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SPATIAL DISTRIBUTION OF COPPER (Cu) IN APPLE ORCHARDS IN THE RESEN REGION

SUMMARY

The soils in apple orchards in the Resen region were examined. The field research was carried out in 2024, during which 26 surface soil samples were taken. In the framework of this master's thesis, an examination of some physical and chemical properties of the soil, as well as the content of the total forms of heavy metals, was carried out. Several soil types are formed in the area covered by the Resen region: regosols, cinnamon forest soils, colluvial soils, and complexes thereof. Based on the obtained values for the mechanical composition, for the most part, the soils in the surface part are sandy clay loam (SCL) at 41%, sandy loam (SL) at 36%, and loamy (L) soils at 23%. The content of total forms of heavy metals in all samples was analysed using atomic emission spectrometry with inductively coupled plasma (AEICP). All statistical analyses were conducted in the R programming environment (version 4.3.2; R Core Team, 2024). The 'FactoMineR' and 'factoextra' packages were used for principal component analysis (PCA), while 'cluster' and 'ggdendro' packages were applied for hierarchical cluster analysis (HCA). Prior to PCA, all variables were standardized (z-score normalization) to eliminate the influence of different measurement scales and to ensure comparability among variables. The selection of principal components was based on eigenvalues >1 (Kaiser criterion) and cumulative explained variance. Cluster analysis was performed using Ward's method and Euclidean distance as the dissimilarity measure to identify similarities among soil parameters. Spatial interpolation of soil properties and total Cu content was performed using the Inverse Distance Weighting (IDW) method in ArcGIS 10.8. The IDW approach was selected because it provides reliable and smooth spatial predictions for datasets with a moderate number of sampling points (n = 26) and

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without a clearly defined spatial trend or anisotropy. The power parameter (p) was set to 2, which emphasizes the influence of closer points while maintaining interpolation stability. Kriging interpolation was tested but not applied, as the dataset size and semivariogram structure did not justify its use due to the lack of a spatially autocorrelated variogram model. The obtained results allow us to distinguish between possible anthropogenic influences on the presence of heavy metals in the soils of in the Resen region and their lithological origin.

Keywords: physical-mechanical properties, characteristics, heavy metals.

INTRODUCTION

Soil has numerous ecological functions that are essential for the environment, but also for the economy and the progress of society as a whole. As a dynamic polydisperse system with many functions, soil provides support for the entire ecosystem (Mitkova *et al.*, 2022). Soil contamination is usually caused by industrial and mining activities; in agriculture, by the improper use of pesticides, mineral fertilizers, and low-quality irrigation water; as well as by traffic in large urban areas (poor fuel quality, outdated technology), wastewater (municipal and industrial), and improper waste disposal (municipal and technogenic).

Soil contamination with heavy metals is one of the most complex and long-term environmental issues (Kabata-Pendias *et al.,* 2001; Artiola *et al.*, 2004; Kabata-Pendias *et al.,* 2007; Mitkova *et al.,* 2009; Prentovic *et al.*, 2010; Markoski *et al.*, 2011; Pelivanoska *et al.*, 2011; Andreevski *et al.*, 2012, Petek *et al.*, 2022; Markoski *et al.*, 2025). In particular, the potential soil contamination with copper in the Resen region known as a fruit-growing area in our country is the subject of research.

Recent research highlights that climatic conditions represent one of the most important determinants controlling the accumulation and mobility of copper (Cu) in vineyard and orchard soils. According to the global review by (Neaman *et al.*, 2024), soil Cu concentrations are directly proportional to precipitation and inversely related to the aridity index (the ratio of potential evapotranspiration to precipitation). In humid regions, where diseases such as Plasmopara viticola (downy mildew) are more prevalent, the need for frequent applications of copper-based fungicides leads to higher Cu accumulation in the surface soil layer.

The study confirmed that climate, farm age, and soil organic matter content are the three key factors explaining the variability of Cu in agricultural soils worldwide. Moreover, increased rainfall enhances Cu losses via surface runoff, but at the same time increases the use of Cu fungicides, resulting in a net positive relationship between precipitation and soil Cu levels in humid regions.

Copper is the first metal that humans used for various purposes. Historical data show that ancient civilizations used it more than 10.000 years ago (Markoski *et al.*, 2025). Its importance throughout human history is evident from the fact that an entire historical period the Bronze Agewas named after an alloy of copper. Today, after iron and aluminum, copper ranks as the third most used metal in the world. Copper is an essential microelement for living organisms and, in small amounts, is necessary for vital physiological processes. On the one hand, its deficiency in organisms leads to various disorders (Romić *et al.*, 2014), while on the other hand, in larger amounts, it causes damage and disease. Whether copper is an essential microelement or a toxin depends on its concentration.

When discussing copper as a chemical soil pollutant, it should be noted that the sources of copper pollution can be diverse and are generally divided into natural and anthropogenic sources. Copper naturally occurs in the Earth's crust in concentrations between 25–75 mg kg^{-1} (Kabata-Pendias and Mukherjee 2007; Zejak *et al*., 2022). It is found in the highest concentrations in igneous rocks, somewhat less in sedimentary rocks, and in very small amounts in carbonate rocks. Depending on the nature of the parent material, copper concentrations in soils worldwide range from 1 to 140 mg kg^{-1} (Romić *et al*., 2014).

Anthropogenic activities also have a significant impact on copper concentrations in soil. The most important sources include the use of copper-based fungicides, the application of liquid fertilizers, the discharge of sewage sludge, industrial activities, mining, emissions of particles from car brakes, and atmospheric deposition of copper (Halamic *et al.,* 2001; Mitkova *et al.,* 2005; Prentovic *et al.,* 2009; Matse *et al.,* 2024).The accumulation of copper in soil depends on various parameters, primarily on the physicochemical properties of the soil (pH, soil structure, organic matter content, clay content, Fe content) (Kelepertzis *et al*., 2015; Jeon *et al.,* 2024). In addition to the above, copper accumulation in soil can also be influenced by vegetation, climate (precipitation), as well as by certain agrotechnical practices such as soil tillage and plant protection measures (Ballabio *et al.* 2018).

STUDY AREA

The Municipality of Resen is located in the Prespa Valley, in the southwestern part of the Republic of North Macedonia, and covers an area of 739 km². It is divided into land (562 km²) and water (177 km²) and represents a distinct spatial unit geographically situated around the intersection of 41°N latitude and 21°E longitude (Figure 1).

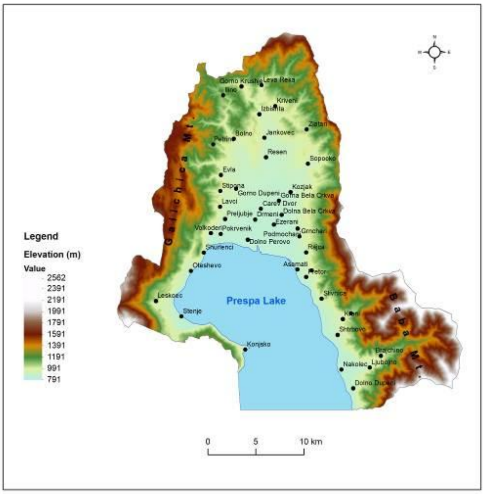


Figure 1. Location of the investigated area Prespa region Republic of North Macedonia

This region of North Macedonia is well known for its fruit production, which is closely linked to its climatic and soil conditions. The climate throughout the Prespa region is moderately continental with Mediterranean influence, while soil fertility also plays a major role.

The Prespa region is characterized by complex geological and tectonic structures, with rocks ranging in age from the oldest Paleozoic formations to the youngest Neogene and Quaternary sedimentary rocks. The Prespa valley and surrounding mountains are composed mainly of rocks of different ages, origins, and mineral compositions. Limestone rocks are the most dominant, although granodiorites and magmatic rocks are also present to a lesser extent. Syenites occur in areas of higher elevation, while Triassic carbonate rock masses are found in many parts of the region. Various types of Quaternary sediments such as proluvial, alluvial, organogenic marsh, deluvial, and fluvio-glacial sediments are dominant in the valleys along riverbeds.

The climatic conditions in the Prespa region determine the quality and uniqueness of apple fruits, as they have a significant influence on their successful cultivation. Most of the Prespa Valley lies within the warm continental zone, while the higher areas belong to the cold continental zone.

The climate can be characterized as continental or modified continental, since continental influence is dominant and Mediterranean influence is weaker. In the northern part, that is, in Upper Prespa, the continental influence is more pronounced, with colder winters, while in the southern part, especially in Lower Prespa, the Mediterranean influence is stronger, resulting in higher temperatures in both winter and summer.

The proximity of Lake Prespa has a major impact on the climate and moderates the extreme values of certain climatic elements that are characteristic of regions at this altitude. Despite the high elevation, the climate is relatively mild, which is due to the large water surface and the penetration of warm Mediterranean air currents from the southern part of the basin. In winter, relatively low temperatures are common, while in summer temperatures are moderately high. Spring is cooler than autumn, and May is cooler than September. Based on these characteristics, the climate can be described as moderately continental in the northern part, and moderately continental with Mediterranean influence in the southern part.

MATERIAL AND METHODS

Samples of surface soil (0–30 cm) were collected for analysis from 26 previously defined locations in the study area (Fig. 2).

All samples were collected in accordance with specific standards for collecting soil. 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.

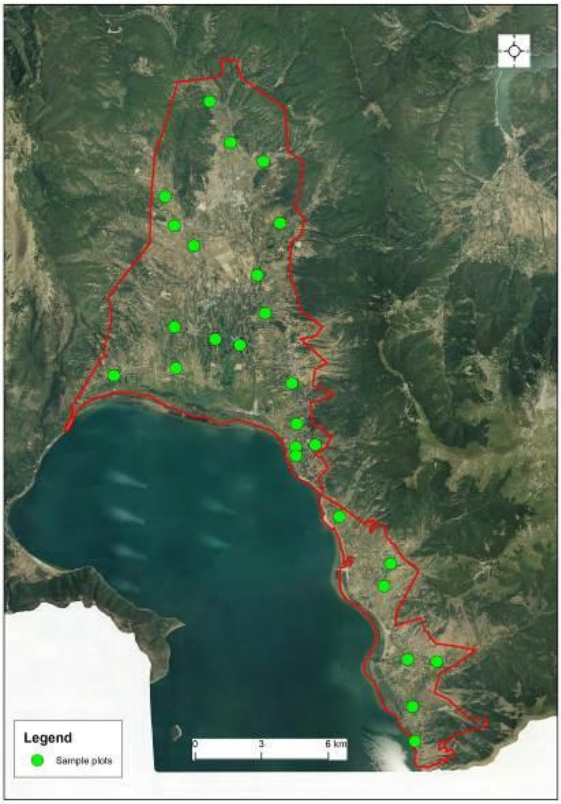


Figure 2. Map of the investigated area with locations, where the soil samples were taken

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. Soil properties were determined, such as; mechanical composition (Mitkova and Markoski, 2022); (Markoski and Mitkova 2020), pH (10390:2005), total nitrogen (11261:1995), The content of organic carbon and humus - Spectrophotometric determination with the dichromatic method according to Walkley and Black, a validated method of the Faculty of Agricultural Sciences and Food in Skopje (Durdjević, 2014), and calcium carbonate equivalent volumetrically (ISO 10693). Additionally total organic carbon (TOC) was determined by dry combustion (according to ISO standard 10694), extractable phosphorus and potassium (ammonium lactate method) while the cation exchange capacity (CEC) was measured by the method described by (Sumner and Miller, 1996). The total form of Cu was analyzed. Soil samples were digested by two methods: Aqua Regia extraction method (ISO 11466) and digestion for determination the total element content with HF method (ISO 14869-1). Aqua regia (HCl and HNO3 3+1) extraction method was done after digestion at 180ºC for 2 h. Soil samples (3.0000 g) were digested directly in the reflux digestion vessels where 21 ml HCl and 7 ml HNO3 were added. The solution was brought to boil and the reflux was kept for 2 hours. The solution of each vessel was quantitatively transferred to 100 ml flasks. For total digestion, soil samples (0.2500 g) were placed in a Teflon digestion vessel and were digested on a hot plate. In the first step, HNO3 was added to remove all organic matter, then a mixture of HF and HClO4 was added, followed by a third step where HCl and water were added to dissolve the residue. The solution was transferred quantitatively to the 25 ml volumetric flask. All reagents were of analytical grade (Merck, Germany). Analytical blanks were included in all extractions. Analysis of soil samples was performed using inductively coupled plasma-atomic emission spectrometry (ICP-AES). From the obtained results descriptive statistics were prepared and multivariate factor analyses by R-method were applied in order to identify the associations of the chemical elements (Reimann *et al.,* 2002). Spatial distribution maps were prepared for each factor using universal kriging method with a linear variogram interpolation. Factor analysis is the methodological basis of a set of statistical techniques used to analyse inter-relations of many variables. The approach includes processing information from a large number of original variables into smaller sets (called factors) with minimal loss of information from the original variables. Factor analysis as a set of statistical and mathematical procedures is useful in investigations whereby a number of variables that are mutually correlated and where is necessary to determine the basic source of covariance between the data (Reimann *et al.,* 2002). Multivariate cluster analysis was also applied to determine the significance of the factor analysis and the stability of the new synthetic variables, that is, associations of elements. The dendrogram of the distances among the individual elements is presented in Fig. 3. Identical results were achieved by application of multivariate factor analysis. All of the obtained clusters correspond to the four obtained factors.

RESULTS AND DISCUSSION

According to the obtained data, the soils in the surface part 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.

Several soil types have formed in the studied area: alluvial, colluvial, leached, brown forest soils, marshy gley soils, calcareous-dolomitic black soils (calcimelanosol), brown soils on limestone and dolomite, complexes of brown forest soils + regosol + leptosol, and leached + regosol, (Fig 3 Pedological map).

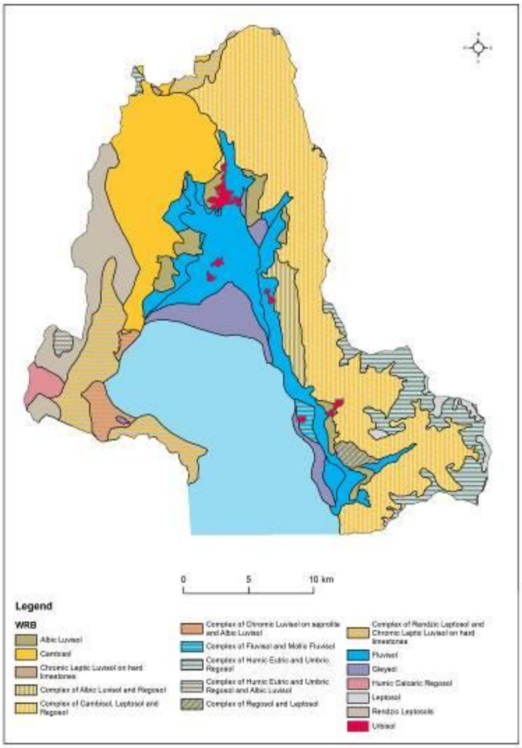


Figure 3. Pedological map of the Resen municipality

From the analyzed soil samples (Table 1), it can be seen that the fraction of total sand is dominated by the fraction of fine sand, on average 30.48% in relation to coarse sand 24.60%. The average value of the physical fraction of sand (fine + coarse sand) is 55.70% and is higher than the physical fraction of clay (clay + silt) which is 42.37%. The median for the total sand fraction is 58.1%. In the physical clay fraction, the clay fraction with the highest average value is 15.25% and ranges from 10.0 to 25.50% in relation to the powder fraction, which averages 27.94%. The median for the powder fraction is 26.60% higher than the median for the clay fraction - 15.7%. The soil samples according to the American classification triangle, with the obtained values for the mechanical composition, are classified into textural classes, (Mitkova and Markoski, 2022). The surface soils are classified as sandy clay loam (SCL), sandy loam (SL), and loam (L), each accounting for 30.77%, and as loamy sand (LS) and silty loam (SiL), each accounting for 3.84%.

The minimum and maximum values of soil bulk density in the surface layer range from 1.39 to 1.58 g/cm³, with an average value for all soil samples of 1.48 g/cm³ and a median of 1.48 g/cm³. The average value of hygroscopic moisture is 2.46%, with a minimum of 1.17%, a maximum of 4.17%, and a median of 2.23%.

Table 1. Descriptive statistics for the content of the analyzed elements in the soil samples

Parameters	Measurement values	n	min	max	X	SD	Md
pH H_2O	/	26	6.28	7.97	6.92	0.36	6.9
$CaCO_3$	[%]	26	0.00	15.82	0.59	3.04	0
Organic mater	[%]	26	0.97	7.25	4.13	1.45	4.24
P_2O_5	[mg/100 g]	26	9.25	61.19	20.34	11.24	19.76
K_2O	[mg/100 g]	26	8.74	75.29	27.53	15.24	24.03
CEC	[cmol(+) kg^{-1}]	26	9.53	27.88	17.67	4.27	17.72
Hygroscopic moisture	[%]	26	1.17	4.17	2.46	1.0	2.23
Coarse sand	[%]	26	6.87	74.17	24.60	14.93	24.39
Fine sand	[%]	26	12.37	61.01	30.48	12.57	30.36
Total sand	[%]	26	36.10	88.10	55.70	12.76	58.1
Silt	[%]	26	0.50	48.40	27.94	11.20	26.6
Clay	[%]	26	10.00	25.50	15.25	3.72	15.7
Clay + Silt	[%]	26	11.90	63.90	42.37	12.76	41.9
ρ_P	[g/cm^3]	26	1.39	1.58	1.48	0.05	1.48
Cu	[mg/kg]	26	14.90	53.50	32.13	12.23	30.85

Figures 4 and 5 show the spatial distribution of the physical clay fraction (clay + silt) and clay in the study area.

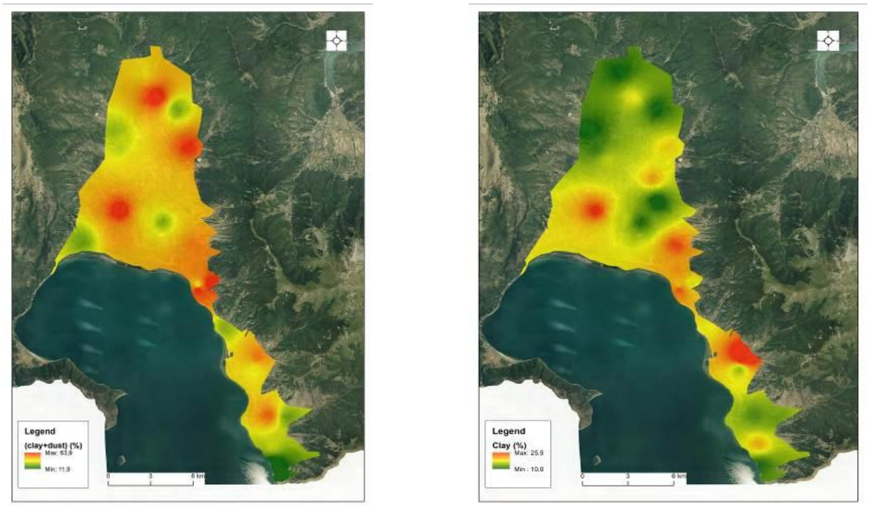


Figure 4 and 5. Spatial distribution of the physical clay fraction (clay+dust) and clay

In Table 1 and the PCA loading matrix, the statistically significant correlations ($p<0.05$) were marked to emphasize the most relevant relationships between soil parameters and copper accumulation. The strongest positive correlations were observed between Cu, organic matter (OM), cation exchange capacity (CEC), silt, and clay, indicating that higher Cu values are associated with soils richer in colloidal and organic fractions capable of binding metal ions. Conversely, a strong negative correlation was found with total sand content, confirming that lighter-textured soils with lower adsorption capacity tend to retain less copper.

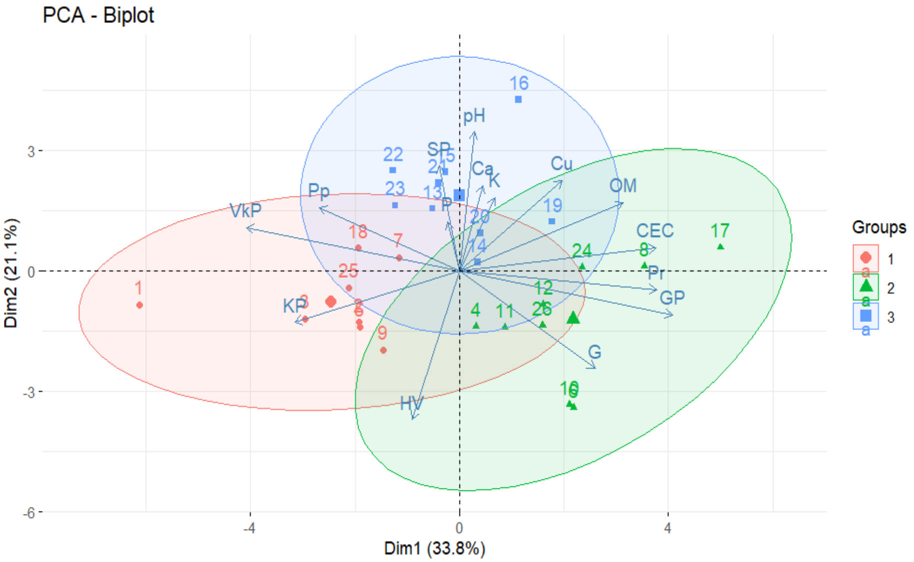
These results suggest that the sorption capacity of soils, governed by organic and fine mineral fractions, plays a dominant role in the retention and spatial distribution of Cu in the studied area. This is done by transforming the original data into a lower-dimensional space, where highly correlated variables are retained together, allowing for better visualization and understanding of the data.

Table 2. Principal Component Analysis

Parameters	PC1	PC2	PC3	PC4	PC5
pH H_2O	0.064	**0.780**	0.102	-0.307	0.300
$CaCO_3$	0.101	0.479	-0.465	-0.327	**0.548**
Organic mater	**0.704**	0.382	0.207	0.235	0.257
P_2O_5	-0.050	0.273	**0.736**	-0.020	0.021
K_2O	0.151	0.412	0.107	**0.620**	-0.282
CEC	**0.844**	0.131	0.063	0.217	0.267
Hygroscopic moisture	-0.201	**-0.829**	-0.175	-0.134	0.076
Coarse sand	**-0.706**	-0.285	0.348	0.238	0.441
Fine sand	-0.089	**0.587**	-0.560	-0.055	-0.417
Total sand	**-0.914**	0.244	-0.144	0.224	0.105
Silt	**0.847**	-0.103	0.262	-0.316	-0.226
Clay	**0.582**	-0.543	-0.279	0.193	0.301
Clay + Silt	**0.914**	-0.244	0.144	-0.224	-0.105
ρ_p	**-0.600**	0.356	0.364	-0.363	-0.063
Cu	0.440	**0.506**	-0.182	0.214	0.051
Eigen-value	5.07	3.17	1.65	1.18	1.15
% variability	33.83	21.12	10.97	7.88	7.68
% cumulative variance	33.83	54.95	65.92	73.80	81.48

Five principal components (PCs) were identified with eigenvalues > 1, which explain 81.48% of the total variability. PC1 explains 33.83% of the total variability, which is due to the high positive correlation of organic matter, CEC, silt, clay, and clay + silt with this component. The highest negative correlation with PC1 was observed with total sand. In the second principal component, pH has the greatest contribution, while P_2O_5 is positively correlated with PC3. The highest positive correlation with PC4 is observed for K_2O and with PC5 for $CaCO_3$.

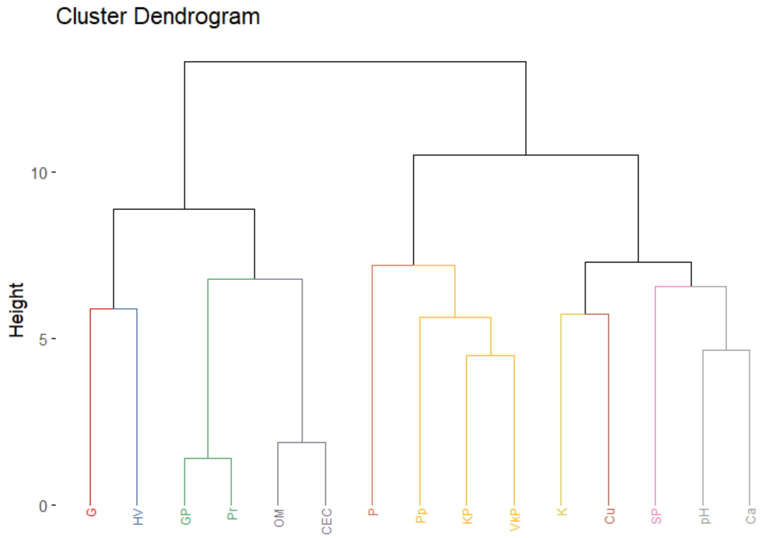
Based on the principal component analysis, a biplot was constructed showing the main components PC1 and PC2. From the graph, it can be observed that the analysed soil types are classified into three groups based on the analysed properties. In the first group (red color), the smallest number of soil samples are included; these are characterized by low contents of organic matter, CEC, silt, and clay + silt. In the second group (blue color), soil types with high values of pH, $CaCO_3$, P_2O_5, K_2O, and fine sand are distributed, while hygroscopic moisture is low. Nine soil samples are positioned in the third group (green color), which are characterized by high contents of organic matter, CEC, silt, clay, and clay + silt (Figure 6).



*Legend: pH; Ca-$CaCO_3$; P-P_2O_5; K-K_2O; O.M-organic matter; CEC-cation exchange capacity; Cu-total copper; KP-coarse sand; SP-fine sand; VkP-total sand; GP-clay + silt; G-clay; Pr-silt; Pp-bulk density; HV-hygroscopic moisture.

Figure 6. Biplot of PC1 and PC2 showing the distribution of the analysed soil samples based on the examined properties.

Based on the cluster analysis, the analysed parameters of the soil samples were divided into ten clusters. In six of them, only one soil property was classified. Clay + silt and silt were grouped in the third cluster. The cation exchange capacity (CEC) and organic matter belonged to the fourth cluster, while bulk density, coarse sand, and total sand were grouped in the sixth cluster. The properties pH and $CaCO_3$ were located in the tenth cluster (Figure 7).



*Legend: pH; Ca–$CaCO_3$; P–P_2O_5; K–K_2O; O.M – organic matter; CEC – cation exchange capacity; Cu – total copper; KP – coarse sand; SP – fine sand; VkP – total sand; GP – clay + silt; G – clay; Pr – silt; Pp – bulk density; HV – hygroscopic moisture.

Figure 7. Dendrogram of the cluster analysis of the analyzed characteristics in the soil samples.

In different soils, the content of organic matter varies widely and depends on the type of vegetation, that is, on the amount of organic residues left by the vegetation in the soil, on the conditions for their decomposition and humus formation (humification), on the rate of humus mineralization, as well as on the manner of soil use (Idrizi *et al*., 2023; Simić *et al*., 2023).

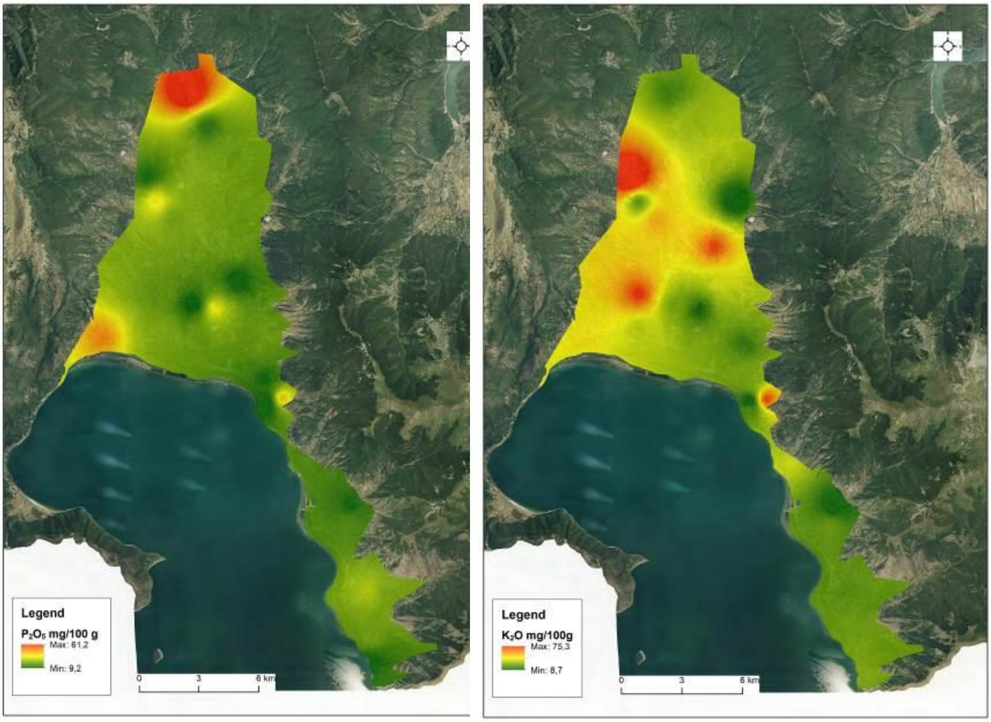
The results obtained from the examination of the chemical properties of the soil samples are presented in Table 6. The organic matter content ranges from 0.97% to 7.25%, with an average of 4.13%, and a median value of 4.24%.

The cation exchange capacity (CEC) depends on the content of organic matter, humus, the mechanical composition and the composition of clay minerals, as well as on the reaction of the solution used to displace the adsorbed ions during their determination. In cultivated soils with an organic matter content of 2–3%, the cation exchange capacity in sandy soils ranges from 5 to 10 cmol/kg^{-1}, in loamy soils between 10 and 20 cmol/kg^{-1}, and in clay soils between 20 and 40 cmol/kg^{-1} (Mitkova and Markoski, 2022).

The values of the analyzed soil samples correlate with the content of organic matter and the mechanical composition of the soil, ranging from 9.53 to 27.88 cmol/kg^{-1}, with an average of 17.67 cmol/kg^{-1} and a median of 17.72 cmol/kg^{-1}.

According to the analyses, the soil samples are non-calcareous, with the exception of one sample that is calcareous (15.82%). In soils containing carbonates, copper solubility decreases, thus reducing its availability, and vice versa. The values of the soil solution reaction (pH) are very important, as they indicate the availability, unavailability, and potential toxicity of nutrients in the soil. According to Filipovski (2003), the uptake of many elements increases with increasing acidity. A strongly acidic reaction (pH below 5.5) can cause toxic levels of Fe, Mn, and Al, as well as Zn, Co, and Cu. In an alkaline reaction, these microelements (Fe, Mn, Zn, Co, Cu) occur in unavailable forms, leading to their deficiency in plant nutrition. The best solubility and availability of most biogenic elements occur at a pH of around 6.5, which is optimal both for plants and microorganisms. The solubility and availability of copper are highest within the pH range of 5 to 7 in the soil solution. In the analyzed soil samples, the pH (in water) ranged from 6.28 to 7.97, with an average value of 6.92 (slightly acidic to moderately alkaline according to the USDA classification) and a median of 6.90.

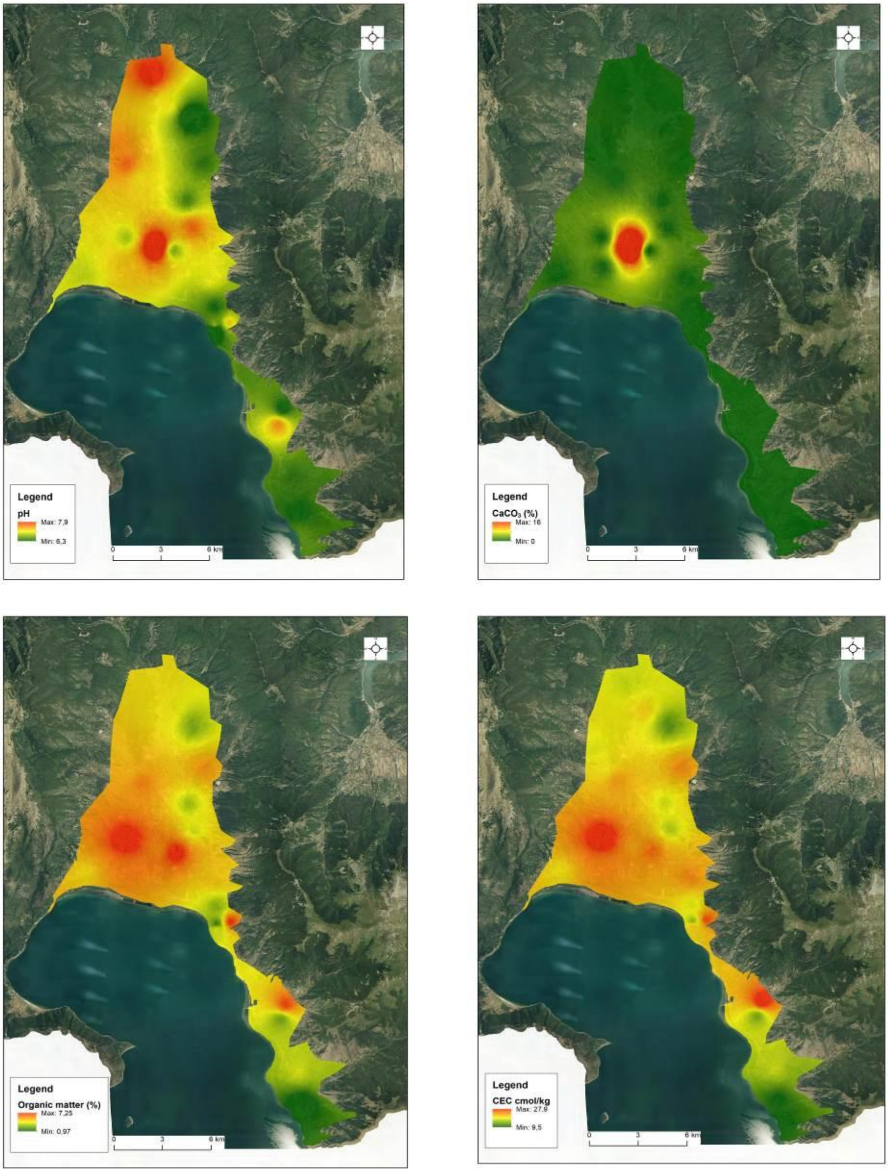
The content of easily available forms of P_2O_5 ranged from 9.25 mg/100 g soil to 61.19 mg/100 g soil, with a median of 19.76 mg/100 g soil. The content of easily available K_2O was higher, ranging from 8.74 to 75.29 mg/100 g soil, with a median of 24.03 mg/100 g soil. Figures 10 and 11 show the spatial distribution of available phosphorus (P_2O_5) and available potassium (K_2O) in the soil samples from the Prespa region.



Figures 8 and 9. Spatial distribution of available phosphorus (P_2O_5) and available potassium (K_2O) in the soil samples from the Prespa region.

The soil samples are slightly, moderately, richly, to very richly supplied with P_2O_5 and K_2O. This indicates uncontrolled fertilization with mineral fertilizers without prior soil fertility testing.

Figures 10, 11, 12, and 13 show the spatial distribution of pH, $CaCO_3$, organic matter, and cation exchange capacity (CEC) in the studied area.



Figures 10, 11, 12, and 13. Spatial distribution of pH, $CaCO_3$, organic matter, and cation exchange capacity (CEC) in the studied area

Table 1 presents the total copper (Cu) content in the soil samples, while table 3 shows a comparison of the obtained results (median, minimum and maximum copper content values in the soil samples from the Prespa region) with those from the entire territory of the Republic of Macedonia (Stafilov *et al.,* 2016), the territory of Skopje (Stafilov *et al.,* 2017) and Europe (Salminen *et al.*, 2005).

Table 3. Comparative analysis of the median, minimum, and maximum copper (Cu) content values in the soil samples from the Prespa region, Skopje, the Republic of North Macedonia, and Europe

Element	**value**	**Prespa**		**Skopje (Stafilov *et al.*, 2017)**		**North Macedonia (Stafilov and Sajn, 2016)**		**Europa (Salminen *et al.*, 2005)**	
		Md	**min-max**	**Md**	**min-max**	**Md**	**min-max**	**Md**	**min-max**
Cu	**mg/kg**	30.85	14.90 – 53.50	33	7.3 – 59.0	16	1.7 – 73.0	13	0.81 – 256

The average copper content in the lithosphere is about 55 ppm. In cultivated soils, its total content varies widely from 1 to 390 ppm, most commonly between 5 and 50 ppm, with an average of approximately 26 ppm. However, most of the copper in the soil is not available to plants. The total copper content in soil depends on the chemical composition of the parent material. Acidic rocks contain the least copper (around 30 ppm), sedimentary rocks slightly more (around 57 ppm), and basic rocks the most (around 140 ppm). Copper also strongly binds to organic matter in the soil. Organic copper complexes play an important role in regulating its movement in the soil and availability to plants. Copper bound to organic matter is poorly available to plants. Therefore, soils with a high organic matter content (e.g., peat soils) may have a copper deficiency for plants. The content of available copper in the soil also depends on the soil's mechanical composition. Sandy soils are poor in copper. Copper deficiency also occurs in humus-rich sandy soils of deluvial and alluvial origin, as well as in some hydromorphic and peat soils. Copper deficiency in the soil does not always correlate with high organic matter content; it can also occur in soils formed under arid conditions with low organic matter content (Mitkova and Markoski 2022).

Excess copper (Cu), however, negatively affects plant growth and productivity. Numerous studies summarize the adverse effects of copper excess on germination, growth, photosynthesis, and antioxidant response in crops. Its inhibitory effect on mineral nutrition, chlorophyll biosynthesis, and antioxidant enzyme activity has been confirmed (Banas *et al.,* 2010). According to (Strumpf *et al.,* 2009), even in heavily contaminated locations, copper content in plants after harvest is low. Based on copper uptake and distribution in plants, for perennial crops (e.g., fruit trees, vineyards), the risk to consumers from the soil–plant connection can be excluded. So far, no references report that high copper content in soils results in high copper content in harvested products, indicating that restrictions on the use of copper-based fungicides are not necessary.

In Germany, estimates of copper pesticide use in 2008 showed that the expansion of organic farming, linked to location, increased copper use by 10 tons to 34.1 tons annually compared to 2005. This input is low compared to fertilizers (around 2.300 t/ha per year) or sewage sludge (around 450 t/ha per year). Continuous application of copper pesticides at the mentioned rates over the next the soil. Furthermore, the development of new low-concentration copper pesticides may reduce copper input in the coming years (Provenzano *et al.,* 2010).

The presence of at least three key factors influencing soil copper content in orchards and vineyards are: climate, age of plantations, and soil organic matter (Neaman *et al*., 2024). Their research showed that soil copper content in orchards and vineyards worldwide is directly proportional to rainfall and inversely affected by drought. Older plantations (orchards and vineyards) globally are characterized by increased copper content. Moreover, higher organic matter content shows an inverse effect on soil copper content. These soil property effects on copper content are also discussed regarding copper losses from the soil through surface runoff. No statistically significant differences were found between organic and conventional orchards and vineyards concerning soil copper content.

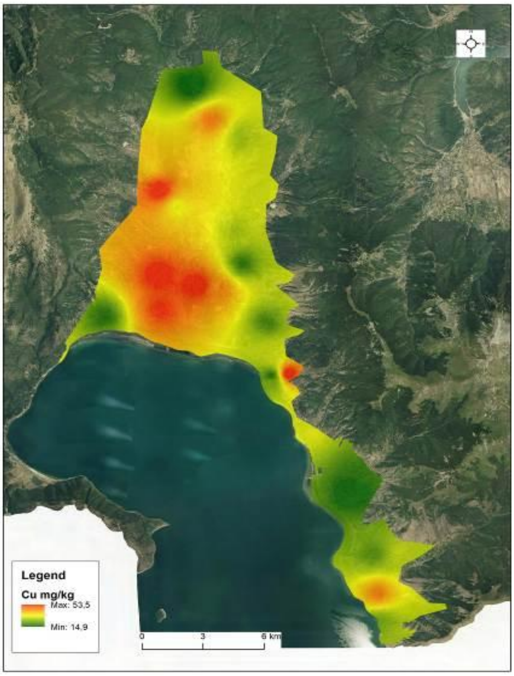


Figure 14. Spatial distribution of copper (Cu) in the soil samples from the Prespa region

The copper content in the soil samples ranged from 14.90 mg/kg to 53.50 mg/kg, with an average of 32.13 mg/kg and a median of 30.85 mg/kg. The minimum copper values in the Prespa region were higher than those reported for soils in the Skopje region (7.3 mg/kg), for the Republic of North Macedonia (1.7 mg/kg), and for European soils (0.81 mg/kg). The highest copper values in the Prespa region were lower than those in the Skopje region (59.0 mg/kg), North

Macedonia (73.0 mg/kg), and Europe (256.0 mg/kg). The median copper content in the analyzed soil samples was 30.85 mg/kg, higher than in soils of North Macedonia (16.00 mg/kg) and Europe (13 mg/kg), but lower than in the Skopje region (33.0 mg/kg). The higher median value in the Prespa region is likely due to greater use of plant protection products and mineral fertilizers containing this element. Similar values for total copper content in hydromorphic soils in the Resen field in surface horizons (13.22 to 33.60 mg/kg) were reported by Andreevski *et al.,* (2010), Savić *et al.,* (1970), in 12 alluvial soils of North Macedonia (0–20 and 20–40 cm), reported total copper content from 4.8 to 41.6 mg/kg, while for Skopje, Petkovski *et al.,* (2001) reported 15.5 to 74.6 mg/kg. When compared to earlier pedological surveys in the Prespa and Ohrid regions, the current study shows a slightly elevated median Cu content (30.85 mg/kg) relative to the values reported by Andreevski *et al*., (2010) for hydromorphic soils in Resen (13.22–33.60 mg/kg) and by Petkovski *et al*., (2001) for the Skopje area (15.5–74.6 mg/kg). In contrast, Cu levels remain well below the threshold values recorded in some European orchard soils (>100 mg/kg; Romić *et al.,* 2014). The observed variability may be attributed to differences in orchard age, intensity of fungicide use, and organic matter content across these regions. This comparison further confirms that, although the Prespa region exhibits moderately increased Cu accumulation, the concentrations remain within ecologically acceptable limits. Figure 16 shows the spatial distribution of copper (Cu) in the soil samples from the Prespa region in apple orchards.

CONCLUSIONS

Based on the obtained results for the spatial distribution of copper (Cu) in the soil samples from the Prespa region, the following conclusions can be drawn:

Several soil types have formed in the studied part of the Prespa region: alluvial, colluvial, leached, brown forest soils, marshy gley soils, calcareous-dolomitic black soils (calcimelanosol), brown soils on limestone and dolomite, complexes of brown forest soils + regosol + leptosol, leached + regosol.

Analyses of the mechanical composition of the samples showed that in the total sand fraction, fine sand dominates, averaging 30.48% compared to coarse sand at 24.60%. The average value of the physical sand fraction (fine + coarse sand) is 55.70%, which is higher than the physical clay fraction (clay + silt) at 42.37%. The median for the total sand fraction is 58.10%. In the physical clay fraction, clay has a lower average value of 15.25%, ranging from 10.00 to 25.50%, compared to silt, which averages 27.94%. The median for silt (26.60%) is higher than for clay (15.70%). Surface soils are sandy clay loam (SCL), sandy loam (SL), and loam (L) at 30.77% each, and loamy sand (LS) and silty loam (SiL) at 3.84% each.

The minimum and maximum soil density values in the surface layer range from 1.39 to 1.58 g/cm^3, with an average and median of 1.48 g/cm^3. The average hygroscopic moisture is 2.46%, with a minimum of 1.17%, a maximum of 4.17%, and a median of 2.23%.

Five principal components (PCs) with eigenvalues >1 were identified, explaining 81.48% of the total variability. PC1 explains 33.83% of the total variability, due to a strong positive correlation of organic matter, CEC, silt, clay, and clay + silt with this component. The strongest negative correlation with PC1 is observed with total sand. In the second principal component, pH has the largest contribution, while P_2O_5 is positively correlated with PC3. K_2O shows the highest positive correlation with PC4, and $CaCO_3$ with PC5.

Based on the principal component analysis, a biplot was constructed showing PCs 1 and 2. The graph shows that the analyzed soil types are classified into three groups based on the studied properties. In the first group (red), the smallest portion of soil samples is included, characterized by low organic matter, CEC, silt, and clay + silt. The second group (blue) includes soil types with high values of pH, $CaCO_3$, P_2O_5, K_2O, and fine sand, and low values of hygroscopic moisture.

Based on cluster analysis, the analyzed soil parameters were divided into ten clusters. Six of these include only one soil property. In the third cluster, clay + silt and silt are grouped. The fourth cluster includes CEC and organic matter, while bulk density, coarse sand, and total sand are grouped in the sixth cluster. The properties pH and $CaCO_3$ are located in the tenth cluster.

Organic matter content ranges from 0.97% to 7.25%, with an average of 4.13% and a median of 4.24%.

Soil samples are non-calcareous, except for one sample (15.82%).

The pH of the soil solution in water ranges from 6.28 to 7.97, with an average of 6.92 (slightly acidic to moderately alkaline according to the USDA classification) and a median of 6.90.

Cation exchange capacity ranges from 9.53 to 27.88 $cmol/kg^{-1}$, with an average of 17.67 $cmol/kg^{-1}$ and a median of 17.72 $cmol/kg^{-1}$.

Easily available P_2O_5 ranges from 9.25 mg/100 g soil to 61.19 mg/100 g soil, with a median of 19.76 mg/100 g soil. Easily available K_2O is higher, ranging from 8.74 to 75.29 mg/100 g soil, with a median of 24.03 mg/100 g soil.

Copper content in the soil samples ranges from 14.90 mg/kg to 53.50 mg/kg, with an average of 32.13 mg/kg and a median of 30.85 mg/kg. The minimum copper values in the Prespa region are higher than those reported for soils in the Skopje region (7.3 mg/kg), North Macedonia (1.7 mg/kg), and Europe (0.81 mg/kg). The maximum copper values in Prespa are lower than those in Skopje (590.0 mg/kg), North Macedonia (73.0 mg/kg), and Europe (256.0 mg/kg).

The results were statistically processed, and spatial distribution maps were prepared for all analyzed elements. The results were compared with international soil standards.

The studies generally indicate a correlation between the presence of copper and the geological formations in the studied area, but also suggest a certain link with insufficiently controlled use of plant protection products and mineral fertilizers containing this element.

Based on the obtained results, it is recommended to implement regular monitoring of Cu levels in orchard soils and to promote the rational and environmentally safe use of copper-based fungicides. Sustainable soil management practices should aim to prevent excessive accumulation of heavy metals while maintaining effective plant protection.

Future research should focus on the analysis of available (mobile) forms of copper and the assessment of Cu content in plant tissues, in order to better understand soil–plant transfer dynamics and potential ecological risks.

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