*Mitkova, T., Markoski, M., Kiprijanovski, M., Naskovska, M., Minchev, I., Todorovska, M. (2026). Spatial distribution of copper in the soils under orchards in the Kumanovo region. Agriculture and Forestry, 72 (1): 163-181. https://doi:10.17707/AgricultForest.72.1.10*

DOI: 10.17707/AgricultForest.72.1.10

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# SPATIAL DISTRIBUTION OF COPPER IN THE SOILS UNDER ORCHARDS IN THE KUMANOVO REGION

## SUMMARY

A total of 22 soil samples from 11 locations under fruit orchards in the Kumanovo region were analyzed to determine total copper content. Samples were collected at depth of 0 - 30 cm and 30 - 60 cm, corresponding the main root zone of fruit trees. The orchards are in their productive phase and regularly treated with copper-containing pesticides, as well as mineral and organic fertilizers. The study aimed to assess whether copper accumulation originates from anthropogenic activities or lithological composition. To interpret copper distribution, soil texture and chemical properties (pH, carbonate content, humus, electrical conductivity, total nitrogen, available $P_2O_5$ and $K_2O$) were analyzed. Results show heterogeneous soil texture, with physical sand fractions dominating the topsoil and physical clay fractions prevailing at deeper layers. Copper concentrations were consistently higher in the topsoil (average 45.33 mg/kg, median 41.6 mg/kg) compared to the subsoil (average 36.31 mg/kg, median 37.7 mg/kg), indicating anthropogenic accumulation. Statistical analyses (correlation, factor analysis, PCA, and cluster analysis) revealed strong associations between copper and clay fractions, phosphorus, humus, and nitrogen, while negative correlations were observed with sand fractions and soil pH. PCA Biplots confirmed that copper distribution is primarily controlled by anthropogenic inputs, with soil texture and chemical properties modulating its bioavailability. Although copper levels remain below the contamination threshold of 100 mg/kg, they exceed WHO’s recommended limit (20-36 mg/kg) in several orchards. These findings highlight the need for careful management of copper-containing agrochemicals to ensure sustainable fruit production and protect soil health.

**Keywords:** copper (Cu), soil texture, chemical properties, orchards, copper distribution maps, PCA, cluster analysis.

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Notes: The authors declare that they have no conflicts of interest. Authorship Form signed online.

*Recieved:13/01/2026* *Accepted:19/02/2026*

## INTRODUCTION

Copper (Cu) is an essential micronutrient for plants, animals, and humans, playing a crucial role in numerous physiological and biochemical processes, including enzymatic reactions, photosynthesis, and oxidative stress regulation. However, its accumulation in agricultural soils has become an increasing environmental concern, particularly in areas subjected to long-term intensive farming practices. In orchard systems, elevated copper concentrations are most commonly associated with prolonged and repeated application of copper-based fungicides and mineral fertilizers, which represent the dominant anthropogenic sources of Cu in cultivated soils (Komárek *et al.*, 2021; Markoski *et al.*, 2025; Kos *et al* 2026).

Modern fruit production relies on intensive management practices, including the use of high-yield cultivars, mechanized soil operations, irrigation, and frequent application of plant protection products. Due to its broad-spectrum antimicrobial activity, copper is widely applied in fruit orchards in various formulations, such as Bordeaux mixture, copper hydroxide, and copper oxychloride, to control fungal and bacterial diseases (La Torre *et al*., 2018; Lamichhane *et al.*, 2018). Although copper-containing agrochemicals are considered effective and relatively persistent, their repeated use often results in gradual Cu accumulation in the topsoil, particularly in perennial cropping systems such as orchards and vineyards (Komárek *et al.*, 2021; Ballabio *et al.*, 2018).

The behavior, mobility, and bioavailability of copper in soils are strongly controlled by a range of physicochemical properties. Soil pH is one of the most influential factors, as copper solubility generally decreases with increasing pH due to enhanced adsorption and precipitation processes (Kabata-Pendias, 2011; Chuancheng *et al.*, 2020). Organic matter plays a dual role by forming stable organo-metal complexes that reduce Cu mobility while simultaneously increasing its retention in surface horizons (Jeon *et al.*, 2024; Hou *et al.*, 2020). Soil texture, particularly the content of fine fractions such as clay, significantly affects copper accumulation due to the high specific surface area and abundance of reactive adsorption sites. In addition, cation exchange capacity (CEC) is closely linked to Cu retention, as soils with higher CEC exhibit a greater capacity to bind copper ions. The presence of carbonates further influences copper behavior by promoting immobilization through co-precipitation and surface complexation mechanisms, especially in calcareous soils (Wang *et al.*, 2009).

Excessive copper accumulation in soils may lead to phytotoxic effects, altered microbial activity, and increased transfer of Cu along the soil-plant-human continuum. While copper deficiency in fruit trees can impair pollen development, reduce fertilization efficiency, and lower yields, excessive copper concentrations may inhibit root growth, disrupt nutrient uptake, and result in elevated Cu levels in edible plant parts (Yruela, 2021; Adrees *et al.*, 2015). Furthermore, long-term copper inputs may negatively affect soil microbial diversity and enzymatic activity, thereby reducing soil biological fertility (Fagnani, *et al.*, 2020).

In recent decades, multivariate statistical techniques have become indispensable tools in pedological and ecotoxicological studies aimed at disentangling the complex interactions between soil properties and trace elements. Among them, Principal Component Analysis (PCA) is widely used to identify dominant factors controlling metal distribution, distinguish between natural (lithogenic) and anthropogenic sources, and reduce data dimensionality while preserving the main variance structure (Reimann *et al*., 2018; Filzmoser *et al.,* 2018). When combined with correlation analysis, factor analysis, and cluster analysis, PCA provides a robust framework for interpreting spatial variability of trace metals in soils and for supporting environmentally sound land management decisions. Despite numerous studies addressing copper accumulation in orchard soils and intensively cultivated regions, quantitative assessments of the relative influence of agricultural practices and intrinsic soil properties on copper distribution in orchard soils of Southeast Europe remain limited. This lack of region-specific evidence constrains the development of targeted soil management strategies and risk assessment frameworks under conditions of increasing agricultural intensification and climate variability. The Kumanovo region, located in the northern part of North Macedonia, represents one of the important agricultural areas characterized by intensive crop production and diversified soil types developed on heterogeneous geological substrates. The region has a long tradition of fruit cultivation, where plant protection practices, including the application of copper-based fungicides, are commonly used to control fungal and bacterial diseases. In addition, the area is characterized by pronounced spatial variability of soil properties, including texture, organic matter content, and carbonate presence, which may significantly influence the mobility and accumulation of trace elements. These characteristics make the Kumanovo region a suitable case study for investigating the spatial distribution and controlling factors of copper in orchard soils under conditions typical for Southeast European agricultural landscapes.

The hypothesis of this study is that the spatial distribution of copper in orchard soils is primarily controlled by soil physicochemical properties-particularly organic matter content, texture, and cation exchange capacity-while anthropogenic inputs from plant protection practices act as an additional, but spatially heterogeneous, enrichment factor. To test this hypothesis, the present study investigates the spatial distribution of copper in orchard soils of the Kumanovo region by integrating soil physicochemical analyses with multivariate statistical methods. The results are expected to improve the understanding of copper dynamics in orchard ecosystems and to support evidence-based soil management practices consistent with the objectives of sustainable agriculture and the EU Soil Strategy for 2030 (European Commission, 2021).

## MATERIAL AND METHODS

### Study area

The Kumanovo region is located in the northeastern part of the Republic of North Macedonia and covers an area of 1293.81 km², representing approximately 4.71% of the national territory. The investigated fruit orchards are distributed across the central and northern parts of the region, as presented in Table 1, while the spatial position of the study area is shown in Figure 1.

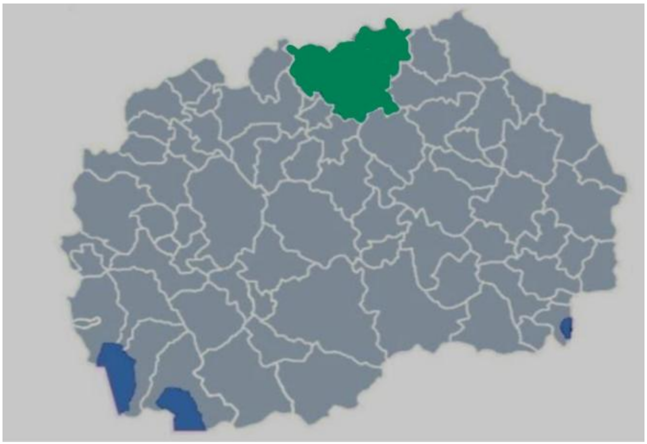


**Figure 1.** Spatial distribution of the Kumanovo region-North Macedonia

From a pedogenetic perspective, the region is characterized by a heterogeneous landscape composed of undulating hills, plains, and slope terrains formed on diverse geological substrates, including metamorphic, magmatic, and sedimentary rocks. Quaternary deposits of lacustrine, deluvial, and alluvial origin are widespread and contribute to considerable variability in soil texture and chemical properties.

The climate of the region is classified as sub-Mediterranean–continental, with a moderately characteristics and local influence of Mediterranean air masses along the Pčinja River valley, while more continental conditions prevail in elevated areas (Markoski *et al.*, 2023).

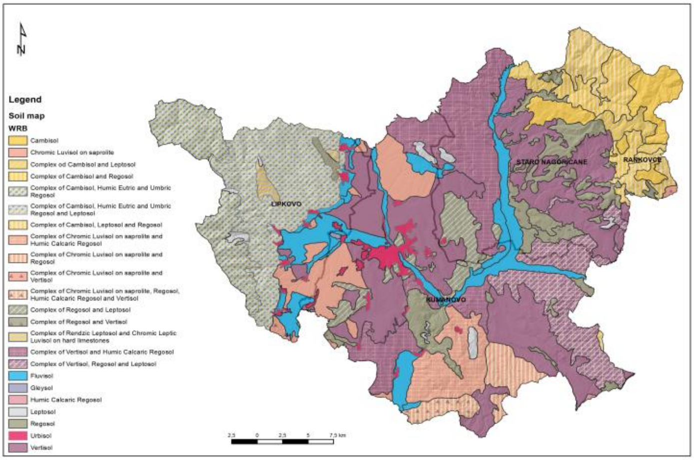


**Figure 2.** Pedological map of the Kumanovo region

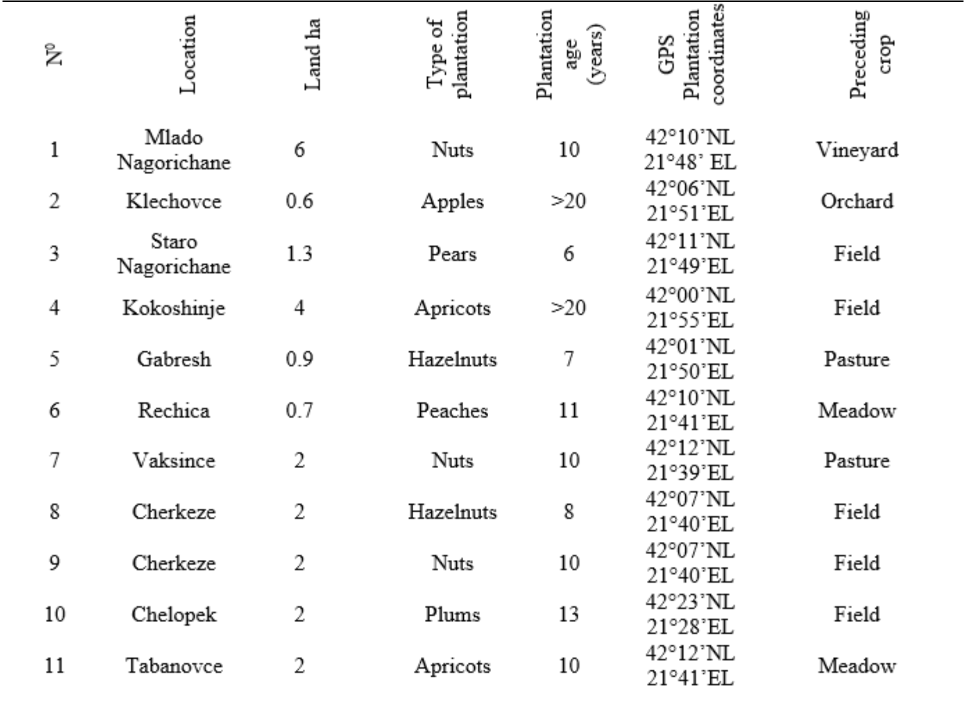
Within the framework of the regional pedological assessment, the spatial distribution and taxonomic classification of soils in the Kumanovo region are presented in the pedological map (Fig. 2).The dominant soil types in the region include Leptosols, Regosols, Cambisols, Vertisols, Fluvisols, and Luvisols, developed on limestone, clays, and heterogeneous Quaternary deposits. Soils under the investigated orchards are predominantly classified as Aric Regosols, characterized by a developed anthropogenic plough (P) horizon formed as a result of long-term cultivation and trenching practices.

### Field, laboratory and data processing workflow

The study was conducted through three main phases: field sampling, laboratory analyses, and data processing.

During the field phase, a total of 22 soil samples were collected from 11 fruit orchard locations in the Kumanovo region (Fig. 1; Table 1). At each location, soil samples were taken from two depths: 0-30 cm and 30-60 cm, corresponding to the main root zone of fruit trees. The orchards are in their productive phase and are regularly treated with pesticides and copper-based fertilizers as part of standard fruit protection and fertilization practices.

**Table 1.** Geographical location of fruit orchards



| N⁰ | Location | Land ha | Type of plantation | Plantation age (years) | GPS Plantation coordinates | Preceding crop |
|---|---|---|---|---|---|---|
| 1 | Mlado Nagorichane | 6 | Nuts | 10 | 42°10'NL<br>21°48' EL | Vineyard |
| 2 | Klechovce | 0.6 | Apples | >20 | 42°06'NL<br>21°51'EL | Orchard |
| 3 | Staro Nagorichane | 1.3 | Pears | 6 | 42°11'NL<br>21°49'EL | Field |
| 4 | Kokoshinje | 4 | Apricots | >20 | 42°00'NL<br>21°55'EL | Field |
| 5 | Gabresh | 0.9 | Hazelnuts | 7 | 42°01'NL<br>21°50'EL | Pasture |
| 6 | Rechica | 0.7 | Peaches | 11 | 42°10'NL<br>21°41'EL | Meadow |
| 7 | Vaksince | 2 | Nuts | 10 | 42°12'NL<br>21°39'EL | Pasture |
| 8 | Cherkeze | 2 | Hazelnuts | 8 | 42°07'NL<br>21°40'EL | Field |
| 9 | Cherkeze | 2 | Nuts | 10 | 42°07'NL<br>21°40'EL | Field |
| 10 | Chelopek | 2 | Plums | 13 | 42°23'NL<br>21°28'EL | Field |
| 11 | Tabanovce | 2 | Apricots | 10 | 42°12'NL<br>21°41'EL | Meadow |

Field sampling was carried out in accordance with the national soil survey methodology (Mitrikeski and Mitkova, 2013) and the requirements of ISO/IEC 17025:2006. Each sample must be representative, which means each sample should be a mixture of five samples collected in an area of 10 × 10 m. It is important to collect the sample at each defined coordinate wed the procedures described in MKS ISO 11464:2015.

The soil samples were packed in polyethylene bags marked with a code and sample number. Samples pretreatment was done in accordance with ISO 11464:2006. First, they were air-dried, and after that crushed and sieved through a 2-mm sieve.

### Laboratory analyses

Laboratory analyses included the determination of selected physical and chemical properties relevant to copper behavior and mobility. Soil texture was determined using standard sedimentation methods. Soil reaction (pH) was measured according to ISO 10390:2022, calcium carbonate ($CaCO_3$) equivalent volumetrically (ISO 10693), humus content by standard wet oxidation procedures, total nitrogen according to ISO 11261:199 and available phosphorus ($P_2O_5$) and potassium ($K_2O$) (ammonium lactate method).

All analyses were performed using accredited and standardized procedures in the Laboratory of Soils and Fertilizers (L-04), Faculty of Agricultural Sciences and Food, which operates under ISO/IEC 17025 accreditation.

### Determination of total copper content

Total copper (Cu) content in soil samples was determined following aqua regia digestion. Soil samples were air-dried at room temperature for approximately two weeks, crushed, and sieved through a 2 mm mesh. A representative subsample was further ground to a particle size below 0.125 mm to ensure homogeneity.

Copper extraction was carried out using aqua regia in accordance with ISO 11466:1995. The concentration of copper in the digested solutions was determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Agilent 715, USA) in the accredited laboratory of RZ ”Technical Control” - AD Skopje. Calibration standards were prepared by serial dilution from a certified stock solution with a concentration of 1000 mg/L.

### Statistical data analysis

Statistical analysis of the data was performed to evaluate the distribution, variability, and controlling factors of copper in the studied soils. Descriptive statistical parameters, including minimum, maximum, mean, median, and standard deviation, were calculated for all analyzed soil properties.

Correlation analysis was applied to assess relationships between copper concentrations and selected physical and chemical soil parameters. Multivariate statistical techniques, including factor analysis and Principal Component Analysis (PCA), were used to identify dominant factors controlling copper distribution and to distinguish between anthropogenic and lithogenic influences. Cluster analysis was applied to group soil samples based on similarities in copper content and soil properties.

All statistical analyses were performed using IBM SPSS Statistics for Windows, version 26.0 (IBM Corp., Armonk, NY, USA). Spatial distribution maps of copper concentrations were generated using inverse distance weighting (IDW) interpolation in ArcGIS version 10.8. Separate maps were produced for the 0-30 cm and 30-60 cm soil layers.

## RESULTS AND DISCUSSION

According to the obtained data, the soils have a heterogeneous mechanical composition. The mechanical composition has an influence on the availability of heavy metals. At the same total content, the availability and mobility of heavy metals is higher in soils with a lighter mechanical composition (sandy), compared to heavier soils (clay). This means that the danger of translocation (moving) of heavy metals to groundwater and their pollution, with all the negative consequences for the ecosystem, is greater in soils with a lighter mechanical composition.

From the analyzed soil samples (Table 2 and 3), it can be seen that at the first depth (0-30 cm), the soil is predominantly composed of the physical sand fraction (coarse sand + fine sand), with an average value of 50.68%, compared to the physical clay fraction (clay + silt), which averages 49.32%. The median for the total sand fraction is 54.00%. In the physical clay fraction, the clay fraction with the highest average value is 32.42%, and ranges from 13.80 to 59.40% in relation to the silt fraction, which averages 16.90%. The median for the clay fraction is 32.90% higher than the median for the silt fraction 16.90%.

At the second depth (30-60 cm), the physical clay fraction becomes dominant, with an average of 55.20%, while the sand fraction accounts for 44.80%. The median for the total sand fraction is 46.60%. In the physical clay fraction, the clay fraction with the highest average value is 31.58%, and ranges from 14.10 to 53.40% in relation to the silt fraction, which averages 23.58%. The median for the clay fraction is 29.10% higher than the median for the silt fraction 21.70%.

Based on the USDA soil texture classification triangle (Mitkova and Markoski, 2022), the analyzed soils are classified into the following textural classes: sandy clay loam (SCL), clay (C), clay loam (CL), sandy loam (SL), loam (L), and sandy clay (SC).

The results obtained from investigations of the Cu content and some chemical properties of the soil samples are presented in Table 2 and 3.

Copper (Cu) is an important micronutrient, essential for fruit crops, required in small quantities, crucial for proper growth and development. Depending on its concentration, copper can act as a necessary micronutrient, but it can also become toxic to fruit crops and lead to reduced yields. On the one hand, its deficiency in organisms leads to various disorders (Xu *et al* 2024; Sharma and Sehkon, 2009), while on the other hand, in higher concentrations it causes harmful effects.

**Table 2.** Descriptive analysis of soil parameters in samples (N=11) at a depth of 0-30 cm

| Parameter | Measurement values | Min | Max | H | SD | Median |
|---|---|---|---|---|---|---|
| Coarse sand | [%] | 5.42 | 28.12 | 16.03 | 7.18 | 14.40 |
| Fine sand | [%] | 16.95 | 51.48 | 34.65 | 10.20 | 31.64 |
| Physical sand | [%] | 23.70 | 71.30 | 50.68 | 12.91 | 54.00 |
| Silt | [%] | 2.30 | 27.90 | 16.90 | 6.50 | 16.90 |
| Clay | [%] | 13.80 | 59.40 | 32.42 | 11.83 | 32.90 |
| Physical clay | [%] | 28.70 | 76.30 | 49.32 | 12.91 | 46.00 |
| Cu | [mg/kg] | 31.1 | 69.9 | 45.33 | 12.09 | 41.6 |
| Humus | [%] | 1.90 | 2.75 | 2.29 | 0.28 | 2.18 |
| Total N | [%] | 0.114 | 0.165 | 0.137 | 0.031 | 0.166 |
| pH in $H_2O$ | / | 7.31 | 8.61 | 8.05 | 0.50 | 8.21 |
| EC | [$dS/m^{-1}$] | 6.28 | 19.35 | 10.54 | 3.24 | 10.41 |
| $CaCO_3$ | [%] | 0.00 | 19.99 | 11.51 | 7.93 | 15.02 |
| $P_2O_5$ | [mg/100 g] | 13.87 | 91.29 | 36.78 | 21.11 | 37.63 |
| $K_2O$ | [mg/100 g] | 30.44 | 77.90 | 50.34 | 13.51 | 52.06 |

**Table 3.** Descriptive analysis of soil parameters in samples (N=11) at a depth of 30-60 cm

| Parameter | Measurement values | Min | Max | H | SD | Median |
|---|---|---|---|---|---|---|
| Coarse sand | [%] | 4.34 | 26.80 | 13.10 | 7.62 | 13.37 |
| Fine sand | [%] | 7.24 | 47.05 | 31.70 | 10.81 | 33.23 |
| Physical sand | [%] | 13.50 | 65.80 | 44.80 | 15.50 | 46.60 |
| Silt | [%] | 9.90 | 39.90 | 23.58 | 8.84 | 21.70 |
| Clay | [%] | 14.10 | 53.40 | 31.58 | 12.09 | 29.10 |
| Physical clay | [%] | 34.20 | 86.50 | 55.20 | 15.50 | 53.40 |
| Cu | [mg/kg] | 26.3 | 49.3 | 36.31 | 6.44 | 37.7 |
| Humus | [%] | 1.10 | 2.01 | 1.42 | 0.29 | 1.37 |
| Total N | [%] | 0.060 | 0.121 | 0.085 | 0.017 | 0.082 |
| pH in $H_2O$ | / | 7.22 | 8.57 | 8.07 | 0.49 | 8.32 |
| EC | [$dS/m^{-1}$] | 7.14 | 24.05 | 11.19 | 4.949 | 9.31 |
| $CaCO_3$ | [%] | 0.00 | 20.41 | 10.86 | 7.58 | 14.16 |
| $P_2O_5$ | [mg/100 g] | 7.95 | 55.37 | 31.41 | 16.31 | 32.30 |
| $K_2O$ | [mg/100 g] | 23.43 | 77.30 | 42.76 | 13.92 | 41.85 |

Copper content in soils is influenced by complex interactions between the mineralogical composition of the parent material, soil texture, chemical properties, and potential anthropogenic inputs such as the use of mineral and organic fertilizers and copper-containing pesticides.

(Chen *et al.,* 2024), in their book on copper in soils, state in Chapter 5 that copper (Cu) is the 25th most abundant component of the Earth's crust and represents an essential microelement for the growth and development of plants, animals, and humans. However, excessive concentrations of Cu in soils are potentially hazardous and may be highly toxic to the microflora, flora, fauna, and humans (Nannipieri *et al.,* 2003).

In the lithosphere, copper concentration is approximately 55 ppm. In arable soils, copper levels vary widely from 1 to 390 ppm, most commonly ranging between 5 and 50 ppm. The total copper content in soil depends largely on the chemical composition of the parent material. For example: acidic rocks contain around 30 ppm, sedimentary rocks around 57 ppm and basic rocks up to 140 ppm.

Copper in soil exists in various forms: in the soil solution, within oxides, embedded in the crystal lattice of primary and secondary minerals, and bound to organic matter. Soil colloids tend to adsorb copper, reducing its availability to plants. The most important available form is water-soluble copper, although its concentration in the soil solution is very low less than 1% of the total copper content in the soil. The bioaccumulation of copper in soils and its bioavailability to fruit crops depends on the physical and chemical properties of the soil, such as mechanical composition (texture), soil sorption capacity, pH reaction, electrical conductivity (EC), humus content, carbonate content, and other factors (Vlcek and Pohanka, 2018; Vukadinović and Vukadinović, 2011, 2013; Alloway, 2013; Mitkova and Markoski, 2022; Kiprijanovski, 2020; Markoski *et al*., 2025). The reaction of the soil solution (pH) influences the availability of copper to plants. With increasing soil pH, copper availability decreases (Mitkova *et al*., 2009; Vukadinovic and Vukadinovic, 2016; Markoski *et al.,* 2011; Mitkova and Markoski, 2022; Kiprijanovski, 2020). This explains the deficiency of copper in carbonate and alkaline soils. Below pH 6, copper availability increases. An exception occurs in strongly acidic soils ($pH<4.5$), where the intensive uptake of other ions may reduce copper absorption. Furthermore, in such soils, aluminium-silicate, phosphate, and other ions can lower the level of water-soluble copper. In acidic soils, due to higher solubility, leaching of available copper may occur, as well as greater removal of copper from the soil through crop yields. The examined soil samples, according to the pH results, are neutral, slightly alkaline, moderately alkaline and strongly alkaline. Only two soils samples at both depths are non-carbonate, while the others are slightly, moderately and highly carlcareous (classification by Penkov, 1996). Fruit trees grow best in slightly carbonate soils ($CaCO_3$ up to 5%). The presence of $CaCO_3$ in the soil prevents acidification (buffer effect), stabilizes organic matter, and improves soil structure. In our research, the average value of the total copper content at a depth of 0 to 30 cm is 45.33 mg/kg and the median is 41.6 mg/kg, and at a depth of 30 to 60 cm, the average value is 36.31 mg/kg and the median is 37.7 mg/kg. Copper has a high potential for accumulation in agricultural soils due to the long-term use of fertilizers and copper-based pesticides. Depending on soil properties, excessive concentrations may become toxic to fruit crops and reduce yields. The recommended maximum level of copper in plants is 10 mg/kg, while the permissible concentration in soils, according to the World Health Organization (1996), ranges from 20 to 36 mg/kg. Concentrations above this threshold can negatively affect plant growth and soil functioning (Ballabio *et.al.,* 2018; Mitkova *et al.,* 2022; Kiprijanovski, 2020; Dube *et al.,* 2000; Artiolaet *et al.,* 2004; Kabata-Pendias *et al.,* 2007; Kabata-Pendias *et al.,* 2001; Kabata-Pendias, 2011; Kopittke *et al.,* 2011; Fagnani *et al*., 2020; Neaman *et al*., 2024). In orchard soils of the Kumanovo region, average copper concentrations were 45.33 mg/kg at 0-30 cm and 36.31 mg/kg at 30-60 cm. These values fall within the global range for arable soils (5-50 ppm), but several exceed WHO's recommended limit, placing them in a borderline to potentially risky category. Although levels remain below the contamination threshold of 100 mg/kg (Decree 214/2007 MEF), continued accumulation from anthropogenic inputs may pose risks to soil quality and fruit production. Copper concentrations are consistently higher in the topsoil compared to the subsoil, confirming that accumulation is primarily due to agricultural practices rather than lithological origin. Overall, the orchards are adequately to well supplied with copper, but careful management of copper-containing agrochemicals is needed to prevent long-term risks.

The comparative assessment of copper (Cu) concentrations in soils from the Kumanovo region reveals notable differences when juxtaposed with data from Skopje (Stafilov *et al.,* 2017), the broader territory of North Macedonia (Stafilov and Šajn, 2016), the Prespa region (Markoski *et al*., 2025), and Europe (Salminen *et al.,* 2005). The median copper content in Kumanovo soils was found to be 37.7 mg/kg, with values ranging between 26.3 and 49.3 mg/kg. In contrast, soils from Skopje exhibited a slightly lower median of 33 mg/kg, though with a wider variability, spanning from 7.3 to 59.0 mg/kg.

Soils from the Prespa region showed comparable copper levels, with concentrations ranging from 14.90 to 53.50 mg/kg, an average value of 32.13 mg/kg, and a median of 30.85 mg/kg, indicating moderate enrichment likely associated with long-term agricultural practices, particularly intensive orchard management. At the national level, the median copper concentration was considerably lower, amounting to 16 mg/kg, with a range between 1.7 and 73.0 mg/kg. European soils, on average, demonstrated the lowest median value of 13 mg/kg, albeit with a much broader distribution, extending from 0.81 to 256 mg/kg.

This comparison highlights that the soils of Kumanovo contain relatively elevated copper levels compared to both national and continental averages. While these concentrations fall within the lower to medium spectrum of European soils, they surpass the thresholds recommended by the World Health Organization (WHO) in several instances. This indicates a potential risk to the environment and human health, particularly in orchards where soil contamination may directly affect both the land and agricultural produce.

Figure 3 illustrates the spatial distribution of total copper in soils under fruit orchards in this region.

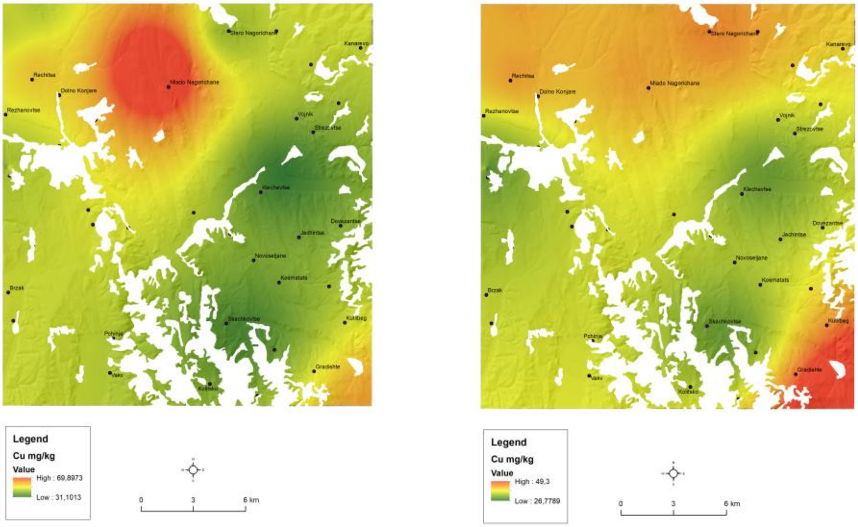


**Figure 3.** Spatial distribution of total copper content in soil samples at depths of 0-30 cm and 30-60 cm

Tables 4 and 5 present the factor analysis, i.e., the loading matrix of dominant rotated factors for soil samples taken at depths of 0-30 cm and 30-60 cm. Through factor analysis, a large number of variables are reduced to a smaller set of variables called factors, which are part of the principal component analysis (PCA). The factors contain significant information about the original variables and typically have a defined meaning. They are obtained by standardizing the data to a zero mean and a unit standard deviation.

In the topsoil layer (0-30 cm), five principal components with eigenvalues greater than 1 were extracted, explaining 93.51% of the total variance, with the first three components accounting for 74.98% of the variability (Table 4). This high explained variance indicates that the selected soil parameters adequately capture the dominant processes controlling copper distribution in the topsoil.

Principal Component 1 (PC1) explains 32.65% of the total variance and represents a texture-controlled sorption and accumulation factor. The strong positive loadings of physical clay, clay fraction, and copper, combined with strong negative loadings of physical sand fractions, clearly indicate that copper accumulation is preferentially associated with fine-textured soils. This relationship reflects the higher specific surface area and cation exchange capacity of clay minerals, which promote copper adsorption and retention.

**Table 4.** Matrix of loading coefficients with dominant rotated factors at a depth of 0-30 cm

| Parameters | PC1 | PC2 | PC3 | PC4 | PC5 |
|---|---|---|---|---|---|
| Humus % | 0.087 | 0.61 | 0.749 | -0.02 | -0.20 |
| Total N % | 0.080 | 0.60 | 0.757 | -0.03 | -0.20 |
| pH in $H_2O$ | 0.095 | -0.86 | 0.425 | -0.08 | -0.001 |
| $CaCO_3$ % | 0.102 | -0.86 | 0.408 | -0.10 | -0.01 |
| EC | -0.050 | 0.65 | -0.544 | -0.23 | 0.01 |
| $P_2O_5$ mg/100g | 0.175 | 0.45 | 0.084 | 0.48 | 0.73 |
| $K_2O$ mg/100g | -0.17 | 0.40 | -0.31 | 0.50 | -0.61 |
| Coarse sand % | -0.68 | 0.14 | -0.38 | -0.43 | 0.19 |
| Fine sand % | -0.77 | -0.11 | 0.40 | 0.43 | -0.02 |
| Physical sand % | -0.98 | -0.01 | 0.11 | 0.10 | 0.09 |
| Clay % | 0.85 | -0.29 | -0.35 | 0.20 | -0.15 |
| Silt % | 0.41 | 0.53 | 0.42 | -0.56 | 0.09 |
| Physical clay % | 0.98 | 0.01 | -0.11 | -0.10 | -0.09 |
| Cu mg/kg | 0.79 | 0.15 | 0.12 | 0.20 | 0.24 |
| Eigenvalue | 4.57 | 3.41 | 2.51 | 1.46 | 1.13 |
| % of Variance | 32.65 | 24.38 | 17.95 | 10.45 | 8.08 |
| Cumulative (%) | 32.65 | 57.03 | 74.98 | 85.42 | 93.51 |

**Table 5.** Matrix of loading coefficients with dominant rotated factors at a depth of 30-60 cm

| Parameters | PC1 | PC2 | PC3 | PC4 | PC5 |
|---|---|---|---|---|---|
| Humus % | 0.15 | 0.87 | 0.42 | -0.02 | 0.15 |
| Total N % | 0.12 | 0.88 | 0.41 | -0.06 | 0.12 |
| pH in $H_2O$ | -0.63 | -0.45 | 0.45 | 0.41 | -0.63 |
| $CaCO_3$ % | -0.49 | -0.46 | 0.46 | 0.56 | -0.49 |
| EC | -0.33 | 0.58 | 0.56 | -0.61 | -0.33 |
| $P_2O_5$ mg/100g | 0.43 | 0.50 | -0.33 | 0.61 | 0.43 |
| $K_2O$ mg/100g | 0.69 | 0.47 | -0.28 | 0.22 | 0.69 |
| Coarse sand % | 0.87 | -0.20 | -0.43 | 0.09 | 0.87 |
| Fine sand % | 0.73 | -0.20 | 0.63 | -0.07 | 0.73 |
| Physical sand % | 0.94 | -0.23 | 0.23 | -0.01 | 0.94 |
| Clay % | -0.75 | -0.10 | -0.62 | -0.10 | -0.75 |
| Silt % | -0.62 | 0.55 | 0.45 | 0.16 | -0.62 |
| Physical clay % | -0.94 | 0.23 | -0.23 | 0.01 | -0.94 |
| Cu mg/kg | -0.11 | 0.69 | -0.31 | 0.51 | -0.11 |
| Eigenvalue | 5.46 | 3.74 | 2.31 | 1.59 | 5.46 |
| % of Variance | 38.97 | 26.74 | 16.53 | 11.35 | 38.97 |
| Cumulative (%) | 38.97 | 65.72 | 82.25 | 93.60 | 38.97 |

Principal Component 2 (PC2) accounts for 24.38% of the variance and is dominated by strong negative loadings of soil pH and $CaCO_3$, indicating a carbonate-alkalinity control factor. This component reflects the buffering capacity of calcareous soils, where elevated pH and carbonate content reduce copper solubility and bioavailability through precipitation and surface complexation mechanisms. The weak association of copper with PC2 confirms that, although alkalinity influences copper mobility, it does not represent the primary driver of copper accumulation in the studied orchards.

Principal Component 3 (PC3) explains 17.95% of the variance and is characterized by strong positive loadings of humus content and total nitrogen. This component represents an organic matter–biological activity factor, highlighting the role of organic matter in copper complexation and stabilization. The association between humus, nitrogen, and copper reflects the strong affinity of copper for organic ligands, which can immobilize copper in the topsoil while simultaneously increasing its persistence over time.

Together, these components indicate that copper distribution in the topsoil is primarily controlled by anthropogenic inputs, with soil texture and organic matter acting as key modulators of copper retention and spatial variability.

In the subsoil layer (30-60) cm depth, four principal components with eigenvalues greater than 1 were extracted, explaining 93.60% of the total variance, with the first three components accounting for 82.25% (Table 5).

Principal Component 1 (PC1) explains 38.97% of the variance and is dominated by strong positive loadings of physical sand fractions and available $K_2O$, coupled with strong negative loadings of clay, physical clay, and soil pH. This component represents a textural differentiation and eluviation factor, reflecting downward redistribution processes and reduced influence of direct anthropogenic inputs compared to the surface layer. The weak loading of copper on PC1 suggests that copper is less controlled by simple textural contrasts at this depth.

Principal Component 2 (PC2) accounts for 26.74% of the variance and shows strong positive loadings of humus, total nitrogen, and copper. This indicates that, even at greater depths, organic matter remains a critical control on copper retention, likely due to downward transport of dissolved organic complexes and bioturbation effects.

Principal Component 3 (PC3) reflects secondary geochemical controls related to nutrient dynamics and minor textural effects, but its influence on copper distribution is comparatively limited.

Overall, the PCA results demonstrate a vertical differentiation in copper-controlling mechanisms, with strong anthropogenic and surface-related controls dominating the topsoil and more pedogenically driven processes influencing the subsoil.

The cluster analysis supports and validates the PCA interpretation by grouping soil parameters according to their degree of similarity. At both investigated depths, copper clusters with humus, total nitrogen, and fine soil fractions rather than with pH or $CaCO_3$, confirming that organic matter and clay fractions are the primary sinks for copper in orchard soils. The separation of electrical conductivity into an independent cluster further indicates that salinity-related processes play a negligible role in copper distribution.

Thus, cluster analysis does not introduce new controlling factors but reinforces the robustness of the PCA-derived conceptual model. These findings are consistent with recent studies indicating that copper accumulation in orchard soils is primarily controlled by soil texture, organic matter, and long-term agricultural inputs (Reimann *et al.*, 2018; Filzmoser *et al.*, 2018).

Figures 4 and 5 present PCA Biplots, which provide a graphical representation of the results obtained from principal component analysis (PCA). They help visualize the relationships between different parameters and the principal components. A PCA Biplot is a two-dimensional diagram that displays the principal components (PC1 and PC2) as axes, while the analyzed parameters are represented as vectors or arrows.

In PCA Biplot 1, the parameters from the analyzed soil samples under fruit orchards at a depth of 0-30 cm are grouped into three clusters. The first group consists of humus content, total nitrogen (N), $CaCO_3$, and the fine sand fraction, which explain most of the variance in PC1. The soil solution pH, electrical conductivity (EC), and clay content influence PC2 and form the second group, while all remaining parameters constitute the third group, having little influence on PC1 and PC2 but contributing to the other components.

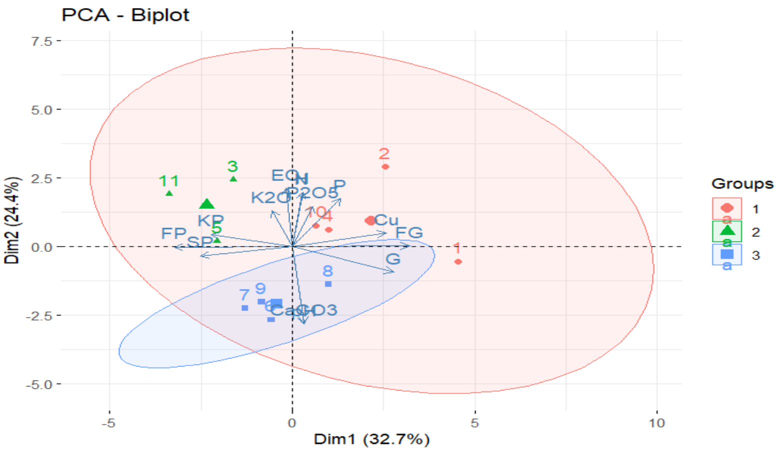


**Figure 4.** PCA Biplot 1 (at a depth of 0-30 cm)

In PCA Biplot 2, the first group consists of soil solution pH, electrical conductivity (EC), available K2O, and the fractions of physical sand and clay, which strongly influence the variance in PC1 and PC2. These parameters show either strong positive or strong negative correlations with PC1. Soil solution pH and clay content are strongly negatively correlated with PC1, whereas available $K_2O$ and the physical sand fraction are strongly positively correlated with PC1.

Electrical conductivity (EC) and available $K_2O$ are strongly positively correlated with PC2, meaning they explain most of the variance in this component. The second group consists of humus content, available $P_2O_5$, coarse sand, and fine sand fractions, which are most strongly associated with PC3 and PC4, while all other parameters fall into the third group.

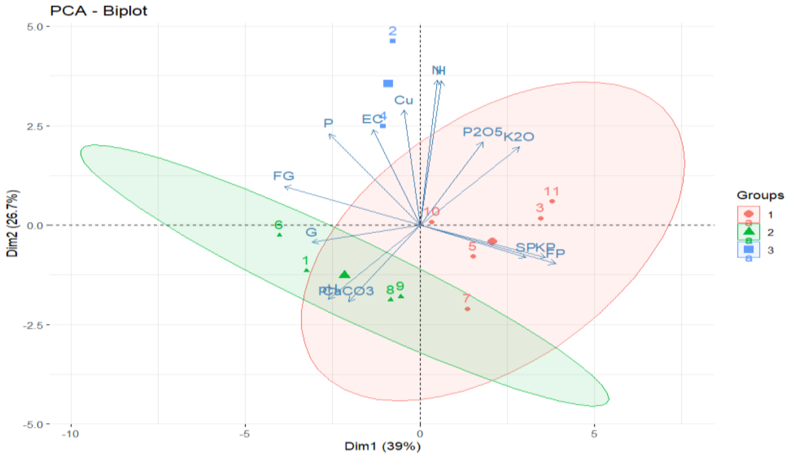
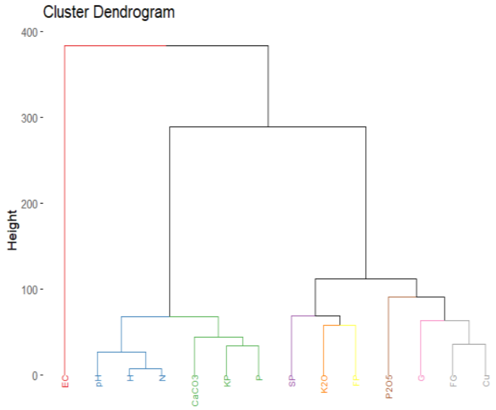


**Figure 5.** PCA Biplot 2 (at a depth of 30-60 cm)



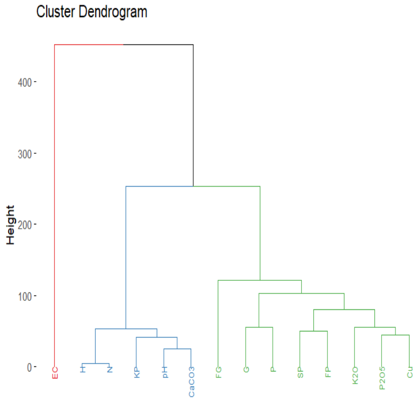


**Figure 6.** Dendrogram 1 from the cluster analysis of the soil samples (0-30 cm)

**Figure 7.** Dendrogram 2 from the cluster analysis of the soil samples (30-60 cm)

A dendrogram is obtained through cluster analysis, in which the results for the elements are grouped into clusters according to their degree of correlation. In Dendrogram 1 (Fig. 6), the elements from the analyzed soil samples at a depth of

0-30 cm are clustered, while in Dendrogram 2 (Fig. 7), the elements from the soil samples at a depth of 30-60 cm are clustered.

In dendrogram 1, the data are divided into three cluster groups. The first cluster includes electrical conductivity (EC), which is negatively correlated with PC1. The second cluster includes soil solution pH, humus content, total nitrogen (N), $CaCO_3$, coarse sand and silt fractions, which are correlated with PC2. The third cluster includes all other variables that are strongly correlated with PC1.

In Dendrogram 2, the data are also divided into three clusters. The first cluster includes electrical conductivity (EC), which is negatively correlated with PC1. The second cluster consists of humus content, total nitrogen (N), $CaCO_3$, coarse sand fraction, and soil solution pH, which have the greatest influence on PC2. The third cluster includes all other parameters that are in strong positive and strong negative correlation with PC1.

## CONCLUSIONS

The results of this study show that copper distribution in orchard soils of the Kumanovo region is primarily controlled by anthropogenic inputs, with soil texture and organic matter acting as key factors regulating copper retention and spatial variability. Multivariate statistical analyses, particularly PCA, proved effective in identifying the dominant mechanisms controlling copper accumulation.

Copper enrichment is most pronounced in the topsoil (0-30 cm), where it is associated with clay fractions, humus, nitrogen, and available phosphorus, indicating the prevailing influence of long-term agricultural practices. In the subsoil (30-60 cm), copper distribution is more strongly influenced by pedogenic processes and organic matter dynamics, reflecting reduced direct anthropogenic impact with depth. Soil pH and carbonate content act mainly as secondary factors affecting copper mobility rather than accumulation.

Average copper concentrations in orchard soils were 45.33 mg/kg in the 0-30 cm layer and 36.31 mg/kg in the 30-60 cm layer. Although these values generally fall within the typical global range for agricultural soils, several locations approach guideline limits, indicating a potential long-term risk under continued intensive management.

Overall, the findings confirm that rational use of copper-based agrochemicals and regular soil monitoring are necessary to prevent excessive accumulation and to ensure sustainable fruit production and long-term soil health.

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