



**HAL**  
open science

## Do rainfall characteristics affect the export of copper, zinc and synthetic pesticides in surface runoff from headwater catchments?

Gwenael Imfeld, Fatima Meite, Charline Wiegert, Benoît Guyot, Jérémy Masbou, Sylvain Payraudeau

### ► To cite this version:

Gwenael Imfeld, Fatima Meite, Charline Wiegert, Benoît Guyot, Jérémy Masbou, et al.. Do rainfall characteristics affect the export of copper, zinc and synthetic pesticides in surface runoff from headwater catchments?. *Science of the Total Environment*, 2020, 741, pp.140437. 10.1016/j.scitotenv.2020.140437 . hal-02988801

**HAL Id: hal-02988801**

**<https://hal.science/hal-02988801>**

Submitted on 5 Jan 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1     **Do rainfall characteristics affect the export of copper, zinc and synthetic**  
2             **pesticides in surface runoff from headwater catchments?**

3

4

5             *Gwenaël Imfeld\**, *Fatima Meite*, *Charline Wiegert*, *Benoît Guyot*, *Jérémy Masbou*,

6

*Sylvain Payraudeau*

7

8     Laboratory of Hydrology and Geochemistry of Strasbourg (LHyGeS), UMR 7517, Université  
9     de Strasbourg/ENGEES, CNRS, 1 Rue Blessig, 67084 Strasbourg Cedex, France

10

11

12

13     \*Corresponding author: [imfeld@unistra.fr](mailto:imfeld@unistra.fr)

14     Laboratory of Hydrology and Geochemistry of Strasbourg (LHyGeS), UMR 7517, Université  
15     de Strasbourg/ENGEES, CNRS, 1 Rue Blessig, 67084 Strasbourg Cedex, France

16

17

18

19

20

21

22

23     Manuscript for Science of the Total Environment

24 **Abstract**

25         Rainfall and runoff characteristics may influence off-site export of pesticides into  
26 downstream aquatic ecosystems. However, the relationship between rainfall characteristics and  
27 pesticide export from small headwater catchments remains elusive due to confounding factors  
28 including the application dose and timing and the variation of pesticide stocks in soil. Here we  
29 examined the impact of rainfall characteristics on the export of copper (Cu), zinc (Zn) and 12  
30 legacy and currently used synthetic pesticides in surface runoff from a headwater vineyard  
31 catchment. Cluster analysis of rainfall intensity, depth and duration of 78 events revealed four  
32 distinct rainfall categories, i.e., Small, Long, Moderate and Intense ( $p < 0.001$ ). Event mean  
33 concentrations of pesticides did not differ among rainfall categories ( $p > 0.05$ ). In contrast,  
34 event loads of both dissolved and solid-bound Cu and Zn significantly differed among rainfall  
35 categories ( $p < 0.001$ ). Rainfall depth and intensity significantly correlated with both Cu and Zn  
36 loads in runoff ( $\rho_s = 0.33$  to  $0.92$ ,  $p < 0.002$ ), and might be the main drivers of Cu and Zn export  
37 at the catchment scale. In contrast, rainfall depth, intensity or duration did not influence the  
38 loads of synthetic pesticides in runoff, even when weekly variations of pesticide stocks in the  
39 soil were accounted for. However, intense rainfall-runoff events, that can fragment soil, may  
40 control the export of persistent and hydrophobic legacy pesticides stocks in the soil, such as  
41 simazine and tetraconazole. Our results emphasise that rainfall characteristics controlled the  
42 off-site export of Cu, Zn and legacy synthetic pesticides in a small headwater catchment,  
43 whereas the application timing drove the export of currently used synthetic pesticides in  
44 runoff. We anticipate our results to be a preliminary step to forecast the influence of regional  
45 rainfall patterns on the export of both metallic and synthetic pesticides by surface runoff from  
46 small headwater catchments.

47 **Keywords:** Rainfall characteristics, pesticide export, surface runoff, headwater catchment,  
48 copper and zinc in vineyard

49

## 50 **1. Introduction**

51           Surface runoff is a major driver of pesticide transport from agricultural land into aquatic  
52 ecosystems. It exports up to 5% of solid-bound and dissolved pesticides during rainfall-runoff  
53 events (Herrero-Hernández et al., 2017; Parajulee et al., 2018; Lefrancq et al., 2018). Pesticide  
54 export eventually affects drinking water resources and the health of aquatic ecosystems (e.g.,  
55 Zubrod et al., 2019). Pesticide export by runoff is primarily controlled by the interplay between  
56 the dose and timing of pesticide applications, pesticide dissipation in soil and hydrological  
57 characteristics of the catchment (Lefrancq et al. 2017; El Azzi et al., 2016; Meite et al., 2018).  
58 In addition, climate change can substantially influences both hydro-climatic characteristics and  
59 aquatic ecosystems by altering pesticide export from the catchment, as well as the pesticide  
60 fraction dissolved in surface runoff or attached to soil particles during soil erosion (Gagnon et  
61 al., 2016; Qiu et al., 2019). In this context, understanding the impact of rainfall characteristics  
62 on pesticide export from agricultural land becomes crucial to anticipate adaptation strategies to  
63 future regional hydro-climatic patterns.

64           Fungicides, which include various forms of copper (Cu) and synthetic molecules, and  
65 herbicides are massively used in vineyards several times across the growing season (Komárek  
66 et al., 2010). Exports of up to 1% of the yearly-applied fungicide and herbicide amount on  
67 vineyard catchments have been observed previously, although export in surface runoff varies  
68 across the seasons and years (Louchart et al., 2001; Dousset et al., 2007; Lefrancq et al., 2014;  
69 Babcsányi et al., 2016). The dose and timing of application as well as pesticide sorption and  
70 degradation in soil mainly determine pesticide export during rainfall-runoff events (Chen et al.,  
71 2018; Parajulee et al., 2018). In addition, the solid-liquid partitioning of pesticides in soil and  
72 runoff controls the proportion of dissolved and solid-bound exports of pesticides (Babcsányi et  
73 al., 2016; El Azzi et al., 2016). For instance, Cu, zinc (Zn) and hydrophobic synthetic

74 pesticides sorb on soil organic matter (SOM) and soil minerals, such as carbonates and clays.  
75 As a result, Cu and Zn export is associated with dissolved organic matter (DOM) and fine-  
76 grained soil particles in runoff, and mainly occurs during intense rainfall events (Komárek et  
77 al., 2010; Babcsányi et al., 2016; Meite et al., 2018). The relationship between pesticide export  
78 and rainfall depth, intensity or duration remains, however, poorly understood in small  
79 headwater catchments.

80 Knowledge of the influence of hydrological characteristics on pesticide export from  
81 small headwater catchments (<100 km<sup>2</sup>) remains scarce in comparison to large catchments  
82 (>100 km<sup>2</sup>) (Meite et al. 2018; Lefrancq et al., 2017). The role of small headwater catchments  
83 in pesticide export is important since they proportionally receive larger pesticide inputs than  
84 downstream areas (Lorenz et al., 2017). Dynamics of pesticide export in small headwater  
85 catchments are discontinuous and difficult to predict because they depend on rainfall  
86 characteristics, the pesticide application timing and seasonal variations of pesticide stocks in  
87 the catchment soil (Leu et al., 2005; Coupe et al., 2012; Lefrancq et al., 2017; Gassmann et al.,  
88 2015). There are two major difficulties when evaluating the influence of rainfall characteristics  
89 on pesticide export while limiting the influence of other confounding variables. First, a  
90 sufficiently large dataset of rainfall-runoff characteristics and pesticide loads in a headwater  
91 catchment is required to understand pesticide export at the time scale of rainfall-runoff events.  
92 Such data sets are generally missing. Secondly, the variability of pesticide stocks in soil can  
93 counteract the influence of rainfall characteristics. Hence, pesticide export in runoff should be  
94 related to the pesticide stocks in soil to account for the variability of pesticide inputs,  
95 accumulation and dissipation when analyzing variables driving pesticide export.

96 In this context, we embarked on a study to examine the influence of rainfall  
97 characteristics on pesticide export from a small headwater vineyard catchment (42.7 ha). We  
98 hypothesized that distinct rainfall categories, featuring specific characteristics including depth,

99 intensity and duration, result in well-distinct export regimes of inorganic (Cu and Zn) and  
100 synthetic (legacy or currently used) pesticides in runoff. The rainfall-runoff events and the  
101 variation of pesticide stocks in soil were monitored over two wine-growing seasons (2015 and  
102 2016). Four categories of pesticides were selected based on their widespread former and  
103 current use, along with the high frequency of their application and detection in soil and runoff  
104 in the studied catchment (Babcsányi et al., 2016; Lefrancq et al., 2014; Lefrancq et al., 2013;  
105 Maillard and Imfeld, 2014):

- 106 1. Cu and Zn, since grapevines receive many applications during the growing season of Cu-  
107 and Zn-bearing fungicides and amendments. This results in the accumulation of Cu and Zn  
108 in soil over years (Komárek et al., 2010; Babcsányi et al., 2016).
- 109 2. Pre-emergence triazine herbicides, including formulations with active ingredients such as  
110 simazine, atrazine and terbuthylazine. These formulations have been banned since the early  
111 2000's in several EU countries. However, they remain of environmental concern due to  
112 their persistence in vineyard soil and potential to contaminate water bodies (Grégoire et al.,  
113 2010; Hildebrandt et al., 2008; Leu et al., 2005).
- 114 3. Widely-used synthetic fungicides including pyrimethanil, metalaxyl-M, cyprodinil,  
115 kresoxim-methyl, tetraconazole, azoxystrobin, dimethomorph, which are used worldwide  
116 for vine protection. These fungicides belong to different chemical classes, and thus display  
117 a broad-spectrum of physico-chemical properties controlling their transformation in soil  
118 and their export in runoff (Komárek et al., 2010; Zubrod et al., 2019).
- 119 4. Herbicides, such as pendimethalin and pyraflufen-ethyl, which are part of weed control  
120 strategies in vineyards worldwide, are commonly found in surface and ground waters  
121 (Herrero-Hernández et al., 2017).

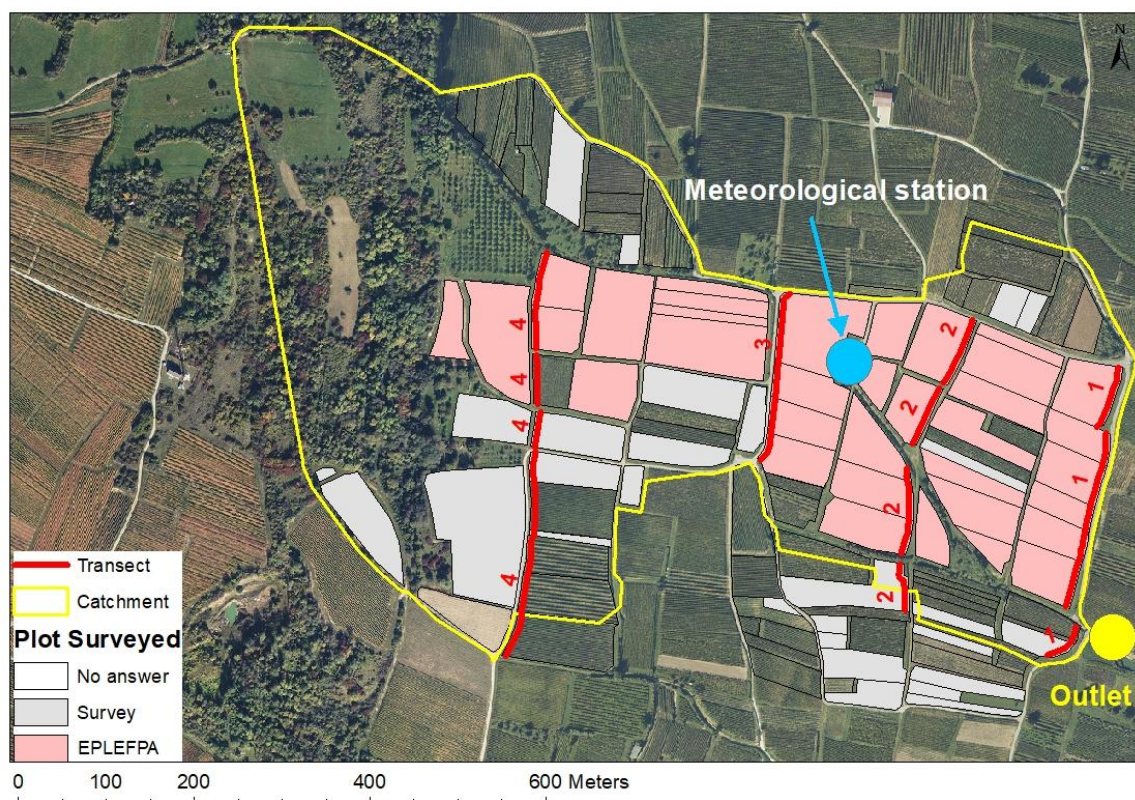
122

123

124 **2. Materials and methods**

125 **2.1. Vineyard catchment description**

126 The 42.7 ha Hohrain vineyard catchment is situated in the Alsatian foothills (47°57'9 N,  
127 07°17'3 E) and representative of northern vineyards (Grégoire et al., 2010; Duplay et al., 2014)  
128 (Figure 1). The catchment has a mean slope of 15%, and is mainly occupied by vineyards  
129 (59%, 25.3 ha), forests and pasture (29%), grassed strips and ditches (7%), as well as roads and  
130 paths (5%). The soil is a calcareous clay loam developed on a loess basement with a bulk  
131 density of 1.4 g cm<sup>-3</sup>. The main soil types are Cambisol (Hypereutric Clayic) and Haplic  
132 Cambisol (Calcaric Siltic) (Duplay et al., 2014). Soil minerals consist of calcite, quartz, and  
133 minor amounts of feldspars, dolomite and clay minerals (Duplay et al., 2014). Vineyard plots  
134 are permanently covered by grass in every second inter-row to limit soil erosion, and grass-free  
135 inter-rows are ploughed up to 5 cm depth to enhance water infiltration. The grass cover was  
136 implemented three to four years after vine planting.



137

138 Figure 1. The Hohrain vineyard catchment (47°57'9 N, 07°17'3 E, Alsace, France). Topsoil  
139 samples were collected weekly from March to October 2015 and 2016 on the catchment across  
140 four transects (in red) to determine monthly average Cu, Zn and weekly synthetic pesticide  
141 concentrations. Dose and frequency of pesticide applications were obtained from surveys  
142 addressed to wine producers of the grey and the pink plots. The pink plots belong to the  
143 Agricultural and Viticulture College of Rouffach, France – EPLEFPA.

144

## 145 **2.2. Vineyard catchment hydrology**

146 Rainfall-runoff events generate intermittent flows in the catchment, which remains dry  
147 otherwise. Discharge at the outlet of the catchment is driven by Hortonian overland flow. The  
148 road network mainly contributes to discharges during rainfall with low intensity (i.e.  $>6$   
149  $\text{mm}\cdot\text{h}^{-1}$ ) (Lefrancq et al., 2014), while vineyard plots contribute when rainfall intensity  
150 overcomes the saturated hydraulic conductivity (i.e.  $58\pm 50 \text{ mm}\cdot\text{h}^{-1}$ ,  $n = 48$ ) (Tournebize et al.,  
151 2012). The saturated hydraulic conductivity can decrease by up to one order of magnitude on  
152 plots when topsoil sealing appears across the season. Grass strips of 2 to 3 m width at the plot  
153 edges limit overland flow on plots (Lefrancq et al., 2014). Fast hydrological response to  
154 rainfall events (i.e., 6 to 12 min between rainfall and runoff peaks) and fast recession period  
155 ( $<1$  h) with total discharge cessation at the outlet of the catchment indicate the prevalence of  
156 Hortonian overland flow. Baseflow is negligible as steep slopes (i.e. 15%) with high vertical  
157 saturated hydraulic conductivity prevent downslope lateral flow.

158

## 159 **2.3. Rainfall monitoring**

160 Rainfall was monitored at a 6-min resolution by a meteorological station (Meteo  
161 France, station n°68287003) located in the catchment (Figure 1). As the hydrological response  
162 time to rainfall event is fast, a rain-free period of 2 h between two rainfall events was used to



163 differentiate the events. Annual rainfall averaged  $635\pm 118$  mm (1998-2016), with 521 and 733  
164 mm in 2015 and 2016, respectively. During the vine-growing season from March to October,  
165 rainfall averaged  $437\pm 91$  mm (1998-2016), with 375 and 434 mm in 2015 and 2016,  
166 respectively.

167

#### 168 **2.4. Survey of pesticide applications**

169 Dose and frequency of pesticide applications were obtained from surveys addressed to  
170 wine producers of the catchment in 2015 and 2016. Answers from producers covered 75% and  
171 74% of the total vineyard area in 2015 and 2016, respectively (Figure 1). Dose and timing of  
172 applications were extrapolated for the non-surveyed area to calculate the seasonal Cu, Zn and  
173 pesticide applications. Amounts applied in 2015 and 2016 and characteristics of Cu, Zn and the  
174 12 synthetic pesticides are provided in Table 1 and in Table S1, respectively.

175

#### 176 **2.5. Soil and runoff sampling**

177 Topsoil samples (0-1cm) were collected weekly from March to October 2015 and 2016  
178 across four transects on the catchment to quantify synthetic pesticides (Figure 1). The top 1 cm  
179 of soil was considered as the relevant soil layer for estimating stocks of synthetic pesticides  
180 that can be exported by runoff since these pesticides concentrate and dissipate in this layer  
181 between soil management operations (Havis et al., 1992; Zhang et al., 1997, 1999). For Cu and  
182 Zn, topsoil samples (0-5 cm) were collected monthly from March to October 2015 and 2016  
183 across the same transects. The top 5 cm of soil was considered as the relevant soil layer to  
184 estimate Cu and Zn stocks in soil. Indeed, Cu and Zn concentrate in this layer and are  
185 influenced by yearly soil management practices homogenising topsoil Cu and Zn  
186 concentrations (Babcsányi et al., 2016). The weekly (synthetic pesticides) and monthly (Cu and  
187 Zn) composite samples (1 kg) were composed of mixed topsoil sub-samples collected each 10

188 m across the four transects. Soil samples were transported in coolers and stored at 4°C until  
189 analysis.

190 Automatic runoff measurement and water sampling at the outlet of the catchment  
191 (Figure 1) was carried out from March 26<sup>th</sup> to October 6<sup>th</sup> 2015 and from March 30<sup>th</sup> to October  
192 10<sup>th</sup> 2016, as previously described (Maillard and Imfeld, 2014). The procedure of sample  
193 collection and storage for pesticide analysis was previously validated (Domange and Grégoire,  
194 2006; Grégoire et al., 2010). Water depth was measured using bubbler flow modules  
195 (Hydrologic, Sainte-Foy, Québec, Canada) combined with a Venturi channel to monitor  
196 discharge runoff, with an uncertainty of  $\pm 8\%$ . Flow proportional samples of runoff water (300  
197 mL every 6 m<sup>3</sup>) were collected during each runoff event using a 4010 Hydrologic automatic  
198 sampler (Hydrologic, Canada). Runoff water was collected in a 24-bottles sampler alternating  
199 pre-cleaned glass bottles for synthetic pesticides and PEHD bottles for Cu and Zn in order to  
200 limit sorption. Flow-proportional runoff water samples were thus collected separately for  
201 synthetic and metallic pesticide measurements. Water samples were immediately stored in  
202 coolers and transported to the laboratory, filtered using a 0.45- $\mu\text{m}$  glass filter membrane, and  
203 frozen ( $-20^{\circ}\text{C}$ ) until extraction and pesticide analysis.

204

## 205 **2.6. Chemical analyses**

### 206 **2.6.1. Cu and Zn quantification**

207 Cu and Zn were quantified in soil, the dissolved phase and the suspended solids of  
208 runoff, as described elsewhere (Lucas et al., 2010; Babcsányi et al., 2014). Briefly, solid  
209 samples were oven-dried (60°C), sieved (2 mm) and powdered using an agate disk mill (<100  
210  $\mu\text{m}$ ) prior to total dissolution of Cu and Zn by double distilled nitric acid under laminar fume  
211 hood in a clean-room. Filtered runoff water was acidified to pH 2 using double distilled nitric  
212 acid. Measurements were carried out using an ICP-AES (ICAP6500, Thermo Fisher

213 Scientific) with geological standards BCR-2 (US Geological survey, Reston, VA, USA) and  
214 SCL-7003 (Analytika, Prague, Czech Republic) for quality control (Babcsányi et al., 2014).  
215 The total analytical uncertainty was  $\pm 5\%$ . Detection (DL) and quantification (QL) limits are  
216 provided in Table S2.

217

### 218 **2.6.2. Synthetic pesticides**

219 Synthetic pesticides were extracted from soil using a sequential solvent extraction and  
220 cleanup procedure as described earlier (Masbou et al., 2018). Runoff water samples were  
221 filtered using a 0.45- $\mu\text{m}$  glass filter membrane. Filtered water samples were extracted by solid-  
222 phase extraction (SPE) using SolEx C18 cartridges (Dionex®, Sunnyvale, CA, USA) and an  
223 AutoTrace 280 SPE system (Dionex®) using a protocol adapted from US EPA method 525.2  
224 and described previously (Elsayed et al., 2014). Synthetic fungicides and herbicides were  
225 quantified by gas chromatography (Trace 1300, Thermo Fisher Scientific, Milan Italy) coupled  
226 with a mass spectrometer (ISQ™, Thermo Fisher Scientific), using isotope-labelled internal  
227 standards of pesticides. Extraction recoveries, DL and QL from water and soil samples are  
228 provided in Table S2.

229 Solid-bound synthetic pesticides were not accounted for in this study because (i) loads  
230 of dissolved pesticides predominate in the studied catchment (Maillard and Imfeld, 2014) and  
231 are preferentially transported to aquatic ecosystems, (ii) loads of total suspended solids in  
232 runoff were modest ( $\bar{X} \pm \sigma$ :  $3.1 \pm 1.5 \text{ g L}^{-1}$ ), and (iii) concentrations were too low ( $< 0.004 \mu\text{g g}^{-1}$ )  
233 for quantification of most pesticides. This limited in our case the relevance to evaluate the  
234 influence of rainfall characteristics on loads of solid-bound synthetic pesticides.

235

236

237

238       **2.7. Data analysis**

239               **2.7.1. Pesticide stocks in soil**

240               The stocks of Cu, Zn and synthetic pesticides in soil of the vineyard catchment were  
241 estimated weekly across the investigation periods in 2015 and 2016 based on the average  
242 pesticide concentrations in soil and the mass of topsoil (Babcsányi et al., 2016). Pesticide stock  
243 estimates were then used to calculate metrics of pesticide export that account for pesticide  
244 stocks (see below). All pesticides were detected in the soil at least once during the study  
245 period. Cu and Zn were systematically quantified. Synthetic pesticide concentrations were  
246 conservatively set at the DL when no pesticide was detected to estimate and account for the  
247 maximal weekly stocks in soil. Correspondingly, synthetic pesticide concentrations were set at  
248 the QL when pesticides concentrations were below the QL but above the DL.

249

250               **2.7.2. Cluster analysis of rainfall events**

251               The hydrological data set comprises 78 rainfall-runoff events. The 78 events  
252 represented 69% in 2015 and 76% in 2016 of the total rainfall depth that generated runoff  
253 during the study period (see Table S3). The 78 rainfall events were categorized based on depth,  
254 maximum intensity and duration data using the R software (R Development Core Team, 2008;  
255 Version 3.5.3). Values were standardized prior to calculation of the distance between rainfall  
256 events based on the Euclidean dissimilarity index (Legendre and Gallagher, 2001). A  
257 hierarchical cluster analysis was performed on the resulting dissimilarity matrix using the  
258 Ward's method. The optimal number of clusters was determined using the Spearman's rank  
259 correlation applied to the binary distance matrix from clusters (Becker et al., 1988). The  
260 obtained clusters correspond to distinct categories of rainfall events, with events in each  
261 category featuring similar rainfall characteristics.

262

263 **2.7.3. Metrics of pesticide export**

264 Four metrics of pesticide export were calculated to compare the influence of rainfall  
265 characteristics on pesticide export from the vineyard catchment.

266 **Event Load.** The Event Load of Cu, Zn and synthetic pesticides ( $EL_p$ ) was calculated  
267 for each event by multiplying the flow-proportional concentration of each pesticide by the  
268 corresponding runoff volume:

269 
$$EL_p = \sum_{i=1}^n C_{pi} V_i \quad (1)$$

270 where  $EL_p$  is the event load for a pesticide  $p$  (in [g] for Cu and Zn, and [mg] for synthetic  
271 pesticides),  $C_{pi}$  is the concentration of  $p$  of the  $i^{\text{th}}$  sample, and  $V_i$  is the corresponding portion of  
272 runoff volume [ $\text{m}^3$ ]. Dissolved and solid-bound  $EL_p$  were calculated for Cu and Zn, whereas  
273 only dissolved  $EL_p$  were calculated for synthetic pesticides.

274

275 **Event Mean Concentration.** The Event Mean Concentration of each pesticide ( $EMC_p$ ) was  
276 calculated for each event according to equation 2:

277 
$$EMC_p = \frac{EL_p}{V} \quad (2)$$

278 where ( $V$ ) is the total volume of the runoff event.

279

280 **Event Export coefficient.** The pesticide event export coefficient ( $EEC_p$ , in [%]) was  
281 calculated for the synthetic pesticides to account for the weekly variation of pesticide stocks in  
282 the vineyard topsoil across the season:

283 
$$EEC_p = 100 \times \frac{EL_p}{Top\ soil\ mass_{wp}} \quad (3)$$

284 where  $Top\ soil\ mass_{wp}$  is the weekly stock of synthetic pesticides in the vineyard soil.

285 Cu and Zn exports by runoff were not related to variations of Cu and Zn stocks in the vineyard  
286 soil because seasonal applications on the catchment represented less than 3% of the initial  
287 stock of Zn and Cu in soil. Hence, minor variations of the monthly stocks of Cu and Zn in  
288 topsoil could not be quantified given the uncertainty of Cu and Zn quantification (5%)  
289 (Babcsányi et al., 2016).

290  
291 **Freshly Applied pesticide Normalized Export Coefficient.** The Freshly Applied  
292 Pesticide Normalized Export Coefficient ( $FANEC_p$ , in [%]) was calculated for each currently  
293 used synthetic pesticides to account for the fraction of freshly applied pesticides. The FANEC  
294 accounts for the difference between the weekly stock of applied pesticide and the initial  
295 background of pesticide in soil:

$$296 \quad FANEC_p = 100 \times \frac{EL_p}{(Top\ soil\ mass_{wp} - Top\ soil\ mass_p\ background)} \quad (4)$$

297 where  $Topsoil\ mass_p\ background$  is the initial mass background amount of pesticide  $p$  in the  
298 soil before pesticide application.

299  
300 **2.7.4. Statistical analysis of pesticide metrics**

301 Non-parametric Kruskal-Wallis and pair-wise Wilcoxon rank sum tests were used to  
302 compare the influence of rainfall categories on pesticide export. Rank-based Spearman's test  
303 was used to assess the correlation between rainfall and runoff characteristics and metrics of  
304 pesticide export. The Bonferroni correction was used to limit the effect of multiple  
305 comparisons by testing each individual hypothesis at a significance level of  $\alpha/m=0.05/4=0.013$ ,  
306 with  $m=4$  rainfall categories.

307  
308

### 309 **3. Results and discussion**

#### 310 **3.1. Pesticide applications and stocks in vineyard soil**

311 The following pesticides, ordered from the heaviest to the lightest mass, were applied in  
312 2015 and 2016: Cu > Zn > dimethomorph > cyprodinil > Pyrimethanil > tetraconazole >  
313 pyraflufen-ethyl (Table 1). Cyprodinil and krezoxim-methyl were exclusively applied in 2015,  
314 while pyrimethanil was only applied in 2016. Overall, 2.223 and 2.158 kg·ha<sup>-1</sup> of vineyard of  
315 elemental Cu and 0.116 and 0.349 kg·ha<sup>-1</sup> of vineyard of elemental Zn were applied on the  
316 catchment in 2015 and 2016, respectively (Table 1). The influence of successive applications  
317 of Cu and Zn across the season on the overall stocks at the catchment scale could not be  
318 quantified since concentrations in the soil remained constant ( $\pm 12\%$ ). Average topsoil Cu and  
319 Zn concentrations and masses in the catchment were similar to those observed in 2011  
320 (Babcsányi et al., 2016). This indicates that soil stocks of Cu and Zn, did not vary much over  
321 the last five years since it built up after several decades of vine management and off-site export  
322 remains limited (see below). In contrast, application timing and doses drove topsoil  
323 concentrations and masses of synthetic pesticides in soil (Figure 2).

324 **Table 1.** Pesticide applications, stocks in soil and export in the Hohrain catchment (Rouffach, France; 25.3 hectare of vineyards) from March 26<sup>th</sup>  
 325 to October 6<sup>th</sup> 2015 and from March 30<sup>th</sup> to October 10<sup>th</sup> 2016.  
 326

|  | Dissolved Cu                            | Particulate Cu | Dissolved Zn                            | Particulate Zn | Simazine           | Atrazine           | Terbutylazine      | Pyrimethanil       | Metaxyl-M | Cyprodinil         | Krezoxim-methyl    | Tetraconazole | Azoxystrobin       | Dimethomorph | Pendimethalin      | Pyraflufen-ethyl   |
|--|---|----------------|---|----------------|--------------------|--------------------|--------------------|--------------------|-----------|--------------------|--------------------|---------------|--------------------|--------------|--------------------|--------------------|
| <b>Applied 2015</b><br>[kg: Cu and Zn and g: synthetic pest.]                              | 56.4*                                   |                | 2.9*                                    |                | ⊖                  | ⊖                  | ⊖                  | n.a                | n.a       | 3163               | 55.3               | 11.1          | n.a                | 118.8        | n.a                | 10.6               |
| <b>Applied 2016</b><br>[kg: Cu and Zn and g: synthetic pest.]                              | 54.6*                                   |                | 8.8*                                    |                | 2001               | 2003               | 2004               | 572.3              | n.a       | n.a                | n.a                | 142.4         | n.a                | 5406         | n.a                | 0.2                |
| <b>Initial topsoil conc. 2015<sup>c</sup></b><br>[mg·kg <sup>-1</sup> <sub>drysoil</sub> ] | 154*                                    |                | 112*                                    |                | 0.001 <sup>b</sup> | 0.001 <sup>b</sup> | 0.07               | 0.057              | 0.013     | 0.03               | 0.001 <sup>b</sup> | 0.071         | 0.037              | 0.021        | 0.001 <sup>b</sup> | 0.001 <sup>b</sup> |
| <b>Initial topsoil conc. 2016<sup>c</sup></b><br>[mg·kg <sup>-1</sup> <sub>drysoil</sub> ] | 120*                                    |                | 80*                                     |                | 0.003 <sup>a</sup> | 0.001 <sup>b</sup> | 0.003 <sup>a</sup> | 0.004 <sup>a</sup> | 0.011     | 0.002 <sup>a</sup> | 0.002 <sup>a</sup> | 0.021         | 0.001 <sup>b</sup> | 0.065        | 0.002 <sup>a</sup> | 0.001 <sup>b</sup> |
| <b>Initial topsoil mass 2015<sup>c</sup></b><br>[kg: Cu and Zn and g: synthetic pest.]     | 2727*                                   |                | 1983*                                   |                | 3.6 <sup>b</sup>   | 4.1 <sup>b</sup>   | 249.7              | 203.5              | 45.5      | 95.3               | 1.9 <sup>b</sup>   | 252.3         | 131.2              | 99.5         | 1.6 <sup>b</sup>   | 3.3 <sup>b</sup>   |
| <b>Initial topsoil mass 2016<sup>c</sup></b><br>[kg: Cu and Zn and g: synthetic pest.]     | 2125*                                   |                | 1417*                                   |                | 10.9 <sup>a</sup>  | 4.1 <sup>b</sup>   | 10.0 <sup>a</sup>  | 13.6 <sup>a</sup>  | 37.2      | 4.6 <sup>a</sup>   | 5.7 <sup>a</sup>   | 74.7          | 2.7 <sup>b</sup>   | 230.2        | 4.9 <sup>a</sup>   | 3.3 <sup>b</sup>   |
| <b>Detection frequency in runoff 2015<sup>d</sup></b> [%]                                  | 100                                     | 100            | 100                                     | 100            | 31                 | 3                  | 3                  | 66                 | 63        | 22                 | 44                 | 31            | 22                 | 63           | 44                 | 3                  |
| <b>Detection frequency in runoff 2016<sup>e</sup></b> [%]                                  | 100                                     | 100            | 100                                     | 100            | 2                  | 0                  | 20                 | 63                 | 54        | 35                 | 20                 | 78            | 46                 | 80           | 28                 | 0                  |
| <b>Load 2015<sup>d</sup></b><br>[kg: Cu and Zn and mg: synthetic pest.]                    | 4×10 <sup>-2</sup>                      | 1.41           | 2×10 <sup>-2</sup>                      | 1.54           | 46.3               | 8.0                | 27.5               | 473.2              | 110.9     | 52.3               | 72.4               | 67.5          | 27.7               | 2301         | 205.6              | 1.2                |
| <b>Load 2016<sup>e</sup></b><br>[kg: Cu and Zn and mg: synthetic pest.]                    | 3×10 <sup>-2</sup>                      | 1.63           | 3×10 <sup>-2</sup>                      | 1.76           | 1.97               | 0                  | 116.7              | 673.4              | 1288      | 58.4               | 29.9               | 142.2         | 58.7               | 4712         | 251.7              | 0                  |
| <b>Event Export coefficients (EEC<sub>p</sub>) 2015<sup>d</sup></b><br>[%]                 | 1×10 <sup>-5</sup> -1×10 <sup>-2f</sup> |                | 5×10 <sup>-6</sup> -1×10 <sup>-2f</sup> |                | 0-0.42             | 0-0.20             | 0-0.84             | 0-0.05             | 0-0.09    | 0-0.03             | 0-1.18             | 0-0.03        | 0-0.54             | 0-0.70       | 0-8.07             | 0-0.04             |
| <b>Event Export coefficients (EEC<sub>p</sub>) 2016<sup>e</sup></b><br>[%]                 | 5×10 <sup>-6</sup> -4×10 <sup>-2f</sup> |                | 5×10 <sup>-5</sup> -7×10 <sup>-2f</sup> |                | 0-0.06             | 0                  | 0-1.4              | 0-1.34             | 0-12.6    | 0-2.35             | 0-0.47             | 0-0.64        | 0-0.32             | 0-0.2        | 0-10.75            | 0                  |

\*Total Cu or Zn

⊖: banned. n.a: not applied, based on the survey covering 75% and 74% of the total vineyard area in 2015 and 2016, respectively. <sup>a</sup>Based on QL. <sup>b</sup>Based on DL. <sup>c</sup>Based on 0-5 cm topsoil layer for Cu and Zn and on 0-1 cm for the synthetic pesticides. <sup>d</sup>Based on the 32 runoff events monitored in 2015. <sup>e</sup>Based on the 46 runoff events monitored in 2016. <sup>f</sup>EEC<sub>p</sub> for total Cu and total Zn was calculated assuming a constant yearly initial topsoil mass.

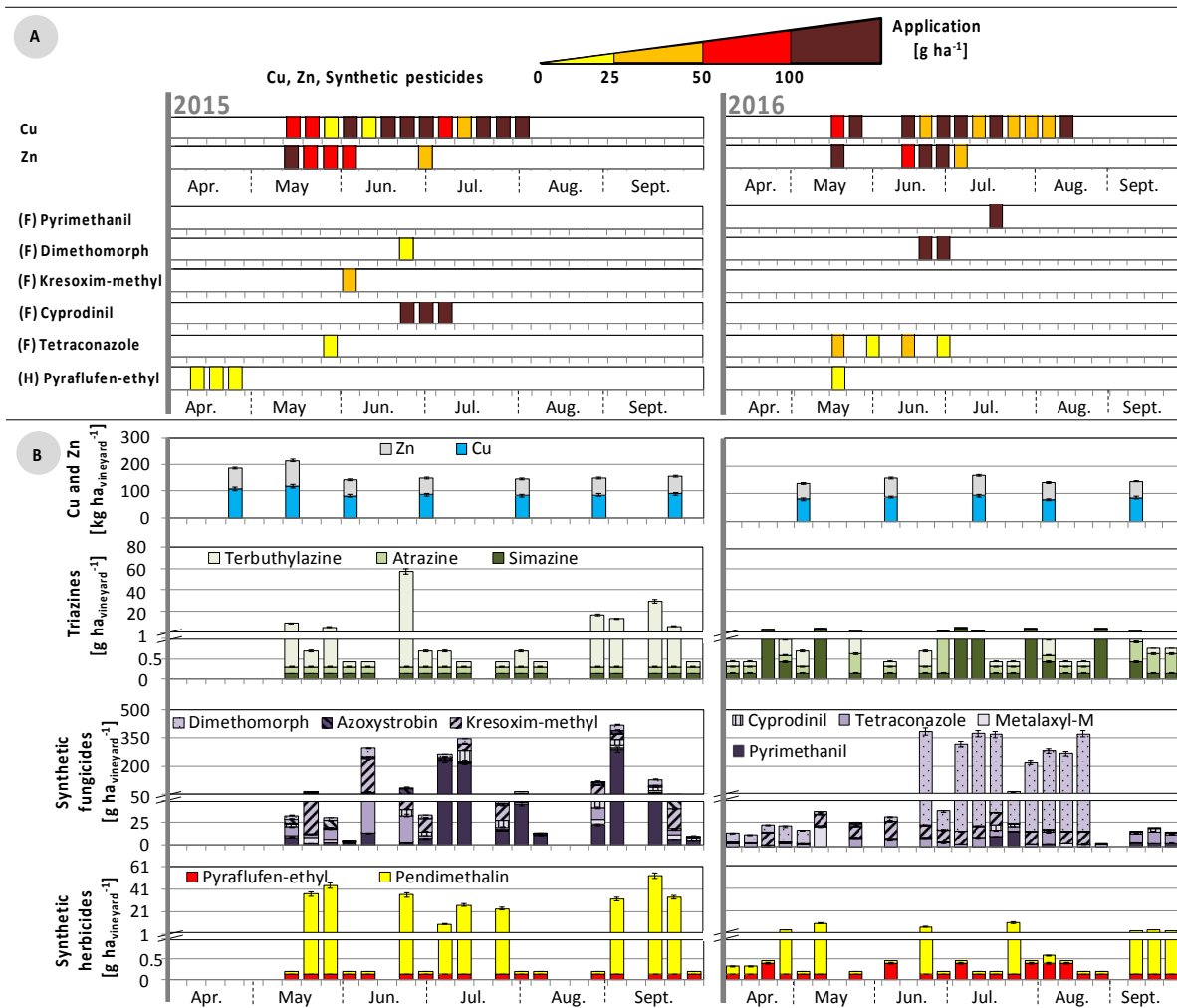


327 In total, 3.359 kg ( $0.133 \text{ kg}\cdot\text{ha}_{\text{vineyard}}^{-1}$ ) and 6.121 kg ( $0.242 \text{ kg}\cdot\text{ha}_{\text{vineyard}}^{-1}$ ) of the twelve  
328 synthetic pesticides were applied on the vineyard catchment in 2015 and 2016, respectively.  
329 Cyprodinil (3.163 kg) was the main fungicide used in 2015, while dimethomorph (5.406 kg)  
330 mainly contributed to pesticide applications in 2016. Worthy of note, polar pesticides applied  
331 on the catchment, i.e. carbendazim, cymoxanil, isoproturon, diuron, isoxaben, oryzalin and  
332 flufenoxuron, were systematically below the DL in both soil and runoff samples (data not  
333 shown) and thus were not considered in this study.

334 Weekly topsoil concentrations of synthetic fungicides and herbicides greatly varied  
335 over the season and ranged from below DL, such as atrazine, simazine, kresoxim-methyl,  
336 pendimethalin, pyraflufen-ethyl in 2015 and azoxystrobin and pyraflufen-ethyl in 2016, up to  
337  $2.57 \text{ mg}\cdot\text{kg}^{-1}$  for dimethomorph in 2016. Stocks of legacy herbicides simazine ( $538\pm 1053$   
338  $\text{mg}\cdot\text{ha}^{-1}$  vineyard) and atrazine ( $189\pm 94 \text{ mg}\cdot\text{ha}^{-1}$  vineyard) remained low across the season or  
339 years compared to the other applied synthetic pesticides. This indicates that the legacy pool of  
340 triazine herbicides persists in the soil and can be progressively released during rainfall-runoff  
341 events. Surprisingly, soil concentrations of the legacy herbicide terbuthylazine in 2015 (banned  
342 in 2004) were similar to those of the currently used pesticides. This suggests illegal use of  
343 terbuthylazine after 2004 in some vineyard plots.

344 Overall, the weekly stocks of pesticide in soil widely varied across the season  
345 depending on the timing of pesticide application and the characteristics of pesticides (Figure  
346 2B and Table S1). The herbicide pyraflufen-ethyl was typically applied in early summer, while  
347 fungicides were applied from early summer (e.g. tetraconazole and kresoxim-methyl) to mid-  
348 and late summer (Figure 2A). Pesticide stocks exceeding 100 g in the catchment topsoil  
349 included the following pesticides, ordered from heaviest to lightest amount in soil:  
350 tetraconazole > terbuthylazine > pyrimethanil > azoxystrobin in 2015, and dimethomorph in  
351 2016 (Table 1). Half-lives of pesticides in soil, estimated based on soil concentrations and

352 sorted here from smallest to largest half-lives, generally were similar or lower compared to  
 353 reference half-lives (Table S1): pyraflufen-ethyl (< 1 d) < pendimethalin (3 d) < pyrimethanil  
 354 (8 d) = azoxystrobin (8 d) < dimethomorph (9 d) < metalaxyl-M (14 d) < tetraconazole (27 d) <  
 355 kesoxim-methyl (50 d) < cyprodinil (92 d).  
 356



357  
 358 **Figure 2.** Applications and stocks of Cu, Zn and synthetic pesticides in the Hohrain catchment  
 359 (Rouffach, France) in 2015 and 2016. **A)** Weekly Cu, Zn and synthetic pesticides applications  
 360 (in grams per hectare of vineyard). **B)** Weekly stocks of synthetic pesticide and monthly stocks  
 361 of Cu and Zn in the vineyard soil. F = fungicide, H = herbicide. The error given for pesticide  
 362 stocks in soil was calculated based on the analytical uncertainty of pesticide measurements  
 363 (Table S2).

364 To sum up, Cu and Zn stocks in soil did not vary much across the season, although  
365 accumulation of Cu and Zn after decades of wine growing can increase the legacy stocks in  
366 vineyard catchments (Komárek et al., 2010). In contrast, stocks of currently applied synthetic  
367 pesticides varied as a function of the application dose and timing (Figure 2) but also of the  
368 dissipation in soil, as previously observed (Moser et al., 2018; Parajulee et al., 2018). Hence,  
369 the variation of synthetic pesticide stocks at the catchment scale should be considered to  
370 evaluate the influence of rainfall characteristics on pesticide export.

371

### 372 **3.2. Rainfall categories**

373 The cluster analysis of the 78 rainfall events created four different rainfall categories  
374 ( $p < 0.001$ ; Table 2 and Table S4, Figure 2). Each category has specific rainfall depth, intensity  
375 and duration characteristics, hereby referred to as Small ( $n = 40$ ), Moderate ( $n = 18$ ), Intense ( $n$   
376  $= 8$ ) and Long ( $n = 12$ ) rainfall events. Overall, maximal rainfall intensities, depths and  
377 durations, but also runoff volumes, maximum discharges and runoff durations differed among  
378 rainfall categories ( $p < 0.001$ ; see Table S4). This confirms that cluster analysis could  
379 disentangle distinct categories of rainfall-runoff events. At least two rainfall characteristics  
380 systematically differed among rainfall categories. However, no significant difference was  
381 found for rainfall depth generated by Long and Intense events, for maximum rainfall intensities  
382 of Small and Long as well as for Moderate and Long events, and for rainfall duration of Small  
383 and Intense categories ( $p > 0.05$ ) (Table S5).

384 The Small category included short (6 to 270 min), less intense events (mean intensity:  
385  $3.0 \pm 3.9 \text{ mm} \cdot \text{h}^{-1}$ ), with a rainfall depth lower than 8.6 mm (Table 2). The Moderate category  
386 included events with similar or higher characteristic values than those of the Small category but  
387 with longer rainfall durations (Table 2 and Table S6). Intense rainfalls were characterized by  
388 high mean rainfall intensities ( $16.3 \pm 16.2 \text{ mm} \cdot \text{h}^{-1}$ ) and rainfall depths similar to those of Long

389 rainfalls. Long events had longer durations (354 to 1554 min), larger rainfall depth (16.8±9.7  
 390 mm) and maximum intensities similar to those of Moderate and Intense categories. We tested  
 391 whether these categories resulted in significantly different export of Cu, Zn and synthetic  
 392 pesticides in runoff.

393

394 **Table 2.** Characteristics of Small, Moderate, Intense and Long rainfall and runoff categories  
 395 (Hohrain catchment, France). Minimum-maximum ranges are provided.

| Rainfall category        |                       | Small         | Moderate   | Intense      | Long         |
|--------------------------|-----------------------|---------------|------------|--------------|--------------|
| <i>n</i>                 |                       | 40            | 18         | 8            | 12           |
| <b>Rainfall depth</b>    | [mm]                  | 0.6 - 8.6     | 1.4 - 10.4 | 5.5 - 56.3   | 3.4 - 36.1   |
| <b>Mean intensity</b>    | [mm·h <sup>-1</sup> ] | 0.4 - 19      | 0.4 - 1.6  | 2.9 - 42     | 0.3 - 3.8    |
| <b>Max intensity</b>     | [mm·h <sup>-1</sup> ] | 2 - 18        | 2 - 8      | 32 - 114     | 2 - 57       |
| <b>Rainfall duration</b> | [min]                 | 6 - 270       | 216 - 480  | 18 - 630     | 354 - 1554   |
| <b>Discharge volume</b>  | [m <sup>3</sup> ]     | 0.3 -<br>27.5 | 1.7 - 90.6 | 40.9 - 773.1 | 7.2 - 295.1  |
| <b>Mean discharge</b>    | [L·s <sup>-1</sup> ]  | 0 - 2.5       | 0.1 - 5.7  | 1.9 - 18.3   | 0.2 - 12.3   |
| <b>Max discharge</b>     | [L·s <sup>-1</sup> ]  | 0.1 -<br>10.6 | 0.2 - 14.9 | 20.1 - 166.5 | 0.9 - 90.2   |
| <b>Runoff duration</b>   | [mn]                  | 31 - 558      | 191 - 662  | 155 - 703.3  | 251.9 - 1553 |

396

### 397 3.3. Cu and Zn export and impact of rainfall characteristics

398 Concentrations of dissolved Cu and Zn in runoff (<0.45 µm particle-size fraction)  
 399 ranged, respectively, from 9.0 to 70 µg·L<sup>-1</sup> ( $\bar{X}\pm\sigma$ : 18.2±18.1 µg·L<sup>-1</sup>) and from 3.0 to 182 µg·L<sup>-1</sup>  
 400 (38.6±51.1 µg·L<sup>-1</sup>). Event mean concentrations and loads for each rainfall category are  
 401 displayed in Table S7. These values were one order of magnitude higher than average  
 402 dissolved concentrations of Cu in rivers worldwide (Vance et al., 2008). While Cu  
 403 concentrations exceeded the US Environmental Protection Agency (EPA) recommendations  
 404 for aquatic environments (chronic level: 9 µg·L<sup>-1</sup>; acute level: 13 µg·L<sup>-1</sup>, respectively), Zn  
 405 concentrations generally were below recommended values (chronic level: 120 µg·L<sup>-1</sup>; acute  
 406 level: 90 µg·L<sup>-1</sup>, respectively). Event export coefficients ( $EEC_p$ ) of dissolved Cu and Zn range

407 from  $5 \times 10^{-6}\%$  to  $<7 \times 10^{-2}\%$ , and were lower or in the same range as those of synthetic  
408 pesticides (Table 1).

409 Overall, our results indicate that rainfall characteristics influenced the export of total  
410 suspended solids (TSS), which in turn governed the export of solid-bound Cu and Zn in runoff  
411 (Figure 3, Table S8 and S9). Event loads ( $EL_p$ ) of TSS, Cu and Zn significantly differed among  
412 rainfall categories ( $p < 0.001$ ; Figure 4 and Table S8). In particular,  $EL_p$  of TSS, Cu and Zn  
413 differed between Small events and Long or Intense rainfall events ( $p < 0.001$ ; Table S9). Long  
414 and Intense runoff events generally resulted in larger soil erosion than Small and Moderate  
415 events since greater raindrop energy and/or runoff amount carry larger soil particles  
416 (Mohammad et al., 2018). Larger soil erosion resulted in proportionally greater export of solid-  
417 bound Cu and Zn in runoff because Cu and Zn were predominantly associated with suspended  
418 solids. Indeed, the export of solid-bound Cu and Zn ( $>0.45 \mu\text{m}$  fraction of runoff) represented  
419 98% (Cu) and 95% (Zn) of the total export for the 78 events (Figure 3). The large contribution  
420 of solid-bound export of Cu and Zn during Intense or Long storm events has major  
421 implications for off-site export towards aquatic ecosystems and runoff management. Buffer  
422 areas within the catchment, such as stormwater wetlands or ponds, may help limiting Cu and  
423 Zn export in runoff. Indeed, solid-bound Cu and Zn in runoff are more efficiently retained  
424 ( $>80\%$ ) in buffer areas than dissolved Cu and Zn (Babcsányi et al., 2014).



425

426

427

428

429

430

431

432

433

434

435

436

437

438

**Figure 3.** Rainfall, discharge and normalized loads of Cu, Zn and synthetic pesticides exported from the vineyard catchment (Rouffach, France; 25.3 hectares of vineyards). 32 and 46 events were monitored in 2015 and 2016, respectively. The error given for discharge measurements corresponds to the measurement precision (8%). The errors given for the pesticide loads were calculated *via* error propagation and incorporate errors associated with discharge measurements and pesticide quantification (see Table S2).

Dissolved Cu and Zn in runoff (<0.45  $\mu\text{m}$  fraction) mainly consist of Cu- and Zn-DOM complexes that can be easily transported into hydrologically connected streams and rivers (Babcsányi et al., 2016). Indeed, mixing of topsoil, soil solution and runoff water during long events and soil fragmentation by raindrop splash during intense events can solubilize and mobilize Cu- and Zn-DOM complexes from the vineyard soil (Jarvis, 2007). This in turn can enhance the transport of lighter aggregate materials during rainfall-runoff events, including Cu-

439 and Zn-DOM complexes associated with the clay and silt fractions. Minteq speciation  
440 modelling with Nica-Donnan and Stockholm Humic models (data not shown) confirmed Cu  
441 and Zn complexation with DOM at pH values above 7 in the dissolved phase of runoff  
442 (Thompson and Ellwood, 2014; Vance et al., 2008).  $EL_p$  of TSS, dissolved and solid-bound Cu  
443 and Zn positively correlated with rainfall depth, intensity and duration ( $\rho_s=0.33$  to  $0.92$ ,  
444  $p<0.002$ ; Figure 3 and Table S10). This is in agreement with the general observation that Cu  
445 loss increases with larger rainfall events and vineyard soil erosion (Komárek et al., 2010;  
446 Babcsányi et al., 2016; Meite et al., 2018). In the present study, correlations between additional  
447 hydrological variables and export of Cu, Zn and synthetic pesticide could be examined.

448 Strong correlations ( $\rho_s=0.73$  to  $0.86$ ,  $p<0.001$ ; Table S10) between rainfall depth and  
449  $EL_p$  of TSS and both dissolved and solid-bound Cu and Zn suggest that rainfall depth is a good  
450 predictor of Cu and Zn export from vineyard headwater catchments. Primary hydrological  
451 signals, such as rainfall depth, may thus prevail over the effect of agricultural practices or dose  
452 and timing of application to determine the export of Cu and Zn in runoff. The strong  
453 relationship between rainfall depth and Cu and Zn export also underscores the relative  
454 homogeneity of Cu and Zn concentrations in the soil across the catchment and over time, as  
455 well as rainfall-proportional export of Cu and Zn whenever runoff is generated.

456 Cu and Zn exports followed a typical pattern of chemostatic export. Chemostatic export  
457 is characterized by limited seasonal and inter-annual variation in concentrations compared to  
458 discharge due to large stocks of Cu and Zn in vineyard soil (Basu et al., 2011). The absence of  
459 significant difference between  $EMC_p$  of Cu and Zn among rainfall categories ( $p>0.05$ ; Table  
460 S8), similar  $EEC_p$  in 2015 and 2016 (Table 1) and the strong positive correlation between  
461 seasonal dissolved loads of Cu and Zn and runoff volume ( $\rho_s>0.74$ ,  $p<0.001$ , Table S10)  
462 altogether suggest the dominance of chemostatic export of Cu and Zn in this vineyard  
463 catchment. The legacy sources of Cu and Zn built up after several decades of vine management

464 are thus gradually released back into the dissolved phase of runoff. The depletion of Cu and Zn  
465 stocks by successive export during rainfall-runoff event is, however, compensated by Cu and  
466 Zn applications. As a result, export of Cu and Zn occurs whenever runoff is generated, while  
467 concentrations in runoff are constant or slightly increase over time due to the inter-annual  
468 accumulation in soil. For instance, the range of dissolved Cu concentrations was slightly higher  
469 in 2015 and 2016 (9.0 to 69.5  $\mu\text{g L}^{-1}$ ) compared to 2011 (7.7 to 32.0  $\mu\text{g L}^{-1}$ ; Babcsányi et al.,  
470 2014).

471 The large influence of hydrological properties on Cu and Zn export at the scale of this  
472 headwater catchment may help to develop simple predictive tools of Cu and Zn export from  
473 vineyard catchments based on hydrologic (Moser et al., 2018) and/or TSS data. From a  
474 conceptual viewpoint, anthropic modifications of the vineyard headwater catchment seem to  
475 overwhelm the local biophysical systems into a structurally and biogeochemically less complex  
476 and more homogeneous system (Basu et al., 2011). Such system might be more predictable in  
477 the case of Cu and Zn export.

478

#### 479 **3.4. Export of synthetic pesticides and impact of rainfall characteristics**

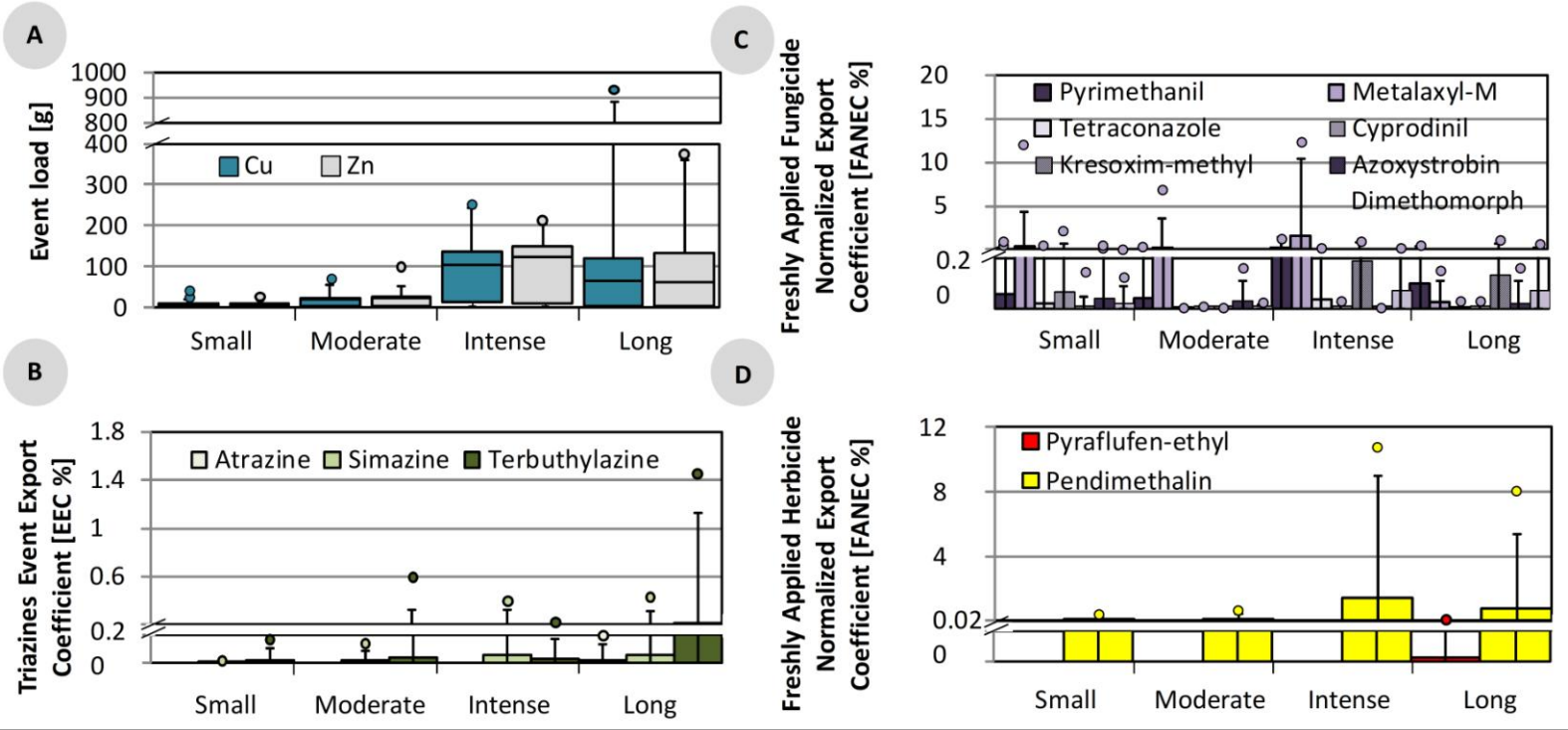
480 The following pesticides were detected in more than 50% of monitored runoff events in  
481 2015 and 2016: dimethomorph (63% and 80%) > pyrimethanil (66% and 63%) > metalaxyl-M  
482 (63% and 54%). Atrazine and pyraflufen-ethyl were detected in only one runoff event (Table  
483 1). Mean concentrations in runoff above 1  $\mu\text{g}\cdot\text{L}^{-1}$  were observed for metalaxyl-M >  
484 dimethomorph > pyrimethanil, with  $EMC_p$  up to 124, 96 and 27  $\mu\text{g}\cdot\text{L}^{-1}$ , respectively (data not  
485 shown). Event Export coefficients ( $EEC_p$ ) of dissolved pesticides ranges from 0% (atrazine and  
486 pyraflufen-ethyl in 2016) up to 12.6% for metalaxyl-M in 2016 (Table 1). The highest  $EEC_p$   
487 values were observed in 2016 for metalaxyl-M > pendimethalin > pyrimethanil >  
488 terbuthylazine > cyprodinil (Table 1). The export of the 12 synthetic pesticides was higher in



489 2016 (total export in runoff of  $7.333 \times 10^{-3}$  kg) than in 2015 ( $3.394 \times 10^{-3}$  kg). This corresponded  
490 to larger applied quantities in 2016 (6.121 kg) than in 2015 (3.359 kg). Larger pesticide export  
491 in 2016 was also due to larger runoff volume (2026 m<sup>3</sup> in 2016 and 1577 m<sup>3</sup> in 2015) and more  
492 frequent rainfall-runoff events in 2016 than in 2015 (46 sampled events in 2016, and 32 in  
493 2015; Figure 3 and Table S3).

494 While rainfall is necessary to export synthetic pesticides offsite, our results indicate that  
495 the rainfall characteristics were not as important as the timing of pesticide applications. Indeed,  
496 the event export coefficient ( $EEC_p$ ) and the freshly applied pesticide normalized export  
497 coefficient ( $FANEC_p$ ) were calculated to account, respectively, for weekly variations of the  
498 total pesticide stock in soil and the fraction of freshly applied pesticides, and did not differ  
499 among rainfall categories ( $p > 0.001$ ; Figure 4 and Table S8). Similarly, event loads of synthetic  
500 pesticides ( $EL_p$ ) did not significantly differ among rainfall categories ( $p > 0.001$ ). This indicates  
501 that normalizing pesticide export by the pesticide stock in soil was not critical in our case to  
502 compare pesticide exports since rainfall conditions only had a weak impact on pesticide export.  
503 In addition, the  $EL_p$  and  $EEC_p$  of currently used synthetic pesticides within 50 days following a  
504 pesticide application were at least one order of magnitude higher than in the following period  
505 ( $p < 0.001$ ; data not shown). In contrast, the pesticide application dose, accounted here from the  
506 weekly concentrations of synthetic pesticides in topsoil, did not correlate significantly with  $EL_p$   
507 or  $EEC_p$  of synthetic pesticides, except for dimethomorph ( $p < 0.001$ , data not shown).  
508 Altogether, this suggests that the application timing, i.e. the period between the application of  
509 synthetic pesticides and a rainfall event, rather than the dose itself, determined the export of  
510 synthetic pesticide in runoff. However, when a soluble pesticide, such as dimethomorph, is  
511 massively applied, thereby increasing the soil stock, both the timing and the dose may  
512 influence  $EL_p$  and  $EEC_p$ .

513           The absence of significant relationship between rainfall categories and the export of  
514 synthetic pesticides suggests that episodic export arising in intermittent pulses predominates  
515 over chemostatic export in the studied vineyard catchment (Basu et al., 2011). In episodic  
516 export, rainfall-runoff events generate episodic pulses, which generally cease a few months  
517 after the initial pesticide application depending on the initial dose of applied pesticide and the  
518 rate of pesticide degradation in soil. Episodic exports can be related to the occurrence of  
519 pesticides in topsoil after initial pesticide application, and the decrease of exported pesticide  
520 loads with increasing time after application (McGrath et al., 2010), in agreement with our  
521 study. As a result, larger export events are generally observed when a large rainfall pulse  
522 directly follows pesticide application, while hydrological characteristics only have a secondary  
523 influence.



525

526 **Figure 4.** Impact of rainfall categories on pesticide export. **A)** Cu and Zn event loads ( $EL_p$ ; boxplot with 5%, first quartile, median, third quartile,  
527 95% and outliers, colored dots, of the 78 events). **B)** Event Export Coefficient ( $EEC_p$ ) for triazines ( $\bar{X} \pm 2\sigma$  and outliers of the 78 events). Freshly  
528 Applied Fungicide Normalized Export Coefficient ( $FANEC_p$ ) for **C)** fungicides and **D)** herbicides ( $\bar{X} \pm 2\sigma$  and outliers of the 78 events).

529 Hence, the confluence of application and intense rainfall determines the process of  
530 intermittent exports. This has also been demonstrated with mechanistic models resolving the  
531 dynamics of individual wetting and concentration fronts in soil (Harman et al., 2011).  
532 However, the low correlation between the export of legacy and currently used synthetic  
533 pesticides and rainfall or runoff characteristics ( $\rho_s=0.08$  to  $0.33$ ; Figure 3 and Table S10) limit  
534 the potential of developing simple predictive tools based on hydrologic data. Indeed, the  
535 seasonal variation of pesticide stocks is mainly controlled by dose and timing of pesticide  
536 application but it also depends on the persistence and degradation of pesticides in soil between  
537 the rainfall-runoff events. As a result, rainfall stochasticity as well as the temporal and spatial  
538 variability of dissipation rates and pathways critically control episodic export. This should be  
539 taken into account when using numerical models to predict the export of synthetic pesticides at  
540 the catchment scale (Basu et al., 2011; Gassmann et al., 2013; Gassmann et al., 2015).

541 Overall, pesticide  $EEC_p$  or  $FANEC_p$  did not correlated with rainfall depth, maximum  
542 intensity and duration ( $\rho_s<0.32$ ; Figure 4 and Table S10), confirming the episodic character of  
543 synthetic pesticide export. However, positive correlation ( $\rho_s>0.29$ ,  $p<0.009$ ; Table S10)  
544 between rainfall intensity and the banned herbicide simazine or the currently used fungicide  
545 tetraconazole suggests that rainfall intensity controls the export of more hydrophobic and  
546 persistent pesticides from the vineyard catchment. Simazine and tetraconazole share higher  
547 persistence, as suggested by their higher  $DT_{50}$  values and  $K_{ow}$  values than the other synthetic  
548 pesticides of this study (see Table S1). The same export mechanism that mobilize Cu and Zn at  
549 the scale of soil aggregates may also mobilize hydrophobic pesticides. The export of simazine  
550 and tetraconazole may be driven by soil fragmentation, depending on raindrop splash during  
551 intense events, followed by solubilization and mobilization of pesticide-DOM complexes  
552 released in surface runoff. Hence, Intense events would generate larger loss of solid-bound  
553 pesticides resulting in larger loads, even some months or years after pesticide applications such

554 as for simazine and terbuthylazine. In particular, soil fragmentation during intense rainfalls  
555 might be critical to mobilize low-concentration, hydrophobic and persistent synthetic  
556 pesticides. In contrast, rainfall depth had a greater impact on the release Cu and Zn, which  
557 might be related to the degree and timing of solubilization and mobilization of Cu- and Zn-  
558 DOM complexes (Herbrich et al., 2017).

559

#### 560 **4. Conclusion**

561         Although physico-chemical characteristics and the dose and timing of applications are  
562 important drivers for Cu, Zn and synthetic pesticides, runoff and rainfall characteristics can  
563 also determine pesticide export from land into downstream aquatic ecosystems. We evaluated  
564 the impact of different rainfall categories on the export by surface runoff of Cu, Zn, legacy and  
565 currently used pesticides in a headwater vineyard catchment during two contrasted wine-  
566 growing seasons. The results support the hypothesis that rainfall characteristics control the  
567 export of TSS, Cu and Zn in small headwater catchments. In contrast, rainfall characteristics  
568 had no significant impact on the event mean concentrations and the export of currently used  
569 synthetic pesticides, even when exports were normalized by the weekly variation of pesticide  
570 stocks in soil.

571         Most importantly, exports of both dissolved and solid-bound Cu and Zn and  
572 hydrophobic pesticides, such as simazine and tetraconazole, correlated with rainfall intensity  
573 and depth. Intense and large rainfall can thus significantly enhance runoff generation from  
574 vineyard plots, topsoil erosion and export of solid-bound pesticides. Together with the  
575 expected increase of maximum rainfall intensity in the coming decades (e.g., Qiu et al., 2019),  
576 this emphasizes the need to design best management practices to reduce runoff, erosion and  
577 associated loads of pollutants. Rainfall characteristics should be considered to improve the  
578 apportionment of Cu and Zn applications and to evaluate the seasonal export dynamics of Cu

579 and Zn and legacy pesticides. Further studies are needed to predict the impact of hydro-  
580 climatic changes on the pesticide export from small agricultural catchments in order to develop  
581 management practices, while evaluating the long-term efficacy of legislation governing their  
582 use. In particular, such management practices should account for both episodic and chemostatic  
583 exports of pesticides to limit pesticide transport from small agricultural catchments into aquatic  
584 ecosystems.

585

### 586 **Author information**

587 \* Corresponding author. e-mail: [imfeld@unistra.fr](mailto:imfeld@unistra.fr) phone: + 33 3 6885 0474

588

### 589 **Author contributions**

590 **Gwenaël Imfeld and Sylvain Payraudeau:** Conceptualization, Methodology, Software,  
591 Visualization, Funding acquisition. **Gwenaël Imfeld:** Project administration, Supervision,  
592 Formal analysis, Writing- Original draft preparation. **Fatima Meite, Charline Wiegert,**  
593 **Benoît Guyot and Jérémy Masbou:** Investigation, Data curation, Writing - Review &  
594 Editing.

595

### 596 **Acknowledgments**

597 This research has been funded by the Agence de l'Eau Rhin-Meuse (AERM) and the  
598 Conseil Interprofessionnel des Vins d'Alsace (CIVA) in the project PACOV. Fatima Meite  
599 was supported by a fellowship of the Alsace Region and the AERM. The authors thank the  
600 Agricultural and Viticulture College of Rouffach (EPLEFPA Les Sillons de Haute Alsace –  
601 Rouffach), the City of Rouffach and the vine producers of the catchment. The authors wish to  
602 acknowledge Eric Pernin and Agnès Herrmann for support in sampling, analyses and surveys.

603 We gratefully acknowledge Richard Coupe (USGS) for enabling significant improvement of  
604 the manuscript and for useful comments.

605

606

607

## 608 **References**

- 609 Babcsányi, I., Chabaux, F., Granet, M., Meite, F., Payraudeau, S., Duplay, J., Imfeld, G.,  
610 2016. Copper in soil fractions and runoff in a vineyard catchment: Insights from  
611 copper stable isotopes. *Sci. Total Environ.* 557–558, 154–162.  
612 <https://doi.org/10.1016/j.scitotenv.2016.03.037>
- 613 Babcsányi, I., Imfeld, G., Granet, M., Chabaux, F., 2014. Copper stable isotopes to trace  
614 copper behavior in wetland systems. *Environ. Sci. Technol.* 48, 5520–5529.  
615 <https://doi.org/10.1021/es405688v>
- 616 Basu, N.B., Thompson, S.E., Rao, P.S.C., 2011. Hydrologic and biogeochemical functioning  
617 of intensively managed catchments: A synthesis of top-down analyses: Managed  
618 catchments. *Water Resour. Res.* 47. <https://doi.org/10.1029/2011WR010800>
- 619 Chen, Y., Yu, K., Hassan, M., Xu, C., Zhang, B., Gin, K.Y.-H., He, Y., 2018. Occurrence,  
620 distribution and risk assessment of pesticides in a river-reservoir system. *Ecotoxicol.*  
621 *Environ. Saf.* 166, 320–327. <https://doi.org/10.1016/j.ecoenv.2018.09.107>
- 622 Coupe, R.H., Kalkhoff, S.J., Capel, P.D., Grégoire, C., 2012. Fate and transport of glyphosate  
623 and aminomethylphosphonic acid in surface waters of agricultural basins. *Pest Manag.*  
624 *Sci.* 68, 16–30. <https://doi.org/10.1002/ps.2212>
- 625 Domange, N., Grégoire, C., 2006. Quality of in situ data about pollutant concentration. *TrAC*  
626 *Trends Anal. Chem.* 25, 179–189. <https://doi.org/10.1016/j.trac.2005.09.002>



627 Dousset, S., Jacobson, A.R., Dessogne, J.-B., Guichard, N., Baveye, P.C., Andreux, F., 2007.  
628 Facilitated transport of diuron and glyphosate in high copper vineyard soils. *Environ.*  
629 *Sci. Technol.* 41, 8056–8061. <https://doi.org/10.1021/es071664c>

630 Duplay, J., Semhi, K., Errais, E., Imfeld, G., Babcsanyi, I., Perrone, T., 2014. Copper, zinc,  
631 lead and cadmium bioavailability and retention in vineyard soils (Rouffach, France):  
632 The impact of cultural practices. *Geoderma* 230–231, 318–328.  
633 <https://doi.org/10.1016/j.geoderma.2014.04.022>

634 El Azzi, D., Probst, J.L., Teisserenc, R., Merlina, G., Baqué, D., Julien, F., Payre-Suc, V.,  
635 Guiresse, M., 2016. Trace Element and Pesticide Dynamics During a Flood Event in  
636 the Save Agricultural Watershed: Soil-River Transfer Pathways and Controlling  
637 Factors. *Water. Air. Soil Pollut.* 227, 442. <https://doi.org/10.1007/s11270-016-3144-0>

638 Elsayed, O.F., Maillard, E., Vuilleumier, S., Nijenhuis, I., Richnow, H.H., Imfeld, G., 2014.  
639 Using compound-specific isotope analysis to assess the degradation of  
640 chloroacetanilide herbicides in lab-scale wetlands. *Chemosphere* 99, 89–95.  
641 <https://doi.org/10.1016/j.chemosphere.2013.10.027>

642 Gagnon, P., Sheedy, C., Rousseau, A.N., Bourgeois, G., Chouinard, G., 2016. Integrated  
643 assessment of climate change impact on surface runoff contamination by pesticides:  
644 Climate change impact on pesticides in surface runoff. *Integr. Environ. Assess.*  
645 *Manag.* 12, 559–571. <https://doi.org/10.1002/ieam.1706>

646 Gassmann, M., Olsson, O., Stamm, C., Weiler, M., Kümmerer, K., 2015. Physico-chemical  
647 characteristics affect the spatial distribution of pesticide and transformation product  
648 loss to an agricultural brook. *Sci. Total Environ.* 532, 733–743.  
649 <https://doi.org/10.1016/j.scitotenv.2015.06.068>

650 Gassmann, M., Stamm, C., Olsson, O., Lange, J., Kümmerer, K., Weiler, M., 2013. Model-  
651 based estimation of pesticides and transformation products and their export pathways

652 in a headwater catchment. *Hydrol. Earth Syst. Sci.* 17, 5213–5228.  
653 <https://doi.org/10.5194/hess-17-5213-2013>

654 Grégoire, C., Payraudeau, S., Domange, N., 2010. Use and fate of 17 pesticides applied on a  
655 vineyard catchment. *Int. J. Environ. Anal. Chem.* 90, 406–420.  
656 <https://doi.org/10.1080/03067310903131230>

657 Harman, C.J., Rao, P.S.C., Basu, N.B., McGrath, G.S., Kumar, P., Sivapalan, M., 2011.  
658 Climate, soil, and vegetation controls on the temporal variability of vadose zone  
659 transport: climate controls on vadose transport. *Water Resour. Res.* 47.  
660 <https://doi.org/10.1029/2010WR010194>

661 Havis, R., Smith, R., Adrian, D., 1992. Partitioning solute between infiltration and overland  
662 flow. *Water Resour. Res.* 28.2569-2580. [https://doi-org.scd-rproxy.u-](https://doi-org.scd-rproxy.u-strasbg.fr/10.1029/92WR01366)  
663 [strasbg.fr/10.1029/92WR01366](https://doi-org.scd-rproxy.u-strasbg.fr/10.1029/92WR01366)

664 Herrero-Hernández, E., Rodríguez-Cruz, M.S., Pose-Juan, E., Sánchez-González, S.,  
665 Andrades, M.S., Sánchez-Martín, M.J., 2017. Seasonal distribution of herbicide and  
666 insecticide residues in the water resources of the vineyard region of La Rioja (Spain).  
667 *Sci. Total Environ.* 609, 161–171. <https://doi.org/10.1016/j.scitotenv.2017.07.113>

668 Hildebrandt, A., Guillamón, M., Lacorte, S., Tauler, R., Barceló, D., 2008. Impact of  
669 pesticides used in agriculture and vineyards to surface and groundwater quality (North  
670 Spain). *Water Res.* 42, 3315–3326. <https://doi.org/10.1016/j.watres.2008.04.009>

671 Jarvis, N.J., 2007. A review of non-equilibrium water flow and solute transport in soil  
672 macropores: principles, controlling factors and consequences for water quality. *Eur. J.*  
673 *Soil sci.* 58, 523–546. <https://doi.org/10.1111/j.1365-2389.2007.00915.x>

674 Komárek, M., Čadková, E., Chrástný, V., Bordas, F., Bollinger, J.-C., 2010. Contamination of  
675 vineyard soils with fungicides: A review of environmental and toxicological aspects.  
676 *Environ. Int.* 36, 138–151. <https://doi.org/10.1016/j.envint.2009.10.005>

677 Lefrancq, M., Imfeld, G., Payraudeau, S., Millet, M., 2013. Kresoxim methyl deposition, drift  
678 and runoff in a vineyard catchment. *Sci. Total Environ.* 442, 503–508.  
679 <https://doi.org/10.1016/j.scitotenv.2012.09.082>

680 Lefrancq, M., Jadas-Hécart, A., La Jeunesse, I., Landry, D., Payraudeau, S., 2017. High  
681 frequency monitoring of pesticides in runoff water to improve understanding of their  
682 transport and environmental impacts. *Sci. Total Environ.* 587–588, 75–86.  
683 <https://doi.org/10.1016/j.scitotenv.2017.02.022>

684 Lefrancq, M., Payraudeau, S., García Verdú, A.J., Maillard, E., Millet, M., Imfeld, G., 2014.  
685 Fungicides transport in runoff from vineyard plot and catchment: contribution of non-  
686 target areas. *Environ. Sci. Pollut. Res.* 21, 4871–4882. [https://doi.org/10.1007/s11356-](https://doi.org/10.1007/s11356-013-1866-8)  
687 [013-1866-8](https://doi.org/10.1007/s11356-013-1866-8)

688 Lefrancq, M., Payraudeau, S., Guyot, B., Millet, M., Imfeld, G., 2018. Correction to  
689 Degradation and transport of the chiral herbicide *S* -metolachlor at the catchment  
690 scale: combining observation scales and analytical approaches. *Environ. Sci. Technol.*  
691 52, 5517–5517. <https://doi.org/10.1021/acs.est.8b01118>

692 Legendre, P., Gallagher, E.D., 2001. Ecologically meaningful transformations for ordination  
693 of species data. *Oecologia* 129, 271–280. <https://doi.org/10.1007/s004420100716>

694 Leu, C., Singer, H., Müller, S.R., Schwarzenbach, R.P., Stamm, C., 2005. Comparison of  
695 Atrazine losses in three small headwater catchments. *J. Environ. Qual.* 34, 1873–1882.  
696 <https://doi.org/10.2134/jeq2005.0049>

697 Lorenz, S., Rasmussen, J.J., Süß, A., Kalettka, T., Golla, B., Horney, P., Stähler, M.,  
698 Hommel, B., Schäfer, R.B., 2017. Specifics and challenges of assessing exposure and  
699 effects of pesticides in small water bodies. *Hydrobiologia* 793, 213–224.  
700 <https://doi.org/10.1007/s10750-016-2973-6>

701 Louchart, X., Voltz, M., Andrieux, P., Moussa, R., 2001. Herbicide transport to surface  
702 waters at field and watershed scales in a mediterranean vineyard area. *J. Environ.*  
703 *Qual.* 30, 982–991. <https://doi.org/10.2134/jeq2001.303982x>

704 Lucas, Y., Schmitt, A.D., Chabaux, F., Clément, A., Fritz, B., Elsass, Ph., Durand, S., 2010.  
705 Geochemical tracing and hydrogeochemical modelling of water–rock interactions  
706 during salinization of alluvial groundwater (Upper Rhine Valley, France). *Appl.*  
707 *Geochem.* 25, 1644–1663. <https://doi.org/10.1016/j.apgeochem.2010.08.013>

708 Maillard, E., Imfeld, G., 2014. Pesticide mass budget in a stormwater wetland. *Environ. Sci.*  
709 *Technol.* 48, 8603–8611. <https://doi.org/10.1021/es500586x>

710 Masbou, J., Meite, F., Guyot, B., Imfeld, G., 2018. Enantiomer-specific stable carbon isotope  
711 analysis (ESIA) to evaluate degradation of the chiral fungicide Metalaxyl in soils. *J.*  
712 *Hazard. Mater.* 353, 99–107. <https://doi.org/10.1016/j.jhazmat.2018.03.047>

713 McGrath, G.S., Hinz, C., Sivapalan, M., Dressel, J., Pütz, T., Vereecken, H., 2010.  
714 Identifying a rainfall event threshold triggering herbicide leaching by preferential  
715 flow: Identifying rapid transport rain events. *Water Resour. Res.* 46.  
716 <https://doi.org/10.1029/2008WR007506>

717 Meite, F., Alvarez-Zaldívar, P., Crochet, A., Wiegert, C., Payraudeau, S., Imfeld, G., 2018.  
718 Impact of rainfall patterns and frequency on the export of pesticides and heavy-metals  
719 from agricultural soils. *Sci. Total Environ.* 616–617, 500–509.  
720 <https://doi.org/10.1016/j.scitotenv.2017.10.297>

721 Mohammad, H., Assefa M, M., Hector R, F., 2018. Raindrop-induced erosion and sediment  
722 transport modelling in shallow waters: a review. *J. Soil Water Sci.* 1.  
723 <https://doi.org/10.36959/624/427>

724 Moser, A., Wemyss, D., Scheidegger, R., Fenicia, F., Honti, M., Stamm, C., 2018. Modelling  
725 biocide and herbicide concentrations in catchments of the Rhine basin. *Hydrol. Earth*  
726 *Syst. Sci.* 22, 4229–4249. <https://doi.org/10.5194/hess-22-4229-2018>

727 Parajulee, A., Lei, Y.D., Cao, X., McLagan, D.S., Yeung, L.W.Y., Mitchell, C.P.J., Wania, F.,  
728 2018. Comparing winter-time herbicide behavior and exports in urban, rural, and  
729 mixed-use watersheds. *Environ. Sci. Process. Impacts* 20, 767–779.  
730 <https://doi.org/10.1039/C7EM00596B>

731 Payraudeau, S., Gregoire, C., 2012. Modelling pesticides transfer to surface water at the  
732 catchment scale: a multi-criteria analysis. *Agron. Sustain. Dev.* 32, 479–500.  
733 <https://doi.org/10.1007/s13593-011-0023-3>

734 Qiu, J., Shen, Z., Leng, G., Xie, H., Hou, X., Wei, G., 2019. Impacts of climate change on  
735 watershed systems and potential adaptation through BMPs in a drinking water source  
736 area. *J. Hydrol.* 573, 123–135. <https://doi.org/10.1016/j.jhydrol.2019.03.074>

737 Thompson, C.M., Ellwood, M.J., 2014. Dissolved copper isotope biogeochemistry in the  
738 Tasman Sea, SW Pacific Ocean. *Mar. Chem.* 165, 1–9.  
739 <https://doi.org/10.1016/j.marchem.2014.06.009>

740 Tournebize, J., Gregoire, C., Coupe, R.H., Ackerer, P., 2012. Modelling nitrate transport  
741 under row intercropping system: Vines and grass cover. *J. Hydrol.* 440–441, 14–25.  
742 <https://doi.org/10.1016/j.jhydrol.2012.03.002>

743 Vance, D., Archer, C., Bermin, J., Perkins, J., Statham, P.J., Lohan, M.C., Ellwood, M.J.,  
744 Mills, R.A., 2008. The copper isotope geochemistry of rivers and the oceans. *Earth*  
745 *Planet. Sci. Lett.* 274, 204–213. <https://doi.org/10.1016/j.epsl.2008.07.026>

746 Zhang, X., Norton, D., Hickman, M., 1997. Rain pattern and soil moisture content effects on  
747 atrazine and métolachlore losses in runoff. *J. Environ. Qual.* 26, 1539-1547.  
748 <https://doi.org/10.2134/jeq1997.00472425002600060013x>

749 Zhang, X., Norton, D., Lei, T., Nearing, M., 1999. Coupling mixing zone concept with  
750 convective-diffusion equation to predict chemical transfer to surface runoff. *Trans*  
751 *ASAE*. 42, 987-994. <https://doi.org/10.13031/2013.13280>

752 Zubrod, J.P., Bundschuh, M., Arts, G., Brühl, C.A., Imfeld, G., Knäbel, A., Payraudeau, S.,  
753 Rasmussen, J.J., Rohr, J., Scharmüller, A., Smalling, K., Stehle, S., Schulz, R.,  
754 Schäfer, R.B., 2019. Fungicides: An overlooked pesticide class? *Environ. Sci.*  
755 *Technol.* 53, 3347–3365. <https://doi.org/10.1021/acs.est.8b04392>