

Pesticides pollution of small streams in Germany

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, and Federal Environmental Agency (UBA), Dessau-Roßlau, Germany

E-mail: szoechs@uni-landau.de

Abstract

Fehlt noch...

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 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 monitoring⁵ and may have adverse effects on biota and ecosystem functioning^{6,7}.

^{*}To whom correspondence should be addressed

[†]Institute for Environmental Sciences

[‡]German Federal Institute of Hydrology

[¶]German Federal Environmental Agency

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 Directive⁸ and further state specific needs. However, currently there is no curated national-wide compilation of this data.

Small water bodies are important refuges of biodiversity⁹ and enabling downstream colonisation of polluted streams¹⁰. At the same time they may be exposed to a high risk of pesticide contamination from adjacent agricultural areas and low dilution effects⁴. Although small streams comprise a major fraction of streams¹¹ relatively little is known 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) How 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 < 100km² 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. 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 flow¹², 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 data¹³ from the sampling date and the day before.

Characterization of chemical pollution

We characterized chemical pollution (excluding sum parameters) using three indicators:

1. National and international Environmental Quality Standards (EQS)^{14,15}: We used only Maximum Annual Concentration EQS (MAC-EQS) for characterization. These were available for 29 compounds (Supplement, Table xxx).  ref

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 105 compounds (Supplement, Table xxx).  ref

We expressed RAC as Risk Quotient (RQ)

$$RQ = \frac{C}{RAC} \quad (1)$$

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

3. Maximum Toxic Units (TU_{max})¹⁷:

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

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 literature⁵, databases^{18,19} or model predictions²⁰, 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 model²¹ and a multiple flow direction algorithm²² as implemented in GRASS GIS 7²³. 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 provided 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

All data-processing and analyses have been performed using R, version 3.3.1²⁴. To display differences in the spectra of analysed compounds between federal states we used Multidimensional Scaling (MDS) based on Jaccard dissimilarity in conjunction with hierarchical clustering using the vegan package²⁵.

Results

Overview and representativeness of compiled data

The compiled dataset comprised only few standing waters (58 sites) and the majority (90%) of samples were 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).

Set
ref to
table

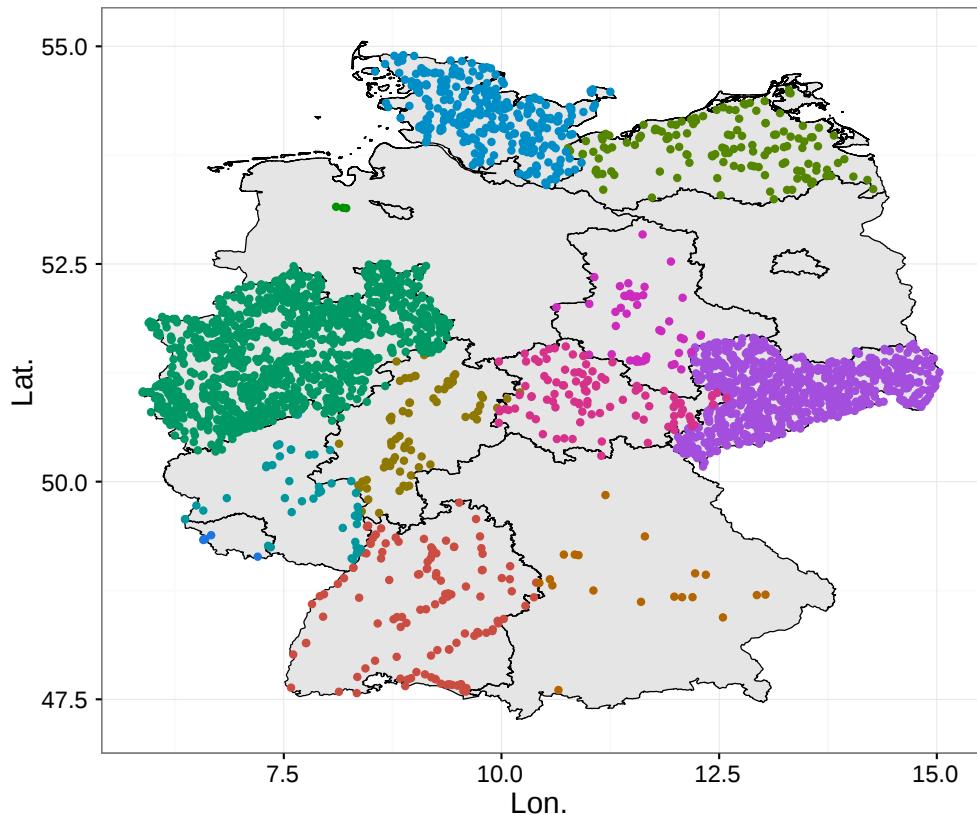


Figure 1: Spatial distribution of the 3109 sampling sites. Colour codes different federal states.

In total 484 different compounds that could be classified as pesticides and their metabolites 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 than 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

Set
ref to
table

were taken at or after days with rainfall events greater than 10mm / day.

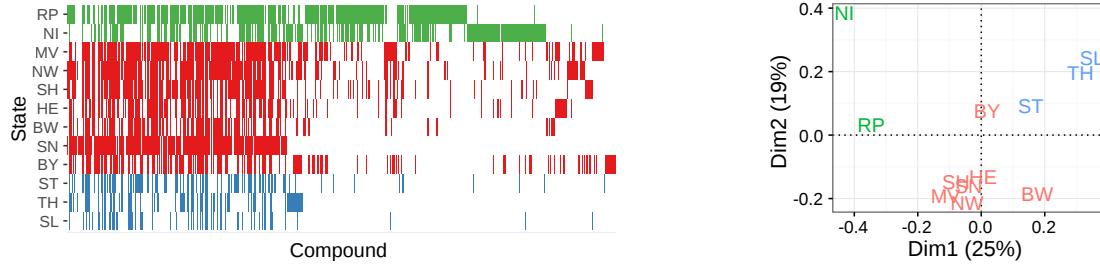


Figure 2: Compound spectra of the different federal states. Left: Barcode plot - Each vertical line is an analysed compound. Right: MDS ordination. Colors according to three groups determined by hierarchical clustering (see Supplement Figure (xxx)).

We were able to derive for 2376 sites catchment sizes and the proportion of agriculture within catchments. . 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.

prettify
figure!
Check
why
there
are so
many
miss-
ing in
BW,
NW,
RP,
SN

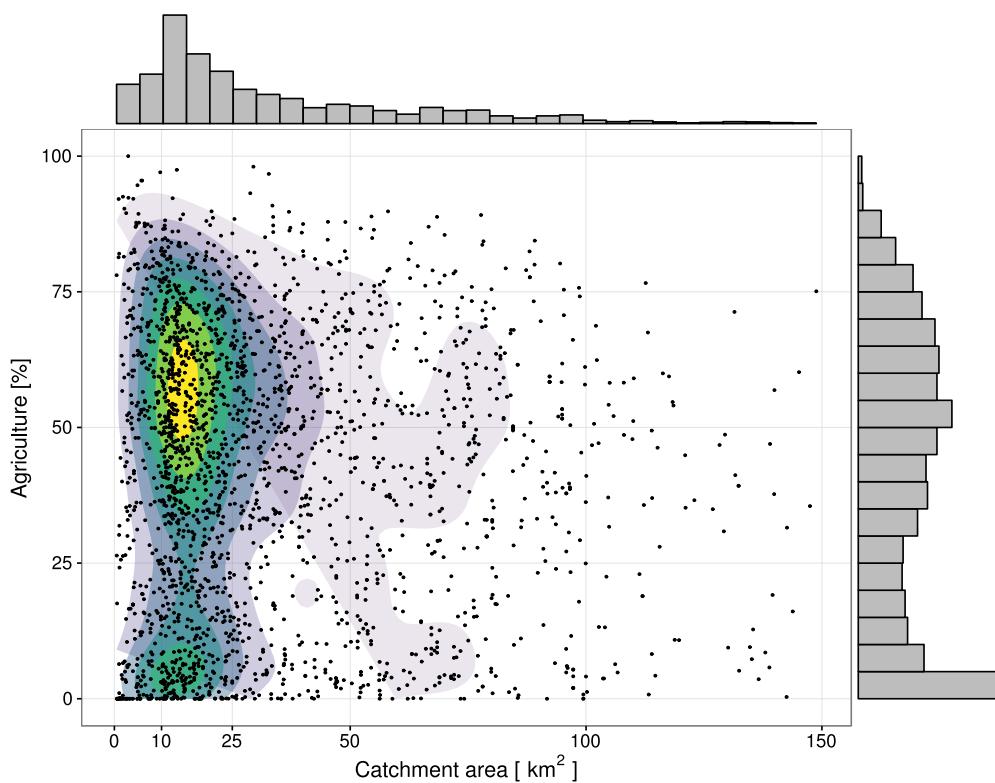


Figure 3: Distribution of catchment area and agriculture within the catchment area across the sampling sites. Only sampling sites with catchment area $< 150 \text{ km}^2$ are displayed. Colour codes the 2-dimensional density of points.

Are small agricultural waters more polluted compared to bigger streams?

Pesticide pollution of small streams

Discussion

Representativeness of the data

Influence of catchment area and agriculture

Pollution of streams

Acknowledgement

The authors thank the authorities for providing chemical monitoring data and the German Federal Environmental Protection Agency (UBA) for funding this project.

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/>.

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) 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.
- (4) 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, Anfragen 38 VG Wort 1/99 Paper Sabine PDF.
- (5) 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 ecosystems on the continental scale. *Proceedings of the National Academy of Sciences* **2014**, *111*, 9549–9554.
- (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, PDF Carola.
- (7) Schäfer, R. B.; Caquet, T.; Siimes, K.; Mueller, R.; Lagadic, L.; Liess, M. Effects of pesticides on community structure and ecosystem functions in agricultural streams of three biogeographical regions in Europe. *Science of the Total Environment* **2007**, *382*, 272–285.
- (8) Quevauviller, P.; Borchers, U.; Thompson, C.; Simonart, T. *The Water Framework Directive: Ecological and Chemical Status Monitoring*; John Wiley & Sons, 2008.
- (9) 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.
- (10) Liess, M.; von der Ohe, P. C. Analyzing effects of pesticides on invertebrate communities in streams. *Environmental Toxicology and Chemistry* **2005**, *24*, 954–965.

- (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) Poisot, T. Best publishing practices to improve user confidence in scientific software. *Ideas in Ecology and Evolution* **2015**, *8*.
- (13) 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.
- (14) OGewV, Verordnung zum Schutz der Oberflächengewässer (Oberflächengewässerverordnung). 2011; BGBl. I S. 1429.
- (15) European Union, DIRECTIVE 2013/39/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. 2013.
- (16) 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.
- (17) Sprague, J. Measurement of pollutant toxicity to fish, II-Utilizing and applying bioassay results. *Water Research* **1970**, *4*, 3–32.
- (18) Pesticide Action Network, PAN Pesticide Database. 2015; <http://www.pesticideinfo.org/>.
- (19) U.S. EPA, The ECOTOXicology knowledgebase (ECOTOX). 2015; <http://cfpub.epa.gov/ecotox/>.

- (20) Schüürmann, G.; Ebert, R.-U.; Kühne, R. Quantitative read-across for predicting the acute fish toxicity of organic compounds. *Environmental Science & Technology* **2011**, *45*, 4616–4622.
- (21) EEA, Digital Elevation Model over Europe (EU-DEM). 2013; <http://www.eea.europa.eu/data-and-maps/data/eu-dem#tab-metadata>.
- (22) Holmgren, P. Multiple flow direction algorithms for runoff modelling in grid based elevation models: An empirical evaluation. *Hydrological Processes* **1994**, *8*, 327–334.
- (23) Neteler, M.; Bowman, M. H.; Landa, M.; Metz, M. GRASS GIS: A multi-purpose open source GIS. *Environmental Modelling & Software* **2012**, *31*, 124–130, pdf RS.
- (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.; Friendly, M.; Kindt, R.; Legendre, P.; McGlinn, D.; Minchin, P. R.; O'Hara, R. B.; Simpson, G. L.; Solymos, P.; Stevens, M. H. H.; Szoecs, E.; Wagner, H. *vegan: Community Ecology Package*; 2016; R package version 2.4-0.

Graphical TOC Entry

Some journals require a graphical entry for the Table of Contents. This should be laid out “print ready” so that the sizing of the text is correct. Inside the `tocentry` environment, the font used is Helvetica 8 pt, as required by *Journal of the American Chemical Society*. The surrounding frame is 9 cm by 3.5cm, which is the maximum permitted for *Journal of the American Chemical Society* graphical table of content entries. The box will not resize if the content is too big; instead it will overflow the edge of the box. This box and the associated title will always be printed on a separate page at the end of the document.