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Title page:

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**Restoring surface water quality: quantitative assessment of the performance of agricultural trajectories for mitigating pesticide concentrations**

Odile Phelpin<sup>a\*</sup>, Françoise Vernier<sup>a</sup>, and Kévin Petit<sup>a</sup> and David Carayon<sup>a</sup>

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16

**Abstract**

17 Most surface water bodies are deteriorating and causing health risks and environmental  
18 damages.

19 The aim of this study was to assess the performance of modeled agri-environmental  
20 transition scenarios for restoring freshwater quality within the protection perimeter of two  
21 strategic surface water drinking water catchments.

22 Realistic agro environmental scenarios with combined agronomic orientations and  
23 gradual implementation were tested, using a well-calibrated ecohydrological model. Their  
24 performance was quantified based on pesticide concentration reductions in freshwater bodies,  
25 focusing on temporal and spatial variability, using non-parametric tests.

26 Our results show that it is possible to differentiate cropping mitigation scenarios  
27 according to their ability to limit pesticide transfers, taking into account the most influential  
28 biogeochemical factors in the catchment, their agronomic orientation, and their progressive  
29 implementation. Our study is applicable to other contexts.

30 Keywords: scenarios; agriculture; pollution; watershed; water source protection;  
31 drinking water

**1. Introduction**

33 Water resources worldwide are facing significant degradation due to various factors. In  
34 Europe, approximately 60% of surface waters exhibit poor ecological and chemical conditions  
35 (István, 2020). The primary culprits behind this degradation are hydromorphological pressures  
36 and agricultural non-point source (NPS) pollution. This deterioration not only impacts  
37 ecosystems but also poses risks to drinking water supplies, thereby endangering human health  
38 (European Union, 1998). In order to sustainably reduce pollution and cut treatment costs for  
39 drinking water production, long-term preventive climate and agri-environmental measures are

40 required. To tackle these challenges sustainably and reduce pollution while cutting treatment  
41 costs for drinking water production, long-term preventive measures are necessary (European  
42 Commission, 2000).

43 Action programs for water quality restoration need to consider the continuum of NPS  
44 pollution in order to act not only on pressures at farm level but also on transport and fate  
45 factors linked to watershed behavior (Bierozza et al., 2021), by collectively involving  
46 territorial stakeholders and water- users and managers (Amblard, 2019). As the financial  
47 resources of water and land managers are limited, action plans often target solely the most  
48 contaminated areas defined as “priority areas” (PA) for action. Agri-environmental and  
49 climate measures have been widely implemented on PAs. They feature non-structural, e.g.  
50 crop rotations (Wang et al., 2019), intercropping, input-reducing, and structural agro-  
51 ecological features e.g. grassing systems) (Lacas et al., 2005; Zhang & Zhang, 2011). Yet,  
52 drinking water sources are still closing down, due contamination from agricultural effluents  
53 causing to agricultural NPS pollution. The holistic approach of water quality governance at  
54 catchment scale requires decision-support methods and tools capable of characterizing the  
55 spatio-temporal dynamics of agricultural NPS pollution. Indeed, for equivalent agrochemical  
56 pressure, some areas contribute disproportionately to NPS pollution.

57 It is therefore essential to identify more specifically these most contributing spatial  
58 areas (CSAs) and identify how temporal variability may affect the effectiveness of action  
59 plans. Ecohydrological modeling enables simulating the agro-ecosystems and agricultural  
60 practices associated with soils and plants, soils and climate heterogeneity, and the non-  
61 linearity of biogeochemical watershed processes responsible for pollutant fate and transport,  
62 as well as the response of hydrosystems to land use and climate changes (Kohne et al., 2009;  
63 Porporato et al., 2015; Veselá et al., 2020). Ecohydrological modeling provides a means to  
64 simulate agro-ecosystems, agricultural practices, biogeochemical processes, and hydrosystem

65 responses, aiding in long-term watershed management (Strehmel et al., 2016). However,  
66 taking into account scenarios complexity and variation in time and space, further analysis are  
67 required to validate the model results.

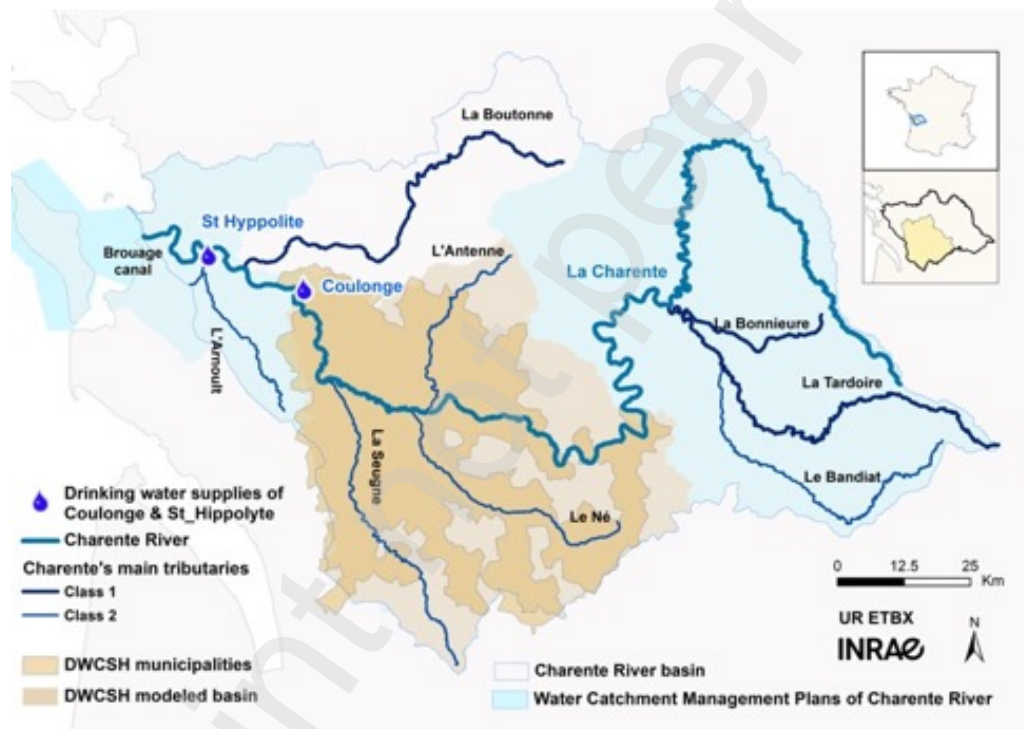
68 We propose an innovative method to analyze model results with statistical  
69 validations. The present study applies to a priority surface drinking water catchment  
70 protection area, embedded in a highly agricultural basin, contaminated by pesticides. Here,  
71 we present several tested mitigation scenarios and evaluate their environmental efficiency in  
72 restoring water quality. We used a well-calibrated SWAT ecohydrological model, whose  
73 performance ranged from 0.65 to 0.85 ( $R^2$ ) and from 0.47 to 0.82 (NSE), during calibration  
74 and validation, respectively (Pryet, 2016), (Vernier et al., 2017). It aims to evaluate thirty-  
75 four scenarios, defined with stakeholders that include targeted Best Management Practices  
76 (BMPs) and gradual areal changes of agrosystems and their agricultural management  
77 practices. Our assessment is based on the last twelve years of daily simulations, for six Plant  
78 Protection Products (PPPs) that have been selected as "markers" of phytosanitary pressure,  
79 taking into account their use, their biophysical characteristics and their concentrations  
80 measured in watercourses. The modeled results are statistically evaluated at the 106-modeled  
81 sub-basins, using nonparametric tests that examine their efficiency over time and space, and  
82 at what level of implementation.

83 Firstly, this study seeks to identify the relative effectiveness of each mitigation  
84 scenario compared to the reference scenario. Secondly, it investigates the spatial variabilities  
85 that could explain the discrepancies between the targeted actions and the significant  
86 efficiencies of the scenarios at sub-basin level. Finally, it looks at monotonic temporal trends  
87 of the scenarios.

## 88 **2. Materials and Methods**

### 89 **2.1. Study area**

90 The Drinking Water Coulonge Saint-Hippolyte (DWCSH) basin, situated in  
 91 southwest France within the Charente basin ( $0^{\circ}45'W$   $45^{\circ}58'N$  /  $0^{\circ}16'E$   $45^{\circ}14'N$ ), serves as a  
 92 critical drinking water source protection area spanning 3,800 km<sup>2</sup> (Fig. 1). The Charente  
 93 River, extending 381 km from east to west, constitutes the primary drainage system within  
 94 the basin, ultimately discharging into the Atlantic Ocean. With an average flow rate of 95 m  
 95 s<sup>-1</sup>, the river's discharge varies from a few m<sup>3</sup> s<sup>-1</sup> to 815 m<sup>3</sup> s<sup>-1</sup> at the furthest downstream  
 96 gauging station, located approximately 40 km from the main outlet where marine influence  
 97 ceases. The alluvial beds of the river exhibit low-density, and dams, canals and reservoirs  
 98 throughout the basin significantly influence the natural hydrologic regime.



99

100 Figure 1: Map of the study area.

101 The climate is generally temperate with an average rainfall of 800 mm yr<sup>-1</sup> over the  
 102 last 30 years and an average temperature of 13°C. However, variability exist; the climate is  
 103 mild and dry and sunny in the center (Cognac area), oceanic on the coast and wetter and less

104 mild in the eastern part of the plateau. The topography is mostly flat, with a minimum  
105 elevation of -1 m to 0 m asl in the west and a maximum of 500 m asl in the East.

106 The DWSCH basin's water supply area is considered strategic for several reasons: it  
107 produces 170 M m<sup>3</sup> y<sup>-1</sup> for 290,000 inhabitants, including over 500,000 during the summer; it  
108 is highly vulnerable to pesticides, particularly herbicides, excessive concentrations of which  
109 are regularly observed despite action plans; and protection of this threatened resource is  
110 required by the Water Framework Directive (WFD) (European Commission, 2000, 2008).  
111 Water managers aim to keep pesticide concentrations below half the Maximum Acceptable  
112 Concentration (MAC) and reduce peak concentrations.

## 113 **2.2. Reference scenario**

114 In the baseline scenario (sRef), the prevailing land use consists mainly of intensive  
115 conventional agricultural practices. Land use patterns vary depending on soil characteristics  
116 and agricultural goals. Unlike many mesoscale crop-modeling studies that covers 2-6 crop  
117 types, our analysis includes 41 distinct cropping systems. These systems are associated with  
118 specific agricultural practices related to eight soil features, and they encompass 17 irrigated  
119 and non-irrigated crops across all scenarios. The crops range from traditional ones like  
120 sunflower, soft winter wheat, durum wheat, oilseed rape, grain corn, maize corn, winter  
121 barley, spring barley, and temporary grassland, to innovative and organic options such as  
122 alfalfa, field pea, temporary pasture, soybean, clover, and triticale, reflecting diverse cropping  
123 practices.

124 The study area primarily consists of deep Campanian soils (ChamP) and shallow  
125 Campanian soils (ChamS), known for their high agronomic potential and clayey-calcareous  
126 properties, making them suitable for vineyards and cereal-maize systems, especially in the



127 Cognac area. Additionally, there are clay-limestone called "Groies," which are fertile but thin  
128 and prone to rapid drying, particularly when shallow (GrSup) or predominantly marly  
129 (GrMar).

130 Cereal cultivation, mainly without irrigation, is common in the southern region on  
131 high potential agricultural soils such as Campanian soils and Groies. In the northern region,  
132 where viticulture and agriculture co-exist, irrigation is used for cereal cultivation, with  
133 diverse growing systems prevailing over monocultures. Alluvial valleys (VaMaT) support  
134 non-irrigated corn cultivation, while specific crop rotations occur on various soil types such  
135 as Groies and hydromorphic loam soils (DHyLI). Sandy loam soils (Dsab) are less prevalent  
136 (Vernier et al., 2017). Pastures and livestock farming, while about 30% of the area comprises  
137 forests, wetlands, urban areas, and water bodies, characterize the eastern plateau.

### 138 **2.3. The Charente SWAT model.**

139 The ecohydrological Soil and Water Assessment Tool (SWAT) model was utilized to  
140 analyze the effects of agri-environmental mitigation strategies aimed at reducing pesticide  
141 contamination in surface waters and assessing long-term impacts on ecosystems in mesoscale  
142 and large-scale watersheds (Arnold et al., 2007). SWAT is recognized as the most suitable  
143 tool for simulating pesticide transport and fate in agricultural watersheds due to its  
144 comprehensive capabilities and ability to handle complex land use change scenarios (Wang et  
145 al., 2019; Kohne et al., 2009) through interfaces such as GenLU2 and BMPs like Vegetative  
146 Filter Strips (VFSs) (White & Arnold, 2009).

147 The DWSCH basin, divided into 106 sub-catchments and 3,659 Hydrologic Response  
148 Units (HRUs), was modeled using SWAT. HRUs represent unique combinations of land use,  
149 soil type, and slope within the catchments. Land use data is derived from a typology

150 developed with agricultural stakeholders, supplemented by cartographic databases and  
151 meteorological data from Météo-France weather stations.

152 Representative herbicides such as glyphosate, acetonifene, MCPA, and tebuconazole,  
153 along with fungicides like mancozeb and a molluscicide, metaldehyde, were studied.

#### 154 **2.4. The mitigation scenarios tested**

155 The mitigation scenarios tested aim to balance the need for well-defined scenarios and  
156 the stakeholders' interest in exploring specific agricultural hypotheses under varying  
157 thresholds of LUC (Table 1). These scenarios include:

- 158 i) Organic farming (Org): Implemented in 35 sub-basins with established organic  
159 farming, focusing on vineyards and field crops. Practices involve reduced fertilization,  
160 cessation of synthetic pesticide usage, extended crop rotations, and residue burial,  
161 primarily on poor agronomic soils.
- 162 ii) Innovative low-input systems (Sdci): Integrating current practices or transitioning to  
163 organic farming for vineyards and field crops. These systems aim to limit pollutant  
164 usage and transfer, lengthen crop rotations, promote intercropping, and substitute  
165 molecules for plant protection.
- 166 iii) Grassed areas (Herb): Involving the implementation of Vegetative Filter Strips  
167 (VFSs) along 551 Hydrologic Response Units (HRUs) at high risk of pollutant  
168 transfer to watercourses. These scenarios transform crops into grasslands, combining  
169 elements of Org, Sdci, and the baseline scenario (sRef). The "Depp" scenario replaces  
170 1% of meadows with crops due to livestock farming issues.

171 Across all mitigation scenarios, vineyard acreage remains constant at 22% of the  
172 Utilized Agricultural Area (UAA). However, innovative scenarios show longer crop

173 durations and increased cultivation of cereals, spring field peas, alfalfa, and temporary  
174 grasslands, with reduced areas for sunflower, rapeseed, and corn. These changes occur while  
175 maintaining overall stability in vineyard acreage. Modifications in farming practices lead to  
176 variations in field crop distribution. For example, wheat cultivation increases from 22% to  
177 24% of the UAA between the reference scenario (sRef) and Sdc1, reflecting current trends.  
178 Sunflower cultivation decreases from 19% to 13%, and corn cultivation decreases from 15%  
179 to 12%, respectively, across scenarios.

## 180 **2.5. Mitigation scenario performance evaluation methods**

181 Simulated daily hydro-meteorological and water-quality outputs present a strong right  
182 skew and several outliers. In the context of water quality for drinking purposes, outliers are  
183 kept. Statistical analysis are performed using each of the simulated PPPs across the 106  
184 outlets over the last 4,383 days of simulation. Various scripts using R v4.3.1. packages enable  
185 performing statistical computations and visualizing visualized (Team et al., 2018).

186 To evaluate the effectiveness of each modeled mitigation scenario compared to the  
187 reference scenario (sRef), the non-parametric Kruskal-Wallis (KW) test (Kruskal & Wallis,  
188 1952) and the post hoc Dunn's test with the Benjamini-Hochberg correction are used. The  
189 KW test is more robust than the ANOVA or t-test (Gibbons & Fielden, 1993) and is more  
190 relevant in the presence of non-normality. H0 indicates that each mitigation scenario is  
191 neither greater nor less than sRef at the 95% confidence level. The p-values of KW pairs are  
192 shown on the boxplots of simulated PPP concentrations. Scenario performance is considered  
193 significant when  $p < 0.05$  (H1) (indicated this way in increasing significance: \*:  $p \leq 0.05$ ;  
194 \*\*:  $p \leq 0.01$ ; \*\*\*:  $p \leq 0.001$ ; \*\*\*\*:  $p \leq 0.0001$ ).

195 Principal Component Analysis (PCA) is employed to identify the contributions of  
196 biogeochemical factors and analyze spatial variability in individual sub-basins. Even in the  
197 presence of non-linear processes, PCAs are suitable for water quality studies, even with  
198 nonlinear processes, as they can transform data optimally (Gamble & Babbar-Sebens, 2012),  
199 accommodating mixed quantitative (i. e. concentrations) and qualitative data. and qualitative  
200 data (i.e. sub-basins) (Agudelo-Jaramillo et al., 2016).

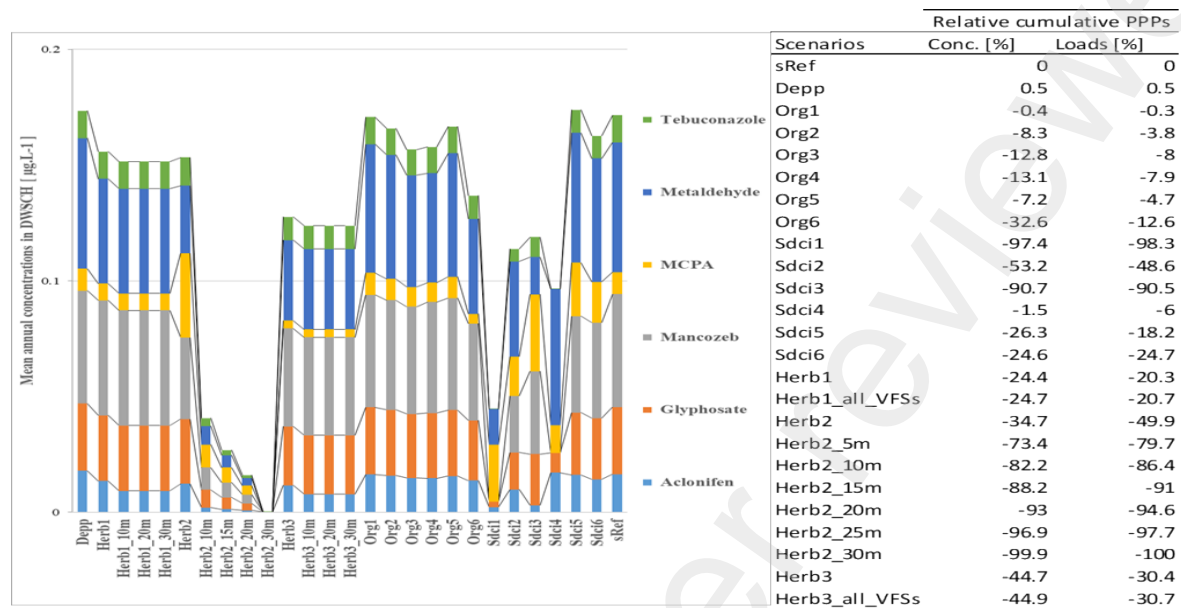
201 Temporal variability within sub-basins is investigated with the non-parametric Man  
202 Kendall (MK) test (Gilbert, 1987), relevant for its robustness (lower sensitivity to gross error)  
203 and efficiency (smaller asymptotic variance) and adjustments for ties (Kendall & Gibbons,  
204 1990). MK assesses that there is no a priori notion of an increasing or decreasing trend notion  
205 for mitigation scenarios towards sRef at the alpha level of 0.05 ( $H_0$ ). If the p-value is less than  
206 0.05, the null hypothesis is discarded and may suggest that there is a significant monotonous trend in daily  
207 water quality outputs ( $H_1$ ).

### 208 **3. Results and discussion**

209 In the DWSCH watershed, trends in mitigation scenario performance indicate varying  
210 average modeled plant protection product (PPP) concentrations over the past 12 years of daily  
211 simulation. Scenarios like Sdc1 and Herb3, extensively implemented along with associated  
212 VFS variants, demonstrate substantial reductions, achieving between 97% and 98% of the  
213 cumulative average PPP concentration drop in water flows over the simulation period.  
214 Innovative scenarios targeting Priority Areas (PAs), such as Sdc3, also show favorable results,  
215 with a notable 90% reduction in cumulative PPP concentrations.

216 Organic farming (Org) scenarios exhibit promising results, especially with significant  
217 land use changes (LUCs). For instance, Org6, with 35% of LUCs devoted to organic farming,  
218 achieves a 33% reduction in concentrations and a 13% reduction in loads. However, scenarios

219 with conversion areas of less than 4% of the UAA, like Org1 and Org2, show less convincing  
 220 results (Fig. 2).



221

222 Figure 2: Simulated average PPP concentrations throughout the DWSCCH basin.

### 223 3.1. Statistical Significance of Scenarios (KW Test)

224 To assess the effectiveness of mitigation scenarios in safeguarding drinking water  
 225 catchments, our analysis focuses on the downstream sub-basin, which mainly consists of  
 226 wheat-based rotations with sunflower, corn, and rapeseed-based rotations.

#### 227 3.1.1. The Organic (Org) and Innovative (Sdci) scenarios

228 Boxplots reveal significant reductions in PPP concentrations across the Org and Sdci  
 229 scenarios, particularly in Sdci1 and Org6, where peak concentrations remain below half the  
 230 MAC. Innovative scenarios successfully maintain concentrations below the MAC threshold,  
 231 except for MCPA.

232 Combining various agronomic orientations within a single scenario proves effective in  
233 water quality restoration efforts. For example, scenario Sdci6, integrating innovative and  
234 organic farming practices, exhibits significant efficacy in reducing aconifen and MCPA  
235 concentrations, moderate efficacy in reducing mancozeb and metaldehyde concentrations,  
236 and limited efficacy in reducing glyphosate concentrations. In contrast, agronomic scenarios  
237 characterized by a single, widely implemented agronomic orientation, such as Sdci1 and  
238 Sdci3, demonstrate significant statistical efficiencies in reducing aconifen and metaldehyde  
239 concentrations. Notably, alterations in practices within these innovative scenarios lead to a  
240 partial substitution of aconifen by MCPA and a decrease in metaldehyde applications.  
241 However, scenarios targeting innovative systems on PAs (Sdci2) and on vines (Sdci4), also  
242 very significantly reduce mancozeb concentrations in watercourses. The KW pairwise test  
243 provides further evidence of the effectiveness of these last massively implemented scenarios  
244 are significantly effective, are significantly effective, but also some other targeted scenarios,  
245 based on progressive swift from intensive farming (Fig.3).

246 For example, Org1 to Org4 scenarios receive runoff from upstream sub-basins where  
247 these scenarios are implemented. Similarly, the Depp scenario increases aconifen  
248 concentrations due to grassland abandonment for corn cultivation in neighboring sub-basins,  
249 exacerbated by silty soils (DHyl).

250 Bio-geophysical factors help explain the discrepancies at the sub-basin level between  
251 the targeted actions and the observed efficiencies. For example, Org1 to Org4 scenarios  
252 receive runoff from upstream sub-basins where these scenarios are implemented. Similarly,  
253 the Depp scenario results in increased aconifen concentrations due to neighboring sub-basins  
254 experiencing grassland abandonment for corn cultivation, exacerbated by the presence of

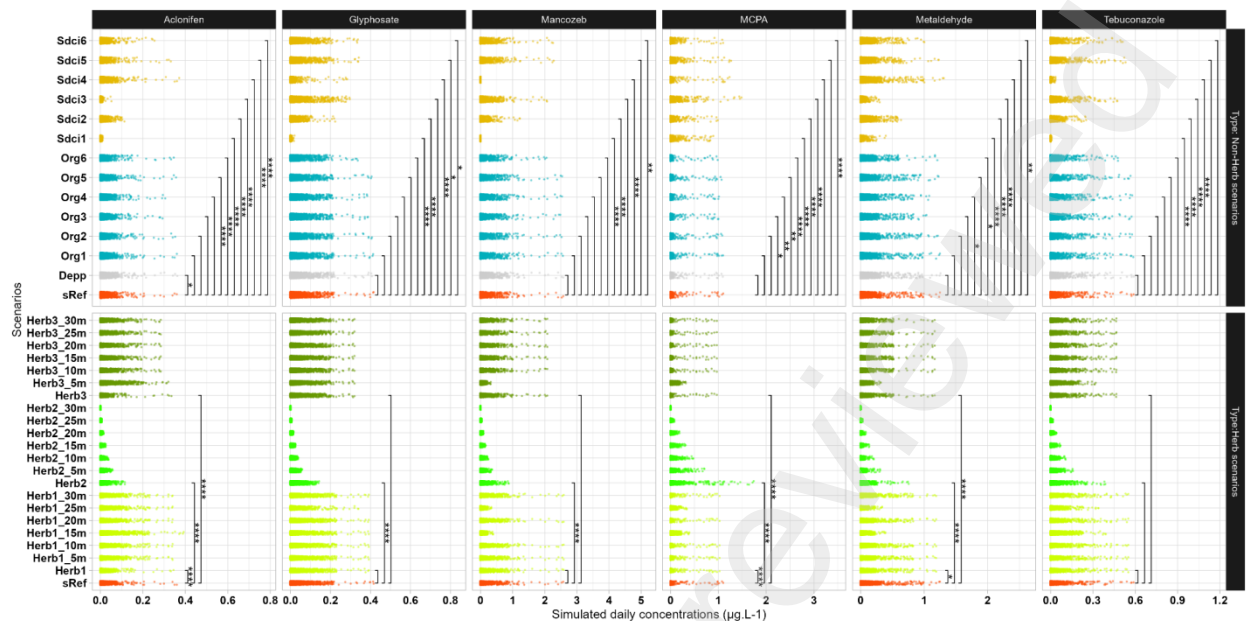
255 silty soils (DHyLi), that may favor particulate transport of this adsorbable contaminant (Fig.  
256 3).

### 257 **3.1.2. Herb Scenarios and their VFS variants**

258 The Herb2 and Herb3 scenarios generally lead to greater reductions in pollutant  
259 concentrations compared to Herb1 especially in targeted areas. While VFS scenarios are  
260 primarily effective for reducing nitrogen (Abimbola et al., 2021), they also demonstrate  
261 efficiencies for pesticides (Tang et al., 2012). Predicting VFS efficiency in trapping  
262 pesticides is complex due to lumped and in-stream empirically based processes and  
263 parameter uncertainties (Munoz-Carpena et al., 2010). However, a general gradient between  
264 VFS width and efficiency is observed, with combined Herb2 and Herb3 scenarios proving  
265 most effective in reducing various pollutant concentrations.

266 Combined Herb2-VFS scenarios are most effective in reducing various pollutant  
267 concentrations, with Herb2 alone efficient for reducing glyphosate and mancozeb  
268 concentrations. Combined Herb2 with the largest VFS scenarios keeps pollutant  
269 concentrations below the Maximum Acceptable Concentration (MAC), while combined  
270 Herb3 scenarios maintain MAC below half and are highly effective in reducing metaldehyde  
271 concentrations.

272 The efficiency of grass strips in purifying pollutants, especially when combined with  
273 organic (Org) and innovative (Sdci) scenarios, confirms the efficacy of VFSs as structural



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Figure 3: Distributions and KW significant efficiencies at the basin outlet

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Best Management Practices (BMPs). Cost-effectiveness modeling studies have demonstrated VFS to be the most cost-effective option. These results highlight the effectiveness of combining non-structural BMPs with different agronomic orientations to enhance water quality restoration efforts.

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### 3.2. Investigation of the main relative contributions of anthropogenic and environmental variables.

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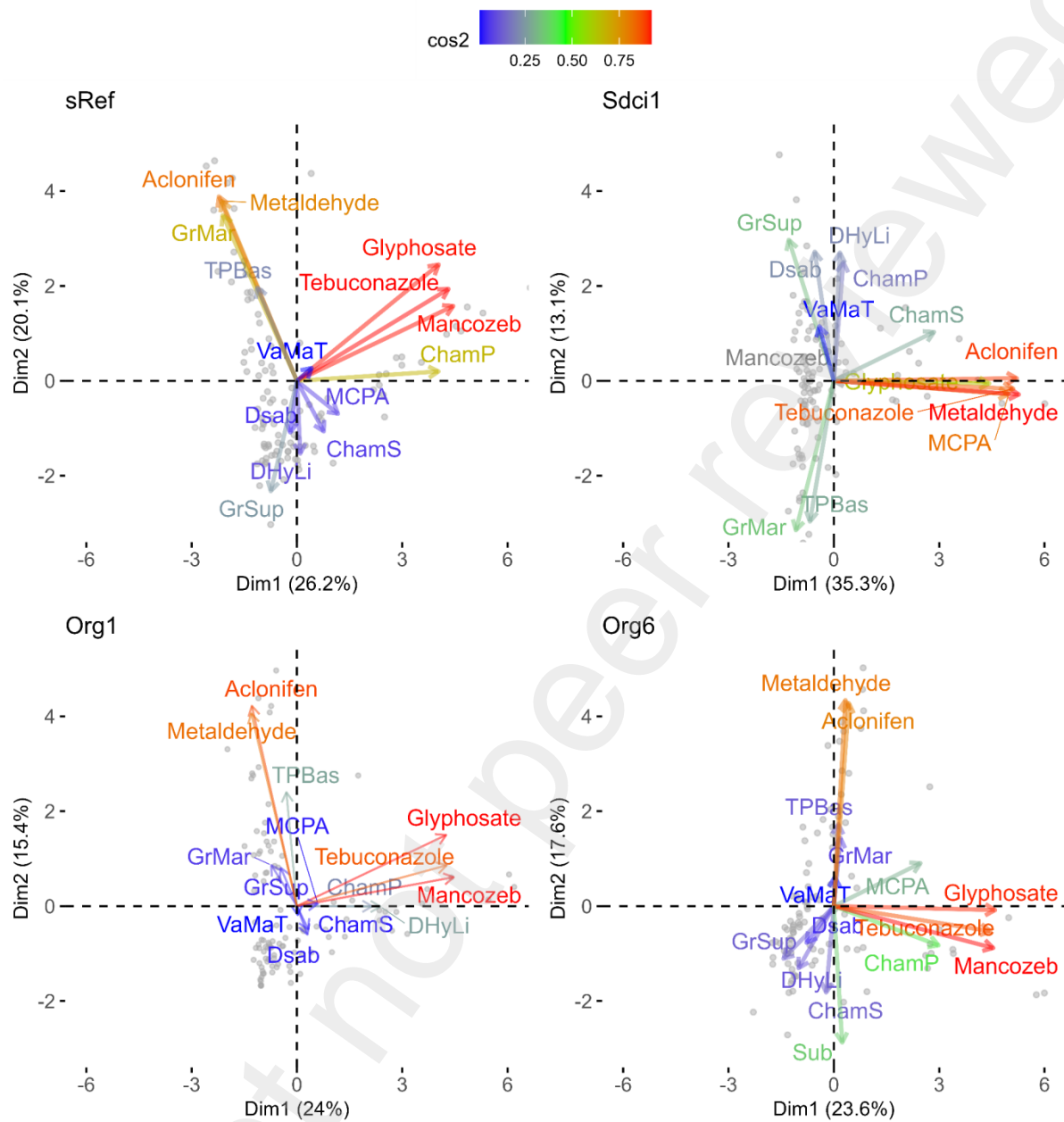
Anthropogenic practices and biogeochemical factors play pivotal roles in PPP transfers, with soil types and climate conditions significantly influencing the temporal distribution of diffuse pollution in watercourses. While precipitation (PCP) exacerbates this phenomenon, it is noteworthy that PCP alone does not determine the extent of pollution (Boithias et al., 2014). Shallow soils such as GrSup and ChamS, along with silty loams like DHyLi and sandy loams such as Dsab, exhibit strong correlations with PCP and are primary contributors to PPP transfers.



290           Within the four illustrated scenarios (Fig. 4), aclonifen and metaldehyde demonstrate  
291 significant correlations with certain soil types, particularly GrMar, TPBas, and VaMaT.  
292 Conversely, glyphosate, tebuconazole, and mancozeb exhibit larger variances within sub-  
293 basins, with tebuconazole showing an average transfer capacity across the sampled PPPs.  
294 Tebuconazole is notable for its ability to transfer in both dissolved and particulate phases,  
295 whereas mancozeb primarily transfers in the adsorbed phase. Agricultural practices further  
296 exacerbate PPP transfers, with intensive conventional agriculture, especially in vineyards and  
297 wheat-dominated rotations, significantly contributing to metaldehyde, aclonifen, and MCPA  
298 concentrations in sub-basins. The hydrological behavior of certain sub-basins, particularly  
299 those experiencing significant groundwater-river exchanges, also plays a role in exacerbating  
300 pollution transfers. In terms of agricultural practices, sub-basins with high contributions of  
301 tebuconazole and mancozeb are located in Priority Areas (PAs), except for certain sub-basins  
302 characterized by intensive conventional agriculture with vines and wheat-dominated  
303 rotations. Tebuconazole is applied to vines, as well as dry and irrigated durum wheat, at  
304 specific rates, while mancozeb is applied at a different rate to vines.

305           Conversely, sub-basins contributing the most to metaldehyde, aclonifen and, to a  
306 lesser extent, MCPA are correlated with the minority TPBa's heavy soil type (Fig. 4).  
307 Metaldehyde is applied to rapeseed ( $113 \text{ g. ha}^{-1}$ ), maize ( $110 \text{ g. ha}^{-1}$ ) and all other straw  
308 cereals and sunflower, depending on soil type and plant, at a rate of between  $9$  and  $38 \text{ g. ha}^{-1}$ .  
309 However, only sub-basins 27 and 17 are classified as PAs. One hypothesis for the factors  
310 aggravating transfers to sub-basins 5 and 37 is the hydrological behavior of these sub-basins,  
311 which are part of the northern median part of the DWSCH basin, characterized by significant  
312 groundwater-river hydrological exchanges.

313



314

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Figure 4: PCA Biplots of factors at the basin outlet

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The analysis of the sRef scenario highlights significant contributions of various Plant

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Protection Products (PPPs) to spatial variance, with the exception of mancozeb. Sub-basins

318

with high contributions of tebuconazole and mancozeb are strongly correlated with the

319

ChamP agricultural soil type (Fig 4). Tebuconazole has an average transfer capacity among

320 the PPPs, being able to transfer in both dissolved and particulate phases, while mancozeb  
321 primarily transfers in the adsorbed phase.

322 Principal component analysis of the scenarios for conversion to organic farming  
323 highlights reductions in the contribution of aconitine and metaldehyde transfers with targeted  
324 actions, even on small areas. Taking sub-basin 27 as an example, conversion of 148 ha and  
325 212 ha significantly reduced the contribution to aconitine and metaldehyde transfers. This  
326 indicates the effectiveness of organic farming in mitigating diffuse pollution markers.  
327 Additionally, the variance of individual sub-basin contributions changes with the intensity of  
328 land conversion to organic farming. We can see that the variances of individual sub-basin  
329 contributions change as the conversion of land to organic farming intensifies. Conversion to organic  
330 farming emerges as a potential mitigation strategy, with targeted actions significantly  
331 reducing the contributions of pesticides, particularly aconitine and metaldehyde. The  
332 effectiveness of organic farming scenarios underscores the potential for small-scale  
333 interventions to mitigate diffuse pollution markers. Spatialized changes in practices, such as  
334 intercropping and alternative techniques to reduce active substance quantities, demonstrate  
335 promise in mitigating PPP transfers and reducing effluent volumes.

336 The results highlight the complex interplay between anthropogenic practices,  
337 biogeochemical factors, and agricultural practices in influencing PPP transfers within the  
338 studied basin. Furthermore, the effectiveness of targeted interventions underscores the  
339 importance of tailored strategies in mitigating diffuse pollution and protecting water  
340 resources.

341 The biplot on the left shows that Sdc11 significantly reduces the contributions of the main  
342 pesticides, with the exception of MCPA, which is used as a substitute herbicide. Notably, the most  
343 contributive sub-basins (CSAs) primarily align with specialization in winegrowing  
344 downstream (particularly Cognac) and concentration of field crops upstream. These areas

345 face significant phytosanitary pressure, with numerous treatments of vineyards generating  
346 PPP effluents that require management. More than a dozen treatments of vineyards with  
347 phytosanitary substances generate PPP effluents that need to be spread or treated.

348         Across the Sdci scenarios, there is a consistent reduction in transfers in the central and  
349 downstream parts of the main section and its northern tributaries. Despite certain molecules  
350 showing a relatively low secondary effect of pesticide substitution in terms of cumulative  
351 concentrations, the innovative scenarios, particularly Sdci1 and Sdci3 targeting all field  
352 crops, prove effective. These scenarios are also highly effective in certain sub-basins,  
353 including priority zones, for specific molecules, while demonstrating a moderate effect on  
354 others. This highlights the necessity of spatialized changes in practices to address diverse  
355 pollution sources effectively.

356         Sdci scenarios implement measures such as intercropping to limit PPP transfer by  
357 runoff, thus safeguarding water resources. Additional techniques like reducing active  
358 substance quantities through methods like grassing of vines and mechanical weeding, along  
359 with adherence to good practices in pesticide application, contribute to reducing effluent  
360 volumes. However, understanding the distribution between surface and underground inputs  
361 remains a challenge, particularly in karstic soils. This underscores the need for ongoing  
362 research and management strategies to address complex pollutant pathways.

### 363 **3.3. Analysis of temporal variability with the Mann Kendall test (MK)**

364         The spatial analysis of the Mann-Kendall (MK) test results, focusing on tebuconazole and  
365 scenarios of conversion to organic farming, reveals notable monotonic trends ranging from  
366 little to high significance (Fig. 5):

367 i. Across the main river continuum, excluding its headwaters, a substantial number of  
368 monotonic trends are observed across all scenarios, including the reference scenario (sRef).

369 The increase in areas converted from conventional to organic farming correlates with the rise  
370 in the number of river sections exhibiting significant monotonic trends, particularly evident  
371 along the main southern tributary, notably in the Org6 scenario.

372 ii. High levels of diffuse tebuconazole pollution are identified in the southern and  
373 southwestern regions, specifically in sub-basins 62, 65, and 71. Within the same impluvium  
374 situated in priority zones, varying degrees of Contaminant Source Areas (CSAs) are  
375 observed. While some CSAs fall within priority action areas designated by water governance,  
376 others, such as CSAs 75, 79, 51, 68, 82, 88, and 98, do not. Nonetheless, significant  
377 monotonic trends are detected outside priority zones, suggesting the potential benefits of  
378 implementing biological scenarios to mitigate tebuconazole contamination. Geological and  
379 hydrological factors may contribute to the observed disparities between actions targeted at  
380 Priority Areas (PAs) and actual responses over time, particularly given shared groundwater  
381 bodies and dynamic surface runoff dynamics.

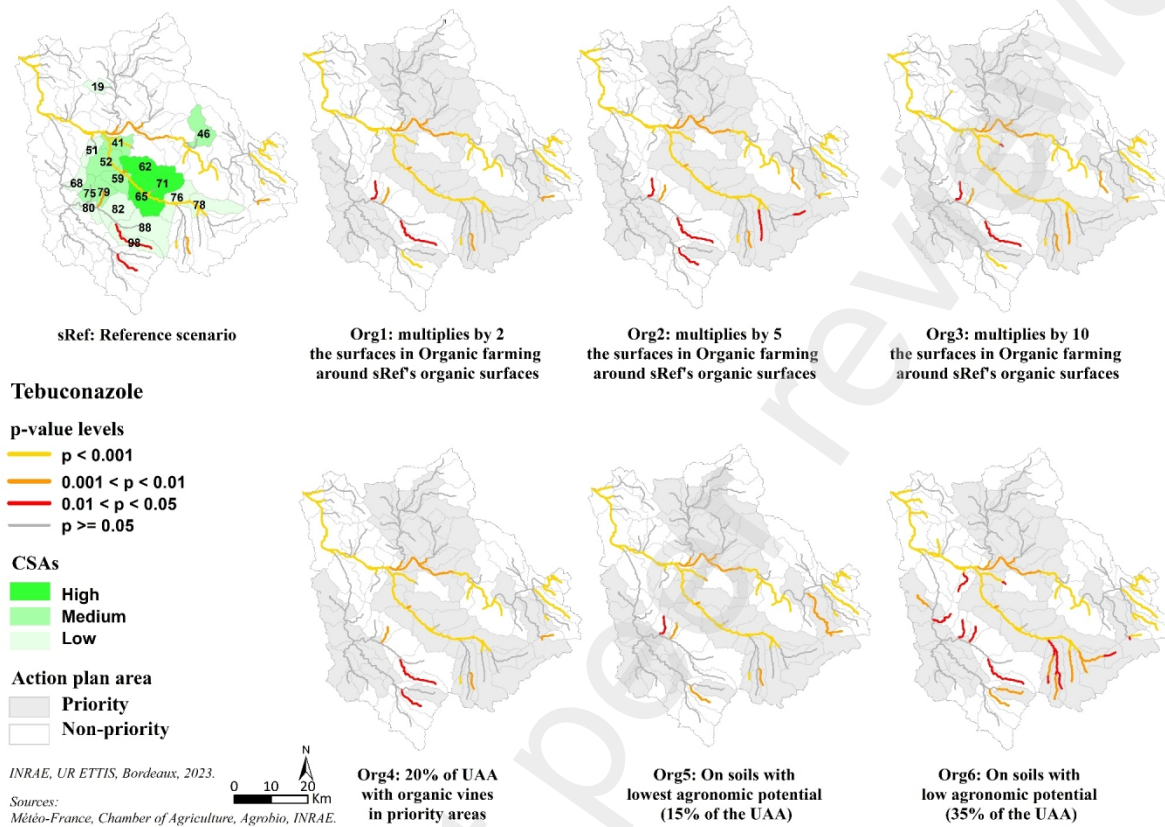
382 iii. In the northern region, sub-basin 19, characterized as a low contributor, exhibits  
383 significant monotonic trends associated with parts heavily cultivated with irrigated durum  
384 wheat. This highlights tebuconazole as a marker of specific agronomic practices, particularly  
385 those related to durum wheat cultivation.

386 iv. To the east, agricultural sub-basin 46, a moderate contributor, demonstrates potential  
387 benefits from inclusion in priority action zones, especially considering its cultivation of  
388 irrigated durum wheat on silty soils (DH<sub>Y</sub>Li), which may facilitate contaminant transfers.

389 The distributions and mean concentrations of tebuconazole from the agri-environmental  
390 scenarios are notably smaller and lower in amplitude compared to the reference scenario.

391 These monotonic downward trends indicate significant reductions in concentrations over the

392 12-year study period, suggesting sustainable and substantial improvements in water quality  
 393 attributed to LUC for this particular PPP in select river sections.



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Figure 5: MK trends in Tebuconazole concentrations in Org scenarios vs sRef

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#### 4. Conclusions and perspectives

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Our study, employing SWAT-GenLU2 spatialized agrohydrological modeling, has yielded valuable insights into the effectiveness of various cropping scenarios in limiting pesticide transfers. By considering combined agronomic orientations, such as organic farming, innovative systems, grass strips, and meadows, along with their progressive implementation, we have elucidated the nuanced relationship between agricultural practices and water quality outcomes. The statistical methods applied to model outputs have provided complementary perspectives for assessing the efficacy of agro-environmental mitigation

404 scenarios, identifying the contributions of anthropogenic and soil factors, and discerning  
405 monotonic trends over time.

406 Our findings highlight that widely deployed scenarios on the Utilized Agricultural  
407 Area (UAA) tend to be more effective over time. However, certain sub-basins exhibit  
408 stronger responses to changes in practices and agrosystems, influenced by specific climatic,  
409 biophysical, and pedomorphological characteristics. Targeting changes within specific  
410 agrosystems, such as field crops and vineyards, can significantly improve surface water  
411 quality, especially when considering the unique characteristics of each sub-watershed.

412 As agroecology gains traction in the study area, it becomes imperative to address the  
413 heterogeneous nature of organic farming practices. The increasing adoption of organic  
414 farming suggests a need to incorporate pesticides authorized for organic farming into  
415 modeling efforts. Identifying highly vulnerable areas to pesticide transfer, such as Critical  
416 Source Areas (CSAs), can aid in defining Priority Areas (PAs) for targeted mitigation efforts,  
417 particularly in the context of climate change.

418 While our modeling approach provides valuable insights, it is essential to  
419 acknowledge its limitations. The complexity of water quality processes and the simplified  
420 representation in the model necessitate caution in its application, requiring validation by field  
421 experts. Improved pesticide monitoring, alongside model calibration and validation efforts,  
422 can enhance our understanding of diffuse pollution and reduce modeling uncertainties.

423 Moving forward, integrating socio-economic drivers into decision support methods  
424 could further enhance our ability to assess and manage water quality effectively. By  
425 considering uncertainties and leveraging multi-criteria decision support methods, integrated

426 water quality modeling, and scenario planning, stakeholders can develop more robust  
427 strategies for sustainable water resource management.

428 Despite these challenges, our spatialized modeling approach offers valuable insights  
429 into the environmental implications of agro-environmental changes and can be extrapolated  
430 to other contexts. Continued research efforts and interdisciplinary collaborations are essential  
431 for addressing the complex challenges associated with water quality management in  
432 agricultural landscapes.

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439 Pryet for their contribution to the model calibration and validation.

### 440 Tables

441 **Table 1** *Description and objectives of the mitigation scenarios tested*

Scenario	Description and LUCs ( [ha]; [% of Total surface]; [% of UAA])	Objectives
<b>sRef</b>	Reference scenario (2558; 70; 100)	Assess model performance (calibration and validation). Detect sensitive parameters. Identify uncertainty sources.
<b>Depp</b>	Turning some fields with mixed cropping systems and temporary grassland into conventional cropping systems (33; 0.9; 1.3)	Modeling the effect of a decrease in livestock activity



<b>Sdci1</b>	Innovative systems throughout the basin (2558; 70; 100)	Identifying the effect of Sdci's massive development
<b>Sdci2</b>	Innovative systems in PAs (1353; 37; 53)	Testing on PAs the massive development of a potential action plan
<b>Sdci3</b>	Low-input field crops throughout the basin (1949; 53; 76)	To isolate the effect of the evolution of field crop practices
<b>Sdci4</b>	Low-input vines throughout the basin (566; 15; 22)	To isolate the effect of the evolution of vineyard practices.
<b>Sdci5</b>	Innovative systems on PAs (503; 14; 20)	Testing an intermediate innovative systems scenario
<b>Sdci6</b>	Combination of 20% of Sdci and 15% of Org (% of UAA) (503; 14; 20)	Testing an intermediate scenario combining Organic and innovative systems
<b>Org1</b>	Doubling the surfaces areas in Org (23; 0.6; 0.9)	Hypothesis tested:
<b>Org2</b>	Multiplication by 5 of Org's UAA (93; 2.5; 3.6)	i) the potential development of Organic farming is stronger in the sub-basins where it is already settled. The increase in Organic
<b>Org3</b>	Multiplication by 10 of the Org's UAA (208; 5.7; 8.1)	UAA is achieved first in these areas and then in the neighbouring sub-basins.
<b>Org4</b>	To reach 20% of UAA of organic vines in the 35 selected sub-basins. (203; 5.5; 7.9)	ii) the development of Organic farming is mostly done on soils with low agricultural potential (valleys, and wetland and terraced soils)
<b>Org5</b>	Org on soils with lower agronomic potential (367; 10; 14)	
<b>Org6</b>	Org on all types of low to medium agricultural potential (904; 25; 35)	To illustrate the maximum potential development of Organic crop production All soil types except on deep Campanian and Groies marl soils
<b>Herb1</b> <b>+ 6 VFS</b>	Introduction of grassed areas in association with Ref practices on the known most vulnerable areas (378; 10.3; 15)	Testing the conversion of fields crops to pasture at 551 targeted fields close to watercourses, in combination with Ref practices
<b>Herb2</b> <b>+ 6 VFS</b>	Testing the consequences of the introduction of grassed areas on PPP pressure (2558; 70; 100)	Testing the conversion of fields crops to pasture at 551 targeted fields close to watercourses, in combination with Sdci1 practices and LUC

**Herb3** Introduction of grassed areas in Testing the conversion of fields crops to  
**+ 6 VFS** association with Org6 practices on the pasture at 551 targeted fields close to  
most vulnerable areas (1064; 29; 42) watercourses, in combination with Org6  
practices and LUC

## 442 **References**

- 443 Abimbola, O., Mittelstet, A., Messer, T., Berry, E., & van Griensven, A. (2021). Modeling  
444 and Prioritizing Interventions Using Pollution Hotspots for Reducing Nutrients, Atrazine and  
445 E. coli Concentrations in a Watershed. *Sustainability*, 13(1), 1-22. doi:ARTN  
446 10310.3390/su13010103.
- 447 Agudelo-Jaramillo, S., Ochoa-Munoz, M., & Zuluaga-Diaz, F. (2016). Principal Component  
448 Analysis for Mixed Quantitative and Qualitative Data Proposal Report Research Practise:  
449 Medellin.
- 450 Amblard, L. (2019). Collective action for water quality management in agriculture: The case  
451 of drinking water source protection in France. *Global Environmental Change*, 58, 101970.  
452 doi:10.1016/j.gloenvcha.2019.101970.
- 453 Bieroza, M. Z., Bol, R., & Glendell, M. (2021). What is the deal with the Green Deal: Will  
454 the new strategy help to improve European freshwater quality beyond the Water Framework  
455 Directive? *Sci Total Environ*, 791, 148080. doi:10.1016/j.scitotenv.2021.148080.
- 456 Council of the European Union (1998). Council Directive 98/83/EC of 3 November 1998 on  
457 the quality of water intended for human consumption. *Off J Eur Communities [Internet]*, 41,  
458 34-54.

- 459 European Commission (2000). Directive 2000/60/EC of the European Parliament and of the  
460 Council of 23 October 2000 establishing a framework for Community action in the field of  
461 water policy. Official Journal of the European Communities, 327(43), 1-72.
- 462 European Commission (2008). Scientific Evidence for Policy-Making. EUR22982EN,  
463 Socio-economic Sciences and Humanities, Directorate-General for Research. Brussels :  
464 European Commission.
- 465 Gamble, A., & Babbar-Sebens, M. (2012). On the use of multivariate statistical methods for  
466 combining in-stream monitoring data and spatial analysis to characterize water quality  
467 conditions in the White River basin, Indiana, USA. *Environ Monit Assess*, 184(2), 845-875.  
468 doi:10.1007/s10661-011-2005-y
- 469 Gibbons, J. D., & Fielden, J. D. G. (1993). *Nonparametric statistics: An introduction*: Sage.
- 470 Gilbert, R. O. (1987). *Statistical methods for environmental pollution monitoring*: John Wiley  
471 & Sons.
- 472 István, P. (2020). *The European environment-state and outlook 2020. Knowledge for*  
473 *transition to a sustainable Europe*. European Environment Agency.
- 474 Kendall, M., & Gibbons, D. (1990). *J. Rank Correlation Methods*: Oxford University Press.
- 475 Kohne, J. M., Kohne, S., & Simunek, J. (2009). A review of model applications for structured  
476 soils: b) Pesticide transport. *J Contam Hydrol*, 104(1-4), 36-60.  
477 doi:10.1016/j.jconhyd.2008.10.003.
- 478 Kruskal, W. H., & Wallis, W. A. (1952). Use of ranks in one-criterion variance analysis.  
479 *Journal of the American statistical Association*, 47(260), 583-621.

- 480 Lacas, J.-G., Voltz, M., Gouy, V., Carluer, N., & Gril, J.-J. (2005). Using grassed strips to  
481 limit pesticide transfer to surface water: a review. *Agronomy for Sustainable Development*,  
482 25(2), 253-266. doi:10.1051/agro:2005001.
- 483 Munoz-Carpena, R., Fox, G. A., & Sabbagh, G. J. (2010). Parameter importance and  
484 uncertainty in predicting runoff pesticide reduction with filter strips. *J Environ Qual*, 39(2),  
485 630-641. doi:10.2134/jeq2009.0300
- 486 Porporato, A., Feng, X., Manzoni, S., Mau, Y., Parolari, A. J., & Vico, G. (2015).  
487 Ecohydrological modeling in agroecosystems: Examples and challenges. *Water Resources*  
488 *Research*, 51(7), 5081-5099. doi:10.1002/2015wr017289.
- 489 Pryet, A., Santos, L., Leccia, O. (2016). Calibration du modèle Soil and Water Assessment  
490 Tool (SWAT) pour le bassin d'alimentation de captage Grenelle : Projet MODCHAR2.  
491 <<https://hal.science/hal-02604830/>>; 2016 [accessed 13.03.24].
- 492 Strehmel, A., Schmalz, B., & Fohrer, N. (2016). Evaluation of Land Use, Land Management  
493 and Soil Conservation Strategies to Reduce Non-Point Source Pollution Loads in the Three  
494 Gorges Region, China. *Environ Manage*, 58(5), 906-921. doi:10.1007/s00267-016-0758-3.
- 495 Tang, X., Zhu, B., & Katou, H. (2012). A review of rapid transport of pesticides from sloping  
496 farmland to surface waters: processes and mitigation strategies. *J Environ Sci (China)*, 24(3),  
497 351-361. doi:10.1016/s1001-0742(11)60753-5.
- 498 Team, R. C., Team, M. R. C., Suggests, M., & Matrix, S. (2018). Package stats. The R Stats  
499 Package.
- 500 Vernier, F., Leccia-Phelpin, O., Lescot, J. M., Minette, S., Miralles, A., Barberis, D., et al.  
501 (2017). Integrated modeling of agricultural scenarios (IMAS) to support pesticide action

- 502 plans: the case of the Coulonge drinking water catchment area (SW France). *Environmental*  
503 *Science and Pollution Research*, 24, 6923-6950, doi:10.1007/s11356-016-7657-2.
- 504 Veselá, T., Nedbal, V., & Brom, J. (2020). Detection of pesticide in a small agricultural basin  
505 after 15 years of application ban. *Int. Multidiscip. Sci. Geoconf. SGEM*, 20, 75-82.
- 506 Wang, R., Yuan, Y., Yen, H., Grieneisen, M., Arnold, J., Wang, D., et al. (2019). A review of  
507 pesticide fate and transport simulation at watershed level using SWAT: Current status and  
508 research concerns. *Science of the total environment*, 669, 512-526.
- 509 Zhang, X., & Zhang, M. (2011). Modeling effectiveness of agricultural BMPs to reduce  
510 sediment load and organophosphate pesticides in surface runoff. *Sci Total Environ*, 409(10),  
511 1949-1958. doi:10.1016/j.scitotenv.2011.02.012.