

Large scale risks from agricultural pesticides in small streams

Eduard Szöcs,[†] Marvin Brinke,[‡] Bilgin Karaoglan,[¶] and Ralf B. Schäfer*,[†]

^{*}*Institute for Environmental Sciences, University of Koblenz-Landau, Fortstraße 7, 76829 Landau, Germany*

[‡]*German Federal Institute of Hydrology (BfG), Koblenz, Germany*

[¶]*German Environment Agency (UBA), Dessau-Roßlau, Germany*

E-mail: schaefer-ralf@uni-landau.de

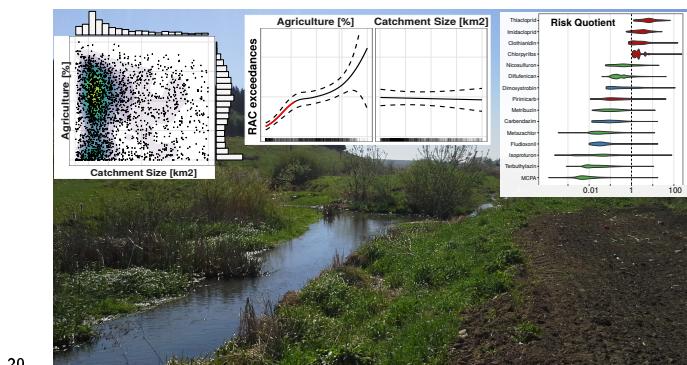
Phone: +49 (0)6341 280 31536. Fax: +49 (0)6341 280 31326

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. Precipitation increased detection probability by 43% and concentrations were the highest from April to June. Overall, this indicates

14 that agricultural land use is a major contributor of pesticides in streams. RACs were
15 exceeded in 26% of streams, with the highest exceedances found for neonicotinoid in-
16 secticides. We conclude that pesticides from agricultural land use are a major threat to
17 small streams and their biodiversity. To reflect peak concentrations, current pesticide
18 monitoring needs refinement.

19 **TOC Art**



20

21 **Introduction**

22 More than 50% of the total land area in Germany is used by agriculture¹. In the year 2014
23 more than 45,000 tonnes of 776 authorised plant protection products were sold for application
24 on this area². The applied pesticides may enter surface waters via spray-drift, edge-of-field
25 run-off or drainage^{3–5}. Once entered the surface waters they may have adverse effects on
26 biota and ecosystem functioning⁶. Although it is known that pesticide pollution and its
27 ecological effects increase with the fraction of agricultural land use in the catchment⁷, the
28 shape of the relationship is unknown and studies on potential thresholds are lacking.

29 Two recent studies indicate that pesticide concentrations in streams might threaten fresh-
30 water biodiversity in the European union. Malaj et al.⁸ analysed data supplied to the Eu-
31 ropean Union (EU) in the context of the Water Framework Directive (WFD) and showed
32 that almost half of European water bodies are at risk from pesticides. Stehle and Schulz⁹

33 compiled 1,566 measured concentrations of 23 insecticides in the EU from scientific publi-
34 cations and found considerable exceedances of regulatory acceptable concentrations (RAC).
35 However, these studies reflect only a small amount of potentially available data (173 sites in
36 predominantly mid-sized and large rivers in Malaj et al.⁸ and 138 measurements in Stehle
37 and Schulz⁹), and it is unclear how representative they are for Germany. Much more com-
38 prehensive data on thousands of sites are available from national monitoring programs that
39 are setup for the surveillance of water quality, which is done independently by the federal
40 states in Germany in compliance with the WFD¹⁰. Despite that these data are providing
41 the opportunity to study pesticide risks and other research questions on a large scale with
42 high spatial density, to date these data have not been compiled.

43 Small streams comprise a major fraction of streams¹¹, accommodate a higher proportion
44 of biodiversity compared to larger streams^{12,13} and play an important role in the recoloniza-
45 tion of disturbed downstream reaches^{14,15}. Nevertheless, a clear definition of small streams
46 in terms of catchment or stream size is currently lacking¹⁶. For example, the WFD defines
47 small streams with a catchment size between 10 and 100 km², without further categorisation
48 of streams <10km² and Lorenz et al.¹⁶ defines small streams with catchment size <10km².
49 Moreover, small streams might particularly be at high risk of pesticide contamination in case
50 of adjacent agricultural areas and given their low dilution potential^{5,7}. Indeed, meta-analyses
51 using data from studies with a few sites reported higher pesticide pollution in smaller streams
52 compared to bigger streams^{7,9}. Despite their ecological relevance and potentially higher pes-
53 ticide exposure, a recent review of pesticide studies showed that a disproportionately small
54 fraction of studies was conducted in small water bodies, and these were largely limited to a
55 few sites¹⁶. Consequently, knowledge on the pesticide pollution of small streams on larger
56 scales is scant. In European law, the Directive 2009/128/EC¹⁷ places an obligation on the
57 EU Member States to adopt National Action Plans (NAP) for the Sustainable Use of Plant
58 Protection Products and the German NAP also addresses the knowledge gap concerning
59 pesticide impact on small streams, specifically including those with catchment size <10km².

60 The aim of this study is to identify drivers and dynamics of pesticide concentrations
61 in streams on large spatial scales. To achieve this, we compiled and analysed large-scale
62 pesticide monitoring data from small streams in Germany and examined four hypotheses: 1)
63 A major fraction of pesticides is applied to agricultural fields. Therefore, we hypothesised
64 that the most frequent exceedances of RACs occur in streams with a high proportion of
65 agricultural land use in the catchment. If agricultural land use was indeed the main source
66 for pesticides in streams, the RAC exceedances should drop to negligible levels in the absence
67 of agricultural land use in their catchments. Given this possible drop we expected a non-
68 linear relationship between exceedances and agricultural land use. In case of a non-linear
69 relationship, our analyses might guide the definition of reference streams without pesticide
70 pollution in future monitoring. 2) Based on previous studies, we hypothesised that an
71 increase in catchment size is associated with an decrease in RAC exceedances^{7,9}. 3) However,
72 also the timing of sampling may influence measured concentrations, as local and regional
73 studies reported higher pesticide concentrations after precipitation events^{5,18}. Therefore,
74 we hypothesised the highest RAC exceedances to be found after precipitation events. 4)
75 Pesticides are not applied throughout the whole year and highest RAC exceedances should
76 be found during the main growing season. Finally, we quantified the current risks from
77 pesticides in small streams in Germany and the compounds accountable for the risk.

78 Methods

79 Data compilation

80 We queried pesticide monitoring data from sampling sites that can be classified as small
81 streams (catchment sizes < 100 km² according to the WFD) from all 13 non-city federal
82 states of Germany (see Supplemental Table S1 for the abbreviations of federal state names)
83 for the years 2005 to 2015. We homogenised and unified all data provided by the federal
84 states into a database and implemented a robust data-cleaning workflow (see Supplemental

85 Figure S1 for details)¹⁹.

86 We identified precipitation at sampling sites by a spatio-temporal intersection of sam-
87 pling events with gridded daily precipitation data (60×30 arcsec resolution) available from
88 the German Meteorological Service (DWD). This data spatially interpolates daily precipi-
89 tation values from local weather stations²⁰. 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)²¹ and the multiple flow direction algorithm²² as implemented
98 in GRASS GIS 7²³ 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 authorities²⁴. 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)²⁵.
₁₁₂ RACs are derived during pesticide authorisation as part of the environmental risk assessment
₁₁₃ (ERA). According to the goals of ERA, exceedances of RACs should not occur after pesticide
₁₁₄ authorisation⁹ and thus no unacceptable ecological effects are expected if the environmental
₁₁₅ concentration remains below the RAC. Stehle and Schulz⁹ showed that RAC exceedances
₁₁₆ reflect a decrease in biodiversity and from this perspective are ecologically relevant indicators.
₁₁₇ The German Environment Agency (UBA) provided RACs for 107 compounds, including
₁₁₈ those with the highest detection rates (Supplemental Table S2). Based on these RACs, we
₁₁₉ calculated Risk Quotients (RQ):

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

₁₂₀ where C_i is the concentration of a compound i in a sample and RAC_i the respective
₁₂₁ RAC.

₁₂₂ **Statistical analyses**

₁₂₃ As outlined in the introduction, we expected non-linear responses to agricultural land use and
₁₂₄ catchment size and searched for potential thresholds (defined as abrupt changes). Therefore,
₁₂₅ we used generalised additive models (GAM) to establish relationships²⁶. We modelled the
₁₂₆ number of RAC exceedances ($RQ > 1$) at a site as:

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

₁₂₇ where $No(RQ > 1)_i$ is the observed number of RAC exceedances at site i . Because of
₁₂₈ overdispersion, we modelled $No(RQ > 1)_i$ as resulting from a negative binomial distribution

129 (*NB*) with mean μ_i and a quadratic mean-variance-relationship ($Var(No(RQ > 1)_i) =$
 130 $\mu_i + \frac{\mu_i^2}{\kappa}$). The proportion of agricultural land use within the catchment ($agri_i$) and the
 131 catchment size of the site ($size_i$) were used as predictors of the number of RAC exceedances.
 132 β_0 is the intercept and f_1 and f_2 are smoothing functions using penalized cubic regression
 133 splines^{27,28}. The number of measurements per site (n_i) was used as an offset to account
 134 for differences in sampling efforts at a site (in terms of number of samples and analysed
 135 compounds) and is equivalent to modelling the rate of exceedances. We used point-wise 95%
 136 Confidence Intervals (CI) of the first derivative of the fitted smooth to identify regions of
 137 statistically significant changes. All data-processing and analyses were performed using R²⁹.
 138 GAMs were fitted using the mgcv package²⁸.

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

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

147 ν_i denotes the probability of a measurement i being above LOQ and f_{Gamma} denotes the
 148 gamma function and is used for values equal to or greater LOQ, with μ being the mean
 149 and σ the standard deviation of RQ. We used the $\log(x + 0.05)$ transformed precipitation
 150 at sampling date ($\log prec_0$) and the day before ($\log prec_{-1}$), as well as quarters of the year
 151 (*Q1: Jan-Mar, Q2: Apr-Jun, Q3: Jul-Sep, Q4: Oct-Dec*) as linear predictors for μ and ν .

152 We used appropriate link functions for μ and ν and assumed σ to be constant. Equation 4
153 summarises the deterministic part of the model for a measurement i .

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

154 To account for differences between federal states we used *site* nested within *state* as
155 random intercepts. We implemented this model using the *gamlss* package.³²

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 separately³³,
160 resulting in an averaged effect of the 22 compounds. The results of individual compounds
161 are provided in the Supplemental Table S4 and Figures S6 and S7. The meta-analysis was
162 performed using the *metafor* package³⁴.

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-

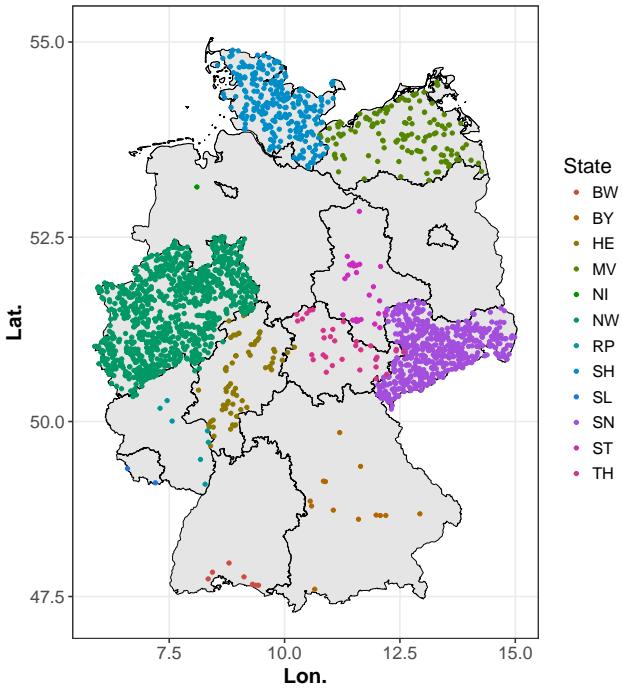


Figure 1: Spatial distribution of the 2,301 small stream sampling sites. Colour codes different federal states (see Supplemental Table S1 for abbreviations).

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 km^2 , with most sampling sites having catchment
 181 sizes between 10 and 25 km^2 (Figure 3).

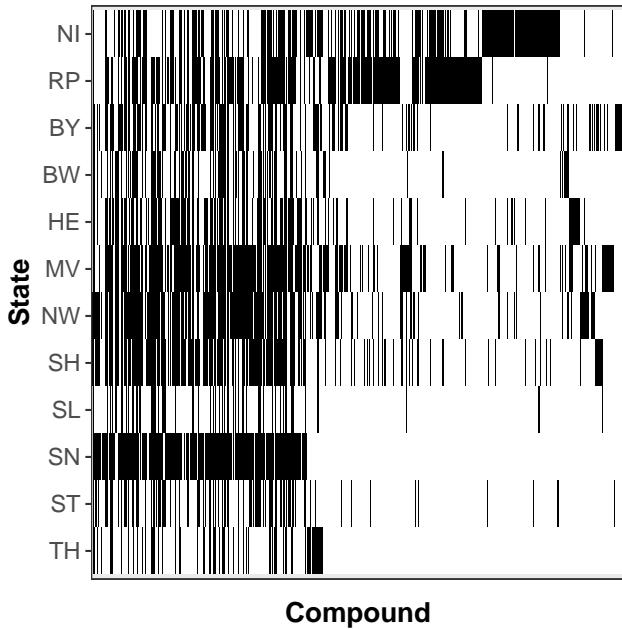


Figure 2: Barcode plot of compound spectra of the federal states. Each vertical line is an analysed compound.

182 Influence of agricultural land use and catchment size

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

189 Effect of precipitation on pesticide risk

190 $prec_0$ and $prec_{-1}$ increased the probability of exceeding LOQ and RQ. In Q2 an increase from
191 0.1 mm to 15 mm of precipitation before sampling ($prec_{-1}$) lead on average to a 43% higher
192 mean RQ of 0.05 (Supplemental Figure S7). The probability to exceed LOQ increases in Q2
193 1.6-fold from 8.7% to 13.5% (Figure 5). Precipitation before sampling ($prec_{-1}$) had a stronger
194 effect than precipitation during sampling ($prec_0$) on the probability of exceeding LOQ. This

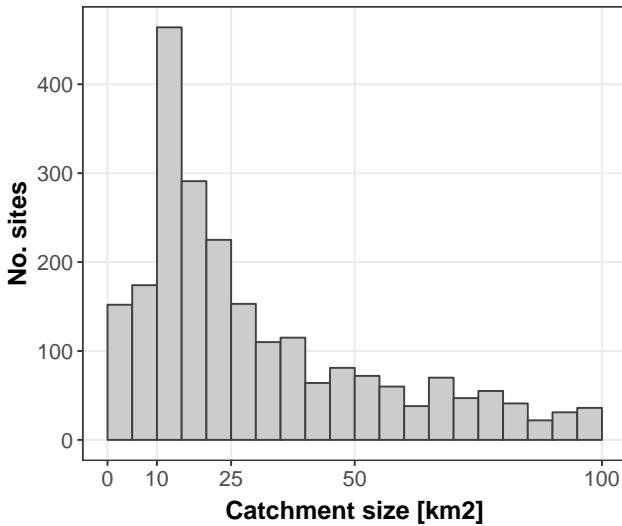


Figure 3: Distribution of catchment sizes across the sampling sites.

195 difference was less pronounced for the mean value of RQ (Supplemental Figure S7, top left).

196 Moreover, effects differed between individual compounds (see Supplemental Table S4).

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

198 in Q2 and decreased towards the end of the year. There was a 2.5-fold higher probability

199 of exceeding LOQ in Q2 (10.6%) than in Q1 (4.6%) (Figure 5). The differences were less

200 pronounced for the mean value of RQ and with less precision (see Supplemental Figure S7,

201 left). Individual compounds showed different temporal patterns (see Supplemental Table S4).

202 Current pesticide risks in small streams

203 We found RAC exceedances in 25.5% of sampling sites and $RQ > 0.1$ in 54% of sites. In

204 23% of sites none of the chemicals, for which RACs were available, were detected (see also

205 Supplemental Figure S8). Neonicotinoid insecticides and Chlorpyrifos showed the highest

206 RQ (Figure 6). For Thiacloprid and Chlorpyrifos the RAC was equal or less than LOQ,

207 therefore, all detections have a $RQ \geq 1$. The herbicides Nicosulfuron and Diflufenican, as

208 well as the fungicide Dimoxystrobin also showed high exceedances of RACs (26.7, 14.1 and

209 21.1 % of measurements $>$ LOQ), see also Supplemental Table S5). RAC exceedances were

210 found in 14% of samples with concentrations $>$ LOQ (and 7.3% of all samples).

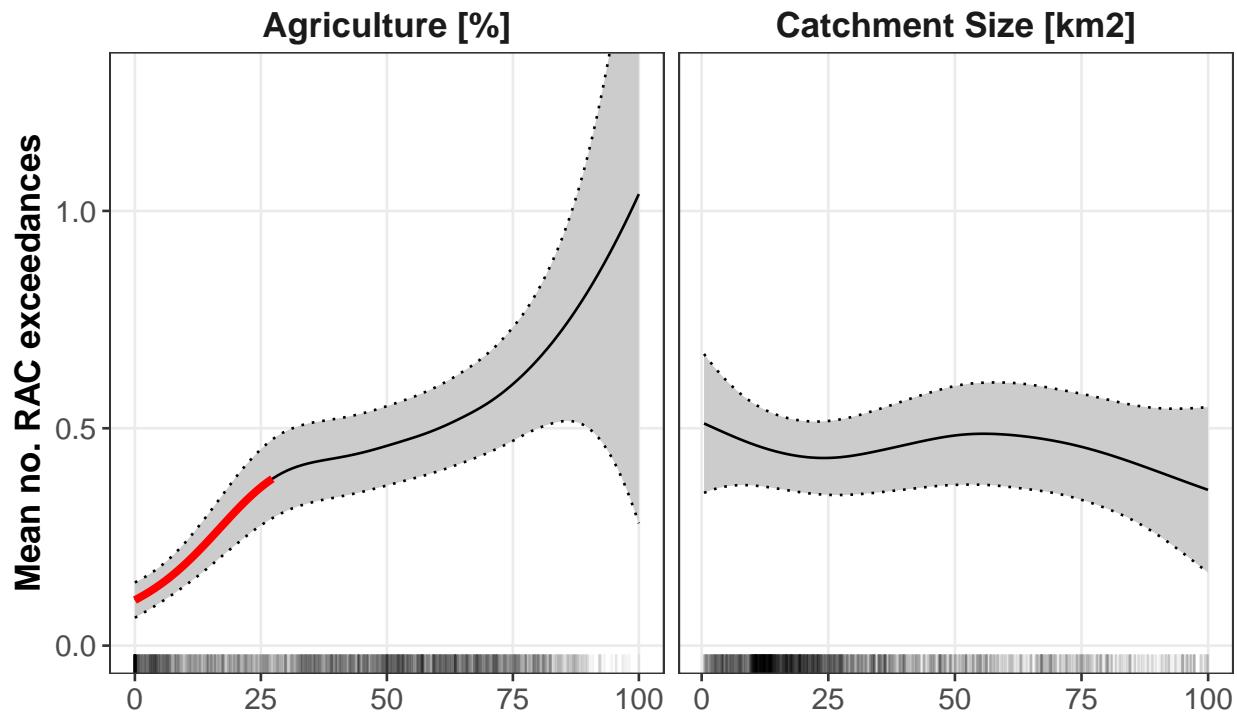


Figure 4: Effect of percent agriculture within the catchment (left) and catchment size (right) on the mean number of RAC exceedances per site. Red line marks statistically significant changes. Dashed lines denote 95% point-wise Confidence Intervals.

211 The highest RQs were observed for Chlorpyrifos ($\text{max}(\text{RQ}) = 220$), Clothianidin ($\text{max}(\text{RQ})$
 212 = 157), Dimoxystrobin($\text{max}(\text{RQ}) = 117$) and Isoproturon ($\text{max}(\text{RQ}) = 80$). Where anal-
 213 ysed, metabolites exhibited the highest detection rates (for example, Metazachlor sulfonic
 214 acid was detected in 84% of all samples where it was analysed ($n = 3038$, see also Supple-
 215 mental Figure S9). Glyphosate was the compound with the highest detection rates (41%, n
 216 = 3557 samples), followed by Boscalid (23%, $n = 9886$) and Isoproturon (22%, $n = 19112$).
 217 However, only the latter showed RAC exceedances (Figure 6). In 45.9% of samples more than
 218 one compound was quantified, with a maximum of 54 different compounds in one sample
 219 (Supplemental Figure S10).

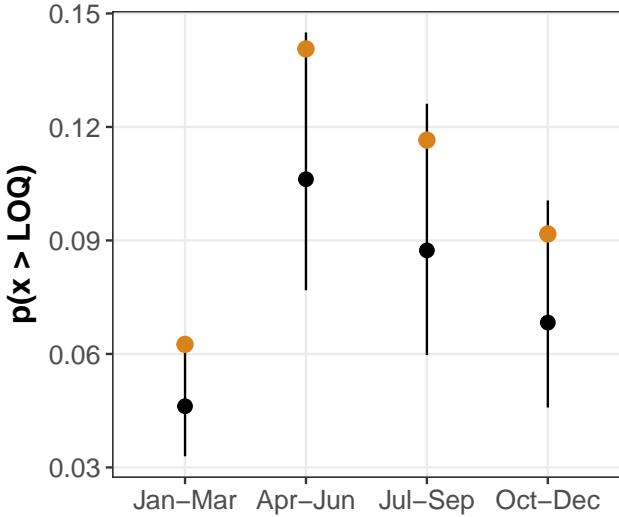


Figure 5: Summarised model predictions for the probability to exceed LOQ throughout the year. Black points indicate the probabilities at 0.1 mm precipitation (and their 95% CI). Orange points indicate the probabilities at 15 mm precipitation. Probabilities have been summarised from a meta-analysis of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

220 Discussion

221 Overview on the compiled dataset

222 The compiled dataset of governmental monitoring data, with a particular focus on small
 223 streams, represents currently the most comprehensive for Germany. Similar nationwide
 224 datasets have been compiled for the Netherlands³⁵, Switzerland³⁶ and the United States³⁷.
 225 While the compilations from Europe are of similar quantity and quality to the data compiled
 226 and analysed here, the compilation used in Stone et al.³⁷ is much smaller, though these data
 227 may be complemented by more data in future analyses.

228 A nationwide assessment of pesticide pollution is hampered by inhomogeneous data across
 229 federal states: Beside large differences in the spatial distribution and quantity of sampling
 230 sites (Figure 1), the spectrum of analysed compounds (Figure 2) and the quality of chem-
 231 ical analyses differed between states. Despite the outlined differences between states, all
 232 ecoregions occurring in Germany^{38,39} and all major stream types were covered by the data

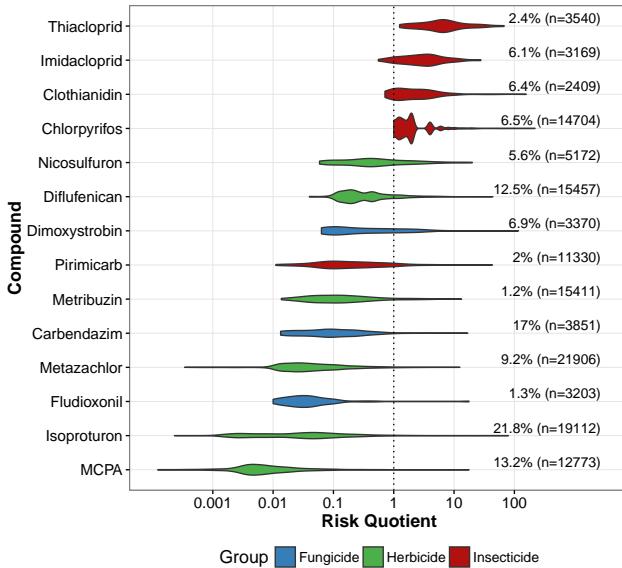


Figure 6: 15 compounds with the highest observed risk quotients in small streams. Non-detects are not shown due to the logarithmic axis. Numbers on the right give the percentage of values >LOQ and the total number of samples were the compound was analysed.

233 set. The unequal distribution of sampling sites and the different sampling strategies hamper
 234 inference on the total population of small streams in Germany. We accounted for differences
 235 in sampling efforts per site by including the total number of measurement into the statistical
 236 models. However, we acknowledge that additional differences such as sampling frequency and
 237 temporal distribution of the samplings might incur bias between states^{3,18}. Consequently,
 238 we did not compare the results between states. Moreover, it is known that differences in
 239 analytical quality can influence estimated effects^{40,41}. However, the used model (Equation 3)
 240 explicitly accounted for LOQs and differences therein.

241 For Thiacloprid and Chlorpyrifos the LOQs were above the RAC, which means that
 242 exceedances are likely underestimated. For compounds with low RACs a lowering of LOQ
 243 through an improvement of chemical analysis is essential for reliable assessment. Moreover,
 244 a nationwide assessment would benefit from a harmonised spectrum of analysed compounds
 245 between federal states.

246 Given their high abundance in the landscape¹¹ small streams below 10 km² are dispro-
 247portionally less sampled in current monitoring (Figure 3). This may be attributed to the

²⁴⁸ missing categorisation in the WFD, but also to technical (e.g. sampling at low flow) and
²⁴⁹ natural reasons (e.g. ephemeral streams).

²⁵⁰ Clearly, there is currently a lack of knowledge on stressor effects on small streams. We
²⁵¹ analysed only data from small streams, however, for lentic small water bodies this lack might
²⁵² be even greater¹⁶.

²⁵³ **Influence of agricultural land use and catchment size**

²⁵⁴ As hypothesised, we found a positive relationship between agricultural land use and the
²⁵⁵ number of RAC exceedances. Especially, we found a statistically significant drop below 28%
²⁵⁶ of agricultural land use (Figure 4, left). This drop indicates that agricultural land use is a
²⁵⁷ major contributor to the observed RAC exceedances. We note that this drop would have
²⁵⁸ been missed by linear modeling (Supplemental Figure S5). The absence of such a drop would
²⁵⁹ have suggested that other inputs such as from urban gardening are relevant contributors to
²⁶⁰ RAC exceedances.

²⁶¹ We did not find a statistically significant relationship between pesticide pollution and
²⁶² catchment size (Hypothesis 2). However, previous studies showed that small streams are
²⁶³ more polluted than bigger streams^{7,9,42}. This can be explained by the relatively short gra-
²⁶⁴ dient of catchment sizes in our dataset, with most of the streams with catchments above
²⁶⁵ 10 km^2 and below 100 km^2 (Figure 3, top). For example, the gradient of Schulz⁷ covered
²⁶⁶ 6 orders of magnitude. Although there is a relationship between catchment size and stream
²⁶⁷ size (Supplemental Figure S11), this might be also influenced by geology and precipitation
²⁶⁸ regime. Therefore, our results cannot be directly translated to stream size.

²⁶⁹ **Effect of precipitation on pesticide risk**

²⁷⁰ We found a 43% higher mean RQ if samples were taken after rainfall events, which conforms
²⁷¹ to the hypothesis that run-off is a major entry path way for pesticides into streams on the
²⁷² large scale. However, samples taken on the day of a rainfall event showed less risk than

273 samples taken one day after a rainfall event. This discrepancy could be explained by a
274 sampling preceding the rainfall event because the temporal resolution of our dataset was 1
275 day. Additionally, this might be explained by a delay between the start of a rain event and
276 the peak in discharge or runoff.

277 The effects of precipitation were more pronounced for the probability to exceed LOQ,
278 with smaller effect sizes for the absolute value of RQ. This may be explained by a higher
279 variability of absolute concentrations. Overall, our results indicate that current pesticide
280 monitoring relying on grab sampling, largely disconnected from precipitation events, under-
281 estimates pesticide risks. Automatic event-driven samplers³ and passive samplers^{43,44} may
282 help overcome these shortcomings and provide a better representation of risks. Our results
283 demonstrate that future monitoring of small water bodies should also capture precipitation
284 events, which is in agreement with other studies, such as Lorenz et al.¹⁶.

285 We found the highest the probability of exceeding LOQ from April to June (10% for
286 Q2) and lowest in the first quarter of the year (4%, Figure 5, bottom right). This annual
287 pattern coincides, as hypothesised, with the main application season for pesticides in Central
288 Europe. Nevertheless, there are compound-specific differences in the annual pattern, which
289 explains the wide CI for the absolute RQ (Figure 5, bottom left). For example, the herbicide
290 Diflufenican showed the highest RQ and the highest probability of exceeding LOQ during the
291 winter quarters Q1 and Q4 (Supplemental Table S4), which coincides with the application
292 period it is registered for in Germany⁴⁵. Moreover, compound properties, like half-life or
293 water solubility, might influence compound dynamics. Our study suggests that pesticide
294 risks display compound specific spatio-temporal dynamics. Currently, little is known about
295 these and further research on those might provide useful information for future environmental
296 risk assessment. For example, the sensitivity of organisms is often life stage dependent⁴⁶ and
297 knowledge on temporal dynamics could inform on concurrent exposure to multiple pesticides,
298 as well as assist to parameterise toxicokinetic and toxicodynamic models⁴⁷. Moreover, our
299 results show that analysing absolute concentrations and probabilities of LOQ together might

300 deliver valuable insights into risk dynamics. The influence of agricultural land use within
301 the catchment area and the coincidence with the growing season indicates that agricultural
302 land use a major contributor of pesticides in streams.

303 Pesticides in small streams

304 Our results suggest that small streams are frequently exposed to ecologically relevant pes-
305 ticide concentrations. In one-quarter of small streams RACs were exceeded at least once.
306 Stehle and Schulz⁹ found the highest percentage of RAC exceedances for organophosphate
307 insecticides. By contrast, we found that neonicotinoid insecticides have highest exceedances
308 of RACs, followed by the organophosphate chlorpyrifos. This difference can be attributed to
309 the low sample size for neonicotinoid insecticides in their study ($n = 33$) compared to the
310 dataset presented here (for example 3,540 samples of Thiacloprid, Figure 6). Overall, our
311 results suggest that neonicotinoids may currently pose a high risk to freshwater ecosystems.
312 Moreover, our results add further evidence to the growing literature on the risks arising from
313 neonicotinoids for aquatic⁴⁸ and terrestrial⁴⁹ ecosystems.

314 Compared to Stehle and Schulz⁹ we found higher rates of RAC exceedances for insec-
315 ticides. They found exceedances in 37.1% of insecticide measurements >LOQ ($n = 1352$,
316 23 insecticides), whereas, we found exceedances in 67% of insecticide measurements with
317 RACs >LOQ ($n = 1855$, 22 insecticides). This could be attributed to different insecticides
318 considered and different underlying RACs. Our study has only 7 insecticides with RACs in
319 common with the insecticides investigated by Stehle and Schulz⁹. Moreover, all RACs were
320 lower in our study (average difference = $-0.71 \mu\text{g/L}$, range = [-2.757; -0.005]). Nevertheless,
321 it must be noted that the dataset compiled here comprised only samples from grab sampling,
322 which may considerably underestimate pesticide exposure^{3,18}.

323 By contrast, Knauer⁴² found exceedances from monitoring data mainly for herbicides
324 and fungicides and only one insecticide Chlorpyrifos-methyl. Moreover, RAC exceedances in
325 Switzerland were generally lower and less abundant (for example 6 exceedances (=0.2%) for

326 Isoproturon with a maximum RQ of 2) compared to our results for Germany. This might
327 reflect differences in pesticide use between countries, ecoregions and RACs used. From
328 the definition of RAC it follows that if the concentration of a compound exceeds its RAC
329 ecological effects are expected. Indeed, Stehle and Schulz⁵⁰ found that the biological diversity
330 of stream invertebrates was significantly reduced by 30% at RQ = 1.12 and by 10% at 1/10
331 of RAC. We found RQ values greater than 1.12 in 25% of small streams and RQ at 1/10 of
332 RAC in 54% of small streams. Consequently, we conclude that agricultural pesticides are
333 on a large scale a major threat to small streams, the biodiversity they host and the services
334 they provide. This threat may exacerbate because pesticides often occur in mixtures⁵¹ and
335 may co-occur with other stressors⁵².

336 Monitoring data, despite the outlined limitations, provides an opportunity to study large-
337 scale environmental occurrence patterns of pesticides. Furthermore, such nationwide com-
338 pilations, may not only be used for governmental surveillance, but also to answer other
339 questions, like validation of exposure modelling,⁵³ retrospective evaluation of regulatory risk
340 assessment^{9,42} or occurrences of pesticide mixtures.⁵¹ However, the sampling design needs
341 to account for precipitation events to provide robust data. Therefore, non-linear modeling
342 can provide additional insights to risk assessment compared to linear modeling²⁶. Our re-
343 sults suggest that exceedances of RACs are landscape dependent and therefore, pesticide
344 regulation should account for landscape features. Moreover, the high exceedances of RACs
345 indicate that greater efforts are needed to describe causal links, which may lead to further
346 developments of the current authorisation procedure.

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³⁵⁵ Supporting Information Available

³⁵⁶ The following files are available free of charge.

- ³⁵⁷ • Supplemental _ Materials.pdf : Supplemental Materials (Figures, Tables, Models).

³⁵⁸ This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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