

# Pesticides in small agricultural streams in Germany

Eduard Szöcs,<sup>\*,†</sup> Marvin Brinke,<sup>‡</sup> Bilgin Karaoglan,<sup>¶</sup> and Ralf B. Schäfer<sup>†</sup>

*Institute for Environmental Sciences, University of Koblenz-Landau, Germany, German Federal Institute of Hydrology (BfG), Koblenz, Germany, and Federal Environmental Agency (UBA), Dessau-Roßlau, Germany*

E-mail: szoechs@uni-landau.de

## Abstract

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## Introduction

More than 50% of the total land area in Germany are used by agriculture<sup>1</sup>. In the year 2014 more than 45,000 tonnes of 766 authorized pesticides were sold for application on this area<sup>2</sup>. 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<sup>3,4</sup>. Once entered the surface waters pesticides are frequently detected in environmental monitoring<sup>5</sup> and may have adverse effects on biota and ecosystem functioning<sup>6,7</sup>.

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<sup>\*</sup>To whom correspondence should be addressed

<sup>†</sup>Institute for Environmental Sciences

<sup>‡</sup>German Federal Institute of Hydrology

<sup>¶</sup>German Federal Environmental Agency

Malaj et al.<sup>5</sup> analyzed 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 study reflected only a small part of data that is available from national monitoring programs. These programs are setup for determination and surveillance of the chemical and ecological status of surface, ground and drinking water. Large amounts of data are generated, 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 WFD<sup>8</sup> and additional state specific needs. However, currently there is no curated national-wide compilation of this data available.

Stehle and Schulz<sup>9</sup> 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 biodiversity<sup>10</sup> and enable downstream colonization of polluted streams<sup>11</sup>. At the same time they may be exposed to a high risk of pesticide contamination from adjacent agricultural areas and low dilution effects<sup>4</sup>. Although small streams comprise a major fraction of streams<sup>12</sup>, 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? Is the current approval process protective for these streams?

# Methods

## Data compilation

We queried chemical monitoring data of pesticides from sampling sites with catchment sizes < 100km<sup>2</sup> 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 reproducible data cleaning work flow (Supplement, Figure S1)<sup>13</sup>, 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.<sup>14</sup>.

## Characterization of chemical pollution

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

1. National and international Environmental Quality Standards (EQS)<sup>15,16</sup>: We used only Maximum Annual Concentration EQS (MAC-EQS) for characterization. These were available for 29 compounds (Supplement, Table S2).
2. Regulatory Acceptable Concentrations (RAC)<sup>17</sup>: This is the lowest concentration at which no acceptable biological effects are expected. These are derived during authorization process of pesticides, incorporate also an uncertainty factor and aim to be protective especially for small streams. The German Federal Environmental Agency provided RACs for 105 compounds (Supplement, Table S2). We expressed RAC as

Risk Quotient (RQ):

$$RQ_i = \frac{C_i}{RAC_i} \quad (1)$$

Where  $C_i$  is the concentration of a compound  $i$  in a sample.

3. Maximum Toxic Units ( $TU_{max}$ )<sup>18</sup>:

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

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 literature<sup>5</sup>, databases<sup>19,20</sup> or model predictions<sup>21</sup>, where experimental data had priority. We could compile  $EC_{50,D.magna}$  values for 394 compounds (Supplement, Table S2)). 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. Additionally, we also calculated the sum of toxic units ( $TU_{sum}$ ). 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<sup>22</sup> and a multiple flow direction algorithm<sup>23</sup> as implemented in GRASS GIS 7<sup>24</sup>. 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<sup>25</sup>. To display differences in the spectra of analyzed compounds between federal states we used Multidimensional Scaling (MDS) based on Jaccard dissimilarity in conjunction with hierarchical clustering using the vegan package<sup>26</sup>. We expected non-linear responses to agriculture and catchment size and therefore, used generalized additive models (GAM) to identify relationships<sup>27</sup>.

We modeled the number of RAC exceedances 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 splines<sup>28</sup>. The degree of smoothness was estimated using restricted maximum likelihood (REML) during model fitting process<sup>29</sup>. Similar models were fitted to the number of EQS-exceedances and the 95th percentile of  $TU_{max}$  (see Supplement for details). We used point-wise 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<sup>29</sup>.

# Results

## Overview of the 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 analyzed 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 S1).

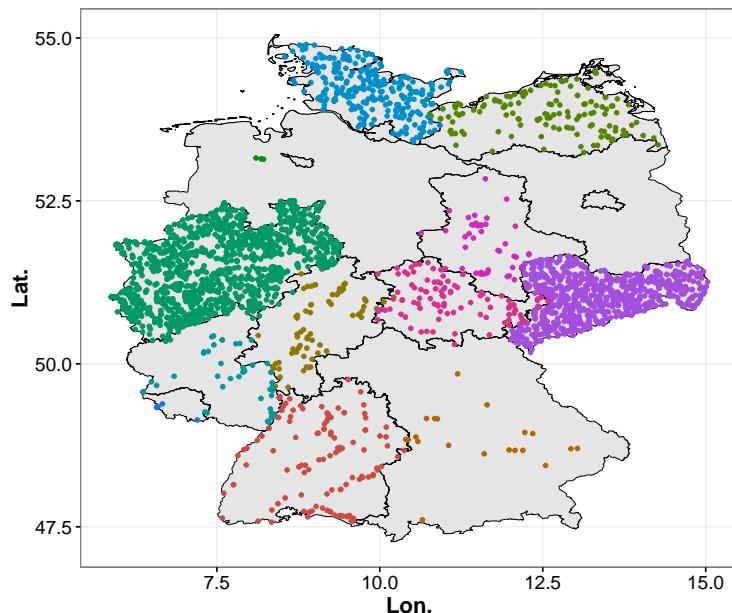


Figure 1: Spatial distribution of the 3109 sampling sites. Colour codes different federal states.

In total 484 different compounds used as pesticides and their metabolites were measured at least once (Supplement, Table S2). Most of the compounds were herbicides (179), followed by insecticides (117) and fungicides (109). We found substantial differences of the spectra of analyzed compounds between federal states (Figure 2 and Supplement Figure S2). Hierarchical clustering revealed three groups: i) with less than 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 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 (Supplement, Figure S3).

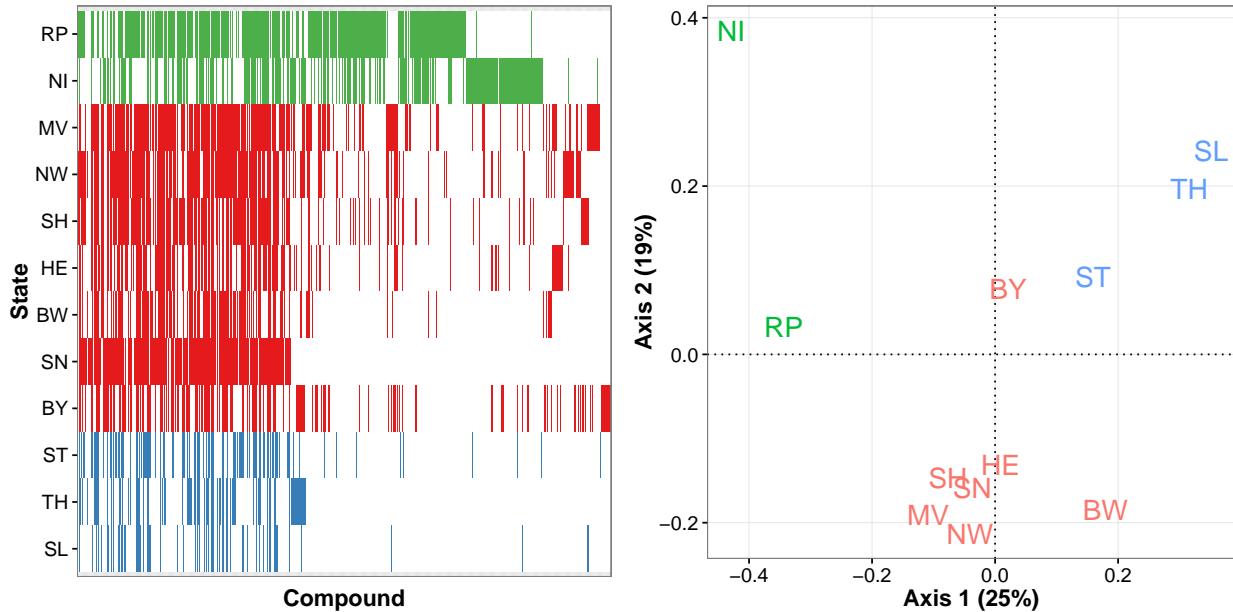


Figure 2: Compound spectra of the different federal states. Left: Barcode plot - Each vertical line is an analysed compound. Right: MDS ordination. Colors according to three groups determined by hierarchical clustering (see Supplement Figure xxx).

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  $10 \text{ km}^2$ , with most sampling sites with catchments between 10 and  $25 \text{ km}^2$  (Figure 3). The proportion of agriculture in the catchments decreased with increasing catchment size.

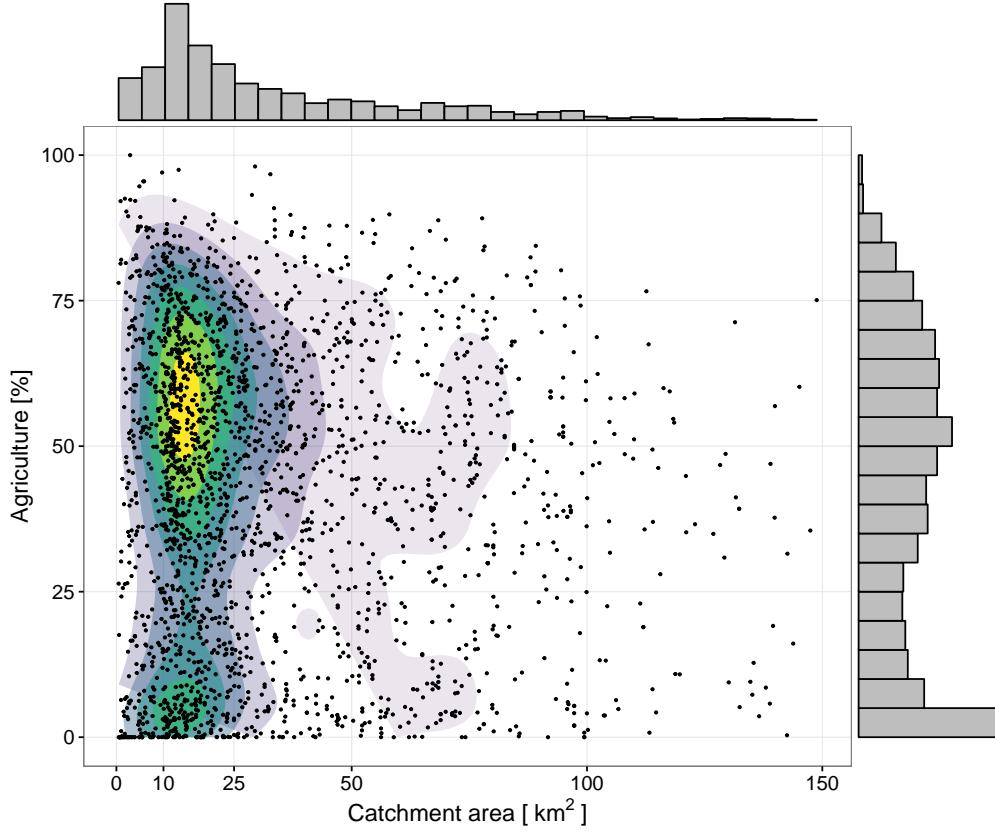


Figure 3: Distribution of catchment area and agriculture within the catchment area across the sampling sites. Only sampling sites with catchment area  $< 150 \text{ km}^2$  are displayed. Colour codes the 2-dimensional density of points.

## 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.

The number of EQS-exceedances and the 95th percentile of  $TU_{max}$  showed similar patterns and thresholds (see Supplement, Figures S4-S8).

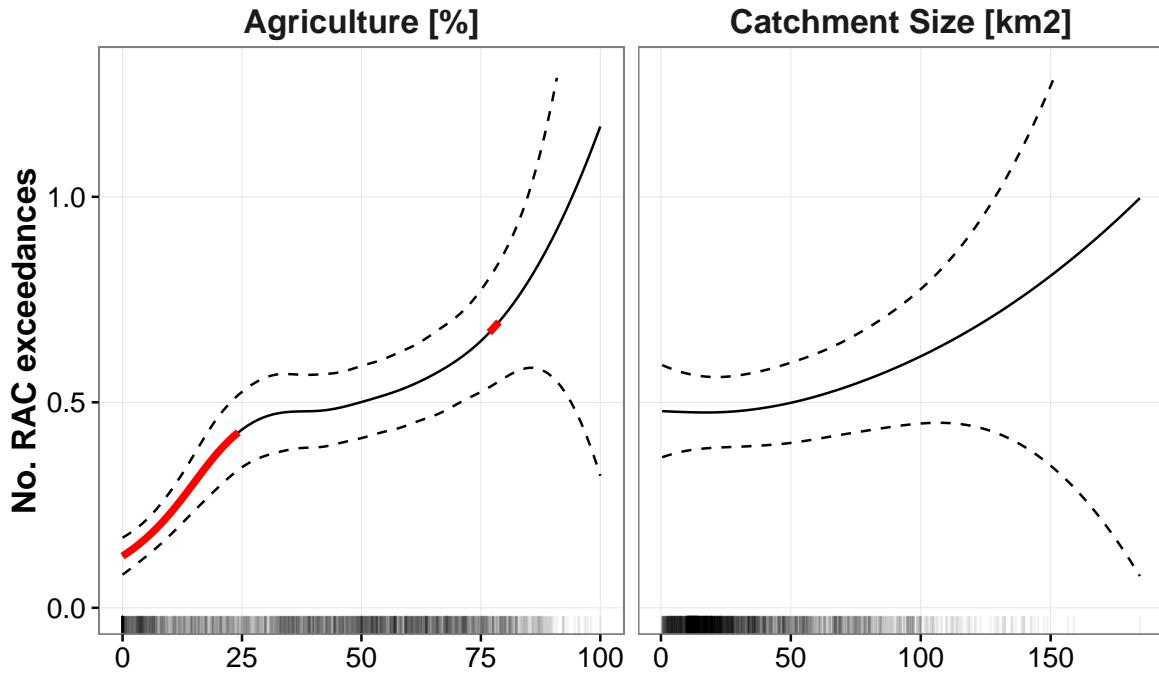


Figure 4: Effect of agriculture within the catchment (left) and catchment size (right) on the number of RAC exceedances. Red line marks statistically significant changes. Dashed lines denote 95% pointwise Confidence Intervals.

## Pollution of small agricultural streams

Based on the results previous results and given the low amount of sample sites with catchment sizes below  $10 \text{ km}^2$  we explored the pollution of small agricultural streams, defined as streams with catchment size less than  $30 \text{ km}^2$  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 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  $\text{RQ} > 1$  (Figure 5B). In 15% of all samples ( $n = 6377$ ) risk quotients higher than 1 were observed. Highest  $\text{RQ}$  were observed for Chlorpyrifos (244), Dimoxystrobin(117) and Isoproturon (80). In 33%

of the samples no pesticides were detected. The mean  $\log_{10}(TU_{max})$  for detects was -4.6. 2.6% of the samples showed  $\log_{10}(TU_{max})$  values greater than -2 (Figure 5C). We found a high correlation of  $\log_{10}(TU_{max})$  and  $\log_{10}(TU_{sum})$  ( $r = 0.985$ , with a maximum higher value of  $\log_{10}(TU_{sum})$  of 0.75 units (Supplement, Figure S9). In most samples (55.5%) more than one compound was detected, with a maximum of 54 different compounds (Figure 5D).

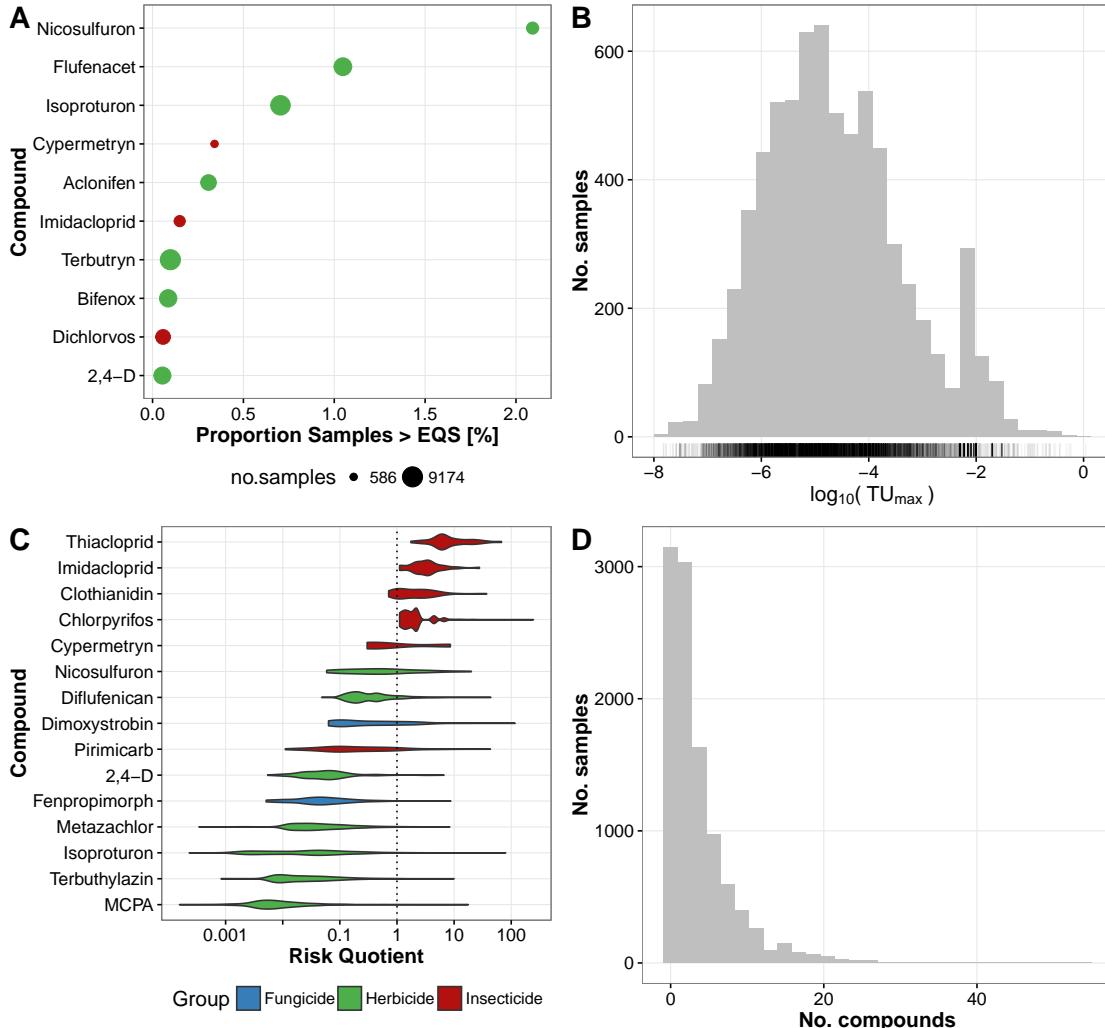


Figure 5: Overview on pesticide pollution of small agricultural streams (catchment size  $<30$  km $^2$  and  $>25\%$  agriculture). **A:** 10 compounds with most frequent EQS exceedances. See B for color legend. **B:** Distribution of  $TU_{max}$  values. Values with  $TU_{max} = 0$  are not displayed (3501 out of 10591 samples). Non-detects are not shown due to the logarithmic axis. **C:** 15 compounds with highest risk quotients. Non-detects are not shown due to the logarithmic axis. **D:** Distribution of the number of detected compounds in a sample.

# Discussion

## Overview on the compiled dataset

The compiled dataset of governmental monitoring data represents currently the most comprehensive one available for Germany. Similar nationwide datasets have been compiled for the Netherlands<sup>30</sup>, Switzerland<sup>31</sup> and the United States (Water Quality Portal (WQP) [www.waterqualitydata.us](http://www.waterqualitydata.us)). The data compiled here for Germany is of similar quantity and quality.

Nevertheless, a nationwide assessment of pesticide pollution is hampered by the inhomogeneity of monitoring data between federal states: There are not only big differences in the spatial distribution and quantity of sampling sites (Figure 1), but also the spectrum of analyzed compounds (Figure 2) and differences in the quality of chemical analyses. An increase of the analyzed compound spectra to all registered compounds and a lowering of LOQ are desirable for a reliable assessment. Our dataset comprised several thousand stream sampling sites, but nearly no data could be compiled for standing waters. Although, standing waters are abundant in the agricultural landscape and may have a high contribution to biodiversity<sup>10</sup>, nearly nothing is known on their chemical status. Small streams comprise most of the total stream length<sup>12</sup>. However, sampling sites with catchment sizes below  $10km^2$  are underrepresented by the current monitoring scheme (Figure 3). This likely arises because catchments under  $10km^2$  are not specified by the WFD. Nevertheless, small streams should not be neglected for ecological and chemical quality assessment. Future monitoring programs should aim at resolving these issues in order to enable a nationwide and representative assessment of freshwaters.

Given the fixed term monitoring design<sup>32</sup> and the low amount of samples taken at precipitation events that could lead to run-off, the data represents a underestimation of the real pollution and peak concentrations. Automatic event-drive samplers and passive samplers may help overcome these shortcomings and provide a better representation<sup>33,34</sup>. Neverthe-

less, such nationwide compilations, may not only be used for governmental surveillance, but also to answer other questions, like validation of exposure modeling,<sup>35</sup> retrospective evaluation of regulatory risk assessment<sup>9,36</sup> or occurrences of pesticide mixtures.<sup>37</sup>

## Influence of catchment area and agriculture

We found a strong influence of agriculture on the pollution of streams. If there is more than 25% agriculture within a catchment pesticides can generally be detected in streams with an increase in fully agricultural catchments (above 75 % agriculture). To our knowledge this is the first study investigating such thresholds of pesticide occurrences. Our results suggest that only catchments with <25% agriculture may be regarded as unpolluted and used as reference sites. Slightly higher thresholds (20-40%) have been found for biological responses of lotic assemblages to land-use<sup>38,39</sup>, though they might be differences between taxonomic groups and landscape<sup>39</sup>.

We did not find support for our hypothesis that small streams are more polluted than big streams, though previous studies have shown such a relationship<sup>6,9,36</sup>. This could be explained by the relatively short gradient of catchment sizes in our dataset, with most of the streams being <100 km<sup>2</sup> (Figure 3, top). For example the gradient of Schulz<sup>6</sup> covered 6 orders of magnitude. Another reason might be the unequal distribution of catchment sizes, with less sites <10 km<sup>2</sup> and >100 km<sup>2</sup> (Figure 3, top).

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## Pollution of streams

Stehle and Schulz<sup>9</sup> found the highest percentage of RAC exceedances organophosphate insecticides. Our results revealed that neonicotinoid insecticides show high exceedances, followed by the organophosphate chlorpyrifos. This difference can be attributed to the low sample size for neonicotinoid insecticides in their study ( $n = 33$ ) compared to the dataset presented here ( $n = 3516-4745$ ) and shows that this particular class of insecticides may currently pose a high risk to freshwater ecosystems. Our results show lower proportions of exceedances com-

pared to Stehle and Schulz<sup>9</sup>, which can be attributed to different aims of the data sources: scientific research aims at finding pollutants, whereas monitoring aims mainly at surveillance of water quality, also during periods with lower pesticide usage. This is also reflected in the different sample sizes (1,566 vs. 1,117,988 measurements of compounds with RAC) and the high number of non-detects in the monitoring data. Contrary, Knauer<sup>36</sup> found exceedances from monitoring data mainly for herbicides and fungicides and only one insecticide Chlorpyrifos. This might reflect differences in pesticide use between countries and defined RACs. For three insecticides all detected values were above the RAC. This highlights that national monitoring programs need to improve chemical analytics and lower the LOQ for these highly toxic compounds.

8.2% of samples showed  $TU_{max}$  values greater than -3 (Figure 5C), a threshold above biological effects have been shown<sup>40</sup>. This suggests that pesticides may act as a common stressor to freshwaters and should not be neglected<sup>41</sup>. The high correlation of TU and the relatively low increase of  $TU_{sum}$  reveals that in compound mixtures occurring in the field there is a skewed distribution of toxicities with mainly one compound dominating the toxicity. Nevertheless, most pesticides did not occur individually but in mixtures<sup>37</sup> and future risk assessment should take mixtures into account.

For only a limited number of compounds EQS have been defined. We found generally low exceedances of EQS with only three herbicides showing higher exceedances. However, compared to the results from RAC comparisons it is clear that the currently defined EQS cannot capture the full risk exposed by pesticides. In order to provide a reliable measure of a good chemical status EQS for additional compounds must be defined.

Monitoring data, despite the outlined limitations, provides an opportunity to study environmental occurrences of pesticides after approval. The high exceedances of RAC indicate that the approval process must be checked and refined.

## 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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# Graphical TOC Entry

