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Copper Risk Assessment in Lands under Different Management Systems

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ABSTRACT

The intensive and long-term use of agrochemicals in intensive agriculture poses significant environmental risks due to the accumulation of heavy metals in soils. This study assessed copper (Cu) fractions, mobility, and ecotoxicity in calcareous soils under horticultural (HO) and field crop (FC) practices in the Atabey Plain, Türkiye. Twenty-seven surface soil samples were collected and analyzed using a seven-step sequential extraction procedure. Chemometric approaches, including Principal Component Analysis (PCA) and Spearman correlation, were applied to identify the sources and distribution patterns of Cu. Results indicated that Cu was predominantly associated with residual fractions in both HO and FC soils, indicating limited overall mobility. However, HO soils exhibited higher total Cu concentration and greater proportions in labile fractions compared to FC soils. PCA revealed clear separation between the soil groups, with Cu enrichment in HO soils strongly influenced by anthropogenic inputs, whereas FC soils reflected more natural processes. Risk factor assessments based on contamination factor (CF) and risk assessment code (RAC) indicated moderated Cu contamination. In conclusion, to avoid high concentrations of mobile Cu in soils, soil properties should be taken into account, and particularly in orchards, alternative formulations to Cu-containing pesticides and cultural practices should be employed.

Keywords: sequential extraction, soil contamination, principal component analysis, plant cover, fate.

INTRODUCTION

Globally, the application of chemical inputs to agricultural production has raised concerns about the deposition of heavy metals in the soil and the resulting effects on human health and the environment in general (Alengebawy et al., 2021). Soils generally provide massive capacity for the adsorption of heavy metals. This is due to the negative charges in the soil components - mainly on the surfaces of clay, oxides, and organic matter - as well as the different specific adsorption mechanisms. While some of the heavy metals may have natural sources that can be linked to the weathering of the parent material, their levels in the soil are always elevated by human activities such as urban waste disposal, industrial processes, fossil fuel combustion and excessive use of pesticides and fertilizers (Nath et al., 2023; Sarkar et al., 2024; Shakti and Pandey, 2024; Nasr and Eissa, 2025).

Despite numerous studies on Cu accumulation, fraction-based ecological risk differentiation between horticultural and field cropping systems in calcareous Mediterranean soils remains insufficiently characterized. Copper (Cu) has attracted particular attention due to its widespread use in agriculture as a bioactive component of fungicides and insecticides in horticultural practices (Ochmian and Malinowski, 2024). Although Cu is a biologically essential element, it can exert toxic effects when accumulated in the soil. Its immobility within the soil profile and high affinity for adsorption to clay minerals, organic matters and oxides contribute to its long persistence in the topsoil layers under continuous application (Tu et al., 2024).

Naturally occurring concentrations of heavy metals in soils remain well below toxic levels, yet their mobility and bioavailability are strongly influenced by soil characteristics. In the case of Cu, factors such as ionic speciation, pH, and organic matter content, concentrations of carbonate ions, salinity, and biological activity are all known to considerably affect its environmental impact

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(Nartowska et al., 2025). Estimating the total concentration of heavy metals in soils tends to be of less value in the context of their source attribution and risk to the environment. This point becomes even more relevant for the case of Cu since the total concentration of Cu in the soil cannot be directly linked to either its bioavailability or the mobility of the metal in the soil (Niesiobędzka, 2023). Instead, the attribution of natural vs. anthropogenic levels of Cu in the ecosystem and the toxic effects of the metal would require the evaluation of Cu distribution in different fractions based on their bioavailability and reactivity.

These assessments can be made difficult due to the complex reactivity of the soil components. Microorganisms in the soil have the capability of binding Cu in the form of organo-mineral complexes. These may act as a supply of bioavailable Cu depending on the chemical nature of the interacting organic molecules in terms of their degree of polymerization (Formentini et al., 2022). Metal extraction methods in soil chemistry can be classified into single-step and sequential techniques. While, bulk concentrations of elements in the soil have been largely used in environmental risk assessments, such approaches overlook the mobility and bioavailability of heavy metals, including Cu. Sequential extraction techniques, by contrast, have greatly advanced the evaluation of Cu binding in soils and have proven crucial in risk assessments across diverse land management contexts (Waris et al., 2021; Kumkrong et al., 2022).

Copper remains a focal point of researches due to its agricultural applications and persistence in soils (Tamm et al., 2022). Although sequential extraction has been widely applied to agricultural soils, relatively few studies have focused specifically on Cu. This study investigates the availability and environmental risk of Cu in horticultural and field crop soils. The research focuses on calcareous soils from different landscapes of the Atabey Plain in Türkiye, employing a seven-step sequential extraction. Chemometric techniques were applied to analyze relationships among soil fractions and associated parameters.

MATERIAL AND METHODS

A total of twenty-seven composite surface soil samples (0-20 cm) was obtained from fourteen horticulture (HO) sites and thirteen field cropping (FC) sites in Atabey Plain, Isparta, Türkiye. The sampling design was guided by expert judgment to ensure adequate representation of contrasting management systems and prevailing soil characteristics in the study area. After being air-dried, the soils were passed through a 2 mm sieve. Subsequently, descriptive analysis and Cu fractionation were performed.

Descriptive Properties of Soils

Routine descriptive soil analyses were conducted using the methods described by Sparks and Bartels (1996) for neutral to alkaline soils. A 1:2.5 soil-to-water ratio was employed to determine pH and electrical conductivity (EC). Organic matter content was measured using the Walkley-Black wet oxidation technique (Nelson and Sommers, 1996). Calcium carbonate equivalence (CCE) was determined with the Scheibler calcimeter (Loeppert and Suarez, 1996). Soil texture was analyzed by the hydrometer method (Gee and Bauder, 1986). Available phosphorus was measured using the Olsen extraction method (Kuo et al., 1996). Available Na, K, Ca, and Mg were determined following the neutral molar ammonium acetate extraction method (Sumner and Miller, 1996). Cation exchange capacity was measured using the sodium acetate method at pH 8.2 (Richard, 1954). Iron and manganese oxides were solubilized with buffered citrate-bicarbonate-dithionite reagents (Mehra and Jackson, 2013). Amorphous iron and manganese oxides were determined by the ammonium oxalate extraction method (Blakemore, 1985). Iron and manganese concentrations were analyzed using an ICP-OES spectrometer (Perkin Elmer Optima 2100-DV).

Determination of Copper Fractions

Soil-Cu was fractionated into seven different geochemical fractions following the procedures described by Leleyter and Probst (1999). Figure 1 below shows the steps of the

fractionation. The residue obtained from the previous step was used to derive the subsequent fractions, beginning with the second step. After each extraction step, the soil was washed using distilled water and dried at a temperature of 40°C to minimize interaction transfer. The Cu content in the filtrates was determined using the inductively coupled plasma-optical emission spectrometry ICP-OES.

Risk Assessment

Various indices, including the contamination factor (Cf), risk assessment code (RAC), and potential ecological risk index (Er), are commonly employed in environmental risk assessments of heavy metals. The contamination factor (Cf) is employed to assess the relative retention time of Cu in soil. It is calculated as the ratio of Cu concentration in the mobile phase (FR1 + FR2 + FR3 + FR4 + FR5 + FR6 = Ci) to that in the residual phase (F7 = Cn) as shown in equation (1).

According to Devi and Saroha (2014), the categorization of Cf is: Cf < 1 represents no pollution; 1-3, low contamination; 3-6, moderate pollution; 6-9, high pollution; >9, very high pollution.

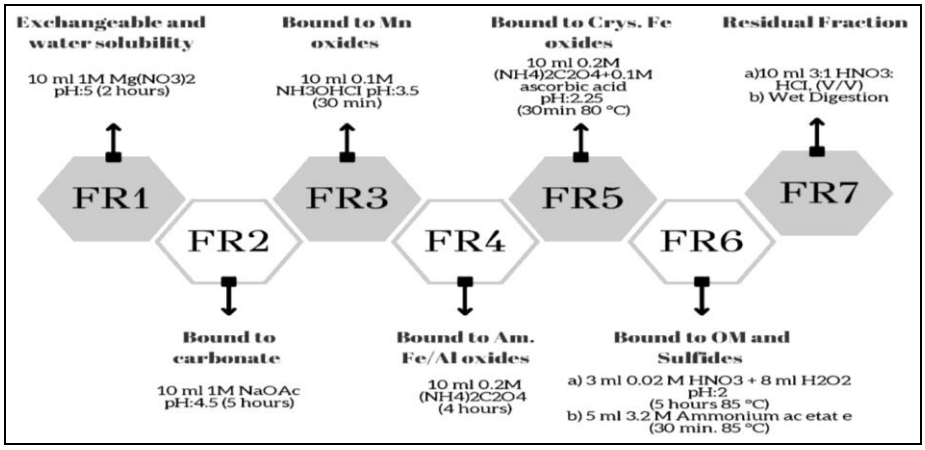


Figure 1. Sequential extraction process with seven steps (Leleyter and Probst, 1999)

The risk assessment code (RAC) is defined by the proportion of the exchangeable and carbonate fractions (FR1 + FR2) obtained through sequential extraction, providing a reliable measure of environmental risk associated with Cu. RAC is calculated using equation (2).

Based on the guidelines, values below <1% indicate the absence of any risk; 1-10% represent low risk; 11-30% represent medium risk; 31-50% high risk; and >50% indicate potential metal toxicity to the ecosystem (Devi and Saroha, 2014).

The potential ecological risk index (Er) is used to assess potential ecological risk of Cu. Er is calculated from the equation (3), where represents the toxic response factor (assigned value of 5 for Cu) (Kowalska et al., 2018).

Based on the assessment criteria, Er can be categorized as follows: Er ≤ 40, low ecological risk; 40 < Er < 80, moderate risk; 80 < Er < 160, considerable risk; 160 < Er < 320, high risk; and Er ≥ 320 very high ecological risk (Devi and Saroha, 2014).

Statistical Analysis

The physicochemical properties of the soils were subjected to descriptive statistical analyses. Subsequently, principal component analysis (PCA), a technique for reducing data dimensionality, was applied to the Cu fractions and descriptive soil properties. Spearman correlation analysis was performed to examine the associations between fractions and soil parameters. The statistical analyses were conducted utilizing the R studio 4.5.2 (R Core Team, 2025).

RESULTS AND DISCUSSION

Physicochemical Properties of Soils

Table 1 represents the descriptive statistics of the physicochemical properties of the soils under investigation. Variability OM content

was also significant, ranging from 0.83% to 3.43% with an average of 2.03%. Calcium carbonate equivalence was also highly varied, ranging from 0.88% to 35.57% in a sample of 9.63%. These soils can therefore largely be classified under the moderately calcareous soils. Soil pH varied from slightly neutral to moderately alkaline conditions (pH 6.92 to 8.00) with a mean of pH 7.69. Electrical conductivity varied considerably, from 153 to 762 µS cm^{-1} with a mean of 338 µS cm^{-1}, indicating non-saline conditions. Soil sand, silt, and clay contents averaged 357 g kg^{-1}, 243 g kg^{-1}, and 401 g kg^{-1} respectively. Cation exchange capacity varied from 19.4 to 61.3 cmol kg^{-1}, with a mean of 36.8 cmol kg^{-1}. Overall, the soil properties exhibited substantial variability, which provides a strong basis for analysing their effects on the Cu total content.

Table 1. Descriptive statistics of the experimental soils

	Min	Max	Mean	Std. dev.	Skew	Kurtosis
OM (%)	0.83	3.43	2.03	0.65	0.18	-0.73
CCE (%)	0.88	35.6	9.63	8.09	1.24	1.74
pH	6.92	8.0	7.69	0.29	-1.53	1.16
EC (µS cm^{-1})	153	762	338	131	1.09	1.72
CEC (cmol kg^{-1})	19.4	61.3	36.8	9.74	0.65	-0.11
Ca (cmol kg^{-1})	6.90	42	27.2	7.75	-0.55	0.04
K (cmol kg^{-1})	0.69	3.51	1.92	0.86	0.37	-1.18
Mg (cmol kg^{-1})	1.62	13.0	5.79	2.94	0.69	-0.39
Na (cmol kg^{-1})	0.05	2.15	0.60	0.39	1.98	7.02
P (mg kg^{-1})	6.10	113	38.3	29.0	1.05	0.07
Sand (g kg^{-1})	71.0	607	357	149	-0.25	-0.95
Silt (g kg^{-1})	137	396	243	77.7	0.28	-1.3
Clay (g kg^{-1})	207	704	401	110	0.55	0.17
MnOx (mg kg^{-1})	80.0	239	165	44.2	0.04	-0.99
AMnOx (mg kg^{-1})	47.0	168	97.0	31.0	0.26	-0.89
TMnOx (mg kg^{-1})	318	2212	494	353	4.25	17.9
AFeOx (mg kg^{-1})	1011	4709	1981	971	1.36	1.05
TFeOx (mg kg^{-1})	11725	23464	17468	2765	-0.03	-0.49
TotCu (mg kg^{-1})	22.3	62.4	39.4	12.2	0.58	-1.17

Chemometric Relations in Soils

The application of the Principal Component Analysis (PCA) for dimensionality reduction was used to evaluate the descriptive soil properties. Table 2 indicates that there are five principal components (PC) whose eigenvalue exceeds the threshold of 1. These components together account for 76.947% of the total variability. The PC1 accounts for 32.136% of the total variability in the soil dataset, followed by PC2 and PC3 for 15.679% and 14.721% variability, respectively. PC1 primarily represents the genetic properties of the soils, PC2 reflects nutritional attributes, and PC3 is mainly associated with soil oxides, as presented in Table 3. The remaining components explain relatively trivial proportions of the variability compared to the first three.

Table 2. The explained variances by the extracted principal component (PC)

Component	Variance %	Cumulative %
1	32.136	32.136
2	15.679	47.815
3	14.721	62.536
4	7.749	70.285
5	6.663	76.947

As shown in Table 3, PC1 has positive loadings for Ca, clay content, CEC, total Mn oxides (TotMnOx), pH, Mg, total Cu (TotCu), CCE, MnOx, silt content, and EC, while negative loadings were observed for exchangeable Na and sand content. Factor

loadings also indicated that the PC2 has positive loadings for P, OM, and K, but negative loading for MnOx. The PC3 has very strong positive loadings for TotCu, amorphous Mn oxides (AMnOx) content, total Fe oxides (TFeOx) content, Cu, and amorphous Fe oxides (AmFeOx) content, with a negative loading for CCE.

Table 2. Loadings between the extracted components and soil properties

Soil Parameters	Components				
	1	2	3	4	5
Ca	0.884				
Sand	-0.866				
Clay	0.831				
CEC	0.828			-0.428	
TMnOx	0.708				
Na	-0.690				
pH	0.664			0.422	
Mg	0.613				
TotCu	0.597		0.533		
CCE	0.586		-0.410	0.441	
MnOx	0.512	-0.507			
P		0.792			
OM		0.755			
K		0.685		-0.440	
AMnOx			0.818		
TFeOx			0.681		
AmFeOx			0.594		0.430
Silt	0.496				-0.651
EC	0.420				0.584

Figure 2 and the PCA scores plot (Figure 3) together show distinct clustering trends between horticultural (HO) and field crop (FC) soils. HO soils always fall in the domains of high organic material amendments, nutrient enrichment, and Cu bound to oxide fractions, thus confirming the major role of anthropogenic inputs. In contrast, the FC soils fall in the domains defined by texture and CCE properties, thereby highlighting the predominant influence of natural soil formation processes on Cu retention in these soils. A small number of samples belonging to the FC soils (FC3 & FC5) fall in the HO soil cluster domain, suggesting possible residual influences of past horticultural practices in these FC soils.

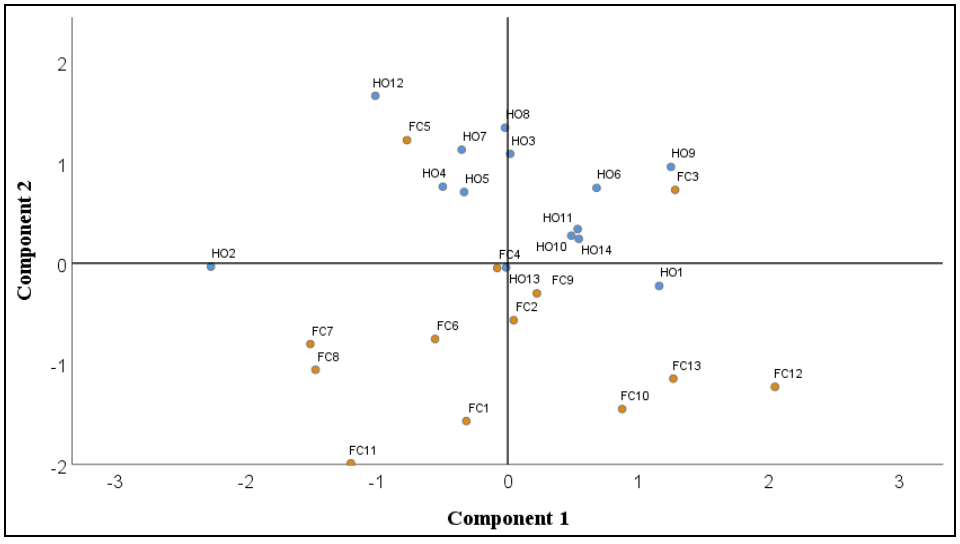


Figure 2. Scatter diagram for Component 1 and Component 2. HO Horticultural area and FC Field crop.

The PCA analysis indicated three possible mechanisms influencing Cu dynamics in the Atabey Plain. These mechanisms include the buffering effects of texture and soil carbonates, the enrichment of OM and nutrients, and the role of Fe-Mn oxides. Together these factors imply that Cu mobility in the HO soils of the Atabey Plain is more strongly affected compared to the FC soils.

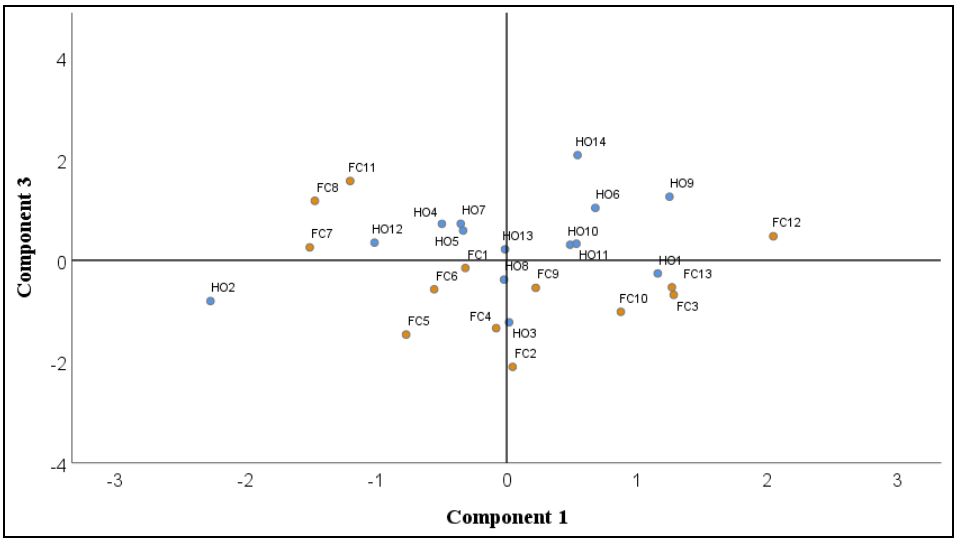


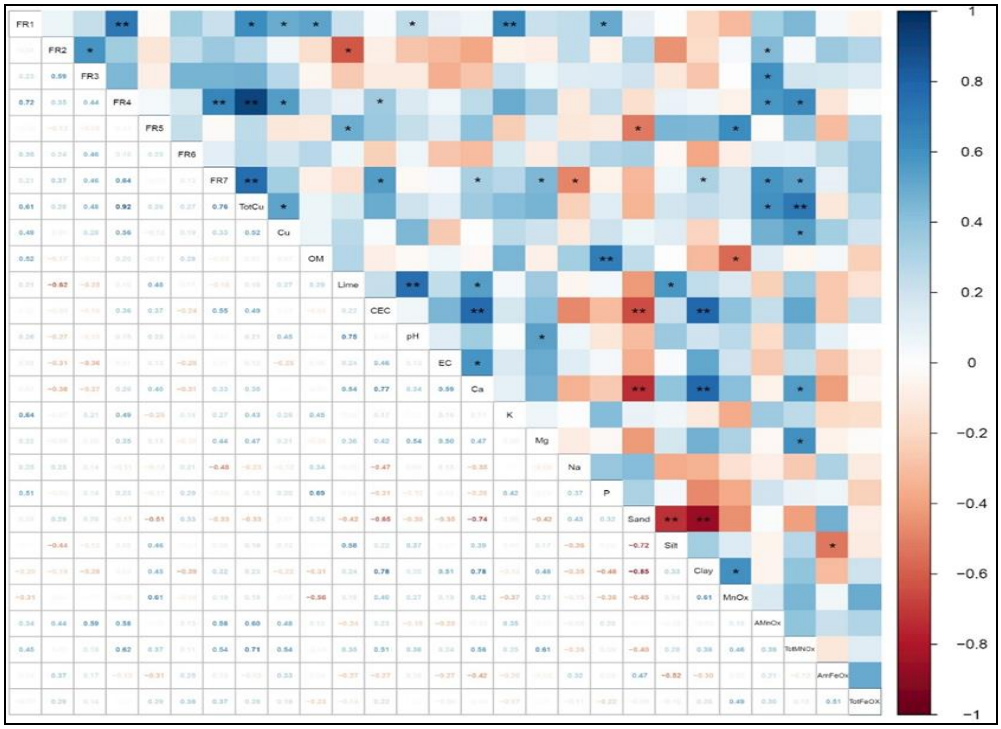
Figure 3. Scatter diagram for Component 1 and Component 3. HO Horticultural area and FC Field crop.

Relationship of Copper Fractions with Soil Properties

The correlation matrix in Figure 4 highlights the relationships between the seven operationally defined Cu fractions (FR1 to FR7) and the selected soil physicochemical properties. These relationships provide important insights into the mechanisms governing the mobility and fixation of applied Cu. The more labile fractions of Cu in the soils, the water-soluble + exchangeable (FR1) and the carbonate-bound (FR2) Cu forms, appeared to have significant positive relationships to the OM content, P, K, and the extractable Mn concentrations. Conversely, these labile fractions had negative correlations with the sand content. These findings suggest that soils of sandier texture, with lower buffering capacity, have higher potentials for Cu mobility, a condition more frequently observed in field crop soils. The moderately labile fraction FR3 (Mn-oxide bound) had strong positive correlations with Mn oxides (AMnOx and TotMnOx), supporting the crucial role of Mn oxides in the control of Cu adsorption in these soils (Figure 5). The high affinity for adsorption and redox reactivity of Mn oxides make them significant sinks for Cu in dynamic soil environment. The intermediate fractions FR4 and FR5 (Cu bound to amorphous Fe oxides and to crystalline Fe oxides) exhibited strong positive relations to concentrations of Fe oxides (AFeOx and TFeOx) and clay content. These significant relationships specifically demonstrate the control of pedogenically formed Fe oxides and fine-textured soils, particularly clay soils, in the long-term immobilization of Cu in soils.

Conversely, the less mobile fraction of Cu, namely FR6 (organic-bound) and FR7 (residual) showed strong positive correlations with clay content, CEC, carbonate content, total Fe/Mn oxides, but negative correlations with OM content. These trends suggest that, under processes such as OM decay and redox cycling of soil constituents, original Cu complexes may be transformed into more firmly bound metal oxides. Alternatively, the strong positive association of FR7 with all the mineral factors clearly indicates the geologically driven nature of the metal in the residual fraction to be solidly trapped in the silicate framework. These findings highlight the contrasting mechanisms of Cu mobility

and stabilization in horticultural versus field crop soils, underscoring the need for tailored management strategies in the Atabey Plain.



2-tailed correlation coefficient is significant at the 0.01 level (**) and 0.05 level (*) for N: 27.

Figure 4. Spearman correlation matrix between the soil properties and fractions

Risk Assessment

The contamination & ecological risk factors (Cf, RAC, & Er) collectively reflect a significantly different degree of Cu ecologically-related risk in HO compared to FC, in a manner that aligns also with Cu fractionation. Additionally, the values of the contamination factor (Cf) show that, while both HO & FC soils generally fall in the low contamination factor class, several HO sites that have higher values of Cf close to the moderate contamination category (Figure 5). These higher values correspond to increased concentrations of labile and moderately labile Cu fractions in HO soils that have long been treated with Cu-based fungicides. In contrast, most FC soils remain well below the contamination threshold.

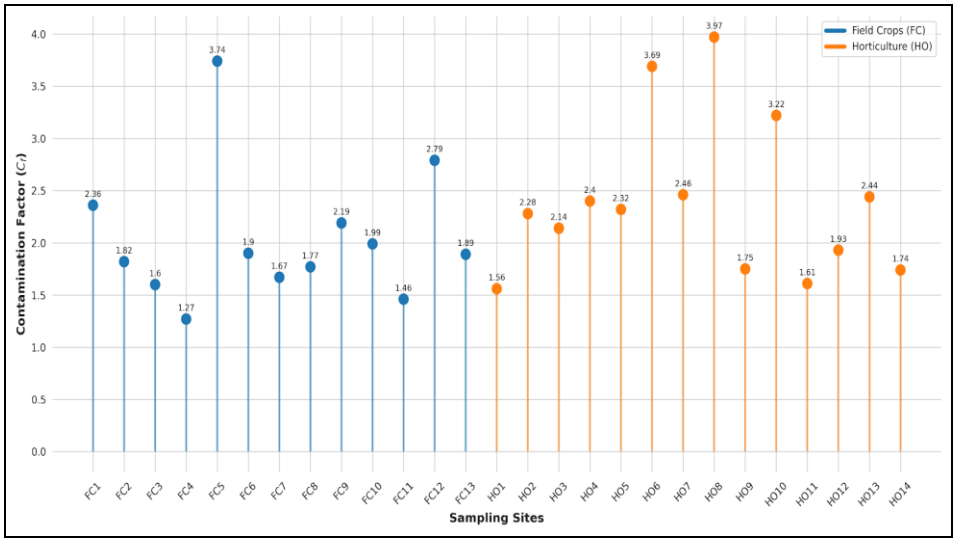


Figure 5. Contamination factor assessment of the soil samples

The risk assessment code (RAC), which evaluates the Cu proportion in mobile pools, further highlights distinction between the two management systems. In the majority of HO soils, the RAC values were in the low to moderate risk categories, although a subset approaches higher risk class due to the elevated proportion of FR1 - FR3 fractions (Figure 6). These results therefore indicate that there may be a significant proportion of the Cu in the HO in a form liable to short-term mobilization. Interestingly, soils with higher total Cu concentrations tend to exhibit lower RAC values.

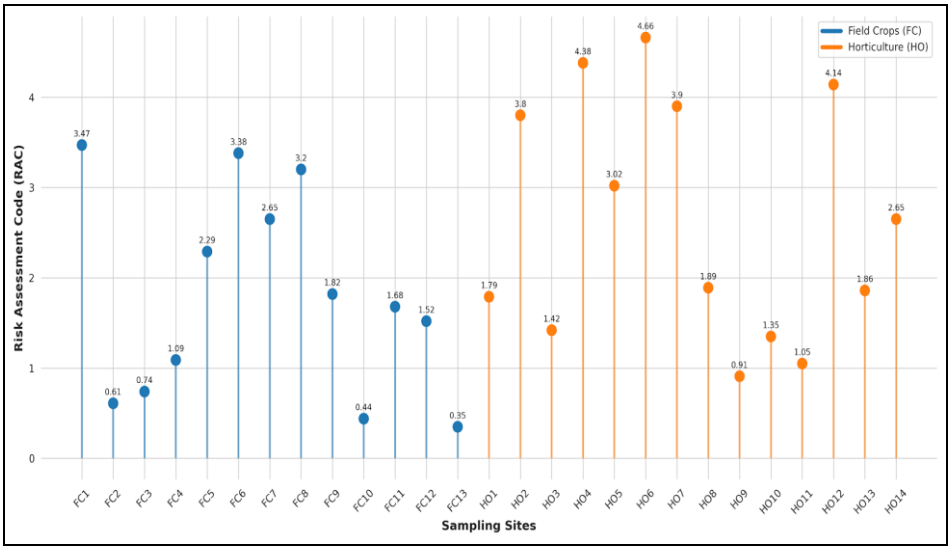


Figure 6. Soil risk assessment code

The ecological risk index (Er), a combination of the degree of contamination and toxicological factors, revealed that most soils had low to moderate ecological risk. Horticultural soils consistently showed the highest degree of Er (Figure 7). Although no site reached the high-risk category, elevated Er values in certain HO soils may reflect localized ecological concerns.

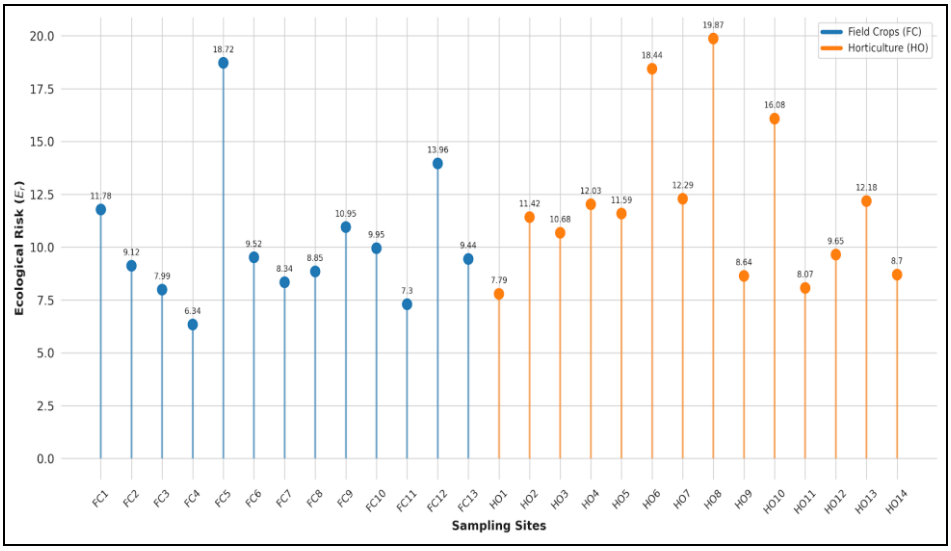


Figure 7. Soil ecological risk assessment

Taken together, the risk indicators demonstrate that the soils in the horticultural regions of the Atabey Plain represent the main Cu accumulation/mobility hotspots. Such a trend can be largely explained by the presence of anthropogenically driven inputs,

overlying the natural buffering capacity of the semi-arid Mediterranean soils. Conversely, FC soils show relatively low degree of contamination/mobility risk, being largely controlled by intrinsic soil properties rather than management-related external inputs. These results underlined the need for long-term monitoring of the different Cu fractions apart from the total concentrations in the soils of intensively cultivated HO sites.

Influence of Soil Physicochemical Properties on Copper Geochemistry

The main factors controlling the Cu geochemistry in the soils under investigation appear to be the unique physicochemical conditions of the calcareous soils. The dominance in the stable Cu fractions in these soils seems to fit well into the general metal mobility in alkaline environments. For instance, the main sink for Cu in calcareous soils was shown to be the carbonate fractions (Siddiqui and Khattak, 2010) due to specific adsorption and co-precipitation of Cu^{2+} ions on the carbonate surface. This explains the strong negative correlation between the carbonate fractions (FR2) and the CCE values in the current studies.

In semi-arid calcareous soils, however, the residual fraction together with the OM have been identified as the main pool for the retention of Cu ions. Jalali and Khanlari (2007) reported that, in contaminated calcareous soils, the residual fraction accounted for up to 41.1% of the total Cu ions in the soil profile, followed by the OM. The results of the current study are consistent with the established affinity between Cu ions and the organic compounds. Furthermore, Farshadirad et al. (2019) pointed out that the Cu ions in the larger aggregates (2.0-4.0mm) play a vital role in the availability of the Cu ions in calcareous soils. The apparent low percentage of the exchangeable Cu ions in the research findings complies with the characteristics of the alkaline soils, which readily convert Cu ions into less mobile fractions. Consequently, the Cu^{2+} ions become less mobile in the soil but establish a thermodynamically more stable organic and carbonate fractions.

Impact of Land Use and Crop Type on Metal Accumulation

The great variation in metal input between HO and FC management systems recorded in the current research has also been supported by the prevailing international literature. The higher Cu content in the HO soils was largely credited to the extensive application of pesticides, particularly Cu-based fungicides. Khan and Nafees (2017) have recorded that orchard soils receiving periodic fungicide applications contained significantly higher Cu concentrations (46.52-53.31 mg kg^{-1}) in comparison to non-orchard agricultural soils (11.18-20.71 mg kg^{-1}). This also matched the current findings, since the contamination degree of HO soils were moderate relative to FC soils. Likewise, the intensive agricultural practices in the Mediterranean region have been promoted to be greatly predisposed to high Cu contamination in the topsoil layers due to past fungicide applications (Peris et al., 2007). Additionally, the variation in metal uptake has a strong linkage to crop physiology. Horticultural crops, particularly leafy vegetables, act more as bioaccumulators. According to the findings presented by Singh et al. (2012), the uptake of heavy metals in spinach leaves was recorded to be significantly higher compared to legume-type field crops. This tendency is even more pronounced in FC with broad leaves, which undergo both root uptake and aerial deposition, as noted by Dala-Paula et al. (2018).

Source Apportionment via Chemometric Analysis

The application of PCA in the current research was successful in distinguishing the anthropogenic sources of Cu. Boruvka et al. (2005) have shown that PCA analysis enables the distinction of lithogenic origin (typically associated with residual fractions) from the anthropogenic inputs (associated with mobile fractions and surface enrichment). In the current research, the specific grouping of the horticultural soils in many particular principal components supports this approach. This finding was also validated by Davis et al. (2009) who used PCA to differentiate industrial-urban pollutants (e.g., Pb, Hg)

from the background natural levels (e.g., Ba, Mn) in topsoils. Similarly, Tume et al. (2018) used multivariate analysis in order to establish that Cr and Ni in urban soil have industrial origin, while other elements reflected natural backgrounds. Furthermore, modern studies incorporating PCA for the analysis of large-scale geochemical surveys also validated the application of PCA in distinguishing the unique geochemical signature of human activity. The correspondence of the relevant factors of Cu to the presented PCA suggests that the major factor of intensive agrochemical inputs exceeds the corresponding natural values in horticultural systems.

Environmental Risk and Management Implications

These risk assessment indices (Cf, RAC, and Er) collectively indicate the presence of localized Cu accumulation "hotspots" in horticultural systems, despite the overall low to medium risk of acute eco-toxicity. Although Cu is predominantly associated with thermodynamically stable fractions, there is the risk of re-mobilization. According to the study of Zinati et al. (2001), even if Cu in compost-treated calcareous soils tends to remain in residual forms despite the application of compost, the process of OM mineralization in the long term may lead to the re-mobilization of organically-bound Cu. This is a particularly relevant factor for our HO plots. Furthermore, excessive Cu bound to reducible fractions - mainly Mn/Fe oxides and acid-soluble carbonate fractions - may also pose potential problems (Piper, 1971). The sensitivity of Mn oxides to changing redox conditions may lead to seasonal periods of toxicity during irrigation cycles (Sparrow and Uren, 2014). Soil under FC, having a higher sand content but a lower CEC value, result in lower total Cu retention. But the lower buffering capacity in these soil types may indirectly indicate the possible ease of the applied Cu being mobilized. For the type of soil mentioned in the case of Jalali and Arfania (2011), the presence of heavy metals in the topsoil may pose a greater risk of contaminating the underground water in the form of more soluble salts when amendments that would make them more soluble are applied. Meanwhile, the in-situ approach to the problem for the two soil categories would require different strategies for their treatment. These would involve the control of copper application in the case of the soil under HO.

Study Limitations and Future Research Directions

Even though this study presents an in-depth evaluation of Cu fractionation and ecological risk under contrasting land use systems, several limitations must be highlighted. First, this study only focused on surface soils (0-20 cm) that primarily contain accumulated agrochemicals, while deeper redistribution processes were not evaluated. Second, ecological risk assessment was carried out using chemical fractionation indices (Cf, RAC, and Er) without incorporating direct biological response measures. Although fractionation methods are widely accepted for assessing mobility and ecological risk, their effectiveness would be improved by incorporating direct biological validation measures.

Future research should focus on improving knowledge on Cu accumulation associated with long-term use of Cu-based fungicides in horticultural systems. Future studies that include soil-plant transfer assessments must be carried out to generate useful information on actual exposure pathways associated with orchard management. Future investigations should also evaluate the effectiveness of alternative plant protection products, integrated pest management (IPM) strategies, and sustainable cultivation practices aimed at reducing Cu inputs and accumulation. Such research would contribute to the development of environmentally sustainable horticultural systems and improve the management of Cu in calcareous Mediterranean soils.

CONCLUSIONS

This study demonstrated that horticultural (HO) soils in the Atabey Plain contain higher total and mobile Cu concentrations than field

crop (FC) soils, primarily as a result of the long-term application of Cu-containing agrochemicals. The factors that dictate the migration and fixation of total Cu in the soils chiefly contain carbonate and Fe-Mn oxides. Even in the majority of soils, the ecological risk factors of Cf, RAC, and Er remain low. Some of the HO soils have localized moderately high ecological risks of contamination besides higher percentages of the more labile Cu fractions. All the above aspects clearly reveal the need for more continuous research into the speciation of Cu in soils instead of the total Cu content analysis. Additionally, there was a great need to decrease the application of Cu compounds in horticulture practices followed by efficient integrated pest management practices to promote the soil organic matter. Future research into the ecological risks of Cu in semi-arid Mediterranean regions of the country would also have to involve additional toxic elements in the studies.

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