Pesticides in small streams in Germany

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Abstract

Small streams are important refugia for biodiversity. In agricultural areas they may be at high risk from pesticides that enter streams during rainfall. However, most related studies have been limited to a few streams on the regional level, hampering extrapolation to larger scales. Data from governmental water quality monitoring provides an opportunity to study occurrences of pesticides on a large scale.

We compiled monitoring data focusing on small streams, resulting in a data set of 2,918,604 measurements from 42,236 samples in 3,049 sampling sites and 484 different pesticides. We investigated the relationships between pesticide exposure and agricultural land use, catchment size, as well as precipitation and seasonal dynamics using new modeling techniques.

Our results show that the influence of agriculture is detectable even if there is only a small proportion of agriculture with a catchment. Precipitation during and before sampling increased measured pesticide concentrations. The highest concentrations were

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found during summer, but with differences between compounds. Small waters are currently underrepresented in German pesticide monitoring. Nevertheless, we show that neonicotinoid and other insecticides frequently exceed regulatory acceptable concentrations.

We conclude that pesticides from agricultural land use are a major treat to small water bodies, the biodiversity they host and the services they provide.

Introduction

More than 50% of the total land area in Germany is used by agriculture[1]. In the year 2014 more than 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[3–5]. Especially run-off after heavy precipitation events has been shown to be one of the major input routes for pesticides[6]. Once entered the surface waters they may have adverse effects on biota and ecosystem functioning[7]. Although, it is known that pesticide pollution and its biological effects increase with agricultural land-use[6], studies investigating the shape of these relationships are currently missing.

Malaj et al.[8] analyzed data supplied to the European Union (EU) in the context of the Water Framework Directive (WFD) and showed that most European water bodies are at risk from pesticides. Stehle and Schulz[9] 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). Both studies indicate that pesticides might be a threat to biodiversity in the European union. However, theses studies reflect only a small amount of data and it is unclear how representative they are: For Germany the study of Malaj et al.[8] lists only 175 sites and Stehle and Schulz[9] only 138 measurements. National monitoring programs are setup for the surveillance of water quality. In Germany these are setup independently by the federal states in compliance with the WFD[10] and additional state specific needs. These programs may provide the most comprehensive data that is currently available for pesticide occurrences in German rivers. However, currently there is no curated nation-wide compilation of this monitoring data available.

Small water bodies (SWB) comprise a major fraction of streams[11], 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[5,6]. It has been shown that SWB are more polluted than bigger streams[6,9]. Especially, compounds from agricultural use show seasonal rain-event-driven short term peak concentrations in SWB[16]. Despite their biological relevance and potential pesticide exposure, only a small fraction of studies were conducted on pesticide pollution of SWB, with only few large scale studies[17]. Moreover, it is currently unknown how precipitation might influence measured pesticide concentrations in national monitoring programs.

In this study we try to fill these gaps and analyze large scale nation-wide chemical monitoring data from Germany. First, we revise the available monitoring data if it is suitable for a large scale description of pesticide pollution. Then we analyse the form of relationship between pesticide exposure, agricultural land use and catchment size. Further, we investigate the influence of precipitation and seasonal dynamics of measure pesticide concentrations. Finally, we give an overview on current pesticide pollution of SWB in Germany.

Methods

Data compilation

We compiled pesticide monitoring data from sampling sites with catchment sizes $< 150\text{km}^2$ 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). We homogenized and unified all data provided by the federal states into a common database and implemented a robust data cleaning workflow (see Supplemental Figure S1 for details)[18]. Nevertheless, parts of the dataset are proprietary and cannot be shared here.

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 stations[19]. We performed the intersection for the actual sampling date and the day before.

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 algorithm[21] as implemented in GRASS GIS 7[22]. Catchment delineation was manually checked for accuracy by comparison with a stream network provided by the government. The delineation algorithm produced only for 30% of the sites accurate results. For the rest we were able to compile catchment size data from authorities (47% of sites) or drainage basins per stream segment provided by authorities (13% of sites). We were not able to compile catchment size data for 10% of the sites.

For each derived catchment (either from DEM or drainage basins) we calculated the relative cover (in %) with agricultural areas based on Official Topographical Cartographic Information System (ATKIS) of the land survey authorities[23]. 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 lacking[17]. The WFD defines SWB with a catchment size between 10 and 100 km^2, without further categorisation of streams $<10km^2$. Lorenz et al.[17] defines SWB with catchment size $<10km^2$ as SWB. Because of data scarcity of streams <10 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):

$$RQ_i = \frac{C_i}{RAC_i} \tag{1}$$

where C_i is the concentration of a compound i in a sample.

Statistical analyses

All data-processing and analyses were performed using R[25]. 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 package[26]. We expected non-linear responses to agriculture and catchment size and therefore, used generalized additive models (GAM) to identify relationships[27]. We modeled the number of RAC exceedances (RQ >1) as:

$$\begin{aligned} No_i &\sim NB(\mu_i, \kappa) \\ log(\mu_i) &= \beta_0 + f_1(agri_i) + f_2(size_i) + log(n_i) \end{aligned} \tag{2}$$

where No_i is the observed number of exceedances at site i. We modeled No_i as resulting from a negative binomial distribution (NB). The proportion of agriculture within the catchment ($agri_i$) and the catchment size of the site ($size_i$) were used as predictors. f_1 and f_2 are smoothing functions using penalized cubic regression splines[28]. The degree of smoothness was estimated using restricted maximum likelihood (REML) during model fitting process[29]. The number of samples per site (n_i) was used as an offset to account different 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 package[29].

While agricultural land use and catchment size vary only between sites, this is not the case for precipitation which changes also with time. Therefore, we modeled the effects of precipitation in a separate model. 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:[30,31]

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

ν_i denotes the probability of an observation i being above LOQ and f_{Gamma} denotes the gamma function and is used for values greater LOQ, with μ being the mean and σ the standard deviation. 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.

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

To account for temporal auto-correlation and differences between federal states we used *site* nested within *state* as random intercepts. Changes on μ can be interpreted as changes in the mean value of RQ, whereas changes in ν can be interpreted as changes in the probability of exceeding LOQ and showing any risk. 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 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 modeled compounds we used a random effect meta-analysis[33].

Results

Overview of the compiled data

The compiled dataset comprised only few standing waters (58 sites) and the majority of samples (91%) where taken via grab sampling. 9% of samples from 33 sites were taken as composite samples of different durations. Therefore, we restricted the analyses to grab samples from streams. The analyzed dataset comprised 2,918,604 pesticide measurements of 42,236 samples in 3,049 sampling sites. We found large differences in the number of sampling sites between federal states and their spatial distribution (Figure 1 and Supplemental Table S1).

In total 484 different compounds used as pesticides and their metabolites were measured 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 detects above the limit of quantification (LOQ). We found substantial differences in the spectra of analyzed compounds between federal states (Figure 2). Hierarchical clustering revealed three groups (see also Supplemental Figure S4):

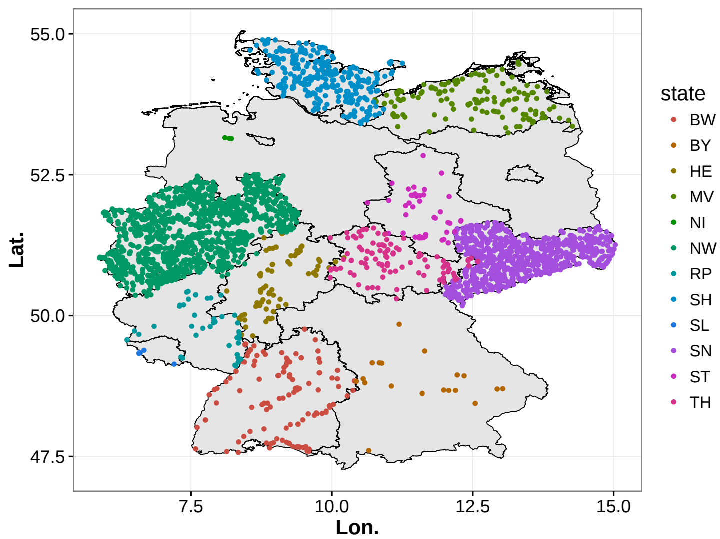

Figure 1: Spatial distribution of the 3109 sampling sites. Colour codes different federal states, see Supplemental Table S1 for abbreviations.

i) with less than 100 compounds (SL, ST and TH)

ii) with medium sized spectra

iii) with a big and distinct spectrum (RP and NI)

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.

Influence of agricultural land use and catchment size

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

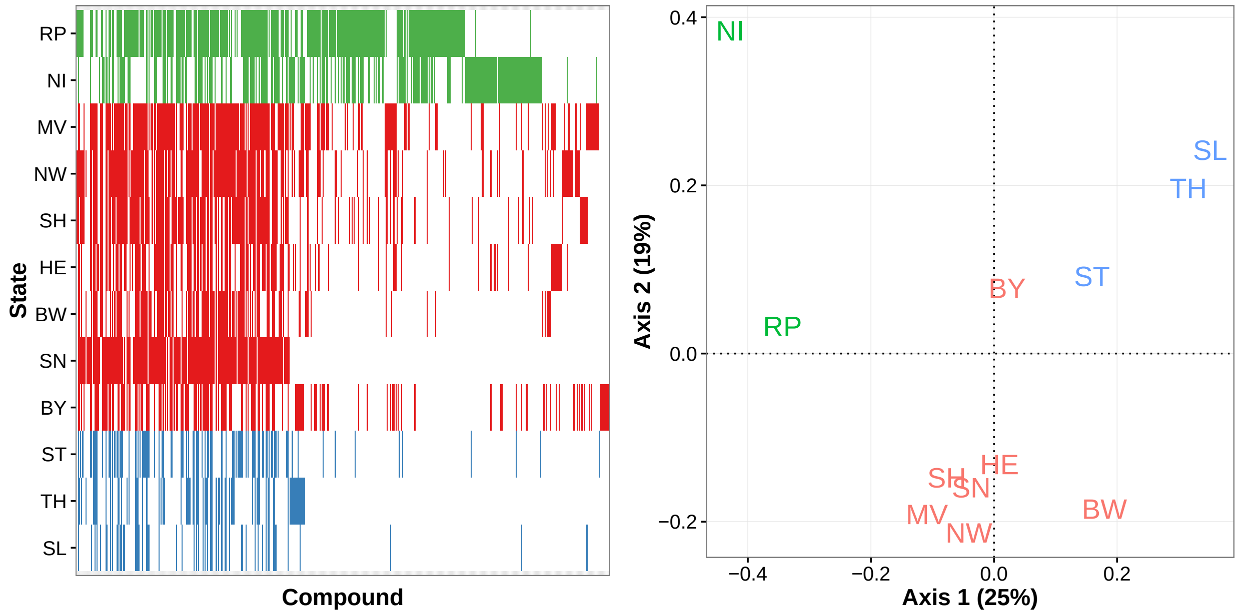

Figure 2: Compound spectra of the different federal states. Left: Barcode plot - each vertical line is an analysed compound. Right: MDS ordination. Colors according to three groups determined by hierarchical clustering (see Supplemental Figure S4).

exceedances (Figure 4, right). We also found no statistically significant interaction between catchment size and agriculture.

Effect of precipitation on pesticide exposure

The spatio-temporal intersection revealed that 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. $prec_{-1}$ had a stronger effect than $prec_0$. This difference was less pronounced for the mean value RQ (Figure 5, top).

The first quarter showed the lowest RQ and probability of exceeding LOQ. Both increased during summer months and decreased towards the end of the year. The differences were less pronounced for the value RQ and with higher variation (Figure 5, bottom).

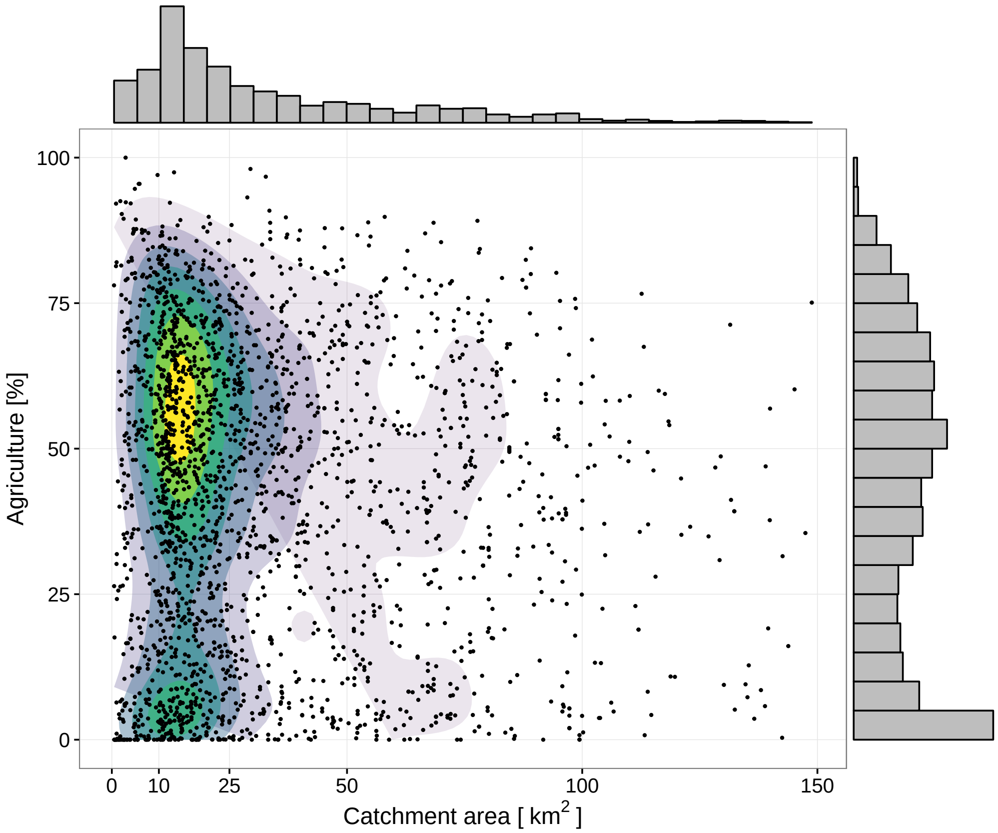

Figure 3: Distribution of catchment area and agriculture within the catchment area across the sampling sites. Only sampling sites with catchment area $< 150\ \mathrm{km}^2$ are displayed. Colour codes the 2-dimensional density of points.

Pesticides in small water bodies

The dataset comprised 12,710 samples from 1,295 small water bodies. In 1,173 samples (0.3% of all and 5.6% of samples with detects) RQ higher than 1 were observed. Neonicotinoid insecticides and Chlorpyrifos showed the highest RQ exceedances (Figure 6). For Thiacloprid, Imidacloprid 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 RQ were observed for Chlorpyrifos (max(RQ) $=$ 244), Dimoxystrobin(max(RQ) $=$ 117) and Isoproturon (max(RQ) $=$ 80). Metabolites were most commonly detected if analysed (for example, Metazachlor sulfonic acid was detected in 82% of all samples were it was analysed, see also Supplemental Figure S9). Glyphosate was the compound with the highest

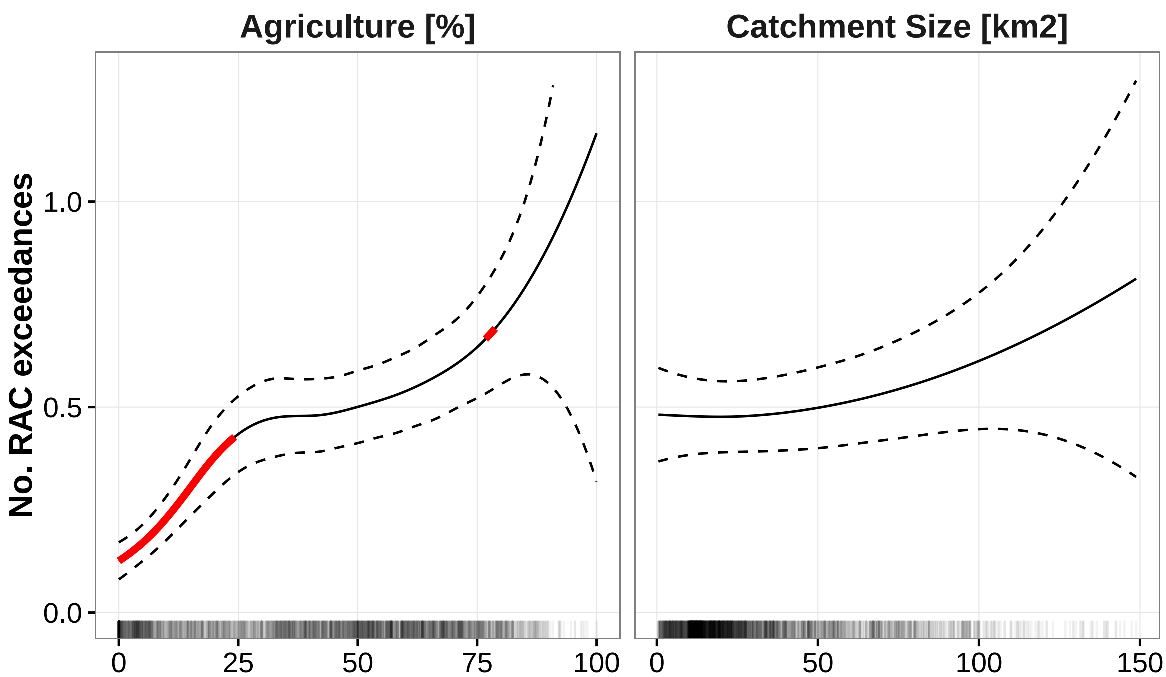

Figure 4: Effect of agriculture within the catchment (left) and catchment size (right) on the number of RAC exceedances. Red line marks statistically significant changes. Dashed lines denote 95% point-wise Confidence Intervals.

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).

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[34], Switzerland[35] 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.

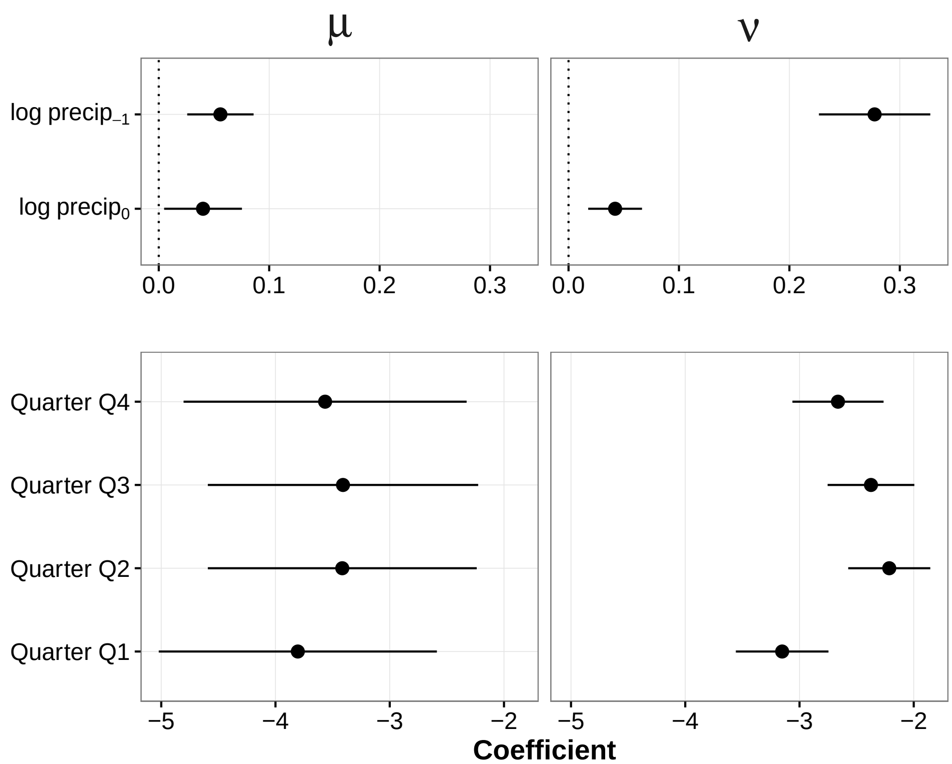

Figure 5: Summarised coefficients (and their 95% CI) for precipitation (top row) and quarter (bottom row) from a meta-anaylsis of the 24 modeled compounds. Left column: coefficients for mean RQ (μ), right column: coefficients for probabilty to exceeed LOQ (ν). Coefficients are shown on the link scale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

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. For Thiacloprid, Imidaclorpid and Chlorpyrifos LOQ were above RAC. For these compounds a lowering of LOQ is essential for reliable assessment. Moreover, would a nation-wide assessment benefit from a harmonized spectrum of analysed compounds between federal states.

Given their high abundance in the landscape[11] SWB are underrepresented in the current monitoring (Figure 3). Especially, streams below 10 km^2 are missing, which could be attributed to the missing categorisation in the WFD.

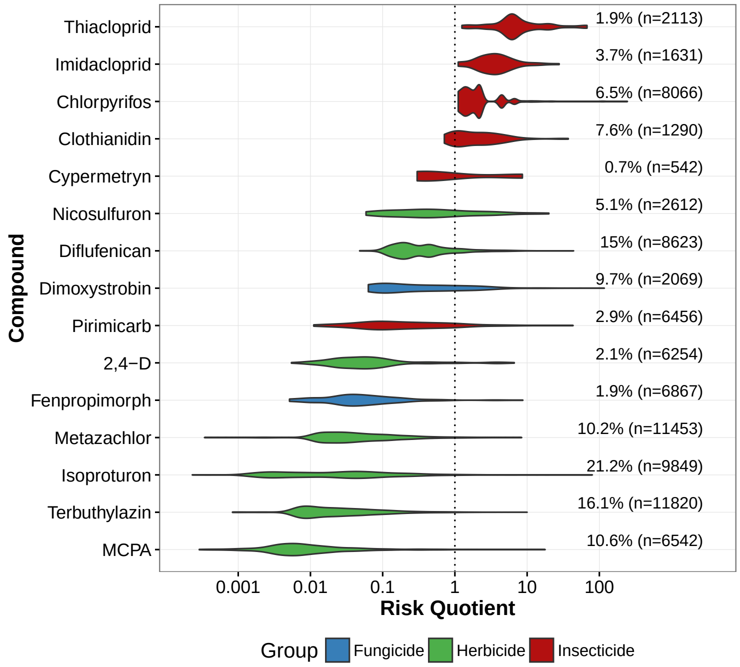

Figure 6: 15 compounds with the highest risk quotients in SWB. Non-detects are not shown due to the logarithmic axis. Numbers on the right give the percentage of values >LOQ and the total number of samples were the compound was analysed.

Influence of agricultural land use and catchment size

We found a strong influence of agriculture on the pollution of streams. If there is more the 25% agriculture within a catchment pesticides, it is likely that RAC will be exceeded with an increase in fully agricultural catchments (above 75 % agriculture). To our knowledge this is the first study investigating such thresholds of pesticide exposure. Thresholds for agricultural land use have only been investigated in the past for biological communities. Feld [36] found change points of biological community metric for agricultural land use at 40% in low lands. Similarly, Waite [37] 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 have shown that SWB are more polluted that bigger streams [6,9,38]. This could be explained by the relatively short gradient of catchment sizes in our dataset, with most of the streams being <100 km^2 (Figure 3, top). For example the gradient of Schulz[6] covered 6 orders of magnitude. Another reason might be the unequal distribution of catchment sizes, with fewer sites below 10 km^2 and above 100 km^2 catchment size (Figure 3, top).

Effect of precipitation on pesticide exposure

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 concentrations[16], 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 strongly underestimates pesticide exposure. Automatic event-drive samplers[3] and passive samplers[39,40] may help overcome these shortcomings and provide a better representation, especially for SWB[17].

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. 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 Germany[41]. Our study suggest that pesticide exposure shows 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 biologically relevant pesticide concentrations. Stehle and Schulz[9] found the highest percentage of RAC exceedances for organophosphate insecticides. By contrast, 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 (between 1,290 and 2,113 samples in SWB, Figure 6). Our results shows that this particular class of insecticides may currently pose a high risk to freshwater ecosystems. Compared to Stehle and Schulz[9] 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. Contrary, Knauer[38] 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. Accordingly, Stehle and Schulz[42] found that biological diversity is 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 pesticides from agricultural land use are a major treat to small water bodies, the biodiversity they host and the services they provide. Additional treat arises when taking into account that most pesticides do not occur individually but in mixtures[43] and may co-occur with other stressors[44].

Monitoring data, despite the outlined limitations, provides an opportunity to study large scale environmental occurrences 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,[45] retrospective evaluation of regulatory risk assessment[9,38]or occurrences of pesticide mixtures.[43] The high exceedances of RAC indicate that the approval process for pesticides 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