

Pesticide exposure in small streams in Germany

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Abstract

Small streams are important refugia for biodiversity. In agricultural areas, they may be at high risk of pesticide pollution. However, most related studies have been limited to a few streams on the regional level, hampering extrapolation to larger scales. In Germany, pesticide monitoring is performed by the federal states as part of water quality surveillance.

Introduction

More than 50% of the total land area in Germany are used by agriculture¹. In the year 2014 more than 45,000 tonnes of 766 authorized pesticides were sold for application on this area². The applied pesticides may enter surface waters via spray-drift, edge-of-field run-off

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or drainage^{3–5}. Especially run-off after heavy precipitation events has been shown to be one of the major input routes for pesticides⁶. Once entered the surface waters they may have adverse effects on biota and ecosystem functioning⁷. Although, it is known that pesticides pollution and its effect increase with agricultural land-use, studies investigating the shape of this relationships are missing.

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Malaj et al.⁸ analyzed data supplied to the European Union (EU) in the context of the Water Framework Directive (WFD) and showed that most European water bodies are at risk from pesticides. Stehle and Schulz⁹ compiled 1566 measured concentrations of 23 insecticides in the EU from scientific publications. They found that many of these measurements exceed regulatory acceptable concentrations (RAC). Both studies indicate that pesticides might be a threat to biodiversity in the European union. However, these studies reflect only a small amount of data and it is unclear how representative they are: For Germany the study of Malaj et al.⁸ lists only 175 sites and Stehle and Schulz⁹ only 138 measurements. National monitoring programs are setup for the surveillance of water quality. In Germany these are setup independently by the federal states in compliance with the WFD¹⁰ and additional state specific needs. These programs may provide the most comprehensive data that is currently available for pesticide occurrences in German rivers. However, currently there is no curated national-wide compilation of this monitoring data available.

Small waters (SW) comprise a major fraction of streams¹¹, accommodate a higher proportion of biodiversity compared to larger freshwater systems^{12,13} and play an important role in recolonization of disturbed downstream reaches^{14,15}. However, SWB might be also at high risk of pesticide contamination from adjacent agricultural areas and lower dilution potential⁶. It has been shown that SW are more polluted than bigger streams^{6,9}. Despite their relevance only a small fraction of studies were conducted on pesticide pollution of SW, with only few large scale studies¹⁶.

In this study we try to fill this gap and analyze large scale nation-wide chemical monitoring data from Germany. First, we revise the available monitoring data if it is suitable for

a large scale description of pesticide pollution. Then we analyse the relationship between agricultural land use and catchment size with pesticide pollution and investigate potential thresholds. We also investigate whether samples taken during or shortly after heavy rainfall events or different seasons are more likely to indicate chemical pollution. Finally, we give an overview on the pollution of SWB in Germany.

Methods

Data compilation

We compiled pesticide monitoring data from sampling sites with catchment sizes < 100km² for the years 2005 to 2015 from all 13 non-city federal states of Germany (see supplemental table S1 for the abbreviations of federal state names). We homogenized and unified all data from the states into a common database. We implemented a robust data cleaning workflow (see supplemental figure S1 for details on data processing)¹⁷. Nevertheless, parts of the dataset are proprietary and cannot be shared here.

Given the relevance of precipitation in causing runoff events, we identified chemical samples taken during heavy rainfall events. We performed a spatio-temporal intersection of sampling events with gridded daily precipitation data available the German Weather service. This data spatially interpolates daily precipitation values from local weather stations¹⁸. We performed the intersection for the actual sampling date and the day before.

Characterization of catchments

We compiled a total of 3,049 sampling sites with pesticide measurements. We delineated catchments upstream for each of the sampling sites using a digital elevation model (DEM)¹⁹ and the multiple flow direction algorithm²⁰ as implemented in GRASS GIS 7²¹. Catchment delineation was manually checked for accuracy by comparison with a stream network provided by the government. The delineation algorithm produced only for 30% of the sites

accurate results. For the rest we were able to compile catchment size data from authorities (47% of sites) or drainage basins per stream segment provided by authorities (13% of sites). For 10% of the sites we were not able to compile catchment size data. For each derived catchment (either from DEM or drainage basins) we calculated the relative cover (in %) with agricultural areas based on Official Topographical Cartographic Information System (ATKIS) of the land survey authorities²². We additionally used agricultural cover data provided by authorities (18% of sites), which resulted to 21% of sites with missing agricultural cover data. For 78% of the sites both, the proportion of agricultural land use and catchment size were available.

A clear definition of SWB in terms of catchment or stream size is currently lacking¹⁶. The WFD defines SWB with a catchment size between 10 and 100 km², without further consideration of streams <10km². Lorenz et al.¹⁶ defines SWB with catchment size <10km² as SWB. Because of data scarcity of streams <10 km² (Figure 3) we define in this study all streams below 25 km² as SWB. This catchment size corresponds to a stream width of approximately 2 meters (see Supplement Figure S2).

Characterization of pesticide pollution

We characterized pesticide pollution using regulatory acceptable concentrations (RAC)²³. RACs are derived during pesticide authorization and no unacceptable ecological effect are expected if the environmental concentration remains below this concentration. The German Federal Environmental Agency provided RACs for the 105 compounds with highest detection rates (Supplement, Table S2). We expressed RACs as Risk Quotient (RQ):

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

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

Statistical analyses

All data-processing and analyses were performed using R²⁴. To display differences in the spectra of analyzed compounds between federal states we used Multidimensional Scaling (MDS) based on Jaccard dissimilarity in conjunction with complete linkage hierarchical clustering using the vegan package²⁵. We expected non-linear responses to agriculture and catchment size and therefore, used generalized additive models (GAM) to identify relationships²⁶. We modeled the number of RAC exceedances (RQ >1) as:

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

where No_i is the observed number of exceedances at site i . We modeled No_i as resulting from a negative binomial distribution (NB). The proportion of agriculture within the catchment ($Agri_i$) and the catchment size of the site ($Size_i$) were used as predictors. f_1 and f_2 are smoothing functions using penalized cubic regression splines²⁷. The degree of smoothness was estimated using restricted maximum likelihood (REML) during model fitting process²⁸. The number of samples per site (n_i) was used as an offset to account different sampling efforts (sampling interval and analysed compound spectrum) at a site and is equivalent to modeling the rate of exceedances. We used point-wise 95% Confidence Intervals (CI) of the first derivative of the fitted smooth to check if there are regions of statistically significant changes. GAMs were fitted using the mgcv package²⁸.

While agricultural land use and catchment size vary only between sites, this is not the case for precipitation that changes also with time. Therefore, we modeled the effects of precipitation in a separate model. RQ showed a skewed distribution with an excess of zeros (no pesticides with RAC detected). Therefore, we modeled these as two processes (one generating values below the limit of quantification (LOQ) and one generating values above LOQ) using a Zero-Adjusted Gamma (ZAGA) distribution.^{29,30}

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

π_i denotes the probability of a observation i being above LOQ and f_{Gamma} denotes the gamma function and is used for values greater LOQ, where μ is the mean of the gamma function. We used the precipitation at sampling date ($prec_0$) and the day before ($prec_{-1}$), as well as quarters of the year ($season_{Q1-Q4}$) as linear predictors for μ and π . To account for temporal autocorrelation and differences between federal states we used the site nested within state as random intercepts:

$$\begin{aligned} \log(\mu_i) &= prec_{0ijk} + prec_{-1ijk} + season_{ijk} + state_j + site_{jk} \\ logit(\pi_{ijk}) &= prec_{0ijk} + prec_{-1ijk} + season_{ijk} + state_j + site_{jk} \\ state_j &\sim N(0, \sigma_{state}^2) \\ site_{jk} &\sim N(0, \sigma_{site}^2) \end{aligned} \quad (4)$$

Changes in μ can be interpreted as changes in the absolute value of RQ, whereas changes in π can be interpreted as changes in the probability that there is any risk. We fitted this model separately to each compound with a RAC, with at least 1000 samples and more then 5% of values above quantification limit (see Supplement, Table S3 for a list of compounds). We implemented the model using the gammalss package.³¹

Results

Overview of the compiled data

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

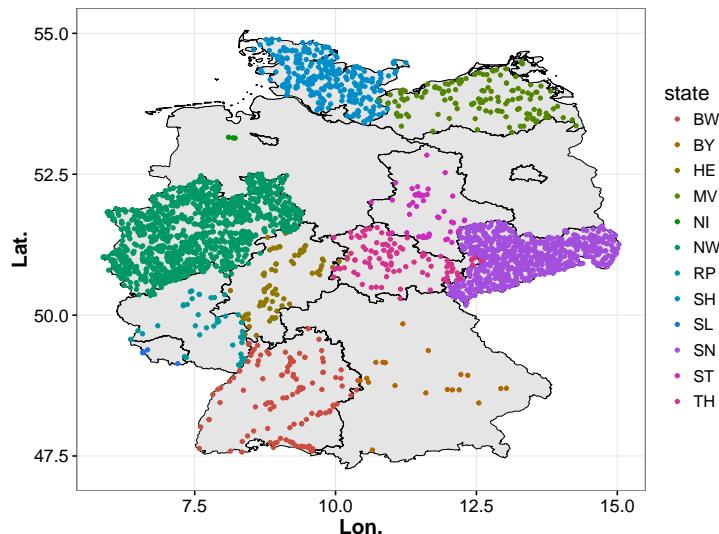


Figure 1: Spatial distribution of the 3109 sampling sites. Colour codes different federal states, see supplemental table S1 for abbreviations.

In total 484 different compounds used as pesticides and their metabolites were measured at least once (Supplement, Table S2). Most of the compounds were herbicides (179), followed by insecticides (117) and fungicides (109). Most samples were taken in the months April till October, with less samples in the winter (see Supplemental Figure S2). Only 5.5% (160,800) of all measurements were detected above the limit of quantification (LOQ). We found substantial differences in the spectra of analyzed compounds between federal states

(Figure 2). Hierarchical clustering revealed three groups (see also Supplement Figure S2):

- i) with less than 100 compounds (SL, ST and TH)
- ii) with medium sized spectra
- iii) with a big and distinct spectrum (RP and NI)

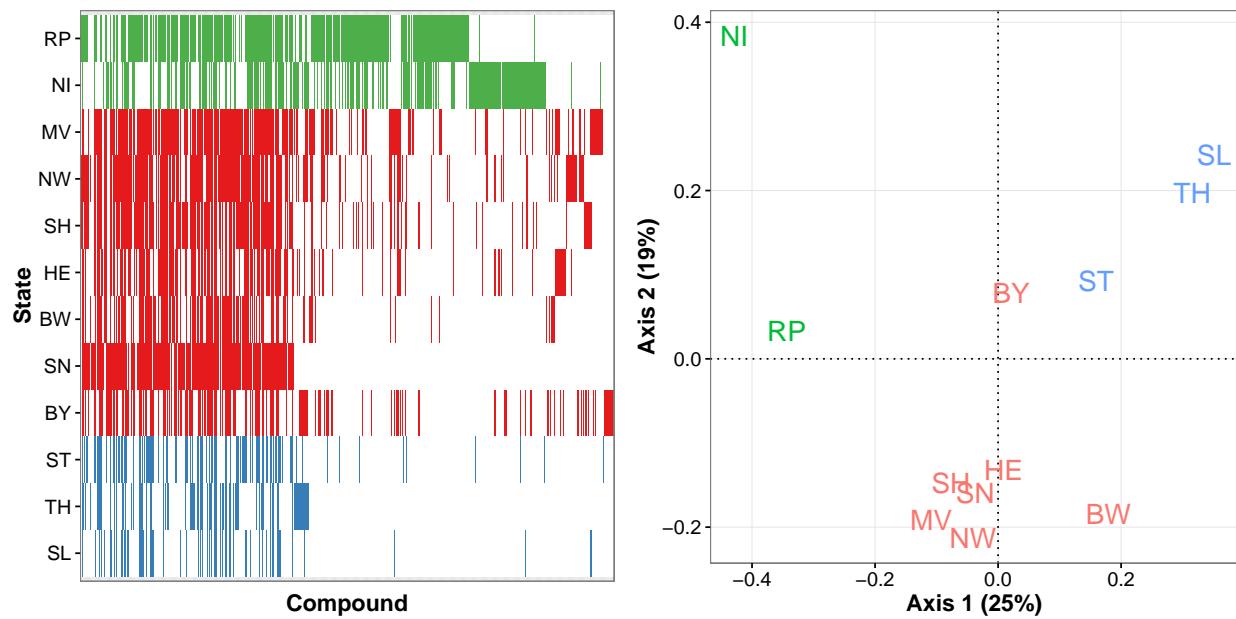


Figure 2: Compound spectra of the different federal states. Left: Barcode plot - each vertical line is an analysed compound. Right: MDS ordination. Colors according to three groups determined by hierarchical clustering (see Supplement Figure S2).

The distribution of sampling sites across catchment area and agricultural area in the catchment revealed a sharp decline in the distribution of catchment-sizes below 10 km^2 , with most sampling sites with catchments between 10 and 25 km^2 (Figure 3). The proportion of agriculture in the catchments decreased with increasing catchment size.

Thresholds for agricultural land use and catchment size

Modeling the number of RAC exceedances as function of agriculture within catchment and catchment size revealed that there is a strong and statistically significant increase up to 25%

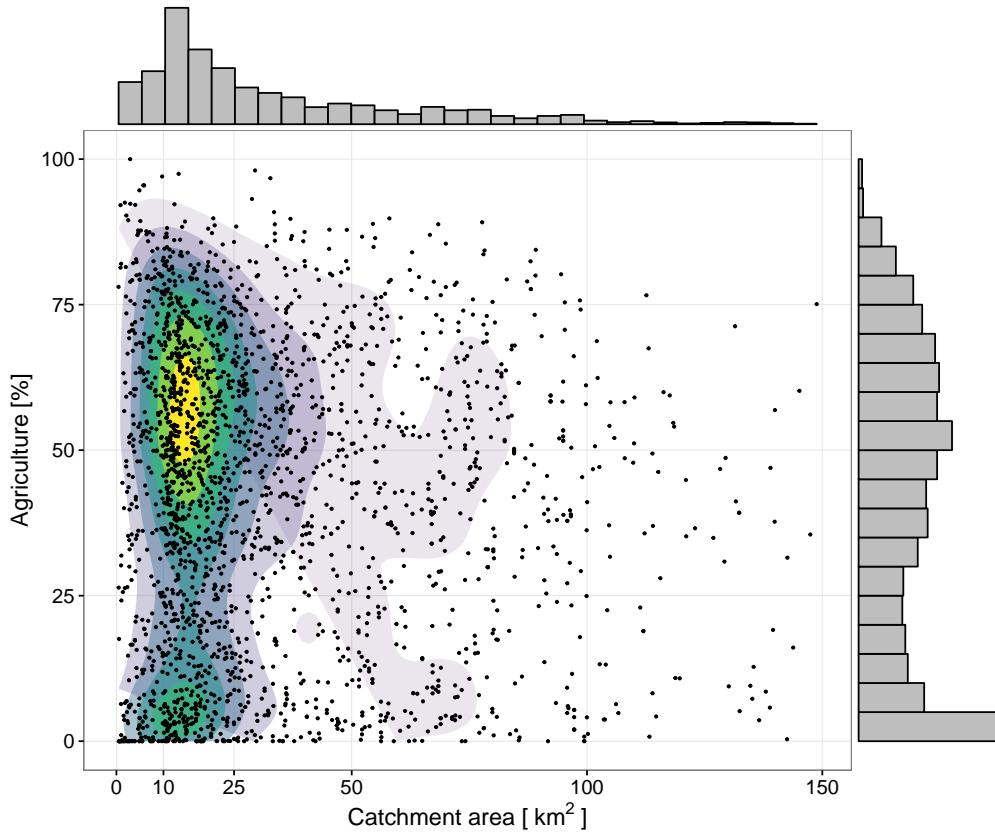


Figure 3: Distribution of catchment area and agriculture within the catchment area across the sampling sites. Only sampling sites with catchment area $< 150 \text{ km}^2$ are displayed. Colour codes the 2-dimensional density of points.

agriculture. Above this threshold the exceedances level off followed by a increase above 75% (Figure 4, left). We could no detect any effect of catchment size on the number of RAC exceedances (Figure 4, right). We also found no statistically significant interaction between catchment size and agriculture.

Effect of precipitation on pesticide exposure

The spatio-temporal intersection revealed that 5% of the samples were taken at or after days with rainfall events greater than 10mm / day (Supplement, Figure S3). Precipitation at the day before (precip_{-1}) sampling increased μ and also π for nearly all modeled compounds. The effects were less pronounced (π) or not directed (μ) for precipitation at the day of sampling (precip_0) (Figure 5, top).

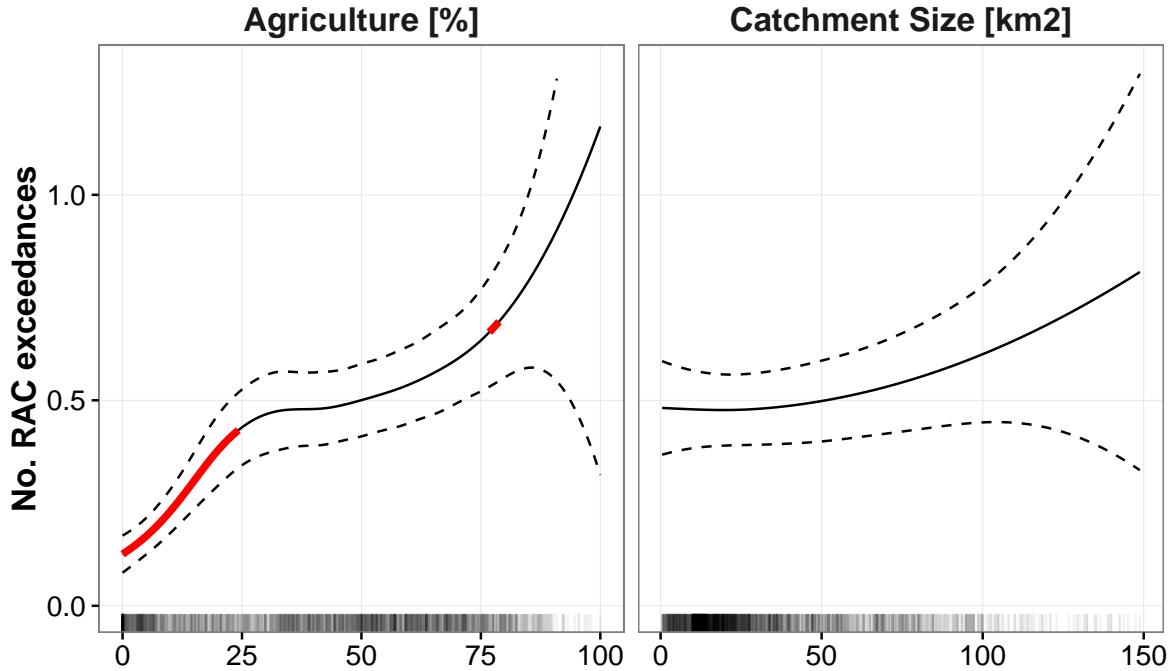


Figure 4: Effect of agriculture within the catchment (left) and catchment size (right) on the number of RAC exceedances. Red line marks statistically significant changes. Dashed lines denote 95% pointwise Confidence Intervals.

Quarters 2-4 showed generally higher μ than in Q1. Exceptions were Diflufenican, that showed lower RQ in Q2-Q4 compared to Q1. Smaller negative effects were found for Clothianidin (Q2) and Isoproturon (Q3) (Figure 5, bottom and Supplement Table S4). We found similar effects on π .

Pesticides in small water bodies

The dataset comprised 12,887 samples from 1313 small water bodies. 1173 samples (0.3% of all and 5.6% of samples with detects) RQ higher than 1 were observed. Neonicotinoid Insecticides and Chlorpyrifos showed highest risk quotients (Figure 6). For Thiacloprid, Imidacloprid and Chlorpyrifos RAC was less than LOQ, therefore, all detections have a RQ >1 . The herbicides Nicosulfuron and Diflufenican, as well as the fungicide Dimoxystrobin showed also high exceedances of RQ (29.5/14.2/21.4 % of all samples with detects). High-

est RQ were observed for Chlorpyrifos ($\text{max}(\text{RQ}) = 244$), Dimoxystrobin($\text{max}(\text{RQ}) = 117$) and Isoproturon ($\text{max}(\text{RQ}) = 80$). Metabolites were most commonly detected in samples (Metazachlor sulfonix acid was in 82% of all samples where it was analysed) (Supplement Figure S8) Glyphosate was the compound with highest detection rates, followed by Boscalid and Isoproturon. However, only the latter showed RQ exceedances (Figure 6). In 44.8% of samples more than one compound was quantified, with a maximum of 54 different compounds in one samples (supplemental figure S7).

Discussion

Overview on the compiled dataset

The compiled dataset of governmental monitoring data represents currently the most comprehensive one available for Germany. Similar nationwide datasets have been compiled for the Netherlands³², Switzerland³³ and the United States (Water Quality Portal (WQP) www.waterqualitydata.us). The data compiled and analysed here for Germany is of similar quantity and quality.

Acknowledgement

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Supporting Information Available

The following files are available free of charge.

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

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

References

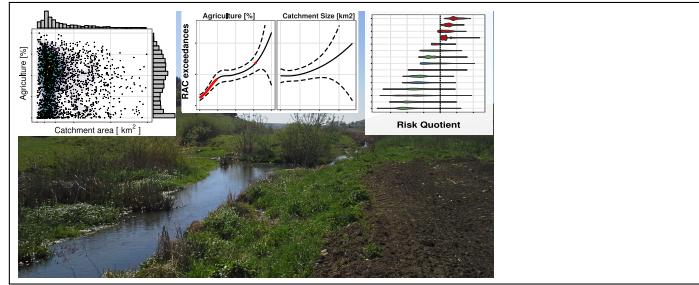
- (1) Statistisches Bundesamt, *Bodenfläche nach Art der tatsächlichen Nutzung*; Fachserie 3 Reihe 5.1; 2014.
- (2) Bundesamt für Verbraucherschutz und Lebensmittelsicherheit, *Absatz an Pflanzenschutzmitteln in der Bundesrepublik Deutschland - Ergebnisse der Meldungen gemäß § 64 Pflanzenschutzgesetz für das Jahr 2014*; 2015.
- (3) Stehle, S.; Knäbel, A.; Schulz, R. Probabilistic risk assessment of insecticide concentrations in agricultural surface waters: a critical appraisal. *Environmental Monitoring and Assessment* **2013**, *185*, 6295–6310.
- (4) Schulz, R. Comparison of spray drift-and runoff-related input of azinphos-methyl and endosulfan from fruit orchards into the Lourens River, South Africa. *Chemosphere* **2001**, *45*, 543–551.
- (5) Liess, M.; Schulz, R.; Liess, M.-D.; Rother, B.; Kreuzig, R. Determination of insecticide contamination in agricultural headwater streams. *Water Research* **1999**, *33*, 239–247.
- (6) Schulz, R. Field Studies on Exposure, Effects, and Risk Mitigation of Aquatic Nonpoint-Source Insecticide Pollution: A Review. *Journal of Environmental Quality* **2004**, *33*, 419–448.
- (7) Schäfer, R. B.; Ohe, P. v. d.; Rasmussen, J.; Kefford, J. B.; Beketov, M.; Schulz, R.; Liess, M. Thresholds for the effects of pesticides on invertebrate communities and leaf breakdown in stream ecosystems. *Environmental Science & Technology* **2012**, *46*, 5134–5142, pdf RS.
- (8) Malaj, E.; Ohe, P. C. v. d.; Grote, M.; Kühne, R.; Mondy, C. P.; Usseglio-Polatera, P.; Brack, W.; Schäfer, R. B. Organic chemicals jeopardize the health of freshwater ecosys-

- tems on the continental scale. *Proceedings of the National Academy of Sciences* **2014**, *111*, 9549–9554.
- (9) Stehle, S.; Schulz, R. Pesticide authorization in the EU—environment unprotected? *Environmental Science and Pollution Research* **2015**,
- (10) Quevauviller, P.; Borchers, U.; Thompson, C.; Simonart, T. *The Water Framework Directive: Ecological and Chemical Status Monitoring*; John Wiley & Sons, 2008.
- (11) Nadeau, T.-L.; Rains, M. C. Hydrological Connectivity Between Headwater Streams and Downstream Waters: How Science Can Inform Policy1: Hydrological Connectivity Between Headwater Streams and Downstream Waters: How Science Can Inform Policy. *JAWRA Journal of the American Water Resources Association* **2007**, *43*, 118–133.
- (12) Davies, B. R.; Biggs, J.; Williams, P. J.; Lee, J. T.; Thompson, S. A comparison of the catchment sizes of rivers, streams, ponds, ditches and lakes: implications for protecting aquatic biodiversity in an agricultural landscape. *Hydrobiologia* **2008**, *597*, 7–17.
- (13) Biggs, N.; Nicolet, P.; Mlinaric, M.; Lalanne, T. *Report of the Workshop on the Protection and Management of Small Water Bodies*; 2014.
- (14) Liess, M.; von der Ohe, P. C. Analyzing effects of pesticides on invertebrate communities in streams. *Environmental Toxicology and Chemistry* **2005**, *24*, 954–965.
- (15) Orlinskiy, P.; Münze, R.; Beketov, M.; Gunold, R.; Paschke, A.; Knillmann, S.; Liess, M. Forested headwaters mitigate pesticide effects on macroinvertebrate communities in streams: Mechanisms and quantification. *Science of The Total Environment* **2015**, *524*, 115–123.
- (16) Lorenz, S.; Rasmussen, J. J.; Süß, A.; Kalettka, T.; Golla, B.; Horney, P.; Stähler, M.; Hommel, B.; Schäfer, R. B. Specifics and challenges of assessing exposure and effects of pesticides in small water bodies. *Hydrobiologia* **2016**, 1–12.

- (17) Poisot, T. Best publishing practices to improve user confidence in scientific software. *Ideas in Ecology and Evolution* **2015**, *8*.
- (18) Rauthe, M.; Steiner, H.; Riediger, U.; Mazurkiewicz, A.; Gratzki, A. A Central European precipitation climatology – Part I: Generation and validation of a high-resolution gridded daily data set (HYRAS). *Meteorologische Zeitschrift* **2013**, *22*, 235–256.
- (19) EEA, Digital Elevation Model over Europe (EU-DEM). 2013; <http://www.eea.europa.eu/data-and-maps/data/eu-dem#tab-metadata>.
- (20) Holmgren, P. Multiple flow direction algorithms for runoff modelling in grid based elevation models: An empirical evaluation. *Hydrological Processes* **1994**, *8*, 327–334.
- (21) Neteler, M.; Bowman, M. H.; Landa, M.; Metz, M. GRASS GIS: A multi-purpose open source GIS. *Environmental Modelling & Software* **2012**, *31*, 124–130.
- (22) AdV, ATKIS - Amtliche Geobasisdaten. 2016; <http://www.adv-online.de/AAA-Modell/ATKIS/>, Arbeitsgemeinschaft der Vermessungsverwaltungen der Länder der Bundesrepublik Deutschland.
- (23) Brock, T. C. M., Alix, A., Brown, C. D., Capri, E., Gottesbüren, B. E., Heimbach, F., Lythgo, C. M., Schulz, R., Streloke, M., Eds. *Linking aquatic exposure and effects: risk assessment of pesticides: EU and SETAC Europe workshop ELINK, Bari, Italy, and Wageningen, Netherlands*; CRC Press: Boca Raton, 2010.
- (24) R Core Team, *R: A Language and Environment for Statistical Computing*; R Foundation for Statistical Computing: Vienna, Austria, 2016.
- (25) Oksanen, J.; Blanchet, F. G.; Kindt, R.; Legendre, P.; Minchin, P. R.; O'Hara, R. B.; Simpson, G. L.; Solymos, P.; Stevens, M. H. H.; Wagner, H. *vegan: Community Ecology Package*; 2016; R package version 2.3-5.

- (26) Fewster, R. M.; Buckland, S. T.; Siriwardena, G. M.; Baillie, S. R.; Wilson, J. D. Analysis of population trends for farmland birds using generalized additive models. *Ecology* **2000**, *81*, 1970–1984.
- (27) Wood, S. N. *Generalized additive models: An introduction with R*; Texts in statistical science; Chapman /& Hall/CRC: Boca Raton and Fla, 2006.
- (28) Wood, S. N. Fast stable restricted maximum likelihood and marginal likelihood estimation of semiparametric generalized linear models. *Journal of the Royal Statistical Society: Series B (Statistical Methodology)* **2011**, *73*, 3–36.
- (29) Rigby, R. A.; Stasinopoulos, D. M. Generalized additive models for location, scale and shape,(with discussion). *Applied Statistics* **2005**, *54*, 507–554.
- (30) Stasinopoulos, M.; Akantziliotou, B. R. w. c. f. C.; Heller, G.; Ospina, R.; Motpan, N.; McElduff, F.; Voudouris, V.; Djennad, M.; Enea, M.; Ghalanos, A. *gamlss.dist: Distributions to be Used for GAMlSS Modelling*; 2016; R package version 4.3-6.
- (31) Stasinopoulos, D. M.; Rigby, R. A. Generalized additive models for location scale and shape (GAMLSS) in R. *Journal of Statistical Software* **2007**, *23*, 1–46.
- (32) Vijver, M. G.; Van 'T Zelfde, M.; Tamis, W. L.; Musters, K. J.; De Snoo, G. R. Spatial and temporal analysis of pesticides concentrations in surface water: Pesticides atlas. *Journal of Environmental Science and Health, Part B* **2008**, *43*, 665–674.
- (33) Munz, N.; Leu, C. Pestizidmessungen in Fließgewässern - schweizweite Auswertung. *Aqua & Gas* **2011**, *11*, 32–41.

Graphical TOC Entry



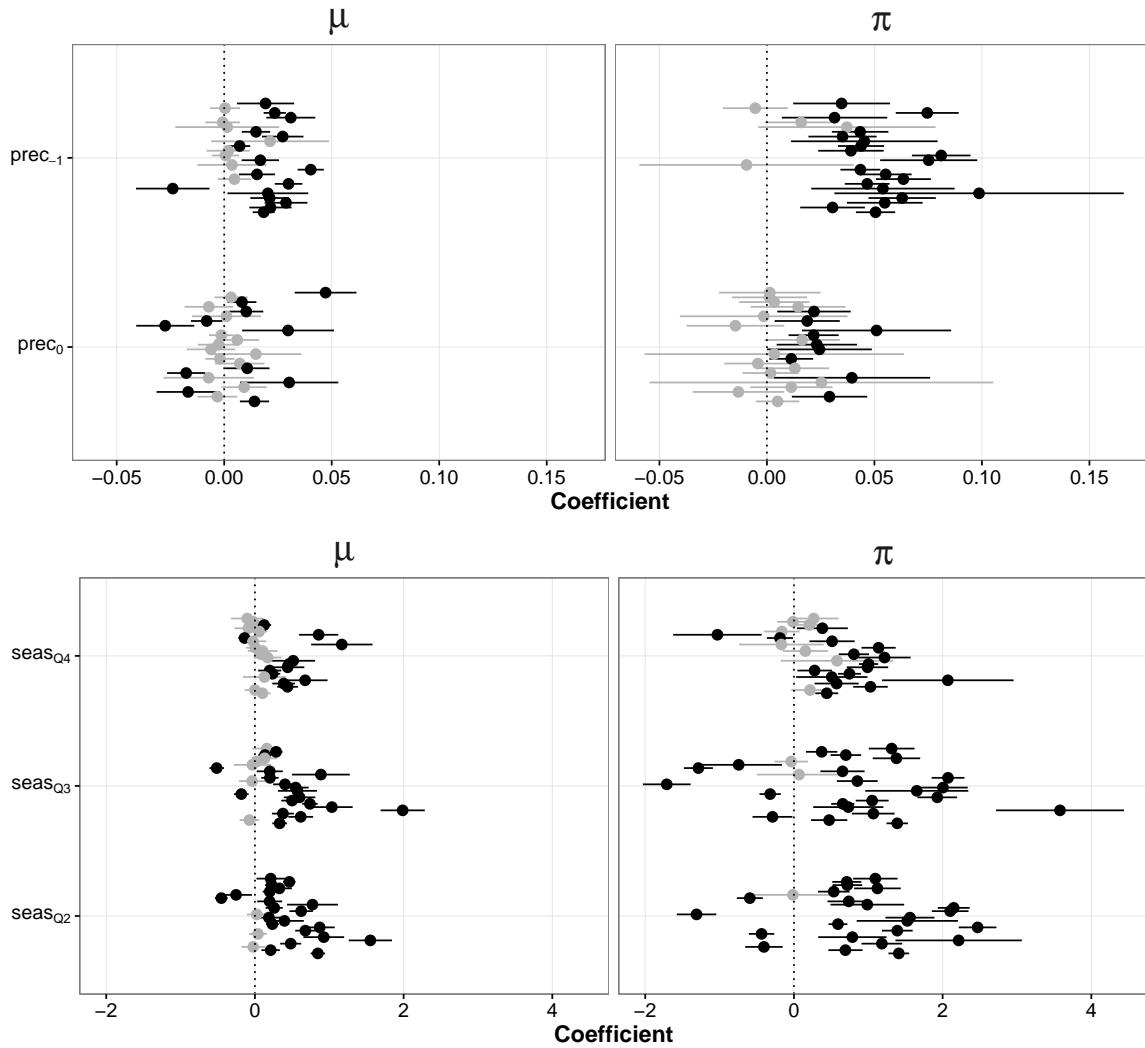


Figure 5: Estimated coefficients and their 95% CI for the model described in equations 3 and 4 for each of the 24 analysed compounds (see Supplement Tables S3 and S4 for a list of compounds from top to bottom and their respective coefficients). Left column: Effect on mean RQ (μ); Right column: effect on the probability that $\text{RQ} > 0$ (π). Coefficients where the CI encompasses zero are shown in gray colour.

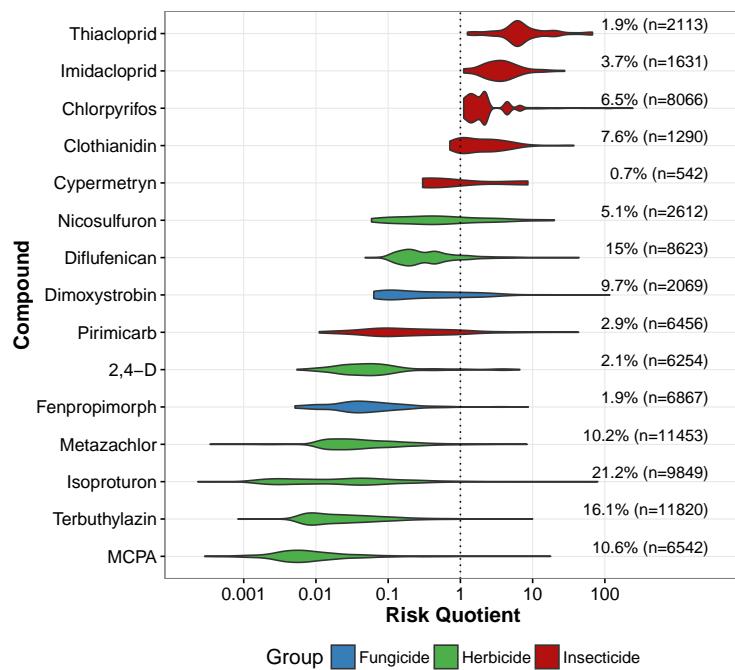


Figure 6: 15 compounds with highest risk quotients in SWB. Non-detects are not shown due to the logarithmic axis. Numbers on the right give the percentage of $RQ > 0$ and total number of samples.