STATISTICAL ECO(-TOXICO)LOGY

IMPROVING THE UTILIZATION OF DATA FOR ECOLOGICAL RISK ASSESSMENT

by

EDUARD SZÖCS

from ZĂRNESTI / ROMANIA

Submitted Dissertation thesis for the partial fulfillment of the requirements for a
Doctor of Natural Sciences
Fachbereich 7: Natur- und Umweltwissenschaften

Universität Koblenz-Landau

3. November 2016

CONTENTS

LIST OF FIGURES

LIST OF TABLES

1

INTRODUCTION AND OBJECTIVES

1.1 PESTICIDES IN FRESHWATER ECOSYSTEMS

1.2 ECOLOGICAL RISK ASSESSMENT

Ecological risk assessment (ERA) tries to estimate risks to animals, populations or ecosystems and is used as a tool for decision making under uncertainty (Newman, 2015). The decision to be made is, whether a (new) pesticide can be approved for usage and a potential release in the environment without a risk to the environment. Ecological risk is defined as a combination of the severity and the probability of occurrence of a potential adverse effect (Suter, 2007). Therefore, ERA is based on two components: Effect- and exposure assessment. A combination of both is needed to characterise ecological risks.

Effect assessment characterizes the strength of effects using laboratory and semi-field experiments. It establishes relationships between the concentration of a compound and the observed ecological effects. In the European Union a tiered approach with increasing complexity and realism. Lower tier assessment is based on highly standardized single species laboratory experiments, whereas higher tier assessment is refined by testing additional species, extended laboratory experiments or model ecosystem experiments. To address the various uncertainties in effect assessment (e.g. experimental variation, variation between species, variation in environmental conditions etc) the retrieved toxicity values are multiplied by a assessment factor between 0.01 (lower tier assessment) and 0.5 (higher tier assessment) depending on data quality, which yields to a regulatory acceptable concentration (RAC) (EFSA, 2013).

Exposure Assessment for freshwaters aims to characterise the probability of a adverse effect by deriving a predicted environmental concentration (PEC) in surface waters and sediments (Newman, 2015). It is mainly based on modeling the fate of chemicals in the environment using computer simulations. In the European Union, the FOCUS models are used (FOCUS, 2001; EFSA, 2013). To calculate PECs these models need many compound specific input parameters like the molecular weight, water solubility, partitioning coefficients and dissipation time. Additionally, information on the application regime and crop type is needed. FOCUS models the concentration within edge-of-field streams of 1 meter width and 30 cm depth (Erlacher and Wang, 2011). Such a stream width corresponds to a catchment size of 7 km^2 (See figure **??**) ref to small streams supplement which is considered as small stream (Lorenz et al., 2016). Nevertheless, recent research showed that FOCUS models fail predict measured field concentrations of pesticides (Knäbel et al., 2012; Knäbel et al., 2014).

The final step in ERA is risk characterisation. It puts together the information gained from effect and exposure assessment. Risk can expressed in several ways, a quantitative way being the risk quotient approach: A PEC / RAC ratio greater than one indicating potential risks (Suter, 2007; EFSA, 2013; Amiard-Triquet, 2015). Substances with a ration lower than one could be approved for usage and potential release to the environment.

1.3 ENVIRONMENTAL MONITORING

1.4 STATISTICAL ECOTOXICOLOGY

Ecological effect assessment generates data on ecological effects using experiments. The produced datasets range from small univariate datasets (lower tier assessment) to medium sized multivariate datasets (higher tier assessment). These datasets are analyzed using statistical techniques in order to deliver usable information for assessment. Therefore, effect assessment relies heavily on statistical methods. Statistical ecotoxicology combines statistics with the specific needs and constraints of ecotoxicology. It aims to provide solutions to statistical challenges in ecotoxicology (Fox and Landis, 2016a), guidance on experimental designs (Johnson et al., 2015) and tools to integrate big data (Van den Brink et al., 2016) to improve accuracy of ERA.

The relationships between the concentration of a compound and the observed effects are usually analysed using using dose-response models (Ritz, 2010), which can be used to derive an effective concentration for x% effect (EC_x). Nevertheless, such relationships cannot always be established from experimental data. For example, model ecosystem experiments are conducted to characterize effects on whole biological communities. However, because of multivariate responses and potential indirect effects, there is no clear dose-response relationship and no models for this kind of data available. There are also other examples were fitting dose-response models is problematic (Green, 2016). In such cases there is usually a no-observed-effect concentration (NOEC) computed. The NOEC is the highest tested concentration that does not lead to significant deviation from the control response and therefore relies on null hypothesis significance testing (NHST). However, the use of NOEC as toxicity measure in ecological effect assessment has been heavily in the past (Laskowski, 1995; Chapman et al., 1996; Warne and Dam, 2008; Fox et al., 2012; Jager, 2012; Fox and Landis, 2016b).

Instead of conducting experiments, toxicity could be also predicted from molecular structures using quantitative structure-activity relationships (QSAR), which are calculated using machine-learning techniques (Murrell et al., 2015; Cortes-Ciriano, 2016). However, improving these models to give sufficient prediction accuracy needs to integrate more input data (Kühne et al., 2013).

Large amount of data are available that could be use for effect and exposure assessment. For example, the US EPA ECOTOX database (U.S. EPA, 2016), the Pesticides Properties Database (Lewis et al., 2016) and ETOX (Umweltbundesamt, 2016) provide toxicity data that could be used for effect assessment. Databases like Physprop (Howard and Meylan, 2016) and Pubchem (Kim et al., 2016) provide chemical properties that are needed as input for exposure models. Monitoring data provides information on realised concentrations, could be used for validation of models and retrospective risk assessment. This big data can provide new information and opportunities for ERA (Dafforn et al., 2015). However, it needs to be linked in order to be used effectively in ERA.

1.5 OBJECTIVES AND OUTLINE OF THE THESIS

The overall goal of this thesis was to contribute to the emerging field of statistical ecotoxicology and ERA. The main objectives were (i) to scrutinize new methods in statistical ecotoxicology, (ii) explore available monitoring data and (iii) provide tools to deal with big data. Figure 1.1 provides a conceptual overview on the parts of this thesis and its relations to ERA as outlined in the previous sections.
The thesis starts with a comparison of statistical methods to analyse ecotoxicological experiments in effect assessment (Chapter **??**). Specific questions addressed were:

- Are newer statistical methods more powerful than currently used methods for NHST?
- How much statistical power do current experimental designs in ecotoxicology exhibit?

Exposure assessment aims at predicting concentrations in small streams. Chapter 2 focuses on large-scale realised environmental concentrations and the drivers thereof. Specific goals were:

- Compile all available monitoring data on pesticides in small streams in Germany
- Explore the relationship between agricultural land use and streams sizze and measured pesticide concentrations.
- Study annual dynamics of pesticide exposure, as well as influence of precipitation on measured pesticide concentrations.
- Assess the current pollution in German streams and identify responsible pesticides.

The compilation of monitoring data from different data sources, lead to a big inhomogeneous amount of data that first needs to be harmonized. Chapters **??** (chemical data) and **??** (biological data) describe software solutions to simplify and accelerate the workflow of:

- validating and harmonizing chemical and taxonomic data

- linking datasets
- retrieving properties and identifiers

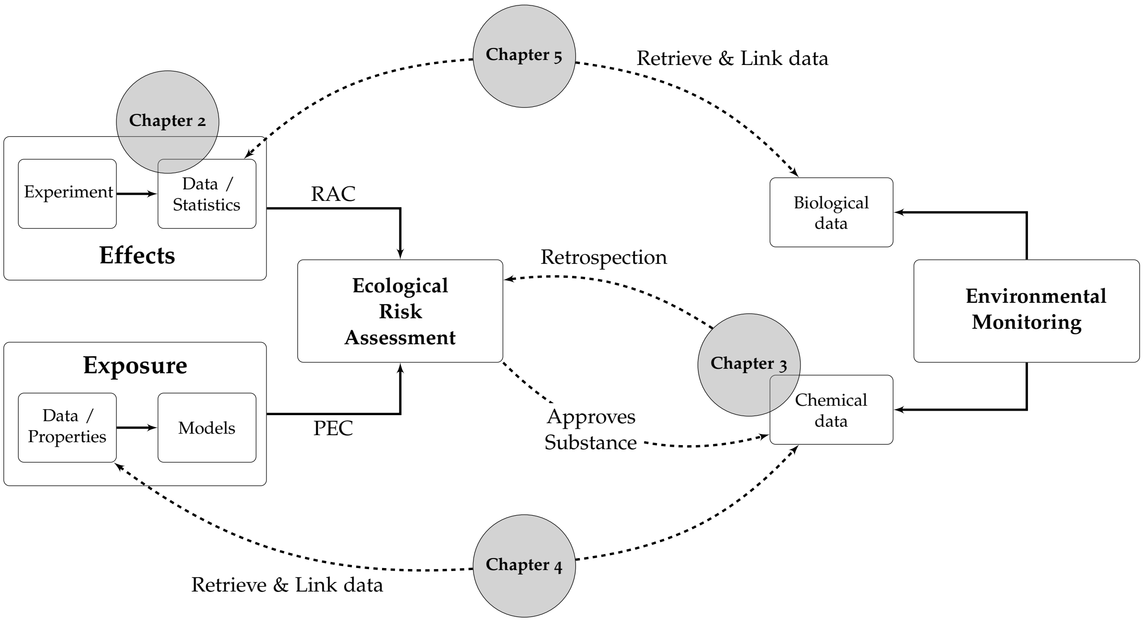

Figure 1.1: Conceptual overview on data in ecological risk assessment, environmental monitoring and the parts addressed by this thesis.

1.6 REFERENCES

Amiard-Triquet, C. (2015). *Aquatic ecotoxicology: advancing tools for dealing with emerging risks*. Boston, MA: Elsevier.

Chapman, P., P. Chapman, and R. Caldwell (1996). "A warning: NOECs are inappropriate for regulatory use". *Environmental Toxicology and Chemistry* 15 (2), 77–79.

Cortes-Ciriano, I. (2016). "Bioalerts: a python library for the derivation of structural alerts from bioactivity and toxicity data sets". *Journal of Cheminformatics* 8 (1). URL: http://www.jcheminf.com/content/8/1/13 (visited on 10/28/2016).

Dafforn, K. A., E. L. Johnston, A. Ferguson, C. Humphrey, W. Monk, S. J. Nichols, S. L. Simpson, M. G. Tulbure, and D. J. Baird (2015). "Big data opportunities and challenges for assessing multiple stressors across scales in aquatic ecosystems." *Marine and Freshwater Research*. URL: http://www.publish.csiro.au/?paper=MF15108 (visited on 02/29/2016).

EFSA (2013). "Guidance on tiered risk assessment for plant protection products for aquatic organisms in edge-of-field surface waters". *EFSA Journal* 11 (7), 3290.

Erlacher, E. and M. Wang (2011). "Regulation (EC) No. 1107/2009 and upcoming challenges for exposure assessment of plant protection products – Harmonisation or national modelling approaches?" *Environmental Pollution* 159 (12), 3357–3363.

FOCUS (2001). *FOCUS Surface Water Scenarios in the EU Evaluation Process under 91/414/EEC.* Report of the FOCUS Working Group on Surface Water Scenarios EC Document Reference SANCO/4802/2001-rev.2.

Fox, D. R., E. Billoir, S. Charles, M. L. Delignette-Muller, and C. Lopes (2012). "What to do with NOECS/NOELS—prohibition or innovation?" *Integrated Environmental Assessment and Management* 8 (4), 764–766.

Fox, D. R. and W. G. Landis (2016a). "Comment on ET&C perspectives, November 2015-A holistic view". *Environmental Toxicology and Chemistry* 35 (6), 1337–1339. URL: http://doi.wiley.com/10.1002/etc.3378 (visited on 07/12/2016).

Fox, D. R. and W. G. Landis (2016b). "Don't be fooled-A no-observed-effect concentration is no substitute for a poor concentration-response experiment: NOEC and a poor concentration-response experiment". *Environmental Toxicology and Chemistry* 35 (9), 2141–2148.

Green, J. W. (2016). "Issues with using only regression models for ecotoxicity studies". *Integrated Environmental Assessment and Management* 12 (1), 198–199.

Howard, P. H. and W. Meylan (2016). *Physical/Chemical Property Database (PHYSPROP)*. http://www.srcinc.com/what-we-do/environmental/scientific-databases.html#physprop. URL: http://www.srcinc.com/what-we-do/environmental/scientific-databases.html#physprop.

Jager, T. (2012). "Bad habits die hard: The NOEC's persistence reflects poorly on ecotoxicology". *Environmental Toxicology and Chemistry* 31 (2), 228–229.

Johnson, P. C. D., S. J. E. Barry, H. M. Ferguson, and P. Müller (2015). "Power analysis for generalized linear mixed models in ecology and evolution". *Methods in Ecology and Evolution* 6 (2), 133–142. (Visited on 04/17/2015).

Kim, S., P. A. Thiessen, E. E. Bolton, J. Chen, G. Fu, A. Gindulyte, L. Han, J. He, S. He, B. A. Shoemaker, J. Wang, B. Yu, J. Zhang, and S. H. Bryant (2016). "PubChem Substance and Compound databases". *Nucleic Acids Research* 44 (D1), D1202–D1213. URL: http://nar.oxfordjournals.org/lookup/doi/10.1093/nar/gkv951 (visited on 01/21/2016).

Knäbel, A., K. Meyer, J. Rapp, and R. Schulz (2014). "Fungicide Field Concentrations Exceed FOCUS Surface Water Predictions: Urgent Need of Model Improvement". *Environmental Science & Technology* 48 (1), 455–463.

Knäbel, A., S. Stehle, R. B. Schäfer, and R. Schulz (2012). "Regulatory FOCUS Surface Water Models Fail to Predict Insecticide Concentrations in the Field". *Environmental Science & Technology* 46 (15), 8397–8404.

Kühne, R., R.-U. Ebert, P. C. von der Ohe, N. Ulrich, W. Brack, and G. Schüürmann (2013). "Read-Across Prediction of the Acute Toxicity of Organic Compounds toward the Water Flea Daphnia magna". *Molecular Informatics* 32 (1), 108–120.

Laskowski, R. (1995). "Some good reasons to ban the use of NOEC, LOEC and related concepts in ecotoxicology". *Oikos* 73 (1), 140–144.

Lewis, K. A., J. Tzilivakis, D. J. Warner, and A. Green (2016). "An international database for pesticide risk assessments and management". *Human and Ecological Risk Assessment: An International Journal* 22 (4), 1050–1064. URL: http://dx.doi.org/10.1080/10807039.2015.1133242 (visited on 07/27/2016).

Lorenz, S., J. J. Rasmussen, A. Süß, T. Kalettka, B. Golla, P. Horney, M. Stähler, B. Hommel, and R. B. Schäfer (2016). "Specifics and challenges of assessing exposure and effects of pesticides in small water bodies". *Hydrobiologia*, 1–12. URL: http://link.springer.com/article/10.1007/s10750-016-2973-6 (visited on 09/13/2016).

Murrell, D. S., I. Cortes-Ciriano, G. J. P. van Westen, I. P. Stott, A. Bender, T. E. Malliavin, and R. C. Glen (2015). "Chemically Aware Model Builder (camb): an R package for property and bioactivity modelling of small molecules". *Journal of Cheminformatics* 7 (1). URL: http://www.jcheminf.com/content/7/1/45 (visited on 10/28/2016).

Newman, M. C. (2015). *Fundamentals of ecotoxicology: the science of pollution*. Boca Raton: CRC Press, Taylor & Francis Group.

Ritz, C. (2010). "Toward a unified approach to dose-response modeling in ecotoxicology". *Environmental Toxicology and Chemistry* 29 (1), 220–229.

Suter, G. W., ed. (2007). *Ecological risk assessment*. Boca Raton: CRC Press/Taylor & Francis.

Umweltbundesamt (2016). *ETOX: Information System Ecotoxicology and Environmental Quality Targets*. http://webetox.uba.de/webETOX/index.do?language=en.

U.S. EPA (2016). *The ECOTOXicology knowledgebase (ECOTOX)*. http://cfpub.epa.gov/ecotox/. (Visited on 11/16/2015).

Van den Brink, P. J., C. B. Choung, W. Landis, M. Mayer-Pinto, V. Pettigrove, P. Scanes, R. Smith, and J. Stauber (2016). "New approaches to the ecological risk assessment of multiple stressors". *Marine and Freshwater Research* 67 (4), 429. URL: http://www.publish.csiro.au/?paper=MF15111 (visited on 06/13/2016).

Warne, M. S. J. and R. van Dam (2008). "NOEC and LOEC data should no longer be generated or used". *Australasian Journal of Ecotoxicology* 14, 1–5.

2

LARGE SCALE RISKS FROM PESTICIDES IN SMALL STREAMS

Eduard Szöcs[a], Marvin Brinke[b], Bilgin Karaoglan[c] & Ralf B. Schäfer[a]

[a]Institute for Environmental Sciences, University Koblenz-Landau, Landau, Germany
[b]German Federal Institute of Hydrology (BfG), Koblenz, Germany
[c]Federal Environmental Agency (UBA), Dessau-Roßlau, Germany

Submitted to *Environmental Science & Technology* in 2016

2.1 ABSTRACT

2.2 REFERENCES

3

DISCUSSION

3.1 STATISTICAL ECOTOXICOLOGY

3.2 LEVERAGING MONITORING DATA FOR ECOLOGICAL RISK ASSESSMENT

3.3 CHALLENGES TO UTILIZE 'BIG DATA' IN ERA

3.4 CONCLUSIONS AND OUTLOOK

3.5 REFERENCES