

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, Germany*

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

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

E-mail: szoebs@uni-landau.de

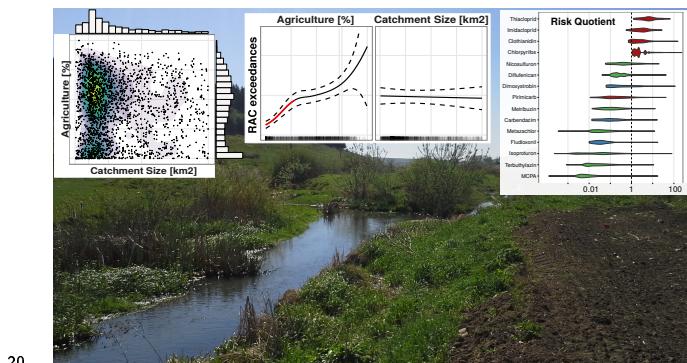
Phone: +49 (0)6341 280 31552

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 from April to June. 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 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 highest concentrations and possible exceedances of RACs occur in streams with
65 a high proportion of agricultural land use in the catchment. If agricultural land use was
66 indeed the main source for pesticides in streams, the RAC exceedances should drop to
67 negligible levels in the absence of agricultural land use in the catchment. Additionally,
68 these relationships may unravel thresholds because of non-linearity which may guide the
69 definition of reference streams without pesticide pollution in future monitoring. 2) Given
70 a higher dilution potential, larger streams should show lower concentrations. 3) However,
71 also the timing of sampling may influence measured concentrations, as local and regional
72 studies reported higher pesticide concentrations after precipitation events^{5,18}. Therefore, we
73 hypothesised the highest concentrations to be found after precipitation events. 4) Pesticides
74 are not applied throughout the whole year and highest concentrations should be found during
75 the main growing season. Finally, we quantified the current risks from pesticides in small
76 streams in Germany and the compounds accountable for the risk.

77 Methods

78 Data compilation

79 We queried pesticide monitoring data from sampling sites that can be classified as small
80 streams (catchment sizes < 100 km² according to the WFD) from all 13 non-city federal
81 states of Germany (see Supplemental Table S1 for the abbreviations of federal state names)
82 for 2005 to 2015. We homogenised and unified all data provided by the federal states into
83 a database and implemented a robust data-cleaning workflow (see Supplemental Figure S1
84 for details)¹⁹.

85 We identified precipitation at sampling sites by a spatio-temporal intersection of sam-
86 pling events with gridded daily precipitation data (60×30 arcsec resolution) available from

87 the German Meteorological Service (DWD). This data spatially interpolates daily precipi-
88 tation values from local weather stations²⁰. We performed the intersection for the actual
89 sampling date and the day before and extracted precipitation during and up to 48 hours
90 before sampling.

91 Characterization of catchments

92 We compiled a total of 2,369 sampling sites in small streams with pesticide measurements.
93 Alongside, we also queried catchment sizes and agricultural land use within the catchment
94 for the sampling sites from the federal states. Catchment size was provided for 59% of sites.
95 Additionally, we delineated upstream catchments for each of the sampling sites using (i) a
96 digital elevation model (DEM)²¹ and the multiple flow direction algorithm²² as implemented
97 in GRASS GIS 7²³ and (ii) from drainage basins provided by the Federal Institute of Hy-
98 drology (BfG). Delineated catchments were visually checked for accuracy by comparison of
99 coverage with stream networks provided by the federal states. Thus, catchment size infor-
100 mation was available for 99% of all sites (59% from authorities, 24% from DEM and 16%
101 from drainage basins).

102 For each derived catchment (either from DEM or drainage basins) we calculated the
103 % agricultural land-use within the catchment based on the Authoritative Topographic-
104 Cartographic Information System (ATKIS) of the land survey authorities²⁴. Thus, agri-
105 cultural land use information was available for 98% of all sites (24% from authorities, 52%
106 from DEM and 22% from drainage basins). 68 sites (3%) that lacked catchment size or land
107 use information were omitted from the analysis, resulting in 2301 sites used in the analyses
108 outlined below.

109 Characterization of pesticide pollution

110 We characterised pesticide pollution using regulatory acceptable concentrations (RAC)²⁵.
111 RACs are derived during pesticide authorisation as part of the ecological risk assessment

112 (ERA). According to the goals of ERA, exceedances of RACs should not occur after pes-
 113 ticide authorisation⁹. No unacceptable ecological effects are expected if the environmental
 114 concentration remains below the RAC. Stehle and Schulz⁹ showed that RAC exceedances re-
 115 flect a decrease in biodiversity and from this perspective are ecologically relevant indicators.
 116 The German Environment Agency (UBA) provided RACs for 107 compounds, including
 117 those with the highest detection rates (Supplemental Table S2). Based on these RACs, we
 118 calculated Risk 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 searched for potential thresholds (defined as abrupt changes). Therefore,
 124 we used generalised additive models (GAM) to establish relationships²⁶. We modelled the
 125 number of RAC exceedances ($RQ > 1$) at a site as:

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

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 μ_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 β_0 is the intercept and f_1 and f_2 are smoothing functions using penalized cubic regression
 132 splines^{27,28}. The number of measurements per site (n_i) was used as an offset to account
 133 for differences in sampling efforts at a site (in terms of number of samples and analysed
 134 compounds) and is equivalent to modelling the rate of exceedances. We used point-wise 95%
 135 Confidence Intervals (CI) of the first derivative of the fitted smooth to identify regions of
 136 statistically significant changes. All data-processing and analyses were performed using R²⁹.
 137 GAMs were fitted using the mgcv package²⁸.

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^{30,31}
 143 (Equation 3). These two processes can be interpreted as changes in the mean value of RQ
 144 (change in μ) and changes in the probability of exceeding LOQ and showing any risk (change
 145 in ν).

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

146 ν_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 μ being the mean
 148 and σ 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 ($Q1$: Jan-Mar, $Q2$: Apr-Jun, $Q3$: Jul-Sep, $Q4$: Oct-Dec) as linear predictors for μ and ν .
 151 We used appropriate link functions for μ and ν and assumed σ to be constant. Equation 4
 152 summarises the deterministic part of the model for a measurement i .

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

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

155 We fitted this model separately to each compound with a RAC, measured in at least 1000
156 samples and with more than 5% of values above LOQ (n = 22 compounds, see Supplemental
157 Table S3 for a list of compounds). To summarise the coefficients across the 22 modelled
158 compounds we used a random effect meta-analysis for each model coefficient separately³³,
159 resulting in an averaged effect of the 22 compounds. The results of individual compounds
160 are provided in the Supplemental Table S4 and Figures S6 and S7. The meta-analysis was
161 performed using the *metafor* package³⁴.

162 Results

163 Overview of the compiled data

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

170 In total 478 different compounds used as pesticides and their metabolites were measured
171 at least once (Supplemental Table S2). Most of the compounds were herbicides (179), fol-
172 lowed by insecticides (117) and fungicides (109). Most samples were taken in the months
173 April till October, while fewer samples were taken during winter (see Supplemental Fig-

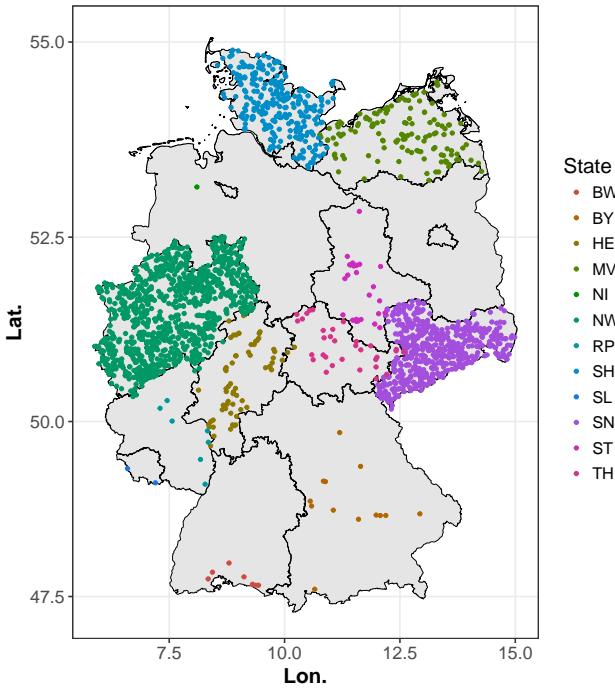


Figure 1: Spatial distribution of the 2,301 small stream sampling sites. Colour codes different federal states (see Supplemental Table S1 for abbreviations).

174 figure S2). We found substantial differences in the spectra of analysed pesticides between
 175 federal states (Figure 2). The number of analysed pesticides per state ranged from 57 (SL)
 176 to 236 (RP) (Supplemental Table S1). 4% (=71,113) of all measurements were concentrations
 177 above LOQ.

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

181 Influence of agricultural land use and catchment size

182 We found a positive relationship between agricultural land use and the number of RAC
 183 exceedances. The non-linear model showed, that below 28% agriculture the mean number of
 184 RAC exceedances dropped statistically significant 3.7-fold from 0.39 (28% agriculture within

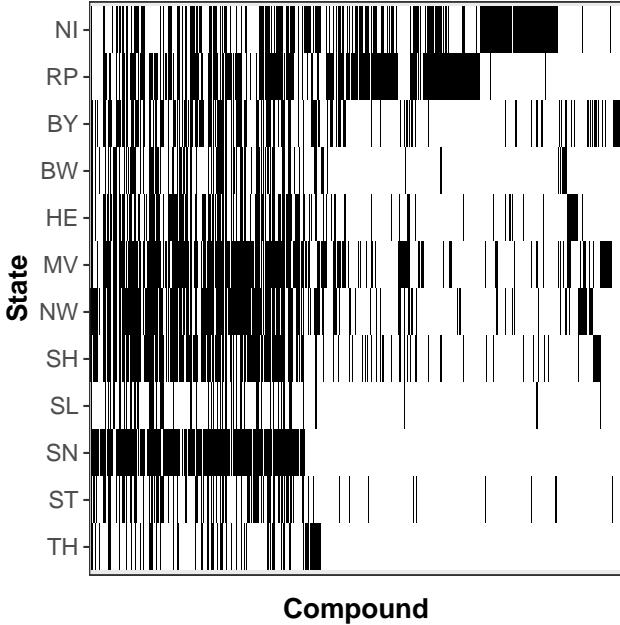


Figure 2: Barcode plot of compound spectra of the federal states. Each vertical line is an analysed compound.

185 the catchment) to 0.10 (no agriculture) (Figure 4, left). Catchment size had no statistically
 186 significant effect on the number of RAC exceedances (Figure 4, right). We also could not
 187 detect a statistically significant interaction between catchment size and agriculture.

188 Effect of precipitation on pesticide risk

189 $prec_0$ and $prec_{-1}$ increased the probability of exceeding LOQ and RQ. In $Q2$ an increase from
 190 0.1 mm to 15 mm of precipitation before sampling ($prec_{-1}$) lead on average to a 43% higher
 191 mean RQ of 0.05 (Supplemental Figure S7). The probability to exceed LOQ increases in $Q2$
 192 1.6-fold from 8.7% to 13.5% (Figure 5). Precipitation before sampling ($prec_{-1}$) had a stronger
 193 effect than precipitation during sampling ($prec_0$) on the probability of exceeding LOQ. This
 194 difference was less pronounced for the mean value of RQ (Supplemental Figure S7, top left).
 195 Moreover, effects differed between individual compounds (see Supplemental Table S4).

196 The first quarter showed the lowest RQ and probability of exceeding LOQ. Both increased
 197 in $Q2$ and decreased towards the end of the year. There was a 2.5-fold higher probability

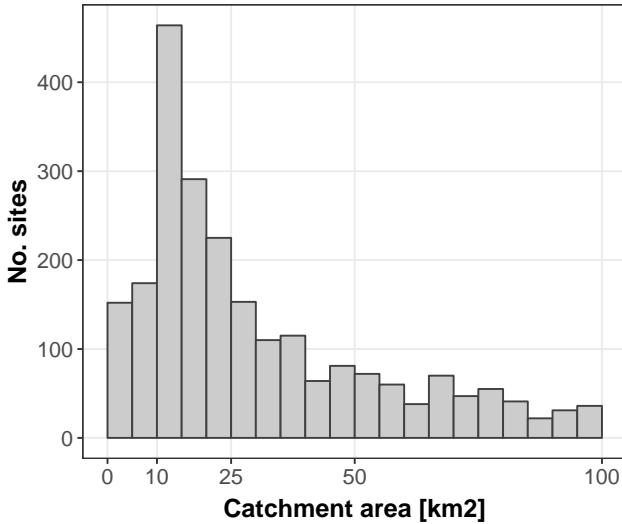


Figure 3: Distribution of catchment area across the sampling sites.

198 of exceeding LOQ in Q_2 (10.6%) than in Q_1 (4.6%) (Figure 5). The differences were less
 199 pronounced for the mean value of RQ and with less precision (see Supplemental Figure S7,
 200 left). Individual compounds showed different temporal patterns (see Supplemental Table S4).

201 Current pesticide risks in small streams

202 We found RAC exceedances in 25.5% of sampling sites and $RQ > 0.1$ in 54% of sites. In
 203 23% of sites none of the chemicals, for which RACs were available, were detected (see also
 204 Supplemental Figure S8). Neonicotinoid insecticides and Chlorpyrifos showed the highest
 205 RQ (Figure 6). For Thiacloprid and Chlorpyrifos the RAC was equal or less than LOQ,
 206 therefore, all detections have a $RQ \geq 1$. The herbicides Nicosulfuron and Diflufenican, as
 207 well as the fungicide Dimoxystrobin also showed high exceedances of RQ (26.7, 14.1 and
 208 21.1 % of measurements $>$ LOQ), see also Supplemental Table S5). RAC exceedances were
 209 found in 14% of samples with concentrations $>$ LOQ (and 7.3% of all samples).

210 The highest RQs were observed for Chlorpyrifos ($\max(RQ) = 220$), Clothianidin ($\max(RQ)$
 211 $= 157$), Dimoxystrobin ($\max(RQ) = 117$) and Isoproturon ($\max(RQ) = 80$). Where anal-
 212 ysed, metabolites exhibited the highest detection rates (for example, Metazachlor sulfonic
 213 acid was detected in 84% of all samples where it was analysed ($n = 3038$, see also Supple-

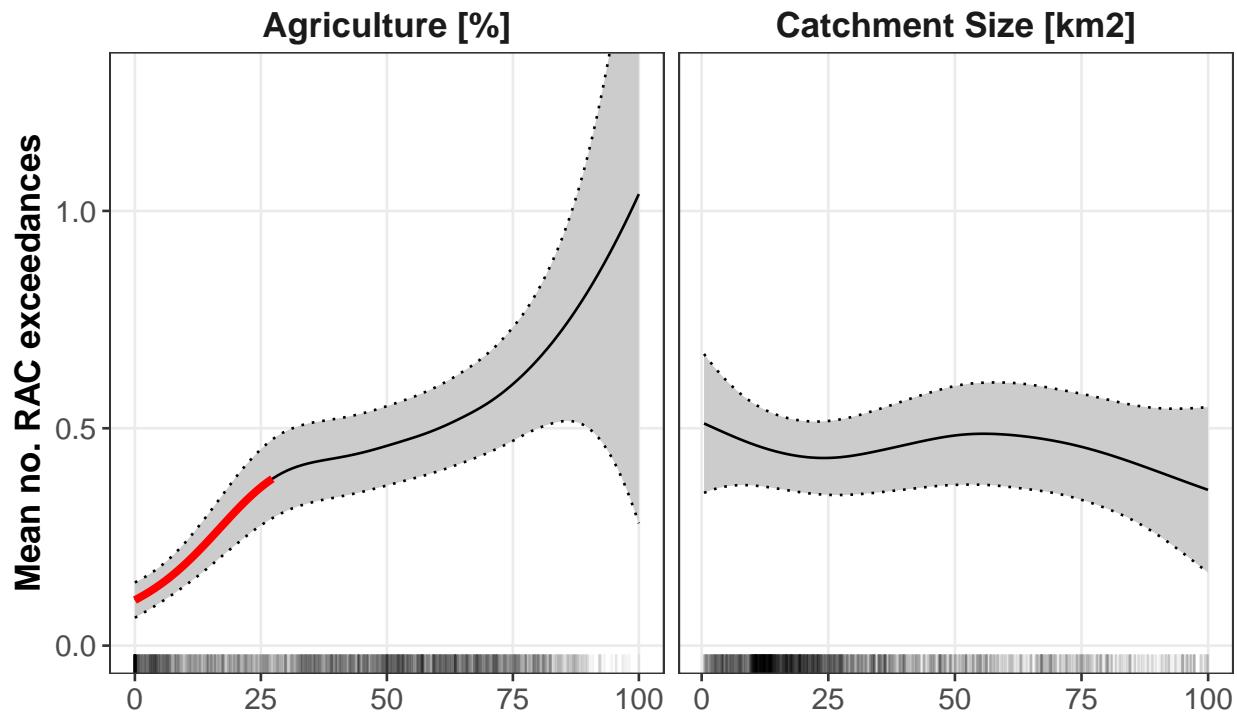


Figure 4: Effect of percent agriculture within the catchment (left) and catchment size (right) on the mean number of RAC exceedances per site. Red line marks statistically significant changes. Dashed lines denote 95% point-wise Confidence Intervals.

²¹⁴ mental Figure S9). Glyphosate was the compound with the highest detection rates (41%, n
²¹⁵ = 3557 samples), followed by Boscalid (23%, n = 9886) and Isoproturon (22%, n = 19112).
²¹⁶ However, only the latter showed RAC exceedances (Figure 6). In 45.9% of samples more than
²¹⁷ one compound was quantified, with a maximum of 54 different compounds in one sample
²¹⁸ (Supplemental Figure S10).

²¹⁹ Discussion

²²⁰ Overview on the compiled dataset

²²¹ The compiled dataset of governmental monitoring data, with a particular focus on small
²²² streams, represents currently the most comprehensive for Germany. Similar nationwide
²²³ datasets have been compiled for the Netherlands³⁵, Switzerland³⁶ and the United States³⁷.

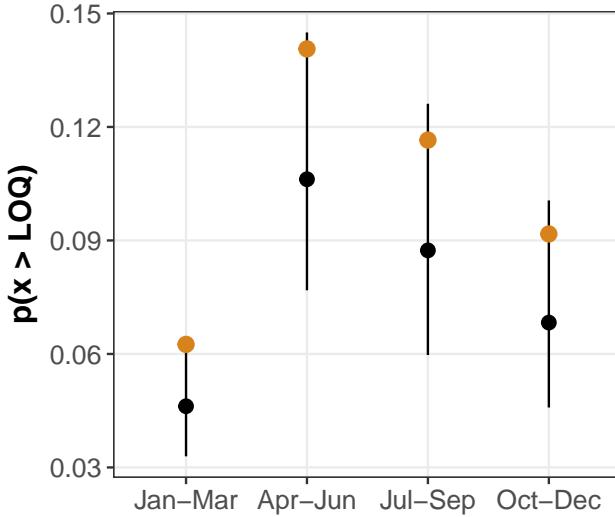


Figure 5: Summarised model predictions for the probability to exceed LOQ throughout the year. Black points indicate the probabilities at 0.1 mm precipitation (and their 95% CI). Orange points indicate the probabilities at 15 mm precipitation. Probabilities have been summarised from a meta-analysis of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

224 While the compilations from Europe are of similar quantity and quality to the data compiled
 225 and analysed here, the compilation used in Stone et al.³⁷ is much smaller, though these data
 226 may be complemented by more data in future analyses.

227 A nationwide assessment of pesticide pollution is hampered by inhomogeneous data across
 228 federal states: Beside large differences in the spatial distribution and quantity of sampling
 229 sites (Figure 1), the spectrum of analysed compounds (Figure 2) and the quality of chem-
 230 ical analyses differed between states. Despite the outlined differences between states, all
 231 ecoregions occurring in Germany^{38,39} and all major stream types were covered by the data
 232 set. The unequal distribution of sampling sites and the different sampling strategies hamper
 233 inference on the total population of small streams in Germany. We accounted for differences
 234 in sampling efforts per site by including the total number of measurement into the statistical
 235 models. However, we acknowledge that additional differences such as sampling frequency and
 236 temporal distribution of the samplings might incur bias between states^{3,18}. Consequently,
 237 we did not compare the results between states. Moreover, it is known that differences in

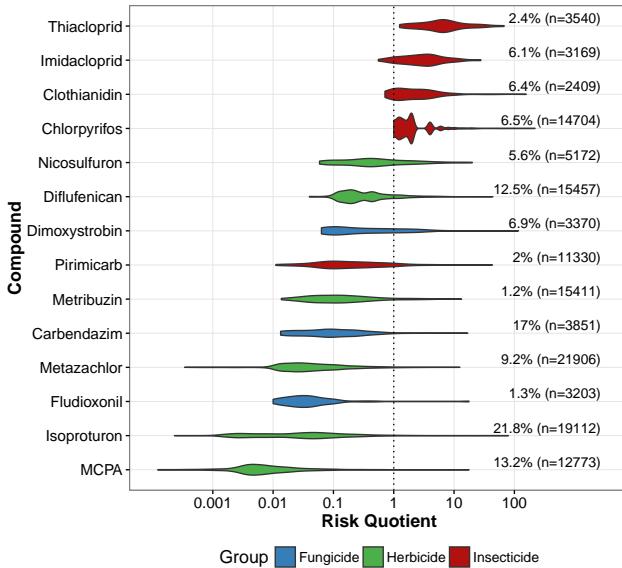


Figure 6: 15 compounds with the highest observed risk quotients in small streams. Non-detects are not shown due to the logarithmic axis. Numbers on the right give the percentage of values >LOQ and the total number of samples were the compound was analysed.

²³⁸ analytical quality can influence estimated effects^{40,41}. However, the used model (Equation 3)
²³⁹ explicitly accounted for LOQs and differences therein.

²⁴⁰ For Thiacloprid and Chlorpyrifos the LOQs were above the RAC, which means that
²⁴¹ exceedances are likely underestimated. For compounds with low RACs a lowering of LOQ
²⁴² through an improvement of chemical analysis is essential for reliable assessment. Moreover,
²⁴³ a nationwide assessment would benefit from a harmonised spectrum of analysed compounds
²⁴⁴ between federal states.

²⁴⁵ Given their high abundance in the landscape¹¹ small streams below 10 km² are dispro-
²⁴⁶portionally less sampled in current monitoring (Figure 3), which may be attributed to the
²⁴⁷ missing categorisation in the WFD. Clearly, there is currently a lack of knowledge on stres-
²⁴⁸sor effects on small streams. We analysed only data from small streams, however, for lentic
²⁴⁹ small water bodies this lack might be even greater¹⁶.

250 Influence of agricultural land use and catchment size

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

258 We did not find a statistically significant relationship between pesticide pollution and
259 catchment size (Hypothesis 2). However, previous studies showed that small streams are
260 more polluted than bigger streams^{7,9,42}. This can be explained by the relatively short gra-
261 dient of catchment sizes in our dataset, with most of the streams with catchments above
262 10 km^2 and below 100 km^2 (Figure 3, top). For example, the gradient of Schulz⁷ covered 6
263 orders of magnitude.

264 Effect of precipitation on pesticide risk

265 We found a 36% higher RQ if samples were taken after rainfall events, which conforms to the
266 hypothesis that run-off is a major input path on the large scale. However, samples taken on
267 the day of a rainfall event showed less risk than samples taken one day after a rainfall event.
268 This discrepancy could be explained by a sampling preceding the rainfall event because the
269 temporal resolution of our dataset was 1 day. Additionally, this might be explained by a
270 delay between the start of a rain event and the peak in discharge or runoff.

271 The effects of precipitation were more pronounced for the probability to exceed LOQ,
272 with smaller effect sizes for the absolute value of RQ. This may be explained by a higher
273 variability of absolute concentrations. Overall, our results indicate that current pesticide
274 monitoring relying on grab sampling, largely disconnected from precipitation events, under-
275 estimates pesticide risks. Automatic event-driven samplers³ and passive samplers^{43,44} may

276 help overcome these shortcomings and provide a better representation of risks. Our results
277 demonstrate that future monitoring of small water bodies should also capture precipitation
278 events, which is in agreement with other studies Lorenz et al.¹⁶.

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

295 Pesticides in small streams

296 Our results suggest that small streams are frequently exposed to ecologically relevant pes-
297 ticide concentrations. In one-quarter of small streams RACs were exceeded at least once.
298 Stehle and Schulz⁹ found the highest percentage of RAC exceedances for organophosphate
299 insecticides. By contrast, we found that neonicotinoid insecticides have highest exceedances
300 of RACs, followed by the organophosphate chlorpyrifos. This difference can be attributed to
301 the low sample size for neonicotinoid insecticides in their study ($n = 33$) compared to the

302 dataset presented here (for example 3,540 samples of Thiacloprid, Figure 6). Overall, our
303 results suggest that neonicotinoids may currently pose a high risk to freshwater ecosystems.
304 Moreover, our results add further evidence to the growing literature on the risks arising from
305 neonicotinoids for aquatic⁴⁸ and terrestrial⁴⁹ ecosystems.

306 Compared to Stehle and Schulz⁹ we found higher rates of RAC exceedances for insec-
307 ticides. They found exceedances in 37.1% of insecticide measurements >LOQ (n = 1352,
308 23 insecticides), whereas, we found exceedances in 67% of insecticide measurements with
309 RACs >LOQ (n = 1855, 22 insecticides). This could be attributed to different insecticides
310 considered and different underlying RACs. Our study has only 7 insecticides with RACs in
311 common with the insecticides investigated by Stehle and Schulz⁹. Moreover, all RACs were
312 lower in our study (average difference = -0.71 µg/L, range = [-2.757; -0.005]). Nevertheless,
313 it must be noted that the dataset compiled here comprised only samples from grab sampling,
314 which may considerably underestimate pesticide exposure^{3,18}.

315 By contrast, Knauer⁴² found exceedances from monitoring data mainly for herbicides
316 and fungicides and only one insecticide Chlorpyrifos-methyl. Moreover, RAC exceedances in
317 Switzerland were generally lower and less abundant (for example 6 exceedances (=0.2%) for
318 Isoproturon with a maximum RQ of 2) compared to our results for Germany. This might
319 reflect differences in pesticide use between countries, ecoregions and RACs used. From
320 the definition of RAC it follows that if the concentration of a compound exceeds its RAC
321 ecological effects are expected. Indeed, Stehle and Schulz⁵⁰ found that the biological diversity
322 of stream invertebrates was significantly reduced by 30% at RQ = 1.12 and by 10% at 1/10
323 of RAC. We found RQ values greater than 1.12 in 25% of small streams and RQ at 1/10 of
324 RAC in 54% of small streams. Consequently, we conclude that agricultural pesticides are
325 on a large scale a major threat to small streams, the biodiversity they host and the services
326 they provide. This threat may exacerbate because pesticides often occur in mixtures⁵¹ and
327 may co-occur with other stressors⁵².

328 Monitoring data, despite the outlined limitations, provides an opportunity to study large-

329 scale environmental occurrence patterns of pesticides. Furthermore, such nationwide com-
330 pilations, may not only be used for governmental surveillance, but also to answer other
331 questions, like validation of exposure modelling,⁵³ retrospective evaluation of regulatory risk
332 assessment^{9,42} or occurrences of pesticide mixtures.⁵¹ However, the sampling design needs to
333 account for precipitation events to provide robust data. Our results suggest that exceedances
334 of RACs are landscape dependent and therefore, pesticide regulation should account for
335 landscape features. Moreover, the high exceedances of RACs indicate that greater efforts
336 are needed to describe causal links, which may lead to further developments of the current
337 authorisation procedure.

338 Acknowledgement

339 The authors thank the federal state authorities and the German Working Group on water
340 issues of the Federal States (LAWA) for providing chemical monitoring data and the Ger-
341 man Environment Agency (UBA) for funding a related project (FKZ 3714 67 4040 / 1).
342 We thank Alexandra Müller, Wolfram König and Volker Mohaupt (German Environment
343 Agency (UBA)), Martin Keller and Beate Bänsch-Baltruschat (German Federal Institute
344 of Hydrology (BfG)), Matthias Liess and Kaarina Foit (Center for Environmental Research
345 (UFZ)) for their contributions to this project.

346 Supporting Information Available

347 The following files are available free of charge.

- 348 • Supplemental _ Materials.pdf : Supplemental Materials (Figures, Tables, Models).
- 349 This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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