# Pesticides pollution of small streams in Germany

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**Abstract**

Fehlt noch...

## Introduction

More than 50% of the total land area in Germany are used by agriculture[1]. In the year 2014 more the 45,000 tonnes of 766 authorized pesticides were sold for application on this area[2]. The applied pesticides may enter surface waters via spray-drift, edge-off-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 monitoring[5] and may have adverse effects on biota and ecosystem functioning[6,7].

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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 by the federal states in compliance with the Water Framework Directive[8] and further state specific needs. However, currently there is no curated national-wide compilation of this data.

Small water bodies are important refuges of biodiversity[9] and enabling downstream colonisation of polluted streams[10]. At the same time they may be exposed to a high risk of pesticide contamination from adjacent agricultural areas and low dilution effects[4]. Although small streams comprise a major fraction of streams[11] relatively little is know about their chemical and ecological status.

The aim of this study was to compile monitoring data on a national scale 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) baHow polluted are small streams and which pesticides are responsible?

# Methods

## Data compilation

We queried chemical monitoring data of pesticides from sampling sites with catchment sizes $< 100\text{km}^2$ 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 then 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 flow[12], 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.[13].

## Characterization of chemical pollution

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

1. National and international Environmental Quality Standards (EQS)[14,15]: 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)[16]: 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):

$$RQ = \frac{C}{RAC} \tag{1}$$

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

3. Maximum Toxic Units ($TU_{max}$)[17]:

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

   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 literature[5], databases[18,19] or model predictions[20], where experimental data had priority. We could compile $EC_{50,D.magna}$ values for 394 compounds (Supplement, Table xxx)) We used the ref 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 model[21] and a multiple flow direction algorithm[22] as implemented in GRASS GIS 7[23]. 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 provide 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 3.3.1[24]. 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 package[25]. We expected non-linear responses to agriculture and catchment size and therefore, used generalized additive models (GAM) to identify relationships[26].

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

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

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 splines[27]. The degree of smoothness was estimated using restricted maximum likelihood (REML) during model fitting process[28]. 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 package[28].

# Results

## Overview and representativeness of compiled data

The compiled dataset comprised only few standing waters (58 sites) and the majority (90%) of samples where 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 ).

In total 484 different compounds used as pesticides and their metobalites were measured at least once (Supplement, Table ). Most of the compounds were herbicides (179), followed

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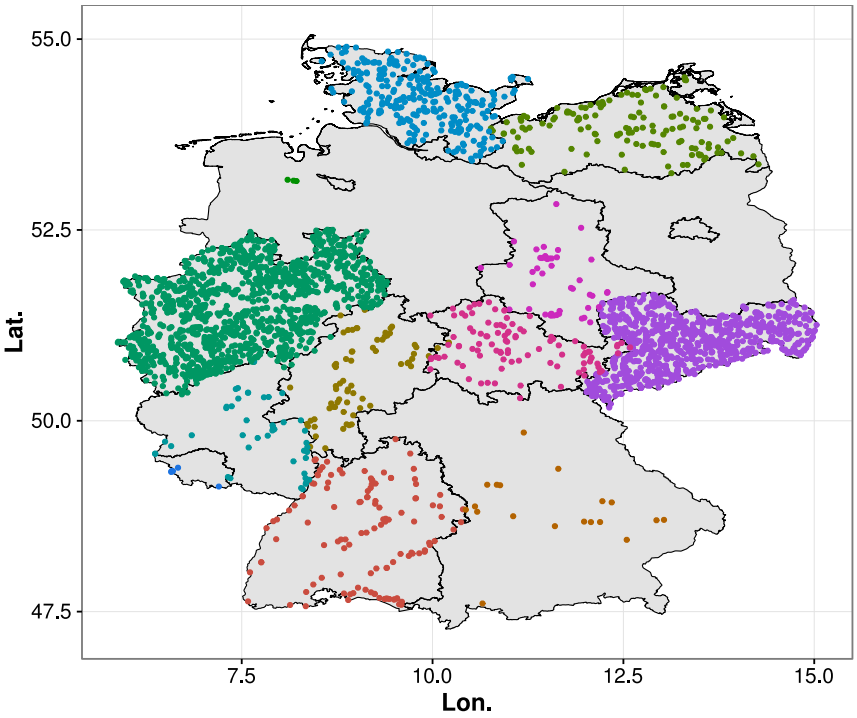


Figure 1: Spatial distribution of the 3109 sampling sites. Colour codes different federal states.

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 then 100 compounds (SL, ST and TH),

ii) with a medium sized spectra and

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

Only 5.5% (160,800) of all measurements were detects 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. .

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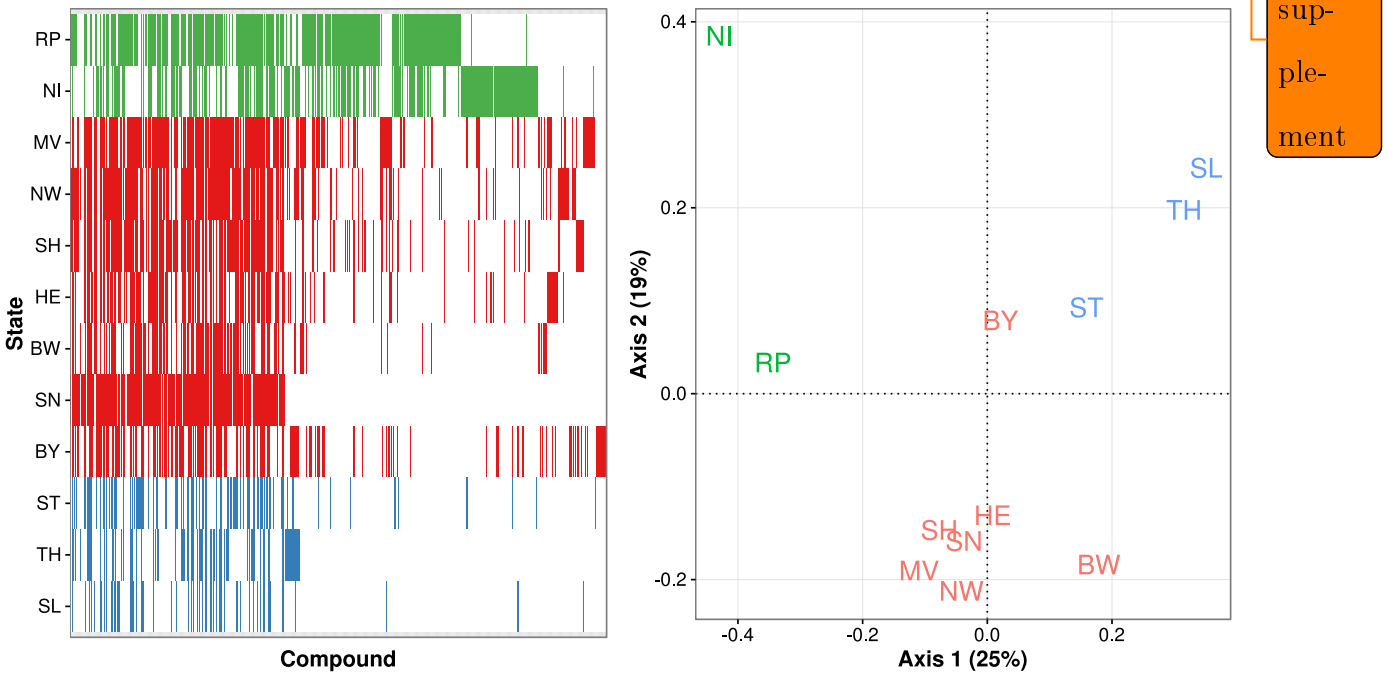


Figure 2: Compound spectra of the different federal states. Left: Barcode plot - Each vertical line is an analysed compound. Right: MDS ordination. Colors according to three groups determined by hierarchical clustering (see Supplement Figure xxx).

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.

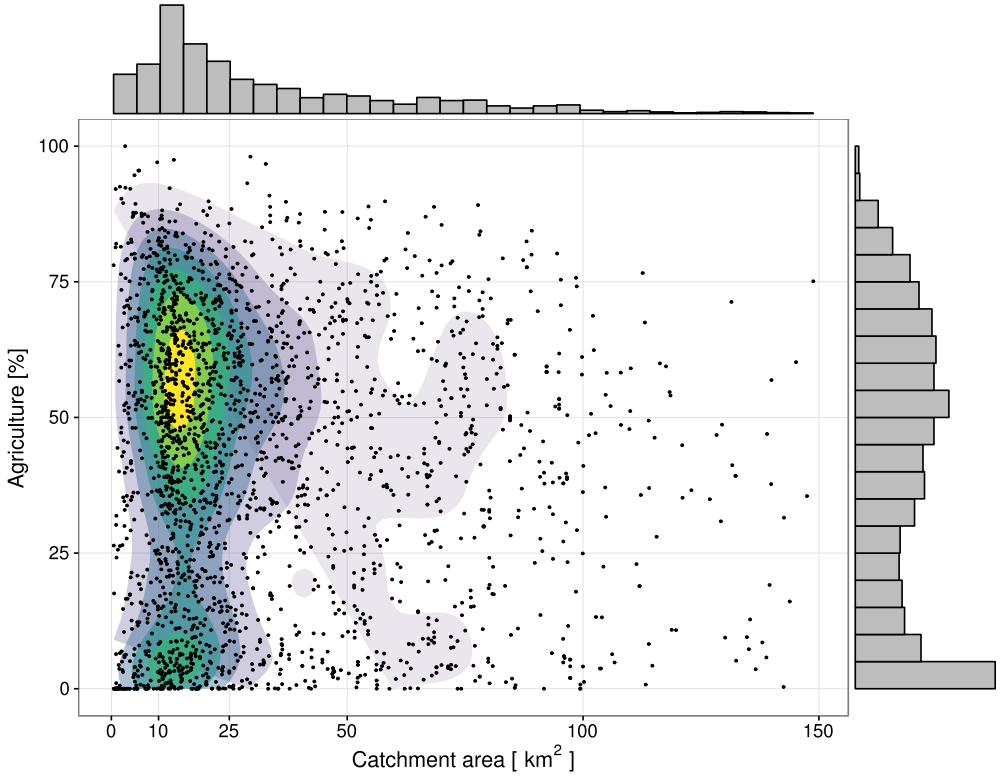


Figure 3: Distribution of catchment area and agriculture within the catchment area across the sampling sites. Only sampling sites with catchment area $< 150$ km$^2$ are displayed. Colour codes the 2-dimensional density of points.

## 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% 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.

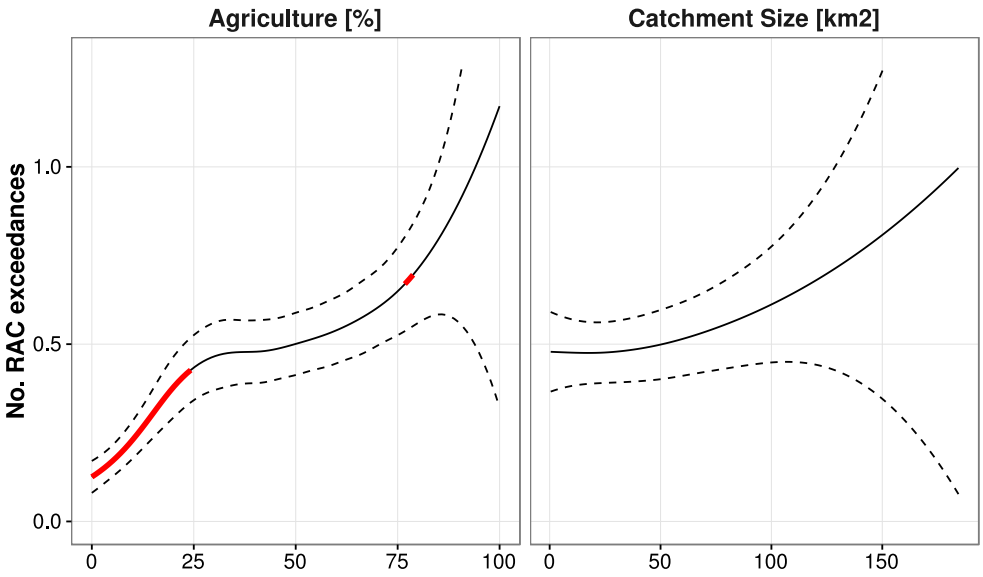


Figure 4: Effect of agriculture within the catchment (left) and catchment size (right) on the number of RAC exceedances. Red line marks statistically significant changes. Dashed lines denote 95% Confidence Intervals.

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

### Pesticide pollution of small agricultural streams in germany

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 (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 then 0.5% of all samples (Figure 5A). Insecticides showed most exceedances of RAC. For Thiacloprid, Imidacloprid and Chlorpyrifos the RAC was less than LOQ, therefore, all detections have a RQ >1 (Figure 5B). Highest RQ was observed for Chlorpyrifos (244), Dimoxystrobin(117) and Isoproturon (80). In 33% of the samples no compounds no compounds 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

### Representativeness of the data

### Influence of catchment area and agriculture

### Pollution of streams

### Acknowledgement

The authors thank the authorities for providing chemical monitoring data and the German Federal Environmental Protection Agency (UBA) for funding this project.

## 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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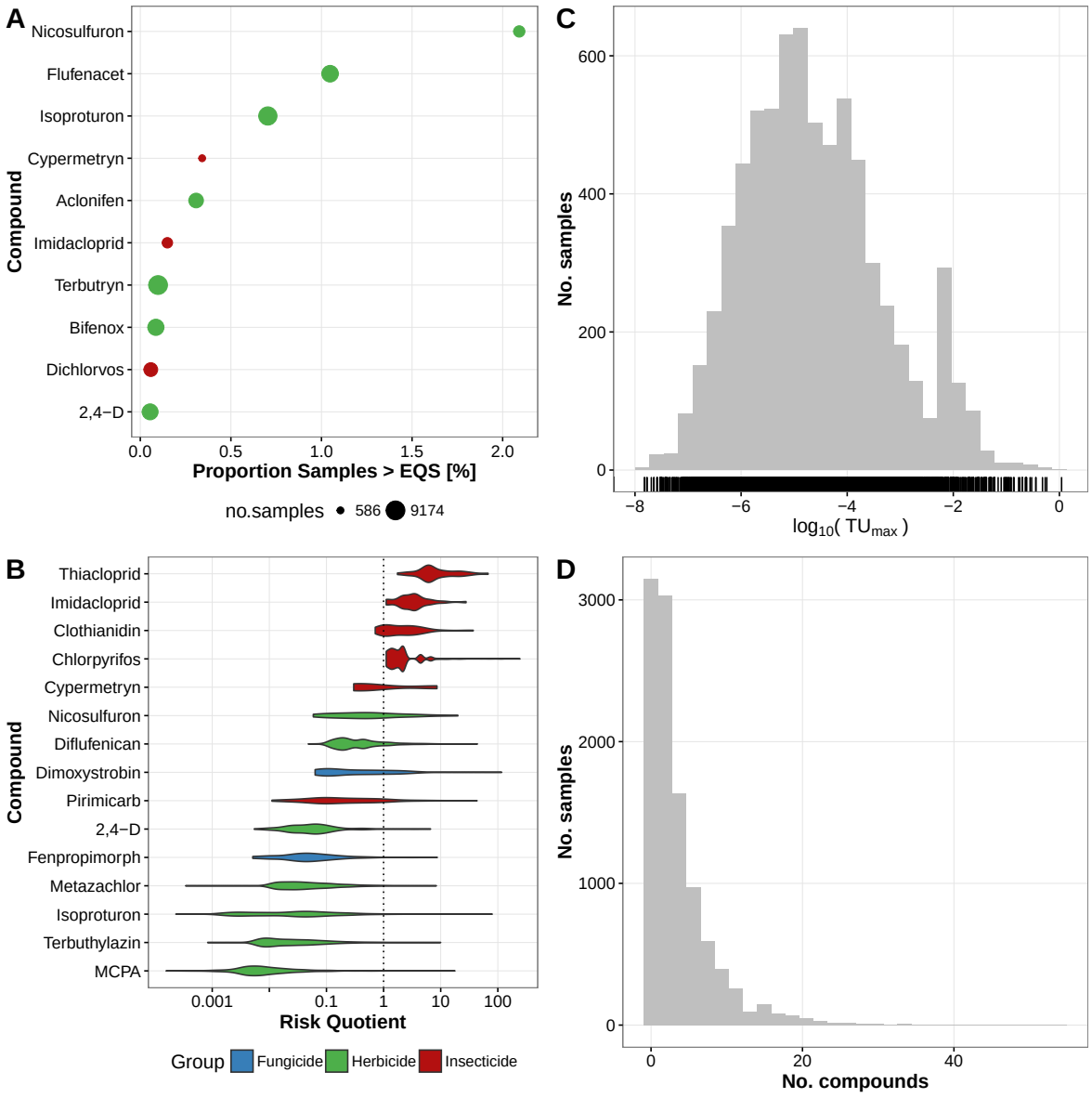


Figure 5: Overview on pesticide pollution of small agricultural streams. A: 10 compounds with most frequent EQS exceedances. See B for color legend. B: 15 compounds with highest risk quotients. C: Distribution of $TU_{max}$ values. Values with $TU_{max} = 0$ are not displayed (3501 out of 10591 samples).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