancing the safety of cultivated crops.

In terms of food safety, crops grown in Mocha generally complied with international reference limits [43], particularly for Hg, Cd, and Pb, while As slightly exceeded the threshold. In contrast, vegetables from Puyo surpassed the FAO reference values for As, Cd, Hg, and Pb, reflecting the elevated metal(loid) content of the soils and the influence of physicochemical parameters such as acidic pH and high OM on metal(loid) mobility and uptake. Overall, Mocha soils demonstrated greater suitability for vegetable production under the evaluated conditions.

These findings provide valuable insights into sustainable soil management in volcanic and non-volcanic regions, emphasizing the role of organic amendments in reducing metal(loid) mobility and enhancing soil quality. However, further research is needed to evaluate the long-term effects of these amendments on soil properties and metal dynamics under varying climatic conditions. Future studies should explore the mechanisms of macroelements, microelements, and metal(loid)s, and their immobilization, along with their uptake and translocation, in a wider range of vegetables. Effective remediation strategies, including alternative amendments and phytoremediation, should be assessed. Additionally, socioeconomic and public health implications—such as farmer adoption and dietary exposure—must be considered.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/agronomy15051166/s1, Table S1: C and N concentrations and C/N ratio in amendments; Table S2 Macro and micronutrient concentrations in amendments; Table S3: Metal(loid) concentrations in amendments. Table S4: Metal(loid) concentrations in Tungurahua ash; Table S5: Macro and micronutrient concentrations in soils; Table S6: Metal(loid) concentrations in soils; Table S7: Metal(loid) concentrations in vegetable samples; Figure S1: Geographic locations of the study areas.

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Abbreviations

The following abbreviations are used in this manuscript:

EC	Electrical conductivity
OM	Organic matter
N	Nitrogen
P	Phosphorus
K	Potassium
C	Carbon
Cu	Copper
Fe	Iron
Mg	Magnesium

Mn	Manganese
Zn	Zinc
Na	Sodium
UV-VIS	Ultraviolet–visible
PSI	Pounds per square inch
W	Watts
LOD	Limit of detection
C/N	Carbon-to-nitrogen ratio
Cr	Chromium
Co	Cobalt
Ni	Nickel
As	Arsenic
Pb	Lead
Cd	Cadmium
Hg	Mercury
ANOVA	Analysis of variance
MAE	Ministerio del Ambiente de Ecuador

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