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Copper contamination in agricultural soils: A review of the effects of climate, soil properties, and prolonged copper pesticide application in vineyards and orchards

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Abstract: Copper contamination stemming from copper-based pesticides poses a grave concern in vineyards and orchards, causing toxicity to soil organisms. Here, we present a comprehensive review of global data encompassing copper levels in these soils, coupled with variables such as the age of agricultural establishments, climate, soil organic matter content, soil pH, and farming practices (organic vs. conventional). The results suggest that there are three pivotal determinants driving copper content in vineyard and orchard soils: climate, the age of agricultural establishments, and soil organic matter content. It was impossible to estimate soil pH's effect on soil copper content because of its dependence on precipitation. Copper content in vineyard and orchard soils worldwide follows a direct correlation with precipitation while inversely correlating with aridity (i.e. potential evapotranspiration divided by precipitation). Furthermore, a clear linkage emerges between farm age and increased copper content in soils globally. Intriguingly, the increased soil organic matter content has shown inverse impacts on soil copper levels. These effects of soil properties on soil copper contents were discussed in terms of copper losses from soil *via* surface runoff. However, no discernible disparities in soil copper content between organic and conventional farming systems were found. This worldwide survey not only underscores the established influence of climate on European vineyards but also sheds novel light on the historical legacy of copper contamination in these landscapes.

Keywords: toxic effect; organic agriculture; conventional agriculture; soil organic carbon; soil remediation

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Copper-based pesticides have been used for over a century to combat bacterial and fungal diseases in crops. In 1880, Pierre Millardet serendipitously stumbled upon the Bordeaux mixture of $\text{CuSO}_4 + \text{Ca}(\text{OH})_2$ (Johnson 1935). Subsequent experiments confirmed its effectiveness against downy mildew (*Plasmopara viticola* (Berk & Curt.) Berl. & de Toni) at a relatively low cost. This discovery marked the advent of the first widely utilised fungicide. The success of the Bordeaux mixture paved the way for commercialising various other copper-based pesticides in modern agriculture, including copper oxychloride and copper octanoate (DuPont et al. 2023).

It is important to emphasise that a significant portion of copper-based pesticides does not firmly adhere to the surfaces of plants (Perez-Rodriguez et al. 2016). Instead, they tend to leach from the foliage, finding their way into the soil. This characteristic leads to a widespread issue of elevated copper levels in soils within vineyards and orchards worldwide (Schoffer et al. 2020).

The high toxicity of copper in soil poses a significant challenge for replanting. Studies have documented this problem for both grapevines (Coïc and Coppenet 1989, Romeu-Moreno and Mas 1999, Komárek et al. 2010, Ambrosini et al. 2015, Brunetto et al. 2019, Cesco et al. 2021) and citrus trees (Alva et al. 1993, 1995, 2000). This has prompted research into copper-based pesticide contamination in these agricultural settings, seeking solutions to overcome this obstacle to replanting (Duplay et al. 2014, Brunetto et al. 2016, Iñigo et al. 2020).

Inadvertent soil ingestion may represent an important pathway for human exposure to trace elements, such as through hand-to-mouth contact (Mielke 2016). In human health risk assessments, the US Environmental Protection Agency recommends using accidental soil ingestion rate estimates of 50 mg/day for children and 20 mg/day for adults (US EPA 2011). It must be emphasised that copper is generally considered safe for public health (Turnlund et al. 2005). Indeed, the regulatory limit for chronic daily copper intake (0.04 mg/kg/day) is considerably higher than that for arsenic (3×10^{-4} mg/kg/day), which is considered a highly toxic element for human health (US EPA 2002).

Under normal circumstances, overwhelming the human body's homeostatic defence mechanisms against copper toxicity through oral ingestion of this element is nearly impossible (Scheinberg 1979). However, instances of copper toxicity in humans

have been reported in cases where copper salt was ingested as part of suicidal attempts, in agricultural workers exposed to CuSO_4 , and when acidic food or beverages were allowed to remain in contact with metallic copper for prolonged periods (Scheinberg 1979, Van Campen 1991, Dameron and Howe 1998). Furthermore, cases of gastrointestinal illnesses have been reported following the consumption of potable water contaminated with copper (with a median level of about 3 mg/L of copper) (Dameron and Howe 1998).

In contrast, copper accumulation in vineyard and orchard soils is concerning. This enrichment can have toxic effects not only on young vines and trees but also on soil organisms. For instance, Van Zwieten et al. (2004) and Schoffer et al. (2024) documented the toxic effect of copper on earthworms exposed to soils treated with copper-based pesticides.

It must be emphasised that current soil remediation options for copper contamination offer limited effectiveness, such as metal phytoextraction (Santa-Cruz et al. 2023), or are complex and expensive, such as *in situ* immobilisation with synthetic sorbents (Smorkalov et al. 2023). This highlights the critical importance of prioritising a preventive approach to reducing the application rate of copper-based pesticides in vineyards and orchards to mitigate copper toxicity. Droz et al. (2021) discuss detailed strategies to achieve this reduction.

A study by Droz et al. (2021) concluded that precipitation and aridity are the key factors explaining the variance in soil copper content in European vineyards. Likewise, Romić et al. (2014) study discussed farm age's effect on soil copper content in Croatian vineyards. Although the studies by Romić et al. (2014) and Droz et al. (2021) significantly contributed to our understanding of factors influencing copper content in agricultural soils, their focus was confined to European vineyards. In the present review, we sought to broaden the geographical scope of data coverage and include vineyards and orchards. To this end, we reviewed worldwide data on copper content in vineyard and orchard soils, along with information on precipitation, aridity, and farm age.

Droz et al. (2021) proposed several hypothetical mechanisms through which soil pH and organic matter could potentially impact copper content in European vineyard soils. Therefore, in the context of the present study, we have included assessments of soil organic matter content and soil pH. This discussion on the effects of soil organic matter on copper mobility in soils focuses on oxic conditions

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typical of vineyards and orchards due to the sensitivity of crops to waterlogging stress (Kreuzwieser and Rennenberg 2014, Salvatierra et al. 2020). The effects of organic matter on copper (im)mobilisation under suboxic conditions are addressed elsewhere (Mehlhorn et al. 2018).

We also assessed the impact of different farming systems on copper content in vineyard and orchard soils. Some researchers have previously compared soil copper levels between organic and conventional vineyards (Probst et al. 2008, Steinmetz et al. 2017). However, these comparisons were constrained by a limited number of data points ($n = 8$ and $n = 9$, respectively). To address this limitation, we conducted a comprehensive review of global data pertaining to copper content in soils from organic ($n = 38$) and conventional ($n = 77$) vineyards and orchards.

DATABASES

In the first database ($n = 157$, Online Supplementary Table 2), we included studies that provided clear indications of (1) the geographical location of the study; (2) the age of the vineyard/orchard (hereafter referred to as "age of the farm" or "farm age"), and (3) the total copper content in the topsoil. In this context, the "age of the farm" refers to the cumulative duration the land has been under cultivation as a vineyard or orchard rather than the current age of the vines or fruit trees. Although growers periodically renew their vines and trees (Brunetto et al. 2019), our analysis is concerned with the overall time the land has been utilised as a vineyard/orchard. The term "total copper content in the topsoil" pertains

to the copper content present within the vineyard or orchard rows, excluding the copper content between the rows. Furthermore, we have incorporated available information on soil pH and soil organic matter.

To assess the influence of geographical areas (Europe, Asia, Oceania, the Americas) and crop types (vineyards and orchards) on total soil copper, we opted for the Kruskal-Wallis test due to the imbalanced number of observations available in different categories for comparison. For instance, there were 43 observations for orchards *versus* 113 observations for vineyards, requiring the use of non-parametric statistical analysis, such as the Kruskal-Wallis test. The results showed that total soil copper content was statistically significantly higher ($P < 0.05$) in South America (median of 456 mg/kg) compared to the rest of the world (median ≤ 60 mg/kg) (Table 1). It is worth noting that the South American data are exclusive to Brazil, where the prevalence of downy mildew is more severe due to the humid climate, requiring higher doses of copper-based pesticides (Komárek et al. 2010). Conversely, there was no statistical difference ($P > 0.05$) between vineyards and orchards concerning total soil copper content in the first database.

In the second database ($n = 116$, Online Supplementary Table 3), we included studies documenting soil copper levels in conventional and organic vineyards/orchards. While some of the papers did not explicitly state "conventional" management, they did reference the use of synthetic products (e.g., synthetic pesticides), which are prohibited in organic farming (European Commission 1991, Ministério da Agricultura 2014). These farms were classified under

Table 1. Distribution of total soil copper in the first database by geographical areas and crop types

Category of the variable	<i>n</i>	Total soil copper (mg/kg)		
		median	mean \pm SD	range
Geographical area				
Asia	17	30 ^A	54 \pm 44	4–148
Europe	85	58 ^A	85 \pm 91	2–442
North America	23	60 ^A	88 \pm 73	5–257
Oceania	10	60 ^A	62 \pm 147	13–126
South America	21	456 ^B	570 \pm 603	33–2 198
Crop type				
Orchard	43	63 ^A	77 \pm 61	4–257
Vineyard	113	72 ^A	171 \pm 329	2–2 198

Mean \pm standard deviation (SD), range, and the number of observations (*n*) are shown. In the median column, different letters for the same group indicate statistically significant differences between categories (Kruskal-Wallis test, $P < 0.05$)

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the "conventional" category in such instances. Two studies that reported data on biodynamic vineyards (Di Giacinto et al. 2020, Hendgen et al. 2020) were categorised as "organic". Three studies that reported data on integrated vineyard management (Di Giacinto et al. 2020, Hendgen et al. 2020, Porizka et al. 2021) were classified as "conventional". These categorisations were based on integrated pest management practices incorporating chemical methods when biological approaches are deemed inadequate or ineffective (Porizka et al. 2021). To ensure consistency, we excluded studies involving vineyards/orchards that transitioned between different farming systems during their cultivation history. For example, if a farm began as conventional and subsequently converted to organic, we excluded it from our analysis.

None of the selected articles addressed pollution resulting from mining activities that might impact copper content in the studied soils. However, we specifically excluded articles that discussed the utilisation of animal manure (e.g., Sonoda et al. 2019, Pham et al. 2022) due to its potential to contribute to copper accumulation in the soil (Ramos et al. 2006, Yamamoto et al. 2018). Despite this exclusion, we opted to include farms in the database where animal manure was used, provided the authors indicated that its usage was limited and insufficient to account for soil copper enrichment (Fan et al. 2011, Wang et al. 2015).

Using the geographical locations of the chosen studies, climate data were obtained from the National Aeronautics and Space Administration Power project (Prediction of Worldwide Energy Resources), accessible at <https://power.larc.nasa.gov>. Specifically, data regarding monthly precipitation, as well as monthly mean maximum and minimum temperatures, were retrieved. For each study in the database, climate data for the ten years preceding its publication were taken into account.

Using the climate data, the mean annual precipitation over the course of ten years was computed (hereafter referred to as "precipitation" for simplicity). Similarly, the mean aridity index (AI) over a ten-year span was computed according to Droz et al. (2021):

$$AI = \frac{ET_0}{P} \quad (1)$$

where: ET_0 – 10-year mean annual potential evapotranspiration (mm); P – 10-year mean annual precipitation (mm). The aridity index is thus unitless. ET_0 was calculated using the "SPEI" package of the RStudio version 1.4.1106, modified from the method of Hargreaves et al. (1985), according to Droogers and Allen (2002):

$$ET_0 = 0.0013 \times 0.408 RA \times (T_{avg} + 17.0) \times (TD - 0.0123 P)^{0.76} \quad (2)$$

where: RA – amount of extraterrestrial radiation ($MJ/m^2/d$); T_{avg} – daily mean temperature ($^{\circ}C$) defined as the average of the daily maximum and minimum mean temperatures; TD ($^{\circ}C$) – temperature range calculated as the difference between the daily maximum and minimum mean temperatures; P – monthly precipitation (mm).

DATA ANALYSIS

The copper content within the examined soils did not follow a normal distribution but exhibited a log-normal pattern. This type of metal content distribution in the soil is typical of anthropogenically contaminated environments (Ott 1990). In such a case of log-normal pattern, the classical mode of statistical analysis involves log transformation of the response variable and the predictor variables before regression analysis (Draper and Smith 1998). The problem with this method is one of interpretation. Fitted values, as well as parameter estimates, are in terms of the log response. This obstacle often proves to be inconvenient (Kutner et al. 2004). A better approach is to internalise the log transformation of the response within the model itself. The log link exponentiates the linear predictor rather than log-transforming the response to linearise the relationship between the response and predictors. This procedure, implicit within the generalised linear model algorithm, allows easy estimates and fitted values interpretation (Hardin and Hilbe 2018).

Therefore, the statistical analysis of the first database involved a generalised linear model of the Gaussian family, with a log-link function, using the "glm2" package in RStudio version 1.4.1106. In this model, the response is expressed as the logarithm of the expected values of the response variable (Hardin and Hilbe 2018).

Our analysis identified a strong negative Pearson correlation (-0.61 , $P < 0.001$) between precipitation and soil pH (Table 2). This aligns with established knowledge about the effects of precipitation on soil pH, with arid regions generally exhibiting neutral or alkaline soils and humid regions having acidic soils (Figueroa and Neaman 2023). It is important to consider this correlation, as r values above 0.7 introduce collinearity into statistical models (Belinda and Peat 2014, Young 2017).

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Table 2. Pearson correlations between the variables of the first database

	Total soil Cu	Farm age	Precipitation	Aridity index	pH	Soil organic matter
Total soil Cu	ns					
Farm age	0.56***	ns				
Precipitation	0.50***	0.25**	ns			
Aridity index	-0.27**	ns	-0.75***	ns		
pH	-0.23**	-0.24**	-0.61***	0.43***	ns	
Soil organic matter	ns	ns	ns	-0.20*	ns	ns

Statistically significant correlations are shown in **bold** (*** $P < 0.001$; ** $P < 0.01$; * $P < 0.05$). ns – not statistically significant

While the absolute value of Pearson correlation between precipitation and soil pH ($r = 0.61$) fell below the commonly used multicollinearity threshold of 0.7, we opted to exclude soil pH from the model with precipitation. This decision was applied similarly to the aridity, even though its correlation with soil pH was weaker ($0.43, P < 0.001$). Consequently, our analysis could not estimate the effect of soil pH on copper content in the studied soils.

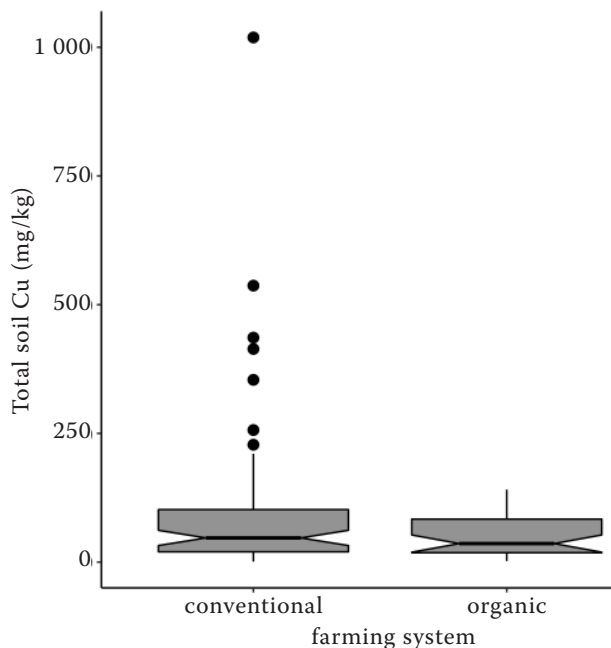


Figure 1. Copper content in the soils was studied as a function of a farming system. The box plots show the lower, median and upper quartile, with whiskers extending to the most extreme data points, while circles represent outliers. The notches display confidence intervals around the median, which are calculated based on the formula: median \pm 1.58* interquartile range/square root of n . Overlapping notches indicate that the medians do not differ statistically

The aridity index, as expected, exhibited a strong negative correlation with precipitation (Table 2) due to its dependence on precipitation in its calculation (Eq. 1). Therefore, we excluded both variables from the same model to avoid redundancy. In all other cases, correlations between other investigated variables – farm age, precipitation (or aridity index, depending on the model), and soil organic matter – remained relatively weak ($r \leq 0.25$, Table 2). This allowed us to incorporate these variables in the model without concerns about multicollinearity.

The data in the second database were analysed using the Kruskal-Wallis test to compare the two management types (organic and conventional), with soil copper content as the response variable. In addition, in order to enhance visual comprehension of the obtained results (Figure 1), we created a boxplot with notches (Marmolejo-Ramos and Tian 2010) using the "ggplot2" package in RStudio version 1.4.1106. The notches display confidence intervals around the median, which are calculated based on the formula: median \pm 1.58* interquartile range/square root of n . Overlapping notches indicate that the medians do not differ statistically (Marmolejo-Ramos and Tian 2010).

THE EFFECTS OF CLIMATE AND FARM AGE

The following equations were obtained for the first database, where Cu_t is total soil copper:

$$\log \text{ expected value of } Cu_t = 5.8 + 0.02 \text{ farm age} - 0.80 \text{ aridity index} \quad (3)$$

$$\log \text{ expected value of } Cu_t = 1.7 + 0.01 \text{ farm age} + 0.002 \text{ precipitation} \quad (4)$$

where: total soil copper is measured in mg/kg, farm age is measured in years, precipitation is measured in mm, and the aridity index is unitless. Eqs. 3 and 4 explained 47% and 60%

of the expected values of total soil copper, respectively, and all predictor variables were highly statistically significant ($P < 0.001$) (Tables 3 and 4), respectively.

Our review suggests that climatic effects have a more pronounced impact in humid regions, where the prevalence of downy mildew is more severe, requiring higher doses of copper-based pesticides (Komárek et al. 2010). As mentioned above, the aridity index has an inverse correlation with precipitation (Eq. 1 in the Databases section and Table 2), which explains the negative sign in Eq. 3. The results derived from the global dataset of vineyards and orchards in this study align with those reported by Droz et al. (2021) for European vineyards. Furthermore, our study provides evidence that the age of the farm plays a pivotal role in influencing copper content in vineyard and orchard soils, echoing the findings of Romić et al. (2014) for Croatian vineyards.

THE EFFECT OF SOIL ORGANIC MATTER

The following equations best explain the variance of total soil copper content in the studied soils, where Cu_t is total soil copper, and SOM is soil organic matter:

$$\log \text{ expected value of } Cu_t = 7.5 + 0.03 \text{ farm age} - 1.7 \text{ aridity index} - 0.23 \text{ SOM} \quad (5)$$

$$\log \text{ expected value of } Cu_t = -0.57 + 0.02 \text{ farm age} + 0.004 \text{ precipitation} - 0.30 \text{ SOM} \quad (6)$$

where: total soil copper is measured in mg/kg, farm age is measured in years, precipitation is measured in mm, and the aridity index is unitless. Eqs. 5 and 6 explained 59% and 74% of the expected values of total soil copper, respectively, and all predictor variables were highly statistically significant ($P < 0.001$) (Tables 5 and 6), respectively.

It is well-established that rainfall can amplify the export of copper-based pesticides from soils *via* surface runoff (Palleiro et al. 2012). Copper can be

exported from the soil through two primary mechanisms: (1) as dissolved copper complexed by dissolved organic carbon, and/or (2) as copper absorbed onto organic matter particles within the soil solid phase (Babcsányi et al. 2016, Imfeld et al. 2020).

It is worth emphasising the negative sign of soil organic matter in Eqs. 5 and 6, suggesting that an increase in soil organic matter content contributes to copper losses from the soil, either indirectly by promoting the formation of dissolved organic substances in the soil solution that complex copper ions, or directly by binding copper to soil organic matter in the solid phase.

These mechanisms align with observations in European soils (Babcsányi et al. 2014, 2016). These studies demonstrated that increased soil organic matter content promotes copper losses *via* runoff. Similarly, Shi and Schulin (2019) reported that dissolved organic carbon (DOC) plays a role in copper losses through surface runoff from arable soils. Their study showed that adding organic residue to soil reduced runoff during heavy rainfall, but the runoff from these amended soils had higher concentrations of DOC and copper compared to the control.

Shi and Schulin (2019) highlight the complex role of soil organic matter in influencing surface runoff and subsequent copper losses. They reveal a double-edged sword effect: soil organic matter reduces surface runoff during rainfall events, but it also increases copper concentrations in the runoff by forming copper complexes with dissolved organic matter. Considering this long-term effect, our analysis suggests a net negative relationship between soil organic matter content and total copper concentration in vineyard and orchard soils.

However, our results diverge from other investigations that reveal a positive correlation between soil organic matter and soil copper content at a regional

Table 3. Results of the generalised linear model of the Gaussian family, with a log-link function (Eq. 3). Response variable: log expected value of total soil copper

Coefficient	Estimate	Standard error	P-value
(Intercept)	5.8438	0.3155	< 2e-16
Aridity index	-0.7982	0.1703	6.9e-12
Farm age	0.0189	0.0017	< 2e-16

Null deviance: 12647188 on 163 d.f.; residual deviance: 6702651 on 161 d.f.; Akaike information criterion (AIC): 2214.8; R^2 : 0.47

Table 4. Results of the generalised linear model of the Gaussian family, with a log-link function (Eq. 4). Response variable: log expected value of total soil copper

Coefficient	Estimate	Standard error	P-value
(Intercept)	1.7187	0.4814	0.00047
Precipitation	0.0024	0.0003	3.15e-12
Farm age	0.0134	0.0014	< 2e-16

Null deviance: 12647188 on 163 d.f.; residual deviance: 5065231 on 161 d.f.; Akaike information criterion (AIC): 2168.9; R^2 : 0.60

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Table 5. Results of the generalised linear model of the Gaussian family, with a log-link function (Eq. 5). Response variable: log expected value of total soil copper

Coefficient	Estimate	Standard error	P-value
(Intercept)	7.4558	0.4432	< 2e-16
Aridity index	-1.7107	0.3037	9.74e-08
Farm age	0.0271	0.0032	2.26e-14
SOM	-0.2317	0.0540	3.33e-05

SOM – soil organic matter; Null deviance: 12308080 on 139 d.f.; residual deviance: 5021333 on 136 d.f.; Akaike information criterion (AIC): 2214.8; R^2 : 0.59

scale in European soils (Duplay et al. 2014, Ballabio et al. 2018). This discrepancy underscores the nuanced nature of the relationship. Consequently, this global review provides new insights into the intricate effects of soil organic matter on soil copper contents globally.

On the other hand, it is widely acknowledged that surface runoff is more pronounced in regions with higher levels of rainfall (Youlton et al. 2010). In this context, it is worth noting that in our analysis, the interaction term SOM \times precipitation exhibited a negative sign and was found to be statistically significant ($P < 0.001$) (Table 6). This suggests that the loss of copper from the soil *via* surface runoff is more likely to occur with increased precipitation.

Likewise, the interaction term SOM \times aridity index exhibited a positive sign and was statistically significant ($P < 0.05$) (Table 5), suggesting that the loss of copper from the soil *via* surface runoff is reduced in more arid conditions. These findings are consistent with the mechanism of losses of copper-based pesticides from soil by surface runoff, which tends to be greater in regions with higher levels of rainfall.

Rainfall acts as a double-edged sword, encouraging copper pesticide export through runoff while driving down mildew outbreaks that necessitate higher pesticide use (Komárek et al. 2010). Our analysis suggests this dual effect results in a net positive relationship between precipitation and copper content in vineyard and orchard soils in humid regions.

CONVENTIONAL VS. ORGANIC FARMING

It is important to emphasise that the use of naturally occurring copper sulfates is permitted in organic agriculture (Barker 2010). However, the use of copper sulfate in organic farming remains a subject of controversy (Lamichhane et al. 2018), and until this

Table 6. Results of the generalised linear model of the Gaussian family, with a log-link function (Eq. 6). Response variable: log expected value of total soil copper

Coefficient	Estimate	Standard error	P-value
(Intercept)	-0.5741	0.6190	0.355
Precipitation	0.0044	0.0004	< 2e-16
Farm age	0.0204	0.0018	< 2e-16
SOM	-0.3048	0.0348	6.81e-15

SOM – soil organic matter; Null deviance: 12308080 on 139 d.f.; Residual deviance: 3165893 on 136 d.f.; Akaike information criterion (AIC): 1811; R^2 : 0.74

controversy is addressed, the broader adoption of organic farming could be hindered. In this study, we observed no statistically significant difference ($P > 0.05$) between organic and conventional management concerning the total copper content in soils, as determined by the Kruskal-Wallis test. Notably, the data from conventional farming exhibited several outliers (Figure 1).

In addition to curbing the use of copper-based pesticides, it is crucial to encourage the search for alternatives to copper compounds. In conventional agriculture, such alternatives might encompass nanoparticle-based metallic formulations (Lamsal et al. 2011). In the context of organic agriculture, options are somewhat more constrained and may involve the use of biological control agents (Dagostin et al. 2011) or the cultivation of pathogen-resistant crop genotypes (Cesco et al. 2021).

In certain countries, including the EU, the use of copper pesticides is tightly regulated within both conventional and organic farming practices (European Commission 2018). This is why soil contamination resulting from copper is more severe in countries lacking such regulations. A pertinent example is Chile, where copper-based pesticides are employed according to guidelines provided on product labels. Unfortunately, these guidelines do not include any information on the potential adverse effects of these compounds on soil or aquatic organisms. Notably, in Chile, applying copper-based pesticides is mandatory under certain circumstances (SAG 2017) to manage *Pseudomonas syringae* pv. *actinidiae*. However, a regulatory authority overseeing soil quality is non-existent. Therefore, there is an urgent need to expedite the establishment of regulations on the use of copper pesticides in conventional agriculture in Chile and other countries that currently lack such directives.

POSSIBLE OTHER FACTORS

Several additional factors, such as soil texture and topography, have been recognised as influential contributors to soil copper content in agricultural soils (Ballabio et al. 2018). Similarly, various agricultural practices, including mulching, could serve as potential confounding factors in our analysis. Notably, mulch can act as a protective barrier, impeding the incorporation of copper-containing pesticides into soils (Schoffer et al. 2020, 2021, 2022). Regrettably, comprehensive information on these factors was not uniformly available across all studies incorporated into this review. Consequently, our ability to assess the nuanced influence of these factors in our global review was constrained, underscoring the need for future studies to provide further depth to our findings.

Furthermore, elevated concentrations of potentially toxic elements in soils cannot solely be attributed to anthropogenic influences; they can also be linked to the natural abundance of these elements in the soil's parent rock (Novoselov et al. 2022). While it is well-established that the composition of soil parent material impacts the concentrations of trace elements in soils (Tapia-Gatica et al. 2022), specific patterns for different rock types remain undefined, given the significant variability in geochemical data across various rock types (GEOROC 2021).

However, the majority of studies examining copper content in vineyard and orchard soils have overlooked the reporting of rock lithology. While large-scale global lithological maps provide valuable insights, they often lack the resolution needed for farm-level analysis (Hartmann and Moosdorf 2012). Rock types can vary significantly within the confines of a single farm, rendering these broad-scale maps insufficient for capturing this crucial detail. Given the unavailability of detailed lithological maps for accurate assessments at the farm scale for our study areas, we could not estimate the impact of rock lithology on soil copper content. Consequently, a notable gap exists in the current understanding of the impact of soil parent rock on the natural copper levels within agricultural soils.

CONCLUSION

This review underscores the presence of at least three key factors influencing soil copper content in vineyards and orchards: (1) climate; (2) farm age, and (3) soil organic matter. The analysis has demonstrated that soil copper content in vineyards

and orchards worldwide is directly proportional to precipitation while inversely impacted by aridity. Furthermore, older farms have been associated with elevated copper content in vineyard and orchard soils on a global scale. Likewise, the increased soil organic matter content has shown inverse impacts on soil copper levels. These effects of soil properties on soil copper contents were discussed in terms of copper losses from soil *via* surface runoff. Finally, no statistically significant distinction between organic and conventional vineyards and orchards about soil copper content has emerged.

This comprehensive overview of vineyards and orchards worldwide not only reaffirms earlier findings regarding the influence of climate and farm age on soil copper content in European vineyards but also introduces novel insights into the importance of vineyard and orchard farming type and the effects of soil processes on copper losses from soil *via* surface runoff.

SUPPLEMENTARY DATA

Supplementary data to this article can be found [online](#).

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REFERENCES

- Alva A.K., Graham J.H., Tucker D.P.H. (1993): Role of calcium in ameliorating copper phytotoxicity for citrus. *Soil Science*, 155: 211–218.
- Alva A.K., Graham J.H., Anderson C.A. (1995): Soil pH and copper effects on young 'Hamlin' orange trees. *Soil Science Society of America Journal*, 59: 481–487.
- Alva A.K., Huang B., Paramasivam S. (2000): Soil pH affects copper fractionation and phytotoxicity. *Soil Science Society of America Journal*, 64: 955–962.
- Ambrosini V.G., Rosa D.J., Prado J.P.C., Borghezani M., de Melo G.W.B., Soares C., Comin J.J., Simao D.G., Brunetto G. (2015): Reduction of copper phytotoxicity by liming: a study of the root anatomy of young vines (*Vitis labrusca* L.). *Plant Physiology and Biochemistry*, 96: 270–280.
- Babcsányi I., Chabaux F., Granet M., Meite F., Payraudeau S., Duplay J., Imfeld G. (2016): Copper in soil fractions and runoff in a vineyard catchment: insights from copper stable isotopes. *Science of the Total Environment*, 557: 154–162.
- Babcsányi I., Imfeld G., Granet M., Chabaux F. (2014): Copper stable isotopes to trace copper behavior in wetland systems. *Environmental Science and Technology*, 48: 5520–5529.

<https://doi.org/10.17221/501/2023-PSE>

- Ballabio C., Panagos P., Lugato E., Huang J.H., Orgiazzi A., Jones A., Fernández-Ugalde O., Borrelli P., Montanarella L. (2018): Copper distribution in European topsoils: an assessment based on LUCAS soil survey. *Science of the Total Environment*, 636: 282–298.
- Barker A.V. (2010): *Science and Technology of Organic Farming*. Boca Raton, CRC Press, 224. ISBN 978-1-4398-1612-7
- Belinda B., Peat J. (2014): *Medical Statistics: A Guide to SPSS, Data Analysis, and Critical Appraisal*. Hoboken, John Wiley and Sons, 392. ISBN: 978-1-118-58993-9
- Brunetto G., de Melo G.W.B., Terzano R., Del Buono D., Astolfi S., Tomasi N., Pii Y., Mimmo T., Cesco S. (2016): Copper accumulation in vineyard soils: rhizosphere processes and agronomic practices to limit its toxicity. *Chemosphere*, 162: 293–307.
- Brunetto G., Rosa D.J., Ambrosini V.G., Heinzen J., Ferreira P.A.A., Ceretta C.A., Soares C., Melo G.W.B., Soriani H.H., Nicoloso F.T., Farias J.G., De Conti L., Silva L.O.S., Santana N., Couto R.R., Jacques R.J.S., Tiecher T.L. (2019): Use of phosphorus fertilization and mycorrhization as strategies for reducing copper toxicity in young grapevines. *Scientia Horticulturae*, 248: 176–183.
- Cesco S., Pii Y., Borruso L., Orzes G., Lugli P., Mazzetto F., Genova G., Signorini M., Brunetto G., Terzano R., Vigani G., Mimmo T. (2021): A smart and sustainable future for viticulture is rooted in soil: how to face Cu toxicity. *Applied Sciences-Basel*, 11: 907.
- Coïc Y., Coppenet M. (1989): *Les Oligo-éléments en Agriculture et Élevage: Incidence sur la Nutrition Humaine*. Versailles, National Institute of Agricultural Research, 144.
- Dagostin S., Scharer H.J., Pertot I., Tamm L. (2011): Are there alternatives to copper for controlling grapevine downy mildew in organic viticulture? *Crop Protection*, 30: 776–788.
- Dameron C., Howe P.D. (1998): *Copper*. Environmental Health Criteria, 200. Geneva, World Health Organization.
- Di Giacinto S., Friedel M., Poll C., Doring J., Kunz R., Kauer R. (2020): Vineyard management system affects soil microbiological properties. *Oeno One*, 54: 131–143.
- Draper N.R., Smith H. (1998): *Applied Regression Analysis*. Wiley Series in Probability and Statistics. 3rd Edition. New York, Wiley-Interscience. ISBN:9780471170822
- Droogers P., Allen R.G. (2002): Estimating reference evapotranspiration under inaccurate data conditions. *Irrigation and Drainage Systems*, 16: 33–45.
- Droz B., Payraudeau S., Martin J.A.R., Toth G., Panagos P., Montanarella L., Borrelli P., Imfeld G. (2021): Copper content and export in european vineyard soils influenced by climate and soil properties. *Environmental Science and Technology*, 55: 7327–7334.
- Duplay J., Semhi K., Errais E., Imfeld G., Babcsanyi L., Perrone T. (2014): Copper, zinc, lead and cadmium bioavailability and retention in vineyard soils (Rouffach, France): the impact of cultural practices. *Geoderma*, 230: 318–328.
- DuPont S.T., Cox K., Johnson K., Peter K., Smith T., Munir M., Baro A. (2023): Evaluation of biopesticides for the control of *Erwinia amylovora* in apple and pear. *Journal of Plant Pathology*. (In Press)
- Fan J.H., He Z.L., Ma L.N.Q., Stoffella P.J. (2011): Accumulation and availability of copper in citrus grove soils as affected by fungicide application. *Journal of Soils and Sediments*, 11: 639–648.
- Figueroa L., Neaman A. (2023): Saline, yet acidic: a quirky soil combo in the Lluta valley in northern Chile. *Idesia (Chile)*, 41: 133–137.
- GEOROC (2021): Database, Geochemistry of Rocks of the Oceans and Continents. Mainz, Max Planck Institute for Chemistry. Available at: <http://georoc.mpch-mainz.gwdg.de/georoc/>
- Hardin J.W., Hilbe J.M. (2018): *Generalized Linear Models and Extensions*. 4th Edition. College Station, Stata Press. ISBN-10: 1-59718-225-7
- Hargreaves G.L., Hargreaves G.H., Riley J.P. (1985): Agricultural benefits for Senegal river basin. *Journal of Irrigation and Drainage Engineering*, 111: 113–124.
- Hartmann J., Moosdorf N. (2012): The new global lithological map database GLiM: a representation of rock properties at the Earth surface. *Geochemistry, Geophysics, Geosystems*, 13: 4370.
- Hendgen M., Doring J., Stohrer V., Schulze F., Lehnart R., Kauer R. (2020): Spatial differentiation of physical and chemical soil parameters under integrated, organic, and biodynamic viticulture. *Plants-Basel*, 9: 1361.
- Imfeld G., Meite F., Wiegert C., Guyot B., Masbou J., Payraudeau S. (2020): Do rainfall characteristics affect the export of copper, zinc and synthetic pesticides in surface runoff from headwater catchments? *Science of the Total Environment*, 741: 140437.
- Iñigo V., Marín A., Andrades M., Jiménez-Ballesta R. (2020): Evaluation of the copper and zinc contents of soils in the vineyards of La Rioja (Spain). *Environments*, 7: 55.
- Johnson G.F. (1935): The early history of copper fungicides. *Agricultural History*, 9: 67–79.
- Komárek M., Cadkova E., Chrastny V., Bordas F., Bollinger J.C. (2010): Contamination of vineyard soils with fungicides: a review of environmental and toxicological aspects. *Environment International*, 36: 138–151.
- Kreuzwieser J., Rennenberg H. (2014): Molecular and physiological responses of trees to waterlogging stress. *Plant, Cell and Environment*, 37: 2245–2259.
- Kutner M., Nachtsheim C., Neter J. (2004): *Applied Linear Regression Models*. Boston, McGraw-Hill Education, 701.
- Lamichhane J.R., Osdaghi E., Behlau F., Kohl J., Jones J.B., Aubertot J.N. (2018): Thirteen decades of antimicrobial copper compounds applied in agriculture. a review. *Agronomy for Sustainable Development*, 38: 28.
- Lamsal K., Kim S., Jung J.H., Kim Y.S., Kim K.S., Lee Y.S. (2011): Inhibition effects of silver nanoparticles against powdery mildews on cucumber and pumpkin. *Mycobiology*, 39: 26–32.
- Marmolejo-Ramos F., Tian T.S. (2010): The shifting boxplot. A boxplot based on essential summary statistics around the mean. *International Journal of Psychological Research*, 3: 37–45.

<https://doi.org/10.17221/501/2023-PSE>

- Mehlhorn J., Besold J., Pacheco J.S.L., Gustafsson J.P., Kretzschmar R., Planer-Friedrich B. (2018): Copper mobilization and immobilization along an organic matter and redox gradient—insights from a Mofette site. *Environmental Science and Technology*, 52: 13698–13707.
- Mielke H.W. (2016): Nature and extent of metal-contaminated soils in urban environments (keynote talk). *Environmental Geochemistry and Health*, 38: 987–999.
- Ministério da Agricultura (2014): Instrução Normativa nº 17, de 18 de junho de 2014. Estabelece o regulamento técnico para os Sistemas Orgânicos de Produção, bem como as listas de substâncias e práticas permitidas para uso nos Sistemas Orgânicos de Produção. Brasília, DF, Diário Oficial da União, Ministério da Agricultura, Pecuária e Abastecimento, 32 pp.
- Novoselov A.A., Hodson M.E., Tapia-Gatica J., Dovletyarova E.A., Yáñez C., Neaman A. (2022): The effect of rock lithology on the background concentrations of trace elements in alluvial soils: implications for environmental regulation. *Applied Geochemistry*, 146: 105440.
- Ott W.R. (1990): A physical explanation of the lognormality of pollutant concentrations. *Journal of the Air and Waste Management Association*, 40: 1378–1383.
- Palleiro L., Rodriguez-Blanco M.L., Taboada-Castro M.M., Taboada-Castro M.T. (2012): Dissolved and particulate metals in the Mero River (NW Spain): factors affecting concentrations and load during runoff events. *Communications in Soil Science and Plant Analysis*, 43: 88–94.
- Perez-Rodriguez P., Soto-Gomez D., De La Calle I., Lopez-Periago J.E., Paradelo M. (2016): Rainfall-induced removal of copper-based spray residues from vines. *Ecotoxicology and Environmental Safety*, 132: 304–310.
- Pham N.T.H., Babcsányi I., Balling P., Farsang A. (2022): Accumulation patterns and health risk assessment of potentially toxic elements in the topsoil of two sloping vineyards (Tokaj-Hegyalja, Hungary). *Journal of Soils and Sediments*, 22: 2671–2689.
- Porizka J., Divis P., Stursa V., Puncocharova L., Slavikova Z., Krikala J. (2021): Impact of organic and integrated pest management on the elemental composition of wine and grapes in a season with high fungal pressure. *Journal of Elementology*, 26: 871–891.
- Probst B., Schuler C., Joergensen R.G. (2008): Vineyard soils under organic and conventional management – microbial biomass and activity indices and their relation to soil chemical properties. *Biology and Fertility of Soils*, 44: 443–450.
- Ramos M.C., Quinton J.N., Tyrrel S.F. (2006): Effects of cattle manure on erosion rates and runoff water pollution by faecal coliforms. *Journal of Environmental Management*, 78: 97–101.
- Romeu-Moreno A., Mas A. (1999): Effects of copper exposure in tissue cultured *Vitis vinifera*. *Journal of Agricultural and Food Chemistry*, 47: 2519–2522.
- Romić M., Matijević L., Bakić H., Romić D. (2014): Copper accumulation in vineyard soils: distribution, fractionation and bioavailability assessment. In: Hernández-Soriano M.C. (ed.): *Environmental Risk Assessment of Soil Contamination*. London, IntechOpen, 799–826. ISBN: 978-953-51-1235-8
- SAG (2017): Resolución exenta No.: 6132/2017. Actualiza y consolida las medidas fitosanitarias para el control obligatorio de la plaga *Pseudomonas syringae* pv. *Actinidiae* (psa), y deroga resoluciones 2.151 y 2.152 de 2013 y sus modificaciones correspondientes. Santiago, Chile Servicio Agrícola y Ganadero, 12 pp.
- Salvatierra A., Toro G., Mateluna P., Opazo I., Ortiz M., Pimentel P. (2020): Keep calm and survive: adaptation strategies to energy crisis in fruit trees under root hypoxia. *Plants-Basel*, 9: 1108.
- Santa-Cruz J., Robinson B., Krutyakov Y.A., Shapoval O.A., Penaloza P., Yanez C., Neaman A. (2023): An assessment of the feasibility of phytoextraction for the stripping of bioavailable metals from contaminated soils. *Environmental Toxicology and Chemistry*, 42: 558–565.
- Scheinberg I.H. (1979): Human health effects of copper. In: Nriagu J.O. (ed.): *Copper in the Environment. Part II: Health Effects*. New York, John Wiley and Sons, 17–31.
- Schoffer J.T., Antilen M., Neaman A., Diaz M.F., de la Fuente L.M., Urdiales C., Ginocchio R. (2021): The role of leaf litter as a protective barrier for copper-containing pesticides in orchard soils. *Environmental Science and Pollution Research*, 28: 60913–60922.
- Schoffer J.T., Aponte H., Neaman A., De la Fuente L.M., Arellano E.C., Gil P.M., Ginocchio R. (2022): Copper content in soils and litter from fruit orchards in Central Chile and its relationship with soil microbial activity. *Plant, Soil and Environment*, 68: 115–128.
- Schoffer J.T., Sauvé S., Neaman A., Ginocchio R. (2020): Role of leaf litter on the incorporation of copper-containing pesticides into soils under fruit production: a review. *Journal of Soil Science and Plant Nutrition*, 20: 990–1000.
- Schoffer J.T., Solari F., Petit-dit-Grézériat L., Pelosi C., Ginocchio R., Yáñez C., Mazuela P., Neaman A. (2024): The downside of copper pesticides: an earthworm's perspective. *Environmental Science and Pollution Research*, 31: 16085.
- Shi P., Schulin R. (2019): Effects of soil organic residue amendment on losses of dissolved organic carbon, P, Cu and Zn *via* surface runoff from arable soils. *Soil and Tillage Research*, 195: 104352.
- Smorkalov I.A., Vorobeichik E.L., Dzeranov A.A., Pankratov D.A., Dovletyarova E.A., Yáñez C., Neaman A. (2023): Field experiment pitting magnetite nanoparticles against microparticles: effect of size in the rehabilitation of metalcontaminated soil. *Revista Brasileira de Ciência do Solo*, 47: e0230017.
- Sonoda K., Hashimoto Y., Wang S.L., Ban T. (2019): Copper and zinc in vineyard and orchard soils at millimeter vertical resolution. *Science of the Total Environment*, 689: 958–962.
- Steinmetz Z., Kenngott K.G.J., Azeroual M., Schafer R.B., Schaumann G.E. (2017): Fractionation of copper and uranium in organic and conventional vineyard soils and adjacent stream sediments studied by sequential extraction. *Journal of Soils and Sediments*, 17: 1092–1100.

<https://doi.org/10.17221/501/2023-PSE>

- Tapia-Gatica J., Selles I., Bravo M.A., Tessini C., Barros-Parada W., Novoselov A., Neaman A. (2022): Global issues in setting legal limits on soil metal contamination: a case study of Chile. *Chemosphere*, 290: 133404.
- Turnlund J.R., Keyes W.R., Kim S.K., Domek J.M. (2005): Long-term high copper intake: effects on copper absorption, retention, and homeostasis in men. *The American Journal of Clinical Nutrition*, 81: 822–828.
- US EPA (2002): Supplemental guidance for developing soil screening levels for superfund sites. Washington. U.S. Environmental Protection Agency, 187. Available at: https://rais.ornl.gov/documents/SSG_nonrad_supplemental.pdf
- US EPA (2011): Exposure Factors Handbook. EPA/600/R-090/052F. Washington, DC, U.S. Environmental Protection Agency.
- Van Campen D.R. (1991): Trace elements in human nutrition. In: Mortvedt J.J., Cox F.R., Shuman L.M., Welch R.M. (eds.): *Micro-nutrients in Agriculture*. Soil Science Society of America, Madison, 663–701. ISBN-10: 9780891187974
- Van Zwieten L., Rust J., Kingston T., Merrington G., Morris S. (2004): Influence of copper fungicide residues on occurrence of earthworms in avocado orchard soils. *Science of the Total Environment*, 329: 29–41.
- Wang Q.Y., Liu J.S., Wang Y., Yu H.W. (2015): Accumulations of copper in apple orchard soils: distribution and availability in soil aggregate fractions. *Journal of Soils and Sediments*, 15: 1075–1082.
- Yamamoto K., Hashimoto Y., Kang J., Kobayashi K. (2018): Speciation of phosphorus zinc and copper in soil and water-dispersible colloid affected by a long-term application of swine manure compost. *Environmental Science and Technology*, 52: 13270–13278.
- Youlton C., Espejo P., Biggs J., Norambuena M., Cisternas M., Neaman A., Salgado E. (2010): Quantification and control of runoff and soil erosion on avocado orchards on ridges along steep-hillslopes. *Ciencia e Investigación Agraria*, 37: 113–123.
- Young D.S. (2017): *Handbook of Regression Methods*. New York, Chapman and Hall. ISBN: 9781315154701

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