# Pesticides pollution of small streams in Germany

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#### Abstract

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## Introduction

The aim of this study was (i) to compile monitoring data on a national scale and to answer the questions:

- (ii) Is the data a representative description of the pollution situation?
- (iii) Are small agricultural waters more polluted compared to bigger streams? Are there thresholds?
- (iv) How polluted are small streams and which pesticides are responsible?

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## Methods

#### Data compilation

We queried chemical monitoring data of pesticides from sampling sites with catchment size  $< 100 \mathrm{km}^2$  for the years 2005 to 2015 from all 13 non-city federal states of Germany. Additionally, we compiled data available from previous studies and searched online databases. This yielded to a total of more than 30 datasets of different formats.

We homogenized and unified these datasets into a common database. We implemented a robust and transparent data cleaning work flow<sup>1</sup>, though parts of the dataset are proprietary. An overview of the data cleaning process is provided in the supplemental materials. The compiled dataset comprised only a small fraction of stand waters and most of the samples where sampled via grab sampling. Therefore, we report only results for grab sampling from streams. To assess whether grab samples were taken during potential rainfall events we intersected sampling coordinates and date with daily precipitation data<sup>2</sup>.

### Characterization of chemical pollution

We characterized chemical pollution using three indicators:

- 1. National and international Environmental Quality Standards (EQS)<sup>3,4</sup>: We used only Maximum Annual Concentration EQS (MAC-EQS) for characterization.
- 2. Regulatory Acceptable Concentrations (RAC)<sup>5</sup>: This is the lowest concentration at which no acceptable biological effects are expected. These are derived during regulatory approval process of pesticides and contains a uncertainty factor. The German Federal Environmental Agency provided RACs for this study.
- 3. Maximum Toxic Units  $(TU_{max})^6$ :

$$TU_{max} = max(\frac{C_i}{EC_{50,D.magna,i}}) \tag{1}$$

Were  $C_i$  is the concentration of compound i in a sample and  $EC_{50,D.magna,i}$  is the concentration of this compound where 50% of the exposed animals showed after 48 hours an effect in a laboratory study. We compiled  $EC_{50,D.magna}$  values from literature<sup>7</sup>, databases<sup>8,9</sup> or model predictions<sup>10</sup>, where experimental data had priority. We used the maximum TU per sample, as it is independent of the number of measured compounds and makes no assumptions on the mode of action.

#### Characterization of catchments

We delineated catchments upstream of the sampling sites using a digital elevation model<sup>11</sup> and a multiple flow direction algorithm<sup>12</sup> as implemented in GRASS GIS 7<sup>13</sup>. Catchment delineation has been manually checked for accuracy. In areas with low relief energy the delineation algorithm did not produce accurate results and we used river catchments provide by federal state authorities in these cases. For each catchment we calculated the relative coverage (%) with agricultural areas based on Official Topographical Cartographic Information System (ATKIS) of the land survey authorities.

### Statistical analyses

## Results

## Overview and representativeness of compiled data

We compiled a national scale dataset comprising 42236 samples from 3049 sampling sites (Figure 1 and Supplement). We found big differences in the number of sampling sites between federal states.

The dataset include 484

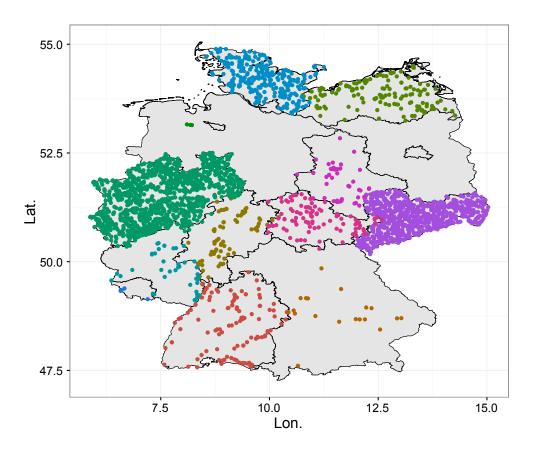


Figure 1: Map of the 3109 sampling sites. Colour codes different federal states.

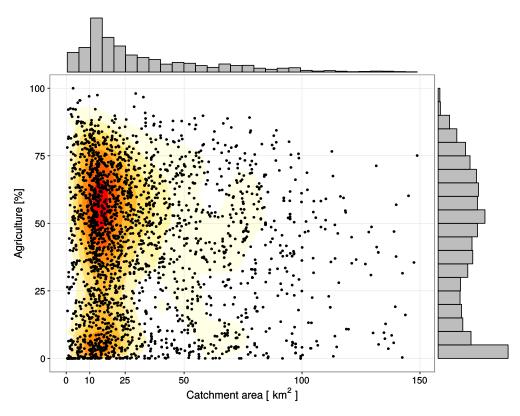


Figure 2: Distribution of catchment area and agriculture within the catchment area across the sampling sites. Only sampling sites with catchment area  $<150~\rm km^2$  are displayed. Colour codes the 2-dimensional density of points

Are small agricultural waters more polluted compared to bigger streams?

#### Pesticide pollution of small streams

## Discussion

Vergleich mit der Schweiz.....

#### Subsection

#### Acknowledgement

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#### Supporting Information Available

The following files are available free of charge.

 $\bullet \ Supplemental\_Materials.pdf: Supplemental\ Materials$ 

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

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