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: szoecs@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 the 45000 tonnes of 766 authorized pesticides were sold for application on these

areas². 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 routes³. Once entered the surface

waters pesticides are frequently detected in environmental monitoring ⁴ and may have adverse

effects on biota and ecosystem functioning 5,6 .

*To whom correspondence should be addressed

[†]Institute for Environmental Sciences

[‡]German Federal Institute of Hydrology

¶German Federal Environmental Agency

1

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?

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 flow⁷, 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 standing 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 with daily precipitation data⁸ 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)^{9,10}: We used only

to results and say that nearl no in forma

Maximum Annual Concentration EQS (MAC-EQS) for characterization.

2. Regulatory Acceptable Concentrations (RAC)¹¹: 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 $(TU_{max})^{12}$:

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

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 literature⁴, databases ^{13,14} or model predictions ¹⁵, 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 model¹⁶ and a multiple flow direction algorithm¹⁷ as implemented in GRASS GIS 7¹⁸. 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 cov-

erage (%) 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 jeccard 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

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

Are small agricultural waters more polluted compared to bigger

streams?

Pesticide pollution of small streams

Discussion

Vergleich mit der Schweiz.....

4

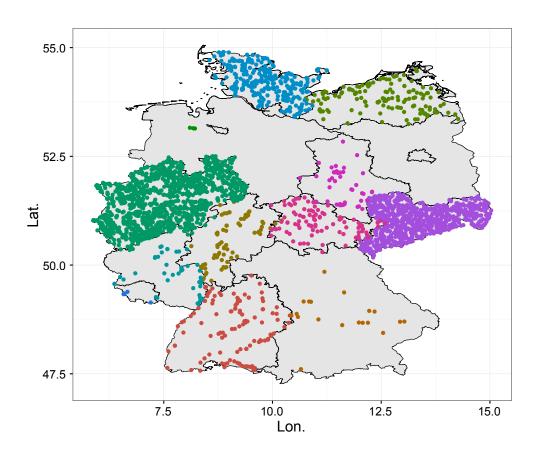


Figure 1: Spatial distribution of the 3109 sampling sites. Colour codes different federal states.

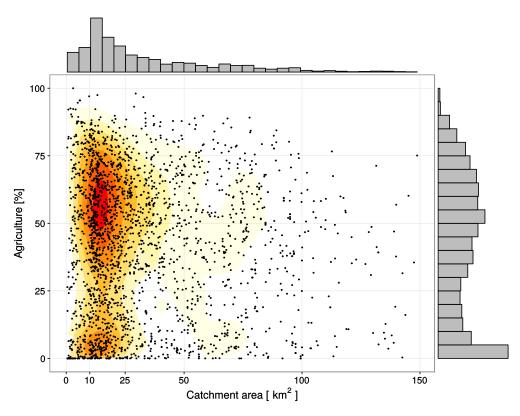


Figure 2: Distribution of catchment area and agriculture within the catchment area across the sampling sites. Only sampling sites with catchment area $< 150 \; \rm km^2$ are displayed. Colour codes the 2-dimensional density of points.

Subsection

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) 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.

- (5) 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.
- (6) 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.
- (7) Poisot, T. Best publishing practices to improve user confidence in scientific software.

 Ideas in Ecology and Evolution 2015, 8.
- (8) 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.
- (9) OGewV, Verordnung zum Schutz der Oberflächengewässer (Oberflächengewässerverordnung). 2011; BGBl. I S. 1429.
- (10) 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.
- (11) 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.
- (12) Sprague, J. Measurement of pollutant toxicity to fish, II-Utilizing and applying bioassay results. Water Research 1970, 4, 3–32.

- (13) Pesticide Action Network, PAN Pesticide Database. 2015; http://www.pesticideinfo.org/.
- (14) U.S. EPA, The ECOTOXicology knowledgebase (ECOTOX). 2015; http://cfpub.epa.gov/ecotox/.
- (15) 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.
- (16) EEA, Digital Elevation Model over Europe (EU-DEM). 2013; http://www.eea.europa.eu/data-and-maps/data/eu-dem#tab-metadata.
- (17) Holmgren, P. Multiple flow direction algorithms for runoff modelling in grid based elevation models: An empirical evaluation. *Hydrological Processes* **1994**, *8*, 327–334.
- (18) 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.

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 3.5 cm, 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.