

# Large scale risks from agricultural pesticides in small streams

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## Abstract

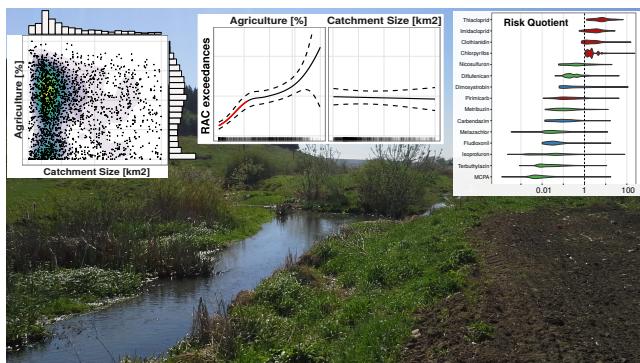
Small streams are important refugia for biodiversity. In agricultural areas they may be at risk from pesticide pollution. However, most related studies have been limited to a few streams on the regional level, hampering extrapolation to larger scales. We quantified risks as exceedances of regulatory acceptable concentrations (RACs) and used German monitoring data to quantify the drivers thereof and to assess current risks in small streams on a large scale. The data set comprised of 1,766,104 measurements of 478 pesticides (including metabolites) related to 24,743 samples from 2,301 sampling sites. We investigated the influence of agricultural land use, catchment size, as well as precipitation and seasonal dynamics on pesticide risk taking also concentrations below the limit of quantification into account. The exceedances of risk thresholds dropped 3.7-fold at sites with no agriculture, indicating that agricultural land use is a major contributor of pesticides in streams. Precipitation increased detection probability by 43% and concentrations were the highest during summer months. RACs were exceeded in 26% of streams. We found the highest exceedances for neonicotinoid insecticides. We

16 conclude that pesticides from agricultural land use are a major threat to small streams  
17 and their biodiversity. To reflect peak concentrations, current pesticide monitoring  
18 needs to be refined.

19

überarbeite

20 **TOC Art**



21

22 **Introduction**

23 More than 50% of the total land area in Germany is used by agriculture<sup>1</sup>. In the year 2014  
24 more than 45,000 tonnes of 776 authorised plant protection products were sold for application  
25 on this area<sup>2</sup>. The applied pesticides may enter surface waters via spray-drift, edge-of-field  
26 run-off or drainage<sup>3–5</sup>. Once entered the surface waters they may have adverse effects on  
27 biota and ecosystem functioning<sup>6</sup>. Although it is known that pesticide pollution and its  
28 ecological effects increase with the fraction of agricultural land use in the catchment<sup>7</sup>, the  
29 shape of the relationship is unknown and studies on potential thresholds are lacking.

30 Two recent studies indicate that pesticides concentrations in streams might threaten  
31 freshwater biodiversity in the European union. Malaj et al.<sup>8</sup> analysed data supplied to  
32 the European Union (EU) in the context of the Water Framework Directive (WFD) and  
33 showed that almost half of European water bodies are at risk from pesticides. Stehle and  
34 Schulz<sup>9</sup> compiled 1,566 measured concentrations of 23 insecticides in the EU from scientific

35 publications and considerable exceedances of regulatory acceptable concentrations (RAC).  
36 However, these studies reflect only a small amount of potentially available data (173 sites in  
37 predominantly mid-sized and large rivers in Malaj et al.<sup>8</sup> and 138 measurements in Stehle  
38 and Schulz<sup>9</sup>), and it is unclear how representative they are for Germany. Much more com-  
39 prehensive data on thousands of sites are available from national monitoring programs that  
40 are setup for the surveillance of water quality, which is done independently by the federal  
41 states in Germany in compliance with the WFD<sup>10</sup>. Despite that these data are providing  
42 the opportunity to study pesticide risks and other research questions on a large scale with  
43 high spatial density, to date these data have not been compiled.

44 Small streams comprise a major fraction of streams<sup>11</sup>, accommodate a higher proportion  
45 of biodiversity compared to bigger streams<sup>12,13</sup> and play an important role in the recoloniza-  
46 tion of disturbed downstream reaches<sup>14,15</sup>. Nevertheless, a clear definition of small streams  
47 in terms of catchment or stream size is currently lacking<sup>16</sup>. For example, the WFD defines  
48 small streams with a catchment size between 10 and 100 km<sup>2</sup>, without further categorisation  
49 of streams <10km<sup>2</sup> and Lorenz et al.<sup>16</sup> defines small streams with catchment size <10km<sup>2</sup>.  
50 Moreover, small streams might particularly be at high risk of pesticide contamination in case  
51 of adjacent agricultural areas and given their low dilution potential<sup>5,7</sup>. Indeed, meta-analyses  
52 using data from studies with a few sites reported higher pesticide pollution in smaller streams  
53 compared to bigger streams<sup>7,9</sup>. Despite their ecological relevance and potentially higher pes-  
54 ticide exposure, a recent review of pesticide studies showed that a disproportionately small  
55 fraction of studies was conducted in small water bodies, and these were largely limited to a  
56 few sites<sup>16</sup>. Consequently, knowledge on the pesticide pollution of small streams on larger  
57 scales is scant. In European law, the Directive 2009/128/EC<sup>17</sup> places an obligation on the  
58 EU Member States to adopt National Action Plans (NAP) for the Sustainable Use of Plant  
59 Protection Products and the German NAP also addresses the knowledge gap concerning  
60 pesticide impact on small streams, specifically including those with catchment size <10km<sup>2</sup>.

61 The aim of this study is to identify drivers and dynamics of pesticide concentrations in

streams. To achieve this, we compiled and analysed large-scale pesticide monitoring data from small streams in Germany in order to identify drivers and dynamics of pesticide concentrations. We expect that the landscape is a determinant of measured pesticide concentrations. Because a major fraction of pesticides is applied to agricultural fields, we hypothesised highest concentrations and possible exceedances of RACs in streams with high proportion of agriculture. Moreover, if agricultural land use is a main source for pesticides in streams, we expect that exceedances drop to zero if there is no agricultural land use in the catchment. Moreover, these relationships may show thresholds that could be used to define reference streams without pollution for a future monitoring. Given their low dilution potential and direct adjacency to agricultural fields we expected that small streams show highest pesticide concentrations. However, also the timing of sampling may influence measured concentrations: A sampling directly after a precipitation might show higher concentrations because of run-off. Furthermore, pesticides are not applied throughout the whole year and we expected highest concentrations during the main growing season. Finally, we quantified the current risks from pesticides in small streams in Germany and the compounds accountable for the risk.

## Methods

### Data compilation

We queried pesticide monitoring data from sampling sites that can be classified as small streams (catchment sizes < 100 km<sup>2</sup> according to the WFD) from all 13 non-city federal states of Germany (see Supplemental Table S1 for the abbreviations of federal state names) for 2005 to 2015. We homogenised 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)<sup>18</sup>.

We identified precipitation at sampling sites by a spatio-temporal intersection of sam-

87 pling events with gridded daily precipitation data ( $60 \times 30$  arcsec resolution) available from  
88 the German Meteorological Service (DWD). This data spatially interpolates daily precipi-  
89 tation values from local weather stations<sup>19</sup>. We performed the intersection for the actual  
90 sampling date and the day before and extracted precipitation during and up to 48 hours  
91 before sampling.

## 92 Characterization of catchments

93 We compiled a total of 2,369 sampling sites in small streams with pesticide measurements.  
94 Alongside, we also queried catchment sizes and agricultural land use within the catchment  
95 for the sampling sites from the federal states. Catchment size was provided for 59% of sites.  
96 Additionally, we delineated upstream catchments for each of the sampling sites using (i) a  
97 digital elevation model (DEM)<sup>20</sup> and the multiple flow direction algorithm<sup>21</sup> as implemented  
98 in GRASS GIS 7<sup>22</sup> and (ii) from drainage basins provided by the Federal Institute of Hy-  
99 drology (BfG). Delineated catchments were visually checked for accuracy by comparison of  
100 coverage with stream networks provided by the federal states. Thus, catchment size infor-  
101 mation was available for 99% of all sites (59% from authorities, 24% from DEM and 16%  
102 from drainage basins).

103 For each derived catchment (either from DEM or drainage basins) we calculated the  
104 % agricultural land-use within the catchment based on the Authoritative Topographic-  
105 Cartographic Information System (ATKIS) of the land survey authorities<sup>23</sup>. Thus, agri-  
106 cultural land use information was available for 98% of all sites (24% from authorities, 52%  
107 from DEM and 22% from drainage basins). 68 sites (3%) that lacked catchment size or land  
108 use information were omitted from the analysis, resulting in 2301 sites used in the analyses  
109 outlined below.

110 **Characterization of pesticide pollution**

111 We characterised pesticide pollution using regulatory acceptable concentrations (RAC)<sup>24</sup>.  
112 RACs are derived during pesticide authorisation as part of the ecological risk assessment.  
113 No unacceptable ecological effects are expected if the environmental concentration remains  
114 below this concentration. Stehle and Schulz<sup>9</sup> showed that RAC exceedances reflect a decrease  
115 in biodiversity and from this perspective are ecologically relevant indicators. The German  
116 Environment Agency (UBA) provided RACs for 107 compounds, including those with the  
117 highest detection rates (Supplemental Table S2). Based on these RACs, we calculated Risk  
118 Quotients (RQ):

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

119 where  $C_i$  is the concentration of a compound  $i$  in a sample and  $RAC_i$  the respective  
120 RAC.

121 **Statistical analyses**

122 As outlined in the introduction, we expected non-linear responses to agricultural land use and  
123 catchment size and search for potential thresholds. Therefore, we used generalised additive  
124 models (GAM) to establish relationships<sup>25</sup>. We modelled the number of RAC exceedances  
125 ( $RQ > 1$ ) at a site as:

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

126 where  $No(RQ > 1)_i$  is the observed number of RAC exceedances at site  $i$ . Because of  
127 overdispersion, we modelled  $No(RQ > 1)_i$  as resulting from a negative binomial distribution  
128 ( $NB$ ) with mean  $\mu_i$  and a quadratic mean-variance-relationship ( $Var(No(RQ > 1)_i) =$

129  $\mu_i + \frac{\mu_i^2}{\kappa}$ ). The proportion of agricultural land use within the catchment ( $agri_i$ ) and the  
 130 catchment size of the site ( $size_i$ ) were used as predictors of the number of RAC exceedances.  
 131  $\beta_0$  is the intercept and  $f_1$  and  $f_2$  are smoothing functions using penalized cubic regression  
 132 splines<sup>26,27</sup>. The number of measurements per site ( $n_i$ ) was used as an offset to account for  
 133 differences in sampling efforts (sampling interval and analysed compound spectrum) at a site  
 134 and is equivalent to modelling the rate of exceedances. We used point-wise 95% Confidence  
 135 Intervals (CI) of the first derivative of the fitted smooth to identify regions of statistically  
 136 significant changes. All data-processing and analyses were performed using R<sup>28</sup>. GAMs were  
 137 fitted using the mgcv package<sup>27</sup>.

138 To assess the influence of precipitation and seasonality, we modelled the RQ of individual  
 139 compounds as the response variable. RQ and concentrations show a skewed distribution  
 140 with an excess of zeros (no pesticides detected and quantified). Therefore, we modelled  
 141 these as two processes (one generating values below the limit of quantification (LOQ) and  
 142 one generating values above LOQ) using a Zero-Adjusted Gamma (ZAGA) distribution<sup>29,30</sup>  
 143 (Equation 3). These two processes can be interpreted as changes in the mean value of RQ  
 144 (change in  $\mu$ ) and changes in the probability of exceeding LOQ and showing any risk (change  
 145 in  $\nu$ ).

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

146  $\nu_i$  denotes the probability of a measurement i being above LOQ and  $f_{Gamma}$  denotes the  
 147 gamma function and is used for values equal to or greater LOQ, with  $\mu$  being the mean  
 148 and  $\sigma$  the standard deviation of RQ. We used the  $\log(x + 0.05)$  transformed precipitation  
 149 at sampling date ( $\log prec_0$ ) and the day before ( $\log prec_{-1}$ ), as well as quarters of the year  
 150 ( $Q1 - Q4$ ) as linear predictors for  $\mu$  and  $\nu$ . We used appropriate link functions for  $\mu$  and  $\nu$   
 151 and assumed  $\sigma$  to be constant. Equation 4 summarises the deterministic part of the model

152 for a measurement  $i$ .

$$\begin{aligned}\log(\mu_i) &= \log \text{prec}_0 + \log \text{prec}_{-1} + Q1_i + Q2_i + Q3_i + Q4_i \\ \text{logit}(\nu_i) &= \log \text{prec}_0 + \log \text{prec}_{-1} + Q1_i + Q2_i + Q3_i + Q4_i\end{aligned}\tag{4}$$

153 To account for temporal autocorrelation and differences between federal states we used  
154 *site* nested within *state* as random intercepts. We implemented this model using the gamlss  
155 package.<sup>31</sup>

156 We fitted this model separately to each compound with a RAC, measured in at least 1000  
157 samples and with more than 5% of values above LOQ ( $n = 22$  compounds, see Supplemental  
158 Table S3 for a list of compounds). To summarise the coefficients across the 22 modelled  
159 compounds we used a random effect meta-analysis for each model coefficient separately<sup>32</sup>,  
160 resulting in an averaged effect of the 22 compounds. The results of individual compounds  
161 are provided in the Supplemental Table S4 and Figure S7. The meta-analysis was performed  
162 using the metafor package<sup>33</sup>.

## 163 Results

### 164 Overview of the compiled data

165 The compiled dataset used for analysis comprised 1,766,104 pesticide measurements in 24,743  
166 samples from 2,301 sampling sites in small streams. These samples were all taken via grab  
167 sampling. We found large differences between federal states in the number of sampling  
168 sites and their spatial distribution (Figure 1 and Supplemental Table S1). The number of  
169 small stream sampling sites per state ranged from 1 (Lower Saxonia, NI) to 1139 (North  
170 Rhine-Westphalia, NW). No data were available from Brandenburg.

171 In total 478 different compounds used as pesticides and their metabolites were measured  
172 at least once (Supplemental Table S2). Most of the compounds were herbicides (179), fol-

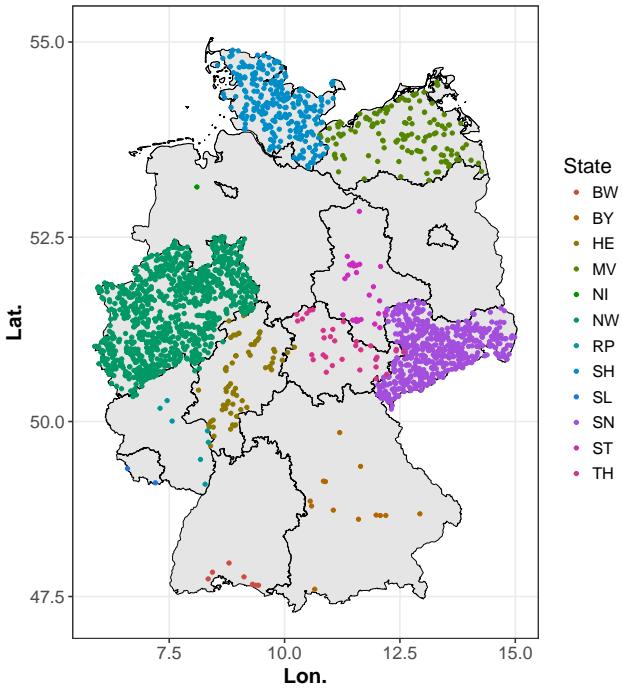


Figure 1: Spatial distribution of the 2,301 small stream sampling sites. Colour codes different federal states (see Supplemental Table S1 for abbreviations).

173 lowered by insecticides (117) and fungicides (109). Most samples were taken in the months  
 174 April till October, while fewer samples were taken during winter (see Supplemental Fig-  
 175 ure S2). We found substantial differences in the spectra of analysed pesticides between  
 176 federal states (Figure 2). The number of analysed pesticides per state ranged from 57 (SL)  
 177 to 236 (RP) (Supplemental Table S1). 4% (=71,113) of all measurements were concentrations  
 178 above LOQ.

179 The distribution of sampling sites across catchment sizes indicated a disproportionately low  
 180 number of sites with catchments below  $10 \text{ km}^2$ , with most sampling sites having catchment  
 181 sizes between 10 and  $25 \text{ km}^2$  (Figure 3).

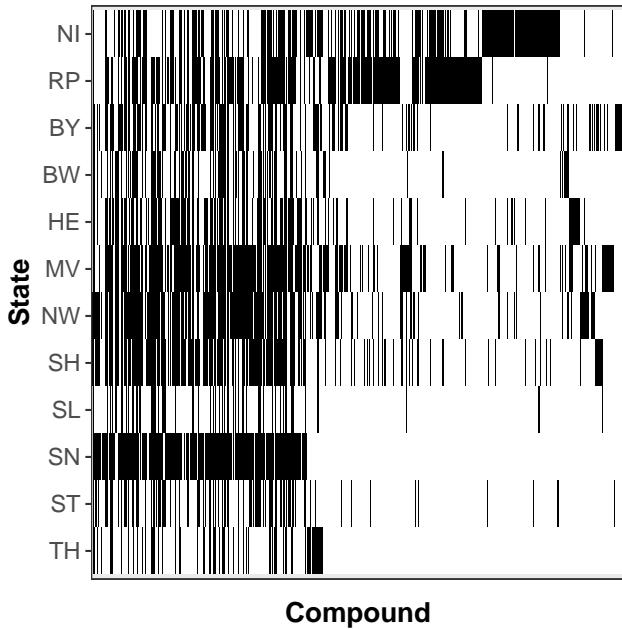


Figure 2: Barcode plot of compound spectra of the federal states. Each vertical line is an analysed compound.

## <sup>182</sup> Influence of agricultural land use and catchment size

<sup>183</sup> We found a positive relationship between agricultural land use and the number of RAC  
<sup>184</sup> exceedances. The non-linear model showed, that below 28% agriculture the mean number of  
<sup>185</sup> RAC exceedances dropped statistically significant 3.7-fold from 0.39 (28% agriculture within  
<sup>186</sup> the catchment) to 0.10 (no agriculture) (Figure 4, left). Catchment size had no statistically  
<sup>187</sup> significant effect on the number of RAC exceedances (Figure 4, right). We also could not  
<sup>188</sup> detect a statistically significant interaction between catchment size and agriculture.

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## <sup>189</sup> Effect of precipitation on pesticide risk

<sup>190</sup> The spatio-temporal intersection revealed that most samples were taken during periods of  
<sup>191</sup> low precipitation. For example, only 5% of the samples were taken at or after days with  
<sup>192</sup> rainfall events greater than 10mm / day that may lead to run-off (Supplemental Figure S6).  
<sup>193</sup>  $prec_0$  and  $prec_{-1}$  increased the probability of exceeding LOQ and RQ. In Q2 an increase  
<sup>194</sup> from 0.1 mm to 15 mm of precipitation before sampling ( $prec_{-1}$ ) lead on average to a 43%

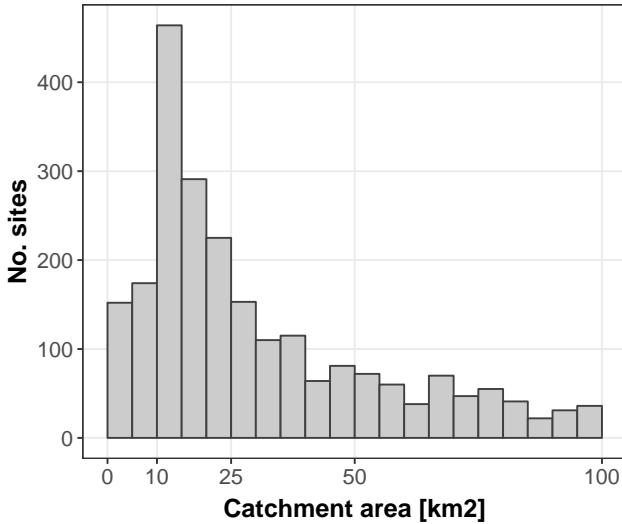


Figure 3: Distribution of catchment area across the sampling sites.

higher mean RQ of 0.05 (Supplemental Figure S7). The probability to exceed LOQ increases in  $Q2$  1.6-fold from 8.7% to 13.5% (Figure 5). Precipitation before sampling ( $prec_{-1}$ ) had a stronger effect than precipitation during sampling ( $prec_0$ ) on the probability of exceeding LOQ. This difference was less pronounced for the mean value of RQ (Supplemental Figure S7). Moreover, effects differed between individual compounds and are provided in the Supplemental Table S4.

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. There was a 2.5-fold higher probability of exceeding LOQ in  $Q2$  (10.6%) than in  $Q1$  (4.6%) (Figure 5). The differences were less pronounced for the mean value of RQ and with less precision (see Supplemental Figure S7, left). Individual compounds showed different temporal patterns (see Supplemental Table S4).

## Pesticide risk in small streams

We found RAC exceedances in 25.5% of sampling sites and  $RQ > 0.1$  in 54% of sites. In 23% of sites none of the chemicals, for which RACs were available, were detected (see also Supplemental Figure S8). Neonicotinoid insecticides and Chlorpyrifos showed the highest

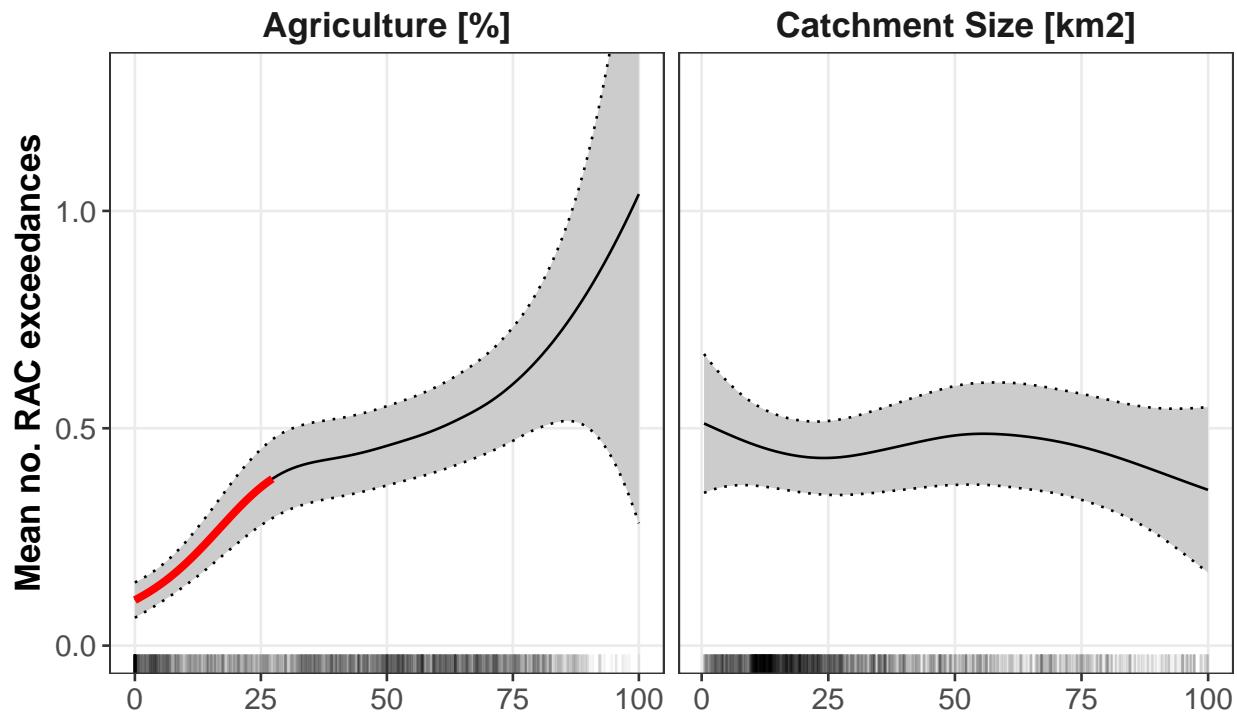


Figure 4: Effect of percent agriculture within the catchment (left) and catchment size (right) on the mean number of RAC exceedances per site. Red line marks statistically significant changes. Dashed lines denote 95% point-wise Confidence Intervals.

211 RQ (Figure 6). For Thiacloprid and Chlorpyrifos the RAC was equal or less than LOQ,  
 212 therefore, all detections have a  $RQ \geq 1$ . The herbicides Nicosulfuron and Diflufenican, as  
 213 well as the fungicide Dimoxystrobin also showed high exceedances of RQ (26.7, 14.1 and  
 214 21.1 % of measurements > LOQ), see also Supplemental Table S5). RAC exceedances were  
 215 found in 14% of samples with concentrations >LOQ (and 7.3% of all samples).

216 The highest RQs were observed for Chlorpyrifos ( $\text{max}(RQ) = 220$ ), Clothianidin ( $\text{max}(RQ)$   
 217  $= 157$ ), Dimoxystrobin( $\text{max}(RQ) = 117$ ) and Isoproturon ( $\text{max}(RQ) = 80$ ). Where anal-  
 218 ysed, metabolites exhibited the highest detection rates (for example, Metazachlor sulfonic  
 219 acid was detected in 84% of all samples where it was analysed ( $n = 3038$ , see also Supple-  
 220 mental Figure S9). Glyphosate was the compound with the highest detection rates (41%,  $n$   
 221  $= 3557$  samples), followed by Boscalid (23%,  $n = 9886$ ) and Isoproturon (22%,  $n = 19112$ ).  
 222 However, only the latter showed RAC exceedances (Figure 6). In 45.9% of samples more than

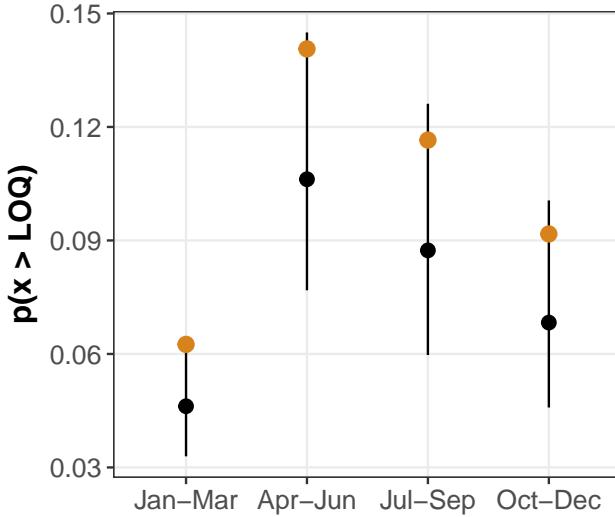


Figure 5: Summarised model predictions for the probability to exceed LOQ throughout the year. Black points indicate the probabilities at 0.1 mm precipitation (and their 95% CI). Orange points indicated the probabilities at 15 mm precipitation. Probabilities have been summaries from a meta-analysis of the 22 modelled compounds. Single compound coefficients are provided in Supplemental Table S4 and Figure S7.

<sup>223</sup> one compound was quantified, with a maximum of 54 different compounds in one sample  
<sup>224</sup> (Supplemental Figure S10).

## <sup>225</sup> Discussion

### <sup>226</sup> Overview on the compiled dataset

<sup>227</sup> The compiled dataset of governmental monitoring data, with a particular focus on small  
<sup>228</sup> streams, represents currently the most comprehensive available for Germany. Similar na-  
<sup>229</sup> tionwide datasets have been compiled for the Netherlands<sup>34</sup>, Switzerland<sup>35</sup> and the United  
<sup>230</sup> States<sup>36</sup>. While the compilations from Europe are of similar quantity and quality to the data  
<sup>231</sup> compiled and analysed here, the compilation used in Stone et al.<sup>36</sup> is much smaller, though  
<sup>232</sup> these data may be complemented by more data in future analyses.

<sup>233</sup> A nationwide assessment of pesticide pollution is hampered by inhomogeneous data across  
<sup>234</sup> federal states: Beside large differences in the spatial distribution and quantity of sampling

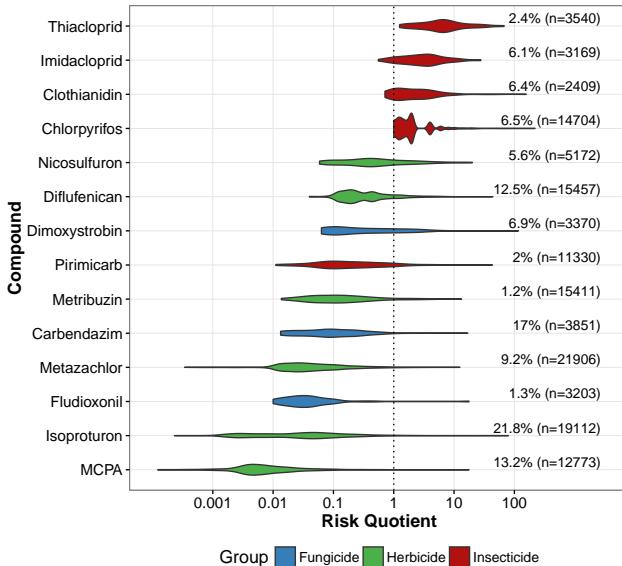


Figure 6: 15 compounds with the highest observed risk quotients in small streams. Non-detects are not shown due to the logarithmic axis. Numbers on the right give the percentage of values >LOQ and the total number of samples were the compound was analysed.

235 sites (Figure 1), the spectrum of analysed compounds (Figure 2) and the quality of chemical  
 236 analyses differed between states. Despite the outlined differences between states, all ecore-  
 237 gions occurring in Germany<sup>37,38</sup> were covered by the presented dataset and thus it might  
 238 nonetheless represent a sample covering all types of small streams in Germany. For Thi-  
 239 acloprid and Chlorpyrifos the LOQs were above the RAC, which means that exceedances  
 240 are likely underestimated. For compounds with low RACs a lowering of LOQ through an  
 241 improvement of chemical analysis is essential for reliable assessment. Moreover, a nation-  
 242 wide assessment would benefit from a harmonised spectrum of analysed compounds between  
 243 federal states.

244 Given their high abundance in the landscape<sup>11</sup> small streams below 10 km<sup>2</sup> are dispro-  
 245portionally less sampled in current monitoring (Figure 3), which may be attributed to the  
 246 missing categorisation in the WFD. Clearly, there is currently a lack of knowledge on stres-  
 247 sor effects on small streams. We analysed only data from small streams, however, for lentic  
 248 small water bodies this lack might be even greater<sup>16</sup>.

<sup>249</sup> **Influence of agricultural land use and catchment size**

<sup>250</sup> We found a strong influence of agriculture on the pollution of streams. Above 28% agriculture  
<sup>251</sup> within a catchment, it is likely that a RAC will be exceeded, with a further increase in entirely  
<sup>252</sup> agricultural catchments (above 75 % agriculture). To our knowledge, this is the first study  
<sup>253</sup> investigating such thresholds of pesticide risk.

<sup>254</sup> We did not find a statistically significant relationship between pesticide pollution and  
<sup>255</sup> catchment size. However, previous studies showed that small streams are more polluted than  
<sup>256</sup> bigger streams<sup>7,9,39</sup>. This can be explained by the relatively short gradient of catchment sizes  
<sup>257</sup> in our dataset, with most of the streams with catchments above 10 km<sup>2</sup> and below 100 km<sup>2</sup>  
<sup>258</sup> (Figure 3, top). For example, the gradient of Schulz<sup>7</sup> covered 6 orders of magnitude.

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<sup>259</sup> **Effect of precipitation on pesticide risk**

<sup>260</sup> Our results revealed that pesticide sampling for chemical monitoring in Germany is mainly  
<sup>261</sup> performed when no precipitation occurs. Nevertheless, we found a 36% higher RQ if samples  
<sup>262</sup> were taken after rainfall events. Samples taken on the day of a rainfall event showed less risk  
<sup>263</sup> than samples taken one day after a rainfall event. This could be explained by the sampling  
<sup>264</sup> preceding the rainfall event and the delay between the start of a rain event and the peak in  
<sup>265</sup> discharge or runoff. The effects of precipitation were more pronounced for the probability to  
<sup>266</sup> exceed LOQ, with smaller effect sizes for the absolute value of RQ. This may be explained  
<sup>267</sup> by a higher variability of absolute concentrations. Overall, our results indicate that cur-  
<sup>268</sup> rent pesticide monitoring relying on grab sampling, largely disconnected from precipitation  
<sup>269</sup> events, underestimates pesticide risks. Automatic event-driven samplers<sup>3</sup> and passive sam-  
<sup>270</sup> plers<sup>40,41</sup> may help overcome these shortcomings and provide a better representation of risks,  
<sup>271</sup> especially for small water bodies<sup>16</sup>.

<sup>272</sup> We found the highest the probability of exceeding LOQ during summer (10% for Q2)  
<sup>273</sup> and lowest in the first quarter of the year (4%, Figure 5, bottom right). This annual pattern  
<sup>274</sup> coincides with the main application season for pesticides in Central Europe. Nevertheless,

275 there are compound-specific differences in the annual pattern, which explains the wide CI  
276 for the absolute RQ (Figure 5, bottom left). For example, the herbicide Diflufenican showed  
277 the highest RQ and the highest probability of exceeding LOQ during the winter quarters Q1  
278 and Q4 (Supplemental Table S4), which coincides with the application period it is registered  
279 for in Germany<sup>42</sup>. Our study suggests that pesticide risks display compound specific spatio-  
280 temporal dynamics. Currently, little is known about these and further research on those  
281 might provide useful information for future ecological risk assessment. For example, the  
282 sensitivity of organisms is often life stage dependent<sup>43</sup> and knowledge on temporal dynamics  
283 could inform on concurrent exposure to multiple pesticides, as well as assist to parameterise  
284 toxicokinetic and toxicodynamic models<sup>44</sup>. Moreover, our results show that analysing abso-  
285 lute concentrations and probabilities of LOQ together might deliver valuable insights into  
286 risk dynamics.

## 287 Pesticides in small streams

288 Our results suggest that small streams are frequently exposed to ecologically relevant pes-  
289 ticide concentrations. In one-quarter of small streams RACs were exceeded at least once.  
290 Stehle and Schulz<sup>9</sup> found the highest percentage of RAC exceedances for organophosphate  
291 insecticides. By contrast, we found that neonicotinoid insecticides have highest exceedances  
292 of RACs, followed by the organophosphate chlorpyrifos. This difference can be attributed to  
293 the low sample size for neonicotinoid insecticides in their study ( $n = 33$ ) compared to the  
294 dataset presented here (for example 3,540 samples of Thiacloprid, Figure 6). Overall, our  
295 results suggest that neonicotinoids may currently pose a high risk to freshwater ecosystems.  
296 Moreover, our results add further evidence to the growing literature on the risks arising from  
297 neonicotinoids for aquatic<sup>45</sup> and terrestrial<sup>46</sup> ecosystems.

298 Compared to Stehle and Schulz<sup>9</sup> we found higher rates of RAC exceedances for insec-  
299 ticides. They found exceedances in 37.1% of insecticide measurements  $>$ LOQ ( $n = 1352$ ,  
300 23 insecticides), whereas, we found exceedances in 67% of insecticide measurements with

301 RACs >LOQ (n = 1855, 22 insecticides). This could be attributed to different insecticides  
302 considered and different underlying RACs. Our study has only 7 insecticides with RACs in  
303 common with the insecticides investigated by Stehle and Schulz<sup>9</sup>. Moreover, all RACs were  
304 lower in our study (average difference = -0.71 µg/L, range = [-2.757; -0.005]). Nevertheless,  
305 it must be noted that the dataset compiled here comprised only samples from grab sampling,  
306 which may considerably underestimate pesticide exposure<sup>3,47</sup>.

307 By contrast, Knauer<sup>39</sup> found exceedances from monitoring data mainly for herbicides  
308 and fungicides and only one insecticide Chlorpyrifos-methyl. Moreover, RAC exceedances in  
309 Switzerland were generally lower and less abundant (for example 6 exceedances (=0.2%) for  
310 Isoproturon with a maximum RQ of 2) compared to our results for Germany. This might  
311 reflect differences in pesticide use between countries, ecoregions and RACs used. From  
312 the definition of RAC it follows that if the concentration of a compound exceeds its RAC  
313 ecological effects are expected. Indeed, Stehle and Schulz<sup>48</sup> found that the biological diversity  
314 of stream invertebrates was significantly reduced by 30% at RQ = 1.12 and by 10% at 1/10  
315 of RAC. We found RQ values greater than 1.12 in 25% of small streams and RQ at 1/10 of  
316 RAC in 54% of small streams. Consequently, we conclude that agricultural pesticides are  
317 on a large scale a major threat to small streams, the biodiversity they host and the services  
318 they provide. This threat may exacerbate because pesticides often occur in mixtures<sup>49</sup> and  
319 may co-occur with other stressors<sup>50</sup>.

320 Monitoring data, despite the outlined limitations, provides an opportunity to study large-  
321 scale environmental occurrence patterns of pesticides. Furthermore, such nationwide com-  
322 pilations, may not only be used for governmental surveillance, but also to answer other  
323 questions, like validation of exposure modelling,<sup>51</sup> retrospective evaluation of regulatory risk  
324 assessment<sup>9,39</sup> or occurrences of pesticide mixtures.<sup>49</sup> However, the sampling design needs to  
325 account for precipitation events to provide robust data. Our results suggest that exceedances  
326 of RACs are landscape dependent and therefore, pesticide regulation should account for  
327 landscape features. Moreover, the high exceedances of RACs indicate that greater efforts

<sup>328</sup> are needed to describe causal links, which may lead to further developments of the current  
<sup>329</sup> authorisation procedure.

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## <sup>338</sup> Supporting Information Available

<sup>339</sup> The following files are available free of charge.

- <sup>340</sup> • Supplemental \_ Materials.pdf : Supplemental Materials (Figures, Tables, Models).

<sup>341</sup> This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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