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Published in:
Science of the Total Environment

Link to article, DOI:
10.1016/j.scitotenv.2017.10.243

Publication date:
2018

Document Version
Peer reviewed version

Modelling Ecotoxicity Impacts in vineyard production: Addressing Spatial Differentiation for Copper Fungicides

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ABSTRACT

Application of plant protection products (PPP) is a fundamental practice for viticulture. Life Cycle Assessment (LCA) has proved to be a useful tool to assess the environmental performance of agricultural production, where including toxicity-related impacts for PPP use is still associated with methodological limitations, especially for inorganic (i.e. metal-based) pesticides. Downy mildew is one of the most severe diseases for vineyard production. For disease control, copper-based fungicides are the most effective and used PPP in both conventional and organic viticulture. This study aims to improve the toxicity-related characterization of copper-based fungicides (Cu) for LCA studies. Potential freshwater ecotoxicity impacts of 12 active ingredients used to control downy mildew in European vineyards were quantified and compared. Soil ecotoxicity impacts were calculated for specific soil chemistries and textures. To introduce spatial differentiation for Cu in freshwater and soil ecotoxicity characterization, we used 7 European water archetypes and a set of 15034 non-calcareous vineyard soils for 4 agricultural scenarios. Cu ranked as the most impacting substance for potential freshwater ecotoxicity among the 12 studied active ingredients. With the inclusion of spatial differentiation, Cu toxicity potentials vary 3 orders of magnitude, making variation according to water archetypes potentially relevant. In the case of non-calcareous soils ecotoxicity characterization, the variability of Cu impacts in different receiving environments is about 2 orders of magnitude. Our results show that Cu potential toxicity depends mainly on its capacity to interact with the emission site, and the dynamics of this interaction (speciation). These results represent a better approximation to understand Cu potential toxicity impact profiles, assisting decision makers to better understand copper behavior concerning the receiving environment and therefore how restrictions on the use of copper-based fungicides should be considered in relation to the emission site.

Keywords: Life cycle assessment (LCA), USEtox, inorganic pesticides, freshwater ecotoxicity, soil ecotoxicity, non-calcareous vineyards.

1. INTRODUCTION

Life Cycle Assessment (LCA) is a comprehensive methodology that aims at quantifying the potential environmental impacts of any product system over its entire lifecycle (ISO-14040, 2006). Within the agricultural sector, LCA has proven to be useful for assessing the environmental performance of many cropping systems (Boone et al., 2016; Parajuli et al., 2017; Torrellas et al., 2012). However, often a limited number of impact categories is evaluated in comparative LCAs of agricultural systems (Meier et al., 2015). Although plant protection products (PPP) are routinely applied in agriculture, one of the critical points within the life cycle impact assessment (LCIA) phase in LCAs of agricultural systems is the lack of characterizing potential toxicity-related impacts for PPP use in crop production. This lack is even more apparent when it comes to the evaluation of inorganic pesticides (i.e. metal-based pesticides), approved for organic farming, as these are not as well understood and characterized as synthetic[1] pesticides. Furthermore, freshwater ecotoxicity is among those LCIA impact categories that, only in recent years, has started to be considered mature enough for inclusion in LCA studies.

Nowadays, the European Commission authorizes more than 500 active ingredients (AI). Around 340,000 tons of PPP are used each year in Europe (EU28), from which fungicides represent the most used AI in conventional and organic agriculture, with a total annual use in the EU28 of 169,000 tonnes for 2014. Furthermore, Inorganic fungicides account for 39-55% of the total applied fungicides in the EU (European Comission, 2009; Eurostat, 2016). PPP have become vital elements in modern agriculture as they provide many benefits, but their extensive and continuous applications also have several negative implications for the environment. Some

[1] The terms synthetic pesticides and synthetic fungicides in this study refer to pesticides that contain xenobiotic organic compounds as active ingredients that are prohibited in organic crop and livestock production (European Comission, 2008).

of these implications include human exposure to crop residues (Fantke et al., 2012), potential impacts on non-target organisms (Felsot et al., 2010), a shift in dominating pest species and increasing pest resistance (Pimentel, 2005). The two latter problems, in turn, push crop growers towards an even more intensified use of PPP, and consequently, crop production costs rise, and potential risks of toxic impacts on humans and the environment may further increase (Nesheim et al., 2015).

European vineyards represent more than 50% of the total world area of vines (OIV, 2016), and the long-term use of PPP in vineyards has contributed to increased concentrations of these substances in different environmental compartments (Hildebrandt et al., 2008; Ribolzi et al., 2002; Wightwick et al., 2008). Concerning PPP use, one of the main differences between conventional and organic viticulture production is that in general synthetic pesticides are not allowed for use in organic pest management, whereas inorganic pesticides are indispensable for organic vine cultivation.

Furthermore, copper-based fungicides are the most efficient and widely used PPP in Europe in both conventional and organic viticulture to control vine fungal diseases, such as downy mildew caused by *Plasmopara viticola*, one of the most severe and devastating diseases for grapevine (Agrios, 2005). Therefore, the extensive use of fungicides to control this and other fungal pests has posed significant environmental problems, such as unwanted residues in plants and water, reduction of the quality and degradation of soils, as well as some ecotoxicological threats in non-target organisms (Fantke et al., 2011a; Komarek et al., 2010).

Different studies have evaluated the environmental profile of viticulture and wine production from a life cycle perspective (Bartocci et al., 2017; Benedetto, 2013; Point et al., 2012). In line with LCA studies of other agricultural systems, one of the repeatedly assessed impact category for viticulture is the evaluation of global warming potential (Bosco et al., 2011; Steenwerth et al., 2015) with particular focus on water or carbon footprint indicators (Bonamente et al., 2016; Bosco et al., 2013; Lamastra et al., 2014). In contrast, impact categories related to toxicity are often disregarded, partly due to missing data for all involved chemicals including PPP and partly due to high perceived and real uncertainties (Fantke et al., 2016; Rosenbaum et al., 2015). Consequently, PPP and their effects on freshwater and terrestrial ecosystems are frequently omitted, even though they are one of the significant environmental concerns linked with agriculture (Meier et al., 2015). Furthermore, including ecotoxicity in LCA does not necessarily mean that the toxic effects of PPP use are being considered. For instance, Benedetto (2013) reports PPP emissions without including the related impact factors despite available characterization models. Other studies evaluated ecotoxicity impacts related to PPP production but do not quantify the impacts in the use phase (Jimenez et al., 2014; Point et al., 2012). Although numerous studies acknowledge the use of copper in vineyard production, and the impacts of the production of copper-based fungicides are included in a few of them (Point et al., 2012; Villanueva-Rey et al., 2014), the impact resulting from the use of these fungicides is not considered.

Freshwater ecotoxicity can be characterized with different available methods, such as the UNEP-SETAC scientific consensus model for toxicity characterization of chemical emissions in LCIA (Rosenbaum et al., 2008) that is endorsed by the UNEP-SETAC Life Cycle Initiative (Westh et al., 2015). In the case of soil ecotoxicity characterization, several emerging approaches exist (Haye et al., 2007; Lofts et al., 2013; Owsianiak et al., 2013), but no method has yet been widely adopted. Finally, there is a lack of agreement on how to assess ecotoxicity-related impacts of metal-based PPP that are currently not adequately characterized by any existing model (Hauschild and Huijbregts, 2015; Meier et al., 2015).

Characterization of the toxic effects of metal-based emissions in LCIA assumes that the toxicity is a function of the activity of the free metal ion (Campbell, 1995; Owsianiak et al., 2015), which is related to the relevant chemical species, Cu(II). Factors such as water pH, dissolved organic carbon (DOC) and water hardness (Allen and Janssen, 2006; Gandhi et al., 2010), and soil organic carbon (SOC), soil pH and texture (Komarek et al., 2010) control metal speciation and thus its potential toxic effects. Consequently, incorporating and defining these geographically distinct characteristics in which the inventory flows (i.e. pesticide emissions) occur will have a significant influence on the ecotoxicological impact assessment of copper-based fungicide AIs in LCA (Gandhi et al., 2011b; Potting and Hauschild, 2006).

The main objective of the present work is to improve the consideration of copper-based fungicides in LCA with focus on three specific aims: First, to characterize fungicide emissions and freshwater ecotoxicity impacts to compare results of copper-based fungicides with commonly used AIs to control downy mildew in European vineyards. Second, to introduce soil ecotoxicity characterization for copper-based fungicides. Third, to include spatial differentiation on the assessment of freshwater and soil ecotoxicity characterization associated with the application of copper-based fungicides in European vineyards.

2. MATERIALS AND METHODS

We identified the most relevant aspects for modelling ecotoxicity in freshwater and soil as direct impact pathways for PPP use. We quantified the freshwater ecotoxicity potential of the main AI (synthetic and copper-based) used to control downy mildew in European vineyards using USEtox 2.02 as characterization model (http://usetox.org). Thereafter, we estimated characterization factors (CF) for non-calcareous soils based on the multiple linear regression model developed by Owsianiak et al. (2013). Finally, we introduced geographic variability for copper-based fungicides used in European vineyards, with the truly dissolved metal fraction as proposed by Dong et al. (2014) evaluated in seven European water archetypes (Gandhi et al., 2011a) and assessed the potential soil ecotoxicity impacts in different application scenarios for specific non-calcareous vineyard soils.

2.1 Selection of active ingredients

The main fungicide AIs used to control downy mildew, their application practices in conventional and organic viticulture for vineyards were investigated. We selected the main AI, accepted in the EU regulation, by their effectiveness, agronomical importance and wide spread use in European vineyards against downy mildew (Aybar, 2008; EFSA, 2013; MAPAMA, 2016; Renaud-Gentié et al., 2015). The European Commission has approved the use of five different AIs of copper-based fungicides (cuprous oxide, copper hydroxide, Bordeaux mixture, copper oxychloride, and tribasic copper sulfate) in both conventional and organic viticulture (European Comission, 2009). In our analysis, all copper-based fungicides will be represented by the copper cation Cu(II) as this is the prevalent species in all related fungicides (Kabata-Pendias, 2011) and the metal ion is considered the relevant part of these fungicides with respect to potential ecotoxicity impacts. As application rate for Cu(II), we used 0.918 kg ha^{-1}, which is the average value of the reported doses for the five copper-based fungicides, ranging from 0.18 kg ha^{-1} for tribasic copper sulfate to 2.0 kg ha^{-1} for tribasic copper sulfate. The 12 synthetic and inorganic fungicide AIs selected are presented in Table 1. Furthermore, all application doses used in our study were based on recommended doses for protecting vineyards against downy mildew for

European standards and regulation (EFSA, 2013; EGTOP, 2014; European Commission, 2016; MAPAMA, 2016). A complete list of the evaluated pesticide AIs, their physicochemical properties, application methods and doses and maximum residue levels are presented in the Supporting Information (SI), Section SI-1.

Table 1. Fungicide active ingredients evaluated with their respective CAS registry numbers (RN) and recommended dose per application.

CAS RN	Active ingredient	Dose per application [kg ha^{-1}]
131860-33-8	Azoxystrobin	0.250
57966-95-7	Cymoxanil	0.121
110488-70-5	Dimethomorph	0.225
39148-24-8	Fosetil-Al	2.000
57837-19-1	Metalaxyl	0.300
70630-17-0	Metalaxyl-M	0.300
133-06-2	Captan	1.250
133-07-3	Folpet	1.500
8018-01-7	Mancozeb	1.600
12427-38-2	Maneb	1.860
9006-42-2	Metiram	1.400
15158-11-9	Cu (II) †	0.918

† The CAS numbers and specific application doses [kg ha^{-1}] for the five copper-based AIs are presented in the Supporting Information, Section SI-1

2.2 Assessment framework

To quantify potential ecotoxicological impacts of the emitted fungicide fractions on exposed ecosystems, we followed the general LCIA emission-to-damage framework (Jolliet et al., 2004):

$$IS_{i,x} = \sum_i m_{i,x} \times CF_{i,x} \quad (1)$$

Where ecotoxicity impact scores ($IS_{i,x}$), in PAF m^3 d ha^{-1}, refer to the potential impact caused by the application of an AI x to compartment i, and is expressed as the product of the characterization factor for ecotoxicity ($CF_{i,x}$), in PAF m^3 d $\mathrm{kg}_{\mathrm{emitted}}^{-1}$, and the inventory output, that is the mass of AI x emitted to compartment i, $m_{i,x}$ [$\mathrm{kg}_{\mathrm{emitted}}$ ha^{-1}].

2.2.1 Emission quantification

PPP emissions as output of the life cycle inventory (LCI) analysis ($m_{i,x}$) can be derived from applied doses and vary with application method. By obtaining information on PPP application methods in European vineyards from experts of viticultural practices, and from statistics or literature (for more information see SI, Section SI-1) we identified that the most common application method is foliar application using air blast sprayers.

Currently, only a restricted number of LCI models provide estimates of emissions to the different environmental compartments, but despite the extensive coverage regarding synthetic pesticides, climates and soils, these models are not suitable to properly assess metal-based pesticides. Based on this limitation, we assumed a static emission distribution that is dependent on the application practices to control downy mildew in vineyard production for the European context. The emission fractions were assumed to be 45% emitted to soil, 17% emitted to air and 1% emitted to freshwater, while the remaining 37% is retained by the treated crops. This assumption was based on specific percentages, or primary distributions, of fungicide application for vineyards with the air-assisted sprayer in Europe (Balsari and Marucco, 2004; Gil et al., 2014; Pergher et al., 2013; Pergher and Gubiani, 1995). This primary distribution takes into account different processes affecting the distribution of the PPP, such as application methods and equipment, the growth stage of the vines (target retention), spray drift and drip.

2.2.2 Ecotoxicity characterization in freshwater

Characterization factors for freshwater ecotoxicity impacts of chemical emissions can be expressed as follows:

$$\mathrm{CF}_{fw} = FF_{fw} \times XF_{fw} \times EF_{fw} \qquad (2)$$

with a fate factor (FF_{fw}), in days, representing transport, distribution and degradation in the environment; a dimensionless ecosystem exposure factor (XF_{fw}) defined as the bioavailable fraction of a chemical in freshwater, and an ecotoxicity effect factor (EF_{fw}) expressing the ecotoxicological effects in the exposed freshwater ecosystems (Hauschild and Huijbregts, 2015).

USEtox 2.02 provided CFs for freshwater ecotoxicity expressed as PAF m^3 d $\mathrm{kg}_{\mathrm{emitted}}^{-1}$ representing the potentially affected fraction (PAF) of ecosystem species integrated over time and exposed water volume per unit of mass of an emitted chemical [$\mathrm{PAF\ m^3\ d\ kg_{emitted}^{-1}}$] (Henderson et al., 2011).

The freshwater impact scores ($\mathrm{IS_{fw}}$) for the 12 AIs studied were calculated using eq. 1, where the CF for each AI was estimated using the landscape dataset for Europe in USEtox.

2.2.3 Ecotoxicity characterization in non-calcareous soils

We applied the modeling approach for terrestrial ecotoxicity characterization (Owsianiak et al., 2013) that introduces the accessibility factor (ACF) into the definition of CFs for soil ecotoxicity:

$$CF_{sl} = FF_{sl} \times ACF_{sl} \times BF_{sl} \times EF_{sl} \qquad (3)$$

where FF_{sl} is the fate factor representing the residential time of total metal mass in soil; ACF_{sl} is the accessibility factor defined as the reactive fraction of total metal in soil; BF_{sl} is the bioavailability factor defined as the free ion fraction of the reactive metal in soil; and EF_{sl} is the terrestrial ecotoxicity effect factor.

2.3 Spatial differentiation

2.3.1 Inclusion of spatial differentiation in the freshwater IS for Cu(II)

For the incorporation of spatial differentiation in the freshwater impact assessment $IS_{fw\text{-}EU}$, we first introduced seven European water archetypes (Gandhi et al., 2011a). These represent the variation of freshwater chemistries in Europe, and each archetype contains a specific data set with water factors of major influence on the speciation of Cu(II) (see SI, Section SI-2 for further details). Furthermore, three application rate scenarios (S1=0.75, S2=1.5 and S3=3 kg ha^{-1}) were derived from the most common use of copper-based fungicides in both conventional and organic viticulture, to introduce spatial aspects also in the emission quantification.

The $IS_{fw\text{-}EU}$ were calculated based on the inventory estimates and using the framework described above (eq. 1). The specific freshwater CFs for the EU water types ($CF_{fw\text{-}EU}$) for Cu(II) introduce in eq.2 the bioavailability factor (BF_{fw}) which is the fraction of truly dissolved metal in freshwater (Dong et al., 2014; Gandhi et al., 2010).

2.3.2 Inclusion of spatial differentiation in non-calcareous soil IS for Cu(II)

We estimated the new CF_{sl} for Cu(II) directly from soil parameters (i.e. pH, SOC, texture) for vineyards in Europe using the multiple linear regression model (MLRm) proposed by Owsianiak et al., (2013). A set of more than 20,000 European vineyards were recorded from the CORINE land cover project (EEA, 2002), and their correspondent soil parameters from the harmonized soil database HWSD (version 1.2) were selected (Fao/Iiasa/Isric/Isscas/Jrc, 2012). Geospatial analysis by means of ArcGIS (ESRI, 2017) was used to correlate the vineyards with the predominant soils of the exact areas where the vineyards were located. We only included soils with pH between 4.4 and 8.0 (typical vine growing range). Since the MLRm is not applicable to calcareous soils, soils that have a pH between 4.4 and 6.5 and carbonate content ($CaCO_3$) above

0% were excluded; also, those soils with pH > 6.5 and $CaCO_3$ higher than 10% were excluded. This resulted in 15034 non-calcareous vineyard soils for which CF_{sl} were calculated.

For estimating the IS_{sl}, we followed the modeling framework described in eq. 3. We estimated the impacts of 4 different application rate scenarios to simulate diverse viticultural practices across Europe. The two first emission scenarios represent standard (So1) and good agricultural practices (So2). For the other two scenarios, we tested the total maximum emission in one year of copper-based fungicide use of 6 kg ha^{-1} (So3) in organic farming (European Commission, 2016) and a reduced rate of 3 kg ha^{-1} (So4) in some viticultural regions (EGTOP, 2014).

3. RESULTS AND DISCUSSION

3.1 Potential freshwater ecotoxicity impacts

Results of the freshwater ecotoxicity impact assessment for the 12 AIs aggregated over all emission compartments are shown in Fig. 1 and impact results for the individual emission compartments are presented in Fig. 2. There was up to 6 orders of magnitude variation in the IS_{fw} for the 12 different fungicide AIs (Fig. 1), with dimethomorph (23.5 PAF m^3 d ha^{-1}) as the least potentially toxic substance and copper-based fungicides (4.6 million PAF m^3 d ha^{-1}) as the most potentially toxic AI.

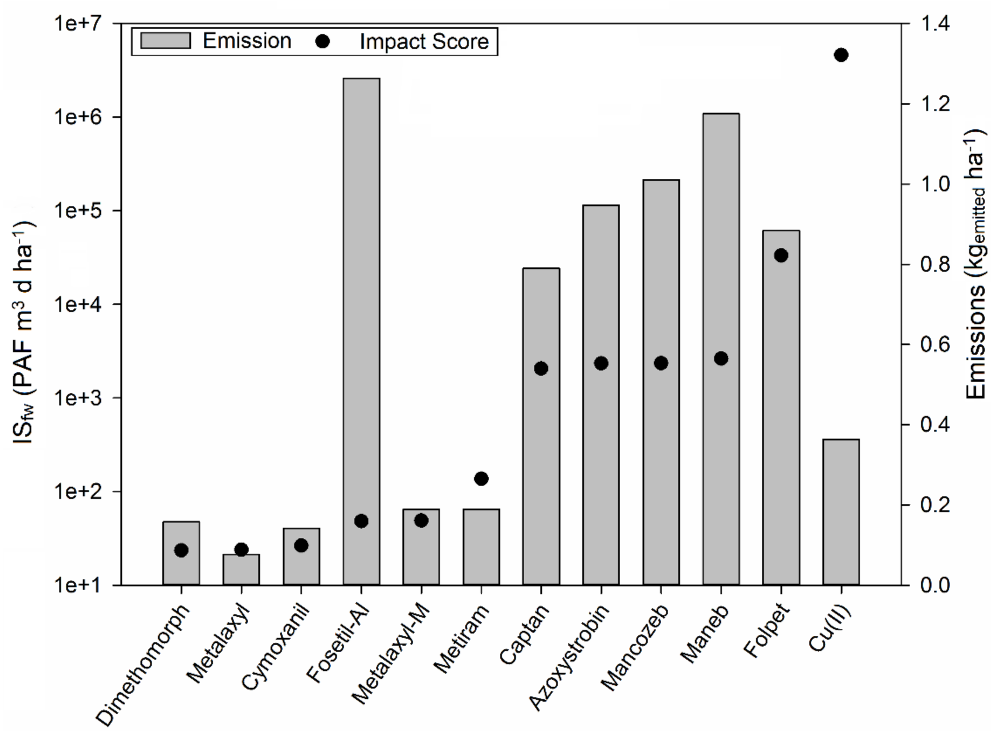

Figure 1. Potential freshwater ecotoxicity impact scores (IS_{fw}) [PAF m^3 d ha^{-1}] and total emissions [$kg_{emitted}$ ha^{-1}] for the 12 fungicide AIs ranked according to increasing impact scores.

In the case of the IS_{fw} for the synthetic pesticides, our findings show that fungicides, such as folpet (33300 PAF m^3 d ha^{-1}), would yield the highest potential freshwater ecotoxicity impacts if Cu(II) is not included (Fig. 1). IS_{fw} for azoxystrobin, mancozeb, captan or maneb presented a lower potential impact despite the fact that they are emitted in similar quantities to folpet, this is mainly due to a higher EF_{fw} with respect to the other AIs (meaning also a hig HC50 value). Fosetyl-aluminum is the AI with the highest application dose, but its relatively low ecotoxicity potential (48.3 PAF m^3 d ha^{-1}) ranked it as one of the less potentially impacting substances. Pesticide application doses across AIs varied ~1 order of magnitude and therefore contributed only little to the variation of the IS_{fw} across AIs over 6 orders of magnitude. These results strongly indicate that the amount of PPP applied (PPP use) is usually not an adequate indicator for toxicity-related freshwater ecosystem impacts in LCA, but that instead a combination of amount applied, fractions emitted, and the characterization of fate, exposure and related potential ecotoxicity effects are required.

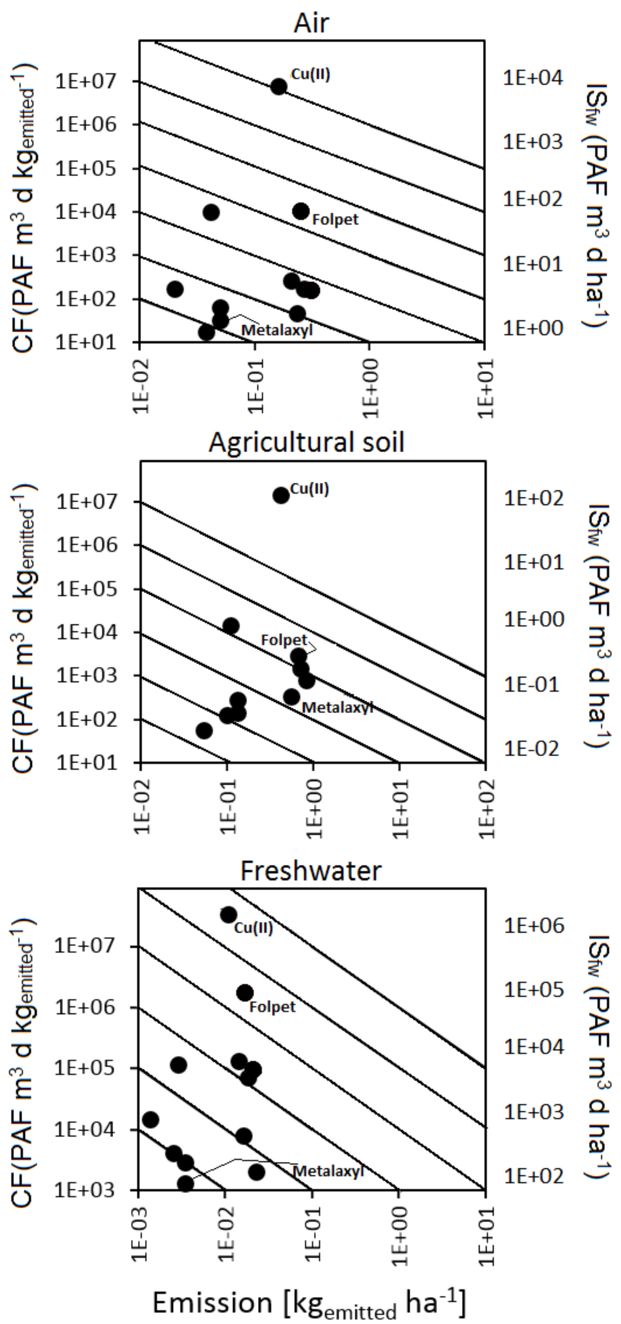

Figure 2. Potential freshwater ecotoxicity impact scores (IS_{fw}) [PAF m^3 d ha^{-1}] diagonalized for the 12 fungicide AIs for each of the receiving emission compartments (right-side y-axis), corresponding emissions [$kg_{emitted}$ ha^{-1}] (x-axis), and CFs [PAF m^3 d $kg_{emitted}^{-1}$] (left-side y-axis).

For the few available vineyard-related LCA studies that contain potential freshwater ecotoxicity impacts, the results are not easily comparable across studies. This may be due to different methodological choices made in these studies, such as the inventory parameters considered, the methods used to estimate emissions and the impact assessment model used. Furthermore, an interesting finding of the comparison of these studies is the lack of transparency in ecotoxicity results, since many studies did not specify whether and how PPP impacts were quantified.

Our findings regarding synthetic fungicides are consistent with results obtained by Villanueva-Rey et al., (2014), where IS_{fw} are dominated by folpet, but contrary to the results of Renaud-Gentié et al., (2015), which shows lower ecotoxicity impacts related to PPP. The contradictory findings may be explained in the assumptions for the inventory analysis, where we have assumed fixed values of emissions for the different environmental compartments across fungicide AIs (Fig. 2), and in consequence, our potential impact values for the synthetic fungicides differ. The authors (Renaud-Gentié et al., 2015) adapted the PestLCI 2.0 emission quantification model to be applied in vineyard production; this tool defined the technosphere as the agricultural field including the air column above it (up to 100 meters) and the soil up to 1-meter depth (Dijkman et al., 2012). This means that PPP emissions to soil are not considered and this could be one reason for the differences between the results in the impact assessment compared to the present study. In the case of folpet, there are further differences that are explained by the use of a CF specifically calculated in the study of Renaud-Gentié and co-authors. This highlights that following different methodological approaches can yield considerably different impact scores.

Although most other studies mention the use of copper in vineyards, only the work by Neto et al., (2013) and Notarnicola, (2003) include impacts for copper-based fungicides in both the production and the use phase. In Notarnicola et al. (2003), the results on impact categories are presented in aggregated percentages and not in absolute values. In that study, ecotoxicity was the most contributing impact category in the agricultural phase and depended mainly on the PPP use. Unfortunately, there is no particular mentioning of the AI contribution to allow a comparison with our own findings. Neto et al., (2013) displayed aggregated results per impact category. They concluded that viticulture stage was the larger contributor to overall impact categories. Freshwater and soil ecotoxicity are due to the use of glyphosate for weed control. The results from these two studies cannot be directly compared with the results from the present study for several reasons, including the use of different inventory models, impact assessment methods and different methods to aggregate results.

Some of the challenges that constitute the main reasons why freshwater ecotoxicity assessments are not routinely included in comparative LCAs are the low availability of data and the perception of a limited reliability upon models that allow the quantification of inventories and impacts.

In fact, the inclusion of potential freshwater ecotoxicity impacts provided valuable additional insight into the environmental performance of different agricultural systems in our study. The potential impacts of PPP in organic crop production are in general lower than those reported for conventional crop production (Meier et al., 2015). However, including copper-based fungicides in the impact assessment may lead to different conclusions.

Our results emphasize that it is necessary to include copper-based fungicides with focus on the development and refinement of characterization factors, as well as, inventory emission fractions.

In the evaluation of the substance ranking, it is also important that the modeling upon which these results are based is inherently complex and subject to many assumptions and simplifications. Therefore, and since impact scores represent potential impacts rather than actual effects, our results cannot be validated against experimental data or compared with risk evaluation and must always be seen in an LCA context, where overall environmental performances of compared product systems are assessed. Furthermore, characteristics of all AIs, such as the usage and the effectiveness for disease control, the mode of action and the metabolite formation, the increment of pest-resistant strains, among other features, should be considered when comparing different AIs for PPP substitution treatments. Otherwise it will be hard to identify the most viable and sustainable alternative (Fantke et al., 2015, 2011b).

Regarding the agronomical importance of copper use against downy mildew, some authors have concluded that under high pressure of the disease on organic viticulture, the only substance to offer effective control was a copper-based fungicide (Komarek et al., 2010; Spera et al., 2007). In low and medium disease pressure, alternative treatments (i.e. biocontrol agents, natural derivatives, plant extracts, etc.) may offer an adequate disease control (La Torre et al., 2011). Therefore, grapevine downy mildew control using reduced copper amounts in organic viticulture is feasible, if pest management is performed in combination with alternative treatments.

Freshwater ecotoxicity impact scores depend on several parameters, with fluctuating uncertainties. For USEtox CFs, an uncertainty range of 1-2 orders of magnitude has been determined, and the major sources of uncertainty are substances half-lives and ecotoxicity effect estimates (Henderson et al., 2011). Therefore, an AI with CF of 1000 PAF m^3 d $kg^{-1}_{emitted}$ may not be (but possibly is), more toxic than an AI with CF of 100 PAF m^3 d $kg^{-1}_{emitted}$. The uncertainty of the emissions has not been quantified before and is also beyond the scope of the present study. Perhaps a more significant and probably more conclusive analysis is the inclusion of spatial differentiation for the AI that may present substantial changes due to natural variations of the emission compartment.

3.2 Characterization results for non-calcareous soils

Site-dependent CFsl for Cu(II) in the 15034 European vineyards non-calcareous soils vary over ~1.5 orders of magnitude, with mean values equal to 2340 PAF m^3 d $\mathrm{kg}_{\mathrm{emitted}}^{-1}$ and spatially differentiated ranges from 155 to 7240 PAF m^3 d $\mathrm{kg}_{\mathrm{emitted}}^{-1}$.

The results from the MLRm show that the CFsl for Cu(II) are determined mainly by OC, that influences Cu(II) mobility (i.e. metal fate) and the effects of soil pH, influencing Cu(II) bioavailability, this trend is represented in Fig. 3. The clay content is rather poorer descriptor for the CFsl of Cu(II) (2 orders of magnitude lower than OC) and did not show a particular trend, although, is interaction with the other parameters is significant.

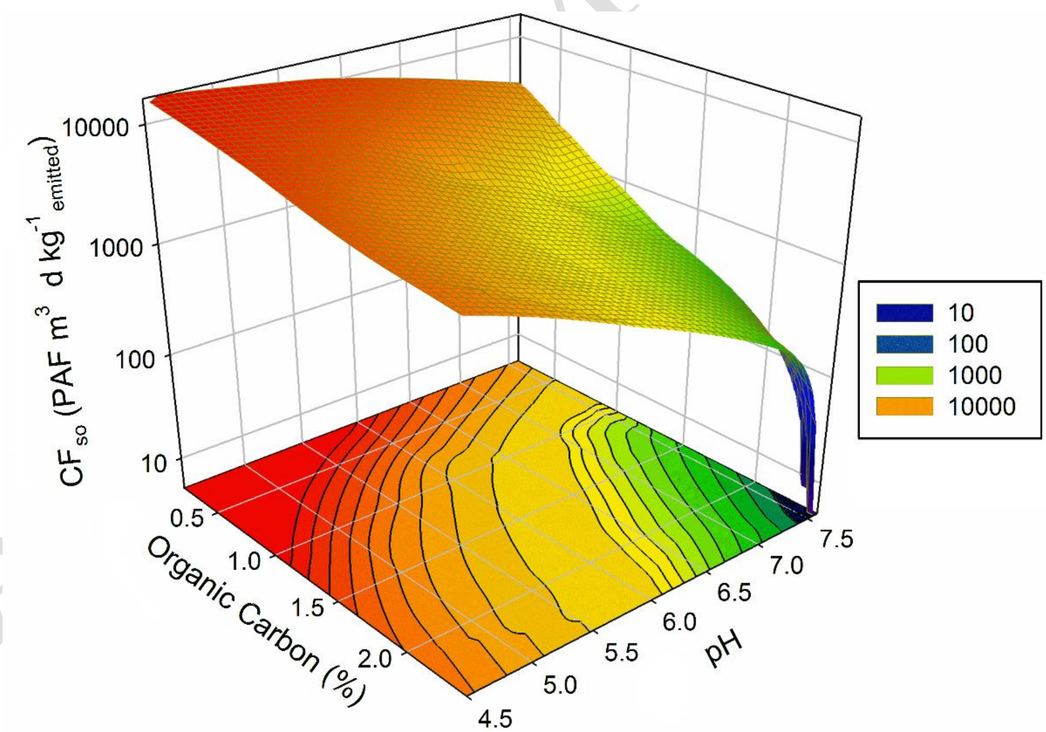

Figure 3. Characterization factors for 15034 non-calcareous vineyard soils CFso [PAF m^3 d $kg^{-1}_{emitted}$], calculated from soil parameters, with respect to soil organic carbon [%] and soil pH.

The parent materials of the soils (e.g., clay content) influence mobility of copper in soils, clay minerals and organo-clay associations together with particular organic matter are the main carrier phases of Cu(II) in soils. Its solubility is highly dependent on the soil pH, and it could be more available at pH values below six. In acidic vineyard soils, copper is more mobile and can more easily reach ground water. Furthermore, the mobility can be affected at pH values above ~7.5 and at this pH the formation of copper complexes (Cu-OC) is promoted by the solubilization of OC. Regarding copper soil ecotoxicity characterization, it is well known that the complexation of Cu(II) with OC reduces significantly its toxicity potential. This is congruent with the trend shown in Fig. 3. Furthermore, in a study on soils contaminated with copper it was shown that in organic soils, less than 0.2% of total copper was in the free ion form Cu^{2+} at pH 4.8–6.3 (Karlsson et al., 2006).

3.3 Spatially differentiated results

Our result have already shown that different factors affect the ecotoxicity of the studied fungicide AIs. In the case of copper-based fungicides, the conditions where emissions occur could be critical to determine its potential ecotoxicity-related impacts. In ecotoxicity characterization models of metals, it is assumed that the potentially ecotoxic effects on ecosystems are a function of the activity of the free metal ion. It is also well known that copper behavior (speciation and mobility) is influenced by, and substantially dependent on, the chemistry of the emission receiving environment (freshwater or soil) and thus influencing the potential ecotoxicity of Cu(II). Hence, spatial differentiation and the inclusion of site-dependent

CF's are relevant when assessing impacts of copper-based fungicides (Potting and Hauschild, 2006). Such evaluation will provide a more accurate assessment of the potential impacts of Cu(II) emissions. Therefore, we present the following results for input parameters that display significant geographical variability in the quantification of IS for Cu(II).

3.2.1 Spatially differentiated freshwater impacts

Results for the freshwater ecotoxicity scenarios evaluated introducing different water chemistries are summarized in Table 2. The IS_{fw-EU} range from 42.1 PAF m^3 d ha^{-1} (S1-EU1 water type) to 168000 PAF m^3 d ha^{-1} (S3-EU6 water type) in the seven European archetypes and across all scenarios.

Table 2. IS_{fw-EU} for Cu(II) in three different scenarios for the seven European water types.

Water type*	IS_{fw-EU} [PAF m^3 d ha^{-1}]			
	Base Scenario†	S1	S2	S3
EU1	1.21E+02	4.21E+01	3.16E+02	6.32E+02
EU2	5.05E+02	1.76E+02	1.32E+03	2.63E+03
EU3	1.21E+03	4.21E+02	3.16E+03	6.32E+03
EU4	2.89E+02	1.01E+02	7.55E+02	1.51E+03
EU5	1.35E+04	4.68E+03	3.51E+04	7.02E+04
EU6	3.23E+04	1.12E+04	8.42E+04	1.68E+05
EU7	1.08E+04	3.74E+03	2.81E+04	5.62E+04

*Water archetypes from (Gandhi et al., 2011a). †Same application dose for copper-based fungicides used for the quantification of IS_{fw}.

These results for copper-based fungicides show that water conditions with low hardness and low DOC, and medium pH, represented by water type EU6, have higher ecotoxicity potential than EU1 water type, wich has a higher pH and hardness. These differences in water chemistry not only influence changes in the IS_{fw-EU} but may also lead to ranking changes when comparing with the other fungicide AIs. The ~3 orders of magnitude of variation among the 7 European water archetypes illustrate the relevance of the inclusion of spatial differentiation. Furthermore, if we consider the $IS_{fw\text{-}EU}$ from the base scenario, we can already see ranking changes for Cu(II) with respect to the other AIs for all European water archetypes.

It is important to stress that the variations in the $IS_{fw\text{-}EU}$ are more dependent on the different water chemistries than the dose of AIs applied. Although copper-based fungicides show higher potential impacts in freshwater ecosystems than the synthetic fungicides, variabilities in the receiving emission environment (soil or water) could make these impacts also highly variable.

On the other hand, Komarek et al., (2010) tested for a study that was conducted from 2004 to 2007 if there were substances that might replace copper in organic viticulture. One of their main findings shows that currently, there is no treatment that is as effective as copper for controlling grapevine downy mildew in organic vineyards (Komarek et al., 2010). In this context, the present study may help to better understand different pest managements in various environments, and give more accurate environmental impacts profiles. This could lead to an integrated management system in which a less efficient product is applied in combination with copper-based fungicides to reduce the total dose of Cu(II) applied, and as a consequence, reduce the overall potential ecotoxicity impacts.

3.2.2 Spatially differentiated non-calcareous soil impacts

Impact scores in non-calcareous soils for Cu(II) showed up to 2 orders of magnitude of difference in the scenarios that simulated different agricultural practices per application So1 and So2. In the same way, So3 and So4 vary 2 orders of magnitude, with values 2 times higher than So1 and So2, thereby keeping in mind that these values evaluate maximum allowed copper application in one year for copper fungicides use.

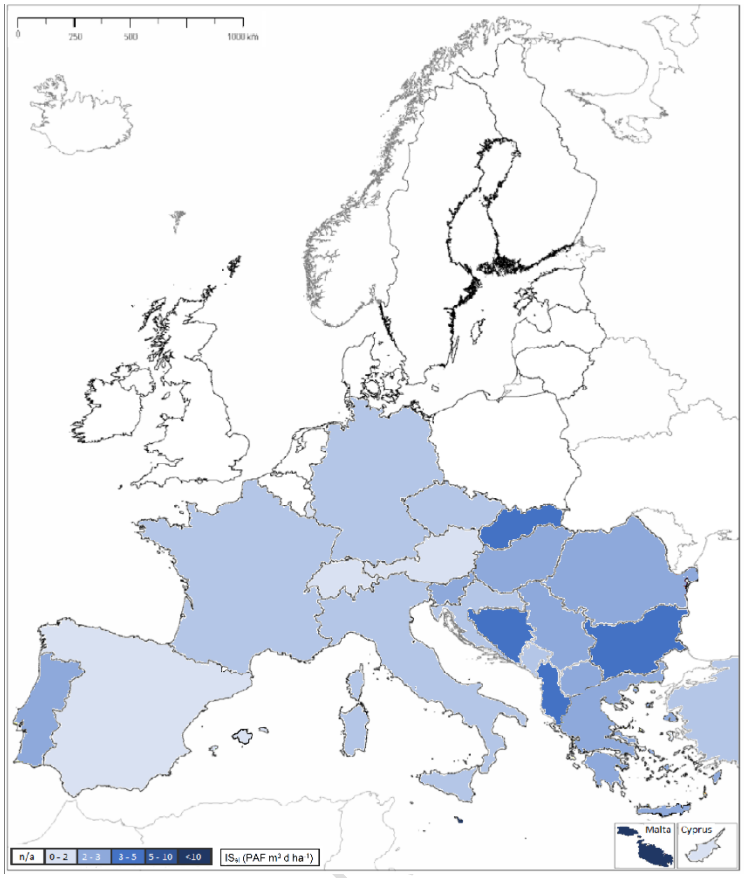

Figure 4. Impact scores for European vineyard non-calcareous soils (IS_{sl}) aggregated by country for the scenario So1 that represent standard agricultural practices for copper-based fungicide application. IS_{sl} in [PAF m^3 d ha^{-1}].

The specific soil texture and chemical composition of the evaluated vineyards varied around 2 orders of magnitude for the same application scenario. Results aggregated by country are shown in Fig. 4 and reflect how potential IS_{sl} could vary depending on emission site. In this context, it is important to note that all calcareous vineyard soils were excluded from our study; therefore, impacts occurred in this type of vineyards have not been considered. In the scenarios with more restrictive copper use, the potential impacts show a lower variation in the aggregated soil ecotoxicity impact potential per country.

4. CONCLUSIONS

4.1 Application of our results and implications for decision making

While the evaluation of global warming potentials in viticulture has been extensively analyzed in most studies, vineyard or wine-related LCAs often neglect to assess ecotoxicity-related impacts, despite their importance at a local and regional level in vineyard areas. Moreover, to the best of our knowledge, the current study constitutes an extended vision of LCIA to an agricultural product, not only through freshwater and terrestrial soil ecotoxicity evaluation but also through the inclusion of spatial differentiation and the use of emerging methodologies.

The main outcome of our work is the potential application of these findings for LCA studies in agricultural systems. Our contribution involves assisting decision makers to better understand copper-related fungicide behavior and the importance of distinguishing its environmental impact depending on the different receiving emission environments and how restrictions on the use of copper-based fungicides should take into account the emission site.

This study has several implications for impact assessment of copper-related compounds. Considering geographic variability both in metal hazard and LCA might provide more accurate results for the evaluation of ecotoxicity impacts, and will help to draw conclusions that are more reliable in environmental impact profiles. The present study has indicated the importance of including spatial differentiation in the ecotoxicity assessment of copper-based fungicides. Accounting and evaluating for PPP potential ecotoxicity (e.g. for substitution of AIs) should include variations of the receiving emission environment. The consistent use of soil and water chemistry values has proven to be particularly important in the ecotoxicity impact evaluation of copper-base fungicides.

4.2 Limitations and future research needs

The methodology applied to characterize Cu(II) do not capture important aspects of metal speciation, such as essentiality or active plant uptake. Although the translation on the LCIA is not straightforward, because specific important spatially varying characteristics, such as cation exchange capacity describing the ionic composition of soil pore water, are not routinely measured. As demonstrated by Owsianiak et al. (2013), CFs for copper are determined mainly by OC (influencing fate) and pH (influencing bioavailability). LCIA models should, therefore, be metal-specific, and the results presented here cannot be extrapolated to other metals. In this respect, the modeling framework used in this study is only applicable to non-calcareous soils, although it is acknowledged that vineyard cultivation in calcareous soils is a typical practice in many European areas.

Further research is needed on how to account for erosion both in the emission quantification and how it might affect the impact assessment of metal-based pesticides. To our knowledge, the methods, both for impact characterization (for terrestrial soil ecotoxicity) and emission modelling of PPP are not mature enough to be extensively applied in LCA. In this sense, this study is a first step towards to a more precise assessment of potential ecotoxicity impacts associated with agricultural production systems in general and in vineyard cultivation in particular.

If these improvements are routinely incorporated into agricultural LCAs, an important issue arises, which is, what is the most representative yet practical spatial information needed and feasible for LCAs on agricultural systems? This is a key issue that will need particular attention upon in future efforts.

ACKNOWLEDGMENTS

This work was financially supported by a scholarship granted by the Colombian Government through COLCIENCIAS, by the Marie Curie project Quan-Tox (grant agreement no. 631910) funded by the European Commission under the Seventh Framework Program, and by the OLCA-Pest project financially supported by ADEME (GA No. 17-03-C0025). Authors would also thank the support from "CERCA Program Generalitat de Catalunya", Anna Levinsson for the proofreading and Immaculada Funes for her contributions to the graphical abstract.

ASSOCIATED CONTENT

Detailed information on pesticide active ingredients, pesticide application methods and practices in European vineyards, and main factors and characteristics of water types and soils included in the study are provided in the Supporting Information.

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