

Large scale risks from pesticides in small streams

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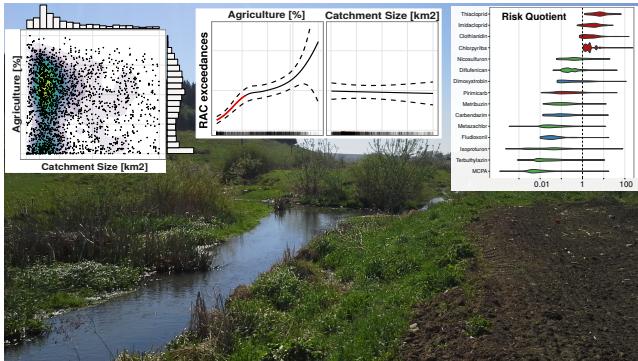
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Abstract

Small streams are important refugia for biodiversity. In agricultural areas they may be at high risk from pesticide pollution. However, most related studies have been limited to a few streams on the regional level, hampering extrapolation to larger scales. We used data from German governmental water quality monitoring to quantify the drivers of pesticide risk and to assess pesticide risk in small streams on a large scale. The data set comprised of 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 using new statistical modelling techniques that explicitly consider the limit of quantification. Agricultural land use lead to a 3.7-fold increase in exceedance of risk thresholds when the proportion of agriculture in a catchment exceeded 28 percent. Precipitation increased pesticide risk by 36% and risk was the highest during summer months. Risk thresholds were exceeded in 26% of streams, with the highest risk related to neonicotinoid insecticides. We conclude that pesticides from agricultural land use

16 are a major threat to small streams and their biodiversity and that a realistic pesticide
17 sampling would be driven by precipitation events.

18 **TOC Art**



19

20 **Introduction**

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

28 Two recent studies indicate that pesticides might threaten freshwater biodiversity in the
29 European union. Malaj et al.⁸ analysed data supplied to the European Union (EU) in the
30 context of the Water Framework Directive (WFD) and showed that almost half of European
31 water bodies are at risk from pesticides. Stehle and Schulz⁹ compiled 1,566 measured con-
32 centrations of 23 insecticides in the EU from scientific publications. They found that many
33 of these measurements exceed regulatory acceptable concentrations (RAC). However, these
34 studies reflect only a small amount of potentially available data (173 sites in predominantly

35 mid-sized and large rivers in Malaj et al.⁸ and 138 measurements in Stehle and Schulz⁹),
36 and it is unclear how representative they are for Germany. Much more comprehensive data
37 on thousands of sites are available from national monitoring programs that are setup for the
38 surveillance of water quality, which is done independently by the federal states in Germany
39 in compliance with the WFD¹⁰ and additional state-specific needs. Despite that these data
40 are providing the opportunity to study pesticide risks and other research questions on a
41 large scale with high spatial density, to date these data have not been compiled and related
42 analyses are lacking.

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

61 In this study, we compiled and analysed large-scale chemical monitoring data from small

62 streams in Germany. First, we analysed the shape of the relationship between pesticide
63 risk, agricultural land use, and catchment size and examined whether related thresholds
64 for pesticide risks can be derived. Second, we investigated the influence of precipitation
65 and seasonal dynamics on pesticide detections, given that precipitation proved an important
66 driver of pesticide exposure in several small-scale studies^{7,18}, but it is unknown whether a
67 precipitation signal prevails on large scales. Finally, we quantified the current risks from
68 pesticides in small streams in Germany and the compounds accountable for the risk.

69 Methods

70 Data compilation

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

77 We identified precipitation at sampling sites by a spatio-temporal intersection of sam-
78 pling events with gridded daily precipitation data (60×30 arcsec resolution) available from
79 the German Meteorological Service (DWD). This data spatially interpolates daily precipi-
80 tation values from local weather stations²⁰. We performed the intersection for the actual
81 sampling date and the day before and extracted precipitation during and up to 48 hours
82 before sampling.

83 Characterization of catchments

84 We compiled a total of 2,369 sampling sites in small streams with pesticide measurements.
85 Alongside, we also queried catchment sizes and agricultural land use within the catchment

86 for the sampling sites from the federal states. Catchment size was provided for 59% of sites.
87 Additionally, we delineated upstream catchments for each of the sampling sites using (i) a
88 digital elevation model (DEM)²¹ and the multiple flow direction algorithm²² as implemented
89 in GRASS GIS 7²³ and (ii) from drainage basins provided by the Federal Institute of Hy-
90 drology (BfG). Delineated catchments were visually checked for accuracy by comparison of
91 coverage with stream networks provided by the federal states. Thus, catchment size infor-
92 mation was available for 99% of all sites (59% from authorities, 24% from DEM and 16%
93 from drainage basins).

94 For each derived catchment (either from DEM or drainage basins) we calculated the
95 % agricultural land-use within the catchment based on the Authoritative Topographic-
96 Cartographic Information System (ATKIS) of the land survey authorities²⁴. Thus, agri-
97 cultural land use information was available for 98% of all sites (24% from authorities, 52%
98 from DEM and 22% from drainage basins). 68 sites (3%) that lacked catchment size or land
99 use information were omitted from the analysis, resulting in 2301 sites used in the analyses
100 outlined below.

101 Characterization of pesticide pollution

102 We characterised pesticide pollution using regulatory acceptable concentrations (RAC)²⁵.
103 RACs are derived during pesticide authorisation as part of the ecological risk assessment.
104 No unacceptable ecological effects are expected if the environmental concentration remains
105 below this concentration. Stehle and Schulz⁹ showed that RAC exceedances reflect a decrease
106 in biodiversity and from this perspective are ecologically relevant indicators. The German
107 Environment Agency (UBA) provided RACs for 107 compounds, including those with the
108 highest detection rates (Supplemental Table S2). Based on these RACs, we calculated Risk
109 Quotients (RQ):

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

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

112 Statistical analyses

113 We expected non-linear responses to agriculture and catchment size and therefore, used
114 generalised additive models (GAM) to establish relationships²⁶. We modelled the number
115 of RAC exceedances ($RQ > 1$) at a site as:

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

116 where $No(RQ > 1)_i$ is the observed number of RAC exceedances at site i . We modelled
117 $No(RQ > 1)_i$ as resulting from a negative binomial distribution (NB) with mean μ_i and
118 a quadratic mean-variance-relationship ($Var(No(RQ > 1)_i) = \mu_i + \frac{\mu_i^2}{\kappa}$). The proportion
119 of agriculture within the catchment ($agri_i$) and the catchment size of the site ($size_i$) were
120 used as predictors of the number of RAC exceedances. β_0 is the intercept and f_1 and f_2 are
121 smoothing functions using penalized cubic regression splines²⁷. The degree of smoothness was
122 estimated using restricted maximum likelihood (REML) during the model fitting process²⁸.
123 The number of measurements per site (n_i) was used as an offset to account for differences
124 in sampling efforts (sampling interval and analysed compound spectrum) at a site and is
125 equivalent to modelling the rate of exceedances. We used point-wise 95% Confidence Intervals
126 (CI) of the first derivative of the fitted smooth to identify regions of statistically significant
127 changes. All data-processing and analyses were performed using R²⁹. GAMs were fitted
128 using the mgcv package²⁸.

129 To assess the influence of precipitation and seasonality, we modelled the RQ of individual
130 compounds as the response variable. RQ and concentrations show a skewed distribution
131 with an excess of zeros (no pesticides detected and quantified). Therefore, we modelled

132 these as two processes (one generating values below the limit of quantification (LOQ) and
 133 one generating values above LOQ) using a Zero-Adjusted Gamma (ZAGA) distribution^{30,31}
 134 (Equation 3). These two processes can be interpreted as changes in the mean value of RQ
 135 (change in μ) and changes in the probability of exceeding LOQ and showing any risk (change
 136 in ν).

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

137 ν_i denotes the probability of a measurement i being above LOQ and f_{Gamma} denotes the
 138 gamma function and is used for values equal to or greater LOQ, with μ being the mean
 139 and σ the standard deviation of RQ. We used the $\log(x + 0.05)$ transformed precipitation
 140 at sampling date ($\log prec_0$) and the day before ($\log prec_{-1}$), as well as quarters of the year
 141 ($Q1 - Q4$) as linear predictors for μ and ν . We used appropriate link functions for μ and ν
 142 and assumed σ to be constant. Equation 4 summarises the deterministic part of the model
 143 for a measurement i .

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

144 To account for temporal autocorrelation and differences between federal states we used
 145 $site$ nested within $state$ as random intercepts. We implemented this model using the *gamlss*
 146 package.³²

147 We fitted this model separately to each compound with a RAC, measured in at least 1000
 148 samples and with more than 5% of values above LOQ ($n = 22$ compounds, see Supplemental
 149 Table S3 for a list of compounds). To summarise the coefficients across the 22 modelled

150 compounds we used a random effect meta-analysis for each model coefficient separately³³,
151 resulting in an averaged effect of the 22 compounds. The results of individual compounds
152 are provided in the Supplemental Table S4 and Figure S7. The meta-analysis was performed
153 using the metafor package³⁴.

154 Results

155 Overview of the compiled data

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

162 In total 478 different compounds used as pesticides and their metabolites were measured
163 at least once (Supplemental Table S2). Most of the compounds were herbicides (179), fol-
164 lowed by insecticides (117) and fungicides (109). Most samples were taken in the months
165 April till October, while fewer samples were taken during winter (see Supplemental Fig-
166 ure S2). We found substantial differences in the spectra of analysed pesticides between
167 federal states (Figure 2). The number of analysed pesticides per state ranged from 57 (SL)
168 to 236 (RP) (Supplemental Table S1). 4% (=71,113) of all measurements were concentrations
169 above LOQ.

170 The distribution of sampling sites across catchment sizes indicated a disproportionately low
171 number of sites with catchments below 10 km², with most sampling sites having catchment
172 sizes between 10 and 25 km² (Figure 3).

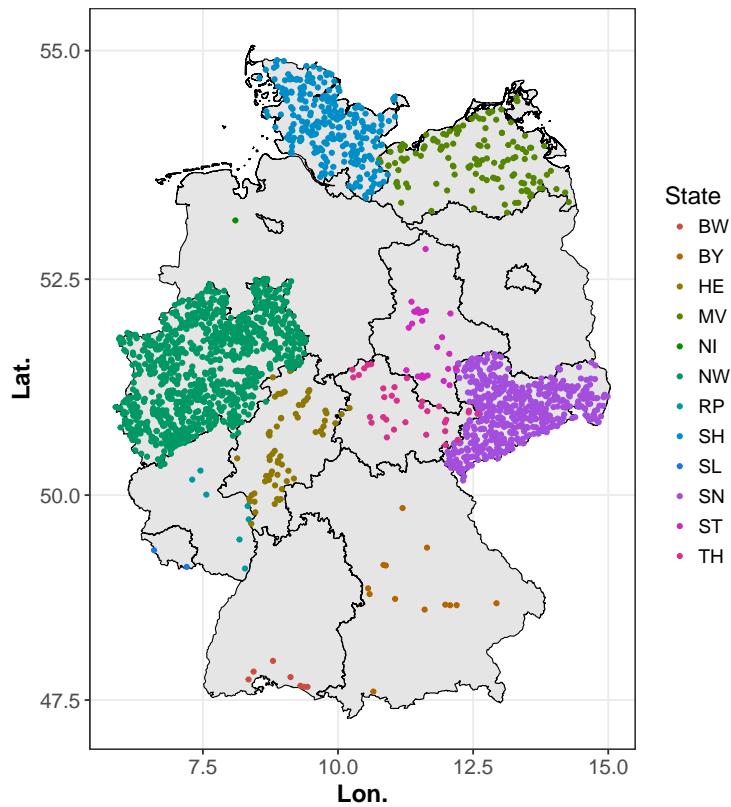


Figure 1: Spatial distribution of the 2,301 small stream sampling sites. Colour codes different federal states (see Supplemental Table S1 for abbreviations).

¹⁷³ Influence of agricultural land use and catchment size

¹⁷⁴ The number of RAC exceedances increased strongly and statistically significant up to 28%
¹⁷⁵ agriculture within the catchment. The mean number of RAC exceedances per site increased
¹⁷⁶ 3.7-fold from 0.10 (no agriculture) to 0.39 (28% agriculture within the catchment). Above
¹⁷⁷ this threshold the exceedances levelled. Above 75% agriculture within the catchment the
¹⁷⁸ number of exceedances further increased, but the increase was not statistically significant
¹⁷⁹ (Figure 4, left). Catchment size had no statistically significant effect on the number of RAC
¹⁸⁰ exceedances (Figure 4, right). We also could not detect a statistically significant interaction
¹⁸¹ between catchment size and agriculture.

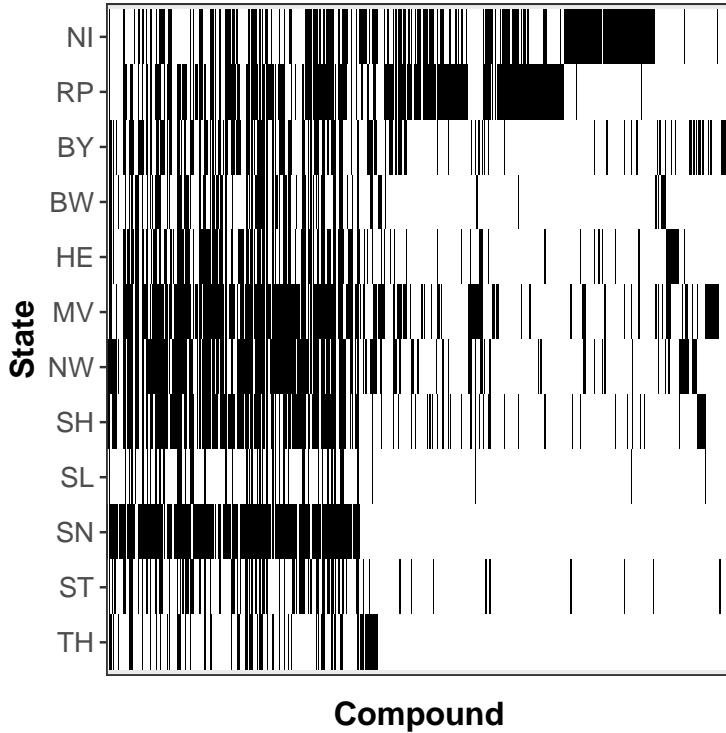


Figure 2: Barcode plot of compound spectra of the federal states. Each vertical line is an analysed compound.

182 Effect of precipitation on pesticide risk

183 The spatio-temporal intersection revealed that most samples were taken during periods of
184 low precipitation. For example, only 5% of the samples were taken at or after days with
185 rainfall events greater than 10mm / day that may lead to run-off (Supplemental Figure S6).
186 $prec_0$ and $prec_{-1}$ increased the probability of exceeding LOQ and RQ. In $Q2$ an increase
187 from 0.1 mm to 10 mm of precipitation before sampling ($prec_{-1}$) lead on average to a 36%
188 higher mean RQ of 0.05. The probability to exceed LOQ increases 1.6-fold from 8.7% to
189 13.5% (Figure 5, top). Effects differed between individual compounds and are provided in
190 the Supplemental Table S4. Precipitation before sampling ($prec_{-1}$) had a stronger effect than
191 precipitation during sampling ($prec_0$) on the probability of exceeding LOQ. This difference
192 was less pronounced for the mean value of RQ (Figure 5, top).

193 The first quarter showed the lowest RQ and probability of exceeding LOQ. Both increased
194 during summer months and decreased towards the end of the year. There was a 2.5-fold

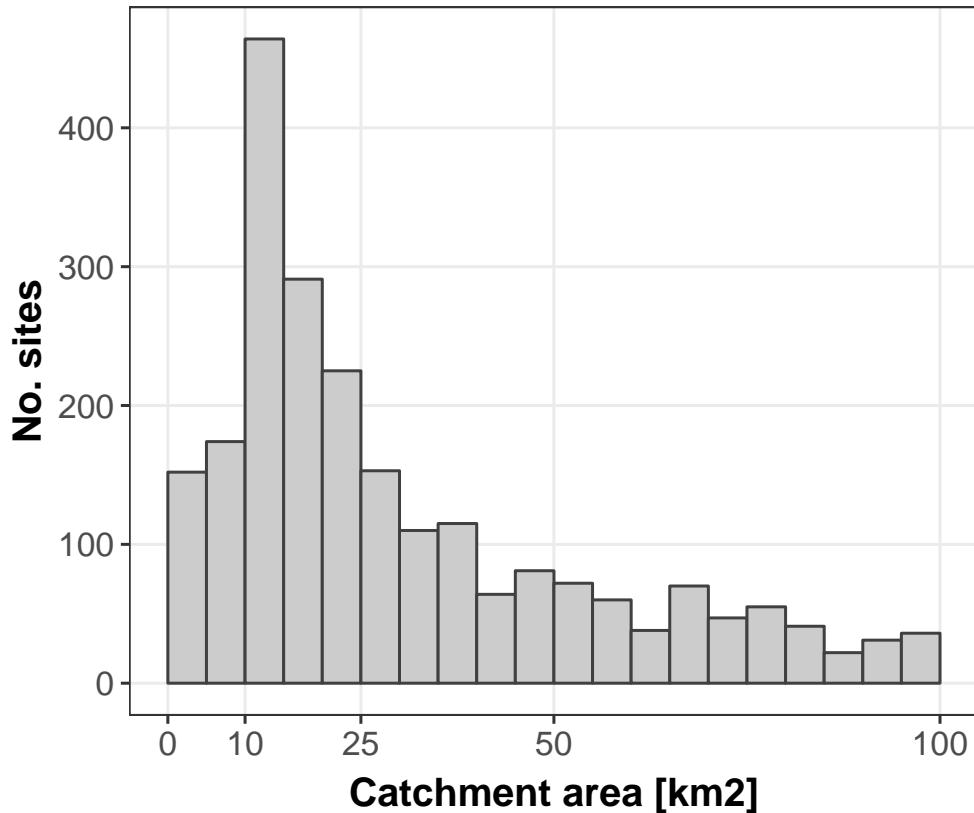


Figure 3: Distribution of catchment area across the sampling sites.

195 higher probability of exceeding LOQ in Q_2 (10.6%) than in Q_1 (4.6%). The differences
 196 were less pronounced for the mean value of RQ and with less precision (Figure 5, bottom).
 197 Individual compounds showed different temporal patterns (see Supplemental Table S4).

198 Pesticide risk in small streams

199 We found RAC exceedances in 25.5% of sampling sites and $RQ > 0.1$ in 54% of sites. In
 200 23% of sites none of the chemicals, for which RACs were available, were detected (see also
 201 Supplemental Figure S8). Neonicotinoid insecticides and Chlorpyrifos showed the highest
 202 RQ (Figure 6). For Thiacloprid and Chlorpyrifos the RAC was equal or less than LOQ,
 203 therefore, all detections have a $RQ \geq 1$. The herbicides Nicosulfuron and Diflufenican, as
 204 well as the fungicide Dimoxystrobin also showed high exceedances of RQ (26.7, 14.1 and
 205 21.1 % of measurements $>$ LOQ), see also Supplemental Table S5). RAC exceedances were

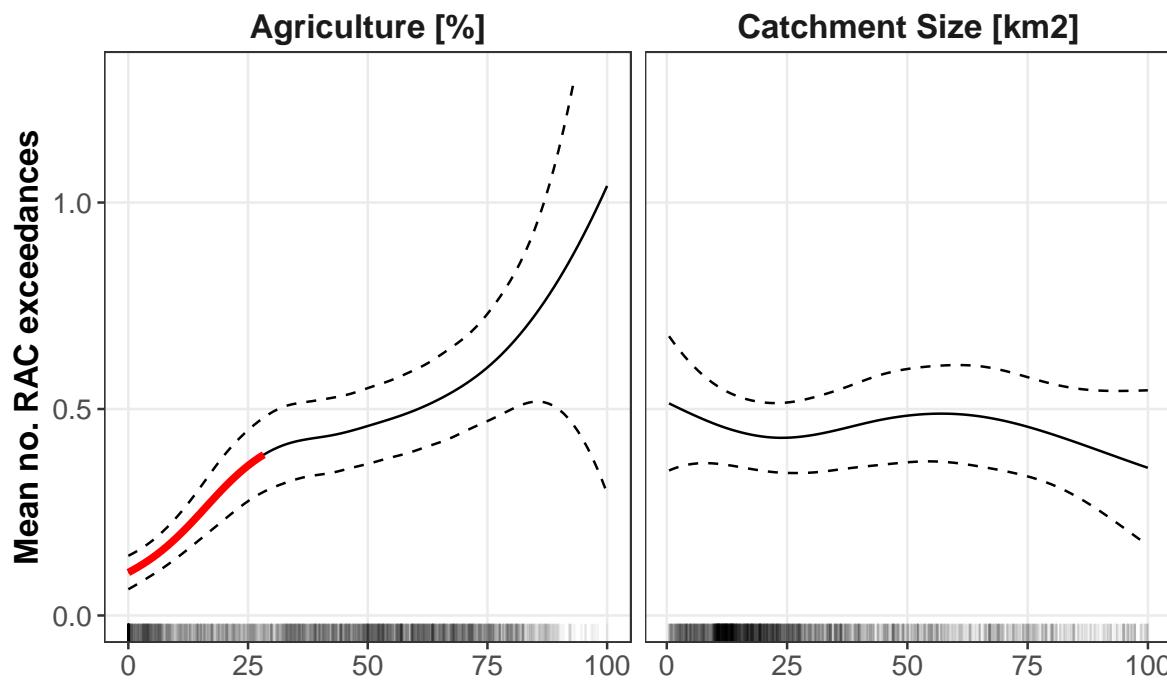


Figure 4: Effect of percent agriculture within the catchment (left) and catchment size (right) on the mean number of RAC exceedances per site. Red line marks statistically significant changes. Dashed lines denote 95% point-wise Confidence Intervals.

²⁰⁶ found in 14% of samples with concentrations >LOQ (and 7.3% of all samples).

²⁰⁷ The highest RQs were observed for Chlorpyrifos ($\text{max}(\text{RQ}) = 220$), Clothianidin ($\text{max}(\text{RQ})$
²⁰⁸ = 157), Dimoxystrobin($\text{max}(\text{RQ}) = 117$) and Isoproturon ($\text{max}(\text{RQ}) = 80$). Where anal-
²⁰⁹ysed, metabolites exhibited the highest detection rates (for example, Metazachlor sulfonic
²¹⁰acid was detected in 84% of all samples where it was analysed ($n = 3038$, see also Supple-
²¹¹mental Figure S9). Glyphosate was the compound with the highest detection rates (41%, n
²¹² = 3557 samples), followed by Boscalid (23%, $n = 9886$) and Isoproturon (22%, $n = 19112$).
²¹³ However, only the latter showed RAC exceedances (Figure 6). In 45.9% of samples more than
²¹⁴one compound was quantified, with a maximum of 54 different compounds in one sample
²¹⁵ (Supplemental Figure S10).

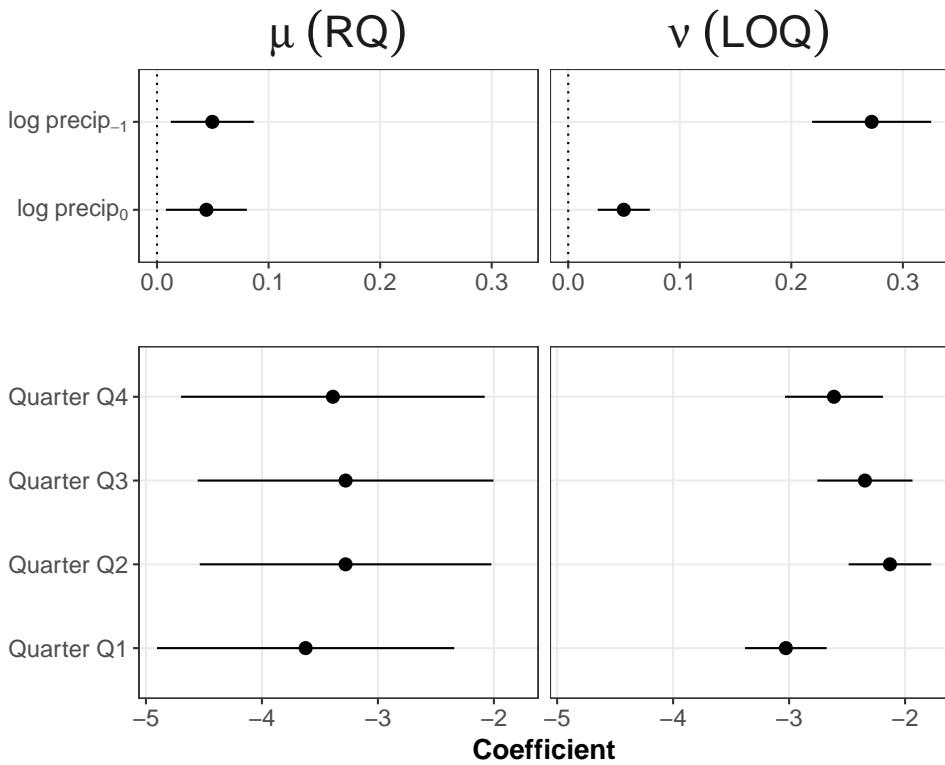


Figure 5: Summarised coefficients (and their 95% CI) for precipitation (top row) and quarter (bottom row) from a meta-analysis of the 22 modelled compounds. Left: coefficients for mean RQ (μ), right: coefficients for probability of exceeding LOQ (ν). Coefficients are shown on the link scale (see Eq. 4). Single compound coefficients are provided in Supplemental Table S4 and Figure S7).

216 Discussion

217 Overview on the compiled dataset

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

224 A nationwide assessment of pesticide pollution is hampered by inhomogeneous data across

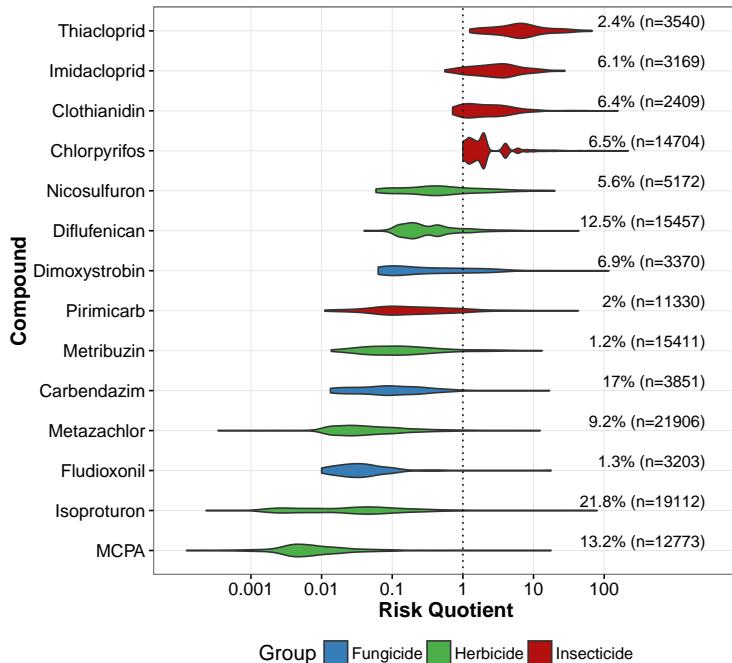


Figure 6: 15 compounds with the highest risk quotients in small streams. Non-detects are not shown due to the logarithmic axis. Numbers on the right give the percentage of values >LOQ and the total number of samples were the compound was analysed.

225 federal states: Beside large differences in the spatial distribution and quantity of sampling
 226 sites (Figure 1), the spectrum of analysed compounds (Figure 2) and the quality of chemical
 227 analyses differed between states. Despite the outlined differences between states, all ecore-
 228 gions occurring in Germany^{38,39} were covered by the presented dataset and thus it might
 229 nonetheless represent a sample covering all types of small streams in Germany. For Thia-
 230 cloprid and Chlorpyrifos the LOQs were above the RAC, which means that exceedances are
 231 likely underestimated. For these compounds a lowering of LOQ through an improvement
 232 of chemical analysis is essential for reliable assessment. Moreover, a nationwide assessment
 233 would benefit from a harmonised spectrum of analysed compounds between federal states.

234 Given their high abundance in the landscape¹¹ small streams below 10 km² are dispro-
 235portionally less sampled in current monitoring (Figure 3), which may be attributed to the
 236 missing categorisation in the WFD. Clearly, there is currently a lack of knowledge on stres-
 237 sor effects on small streams. We analysed only data from small streams, however, for lentic

²³⁸ small water bodies this lack might be even greater¹⁶.

²³⁹ Influence of agricultural land use and catchment size

²⁴⁰ We found a strong influence of agriculture on the pollution of streams. Above 28% agriculture
²⁴¹ within a catchment, it is likely that a RAC will be exceeded, with a further increase in entirely
²⁴² agricultural catchments (above 75 % agriculture). To our knowledge, this is the first study
²⁴³ investigating such thresholds of pesticide risk.

²⁴⁴ We did not find a statistically significant relationship between pesticide pollution and
²⁴⁵ catchment size. However, previous studies showed that small streams are more polluted than
²⁴⁶ bigger streams^{7,9,40}. This can be explained by the relatively short gradient of catchment sizes
²⁴⁷ in our dataset, with most of the streams with catchments above 10 km² and below 100 km²
²⁴⁸ (Figure 3, top). For example, the gradient of Schulz⁷ covered 6 orders of magnitude.

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²⁴⁹ Effect of precipitation on pesticide risk

²⁵⁰ Our results revealed that pesticide sampling for chemical monitoring in Germany is mainly
²⁵¹ performed when no precipitation occurs. Nevertheless, we found a 36% higher RQ if samples
²⁵² were taken after rainfall events. Samples taken on the day of a rainfall event showed less risk
²⁵³ than samples taken one day after a rainfall event. This could be explained by the sampling
²⁵⁴ preceding the rainfall event and the delay between the start of a rain event and the peak in
²⁵⁵ discharge or runoff. The effects of precipitation were more pronounced for the probability to
²⁵⁶ exceed LOQ, with smaller effect sizes for the absolute value of RQ. This may be explained
²⁵⁷ by a higher variability of absolute concentrations. Overall, our results indicate that cur-
²⁵⁸ rent pesticide monitoring relying on grab sampling, largely disconnected from precipitation
²⁵⁹ events, underestimates pesticide risks. Automatic event-driven samplers³ and passive sam-
²⁶⁰ plers^{41,42} may help overcome these shortcomings and provide a better representation of risks,
²⁶¹ especially for small water bodies¹⁶.

²⁶² We found the highest the probability of exceeding LOQ during summer (10% for Q2)

and lowest in the first quarter of the year (4%, Figure 5, bottom right). This annual pattern coincides with the main application season for pesticides in Central Europe. Nevertheless, there are compound-specific differences in the annual pattern, which explains the wide CI for the absolute RQ (Figure 5, bottom left). For example, the herbicide Diflufenican showed the highest RQ and the highest probability of exceeding LOQ during the winter quarters Q1 and Q4 (Supplemental Table S4), which coincides with the application period it is registered for in Germany⁴³. Our study suggests that pesticide risks display compound specific spatio-temporal dynamics. Currently, little is known about these and further research on those might provide useful information for future ecological risk assessment. For example, the sensitivity of organisms is often life stage dependent⁴⁴ and knowledge on temporal dynamics could inform on concurrent exposure to multiple pesticides, as well as assist to parameterise toxicokinetic and toxicodynamic models⁴⁵. Moreover, our results show that analysing absolute concentrations and probabilities of LOQ together might deliver valuable insights into risk dynamics.

Pesticides in small streams

Our results suggest that small streams are frequently exposed to ecologically relevant pesticide concentrations. In one-quarter of small streams RACs were exceeded at least once. Stehle and Schulz⁹ found the highest percentage of RAC exceedances for organophosphate insecticides. By contrast, we found that neonicotinoid insecticides have highest exceedances of RACs, followed by the organophosphate chlorpyrifos. This difference can be attributed to the low sample size for neonicotinoid insecticides in their study ($n = 33$) compared to the dataset presented here (for example 3,540 samples of Thiacloprid, Figure 6). Overall, our results suggest that neonicotinoids may currently pose a high risk to freshwater ecosystems. Moreover, our results add further evidence to the growing literature on the risks arising from neonicotinoids for aquatic⁴⁶ and terrestrial⁴⁷ ecosystems.

Compared to Stehle and Schulz⁹ we found higher rates of RAC exceedances for insec-

ticides. They found exceedances in 37.1% of insecticide measurements >LOQ (n = 1352, 23 insecticides), whereas, we found exceedances in 67% of insecticide measurements with RACs >LOQ (n = 1855, 22 insecticides). This could be attributed to different insecticides considered and different underlying RACs. Our study has only 7 insecticides with RACs in common with the insecticides investigated by Stehle and Schulz⁹. Moreover, all RACs were lower in our study (average difference = -0.71 µg/L, range = [-2.757; -0.005]). Nevertheless, it must be noted that the dataset compiled here comprised only samples from grab sampling, which may considerably underestimate pesticide exposure^{3,48}.

By contrast, Knauer⁴⁰ found exceedances from monitoring data mainly for herbicides and fungicides and only one insecticide Chlorpyrifos-methyl. Moreover, RAC exceedances in Switzerland were generally lower and less abundant (for example 6 exceedances (=0.2%) for Isoproturon with a maximum RQ of 2) compared to our results for Germany. This might reflect differences in pesticide use between countries, ecoregions and RACs used. From the definition of RAC it follows that if the concentration of a compound exceeds its RAC ecological effects are expected. Indeed, Stehle and Schulz⁴⁹ found that the biological diversity of stream invertebrates was significantly reduced by 30% at RQ = 1.12 and by 10% at 1/10 of RAC. We found RQ values greater than 1.12 in 25% of small streams and RQ at 1/10 of RAC in 54% of small streams. Consequently, we conclude that agricultural pesticides are on a large scale a major threat to small streams, the biodiversity they host and the services they provide. This threat may exacerbate because pesticides often occur in mixtures⁵⁰ and may co-occur with other stressors⁵¹.

Monitoring data, despite the outlined limitations, provides an opportunity to study large-scale environmental occurrence patterns of pesticides. Furthermore, such nationwide compilations, may not only be used for governmental surveillance, but also to answer other questions, like validation of exposure modelling,⁵² retrospective evaluation of regulatory risk assessment^{9,40} or occurrences of pesticide mixtures.⁵⁰ However, the sampling design needs to account for precipitation events to provide robust data. Our results suggest that exceedances

³¹⁶ of RACs are landscape dependent and therefore, pesticide regulation should account for
³¹⁷ landscape features. Moreover, the high exceedances of RACs indicate that greater efforts
³¹⁸ are needed to describe causal links, which may lead to further developments of the current
³¹⁹ authorisation procedure.

³²⁰ Acknowledgement

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³²⁷ (UFZ)) for their contributions to this project.

³²⁸ Supporting Information Available

³²⁹ The following files are available free of charge.

- ³³⁰ • Supplemental_Materials.pdf : Supplemental Materials (Figures, Tables, Models).

³³¹ This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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