

Large scale risks from pesticides in small streams

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Abstract

Small streams are important refugia for biodiversity. In agricultural areas they may be at high risk from pesticide pollution. However, most related studies have been limited to a few streams on the regional level, hampering extrapolation to larger scales. We used data from German governmental water quality monitoring to quantify the drivers of pesticide risk and to assess pesticide risk in small streams on a large scale. The data set comprised of 2,918,604 measurements related to 42,236 samples in 3,049 sampling sites and of 484 pesticides. We investigated the influence of agricultural land use, catchment size, as well as precipitation and seasonal dynamics on pesticide risk using new statistical modeling techniques that explicitly consider the limit of quantification. Agriculture land use lead to an 3.5-fold increase in exceedance of risk thresholds once the proportion of agriculture in a catchment exceeded 25 percent. Precipitation increased

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measured pesticide concentrations xxx-fold. The highest concentrations were found during summer. Risk thresholds were exceeded in 27 percent of small streams, with neonicotinoid and other insecticides exhibiting highest frequencies of exceedance. We conclude that pesticides from agricultural land use are a major threat to small streams and their biodiversity, and that governmental pesticide sampling should be adapted to precipitation events in summer.

Introduction

More than 50% of the total land area in Germany is 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^{3–5}. Once entered the surface waters they may have adverse effects on biota and ecosystem functioning⁶. Although it is known that pesticide pollution and its ecological effects increase with the fraction of agricultural land use in the catchment⁷, the shape of the relationship is unknown and studies on potential thresholds are lacking.

Two recent studies indicate that pesticides might threaten freshwater biodiversity in the European union. Malaj et al.⁸ analyzed data supplied to the European Union (EU) in the context of the Water Framework Directive (WFD) and showed that almost half of European water bodies are at risk from pesticides. Stehle and Schulz⁹ compiled 1,566 measured concentrations of 23 insecticides in the EU from scientific publications. They found that many of these measurements exceed regulatory acceptable concentrations (RAC). However, these studies reflect only a small amount of potentially available data (173 sites in predominantly mid-sized and large rivers in Malaj et al.⁸ and 138 measurements in Stehle and Schulz⁹), and it is unclear how representative they are for Germany. Much more comprehensive data on thousands of sites are available from national monitoring programs that are setup for the surveillance of water quality, which is done independently by the federal states in Germany in compliance with the WFD¹⁰ and additional state specific needs. Despite these data pro-

viding the opportunity to study pesticide risks and other research questions on a large scale with high spatial density, to date these data have not been compiled and related analyses are lacking.

Small water bodies (SWB) comprise a major fraction of streams¹¹, accommodate a higher proportion of biodiversity compared to larger freshwater systems^{12,13} and play an important role in recolonization of disturbed downstream reaches^{14,15}. However, SWB might be also at high risk of pesticide contamination from adjacent agricultural areas and lower dilution potential^{5,7}. Indeed, meta-analyses using data from studies with a few sites reported higher pesticide pollution in smaller streams compared to bigger streams^{7,9}. Despite their ecological relevance and potentially higher pesticide exposure, a recent analysis of pesticide studies showed that a disproportionately small fraction of studies were conducted in SWB, and these were largely limited to a few sites¹⁶. Consequently, knowledge on the pesticide pollution of SWB on larger scales is scant.

In this study we compiled and analyzed large scale chemical monitoring data from SWB in Germany. First, we analysed the shape of the relationship between pesticide risk, agricultural land use and catchment size and examined whether related thresholds for pesticide risks can be derived. Second, we investigated the influence of precipitation and seasonal dynamics on pesticide detections, given that precipitation proved an important driver of pesticide exposure in several small scale studies¹⁷, but it is unknown whether a precipitation signal prevails on large scales. Finally, we quantified the current risks from pesticides in SWB in Germany.

Methods

Data compilation

We requested pesticide monitoring data from sampling sites with catchment sizes < 100km² for the years 2005 to 2015 from all 13 non-city federal states of Germany (see Supplemental

Table S1 for the abbreviations of federal state names). Additionally, we used data available from previous projects with bigger catchment sizes. We homogenized and unified all data provided by the federal states into a database and implemented a robust data cleaning workflow (see Supplemental Figure S1 for details)¹⁸.

We identified chemical samples taken during heavy rainfall events by spatio-temporal intersection of sampling events with gridded daily precipitation data available from the German Weather service (DWD). This data spatially interpolates daily precipitation values from local weather stations¹⁹. We performed the intersection for the actual sampling date and the day before, to identify rain events during and up to 48 hours before sampling.

Characterization of catchments

We compiled a total of 3,049 sampling sites with pesticide measurements. We delineated catchments upstream for each of the sampling sites using a digital elevation model (DEM)²⁰ and the multiple flow direction algorithm²¹ as implemented in GRASS GIS 7²². Catchment delineation was manually checked for accuracy by comparison with state stream networks. Given that the delineated catchments were accurate only for 30% of the sites, we compiled complementary catchment size data from authorities that provided catchments for an additional (60% of sites). Ten percent of sites lacked catchment size data and were omitted from the operations outlined below.

For each derived catchment (either from DEM or drainage basins) we calculated the relative cover (in %) with agricultural area based on Official Topographical Cartographic Information System (ATKIS) of the land survey authorities²³. Additionally, we used agricultural cover data provided by authorities (19% of sites). For 78% of the sites both, the proportion of agricultural land use and catchment size were available.

A clear definition of SWB in terms of catchment or stream size is currently lacking¹⁶. The WFD defines SWB with a catchment size between 10 and 100 km², without further categorisation of streams <10km². Lorenz et al.¹⁶ defines SWB with catchment size <10km²

as SWB. Because of data scarcity of streams $<10 \text{ km}^2$ (Figure 3) we define in this study all streams below 25 km^2 as SWB. This catchment size corresponds to a stream width of approximately 2 meters (see Supplemental Figure S2).

Characterization of pesticide pollution

We characterised pesticide pollution using regulatory acceptable concentrations (RAC)²⁴. RACs are derived during pesticide authorization as part of the ecological risk assessment. No unacceptable ecological effect are expected if the environmental concentration remains below this concentration. The German Federal Environmental Agency (UBA) provided RACs for the 105 compounds with highest detection rates (Supplemental Table S2). We expressed RACs 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.

Statistical analyses

All data-processing and analyses were performed using R²⁵. To display differences in the spectra of analyzed compounds between federal states we used Multidimensional Scaling (MDS) based on Jaccard dissimilarity in conjunction with complete linkage hierarchical clustering using the vegan package²⁶. We expected non-linear responses to agriculture and catchment size and therefore, used generalized additive models (GAM) to establish relationships²⁷. We modeled the number of RAC exceedances as:

$$\begin{aligned} No(RQ > 1)_i &\sim NB(\mu_i, \kappa) \\ \log(\mu_i) &= \beta_0 + f_1(agri_i) + f_2(size_i) + \log(n_i) \end{aligned} \quad (2)$$

where $No(RQ > 1)_i$ is the observed number of RAC exceedances at site i . We modeled $No(RQ > 1)_i$ as resulting from a negative binomial distribution (NB) with mean μ_i and a quadratic mean-variance-relationship ($Var(No(RQ > 1)_i) = \mu_i + \frac{\mu_i^2}{\kappa}$). The proportion of agriculture within the catchment ($agri_i$) and the catchment size of the site ($size_i$) were used as predictors of the number of RAC exceedances. f_1 and f_2 are smoothing functions using penalized cubic regression splines²⁸ and β_0 is the intercept. The degree of smoothness was estimated using restricted maximum likelihood (REML) during model fitting process²⁹. The number of measurements per site (n_i) was used as an offset to account for differences in sampling efforts (sampling interval and analysed compound spectrum) at a site and is equivalent to modeling the rate of exceedances. We used point-wise 95% Confidence Intervals (CI) 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.

To assess the influence of precipitation and seasonality we modeled the RQ of individual compounds as response variable. RQ and concentrations show a skewed distribution with an excess of zeros (no pesticides detected and quantified). Therefore, we modeled these as two processes (one generating values below the limit of quantification (LOQ) and one generating values above LOQ) using a Zero-Adjusted Gamma (ZAGA) distribution (Equation 3).^{30,31} These two processes can be interpreted as changes in the mean value of RQ (change in μ) and changes in the probability of exceeding LOQ and showing any risk (change in ν).

$$RQ_i \sim ZAGA(\mu_i, \sigma, \nu_i) = \begin{cases} (1 - \nu_i) & \text{if } y < LOQ \\ \nu_i \times f_{Gamma}(\mu_i, \sigma) & \text{if } y \geq LOQ \end{cases} \quad (3)$$

ν_i denotes the probability of an observation i being above LOQ and f_{Gamma} denotes the gamma function and is used for values equal to or greater LOQ, with μ being the mean and σ the standard deviation of RQ. We used the $\log(x + 0.05)$ transformed precipitation at sampling date ($\log prec_0$) and the day before ($\log prec_{-1}$), as well as quarters of the year

$(Q1 - Q4)$ as linear predictors for μ and ν . We used appropriate link functions for μ and ν and assumed σ to be constant. Equation 4 summarises the deterministic part of the model.

$$\begin{aligned}\log(\mu_i) &= \log prec_{0i} + \log prec_{-1i} + Q1_i + Q2_i + Q3_i + Q4_i \\ \text{logit}(\nu_i) &= \log prec_{0i} + \log prec_{-1i} + Q1_i + Q2_i + Q3_i + Q4_i\end{aligned}\tag{4}$$

To account for temporal auto-correlation and differences between federal states we used *site* nested within *state* as random intercepts. We implemented this model using the *gamlss* package.³²

We fitted this model separately to each compound with a RAC, measured in least 1000 samples and with more than 5% of values above LOQ ($n = 24$ compounds, see Supplemental Table S3 for a list of compounds). To summarise the coefficients across the 24 modeled compounds we used a random effect meta-analysis for each model coefficient separately³³. The results of individual compounds are provided in the Supplemental Table S4 and Figure S7. The meta-analysis was performed using the *metafor* package³⁴.

Results

Overview of the compiled data

The compiled dataset used in analysis comprised 2,918,604 pesticide measurements of 42,236 samples in 3,049 sampling sites. These samples were taken via grab sampling. Composite samples of different durations that were taken in 33 sites were not considered in analysis, given a potential methodical bias and the low sample size. We found large differences in the number of sampling sites between federal states and their spatial distribution (Figure 1 and Supplemental Table S1). The number of sampling sites per state ranged from 3 (Lower Saxonia, NI) to 1320 (North Rhine-Westphalia, NW).

In total 484 different compounds used as pesticides and their metabolites were measured

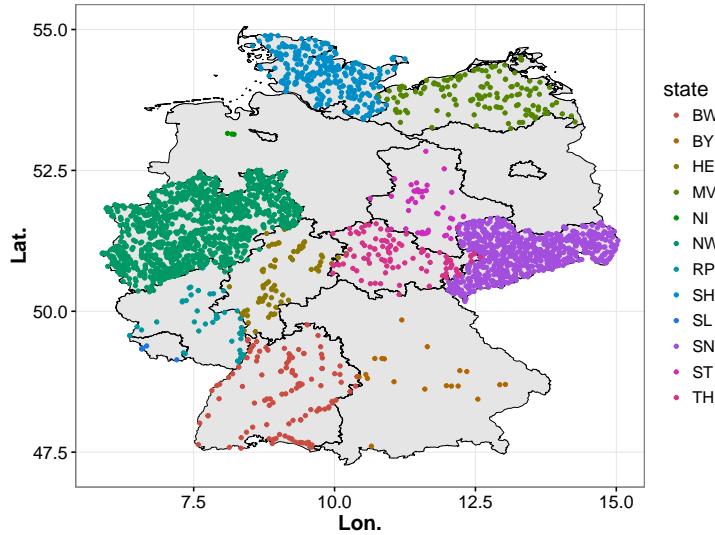


Figure 1: Spatial distribution of the 3109 sampling sites. Colour codes different federal states, see Supplemental Table S1 for abbreviations.

at least once (Supplemental Table S2). Most of the compounds were herbicides (179), followed by insecticides (117) and fungicides (109). Most samples were taken in the months April till October, with fewer samples during winter (see Supplemental Figure S3). Only 5.5% (160,800) of all measurements were detected above the limit of quantification (LOQ). We found substantial differences in the spectra of analyzed pesticides between federal states (Figure 2). The number of different pesticides per state ranged from 57 (Saarland, SL) to 278 (Rhineland-Palatinate, RP). Hierarchical clustering revealed three groups (see also Supplemental Figure S4):

- i) SL, ST and TH with a small (less than 100 compounds) compound spectra.
- ii) RP and NI with a big (278 and 226 compounds) and distinct compound spectra
- iii) the other states showed a similar spectra of medium to big size (between 127 and 227 compounds)

The distribution of sampling sites across catchment sizes indicated a disproportionately

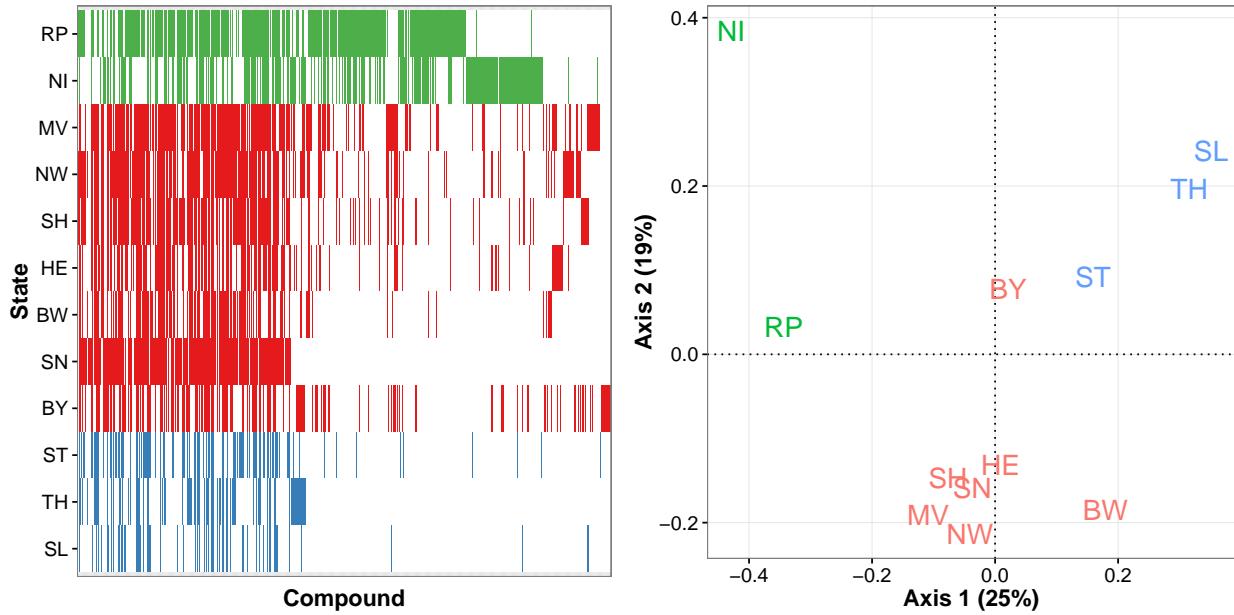


Figure 2: Compound spectra of the different federal states. Left: Barcode plot - each vertical line is an analysed compound. Right: MDS ordination. Colors according to three groups determined by hierarchical clustering (see Supplemental Figure S4).

low number of sites of catchments below 10 km^2 , with most sampling sites having catchment sizes between 10 and 25 km^2 (Figure 3). The proportion of agriculture in the catchments tended to decrease with increasing catchment size. For example, only 3 sites had more than 75% agriculture in catchments larger 100 km^2 , whereas in catchments below 100 km^2 , 245 sites had more than 75% agriculture in their catchment.

Influence of agricultural land use and catchment size

The number of RAC exceedances increased strongly and statistically significant up to 25% agriculture within the catchment. Above this threshold the exceedances levelled followed by an increase above 75% (Figure 4, left). Catchment size had no statistically significant effect on the number of RAC exceedances (Figure 4, right). We also found no statistically significant interaction between catchment size and agriculture.

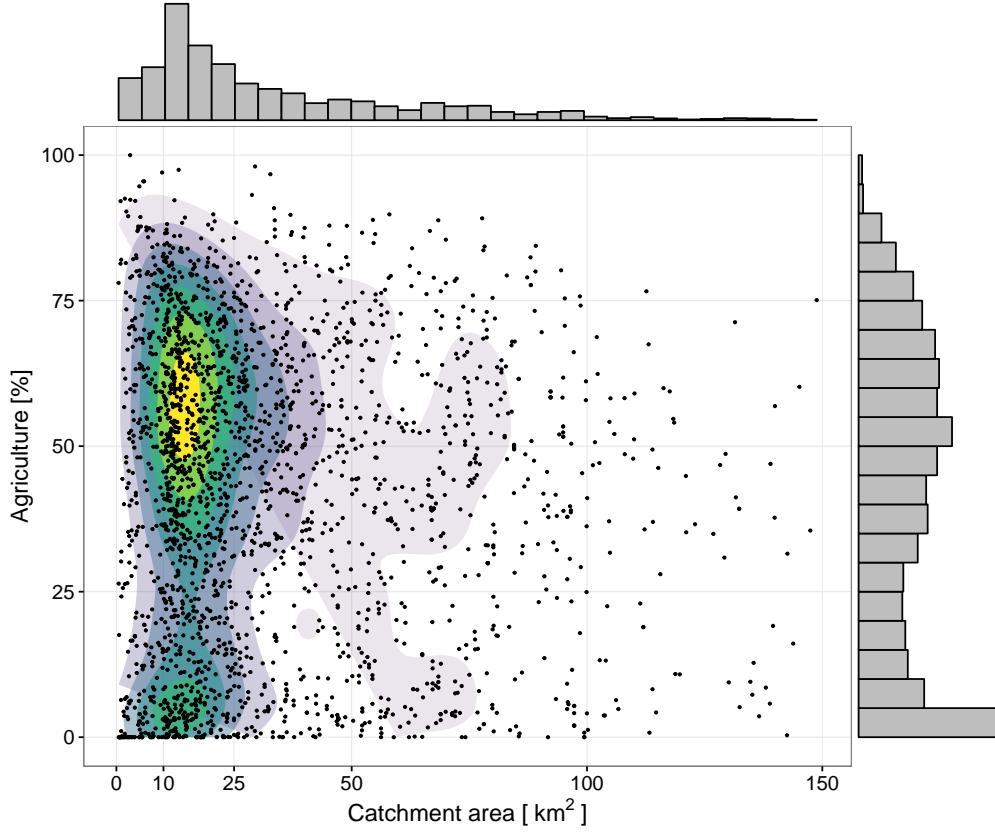


Figure 3: Distribution of catchment area and agriculture within the catchment area across the sampling sites. Only sampling sites with catchment area $< 150 \text{ km}^2$ are displayed. Colour codes the 2-dimensional density of points.

Effect of precipitation on pesticide risk

The spatio-temporal intersection revealed that most samples were taken during periods with low precipitation. For example, only 5% of the samples were taken at or after days with rainfall events greater than 10mm / day (Supplemental Figure S6).

$prec_0$ and $prec_{-1}$ increased the probability of exceeding LOQ and the mean value of RQ. An increase of precipitation before sampling ($prec_{-1}$) from 1mm to 10mm precipitation lead to a 6% higher mean RQ in Q2. The probability to exceed LOQ increases in Q2 from 12% to 16%. Precipitation before sampling ($prec_{-1}$) had a stronger effect than precipitation during sampling ($prec_0$). This difference was less pronounced for the mean value of RQ (Figure 5, top).

The first quarter showed the lowest RQ and probability of exceeding LOQ. Both increased

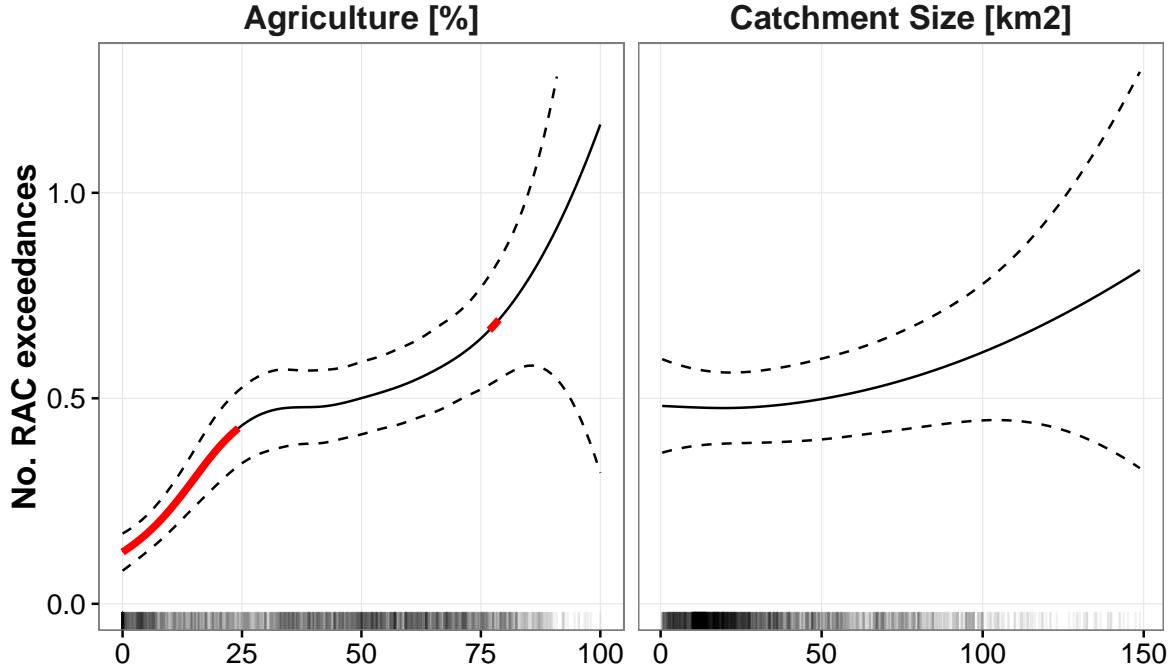


Figure 4: Effect of percent agriculture within the catchment (left) and catchment size (right) on the number of RAC exceedances. Red line marks statistically significant changes. Dashed lines denote 95% point-wise Confidence Intervals.

during summer months and decreased towards the end of the year. There was a probability of 4% to exceed LOQ in Q_1 and 10% in Q_2 . The differences were less pronounced for the value of RQ and with higher variation (Figure 5, bottom).

Pesticides in small water bodies

The dataset comprised 12,710 samples from 1,295 small water bodies. In 346 (26.7%) of these streams RQ were exceeded. In total 1,173 samples (0.3% of all and 5.6% of samples with detects) showed RQ higher than 1 were observed. Neonicotinoid insecticides and Chlorpyrifos showed the highest RQ exceedances (Figure 6). For Thiacloprid, Imidaclorpid and Chlorpyrifos the RAC was less than LOQ, therefore, all detections have a $RQ > 1$. The herbicides Nicosulfuron and Diflufenican, as well as the fungicide Dimoxystrobin also showed high exceedances of RQ (29.5, 14.2 and 21.4 % of all samples with detects). The highest

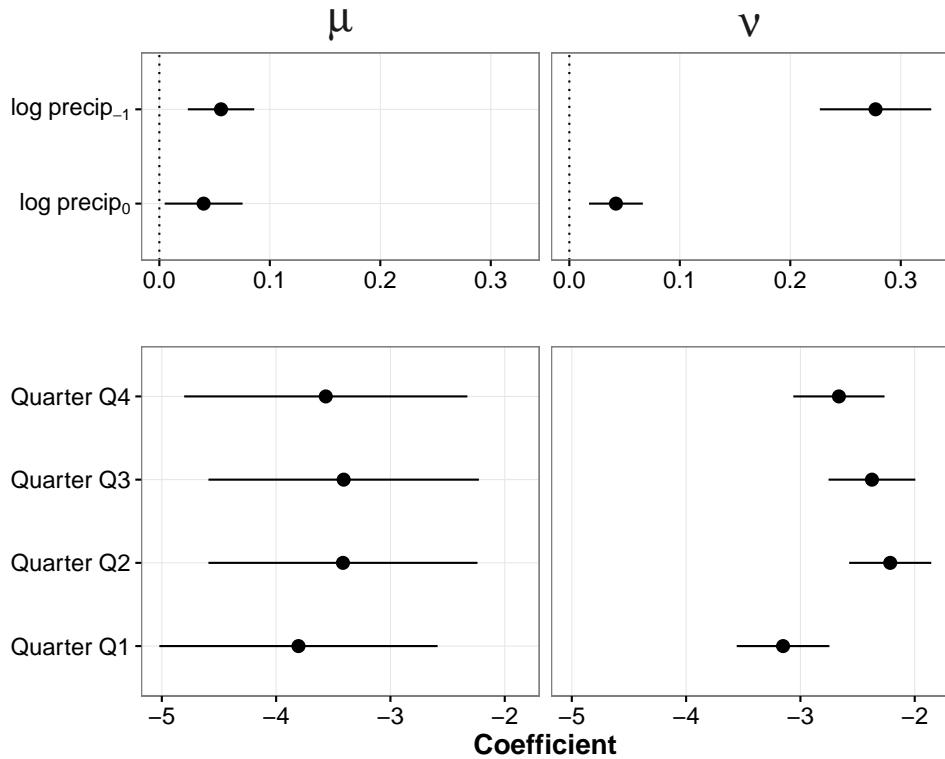


Figure 5: Summarised coefficients (and their 95% CI) for precipitation (top row) and quarter (bottom row) from a meta-analysis of the 24 modeled compounds. Left column: coefficients for mean RQ (μ), right column: coefficients for probability to exceed LOQ (ν). Coefficients are shown on the link scale (see Eq. 4). Single compound coefficients are provided in the Supplemental Table S4 and Figure S7).

RQ were observed for Chlorpyrifos ($\text{max}(\text{RQ}) = 244$), Dimoxystrobin ($\text{max}(\text{RQ}) = 117$) and Isoproturon ($\text{max}(\text{RQ}) = 80$). Where analysed, metabolites exhibited the highest detection rates (for example, Metazachlor sulfonic acid was detected in 82% of all samples where it was analysed, see also Supplemental Figure S9). Glyphosate was the compound with the highest detection rates, followed by Boscalid and Isoproturon. However, only the latter showed RQ exceedances (Figure 6). In 44.8% of samples more than one compound was quantified, with a maximum of 54 different compounds in one sample (Supplemental Figure S8).

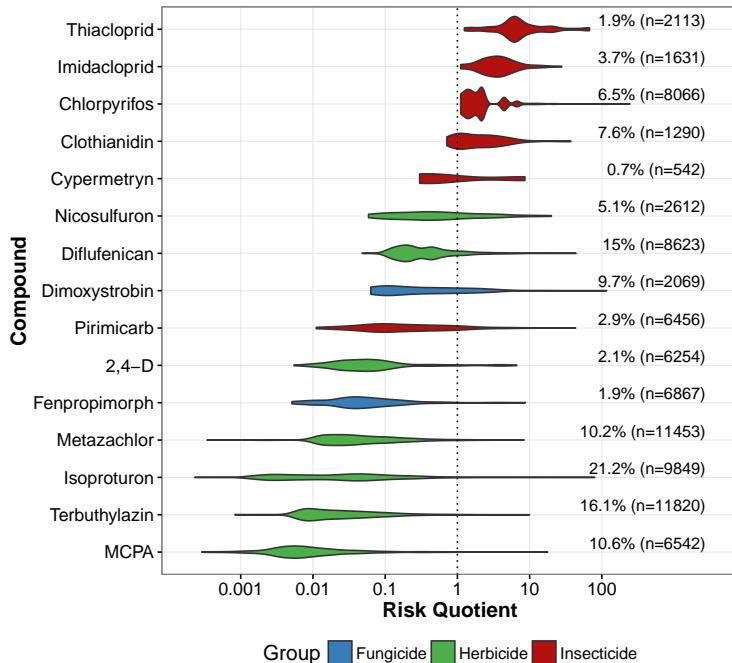


Figure 6: 15 compounds with the highest risk quotients in SWB. Non-detects are not shown due to the logarithmic axis. Numbers on the right give the percentage of values >LOQ and the total number of samples were the compound was analysed.

Discussion

Overview on the compiled dataset

The compiled dataset of governmental monitoring data, with a particular focus on small streams, represents currently the most comprehensive one available for Germany. Similar nationwide datasets have been compiled for the Netherlands³⁵, Switzerland³⁶ and the United States (Water Quality Portal (WQP) www.waterqualitydata.us). The data compiled and analysed 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: Beside large differences in the spatial distribution and quantity of sampling sites (Figure 1), the spectrum of analyzed compounds (Figure 2) and the quality of chemical analyses differed between states. For Thiacloprid, Imidaclorpid and Chlorpyrifos the LOQs were above the RAC, which means that some ex-

ceedances were likely not detected. For these compounds a lowering of LOQ is essential for reliable assessment. Moreover, a nation-wide assessment would benefit from a harmonized spectrum of analysed compounds between federal states.

Given their high abundance in the landscape¹¹ SWB are underrepresented in the current monitoring (Figure 3). Especially, sampling sites in streams below 10 km² are disproportionately low, which may be attributed to the missing categorisation in the WFD.

Influence of agricultural land use and catchment size

We found a strong influence of agriculture on the pollution of streams. If there is more than 25% agriculture within a catchment pesticides, it is likely that a RAC will be exceeded, with a further increase the likelihood of RAC exceedance in fully agricultural catchments (above 75 % agriculture). To our knowledge this is the first study investigating such thresholds of pesticide risk. Previous studies examined thresholds for percent agricultural land use with respect to the response of biological communities, integrating different agricultural stressors. Feld³⁷ found change points of biological community metrics at 40% agricultural land use in low land streams. Similarly, Waite³⁸ found a threshold for aquatic diatoms at 40%. Our results coincide with these thresholds and suggest that pesticides might contribute to the observed biological changes.

We did not find a relationship between pesticide pollution and catchment size. However, previous studies showed that SWB are more polluted than bigger streams^{7,9,39}. This can be explained by the relatively short gradient of catchment sizes in our dataset, with most of the streams with catchments above 10 km² and below 100 km² (Figure 3, top). For example the gradient of Schulz⁷ covered 6 orders of magnitude.

Effect of precipitation on pesticide risk

Our results revealed that pesticide sampling for chemical monitoring in Germany is mainly performed when no precipitation occurs. Nevertheless, we found higher RQ if samples where

taken after rainfall events. Samples taken at the day of a rainfall-event showed less risk, than samples taken one day after a rainfall-event. This could be explained by a sampling just before the actual rainfall event. Pesticide concentrations in agricultural SWB generally show short term peak concentrations¹⁷, therefore, a sampling at the day after a rainfall-event might miss peak concentrations. The effects of precipitation were more pronounced for the probability to exceed LOQ, with smaller effect sizes for RQ. This could be attributed to a higher variability of absolute concentrations. Overall, our results indicate that current pesticide monitoring relying on grab sampling, largely disconnected from precipitation events, underestimates pesticide risks. Automatic event-drive samplers³ and passive samplers^{40,41} may help overcome these shortcomings and provide a better representation, especially for SWB¹⁶.

We found highest the probability of exceeding LOQ during summer (9.9% for Q2) and lowest in the first Quarter (2.8%, Figure 5, bottom right). This yearly pattern coincides with their main application season for pesticides in Central Europe. Nevertheless, there are compound specific differences in the yearly pattern, which explain the wide CI for the absolute RQ (Figure 5, bottom left). For example, the herbicide Diflufenican showed highest RQ during the winter quarters (Supplemental Table S4), which is the application period it is registered for in Germany⁴². Our study suggests that pesticide risks display compound specific spatio-temporal dynamics. Currently, little is known on these and further research on those might provide useful information for future ecological risk assessment.

Pesticides in small water bodies

Our results suggest that SWB are frequently exposed to ecologically relevant pesticide concentrations. Stehle and Schulz⁹ found the highest percentage of RAC exceedances for organophosphate insecticides. By contrast, our results that neonicotinoid insecticides showed highest exceedances of RACs, 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 (for example 2,113 samples of Thiacloprid, Figure 6). Overall, our results suggest that neonicotinoids may currently pose a high risk to freshwater ecosystems. Compared to Stehle and Schulz⁹ we found much lower rates RAC exceedances (0.3% of 372,304 samples with RAC vs 44% of 1,566 samples). This 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 and at natural sites. By contrast, Knauer³⁹ 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.

From the definition of RAC it follows that if the concentration of a compound exceeds its RAC ecological effects are expected. Indeed, Stehle and Schulz⁴³ found that biological diversity of stream invertebrates was significantly reduced at a RQ of 1.12. We found RQ values greater than 1.12 at 25% of all SWB sites. Consequently, we conclude that agricultural pesticides are a major threat to small streams, the biodiversity they host and the services they provide. This threat may exacerbate because pesticides often occur in mixtures⁴⁴ and may co-occur with other stressors⁴⁵.

Monitoring data, despite the outlined limitations, provides an opportunity to study large scale environmental occurrence patterns of pesticides. Nevertheless, such nationwide compilations, may not only be used for governmental surveillance, but also to answer other questions, like validation of exposure modeling,⁴⁶ retrospective evaluation of regulatory risk assessment^{9,39} or occurrences of pesticide mixtures,⁴⁴ though the sampling design need to account for precipitation events to provide robust data. The high exceedances of RAC indicate that the authorisation process for pesticides may require further development.

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

