



Article

Cu Concentration in Vegetable-Cultivated Soil: Comparison Between Open Fields and Protected Environments in Brazil

Odair J. Schmitt¹, Jerônimo L. Andriolo¹, Tadeu L. Tiecher² , Lessandro De Conti³, Cledimar R. Lourenzi⁴ , Renan Costa Beber Vieira⁵ , Douglas R. Kaiser⁵, Carina Marchezan⁶, Aparecida Miranda Corrêa⁶, Isley C. Bicalho Silva⁶, Tatiane Chassot⁵, Mario S. Wolski⁵, Letícia Morsch⁴, Edicarla Trentin⁶, Moreno Toselli⁷ , Elena Baldi⁷ , Paulo Ademar Avelar Ferreira⁶ and Gustavo Brunetto^{6,*}

- ¹ Plant Science Department, Federal University of Santa Maria (UFSM), Santa Maria 97105-900, RS, Brazil; odair.schmitt@uffs.edu.br (O.J.S.); jeronimoandriolo@gmail.com (J.L.A.)
 - ² Federal Institute Rio Grande do Sul, Campus Restinga, Porto Alegre 91791-508, RS, Brazil; tadeu.t@hotmail.com
 - ³ Federal Institute Farroupilha, Campus Santo Augusto, Santo Augusto 98590-000, RS, Brazil; lessandrodeconti@gmail.com
 - ⁴ Rural Engineering Department, Center of Agricultural Science, Federal University of Santa Catarina (UFSC), Florianópolis 88034-001, SC, Brazil; lourenzicr@gmail.com (C.R.L.); lehorsch@gmail.com (L.M.)
 - ⁵ Department of Agronomy, Federal University of Fronteira Sul–Campus Cerro Largo (UFFS), Cerro Largo 97900-000, RS, Brazil; renan.vieira@uffs.edu.br (R.C.B.V.); douglasrodrigokaiser@gmail.com (D.R.K.); tatianechassot@yahoo.com.br (T.C.); mario.wolski@uffs.edu.br (M.S.W.)
 - ⁶ Soil Science Department, Federal University of Santa Maria (UFSM), Santa Maria 97105-900, RS, Brazil; marchezancarina@yahoo.com.br (C.M.); aparecida.correa@acad.ufsm.br (A.M.C.); isleybicalho@yahoo.com.br (I.C.B.S.); edicarlatrentin@gmail.com (E.T.); ferreira.aap@gmail.com (P.A.A.F.)
 - ⁷ Department of Agricultural and Food Sciences, University of Bologna, Viale Fanin, 46 40127 Bologna, Italy; moreno.toselli@unibo.it (M.T.); elena.baldi7@unibo.it (E.B.)
- * Correspondence: brunetto.gustavo@gmail.com; Tel.: +55-55-99984-0302



Citation: Schmitt, O.J.; Andriolo, J.L.; Tiecher, T.L.; De Conti, L.; Lourenzi, C.R.; Vieira, R.C.B.; Kaiser, D.R.; Marchezan, C.; Corrêa, A.M.; Silva, I.C.B.; et al. Cu Concentration in Vegetable-Cultivated Soil: Comparison Between Open Fields and Protected Environments in Brazil. *Horticulturae* **2024**, *10*, 1183. <https://doi.org/10.3390/horticulturae10111183>

Academic Editors: Simona Fabroni, Francesco Montemurro and Luana Bontempo

Received: 25 September 2024
Revised: 29 October 2024
Accepted: 4 November 2024
Published: 8 November 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Abstract: High copper (Cu) concentration in soils used for vegetable production is an agricultural, social and environmental issue. The excess of Cu in soil can cause toxicity in plants, reducing growth and yields. Moreover, Cu can also be absorbed and accumulated in edible organs, increasing risks for human health. This study aimed to compare Cu fractions in soils: (1) non-cultivated, natural soil (NC), (2) soils cultivated with open field crops (FCs) and (3) soils cultivated in controlled environments (CEs). The survey was carried out on 25 sites in Rio Grande do Sul (Southern Brazil), with each site containing the three types of soils described above. From these sites, the four with the highest soil Cu concentrations were selected to compare soluble (Cu-CaCl₂), available (Cu-EDTA) and total (Cu-EPA) Cu. Both total and available soil Cu concentration in soil solution, in CE and FC areas were higher than in NC. At sites 23R1 (Oxisol) and 11R1 (Molisol) the soluble and available Cu content was higher in the FC environment than in CEs, and the same was observed for the total Cu content at sites 23R1 (Oxisol) and 9R1 (Molisol). Some FC soils showed total Cu concentrations higher than the limits established by Brazilian environmental legislation, being, as a consequence, potentially contaminated. Soil monitoring and cropping practices must be adopted to reduce the Cu content in soils of vegetable crops in this region.

Keywords: heavy metals; environmental contamination; Cu-soil solution; available Cu; total Cu

1. Introduction

Vegetable production stands out by the intensive use of chemical and organic agricultural inputs, mainly of fertilizers [1,2]. Indiscriminate agricultural fertilizer use is mainly associated with: (i) inexistence and/or lack of research indicating mineral nutrient requirements during the growth and development of more than 50 species of vegetables cultivated in Brazil [3]; (ii) short development cycles of vegetables, generally between

30 and 150 days, associated with concerns on high yield obtainment; and (iii) the use of several intensive cropping systems, such as cultivation in an open field, in a protected environment and soilless. This generates several variables and specificities to be considered in the formulation, recommendation and management of the crop fertilization.

In agricultural soils, copper (Cu) concentration is usually naturally low, but may increase due to intensive application via chemical and/or organic fertilization, since high fertilizer rates are used in vegetable cultivation [4,5]. Also, Cu product use in phytosanitary treatments, especially fungicides, can contribute to increased soil Cu [6]. In Brazil, there are 28 products formulated with Cu, which are recommended for at least one vegetable species [7]. This way, frequent use of these products, associated with successive crops in the same area and high rates of fertilization, can cause Cu accumulation in the soil [8–10], especially since Cu is a micronutrient and, therefore, absorbed by plants in small quantities [11].

Moreover, Cu can be absorbed and accumulated in edible plant organs at levels that are considered toxic [12], representing a risk to consumer health due to its cumulative potential in the human organism [13], as well as reducing crop productivity and causing economic losses to producers. Although this study does not evaluate Cu levels in vegetables, the literature indicates that increased soil Cu can lead to absorption by plants, causing accumulation that may negatively affect plant growth and pose health risks when consumed. It is important to note that the available Cu fraction is the result of several physicochemical reactions between the element and soil constituents, mainly clay, iron (Fe) and aluminum (Al) oxides, organic matter content, pH and the cation exchange capacity (CEC) in soil [14,15]. Therefore, Cu availability can vary according to soil classes and the management practices adopted in production systems.

In this context, it is essential to monitor soil Cu availability to ensure safe and sustainable vegetable production. Studies on heavy metal presence in soils cultivated with vegetables remain limited. This study aims to address this gap by diagnosing Cu concentration and availability in soils used for open-field and protected-environment vegetable cultivation. Out of the initial 25 sampling sites, four were selected for detailed analysis due to their higher Cu concentrations, representing higher-risk scenarios. Protected environments refer to covered cultivation areas, such as greenhouses or plastic tunnels, where climatic conditions are partially controlled.

2. Materials and Methods

2.1. Soil Sampling Sites

Sites where soil samples were collected were defined with the aim of covering the five regions classified and presented in Ordinance No. 85, issued by the State Foundation for Environmental Protection and published on 5 September 2014. This ordinance establishes soil Quality Reference Values (QRVs) for nine chemical elements, among them Cu, naturally present in the different geomorphological/geological provinces of Rio Grande do Sul state, Southern Brazil.

Preliminary selection of sampling sites was carried out by using satellite images (Google Earth Pro, version 7.3.3.) and the choice was made according to the following criteria: (i) existence of two cropping systems, i.e., field and greenhouse cultivation; (ii) successive cultivation of vegetables for at least 5 years; and (iii) the presence of a non-anthropized area (uncultivated field or native forest) close to cultivated areas (used as a control). Sampled sites identification was performed through the collection and annotation of geographical coordinates, from a portable GPS navigator, as shown in Table 1 and Figure 1.

Table 1. Identification, municipalities, soil class and geographic coordinates of the 25 experimental sites.

Identification	Municipalities	Soil Class (1)	Geographic Coordinates
1R3	Santa Maria	Alfisol	29°41'27.67" S; 53°42'34.38" O
2R3	Santa Maria	Alfisol	29°38'51.81" S; 53°40'36.51" O
3R1	Cruz Alta	Oxisol	28°36'29.69" S; 53°37'43.50" O
4R4	Cruz Alta	Oxisol	28°34'49.23" S; 53°32'28.35" O
5R2	Caçapava do Sul	Entisol	30°33'18.41" S; 53°28'40.26" O
6R4	Caçapava do Sul	Alfisol	30°35'42.87" S; 53°22'39.61" O
7R5	Turuçu	Alfisol	31°26'27.23" S; 52°13'40.39" O
8R3	São Vicente do Sul	Alfisol	29°41'1.18" S; 54°41'12.78" O
9R1	Feliz	Molisol	29°31'3.96" S; 51°19'30.71" O
10R4	Cacequi	Alfisol	29°51'55.86" S; 54°49'47.29" O
11R1	Bom Princípio	Molisol	29°30'39.29" S; 51°21'21.17" O
12R1	Cruzeiro do Sul	Oxisol	29°32'59.30" S; 52° 3'36.62" O
13R1	Venâncio Aires	Alfisol	29°34'14.05" S; 52°12'2.29" O
14R3	Santa Cruz do Sul	Alfisol	29°40'42.11" S; 52°19'16.01" O
15R2	São Sepé	Alfisol	30°11'4.21" S; 53°36'47.98" O
16R3	São Gabriel	Alfisol	30°21'7.08" S; 54°16'57.43" O
17R1	Erechim	Oxisol	27°39'56.73" S; 52°18'41.99" O
18R1	Caxias do Sul	Inceptisol	29°13'18.26" S; 51° 1'13.13" O
19R2	Canguçu	Entisol	31°25'44.40" S; 52°40'3.07" O
20R5	Camaquã	Alfisol	30°49'6.77" S; 51°46'44.64" O
21R1	Passo Fundo	Oxisol	28°14'30.07" S; 52°33'20.33" O
22R4	Tabaí	Alfisol	29°41'31.80" S; 51°42'18.08" O
23R1	Santa Rosa	Oxisol	27°46'56.37" S; 54°27'29.19" O
24R1	Itaqui	Alfisol	29° 7'47.54" S; 56°33'48.01" O
25R1	Júlio de Castilhos	Alfisol	29° 9'54.77" S; 53°39'37.96" O

In identification, the "R" followed by the numbers (1, 2, 3, 4, 5) represents the geomorphological region in which the state is inserted. See Figure 1. (1) The soils were classified according to the Soil Survey Staff (2014).

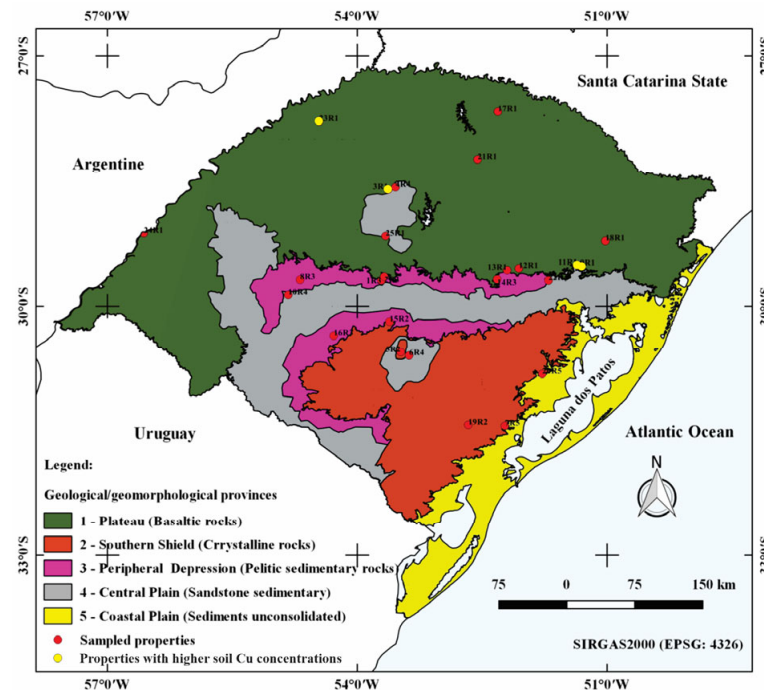


Figure 1. Georeferenced location of sampled properties across the five geomorphological/geological provinces according to FEPAM Ordinance No. 85/2014. Sites sampled for this study are marked in red, while those selected for discussion due to higher soil Cu concentrations are shown in yellow. More information about the sampling sites can be found in Table S1. Created by the author. Source: Geological Map [16], adapted from FEPAM [17].

2.2. Soil Sampling Procedure

Twenty-five sites were chosen and, within the same site, soil samples were collected in three different environments: non-cultivated, natural soil (NC), cultivated with open field crops (FCs) and cultivated in controlled environments (CEs), at the depth of 0.0–0.20 m according to the methodology proposed by CONAMA [18] and recommendations from CQFS RS/SC [19]. In all the areas, 15 subsamples were collected with a cutting blade and mixed together to create a composite sample, used for analysis. In areas under FCs and CEs, soil samples were collected between planting lines, while in native or forest areas, soil sampling was performed according to a zigzag design. Samples were placed in plastic bags, properly labeled and sealed. Subsequently, they were air dried, ground, sieved with 2 mm mesh and stored.

2.3. Chemical Analysis of Soil

Soil samples collected in the CE environment were extracted by Mehlich-1 [20] to evaluate Cu concentration. Based on these results, the four sites with the highest Cu concentrations were selected (sites 23R1, 3R1, 11R1 and 9R1) since they were those with the highest potential for environmental contamination or toxicity to plants. The sites have 31, 24, 28 and 23 years of cultivation with vegetables, respectively. The samples deriving from FCs, CPs and NCs of the four soils were analyzed for clay, organic matter, pH in water, CEC (pH 7.0), Cu-CaCl₂, Cu-EDTA and Cu-EPA.

Soluble Cu was extracted by CaCl₂ (0.01 mol L⁻¹), according to Novozamsky et al. [21]; briefly, 1.0 g of dry soil was mixed with 10 mL of CaCl₂ (0.01 mol L⁻¹) and stirred for 2 hours. Samples were then centrifuged for 15 min at 3200 rpm, filtered (Whatman No 1 filter paper, Germany, medium weight with a particle retention capacity of approximately 11 µm) and stored since analysis.

Available Cu (Cu-EDTA) was extracted with EDTA (Na₂-EDTA 0.01 mol L⁻¹/1.0 mol L⁻¹ ammonium acetate, pH adjusted to 7.0 [22]. Total Cu concentration (Cu-EPA) was determined according to USEPA [23], by oxidation and acid attack using concentrated HNO₃, H₂O₂ and HCl under heating. In all extraction methods, Cu concentration was determined by an atomic absorption spectrophotometer (EEA; Perkin Elmer, Analyst 200, Shelton, CT, USA).

2.4. Statistical Analysis

Copper concentration determined by different extraction (CaCl₂, EDTA and EPA) was compared by orthogonal contrasts at 1% error probability, using the SISVAR software version 5.2 [24].

3. Results

3.1. Physical-Chemical Characteristics in Soils

The four sites selected for a more detailed analysis (23R1, 3R1, 11R1 and 9R1) were classified and inserted in geomorphological region 1 (Figure 1), whose source material is Plateau volcanic rocks [17]. Soils from 23R1 and 3R1 sites were classified as Oxisol (Table 1), while soils from the 11R1 and 9R1 sites were classified as Molisol (Tables 1 and 2). These sites were chosen due to their significantly higher Cu concentrations compared to the other sites. Sites 23R1 and 3R1 showed average clay contents, which were higher than the values observed in 11R1 and 9R1. The clay contents in CEs were lower than the values observed in FCs in all sites (Table 2). The organic matter contents ranged from 12 g kg⁻¹ to 31 g kg⁻¹ among the sites. In the four sites, the organic matter contents in the CE environment were higher than those observed in FCs (Table 2).

Table 2. Soil clay, organic matter (O.M.), pH, cation exchange capacity ($CEC_{pH7.0}$) and Cu evaluated in samples referring to the following environments: non-cultivated, natural soil (NC); cultivated with open field crops (FCs) and cultivated in controlled environments (CEs) from the four selected properties for further determination of Cu contents by $CaCl_2$, EDTA and EPA.

Environment	Clay ($g\ kg^{-1}$)	O.M.	pH (1:1)	$CEC_{pH7.0}$	Cu ($mg\ dm^{-3}$)
23R1					
NC	690	31	5.7	13.1	7.40
FC	790	22	5.5	11.5	10.38
CE	470	31	5.3	17.0	60.00
3R1					
NC	360	18	5.3	7.9	1.08
FC	600	24	4.8	10.1	11.32
CE	470	30	5.3	22.6	13.90
11R1					
NC	170	12	4.6	6.9	1.54
FC	140	17	6.3	6.0	7.47
CE	90	29	5.9	8.4	10.00
9R1					
NC	320	23	5.3	16.2	3.00
FC	200	17	7.2	14.6	2.67
CE	140	28	7.4	12.9	12.5

The pH values in water were similar in soils from sites 23R1 and 3R1 (Table 2). But the pH values in water in the soils of the 11R1 and 9R1 sites in the FC and CE environments were higher than the values verified in the NC environment (Table 2). The highest CEC (pH 7.0) values were observed in the CE environment at sites 23R1, 3R1 and 11R1. In the soil of the 9R1 site, the highest CEC (pH 7.0) values were observed in the NC environment (Table 2). The lowest Cu extracted by Mehlich-1 (Cu Mehlich-1) at sites 23R1, 3R1 and 11R1 was observed in the sequence $NC < FC < CE$ (Table 2). At the 9R1 site, the lowest Cu-Mehlich-1 content was observed in the $FC < NC < CE$ sequence (Table 2).

3.2. Cu Availability in Soils

The Cu fractions extracted by $CaCl_2$, EDTA and EPA in the soil of the NC environment were different from those observed in FCs and CEs in the four sites (Table 3). In the 3R1, 11R1 and 9R1 sites, the Cu- $CaCl_2$, Cu-EDTA and Cu-EPA contents in the FC and CE environments were higher than the values verified in the NC sites. At the 23R1 site, Cu contents in the FC environment did not differ from the NCs when the element was extracted by $CaCl_2$ and EPA (Table 3).

At sites 23R1 and 11R1, Cu- $CaCl_2$ contents in the CE environment were approximately 68% and 14% higher than those observed in the FCs (Table 3), while the Cu-EDTA contents at the 23R1 and 11R1 sites were approximately 79% and 14% higher in the CE environment compared to the FCs (Table 3). The Cu-EPA contents in the 23R1 and 9R1 sites were approximately 55% and 11% higher in the CE environment in relation to the FCs, but the Cu-EPA contents did not differ in the CE and FC environments for the other sites (Table 3).

Table 3. Orthogonal contrasts of Cu-CaCl₂, Cu-EDTA and Cu-EPA present in non-cultivated, natural soil (NC); cultivated with open field crops (FCs) and cultivated in controlled environments (CEs) from the four states (23R1, 3R1, 11R1 and 9R1).

Environment	23R1	3R1	11R1	9R1
Cu-CaCl ₂ (mg kg ⁻¹)				
NC	0.14	0.34	0.60	0.76
FC	0.18	0.55	0.73	0.93
CE	0.57	0.64	0.85	0.99
Orthogonal Contrast F Test				
NC × FC e CE	**	**	**	**
NC × FC	ns	**	**	**
NC × CE	**	**	**	**
FC × CE	**	ns	**	ns
Cu-EDTA (mg kg ⁻¹)				
NC	18.65	1.79	2.06	7.81
FC	21.70	18.23	10.67	10.88
CE	105.41	18.72	12.42	11.66
Orthogonal Contrast F Test				
NC × FC e CE	**	**	**	**
NC × FC	**	**	**	**
NC × CE	**	**	**	**
FC × CE	**	ns	**	ns
Cu-EPA (mg kg ⁻¹)				
NC	110.12	18.97	10.90	22.57
FC	116.17	116.80	21.33	28.10
CE	260.23	117.60	22.70	31.60
Orthogonal Contrast F Test				
NC × FC e CE	**	**	**	**
NC × FC	ns	**	**	**
NC × CE	**	**	**	**
FC × CE	**	ns	ns	**

** Significant at 0.001 significance level. ns: not significant.

4. Discussion

Based on Cu concentrations extracted by Mehlich-1 it is possible to observe (Table 2) that in environments that were not previously cultivated (NC), in the four sites, the Cu concentration is higher than 0.5 mg/dm³ and therefore classified in the class of “high” availability according to reference levels from CQFS RS/SC [19]. This is probably associated with the material source in these soils, which are basaltic rocks, and have high Cu concentrations in their composition [25,26]. Consequently, Cu additions would not be necessary for cultivating the majority of vegetables, as the native soil Cu is sufficient to meet crop needs.

In the two cultivated soils (FCs and CEs) with vegetable crops, Cu concentrations were higher than in native soils. The increase may be associated with the use of chemical and organic fertilizers, and fungicides that contain Cu in the composition, whose most common active principles are Cu oxychloride and Cu sulfate, which are highly effective and low cost [12]. The Cu accumulation in soil can occur since application of these fungicides in vegetable cultivation areas was listed as routine by farmers, being carried out weekly in the four sites studied.

Vegetable cultivation in the CE environment accumulated the highest Cu in the soil, compared to cultivation in FCs. This can be explained by the higher binding of Cu to functional groups present in soil organic matter [27,28]. In fact, a trend towards higher

organic matter values in the four sites of the CE environment was observed (Table 2). The electronic configuration of Cu, $[Ar]3d^{10}4s^1$, confers high adsorption affinity to carboxylic and phenolic groups of organic matter [29]. Over time, some of the soil organic matter can be decomposed, which contributes to higher Cu availability [30]. In addition, protected cultivation has less water flow in the soil profile, reducing the likelihood of soluble Cu movement and surface runoff [27]. These factors contribute to the maintenance of higher concentrations of Cu in the soil. On the other hand, the higher organic matter content in CE may be contributing to the higher values of $CEC_{(pH7.0)}$ in sites 23R1, 3R1 and 11R1. In higher CEC environments, a higher Cu adsorption and lower metal availability is expected, as this is an important factor in soil Cu dynamics, since it acts directly on ion concentrations present in soil solution and in sites [14,30].

In the FC and CE environments, the 23R1 and 3R1 sites were classified as Oxisol, and have the highest Cu-EPA and the lowest Cu-CaCl₂ soil concentration. On the other hand, sites 11R1 and 9R1, classified as Molisol, had the lowest Cu-EPA and the highest Cu-CaCl₂ concentration. According to Brunetto et al. [31], Cu concentration in soil solution (for example, extracted with CaCl₂) is generally low, approximately 2% of total Cu content. In our study, the Cu extracted by both the CaCl₂ and the EPA method showed percentages varying from 0.1 to 1.7%, in Oxisol (23R1 e 3R1) and from 3.1 to 5.5% in Molisols (11R1 e 9R1). The Cu present in the soil solution is the result of adsorption/desorption, complexing and precipitation reactions, which affect metal distribution between soil solid and liquid fractions, being responsible for its mobility and bioavailability [32]. Higher concentrations of Cu in the solution can increase toxicity in plants [12], but also the potential for water contamination [33].

The Cu-EDTA contents were lower in soils at sites 11R1 and 9R1 in both cultivated environments. In these areas, the highest pH values were also observed. This can be attributed to recent applications of soil acidity correctives, such as limestone [34]. The free ion Cu²⁺ predominates in acidic soils and with the increase in pH, the deprotonation of the functional groups of minerals and organic matter occurs, which increases the CEC of the soil and consequently the adsorption of Cu, thus decreasing its availability [9,35]. In addition, an increase of soil anions such as carbonates (CO₃²⁻) and hydroxyls (OH⁻) promotes Cu precipitation, thus reducing its mobility [14,30].

Total Cu content (Cu-EPA) in soil is the reference for assessing the potential of environmental contamination by heavy metals in several countries such as Brazil [18], United States of America [36], Australia and New Zealand [37] and also in the European continent [38]. In Brazilian environmental legislation, total Cu concentrations values were stipulated, as reference, in areas exploited by agriculture, for prevention (PV) and investigation value (IV), being 60 and 200 mg kg⁻¹, respectively [18]. However, state legislations have different values and parameters. For Rio Grande do Sul state QRVs, they were determined according to the soils from the five geomorphological regions, ranging from 9 to 203 mg Cu kg⁻¹ in agricultural soils, with VI = QRV = PV corresponding to 203 mg Cu kg⁻¹ in agricultural soils from region 1 [17] in which the four sites evaluated in the present study are inserted. Considering these references, although they show differences, it is possible to observe that the soils sampled in NCs, FCs and CEs of 23R1 and FCs and CEs of 3R1 exceeded the respective QRVs according to the legislation of CONAMA and CETESB. Only the total Cu content from soil sampled in CP of 23R1 (Table 3), 260 mg Cu kg⁻¹, exceeds CONAMA and FEPAM investigation values, which indicates the need for practices reducing Cu content in soils of these areas [18].

The high Cu concentrations observed in soils of some areas of this study can hinder plant growth and production of these crops. The adoption of conservation practices, such as minimum cultivation and direct planting of vegetables, could minimize Cu transfer via erosion and leaching. However, this could lead to an increased Cu concentration in the surface layer (0–20 cm) that is the most exploited by most vegetables root system [3]. On the other hand, reduced tillage contributes to limiting OM mineralization, thus increasing Cu complexing [31,39], leading to decreased Cu availability.

5. Conclusions

The Cu concentration in soils cultivated with vegetables increased in comparison to native soil as a result of agricultural management. This has led to alterations in Cu concentration in the soil solution, in the available fraction and total Cu in both open field (FC) and under protected cultivation (CE) areas. This increase in Cu contents in more labile forms favors the metal bioavailability in soil, which can cause damage to plants and soil microorganisms, as well as increase of environmental contamination risks. In addition, soil from CE environment of site 23R1 presented a total Cu content with high contamination potential, which surpassed the quality referential value and constant intervention value in environmental legislation of Rio Grande do Sul state, Southern Brazil, deserving attention and monitoring, as well as the adoption of measures to reduce or stabilize the content of this metal in soil. This emphasizes the importance of conducting future studies involving the collection and determination of Cu contents in vegetables cultivated in soils with high Cu levels. Such research will help elucidate the occurrence of phytotoxicity and prevent risks associated with consumer health regarding vegetables grown in these soils.

Additionally, it is important to discuss the limitations of this study, including potential biases in sampling and analysis methods. Future research should aim to incorporate a larger sample size and diverse geographical locations to enhance the robustness of the findings. Addressing these limitations could provide a more comprehensive understanding of Cu dynamics in agricultural systems and inform better management practices.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/horticulturae10111183/s1>, title; Table S1: Chemical, physical and mineralogical properties evaluated in samples from the protected cultivation environment (CE) from the 25 sampled sites and extractor/methodology used; Table S2: Identification, municipalities, chemical, physical and mineralogical properties evaluated at 25 sample sites of the protected cultivation environment (CE).

Author Contributions: Conceptualization, O.J.S., J.L.A. and G.B.; methodology, C.M., A.M.C. and L.M.; investigation, O.J.S., R.C.B.V., D.R.K., T.C., M.S.W., G.B., T.L.T., L.D.C. and C.R.L.; writing—review and editing, C.M., I.C.B.S., L.M., E.T., A.M.C., M.T., E.B. and G.B.; visualization, C.M.; supervision, G.B. and J.L.A.; project administration, P.A.A.F. and G.B. All authors have read and agreed to the published version of the manuscript.

Funding: We are grateful to Conselho Nacional de Desenvolvimento Científico e Tecnológico—CNPq (Brazilian National Council for Scientific and Technological Development) for the research productivity scholarship, granted to the second author.

Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

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

References

1. Franco, T.F.; Lima, E.S.A.; Amaral Sobrinho, N.M.B.; Carmo, M.G.F.; Breda, F.A.D.F. Enrichment and bioavailability of toxic elements in intensive vegetable production areas. *Rev. Caatinga* **2020**, *33*, 124–134. [[CrossRef](#)]
2. Silva, L.S.; Galindo, I.C.L.; Nascimento, C.W.A.; Gomes, R.P.; Campos, M.C.C.; Freitas, L.; Oliveira, I.A. Heavy metal contents in Latosols cultivated with vegetable crops. *Pesqui. Agropecu. Trop.* **2016**, *46*, 391–400. [[CrossRef](#)]
3. Filgueira, F.A.R. *Novo Manual de Olericultura: Agrotecnologia Moderna na Produção e Comercialização de Hortaliças*; UFV: Viçosa, Brazil, 2012.
4. Silva, L.S.; de Luna Galindo, I.C.; Gomes, R.P.; Filla, V.A.; Campos, M.C.C.; de Freitas, L.; de Oliveira, I.A.; Marques, K.P.P.; de Souza, E.D.; Cazzeta, J.O. Investigation of heavy metal accumulation in soil, water and plants in areas with intensive horticulture. *Aust. J. Crop Sci.* **2019**, *13*, 192–198. [[CrossRef](#)]
5. Zhen, H.; Jia, L.; Huang, C.; Qiao, Y.; Li, J.; Li, H.; Wan, Y. Long-term effects of intensive application of manure on heavy metal pollution risk in protected-field vegetable production. *Environ. Pollut.* **2020**, *263*, 114552. [[CrossRef](#)]
6. Fernández-Calviño, D.; Soler-Rovira, P.; Polo, A.; Arias-Estévez, M.; Plaza, C. Influence of humified organic matter on copper behavior in acid polluted soils. *Environ. Pollut.* **2010**, *158*, 3634–3641. [[CrossRef](#)]

7. Brasil. Sistema de Agrotóxicos Fitossanitários (AGROFIT). 2018. Available online: http://agrofit.agricultura.gov.br/agrofit_cons/principal_agrofit_cons (accessed on 12 July 2024).
8. Wang, J.; Guo, W.; Chen, X.; Shi, Y. Effect of cultivation ages on Cu accumulation in Greenhouse Soils in North China. *IOP Conf. Ser. Earth Environ. Sci.* **2017**, *94*, 012071. [CrossRef]
9. Yang, L.; Huang, B.; Hu, W.; Chen, Y.; Mao, M.; Yao, L. The impact of greenhouse vegetable farming duration and soil types on phytoavailability of heavy metals and their health risk in eastern China. *Chemosphere* **2014**, *103*, 121–130. [CrossRef]
10. Zhang, H.Z.; Li, H.; Wang, Z.; Zhou, L.D. Accumulation Characteristics of Copper and Cadmium in Greenhouse Vegetable Soils in Tongzhou District of Beijing. *Procedia Env. Sci.* **2011**, *10*, 289–294. [CrossRef]
11. Kabata-Pendias, A. *Trace Elements in Soils and Plants*; CRC Press: Boca Raton, FL, USA, 2011.
12. Tiecher, T.L.; Soriani, H.H.; Tiecher, T.; Ceretta, C.A.; Nicoloso, F.T.; Tarouco, C.P.; Clasen, B.E.; De Conti, L.; Tassinari, A.; Melo, G.W.B.; et al. The interaction of high copper and zinc doses in acid soil changes the physiological state and development of the root system in young grapevines (*Vitis vinifera*). *Ecotoxicol. Environ. Saf.* **2018**, *148*, 985–994. [CrossRef]
13. Mendoza, J.C.; Garrido, T.R.; Quilodrán, C.R.; Segovia, M.C.; Parada, J.A. Evaluation of the bioaccessible gastric and intestinal fractions of heavy metals in contaminated soils by means of a simple bioaccessibility extraction test. *Chemosphere* **2017**, *176*, 81–88. [CrossRef]
14. Brunetto, G.; de Melo, G.W.B.; Terzano, R.; Del Buono, D.; Astolfi, S.; Tomasi, N.; Pii, Y.; Mimmo, T.; Cesco, S. Copper accumulation in vineyard soils: Rhizosphere processes and agronomic practices to limit its toxicity. *Chemosphere* **2016**, *162*, 293–307. [CrossRef] [PubMed]
15. Kumar, V.; Pandita, S.; Sidhu, G.P.S.; Sharma, A.; Khanna, K.; Kaur, P.; Bali, A.S.; Setia, R. Copper bioavailability, uptake, toxicity and tolerance in plants: A comprehensive review. *Chemosphere* **2021**, *262*, 127810. [CrossRef] [PubMed]
16. CPRM—Comissão de Pesquisa em Recursos Minerais. Mapa Geológico do Estado do Rio Grande do Sul. Projeto Geologia do Brasil ao Milionésimo. 2006. Available online: http://www.cprm.gov.br/publique/media/geologia_basica/cartografia_regional/mapa_rio_grande_sul.pdf (accessed on 7 May 2024).
17. FEPAM—Fundação Estadual de Proteção Ambiental. Portaria FEPAM nº 85/2014. 2014. Available online: <https://www.fepam.rs.gov.br/upload/arquivos/202301/27114351-portaria085-2014.pdf> (accessed on 21 March 2024).
18. CONAMA—Conselho Nacional do Meio Ambiente. Resolução CONAMA no 420 de 28/12/2009. 2009. Available online: https://www.normasbrasil.com.br/norma/resolucao-420-2009_110436.html (accessed on 21 March 2024).
19. CQFS RS/SC—Comissão de Química e Fertilidade do Solo. *Manual de Aducação e de Calagem Para os Estados do Rio Grande do Sul e de Santa Catarina*; SBCS/Núcleo Regional Sul: Porto Alegre, Brazil, 2016.
20. Tedesco, M.J.; Gianello, C.; Biassani, C.A.; Bohnen, H.; Volkweiss, S.J. Análise de solo, plantas e outros materiais. In *Boletim Técnico*; Universidade Federal do Rio Grande do Sul: Porto Alegre, Brazil, 1995; p. 174.
21. Novozamsky, I.; Lexmond, T.M.; Houba, V.J.G. A Single Extraction Procedure of Soil for Evaluation of Uptake of Some Heavy Metals by Plants. *Int. J. Environ. Anal. Chem.* **1993**, *51*, 47–58. [CrossRef]
22. Chaignon, V.; Hinsinger, P. A Biotest for Evaluating Copper Bioavailability to Plants in a Contaminated Soil. *J. Environ. Qual.* **2003**, *32*, 824–833. [CrossRef]
23. USEPA. (n.d.). EPA Method 3050B: Acid Digestion of Sediments, Sludges, and Soils. Available online: <https://www.epa.gov/homeland-security-research/epa-method-3050b-acid-digestion-sediments-sludges-and-soils> (accessed on 28 March 2024).
24. Ferreira, D.F. SISVAR: Um programa para análises e ensino de estatística. *Rev. Symp.* **2008**, *6*, 36–41.
25. Althaus, D.; Gianello, C.; Tedesco, M.J.; Justin, K. Natural Fertility and Metals Contents in Soils of Rio Grande do Sul (Brazil). *Rev. Bras. Ciênc. Solo* **2018**, *42*, e0160418. [CrossRef]
26. Zinn, Y.L.; de Faria, J.A.; Araujo, M.A.; Skorupa, A.L.A. O material de origem do solo é o principal controle sobre as concentrações de metais pesados nas terras altas tropicais do Brasil. *Catena* **2020**, *185*, 104319. [CrossRef]
27. De Conti, L.; Ceretta, C.A.; Ferreira, P.A.; Lourenzi, C.R.; Giroto, E.; Lorensini, F.; Tiecher, T.L.; Marchezan, C.; Anchieta MGBrunetto, G. Soil solution concentrations and chemical species of copper and zinc in a soil with a history of pig slurry application and plant cultivation. *Agric. Ecosyst. Environ.* **2016**, *216*, 374–386. [CrossRef]
28. Tiecher, T.L.; Ceretta, C.A.; Comin, J.J.; Giroto, E.; Miotto, A.; Moraes, M.P.; Benedet, L.; Ferreira, P.A.A.; Lorenzi, C.R.; Couto, R.R.; et al. Forms and accumulation of copper and zinc in a sandy typic hapludalf soil after long-term application of pig slurry and deep litter. *Rev. Bras. Ciênc. Solo* **2013**, *37*, 812–824. [CrossRef]
29. Dresler, S.; Hanaka, A.; Bednarek, W.; Maksymiec, W. Accumulation of low molecular-weight organic acids in roots and leaf segments of *Zea mays* plants treated with cadmium and copper. *Acta Physiol. Plant* **2014**, *36*, 1565–1575. [CrossRef]
30. Trentin, E.; Facco, D.B.; Hammerschmitt, R.K.; Avelar Ferreira, P.A.; Morsch, L.; Belles, S.W.; Ricachenevsky, F.K.; Nicoloso, F.T.; Ceretta, C.A.; Tiecher, T.L.; et al. Potential of vermicompost and limestone in reducing copper toxicity in young grapevines grown in Cu-contaminated vineyard soil. *Chemosphere* **2019**, *226*, 421–430. [CrossRef] [PubMed]
31. Brunetto, G.; Comin, J.J.; Miotto, A.; de Moraes, M.P.; Sete, P.B.; Schmitt, D.E.; Gatiboni, L.C.; de Melo, G.W.B.; Morais, G.P. Copper and zinc accumulation, fractionation and migration in vineyard soils from Santa Catarina State, Brazil. *Bragantia* **2017**, *77*, 141–151. [CrossRef]
32. McBride, M.; Sauve, S.; Hendershot, W. Solubility control of Cu, Zn, Cd and Pb in contaminated soils. *Eur. J. Soil Sci.* **1997**, *48*, 337–346. [CrossRef]

33. Ouyang, W.; Wang, Y.; Lin, C.; He, M.; Hao, F.; Liu, H.; Zhu, W. Heavy metal loss from agricultural watershed to aquatic system: A scientometrics review. *Sci. Total Environ.* **2018**, *637*, 208–220. [[CrossRef](#)] [[PubMed](#)]
34. Tiecher, T.; Denardin, L.G.D.O.; Martins, A.P.; Pias, O.H.; Nunes, L.R.; Tiecher, T.L.; Alvarez, J.W.R.; Mallmann, F.J.K.; Brunetto, G.; Rheinheimer Dos Santos, D. Dynamics of sulfate and basic cations in soil solution as affected by gypsum fertilization in an Ultisol of Southern Brazil. *Arch. Agron. Soil Sci.* **2019**, *65*, 1272–1286. [[CrossRef](#)]
35. CETESB—Companhia de Tecnologia de Saneamento Ambiental. Decisão de Diretoria nº 256/2016. *Rev. Meio Ambiente* **2016**, *126*, 55–56.
36. USEPA—United States Environmental Protection Agency. *40 CFR-Standards for the Use and Disposal of Sewage Sludge*; USEPA: Washington, DC, USA, 1993; pp. 9387–9415.
37. ANZECC. Australian and New Zealand Guidelines for the Assessment and Management of Contaminated Sites [Electronic Resource]/Australian and New Zealand Environment and Conservation Council, National Health and Medical Research Council. Version Details—Trove. 1992. Available online: <https://trove.nla.gov.au/work/18093032?q&versionId=21236483> (accessed on 15 February 2024).
38. Council Directive 86/278/EEC. Protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. *Off. J. Eur. Union* **1986**, *181*, 6–12.
39. Giroto, E.; Ceretta, C.A.; Brunetto, G.; Santos, D.R.; Silva, L.S.; Lourenzi, C.R.; Lorensini, F.; Vieira, R.C.B.; Schmatz, R. Acúmulo e formas de cobre e zinco no solo após aplicações sucessivas de dejetos líquidos de suínos. *Rev. Bras. Ciênc. Solo* **2010**, *34*, 955–965. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.