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Challenges of spatially extrapolating aquatic pesticide pollution for policy evaluation

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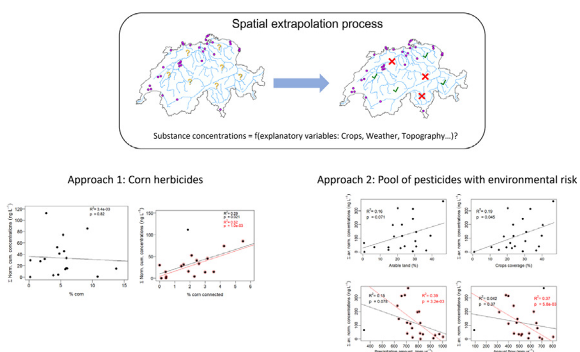
HIGHLIGHTS

- Our study explores relationships between aquatic pesticide pollution and explanatory variables.
- Extrapolating data from monitoring sites to the entire river network is highly uncertain, even with detailed datasets.
- Improving the data on pesticide applications will be essential to progress in modelling pesticide transport.

GRAPHICAL ABSTRACT



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ABSTRACT

Aquatic pesticide pollution is an important issue worldwide. Countries rely on monitoring programs to observe water bodies quality and on models to evaluate pesticide risks for entire stream networks. Measurements are typically sparse and discontinuous which lead to issues in quantifying pesticide transport at the catchment scale. Therefore, it is essential to assess the performance of extrapolation approaches and provide guidance on how to extend monitoring programs to improve predictions. Here we present a feasibility study to predict pesticide levels in a spatially explicit manner in the Swiss stream network based on the national monitoring program quantifying organic micropollutants at 33 sites and spatially distributed explanatory variables. Firstly, we focused on a limited set of herbicides used on corn crops. We observed a significant relationship between herbicide concentrations and the areal fraction of hydrologically connected cornfields. Neglecting connectivity revealed no influence of areal corn coverage on the herbicide levels. Considering chemical properties of the compounds slightly improved the correlation. Secondly, we analysed a set of 18 pesticides widely used on different crops and monitored across the country. In this case, the areal fractions of arable or crop lands showed significant correlations with average pesticide concentrations. Similar results were found with average annual discharge or precipitation if two outlier sites were neglected. The correlations found in this paper explained only about 30 % of the observed variance leaving most of the variability unexplained. Accordingly, extrapolating the results from the existing monitoring sites to the Swiss river network comes with substantial uncertainty. Our study highlights possible reasons for weak matches, such as missing pesticide application data, limited set of compounds in the monitoring program, or a limited understanding of factors differentiating the loss rates from different catchments. Improving the data on pesticide applications will be essential to progress in this regard.

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1. Introduction

Pesticides are commonly used in agriculture to improve crop production and secure global food supplies (Hedlund et al., 2020). However, pesticides can enter non-target environments such as surface water, threatening aquatic ecosystems and human health (Beketov et al., 2013; Brühl and Zaller, 2019; Chetty-Mhlanga et al., 2021). Monitoring in-stream pesticide concentrations is essential to evaluating exposure risk and preventing pollution in aquatic ecosystems (Federal Office for the Environment (FOEN), 2022). Monitoring is often the basis for demonstrating the need for implementing mitigation measures to reduce in-stream pesticide levels and improve water quality in the river network (Reichenberger et al., 2007).

A prerequisite to assessing the impacts of mitigation measures at the regional scale is characterising the spatial distribution of pesticide concentrations throughout the stream network (Ryberg and Gilliom, 2015; Boye et al., 2019). As data is generally sparse and discontinuous, modelling tools are needed to extrapolate this data to the required extent. Many models were applied from field to catchment scale to assess water pollution by pesticides (Ippolito and Fait, 2019; Ammann et al., 2020). The processes that govern pesticide fate and transport in the environment have been an area of research for many years and have been integrated into current modelling tools (Ippolito and Fait, 2019). However, the main issues in modelling pesticide dynamics at the watershed scale are the difficulties in accounting for the multiple sources of pesticide pollution. Sources of pesticide pollution can be diffuse or non-point, e.g., spray drift, surface runoff, hydraulic shortcuts, and drainage (Ippolito and Fait, 2019; Schönenberger and Stamm, 2021). Agricultural point sources, e.g., accidental spills during tank filling, can also significantly contribute to water contamination (Müller et al., 2002). Unpredictable misuses, such as inappropriate handling, spillage during tank filling, or cleaning of equipment (Vasiljević et al., 2012), can be challenging to represent in large-scale models (Wenneker et al., 2010).

The first models to estimate pesticide transport and fate in stream networks were empirical or semi-empirical, linking in-stream pesticide concentrations with pesticide use and precipitation or discharge (Brown and Hollis, 1996). This method is still used for large-scale studies (Guo et al., 2004; Leu et al., 2010; Ryberg and Gilliom, 2015; Stackpoole et al., 2021), but uncertainties remain high (Brown et al., 2002; Stackpoole et al., 2021).

Physically based models can represent pesticide dynamics at an hourly or daily time step (Holvoet et al., 2007; Gevaert et al., 2008; Boithias et al., 2014; Ammann et al., 2020). Current models can represent various processes influencing pesticide transport and fate in soils and surface waters (Holvoet et al., 2007; Ippolito and Fait, 2019; Wang et al., 2019). However, these models need continuous input and detailed landscape data and are time-consuming to set up. Moreover, they are usually applied at the scale of headwater catchments, and they are challenging to up-scale to larger areas (Gassmann et al., 2014).

Another method to predict pesticide risks relies on using indicators, combining multiple large-scale datasets related to pesticide application and transport, such as slope, land use, soil types, or distance to the stream. This approach has been applied at the watershed, regional, and global scales (Macary et al., 2014; Strokal et al., 2019; Koch and Prasuhn, 2021). Nevertheless, this approach only provides a pollution risk but does not quantify loads or concentrations of pesticides in the streams.

Arguably, the most common approach in large-scale studies is based on the spatial extrapolation of pesticide concentration summary statistics. This approach is based on regression equations using various landscape and meteorological indicators and results in a static picture of pesticide pollution in a stream network (Ippolito and Fait, 2019). Parametric regression models (e.g., SEAWAVE-Q) have also been developed to assess variability and trends of pesticide concentration time series (Ryberg and Vecchia, 2013).

Switzerland issued a national action plan (NAP) to reduce the risk from plant protection products. One objective of the Swiss NAP is to halve the stream length exceeding legal threshold values for pesticides by 2027 (Conseil Fédéral, 2017). To assess whether this objective will be achieved, an existing monitoring program for micropollutants was used with a selection of watersheds representing multiple conditions (e.g., size, crop type, hydrology), which is essential to highlight regional effects of the NAP (e.g., Boye et al., 2019; Stackpoole et al., 2021). This monitoring program implemented in 2017 provides detailed pesticide concentrations with a frequency of 14 days (composite samples) in multiple sites across Switzerland (Doppler et al., 2020).

This study aims to test the feasibility of predicting the spatial variability of pesticide concentrations in the Swiss stream network based on the available monitoring data. It includes a focus on predicting stream network length without Environmental Quality Standard (EQS) exceedances to align directly with the NAP objectives. In particular, we aim to construct meaningful summary statistics of pesticide concentrations in streams and to relate them with simple relationships to explanatory variables available at the national scale, including climatic and landscape indices, to build a reliable model that can extrapolate to the national scale. Moreover, we want to identify the main factors that influence this extrapolation process to provide guidance on achieving better predictive performance.

One the one hand, we focus on herbicides applied to corn because i) corn is a major crop across the entire country and ii) the respective herbicides are generally used only once per year during a well-defined period. Moreover, the number of pesticides applied to corn is limited. Therefore, we expect results to be easier to interpret than other crop types, which generally have more complex pesticide application patterns. On the other hand, we look at groups of pesticides monitored in the Swiss monitoring program. In both cases (i.e., corn herbicides and pesticide groups), we aim to quantify the average concentrations of pesticides and empirically model them with spatially distributed explanatory variables. Finally, we evaluate to which degree it is possible to predict the stream length without EQS exceedances.

2. Methods

The evaluation of the Swiss NAP will be partly based on the monitoring data obtained from the Swiss National Surface Water Quality Monitoring Program (NAWA TREND), jointly run by the cantonal authorities and the Federal Office for the Environment (FOEN). Accordingly, this study used 2019 NAWA TREND data to evaluate methods to extrapolate in-stream pesticide concentrations to the Swiss stream network.

2.1. Database of monitoring sites

The NAWA TREND program consists of multiple monitoring sites draining watersheds of different sizes and various anthropogenic pressures. We excluded large watersheds with stream orders (the number representing the branching level in a river system) greater than five for most analyses, as they make up only a small part of the Swiss river network (Appendix 1). In this study, we used the Strahler stream order attributing the first order to each headwater reach (Strahler, 1957, 1964).

We also excluded sites not operational before May 2019. The final set contains 21 independent, non-nested stations across the Swiss Plateau and the Rhône valley (Fig. 1). These sites represent various hydrological and agricultural characteristics with an average elevation ranging from 415 to 683 m.a.s.l. and sizes ranging from 2.0 km^2 to 78.4 km^2 (Appendix 2).

2.2. Explanatory variables

Table 1 shows several explanatory variables that represent either source of pesticides or potential factors influencing pesticide transport to streams. These variables were used to model the spatial variability of pesticide concentrations in the Swiss river network and extrapolate the results to the unmonitored streams. Further details about selected variables are provided as supporting information.

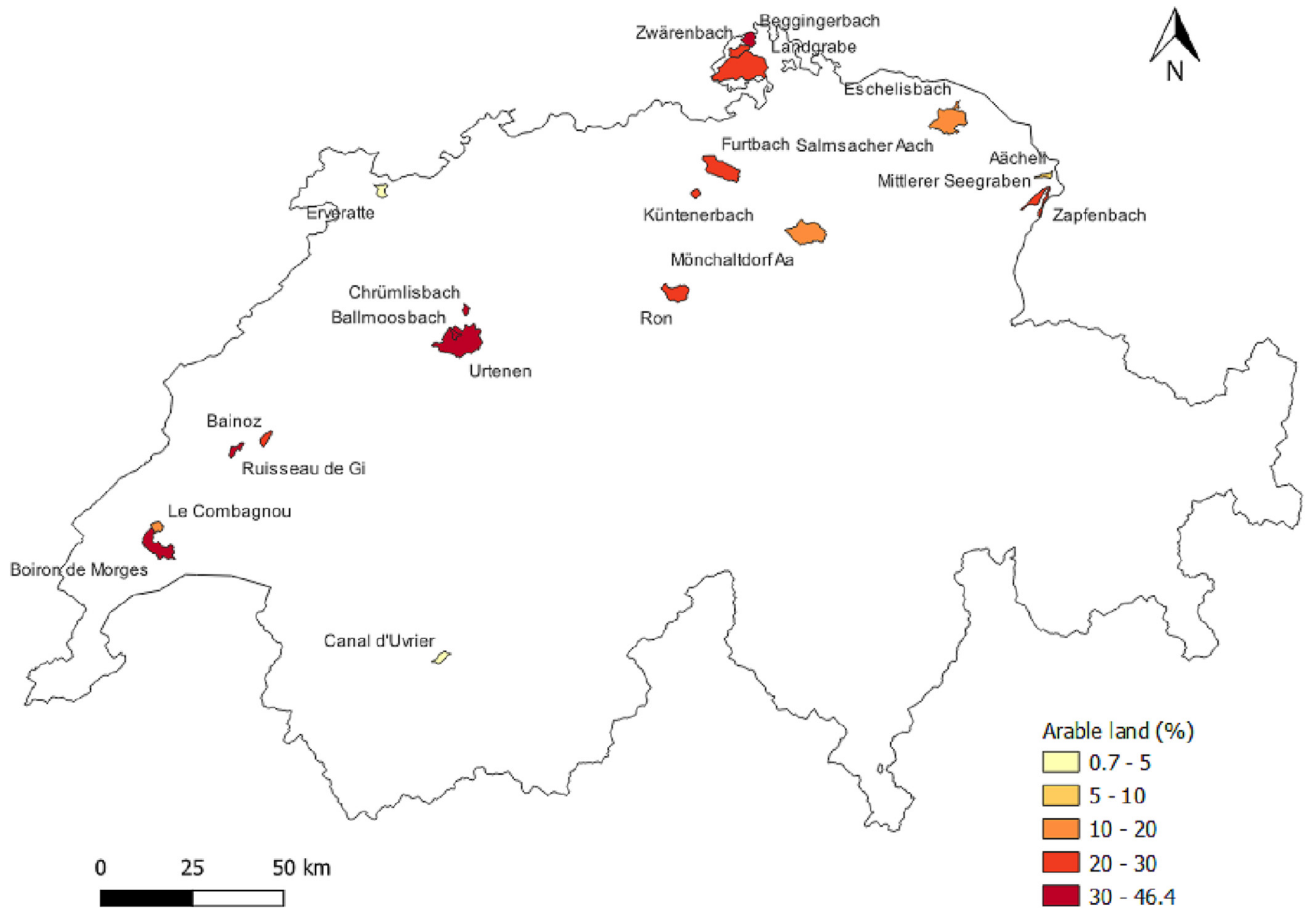

Fig. 1. Distribution of the watersheds within the Swiss NAWA TREND monitoring program selected for this study. The 21 watersheds are mostly distributed along the Swiss Plateau in the North and the West of the country. Appendix 2 contains detailed information regarding each watershed.

2.3. Modelling approaches

2.3.1. Approach 1: Corn cultivation and average concentrations of corn herbicides

2.3.1.1. Evaluation of average herbicide concentrations. In Approach 1, we chose to study herbicides frequently used on corn. We assume that the cumulative pesticide concentrations $C_{i,k}$ during the entire application period is the relevant metric to be used (Spycher et al., 2018). We focused on the concentrations between March and October 2019. We assumed that pesticide peaks during that period of the year are mostly attributed to agricultural use. The rationale for using the cumulative concentrations is that it is less sensitive to the actual timing of applications and rainfall events than the maximum concentration (Spycher et al., 2018). Accordingly, we calculated cumulative concentrations during the growing season (March to October) in 2019 for each selected substance and monitoring site. The direct link between explanatory variables such as land use and herbicide concentrations is non-trivial because some corn herbicides are also applied to other crops, and catchment-specific application data are absent. As not all catchments have the same sampling frequency, we normalised the concentration values by the number of samples to obtain the average concentration:

$$C_{i,k,\mathrm{av}} = \frac{C_{i,k}}{n_{i,k}}$$

where $C_{i,k}$ is the cumulative herbicide concentrations for compound i in catchment k and $n_{i,k}$ is the number of samples for compound i in catchment k during the application period. From these concentrations, we need to focus on the part that is coming from corn fields. Indeed, corn herbicides can be applied to corn and other crops in various amounts (Appendix 3). Therefore, we calculated the total use $M_{\mathrm{in},i,k}$ in kg of a single herbicide i in any given catchment k as:

$$M_{\mathrm{in},i,k} = \sum_j f_{j,k}\, \overline{m}_{\mathrm{in},i,j} = \sum_j \frac{A_{j,k}}{A_{total\ crops,k}}\, \overline{m}_{\mathrm{in},i,j}$$

where $f_{j,k}$ is the areal fraction of crop j among crops where the herbicide i is used in catchment k, $A_{j,k}$ the area of crop j in catchment k (Appendix 4), $A_{total\ crops,k}$ is the total area of crops where the herbicide i is used in catchment k, and $\overline{m}_{\mathrm{in},i,j}$ is the average application rate across the entire country of compound i on crop j (kg.ha^{-1}; Appendix 3; Spycher and Daniel, 2013).

Then, we assume that $C_{i,k,\mathrm{av}}$ is proportional to the herbicide mass applied in the catchment irrespective of the crop, as the signal received at the watershed outlet is related to the mass applied in the catchment (Doppler et al., 2014):

$$C_{i,k,\mathrm{av}} \sim M_{in,i,k}$$

Based on the application rates on each crop (Appendix 3) and the spatial fraction of each crop per catchment (Appendix 4), we can attribute a

Table 1
Explanatory variables considered for the spatial analysis and extrapolation.

Category	Sub-category	Variable	Data source
PPP source	Pesticide Risk map	Point sources map (farmyards)	Risk Maps for Plant-Protection Product Input into Surface Waters (Koch and Prasuhn, 2021; Federal Office for Agriculture)
	General land use (areal fraction)	Arable land	Land use dataset (details below)
		Orchards	
		Vineyards	
	Major crops (areal fraction)	Cereals	
		Corn	
		Sugar beet	
		Rape seed	
		Vegetables	
		Potatoes	
		Legume	
	Urban influence	Urban areas	swissTLMRegio (Federal Office of Topography)
	Wastewater	Number Wastewater Treatment Plant	Wastewater treatment plants map (Federal Office for the Environment)
		Fraction of Wastewater	
Risk of transport	Pesticide Risk map	Connectivity map	Risk Maps for Plant-Protection Product Input into Surface Waters (Koch and Prasuhn, 2021; Federal Office for Agriculture)
		Drainage map	
		Pesticide risk index	
	Catchment and river characteristics	Size	Topographical catchment areas of Swiss water bodies 2 km^2 (Federal Office for the Environment)
		Compactness coefficient (K_G)	
		Mean elevation	Digital Elevation Model 25 m (Federal Office of Topography)
		Topography: mean slope	Digital Elevation Model 25 m (Federal Office of Topography)
		Precipitation amount (mm/year)	Monthly and Yearly Precipitation (MeteoSwiss)
		Annual mean flow (mm yr^{-1})	Mean runoff and flow regime types for the river network of Switzerland (Federal Office for the Environment FOEN)
	Soil properties	Soil organic carbon content (%)	Topsoil Organic Carbon Content for Europe (Jones et al., 2005)
		Depth index	Digital soil suitability map of Switzerland (Federal Office for Agriculture FOAG)
		Stone index	
		Water storage index	
		Nutrient storage index	
		Permeability index	
		Waterlogging index	

specific fraction ($f_{\mathrm{load,corn},i,k}$) of the measured cumulative concentration to corn (Appendix 5):

$$f_{\mathrm{load,corn},i,k} = \frac{f_{\mathrm{corn},k}\ \overline{m}_{in,i,\mathrm{corn}}}{\Sigma_j f_{j,k}\ \overline{m}_{\mathrm{in},i,j}}$$

For example, S-Metolachlor has average national application rates of 0.15 kg ha^{-1} for corn, 0.32 kg ha^{-1} for beets, and 0.25 kg ha^{-1} for other uses (Appendix 3). At monitoring site 4, we have 1816 ha of corn, 2017 ha of beets, and 1067 ha of other uses resulting in masses of S-Metolachlor of 272 kg, 323 kg, and 267 kg applied to the fields, respectively. Thus, 23 % of the total mass is applied to corn, giving $f_{\mathrm{load,corn},S-Metolachlor,4} = 0.24$. For monitoring site 10, there are no beets or other uses, resulting in $f_{\mathrm{load,corn},S-Metolachlor,10} = 1$, as the total S-Metolachlor found in-stream should come exclusively from corn fields.

Relation with corn fields.

We used land use data and information about average application rates to estimate the average concentration from application to corn:

$$C_{i,\mathrm{corn},k,\mathrm{av}} = f_{\mathrm{load,corn},i,k} \cdot C_{i,k,\mathrm{av}}$$

Assuming spatially uniform application rates for any given herbicide *i* on a given crop across catchments, we may also expect the cumulative concentration to be proportional to the areal fraction of corn:

$$C_{i,\mathrm{corn},k,\mathrm{av}} \sim f_{\mathrm{corn},k}$$

As for single compounds, we tested the hypothesis that the sum of the normalised, corn-specific cumulative herbicide concentrations varied linearly with the fraction of corn. As an alternative hypothesis, we combined $f_{\mathrm{corn},k}$ with the connectivity map (see Table 1) to obtain the fraction of corn connected to the stream in each catchment ($f_{\mathrm{corn\ connected},k}$), which has been compared to $\sum_i C_{i,\mathrm{corn},k,\mathrm{av}}$. Nevertheless, this comparison was performed in 18 sites instead of 21 as the high-resolution land use data was not available for sites 7, 8, and 9 (Appendix 2):

$$\sum_i C_{i,\mathrm{corn},k,\mathrm{norm}} \sim f_{\mathrm{corn},k}\ or\ f_{\mathrm{corn\ connected},k}$$

2.3.1.2. Herbicides selection. To calculate average concentrations, we had to consider which corn herbicides were included in the NAWA TREND program. Corn herbicides were characterised by three factors: i) the fraction of corn fields treated with these herbicides ($\frac{\text{area of corn fields receiving the herbicide}}{\text{total area of corn fields}}$; x-axis in Fig. 2), ii) the fraction of the total use being applied on corn ($\frac{\text{fraction applied on corn}}{\text{total amount applied on all crops}}$; y-axis in Fig. 2), and iii) whether they are being monitored in the NAWA TREND program. Fig. 2 shows the substances (grey and black font) measured within the NAWA TREND program.

We decided to keep substances where >40 % of the total herbicide use goes to corn and where at least 10 % of the entire Swiss corn fields receive this herbicide, as their detection in the streams should be due to the presence of corn fields in the corresponding catchment (Fig. 2). Therefore, we included the following six herbicides in the analysis: Dimethenamid-P, Flufenacet, Foramsulfuron, Nicosulfuron, S-Metolachlor, and Terbuthylazine. Their average application rates were assessed based on surveys conducted by the Zentrale Auswertung der Agrarumweltindikatoren (ZA-AUI; Spycher and Daniel, 2013; Appendix 3).

2.3.2. Approach 2: Concentrations of multiple pesticides from multiple crops

The NAWA TREND program monitors 48 mandatory pesticides and ten optional ones. As of 2021, the Waters Protection Ordinance (Gewässerschutzverordnung; GSchV) defines Environmental Quality Standards (EQS; Appendix 6) for 17 of the mandatory analytes, selected to cover a significant part of the ecotoxicological risk, which we selected in our study (Appendix 6). We excluded two substances (Diazinon and Terbutryn) from the analysis because they are no longer registered as

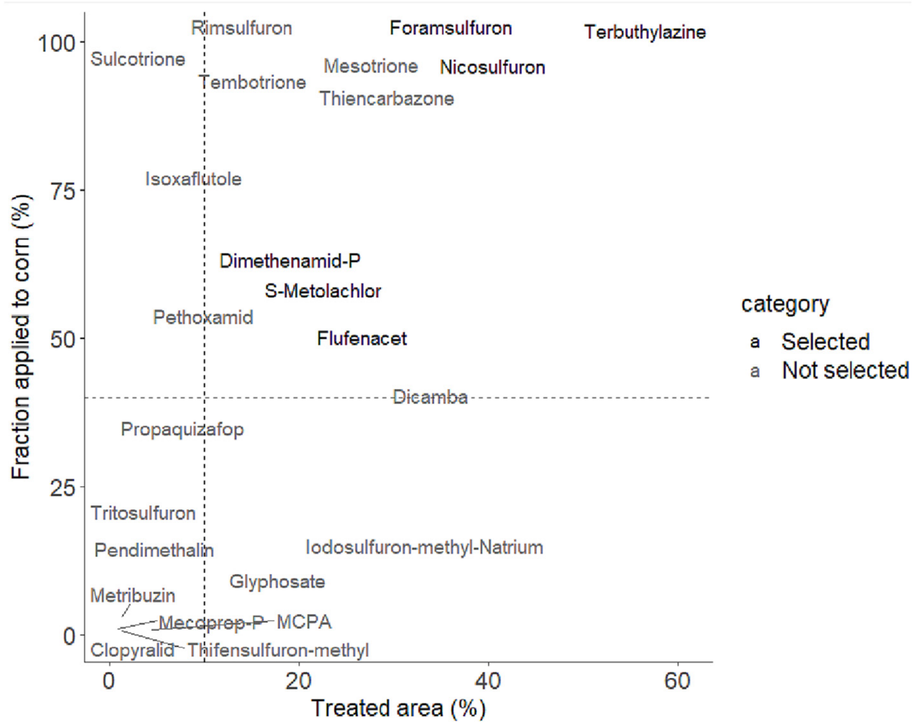

Fig. 2. Selection of compounds used in Approach 1 analysis. Estimated fractions of corn treated with herbicides (x-axis) and their specific use on corn (y-axis). These data are based on surveys conducted by the Zentrale Auswertung der Agrarumweltindikatoren (ZA-AUI; Spycher and Daniel, 2013).

Plant Protection Products (PPP) in Switzerland. The final list comprises three fungicides, eight herbicides, and six insecticides. We computed average expected concentrations at the NAWA TREND sites for the pesticides listed in Appendix 6.

We calculated an average concentration C_k for each NAWA TREND site during the growing season, i.e., between March and October 2019, by normalising the concentration by the number of samples, which was not the same for every compound and each catchment:

$$C_k = \sum_i C_{i,k,av}$$

where C_k is the average concentration for watershed k, $C_{i,k,av}$ represents the average concentration between March and October 2019 for compound i and watershed k.

Next, we compared these average concentrations with the set of explanatory variables in Table 1. First, we tested the relationship between the concentrations and the pesticide risk map (Koch and Prasuhn, 2021). We hypothesise that a watershed with a high pesticide pollution risk should have a high concentration at its outlet. This test is also essential to evaluate the link between pesticide risk maps and water quality in observed data. Second, we assessed the relationship between average concentrations and several agricultural and hydrological characteristics, such as crop coverage, arable land coverage, crop intensity, river and watershed features (Table 1). We tested each crop separately. Finally, we looked at multiple variable regressions to refine our predictions.

2.3.2.1. Chemical properties consideration. It was shown that half-life in soils (DT50) or OC-water partition coefficient (K_{OC}) may help predict the concentrations in water (Ryberg and Gilliom, 2015). In this paper, we also tried to consider this effect by changing the calculation of normalised concentrations in both approaches as follows:

$$C_k = \sum_i \frac{C_{i,k},av}{DT50} \text{ or } C_k = \sum_i \frac{C_{i,k,av}}{K_{OC}} \text{ or } C_k = \sum_i \frac{C_{i,k,av}}{DT50\ K_{OC.}}$$

DT50 and K_{OC} values for each substance can be found in Appendix 6.

3. Results

3.1. Modelling corn herbicides

When aggregating across all six corn herbicides, the data suggest that the larger the fraction of corn in catchment the higher the average concentrations. This correlation however, ($p = 0.02$ for all data) explaining about 30 % of the variance (52 % if leaving out an outlier, see Fig. 3, right bottom panel), only holds when considering the fraction of corn field hydrologically connected to the stream network. Relationships were also absent when analysing the data from individual compounds irrespective of whether or not the hydrologic connectivity was considered (S-metolachlor was the single exception with a weak correlation, see Fig. 3). Because some of these compounds can also be applied to other crops, we attributed only a fraction to corn according to land use and crop-specific application data (see above) and used only this fraction for the analysis.

These findings demonstrate that the resulting herbicide patterns in the streams vary substantially, even for a crop with a simple herbicide application pattern (one application per year). Based on the available data and information, predicting the respective herbicide concentrations seems challenging. There are many possible reasons for this high uncertainty. Firstly, only a fraction of all corn herbicides is measured within the NAWA TREND program (Fig. 2). If the application of corn herbicides was spatially uniform, this fact would not be problematic. However, comparing corn herbicides across the monitoring sites (Appendix 7) suggests a very heterogeneous application pattern in space, especially for Foramsulfuron and Dimethenamid-P. Hence, one major limitation for the successful prediction of corn herbicides is the poor knowledge of the actual input in each catchment. Secondly, we also lack information about potentially relevant factors driving the transport of the applied compounds. For example, the analysis does not consider the timing between application and rainfall, which can affect sensibly the concentration dynamics (Doppler et al., 2014; Chow et al., 2020). These limitations originate from the lack of application data and the sampling strategy, which can only provide temporally averaged concentrations for 14 days.

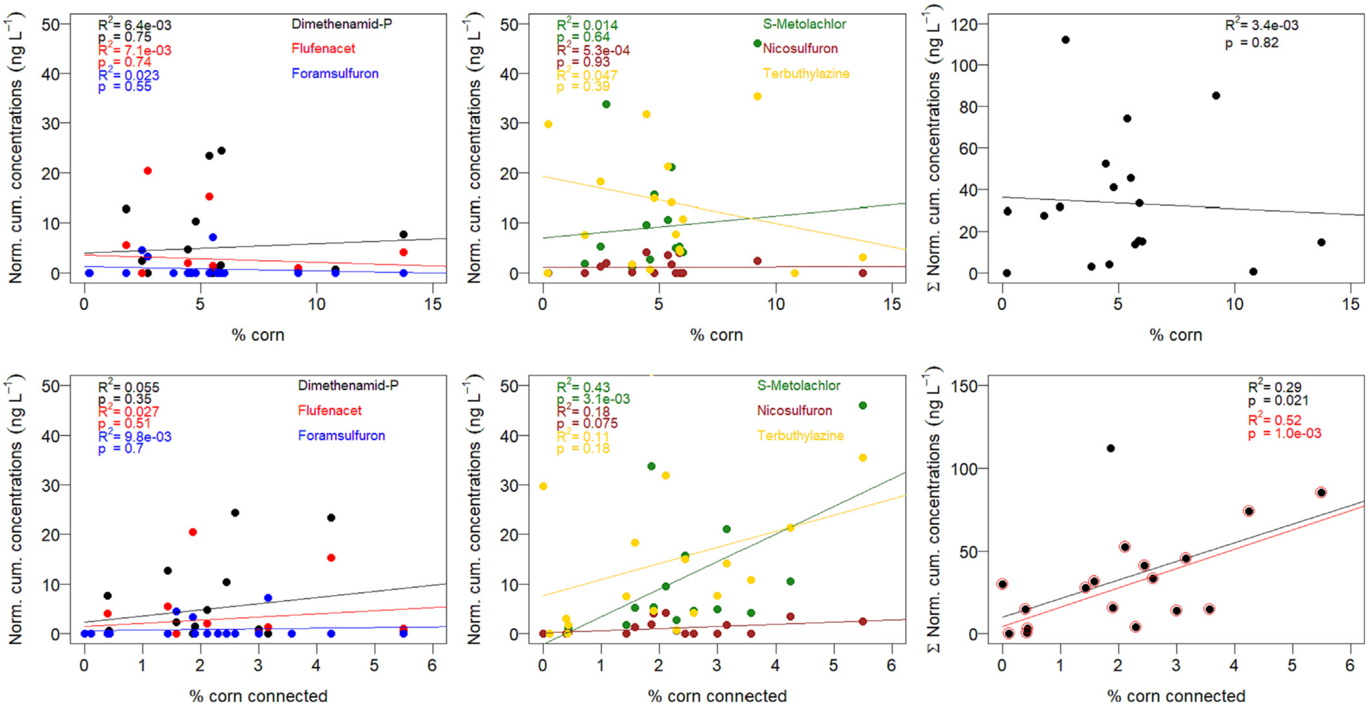

Fig. 3. Correlations between the cumulative concentrations of each corn herbicide with the percentage corn coverage in the catchment (left and middle panels). Right panel: correlation between the sum of the cumulative concentrations with the percentage corn in the catchments. The top row depicts the results for the entire corn area per catchment, the lower one shows the results when only considering the corn field connected to the stream network. Each dot represents a catchment of the NAWA TREND program. Red lines, dots and coefficients refer to the regressions without outliers.

Given these results for corn herbicides, it seems unlikely that better predictions would be possible for other crops and pesticides. For all these cases, the same limitations apply but may be more severe due to more complex application patterns (more diverse sets of compounds, several applications during the vegetation period). For these reasons, we decided to concentrate on aggregated endpoints, such as the total concentrations for a group of pesticides. The reason why such a coarser approach might work despite the failure with a single crop is that by adding data from many crops, patterns may emerge that also existed for single crops but were not detectable for a single crop due to the variance being too significant for the number of available data (as suggested by the Central Limit Theorem).

3.2. Modelling pesticide concentrations for multiple crops

The sums of the average concentrations per sample vary widely between the catchments for all monitored pesticides (Appendix 8). This figure demonstrates no regional difference in the concentrations between the Western and the Eastern parts of Switzerland. In the same way, there is no clear link between the average concentrations and the size of the watershed (with the exclusion of large watersheds; see Section 2) and no clear groups in terms of the sum of concentrations.

3.2.1. Relationships with explanatory variables

To predict concentrations across the stream network, we need to find statistical relationships between concentrations and independent explanatory variables available at the national level. Potential explanatory variables are crop coverage, the presence of additional pesticide sources (e.g., effluent from wastewater treatment plants) and catchment characteristics (e.g., soil properties). We first describe the relationships with single factors (crop coverage, catchment properties) and then move to multivariate approaches such as the Risk Index (Koch and Prasuhn, 2021) and multi-linear regression models.

First, we found a positive correlation between the fraction of crop coverage and the average concentrations ($p = 0.045$, Fig. 4). The explained variance, though, is limited (19 %). A similar trend was observed with arable land only, i.e., without orchards and vineyards, although the relationship was non-significant ($p = 0.07$; Fig. 4).

Moreover, we evaluated the relationship between the average concentrations and the pesticide risk map provided by Koch and Prasuhn (2021). There is only a weak positive correlation between the average concentrations and the pesticide risk index (Fig. 4). We also analysed relationships with the individual components used to calculate the pesticide risk index (connectivity, drainage, and point sources influences). No relationship with any of these components were observed (see Appendix 9 for details).

We also tested the correlations between the average concentration and various watershed characteristics. Fig. 4 shows that the less annual rainfall, the larger the range of observed concentrations and the larger the mean per site, possibly due to a dilution effect from rainfall in non-critical source areas. The same conclusion is observed with annual flows in each catchment. Similarly, Masiá et al. (2013) found that lower streamflows were associated with higher in-stream pesticide concentrations in Spain. Finally, we also tested the relationships with soil characteristics detailed in Table 1. Only for soil organic carbon (SOC), a certain pattern was observed in that all three sites with SOC > 10 % had low pesticide concentrations. This might indicate that high SOC levels caused stronger pesticide sorption decreasing concentrations, but the data is too sparse to draw solid conclusions.

We used Multiple Linear Regressions (MLR) to test whether combinations of explanatory variables (Appendix 10) would result in better predictions.

All models indicate that a low concentration can only be expected without the relevant potential pesticide sources. This fact can be nicely illustrated with the best model according to the Akaike Information Criterion

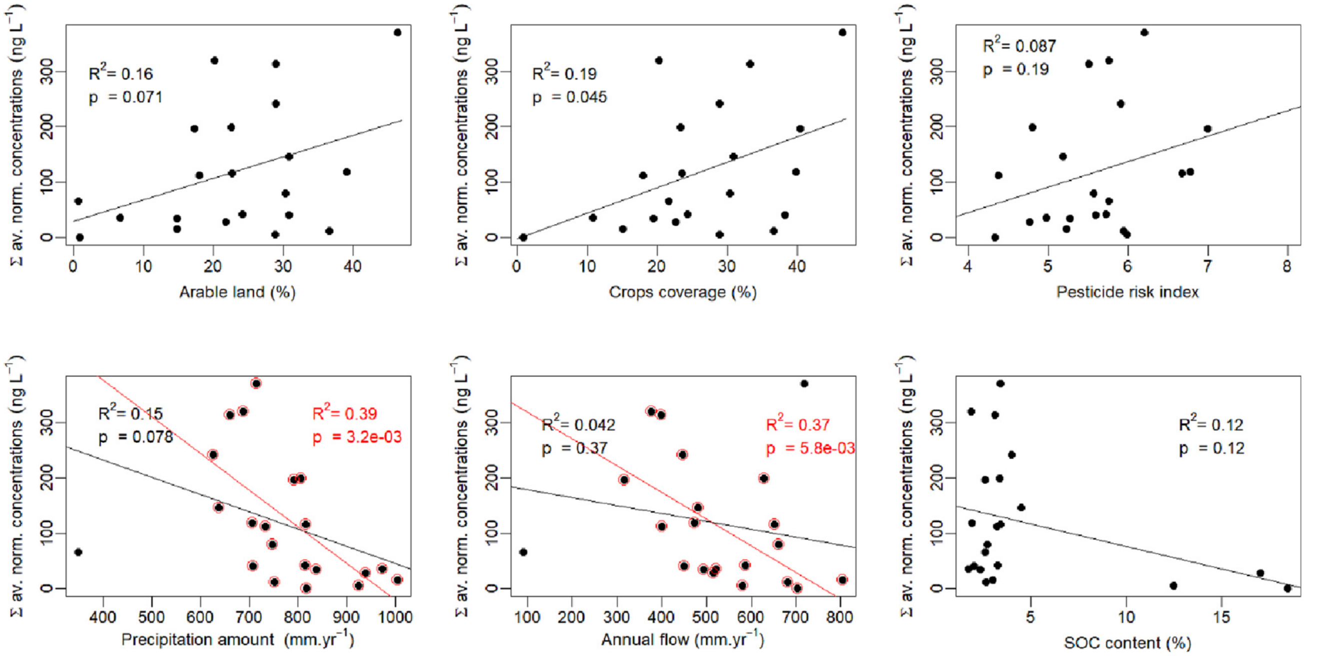

Fig. 4. Correlations between average pesticide concentrations and various explanatory variables. Crop coverage includes arable land plus orchards and vineyards. Each dot represents a catchment of the NAWA TREND program. Red lines, dots and coefficients refer to the regressions without outliers.

(Appendix 10; Akaike, 1974). The model, including the percentage of arable land and the precipitation amount, was selected as it performed better and was significant (AIC = 260.5; R^2 = 0.30; p-value = 0.04). It explained about 30 % of the variance (Appendix 11):

$$C_{calc} = 3.68 \cdot Arable - 0.29 \cdot Precipitation + 257.5$$

By removing the outlier as suggested in Fig. 4, the performance is slightly increased (AIC = 246.5; R^2 = 0.40; p-value = 0.01; Appendix 10).

3.3. Prediction of the number of exceedances for multiple crops

By comparing the concentrations with Environmental Quality Standards (EQS) defined by the Water Protection Ordinance (Appendix 1), we could calculate an average number of EQS exceedances for each watershed on the list of compounds from the Water Protection Ordinance. Subsequently, we tested regressions between the number of exceedances (N_{calc}) and the explanatory variables. The best results came from the same variables and the percentage of wastewater in

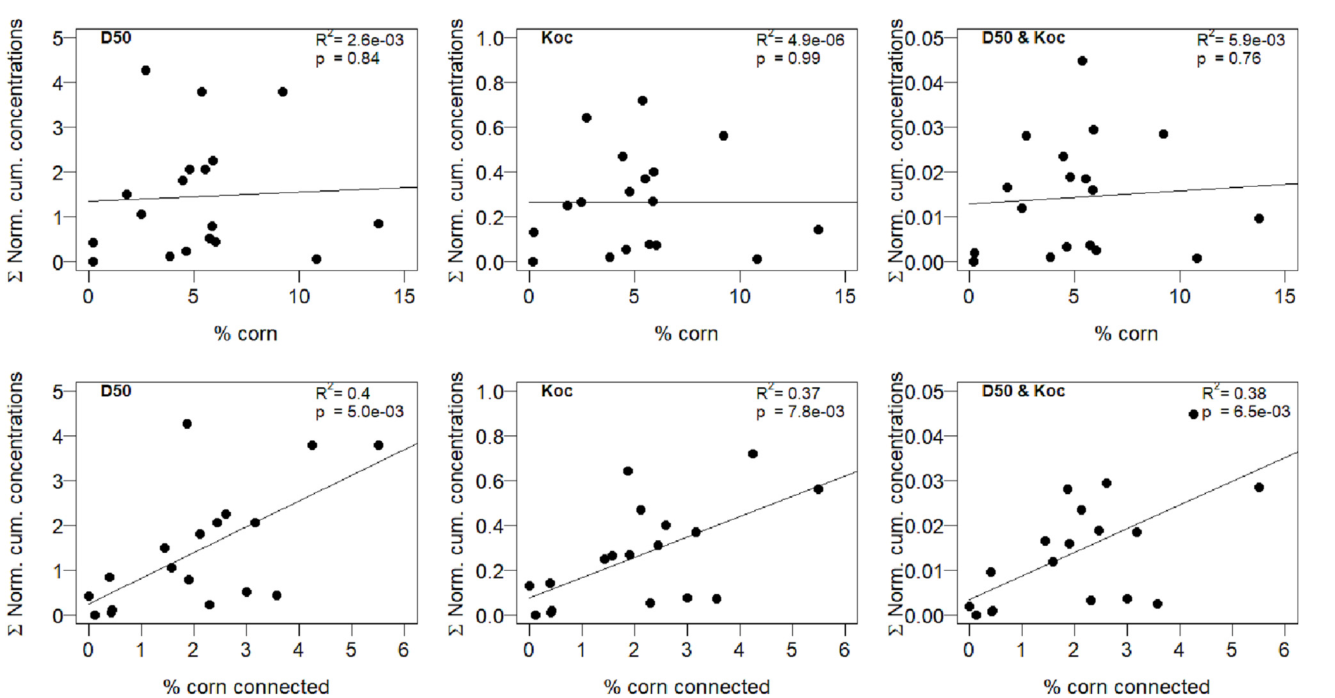

Fig. 5. Cumulative concentrations of corn herbicides normalised by the half-life in soils ($DT50$) and the OC-water partition coefficient (K_{OC}).

the total water discharged (*Fraction WW*; Appendix 12 & Appendix 13):

$$N_{calc} = 0.023.Arable + 3.69.Fraction\ WW - 0.0016.Precipitation + 1.22$$

This time, the statistical performance is slightly better, with an R^2 of 0.50 (p-value = 7e-3).

3.4. Chemical properties influence

In Approach 1, normalising the concentrations by DT50 and K_{OC} increase the correlation with the corn crops connected to the stream network ($R^2 = 0.4$ against $R^2 = 0.29$; Fig. 5). Without considering the connectivity of corn crops, the normalization does not improve the relationship.

Concerning Approach 2, normalising the cumulative concentrations by the chemical properties of each substance can improve the relationships depending on the considered explanatory variable (Table 2). As an example, the coefficients of correlations increase for arable lands but decrease for the precipitation amount or the annual mean flow.

4. Discussion

4.1. Model validity

4.1.1. Methodology

This paper explores relationships to predict in-stream pesticide concentrations with explanatory variables. We tried various approaches with a large dataset concerning pesticide concentrations, i.e., high frequency and numerous stations, and detailed explanatory variables (e.g., detailed land use data at the parcel scale). Our analyses indicate that moderate relationships between aquatic pesticide pollution levels and land use data only appear with a combination of high-resolution land use and connectivity data sets for specific crops, e.g., corn fields, in this study. The high uncertainty shown by our spatial extrapolation models can be attributed to many sources, where the limited knowledge about the pesticides inputs plays a major role.

Although different models showed high uncertainty when extrapolating in space, interannual variability showed a more consistent pattern. In particular, based on preliminary data in 2020, we compared to which extent the cumulative concentrations per sample remained stable between 2019 and 2020 (Appendix 14). Such high temporal correlation suggests that the limited knowledge of factors that might affect interannual variability, such as time of application, or interval between application and precipitation events, are of less importance than factors that might affect spatial variability, such as application rates, which can be assumed to be more uniform in time than in space. However, more data are required to make a more robust evaluation in this regard.

Concerning Approach 1, we tried to extract from the cumulative concentrations the signal from corn fields based on the areal fraction of corn and its connected part in the respective watersheds and the average application rates at the national scale. This approach shows weak correlations with the connected fraction of corn, not appearing only with the fraction of corn. Collecting actual application rates in each catchment and using them to extract the signal may reduce the uncertainties in this approach. Moreover, high-resolution data sets of land use and connectivity seem needed to obtain significant relationships and may be encouraged. In this approach, some herbicides are not detected in a few catchments. These herbicides may be stored or degraded before reaching the outlet, may not be used in these catchments, or may be used in low amounts leading to a concentration in each sample below the limit of quantification.

The approaches in this paper try to relate the full signal from one crop or a list of substances to explanatory variables by summing the cumulative concentrations. This method assumes that the pesticides considered behave approximately in the same way. It does not consider the physical-chemical and environmental fate properties of the substances that could influence their transport, storage, or degradation in soil and water.

Table 2
Coefficients of correlation between the cumulative concentrations of pesticides considered in Approach 2, or the normalised concentrations by the half-life in soils (*DT*50) and the OC-water partition coefficient (K_{OC}) and the respective explanatory variables. The values in parenthesis for the precipitation amount and the annual mean flow correspond to the coefficients of correlation without the outliers (see Fig. 4).

Category	Sub-Category	Variable	Base	D50	Koc	D50 & Koc
PPP source	Pesticide Risk map	Point sources map (farmyards)	4.73E-03	0.01	0.03	0.02
	General land use (areal fraction)	Arable land	0.16	0.24	0.26	0.29
		Crops	0.19	0.31	0.17	0.19
		Orchards	0.01	0.04	0.02	0.02
		Vineyards	0.01	0.04	0.04	0.04
	Major crops (areal fraction)	Cereals	0.16	0.16	0.19	0.16
		Corn	0.01	0.01	4.56E-03	0.02
		Sugar beet	0.42	0.40	0.37	0.34
		Rape seed	0.12	0.06	0.11	0.08
		Vegetables	0.02	0.01	0.01	0.01
		Potatoes	0.1	0.31	0.28	0.43
		Legume	0.03	2.26E-03	0.01	3.95E-03
	Urban influence	Urban areas	0.14	0.17	0.11	0.11
	Wastewater	Number Wastewater Treatment Plant	1.69E-03	2.47E-03	3.33E-05	4.57E-04
		Fraction of Wastewater	0.01	2.93E-04	1.95E-03	4.96E-04
Risk of transport	Pesticide Risk map	Connectivity map	0.17	0.08	0.05	0.03
		Drainage map	0.11	0.22	0.20	0.24
		Pesticide risk index	0.09	0.14	0.02	0.14
	Catchment and river characteristics	Size	0.01	0.01	1.37E-04	0.03
		Compactness coefficient (K_G)	0.17	0.12	0.18	0.01
		Mean elevation	2.07E-03	0.01	1.92E-03	1.15E-04
		Topography: mean slope	1.89E-03	0.01	0.01	0.01
		Precipitation amount (mm)	0.15 (0.39)	0.07 (0.34)	0.08 (0.31)	0.05 (0.39)
		Annual mean flow ($mm.yr^{-1}$)	0.04 (0.37)	1.23E-03 (0.4)	1.38E-03 (0.17)	0.02 (0.22)
	Soil properties	Soil organic carbon content (%)	0.12	0.05	0.07	0.03
		Depth index	0.11	0.14	0.10	0.09
		Stone index	0.05	0.06	0.10	0.10
		Water storage index	9.39E-04	0.01	8.86E-04	3.56E-05
		Nutrient storage index	0.02	0.05	0.04	0.05
		Permeability index	0.04	0.01	0.02	0.01
		Waterlogging index	0.15	0.08	0.08	0.06

Nevertheless, we tried to incorporate the chemical properties of the selected substances to incorporate their different behaviour in the calculation of the cumulative concentrations. In Approach 1, we found better correlations in all scenarios. Concerning Approach 2, interesting correlations were found only by normalising by DT50. The issues with the normalization by K_{OC} might be linked to the variability of SOC in the watersheds. Indeed, the variability of the soil quality is not considered in our calculations. More research should be conducted to understand better the impact of the chemical properties of pesticides on the signal received at the outlet of each catchment.

4.1.2. Missing samples, substances, and catchments

The number of samples in each catchment is not always the same due to differences in sampling protocols. As was done in this paper, normalising the number of samples may attenuate the problem. However, lacking samples may induce missing parts of the signal important to reflect the total amount of pesticides exported to the outlet, as concentration patterns are highly dynamic. Therefore, missing samples will impact the average concentrations we calculated for 2019 and may influence all the correlations with the explanatory variables we tried to highlight in this paper. This statement is even more true if missing samples occur during the growing season, which typically have higher concentrations than in the non-growing season. To avoid this issue, future research may focus on multiyear datasets in order to attenuate the impact of missing samples on the final signal.

This study focused on two lists of compounds. The first list considers the herbicides used on corn crops. We selected herbicides applied to corn fields as the application frequencies should be the easiest to understand. We found a weak relationship between the concentrations calculated with this selection and the percentage of corn fields connected to the stream. Nevertheless, the relationship with connected corn was performed only with 18 catchments instead of 21 as the fraction of connected corn was unavailable in sites where we do not have high-resolution land use data, i.e., sites 7, 8, and 9 (see Appendix 2). Then, the improvement could be linked to the reduction of the heterogeneity in the catchments than the selected explanatory variable.

Moreover, the underestimations of cumulative concentrations in Fig. 3 could be due to the selection of pesticides performed in Approach 1 (Fig. 2). This study is limited by the number of substances measured at all selected sites within the NAWA TREND program. Appendix 15 shows the status of each pesticide applied to corn fields in Switzerland. Even if we selected the pesticides that may play a major role in the corn signal expected in surface waters, some of the excluded substances may be used in large amounts in specific parts of the country to replace widely used pesticides. This statement may distort the comparison of cumulative concentrations between catchments. Considering these spatial differences in the application of herbicides may decrease the uncertainties observed. The same issues may be found with other crops, as they present more complex pesticide application frequencies.

In Approach 2, we explore multiple compounds from the Water Protection Ordinance of Switzerland, selected to cover a significant part of the ecotoxicological risk. In this paper, we selected substances based on their impact on freshwater ecosystems but also depending on the sampling frequencies in the NAWA TREND program. It was important to choose compounds measured at all the sites selected in our study to cover Switzerland and keep as many watersheds of the NAWA TREND program as possible. However, these selections imply that we miss signals from unselected compounds, as in Approach 1 with the unselected corn herbicides in Fig. 2. These missing substances may be applied in substantial amounts in some watersheds and not others, which may influence the total signal received at the outlet. Therefore, the correlations could be improved by analysing more compounds and representing a broader picture of the pesticides used on the national scale.

4.1.3. Explanatory variables

Multiple correlations between pesticide concentrations and explanatory variables were tested in this study. In approach 1, we related corn herbicides with the fraction of corn in each catchment, whether it is connected to the stream or not. Single herbicide analysis returned weak relationships except for S-Metolachlor with the fraction of corn connected to the stream ($R^2 = 0.43$; p-value $= 3.1\ e^{-3}$; Fig. 3). As this molecule is used only on corn and beets (if we neglect other uses; Appendix 3), we could assume that the extraction of the corn signal from the total concentration works better with a combination of beets and corn fields than with other crops. It is supported by the results obtained in Approach 2, with a substantial correlation between the pesticide concentrations and the fraction of beets ($R^2 = 0.42$; p-value $= 0.001$; Appendix 9).

Increasing water fluxes could lead to higher erosion resulting in greater pesticide loads to surface waters. On the contrary, we found in most catchments that pesticide concentrations show a significant decreasing trend with increasing precipitation or discharge (Fig. 4). This is consistent with findings from an aquatic pesticide study in Spain, which showed that lower streamflows were associated with higher concentrations (Masiá et al., 2013). We could explain this tendency by a dilution effect. In this plot, the outlier with a low water flux and a low precipitation amount is an artificial waterway, which could explain its different behaviour. Site 8 is also an outlier presenting a high pesticide concentration facing high discharge or precipitation. It is due to high detections of Metribuzin in late spring. This pesticide is mainly used on potatoes (Appendix 6), which could explain the outlier as the fraction of potatoes in site 8 is much higher than in other sites (12 % against 1 % on average).

The models provided in this paper depend on the pesticide concentration and the quality of the explanatory datasets. As mentioned in Section 2, land use data are available at a high-resolution in many cantons but only at the municipality scale in others. This difference may impact the spatial extrapolation depending on the land use datasets. For example, the unavailability of high-resolution land use data in watersheds 7, 8, and 9 did not allow calculating a fraction of connected corn fields in these areas. In the same way, soil characteristics are qualitative indices that limit the statistical analysis. There is a need for a detailed soil map at the national scale to better highlight the links between soil quality and pesticide fate.

4.2. Number of exceedances

The relationship between N_{calc} and the explanatory variables reveals that for catchments with precipitation below 1000 mm y^{-1}, exceedances may be expected. This model gives no exceedances detected if the drained catchment has no arable lands, no wastewater effluent, and precipitation >1000 mm y^{-1}. The arable lands and the wastewater factors are related to pesticide contributions to surface waters. Higher precipitation in noncritical source areas may dilute in-stream pesticides, leading to the absence of exceedances.

4.3. Spatial extrapolation

We used the model with the lowest AIC to extrapolate concentrations to the entire stream network in the Swiss Plateau (Section 3.2.1). We decided to exclude subwatersheds with an elevation >1000 m.a.s.l., because they typically have low to null crop coverage. Fig. 6 shows the distribution of average concentration within the subwatersheds. We found that the compounds studied in this paper might not be detected in about 45 % of the Swiss stream network. As expected, the Swiss plateau and the Rhône valley contain the subwatersheds with the highest predicted concentrations and the most significant numbers of exceedances, as these areas concentrate the highest anthropogenic pressures in the country.

4.4. Perspectives

This study provides a feasibility study on whether cumulative pesticide concentrations in Swiss streams can be spatially extrapolated. High uncertainties remain in our model regarding the statistical performances. Our model is based on data between March and October 2019. The fate of the pesticide concentrations at the outlet of the different watersheds is

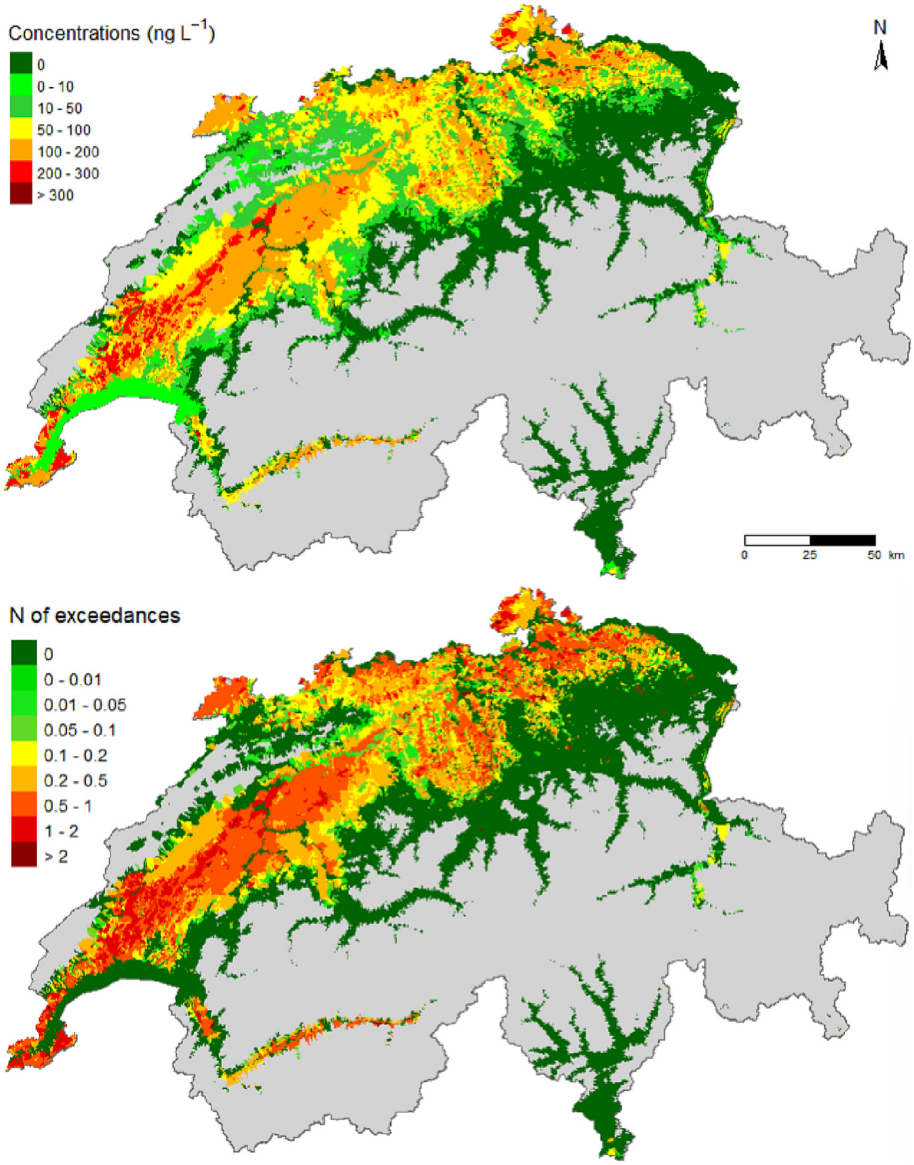

Fig. 6. Spatial representation of the average concentration (ng L^{-1}) and the number of exceedances in the various subwatersheds in Switzerland. The values are calculated based on the multiple regression model described in Section 3.2.1. Subwatersheds with an average elevation >1000 m.a.s.l. were excluded as they present a low crop coverage and are less subjected to pesticide exceedances.

uncertain due to many issues, e.g., assumptions in the model, limited data on pesticide input, and limitations from monitoring (i.e., missing samples, restricted number of pesticides tested). Governmental decisions on the future use of some compounds may impact the total concentrations. Similarly, modifications in the hydrological cycle due to climate change or land use distribution may affect our conclusions.

5. Conclusion

This study explores relationships between aquatic pesticide pollution levels and explanatory variables to extrapolate pesticide levels to other parts of the stream network with little to no monitoring. We performed two approaches. Firstly, we focused on corn fields and corn herbicides. Secondly, we studied a list of pesticides used on various crops. For the corn approach, we saw a weak relationship between the amount of corn cultivated and connected to the stream and the concentrations of corn herbicides in the river. For multiple pesticides coming from various crops, a moderate relationship was found between in-stream pesticide concentrations, crop coverage in the watershed, and the annual precipitation rate. Our analysis suggests that the primary source of uncertainty comes from the lack of knowledge on inputs of pesticides. This paper provides support towards developing a simple method that can lead to more sustainable agricultural practices that keep freshwater ecosystems healthy and safe. However, predicting pesticide concentrations in an unobserved stream is challenging based on readily available catchment information, even with an existing monitoring program established to quantify pollution levels in impacted streams.

CRediT authorship contribution statement

CF performed and analysed the modelling with the help of TD, RC, FF, RS, AD, and CS. CF wrote the paper with considerable contributions from TD, RC, FF, and CS.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.162639.

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