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# Assessing agri-environmental strategies to reduce pesticide concentrations in surface drinking water sources, Coastal Charente River basin, SW France

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## Abstract

Most surface water bodies are deteriorating, resulting in health risks and environmental damage. This study aimed to assess the performance of the modeled agri-environmental transition scenarios for restoring freshwater quality within the protection perimeter of strategic surface water drinking water catchments. Realistic agri-environmental scenarios with combined agronomic orientations were tested using a well-calibrated ecohydrological model. Their performance was quantified based on pesticide concentration reductions in freshwater bodies, focusing on temporal and spatial variability, using non-parametric tests. Our results show that it is possible to differentiate cropping mitigation scenarios according to their ability to limit pesticide transfers, taking into account the most influential biogeochemical factors in the catchment, their agronomic orientation, and their progressive implementation. Our study is also applicable to other contexts.

*Keywords: agriculture; drinking water; pesticide; scenarios; watershed; water source protection*

## 1. Introduction

In Europe, despite decades of directives and policies aimed at protecting water resources (EC, 2000), and notably the quality of water intended for human consumption (EC, 1998, recast with EC, 2020), and the sustainable use of pesticides (EC, 2009), approximately 60% of surface water bodies exhibit poor ecological and chemical conditions (István, 2020). This deterioration not only impacts ecosystems long-term after their ban (Veselá, et al., 2020) but also poses risks to drinking water abstraction points, thereby endangering human health (Budzinski and Couderchet, 2018; Baldi et al., 2022).

Effective water quality restoration requires comprehensive action programs addressing diffuse pollution, incorporating holistic farm-level interventions and broader watershed management strategies (Bieroza et al., 2021), and collectively involving territorial stakeholders and water users and managers (Amblard, 2019). However, because financial resources are limited, water managers target the most contaminated areas, identified by water development and management plans as "Priority Areas” (PAs), with agri-environmental and climate measures. Despite these efforts, persistent diffuse pollution continues to affect drinking water sources (Amblard, 2019). In France, around 500 catchments affected by diffuse agricultural pollution have been classified as 'Grenelle' strategic catchments as part of the Grenelle de l'Environnement initiative launched in 2007 to prioritize actions to protect drinking water. This number has since increased to an estimated 3000 catchments (Amblard, 2019).

Decision-support tools are needed to characterize the spatiotemporal dynamics of agricultural diffuse pollution and improve water quality governance at the catchment scale. Identifying critical source areas (CSAs) (Giri et al., 2016) and understanding the temporal variability in pollution levels are essential for the efficient implementation of diffuse pollution mitigation strategies.

Ecohydrological modeling simulates the agro-ecosystems and agricultural practices associated with soils and plants, soils and climate heterogeneity, and the non-linearity of biogeochemical watershed processes responsible for pollutant fate and transport, as well as hydrosystem response to land use and climate change (Kohne et al., 2009; Porporato et al., 2015; Veselá et al., 2020). Thus, it helps improve long-term watershed management (Strehmel et al., 2016). However, for enhanced decision support and considering the complexity of scenarios and biophysical variations in time and space, further analysis is required to discriminate the respective contributions of anthropogenic and biophysical factors, in time and space and evaluate the statistical efficiencies of the modeled scenarios.

This study focusses on a 3,800 km $^2$ wide priority surface water catchment area~~,~~ endangered by pesticide diffuse pollution, and aims to shed light on the anthropogenic and biophysical factors that significantly contribute to the reduction of plant protection product (PPP) pollution in freshwater using statistical methods on the ecohydrological model output of the tested mitigation scenarios. We aim to differentiate these scenarios based on their ability to limit pesticide transfers by considering the most influential biogeochemical factors in the catchment, their agronomic orientation, and their progressive implementation in time and space. By applying indirect methods through a well-calibrated ecohydrological model (SWAT) and using statistical analysis of its outputs, this study evaluates mitigation strategies for improving water quality. The findings provide insights applicable to other contexts and contribute to enhancing the overall approach to water quality management in agricultural landscapes.

## 2. Materials and Methods

### 2.1. Study area

The Drinking Water Coulonge Saint-Hippolyte (DWSCH) basin, situated in southwest France within the Charente basin (0°45W 45°58N / 0°16E 45°14N), serves as a critical area or protection area for surface drinking water abstraction sources, spanning 3,800 $km^2$ (Fig. 1). The Charente River extends 381 km from east to west and is the primary drainage system in the basin, ultimately discharging into the Atlantic Ocean. With an average flow rate of 95 $m^3 s^{-1}$, the river discharge varies from a few $m^3 s^{-1}$ to 815 $m^3 s^{-1}$ at the furthest downstream gauging station, located approximately 40 km upstream from the Ocean estuary, where tidal influences become significant. The main outlet of the DWSCH basin is located about 30 km from the coast, however, due to the meandering course of the river, it can be up to 40 km upstream from the estuary. While tidal effects are more pronounced closer to the estuary, they exert less influence within the DWSCH basin. The alluvial beds of the river exhibit low density, and dams, canals, and reservoirs throughout the basin significantly influence the natural hydrological regime (Fig. 1).

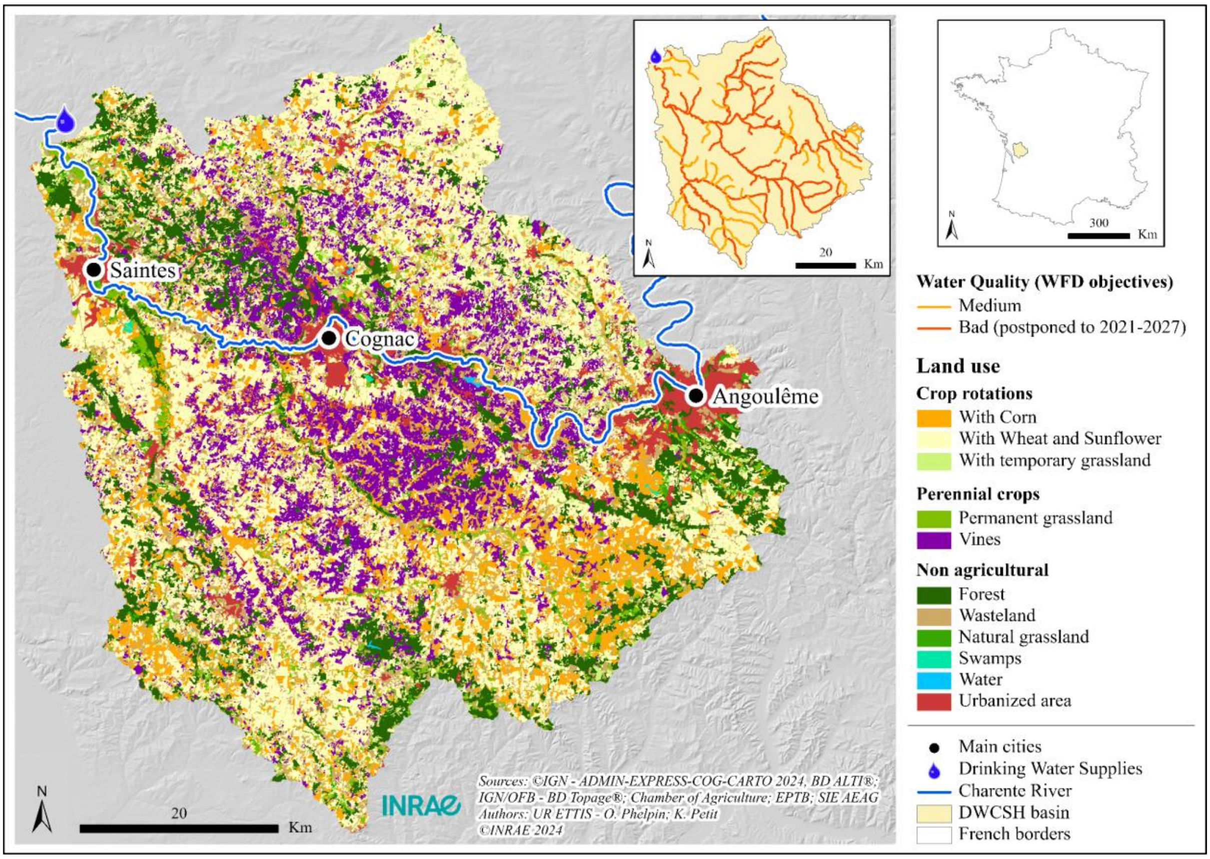

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Figure 1: Map of the study area.

The DWSCH basin‘s water supply area is considered strategic for several reasons: it produces 170 millions m$^3$ y$^{-1}$ to serve 290,000 residents, with this number increasing to over 500,000 during the summer months; it is highly vulnerable to pesticides, particularly herbicides, excessive concentrations of which are regularly observed despite action plans; and protection of this threatened resource is required by the Water Framework Directive (WFD) (EC, 2000, EC, 2008). To comply these requirements, local water managers aim to reduce pesticide peak concentrations and maintain levels below 0.05 µg/L for each pesticide, which is set as half of the maximum acceptable concentration (MAC) outlined in the EU regulations. To comply with the Water Framework Directive (WFD) and other EU regulations, local water managers aim to reduce pesticide peak concentrations and maintain levels below 0.05 µg/L for each pesticide, which corresponds to half of the maximum acceptable concentration (MAC) outlined in the EU regulations.

The climate is generally temperate, with an average rainfall of 800 mm yr$^{-1}$ over the last 30 years and an average temperature of 13°C. However, variability exists: the climate is mild and dry and sunny in the center (Cognac area), oceanic on the coast, and wetter and less mild in the eastern part of the plateau. The topography is mostly flat, with a minimum elevation of -1 m to 0 m a.s.l. in the west and a maximum elevation of 500 m a.s.l. in the East. Agriculture is the predominant activity in the area, significantly impacting pesticide concentrations. The most frequent exceedances were over 40% for metaldehyde and mancozeb, over 25% for glyphosate and 35% for its metabolite (Source: SIE AEAG).

## 2.2. Reference scenario

The "reference scenario" serves as the baseline against which all mitigation scenarios are evaluated. It is important to note that this scenario is not the current state of the catchment but rather a baseline established in 2017 with the expertise and consensus of various stakeholders, including agricultural experts, environmental scientists, and local water managers (Vernier, 2017). The reference scenario reflects the agricultural practices, land use, and management strategies that were prevalent at that time. In this scenario, the dominant land use consists mainly of intensive conventional agricultural practices. Land use patterns vary with soil characteristics and agricultural goals. Unlike many mesoscale crop modeling studies that cover only 2-6 crop types, our study simulates 41 distinct cropping systems (Fig. 1).

These systems are associated with specific agricultural practices related to eight soil features (Table 2) and encompass 17 irrigated and unirrigated crops. The crops grown in the region include: i) Traditional crops: sunflower, soft winter wheat, durum wheat, oilseed rape, grain corn, maize corn, winter barley, spring barley, and temporary grassland. ii) Innovative and organic options: alfalfa, field pea, temporary pasture, soybean, clover, and triticale.

**Table 1** *Agricultural Soil Types Table*

| **Common name, cover age (%), FAO Types** | **Description** | **Agronomic Properties & Use** | **Vulnerabilities** |
|---|---|---|---|
| **Groies, 36%. Calcosols, rendosols.** | Calcareous clay-loam soils ; differentiated into shallow (**GrSup**) that are stony, low water-holding capacity; and silty clay soils over marl or limestone, non-hydromorphic, irregular stone content, with local clayey hydromorphic zones (**GrMar**). | Fertile, with **GrSup** requiring irrigation; and suitable for polyculture; requires irrigation for corn due to drought; **GrMar** suitable for cereals, easy to cultivate due to its well-drained structure. | Moderate runoff in summer for GrSup; low runoff throughout the year for GrMar. |
| **Campanian soils, 33%. Calcisols, calcosols, rendosols..** | Clayey-calcareous soils, gray to black in color, overlying chalk, marl, or soft limestone, differentiated into shallow (**ChampS**) with high calcium carbonate content from the surface; Deeper soils (ChampP) have greater water capacity, benefiting from capillary rise. | High potential for **ChampS** used in dry farming, and vineyards; **ChampP** are very suitable for corn and mixed crops. | High runoff potential, especially in winter, due to low surface infiltration, especially in winter. |
| **Doucins, 16% Planosols, neoluvisols, brunisols**, calcisols, calcosols. | Mixed clayey, loamy, sandy soils, acidic, with low water-holding capacity, subdivided into hydromorphic sandy-loamy (**Dsab**) with low fertility and sandy-clayey (**Dmar**), often waterlogged. | Soil pH management and structure improvement required. **Dsab** moderately suitable for cereals, requiring irrigation, **Dmar** poor to cultivate, requiring minimum to no tillage, in dry conditions. | Vulnerable to surface runoff, desiccation and leaching (Dsab); strong runoff and waterlogging (**Dmar)**. |
| **Pays Bas, 7%. Calcosols, rendosols.** | Very heavy clay soils (up to 60% clay content) with poor drainage located in the depressions in northern Cognac (**Tpbas**). | Limited agricultural use; best suited to specific crop rotations with adapted management practices. | High risk of waterlogging and surface runoff, especially in winter; slow infiltration.. |
| **Valleys and terraces 7%. Fluviosols, histosols, calcosols.** | Alluvial soils ranging from sandy to loamy textures with variable hydromorphology, in valleys (**VaMt**). | Suitable for pasture; some cereal farming in well-drained areas. | Moderate runoff risk of winter runoff due to fluctuating water levels; low risk of water saturation and seasonal flooding. |

The soils are predominantly sedimentary, varied in composition and generally thin, with calcareous and marly characteristics shaped by the local geology. The main soil types include calcosols, calcisols and rendosols, which largely determine the agronomic potential of the area (Table 1).

Representative herbicides such as glyphosate, aclonifen, MCPA, and tebuconazole, along with fungicides like mancozeb and the molluscicide metaldehyde, were studied. These pesticides were selected based on their frequent detection in freshwater environments and their extensive use in areas dedicated to field crop and vine cultivation. The selection criteria were based on current agricultural practices' prevalence, environmental impact, and relevance (Vernier, 2017).

The widespread use of these pesticides in agriculture is a significant concern due to their potential genotoxic effects on both the environment and human health. Glyphosate, the most widely used herbicide, causes DNA damage and oxidative stress (Lebailly et al., 1998). Mancozeb has been associated with genotoxicity for over 40 years (Perocco et al., 1989), while tebuconazole has demonstrated similar effects (Andrioli et al., 2023). Aclonifen is known to cause developmental abnormalities (Lee et al., 2021; Park et al., 2022), and the molluscicide metaldehyde poses significant risks to aquatic life (Macar et al., 2023). The increased use of the herbicide MCPA is also of concern.

Exposure to a mixture of plant protection products (PPPs) increases the risk of genotoxicity (Dhananjayan et al., 2019). Although the EU banned the sale of mancozeb and metaldehyde by the EU in 2020 and 2021, respectively, these substances are still used as anti-mildew and anti-slug agents and continue to be detected in streamflows within the DWSCH basin.

The persistent presence of these pesticides in excess underscores the pressing need for effective management strategies to mitigate their impact on drinking water sources.

### 2.3. The Charente SWAT model

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

The GenLU2-SWAT model was extensively calibrated and validated using observed streamflow and pesticide concentration data from the DWSCH basin, previously collected and referenced (Pryet et al., 2016), (Vernier et al. 2017). These data, sourced from institutional datasets (SIE AEAG and Météo-France), ensured accurate simulation of hydrological processes and contaminant transport. The calibration process included both streamflow measurements and pesticide concentration data, allowing the model to reliably simulate pollutant transfers within the hydrosystem at four available gauging stations and over 15 water quality stations. Although no new field measurements of pesticide concentrations were collected for this study, the previously validated SWAT model was used to simulate contaminant transfers and hydrosystem responses to land use changes (LUCs) and agronomic interventions, accros the 106 modeled sub-basins. The statistical analyses employed in this study (Kruskal-Wallis, Dunn's post hoc, Mann-Kendall, and PCA) are designed to explore spatio-temporal trends and relationships among biophysical factors based on model outputs. This indirect modeling approach provides insight into how these interventions affect water quality and pollutant transfer to surface waters.

## 2.4.The tested mitigation scenarios

The mitigation scenarios were developped to explore the impact of various agricultural practices and land-use changes (LUCs) on environmental quality, considering stakeholder interests (Table 2).

**Table 2** *Description and objectives of the tested mitigation scenarios*

| **Scenario** | Description & LUC (ha; % Total Area; % UAA) | **Objectives** |
|---|---|---|
| **sRef** | Reference scenario (2558; 70; 100) | Assess model performance, detect sensitive parameters. |
| **Depp** | Conversion of mixed/temporary grasslands to crops (33; 0.9; 1.3) | Model decreased livestock activity. |
| **Sdci1** | Full-basin innovative crop systems (Sdci) (2558; 70; 100) | Assess effects of large-scale Sdci practices. |
| **Sdci2** | Sdci in Protected Areas (PAs) (1353; 37; 53) | Test implementation within Pas. |
| **Sdci3** | Low-input field crops (1949; 53; 76) | Isolate impacts of changes in field crops. |
| **Sdci4** | Low-input vineyards (566; 15; 22) | Isolate impacts of changes in vineyards. |
| **Sdci5** | Intermediate Sdci in PAs (503; 14; 20) | Test intermediate Sdci in PAs. |
| **Sdci6** | 20% Sdci, 15% Organic (503; 14; 20) | Test combined practices. |
| **Org1** | Double organic area (23; 0.6; 0.9) | Test growth in existing and marginal areas. |
| **Org2** | 5-fold organic area increase (93; 2.5; 3.6) | Evaluate short-term organic expansion. |
| **Org3** | 10-fold organic area increase (208; 5.7; 8.1) | Evaluate medium-term organic expansion. |
| **Org4** | 20% organic vineyards in select areas (203; 5.5; 7.9) | Test organic vineyards in specific areas. |
| **Org5** | Organic on low-potential soils (367; 10; 14) | Explore organic farming on less fertile soils. |
| **Org6** | Organic on low-to-medium potential soils | Demonstrate potential on diverse soils. |

| | | |
|---|---|---|
| | (904; 25; 35) | |
| **Herb1, 2, 3** | Grassed areas with VFSs near watercourses:<br>- Herb1: sRef practices (378; 10.3; 15).<br>- Herb2: Sdci1 practices (2558; 70; 100).<br>- Herb3: Org6 practices (1064; 29; 42). | Test crop-to-pasture conversion with VFSs (5-30 m). |

Scenarios are grouped according to their agronomic drivers as follows:

i) Organic Farming (Org) explore different scales and targets of organic farming expansion, with prioritization in soils of lower agronomic potential (valleys, wetlands, and terraced areas). Organic practices involve reduced fertilization, cessation of synthetic pesticide use, extended crop rotations, and residue management.

ii) Innovative Crop Systems (Sdci) integrate transitioning pratices to organic farming for vineyards and field crops, at different scales. These systems limit pollutant use and transfer, lengthen crop rotations, promote intercropping, and provide alternative molecules for plant protection.

iii) Grassed Areas (Herb): integrate temporary grasslands into crop rotations, in combinination with practices from the baseline (Herb1), innovative crop systems (Herb2) and organic farming (Herb3). Each of this Herb scenario has its VFSs scenarios, with filter strips from 5 to 30 m wide along the 551 fields at high pollutant transfer risk to watercourses.

Modifications in farming practices lead to variations in field crop distribution. For example, wheat cultivation increased from 22% to 24% of the UAA between the reference scenario (sRef) and the innovative low-input scenario (Sdci1), reflecting current trends. Sunflower cultivation decreases from 19% to 13% and corn cultivation decreases from 15% to 12% in all scenarios.

Across all scenarios, vineyard acreage remains constant at 22% of the Utilized Agricultural Area (UAA). However, innovative scenarios show longer crop rotations and increased surfaces of cereals, spring field peas, alfalfa, and temporary grasslands, with reduced areas for sunflower, rapeseed, and corn. These changes occur while  maintaining overall vineyard acreage stability.

Crop rotations vary in length from 1 year (e.g., maize monoculture or temporary pasture) to 7 years (e.g., Sdci scenario with three years of maize, followed by barley, then three years of alfalfa, or two years of silage corn, sunflower, winter wheat, and three years of alfalfa). These repeated cycles ensured that the simulations realistically captured the impacts of agronomic practices over time, providing reliable predictions of potential environmental benefits.

The mitigation scenarios were simulated to assess potential improvements in freshwater quality over an extended period. This long-term approach accounts for ecosystem inertia and response to agricultural changes. By systematically modeling crop rotations, soil practices, and agricultural techniques across reference and mitigation scenarios, we aimed to provide reliable predictions of environmental benefits.

### 2.5.Mitigation scenario performance evaluation methods

Simulated daily hydro-meteorological and water-quality outputs exhibited a strong right skew and several concentration peaks, as observed. The well-calibrated Soil and Water Assessment Tool (SWAT) model was used to route the PPPs from fields to water reach, reporting at each of the 106 outlets.

Statistical analyses were performed on each of the simulated PPP across the 106 outlets over the last 4,383 days. Various scripts using R v4.3.1 package executed statistical computations and visualization (R Core Team, 2022).

To evaluate the effectiveness of each modeled mitigation scenario compared to the reference scenario (sRef), the non-parametric Kruskal-Wallis (KW) test (Kruskal and Wallis, 1952) and post hoc Dunn’s test with the Benjamini-Hochberg correction was used. The KW test was chosen for its robustness over the ANOVA or t-test in the presence of non-normality (Gibbons and Fielden, 1993). The null hypothesis (H0) states that each mitigation scenario is neither greater nor less than sRef at the 95% confidence level. For visualization, p-values from the KW pairs were prepared and presented as boxplots of the simulated PPP concentrations. Scenario performance was considered significant when $p < 0.05$, as follows: *: $p \leq 0.05$; **: $p \leq 0.01$; ***: $p \leq 0.001$; ****: $p \leq 0.0001$.

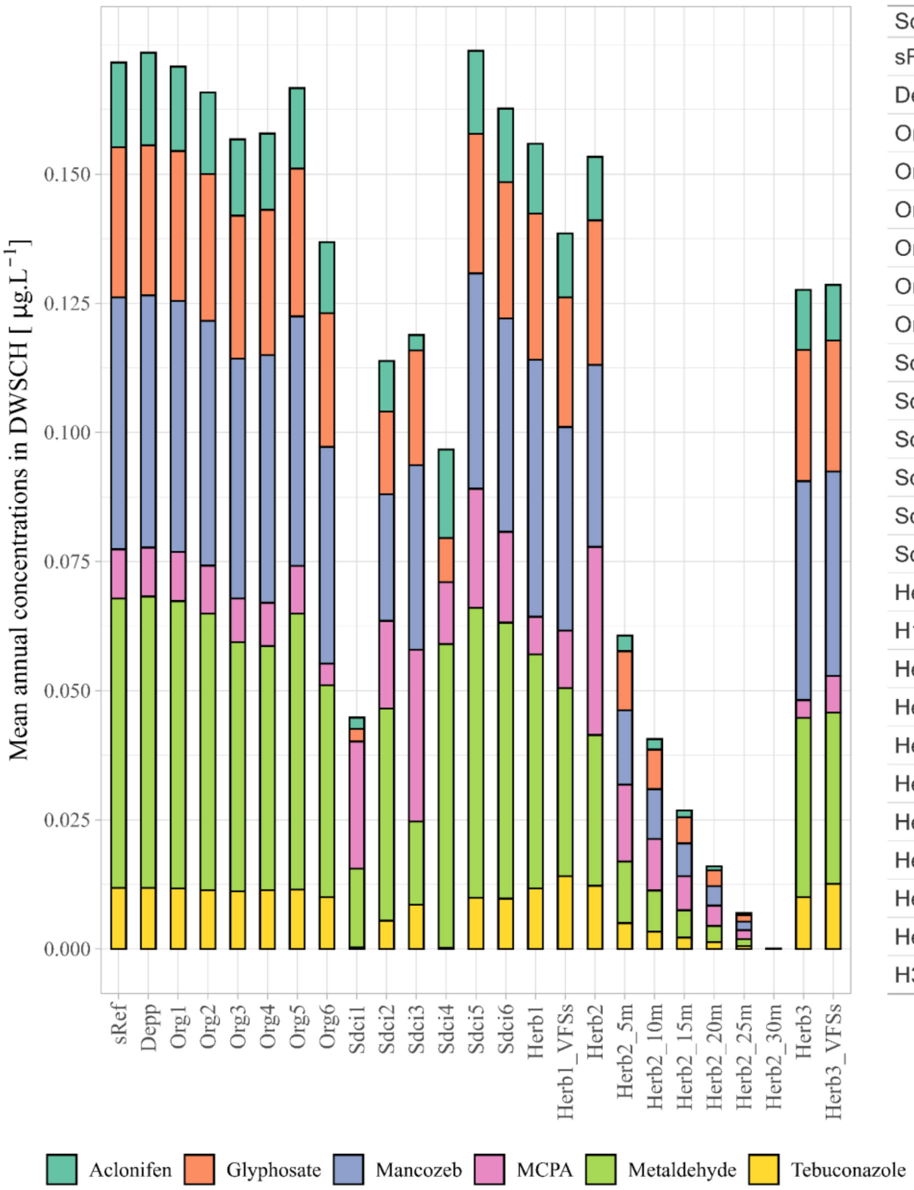
Principal Component Analysis (PCA) was employed to identify the contributions of biogeochemical factors and analyze the spatial variability in individual sub-basins. PCA was chosen because it is suitable for water quality studies, even in the presence of nonlinear processes, as it can optimally transform data (Gamble and Babbar-Sebens, 2012). Biplots were used as part of PCA to graphically represent the results by combining scores and loadings into a single plot. This approach allows simultaneous analysis of categorical (e.g., sub-basin identities) and quantitative (e.g., pollutant concentrations) multivariate data (Agudelo-Jaramillo et al., 2016). Biplots facilitate the identification of relationships and contributions among different variables, making them a powerful tool for interpreting the complex data generated in this study.

Temporal variability within sub-basins was investigated using the non-parametric Mann-Kendall (MK) test (Gilbert, 1987), chosen for its robustness (lower sensitivity to gross errors) and efficiency (smaller asymptotic variance) with adjustments for ties (Kendall and Gibbons, 1990). The MK test evaluated trends in daily water quality outputs, with the null hypothesis (H0) suggesting no a priori notion of an increasing or decreasing trend in mitigation scenarios compared to sRef at an alpha level of 0.05. A p-value of less than 0.05 led to the rejection of the null hypothesis, indicating a significant monotonic trend (H1).

## 3. Results and discussion

In the DWSCH watershed, trends in mitigation scenario performance indicate varying average modeled PPP concentrations over the past 12 years of the daily simulation. Scenarios like Sdci1 and Herb3 (Table 1), which were extensively implemented along with their associated VFS variants, demonstrated substantial reductions, achieving between 97% and 98% of the cumulative average PPP concentration drop in water flows over the simulation period. Innovative scenarios targeting PAs, such as Sdci3, also show favorable results, with a notable 90% reduction in cumulative PPP concentration.

Organic farming (Org) scenarios exhibit promising results, especially with significant LUCs. For instance, Org6, which accounts for 35% of LUCs devoted to organic farming, achieves a 33% reduction in the concentration. However, scenarios with conversion areas of less than 4% of the UAA, like Org1 and Org2, showed less significant relative reductions (Fig. 2).



| Scenarios | Cum.conc.[%] |
|---|---|
| sRef | 0.0 |
| Depp | 0.5 |
| Org1 | -0.4 |
| Org2 | -8.3 |
| Org3 | -12.8 |
| Org4 | -13.1 |
| Org5 | -7.2 |
| Org6 | -32.6 |
| Sdci1 | -97.4 |
| Sdci2 | -53.2 |
| Sdci3 | -90.7 |
| Sdci4 | -1.5 |
| Sdci5 | -26.3 |
| Sdci6 | -24.6 |
| Herb1 | -24.4 |
| H1_VFSs | -24.7 |
| Herb2 | -34.7 |
| Herb2_5m | -73.4 |
| Herb2_10m | -82.2 |
| Herb2_15m | -88.2 |
| Herb2_20m | -93.0 |
| Herb2_25m | -96.9 |
| Herb2_30m | -99.9 |
| Herb3 | -44.7 |
| H3_VFSs | -44.9 |

Figure 2: Simulated average PPP concentrations throughout the DWSCH basin.

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

To assess the effectiveness of the mitigation scenarios in safeguarding drinking water catchments, our analysis focused on the downstream sub-basin, i.e. the sub 6, which mainly consisted of wheat-based rotations with sunflower, corn, and rapeseed-based rotations.

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

Boxplots reveal significant reductions in PPP concentrations across the organic and innovative system scenarios, particularly for Sdci1 and Org6, where the peak concentrations remain below half the MAC. Innovative scenarios successfully maintained concentrations below the MAC threshold, except for MCPA.

The KW pairwise test provides further evidence of the effectiveness of these last massively implemented scenarios as significantly effective, but also some other targeted scenarios based on the progressive shift from intensive farming (Fig.3). Combining various agronomic orientations within a single scenario is effective for water quality restoration. For example, scenario Sdci6, which integrates innovative and organic farming practices, exhibits significant efficacy in reducing aclonifen and MCPA concentrations, moderate efficacy in reducing mancozeb and metaldehyde concentrations, and limited efficacy in reducing glyphosate concentrations. In addition, the scenarios characterized by a single, widely implemented agronomic orientation, such as Sdci1 and Sdci3, demonstrated significant statistical efficiencies in reducing aclonifen and metaldehyde concentrations. Notably, alterations in practices within these innovative scenarios led to partial substitution of aclonifen by MCPA and a decrease in metaldehyde applications. However, scenarios targeting innovative systems on PAs (Sdci2) and vines (Sdci4) also significantly reduce the concentration of mancozeb in watercourses. Targeting LUCs efficiently on relatively small surfaces using these combined scenarios is interesting for water management with limited financial resources.

Bio-geophysical factors help explain the sub-basin discrepancies between targeted actions and observed efficiency. For example, the Org1-Org4 scenarios receive runoff from the upstream sub-basins where these scenarios are implemented. Similarly, the Depp scenario results in increased aclonifen concentrations due to neighboring sub-basins experiencing grassland abandonment for corn cultivation, exacerbated by the presence of silty soils (DHyLi), which may favor the particulate transport of this adsorbable contaminant (Fig. 3).

### 3.1.2. Herb Scenarios and their VFS variants

The Herb2 and Herb3 scenarios generally lead to greater reductions in pollutant concentrations than Herb1, especially in targeted areas. Although VFS scenarios are primarily effective for nitrogen reduction (Abimbola et al., 2021), they also demonstrated the efficiency of PPP reduction (Tang et al., 2012). Predicting the VFS efficiency of pesticide trapping is a complex task due to lumped and in-stream empirical processes and parameter uncertainties (Munoz-Carpena et al., 2010). However, a general gradient between VFS width and efficiency was observed, with the combined Herb2 and Herb3 scenarios being the most effective at reducing various pollutant concentrations.

Combined Herb2-VFS scenarios are most effective at reducing various pollutant concentrations, with Herb2 alone effectively reducing glyphosate and mancozeb concentrations. Combined Herb2 with the largest VFS scenario maintained pollutant concentrations below the MAC, whereas combined Herb3 scenarios maintained the MAC below half and were highly effective at reducing metaldehyde concentrations.

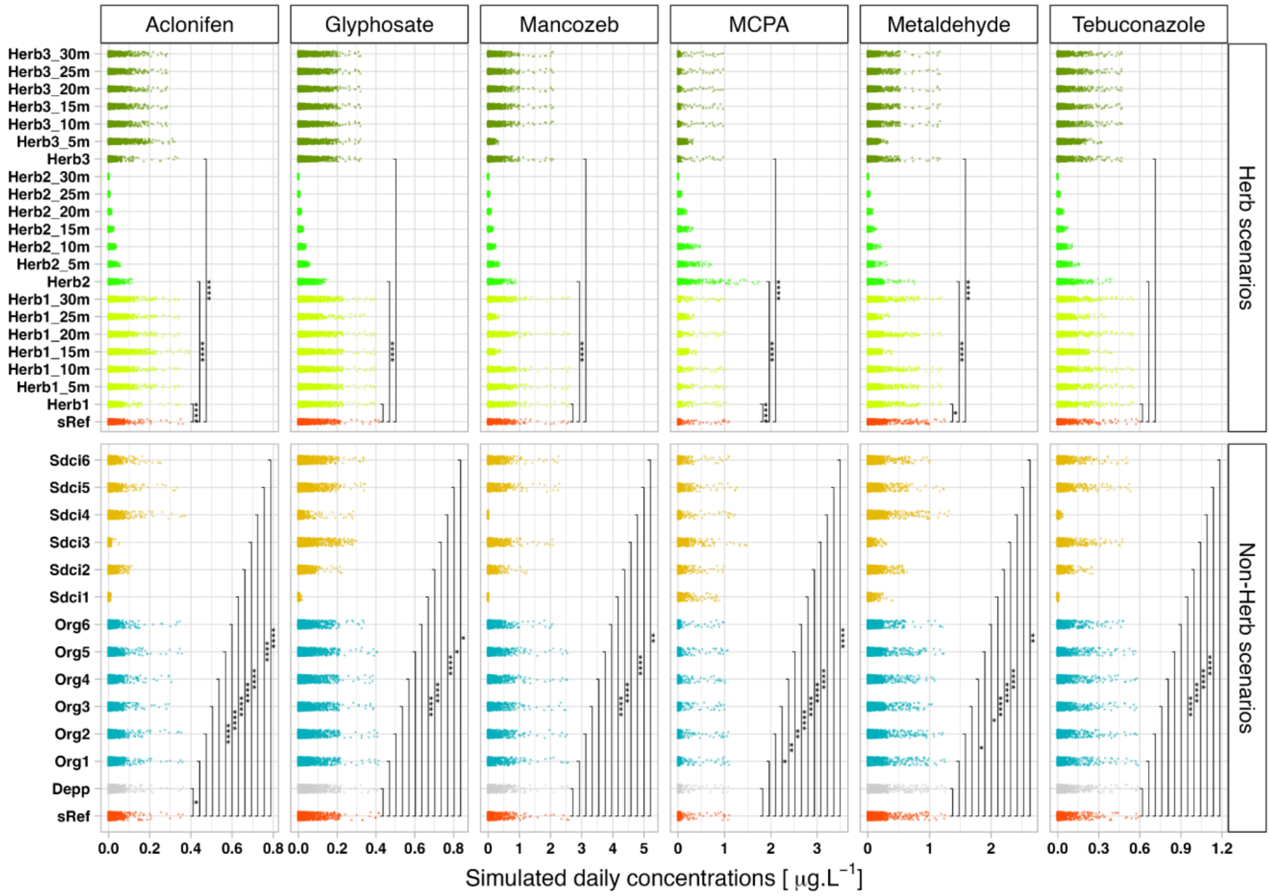


Figure 3: Distributions and KW efficiencies at basin outlet.

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

Anthropogenic practices and biogeochemical factors play pivotal roles in PPP transfers, with soil type and climate significantly influencing the temporal distribution of diffuse pollution in watercourses. Although precipitation (PCP) worsens this phenomenon, it is noteworthy that PCP alone cannot 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.

Within the four illustrated scenarios (Fig. 4), aclonifen and metaldehyde demonstrated significant correlations with certain soil types, particularly GrMar, TPBas, and VaMaT. Conversely, glyphosate, tebuconazole, and mancozeb exhibited larger variances within sub-basins, with tebuconazole showing an average transfer capacity across the sampled PPPs. Tebuconazole is notable for its ability to transfer in both dissolved and particulate phases, whereas mancozeb primarily transfers in the adsorbed phase. Agricultural practices further intensify PPP transfers, with intensive conventional agriculture, especially in vineyards and wheat-dominated rotations, significantly contributing to metaldehyde, aclonifen, and MCPA concentrations in sub-basins. The hydrological behavior of certain sub-basins, particularly those experiencing significant groundwater-river exchanges, also plays a role in intensifying pollution transfers. Regarding agricultural practices, sub-basins with high contributions of tebuconazole and mancozeb are located in PAs, except for certain sub-basins characterized by intensive conventional agriculture with vine and wheat-dominated rotations. Tebuconazole is applied to vines and dry and irrigated durum wheat at specific rates, whereas mancozeb is applied at different rates to vines.

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

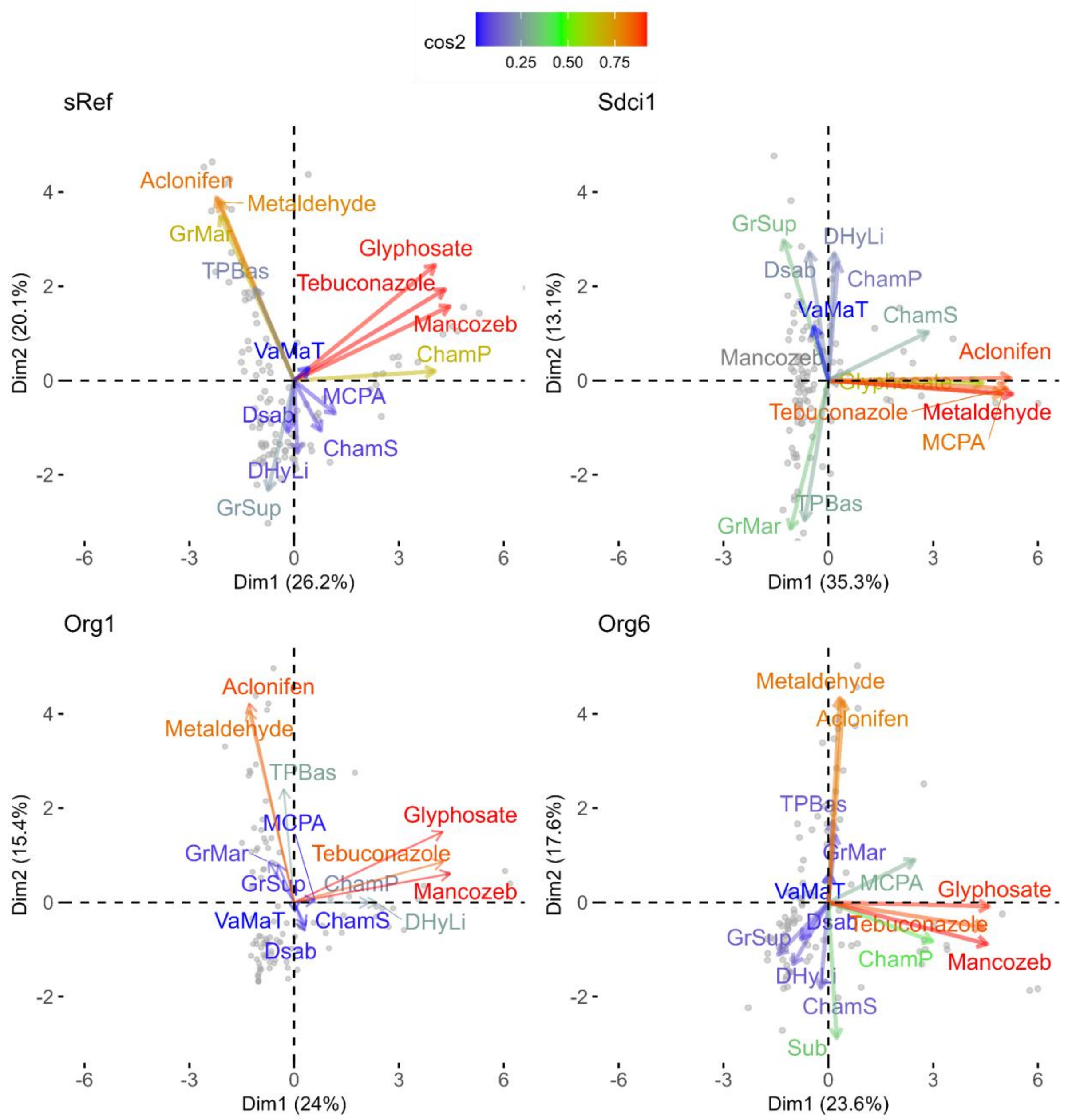


Figure 4: PCA Biplots of factors at the basin outlet.

The analysis of the sRef scenario highlights the significant contributions of various PPPs to spatial variance, except for mancozeb. Sub-basins with high contributions of tebuconazole and mancozeb are strongly correlated with the ChamP agricultural soil type (Fig 4). Tebuconazole has an average transfer capacity among the PPPs, being able to transfer in both the dissolved and particulate phases, whereas mancozeb primarily transfers in the adsorbed phase.

Principal component analysis of the scenarios for conversion to organic farming revealed reductions in the contributions of aclonifen and metaldehyde transfers with targeted actions, even in small areas. Taking sub-basin 27 as an example, the conversion of 148 ha and 212 ha significantly reduced the aclonifen and metaldehyde transfers. This indicates the effectiveness of organic farming in mitigating diffuse pollution. Additionally, the variance in individual sub-basin contribution changes as the conversion of land to organic farming intensifies. Conversion to organic farming is a potential mitigation strategy, with targeted actions significantly reducing PPP contributions, particularly aclonifen and metaldehyde. The effectiveness of organic farming scenarios underscores the potential of small-scale interventions to mitigate diffuse pollution markers. Spatializing changes in practices, such as intercropping and alternative techniques, to reduce active substance quantities demonstrate promise in mitigating PPP transfers and reducing effluent volumes.

The results highlight the complex interplay among anthropogenic, biogeochemical, and agricultural practices in influencing PPP transfers within the basin studied. Furthermore, the effectiveness of targeted interventions underscores the importance of tailored strategies for mitigating diffuse pollution and protecting water resources.

The biplot on the left shows that Sdci1 significantly reduces PPP contributions, except MCPA, which is used as a substitute herbicide. Notably, the most contributive sub-basins (CSAs) align primarily with specialization in winegrowing downstream (particularly Cognac) and the concentration of field crops upstream. These areas face significant phytosanitary pressure, with numerous vineyard treatments generating PPP effluents that require management. More than a dozen treatments of vineyards with phytosanitary substances generate PPP effluents that need to be spread or treated.

Across all Sdci scenarios, there was a consistent reduction in transfers in the central and downstream parts of the main section and its northern tributaries. Although certain molecules showed a relatively low secondary effect of PPP substitution in terms of cumulative concentrations, the innovative scenarios, particularly Sdci1 and Sdci3, which target all field crops, proved effective. These scenarios are also highly effective in certain sub-basins, including priority zones, for specific molecules, while demonstrating a moderate effect on other molecules. This highlights the need for spatializing changes in practices to address diverse pollution sources effectively.

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

### 3.3. Temporal variability analysis using the Mann-Kendall test (MK)

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

i. Across the main river continuum, excluding the headwaters, a substantial number of monotonic trends was observed across all scenarios, including the reference scenario (sRef). The increase in areas converted from conventional to organic farming is correlated with the increase in the number of river sections that exhibit significant monotonic trends, which is particularly evident along the main southern tributary, notably in the Org6 scenario.

ii. High levels of diffuse tebuconazole pollution were identified in the southern and southwestern regions, specifically sub-basins 62, 65, and 71. In the same impluvium situated in priority zones, some CSAs fall within priority areas designated by water governance, whereas others, such as CSAs 75, 79, 51, 68, 82, 88, and 98, do not. Nonetheless, significant monotonic trends were detected outside priority areas; the potential benefits of implementing biological scenarios to mitigate tebuconazole contamination. Geological and hydrological factors may contribute to the observed disparities between actions targeted at PAs and actual responses over time, particularly given shared groundwater bodies and dynamic surface runoff dynamics.

iii. In the northern region, sub-basin 19, which is characterized as a low contributor, exhibits significant monotonic trends associated with parts heavily cultivated with irrigated durum wheat. This study highlights tebuconazole as a marker of specific agronomic practices, particularly durum wheat cultivation.

iv. To the east, agricultural sub-basin 46, a moderate contributor, shows potential benefits from inclusion in priority action zones, especially for its cultivation of irrigated durum wheat on silty soils (DHyLi), which may facilitate contaminant transfers.

The distribution and mean concentrations of tebuconazole in the agri-environmental scenarios were notably smaller and lower in amplitude than those in the reference scenario. These monotonic downward trends indicate significant reductions in pollutant concentrations over the 12-year study period, indicating sustainable and substantial improvements in water quality attributed to LUC for this particular PPP in select river sections.

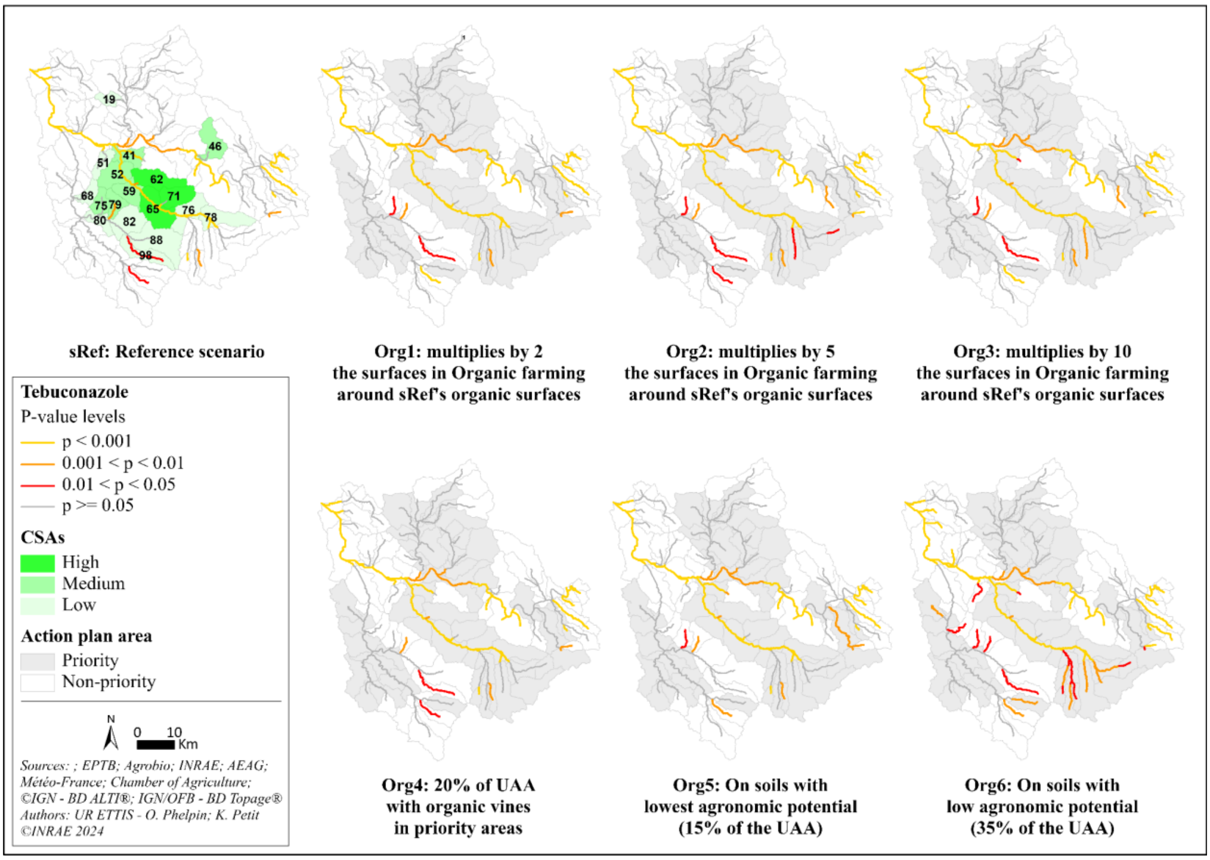


Figure 5: MK trend significance (p-values) for tebuconazole concentrations under organic scenarios vs. baseline (sRef).

## 4. Conclusions

Our SWAT-GenLU2 spatialized agrohydrological modeling yielded valuable insights into the effectiveness of various cropping scenarios in limiting PPP 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 scenarios, identifying the contributions of anthropogenic and soil factors, and discerning monotonic trends over time.

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

As agroecology gains traction in the study area, it becomes imperative to address the heterogeneous nature of organic farming practices. The increasing adoption of organic farming highlights the need to incorporate PPPs authorized for organic farming into modeling efforts. Identifying highly vulnerable areas to PPP transfer, such as Critical Source Areas (CSAs), can help define PAs for targeted mitigation efforts, particularly in the context of climate change.

Although our modeling approach provides valuable insights, it is essential to acknowledge its limitations. The complexity of water quality processes and the simplified representation in the model necessitate caution in its application, which requires validation by field experts, as was the case in this study. Improved PPP monitoring, along with model calibration and validation efforts, can enhance the understanding of diffuse pollution and reduce modeling uncertainties.

Moving forward, integrating socio-economic drivers into decision support methods could further enhance our ability to assess and manage water quality effectively. By considering uncertainties and leveraging multi-criteria decision-support methods, integrated water quality modeling, and scenario planning, stakeholders can develop more robust strategies for sustainable water resource management.

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

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