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Soil management drives copper and zinc export in runoff from vineyard plots

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1 **Soil management drives copper and zinc export in runoff**
2 **from vineyard plots**

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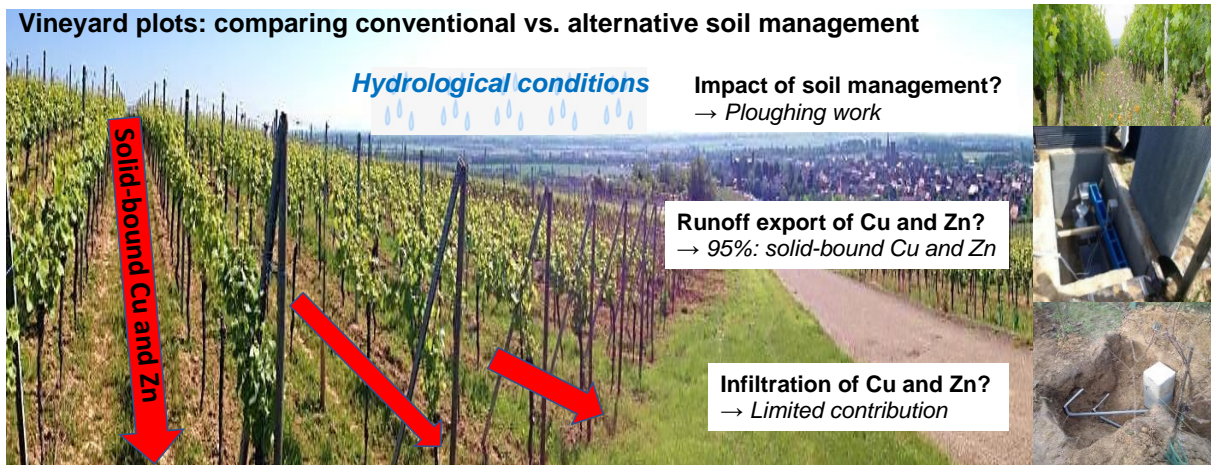
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13 **Acknowledgments**

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24 Manuscript for Water, Air, & Soil Pollution

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26 **Graphical abstract**



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29 **Highlights**

- 30 • Zn and Cu exports from vineyard plots under conventional and alternative management
- 31 practices
- 32 • Surface runoff drove Cu and Zn exports since vertical flows were limited
- 33 • Runoff export amounts of Cu and Zn from the topsoil stock ranged from 0.001 to 0.071%
- 34 • Solid-bound exports of Cu and Zn accounted for more than 95% of the total export
- 35 amount
- 36 • Ploughing followed by a storm led to extensive Cu and Zn exports

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43 **Abstract**

44 Copper (Cu)- and zinc (Zn)-based formulations are used globally in vineyards for
45 fungicide protection. Both soil management and rainfall characteristics control the exports of
46 Cu and Zn in runoff from vineyard plots. However, quantitative field studies investigating the
47 influence of soil management on the dissolved and solid-bound exports of Cu and Zn are
48 mostly lacking. Runoff exports of Zn and Cu from northern vineyard plots (Rouffach, Alsace)
49 under conventional (chemical) and alternative (mechanical) soil management practices were
50 compared during two vine-growing seasons. Our results emphasize that mechanical soil
51 management before intense or long rainfall-runoff events favoured Cu and Zn seasonal mass
52 export. Overall, Cu and Zn runoff from the alternative management plot was lower than that
53 in the conventional management plot since grass cover reduced the runoff coefficients. The
54 seasonal Cu and Zn exports during runoff were related to the historical stocks in the topsoil
55 and ranged from 0.001 to 0.071% in the alternative management plot. However, ploughing on
56 the alternative plot followed by a single intense storm event led to extensive Cu and Zn
57 exports, accounting for more than 95% of the total amount exported during the season. In both
58 plots, Cu and Zn were mainly (<95%) exported from the vineyard plots in association soil
59 particles. Overall, this study underscores that soil management, including soil disturbance
60 before a storm event, can lead to extensive export of Cu and Zn by runoff from vineyard plots.

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67 **1. Introduction**

68 The wine sector is the most dynamic in terms of conversion to organic farming
69 worldwide (Provost and Pedneault 2016). One objective of organic vineyard farming is to
70 preserve water and soil quality. Conversion to organic farming is generally accompanied by a
71 change in agricultural practices, including mechanical weeding and spontaneous vegetation
72 management in vineyard plots (Bond and Grundy 2001; Coll et al. 2011). Compared to tillage
73 practices, mechanical control of weeds may improve soil quality and limit disturbances while
74 increasing soil organic carbon, water retention, soil microbial biomass and biodiversity
75 (López-Piñeiro et al. 2013). However, information on the impacts of soil management on the
76 hydrological and biogeochemical functioning of vineyard soil, including the mobilization of
77 copper (Cu) and zinc (Zn) during rainfall-runoff events, remains scarce. In particular, the
78 export of Cu and Zn in runoff from agricultural plots may alter receiving ecosystems
79 (Alengebawy et al. 2021), but the export amount is rarely quantified with respect to soil
80 management practices.

81 Vineyard soil is considered an essential component of the terroir, which in turn
82 modulates wine quality (Van Leeuwen et al. 2018). However, many soils in the European
83 vineyard are considered degraded due to erosion and depletion of nutrient reserves (Rodrigo-
84 Comino 2018); accumulation of pollutants, including Cu and Zn (Komárek et al., 2010); and
85 compaction (Cataldo et al. 2021). Cu and Zn concentrations that are more than 100 mg kg⁻¹ in
86 topsoil, depending on their speciation and availability, can have toxic effects on soil
87 organisms. In the long term, this may reduce soil fertility and generate phytotoxic stress.
88 During rainfall events, heavy metals are mainly transported via runoff in suspended matter
89 (Imfeld et al. 2020). Cu and Zn enrichment in eroded sediment from vineyard plots may
90 contribute to the ecological risk from these toxic elements (Pham et al. 2022) that can affect

91 downstream aquatic ecosystems (Pompermaier et al. 2021). While the amount of solid-bound
92 Cu and Zn export from vineyard plots may be significant, quantitative knowledge of the
93 influence of soil management and hydrological conditions on the export of both solid-bound
94 and dissolved Cu and Zn from vineyard plots is scarce.

95 At the catchment scale, Cu and Zn export in runoff is primarily controlled by the
96 interplay between application dose and timing (Imfeld et al. 2020). However, Cu and Zn
97 ageing, i.e., the distribution and diffusion of Cu and Zn over time in soil porewater, minerals
98 and organic matter, in topsoil and hydrological characteristics also play a critical role (Meite
99 et al. 2018). In a previous study, we showed that rainfall depth mainly drove soil erosion from
100 a small headwater vineyard catchment (Imfeld et al. 2020). In turn, soil erosion caused
101 rainfall-proportional export of solid-bound Cu and Zn whenever runoff was generated. This
102 finding led to a new and unresolved question: do primary hydrological signals prevail over the
103 effect of soil management in determining the export of Cu and Zn in runoff? This effect can
104 be preferably examined at the scale of the vineyard plot because soil management varies
105 across a catchment and over time, thus confounding hydrological and soil management
106 signals. In addition, climatic data, erosion, and *in situ* measurements of hydrological factors,
107 including infiltration and runoff, generally enable the establishment of a water balance at the
108 vineyard plot scale (Lefrancq et al. 2014). However, the water balance at the plot scale is
109 rarely coupled with chemical indicators, such as the distribution of Cu and Zn in soil and
110 runoff and the dissolved and solid fractions, to estimate the stocks, fluxes and exports of Cu
111 and Zn from vineyard soil.

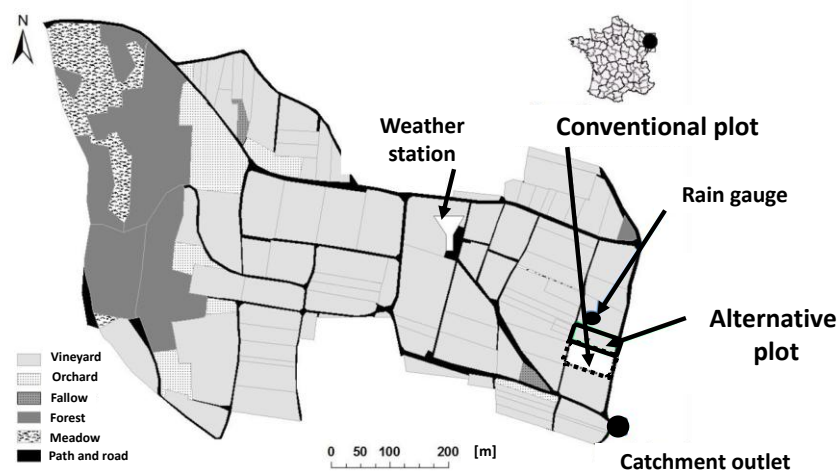
112 In this context, the purpose of this study was to evaluate the influence of soil
113 management on the dissolved and solid-bound exports of Cu and Zn from vineyard soil.
114 During two hydrologically contrasting vine-growing seasons (March to October 2015 and
115 2016), we compared two adjacent plots in a northern vineyard (Rouffach, Alsace, France),

116 one under conventional soil management, involving chemical weeding, and another under
117 alternative soil management with mechanical weeding, in terms of (i) hydrological
118 functioning, (ii) changes in vegetation cover, and (iii) exports of Cu and Zn.

119 2. Materials and Methods

120 2.1. Catchment characteristics

121 The 42.7 ha Hohrain vineyard catchment is situated in the Alsatian foothills (47°57'9
122 N, 07°17'3 E) and is representative of northern vineyards (Duplay et al. 2014; Gregoire et al.
123 2010) (Fig. 1). The catchment is mainly occupied by vineyards (59%, 25.3 ha), orchards,
124 fallow areas and forest (29%), grass strips and ditches (7%), and roads and paths (5%). The
125 vineyards in the region and the catchment are exclusively rainfed.



126

127 **Fig. 1.** Rouffach vineyard catchment (Haut-Rhin, France).

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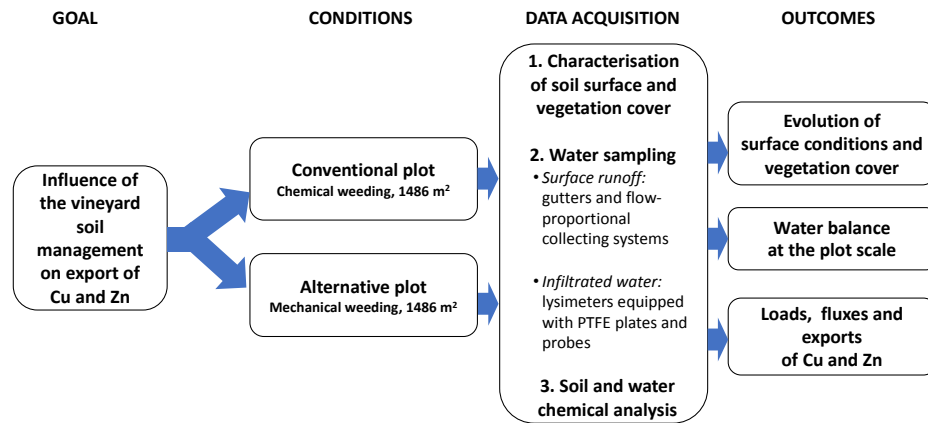
129 Rainfall was monitored at a 6 min resolution by a meteorological station (Météo
130 France, Station n°68287003) located in the catchment. During the vine-growing season
131 (March to October), cumulated rainfall averaged 437 ± 91 mm (1998-2016). Vineyard plots
132 contribute to runoff when the rainfall intensity exceeds the saturated hydraulic conductivity
133 (i.e., 58 ± 50 mm h⁻¹) (Lefrancq et al. 2014; Tournebize et al. 2012). The saturated hydraulic
134 conductivity within plots can decrease by up to one order of magnitude when topsoil sealing

135 occurs across the season.

136 The soil is a calcareous clay loam developed on a loess base. The soils are Haplic
137 Cambisol Calcaric Siltic and Cambisol Hypereutric Clayic (Endoskeletal) (IUSS Working
138 Group WRB, 2006), with soil minerals consisting of calcite, quartz, and minor amounts of
139 feldspars, dolomite and clay (Duplay et al. 2014). The clay minerals are generally composed
140 of kaolinite and illite. The soil pH ranges from 7.7 to 8.3. The organic matter varies from 2‰
141 in the deepest soil horizon to 34‰ in the topsoil (i.e., the first 5 cm). The background contents
142 of Cu and Zn in the soil before the study ranged from 10 to 188 mg kg⁻¹ and from 39 to 132
143 mg kg⁻¹, respectively, with the highest contents occurring in the top 20 cm (Duplay et al.
144 2014).

145 **2.2. Characteristics of the experimental plots**

146 The experimental design was restricted to two plots to enable a detailed and
147 quantitative comparison of Cu and Zn exports associated with typical conventional and
148 alternative vineyard soil management practices. Each plot included (i) a large surface area
149 (>0.1 ha) to generate sufficient and representative runoff water, (ii) gutters and flow-
150 proportional collecting systems to monitor and collect surface runoff, and (iii) lysimeters
151 equipped with polytetrafluoroethylene (PTFE) plates and probes to monitor and collect
152 infiltrated water. Both the availability of vine areas with similar characteristics (i.e., soil,
153 rootstock, and management) and costs prevented the replication of such monitoring facilities.
154 However, the two plots were thoroughly monitored weekly over the entire vine growing
155 season (8 months) and two contrasting vine growing seasons. The overall methodology is
156 summarized in Fig. 2.



157

158 **Fig. 2.** Overall methodology and outcomes of the study.

159

160 The two experimental plots, each covering an area of 1486 m² (87.4 m × 17 m), were
 161 planted in 1998 with Riesling (rootstock 161-49). Each plot contained 10 rows of vines, with
 162 alternating interrows permanently grassed to limit soil erosion and facilitate the passage of
 163 machinery and a weeded interrow. The interrow spacing was 170 cm, while the space
 164 between each vine was 130 cm. The planting density was approximately 4000 vines ha⁻¹,
 165 corresponding to a typical density in Alsace. The plots had a mean slope of 10.8%, and their
 166 soils were classified as type C (moderately high runoff potential) (SCS-CN, 1997). The yearly
 167 vertical drainage at 2 m depth of the studied plots was estimated at 128 ± 25 L m⁻² a⁻¹ ($\bar{X} \pm \sigma$),
 168 i.e., 23 ± 4.7% of the effective recharge by rain, which was the difference between rainfall
 169 and actual evapotranspiration over two hydrological years (1998-1999 and 1999-2000)
 170 (Tournebize et al. 2012). A field survey carried out on one soil profile per plot at three depths
 171 up to 1.5 m, and a laser grain size analysis indicated that the plots had similar and
 172 homogeneous grain sizes (i.e., silt loam with 77 ± 6% silt) and bulk density (1.4 ± 0.2 g cm⁻³).

173 The fungicides used in the experimental plots were identical and contained Cu and
 174 sulfur only. The Cu fungicides were applied directly to the vine canopy of both plots to
 175 control downy mildew (*Plasmopara viticola*) (MacKie et al., 2012), and these fungicides
 176 (expressed as elemental Cu) were applied from May to August in the form of Cu sulfate

177 ('Bordeaux mixture', $\text{CuSO}_4 + \text{Ca}(\text{OH})_2$), Cu oxide (Nordox[®], Cu_2O), and Cu hydroxide
178 (Kocid[®], Cuproxat[®] and Champ flo[®], $\text{Cu}(\text{OH})_2$) (Fig. 5). The dose and frequency of the Cu
179 applications were obtained from surveys of wine producers in the catchment in 2015 and
180 2016. Producer responses covered 75% and 74% of the total vineyard area in 2015 and 2016,
181 respectively. The contribution of atmospheric Cu and Zn to the catchment over the period was
182 negligible, i.e., $\leq 0.5\%$ of the total input mass (Chabaux et al. 2005). No Zn application was
183 reported during the study period.

184 *Conventional plot.* The conventional soil management practices followed the
185 traditional soil management approach in Alsace. The cavaillon, referring to the zone below
186 the vine line, was chemically weeded first at the budburst of the vine (May) and then one
187 month before harvesting (August) using a combination of pyraflufen-ethyl and glyphosate
188 (Vertical[®], Arysta LifeScience, 1 L ha^{-1}). The grass-covered interrows were controlled by
189 mowing, while the other interrow was mechanically weeded. Between two and five mowing
190 were carried out yearly. Soil mechanical weeding consisted of three to five passes, alternating
191 between a coarse and deep weeding, using a tool with rigid teeth, and a finer and more
192 superficial weeding, using a rotary harrow (Fig. 4).

193 *Alternative plot.* The alternative soil management practices aimed to limit additional
194 work by not chemically weeding the cavaillon. In the plot, one interrow out of two was
195 grassed, while the two adjoining half-cavaillons were spontaneously grassed. The other row
196 and the two adjoining half-cavaillons were worked mechanically (harrowing and ploughing).
197 Each cavaillon was thus half grassed and mowed and half worked. This management
198 approach allowed simultaneous mowing or tilling of the interrow and the cavaillon by
199 combining a tine cultivator (10-30 cm deep) or a rotary flail for the interrow with interceps for
200 the cavaillon (Fig. 4).

201 **2.3. Experimental plots**

202 The experimental plots were separated hydrologically from the adjacent plots with a
203 30 cm high waterproof border. Each plot was equipped with a gutter leading to two stainless
204 steel manifolds (68 L) in series with a tundish to monitor runoff discharge. This setting of
205 collectors, with a first tank of 68 L, of which 1/10 of the overflow contributed to the filling of
206 the second tank, increased the capacity of the runoff volume measurement up to 748 L. The
207 gutters and collectors were covered with a PTFE film to limit metal sorption. The gutters were
208 covered on top with metallic grids wrapped in PTFE films to prevent contamination from
209 machinery passages. The flow at the outlet of the plots was monitored continuously using an
210 ultrasonic height sensor (ISMA, Forbach, France) connected to a flowmeter and combined
211 with an exponential section venturi channel (ISMA) and flow-controlled refrigerated
212 automatic sampler (Teledyne ISCO, Lincoln, NE, USA).

213 To monitor water infiltration, the soil was excavated in each plot in December 2014 to
214 install lysimeters between the cavaillon and the grassed interrow. The PTFE lysimetric plates
215 (40 × 30 cm) were installed at 40 and 80 cm below the soil surface to collect by gravity the
216 free water in manholes located downstream of the pits. In parallel, probes (Campbell CS655)
217 were installed to monitor the water content and the temperature at 40 and 80 cm below the
218 soil surface throughout the year, with a frequency of every 15 min.

219 **2.4. Characterization of the soil surface**

220 Surface conditions were characterized based on (Roose 1996) on the cavaillons and
221 the worked interrows of the experimental plots. Since the entire surface of the interrow
222 remained grass, its contribution to runoff was assumed to be very limited. The
223 characterization of the soil surface allowed to (i) separate coarse elements and clumps
224 according to their size and shape, (ii) identify macropores, (iii) estimate the rate of structural
225 and sediment crust, (iv) determine the rate of vegetation cover and its height, and (v)
226 determine the threshold height that needed to be crossed for a possible dripping blade to

227 evaluate the roughness of the soil.

228 **2.5. Sampling**

229 *Soil.* From March to October 2015 and 2016, topsoil (0-5 cm) subsamples were
230 collected monthly every 10 m in the middle of the two interrows and under the cavaillon.
231 Topsoil subsamples were pooled into one composite sample for each plot and sampling date,
232 yielding a total of 28 soil samples. Geogenic Cu (i.e., naturally occurring in soil) was
233 determined from a reference sampled at 70 cm below the soil surface (near bedrock) in the
234 forested area upstream of the vineyard catchment (Babcsányi et al. 2016).

235 *Water.* Runoff water from the two plots was collected from March to October 2015
236 and 2016. Runoff water samples were collected at each event in proportion to the flow rate
237 (100 mL every 3 L). Water samples were collected in PE bottles previously washed with HCl
238 (0.5 M) and rinsed with distilled water. Water samples were refrigerated during sampling and
239 combined weekly into one composite sample per plot, yielding 28 and 22 water samples in
240 2015 and 2016, respectively. The runoff water samples were placed on ice during transport to
241 the laboratory and filtered through 0.45 µm membranes to separate the solid-bound and
242 dissolved phases. Samples were stored at 4 °C until analysis. Water infiltration and water
243 content at 40 and 80 cm below the soil surface were monitored in the lysimeters throughout
244 the two years.

245 **2.6. Chemical analyses**

246 *Soil physicochemical analyses and hydrochemical analyses.* Soil physicochemical
247 characteristics were determined as described previously (Duplay et al., 2014).
248 Hydrochemical analyses were carried out as described previously (Lucas et al. 2010).

249 *Cu and Zn quantification.* Soil samples were oven-dried (60 °C), sieved (2 mm) and
250 powdered using an agate disk mill (<100 µm) prior to total dissolution in double distilled
251 nitric acids under a laminar fume hood in a clean room (Babcsányi et al., 2016). Filtered

252 runoff water was acidified to pH 2 using double distilled nitric acid. Measurements were
253 carried out by ICP–AES (ICAP6500, Thermo Fisher Scientific) with the geological
254 standards BCR-2 (US Geological Survey, Reston, VA, USA) and SCL-7003 (Analytika,
255 Prague, Czech Republic) for quality control (Babcsányi et al. 2014). The total analytical
256 uncertainty of the measurements was $\pm 5\%$, and the detection limit was $<3 \mu\text{g L}^{-1}$.

257 **2.7. Water balance calculations**

258 A water balance was used to estimate the monthly soil water content and the
259 associated water excess or deficit considering the available water capacity of each plot. The
260 available water capacity corresponds to the amount of water stored across a soil profile. It was
261 calculated as the difference between the water content at field capacity and the permanent
262 wilting point. These two thresholds of water content were estimated using a pedotransfer
263 function (Rawls et al. 1982) across the 1.5 m soil profile, considering the soil granulometric
264 parameters and the organic matter contents. The initial soil water content corresponded to the
265 available water content in January 2015. The change in the soil water content over time was
266 then estimated using the monthly rainfall and the Penman–Monteith potential
267 evapotranspiration (PET) recorded at the meteorological station. When the soil water content
268 was below the available water capacity, a PET fraction was determined based on the water
269 content to available water capacity ratio to retrieve the real evapotranspiration (ET_0). The ET_0
270 was then compared to the PET to estimate the water deficit (Fig. 3).

271 **2.8. Metrics of Cu and Zn export**

272 Two metrics were calculated to compare the influence of vineyard soil management
273 practices on the export of Cu and Zn at the plot scale.

274 *Weekly specific load.* The weekly specific loads of Cu and Zn ($WL_{Cu \text{ or } Zn}$ [mg ha^{-1}])
275 were calculated by multiplying the weekly concentrations of Cu or Zn by the corresponding
276 runoff volume:

$$277 \quad WL_{Cu \text{ or } Zn} = \frac{C_{Cu \text{ or } Zn} \times V}{S} \quad (1)$$

278 where C is the weekly concentration of Cu or Zn, V is the corresponding weekly portion of
 279 runoff volume [L] and S is the plot surface [ha]. Dissolved and solid-bound $WL_{Cu \text{ or } Zn}$ values
 280 were calculated separately for Cu and Zn.

281 *Seasonal export coefficient.* The seasonal export coefficient ($SEC_{Cu \text{ or } Zn}$ [%]) was
 282 calculated to compare the Cu and Zn exports accounting for the Cu and Zn stocks in the
 283 topsoil:

$$284 \quad SEC_{Cu \text{ or } Zn} = 100 \times \frac{WL_{Cu \text{ or } Zn}}{Topsoil \ mass_{Cu \text{ or } Zn}} \quad (2)$$

285 where $Topsoil \ mass_{Cu \text{ or } Zn}$ is the stock of Cu or Zn [$mg \ ha^{-1}$] in the vineyard topsoil (0-5 cm).

286 The Cu and Zn stocks in the vineyard soil did not vary significantly because seasonal
 287 applications in the catchment represented less than 5% of the initial stock of Cu and Zn in soil.
 288 This amount was within the uncertainty range of the Cu and Zn quantification (5%) (Babcsányi
 289 et al., 2016).

290 **2.9. Statistical analysis**

291 Statistical tests were performed using the R program (Copyright 2005, The R
 292 Foundation for Statistical Computing, Version 2.15.1). Nonparametric Wilcoxon and
 293 Kruskal–Wallis tests were applied to compare the soil characteristics, Cu and Zn
 294 concentrations and exports in the vineyard plots.

295

296 **3. Results and discussion**

297 **3.1. Water balance in the vineyard plots**

298 The two vine-growing seasons differed in terms of rainfall, rainfall intensity,
 299 occurrence and runoff volumes in both plots. The rainfall volume from March to October
 300 was lower in 2015 (387 mm) than in 2016 (428 mm, with 90% of rainy weeks). Accordingly,
 301 the runoff volume in 2016 from the vineyard plots was >80% larger than that in 2015 (Table

1). However, the average rainfall intensity was twice as high in 2015 (4.3 mm h⁻¹) than in 2016 (2.5 mm h⁻¹). The weekly runoff coefficients in 2015 were similar in both plots (Table 1) and were as high as 1.37% in the conventional plot during an intense storm on July 22nd (36.8 mm in 54 min). In contrast, the weekly runoff coefficients in 2016 were one order of magnitude lower than those in 2015 (Table 1). Overall, the runoff coefficients in the Hohrain vineyard plots were more than one order of magnitude lower than those in other European vineyards (Rodrigo Comino et al. 2016) because half of the interrows were grassed.

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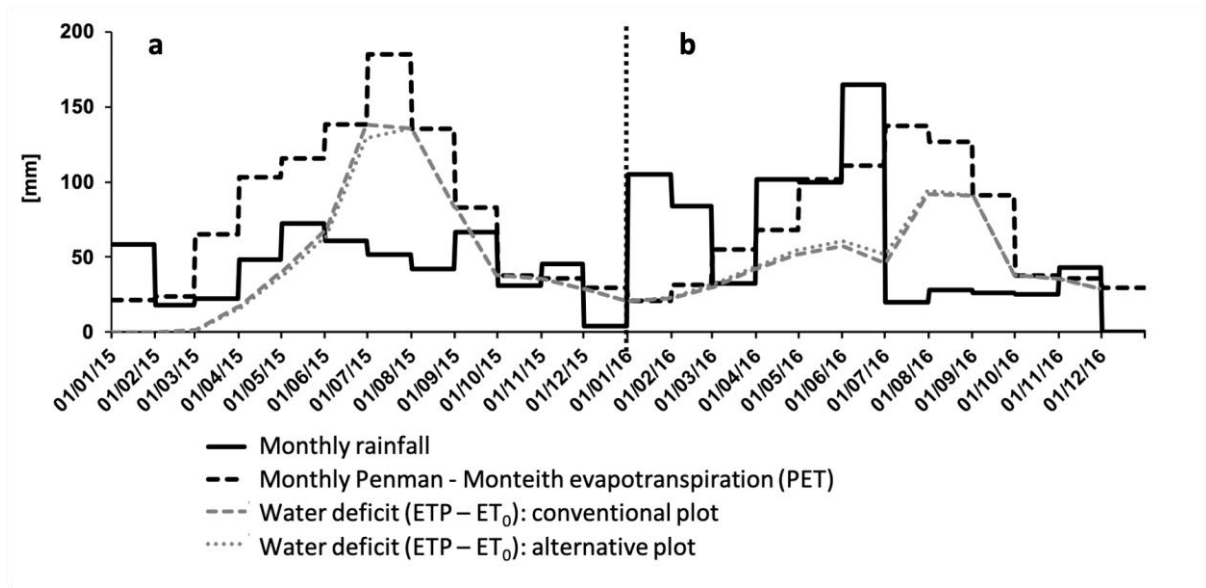
Table 1. Surface runoff from the conventional and alternative vineyard plots. The error given for the mean weekly runoff coefficient corresponds to $\pm\sigma$.

	Conventional		Alternative	
	2015 (n=14)	2016 (n=14)	2015 (n=14)	2016 (n=12)
Total runoff volume [L]	252	1259	149	1117
Weekly runoff coefficient [%]	0.15 ± 0.36	0.03 ± 0.04	0.13 ± 0.34	0.02 ± 0.03

314

The available water content was similar in both plots (conventional: 301 mm, alternative: 321 mm) (Fig. 3) since their soil texture and organic matter content did not significantly differ ($p>0.01$). From March 2015 to December 2016, the monthly water content in the soil was always below the available water content, indicating a constant water deficit (Fig. 3) with limited infiltration in soil. The lack of collected water at depths of 40 and 80 cm over the vine-growing seasons confirmed limited water infiltration. However, water infiltration at depths of 40 and 80 cm in January and February 2016 corresponded to 2.2% (conventional plot) and 12% (alternative plot) of the rainfall depth, respectively. However, the

323 collected leached water volumes did not allow reliable Cu and Zn quantification.



324

325 **Fig. 3.** Monthly water balance in 2015 (A) and 2016 (B). Water deficit represents the
326 difference between the potential evapotranspiration (PET) and the real evapotranspiration
327 (ET_0). The water deficit was ≥ 0 , and no water excess occurred in either the conventional or
328 alternative management plots.

329

330 The soil water content measured across the soil profiles also indicated limited vertical
331 flows. The soil water content was systematically higher at a depth of 40 cm than at a depth of
332 80 cm, particularly in the alternative management plot. Different volumetric water contents
333 between the 40 and 80 cm depths in the alternative management plot (9% in 2015 and 6% in
334 2016) and the conventional management plot (<3%) further confirmed the lower dynamics of
335 vertical fluxes in the alternative management plot. Hence, the alternative management plot
336 was less affected by rainfall events than the conventional plot, which may be due to different
337 hydraulic conductivities at saturation between the plots (conventional: 35 mm h^{-1} , alternative:
338 10 mm h^{-1}), mirroring the different soil management practices. However, in both plots and at
339 both depths, the water content decreased by 10% in spring and summer compared to that in
340 autumn. This finding is mainly attributed to the evaporation associated with climatic

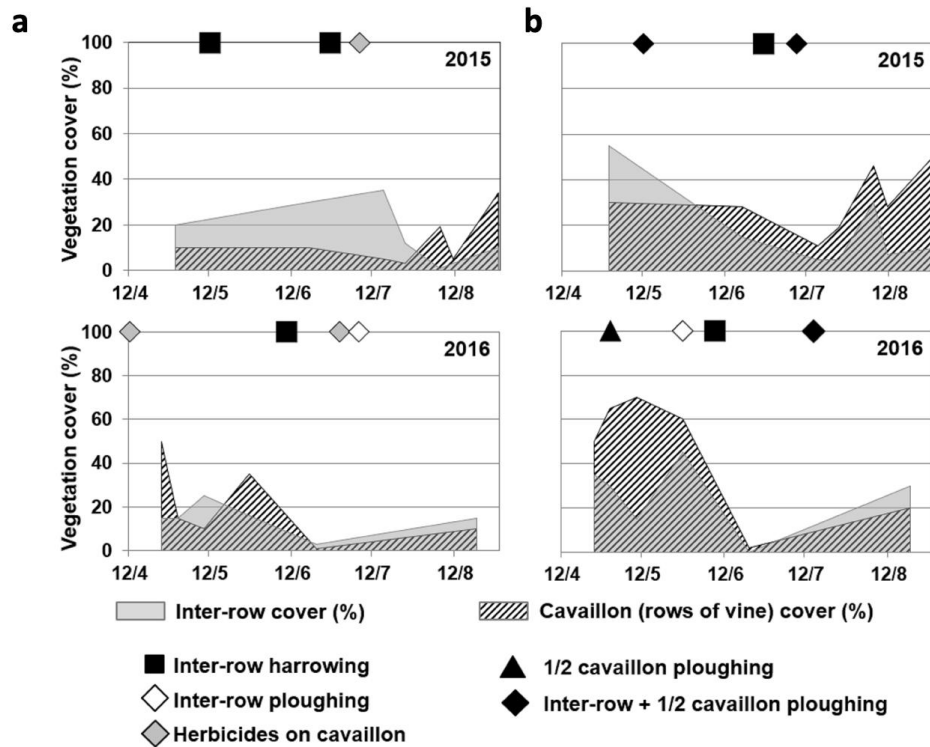
341 conditions and the water demand of vines.

342 Thus, the minimal contribution of runoff and water infiltration to the overall water
343 budget underlines the prevalence of evaporation and water uptake by the vine and grass in the
344 interrows during the study periods. The minor contribution of water infiltration to the soil was
345 also expected to limit the vertical transport of trace metals, including Cu and Zn, downwards
346 in the soil (Meite et al. 2018).

347

348 **3.2. Soil surfaces and vegetation cover**

349 The vegetation cover in the alternative management plot (15 to >60%) was greater
350 than that in the conventional management plot (0 to 40%) for both the cavaillon and the
351 interrows (Fig. 4). The dominant species (>95%) in both plots included English ryegrass
352 (*Lolium perenne* L.), white clover (*Trifolium repens* L.), lanceolate plantain (*Plantago*
353 *lanceolata* L.) and dandelion (*Taraxacum officinale* Weber ex F.H. Wigg.). In 2016, increased
354 tillage operations from June to August (Fig. 4) generally limited the vegetation development
355 on the interrows. Although downslope tilled vineyards are generally the most eroded,
356 vegetation cover between vine rows significantly reduces soil erosion (Lieskovský and
357 Kenderessy 2014). Lower exports of solid-bound Cu and Zn with eroded soil from the
358 alternative vineyard management plot than from the conventional vineyard management plot
359 were thus expected. However, soil management can also influence the regrowth of the
360 vegetation cover since coarse-scale soil management practices do not completely destroy
361 weeds, as opposed to fine-scale management practices.



362

363 **Fig. 4.** Soil management and vegetation cover in the conventional (A) and alternative (B)
 364 management plots.

365

366 A total encrustation of surface soil was observed in 70% and 40% of the observations
 367 in 2015 and 2016, respectively. Soil management quickly destroyed the structural crust, partly
 368 after coarse-scale management practices and completely after fine-scale management
 369 practices work. However, rainfall can quickly alter the porosity generated by soil
 370 management. For instance, encrustation increased from 0% to 100% in the interrow of the
 371 alternative management plot from July 16 to 24, 2015, which could have been related to the
 372 high volume and intensity of successive rainfalls. Similarly, the encrustation in the
 373 conventional management plot increased from 9% to 100% due to the absence of tillage and a
 374 cumulative rainfall volume of 80 mm from April 27 to May 26, 2016. On the other hand,
 375 coarse-scale soil management using a rigid-tine cultivator created more clods than fine-scale
 376 harrowing, thereby increasing the soil roughness. The estimated height of the thresholds to be

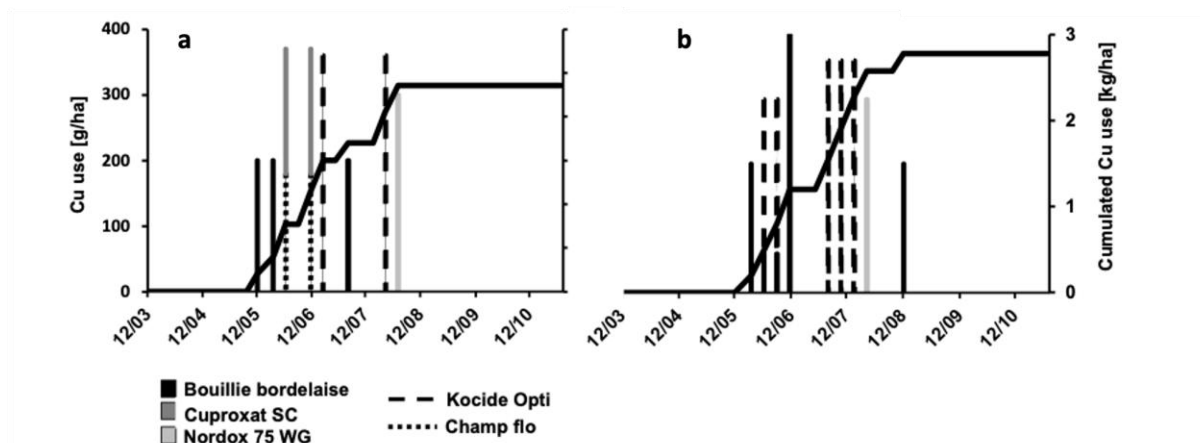
377 crossed to generate surface runoff from the soil was 1 to 2 cm. However, water likely also
378 flowed between clods when the surface was completely encrusted and clods were sealed to
379 the soil matrix. It is also notable that the crusted soil surface on the chemically weeded
380 cavaillon was always greater than 70%, while that on the cavaillon in the alternative
381 management plot could fall below 10%.

382 Overall, soil mechanical work may temporarily increase the soil structural porosity
383 and thus water infiltration. However, this effect is transient, and its duration depends on the
384 volume and intensity of the successive rainfall events and vegetation regrowth. In addition,
385 tillage and harrowing reduced soil encrustation, which may favour the mixing of topsoil, soil
386 solution and runoff water during long events as well as soil fragmentation by raindrop splash
387 during intense events (Jarvis 2007). Hence, it is expected that rainfall-runoff events following
388 soil mechanical work favour the solubilization and mobilization of Cu and Zn from the
389 vineyard soil and the plots, together with the transport of soil aggregates.

390

391 **3.3. Soil stocks and concentrations of Cu and Zn in runoff**

392 The total amount of Cu applied to the plots was less than 2.4 kg ha⁻¹ in 2015 and 2.8
393 kg ha⁻¹ in 2016 (Fig. 5). These amounts corresponded to higher downy mildew pressure in
394 2016 than in 2015, corresponding to higher rainfall volumes in 2016 (428 mm) than in 2015
395 (387 mm). No Zn application was reported in 2015 and 2016.



396

397 **Fig. 5.** Cu-based fungicides used in 2015 (A) and 2016 (B) in the conventional and
 398 alternative management plots and the cumulative use of elemental Cu. Bouillie bordelaise
 399 ($\text{CuSO}_4 + \text{Ca}(\text{OH})_2$), Nordox[®] 75 WG: Cu_2O (Cu oxide), Kocid[®] Opti, Cuproxat[®] SC and
 400 Champ flo[®]: $\text{Cu}(\text{OH})_2$ (Cu hydroxide). The dose and frequency of the Cu applications were
 401 estimated from surveys of wine producers in the catchment area.

402

403 The mean concentrations in topsoil (0-5 cm) were ($\bar{X} \pm \sigma$) $129 \pm 30 \text{ mg Cu kg}^{-1}$ and 97
 404 $\pm 19 \text{ mg Zn kg}^{-1}$, with no significant difference ($p < 0.01$) between the plots and the vine-
 405 growing seasons. These concentrations corresponded to $90 \pm 21 \text{ kg Cu ha}^{-1}$ and $67 \pm 13 \text{ kg Zn}$
 406 ha^{-1} in the top 5 cm of the soil accumulated after five decades of vine growing in the plots
 407 (Babcsányi et al. 2016). Since the annual input of Cu accounted for less than 5% of the initial
 408 stock in the topsoil, the stocks of Cu and Zn in topsoil did not vary much over the season. In
 409 fact, the coefficients of variation (i.e., σ/\bar{x}) of monthly Cu and Zn concentrations in the
 410 topsoil and amounts per hectare of vineyard were less than 20% in both plots and over the
 411 two growing seasons. Hence, sampling heterogeneity mainly drove the variability in the Cu
 412 and Zn concentrations in the soil, as observed previously at the catchment scale (Imfeld et al.
 413 2020).

414 Strong correlations ($\rho_s > 0.8$, $p < 0.001$) between the runoff volume and the mass export

415 of total suspended solids (TSS) and both dissolved and solid-bound Cu and Zn
416 concentrations indicated that the export of Cu and Zn increased with vineyard soil erosion.
417 Solid-bound Cu and Zn concentrations were at least three times higher during larger runoff
418 events (>10 L) than during smaller runoff events from the plots in 2015 and 2016 (Table 2).
419 In contrast, dissolved Cu and Zn concentrations were twice as high during small than during
420 large runoff events (Table 2). This finding highlights that a dilution effect occurred during
421 large runoff events, although the Cu concentrations during the smaller and larger runoff
422 events from the alternative management plot did not substantially differ.

423 It is also notable that the ranges of dissolved Cu (7 to 264 $\mu\text{g L}^{-1}$) and Zn (10 to 1300
424 $\mu\text{g L}^{-1}$) concentrations in the surface runoff from the vineyard plots were large. A previous
425 study emphasized that Cu mobilized by rainwater and dissolved in runoff mainly consisted of
426 Cu-dissolved organic matter complexes in this vineyard catchment (Babcsányi et al. 2016).
427 The sorption of heavy metals on dissolved organic matter in runoff water is expected to
428 significantly reduce the bioavailability, uptake and ecotoxicity of free Cu^{2+} and Zn^{2+} (Adams
429 et al. 2020). However, transient ecotoxicological effects of runoff water from vineyard plots
430 cannot be excluded for some events.

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437 **Table 2.** Weekly mean concentrations ($\mu\text{g L}^{-1}$) of dissolved and solid-bound Cu and Zn in
438 the surface runoff from the conventional and alternative management plots over the vine-

439 growing seasons (March to October 2015 and 2016). The error given for the weekly
 440 concentrations corresponds to the standard deviation ($\pm\sigma$).

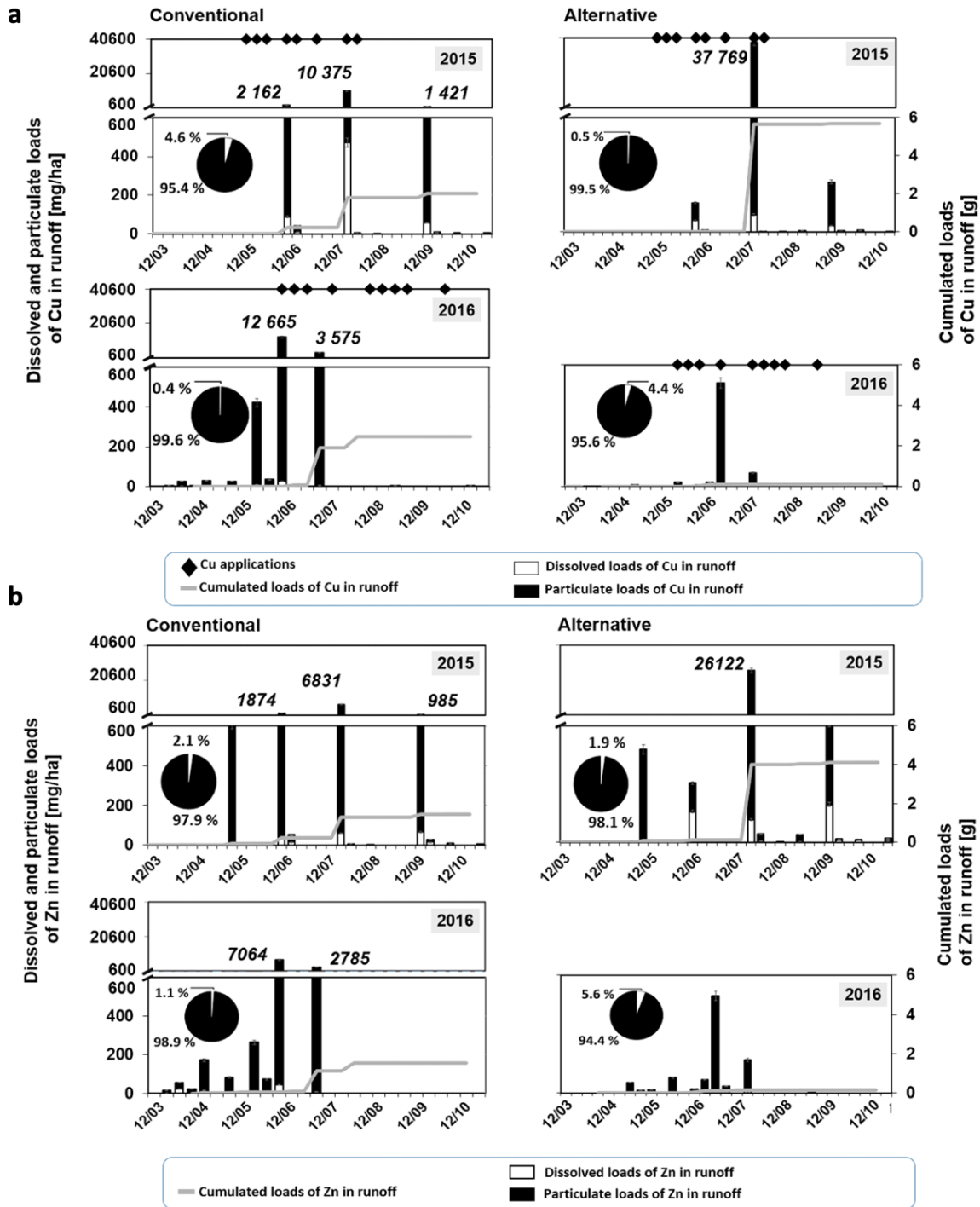
		Small runoff events (<10 L)	Large runoff events (>10 L)	
Conventional	Cu	Dissolved	119 ± 75	51 ± 32
		Solid-bound	150 ± 217	3394 ± 6561
	Zn	Dissolved	201 ± 168	89 ± 76
		Solid-bound	508 ± 844	2754 ± 3708
Alternative	Cu	Dissolved	45 ± 24	43 ± 30
		Solid-bound	232 ± 214	1203 ± 2347
	Zn	Dissolved	268 ± 363	12 ± 106
		Solid-bound	1635 ± 2612	158646

441

442 **3.4. Exports of Cu and Zn in runoff**

443 The solid-bound amount of Cu and Zn exported in the runoff accounted for more than
 444 95% of the total Cu and Zn amount exported during both seasons and for both plots (Fig. 6).
 445 This result is consistent with those of previous study showing that Cu in runoff was mainly
 446 exported in the silt fraction due to complexation with soil organic matter and in the clay
 447 fraction due to preferential Cu sorption on clay minerals (Babcsányi et al. 2016). Moreover,
 448 the Cu and Zn amount exported during large runoff events was up to five orders of
 449 magnitude higher than that during small runoff events. In particular, more than 75% and
 450 52% of the total seasonal exports of Cu and Zn, respectively, occurred within one week
 451 during larger runoff events (Fig. 6). This finding highlights the major influence of
 452 hydrological conditions on Cu and Zn export and its seasonal distribution. Overall, large
 453 runoff events resulted in greater soil erosion than small runoff events since greater raindrop

454 energy and runoff amount carry larger soil particles (Mohammad et al. 2018). This scenario
455 led to proportionally greater exports of solid-bound Cu and Zn in the runoff (Imfeld et al.
456 2020).



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Fig. 6. Specific loads (mg ha^{-1}) of Cu (a) and Zn (b) exported in the dissolved and solid-bound phases and cumulative loads of Cu and Zn in the runoff from the conventional and alternative management plots. The error given for the dissolved and particulate loads was calculated via error propagation and incorporates errors associated with discharge measurements and the analytical uncertainty of the Cu and Zn measurements.

463 Overall, our results indicated that slightly lower runoff volumes and greater vegetation
464 cover preventing soil fragmentation in the alternative management plot significantly reduced
465 Cu and Zn export. However, the timing of soil management favouring the solid-bound
466 transport of heavy metals in relation to large rainfall-runoff events controlled the extent of Cu
467 and Zn export. In fact, the total amount of Cu (conventional: 14.0 g ha⁻¹, alternative: 38.2 g
468 ha⁻¹) and Zn (conventional: 10.4 g ha⁻¹, alternative: 27.7 g ha⁻¹) exports were higher in the
469 alternative management plot than in the conventional management plot in 2015. Ploughing in
470 the alternative management plot followed by the intense storm event on July 22nd led to the
471 extensive export of both Cu and Zn (Fig. 6). Although this storm event accounted for only
472 10% of the total rainfall depth during the growing season in 2015, it accounted for 85%, 99%
473 and 94% of the total amounts of TSS, Cu and Zn, respectively, exported in the surface runoff
474 from the alternative management plot during the vine-growing season.

475 In addition, mechanical work fractured the vineyard soil and likely temporarily altered
476 the soil structure and decreased the aggregate size and the bulk density. This, in turn,
477 increased surface runoff, soil erosion (Roger-Estrade et al. 2009) and Cu and Zn solid-bound
478 exports. Based on the surface soil characterization, the rate of structural soil crust reached 0%
479 after ploughing in the alternative plot. During the intense storm event on July 22nd, it was thus
480 expected that runoff quickly funnelled the finer soil fraction from raindrop splash effects and
481 interrill erosion, while excess shear stresses mobilized coarser soil particles from the plot
482 (Hou et al. 2021). Nevertheless, the amount of Cu exported from both the conventional and
483 the alternative management plots was lower than the average net amount of Cu exported
484 during the vine-growing season, i.e., 170 g Cu ha⁻¹, estimated in European vineyards (Droz et
485 al. 2021).

486 The seasonal export coefficients in 2015 were at least three times higher in the
487 alternative management plot than in the conventional management plot for both Cu and Zn

488 (Table 3). This finding confirmed that the soil mechanical work significantly enhanced the
 489 mobilization and transport of solid-bound Cu and Zn from the vineyard soil. In contrast, the
 490 export coefficients in 2016 for both Cu and Zn were one order of magnitude lower in the
 491 alternative management plot than in the conventional management plot (Table 3). This result
 492 can be explained by the absence of large surface runoff events in the alternative
 493 management plot, resulting in a lower maximum runoff coefficient than that in the
 494 conventional management plot (conventional: 1.5%, alternative 0.08%). Notably, the
 495 seasonal export of freshly applied Cu from the conventional management plot (0.6% of Cu
 496 applied) was 30 times higher than that in the alternative management plot (0.02%). This
 497 result indicates that it may be critical to account for not only the historical background of Cu
 498 in topsoil but also the fraction of Cu freshly applied during the vine-growing season to
 499 evaluate the effect of soil management on Cu export.

500

501 **Table 3.** Seasonal export coefficient (SEC) [%] of Cu and Zn from the conventional and
 502 alternative management plots.

	Conventional		Alternative	
	2015	2016	2015	2016
Cu [%]	0.022	0.026	0.084	0.001
Zn [%]	0.024	0.023	0.071	0.002

503

504 Since a limited fraction (<15%) of the rainfall volume infiltrated the soil of both plots
 505 in the winter, the Cu and Zn leaching across the soil was one order of magnitude lower than
 506 that being exported via surface runoff. The contribution of vertical transport to Cu and Zn
 507 exports evaluated from the samples collected by lysimetric plates in January and February
 508 2016 accounted for less than 0.0005% and 0.002% of the initial Cu and Zn stocks in topsoil,

509 respectively. This finding confirmed the low risk of vertical Cu and Zn transport in the
510 studied vineyard soil, as also observed in laboratory leaching experiments (Meite et al.
511 2018). However, the leaching coefficient for Zn (0.0016%) was one order of magnitude
512 higher than that for Cu in the alternative management plot, which may reflect different
513 interactions of Cu and Zn with soil oxides, clays and carbonates. In fact, the decrease in
514 labile and leachable forms in soil during ageing may be larger for Cu than for Zn. Cu is
515 expected to undergo diffusive penetration in soil and interact with organic ligands, oxides,
516 clays and soil carbonates (Meite et al. 2022). This may result in less leaching of Cu than Zn.
517 In particular, the increase in the Cu reducible fraction of soil mainly corresponded to the Cu
518 bound to soil oxides (Huang et al. 2015). In contrast, Zn was previously found in association
519 with clays and carbonates in Rouffach soil (Duplay et al. 2014), and Zn ageing in soil may
520 not significantly affect its mobility.

521

522 **4. Conclusions**

523 Here, we examined how conventional and alternative vineyard plot management
524 practices affected hydrological functioning, vegetation cover and the mass export of Cu and
525 Zn from soil during two contrasting wine growing seasons. Our main findings were that (i)
526 surface runoff mainly drove Cu and Zn exports since vertical flows were limited; (ii) the
527 seasonal Cu and Zn export during runoff relative to the historical stocks in topsoil ranged
528 from 0.001 to 0.071% in the alternative plot; (iii) ploughing for mechanical weeding
529 followed by an intense storm event resulted in extensive Cu and Zn mass export, accounting
530 for more than 95% of the total Cu and Zn mass exported in the surface runoff during the
531 season; and (iv) Cu and Zn were mainly (<95%) exported in surface runoff in association
532 soil particles. Overall, our results support the hypothesis that mechanical soil management
533 before intense or long rainfall-runoff events favours the export of a large fraction of the

534 overall Cu and Zn seasonal mass export. Compared to previous studies, the present study
535 underscores that soil management, including soil disturbance before a storm event, can lead
536 to extensive Cu and Zn export by runoff from vineyard plots. This emphasizes that the
537 timing of soil management may drive Cu and Zn export in runoff from vineyard plots at the
538 plot scale. The main implication of our results is that soil management type should be
539 considered when evaluating the dynamics of Cu and Zn export at the plot scale. To limit the
540 mass export of Cu and Zn associated with eroded particles in surface runoff, grass interrows
541 should be a priority, and tillage before stormy periods should be avoided. In the future, the
542 variability in Cu and Zn exports from vineyard plots and the associated ecotoxicological
543 risks may be examined with respect to the ageing and speciation of historical Cu and Zn
544 accumulated in soil and the diversity of soil management practices.

545

546

547 **Data availability statement**

548 The datasets generated during and/or analysed during the current study are available from the
549 corresponding author on reasonable request.

550

551 **Author Contributions**

552 **Gwenaël Imfeld:** Conceptualization, Methodology, Formal analysis, Funding
553 acquisition, Project administration, Resources, Supervision, Writing - original draft. **Benoît**
554 **Guyot and Charline Wiegert:** Conceptualization, Investigation, Methodology, Formal
555 analysis, Writing - review & editing. **Sylvain Payraudeau:** Conceptualization,
556 Methodology, Formal analysis, Resources, Supervision; Writing - review & editing.

557

558 **Declaration of Competing Interests**

559 The authors have no relevant financial or non-financial interests to disclose.

560

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