Development of a quantitative tool for environmentally sustainable copper fungicide application and tracking within vineyards.

By

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Development of a quantitative tool for environmentally sustainable copper fungicide application and tracking within vineyards.

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Abstract

Copper-based fungicides (CuFs) are used in vineyards and fruit-farms as a preventive form of pathogen control. These have a fungicidal impact against mildew infections (*Plasmopara viticola*) and other fungi that attack grapevines causing poor plant development, fruit rot, and ultimately, poor wine production. If applied annually in large quantities, copper pollutes both the vineyard soil and the surrounding freshwaters. This research combines a copper soil transport model within vineyard systems, a downy mildew germination model, and a copper dosage model with the ultimate aim of diminishing copper usage to concentrations as low as reasonably achievable while determining its environmental fate. The copper soil transport model is based on a solid-solution partitioning model, water balance model, and biotic ligand model. The downy mildew model is built according to a mechanistic model which separates the morphological development of mildew into discrete variables. The copper dosage model is built by combining a grapevine development model, a spray efficiency model, and a deposition efficiency model. Running the simulation from 2009 to 2018 for a vineyard in the Bordeaux Graves region, the model predicts that copper usage could have been reduced to 4.7 $kg_{Cu}*ha^{-1}$ annually by only applying during mildew infection events and accounting for leaf area dependent spray deposition rates. Improving spray efficiency by 10% could further reduce copper demand to 3.9 $kg_{Cu}*ha^{-1}$, below the new European limit of 4 $kg_{Cu}*ha^{-1}$. Soil pH and organic matter adjustments most affected copper speciation, controlling biological uptake rates, soil matrix storage, and leaching rates; while varying the clay content did not present significant impacts.

Keywords: copper, emission, modeling, mildew, application efficiency, systems approach, soil transport.

1. Introduction

Copper-based fungicides (CuFs) protect grapevines from downy mildew (Dagostin et al., 2011), a pathogen that has previously led to nearly total harvest loss for the most economically important fruit species globally (FAO, 2012). In Europe, vineyards represent 67% of all pesticide application, of which 10% is specifically CuFs (Panagos et al., 2018), despite occupying a mere 3.3% of agricultural land (European Commission, 2007, Delaunois et al., 2014). Historically, these CuFs have been applied disproportionately and inefficiently, leading to environmental concerns of excess residual copper (Cu) in soils (Vogelweith & Thiéry, 2018). Today, vineyard soil Cu concentrations average 49 $mg_{Cu}*kg^{-1}$ (Figure 1, Ballabio et al., 2018), with certain samples exceeding 1000 $mg_{Cu}*kg^{-1}$, 70 times higher than the European average of 17 $mg_{Cu}*kg^{-1}$.

At high concentrations, Cu's micronutrient properties lead to accumulation in plant tissue decreasing photosynthetic rates, causing oxidative stress, and damaging cell membrane lipids (Brunetto et al., 2015). These symptoms and stresses inhibit phenological development and reduce fruit yields (Baldi et al., 2018) in grapevines at free Cu concentrations as low as 5 μM (Chen et al., 2012; J.Cambrollé et al., 2015;). Elevated Cu concentrations in the soil stock also significantly reduce soil fertility and structure by disturbing the interaction between soil meso, micro, and macrofauna. Fauna populations decrease with increased Cu concentrations; for instance, concentrations in excess of 30 $mg_{Cu}*kg_{-1}$ lead to a decrease in earthworm populations (Komárek et al., 2010). This macrofauna, in particular, stabilizes soils by digging burrows and redistributes nutrient-rich particles, facilitating root development, water infiltration, and delivering oxygen to the sediment. High Cu concentrations also decrease microbiological activity reducing, humified organic matter levels and impairing nutrient and chemical exchanges (Fusaro et al., 2018).

As a result of these environmental concerns, techniques to reduce and track Cu in vineyards have been increasingly developed. In order to reduce usage, relations between the leaf area index (LAI) of a vineyard on the particle deposition efficiency (Siegfried et al., 2007; Pergher and Petris, 2013) have been developed to optimize spray dosage. Variable dosage sprayers have been researched to adapt dosages in real time, improving sprayer efficiencies by accounting for leaf area heterogeneity throughout vineyard systems (Escolà et al., 2013). Further, studies have identified that 5 $mg_{Cu}*m_{leaf-2}$ (leaf surface area) is the optimal deposition required to prevent mildew outbreaks, significantly lower than the 15 $mg_{Cu}*m_{leaf-2}$ recommended by fungicide producers (Cabús et al., 2017). Bioengineers are also studying the commercial potential of mildew resistant grapevines (Ferreira et al., 2004; Toffolatti et al., 2018) to further reduce the required deposition quantity. Biofungicides are emerging as alternatives to CuFs altogether, however their lack of efficacy, high cost, sensitive storage requirements, and low persistency, all remain major barriers to widespread production and adoption (Dagostin et al., 2011). Reducing the initial inoculum dose of mildew spores which overwinter has been considered, however this strategy can lead to negative side effects such as sour rot (Pertot et al., 2017). Finally, modeling systems have been developed focusing on mildew germination (Rossi et al., 2008) and precipitation-based warning recommendations (Pellegrini et al., 2010), estimating that Cu usage could be reduced by 50%.

In soils, Cu partitioning has been extensively studied, establishing that Cu binds strongly to organic matter and clays (Babcsányi et al., 2016) and that its solubility is driven by soil pH (Bravin et al., 2012). At low pH the adsorption capacity of soils decreases, making Cu more biologically available (Brun et al., 2001) in the soil solution phase. Biological remediation strategies have been explored due to their potential (Mackie et al., 2012), however current in-situ extraction rates have not been sufficient to significantly offset current application rates (Mackie et al., 2014). Despite low removal rates, research has found that Cu soil concentrations, though elevated, are lower than expected, implying an additional unknown loss factor, theorized to be erosion losses (Brun et al., 1998).

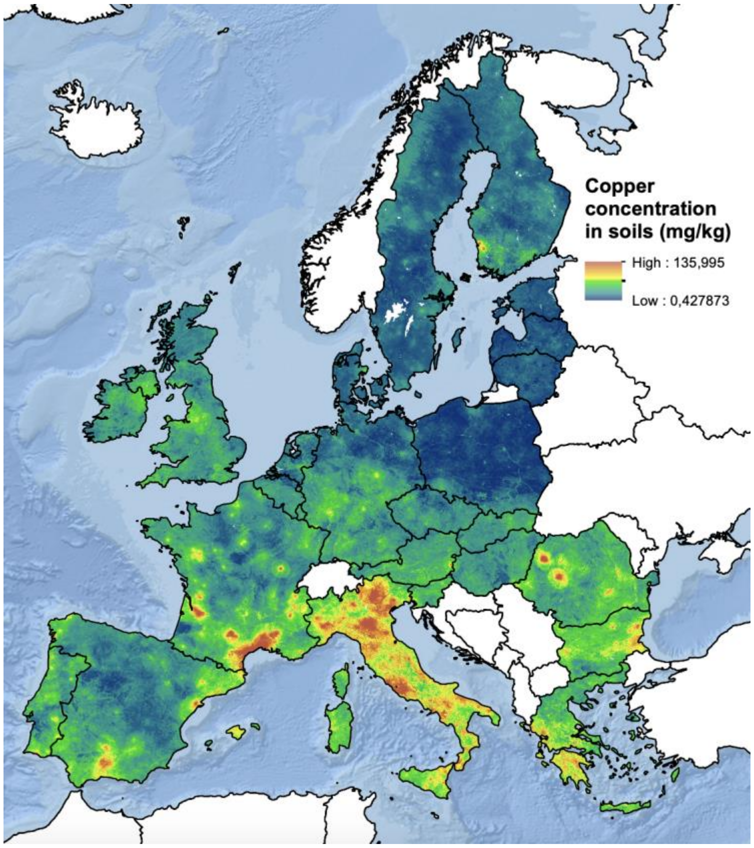

Figure 1. European Cu soil concentration (from Ballabio et al., 2018)

Our objective is to develop an open source tool (available upon request) enabling the spatiotemporal simulation of Cu demand and fate in vineyards to predict the most efficient mildew controlling practice. The Cu demand model is developed accounting for mildew life stages, grapevine development, and deposition and spraying efficiency. The Cu fate model is developed using a solid-solution partitioning model, biotic ligand model, and water balance model. These models are unified to provide a complete simulation of the demand and distribution of Cu within a vineyard over the course of an application season. Finally, preliminary sensitivity analyses are done to provide a simplistic understanding of the impact each process and site characteristic has on the final Cu demand and distribution within the system.

2. Methodology

A Cu transport model is developed tailored to vineyards and relies on chemical transport and fate principles of heavy metals. As such, the model uses equations to estimate the Cu flows in air, soil, water, and biota (Figure 2, Gulliver 2007).

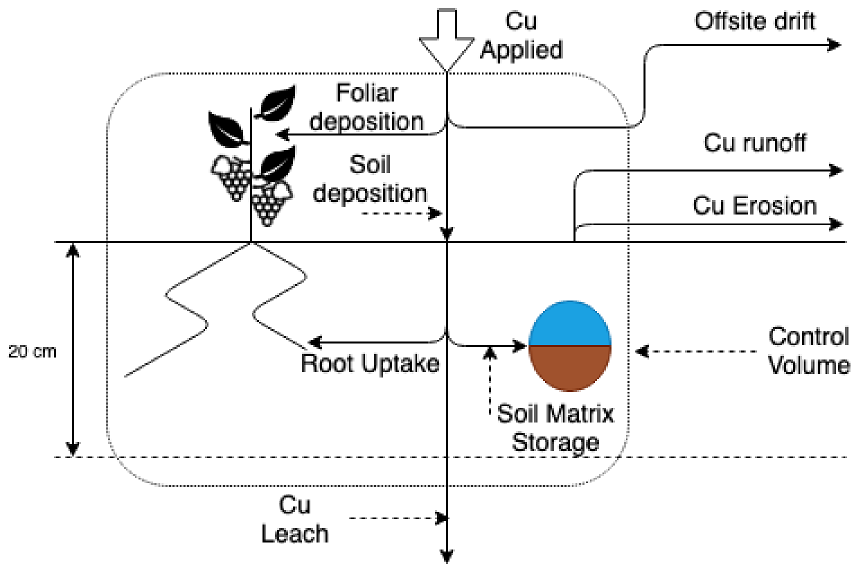

Figure 2. Schematic representation of Cu transport in vineyards

The control volume input considered is the CuF sprayer nozzle output. The control volume outputs considered are losses due to drift, erosion, runoff, and leach occurring 20cm below the soil surface. The model is simplified by assuming the applied Cu which is not lost to offsite drift eventually enters the soil matrix. This is assumed because, during rain events, the majority of the Cu is washed off the grapevine before sheet flows form, entering the soil matrix (Pérez-Rodríguez et al., 2015) and yielding negligible surface losses (Babcsányi et al., 2016). Additionally, the model assumes that, over the course of an entire application season, all applied Cu will be restored through leaf fall and that the mass uptaken by the grapes is negligible (Brun et al., 1998). This results in assuming that all the Cu applied to the site will eventually enter the soil matrix.

The flows represented (Figure 2) were quantified by developing a two-phase model (Figure 3) based on the coupling of existing models. The Phase-1 model output is the Cu demand of the site, while the Phase-2 model outputs are the Cu storage and emission of the vineyard system. A full description of all equations used is provided in the supplemental methods document.

In this study, the model is used to simulate the Cu demand and distribution of a vineyard in the Bordeaux Grave region from 2009 to 2018.

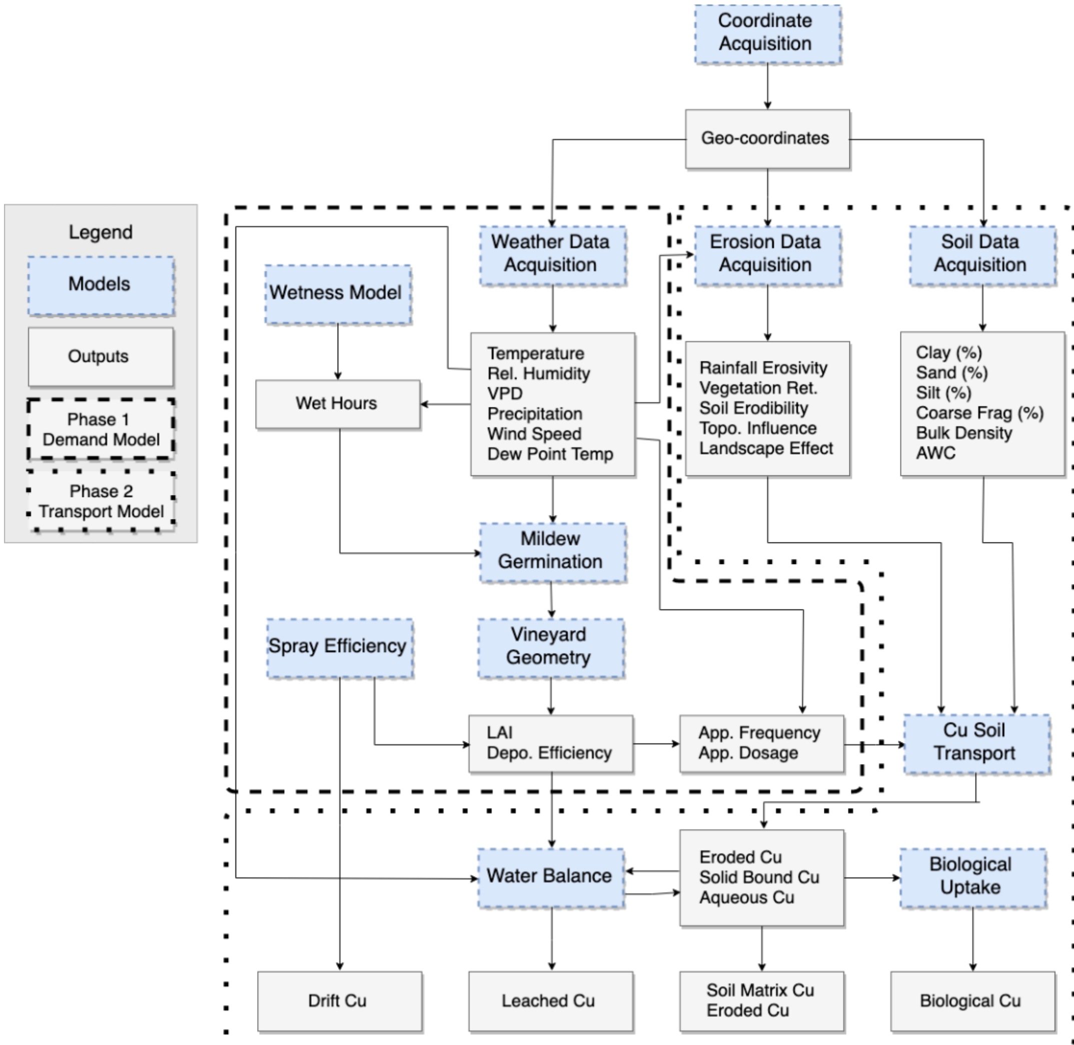

Figure 3. Schematic diagram of each phase model.

Data Acquisition

The geographical coordinates of the vineyard are acquired via the *Geocoder* API (Application Programming Interface). All yearly meteorological data sets were developed via the *World Weather Online* API which provides data generated from the ECMWF atmospheric model output, World Meteorological Organization and buoy observations. All soil properties were acquired via soil atlases made available by the European Soil Data Centre (ESDAC). The standard practice (SP) seasonal dosage used as the comparison benchmark of the model scenarios was adapted from Pellegrini et al. (2010).

Phase One: Copper Demand Modeling.

As mildew infections are the primary driver of Cu usage in vineyards (Cavani et al., 2016), simulating the timing of infection events based on weather forecasting and thereby quantifying the required protection events is mandatory to reduce environmental burdens. To determine mildew infection events, a mechanistic mildew germination model (Rossi et al., 2007), supplemented with a leaf wetness model (Kim et al., 2002), is utilized. The model tracks the germination events of mildew cohorts based on the on-site meteorological conditions to determine whether a mildew cohort will successfully infect a grapevine. Once the infection times are determined, a grapevine development model is utilized to calculate the LAI of the vineyard (Williams & Ayars, 2005) at the time of infection, determining the particle deposition efficiency (Siegfried et al., 2007; Pergher & Petris, 2013). The deposition efficiency model is supplemented with a sprayer efficiency coefficient (Garcerá et al., 2017) in order to determine a Cu spray dosage. This process is repeated for each infection event throughout the growing season, providing the seasonal minimum required Cu usage.

Certain logic checks are incorporated in order to avoid excessive application. First, mildew spores cannot infect a grapevine before budburst (Pellegrini et al., 2010), therefore no spraying event is recommended before this date. The budburst date is simulated using a growing degree day model with a base temperature of $5^{o}C$ (Bonhomme, 2000; García de Cortázar-Atauri et al., 2009). Furthermore, in addition to using a factor of safety of 30%, each dosage recommendation is rounded up to the nearest multiple of 50 in order to avoid overly specific dosages which are impractical to measure (Gil et al., 2011). It is also assumed that the maximum LAI vineyards achieve before viticulturists manage the canopy is 2.5 (Williams & Ayars 2005; Siegfried et al., 2007; Valdés-Gómez et al., 2009). This value is thus considered constant from the time it is reached until the end of the season. The model incorporates a rudimentary particle washout check, assuming that rain events with less than 5mm of precipitation remove 50% of the previously applied Cu (Pérez-Rodríguez et al., 2015), halving the subsequent required spray deposition. This is only considered valid if the following application event is less than 7 days away in order to account for new leaf growth which would require a full dose (Pellegrini et al., 2010). Finally, it is assumed that spraying events end one month before harvest. The harvest date varies annually but typically occurs in the middle of September, as such, August 15th was considered a reasonable final spray date for the vineyard considered (personal communication, 2019).

Phase Two: Copper Transport Modeling

After the site-specific Cu demand is determined, a Cu transport model is incorporated to determine the Cu storage and emission of the vineyard. First, the site-specific soil properties (Table 1) are determined through the ESDAC online soil atlases.

Table 1. Initial Site Conditions

Symbol Soil Property	Units	Value
Soil pH	-	3.84
Organic Matter Content	%	5.83
Sand Content	%	49.9
Clay Content	%	17.45
Bulk Density	t/m3	1.08
Available Water Content	cm/cm	0.08
Hydraulic conductivity	cm/day	0.47
Field capacity	cm3/cm3	0.36
Wilting point	cm3/cm3	0.23

The Cu distribution in soil is determined by calculating the reactive metal concentration, which can partition to the solution phase where its transport is dependent on its speciation (Krishnamurti et al., 2002; De Vries & Groenenberg, 2009). By determining the available free Cu in solution, its grapevine root uptake can be calculated with a biotic ligand model (Chen et al., 2012) while the fate of the remaining Cu fractions both in solid and solution phases can be calculated based on multi-phase equilibrium principles. The water balance simply assumes a certain fraction of the monthly rainfall infiltrates the soil matrix, driving the flux of Cu lost to leaching (Ebrahimi et al., 2017).

Once the biogeochemical processes are determined, a soil erosion by water model, in accordance with the G2 model principles, is implemented to determine the mechanical Cu losses retroactively (Karydas & Panagos, 2018). The model assumes constant Cu concentration over the depth of the control volume, therefore, the erosion model does not affect the soil Cu concentration.

Model Scenarios

The impact of each site characteristic is isolated within the model to determine how each component impacts Cu demand, storage, and emissions. Multiple scenarios representing certain innovations are developed and compared relative to the initial model results.

The phase-1 scenarios include the following adjustments: exclusion of the vine development model, a 10% improvement in spray efficiency, grapevine bioresistance, and Cu foliar sorption. Each scenario is simulated independently. To implement these scenarios, the following parameters are adjusted: the maximum LAI dosage is considered for all application events, spray efficiency is increased from 46% to 56%, the minimum required Cu deposition is decreased from 0.5 to 0.45 $mg_{Cu}*m_{leaf}^{-2}$, and the half-removal washout logic check is increased from 5 to 5.5mm of rainfall.

For the phase-2 portion of the model, soil properties are adjusted to determine their impact on the final distribution of Cu within the vineyard system. The following parameters are adjusted independently: soil pH is increased by 10%, clay content is reduced by 10%, and soil organic matter (OM) is increased by 10%. These parameters are selected because of their known impacts on Cu speciation within the soil matrix (Babcsányi et al., 2016). The scenarios simulating a change in clay and OM content assume that the adjusted fraction is compensated with a non-reactive soil characteristic.

Ecotoxicity

Subsequently, the model outputs are coupled to an ecological impact model to determine the changes in potential ecotoxicity impacts of the Cu flows under each scenario. To do this, yearly changes in soil stocks and emission pathways are compared between all simulations using the characterization factors (CFs) of Cu in air, water, and soil (Table 2, Dong et al., 2014).

Table 2. Characterization factors of Cu^{2+}

	CF (PAF. day. m3 /kg)
Air	7.64E+06
Water	7.50E+05
Soil	1.40E+07

3. Results

System Simulation

Over the ten-year simulation period, the model simulated an average yearly Cu demand of 4.7 $kg_{Cu}*ha^{-1}$ with a maximum of 11.3 $kg_{Cu}*ha^{-1}$ and a minimum of 1.2 $kg_{Cu}*ha^{-1}$ (Table 3) and a total ten-year demand of 46.7 $kg_{Cu}*ha^{-1}$. If the system recommendation had been utilized, reductions of 6.7 $kg_{Cu}*ha^{-1}$ in Cu usage could have been achieved annually compared to the common practice dosage considered. In eight of the ten years simulated, Cu usage was below the former legislative maximum of 6 $kg_{Cu}*ha^{-1}$, and five of these were also below the new legislative maximum of 4 $kg_{Cu}*ha^{-1}$. The model simulated an average of 10 infection events per year with a maximum of 19 and a minimum of 3 events. The average budburst date and maximum LAI development were simulated to be on April 6th and June 20th respectively. The earliest budburst date was found to be March 24th while the latest was simulated to be on April 18th. The maximum LAI development exhibited more variance with the earliest date of June 6th and the latest date of July 7th.

Table 3. Yearly meteorological patterns and Cu usage. Precipitation is the amount of rainfall from April 1st to August 15th, $Date_{buburst}$ is the date at which the budburst was recorded, and $Date_{max\text{-}LAI}$ is the date at which the LAI of the vineyard 2.5. CP is the common practice annual dosage adapted from Pellegrini et al. (2010).

Year	Precipitation (mm) (Apr. - Aug.)	$Date_{budburst}$	$Date_{max\text{-}LAI}$	No. of Treatments	Copper ($kg_{Cu}*ha^{-1}$)
2009	148.1	April 14th	June 19th	3	1.9
2010	123.1	April 18th	June 26th	4	2.6
2011	230.2	April 3rd	June 6th	17	11.3
2012	206.4	April 5th	June 22nd	10	4.9
2013	209.9	April 15th	July 7th	12	3.4
2014	213.6	March 24th	June 19th	19	10.0
2015	133.7	April 12th	June 16th	7	4.1
2016	101.2	March 30th	June 30th	9	2.0
2017	126.7	March 29th	June 14th	5	1.2
2018	158.2	April 3rd	June 18th	11	5.4
Average	165.1	April 6th	June 20th	10	4.7
CP	-	-	-	12	11.4

Copper Distribution

Given the soil properties (Table 1), the soil stock accumulated 15% of the total applied Cu (6.5 $kg_{Cu}*ha^{-1}$, Table 4), increasing the soil concentration from 26.46 $mg_{Cu}*kg^{-1}$ to 29.55 $mg_{Cu}*kg^{-1}$. Grapevine root uptake, the only other considered on-site stock, accounted for 3% (1.5 $kg_{Cu}*ha^{-1}$) of the Cu applied. The primary emission occurred through water losses, where 66% (30.9 $kg_{Cu}*ha^{-1}$) of the Cu was transported offsite. The second emission flow considered, drift, accounted for 16% (7.5 $kg_{Cu}*ha^{-1}$) of the site Cu losses.

Table 4. Yearly Cu distribution in soil for each year simulated based on the Cu dosage recommended by all standard phase 1 and 2 models.

Year	Copper $kg_{Cu}*ha^{-1}$	Offsite Drift $kg_{Cu}*ha^{-1}$	Onsite Deposition $kg_{Cu}*ha^{-1}$	Final Soil Stock ($mg_{Cu}*kg_{soil}^{-1}$)*	Water Losses ($kg_{Cu}*ha^{-1}$)	Δ Soil stock ($kg_{Cu}*ha^{-1}$)	Δ Root stock ($kg_{Cu}*ha^{-1}$)
2009	1.9	0.30	1.58	26.46	1.40	0.15	0.03
2010	2.6	0.42	2.18	26.58	1.87	0.26	0.06
2011	11.3	1.81	9.51	27.51	7.08	1.99	0.44
2012	4.9	0.78	4.12	27.85	3.20	0.75	0.17
2013	3.4	0.54	2.81	28.02	2.38	0.35	0.08
2014	10.0	1.60	8.42	28.80	6.36	1.68	0.38
2015	4.1	0.65	3.40	29.07	2.68	0.59	0.13
2016	2.0	0.32	1.66	29.16	1.43	0.19	0.04
2017	1.2	0.19	1.01	29.18	0.95	0.05	0.01
2018	5.4	0.86	4.49	29.55	3.51	0.80	0.18
Average	4.7	0.75	3.92	-	3.09	0.68	0.15
Total	46.7	7.5	39.2	-	30.9	6.8	1.5

*December of the same year and initial condition of the following year

Phase One Scenarios

Each model scenario output was recorded for total Cu demand (Table 5) on an annual basis. Improvements in spray efficiency yielded the lowest Cu demand at 38 $kg_{Cu}*ha^{-1}$ while the scenario excluding LAI dependent dosage simulated the largest Cu demand at 58.3 $kg_{Cu}*ha^{-1}$.

Table 5. Yearly Cu demand of each simulated scenario. $Dose_{original}$ is the original recommendation using all models at their initial state. $Dose_{lai}$ is the dosage excluding a dynamic dosage based on LAI, $Dose_{spray}$ is the dosage using a 10% improvement in spray efficiency, $Dose_{bioresistant}$ is the dosage using a 10% improvement in grapevine bioresistance, and $Dose_{sorption}$ is the dosage using a 10% improvement in foliar sorption.

	Model Recommended Dosage ($kgCu*ha^{-1}$)				
Year	$Dose_{original}$	$Dose_{LAI}$	$Dose_{spray}$	$Dose_{bioresistant}$	$Dose_{sorption}$
2009	1.9	1.9	1.5	1.6	1.9
2010	2.6	3.0	2.3	2.4	2.6
2011	11.3	13.1	9.3	10.0	11.3
2012	4.9	7.1	4.0	4.3	4.9
2013	3.4	6.8	2.7	3.0	3.4
2014	10.0	11.3	8.1	8.8	10.0
2015	4.1	4.1	3.3	3.5	4.1
2016	2.0	2.8	1.6	1.8	2.0
2017	1.2	1.5	1.0	1.1	1.2
2018	5.4	6.8	4.4	4.7	5.4
Average	4.7	5.8	3.8	4.1	4.7
Total	46.7	58.3	38.0	41.2	46.7

Static Geometry Dosage

When the model is run without the contribution of a dynamic LAI, the average Cu usage increases from 4.7 $kg_{Cu}*ha^{-1}$ to 5.8 $kg_{Cu}*ha^{-1}$ (Table 5), leading to an additional 11.6 $kg_{Cu}*ha^{-1}$ applied over the 10-year simulation (Table 6). The maximum impact is seen in 2013 where an additional 3.5 $kg_{Cu}*ha^{-1}$ is required, while there was no difference between the two scenarios in 2009. The increase in Cu usage led to increases in the stock and emissions of the site. The model simulated a rise in soil accumulation from 6.8 $kg_{Cu}*ha^{-1}$ to 9.1 $kg_{Cu}*ha^{-1}$, leading to an average soil Cu concentration increase from 29.55 $mg_{Cu}*kg_{soil}^{-1}$ to 30.6 $mg_{Cu}*kg_{soil}^{-1}$. Root stock increased from 1.5 $kg_{Cu}*ha^{-1}$ in the original scenario to 2.0 $kg_{Cu}*ha^{-1}$. Drift emissions increased from 7.5 $kg_{Cu}*ha^{-1}$ to 9.3 $kg_{Cu}*ha^{-1}$ and water-related losses increased to 37.9 $kg_{Cu}*ha^{-1}$ compared to an original loss of 30.9 $kg_{Cu}*ha^{-1}$.

Table 6. Annual Cu distribution excluding dynamic LAI model from simulations.

Year	Copper $kg_{Cu}*ha^{-1}$	Offsite Drift $kg_{Cu}*ha^{-1}$	Onsite Deposition $kg_{Cu}*ha^{-1}$	Final Soil Stock ($mg_{Cu}*kg_{soil}^{-1}$)*	Water Losses ($kg_{Cu}*ha^{-1}$)	Δ Soil stock ($kg_{Cu}*ha^{-1}$)	Δ Root stock ($kg_{Cu}*ha^{-1}$)
2009	1.9	0.30	1.58	26.46	1.40	0.15	0.03
2010	3.0	0.48	2.52	26.62	2.11	0.34	0.07
2011	13.1	2.10	11.03	27.71	8.16	2.35	0.52
2012	7.1	1.14	5.99	28.26	4.53	1.19	0.27
2013	6.8	1.09	5.71	28.73	4.46	1.10	0.23
2014	11.3	1.80	9.45	29.62	7.11	1.90	0.43
2015	4.1	0.66	3.47	29.89	2.74	0.59	0.14
2016	2.8	0.44	2.33	30.05	1.92	0.34	0.08
2017	1.5	0.24	1.26	30.09	1.14	0.09	0.02
2018	6.8	1.08	5.67	30.59	4.36	1.07	0.25
Average	5.8	0.93	4.90	-	3.79	0.91	0.20
Total	58.3	9.3	49.0	-	37.9	9.1	2.0

*December of the same year and initial condition of the following year

Improved Spraying Efficiency

The initial model assumes a spraying efficiency of 46%. When this value is increased 10% to 56%, the average annual Cu usage decreased from 4.7 $kg_{Cu}*ha^{-1}$ to 3.8 $kg_{Cu}*ha^{-1}$ (Table 7), with a maximum and minimum reduction of 2.1 kgCu/ha in 2011 and 0.2 kgCu/ha in 2017. This led to a total decrease of 8.7 $kg_{Cu}*ha^{-1}$ (18.5%) over the ten-year simulation.

Table 7. Annual Cu distribution implementing a 10% improvement in spraying efficiency

Year	Copper $kg_{Cu}*ha^{-1}$	Offsite Drift $kg_{Cu}*ha^{-1}$	Onsite Deposition $kg_{Cu}*ha^{-1}$	Final Soil Stock $(mg_{Cu}*kg_{soil}^{-1})$*	Water Losses $(kg_{Cu}*ha^{-1})$	Δ Soil stock $(kg_{Cu}*ha^{-1})$	Δ Root stock $(kg_{Cu}*ha^{-1})$
2009	1.5	0.24	1.26	26.43	1.17	0.07	0.16
2010	2.3	0.36	1.89	26.51	1.60	0.17	0.04
2011	9.3	1.48	7.77	27.24	5.84	1.58	0.35
2012	4.0	0.64	3.36	27.51	2.65	0.58	0.13
2013	2.7	0.43	2.27	27.61	1.99	0.23	0.05
2014	8.1	1.30	6.80	28.22	5.20	1.31	0.29
2015	3.3	0.52	2.73	28.42	2.20	0.43	0.10
2016	1.6	0.26	1.37	28.48	1.21	0.13	0.03
2017	1.0	0.16	0.84	28.49	0.83	0.01	0.00
2018	4.4	0.70	3.65	28.77	2.90	0.62	0.14
Average	3.8	0.6	3.2	-	2.6	0.5	0.1
Total	38.0	6.1	31.9	-	25.6	5.1	1.3

*December of the same year and initial condition of the following year

The decrease in Cu inputs results in reduced soil stock. Cu losses to water decreased by 5.3 $kg_{Cu}*ha^{-1}$ (17%) and losses to drift a reduced from 7.5 to 6.1 $kg_{Cu}*ha^{-1}$. The soil stock decreased to 5.1 $kg_{Cu}*ha^{-1}$ over the ten simulated years, 1.7 $kg_{Cu}*ha^{-1}$ less than the original simulation, while root stocks accumulated 0.2 $kg_{Cu}*ha^{-1}$ less than initially simulated.

Improved Grapevine Resistance

When the minimum deposition dosage required to prevent infection is decreased from 0.5 $mg_{Cu}*m^{-2}$ to 0.45 $mg_{Cu}*m^{-2}$ (10% reduction), the Cu demand decreased by an average of 0.6 $kg_{Cu}*ha^{-1}$ annually (Table 8). The largest decrease was seen in 2011, where 1.3 $kg_{Cu}*ha^{-1}$ less were required to prevent infection. The least affected year was 2017, when a reduction 0.1 $kg_{Cu}*ha^{-1}$ was simulated. The annual reduction led to a total decrease of 5.5 $kg_{Cu}*ha^{-1}$ over the simulated years.

Again, the decrease in Cu inputs results in reduced soil stock. Cu losses to water decreased by 3.3 $kg_{Cu}*ha^{-1}$ (10%) and losses to drift reduced 0.9 $kg_{Cu}*ha^{-1}$ (12%). The soil stock decreased by 1 $kg_{Cu}*ha^{-1}$ over the ten simulated years while root stocks decreased by 0.2 $kg_{Cu}*ha^{-1}$ (13%) compared to the initial simulation.

Table 8. Annual Cu distribution implementing a 10% increase in grapevine resistance

Year	Copper $kg_{Cu}*ha^{-1}$	Offsite Drift $kg_{Cu}*ha^{-1}$	Onsite Deposition $kg_{Cu}*ha^{-1}$	Final Soil Stock $(mg_{Cu}*kg_{soil}^{-1})$*	Water Losses $(kg_{Cu}*ha^{-1})$	Δ Soil stock $(kg_{Cu}*ha^{-1})$	Δ Root stock $(kg_{Cu}*ha^{-1})$
2009	1.6	0.3	1.4	26.44	1.2	0.1	0.0
2010	2.4	0.4	2.0	26.54	1.7	0.2	0.0
2011	10.0	1.6	8.4	27.34	6.3	1.7	0.4
2012	4.3	0.7	3.6	27.64	2.9	0.6	0.1
2013	3.0	0.5	2.5	27.77	2.1	0.3	0.1
2014	8.8	1.4	7.4	28.44	5.6	1.5	0.3
2015	3.5	0.6	3.0	28.67	2.4	0.5	0.1
2016	1.8	0.3	1.5	28.74	1.3	0.2	0.0
2017	1.1	0.2	0.9	28.75	0.9	0.0	0.0
2018	4.7	0.8	3.9	29.07	3.1	0.7	0.2
Average	4.1	0.7	3.5	-	2.8	0.6	0.1
Total	41.2	6.6	34.6	-	27.6	5.8	1.3

*December of the same year and initial condition of the following year

Improved Copper Foliar Sorption

In order to simulate improved foliar sorption of Cu fungicides on the surface of the grapevine leaves, the 50% washout standard was shifted from 5 mm of precipitation to 5.5 mm. The new simulation resulted in no changes in Cu demand in any of the simulated years (Table 9), matching the initial simulation annual average of 4.7 $kg_{Cu}*ha^{-1}$ and total of 46.7 $kg_{Cu}*ha^{-1}$. Due to their identical application schedules, the Cu distribution (Table 9) simulated identical results to the original full model simulation.

Table 9. Annual Cu distribution implementing a 10% increase in foliar sorption

Year	Copper $kg_{Cu}*ha^{-1}$	Offsite Drift $kg_{Cu}*ha^{-1}$	Onsite Deposition $kg_{Cu}*ha^{-1}$	Final Soil Stock $(mg_{Cu}*kg_{soil}^{-1})$*	Water Losses $(kg_{Cu}*ha^{-1})$	Δ Soil stock $(kg_{Cu}*ha^{-1})$	Δ Root stock $(kg_{Cu}*ha^{-1})$
2009	1.9	0.3	1.6	26.46	1.4	0.1	0.0
2010	2.6	0.4	2.2	26.58	1.9	0.3	0.1
2011	11.3	1.8	9.5	27.51	7.1	2.0	0.4
2012	4.9	0.8	4.1	27.85	3.2	0.8	0.2
2013	3.4	0.5	2.8	28.02	2.4	0.4	0.1
2014	10.0	1.6	8.4	28.80	6.4	1.7	0.4
2015	4.1	0.6	3.4	29.07	2.7	0.6	0.1
2016	2.0	0.3	1.7	29.16	1.4	0.2	0.0
2017	1.2	0.2	1.0	29.18	1.0	0.0	0.0
2018	5.4	0.9	4.5	29.55	3.5	0.8	0.2
Average	4.7	0.7	3.9	-	3.1	0.7	0.2
Total	46.7	7.5	39.2	-	30.9	6.8	1.5

*December of the same year and initial condition of the following year

Phase Two Scenarios

As soil properties have no bearing on the drift emissions, this loss remains constant in all the following scenarios and is not further presented.

Increased Soil pH

When the pH is increased by 10%, the soil accumulated 6.4 $kg_{Cu}*ha^{-1}$, decreasing the final soil concentration to 29.39 $mg_{Cu}*kg^{-1}$ (Table 10). The grapevine root accumulation decreased from 1.5$kg_{Cu}*ha^{-1}$ (3% of total Cu applied) to 1.0$kg_{Cu}*ha^{-1}$ (2% of total Cu applied). Finally, the Cu losses to water increased from 66% (30.9 $kg_{Cu}*ha^{-1}$) to 68% (31.8 $kg_{Cu}*ha^{-1}$).

Table 10. Annual Cu distribution raising the pH 10%

Year	Final Soil Stock ($mg_{Cu}*kg_{soil}^{-1}$)*	Water Losses ($kg_{Cu}*ha^{-1}$)	Δ Soil stock ($kg_{Cu}*ha^{-1}$)	Δ Root stock ($kg_{Cu}*ha^{-1}$)
2009	26.46	1.4	0.1	0.0
2010	26.58	1.9	0.3	0.0
2011	27.44	7.4	1.9	0.3
2012	27.77	3.3	0.7	0.1
2013	27.93	2.4	0.3	0.1
2014	28.67	6.6	1.6	0.2
2015	28.93	2.8	0.6	0.1
2016	29.01	1.4	0.2	0.0
2017	29.04	0.9	0.1	0.0
2018	29.39	3.6	0.8	0.1
Average	-	3.2	0.64	0.1
Total	-	31.8	6.4	1.0

*December of the same year and initial condition of the following year

Increased Clay Content

When the clay content of the soil is increased by 10% (Table 11), the soil accumulation rose slightly from 6.8 $kg_{Cu}*ha^{-1}$ to 6.9 $kg_{Cu}*ha^{-1}$. The grapevine root accumulation increased by less than 0.005 $kg_{Cu}*ha^{-1}$ thereby remaining at 3% of the total Cu applied. Finally, a minor 0.2 $kg_{Cu}*ha^{-1}$ decrease in Cu emissions to water was observed.

Table 11. Annual Cu distribution raising the clay content 10%

Year	Final Soil Stock ($mg_{Cu}*kg_{soil-1}$)*	Water Losses ($kg_{Cu}*ha_{-1}$)	Δ Soil stock ($kg_{Cu}*ha_{-1}$)	Δ Root stock ($kg_{Cu}*ha_{-1}$)
2009	26.46	1.4	0.2	0.0
2010	26.59	1.9	0.3	0.1
2011	27.53	7.0	2.0	0.4
2012	27.88	3.2	0.8	0.2
2013	28.05	2.4	0.4	0.1
2014	28.85	6.3	1.7	0.4
2015	29.13	2.7	0.6	0.1
2016	29.22	1.4	0.2	0.0
2017	29.24	0.9	0.0	0.0
2018	29.62	3.5	0.8	0.2
Average	-	3.1	0.69	0.2
Total	-	30.7	6.9	1.5

*December of the same year and initial condition of the following year

Increased Organic Matter Content

Similarly to changing the pH, the OM adjustment impacted the soil distribution in the vineyard (Table 12) by decreasing the soil stock to 6.3 $kg_{Cu}*ha_{-1}$ while increasing losses to water emissions to 31.6 $kg_{Cu}*ha_{-1}$ and bioaccumulation to 1.3 $kg_{Cu}*ha_{-1}$.

Table 12. Annual Cu distribution raising the OM 10%

Year	Final Soil Stock ($mg_{Cu}*kg_{soil-1}$)*	Water Losses ($kg_{Cu}*ha_{-1}$)	Δ Soil stock ($kg_{Cu}*ha_{-1}$)	Δ Root stock ($kg_{Cu}*ha_{-1}$)
2009	26.46	1.4	0.1	0.0
2010	26.57	1.9	0.2	0.0
2011	27.42	7.3	1.8	0.4
2012	27.74	3.3	0.7	0.1
2013	27.89	2.4	0.3	0.1
2014	28.61	6.6	1.6	0.3
2015	28.86	2.8	0.5	0.1
2016	28.94	1.4	0.2	0.0
2017	28.96	1.0	0.0	0.0
2018	29.31	3.6	0.7	0.2
Average	-	3.2	0.63	0.1
Total	-	31.6	6.3	1.3

*December of the same year and initial condition of the following year

Erosion

The annual site erosion varied considerably every year. Five of the ten years simulated no erosion loss while a maximum of 63,560 $kg_{soil}*ha_{-1}$was simulated in 2015 (Table 13). The average annual loss of Cu due to erosion was 0.5 $kg_{Cu}*ha_{-1}$, with a total of 5.4 $kg_{Cu}*ha_{-1}$ lost over the ten-year period.

Table 13. Annual site erosion

Year	Final Soil Stock ($mg_{Cu}*kg_{soil}^{-1}$)*	Soil Erosion ($kg_{soil}*ha^{-1}$)	Copper Emissions ($kg_{Cu}*ha^{-1}$)
2009	26.46	17366	0.5
2010	26.58	0	0
2011	27.51	56304	1.5
2012	27.85	0	0
2013	28.02	0	0
2014	28.80	16814	0.5
2015	29.07	63560	1.8
2016	29.16	0	0
2017	29.18	35005	1.0
2018	29.55	0	0
Average	-	18905	0.5
Total	-	189048	5.4

*December of the same year and initial condition of the following year

Ecotoxicity

The ecotoxicity of each model scenario is considered according to the CF of Cu^{2+} in air, water, and soil. The improved foliar sorption and clay adjustment scenarios are excluded due to their negligible difference with the standard simulation. The ecotoxicity of each model (Table 14) followed the same pattern as the Cu demand with the 10% spray improvement simulating the lowest ecotoxicity at 1.55E+08 $PAF*day*m^3*ha^{-1}$. The scenario excluding the dynamic LAI simulated the largest ecotoxicity with a value of 2.56E+08 $PAF*day*m^3*ha^{-1}$. The increased pH and OM scenarios simulated at 1.85E+08 and 1.87E+08 $PAF*day*m^3*ha^{-1}$ respectively, each had a slightly lower ecotoxicity impact than the standard simulation of 1.97E+08 $PAF*day*m^3*ha^{-1}$, despite having the same Cu input.

Table 14. Ecotoxicity of each model scenario

	Impact Factor ($PAF*day*m^3*ha^{-1}$)					
	IF_{MR}	IF_{LAI}	IF_{Spray}	$IF_{bioresisant}$	IF_{pH}	IF_{OM}
Air	5.70E+07	7.13E+07	4.65E+07	5.04E+07	5.70E+07	5.73E+07
Water	2.31E+07	2.85E+07	1.92E+07	2.07E+07	2.38E+07	2.37E+07
Soil	1.17E+08	1.56E+08	8.97E+07	9.86E+07	1.04E+08	1.06E+08
Total	1.97E+08	2.56E+08	1.55E+08	1.70E+08	1.85E+08	1.87E+08

4. Discussion

The model recommendations present a significant reduction in Cu usage in contrast to the standard practice considered, simulating a 58% decrease in annual usage despite including a 30% factor of safety. However, the modeled recommendation of 4.7 $kg_{Cu}*ha^{-1}$ remains above the new European legislation maximum average annual use of 4 $kg_{Cu}*ha^{-1}$ (28 $kg_{Cu}*ha^{-1}$ over a 7-year period, European Commission, 2018). Previous Cu demand models also present savings between 46% and 60%, which also result in recommendations exceeding the 4 $kg_{Cu}*ha^{-1}$ ceiling (Pellegrini et al., 2010; Caffi et al., 2010). By excluding the 30% factor of safety however, the recommendation from this model decreases to 3.6 $kg_{Cu}*ha^{-1}$, below the new legislative ceiling.

There were two significant outlier years, 11.3 $kg_{Cu}*ha^{-1}$ in 2011 and 10.0 $kg_{Cu}*ha^{-1}$ in 2014. These were the only two years to exceed 5.5 $kg_{Cu}*ha^{-1}$ and their exclusion would reduce the average annual demand to 3.2 $kg_{Cu}*ha^{-1}$. These years had two of the earliest budburst dates and maximum LAI dates. The early phenological development led to higher dose requirement per treatment earlier in the season, increasing the overall seasonal demand. In addition, these were the two rainiest years recorded, creating many infection events when the LAI had reached its maximum, significantly increasing the Cu demand. Other years had similar rainfalls, or similarly timed phenological development, however no other year had the combination of the two. For example, in 2013, despite experiencing similar rainfall to 2014, a later budburst date led to small Cu dosages per treatment due to the LAI increasing later in the year. As a result, despite experiencing 98% of the 2014 rainfall, 2013 required 66% less Cu to prevent mildew infections. The 2017 simulation had a similar budburst date to 2011, however it only experienced 55% of the rainfall that 2011 did, resulting in 2017 requiring 90% less Cu. Overall, 4 years experienced budburst dates before April 5th and rainfall exceeding 150 mm. These required an average of 7.9 $kg_{Cu}*ha^{-1}$, while the 6 years which experienced budburst dates after April 5th or less than 150 mm of rainfall required an average of 2.5 $kg_{Cu}*ha^{-1}$, highlighting the important interaction between budburst and rainfall on Cu demand.

When considering model scenarios, the first factor considered is the exclusion of the dynamic LAI factor. In this scenario, the model is simply a mildew infection model which provides application frequency requirements, similar to that of Rossi et al., (2007). In this iteration, the model simulates a 49% reduction (5.8 $kg_{Cu}*ha^{-1}$) in Cu demand from the standard practice of 11.4 $kg_{Cu}*ha^{-1}$. This indicates that much of the current application schedules apply Cu despite no risks of infection and is therefore the most important parameter to consider. The inclusion of the seasonally dynamic LAI factor decreases dosage recommendations by an additional 25% representing a 1.1 $kg_{Cu}*ha^{-1}$ saving annually; thereby reducing the total demand to 4.7 $kg_{Cu}*ha^{-1}$ as indicated in the baseline scenario.

When exploring the process specific improvements considered, the 10% improvement in spray efficiency yielded the largest additional savings at 0.9 $kg_{Cu}*ha^{-1}$annually compared to the 10% increase in bioresistance and foliar sorption, which respectively simulated 0.6 $kg_{Cu}*ha^{-1}$ and 0 $kg_{Cu}*ha^{-1}$savings annually. The spray efficiency savings result in a total Cu demand of 3.8 $kg_{Cu}*ha^{-1}$, breaking the 4 $kg_{Cu}*ha^{-1}$threshold, while the bioresistance scenario reduces Cu demand to 4.1 $kg_{Cu}*ha^{-1}$. The improvements in spray efficiency are most impactful when the spray events occur later in the year as they reduce the maximum dosage recommendation from 750 gCu/ha to 600 gCu/ha (Table shown in supplemental results, Table SR1). This difference is less pronounced early in the year as the deposition efficiency is much higher at lower LAIs, only saving 0-50 gCu/ha per treatment. The same holds true for the improved bioresistance, however the maximum dosage only decreases to 650 gCu/ha (Table SR2), leading to a slightly lower overall improvement.

The improvements in foliar sorption did not provide any benefits over the course of the simulation as there were no precipitation events between 5 mm and 5.5 mm recorded. Two rain events where a half dosage was possible were recorded between 5.5 mm and 6.0 mm, meaning the maximum possible reduction from this implementation would be 0.08 kg_{Cu}*ha_{-1} if foliar sorption increased by 20%. Though this value is significantly smaller than the other options considered at this location, precipitation conditions vary significantly between vineyards globally. At locations where there are frequent small precipitation events (< 5mm), this innovation could present more impactful Cu reductions.

Considering the research currently conducted in relation to these scenarios, managing the canopy development of grapevines within vineyards is an extremely common practice, though its potential may be more limited than other Cu reducing techniques because the LAI of a vineyard cannot be maintained artificially low without affecting wine quality (Keller, 2010). The importance of improving spray efficiencies and bioresistance is highlighted by the observed results despite limited improvements. Current solutions to improve spray efficiency often rely on sensitive high-tech equipment that can be difficult to calibrate consistently (Gil et al., 2011). For improved bioresistance, the primary bottleneck encountered is the ability of bioresistant grapevines to produce quality wines on a consistent basis (Toffolatti et al., 2018). As a result, these solutions are not currently available for viticulturists to consider at an industrial level. However, if future tests provide improved results, these could be implemented without significantly adapting current practices. There is research focused on improving CuF formulations which release Cu ions at slower rates thereby improving foliar sorption and reducing rainfall induced wash off (Gessler et. al, 2011). Despite its comparatively poor results, this solution holds the potential to significantly reduce Cu usage, particularly in high usage years such as 2011 and 2014, if protection efficacy can be maintained.

The change in clay content yielded no significant changes in the distribution of Cu in the system, whereas increasing the pH and OM each provided a noticeable difference in the Cu's ultimate fate. The results indicated a decrease in soil concentration as pH and OM increased, with larger water emissions and less bioaccumulation. The reduction in bioaccumulation is expected due to its direct relationship to free Cu (Chen et al., 2012), which decreases as pH or OM increase (Supp-1, equation 31), however previous studies have determined that higher pH values decrease the mechanical mobility of Cu, contradicting the results found in the model. The model predicts a reduction in soil stock because the partitioning coefficient increases with pH (Supp-1, equation 34). Subsequently, the increased partitioning coefficient leads to a reduction in Cu input interacting with the soil matrix according to equation 42 of the supplemental methods. The model calculates that the reduction in total Cu interacting with the soil negates the impacts of the decreased reactive concentration, thus leading to increased water emission and reduced soil and biological stocks. The increase in OM also increases the overall reactive fraction of Cu in the soil matrix (Supp-1 equation 32), thereby increasing the soluble fraction of Cu. This additional fraction, however, will provide less free Cu to bioaccumulate as it binds with the increased dissolved OM, explaining the additional losses to water emissions and reduced biological uptake. The increase in pH limits the potential for phytoextraction of Cu in soils, a process which requires biological mobility, however, it may represent further potential for mechanical treatment processes.

Overall, the major emission factor simulated was losses to water. Previous work has established that surface runoff represents a minor fraction of the Cu applied (Babcsányi et al., 2016), therefore it could be considered that the majority of the water losses simulated are related to subsurface flows. Others have theorized erosion losses play a significant role in the offsite transport of Cu (Brun et al., 1998) however, according to the model simulations, annual water related losses (3.1 $kg_{Cu}*ha^{-1}$) are nearly an order of magnitude higher than erosion losses (0.5 $kg_{Cu}*ha^{-1}$). The difference among these losses, however, is highly dependent on the soil Cu concentration. At the site simulated, the initial concentration of 26.4 $mg_{Cu}*kg^{-1}$ is generally low for a vineyard (Ballabio et al., 2018), and as a result, a site with concentrations exceeding 100 $mg_{Cu}*kg^{-1}$ could see the annual Cu loss from erosion on the same order of magnitude as water losses. The average annual erosion rate for the vineyard was 18.95 $t_{soil}*ha^{-1}$, slightly higher than the average agricultural land rate of 14 $t_{soil}*ha^{-1}$ found by Panagos et al. (2014). Erosion rates are unlikely to increase by an order of magnitude, implying that the primary erosion related losses are dependent on the site Cu soil concentration. Nevertheless, the annual water losses are significantly higher than the annual soil accumulation rate found (0.7 $kg_{Cu}*ha^{-1}$) despite an extremely low site pH, implying that the majority of the Cu does not interact with the top 20cm of the soil, and much of it may enter the groundwater or bind to the soil at lower depths.

The fraction which does interact with the soil appears to be a net irreversible process at the current dosages required to protect the grapevines. Regardless of the dosage in a given year, an increase in soil Cu concentration was observed, implying that any Cu input to soil may be greater than the corresponding soil output. This is due to the relationship between precipitation, infection events, and Cu application, as years with higher precipitation demand more Cu usage as a result of more frequent infection events; dryer years will have a lower Cu demand but also a smaller water flux transporting Cu out of the system. This trend is seen globally, as vineyards in regions with higher annual precipitation also experience higher Cu accumulation rates (Miotto et al., 2017).

An important factor not considered in the model is the dynamic resistance of grapevine to mildew over the course of a season. Grapevines are primarily susceptible to infection in the first three weeks after their flowers bloom, however after this period, they develop a natural resistance due to their stomata losing functionality over the course of the growing season (Gindro et al., 2012). This was not considered as the specific timing of the change to closed-like stomata is still unclear. In addition to this, mildew cohorts have varying degrees of intensity, with the initial infection cohorts considered the most critical to harvest loss in (Rossi et al., 2007). Effectively modeling the seasonal change in resistance of the grapevines with the cohort intensity could provide crucial information to further reduce Cu usage late in the application season, when the recommended spray dosages are highest.

The model includes additional simplifying assumptions which can affect the accuracy of the results. The rain wash-off, spray efficiency, root density, Mg^{2+} pore water concentration, OM content, and water balance are calculated using static coefficients. These, however, are dynamic variables under in-situ conditions, therefore future research implementing models which account for their seasonal variations could lead to changes in Cu demand and its final fate.

5. Conclusion

According to the model developed, the total Cu applied in vineyards annually can be significantly reduced by incorporating precision application schedules which closely monitor the germination of mildew cohorts and canopy development simultaneously. Innovations in spray efficiency and grapevine bioresistance present a high potential for further reducing Cu usage while improved foliar sorption requires larger advances before significant impacts can be consistently observed. As it stands, current application methods are not sufficiently efficient to meet the European standard of 4 $kg_{Cu}*ha^{-1}$ without incurring additional infection risks. This model, however, offers viticulturists the opportunity to incorporate new innovations to systematically reduce their Cu by interconnecting these factors while demanding little informational input, an important consideration in its usability. The accumulation of Cu increases continually, regardless of application dosages, implying research efforts should continue to develop technologies which reduce the necessary Cu input as Cu's bioavailability after application significantly limits the potential of phytoextraction. This model also allows for a better understanding of Cu transport in soils, indicating that pH and OM adjustments are the primary drivers of Cu fractionation and speciation in soil solution, significantly affecting its mechanical and biological mobility. Further research to validate these findings are required, but could help future legislations incorporate specific Cu related stock and emissions goals, rather than input based objectives.

Despite including many simplifying assumptions, the model provides a proof of concept that the processes of a vineyard system, and potentially other agricultural systems, can be systematically simulated to predict the plant protection products required to maintain a healthy crop. Additional process considerations can be introduced to the model to further assess the optimal recommended dosage, which may present savings not considered in this study in order to reach acceptable European legislative levels.

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