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Research Paper

# Copper and zinc as a window to past agricultural land-use

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ABSTRACT

Intensive agricultural management significantly affects soil chemical properties. Such impacts, depending on the intensity of agronomic practices, might persist for several decades. We tested how current soil properties, especially heavy metal concentrations, reflect the land-use history over a 24,000 ha area dominated by intensive apple orchards and viticulture (South Tyrol, ITA). We combined georeferenced soil analyses with land-use maps from 1850 to 2010 in a space-for-time approach to detect the accumulation rates of copper and zinc and understand how present-day soil heavy metal concentrations reflect land-use history. Soils under vineyards since the 1850s showed the highest available copper concentration (median of 314.0 mg $kg^{-1}$, accumulation rate between 19.4 and 41.3 mg $kg^{-1}\cdot 10\ y^{-1}$). Zinc reached the highest concentration in the same land-use type (median of 32.5 mg $kg^{-1}$, accumulation rate between 1.8 and 4.4 mg $kg^{-1}\cdot 10\ y^{-1}$). Using a random forest approach on 44,132 soil samples, we extrapolated land-use history on the permanent crop area of the region, reaching an accuracy of 0.72. This suggests that combining current soil analysis, historical management information, and machine learning models provides a valuable tool to predict land-use history and understand management legacies.

## 1. Introduction

Soil is a complex medium and one of the most valuable assets for humankind (Council of Europe, 1973). It is a dynamic, living, non-renewable resource that plays several vital roles in terrestrial ecosystems and sustains plant and animal life on Earth (Doran et al., 1996, 1994). Soil degradation, such as erosion, fertility loss, salinity, acidification, soil carbon decline, and compaction are recognized as threats by the European Union (Commission of the European Communities (CEC), 2006; Stolte et al., 2016). These threats have detrimental consequences for secure supplies of food, clean freshwater, landscape diversity, and the production of renewable energy sources (Carré et al., 2017; Koch et al., 2013). Therefore, soil security, associated with the maintenance and improvement of soil resources, should be considered as a global existential challenge (Bouma, 2019; McBratney et al., 2014).

Heavy metal accumulation in soils is a major risk for soil function and fertility and can occur due to a specific geology or the occurrence of ore deposits (Abrahams, 2002; Zhang and Wang, 2020). However, heavy metals are mostly released into the environment by human activity, agricultural practices in particular (Vareda et al., 2019). Specifically, fertilizer and animal manure application, sewage sludge use, and pesticide application are assumed to be major causes of heavy metal pollution in agricultural soils (Guo et al., 2018; Wagner, 1993). Pesticides used in the past may have contained a significant amount of metals; in addition, insecticides and fungicides may be based on compounds containing copper (Cu), mercury (Hg), manganese (Mn), lead (Pb), and zinc (Zn), e.g., fungicidal sprays such as Bordeaux mixture ($CuSO_4$) and Cu oxychloride for Cu (Jones and Jarvis, 1981), and Mancozeb® for Zn (National Center for Biotechnology Information, 2017). Under certain soil characteristics (low pH, low soluble organic carbon) or extent of plant cover (e.g., absence of grass uptake), heavy metals added to soils through biosolid applications can be leached downwards through the soil profile and may contaminate groundwater (McLaren et al., 2005; Sharma et al., 2017).

Soils may widely differ in their response to heavy metal accumulation depending on abiotic factors affecting the metal availability, mainly

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pH and soil organic matter (SOM). In addition, heavy metals can affect soil microbial community biomass, composition, and diversity (Li et al., 2017; Smolders et al., 2004; Zhen et al., 2019). Several studies have reported a decrease in microbial biomass (Kuperman and Carreiro, 1997) as well as alterations of microbial diversity (Abdu et al., 2017) and structure as a consequence of heavy metal accumulation (Borruso et al., 2015; Cavani et al., 2016; Giller et al., 2009; Linton et al., 2007).

Both Cu and Zn are essential plant micronutrients. However, when their available fractions exceed certain thresholds, they might induce toxicity symptoms to plants and soil organisms (Brunetto et al., 2016). For instance, Cu causes a decrease in the number and diversity of Collembola and earthworms, as well as a decline in microbial biomass and inhibition of cyanobacterial metabolic activities (Karimi et al., 2021; Pipe, 1992). Soil respiration activity is severely compromised and limited at high Cu concentrations (Fritze et al., 1996; Romero-Freire et al., 2016). Meanwhile, Zn can negatively influence the activity of microorganisms and earthworms, retarding the breakdown of organic matter (García-Gómez et al., 2020; Greaney, 2005; Yausheva et al., 2016) and, subsequently, the biogeochemical cycles of the nutrients linked with this process. Furthermore, Zn decreases bacterial population and inhibits phosphatase, urease, and dehydrogenase activities in metal-polluted soils (Gao et al., 2010; Rajput et al., 2018). Moreover, high levels of Cu and Zn can cause unbalanced uptake of other essential nutrients and synergistic or antagonistic interactions among elements (Marastoni et al., 2019).

Among agricultural systems, soil characteristics differ in space and time according to the agricultural practices applied. In recent years, integrated geographical information science and multivariate statistical analysis have been used to assess the heavy metal distribution and temporal trends in soils (Hou et al., 2017). Space-for-time substitutions are defined as measuring the effect of a long-lasting process by studying a spatial gradient that replicates that process in space and are widely used in soil science (Huggett, 1998; Lucas et al., 2019; Stevens and Walker, 1970). Space-for-time substitutions form chronosequences, which have been used to evaluate the concentration of pesticides in reclamation areas under different land-uses (Bai et al., 2015), metal concentrations in urban soils (Howard and Olszewska, 2011), and adsorption of copper in flood plains (Graf et al., 2007).

High-resolution time series of digital land-use maps are becoming increasingly available, covering all continents, such as CORINE Land Cover project in Europe. These multi-temporal land-use/land-cover series combined with soil survey databases provide an enormous potential to evaluate the relationship between soil characteristics and land-use history (Baude et al., 2019; Della Chiesa et al., 2019b; Hengl et al., 2017). Moreover, machine learning algorithms (Hastie et al., 2009; Yaseen, 2021) strongly support this approach in data exploration, pattern recognition, modeling, and prediction. For instance, digital soil mapping has received considerable benefits in spatial interpolation from machine learning algorithms (Wadoux et al., 2020) such as random forest (Hengl et al., 2007; Liaw and Wiener, 2014), and was successfully applied in modeling heavy metal distribution in agricultural ecosystems (Hu et al., 2020). Random forest is a relatively simple and accurate algorithm when dealing with several covariates and aiming mainly at predicting a response or class (Breiman, 2001; Fawagreh et al., 2014).

This study used a robust data set of about 44,132 soil samples from different management types and analyzed their variability based on historical land-use maps that date back to the 19th century through machine learning algorithms. With this interdisciplinary combination of soil science, landscape research, and geospatial modeling, we aimed at i) describing the temporal accumulation of Cu and Zn in intensively used permanent crop soils, ii) investigating how current soil heavy metal concentrations reflect land-use history, and iii) demonstrating the feasibility of retracing land-use history by modeling its effect on soil characteristics.

## 2. Materials and Methods

### 2.1. Study area

This study focused on the topsoil (0–20 cm) from highly productive agricultural areas in the Province of Bolzano, South Tyrol (Northern Italy). South Tyrol is Europe's largest apple-growing area, with orchards covering around 19,000 ha and vineyards covering about 5500 ha. Apple orchards are managed with integrated, conventional, and organic farming (the latter being practiced in approximately 10% of the total area), with a density between 3000 and 5000 plants ha$^{-1}$. Vineyards are mostly cultivated with conventional farming (organic farming being practiced in around 1% of the total area) with 4000 to 6000 plants ha$^{-1}$, mostly Guyot pruned. The study area has a continental climate with maximum precipitation in summer and relatively cold and dry winters (Adler et al., 2015). The total annual precipitation is 450–850 mm at the cultivated valley bottom. The valley sediments, where most of the permanent crops grow, are derived from flood plain post-glacial deposits starting the Holocene era until recent years (Avanzini et al., 2003). Furthermore, large alluvial fans are part of this geological formation (Jarman et al., 2011). The texture of these sediments is diverse, including clays, silts, sands, and gravels. The depth of the Holocene sediments varies from 1 to 100 m. Furthermore, glacial Pleistocene sediments are also present throughout the valleys, mainly with Tillite (silt-sands with stones). On both valley slopes, covered primarily with vineyards, hard rocks such as rhyodacitic lavas and granodiorites come to the surface (Avanzini et al., 2003; Bargossi et al., 2010). According to the Ecopedological Map of Italy (Rusco et al., 2003) the study area is included in sub-region "02 o" "Large valley bottoms of central Alps" and sub-region "02 n" " Medium and lower portions of the sides of the alpine valleys." These two sub-regions have Dystri-Skeletic Fluvisol, Fluvi-Dystric Cambisol, Skeleti-Calcaric Fluvisol, Dystri-Skeletic Cambisol, Skeletic Umbrisol, and Eutric Cambisol, as dominant soil types based on FAO classification (IUSS Working Group WRB, 2015).

To assess the effect of land-use history on heavy metal concentration, we used a subset of about 7400 ha as the training area, i.e., around one-third of the total study area (Fig. 1). The training area is mainly located in the Venosta/Vinschgau and Adige/Etsch Valley and was selected to represent the typical agricultural development pattern in the region, i.e., long-term apple orchards and vineyards as well as areas with a high land-use turnover throughout the last 150 years (Tasser et al., 2009). Then, exploratory data analysis and land-use prediction were applied to the entire study area (South Tyrolean orchards and vineyards; 24,400 ha in total).

### 2.2. Land-use history

Digital land-use maps dating from the 1850s were derived from historical maps and aerial photos provided by the Autonomous Province of Bolzano/Bozen. The Francisco-Francisco-Josephinian Cartographical Register (third cartographical register of the Austrian crownlands; 1:25,000) was used as the starting point. These historical land-use maps distinguish with specific symbols the areas between apple orchards and vineyards. Additionally, the quality of the aerial photos from 1950 onwards was also sufficient to identify the main land-use types used in this analysis. To corroborate the resulting land cover/land-use maps, current and historical data on the meta-level were used, e.g., agricultural census and village chronicles. The land-use maps produced were slightly space-time discontinuous, as they rely on the area and year of the historical map or aerial photos taken throughout the years. Thus, we grouped these maps in three time steps: a) the 1850s, which included maps drawn up from 1855 to 1861, b) the 1950s, which included maps from 1954, 1955, and 1956, and c) the 1980s, which included maps from 1981, 1982, and 1985. Finally, we identified the 2010s land use with orthophotos from 2013. A minimum homogeneous area of 4 ha was defined for the digitalization of the historical maps and photos, and smaller areas with mixed land-use types were classified according to the prevailing

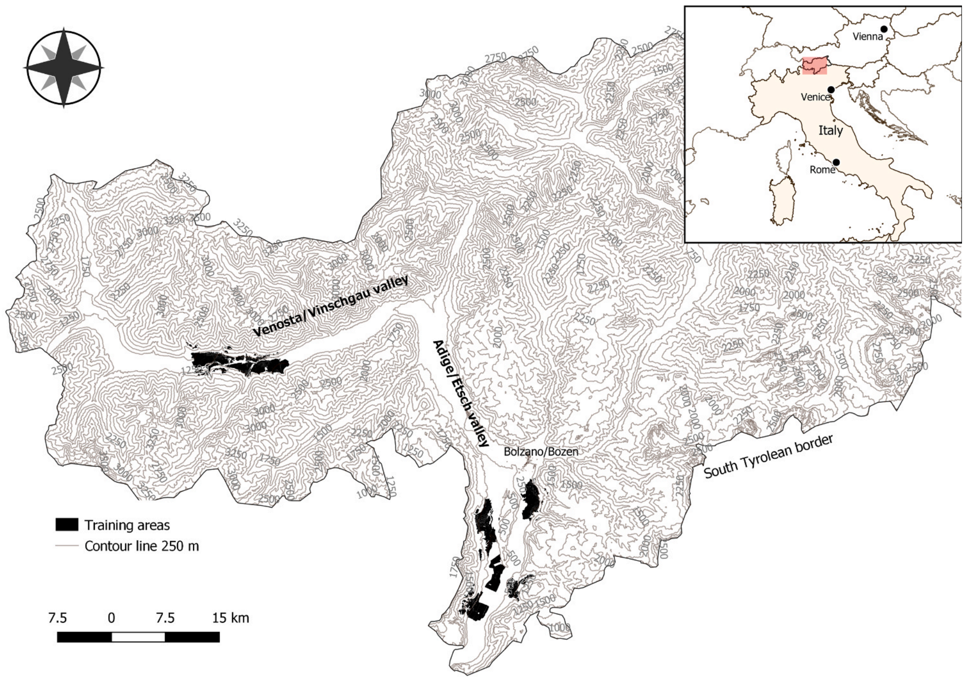


**Fig. 1.** Study area, main valleys of South Tyrol, Italy. Dark polygons represent the training areas, where both land-use history and soil samples are available.

type. To address the specific research questions of this study, we clustered the land-use categories as follows: "Grassland" (containing mainly meadows and pastures and a small percentage of arable land), "Vineyards," "Orchards," and "Settlements" (containing settlements and other artificial surfaces).

### 2.3. Soil samples dataset and analysis

This study was based on a total of 44,132 soil samples collected by farmers and analyzed by the Laboratory of Agricultural Chemistry, Public Research Centre of Agriculture and Forestry, Laimburg (Dalla Via and Mantinger, 2012). A minimum of 15 soil sub-samples from every agricultural field was collected at 0–20 cm depth and 1 kg of mixed soil material was used for analysis. Overall, the mean sample density in the study area was 54 points/km$^2$. For a detailed description of the soil sampling framework, please refer to Della Chiesa et al. (2019a, 2019b). Soil samples were collected between 2006 and 2016. A total of 38,613 samples were collected from apple orchards and vineyards, while 316 were collected from grasslands. Approximately 59% of soil samples in the dataset have been georeferenced using the cadastral code (Della Chiesa et al., 2019b). Among these, 5203 georeferenced samples (11.8%) originated from the training area (Fig. 1). Soil analysis was carried out (parameters listed in Table 1) to gain a better understanding of soil variability and the relationship between heavy metals, other soil characteristics, and land use.

Texture classes were estimated by feel (Thien, 1979) according to the German classification (AD-HOC AG, 2005). We converted each textural class to percentage values using the centroid of the classes (clay, sand, and silt). This simplified the comparison with other variables in the exploratory data analysis. The nutrient elements in the dataset were extracted using methods to assess the available plant fraction (Table 1) (Accredited laboratory under ISO 17025:2005, methods: ISO 10694:1995, DIN EN 15933:2012, ÖNORM L 1087:2012 A.5). Total Cu and Zn could be compared with available Cu and Zn, keeping in mind that available values are always lower than the total Cu and Zn (Lončarić et al., 2010; Nogueirol et al., 2010; Romić et al., 2004). As scientific literature commonly refers to total Cu and Zn, for comparison purposes, we built a multivariate linear model that converted the $CaCl_2$/DTPA (CAT) extraction to aqua regia extraction because our dataset contained 693 soil samples analyzed with both CAT and aqua regia.

**Table 1**
Measured parameters, analysis methods (VDLUFA, 1991), units and variable type.

| Parameter | Analysis method | Units | Variable type |
|---|---|---|---|
| SOM | Elemental analysis | % | Numerical |
| pH | $CaCl_2$ glass electrode | – | Numerical |
| Soil texture | Feel test | Soil texture class | Categorical |
| $P_2O_5$ | CAL colorimetry | mg 100 g$^{-1}$ | Numerical |
| $K_2O$ | CAL flame photometry | mg 100 g$^{-1}$ | Numerical |
| Mg | CAT ICP-OES | mg 100 g$^{-1}$ | Numerical |
| B | CAT ICP-OES | mg kg$^{-1}$ | Numerical |
| Mn | CAT ICP-OES | mg kg$^{-1}$ | Numerical |
| Cu | CAT ICP-OES | mg kg$^{-1}$ | Numerical |
| Zn | CAT ICP-OES | mg kg$^{-1}$ | Numerical |

ICP-OES, inductively coupled plasma optical emission spectrometry; CAL, calcium acetate-lactate; CAT, extraction solution 0.01 M $CaCl_2$ + 0.002 M DTPA-solution.

For the land-use history analysis in the training areas, only the georeferenced samples were used. The soil dataset, together with the cadastral information and all land-use maps, were stored in a PostgreSQL database with the PostGIS extension. This approach greatly facilitates data exploration and analysis and allows the connection with the R environment (R Core Team, 2018) to deepen the statistical analysis further.

### 2.4. Exploratory data analysis

We conducted an exploratory data analysis that comprised a principal component analysis (PCA) and a distribution visualization of Cu and Zn concentrations by land use. PCA was carried out in R with the package *FactoMineR* (Lê et al., 2008) on the following variables: pH, SOM, phosphorous, potassium, magnesium, manganese, boron, zinc, copper, clay (%), and sand (%). Land use was included as a supplementary categorical variable. The variables were scaled to unit variance before computation. We used the *dimdesc* function of the *FactoMineR* (Lê et al., 2008) package to identify variables and the most characteristic categories according to each component of the PCA. Results include significance tests with a significance threshold of 0.05 and are shown in the Supplementary Materials.

### 2.5. Modeling and predicting land-use history

We combined land-use history derived from land-use maps and soil analysis data by building a random forest model (Liaw and Wiener, 2014). The model is a classifier that uses soil physical and chemical properties to predict the probability of a sample belonging to a particular chronosequence class. The independent variables of the model were the same as those used for PCA (Supplementary Table S1). The dependent variable is a chronosequence class of land-use history in the four available time steps (1860, 1950, 1980, 2010) so that for each time step, we have three possible land-use types (grasslands, orchards, or vineyards). We used the random forest implementation in the Python library scikit-learn (Pedregosa et al., 2011). Random forest can also provide model accuracy and variable importance and output the significance of the importance measures for each predictor on the response variable. Therefore, it was a good choice for this case study, where wanted to predict a certain land-use history using soil physical and chemical data. We retained 15% of the samples to use them as an independent validation set to measure model accuracy and stratified the random choice on the chronosequence classes as these were uneven in the dataset. We presented each independent variable's importance in defining the model (Fig. 7), which is useful for understanding which variables had greater links to land-use history (dependent variable). We presented model accuracy with the overall accuracy, cross-entropy loss, and out-of-bag (OOB) accuracy. A confusion matrix and a classification report with precision, recall, f1-score, and support were also provided (Supplementary Tables S3 and S4). Then, we used the model to predict the chronosequence classes of the soil samples (around 38,600) lacking such information and presented the prediction in a map showing soil sample locations per chronosequence class.

## 3. Results and Discussion

### 3.1. Land-use history

From the 1850s onward, land use changed mainly from grasslands to permanent crops (Figs. 2 and 3) and started increasing before the 1950s. Vineyards initially increased after 1850 and remained stable thereafter, while apple orchards are still currently gaining space and cover most of the training area. In the 2010s, the percentages of agricultural land use (excluding settlements) were 73.1%, 22.4%, and 4.5% in orchards, vineyards, and grasslands/arable land, respectively (Fig. 3). This specialization and intensification of agricultural management within the study area occurred with different timing and magnitude. In the Adige/Etsch Valley, permanent crops began earlier, with a significant area covered by vineyards for centuries (Tasser et al., 2007). In the Venosta/Vinschgau Valley, almost no vineyards were present (Fig. 2), and the change was mainly from hay meadows and arable land to apple orchards. The abrupt conversion from extensive to intensive farming contrasted with that of other agricultural regions in the Alps (Tasser et al., 2007). However, it is a development that is in line with the global trend of land-use intensification (Ellis et al., 2013). This change in management apparently affects soil quality and functions (Adhikari and Hartemink, 2016; Herrick, 2000; Vogel et al., 2019), biogeochemistry of agricultural and mountain soils (Verchot et al., 1999), and C fluxes (Mojeremane et al., 2010). Moreover, intensive agriculture decreases SOM (Pulleman et al., 2000; Riezebos and Loerts, 1998), whereas tillage can reduce soil stability (Herrick, 2000) and increase bulk density, which in turn alters several soil physical properties by reducing permeability to air, water, and roots (Batey, 2009).

### 3.2. Exploratory data analysis

Although this study focused on Cu and Zn, because an overall characterization of the soil samples and their land use is crucial for a better understanding of the correlation between metal concentrations and other soil characteristics, we also performed an exploratory data analysis on all available soil parameters. Fig. 4 shows the PCA results for all the available samples from vineyards, orchards, and grasslands in South Tyrol. Grassland samples were distributed across all agricultural land in South Tyrol. Supplementary Fig. S1 shows the contribution of soil variables to each principal component (PC).

The first and second principal components (PC1 and PC2, respectively) explained 43.3% of the total dataset variance and were characterized by variables such as P, K, SOM, Mg, and pH. This indicated that a large part of soil variability was explained by chemical characteristics, likely a consequence of land management and fertilization. Nevertheless, 10.6% of the variance was explained by PC4, which was strongly characterized by Cu. In this component, vineyard soils were highly correlated with Cu, confirming the patterns shown in Fig. 5. Furthermore, some orchard soils were grouped with vineyards, probably owing to land-use changes. In fact, in the study area, soils that were historically cultivated as vineyards were recently converted to apple orchards. Our results confirmed a memory effect (Farlin et al., 2013) for those soils in terms of Cu concentrations, appearing closer to vineyard soils than to other apple orchard soils.

### 3.3. Copper and zinc accumulation

This work was original as it considered the available fraction of heavy metals in soils (CAL method, Önorm L 1075 - Austrian Standard), while most studies and national and international regulations on threshold values report the total metal content (Carlon, 2007). However, the available content is always a fraction of the total, and the correlation between total and available concentration was mostly linear in previous studies (Lončarić et al., 2010; Nogueirol et al., 2010; Romić et al., 2004). These studies suggested that total Cu content is about 2-fold higher than that of available Cu (DTPA extraction, Nogueirol et al., 2010). Contrastingly, this equation was found for Zn according to Lončarić et al. (2010): $Zn_{available\text{-}DTPA} = Zn_{total\text{-}aqua\ regia} * 0.015 + pH * 0.259$. To the best of our knowledge, there are no reports presenting regressions between the CAT method used in this study and the aqua regia method used for determining the total metal fraction (Hseu et al., 2002). Therefore, we fitted a multivariate linear model on our data, and the output for Cu and Zn was described in Table 2.

Models had an $R^2$ of 0.98 and 0.92 for Zn and Cu, respectively, were statistically significant and made it possible to compare the results of this study with studies that only considered aqua regia extraction. These comparisons must be treated with caution as the model has been built using our dataset and could not be as accurate on soils that fall outside the model domain (e.g., high or low pH or Cu). Nevertheless, the number of samples (i.e., 693) was 10–30-fold larger than those in other studies (Hseu et al., 2002; Lončarić et al., 2010) and could contribute to a robust knowledge base to the scientific community.

Based on the main land-use changes throughout the last 160 years, we obtained six prevailing chronosequence classes and discarded those with fewer than 15 observations. Figs. 5 and 6 show the distribution of available Cu and Zn concentrations in soils grouped according to the chronosequence classes. The reference values for available Cu and Zn (calculated as the median concentration of nearby permanent grasslands in similar environmental conditions) were 4 and 10 mg $kg^{-1}$, respectively. Fig. 5 showed that soils cultivated as vineyards, at least from the 1950s (class 1 and 2), showed Cu concentrations 4- to 65-fold higher than the reference values. Additionally, soils cultivated as vineyards since the 1850s showed the highest Cu concentration (median and absolute maximum value 314.0 and 752.0 mg $kg^{-1}$, respectively), followed by that of soils cultivated as vineyards since the 1950s (median

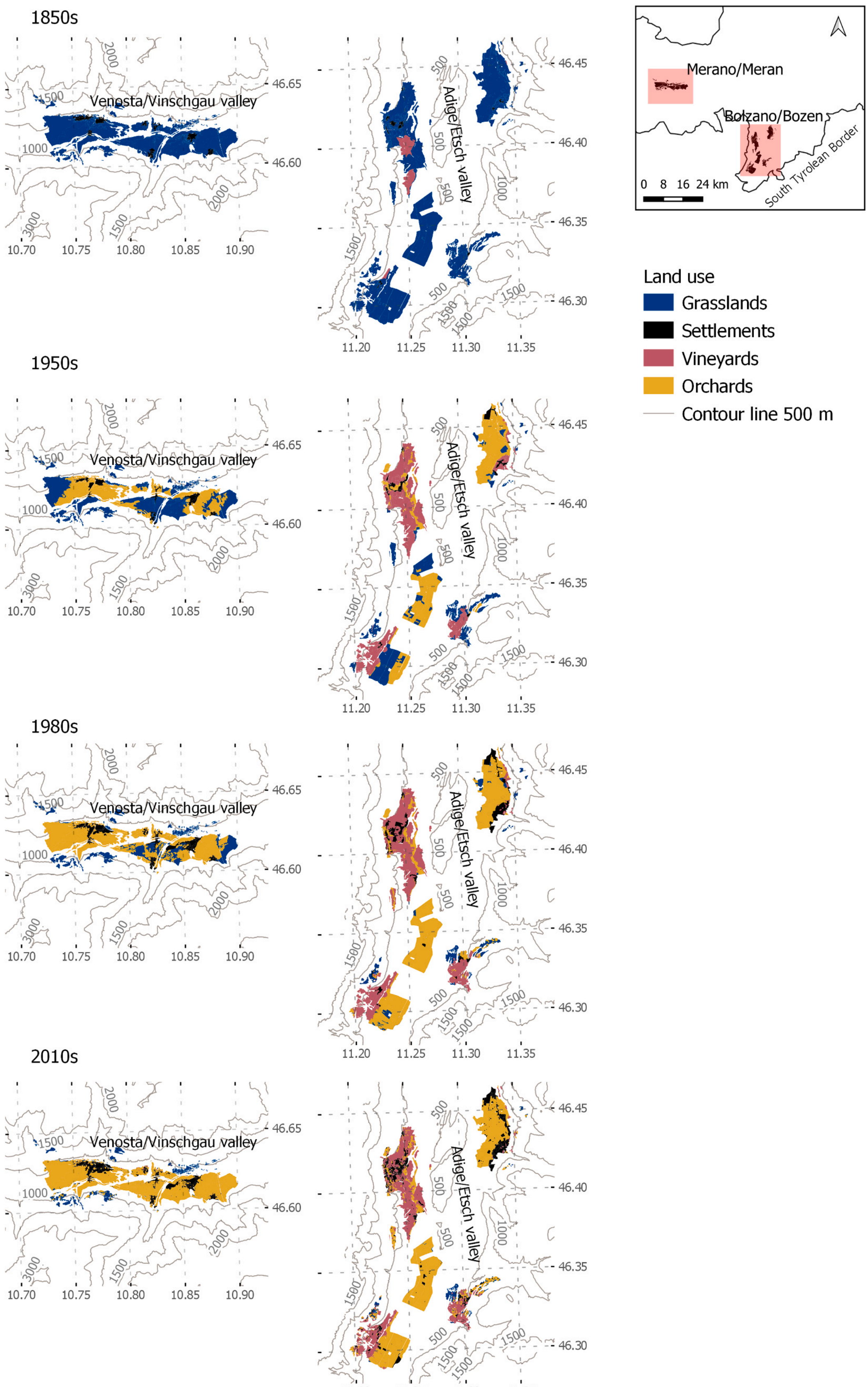


**Fig. 2.** Land-use maps in the study area at different time steps: 1850s, 1950s, 1980s, 2010s. Blue = Grasslands, Black = Settlements, Yellow = Orchards, Red = Vineyards. These areas correspond to the dark training areas of Fig. 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

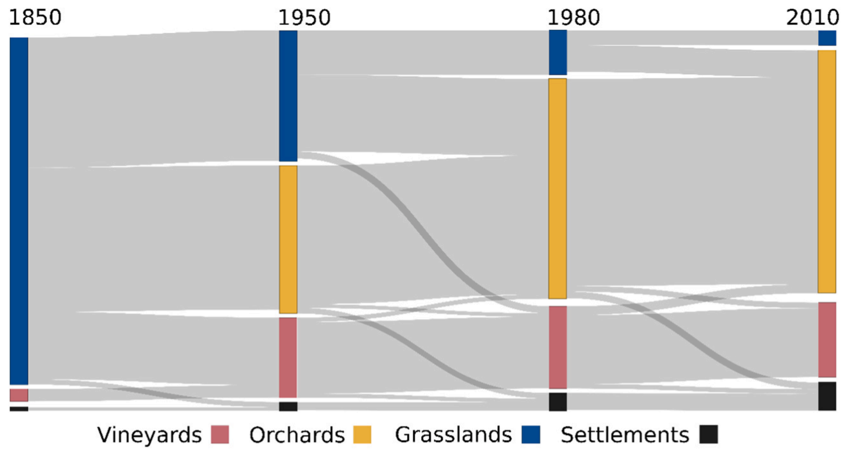


**Fig. 3.** Land-use change fluxes in the Vinschgau and Etsch Valleys. Every bar has a color representing land use with heights proportional to the corresponding area, every stack of bars represents a time step starting from the 1850s onto 2010s.

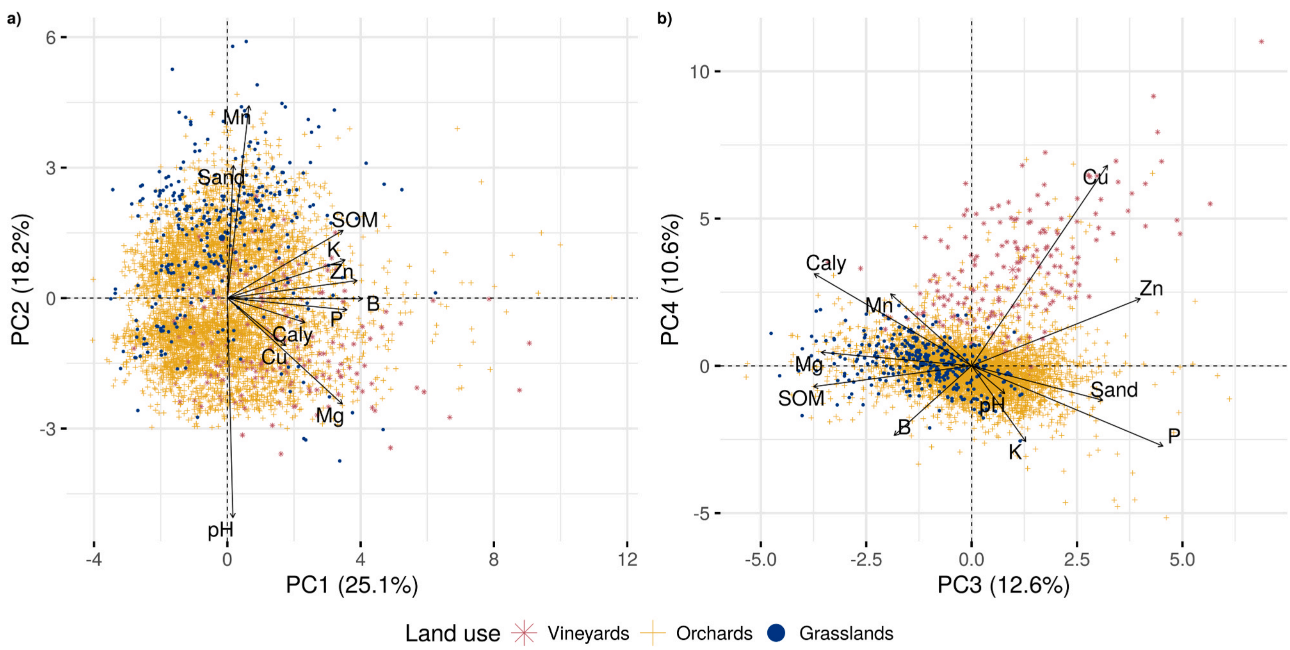


**Fig. 4.** Principal Component biplot, both individuals and variables are plotted. Land use is used as explanatory categorical variable. The land-use history is described using colors (blue: grasslands, yellow: orchards, red: vineyards). a) The first principal component (PC1) and the second principal component (PC2) are shown. b) The third principal component (PC3) and the fourth principal component (PC4) are also shown. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

252.0 mg $kg^{-1}$) and by that of soils cultivated as vineyards since the 1950s that changed to orchards in the 2010s (class 3, median of 135.5 mg $kg^{-1}$). Classes 1, 2, and 3 had a high standard deviation (163.5, 142.0, and 104.0, respectively) and were thus not significantly different from each other in Cu content but were significantly different from soils cultivated as grasslands and orchards only (Fig. 5). Among orchards, orchards since the 1950s (Class 4) showed the highest Cu concentration (median of 21.0 mg $kg^{-1}$) followed by orchards since the 1980s (Class 5, median of 15.0 mg $kg^{-1}$) and those soils with orchards only since the 2010s (Class 6, median of 13.0 mg $kg^{-1}$). These last three groups were significantly different from each other in Cu content, proving a temporal accumulation of Cu in the soil, but one order of magnitude lower than that in vineyards. For vineyards, we estimated a linear accumulation rate of available Cu between 19.4 and 41.3 mg $kg^{-1}\cdot 10\ y^{-1}$, while for apple orchards, this value was between 2.8 and 3.6 mg $kg^{-1}\cdot 10\ y^{-1}$.

As observed for Cu, Zn concentrations increased with the age of the permanent crop. Soils cultivated as vineyards since the 1860s, 1950s, and those that were vineyards after the 1950s and then changed to orchards in the 2010s (classes 1, 2, and 3, respectively) showed similar concentrations with medians of 32.5, 28.0, and 30.5 mg $kg^{-1}$, respectively, and no statistical differences among them. This lack of difference posed an uncertainty on which cultivation, vineyards, or orchards, contributed more to Zn accumulation in the soil. Nevertheless, soils cultivated as vineyards since the 1950s had a Zn concentration 1.4-fold higher than that of orchards of the same age, and the difference was statistically significant (Fig. 5). Comparing Zn concentration between soils that were cultivated only as grasslands/arable land or orchards, the highest concentration (median of 18.0 mg $kg^{-1}$) was seen in those cultivated as orchards since the 1950s (Class 4) followed by that of orchards since the 1980s (Class 5, median of 13.0 mg $kg^{-1}$), and, finally, that of orchards since the 2010s (Class 6, median of 9.0 mg $kg^{-1}$), with significant differences between them. This proved the temporal accumulation of Zn in the soil for these land-use classes. For vineyards, we estimate a linear accumulation rate of available Zn between 1.8 and

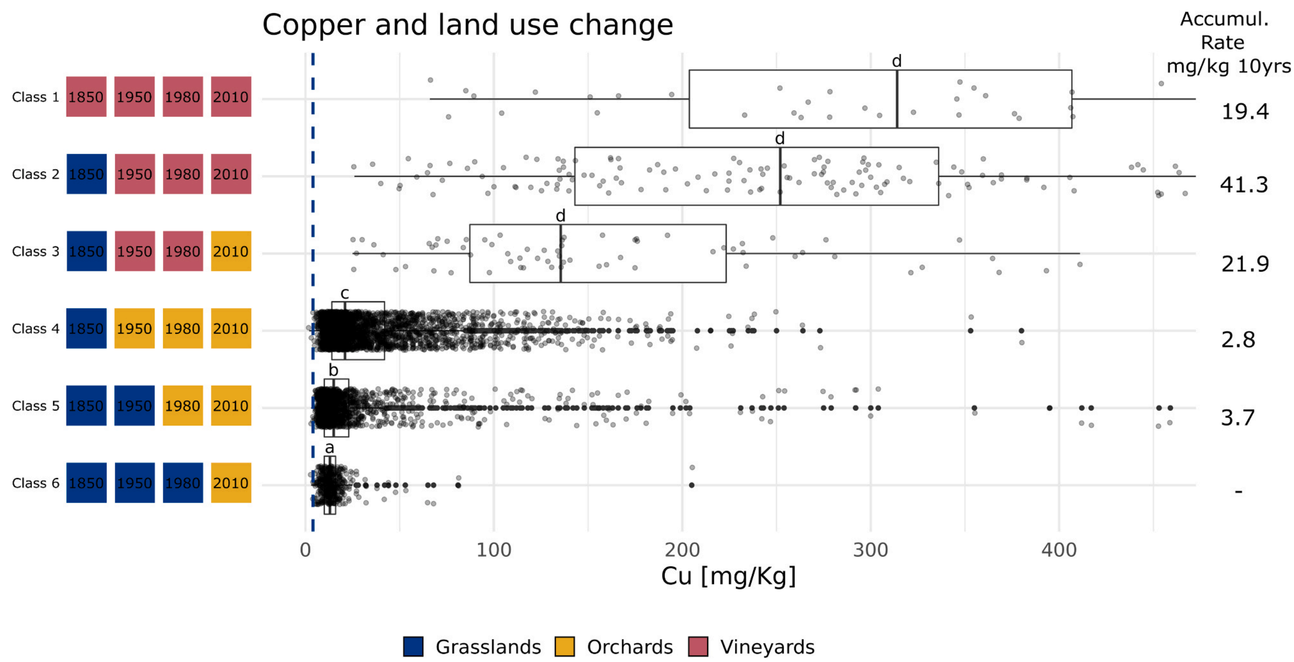


**Fig. 5.** Cu concentrations (available fraction) distribution according to the chronosequence classes. The samples are included in different boxplots according to a common land-use history. The land-use history is described using colored squares (blue: grasslands, yellow: orchards, red: vineyards) and the years written inside the squares. The vertical blue dashed line refers to the background value. Accumulation rate values are given for each chronosequence class. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 2**
Summary of the multivariate linear model parameters to convert aqua regia extraction of Cu and Zn into CAT extraction.

| Element | Term | Estimate | std.error | t-statistic | p.value |
|---|---|---|---|---|---|
| $Cu_{ar}$ | $Cu_{cat}$ | 1.64 | 0.01 | 157.51 | * |
| | pH | 4.72 | 0.15 | 31.52 | * |
| $Zn_{ar}$ | $Zn_{cat}$ | 1.61 | 0.13 | 12.69 | * |
| | pH | 16.99 | 0.37 | 46.01 | * |

Element represents dependent variables ($Cu_{ar}$: Copper extracted with aqua regia, $Zn_{ar}$: Zinc extracted with aqua regia). Term includes independent variables ($Cu_{cat}$: Copper extracted with CAT, $Zn_{cat}$: Zinc extracted with CAT). Estimate represents the coefficient for each independent variable.

* indicated p-value ≤ 0.001.

4.4 mg $kg^{-1}$·10 $y^{-1}$, while this value was between 2.3 and 3.0 mg $kg^{-1}$·10 $y^{-1}$ for apple orchards.

Several studies have reported metal accumulation in agricultural soils (Gulf et al., 2003; Huang and Jin, 2008; Merry et al., 1983; Morgan and Bowden, 1993). However, to the best of our knowledge, none followed a space-for-time approach to compare different land uses and their effect on heavy metal accumulation. In this study, the calculated accumulation rate has the disadvantage of land-use maps holding information of cultivation patterns only for four time-steps within a 160-year period. Agricultural practices might have changed during the decades, affecting Cu and Zn accumulation in soil. In addition, within the same land-use type, management intensity might have increased, e.g., plant density has doubled from 2000 plants $ha^{-1}$ in the 1950s to the current 3000–5000 plants $ha^{-1}$ (personal communication from local farmers). Therefore, we only estimated an average of what happened in the past, with consequent loss of predictive power for the future. Nevertheless, the accumulation rate gives us a baseline on the past that can be used to interpret present and future accumulation. For instance, Morgan and Bowden (1993) stated that Cu accumulation is clear over time but is not simply a function of age, as factors other than time, such as SOM and pH, may have an effect.

Copper is related to agricultural pest management in vineyards and orchards with the use of Bordeaux mixture (Cu sulfate) and Cu oxychloride (Jones and Jarvis, 1981) as well as fertilizers and manure (Alloway, 2013). Li et al. (2005) reported an average annual total Cu increase in apple orchards ranging from 2.5 to 9 mg $kg^{-1}$ $y^{-1}$. These concentrations were obtained by nitric acid extraction. Aqua regia extracts about twice the Zn extracted by nitric acid (Száková et al., 2000). By translating the values of nitric acid to aqua regia and then to the available fraction, we can conclude that the accumulation rate we found in orchards is about twice that found by Li et al. (2005). In the soils of this study, Cu accumulation over time has led to concentrations that often exceed background values in European soils, which are between 4 and 40 mg $kg^{-1}$ of total Cu (Gawlik and Bidoglio, 2006a; Reimann et al., 2018). Concentrations above 150 mg $kg^{-1}$ of total Cu can be toxic to annual plant species (Vácha et al., 2014) and inhibit microbial growth and activity (Aoyama and Nagumo, 1996). According to our model, this concentration range would correspond to approximately 80 mg $kg^{-1}$ of available Cu, with 18.2% of the samples in this study being above this limit.

Addition of Cu to soils may result in pH changes that could directly and negatively affect soil microbial biomass and diversity (Fernández-Calviño and Bååth, 2016). Although the concentrations in this study could be as high as 600 mg $kg^{-1}$ of available Cu, this metal was mainly accumulated in vineyards and in the topsoil layer (Merry et al., 1983), as confirmed by the low concentrations detected in the 20–40 cm layer, data not shown. As accumulation was confined only to the topsoil, there should be no concern about vineyard growth inhibition or phytotoxicity, as grapevine plants have a rather deep rooting system, depending on the rootstock (Smart et al., 2006). In addition, grapevine plants can adopt a range of detoxification mechanisms to cope with heavy metal-induced stress, and some agronomic practices can further alleviate Cu toxicity (Bachmann et al., 1999; Brunetto et al., 2016; Hall, 2002; Rosaria et al., 2010). Nevertheless, in this study, several apple orchard soils had relatively high Cu concentrations owing to their long-lasting vineyard land-use history. Moreover, apple orchards are regularly plowed every 20–30 years, depending on the management. This could lead to a Cu distribution throughout the soil profile in the long term. Although few apple orchards have this land-use history, little is known about the potential transfer of

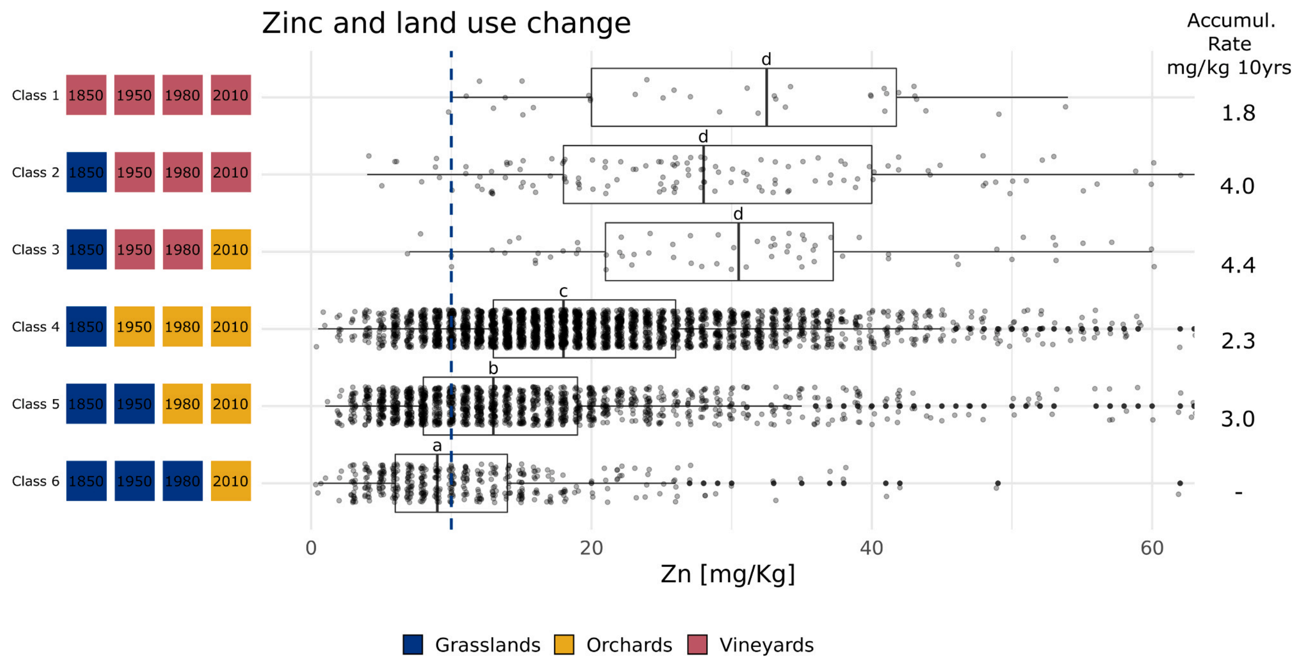


**Fig. 6.** Zn concentrations (available fraction) distribution according to the chronosequence classes. The samples are included in different boxplots according to a common land-use history. The land-use history is described using colored squares (blue: grasslands, yellow: orchards, red: vineyards), and the years are written inside the squares. The vertical blue dashed line refers to the background value. Accumulation rate values are given for each chronosequence class. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Cu from soil to fruits, which requires further investigation (Chojnacka et al., 2005; Park and Cho, 2011; Wang et al., 2015a, 2015b). Therefore, future land-use changes to crops with shallower root systems or vineyard replanting systems could induce Cu toxicity symptoms, affecting the sustainability and, potentially, productivity and quality of these agro-ecosystems (Brun et al., 2001; Fernández-Calviño et al., 2008; Michaud et al., 2007). Soil management practices should also consider the highly dynamic interactions occurring in the rhizosphere due to intimate interactions among plant roots, soil, and microorganisms, which determine the availability and acquisition of essential nutrients and the toxicity of heavy metals such as Cu and Zn.

Similar to Cu, Zn is also related to agricultural pest management in vineyards and orchards using Zn-containing fungicides, such as Mancozeb® (National Center for Biotechnology Information, 2017), and fertilizers (Alloway, 2013). Zn is frequently applied in permanent crops and accumulates in soils over time (Bahadur et al., 1998; Orphanos, 1982; Weingerl and Kerin, 2000). Moreover, the concentrations observed in this study are comparable with background concentrations in European soils, i.e., between 17 and 85 mg $kg^{-1}$ of total Zn (Gawlik and Bidoglio, 2006b). Nevertheless, considering the conversion from CAT to aqua regia, older permanent crops reached values that were 2-fold higher than the upper limit of the background values. Phytotoxicity or microbial toxicity can be expected only when the total content of Zn exceeds 700 and 500 mg $kg^{-1}$, respectively (Podlesakova et al., 2002; Smolders et al., 2004). According to our model, this concentration corresponds to an available Zn range of 255–382 mg $kg^{-1}$, and no samples in this study reached this limit (maximum value of 195 mg $kg^{-1}$ of available Zn, Fig. 5). Therefore, Zn toxicity on plants or microbial communities is unlikely to occur in the study area. In addition, slightly acidic and alkaline soil conditions further reduce Zn toxicity to soil microorganisms or algae, as shown in pure (solution) cultures (Smolders et al., 2004). Heavy metal contamination is also considered to be involved in apple replant disease (Peruzzi et al., 2017) and could be taken into account when assessing risk factors in public places near agricultural fields (Linhart et al., 2019).

### 3.4. Modeling and predicting land-use history

If land-use history is strictly related to soil chemical and physical parameters, in particular heavy metals, this relationship can be used to build a model and predict the land-use history of soils with an unknown history. The random forest classifier generally performed well and yielded an overall accuracy of 0.72, an OOB accuracy of 0.72, and a cross-entropy loss of 0.68. Overall, the samples were grouped into six chronosequence classes according to land-use history (Figs. 4 and 5). The classification report (Table S3) and the confusion matrix (Table S4) described differences in performance among classes. Class 3 had the highest precision and recall of 0.76 and 0.90, respectively, and is also the most represented class in the test set (453 soil samples). Contrastingly, class 6 had a precision and recall of zero and was the least represented in the test set with only six samples. This difference in performance might be caused by the unbalanced dataset. Unbalanced data is often considered an issue in machine learning and data mining, but random forest proved to perform better than other methods with such data (Shearman et al., 2019). It is important to note that when the model misclassifies a class, it often chooses a similar class, e.g., class 6, which is classified as a similar class (class 5) five out of six times. Variable importance (Fig. 7) in the random forest classifier showed Cu, Zn, Mn, and SOM as the four important variables (Breiman et al., 1984), with Cu and Zn as the most important. This confirmed that, for the study area, heavy metals and SOM are the most useful soil parameters for predicting land-use history. If a land-use change affects SOM, this will decrease soil carbon stock, which will contribute to climate change. This process will cause the reduction of arable soil surface owing to soil degradation (Indoria et al., 2020) and drive land-use change further (Jones and Webb, 2010).

We used the classifier on the entire dataset (38,613 samples, excluding training and test data) to predict the land-use history class of each sample. This approach allowed the reconstruction of land-use history for most of the apple orchard and vineyard areas in South Tyrol (Fig. 8). These maps clearly showed that the oldest vineyards (Fig. 8f) concentrated in the southern part, as opposed to the newly planted orchards (class 5 and 6; Fig. 8, top-left) that were grasslands until the 1980s, which were in the west (Vinschgau Valley) and east

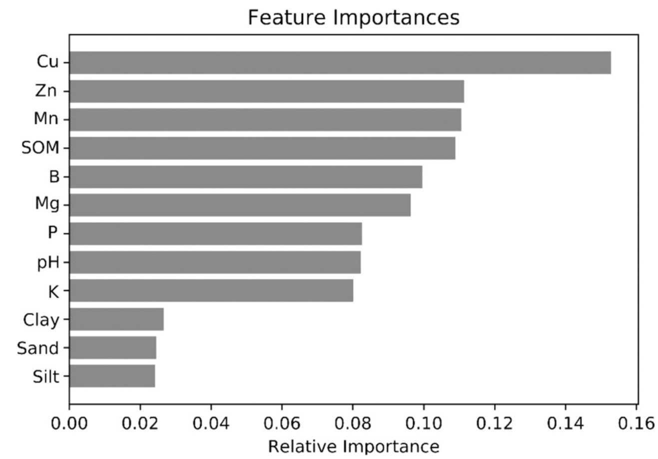


**Fig. 7.** Variable importance for the random forest classifier, the higher the value, the higher the importance. The importance of a variable is computed as the normalized total reduction of the Gini's impurity (Breiman et al., 1984) brought by that variable.

(Eisack Valley) of the study area. This classifier proved reliable and could be used by farmers or other stakeholders to discover the history of a field when this is unknown or uncertain. A better understanding of a field's history could sustainably optimize agricultural management, e.g., by avoiding practices that cause soil contamination or decreased fertility. This would also allow early detection and targeted solutions for potential ecosystem service reductions in soils (Awuah et al., 2020). Moreover, the model output could be used to improve the development of historical land-use cartography. Land-use history affects the ecosystem services provided by soils (Liiri et al., 2012), and modeling its change in time and space could provide the base knowledge for ecosystem service assessment. Because its effects can last decades or even centuries and are ubiquitous throughout the environment, land-use history is of great importance for ecological science and conservation planning (Foster et al., 2003).

## 4. Conclusions

Combining the results from up-to-date soil analysis with information on land-use history proved to be a valuable instrument for understanding the spatio-temporal patterns of Cu and Zn concentrations and accumulation in intensively managed permanent crop soils.

By testing the effect of agricultural practices and their change through time on soil properties, this study established that land use does indeed have a significant effect on Cu and Zn concentrations. We found a strong correlation between the amount of time an agricultural field was a vineyard and the concentration of soil-available Cu. The same trend, but with smaller effects, can be seen in apple orchards. Soil-available Zn presents lower accumulation rates, and the difference between apple orchards and vineyards is less evident.

The derived chronosequence showed that heavy metals are still accumulating with current land-use practices. This process should be critically monitored in the future in terms of possible shifts to shallow-rooted crops, rhizosphere dynamics, and potential accumulation in agricultural products. Further research and monitoring are needed to understand the effect of Cu and Zn pollution on taxonomical and functional fungal and bacterial diversity. In this study, model applicability is constrained to the land uses and land-use history classes used for training. However, we expect the methodological framework to be robust enough to be applied in other agricultural scenarios. This could lead to a better understanding of the legacy of historical heavy metal applications and improve current management practices aimed at conservative and sustainable food production.

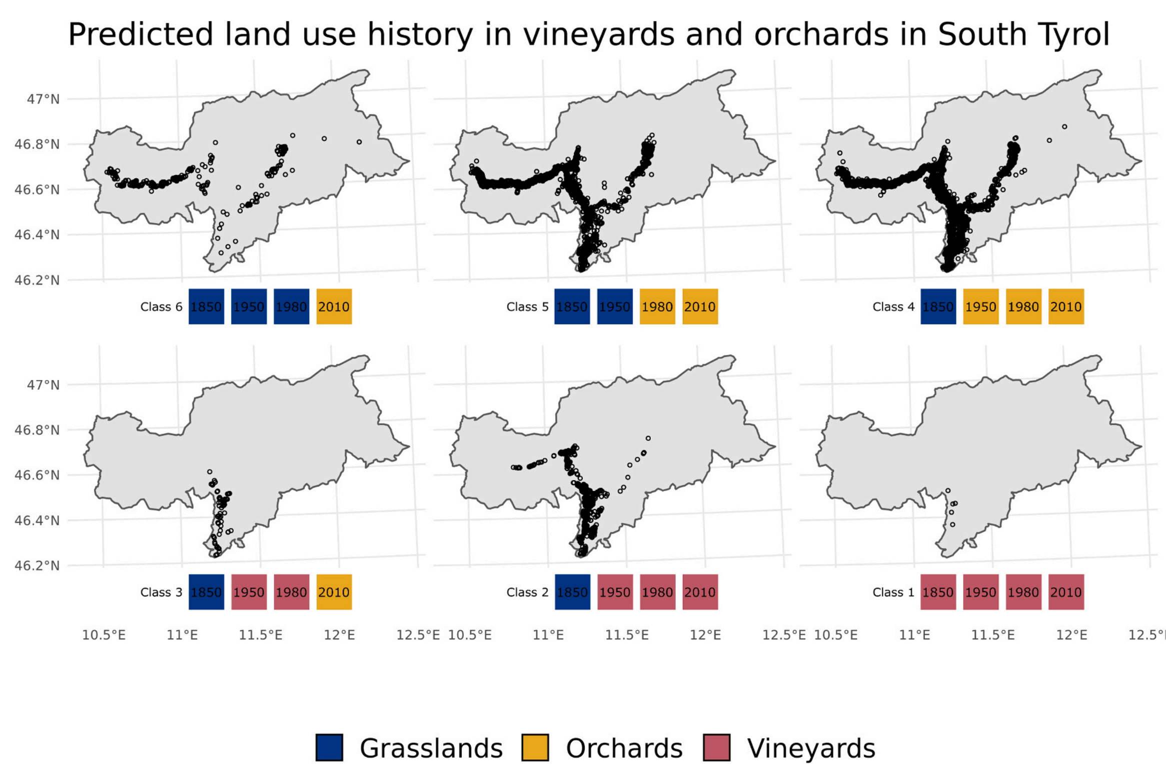


**Fig. 8.** Land-use history predicted by the random forest classifier. Black points represent sample locations. Each panel presents samples with a common land-use history. Colored squares indicate land-use history (blue: grasslands, yellow: orchards, red: vineyards) with the years written inside. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

## CRediT authorship contribution statement

**G. Genova:** Conceptualization, Methodology, Formal analysis, Data curation, Writing – original draft, Writing – review & editing, Visualization, Software. **S. Della Chiesa:** Conceptualization, Methodology, Data curation, Writing – original draft, Writing – review & editing, Visualization. **T. Mimmo:** Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Visualization. **L. Borruso:** Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Visualization. **S. Cesco:** Writing – original draft, Writing – review & editing. **E. Tasser:** Data curation, Writing – original draft, Writing – review & editing. **A. Matteazzi:** Resources, Data curation, Writing – original draft. **G. Niedrist:** Conceptualization, Methodology, Writing – original draft, Writing – review & editing.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2021.126631.

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