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1 Copper Content and Export in European Vineyards  
2 Soils Influenced by Climate and Soil Properties

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16

17 ABSTRACT

18 Copper-based fungicides ( $\text{Cu}_f$ ) are used in European (EU) vineyards to prevent fungal  
19 diseases. Soil physicochemical properties govern locally the variation of total copper  
20 content ( $\text{Cu}_t$ ) in EU vineyards. However, variables controlling  $\text{Cu}_t$  distribution at larger  
21 scale are poorly known. Here machine learning techniques were used to identify  
22 governing variables and to predict the  $\text{Cu}_t$  distribution in EU vineyards. Precipitation,  
23 aridity and soil organic carbon are key variables explaining together 45% of  $\text{Cu}_t$   
24 distribution across EU vineyards. This underlines the effect of both climate and soil  
25 properties on  $\text{Cu}_t$  distribution. The average net export of Cu at the EU scale is 0.29 kg  
26  $\text{Cu ha}^{-1}$  which is two orders of magnitude less than the net accumulation of Cu (24.8 kg  
27  $\text{Cu ha}^{-1}$ ). Four scenarios of  $\text{Cu}_f$  application were compared. The current EU regulation  
28 with a maximum of 4 kg  $\text{Cu ha}^{-1} \text{ year}^{-1}$  may increase by 2% the EU vineyard area  
29 exceeding the predicted no-effect concentration (PNEC) in soil in the next 100 years.  
30 Overall, our results highlight vineyard areas requiring specific remediation measures  
31 and strategies of  $\text{Cu}_f$  use to manage a trade-off between pest control and soil and water  
32 contamination.

## 33 INTRODUCTION

34 Copper-based fungicides ( $\text{Cu}_f$ ) are intensively used in European vineyards since the  
35 end of the 19<sup>th</sup> century to prevent fungal disease such as 'Downy Mildew'.<sup>1</sup>  $\text{Cu}_f$   
36 application doses and timing vary across regions depending on practices, regulation,  
37 hydro-climatic conditions and vine variety. The European Union (EU 2018/1981)  
38 regulation recently decreased from 6 to 4 kg Cu ha<sup>-1</sup> year<sup>-1</sup> the maximal dose allowed.<sup>2</sup>  
39 However, doses as high as 50 kg Cu ha<sup>-1</sup> year<sup>-1</sup> were applied frequently for decades in  
40 the mid-20<sup>th</sup> century.<sup>3</sup> Today, the total copper content in topsoil ( $\text{Cu}_t$ ) exceeds 100 mg  
41 Cu kg<sup>-1</sup> in 15% of the European vineyard area. This corresponds to the average  
42 proposed threshold values for which soil remediation is needed.<sup>4-6</sup> European vineyards  
43 represent more than 50% of the total vineyard surface worldwide.<sup>7</sup> Although vine  
44 growing accounts for only 3.3% of the agricultural area in Europe, it uses 86% of total  
45 fungicides consumed in Europe.<sup>8</sup> Hence, vineyard soil is often more contaminated by  
46  $\text{Cu}_f$  than soils of any other agricultural soils.  $\text{Cu}_f$  accumulates in soil and can impact soil  
47 organisms and plants,<sup>9</sup> thereby reducing soil fertility<sup>10</sup> and productivity.<sup>11</sup> In contrast,  
48 leaching<sup>12</sup> and surface runoff<sup>13,14</sup> export  $\text{Cu}_f$  from vineyard soil, which can contaminate  
49 aquatic ecosystems<sup>15</sup> and drinking water resources.<sup>16</sup>

50  $\text{Cu}_f$  mobility in topsoil controls  $\text{Cu}_t$  accumulation and off-site export. Cu mobility in soil  
51 is mainly controlled by (i) sorption on organic matter,<sup>17</sup> and to a lesser extent on clay  
52 and Fe-, Mn-(hydr)oxide and carbonate,<sup>18</sup> (ii) pH-redox dependency since alkaline soil  
53 increase the proportion of available binding sites on organic matter.<sup>17,19</sup> Cu sorbed on  
54 fine particle matter may result in Cu export in runoff.<sup>13,14</sup> Hydro-climatic and field  
55 conditions indirectly control Cu export by (i) affecting soil properties,<sup>20</sup> (ii) mediating

56 dissolved and particulate  $Cu_f$  transport, and (iii) modifying preferential transport.<sup>21</sup>  
57 Accordingly, presumed or established processes governing  $Cu_t$  mobility in vineyard soil  
58 may co-occur and/or may be interrelated (Table 1). Variables governing  $Cu_t$  and  
59 dynamics in vineyard soil are, however, examined in laboratory and field studies  
60 separately. As a result, the understanding of variables governing  $Cu_t$  in soil remains  
61 study- or site-specific. The identification of variables governing  $Cu_t$  in vineyard soil and  
62 leading to Cu accumulation and/or off-site export over time is necessary to evaluate the  
63 current and future distribution of  $Cu_t$  at the European scale.

64 In this context, a major issue is to predict the spatial variation of  $Cu_t$  in the European  
65 vineyards, to quantify Cu accumulation and export and to identify priority areas requiring  
66 soil remediation. The purpose of this study was (i) to identify key variables potentially  
67 governing  $Cu_t$  in vineyard topsoil (0 – 30 cm), (ii) to predict average  $Cu_t$  at European  
68 vineyards scale using machine learning technics, and (iii) to estimate  $Cu_t$  accumulation,  
69 export and associated toxicity for terrestrial trophic levels, for historical, current and  
70 future scenarios of  $Cu_f$  application (i.e, 0, 2, 4 or 8 kg Cu ha<sup>-1</sup> y<sup>-1</sup>).

71

## 72 MATERIALS AND METHODS

### 73 **Topsoil total Copper Datasets.**

74  $Cu_t$  datasets ( $Cu_{t, \text{dat}}$ ; i.e., soils within 0–30 cm) were obtained from several soil  
75 surveys across European vineyards (–9.4° to 42° E; 35° to 53° N; SI, Figure S1)  
76 delineated by the Corine Land Cover (CLC 2012; v18.5.1; <http://land.copernicus.eu>). In  
77 total, 1,202  $Cu_{t, \text{dat}}$  measurements (average: 27.8 mg Cu kg<sup>-1</sup>; min–max: 0.54–774 mg  
78 Cu kg<sup>-1</sup>) were sampled between 1992 and 2016 (median = 2008, standard deviation

79 (SD) = 5) and used in our study. Summary of the studied  $Cu_{t, \text{dat}}$  are provided in Table  
80 S1 of the Supporting Information (SI). Although the Cu quantification methods differ  
81 among datasets, inter-comparability between datasets has been demonstrated  
82 previously for the methods used in our study.<sup>22</sup> The impact of topsoil sampling depth  
83 (first 20 or 30 cm) and sampling time span on the average prediction of  $Cu_t$  ( $Cu_{\text{pred}}$ ) at  
84 the European scale remains low (SI, section Influence of heterogeneous sampling  
85 depths and time on the Cu prediction). The heterogeneity of topsoil sampling depth and  
86 time span did not significantly (within  $2\sigma$ ) impact the average predictions of  $Cu_t$  at the  
87 European scale.

88

#### 89 **Predictive Variables.**

90 Soil properties, topology, climate and land cover were selected and evaluated as  
91 hypothetical predictive variables of  $Cu_t$  (Table 1 & SI, Table S2). Geogenic, i.e., from bed  
92 rocks,<sup>23</sup> and atmospheric non-agricultural anthropogenic inputs of Cu, i.e., mining,  
93 smelter, sewage sludge and vehicle brake pads are sources of Cu contributing from 5 to  
94  $100 \text{ g Cu ha}^{-1} \text{ year}^{-1}$  whereas about  $8 \text{ kg Cu ha}^{-1} \text{ years}^{-1}$  of  $Cu_f$  are applied on  
95 vineyards.<sup>24</sup> Topsoils surrounding Cu mining or smelter, that may reach up to  $6 \text{ g Cu kg}^{-1}$   
96 <sup>1, 25, 26</sup> were not identified close to vineyard areas. Consequently, geogenic and industrial  
97 sources of Cu were not considered in this study.

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100

101

102 **Table 1.** Hypothetic Predictive Variables Governing the Total Copper Content in  
 103 Vineyard Topsoil ( $Cu_t$ ) Leading to  $Cu_t$  Accumulation and/or off-site Export.

Variables <sup>a</sup>	Processes
<b>Soil properties</b>	
Soil physicochemical properties affect $Cu_t$ mobility	$Cu_t$ correlates positively to soil organic matter since Cu preferentially sorbs to organic matter in soil, <sup>13,17</sup> which affects $Cu_t$ mobility. Higher pH increases sorption sites (e.g. negative charge) for $Cu_t$ on clay, organic matter and sand containing carbonate, <sup>19</sup> and reduces $Cu_t$ leaching. <sup>12</sup>
Soil moisture influences soil biogeochemistry	Soil moisture directly affects microbial respiration and activities in soil resulting in biogeochemical gradients. <sup>27,28</sup> Cu occurs as Cu(II) in oxic soils. In contrast, Cu(II) may potentially precipitate to less mobile Cu(I) forms in anoxic soils. <sup>17,29</sup>
<b>Topography/climate</b>	
Topography and climate conditions drive soil erosion	Greater rainfall depth and higher slope length enhance soil erosion by runoff. <sup>21</sup> $Cu_t$ is mostly bound to suspended particles matter (SPM) in topsoil (~85% <sup>13, 14</sup> ) where SPM-bound Cu can account for 84.4% of the total $Cu_t$ exported by runoff. <sup>14</sup>
Hydro-climatic conditions influence Cu application doses	Intense rainfalls during warm conditions favor the development of 'Downy Mildew'. This increases the frequency and amount of $Cu_t$ use in some areas to control it. <sup>30,31</sup>
Hydro-climatic conditions influence (i) soil chemistry	Arid environments (with higher Al values), characterized by higher soil pH and oxidizing soils, <sup>20</sup> favor $Cu_t$ accumulation (see soil physicochemical properties above). In contrast, arid soils tend to lose more soil organic matter and associated $Cu_t$ since Cu is preferentially associated to soil organic matter. <sup>13,17</sup>
(ii) Vegetation growth	Optimal conditions for vegetation growth depend on temperature, soil moisture and solar radiation, and vary across plant growth stages. <sup>32</sup> Vegetation growth controls $Cu_t$ mobility indirectly by limiting erosion via surface runoff and thus can be related to $Cu_t$ .

(iii) Plant uptake Cu uptake from soil by plants remains limited: 0.1–7.2% by wild<sup>33</sup> and 0.1–3.8% by the vineyard<sup>34</sup> plants of the Cu<sub>t</sub>. Hence, plants only marginally decrease Cu<sub>t</sub> in soil.

#### Plant cover

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Plant cover affects surface runoff and organic matter content in topsoil

Plant cover, i.e., vine and grass in vineyards, can stabilize the vineyard soil and thus limit erosion via surface runoff.<sup>35</sup> In addition, plant decomposition can slightly increase organic matter content in topsoil,<sup>36</sup> thereby reducing Cu mobility.

104 <sup>a</sup> Hypothetic predictive variables governing Cu<sub>t</sub> in vineyard soil. Variables associated  
105 with each process are provided in the SI, Table S2. Processes were identified based on  
106 experimental studies in vineyard or related soil.

107

108 Predictive variables were computed or directly obtained on a grid cell of 250x250 m  
109 for the study area. Details concerning building spatial variables are provided in the in SI,  
110 Table S2 & S3. Cu<sub>t, dat</sub> coordinates were used to extract values of each predictive  
111 variable in the corresponding grid cells. Extracted data were then used to select  
112 variables and calibrate the model (details in SI). Extracted data represented adequately  
113 the range of predictive variables within the prediction domain (details given in SI; paired  
114 t-test; p-value<sub>average</sub> >0.01) and did not display any spatial correlation (Moran's test;  
115 I<sub>average</sub> = -0.211 ± 0.09; p-value >0.01). The selection of variables was carried out from  
116 the 24 original predictive variables (SI, Table S2) to limit collinearity between predictive  
117 variables and optimize model predictions as described elsewhere.<sup>37</sup> (i) Pearson  
118 correlation was used to discard variables providing the similar information and (ii)  
119 principal component analysis (PCA) was used to discard noise variables containing the  
120 least information.<sup>38</sup>

121

122

### 123 **Prediction of Total Copper Content in European Vineyard Topsoil.**

124 The variable selection procedure highlight that the following variables were predictive  
125 of the average  $Cu_t$  in European vineyards: clay and silt fractions (%), soil organic carbon  
126 content ( $C_{org}$ ; %), soil pH (unitless), aridity index (AI; unitless), annual average  
127 temperature ( $T_{av}$ ; °C), annual rainfall (rainfall; mm), soil moisture content (moisture; %),  
128 the enhanced vegetation index (EVI; unitless) and slope (degree; SI, Table S3). This  
129 selection is consistent with predictive variables reported previously (Table 1). Three  
130 independent machine learning techniques, i.e., neural networks (R package nnet v 7.3-  
131 12), random forest (R package randomForest v.4.6-12) and bagging tree (R package  
132 ipred v.0.9-5), were used in parallel and were averaged into an ensemble model (ENS;  
133 details in SI) for the final prediction, as described elsewhere.<sup>39</sup> The ENS resulted in  
134 fewer false predictions and higher predictive accuracy than a single model. Consistency  
135 of  $Cu_{pred}$  was evaluated for each grid cell on a SD of 1,000 predictions for each machine  
136 learning technique. Model performance was evaluated using a 10-fold cross-validation  
137 (CV). Model spatial transferability was evaluated using a spatially constrained 10-fold  
138 CV (details in SI). For each model, the averaged relative importance (ARI) of each  
139 variable in the model was calculated with an input permutation technique and one-  
140 factor-at-a-time (OFAT) sensitivity analysis (details in SI). The complete modelling  
141 framework to select variables, calibrate the model and predict  $Cu_t$  is available for  
142 download at [https://github.com/Boris-Droz/ML\\_soil\\_predi\\_conc](https://github.com/Boris-Droz/ML_soil_predi_conc).

143

144

145

## 146 **Copper Accumulation and Export.**

147  $Cu_t$  net mass accumulation since the beginning of the  $Cu_f$  application was estimated  
148 assuming that  $Cu_t$  is distributed similarly across a homogenous topsoil layer, following  
149 eq. 1,

$$150 \text{ net acc.} = (Cu_{Pred} - Cu_{bgd}) \times BD \times h_{topsoil} \quad (1)$$

151 where *net acc.* stands for the  $Cu_t$  net mass accumulation ( $\text{kg Cu ha}^{-1}$ ),  $Cu_{bgd}$  the  
152 background of geogenic and atmospheric non-agricultural anthropogenic  $Cu_t$  ( $\text{mg Cu}$   
153  $\text{kg}^{-1}$ ; SI, Figure S2),  $BD$  is the soil bulk density (<https://soilgrids.org/>, series M\_sl1,  
154 v18.4.2017; in  $\text{kg m}^{-3}$ )<sup>40</sup> and the average topsoil thickness where Cu mainly  
155 accumulates ( $h_{topsoil} = 30 \text{ cm}$ ; SI, Table S1). The net mass export of  $Cu_t$  (*net exp.*;  $\text{kg of}$   
156  $\text{Cu ha}^{-1}$ ) was assumed to be the sum of  $Cu_t$  exported from topsoil via runoff and  
157 leaching, and was calculated yearly following eq. 2,<sup>13, 14</sup>

$$158 \text{ net exp.} = (\dot{q}_{RUSLE} + f_{sol} \times BD \times h_{topsoil}) \times Cu_{Pred} \quad (2)$$

159 where  $\dot{q}_{RUSLE}$  is the soil loss rate ( $\text{kg ha}^{-1}$ ) as defined elsewhere<sup>21</sup> and  $f_{sol}$  the soluble  
160 fraction of  $Cu_{Pred}$  estimated from soil properties (both details in SI).

161

## 162 **Scenarios of Copper-Based Fungicides Application Doses.**

163 Four scenarios of  $Cu_f$  application doses were compared: (i) an historical scenario with  
164  $8 \text{ kg Cu ha}^{-1} \text{ year}^{-1}$  inferred from sold  $Cu_f$  amount before the 2002 European  
165 regulation,<sup>2</sup> and/or speculated illegal usage in some areas,<sup>41</sup> (ii) current regulation  
166 scenarios, with either (iii) 2 or (iii) 4  $\text{kg Cu ha}^{-1} \text{ year}^{-1}$  as average and maximum doses,

167 respectively,<sup>2, 42</sup> and (iv) a scenario of Cu<sub>f</sub> substitution, i.e., no Cu<sub>f</sub> application or 0 kg Cu  
168 ha<sup>-1</sup> year<sup>-1</sup>.

169 For the scenario with 8 kg Cu ha<sup>-1</sup> year<sup>-1</sup> and current regulation scenarios, a stepwise  
170 mass balance calculation based on a year t was established (eq. 3 and detail in SI)  
171 assuming no temporal variation of the topsoil volume and a homogeneous topsoil layer  
172 (0–30 cm),

$$173 \quad Cu_{pred,t+1} = Cu_{pred,t} + (APP_{Cu,f} - Cu_{pred,t} \times net\ exp. - Cu_{input} \times f_{sol}) / (BD \times h_{topsoil}) \quad (3)$$

174 where  $Cu_{pred}$  is the average predictions of Cu<sub>t</sub> (mg Cu kg<sup>-1</sup>),  $APP_{Cu,f}$  the yearly  
175 application dose of Cu<sub>f</sub> (kg Cu ha<sup>-1</sup> year<sup>-1</sup>) and  $f_{sol}$  the soluble fraction as calculated in  
176 eq S3–6. The *net exp.* was previously calculated in eq. 2.  $Cu_{pred,t+1}$  accounted for the  
177 yearly Cu application dose to which the soluble fraction of Cu<sub>f</sub> ( $f_{sol}$ ) and the *net exp.*  
178 were deducted. For each, pixel, the scenario was applied until  $Cu_{pred}$  at year  $t + 1$   
179 reaches for the given pixel the predicted no-effect concentration (PNEC; SI, building  
180 spatial variables). In contrast, the time required to export the accumulated Cu<sub>f</sub> via runoff  
181 and associated suspended solids and reach back  $Cu_{bgd}$ , i.e., assuming the existence of  
182 alternatives to Cu<sub>f</sub>, was estimated by dividing eq. 1 by eq. 2.

183 The uncertainty associated with each scenario was estimated by numerical  
184 propagation of uncertainties across the entire modelling framework. Briefly, each  
185 variable was associated with lower and an upper uncertainty limits accounting for the  
186 analytical or monitoring uncertainty or calculation steps, depending on the variable (SI,  
187 Table S4). All combinations of lower and upper uncertainty limits for the selected  
188 variables were then included to propagate uncertainties and estimate the lower and  
189 upper uncertainty limits associated to each scenario for each pixel independently.

190

191

## 192 RESULTS AND DISCUSSION

### 193 **Prediction of Total Copper in Topsoil.**

194 Ten variables governing  $Cu_t$  in vineyard topsoil were considered (see above Materials  
195 and Methods and SI, Figure S4. b). Using these climate and soil variables, the ENS  
196 accurately predicted  $Cu_t$  (slope of 1.13, intercept of 0.01; SI, Figure S4. a), and  
197 predictions were fairly precise (averaged  $R^2 = 0.61$ ). Comparison between ENS and CV  
198 (averaged  $R^2$ -CV =  $0.58 \pm 0.06$ ) indicates no over-fitting of the ENS. For the three  
199 machine learning technics,  $Cu_{pred}$  fit  $Cu_{t, dat}$  ( $SD\ Cu_{pred}/Cu_{t, dat} \times 100 = 13 \pm 2\%$ ),  
200 indicating a good overall agreement of predictions between the three technics. Average  
201 uncertainty of the  $Cu_{pred}$  falls within  $\pm 11\text{ mg Cu kg}^{-1}$  for 75% of the data (RMSE of  $0.63$   
202  $\pm 0.06$ ). The scattering observed in the predictions (SI, Figure S4) mainly concerns data  
203 above  $130\text{ mg Cu kg}^{-1}$ , corresponding to 6.3% of the dataset only. ENS predictions  
204 failed to reproduce observed  $Cu_t$  in the corresponding vineyard areas, which potentially  
205 received larger historical  $Cu_f$  applications than other areas under similar climatic and  
206 soil conditions. Additional model performances and limits are provided in SI.

207

### 208 **Climate Variables rather than Soil Variables Determine Total Copper in Topsoil.**

209 Climate variables (i.e., rainfall and aridity index) mainly determined  $Cu_{pred}$  at the  
210 European scale, possibly by controlling physicochemical processes, including Cu  
211 leaching and the redox state of soil. Hydro-climatic conditions likely determined regional  
212 Cu application practices as 'Downy Mildew's' pressure increases in more humid and

213 warmer areas in early summer.<sup>30,31</sup> In contrast, soil physicochemical properties (i.e., pH)  
214 predominantly governed  $Cu_t$  on the local scale and under homogeneous climatic  
215 conditions. The averaged relative importance (ARI) from the ENS and the sensitivity  
216 analyses confirmed the relationship between climate variables and  $Cu_{pred}$ .  $Cu_{pred}$   
217 correlated positively with both the annual rainfall (rain;  $R^2 = 0.71$ ) and the aridity index  
218 (AI; potential evapotranspiration divided by rainfall;  $R^2 = 0.79$ ), while the combined  
219 effect of rainfall and AI accounted for 32.6% of the  $Cu_{pred}$  ARI (rainfall =  $17.4 \pm 0.9\%$ , AI  
220 =  $15.2 \pm 1.3\%$ ; SI, Figure S4. b).

221 Although rainfall was negatively correlated with AI, both variables were positively  
222 correlated to  $Cu_{pred}$ , suggesting that two different mechanisms control  $Cu_t$  in vineyard  
223 soil. First, rainfall could increase temporally soil water content and reduce oxygen  
224 diffusion in water, leading to reducing soil conditions.<sup>43</sup> Under anoxic conditions,  
225 biological activity may decrease Cu mobility by precipitating soluble Cu(II) to Cu(I),<sup>44,45</sup>  
226 which is strongly complexed and stabilized with reduced organic sulfur.<sup>46</sup> Additionally,  
227 depending on the solutes present in soil, e.g., carbonate, sulphide, biotic and abiotic  
228 processes may form minerals and further reduce the  $Cu_t$  mobility.<sup>33, 47, 48</sup>

229 In contrast, higher AI leads to drier soil,<sup>49</sup> which facilitates the formation of soil  
230 macropores favoring oxygen transfer.<sup>50</sup> As a result, Cu(I) may partly re-oxidize into  
231 mobile Cu(II) in oxic soil. However, an opposite trend is observed as AI may indirectly  
232 increase the Cu-binding affinity of soil organic matter (ARI of  $13.1 \pm 0.1\%$ ). Indeed, the  
233 oxidation of organic matter under oxic conditions increases the contribution of carboxylic  
234 and hydroxylic groups as preferential binding partners for Cu in organic matter.<sup>51</sup> In

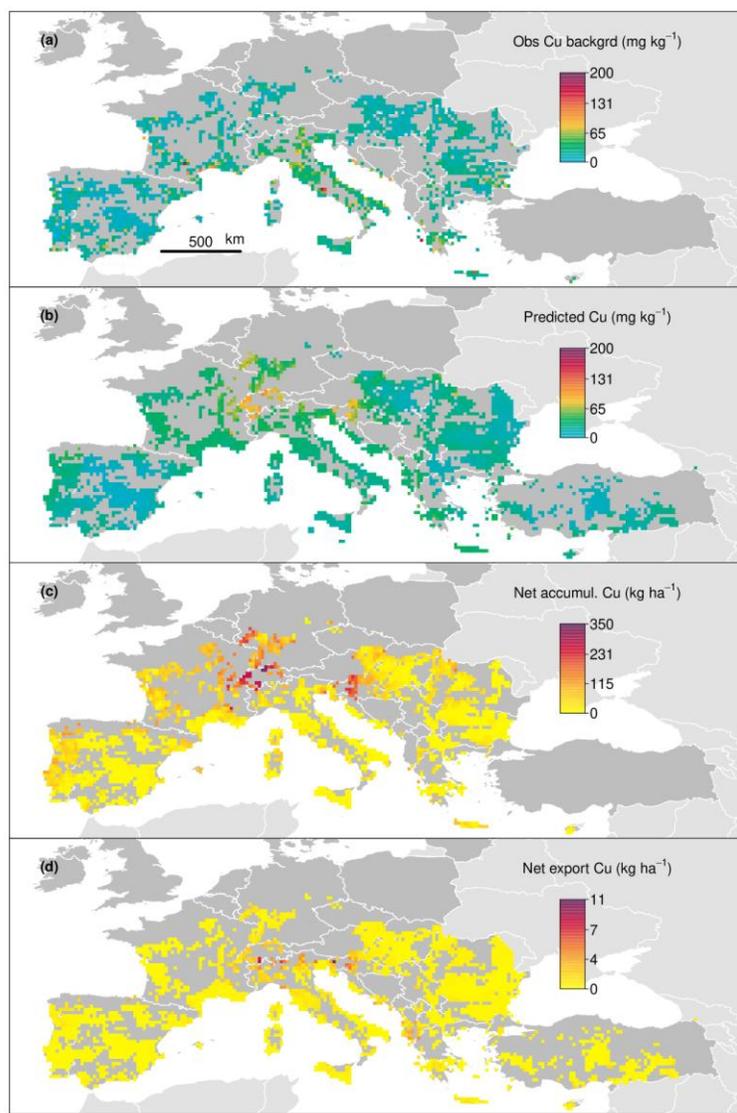
235 addition, pH (ARI of  $7.5 \pm 1.3\%$ ) directly controls the deprotonation of sorption sites on  
236 soil constituent. Hence, higher pH increases available sorption sites for Cu binding.<sup>19</sup>

237

### 238 **Distribution of the Total Copper in Topsoil Across European Vineyards.**

239  $Cu_{pred}$  in European vineyards were successfully made as the datasets covered the  
240 range of predictive variables within the domain of prediction. The ENS also displays  
241 good model transferability in space evaluated on four equivalent geographical sub-  
242 domains (average  $R^2 = 0.84 \pm 0.07$ , details in SI). This suggests a homogenous  
243 influence of predictive variables within the European vineyards. Overall,  $Cu_{pred}$  for  
244 vineyards is  $25.4 \text{ mg Cu kg}^{-1}$  which is 30.5% higher than  $Cu_{bgd}$  including geogenic and  
245 atmospheric non-agricultural anthropogenic Cu (Figure 1. a–b).

246



247  
 248 **Figure 1.** Distribution of the total copper content in vineyard topsoil ( $Cu_t$ ), accumulation  
 249 and net export of Cu in European Vineyards. (a) Observed background  $Cu_t$ . (b)  
 250 Predicted  $Cu_t$  ( $Cu_{pred}$ ). (c) Estimated net accumulation of  $Cu_t$ . (d) Estimated net export of  
 251  $Cu_t$ . Dark grey: Area of the European Corine Land Cover (CLC). Pixels depict average  
 252 predictive values at a spatial resolution of  $20\text{ km}^2$ . Net accumulation was not computed  
 253 for Turkey due to absence of background data. Overall,  $Cu_{pred}$  were higher for vineyards

254 in the alpine regions (Figure 1. b; average = 57 mg Cu kg<sup>-1</sup>) than in other European  
255 biogeographic regions (SI, Table S5).

256

257 The threshold of contamination (>100 mg Cu kg<sup>-1</sup>)<sup>5</sup> was reached for 2% of Cu<sub>pred</sub>  
258 within the prediction domain. Contaminated areas were mainly located in central  
259 Western Europe, i.e., northern Italy, eastern France, Switzerland and Slovenia. In those  
260 regions, C<sub>org</sub> is medium (up to 14%) while Cu<sub>pred</sub> >100 mg Cu kg<sup>-1</sup> accounted for 70% of  
261 vineyard soil.<sup>52</sup> Data points above the contamination threshold in those regions are  
262 characterized by high AI, soil moisture and annual rainfall, although only C<sub>org</sub> was  
263 significantly higher (>9.0%) than in other regions of southern Europe (t-test; p-value  
264 <0.01). This suggests that higher annual rainfall correlates with higher temperature in  
265 central Western Europe. This may favor 'Downy Mildew' emergence and concomitant  
266 use of higher doses and more frequent applications of Cu<sub>f</sub>. In central Western Europe,  
267 soil with higher C<sub>org</sub> may influence the Cu<sub>pred</sub> predominantly and locally, although C<sub>org</sub>  
268 accounted in total for 13.1% ARI of the Cu<sub>pred</sub>.

269

### 270 **Accumulation and Export of Copper in Topsoil.**

271 The estimated average net accumulation and net export of Cu in topsoil in European  
272 vineyards are 24.8 (SD = 42.7) and 0.29 kg Cu ha<sup>-1</sup> (SD = 0.64), respectively (Figure 1  
273 c–d). This corresponds to 112,400 tons of Cu accumulated over time, and a yearly Cu  
274 export from vineyards of 1,466 tons across Europe. The distribution of Cu net export  
275 fitted with that of Cu<sub>pred</sub> (R<sup>2</sup> = 0.65). On average, predicted loss rate of vineyard soil  
276 (9.47 tons ha<sup>-1</sup> year<sup>-1</sup>) is 3.5 times greater than any other European arable land due to

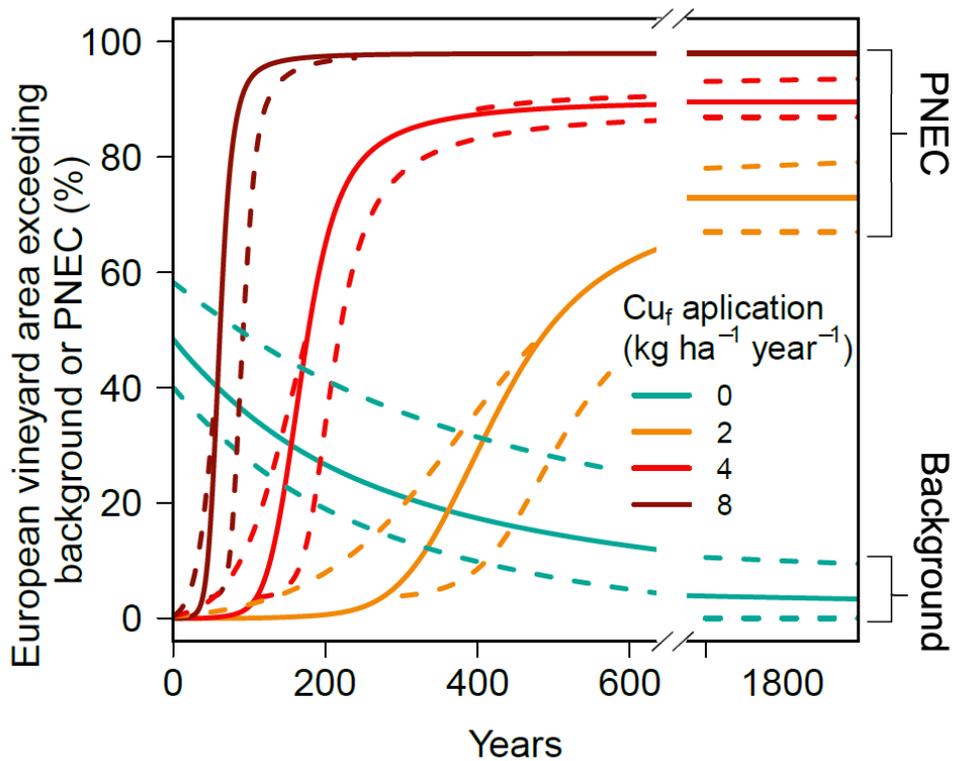
277 low vegetation and sloping area in vineyards. Consequently, net Cu export is  
278 particularly large in the Southern Alps due to intense soil erosion. Large soil loss is  
279 associated to higher slope ( $>25^\circ$ ) and greater rainfall amounts ( $>1,600 \text{ mm year}^{-1}$ ) in  
280 the Southern Alps than in other vineyard areas.<sup>21</sup>

281

### 282 **Potential Future Copper Accumulation in European Vineyards.**

283 Overall, the proportion of European vineyard area exceeding PNEC values (i.e.,  
284 ranged from 30 to 290 mg Cu kg<sup>-1</sup> according to soil properties calculate elsewhere,<sup>53, 54</sup>  
285 details in SI) may largely vary in the future depending on the application dose of Cu<sub>f</sub>  
286 (Figure 2). Cu accumulation due to Cu<sub>f</sub> application doses of 2, 4 and 8 kg Cu ha<sup>-1</sup> year<sup>-1</sup>  
287 may be balanced with Cu export after 1,200, 750 and 150 years, with 75, 89, 97% of  
288 European vineyards areas exceeding PNEC values, respectively. Assuming constant  
289 soil properties, we speculate that the current European regulation with a maximum  
290 application of 4 kg Cu ha<sup>-1</sup> year<sup>-1</sup> will increase by only 2% the proportion of vineyard  
291 areas exceeding PNEC in the next 100 years.

292 In contrast, 94% of vineyard areas may exceed PNEC in the historical application  
293 scenario of 8 kg Cu ha<sup>-1</sup> year<sup>-1</sup>. With an application of 2 kg Cu ha<sup>-1</sup> year<sup>-1</sup>, vineyards  
294 areas exceeding PNEC values may increase by less than 0.5% for the next 100 years.  
295 In contrast, a substitution of Cu<sub>f</sub> (0 kg Cu ha<sup>-1</sup> year<sup>-1</sup>) may decrease the proportion of  
296 vineyard areas exceeding the background Cu<sub>bgd</sub> from 48 to 38% after 100 years. Such  
297 long-term indicative estimation for different Cu application dose provides critical  
298 temporal trend to support the reduction of Cu application in vineyard.



299

300 **Figure 2.** Proportion of European vineyards area exceeding predicted no-effect  
 301 concentration (PNEC) values of total Cu in topsoil (scenarios with  $Cu_f$  application dose  
 302 of 2, 4, 8  $kg\ ha^{-1}\ year^{-1}$ ) or equal to or lower than the background (bgd) Cu content  
 303 (scenario with no  $Cu_f$  application). Predictions account for the balance between yearly  
 304  $Cu_f$  application at a given application dose and Cu export over time. Dashed lines  
 305 indicate the upper and lower uncertainties of predictions.

306

307 Our back-envelope is a first attempt to evaluate Cu accumulation and export at the  
 308 European scale and the proposed mass balance approach may lead to inaccurate  
 309 estimations of  $Cu_t$  export. For instance, freshly applied  $Cu_f$  is a soluble Cu pool that can  
 310 be directly exchanged with the labile cation present in vineyard soil following  $Cu_f$

311 application. Depending on the time following  $Cu_f$  application,  $Cu_f$  may be partly mobilized  
312 during rainfall-runoff events<sup>14</sup> and thus bias estimations of  $Cu_t$  in soil. Since rainfall  
313 erosivity is predicted to increase by 18% in Europe over time,  $Cu_f$  export may also  
314 increase.<sup>55</sup> In addition, estimations using the semi empirical model account for Cu aging  
315 in contaminated soil and rely on realistic desorption experiments, which may  
316 underestimate  $Cu_f$  export.<sup>12</sup> However,  $Cu_f$  accumulation over time may be also  
317 underestimated. Climate change models predict an average of 10% increase of soil  
318 organic matter content by 2100 in regions of European vineyards,<sup>56</sup> which may in turn  
319 reduce  $Cu_t$  mobility and increase the amount of Cu accumulated in the vineyard soil.

320

### 321 **Implications for Winegrowing Practices.**

322 Cu is an element that cannot be degraded in soil and soil remediation processes,  
323 such as phyto-extraction<sup>57</sup> or enhanced mobilization by plants,<sup>58</sup> have limited  
324 efficiencies. The most efficient strategies to limit the increase of  $Cu_t$  is thus to reduce  
325 application doses of  $Cu_f$ . Reducing strategies consist in applying  $Cu_f$  during long humid  
326 periods only<sup>42</sup> and in reducing preventively the use of  $Cu_f$ . Forecast models of  
327 grapevine 'Downy Mildew'<sup>59</sup> relying on climate variables can help to improve the  
328 efficiency of  $Cu_f$  reduction strategies. Alternatives to  $Cu_f$  include replacing current grape  
329 varieties with new grape varieties with a higher resistance to fungus pests,<sup>60</sup> using  
330 microorganisms for biocontrol,<sup>61</sup> introducing plant defense stimulators<sup>62</sup> and/or applying  
331 plant extracts to substitute  $Cu_f$ .<sup>63</sup> Alternative scenarios without  $Cu_f$  are still debated, but  
332 are currently used in some Biodynamic approaches accounting for only ca. 1% of  
333 vineyards worldwide (<http://www.demeter.net>). Additional benefits of biodynamic wine

334 growing include the higher soil biodiversity and microbiological activity<sup>10</sup> and potentially  
335 greater resilience to climatic and pathogenic threats in vineyards<sup>64</sup> as opposed to most  
336 conventional wine growing.<sup>65</sup>

337 Cu export is mainly driven by soil erosion with concomitant loss of solid-bound Cu,  
338 which should be prevented and lessened in regions prone to soil loss to reduce  
339 contamination of connected aquatic ecosystems. In fact, 10% of the vineyards are  
340 located close to a river (<500 m)<sup>66</sup> and the associated catchment may act as a point  
341 source of contamination. The transport of solid-bound Cu into aquatic ecosystems may  
342 also affect the downstream areas due to the progressive release of toxic Cu(II) resulting  
343 from a change in pH and/or redox conditions. Anti-erosion soil management strategies  
344 should thus be prioritized and designed to retain Cu on the vineyard plots. In particular,  
345 traditional soil management strategies, including grass or mulch cover, reduced tillage,  
346 contour planting and terraced vineyards are most effective in limiting soil erosion and  
347 associated Cu runoff.<sup>35</sup> Complementarily, stormwater wetlands may be deployed at the  
348 outlet of vineyard catchments. Stormwater wetlands have the potential to retain >68% of  
349 the dissolved Cu and >92% of the solid-bound Cu, the principal contributions to Cu  
350 export in runoff.<sup>14</sup>

351

## 352 ASSOCIATED CONTENT

### 353 Supporting Information

354 The Supporting Information is available free of charge on the ACS Publications  
355 website at DOI: XXX/XXXXX.

356 Texts, tables, and figures provide detailed methods (total copper in the topsoil dataset,  
357 spatial variable building, data pre-processing, variable selection, machine learning  
358 building, performance and evaluation, scenario of copper-based fungicide application)  
359 and supporting results and discussion (model performance, regional prediction, limit of  
360 the approach).

361  
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374

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376 B.D., S.P. and G.I. designed research, B.D. performed research; S.P., J.A., R.M., G.T.,

377 P.P., L. M. and P.B. contributed to the acquisition of data/soil samples; B.D. and S.P.

378 analyzed data; and B.D., S.P. and G.I. wrote the manuscript with critical review from all  
379 authors. The authors declare no conflict of interest.

380

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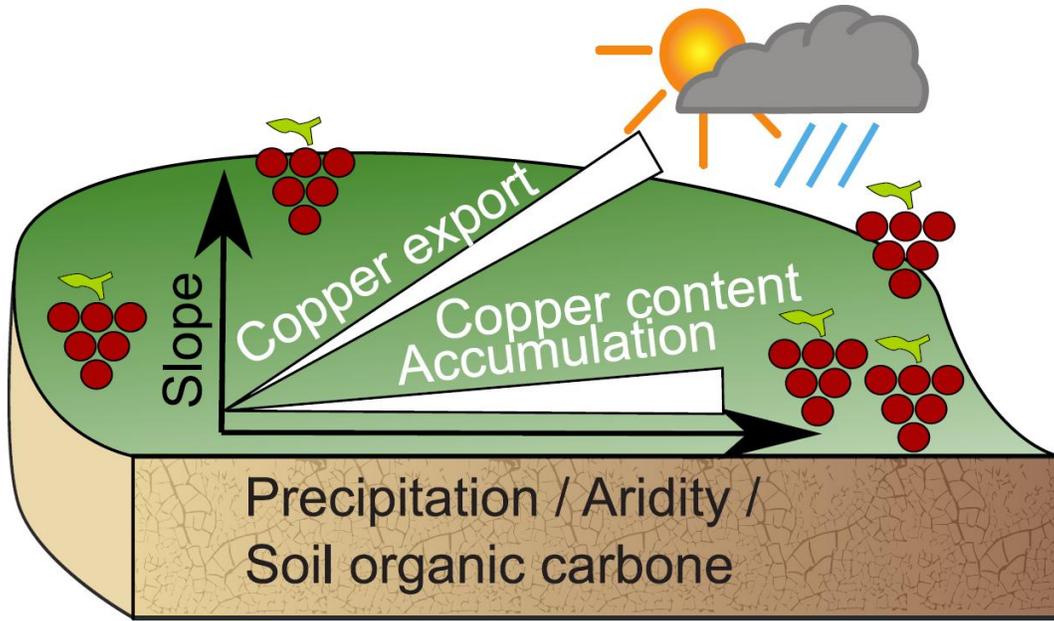
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