

Pesticides in small agricultural streams in Germany

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Abstract

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Introduction

More than 50% of the total land area in Germany are used by agriculture¹. In the year 2014 more than 45,000 tonnes of 766 authorized pesticides were sold for application on this area². The applied pesticides may enter surface waters via spray-drift, edge-of-field run-off or drainage, with run-off being one of the major input routes^{3,4}. Once entered the surface waters pesticides are frequently detected in environmental monitoring⁵ and may have adverse effects on biota and ecosystem functioning^{6,7}.

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Malaj et al.⁵ analysed data supplied to the European Union (EU) in the context of the Water Framework Directive (WFD) and showed that pesticides jeopardize the health of freshwater ecosystems. However, this reflects only a small part of data from national scale monitoring programs. National monitoring programs are setup for determination and surveillance of the chemical and ecological status of surface, ground and drinking water. These monitoring programs produce large amounts of data, which possibly can also be used to answer other questions. In Germany monitoring programs are setup independently by the federal states in compliance with the Water Framework Directive⁸ and additional state specific needs. However, currently there is no curated national-wide compilation of this data available. Stehle and Schulz⁹ compiled 1566 measured concentrations of 23 insecticides in the EU from scientific publications. They found that insecticides that many of these measurements exceed regulatory acceptable concentrations (RAC), especially in very small catchments $<1\ km^2$.

Small water bodies are important refuges of biodiversity¹⁰ and enable downstream colonisation of polluted streams¹¹. At the same time they may be exposed to a high risk of pesticide contamination from adjacent agricultural areas and low dilution effects⁴. Although small streams comprise a major fraction of streams¹² relatively little is known about their chemical and ecological status.

The aim of this study was to compile all available chemical monitoring data in Germany and to answer the questions:

- (i) Can the currently available monitoring data used for a representative description of the pollution situation?
- (ii) Are small agricultural waters more polluted compared to bigger streams? Are there thresholds in these relationships?
- (iii) How polluted are small streams and which pesticides are most important?

Methods

Data compilation

We queried chemical monitoring data of pesticides from sampling sites with catchment sizes < 100km² for the years 2005 to 2015 from all 13 non-city federal states of Germany. Additionally, we compiled data available from previous studies and searched online databases. This yielded to a total of more than 30 datasets of different formats. In the following we will use the ISO 3166-2:DE standard abbreviations for federal states.

We homogenized and unified these datasets into a common database. We implemented a robust and transparent data cleaning work flow¹³, though parts of the dataset are proprietary. An overview of the data cleaning process is provided in the supplemental materials. To assess whether samples were taken during potential rainfall events we performed spatio-temporal intersection of sampling events with daily precipitation data from the sampling date and the day before.¹⁴.

Characterization of chemical pollution

We characterized chemical pollution (excluding sum parameters) using three indicators:

1. National and international Environmental Quality Standards (EQS)^{15,16}: We used only Maximum Annual Concentration EQS (MAC-EQS) for characterization. These were available for 29 compounds (Supplement, Table xxx). ref
2. Regulatory Acceptable Concentrations (RAC)¹⁷: This is the lowest concentration at which no acceptable biological effects are expected. These are derived during authorization process of pesticides and contain an uncertainty factor. The German Federal Environmental Agency provided RACs for 105 compounds (Supplement, Table xxx). ref

We expressed RAC as Risk Quotient (RQ):

$$RQ = \frac{C}{RAC} \quad (1)$$

Where C is the concentration of a compound in a sample.

3. Maximum Toxic Units (TU_{max})¹⁸:

$$TU_{max} = \max\left(\frac{C_i}{EC_{50,D.magna,i}}\right) \quad (2)$$

Where C_i is the concentration of compound i in a sample and $EC_{50,D.magna,i}$ is the concentration of this compound where 50% of the exposed animals showed after 48 hours an effect in a laboratory study. We compiled $EC_{50,D.magna}$ values from literature⁵, databases^{19,20} or model predictions²¹, where experimental data had priority. We could compile $EC_{50,D.magna}$ values for 394 compounds (Supplement, Table xxx)). We used the maximum TU per sample, as it is independent of the number of measured compounds and makes no assumptions on the mode of action. A table of all included compounds can be found in the supplement.

Characterization of catchments

We delineated catchments upstream of the sampling sites using a digital elevation model²² and a multiple flow direction algorithm²³ as implemented in GRASS GIS 7²⁴. Catchment delineation has been manually checked for accuracy. In areas with low relief energy the delineation algorithm did not produce accurate results and we used river catchments provided by federal state authorities in these cases. For each catchment we calculated the relative coverage (%) with agricultural areas based on Official Topographical Cartographic Information System (ATKIS) of the land survey authorities.

Statistical analyses

All data-processing and analyses have been performed using R, version 3.3.1²⁵. To display differences in the spectra of analysed compounds between federal states we used Multidimensional Scaling (MDS) based on Jaccard dissimilarity in conjunction with hierarchical clustering using the vegan package²⁶. We expected non-linear responses to agriculture and catchment size and therefore, used generalized additive models (GAM) to identify relationships²⁷.

We modeled the number of RAC exceedances (No) as:

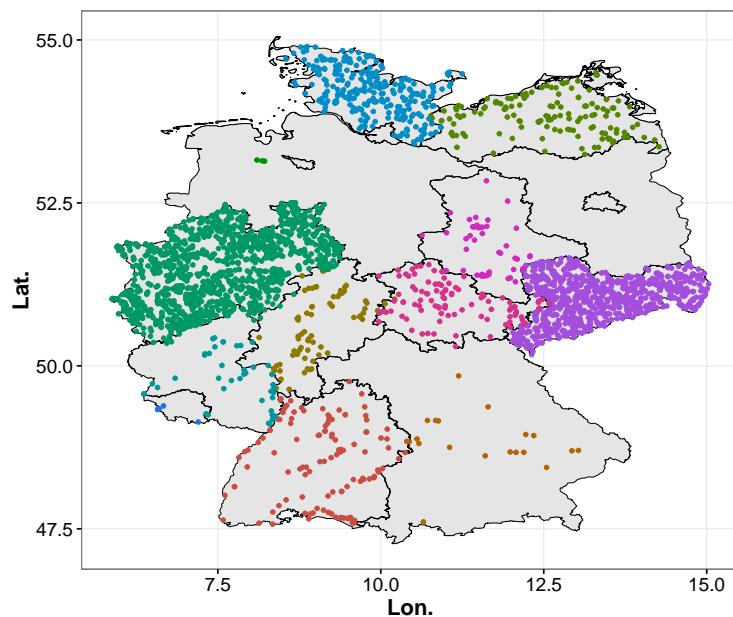
$$\begin{aligned} No_i &\sim NB(\mu_i, k) \\ E(No_i) &= \mu_i \text{ and } Var(No_i) = \mu_i + \frac{\mu_i^2}{k} \\ log(\mu_i) &= \beta_0 + f_1(Agri_i) + f_2(Size_i) + log(n_i) \end{aligned} \quad (3)$$

where No_i is the observed number of exceedances at site i , $Agri_i$ the proportion of agriculture within the catchment and $Size_i$ the catchment size of the site. We modeled No_i as resulting from a negative binomial distribution (NB) and used the number of sampling events per site (n_i) as an offset to account different sampling efforts. f_1 and f_2 are smoothing functions using thin plate regression splines²⁸. The degree of smoothness was estimated using restricted maximum likelihood (REML) during model fitting process²⁹. Similar models were fitted to the number of EQS-exceedances and the 95th percentile of TU_{max} (see Supplement for details). We used pointwise 95% Confidence Intervals of the first derivative of the fitted smooth to check if there are regions of statistically significant changes. GAMs were fitted using the mgcv package²⁹.

Results

Overview and representativeness of compiled data

The compiled dataset comprised only few standing waters (58 sites) and the majority (90%) of samples were taken via grab sampling. Therefore, we report only results of grab samples from streams. The analysed dataset comprised 2,918,604 measurements from 42,236 samples from 3,049 sampling sites. We found big differences in the number of sampling sites between federal states (Figure 1 and Supplement, Table).



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Figure 1: Spatial distribution of the 3109 sampling sites. Colour codes different federal states.

In total 484 different compounds used as pesticides and their metabolites were measured at least once (Supplement, Table). Most of the compounds were herbicides (179), followed by insecticides (117) and fungicides (109). We found substantial differences of the spectra of analysed compounds between federal states (Figure 2). Hierarchical clustering revealed three groups: i) with less than 100 compounds (SL, ST and TH), ii) with a medium sized spectra and

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iii) with a big and distinct spectra (RP and NI).

Only 5.5% (160,800) of all measurements were detected above the limit of quantification (LOQ). The spatio-temporal intersection revealed that 5% of the samples were taken at or after days with rainfall events greater than 10mm / day. .

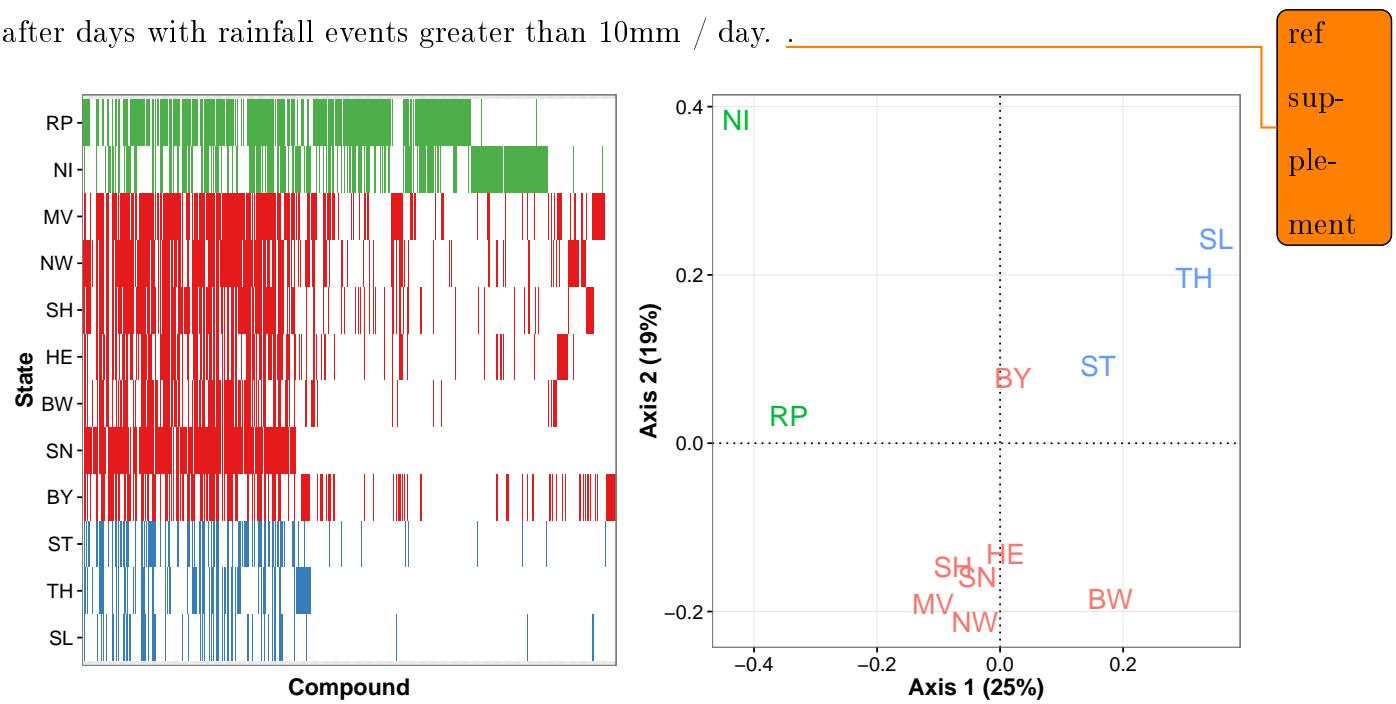


Figure 2: Compound spectra of the different federal states. Left: Barcode plot - Each vertical line is an analysed compound. Right: MDS ordination. Colors according to three groups determined by hierarchical clustering (see Supplement Figure xxx).

We were able to derive for 2376 sites catchment sizes and the proportion of agriculture within catchments. The distribution of sampling sites across catchment area and agricultural area in the catchment revealed a sharp decline in the distribution of catchment-sizes below 10 km^2 , with most sampling sites with catchments between 10 and 25 km^2 (Figure 3). The proportion of agriculture in the catchments decreased with increasing catchment size.

Are small agricultural waters more polluted compared to bigger streams?

Modeling the number of RAC exceedances as function of agriculture within catchment and catchment size revealed that there is a strong and statistically significant increase up to 25%

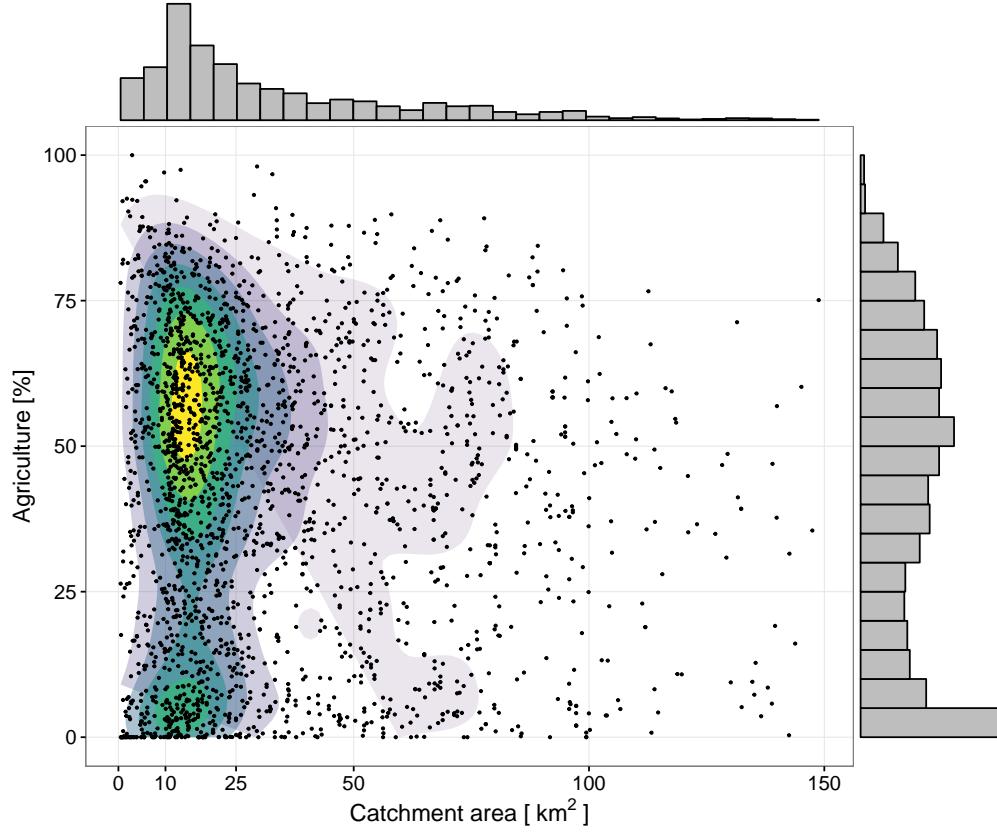


Figure 3: Distribution of catchment area and agriculture within the catchment area across the sampling sites. Only sampling sites with catchment area $< 150 \text{ km}^2$ are displayed. Colour codes the 2-dimensional density of points.

agriculture. Above this threshold the exceedances level off followed by a increase above 75% (Figure 4, left).

We could no detect any effect of catchment size on the number of RAC exceedances (Figure 4, right) and no interaction between these two predictors.

The number of EQS-exceedances and the 95th percentile of TU_{max} showed similar patterns and thresholds (see Supplement Figure Sxxx - Sxxx). references

Pollution of small agricultural streams

Based on the results previous results and given the low amount of sample sites with catchment sizes below 10 km^2 we explored the pollution of small agricultural streams, defined as streams with catchment size less than 30 km^2 and more than 25% agriculture within the catchment

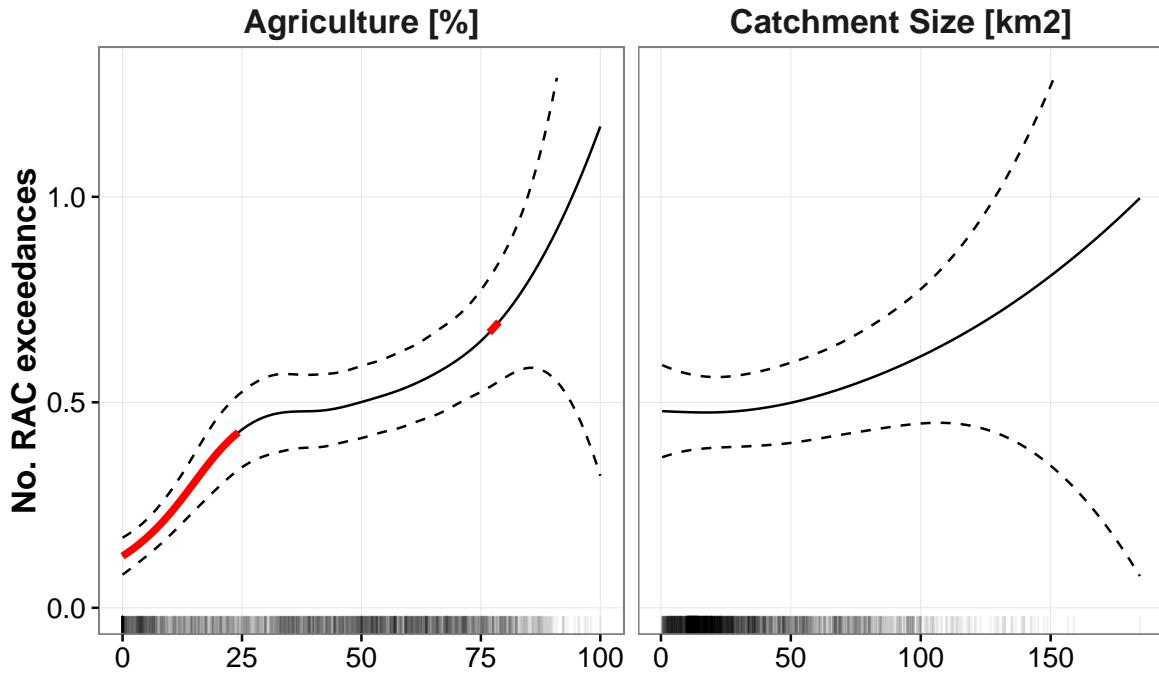


Figure 4: Effect of agriculture within the catchment (left) and catchment size (right) on the number of RAC exceedances. Red line marks statistically significant changes. Dashed lines denote 95% pointwise Confidence Intervals.

($n = 1030$ sites with 10591 samples and 36550 measurements). Out of the 29 compounds with EQS, the most frequent EQS exceedances were recorded for the herbicides Nicosulfuron (2.1%, $n = 1769$), Flufenacet (1.1%, $n = 6301$) and Isoproturon (0.7%, $n = 8380$). Other compounds show exceedances only at less than 0.5% of all samples (Figure 5A). Neonicotinoid Insecticides and Chloryrifos showed highest risk quotients. For Thiacloprid, Imidacloprid and Chlorpyrifos RAC was less than LOQ, therefore, all detections have a RQ >1 (Figure 5B). In 15% of all samples ($n = 6377$) risc quotients higher then 1 were observed. Highest RQ were observed for Chlorpyrifos (244), Dimoxystrobin(117) and Isoproturon (80). In 33% of the samples no pesticides were detected. The mean $\log(TU_{max})$ for detects was -4.6. 2.6% of the samples showed $\log(TU_{max})$ values greater then -2 (Figure 5C). In most samples (55.5%) more then one compound was detected, with a maximum of 54 different compounds (Figure 5D).

Discussion

The compiled dataset of governmental monitoring data represents the

Representativeness of the data

Influence of catchment area and agriculture

Pollution of streams

Acknowledgement

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Supporting Information Available

The following files are available free of charge.

- Supplemental_Materials.pdf : Supplemental Materials (Figures, Tables, Models).

This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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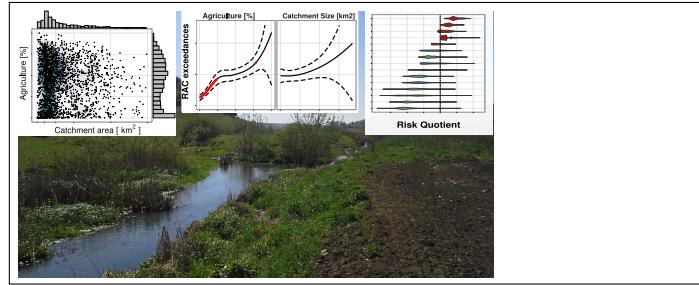
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Graphical TOC Entry



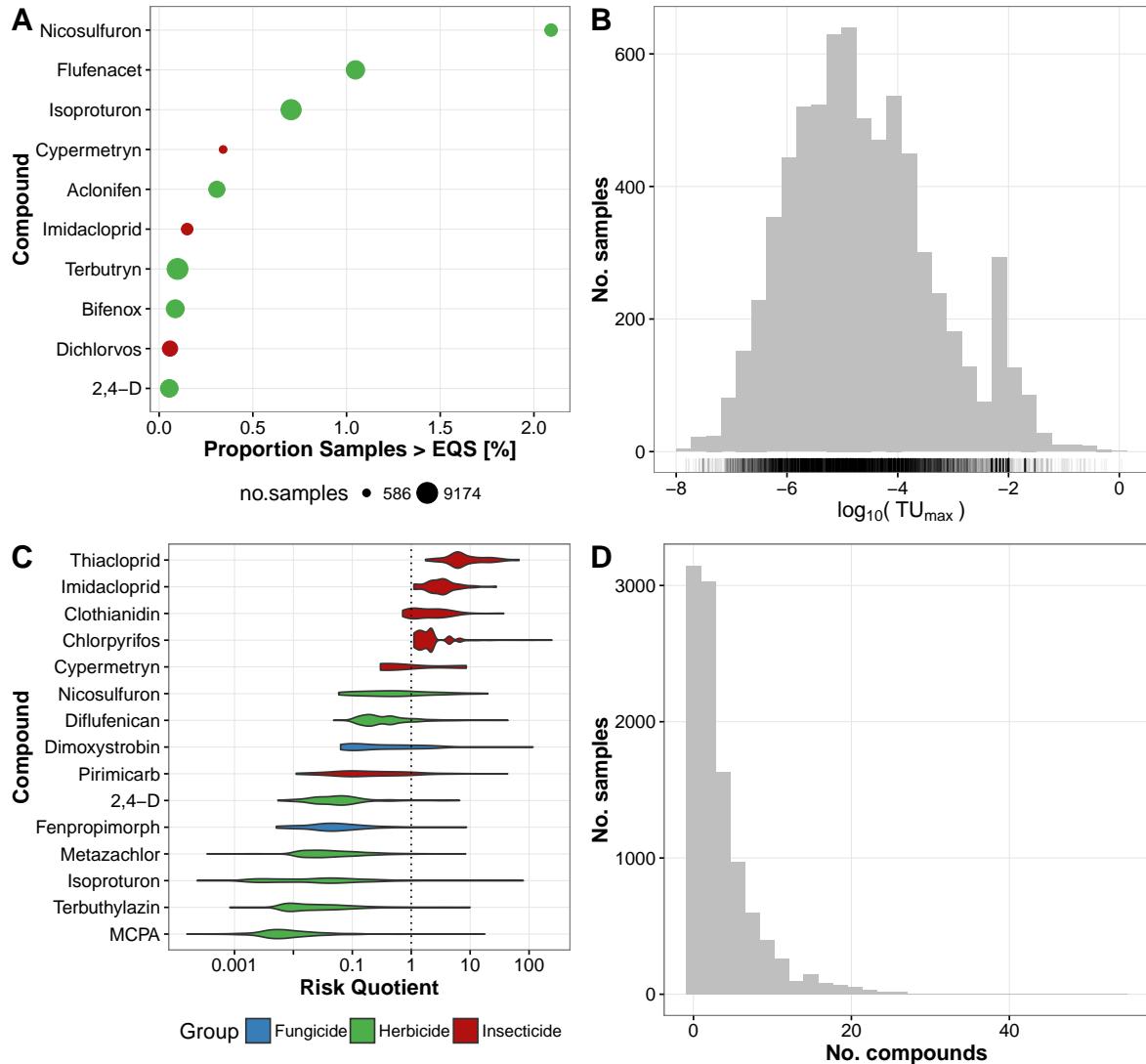


Figure 5: Overview on pesticide pollution of small agricultural streams. **A:** 10 compounds with most frequent EQS exceedances. See B for color legend. **B:** Distribution of TU_{\max} values. Values with $TU_{\max} = 0$ are not displayed (3501 out of 10591 samples). **C:** 15 compounds with highest risk quotients. **D:** Distribution of the number of detected compounds in a sample.