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Regionalizing eco-toxicity characterization factors for copper soil emissions considering edaphic information for Northern Spain and Portuguese vineyards

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Abstract

The management of vineyards depends on the use of plant protection agents. Regardless of the numerous environmental impacts that these pesticides generate during their production, their dosage as pest control agents in vineyards causes an important toxic effect that must be monitored. Copper-based inorganic pesticides are the most widely used agents to control fungal diseases in humid wine-growing regions. It is, however, significant that the environmental analysis of their use through the Life Cycle Assessment (LCA) methodology does not provide detailed information on the potential toxicity of this type of pesticides. Hence, most studies report average values for copper characterization factors (CFs), excluding local soil characteristics. The objective of the study was the spatial characterization of the ecotoxicity factors of copper soil emissions as a function of the chemical characteristics of vineyard soils located in Portugal and Galicia (NW Spain). A multiple linear regression model was applied to calculate the comparative toxic potential. Subsequently, CFs for copper were calculated based on spatial differentiation considering the variable properties of the soil within each wine appellation. The CFs obtained for the area evaluated ranged from 141 to 5,937 PAF·m^3·day/kg$_{\mathrm{Cu\ emitted}}$, for fibric histosols (HSf) and dystic cambisols (CMd), respectively. Moreover, the average values obtained for Galician and Portuguese soils were 1,145 and 2,274 PAF·m^3·day/kg$_{\mathrm{Cu\ emitted}}$, respectively. The results obtained illustrate the high variability of CF values as a function of the chemical characteristics of each type of soil. For example, Cu soil mobility was linked to organic carbon content and pH. Finally, to validate the representativeness of the calculated CFs, these were applied to the results of 12 literature life cycle inventories of grape production in the area evaluated, revealing that impact scores associated with Cu emissions can considerably vary when spatially-differentiated CFs are implemented.

Keywords: comparative toxic potential; grape production; Life Cycle Assessment; metal mobility; terrestrial eco-toxicity; wine.

1. Introduction

Life cycle assessment (LCA) is a methodology that allows the quantification of environmental impacts related to products and services (ISO, 2006). This methodology has been broadly implemented to the primary sector aiming at analyzing the whole supply chain of agri-food products (Nijdam et al., 2012; Clune et al., 2017; Notarnicola et al., 2017). When delving into the application of this methodology in the agrifood sector, there are different works in products related to shellfish, aquaculture, agriculture or livestock evaluated using LCA (Castanheira et al., 2010, Henriksson et al., 2012; Gonzalez-Garcia et al., 2015, Ziegler et al., 2016; McClelland et al., 2018).

Despite the methodological advances in LCA in the past decade, in the particular case of agricultural systems it is difficult for LCA practitioners to tackle certain methodological limitations. These include the availability of primary data to construct robust life cycle inventories (Villanueva-Rey et al., 2017) or the availability of spatially differentiated characterization factors – CFs (Peña et al., 2018). As for the availability of primary data, on the one hand, and although pesticide production has traditionally been included within the system boundaries of agricultural production, it is common, especially for those that are metal-based, to disregard on-field emissions (Villanueva-Rey et al., 2014a; Renaud-Gentié et al., 2015). Therefore, LCA practitioners seek alternative approaches, which add uncertainty to the analysis and complicate results benchmarking (Rosenbaum et al., 2015). Additionally, current methods cannot account for inorganic active compounds – i.e., metal-based (Birkved and Hauschild, 2006; Dijkman et al., 2012). On the other hand, some efforts have been developed to calculate the CFs to assess the impacts of terrestrial eco-toxicity (also known as Comparative Toxic Potentials —CTPs) of metal-based pesticides (Peña et al., 2017; Owasianiak et al., 2013; Aziz et al., 2018; Viveros Santos et al., 2018; Plouffe et al., 2016), as well as of metallic elements presented in manure (Sydow et al. 2018). Owasianiak et al. (2013) calculated CFs for metal terrestrial toxicity based on multiple linear regression models to analyze the influence of soil properties on the CFs. Peña et al. (2017) and Viveros Santos et al. (2018) also calculated CFs for metal-based fungicides following the Owsianiak et al. (2013) approach, and Plouffe et al. (2016) and Aziz et al. (2018) used modified USEtox fate factors. Owasianiak et al. (2013), Peña et al., (2018) and Viveros Santos et al. (2018) focused on non-calcareous soils, while Plouffe et al. (2016) and Aziz et al. (2018) studied calcareous and non-calcareous soils. However, none of the abovementioned CFs consider the locally-differentiated characteristics of soils. Although these studies developed certain efforts to consider spatial differentiation, the lack of a high level spatial differentiation in the Life Cycle Impact Assessment (LCIA) of agricultural production, particularly for eco-toxicity impacts, remains a critical gap in LCA, as eco-toxicity CFs depend on specific soil characteristics, which affect mobility of the applied metal-based pesticides in crop production.

The environmental profile of grape and wine production has been widely evaluated using the LCA methodology (Gazulla et al., 2010, Point et al. 2012; Vázquez-Rowe et al., 2012a; Herath et al, 2013; Neto et al. 2013, Rugani et al., 2013; Villanueva-Rey et al., 2014b; Steenwerth et al., 2015; Bartocci et al., 2017). The most common environmental impacts reported in the literature include climate change, acidification, or eutrophication, with an emphasis on carbon footprint or water footprint (Rugani et al., 2013; Quinteiro et al., 2014, 2018; Vázquez-Rowe et al., 2017; Villanueva-Rey et al., 2017). Toxicity impacts have been systematically ignored in many studies due to the availability of data, uncertainty in the calculation or the fact that adding these impacts takes much more time than other impact categories (Costa et al., 2018).

In this context, it must be noted that vineyards are typically intensively treated with pesticides to control fungal diseases such as downy mildew (*Plasmopara viticola*) and powdery mildew (*Uncinula necator*). Due to humid climatic conditions, wine-growing regions subject to the Atlantic influence suffer from recurrent fungal diseases during the period from April to June in the northern hemisphere (Point et al., 2012; Vázquez-Rowe et al., 2012a). In addition to synthetic pesticides (e.g., captan, cymoxanil, folpet, mancozeb, etc.), inorganic copper- and sulfur-based pesticides are traditionally used (Dagostin et al., 2011; Bereswill et al., 2012). Synthetic pesticides are man-made plant protection agents intended to kill or repel pests. In contrast, inorganic pesticides are derived from minerals ground into a fine powder, acting as a pest poison. In the 19th century, Bordeaux broth and sulfur dust were used to treat fungal diseases (Sabatier et al., 2014). Currently, inorganic pesticides maintain compositions similar to those used more than 100 years ago. In addition, it should be noted that synthetic pesticides are not permitted in organic viticulture and, therefore, pest management in organic viticulture relies heavily on inorganic pesticides to control insects/fungal diseases.

Due to their efficiency, copper-based fungicides (hereafter represented as copper cation – Cu(II)) are the most widely used active compounds to control downy mildew, which is the most recurrent fungal disease in viticulture regions under the influence of Atlantic climate conditions (e.g., Western Iberian Peninsula: Spain and Portugal). The main copper (Cu) formulations applied in vineyards are the Bordeaux blend, which is a mixture of calcium hydroxide ($Ca(OH)_2$) and cupric sulfate ($CuSO_4$), and copper oxychloride ($Cu_2(OH)_3Cl$). In fact, in this area some studies have reported high concentrations of Cu in soils and sediments, which, in many cases, reach a concentration several times higher than the maximum allowed by the

European Union for agricultural soils (50-150 mg/kg, with lower levels for acid soils) (European Commission, 1986; Arias et al., 2004; Fernández-Calviño et al., 2009; Díaz-Raviña et al., 2007; Patinha et al., 2017).

The natural occurrence of micronutrients such as Cu in soils generally reflects the influence of the bedrock type, climatic conditions influenced by physicochemical weathering, soil age, biological conditions, among others (Harmsen and Vlek, 1985). In terms of natural abundance, soils formed from acid rock materials, such as granites, are expected to have lower concentrations of elements such as Cu and Zn than soils composed of predominantly basic materials, such as basalts. Interestingly, for soils formed from sedimentary bedrocks, these differences are even more pronounced. Soils formed from sandstones usually have relatively low concentrations of elements such as Mo, Mn, Cu or Zn. Similarly, soils formed from limestones tend to be deficient in Fe, Zn, or Cu due to the generally high pH values in these soils, decreasing the availability of these elements (Harmsen and Vlek, 1985). Cu bioavailability and mobility is strongly correlated with pH and organic matter content (Fernández-Calviño et al., 2008a), clay type and content (Wäldchen et al., 2012), cation exchange capacity (Rashidi and Seilsepour, 2008), carbonate and phosphate content (Kabata-Pendias, 2010), among others. Solubility increases in acid soils, but clay content and organic matter play a key role in adsorbing Cu (II) and reducing movement. As a result, the incorporation of spatially differentiated soil chemistry characteristics will influence the assessment of the impact of the ecotoxicity of copper-based pesticides (Hauschild, 2006; Peña et al., 2018).

Toxicity impacts are usually computed independently for human and ecosystem effects. For the latter, eco-toxicity impacts can be analyzed using different methods. However, the UNEP-SETAC scientific consensus model for human toxicity and freshwater eco-toxicity (i.e., USEtox) is recommended for LCA studies (Rosenbaum et al., 2008). Despite this recommendation, it should be noted that USEtox, in its current version, is not capable of differentiating impacts at a high level of spatial resolution and presents limitations in terms of its metal database coverage (Belyanovskaya et al., 2019). Moreover, the modelling behind

USEtox provides a higher level of certainty for nonionic, organic chemicals in a liquid or gaseous state, whereas metals with high vapor pressure, such as copper or mercury, tend to pose problems (Fantke et al., 2017). More importantly for the current study, exposure and effect modeling in the marine and terrestrial compartments are yet to be totally identified, due to data gaps in terms of chemical behavior and effects on living organism (Henderson et al., 2011).

In this context, considering the importance of metal-based pesticides in terms of vineyard soil degradation, the main objective of the study is to develop spatially differentiated CFs to assess the impacts of terrestrial eco-toxicity for Cu emissions into the soil. These CFs are estimated taking into account the soil features of the wine-growing areas located in the Northwestern section of the Iberian Peninsula, focusing on 12 wine appellations in Galicia and the northern and central regions of Portugal. In addition, this study revisits the results of the impact of eco-toxicity on Cu emissions in the field using the newly developed and spatially differentiated CFs.

2. Materials and methods

2.1. Terrestrial eco-toxicity CFs framework

The proposed framework for terrestrial eco-toxicity impact assessment is based on the Multiple Linear Regression (MLR) model developed by Owsianiak et al. (2013) to calculate the characterization factor (CF) of Cu emitted into the air in non-calcareous soils. This model revisits the method proposed by Gandhi et al. (2010) for calculating the CF of cationic metals in freshwater. The novelty of the previous model relies on the introduction of the accessibility factor (ACF) into the CF definition, decoupling the ACF from the bioavailability factor (BF), redefining the equation as follows:

$$CF_{i,s} = FF_{i,s} \times \underbrace{ACF_s \times BF_s}_{\text{exposure}} \times EF_s \qquad (1)$$

where $CF_{i,s}$ ($PAF \cdot m^3 \cdot day/kg_{total\ emitted}$) is the characterization factor of total metal *s* emitted to the environmental compartment *i*; $FF_{i,s}$ (day) is the fate factor calculated for total metal *s* in soil; ACF_s ($kg_{reactive}/kg_{total}$) is the accessibility factor defined as the reactive fraction of total metal *s* in soil; BF_s ($kg_{free}/kg_{reactive}$) is the bioavailability factor defined as the free ion fraction of the reactive metal *s* in soil; and, EF_s (m^3/kg_{free}) is the terrestrial eco-toxicity effect factor defined as potentially affected fraction (PAF) of organisms for the free ion form of the metal. The soil exposure factor, taking into account both ACFs and BFs, expresses the quantity of free Cu ions transferred to the soil.

2.1.2 Soil spatial differentiation

The inclusion of spatial differentiation for CFs was possible through the application of the MLR model proposed by Owsianiak et al. (2013). Based on equation 1, the model analyses the influence of soil properties on CF, allowing direct calculation of endpoint terrestrial ecotoxicity from soil parameters, as shown in equation 2:

$$\log_{10} CF_i = a + b \cdot pH + c \cdot \log_{10}(ORG) + d \cdot \log_{10}([Mg^{2+}]) + e \cdot \log_{10}(CLAY) \qquad (2)$$

where CF ($PAF \cdot m^3 \cdot day/kg_{Cu\ emitted}$) is the characterization factor of the total metal emitted into air for soil type category *i* within each appellation evaluated; pH is the measure of the acidity or basicity of a soil; ORG (%) is the organic carbon in the soil; $[Mg^{2+}]$ (mol/L) is the magnesium concentration in soil pore water; CLAY (%) is the clay content in soil; and, a,b,c,d and e are the linear regression coefficients. The coefficients of equation 2 can be found in Table S1 of the Supporting Material (SM). The model is not applicable to calcareous soils or soils with carbonate ($CaCO_3$). In addition, soils with pH values > 6.5 and saline soils (ionic strength of soil pore water above 0.5 mol/L) are also excluded due to the uncertainties related to calculations (Owsianiak et al., 2013). According to Owsianiak et al. (2013), terrestrial eco-toxicity CFs are poorly correlated with the concentration of Mg^{2+} in soils. Therefore, and due to unavailable spatially differentiated data for Mg^{2+}, a concentration value of 3.80E-4 mol/L —as reported by Owsianiak et al. (2013) as median for the set of 760 soils employed for the model— was assumed for soils under analysis. Additionally, a sensitivity analysis was conducted implementing the minimum and maximum Mg^{2+} concentration obtained by Owsianiak et al. (2013): 6.00E-8 mol/L and 7.50E-2 mol/L respectively. Likewise, the linear regression equation was also implemented using only organic carbon and pH as parameters. Finally, according to the research performed by Miotto et al. (2014) the increased availability of Cu in soil slightly affects the concentration and accumulation of Cu in leaves and branches, but appears to have no significance on berries.

2.2. Soil data

2.2.1. Data processing

The selected area includes a total of 12 appellations throughout Galicia (NW Spain) and Portugal (Northern and Central regions) (Figure 1). Appellations are wine and grape Protected Designation of Origin regulations used to describe a wine producing region that complies with the following requirements: i) its quality and characteristics are essentially or exclusively due to a particular geographical environment with its inherent natural and human factors; ii) the grapes come exclusively from that geographical area; and, iii) wine production takes place in that geographical area. In Spain, these geographical indications receive the name of *Denominación de Origen*, whereas in Portugal they are regulated under the name of *Denominação de Origem Controlada*. Although Galicia only accounts for 2% of the total area dedicated to vine cultivation in Spain, in recent years this region has acquired international notoriety thanks to the quality of its vineyards (Decanter, 2011). In contrast, in the case of Portugal, the areas evaluated represent around 76% of the total national wine-growing area (INE, 2015).

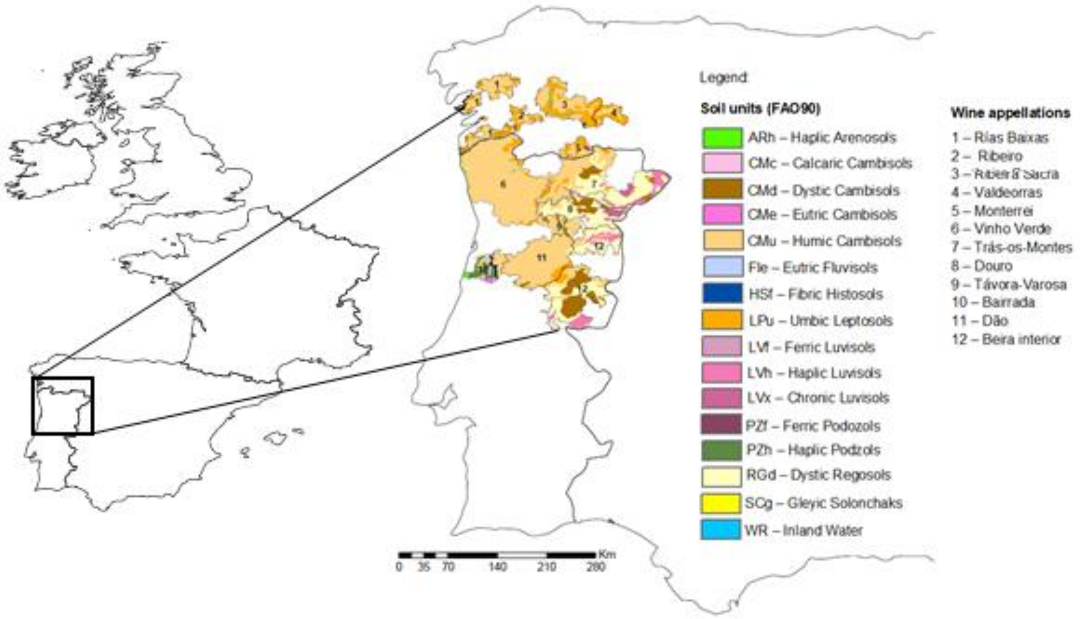

Figure 1. Map of the area under consideration including details of soil types in the 12 appellations evaluated.

ArcGIS v.10.3.1 (Esri, 2015) was the software applied to identify the soil units for the area under analysis and to georeference the appellations (Figure 1). The classification of soil units was obtained from the Harmonized World Soil Database (HWSD) developed by FAO/IIASA/ISRIC/ISS-CAS/JRC (2012). Data on organic carbon, pH and clay content, required to calculate CFs from equation 2, were collected from this database. Moreover, the digital maps for the aforementioned appellations were delimited according to the Local Administrative Units (LAU). The LAUs are the basic components of the Nomenclature of Territorial Units for Statistics NUTS (i.e., a hierarchical system used to divide the territory of the European Union) (Eurostat, 2013).

Both soil classification and region delimited maps were overlapped aiming at mapping vineyard-devoted soils per producing area, as shown in Figure 1. Subsequently, from the resulting map, soil chemistry characteristics were used to calculate CFs on the basis of equation 2. As mentioned in section 2.1, CFs were derived for non-calcareous soils showing zero content of $CaCO_3$ and pH < 6.5. Thereafter, CFs were weighted for each appellation according to the soil surface area, following Equation 3. This procedure allowed the weighted CFs for each denomination to be calculated individually, taking into account the different soil types within each appellation. The rationale behind the latter is to help LCA practitioners when selecting an appropriate CF for the computation of eco-toxicity environmental impact scores.

$$CF_{w,j} = \frac{CF_j x\, A_j}{A_t} \quad (3)$$

where $CF_{w,j}$ (PAF·m^3·day/kg$_{\text{total emitted}}$) is the weighted average CF of each appellation *j*; A (ha) is the area for each soil type category *i* within each appellation; and A_t(ha) is the total area of each appellation under study.

2.2.2. Soils characterization

From a lithological perspective, the regions of Galicia and Northwest Portugal are very homogenous. According to Fernández-Calviño et al. (2008a), vineyard-devoted soils in most of the areas under analysis are either granite- or granodiorite- based. However, in Galicia there are also small proportions of other bedrocks, such as shales and gneiss (e.g., in Ribeiro and Ribeira Sacra), slates (e.g., in Ribeira Sacra and Valdeorras), Tertiary sediments, limestones and Quaternary terraces (e.g., in Ribeiro, Monterrei and Valdeorras). Shale- and granite-based soils predominate in Portugal, and their contribution may vary from region to region (e.g. Trás-os-Montes, Douro, Dão and Beira interior). The vineyards in the region of Bairrada were planted mostly in clay-calcareous soils, but also in sandy and alluvial soils. Finally, in the Távora – Varosa appellation most soils are granitic or sandy-clay (Atlas do Ambiente Digital, 2018).

In vineyard regions, the associated soils have undergone profound changes in the original morphology due to secular work, which involves vine planting, plus the additions of organic and inorganic materials (fertilizers, pesticides, etc.), long-continued irrigation, etc. Hence, according to FAO classification (FAO/IIASA/ISRIC/ISS-CAS/JRC, 2012), this type of soils are called anthrosols. Where anthropogenic action was less intense and the soil maintained its original profile despite modifications in the superficial layer, three main units are distinguished: cambisols (CM), regosols (RG) and leptosols (LP) (Figure 1). Cambisols are moderately developed soils, showing a slight evidence of the soil formation process. These soils are located mainly in valleys. Regosols are very weakly developed soils, characterized by the topographic conditions (i.e., eroding lands and hillsides). Leptosols are very shallow soils deposited over hard rock and very susceptible to erosion, presenting little evidence of soil formation with slight or no horizonation (FAO/IIASA/ISRIC/ISS-CAS/JRC, 2012).

Most of the soils dedicated to the vineyard are cambisols - dominated by humic cambisols (CMu) - and leptosols - mainly umbric leptosols (LPu) (Vinho Verde, Dão and Galician appellations). In addition, there are vineyards mainly established on dystic regosols (RGd) and dystic cambisols (CMd) (Douro and Beira Interior). However, there are also other appellations such as Trás-os-Montes, established on humic cambisols (CMu) and dystic regosols (RGd). The region of Távora-Varosa is mainly established on cambisols (CMu and CMd). Finally, Bairrada is undoubtedly the region with the greatest variety of soils due to its bedrock diversity. In this region, vineyards grow on cambisols - including humic cambisols (CMu) and calcaric cambisols (CMc), but also on podzols - which are dominated by haplic podzols (PZh) (Atlas do Ambiente Digital, 2018). Tables S2 and S3 in the SM summarize the chemical features of soil in each appellation.

In general, vineyard-devoted soils are characterized by low pH (acid to moderately acid), small thickness, sandy loam texture and low to moderate organic carbon content. In addition, soils are dominated by the sand fraction rather than by their content in clay and silt. Clay is generally the lowest fraction in these soils. As mentioned previously, these factors (i.e., pH, clay, silt and sand percentage and organic carbon content) influence the availability of important soil micronutrients and metals, such as Cu. Furthermore, high annual rainfall leads to leaching of nutrients and, consequently, problems in terms of soil fertility. Many soils have limitations for agriculture: small thickness and nutrient scarcity. Therefore, agriculture is found in the valleys, while shrubs and bushes thrive on the slopes. However, due to the lack of available land, crops such as vines are established on terraces, avoiding the effects of erosion and allowing cultivation. In this sense, terraced vineyards dominate the landscape of riversides in some of the appellations aforementioned (e.g., Ribeira Sacra, Ribeiro, Douro, Trás-os-Montes).

3. Results and discussion

3.1. Characterization factor for soils: Spatially differentiated results

The CFs, as abovementioned, also known as Comparative toxic Potentials —CTPs, obtained for non-calcareous soils in the area ranged from 141 to 5,937 PAF·m^3·day/$kg_{Cu\ emitted}$, for fibric histosols (HSf) and dystic cambisols (CMd), respectively, according to the results obtained using Equation 2. The average values obtained for Galician and Portuguese soils were 1,145 and 2,275 PAF·m^3·day/$kg_{Cu\ emitted}$, respectively. As mentioned in section 2.2, cambisols are the dominant soils, ca. 50% in terms of total area. The CF obtained for the dominant cambisol (CMu) was 987 PAF·m^3·day/$kg_{Cu\ emitted}$ (Figure 2). Additionally, significant differences were found within CMu. Hence, some CMu soils obtained higher CF values (1,891 PAF·m^3·day/$kg_{Cu\ emitted}$) emitted due to the lower organic carbon content of these soils. Similarly, dystic cambisols (CMd) attained CF values higher than those of CMu, 5,937 PAF·m^3·day/$kg_{Cu\ emitted}$, but it should be noted that the latter account for only 6% of the surface share and are only found in Portuguese soils.

Regosols are the second type of soil in terms of surface share, representing 30% of total area, being dystic regosols (RGd) predominant within regosols. The CF obtained for RGd ranged from 2,618 to 3,645 PAF·m^3·day/$kg_{Cu\ emitted}$, based on soil features: different clay and organic carbon content. Eutric regosols (RGe) can also be found, but they are negligible in terms of surface —less than 1%. Interestingly, the aforementioned RGe reached lower CF values: 1,096 PAF·m^3·day/$kg_{Cu\ emitted}$, due to its higher pH, regardless of its lower organic carbon and clay content.

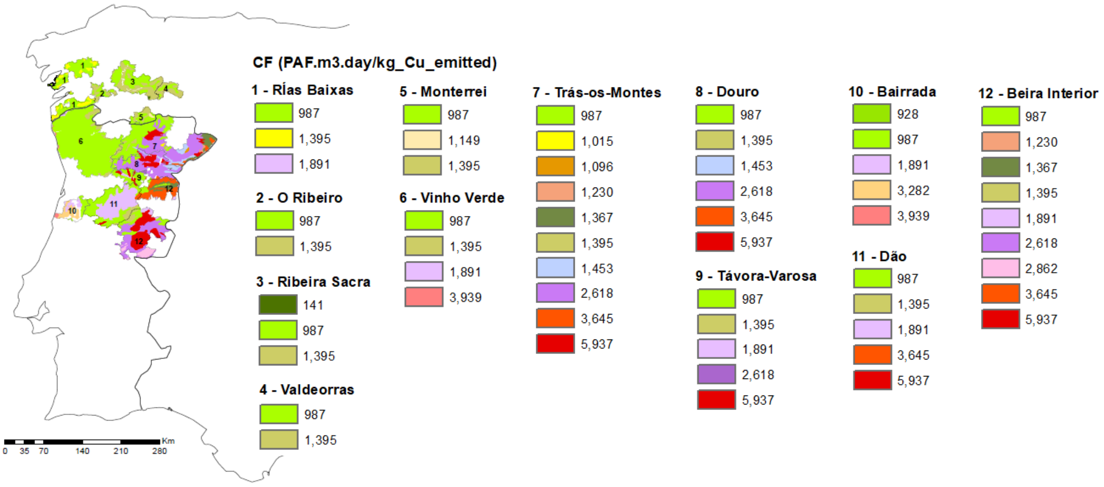

Figure 2. Characterization factors of terrestrial eco-toxicity (CFs) for copper (Cu) calculated for 16 soils in the northwest of the Iberian Peninsula.

Umbric leptosols (LPu) are the third soils in terms of surface, with 11% in share. The calculated CF was 1,395 PAF·m^3·day/kg$_{\text{Cu emitted}}$, which is slightly higher than the CF obtained for CMu, even though both share features in terms of pH, organic carbon and clay content.

Luvisols are also relevant in terms of surface share, accounting for 10%. Humic luvisols (LVh) are the main luvisol followed by chromic luvisol (LVx) and ferric luvisol (LVf). The results obtained for these subtypes vary considerably depending on the soil chemistry. Hence, the CF ranges between 928 to 2,862 PAF·m^3·day/kg$_{\text{Cu emitted}}$ for LVx and LVh, respectively. Additionally, significant differences were found within haplic luvisols (LVh). Finally, podzols, histosols and arenosols are negligible in terms of surface, representing only 3% of total surface area. Comprehensive and detailed data on CF results can be consulted in Table S3 of the SM.

As Figure 1 depicts, soils in the appellations are heterogeneous and consist of several soil units. In this regard, the CF of each appellation was estimated for the total area of each appellation due to the difficulty of mapping specific vineyard areas within each appellation. Hence, the weighted average CF of each appellation (CF$_W$) was obtained for each of them, taking into account the surface area of the soil type. The weighted average CF ranged from 1,030 to 2,884 PAF·m^3·day/kg$_{\text{Cu emitted}}$ for Vinho Verde and Douro, respectively (Table 1).

Interestingly, the Galician appellations, together with the Vinho Verde appellation, attained lower CFs values when compared to the other Portuguese appellations. The lithological similarities between Northwest Portugal and Galicia, and the derived soils thereby (Figure 1), explain the results obtained for the Cu soil eco-toxicity CFs. Dão and Távora-Varosa achieved higher CF values, despite having soil classes similar to those of the Northern appellations. The existence of cambisols with low clay and carbon contents combined with low pH values explain this phenomenon. Furthermore, Trás-os-Montes attained a high CF_W despite sharing soil types with Vinho Verde in the Western area. In this sense, the presence of regosols, luvisols and dystic cambisols caused an increase in the CF_W due to the lower organic carbon and clay contents in these soils. Moreover, the CF_W obtained for Bairrada is also noteworthy, since it is highly influenced by the lower clay and organic carbon contents of its soils. Finally, the high CF_W value obtained for Beira interior is related to the lower organic carbon content (below 1%) of regosols (RGd) and cambisols (CMd).

Table 1. Weighted average of terrestrial eco-toxicity characterization factors (CF_W) for each appellation evaluated.

Designation of Origin	CF_W (PAF•m3•day/$kg_{Cu\ emitted}$)		
	Weighted average	Higher	Lower
Rías Baixas	1,103	1,891	987
Ribeiro	1,214	1,395	987
Ribeira Sacra	1,177	1,395	141
Valdeorras	1,267	1,395	987
Monterrei	1,154	1,395	987
Vinho Verde	1,030	3,939	987
Trás-os-Montes	2,052	5,937	987
Douro	2,884	5,937	987
Távora Varosa	1,880	5,937	987
Bairrada	2,366	3,939	987
Dão	1,574	5,937	987
Beira interior	2,513	5,937	987

Furthermore, as abovementioned, a sensitivity analysis was conducted for the calculation of CFs, taking into account different Mg^{2+} concentration and using only organic carbon and pH as parameters for the regression model. Thus, the CFs calculated using only pH and organic carbon as parameters, approach followed by Peña et al. (2018), are in a similar range as those CFs obtained when the concentration of Mg^{2+} is established in the median value reported by Owsianiak et al. (2013): i.e., the approach used in the current study. The latter is not strange due to the fact that the model is determined mainly by soil organic carbon (Owsianiak et al., 2013). In contrast, variations in the CFs were found when the lower and higher Mg^{2+} concentration values are used. Detailed results for sensitivity analysis can be consulted in Table S3 of the SM.

The CFs obtained for each soil depend on the chemical characteristics. Hence, Cu soil mobility depends largely on the organic carbon content, which influences metal mobility, and pH, which influences bioavailability (Arias et al., 2004). Clay content (soil texture), in contrast, has less overall influence (Owsianiak et al., 2013; Peña et al., 2018). Having said this, on the one hand, it is not surprising that soils with higher organic carbon rates, such as fibric histosols —HSf— or CMu, have reached lower CFs values since organic matter bounds the largest fraction of Cu (Fernandez-Calviño et al., 2009). On the other hand, soils with low organic carbon content (e.g. CMd) attained the highest CF value. As for pH, its values influence the final CF value. Hence, slightly acidic soils (i.e., with a pH between 6 and 6.4) lead to reduced CF values in many cases, especially in soils with low organic carbon (OC) content (<1%): RGe and luvisols. The results obtained for the spatially differentiated CFs are aligned to those abovementioned. Thus, the high organic matter and clay contents are related to copper bounds and, therefore, to lower Cu soil mobility.

3.2 Limitations and further research

A few constraints were identified regarding the soils units analyzed, the effects of LUCs on terrestrial eco-toxicity impacts, and the management techniques for land-use systems. Following the conditions established by Owsianiak et al. (2013) for the application of eq. 2, some soil units were excluded due to pH value and $CaCO_3$ content, both collected from the HWSD database. Hence, it was not possible to calculate CFs for some soil classes, although it should be remarked that the excluded soils represent less than 2% of the total area evaluated. For instance, some soils in Trás-os-Montes, Bairrada and Douro were excluded due to pH values higher than 6.5 and the presence of $CaCO_3$. The main soil classes excluded were cambisols (eutric cambisols —CMe and —CMc), followed by fluvisols (eutric fluvisols —FLe) in Trás-os-Montes, Douro and Bairrada. These soils are expected to reach lower CF values due to their basic to moderately basic pH values, which will lead to lower Cu mobilization. Furthermore, there was also exclusion related to soil salinity due to the presence of gleyic solonchaks (SCg) in Bairrada.

Land use changes (LUCs) also influence metal concentrations and their mobility in soils (de Santiago-Martín et al., 2016). For instance, abandonment of vineyards has been a common trend in some areas of Galicia in recent decades, shifting from small vineyard plots to larger ones in hillslopes and forests (Fernández-Calviño et al., 2008a; Villanueva-Rey et al., 2015). These abandoned vineyards reconverted to new uses —mainly forest— may give rise to Cu mobilization due to soil acidification (Fernández-Calviño et al., 2008a). In fact, Fernández-Calviño et al. (2008b) have reported different Cu distribution based on vineyard age and abandonment. Moreover, reforestation processes may lead to soil acidification, which increases Cu mobilization, although this phenomenon is highly dependent on the tree species. A particular high-risk scenario is related to the recurrent forest fires that occur annually in this area (Nunes, 2012; Loureiro and Barreal, 2015; Tonini et al., 2017). Reforested areas tend to recover, naturally or artificially, with coniferous or eucalyptus species, widely present in the landscape of the NW Iberian Peninsula (Calviño-Cancela et al., 2017). These species not only imply higher mobilization of Cu due to the acid characteristics of their soils, but are also pyrophyte species prone to favor future forest fire conditions. Moreover, mercury and other heavy metals may be released into the environment as a result of soil erosion due to increased runoff in deforested or burned areas associated with a variety of anthropogenic activities due to high natural accumulation of these metals in the environment (Roulet et al., 2000). When heavy rainfall episodes occur immediately after forest fires, there is a high risk of Cu mobilization and other metals due to runoff (Vieira et al., 2015). The application of mulching techniques with agricultural residues appears to be an efficient option to reduce the risk of runoff due to post-fire erosion processes while vegetation cover has not yet recovered (Fernández et al., 2016).

Villanueva-Rey et al. (2015) assessed the influence of afforestation and forest fires on the LUCs in the Ribeiro appellation in the period 1990-2009, suggesting that conifers and eucalyptus species expansion are the leading afforestation processes in abandoned vineyards. In other words, the reforestation process (natural or artificial) in this area of the Iberian Peninsula has occurred with exotic species, based in many cases on economic profitability (Calviño-Cancela and Rubido-Bará, 2013). Therefore, human-induced afforestation strategies should include deciduous species, rather than coniferous species, which have greater acidifying potential (Rigueiro-Rodríguez et al., 2012).

Different management techniques, climatic conditions and vineyard age have also shown some influence in terms of Cu concentrations (Duplay et al., 2014). Furthermore, hillside erosion and terraced vineyards lead to transportation and accumulation of Cu in sediments due to mobilization of metal bounds with organic matter and inorganic amorphous colloids (Fernández-Calviño et al., 2009). Finally, soil Cu influences the adsorption of herbicides in the soil rather than depending on clay or organic content, as it competes with ammonium herbicides for adsorption sites (Conde-Cid et al., 2017). Therefore, further research is needed to properly quantify the effects of LUCs, including management techniques, mulching techniques and post-fire erosion processes on CFs of Cu. In addition, policy measures should be implemented in this regard in order to avoid future toxicity problems of Cu arising from mobilization.

3.3. Practical implications

Several studies have analyzed the accumulation of Cu in vineyard soils. For instance, Fernandez-Calviño et al. (2009) stated that Cu concentration in soils dedicated to vines in the northwest of the Iberian Peninsula ranges from 25 mg/kg to 666 mg/kg, which is significantly higher than in uncultivated soils (12-39 mg/kg). Therefore, there is clear evidence of Cu accumulation, obtaining values above the permitted range of 50 mg/kg to 140 mg/kg, being 50 mg/kg the maximum content established for acid soils (European Commission, 1986). Interestingly, despite higher Cu concentrations, there is evidence that these concentrations tend to present low mobility, with only a minor fraction representing exchangeable Cu (Fernandez-Calviño et al., 2009).

USEtox is the most widely and recommended consensus model to characterize human and eco-toxicity impacts of chemical emissions in LCA (European Commission et al., 2010). However, despite having an impressive database of hundreds of CFs to account for freshwater eco-toxicity of inorganic and organic substances, there are gaps in the characterization of soil eco-toxicity impacts due to lack of appropriate data and models (Henderson et al., 2011; Rosenbaum et al., 2015). In this context, the CFs obtained from the current study were applied to some LCA studies of Portuguese and Galician grape production available in the bibliography (Vázquez-Rowe et al., 2012a,b; Villanueva-Rey et al., 2014; Neto et al., 2012; Figueiredo et al., 2014) and the results of their comparison are depicted in Figure 3. The results reveal that different impact scores can be attained when spatially differentiated CFs are implemented. The studies performed in the appellations located in Galicia and Northern Portugal (i.e., Rías Baixas, Ribeiro, and Vinho Verde) achieved the lowest impact scores. This makes sense taking into account that the soils from these appellations presented the lowest CFs. In contrast, higher impact scores are achieved in the studies carried out in Central Portugal (i.e., Douro and Bairrada) due to the fact that these appellations presented the highest CFs. Additionally, the different impact scores attained in the studies conducted within the same appellation are remarkable (i.e., Rías Baixas, Ribeiro and Vinho Verde). The rationale behind the latter is related to Cu-based pesticides dosage per year (number of treatments based of weather conditions and fungal infections recurrence) and vineyards production yield: viticulture type and/or harvest year.

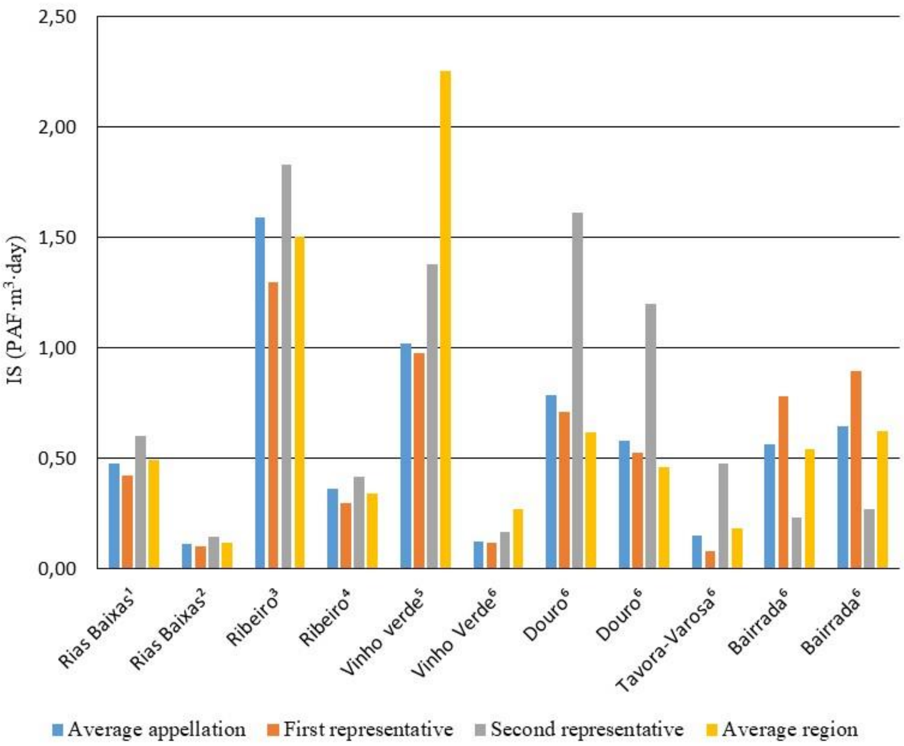

Figure 3. Terrestrial eco-toxicity impact results for Cu on-field emission in some LCA studies performed in the area evaluated. Note: Average appellation, weighted average CF; First representative, CF for larger soil type in surface share; Second representative, CF for second soil type in surface share; Average region, CF for the region (i.e. Galicia, Northern Portugal and Central Portugal); FU, 1 kg of grapes was the selected functional unit; IS, Impact Score (PAF·m^3·day). References: 1, Vázquez-Rowe et al. (2012b); 2, unpublished; 3, Vázquez-Rowe et al. (2012a); 4, Villanueva-Rey et al. (2014); 5, Neto et al. (2012); 6, Figueiredo et al. (2014).

4. Conclusions

The results of this study reveal the wide range of eco-toxicity impact results that can be attained when specific edaphic information is available to compute spatially-differentiated CFs. This constitutes an important finding since it demonstrates the high uncertainty inherent to generic CFs used in many LCA studies and the limitations in terms of scientific relevance and policy-making advice. For the former, it is hypothesized that the influence of soil characteristics could be extended to many other active compounds used in agriculture, although the results from this study cannot be extrapolated to other chemicals, since interactions between soils and toxic elements do not follow linear patterns. For the latter, decision makers could benefit from site- or local-specific emission values to set guidelines or restrictions on the use of copper-based pesticides. Therefore, we advocate that future LCA studies in the agri-food sector include edaphic information in their analysis in order to take into account the specific characteristics of the soil when reporting toxic environmental impacts.

The implementation of spatially-differentiated CFs demonstrates the variety of eco-toxicity impact scores for Cu on-field emissions that can be attained for grape devoted soils. The organic carbon content in soils was found to be one of the main driving factors influencing the toxicity potential: higher content is related to lower eco-toxicity potential. In general, large copper bioavailability and chemical mobility occurs at low pH (pH<6.5), but these skills are heavily influenced by a range of other soil properties, such as organic matter content, clay content, cation exchange capacity, carbonate and phosphate content, among others. However, the most important sink is copper complexation with organic matter, being one of the most efficient mechanisms of copper retention in soil and being one of the most efficient mechanisms of copper retention in soil and lower eco-toxicity potential thereby. Consequently, the appellations of Galicia and Northern Portugal attained the lowest CFs due to the fact that vineyard devoted soils are mainly established in cambisols (CMu) and leptosols (LPu), which are characterized by moderate-high levels of organic carbon and low pH values.

Finally, this work establishes the foundations for assessing the toxicity of inorganic pesticides used in vineyards, and at the same time builds a bridge to apply a similar approach to organic pesticides that are also frequently applied in viticulture.

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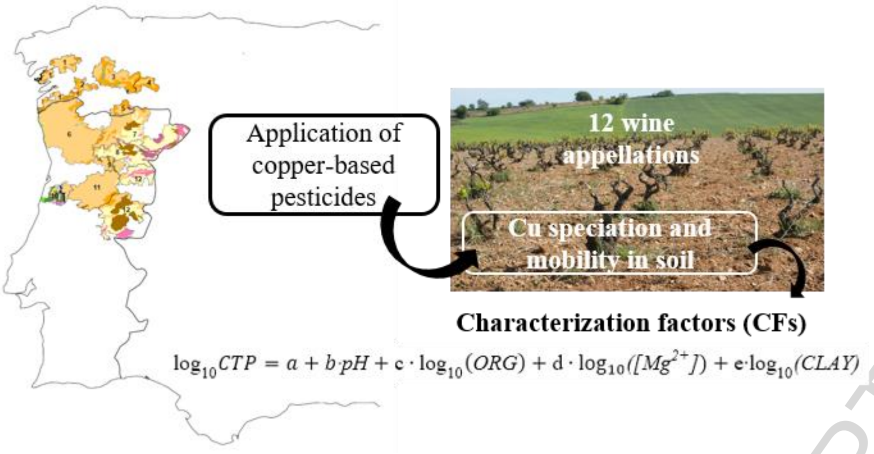

Graphical abstract

Research highlights

- Vineyard devoted soils were characterized for wine appellations in Northern Spain and Portugal
- Spatially-differentiated characterization factors for terrestrial eco-toxicity were obtained for copper
- Characterization factors range considerably as a function of the chemical characteristics of each type of soil
- The organic carbon content in soils was found to be one of the main driving factors influencing the toxicity potential