Pesticides pollution of small streams in Germany

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Abstract

Fehlt noch...

Introduction

More than 50% of the total land area in Germany are used by agriculture[1]. In the year 2014 more the 45,000 tonnes of 766 authorized pesticides were sold for application on this area[2]. The applied pesticides may enter surface waters via spray-drift, edge-off-field run-off or drainage, with run-off being one of the major input routes[3,4]. Once entered the surface waters pesticides are frequently detected in environmental monitoring[5] and may have adverse effects on biota and ecosystem functioning[6,7].

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National monitoring programs are setup for determination and surveillance of the chemical and ecological status of surface, ground and drinking water. These monitoring programs produce huge amounts of data, which possibly can also be used to answer other questions. In Germany monitoring programs are setup by the federal states in compliance with the Water Framework Directive[8] and further state specific needs. However, currently there is no curated national-wide compilation of this data.

Small water bodies are important refuges of biodiversity[9] and enabling downstream colonisation of polluted streams[10]. At the same time they may be exposed to a high risk of pesticide contamination from adjacent agricultural areas and low dilution effects[4]. Although small streams comprise a major fraction of streams[11] relatively little is know about their chemical and ecological status.

The aim of this study was to compile monitoring data on a national scale and to answer the questions:
(i) Can the currently available monitoring data used for a representative description of the pollution situation?
(ii) Are small agricultural waters more polluted compared to bigger streams? Are there thresholds in these relationships?
(iii) baHow polluted are small streams and which pesticides are responsible?

Methods

Data compilation

We queried chemical monitoring data of pesticides from sampling sites with catchment size $< 100\text{km}^2$ 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 then 30 datasets of different formats. In the following we will use the ISO 3166-2:DE standard abbreviations for federal states.

We homogenized and unified these datasets into a common database. We implemented a robust and transparent data cleaning work flow[12], though parts of the dataset are proprietary. An overview of the data cleaning process is provided in the supplemental materials. To assess whether samples were taken during potential rainfall events we intersected sampling coordinates with daily precipitation data[13] from the sampling date and the day before.

Characterization of chemical pollution

We characterized chemical pollution using three indicators:

1. National and international Environmental Quality Standards (EQS)[14,15]: We used only Maximum Annual Concentration EQS (MAC-EQS) for characterization.

2. Regulatory Acceptable Concentrations (RAC)[16]: This is the lowest concentration at which no acceptable biological effects are expected. These are derived during authorization process of pesticides and contain an uncertainty factor. The German Federal Environmental Agency provided RACs for this study. We expressed RAC as Risk Quotient (RQ)

$$RQ = \frac{C}{RAC} \tag{1}$$

   Where C is the concentration of a compound in a sample.

3. Maximum Toxic Units ($\mathrm{TU}_{\mathrm{max}}$)[17]:

$$TU_{max} = max(\frac{C_i}{EC_{50,D.magna,i}}) \tag{2}$$

   Where 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[5], databases[18,19] or model predictions[20], 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. A table of all included compounds can be found in the supplement.

Characterization of catchments

We delineated catchments upstream of the sampling sites using a digital elevation model[21] and a multiple flow direction algorithm[22] as implemented in GRASS GIS 7[23]. 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

We used Multidimensional Scaling (MDS) based on jaccard dissimilarity in conjunction with hierarchical clustering to display differences in the spectra of analysed compounds per federal state.

Results

Overview and representativeness of compiled data

The compiled dataset comprised only few standing waters (58 sites) and the majority (90%) of samples where taken via grab sampling. Therefore, we report only results of grab samples from streams. The analysed dataset comprised 42236 samples from 3049 sampling sites. We found big differences in the number of sampling sites between federal states (Figure 1 and Supplement, Table).

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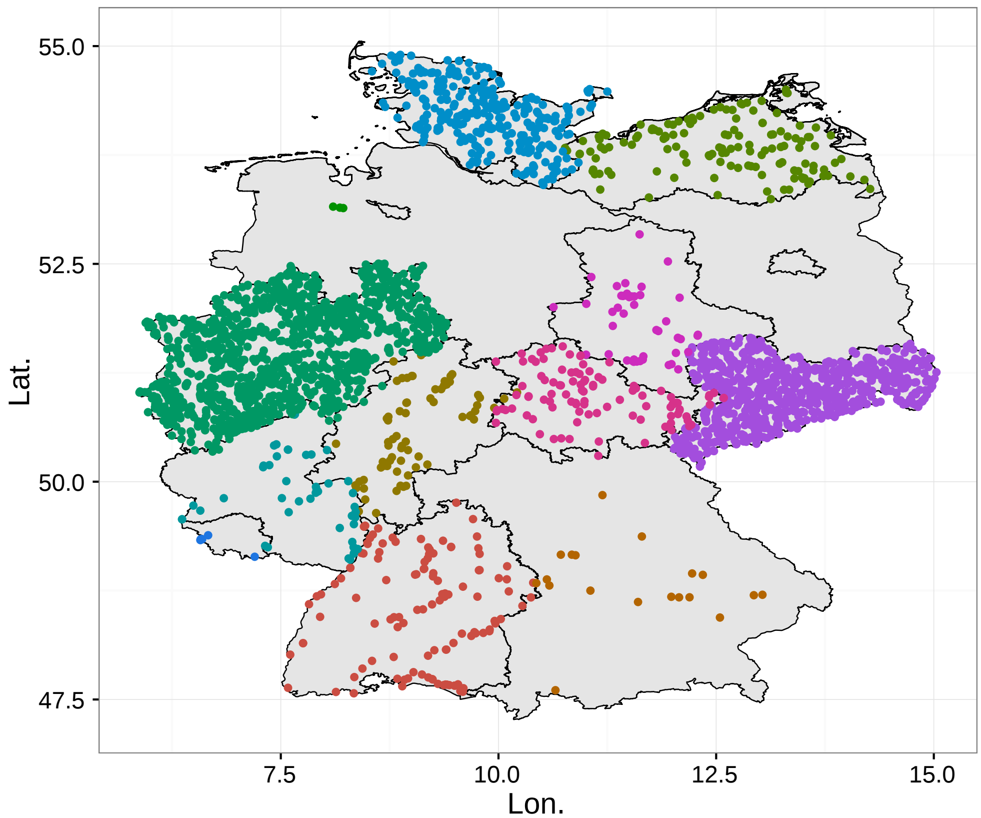

Figure 1: Spatial distribution of the 3109 sampling sites. Colour codes different federal states.

In total 484 different compounds that could be classified as pesticides and their metobalites were measured at least once (Supplement, Table). Most of the compounds were herbicides (179), followed by insecticides (117) and fungicides (109). We found substantial differences of the spectra of analysed compounds (Figure 2). Hierarchical clustering revealed three groups of states: i) with less then 100 compounds (SL, ST and TH), ii) with a medium sized spectra and iii) with a big and distinct spectra (RP and NI). Only 5% of the samples were taken at or after days with rainfall events greater than 10mm / day.

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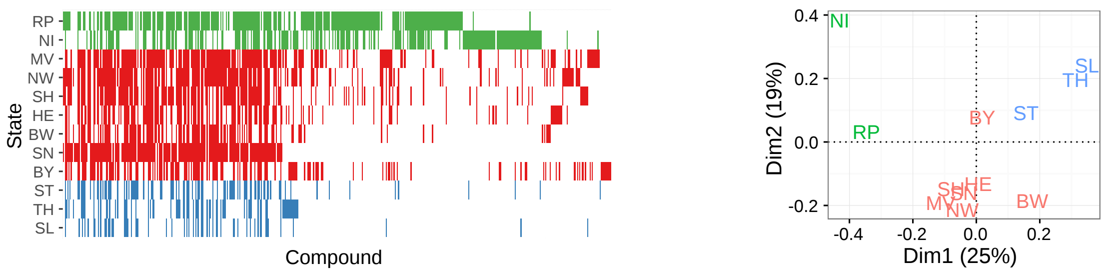

Figure 2: Compound spectra of the different federal states. Left: Barcode plot - Each vertical line is an analysed compound. Right: MDS ordination. Colors according to three groups determined by hierarchical clustering (see Supplement Figure (xxx).

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.

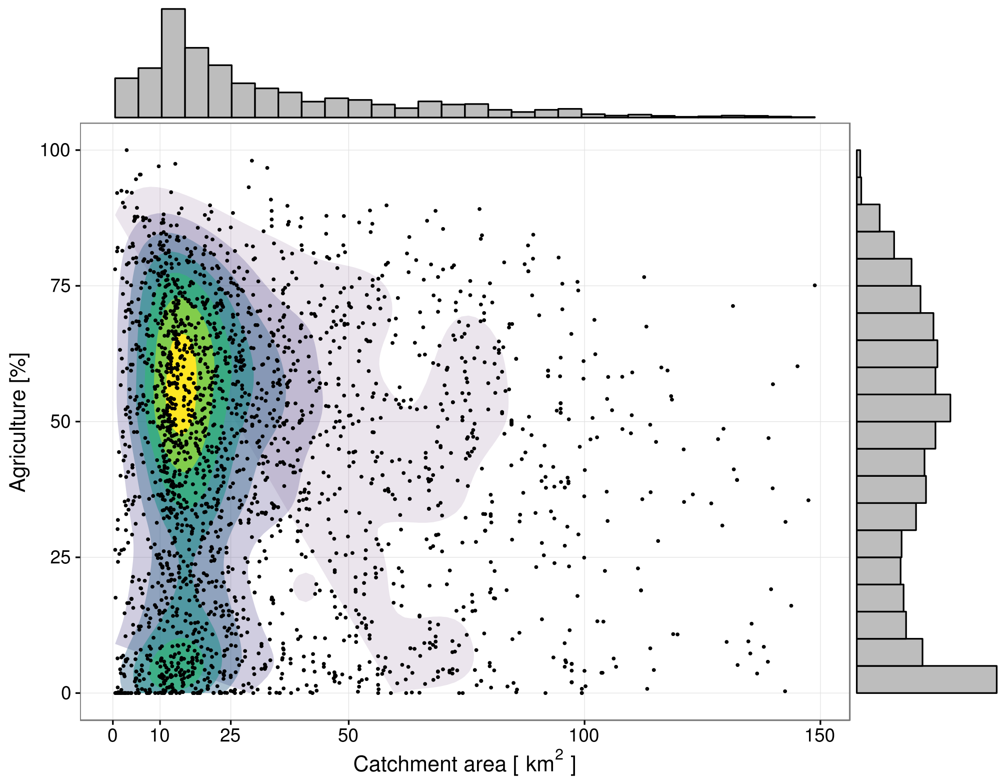

Figure 3: Distribution of catchment area and agriculture within the catchment area across the sampling sites. Only sampling sites with catchment area < 150 km^2 are displayed. Colour codes the 2-dimensional density of points.

Are small agricultural waters more polluted compared to bigger streams?

Pesticide pollution of small streams

Discussion

Subsection

Acknowledgement

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Supporting Information Available

The following files are available free of charge.

- Supplemental_Materials.pdf : Supplemental Materials

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

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