Supplementary Methodology – Nicolas Navarre - *Development of a quantitative tool for environmentally sustainable copper fungicide application and tracking within vineyards*.

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Modeling Mildew Growth

The mechanistic model developed by Rossi et al. is used to simulate the primary infection of mildew in vineyards (Rossi et al., 2008). The model is based on a series of governing equations and disease cycle processes which rely on temperature, relative humidity (RH), vapor pressure deficit (VPD), and wetness (W). All of the input data, except wetness (wet hours), is acquired via the weather APIs described in the previous section. Equations (1-10 & 14-17) and their derivations are all according to the model published by Rossi et al. (2008).

Table SM1 List of nomenclature and parameters used in modeling mildew germination from Rossi et al. (2008)

Symbol	Description	Unit
SOD	Seasonal oospore dose	Number (set at 1)
MMO	Morphologically mature oospores	Number (0–1)
PMO	Physiologically mature oospores	Number (0–1)
GEO	Germinated oospores (i.e. oospores with sporangia)	Number (0–1)
ZRE	Zoospores released from sporangia	Number (0–1)
ZDI	Zoospores dispersed from soil to leaves	Number (0–1)
ZIN	Zoospores causing infection	Number (0–1)
OSL	Oil spots on leaves	Number (0–1)
DOR	Progress of dormancy breaking in the oospore population	Proportion/h
GER	Germination of oospores (i.e. formation of sporangia)	Number
SUS	Survival of sporangia	Number
REL	Zoospore release	0 (no) or 1 (yes)
SUZ	Survival of zoospores	Number
INF	Infection by zoospores	0 (no) or 1 (yes)
INC	Incubation	0–1
PIS	Length of the primary inoculum season	Days
PMOc	Density of the cth oospore cohort	Number (0–1)
h	Counter for the time (hours), with h = 1 on 1st January, 01.00 h	h
η	Current hour	h
ε	Time when an oospore cohort begins germination	h
φ	Time when an oospore cohort ends germination	h
ρ	Time of the zoospore release	h
δ	Time of zoospore dispersal	h
ι	Time of infection	h
τ	Time of disease onset	h
j	Subscript for the oospore germination events	Number

J	Total oospore germination events in the PIS	Number
c	Subscript for the oospore cohort	Number
C	Total oospore cohorts	Number
DOY	Day of the year	Number
T	Air temperature	°C
R	Rainfall	mm
RH	Relative humidity	%
W	Presence of wetness	0 (no) or 1 (yes)
VPD	Vapour pressure deficit	hPa
WD	Wetness duration	h
HT	Hydro-thermal time	°C × h
M	Moisture of the leaf litter	0 (no) or 1 (yes)
TWD	Average T over WD	°C

The initial consideration of the model is the seasonal oospore dose. In order to estimate most conservatively, it is assumed 100% of the spores have the potential to break dormancy, therefore:

$$SOD = 1 \quad (1)$$

The model tracks this seasonal dose from the first hour of the year (January 1st at 01h00 of any given year) until an hour 'h'. At $h = 1$, none of the spores have had time to break dormancy, therefore the entire oospore population is considered morphologically mature oospores (MMO). As a result, at $h = 1$:

$$MMO_h = SOD \quad (2)$$

The MMO then break dormancy to become physiologically mature oospores (PMO). These are the oospores that have the potential to germinate and later cause infection. This conversion rate is regulated by a dormancy breaking factor where:

$$PMO_h = MMO_h * DOR_h \quad (3)$$

$$DOR_h = exp(-15.891 * exp(-0.653(HT_h + 1))) \quad (4)$$

HT_h is the hydro-thermal time at any given hour 'h' and calculated as:

$$HT_h = \sum_{h=1}^{\eta} \frac{M_h}{(1330.1 - 116.19T_h + 2.6256T_h^2)} \quad (5)$$

T_h is the temperature (^oC) at any given hour. When $T_h \leq 0^oC$, $\frac{M_h}{f(T_h)} = 0$. Additionally, if:

$R_h > 0\ mm$ or $VPD_h = 4.5\ hPA, M_h = 1$

$R_h = 0\ mm$ and $VPD_h > 4.5\ hPA, M_h = 0$

Where R_h is the rainfall amount in mm and VPD_h is the vapor pressure deficit in hPa at hour h. Each parameter is acquired through the World Weather Online API.

The model then tracks oospore cohorts, which are triggered by rain events where $R_{h=\varepsilon} > 0.2\ mm$. When such a rain event occurs, the hour 'h' is considered the initial hour 'ε' of the j^{th} cohort event. The length of the germination process is regulated by:

$$GER_h = \sum_{h=\varepsilon}^{\eta} \frac{M_h}{(1330.1 - 116.19T_h + 2.6256T_h^2)} \quad (6)$$

When $T_h \leq 0^o C, \frac{M_h}{f(T_h)} = 0.$

The intensity of the event, or the relative number of seasonal spores which make up the cohort is regulated by

$$PMO_c = \int_{\varepsilon(j-1)}^{\varepsilon-1(j)} DOR_h \quad (7)$$

Where PMO_c is the physiologically mature oospores, '$\varepsilon(j-1)$' is the first hour of the previous cohort event and $\varepsilon - 1(j)$ is the final hour of the current cohort event.

When $GER_h = 1,\ \phi = \eta$ where ϕ is the hour when the germination process is completed and $GEO_\phi = PMO_c$. This implies that the germinated oospore dose at hour ϕ is equal to the PMO_c of the current cohort event.

When the process is complete, the oospores have formed sporangia. The survival of sporangia (SUS) is modeled as:

$$SUS_h = \sum_{h=\phi}^{\eta} \frac{1}{(24(5.67 - 0.47(T_h(1 - RH_h/100)) + 0.01(T_h(1 - RH_h/100))^2))} \quad (8)$$

Where RH_h is the relative humidity at hour 'h'. The sporangia survive as long as $SUS_h \leq 1$ at which point $GEO_h = GEO_\phi$. If $SUS_h > 1$, the sporangia have not survived and $GEO_h = 0$.

While the sporangia are alive (ZRE), they will release their zoospores (REL) given the following conditions:

$$WD_h \geq exp(\frac{-1.022 + 19.634)}{TWD_h}),\ REL_h = 1, \rho = h, ZRE_\rho = GEO_h \quad (9)$$

Where REL is a dichotomous variable assuming the value of 1 (release) or 0 (no release) and hour 'ρ' represents the hour at which zoospore release occurred, and at intensity GEO_h. WD is the duration of wetness (in hours) calculated by summing a dichotomous variable, W, wet hour (1) or dry hour (0). This variable is summed as:

$$\sum_{h=\phi+1}^{\eta} W_h \quad (10)$$

Where TWD_h is the average temperature of the current wet period.

The Rossi et al. (2008), germination model does not include a clear definition of wetness, or wet hours. To compensate for this, a classification and regression tree/stepwise linear discriminant model (CART/SLD/Wind model) developed by Kim et al. (2002) was incorporated. The model factors in dew point temperature, wind speed, and RH to estimate whether or not an hour should be considered wet or dry according to equations (11-13). The results of the CART model are incorporated into the germination model to provide the necessary input to determine whether

$W_h = 1$ or $W_h = 0$. The CART model was favored over other leaf wetness models due to its superior robustness and simpler data demands (Montone et al., 2016).

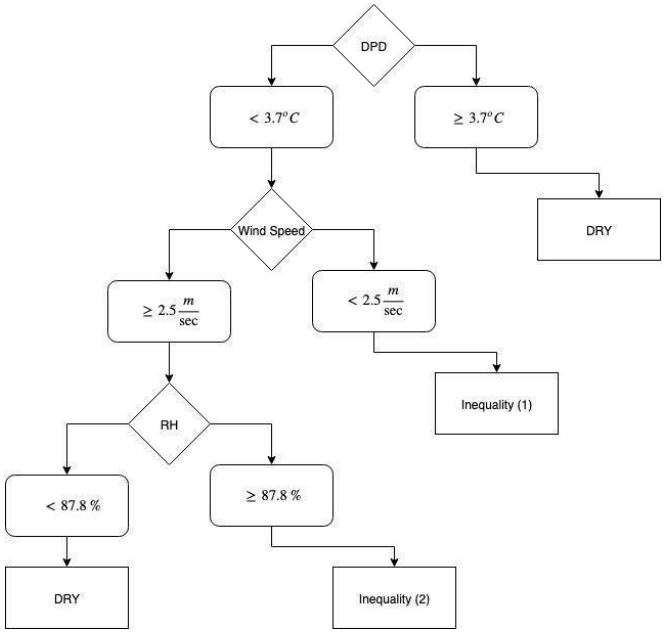

Figure SM1. from Kim et al. 2002 governing conditions of CART model

Where DPD_h is the dew point temperature difference and DT_h is the dew temperature at hour 'h'

$$DPD_h = T_h - DT_h \quad (11)$$

$$Inequality\ (1) = 1.6064\sqrt{T_h} + 0.0036T_h^2 + 0.1531RH_h - 0.499WS_h * DPD_h - 0.0035T_h * RH_h > 14.4674 \quad (12)$$

$$Inequality\ (2) = 0.7921\sqrt{T_h} + 0.0046RH_h - 2.3889WS_h - 0.0390T_h * WS_h - 1.0613WS_h * DPD_h > 37.0 \quad (13)$$

Once the zoospores are released, survival (SUZ) is modeled as:

$$SUZ_h = \frac{\sum_{h=1}^{\eta}(h-\rho)}{\sum_{h=\rho+1}^{\eta} W_h} \quad (14)$$

If $SUZ_h > 1$ the wet period has ended and the zoospores have died. Therefore $ZRE_h = 0$. While the zoospores are alive, dispersion through a rain event can occur when $R_h \geq 0.2\ mm$. When this happens hour $h = \delta$ and $ZDI_\delta = ZRE_\rho$ and the current quantity of viable released zoospores (ZRE) become viable dispersed zoospores (ZDI). Once dispersed, the ZDI cause infection to the grapevine under the following condition:

$$WD_h * TWD_h \geq 60 \quad (15)$$

If this condition is met, infection occurs and hour $h = \iota$. Once an infection has occurred there is an incubation period, before symptoms appear on the grapevine, which last within the following time interval:

$$INC'_h = \frac{1}{(24*(45.1-3.45*T_h+0.073*T_h^2))} \quad (16)$$

$$INC''_h = \frac{1}{(24*(59.9-4.55*T_h+0.095*T_h^2))} \quad (17)$$

When $\sum_{h=\iota}^{\eta} INC'_h \leq 1 \; and \; \sum_{h=\iota}^{\eta} INC''_h \leq 1$the time range in which symptoms will appear has been established.

Modeling Vineyard Parameters and Spray Deposition

Once the mildew germination cycle is modelled, copper (Cu) demand can be simulated. First the model simulates the budburst date of the grapevine. Infection can only occur if the grapevine buds have broken, as the leaf surface area is too small for spores to cause infection before this (Pellegrini et al., 2010). The growing degree day model (GDD; Bonhomme, 2000) is used to determine the timing of budburst. The model predicts budburst when a fixed thermal time (G_c (^oC)) has been reached:

$$G_c = \sum_{n=1}^{N_{bb}} A_C(n) \quad (18)$$

$$A_c(n) = \max(T(n) - T_0, 0) \quad (19)$$

$$T_0 = 5^oC \quad (20)$$

Where $T(n)$ is the daily mean temperature, T_0 is the base temperature, and $N_{bb}$is the date of budburst (Cortázar-Atauri et al., 2009).

If the budburst date has passed, the recommended dosage $Cu_{dose}(grams * ha^{-1})$ is calculated using equation (21) developed by Pergher and Petris (2008), which factors the leaf area index (LAI) of a vineyard, the spray efficiency, and deposited dose.

$$Cu_{dose} = 2 * 10^2 d_{norm} \frac{LAI}{\varepsilon} \quad (21)$$

The parameters needed to solve the equation are $d_{adj}(\mu gCu * cm_{leaf}^{-1})$, LAI $(m^2 * m^{-2})$, andε $(unitless)$. To calculate d_{adj}, models developed empirically by Siegfried et al. (2007; equ. 22) and Pergher and Pertis (2008; equ. 23) were used. These models calculate a normalized deposition efficiency as a function of LAI, indicating that this is a dynamic parameter over the course of a growing season. Both models were considered because LAI is a sensitive parameter leading to large variances in estimated $d_{norm}(\mu gCu * cm_{leaf}^{-1})$. The smallest d_{norm} was used as this would represent the least efficient spraying and therefore demand the largest dose.

$$d_{norm} = -2.6422 * ln(LAI) + 3.947 \quad (22)$$

$$d_{norm} = 0.2269 * LAI^{-0.5187} \quad (23)$$

A target deposition dose (d_0) of 0.5 $\mu gCu * cm_{leaf}^{-1}$is considered the optimum dose needed to achieve effective leaf protection (Cabùs et al., 2017). As this is the desired deposition in order to

avoid excess Cu usage, an adjustment factor is needed to correct the dosage based on the LAI. To compensate for this an adjustment term d_{adj} was developed as:

$$D_{adj} = \frac{0.5}{d_{norm}}. \quad (24)$$

The relationship was assumed to be linear due to the linear relationship of $d_0$and Cu_{dose}. As a result, equation 21 can be generalized to be:

$$Cu_{dose} = 2 * 10^2 d_{norm} \frac{LAI}{\varepsilon} * D_{adj} \quad (25)$$

The model assumes approximately 50% of Cu is washed off after 5 mm of rain (Pérez-Rodríguez et al., 2015). This principle is validated with vineyard owners and is commonly relied upon to adjust dosage in current practice (personal communication). As such, if the previous rain event had less than 5 mm of precipitation, the target deposition dose is lowered from $0.5\ \mu gCu * cm_{leaf}^{-1}$ to $0.25\ \mu gCu * cm_{leaf}^{-1}$. This assumption is only valid if the interval between rain events is smaller than 5 days (Pellegrini et al., 2010). If the interval is larger than 5 days, it is assumed new leaf growth must be accounted for, therefore the full dose requirement is utilized.

With the adjusted deposition established, a spraying efficiency model is incorporated to calculate a recommended spray dosage. To acquire data on spray efficiency, results from a study carried out by Garcera et. Al (2017), which tracked the Cu flows from nozzle to final deposition were used to estimate the Cu spraying efficiency (Garcerà et al., 2017). This estimate was validated with the vineyard chief of culture and additional research publications (Balsari and Marucco, 2004; Pergher et al., 2013, Gil et al., 2014).

$$\varepsilon = 0.46$$

Additionally, from the same research conducted by Garcera et al. (2017), it is estimated that 16% of the mass applied is lost to offsite drift. Therefore:

$$Cu_{drift} = 0.16 * Cu_{dose} \quad (26)$$

To determine the LAI of each vineyard, a series calculation based on the degree days of the location is used (Williams & Ayars, 2005) to determine the shaded area (SA, $m^2 * vine^{-1}$), leaf area (LA, $m^2 * vine^{-1}$), crop coefficient (K_c, $unitless$), and finally LAI $m^2 * m^{-2}$. These are calculated according to the following equations:

$$SA = -2.6 + 6.638 * (1 - e^{-0.0042 * x}) \quad (27)$$

$$x = Degree\ Days > 10^o C\ if\ Day > March\ 15^{th} \quad (28)$$

$$LA = 0.552 + 0.134 * SA \quad (29)$$

$$K_c = 0.115 + 0.0309 * LA \quad (30)$$

$$LAI - 0.115 + 0.235 * K_c \quad (31)$$

With the necessary spray deposition parameters acquired, Pergher and Petris' spray deposition governing equation is used to provide a dynamic dosage required which varies based on the grapevine LAI.

Modeling Soil Transport

The Cu transport in soil is modelled on a monthly resolution based on the partition and speciation relationships derived by Römkens et. al (2004) and De Vries and Groenenberg (2009) and the biological uptake rates derived by Chen et al. (2013). The model relies on initial Cu concentration in the soil ($ctCu_{tot}$; $mol * kg_{soil}^{-1}$), soil organic matter (OM) content, soil clay content, soil pH, bulk density, available water capacity, and root density (De Vries and Groenenberg, 2009) to calculate the final fate of Cu in soil. The model output is the partitioning and the quantification Cu in the solid ($mgCu * kg_{soil}^{-1}$), liquid ($mgCu * L^{-1}$), and biological ($mgCu * kg_{root}^{-1}$) phases. The topsoil (<20cm) is most relevant for the Cu enrichment (Wang et al., 2015), and is therefore established as the lower boundary of the system.

First, the reactive fraction of Cu ($ctCu_{re}$; $mol * kg_{soil}^{-1}$) in the soil is determined through equation.

$$ln(ctCu_{re}) = \beta_0 + \beta_1 * ln(ctCu_{tot}) + \beta_2 * ln(\%OM) + \beta_3 * ln(\%clay) \quad (32)$$

$$\beta_0 = 400$$

$$\beta_1 = 1.152$$

$$\beta_2 = 0.023$$

$$\beta_3 = -0.171$$

With the reactive concentration calculated, a linear solid solution partitioning equation (Krishnamurti et al., 2002) can be used to calculate the total solution phase Cu concentration $[Cu]_{tots,ss}$ $(mol * L^{-1})$.

$$ctCu_{re} = k_d * [Cu]_{tots,ss} \quad (33)$$

$$k_d = 0.68 + 0.15 * pH \quad (34)$$

A Freundlich equation is then used to calculate the Cu^{2+} concentration in solution:

$$ctCu_{re} = K_f * [Cu]_{free}^{n} \quad (35)$$

$$ln(K_f) = \alpha_0 + \alpha_1 * pH + \alpha_2 * ln(OM) \quad (36)$$

$$n = 0.85$$

$$\alpha_0 = -2.26$$

$$\alpha_1 = 0.89$$

$$\alpha_2 = 0.90$$

With the free Cu concentration calculated, a biotic ligand model (BLM) can be included to determine the root uptake. The mechanisms and rates by which grapevine roots uptake Cu is still poorly understood (Chopin et al., 2008). There are a multitude of soil and biological parameters which drive the biotic interaction with the Cu available in the soil, we followed the aka razor principle. The distinction between established and juvenile roots is not considered nor is the average root depth. These are difficult parameters to simulate and can vary significantly within a single vineyard (Chopin et al., 2008). A BLM model accounts for uptake via the free ion activity as well incorporates the competition with cations that significantly impact the uptake a BLM

model specifically for Kyoho grapevine (*Vitis vinifera* L.) is derived (Chen et al 2013). As a result, a BLM is used to calculate the root accumulation Cu_{root} $(mgCu * kg_{root})$ shown in equation 37.

$$Cu_{ru} = \frac{n_{blm} * K_{Cu}^{A}\{Cu^{2+}\}}{1 + K_{Mg}^{A}\{Mg^{2+}\}} \quad (37)$$

$$n_{blm} = 16{,}005.86 \ \ (unitless)$$

$$\ln(K_{Cu}^{A}) = 4.29 \ \ (unitless)$$

$$\ln\left(K_{Mg}^{A}\right) = 2.35 \ \ (unitless)$$

$$\{Cu^{2+}\} = [Cu^{2+}] \ \ (mg * L^{-1})$$

$$\{Mg^{2+}\} = [Mg^{2+}] = 0.95 \ (mg * L^{-1})$$

The model's only data input demand is free Cu activity. It was assumed that the effective Cu concentration was equal to the actual free Cu concentration due to limited information on the activity of the soil water as discrete locations throughout Europe.

After the initial Cu distribution in the soil is determined, the following mass balance is used to determine the changes in concentration due to Cu application, leaching, and biological uptake on a monthly resolution.

$$Cu_{in} = Cu_{ru} + Cu_{le} + \rho * z * \frac{d}{dt} ctCu_{re} + \ \sigma * z * \frac{d}{dt}[Cu]_{tot,ss} \quad (38)$$

Combining equation 33 with equation 37, equation 38 can be rearranged as:

$$Cu_{in} = Cu_{ru} + Cu_{le} + \frac{d}{dt}[Cu]_{tot,ss}(\rho * z * k_d + \ \sigma * z) \quad (39)$$

Where ρ is the soil bulk density $(\text{kg} * \text{m}^{-3})$, z is the soil depth (m), k_d is the partitioning coefficient in $(\text{m}^3 * kg^{-1})$, σ is the soil water content in $(\text{m}^3 * \text{m}^{-3})$, and Q_{le} is the water fraction $m * month^{-1}$ which exits the system through subsurface leaching.

$$Cu_{le} = Q_{le} * \ [Cu]_{tot,ss} \quad (40)$$

$$Q_{le} = Precip_{monthly} * 0.108 \quad (41)$$

Defining A and B as:

$$A = \frac{Cu_{in}}{\rho * z * k_d + \sigma * z} \quad (42)$$

$$B = \frac{Q_{le}}{\rho * z * k_d + \sigma * z} \quad (43)$$

Equation 39 can be rewritten as:

$$A = \frac{Cu_{ru}}{\rho * z * k_d + \sigma * z} + \ B * [Cu]_{tot,ss} + \ \frac{d}{dt}[Cu]_{tot,ss} \quad (44)$$

By combining the biotic ligand model (equ. 37) with the partitioning model (equ 33) and Freundlich equation (equ. 35) Cu_{ru} can be defined as a function of $[Cu]_{tot,ss}$ such that:

$$Cu_{ru} = \frac{z * n_{blm} * K_{Cu}^{A}}{\rho_{root} * (1 + K_{Mg}^{A}\{Mg^{2+}\})} * \left(\frac{k_d}{k_f} * [Cu]_{tot,ss}\right)^{\frac{1}{n}} \quad (45)$$

And we define a coefficient C as:

$$C = \frac{z * n_{blm} * K_{Cu}^{A}}{\rho_{root} * \left(1 + K_{Mg}^{A}\{Mg^{2+}\}\right) * (\rho * z * k_d + \sigma * z)} * \left(\frac{k_d}{k_f}\right)^{\frac{1}{n}} \quad (46)$$

Where ρ_{root} is the root density in soil $mg_{root} * kg^{-1}$. Combining equation 45 and 46 with equation 44, the change in Cu concentration can thus be defined as:

$$\frac{d}{dt}[Cu]_{tot,ss} = A - B * [Cu]_{tot,ss} - C * [Cu]_{tot,ss}^{\frac{1}{n}} \quad (47)$$

Modeling Soil Erosion

Soil erosion was modeled according the G2 erosion model governing equation (Karydas and Panagos, 2018):

$$E_m = R_m * V_m * S * T * L \quad (48)$$

Where E_m is the soil erosion loss in a month $(t * ha^{-1})$. R_m is the rainfall erosivity $(MJ * mm * ha^{-1} * h^{-1})$ calculated according to the following equation:

$$R_m = 524 + 222 * log_{10}\left(\frac{P}{t}\right) \quad (49)$$

Where P is equal to the rainfall in a given month (mm) and t is the rainfall duration during that month (h). The vegetation retention factor V_m and f_{cover} (Mougin et al., 2014) is calculated as:

$$V_m = e^{LU * f_{cover}} \quad (50)$$

$$f_{cover} = 1 - e^{0.475 * LAI} \quad (51)$$

The land use factor (LU) is assumed to be 7 for vineyards according to the Corine code (Karydas and Panagos, 2018). The remaining parameters S, T, L are imported through the soil atlases made available by the ESDAC.

Finally, in order to estimate the Cu lost to erosion the following equation is used:

$$Cu_{erosion} = E_m * ctCu_{tot} * \rho \quad (52)$$

Calculating Ecotoxicity

To calculate the ecotoxicity of each Cu outflow, characterization factors (CF) of Cu^{2+} emissions to air, water, and soil were used (Peña and Antón, 2016). The impact score $(IS; PAF * day * m^3 * ha^{-1})$ of each flow was calculated according to the following equation (Peña and Antón, 2016):

$$IS_i = m_i * CF_i \quad (53)$$

Where m_i is the mass of a Cu^{2+} in flow i $(kg * ha^{-1})$. The total impact score for a given vineyard is then given as:

$$IS_{tot} = \sum IS_i \quad (54)$$