EVALUATION OF EXPOSURE MODELLING STRATEGIES IN THE CONTEXT OF THE ENVIRONMENTAL RISK ASSESSMENT FOR PESTICIDES

by
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Overview of Publications

This cumulative dissertation includes four scientific publications and one response to a comment on the first scientific publication. The fourth publication is part of the dissertation thesis of Sebastian Stehle (first author), but was included in the present thesis because of thematic relevance and because it was co-authored by Anja Knäbel, who conducted the exposure modelling part of this publication.

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

1.1 **Knäbel, A.** and Schulz, R. (2014) Response to Comment on Fungicide Field Concentrations Exceed FOCUS Surface Water Predictions: Urgent Need of Model Improvement. *Environmental Science and Technology*, 48, 5347–5348.

2 **Knäbel, A.**; Bundschuh, M.; Kreuzig, R.; Schulz, R. (2015) Runoff of veterinary pharmaceuticals from arable and grassland – A comparison between predictions from model simulations and experimental studies. *Agriculture, Ecosystems and Environment*, 218, 33-39.

3 **Knäbel, A.**; Scheringer, M.; Schulz, R. (2016) Aquatic exposure predictions of insecticide field concentrations using a multimedia mass-balance model. *Environmental Science and Technology,* DOI: 10.1021/acs.est.5b05721.

4 Stehle, S.; **Knäbel, A**.; Schulz, R. (2013) Probabilistic Risk Assessment of Insecticide Concentrations in Agricultural Surface Waters: A Critical Appraisal. *Environmental Monitoring and Assessment*, 185, 6295-6310.

Annotation

This cumulative dissertation is based on publications written by multiple authors. Therefore, the first person plural is used throughout the thesis.

Contents

Abbreviation list

AIC	Akaike's Information Criterion
ANOVA	ANalysis Of VAriance
EFSA	European Food Safety Authority
EMEA	European Medicines Agency
EU	European Union
FOCUS	FOrum for the Co-ordination of pesticide fate models and their USe
GAP	Good Agricultural Practice
HSD	Honest Significant Differences
K_{OC}	Soil organic carbon-water partitioning coefficient
MFC	Measured Field Concentration
PEC	Predicted Environmental Concentration
PRZM	Pesticide Root Zone Model
RAC	Regulatory Acceptable Concentration
$\text{ratio}_{S/M}$	PEC-MFC ratio
SCS	Soil Conservation Service
SED	Sediment
SI	Supporting Information
SRM	Small Region Model
SWAN	Surface Water Assessment eNabler
SWASH	Surface WAter Scenarios Help
SW	Surface-Water
TER	Toxicity Exposure Ratio
TOXSWA	TOxic Substances in Surface WAter
USLE	Universal Soil Loss Equation
VP	Veterinary Pharmaceuticals

Abstract

The application of pesticides to agricultural areas can result in transport to adjacent non-target environments. In particular, surface water systems are likely to receive agricultural pesticide input. When pesticides enter aquatic environments, they may pose a substantial threat to the ecological integrity of surface water systems. To minimize the risk to non-target ecosystems the European Union prescribes an ecotoxicological risk assessment within the registration procedure of pesticides, which consists of an effect and an exposure assessment. This thesis focuses on the evaluation of the exposure assessment and the implications to the complete regulatory risk assessment, and is based on four scientific publications. The main part of the thesis focuses on evaluation of the FOCUS modelling approach, which is used in regulatory risk assessment to predict pesticide surface water concentrations. This was done by comparing measured field concentrations (MFC) of agricultural insecticides (n = 466) and fungicides (n = 417) in surface water to respective predicted environmental concentrations (PEC) calculated with FOCUS step 1 to step 4 at two different levels of field relevance. MFCs were extracted from the scientific literature and were measured in field studies conducted primarily in Europe (publications 1 and 3). In addition, an alternative fugacity-based multimedia mass-balance model, which needs fewer input parameters and less computing effort, was used to calculate PECs for the same insecticide MFC dataset and compared to the FOCUS predictions (publication 3). Furthermore, FOCUS predictions were also conducted for veterinary pharmaceuticals in runoff from an experimental plot study, to assess the FOCUS predictions for a different class of chemicals with a different relevant entry pathway (publication 2). In publication 4, the FOCUS step-3 approach was used to determine relevant insecticide exposure patterns. These patterns were analysed for different monitoring strategies and the implications for the environmental risk assessment (publication 4).

The outcome of this thesis showed that the FOCUS modelling approach is neither protective nor appropriate in predicting insecticide and fungicide field concentrations. Up to one third of the MFCs were underpredicted by the model calculations, which means that the actual risk might be underestimated. Furthermore, the results show that a higher degree of realism even reduces the protectiveness of model results and that the model predictions are worse for highly hydrophobic and toxic pyrethroids. In addition, the absence of any relationship between measured and predicted concentrations questions the general model performance quality (publication 1 and 3). Further analyses revealed that deficiencies in protectiveness and predictiveness of the environmental exposure assessment might even be higher than shown in this thesis, because actual short-term peak concentrations are only detectable with an event-related sampling strategy (publication 4). However, it was shown that the PECs of a much simpler modelling approach are much more appropriate for the prediction of insecticide MFC, especially for calculations with a higher field relevance (publication 3). The FOCUS approach also failed to predict concentrations of veterinary pharmaceuticals in runoff water (publication 2). In conclusion, the findings of this thesis showed that there is an urgent need for the improvement of exposure predictions conducted in the environmental risk assessment of pesticides as a group of highly relevant environmental chemicals, to ensure that the increasing use of those chemicals does not lead to further harmful effects in aquatic ecosystems.

1 Introduction

1.1 The significance of pesticides in global agriculture

The human population is growing today by 1.18% per year. This means that there are an additional 83 million people every year, which will result in 8.5 billion people by the year 2030 (United Nations 2015). The increasing world population, together with the increasing use of grains for livestock feed and energy plants, will lead to an agricultural intensification. For example, the worlds' grain production increased over the last ten years by almost 16%, and will further increase by 11% until 2024 to 4.1 tonnes per hectare (OECD 2015). Agricultural intensification, also known as the Green Revolution, was possible through the introduction of genetically improved crops, chemical fertilisation and pest control via synthetic pesticides. Green et al. (2005) mentioned that from all factors that contributed to the overall increase of 106% in food crop yield per area between 1961 and 1999, pesticide production increased the most (854%). It was estimated by Tilman et al. (2001) that, if past patterns continue, global pesticide production will increase by a factor of 1.7 from 2000 to 2020 and by a factor of 2.7 by 2050, reaching a volume of 10.1 million tonnes per year. Even if population growth in the European Union (EU) is declining at the moment, the use of pesticides will become even more important in the future. Beside those factors that lead to agricultural intensification, resistance and climate change will further increase pesticide significance. Oerke and Dehne (2004) stated that the possible loss of crops by pests varies from less than 50% (on barley) to more than 80% (on sugar beet and cotton), while the efficacy of crop protection lies between 43 and 50% in food crops. From this perspective it seems that pesticides are indispensable in today's agricultural food production in preventing and controlling pests and diseases, and to maintain yields at a level sufficient for a growing human population (Oerke and Dehne 2004). Nevertheless, those forecasts do not consider developments in technology, social and environmental regulations, and consumers' behavioural changes.

1.2 Environmental relevance of pesticides for aquatic systems

Pesticides are highly biologically active substances that are applied to the environment deliberately to control or eliminate targeted organisms. The application of pesticides to agricultural areas can result in transportation of these chemicals to surrounding non-target environmental compartments like surface water bodies (Jergentz et al. 2005; Schäfer et al. 2008). Small artificial ditches, constructed to drain fields, constitute a substantial share of the aquatic systems present in the European agricultural landscape (Schulz 2004; Bereswill et al. 2012). Each of those systems represents a habitat for a multitude of different organisms. Furthermore, those systems play a significant role in influencing successional surface water systems of higher order. The existence of such surface water systems in the agricultural landscape leads them to constitute habitats likely to receive agricultural pesticide input after pesticide application (Schwarzenbach et al. 2006). The exposure of a chemical is defined as the presence in the environment and is normally described as the chemical's long or short term concentration within the respective environmental media (Scheringer 1999). Exposure level and duration are determined by the chemicals' emission rate and the environmental fate. The emission rate of a pesticide is equal to the application amount and conditions. The application conditions are generally very different for different substance groups. Insecticides are normally applied in the field to acute infestations in comparably small application amounts, while herbicides and fungicides are often applied preventively and repeatedly throughout the vegetation period (Stehle et al. 2013). The environmental fate of pesticides depends on the partitioning between the different environmental media and the chemical transformation processes. It has been reported that the edge-of-field loss of pesticides can reach a significant (>10%) amount of the total mass applied to the field (Schulz 2004). In particular non-point source pollution from agricultural areas has often been reported as an important factor for surface water contamination (Jergentz et al. 2005; Schwarzenbach et al. 2006; Schäfer et al. 2012). Surface runoff after heavy precipitation events, spray drift during spray application, and leaching to field drains constitute the predominant routes of pesticide non-point source pollution of water bodies (Holvoet et al. 2007). Generally, the different entry routes depend on different environmental and substance conditions. Surface runoff is induced by irrigation or precipitation events. If the precipitation amount exceeds the rate of infiltration, pesticides can be transported in the aqueous phase or sorbed to soil particles with soil erosion to water bodies (Holvoet et al. 2007). The amount of the pesticide that is transferred depends on the precipitation height and watershed characteristics like soil properties, vegetation, soil moisture conditions, and slope, as well as pesticide properties (e.g., soil half life, soil organic carbon - water partitioning coefficient: K_{OC}). Spray drift occurs during pesticide application and depends mainly on application techniques, distance between crop and water bodies, and wind speed. Pesticide leaching to field drains is especially important if the soil is drained and mostly depends on soil (e.g., organic carbon content, moisture) and pesticide properties.

Subsequent to their entry in aquatic environments, pesticides can pose a substantial threat to the ecological integrity of surface water systems as they exhibit effects on individuals, populations and communities (Schäfer et al. 2011; Schulz and Liess 2001). The kind of effect a substance evokes largely varies between substance groups and mode of action, but also within substance classes and active substance. Insecticides are generally very toxic to a wide range of aquatic organisms (Brock et al. 2007; US EPA 1995), but especially aquatic arthropods are affected, because of the acute mode of action of insecticides, and the similarity of non-target and target organisms (van Wijngaarden et al. 2005). A lot of fungicides act on consecutive cell processes, like energy production or cell division, which are not specific for fungi and they can therefore affect a lot of different organisms (Maltby et al. 2009). Recent studies have also shown that fungicides have direct toxic effects on amphibians (Brühl et al. 2009; Belden et al. 2010), which is also known to be true of herbicides (Hayes et al. 2010; Relyea 2009). Beside this, the toxicity of herbicides to aquatic organisms is classified as comparably low.

1.3 Actual exposure of agricultural surface waters

Numerous field studies on pesticide exposure in global surface waters due to agricultural non-point source pollution exist, reporting detection of all major pesticide groups and substance classes, in water and sediments of aquatic ecosystems (Stehle and Schulz 2015a; 2015b). Stehle and Schulz (2015b) showed that in surface water samples measured in Europe which contain multiple pesticides, fungicides showed higher absolute concentrations compared to herbicides and insecticides. If the measured concentrations were compared to tier-1 regulatory acceptable concentrations (RAC) used in environmental risk assessment, insecticides and fungicides showed higher exceedance frequencies compared to herbicides. Only 3.8% of the herbicide concentrations were higher than the respective RACs, whereas 53% and 31% of the insecticide and fungicide concentrations exceeded the relevant RAC, with a factor of 1.25 for the median insecticide concentrations. Therefore, it can be concluded that the importance of insecticide and fungicide surface water exposure is much higher than herbicides because it is more likely that occurring concentrations cause harmful effects to the non-target environment.

Exposure profiles depend on various environmental and substance-specific factors, and differ between different pesticide groups. Non-point source entries of insecticides into surface waters are to a large extent associated with edge-of-field runoff or spray drift events, whereas input via drainage only plays a minor role. This results in an extremely high temporal variability of insecticide concentrations with only a few, but highly ecotoxicologically relevant, peak concentrations. For instance, especially small agricultural surface waters are at high risk for insecticide contamination. Schulz (2004) found that maximum insecticide concentrations measured in field studies were significantly negatively correlated with catchment sizes. Insecticides measured in agricultural surface water often reach concentrations at levels that can cause harmful effects to aquatic organisms. In detail, Stehle and Schulz (2015a) reported that approximately 50% of the global insecticides detected in small agricultural surface waters exceed the tier-1 ecotoxicological threshold levels used in regulatory risk assessment.

In contrast, fungicides are used at comparably high application rates and multiple applications per season, which can lead to a more continuous entry into surface water bodies than that observed in insecticides (Bereswill et al. 2012). In addition, several fungicides are often applied in defined application cycles to prevent fungal resistance, which results in the detection of diverse fungicide compounds per sample (Bereswill et al. 2012; Maillard et al. 2011).

1.4 Regulatory risk assessment for pesticides in the European Union

1.4.1 Principles of environmental risk assessment for pesticides

In order to prevent unacceptable effects of pesticides released to non-target ecosystems, there is a need for an environmental risk assessment for new compounds during the registration procedure prior to authorization, and also for pesticides already on the market during re-registration processes (e.g., European Commission 2009). The European aquatic environmental risk assessment combines effect and exposure assessment to make sure that no pesticide concentrations appear in the environment that lead to unacceptable ecological effects. Generally, the risk assessment follows a tiered approach with increasing ecosystem relevance, i.e. higher tiers are less conservative with a lower degree of standardisation, but with an increase in complexity and realism. The effect characterisation at lower tiers is based on single species laboratory toxicity tests conducted under standardised conditions for determined test duration times, depending on the test species and the evaluation of acute or chronic toxicity (EFSA 2013). The pesticide exposure assessment is based on computer simulations, as the compounds under assessment are usually not yet on the market (Adriaanse et al. 1997), and monitoring data are usually not available for substances under re-evaluation. In the European Union, the FOCUS

(FOrum for the Coordination of pesticide fate models and their USe, see below for details on these models) modelling approach is used to calculate predicted environmental concentrations (PEC) in surface water and sediments, which is intended to reflect exposure levels of a specific pesticide compound under (realistic) worst-case conditions. The FOCUS pesticide exposure model conception started in 1993 with the FOCUS leaching modelling work-group. The work group was founded to harmonise the calculation of pesticide PECs in the framework of the EU Directive 91/414/EEC and is based on the co-operation of scientists of regulatory agencies, academia, and industry (FOCUS 2001). In 2001, the FOCUS surface water working group introduced a final tiered approach comprised of four steps, where each step describes different levels of protection and complexity (FOCUS 2001, details on the individual FOCUS steps are given below). Basically, FOCUS step-1 and 2 PECs play a minor role in the regulatory risk assessment of insecticides and fungicides in the EU. In detail, 83% and 62% of the insecticide and fungicide substances authorised under EU Directive 1107/2009 for which the European Food Safety Authority (EFSA) risk assessment was publicly available and the PEC estimation is conducted with FOCUS, are based on step-3 or step-4 calculations. Within the acute environmental risk assessment, maximum PECs are used, while for evaluation of chronic risk, time-weighted-average PECs for the relevant time-spans are considered. Generally, all FOCUS tiers are used in tier-one risk assessment in the common regulatory practice including the highest, step-4, as long as it maintains standard step-3 scenario definitions in agreed standardized approaches (Brock et al. 2007). FOCUS step-4 can also be considered as higher-tier exposure assessment in case of additional substance or scenario properties that differ from the official standard scenarios.

In the lower-tier risk assessment, toxicity data are divided by the maximum PECs to generate toxicity exposure ratios (TER). In order to address uncertainties in the effect characterisation, assessment factors are used. For example, the acute TER values should be not less than 100 for the most sensitive animal species and not less than 10 for aquatic plants (EFSA 2013). In case a TER value smaller than the respective assessment factor is derived for a specific substance, a refined higher-tier exposure and effect assessment has to be conducted. The higher-tier effect assessment can consist for example of extended laboratory tests (e.g. additional species, modified exposure), indoor microcosm studies, or complex outdoor mesocosm systems (Campbell et al. 1999), where factors like recovery or recolonisation can be considered. For the higher-tier risk assessment, the respective assessment factors are substantially reduced compared to the lower-tier assessment (1-10) depending on the data background, and are applied as case-by-case decisions. If the TER value of the higher-tier risk assessment is still smaller than the relevant assessment factor, no authorisation can be granted. The overall goal of the environmental risk assessment is therefore to ensure that there are no cases in actual agricultural surface water systems in which the measured pesticide concentration is higher than the relevant RAC at which transient effects are allowed, which are assumed to be ecologically acceptable.

1.4.2 The tiered FOCUS surface water modelling approach

As mentioned before, the FOCUS surface water modelling approach consists of four different steps named FOCUS step-1 to FOCUS step-4. It starts with simple extreme worst-case conditions and progresses to more detailed and realistic procedures. If at one stage the use is considered safe, no further surface water risk assessment and therefore no further exposure predictions have to be conducted (Figure 1). Step-1 is based on very simple assumptions and scenarios and accounts for one extreme worst-case pesticide loading without consideration of specific additional characteristics for pesticide application or climate. For the amount of spray drift, the 90th percentile value from the experimental drift values determined by the Biologische Bundesanstalt (BBA 2001) were calculated for 1m distance for arable crops and 3m distance for vines, orchards, and hops. This resulted in a value of 2.8% for all arable crops and between 2.7 and 29.2% for other crops (FOCUS 2001). In addition, it is assumed that a simultaneous runoff/drainage event occurs where 10% of the total applied amount is loaded to the water body. Step-2 also characterizes pesticide input from drift,

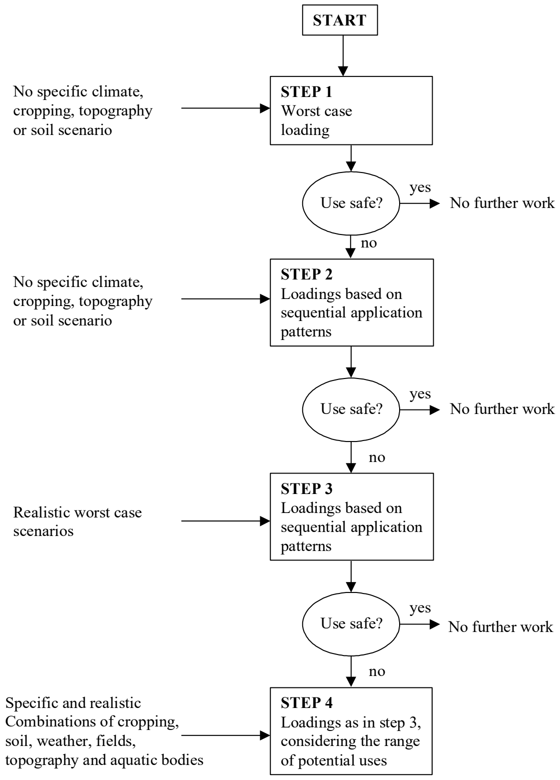

Figure 1. Principle of the tiered FOCUS surface water approach (taken from FOCUS 2001)

runoff and drainage input as a percentage of the individual applied amount. Within step-2, sequential application patterns with pesticide degradation between each particular application are taken into account. It is assumed that during pesticide application, spray drift to the water body occurs, and an additional runoff/drainage event takes place four days after application. The amount of spray drift is based on the same calculated drift values as in step-1, but additionally the number of applications were taken into account such that the drift from the total number of applications represents the 90th percentile value. This means that for a single application, the same drift loading as in step-1 is considered, but for an increasing number of applications each single drift loading becomes lower than the 90th percentile value. The combined runoff and drainage entry is calculated as a given percentage (2-5%) of the soil residue (considering plant interception and degradation) and depends on the application region (northern or southern Europe) and season (FOCUS 2001). For both steps a static ditch of 30 cm water depth and a 5 cm deep sediment layer is considered as a water body. The partition between water-phase and sediment is based on the K_{OC}.

For the more important step-3, the FOCUS surface water working group developed ten realistic worst-case climate and soil scenarios which represent approximately 33% of the total agricultural area of the European Union (FOCUS 2001). The representative weather stations are located in nine different European countries and the soil data were taken from specific fields in these areas but have been manipulated to represent wider areas. The defined scenarios differ in soil type, slope, climatic conditions (e.g., temperature and precipitation), and three different water bodies (i.e., pond, ditch, stream) typical for the regions where they are located (Table 1).

Table 1. Overview of the most important FOCUS surface water scenario properties (taken from FOCUS 2001)

Name	**Mean annual Temp. (°C)**	**Annual Rainfall (mm)**	**Topsoil**	**Organic carbon (%)**	**Slope (%)**	**Water bodies**	**Weather station**
D1	6.1	556	Silty clay	2.0	0 – 0.5	Ditch, stream	Lanna
D2	9.7	642	Clay	3.3	0.5 – 2	Ditch, stream	Brimstone
D3	9.9	747	Sand	2.3	0 – 0.5	Ditch	Vreedepeel
D4	8.2	659	Loam	1.4	0.5 – 2	Pond, stream	Skousbo
D5	11.8	651	Loam	2.1	2 – 4	Pond, stream	La Jailliere
D6	16.7	683	Clay loam	1.2	0 – 0.5	Ditch	Thiva
R1	10.0	744	Silt loam	1.2	3	Pond, stream	Weiherbach
R2	14.8	1402	Sandy loam	4	20*	Stream	Porto
R3	13.6	682	Clay loam	1	10*	Stream	Bologna
R4	14.0	756	Sandy clay loam	0.6	5	Stream	Roujan

The step-3 exposure assessment uses mechanistic models to consider pesticide leaching via drainage, surface runoff, and spray drift as well as fate and transport processes in respective water bodies. These specific exposure models are MACRO (Jarvis 2001) for drainage entries, PRZM (Pesticide Root Zone Model, Carsel et al. 1998) for runoff entries, and TOXSWA (TOxic Substances in Surface WAter, Adriaanse and Beltman 2009) for pesticide fate modelling. Either MACRO (Drainage scenario) or PRZM (Runoff scenario) is always combined with the fate model TOXSWA. The integration of these models occurs by the graphical user interface SWASH (Surface Water Scenarios Help, FOCUS 2001), which calculates the input via spray drift, organizes the database, the user input, and the coordination of data exchange between the individual models. The drift calculator uses in principle the same determined drift values based on the experimental data of the BBA (2001) as assumed in the lower steps, but other distances between crop and water body were taken into account that depend on both the water body and the relevant crop. It is also assumed that the cumulative drift loadings of all applications represent the 90th percentile from the experimental values. For the FOCUS pond and ditch scenario, only spray drift loadings from the adjacent field are considered, while for the stream scenario it is assumed that an additional 20% spray drift loading occurs at the upstream catchment. The PRZM model that is used for runoff calculation is a one dimensional, dynamic compartment model that calculates chemical movement in unsaturated soils. The hydrology that determines runoff and erosion are based on the USDA Soil Conservation Service (SCS) curve number methodology and a watershed -scale variation of the Universal Soil Loss Equation (USLE). The SCS Curve number methodology estimates a direct runoff or infiltration from a rainfall excess dependent on the hydrological soil group and land use. The USLE describes soil erosion processes and was developed from erosion plot and rainfall simulator experiments. The factors included describe erosivity, erodibility, topographies, and cropping management. The water movement in soil is simulated by the use of generalised soil parameters, including field capacity, wilting point and saturation water content (FOCUS 2001).

The MACRO model simulates pesticide losses through macropore and bulk matrix flow. The water flow in soil micropores is simulated using the Richards' equation and the solute chemical transport follows the convection-dispersion equation. For the fluxes in macropores the model uses a simplified capacitance type-approach. Details on the modelling processes of the MACRO model are described elsewhere (Jarvis 2001). For step-4 modelling, the FOCUS surface water working group developed several model refinements and mitigation options with different levels of complexity (FOCUS 2007). These include, for example, extension of substance input parameters that affect the pesticide behaviour, regional and landscape level approaches or mitigation options like no-spray buffer zones or vegetated filter strips. The SWAN (Surface Water Assessment eNabler) model (ECPA and Tessella Support services plc. 2008) is used within FOCUS step-4 calculations to implement different risk mitigation options, like runoff reduction through vegetated filter strips, and a reduced spray drift input via nozzle reduction techniques or no-spray buffer zones.

Overall, for the regulatory risk assessment of fungicides and insecticides, step-3 and step-4 are of major importance because most of the substances are regulated with those steps (cf. chapter 1.4.1). For step-3, in which no mitigation options are included, the FOCUS working group claims that the model predicts the 90th percentile field concentration. In consequence, one can interpret that a maximum of 10% of a representative sample of field concentrations should be underpredicted by the modelling results. In addition, taking into account only the 90th percentile field concentration per substance and study of the same dataset, no field concentration should be underpredicted by the model estimation. For the evaluation of step-4 predictions it is important that the considered mitigation options are implemented in actual field conditions. Otherwise an underestimation of the field concentration by the model prediction could also occur due to farmers' malpractice. Nevertheless, a recent study (Knäbel et al. 2012) showed for insecticides that there are indications that the predictions of the FOCUS modelling approach does not reflect measured field concentrations (MFC) with an acceptable degree of uncertainty. It was shown that more than 20% of the MFCs used in this study were underpredicted by the respective step-3 PECs. Nevertheless, the used dataset of this study is rather small and not all of the used field concentrations were measured in Europe.

1.5 Multi-media mass-balance models

Beside the process-driven mechanistic fate and transport models used in the FOCUS surface water modelling approach, there are also other environmental fate models, such as multimedia mass-balance models. These models have a different spatial and temporal resolution and employ different mathematical methods (Scheringer 1999). Multimedia mass-balance models describe a system of different environmental compartments with exchange processes between the compartments, and with chemical and biological degradation in every compartment simultaneously. For these models, “the power lies in demonstrating the connections among different factors that determine the chemical concentrations and the rates of transport and transformation of chemicals in the environment," (MacLeod et al. 2010) and they are a well-established technique in risk assessment of organic chemicals (MacLeod et al. 2010; Scheringer 2009). The most important advantage is that the use of multimedia models is less time-consuming because of the efficient mathematical treatment, relatively low computing effort, and small set of input data needed. One model publicly available is the Small Region Model (SRM) that is part of the Small Models (MacLeod and Scheringer 2011, Scheringer 2012). The SRM is a four-box model that consists of tropospheric air, soil, water and sediment. The model principles and the arrangement of the environmental compartments are shown in Figure 2.

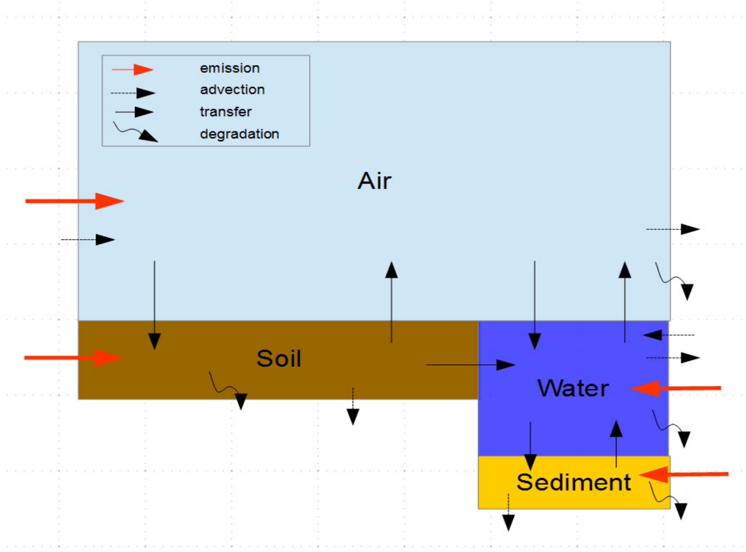

Figure 2. Principles and spatial arrangement of the fugacity-based Small Region Model. The arrows shows the processes named in the legend which are considered in the model. Figure adapted from MacLeod and Scheringer (2011).

The substance-specific input data required by the SRM are the Henry´s law constant, the octanol-water partition coefficient, and the degradation half-lives for every compartment. Furthermore, scenario-specific input data are needed that describe the compartment sizes (i.e., volume) and specify the model processes (e.g., wind speed, precipitation amount, and concentration of atmospheric aerosols). The model estimates the concentration of a chemical in a box as the combination of the total emission rate, the available volume, and the losses by degradation and outflow under the steady-state assumption. Degradation within each compartment is considered as a first-order-kinetic model and is determined by $T_{1/2} = \ln 2/k_{deg}$. The capacity of an environmental compartment is described by the fugacity capacity that is determined by the chemical partition coefficients. In addition, the model system includes outflow with moving air and water. All losses, outflow and degradation are combined in an overall removal rate constant. Overall, the model estimates for every compartment the substance's fugacity [Pa], the inventory [mol], the concentration [mol/m^3 or ng/l], and the distribution between the compartments [%].

2 Research objectives and thesis outline

The overall goal of this thesis was to contribute to the assessment of the adequacy of the regulatory exposure assessment of pesticides. The state of the art represented in the introduction suggests that pesticides can be claimed a relevant environmental stressor for agricultural surface water systems. To identify their actual environmental risks, caused by the pesticides' release to non-target ecosystems, it is essential that exposure predictions cover the range of actual field exposure. The 90th percentile protection goal, claimed by the FOCUS surface water working group (FOCUS 2001), suggests that a maximum of 10% of the field data should be underestimated by the model predictions. A recent study (Knäbel et al. 2012) indicated that the FOCUS surface water modelling approach, which is used in environmental risk assessment of pesticides and veterinary pharmaceuticals, underestimates a relevant amount of insecticide field concentrations.

Therefore, the thesis aims at the evaluation of the FOCUS surface-water approach with the evaluation of influencing factors and uncertainties, and to assess the accuracy of an alternative modelling approach. The overall outcome should be to offer new perceptions on the exposure assessment and to show concrete weak points of the current exposure assessment, and alternative possibilities that are highly relevant for the complete regulatory risk assessment of highly toxic chemicals intentionally applied to the environment.

To achieve the overall aim of the present thesis four objectives have been investigated. The complete thesis concept including the context of the single research objectives are displayed in Figure 3.

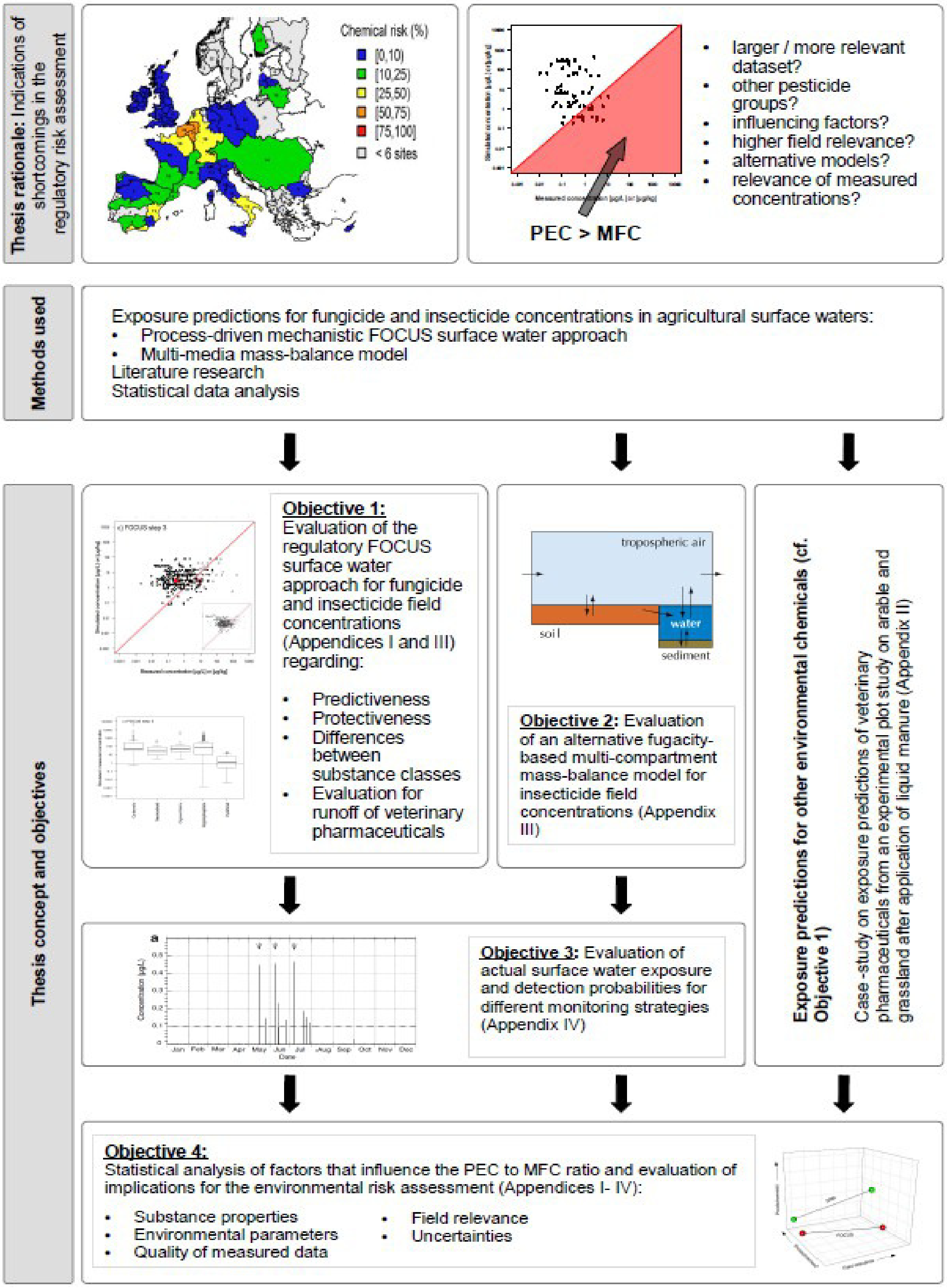

Figure 3: Overview and thesis concepts with placement of the four research objectives. References to the publications are marked with Appendix I-IV. The map in the thesis rationale indicating acute chemical risk in European river basins was taken from Malaj et al. (2014). The second figure in the thesis rationale that compares predicted and measured insecticide concentrations was taken from Knäbel et al. (2012). The scheme of the multi-compartment model shown in the context of objective 2 was taken from Scheringer (2012). All other figures are taken from the publications shown in Appendices I-IV.

3 Overview of data background and methods

In this chapter only a brief overview on the main methods is given. A detailed description can be found in the individual manuscripts attached in the Appendices I-IV of this thesis.

3.1 Outline of model calculations

In all parts of this thesis, exposure models were used for the calculation of chemical input into surface water.

First, in Appendices I and III, the predictions of the complete FOCUS surface water modelling approach (FOCUS 2001) were evaluated for fungicide and insecticide field concentrations. PECs were calculated as applied in official EU regulatory risk assessment for pesticides (FOCUS standard calculations; EU 1107/2009) and for insecticide concentrations, with an adaptation of the FOCUS step-3 standard scenarios, and input data to the field study conditions to overcome the generalising nature of the scenarios, and to improve the field relevance (FOCUS step-3 realistic calculations). The second model, which was used in Appendix III to predict insecticide concentrations in surface water and sediment, was the Small Region Model (MacLeod and Scheringer 2011), a fugacity-based chemical model for multi-compartments. SRM simulations were also conducted with parametrisation to the FOCUS step-3 standard scenarios (SRM standard calculations) and adapted to the field conditions (SRM realistic calculations). The FOCUS step-3 models were also used for the prediction of veterinary pharmaceuticals (VP) in runoff from arable- and grassland after application of liquid manure in Appendix II. FOCUS simulations were conducted for concentrations of five different veterinary pharmaceuticals and were compared to measured concentrations determined in an experimental plot study from Kreuzig et al. (2005). Again, two types of simulations were conducted. On the one hand, VP concentrations in runoff were predicted as recommended in the environmental impact assessment for VPs (EMEA 2008). On the other hand, calculations have also been conducted by adapting the standard conditions to the field situation.

In addition, the FOCUS step-3 models (FOCUS 2001) were used in Appendix IV for the prediction of insecticide exposure profiles in agricultural surface waters for different crop and application scenarios. This was done for generalized and realistic application scenarios of a typical model insecticide, and for three different example insecticide compounds. The determined exposure profiles were used to evaluate the adequacy of different sampling strategies in terms of peak detection probability (Appendix IV).

In total, approximately 6000 FOCUS calculations have been conducted for the present thesis. The majority of physicochemical substance properties were taken from the Pesticide Property Database (Lewis et al. 2015a) and from the Veterinary Substance Database (Lewis et al 2015b). Application data (application rate, number and interval of applications, and application timing) for pesticides were taken from the official EU registration documents according to the Good Agricultural Practice (GAP), or were selected according to the experimental study. Details on the selection of input data can be found in Appendices I-IV.

3.2 Evaluation of exposure models for pesticides (Appendices I and III)

3.2.1 Data background for model evaluation

Fungicide and insecticide concentrations measured in small agricultural surface waters (lotic or lentic) that resulted from agricultural non-point source pollution were extracted from scientific field studies. For fungicide concentration, a literature research was conducted in multiple literature databases (i.e., ISI Web of knowledge, BIOSIS Previews) on studies that reported fungicide concentrations measured in surface water or sediment. With some exceptions, all of the detected substances were considered. Insecticide concentrations measured in Europe were taken from a dataset of Stehle and Schulz (2015a), who conducted a comprehensive literature search in multiple literature databases for the most important insecticide substances. Further criteria for the selection of field studies for pesticide groups were (i) comparably small water-body size or catchments smaller than 10,000 km², and (ii) the presence of agricultural land in the surrounding area. In addition, all studies in which the pesticide concentrations were measured in rice paddies or were influenced by entries from rice paddies were not considered in this analysis because there is no corresponding FOCUS scenario. Multiple concentrations reported in one publication can be regarded as independent because only those peak concentrations that originated from different entry events (i.e., measured after different precipitation or application events or in different seasons) were considered. For fungicides this resulted in a data set of 56 field studies covering 46 active ingredients (Appendix I) and 482 fungicide concentrations. The selected field studies were conducted in Europe (n = 40), the United States (n = 9), Canada (n = 4), and Australia (n = 3) and published between 1996 and 2012, with the majority of studies published after 2000 (approximately 90%). For insecticides, the dataset consists of 64 studies and 466 MFCs for the EU published between 1978 and 2012, covering 21 active ingredients (Appendix III).

3.2.2 Details on FOCUS exposure modelling

The selected measured concentrations were compared to the respective PECs calculated using the tiered FOCUS surface water approach (step-1 to step-4) in accordance with the EU Directive 1107/2009. The versions of the models used are given in Appendices I and III. Scenario selection was mainly based on climatic conditions relevant for the respective field study, cultivated crops, and the pesticide input pathway. If no crop type was specified in a field study, then the crops commonly grown in the specific study region and for which the use of the particular fungicide was permitted were selected. If several crops were cultivated in an agricultural area where a field study was conducted, then multiple FOCUS PEC calculations were performed. For most of the selected studies, it was not possible to define only one climate scenario that represented the respective conditions. In such cases, step-1 and step-2 calculations were performed for northern and southern Europe and for all relevant drainage and runoff scenarios in FOCUS step-3. Step-4 calculations were only performed if the application restrictions for the respective substances are mandatory. In general, for all standard calculations the, considered procedure was as close as possible to those used for regulatory exposure assessment within pesticide registration in the EU. Taking all crop-scenario combinations into account, for fungicides a total of approximately 600 step-1 and 600 step-2 calculations and approximately 2000 step-3 and 4 calculations were conducted during this study. For insecticides 280 step-1 and step-2 calculations, approximately 750 step-3, and 800 step-4 calculations were performed.

For the FOCUS step-3 realistic calculations, which were conducted to overcome the generalizing nature of the standard FOCUS scenarios only for insecticide substances, PECs were taken from Knäbel et al. (2012) for all measured concentrations from studies that were also considered in the earlier study (n = 34). Further step-3 realistic calculations were conducted for MFCs (n = 16) for which enough information on the actual field conditions were provided in the respective publication. These calculations were performed using all available realistic field information regarding insecticide use patterns, climate conditions, landscape, and water body characteristics. If the reported field conditions differed from the FOCUS scenario assumptions, then the standard parameters and scenario conditions of the FOCUS model were adjusted. An exact description of the adaptations and methods for the calculation of FOCUS step-3 realistic PECs is given in Knäbel et al. (2012). Overall, a total of 50 step-3 realistic PECs were used in this study.

3.2.3 Details on SRM exposure modelling

PEC_{SRM} calculations for insecticides were conducted with the Small Region Model that belongs to the Small Models® LEVEL-III Version 2.0 (MacLeod and Scheringer 2011, Scheringer 2012), developed for a wide range of chemicals. These models can be used to provide estimates of chemical concentrations in air, water, soil, and sediment in a region of interest (Scheringer 2012). Beside the scenario description (proportion of environmental compartments), only the overall emission rate of the chemical and the chemical phase partitioning and degradation properties are needed as model input (Scheringer 2012). To make the two model outcomes comparable, the SRM model was scaled to the proportion of the landscape and water body conditions of the FOCUS stream, pond and ditch scenarios (FOCUS 2001). In addition, the model was parametrized to the climate and soil conditions of the ten runoff and drainage step-3 FOCUS surface water scenarios (R1-R4, D1-D6; FOCUS 2001). All input parameters are given in Appendix III. For each MFC several calculations were conducted with the parametrization for the same water body and climate scenario combinations as selected for the FOCUS calculations. In the SRM model the application rate is considered as emission rate to different compartments (soil, air, water, sediment) in mol h^{-1}. To account for the fact that the application of pesticides doesn't take place directly on the soil surface and that spray-drift can occur during application, total emission rates were split into emission to soil and emission to air, while interception by plants was not considered. The percentage of emission to soil and air from the total emission rate were based on the BBA drift values (BBA 2001), also used in the FOCUS surface water approach. Therefore, the emission to air was calculated as the total emission rate multiplied by the FOCUS drift value for the respective crop-water body combination. In addition, SRM realistic calculations were conducted for the same MFCs as the FOCUS step-3 realistic calculations for insecticides and for two further studies. For the SRM realistic calculations, adaptations of the standard calculations were conducted regarding application amount, compartment sizes, wind speed, organic carbon content in soil, and application method.

3.2.4 Outline of main statistical analyses

The MFCs were compared to the calculated FOCUS and SRM PECs and the extent of over- and underprediction was determined. If multiple PECs were calculated because of different crop-scenario combinations, the maximum PECs were compared to the respective MFCs. The relationships between PECs and MFCs were analysed using linear regression. The effect of different insecticide or fungicide substance classes on the ratio of simulated to measured concentrations (PEC divided by MFC; $\text{ratio}_{S/M}$) was analysed by a single-factor analysis of variance (ANOVA) test followed by Tukey's Honest Significant Differences (HSD) post hoc test for pairwise multiple comparisons. For insecticides the relationship between $\text{ratio}_{S/M}$ and catchment-size as well as the K_{OC} were analysed using linear regression. In addition, a multiple linear regression analysis was conducted with the $\text{ratio}_{S/M}$ as the dependent variable to identify interactions between different independent variables. The independent variables investigated in the analysis were K_{OC}, catchment-size and sampling interval. First, a main effect model was used to test all individual independent variables, followed by models containing all relevant interactions. Automated model building was used to identify the best-fit linear model containing variables and interactions with the highest explanatory power. The model building started with the most complex model, including all variables and interactions, and used a stepwise backward method with the Akaike´s Information Criterion (AIC) as the goodness-of-fit measure. All data were transformed (ln[x]) prior to statistical analysis to satisfy the assumption of normally distributed residuals. The models were also checked for heteroscedasticity and outliers (leverage plots and Cook´s distance). In addition, the relationship between PEC_{SRM} and PEC_{FOCUS} (for FOCUS steps 1-4) was also determined using linear regression. All of the statistical analyses and graphics were made with the open-source software package R (www.r-project.org). Details on program versions are given in Appendices I and III.

3.3 Exposure predictions for veterinary pharmaceuticals in runoff (Appendix II)

Exposure concentrations of five different VPs including three sulfonamides (sulfadiazine, sulfadimidine, sulfamethoxazole) and two benzimidazoles (flubendazole, fenbendazole) were measured in runoff water from arable and grassland plots after manure application in an experimental field study by Kreuzig et al. (2005). Details of the experimental field study are given in Appendix II and in Kreuzig et al. (2005). The concentrations of the VPs in the runoff water were predicted using the FOCUS surface water step-3 modelling approach. Details on used model versions are given in Appendix II. Two different types of calculations were performed for the five VPs. Within the first model exercise, the calculations were conducted as recommended for the exposure assessment of veterinary medicinal products in Europe (EMEA 2008), assuming one granular application with an incorporation depth of 15cm at the drilling time for winter cereals to meet the requirements of manure application.

In addition to the calculations performed as recommended by European Medicines Agency (EMEA 2008), in the second model exercise FOCUS step-3 calculations were conducted by adapting the input data to the site-specific plot conditions. The adaptations were made for application timing, crop scenarios (winter cereals or grass alfalfa), and precipitation amount (50 mm/d). Thus, the field situation was reflected as realistically as possible in the model. Furthermore, the application rates were adapted to the actual substance concentrations that remained following the ageing of the manure prior to the field application in the experimental plot study. For the plots located in the arable land, the calculations were conducted based on the FOCUS scenario R1, because this scenario fits the climate and soil conditions of the field sampling sites, using granular application and an incorporation depth of 15 cm. For the plots located in grassland, it was not possible to use the R1 climate and soil scenario because the FOCUS surface water scenarios assume no cultivation of “grass or alfalfa” in this climatic region (FOCUS 2001). Therefore, the calculations for the grassland plots were conducted for all other available runoff scenarios, and the maximum concentration from all considered scenarios was used for comparisons. In accordance with the procedure employed during the plot experiments, the incorporation depth of the manure was set at zero for both G1 and G2. All further parameters involved in the FOCUS modelling are given in Appendix II.

3.4 Insecticide's exposure profiles, detection probability of monitoring strategies and risk assessment (Appendix IV)

Exposure profiles were derived for a typical “model insecticide” that exemplifies median physicochemical properties, application rates, and ecotoxicity of all insecticide compounds approved in the EU (specifications are given in Appendix IV), and three real insecticides (malathion, acetamiprid, deltamethrin), that cover a wide range of physicochemical properties. Exposure profiles for these substances were derived with the FOCUS step-3 models for both arable and permanent crops. The results of the FOCUS calculations for the model insecticide were added into two generalized insecticide exposure patterns using the model insecticide results for arable and permanent crops to generate representative insecticide exposure patterns not influenced by individual compound properties. In addition, we synthesized two realistic insecticide exposure patterns using FOCUS simulation results for the application of the three real compounds to arable and permanent crops. Six typical sampling strategies used in pesticide monitoring programs with different intervals between the individual samplings were applied to the generalized and realistic insecticide exposure patterns synthesized from FOCUS scenarios using Monte Carlo simulations. In detail, we randomly sampled the model insecticide concentrations using a fixed monthly, 14 day, weekly and 3.5 day sampling strategy. The day of the first sampling within the model year was taken randomly. The exact intervals between the individual samplings were allowed to vary randomly within a specific amount of time (depending on the sampling strategy) to simulate the variability in sampling programs due to logistic restrictions. A total of 100,000 Monte Carlo simulations were run for each of these sampling strategies, and the mean, minimum, and maximum numbers of insecticide detections per model year were computed. The exposure patterns were subsequently evaluated for three different risk assessment procedures including a deterministic, a probabilistic and a relevance-driven risk assessment concept. Most of the exposure modelling was conducted by Anja Knäbel.

4 Results and discussion

4.1 Evaluation of the regulatory FOCUS surface water approach (Objective 1)

4.1.1 Protectiveness of FOCUS predictions

The fact that the degree of conservatism decreases from FOCUS step-1 to step-4 is clearly visible in our data (Figure 4 for fungicide concentrations, figures from the study on insecticides are given in Appendix III). More realistic model assumptions resulted in lower PECs, and consequently, the frequency of MFCs that exceed the PECs increased from 0% and 4% to 28% and 20% for fungicides and insecticides, respectively (Table 2). In general, a criterion is needed to decide whether the model outcomes are valid (Kirchner et al. 1996). The FOCUS surface water working group claims that the FOCUS scenarios “provide a mechanism for assessing pesticide PECs in surface water and sediment with an acceptable degree of uncertainty” and that the highest PEC in surface water (PEC_{SW}) estimates from the 10 scenarios would represent at least the 90th percentile for surface water exposures (FOCUS 2001). These criteria appear to be subjective to a certain extent and also the EFSA states that the level of protection achieved by the current FOCUS surface water exposure assessment methodology is unknown (EFSA 2013).

Table 2. Frequencies of over- and underprediction from FOCUS step-1 to step-4 calculations for agricultural pesticides measured in Europe[a,b]

	Fungicides			Insecticides		
	n	Overprediction PEC > MFC [%]	Underprediction PEC < MFC [%]	n	Overprediction PEC > MFC [%]	Underprediction PEC < MFC [%]
FOCUS step-1	327	100	0	397	96	4
FOCUS step-2	327	98	2	397	91	9
FOCUS step-3	327	85	15	397	89	11
FOCUS step-4	187	72	28	322	80	20

[a]PEC = Predicted environmental concentration; [b]MFC = Measured field concentration

Nevertheless, taking the ±10% deviation value as a quality threshold, the results of the present thesis on fungicides and insecticides clearly support the conclusion, which was previously reached for the first insecticide study (Knäbel et al. 2012), that the degree of uncertainty is not acceptable. Even if the predictions of the very conservative step-1 and step-2 calculations generally overestimated the respective MFCs, those for step-3 and step-4 calculations, underpredicted the MFCs by 15% and 28%, respectively. This finding is substantial because FOCUS step-3 and 4 are the most realistic standard tiers available in European regulatory exposure modelling and are used for the risk assessment of 62% of the fungicides and 82% of the insecticides registered in the European Union for which the risk assessment was publicly available. Thus, because values that are lower than the actual surface water concentrations are considered in the regulatory risk assessment, pesticides might exhibit unacceptable ecological effects in the field. In addition to the complete dataset, we also compared the calculated PECs to the 90th percentile concentrations of every substance's MFCs from each study. This was done to exclude particularly low water-phase concentrations and to increase the chance that measured concentrations are peak concentrations, because the FOCUS approach also aims at predicting maximum peak concentrations. For insecticide concentrations we further reduced the dataset to only concentrations which are definitely agricultural origin. The analyses of these datasets showed that the frequency of MFC underestimation is considerably higher than for the complete dataset. FOCUS step-3 predictions which did not include mitigation options underestimated 26% of insecticide MFCs and 19% of fungicide MFCs (Appendices I and III). This finding is substantial because the reduced dataset has a higher relevance for the evaluation of the FOCUS approach, as it represents peak concentrations stemming from non-point source entries also predicted within the FOCUS approach, taking into account the 90th percentile protection goal claimed by the FOCUS surface water group. For the reduced dataset no field concentrations should be underestimated considering the protection goal claimed by the FOCUS surface water group, that the highest PEC represent the 90th percentile field concentration. Mackay et al. (1996) stated that it is unlikely for exposure models to be universally valid but they may produce results that are deemed to be reliable with a level of accuracy that depends on the nature of the chemical, the environment, and regulatory requirements. Regarding only the aspect of the regulatory requirements, the FOCUS approach failed to meet the demanded protection goal. As mentioned before, in addition to model inaccuracies, the underestimation of MFCs might also be a result of farmers' malpractice, for example the non-adherence to spray buffer zones. But this would only explain a theoretical difference between the underestimation frequencies of step-3 and step-4, since step-3 does not include mitigation options. This means that for example for fungicides only 13% of the cases might be due to farmers malpractice (difference between 28% and 15% underestimation in step-4 and step-3, respectively).

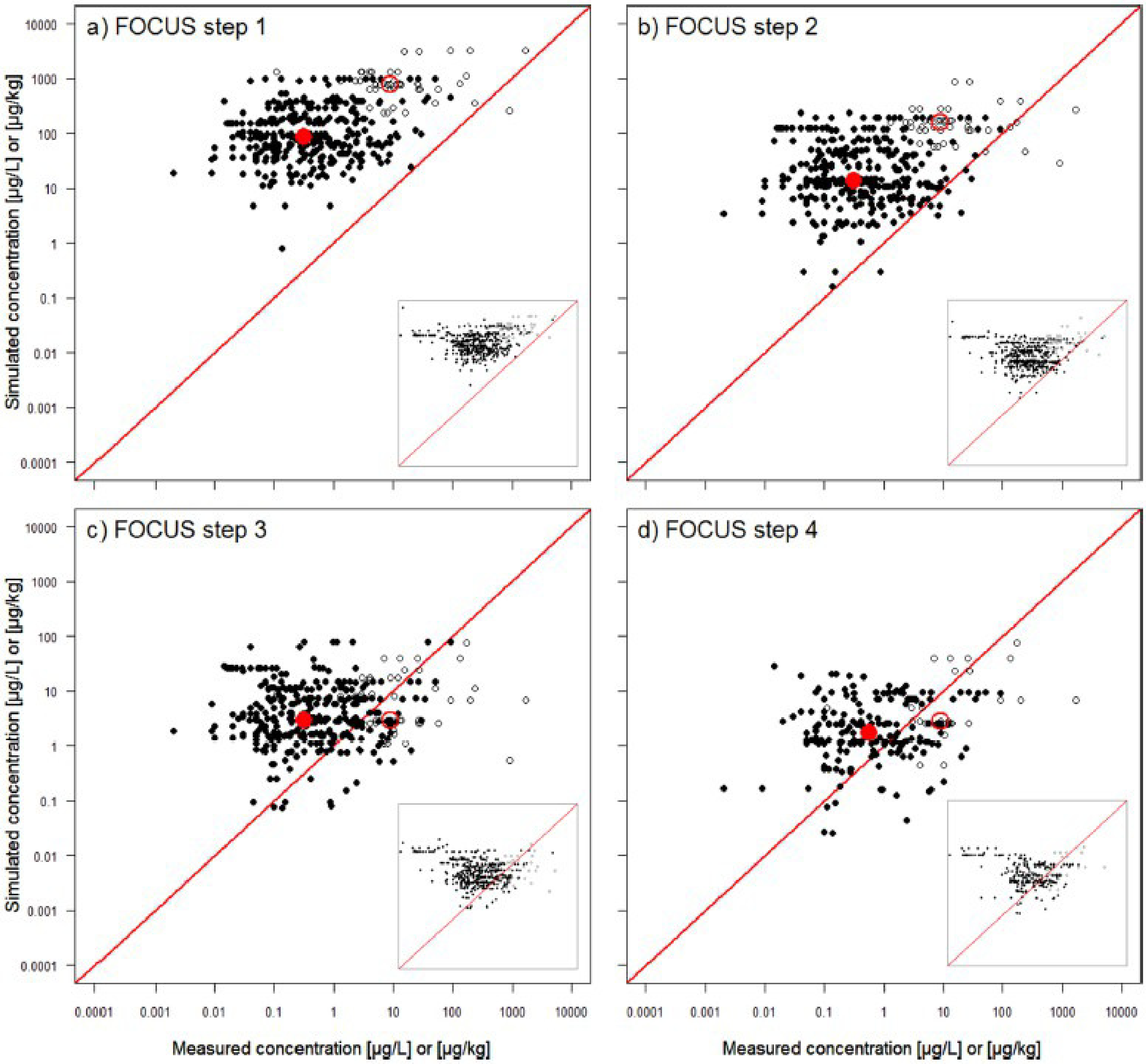

Figure 4. Relationship between simulated and measured fungicide concentrations from EU studies for FOCUS steps 1−4. Black dots = water (step 1−3: n = 327; step-4: n = 187); white dots = sediment (step 1−3: n = 57; step-4: n = 37); large red dot = overall median surface water concentration, large red circle = overall median sediment concentration. Small figures = respective data for EU plus rest of the world (water: step 1−3: n = 417, step-4: n = 223; sediment: step 1−3: n = 65, step-4: n = 38). The 45° line denotes identity between PEC and MFC. The simulated concentrations are displayed on the y-axis such that the MFC underestimations are plotted below the 45° line. Figure taken from Appendix I.

The underestimation of the actual pesticide concentration was also described by Jung et al. (2012) using an environmental exposure model (KOIEM) to predict insecticide concentrations in water bodies in Korea. These researchers compared the average measured deltamethrin concentrations with the PECs and found that the calculated PECs for ditches underestimated the real concentrations with a median factor of approximately 3. Most important, they found that estimated maximum concentrations predicted by KOIEM were higher than those obtained from FOCUS, which indicates that the underestimation obtained with FOCUS could even be worse. Only a few other published studies have compared predicted environmental pesticide concentrations and field data; however, most of these studies studied only a very limited number of cases or did not use the FOCUS surface water approach ($n < 5$; Padovani and Capri 2005; Singh and Jones 2002; Jackson et al. 2005). However, this thesis includes the first studies that has evaluated the complete FOCUS approach using a larger number of fungicide and insecticide concentrations from several field studies, most of which were conducted in the EU.

4.1.2 Predictiveness of FOCUS predictions

Predicted pesticide concentrations used in aquatic risk assessment should provide some degree of realistic estimates of field concentrations, i.e., there should ideally be some kind of relationship between measured and predicted concentrations. The results of this thesis show that there are only very few matches between predicted and measured fungicide concentrations, most likely due to coincidence. If a difference of ±10% is regarded as adequate (FOCUS 2001; US EPA 1988) then less than 7% of the step-4 fungicide PEC_{SW} and less than 1% of the insecticide PEC_{SW} matched the MFC_{SW}. Even when the performance threshold was set at ±30% to account for uncertainties in the field studies, almost all predictions, i.e., 92% and 96% of all step-4 fungicide and insecticide PECs, did not match the MFC_{SW}. Furthermore, Figure 4 shows that there is no positive relationship in terms of a statistically significant slope with a value greater than 0, e.g., in a linear regression model between predicted and measured fungicide concentrations. The same was shown for insecticides (Appendix III). In response to the results obtained in the preliminary study on insecticides (Knäbel et al. 2012), Reichenberger (2013) criticized that one modelled data point was plotted against several measured data points and claimed that only the measured peak concentrations should be used to evaluate the linear relationship (see also Knäbel et al. 2013). Even if the fungicide concentrations considered here were measured either during different seasons or originated from clearly distinguishable entry events, it cannot be ensured that they are absolute peak concentrations. For this reason, we additionally analysed the relationship between step-3 and step-4 PECs and the 90th percentile MFCs for every substance per study and either event-related MFCs (in case of fungicides) or concentrations that are definitely agricultural origin (in case of insecticides). The results for this analysis showed, that there is still a very week (maximum $r^2 = 0.08$, 90th percentile MFCs + only EU data Appendix I, Supporting

Information (SI) and Appendix III) yet due to the large n, significant linear relationship for the fungicide data but no relationship for the reduced insecticide dataset (Appendix III). However, the results of this thesis confirm the observation made earlier (Knäbel et al. 2012) that the quality of FOCUS predictions, regarding a relationship between measured and predicted fungicide and insecticide concentrations, is not sufficient. This is important in the context of the evaluation of the model validity, even if the FOCUS working group does not aim at an accurate prediction of actual field concentrations. A prediction of field concentrations “with an acceptable degree of uncertainty” (FOCUS 2001) should result at least in some kind of relationship between PECs and MFCs even if there might be uncertainties in the considered field data. Bach and Hollis (2013) also questioned the quality of the FOCUS models, although their argument was not based on any empirical evidence. Kirchner et al. (1996) stated that a model is valid if it is adequate for a specific purpose, rather than absolute truth in every respect. Assuming that the only purpose of the FOCUS approach is to be protective and not to lead to underestimations of the real contamination in the field, then FOCUS step-1 and 2 might achieve this aim, but step-3 and step-4 predictions are unacceptable in their present form. Possible reasons for the low quality of the FOCUS predictions, such as the too-simplified integration of upstream catchment, translation of runoff fluxes from PRZM to TOXSWA, and the impossibility of a simultaneous calculation for drainage and runoff entries, are described elsewhere (Knäbel et al. 2012; Bach and Hollis 2013). Another shortcoming, which seems to be particularly relevant for fungicides, is that not all relevant entry pathways are included in the FOCUS modelling approach. It has for instance been shown that the wash-off from paved edge-of-field farm pathways in vineyards, on which the fungicides dropped during the turn of the spraying machines, is a highly relevant entry pathway into aquatic ecosystems (Bereswill et al. 2012; Lefrancq et al. 2013). Nevertheless, vineyards are only relevant in 10 of the 56 field studies that reported fungicide concentrations in surface water considered here (Appendix I).

4.1.3 Predictiveness for different substance classes

As was shown in the earlier study on insecticides (Knäbel et al. 2012), the FOCUS modelling approach is not similar for all substance classes. The results of this thesis, with a much larger sample size, confirm that the FOCUS approach is less protective for highly toxic pyrethroids, compared to organochlorines, organophosphates, and neonicotinoids, even when neonicotinoids as an additional substance class are included. For the insecticide study we found that highly toxic pyrethroids had significantly lower ratio$_{S/M}$ for all FOCUS steps (Appendix III; SI). This result is remarkable, as over the past decades pyrethroids have become increasingly important agricultural insecticides (Hendley et al. 2008). Pyrethroids generally have a low water solubility and consequently high K_{OC} values, which leads to a rapid and strong sorption to soil and sediment (Domagalski et al. 2010; Hill 1989) which should reduce both the entry into surface water and the concentration within the water column after the entry into the water body. Therefore, we tested if exclusion of sorption to sediment had an impact, but neither the extent of underestimation of MFCs by step-3 PEC$_{FOCUS}$ nor the ratio$_{S/M}$ for different substance classes changed. Luo and Zhang (2011) stated that PRZM is known to inadequately predict the pesticide transport associated with soil erosion. This assertion may explain the underestimation of insecticide PECs arising from runoff entries for strongly sorbing pyrethroids, as the pesticides associated with eroded soils are removed only from the uppermost soil compartment (US EPA 2012). In addition, Jones and Mangels (2002) list several PRZM deficiencies (e.g., overestimation of downward movement, underestimation of pesticide persistence in soil) that could also lead to the underestimation of field concentrations.

Compared to insecticides, for fungicides we found only small differences in the ratios$_{S/M}$ between different fungicide substance classes for all FOCUS steps (Appendix I). Chloronitril and chlorophenol fungicides exhibited significantly higher ratios than most of the other fungicide classes in all FOCUS steps. The reason for this is most likely that chloronitril (e.g., chlorothalonil) and chlorophenol (e.g., dicloran and quintozene) fungicides were measured at relatively low concentrations but the predicted concentrations were comparatively high due to high application rates. In addition, only the PEC$_{SW}$ to MFC$_{SW}$ ratio for carbamate fungicides in step-4 were significantly lower than 1 because all of the MFC$_{SW}$ were underpredicted by the respective PECs. Nevertheless, no general conclusion should be derived from this finding because the sample size is rather low (n = 3).

4.1.4 Evaluation of the FOCUS approach for the prediction of veterinary pharmaceuticals in runoff

The evaluation of the FOCUS predictions for veterinary pharmaceuticals in runoff was done for concentrations measured in an experimental plot study from Kreuzig et al (2005). In the experimental study the application of liquid manure containing VPs and subsequent irrigation to both arable and grassland plots resulted in substance specific concentrations in the runoff water. Between 2.5 and 27.6% of the total applied amount were measured in the surface runoff water from the plots with a general higher loss from grassland plots which can be explained by the fact that the manure was not incorporated into the soil on the grassland plots.

The predictions of the VP concentrations in runoff water by the FOCUS step-3 modelling approach generally differ very much between the two different modelling exercises conducted in this study. The overall predicted runoff concentrations are much higher than the measurements for four of the five VPs applied during the plot experiments, if calculations are performed as recommended for the risk assessment for VPs on arable land. The high protection level of the first modelling exercise, may be primarily explained by the fact that the application rate for each VP corresponded to its initial (spiked) concentration and not its concentration after ageing This overprediction was reduced if the FOCUS step-3 scenarios were parametrized to the site- and hence, the situation -specific conditions (Appendix II). Even if the predictions of the site-specific FOCUS modelling approach were higher than the measured concentrations (up to a factor of 415) for most of the cases, in 35% of the cases, the measured concentrations in the runoff are underestimated by up to 24-fold by the model output. This frequent underestimation of the runoff concentrations was mainly (85% of the underestimated situations) observed for the grassland plots, whereas the FOCUS predictions overestimated the concentrations in the runoff from the arable plots. This phenomenon may be partly explained by the overestimation of the infiltration rate during the runoff causing an underestimation of the runoff-induced translocation inter alia VPs (Jones and Mangels 2002). Therefore, considering the general substantial overestimation of the runoff concentrations generated by the models that were parametrised for the site-specific situations during the arable land plot experiments (up to 415-fold), the reliability of the predictions generated by the FOCUS step-3 models are questionable— irrespective of the partly high level of protectiveness with regard to the risk assessment associated with their predictions. More importantly, the FOCUS modelling approach was not designed to estimate the runoff of VPs after the application of manure, a fact that likely substantially contributed to the detected differences between the predicted and measured concentrations. In addition, the FOCUS modelling approach aims at the prediction of the fate of pesticides, which are applied as formulations directly to the soil surface but are not bound to other organic material, such as manure, which explains the large overestimation of the actual VP concentrations in certain cases. Altogether, these observations shows that there are substantial differences between the predicted and measured VP concentrations in the runoff. Therefore, the present results calls for a more targeted analysis questioning, for instance, the representativeness of the FOCUS modelling approach for substances applied to agricultural fields in combination with manure and the analysis of the sensitivity of important input parameters.

4.2 Comparison between predictions of the fugacity-based Small Region Model and the FOCUS approach (Objective 2)

Compared to the result of the step-3 FOCUS calculations, the PEC values from the SRM generally overestimate the corresponding MFCs by several orders of magnitudes (Figure 5). Only 1% of all PECs calculated with SRM underpredicted the respective surface water field concentrations. Even for the reduced dataset (90th percentile concentration per substance and study that are definitely agricultural origin), the frequency of underprediction increased only slightly to 2%. This means that the SRM exposure predictions are much more protective than the predictions of the regulatory FOCUS step-3 approach. The most important reason for the generally higher PEC_{SRM} might be that within the SRM model the total amount of the applied substance is available for the partitioning between the different compartments within the system because the model does not consider some small-scale processes that might reduce the transfer of the chemical to surface water.

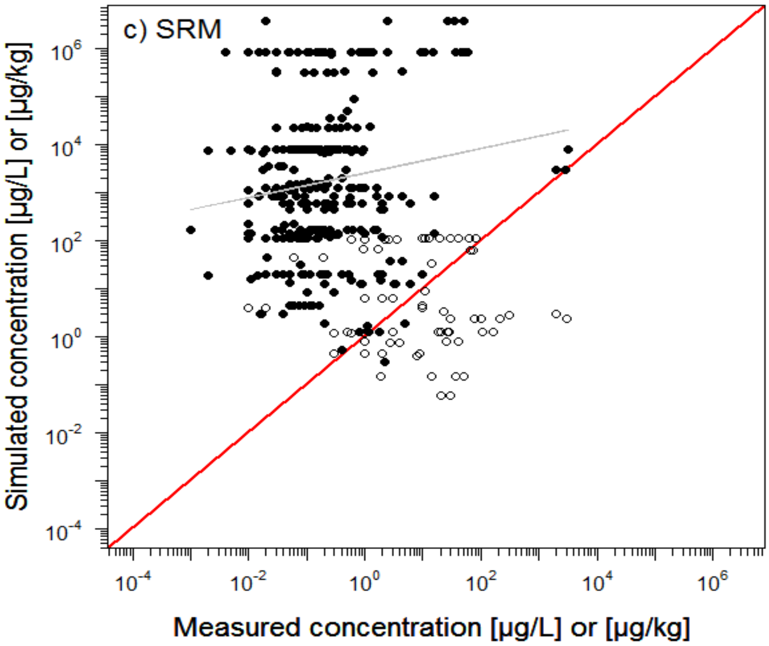

Figure 5. Relationship between insecticide concentrations predicted with the Small Region Model adapted to the FOCUS step-3 standard scenarios and measured concentrations. Black dots = water-phase concentrations (n = 397), white dots = sediment concentrations (n = 69). Figure taken from Appendix III.

This includes, for example, plant interception and photodegradation on the soil surface, which generally results in lower chemical amounts available for surface water entry within the system. Nevertheless, there are indications that within the FOCUS approach especially the extent of plant interception is overestimated for some crops (Olesen and Jensen 2013).

Another study from Di Gurado et al. (1994) that compared measured herbicide concentrations to concentrations predicted with a fugacity model showed that the model has a tendency to overestimate actual measured concentrations and concluded that the worst-case scenario results in concentrations “protective for the environment”. Di Guardo et al. (1994) concluded that in reality the transfer process of pesticides from soil to surface water may only depend on a mixing layer of a few centimetres of the soil from which the pesticide can be extracted. During a rainfall event, a relevant amount of the substance can be moved downward, such that the chemical is not available for runoff, which might even be increased by the presence of cracks and macropores. This might also be true for the predictions conducted in the present thesis.

In our study, the frequency of MFC_{SW} underprediction by PEC_{SRM} is even lower than that from the PEC_{FOCUS} calculated with the very conservative FOCUS steps 1 and 2 (Table 2), especially for the reduced dataset (frequency of underprediction: step-1: 14%, step-2: 23%; Appendix III). Mackay et al. (1996) stated that it is unlikely for exposure models to be universally valid, but they may produce results that are deemed to be reliable with a level of accuracy that depends on the nature of the chemical, the environment, and regulatory requirements. Regarding only the aspect of the regulatory requirements, the FOCUS approach failed to meet the demanded protection goal, while the SRM showed a very high level of protectiveness. In terms of accuracy of the model results, the standard SRM calculations do not show a better performance than the FOCUS predictions because the standard SRM PECs generally overestimate the MFCs by several orders of magnitude.

Box 2: Conclusions reached from objective 2

The predictions from the fugacity-based SRM model results in concentrations higher than the MFCs. Only 2% of the field concentrations were underpredicted by the model results. No linear relationship was found between PECs from the SRM and the field data. The predictions are much more conservative compared to that of the FOCUS approach and provides estimations "protective for the environment". Nevertheless, the predictive capability of the SRM model seems to be as low as that of the regulatory FOUCS approach when the model is parametrized to the FOCUS standard scenarios.

4.3 Actual surface water exposure of insecticides and detection probabilities for different monitoring strategies (Objective 3)

The simulated exposure patterns of the generalized insecticide resulted in 11 and 16 peak concentrations for arable and permanent crops respectively (Figure 6). The analysis of the exposure durations revealed that insecticides are only detectable with a maximum of 2.3% of the time. For real insecticides the simulations showed that the amount of time in which insecticides are detectable within the surface water system is even lower than for the generalized insecticide with less than 1% for both arable and permanent crops (arable crops: 0.62% of the time; mean exposure duration, 9.1 h; permanent crops: 0.97% of the time, mean exposure duration, 9.7 h). The highest simulated concentrations were caused by spray drift entries, while drainage and runoff entries led to lower concentrations.

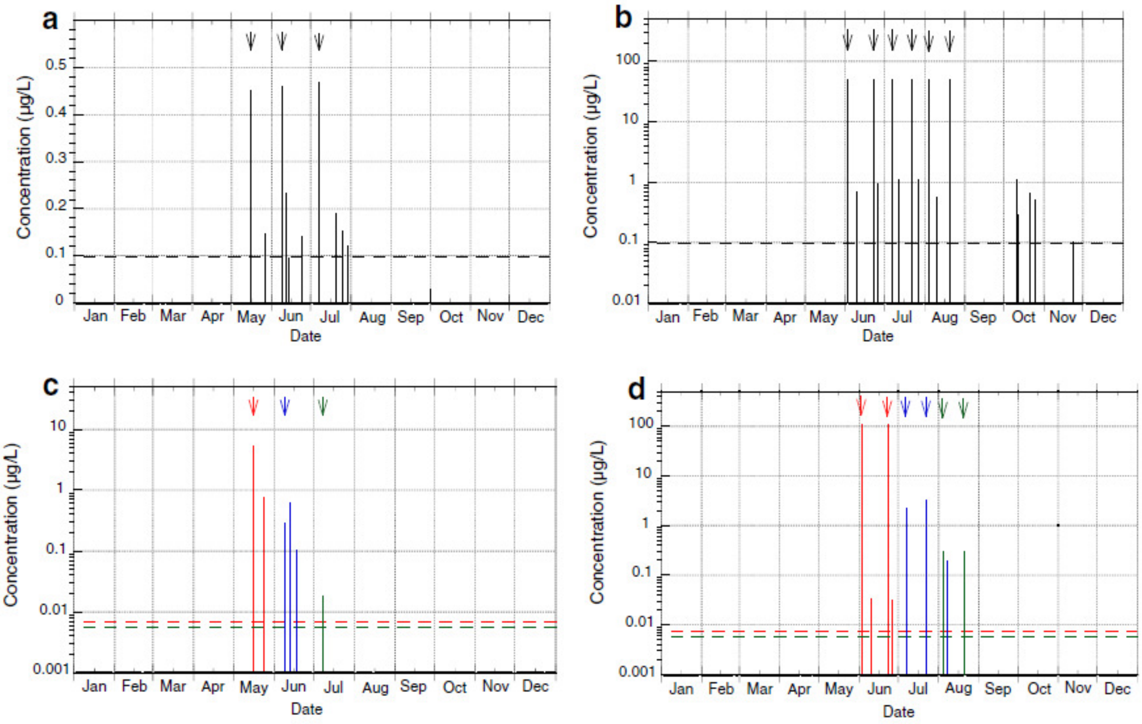

Figure 6. Generalized (a, b) and realistic (c, d) insecticide exposure profiles in a stream receiving agricultural non-point source pollution as synthesized from respective FOCUS surface water scenarios (see Appendix IV, Supporting Information for detailed FOCUS scenario results). a, c Arable crops with three insecticide applications (arrows above bars, application dates); b, d six applications to permanent crops. The dashed horizontal lines indicate the RAC for the insecticides (see Appendix IV for details on the RACs). Figure was taken from Appendix IV (Stehle et al. 2013).

However, 80% and 93% of the model insecticide and 50% and 67% of the real insecticide peaks exceeded the relevant regulatory threshold level. Even if it was shown in this thesis that the FOCUS modelling approach do not adequately predict insecticide peak concentrations, it has been shown that the general exposure patterns (peak intervals and decrease in concentration height) are reasonably represented (Ashauer and Brown 2007; Brock et al. 2007). The investigation of different fixed-interval sampling strategies showed that less than 50% of the simulated concentrations of the realistic insecticide exposure pattern were detected. This in consequence means that all static-fixed monitoring intervals result in high percentages of non-detects (99 to 100%, Appendix IV). Only the application of an event-related sampling resulted in the detection of all occurring insecticide peak concentrations with a peak detection error of 0%. In addition, it was shown in a cost benefit analysis (Appendix IV), that the costs for a positive detection by a fixed-interval sampling were more than a factor of 30 higher compared to an event-based sampling. These findings are substantial for the present thesis, because it means that the insecticide field concentrations measured by a fixed-interval sampling used for the evaluation of the exposure models do not represent maximum peak concentrations which are predicted within the environmental risk assessment. The results of the present thesis showed that for low (i.e., < 0.5 µg/l) water-phase insecticide concentrations, almost all PECs are higher than the MFCs in all FOCUS steps (Figure 4). Knäbel et al. (2012) showed that 50% of the considered MFCs below 0.5 µg/l were measured by an event-related sampling, which was the case for 86% of the concentrations > 0.5 µg/l. this clearly indicates that the amount of underestimation of actual insecticide field concentrations might even be higher than shown in the present thesis. These findings might even be worse for fungicides in context of the present thesis. In contrast to insecticides, fungicides are used at comparably high application rates and multiple applications per season, which can lead to a more continuous entry of fungicides into surface water bodies than that observed with insecticides (Bereswill et al. 2012). With an almost continuous exposure throughout the season, static fixed sampling intervals may lead to the detection of more concentrations lower than the maximum peak concentration instead of non-detects (Rabiet et al. 2010). For the model evaluation this could mean that an even higher amount of the field concentrations do not represent actual peak concentrations compared to insecticides (Appendices I and III). This was further underpinned by the fact that fraction of the MFC underprediction is higher for the 90th percentile concentration per substance and study compared to the complete dataset for both fungicide and insecticide concentrations, but the difference in the underestimation frequencies for this dataset compared to the complete dataset was higher for insecticides than for fungicides. Nevertheless, also for fungicide concentrations it was shown that more of the considered concentrations higher than 0.5 µg/l were measured by an event-related sampling than of the concentrations smaller 0.5 µg/l (64% instead of 48%, Appendix I).

Box 3: Conclusions reached from objective 3

It has been shown that the surface water monitoring for insecticides using any kind of fixed-interval strategy is inadequate for the detection of short term insecticide concentrations, because less than 50% of the seasonal insecticide peaks were detected. Compared to that an event-related sampling strategy results in the detection of all occurring insecticide peak concentrations and is also less cost and time intensive. These findings implicate that the measured concentrations used for the evaluation of the FOCUS approach do not reflect actual peak concentrations and that the amount of MFC underestimation is even higher than shown for objective 1.

4.4 Factors that influence the predictive model capability and implications for environmental risk assessment (Objective 4)

The evaluation of the realistic simulations conducted in the study on insecticides (Appendix III) in which the standard scenarios were adapted to the respective study conditions showed that the extent of underprediction is higher than for the standard calculations. For FOCUS step-3 realistic calculations, the frequency of MFC underprediction is more than three times the frequency of the step-3 standard calculations (64%; Table 1) and even higher than shown in the earlier insecticide study (43%, Knäbel et al. 2012). The frequency of MFC underprediction by realistic PEC_{SRM} values is also higher than for the standard SRM calculations, but there is only a small difference between standard and realistic calculations (8% instead of 1%). This fact demonstrates that the substitution of the worst-case assumptions included in the step-3 standard scenarios, to which the SRM model was also parametrized, by real-world field data generally results in lower PECs. Nevertheless, the frequency of MFC underestimation by PECs calculated with the SRM realistic scenarios remains within the range of 10%, which is often used a quality criterion for model evaluations, and can therefore still be claimed as protective.

In addition, as shown in the earlier insecticide study (Knäbel et al. 2012) the relationship between realistic PEC_{FOCUS} and MFC was not improved compared to the standard calculations. However, for the SRM results, there is a significant relationship between realistic PEC_{SRM} and MFCs of the reduced dataset ($p = 0.03$, $r^2 = 0.31$), which clearly shows that the SRM's predictiveness increases with a higher field relevance to the measured data (i.e., an increase in realism of input parameters and scenario, Figure 7). This higher predictiveness is important in the context of ERA because it means that a relatively simple multi-media mass balance model serves the purpose better than the FOCUS models do. Furthermore, it was shown that for the SRM realistic calculations some points directly lie along the 45 degree line and the distance of the data-points is even lower when only concentrations are considered that were measured by an event-related sampling (Appendix III, Figure 1h). Even if the dataset is rather small for this evaluation, this result indicates that there is a need for the development of more realistic exposure scenarios because a higher field relevance resulted in a higher predictive performance of the SRM model. Also Di Guardo and Hermens (2013) concluded that for an improvement of the exposure assessment the current environmental scenarios should be improved to describe realistic conditions and that more evaluation datasets should be made publicly available.

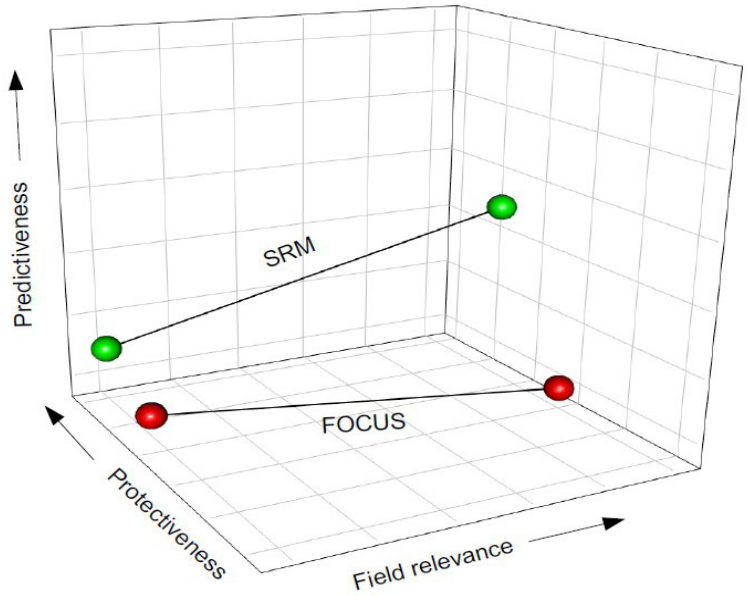

Figure 7. Schematic illustration of FOCUS and SRM predictions at two different levels of field relevance. Taken from Appendix III.

As mentioned before, the FOCUS modelling approach is not similar for all substance classes and underpredicts especially highly toxic pyrethroids which generally have a low water solubility and consequently high K_{OC} values. This leads to a rapid and strong sorption to soil and sediment and should reduce both the entry into surface water and the concentration within the water column after entry into the water body. Therefore, we tested if exclusion of sorption to sediment had an impact, but neither the extent of underestimation of MFCs by step-3 PEC_{FOCUS} nor the $ratio_{S/M}$ for different substance classes did change. Possible reasons for the significantly lower $ratio_{S/M}$ for pyrethroids, like the overestimation of pesticide downward movement in soil in the PRZM model are discussed elsewhere (Knäbel et al. 2012). Also for the SRM, the lowest $ratio_{S/M}$ was found for pyrethroids, but almost no underprediction occurred even for this insecticide class (Appendix III).

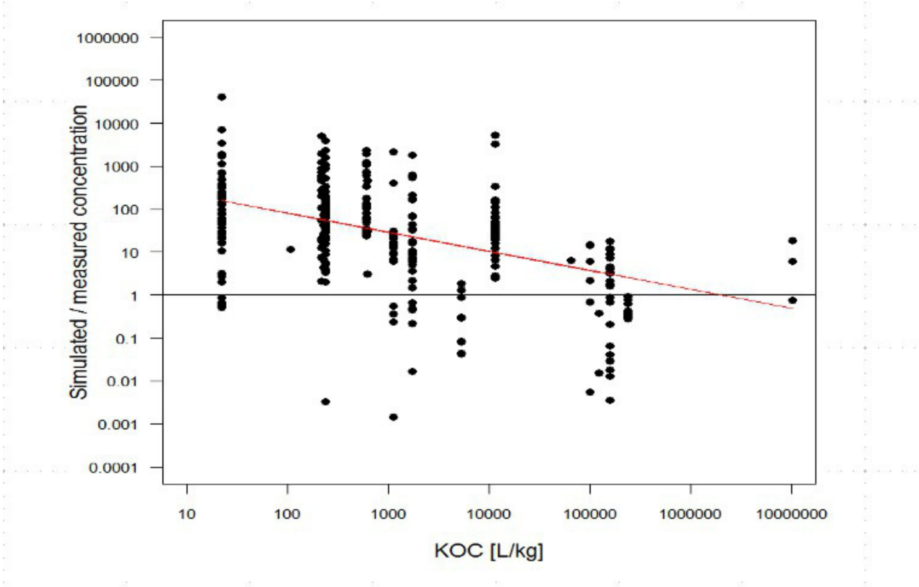

Figure 8. Relationship between simulated to measured concentration ratios in the water phase and substances K_{OC} for FOCUS step-3. Red lines shows linear regression between simulated to measured concentration ratios and substance K_{OC} ($p < 0.001$; $r^2 = 0.21$). Figure taken from Appendix III.

Therefore, we analysed the relationship between the ratios$_{S/M}$ and the substance K_{OC} value. A significant negative linear relationship was found for all FOCUS steps (Figure 8, for step-3 results), which shows that the chance that MFCs are underestimated by the respective PECs increases with increasing K_{OC} values (also shown in the multiple regression analysis, Appendix III, SI). This result confirms the fact that highly hydrophobic pyrethroids are especially underpredicted by the PEC$_{FOCUS}$ results. Overall the MFC underestimation depends on a variety of factors including substance properties and environmental parameters. In addition, Stehle and Schulz (2015a) showed that the frequency of regulatory threshold level exceedances by MFCs is significantly higher for pyrethroids compared to organophosphorus and organochlorine insecticides.

Box 4: Conclusions reached from objective 4

The higher field relevance of the realistic calculations resulted in lower PECs and a higher undeprediction frequency for all FOCUS steps, while those of the SRM predictions did not increase noticeably. The results of the SRM realistic calculations indicate that the SRM might estimate insecticide concentrations with an acceptable degree of uncertainty if the model is parametrized in a more realistic way than simply to the FOCUS standard scenarios.

5 Conclusion

The control of pests and diseases is important in modern agriculture. Therefore, the use of pesticides on agricultural areas is indispensable to prevent yield losses and to safeguard the world food supply for a growing human population. The application of these highly toxic and biologically active substances require an individual environmental risk assessment prior to the legalization of the chemical to ensure that there are no harmful effects to non-target ecosystems. The prevention of harmful ecological effects postulates that both effect and exposure assessment reflect actual field conditions with an acceptable degree of uncertainty. The results of the present thesis clearly showed that the FOCUS exposure modelling approach used within the regulatory risk assessment of the European Union, to predict pesticide concentrations in surface water and sediment, does not provide estimations that reflect actual field exposure. In detail, the work presented here shows for the first time that a considerable amount of two representative datasets of measured field concentrations were underestimated by the FOCUS modelling approach. Up to one-third of the field concentrations were underpredicted by the respective model predictions for the most important FOCUS tier, which means that in 30% of the cases the actual risk might be underestimated within the regulatory risk assessment. In addition, it was also shown that the FOCUS approach especially underestimates hydrophobic and highly toxic pyrethroids and that the predictive capability is negative correlated with the substance K_{OC}. Beside the insufficient protectiveness, it was also shown that the general model performance quality is low. No relationship in form of a linear regression was detected between predicted and measured field concentrations for fungicides and insecticides. The presented work also showed that the amount to which the FOCUS approach underestimated the actual surface water exposure with pesticides might even be higher than in the results presented here, because there are several hints that a relevant amount of the considered MFCs does not represent actual peak concentrations.

Compared to the results of the FOCUS predictions it has been shown that a less complex fugacity-based multi compartment model provides predictions that can be claimed protective for the environment, when the model is parametrized to the regulatory FOCUS standard scenarios. Moreover, if this parametrization is adapted to the actual conditions of the field sampling sites to reach a higher degree of field relevance the model performance quality significantly increase compared to the standard calculations and can even result in predictions with an acceptable degree of uncertainty. Therefore, this thesis uncovered for the first time that a less complex modelling approach than used in the regulatory risk assessment exhibits a higher level of protectiveness and predictiveness and that there is a need to develop and evaluate new ecologically relevant scenarios in the context of exposure modelling.

Overall, the present thesis contribute significantly to the overall knowledge on the adequacy of the actual environmental exposure assessment and might explain partly why pesticides pose a substantial threat to the ecological integrity of aquatic ecosystems, because it shows that the actual risk of pesticides might be underestimated already within the registration procedure. The fact that a less complex and much simpler modelling approach resulted in more reliable predictions than the complex FOCUS approach are highly relevant and should be taken on the agenda of the relevant authorities.

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7 Declaration

I, the undersigned, author of this work, declare that this thesis is my own work and has not been submitted in any form for another degree or diploma at any university or other institution of tertiary education.

Information derived from the published or unpublished work of others has been acknowledged in the text and a list of references is given.

....

Date Signature

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9 Curriculum Vitae

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10 Appendices

Appendix I

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

Knäbel, A. and Schulz, R. (2014) Response to Comment on Fungicide Field Concentrations Exceed FOCUS Surface Water Predictions: Urgent Need of Model Improvement. *Environmental Science and Technology*, 48, 5347–5348.

Appendix II

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Appendix III

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Appendix IV

Stehle, S.; Knäbel, A.; Schulz, R. (2013) Probabilistic Risk Assessment of Insecticide Concentrations in Agricultural Surface Waters: A Critical Appraisal. *Environmental Monitoring and Assessment*, 185, 6295-6310.

Appendix I

- Knäbel, A.; Meyer, K.; Rapp, J.; Schulz, R. (2014) Fungicide Field Concentrations Exceed FOCUS Surface Water Predictions: Urgent Need of Model Improvement. *Environmental Science and Technology*, 48, 455−463.
- Supporting Information for: Knäbel, A.; Meyer, K.; Rapp, J.; Schulz, R. (2014) Fungicide Field Concentrations Exceed FOCUS Surface Water Predictions: Urgent Need of Model Improvement. *Environmental Science and Technology*, 48, 455−463.

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Fungicide Field Concentrations Exceed FOCUS Surface Water Predictions: Urgent Need of Model Improvement

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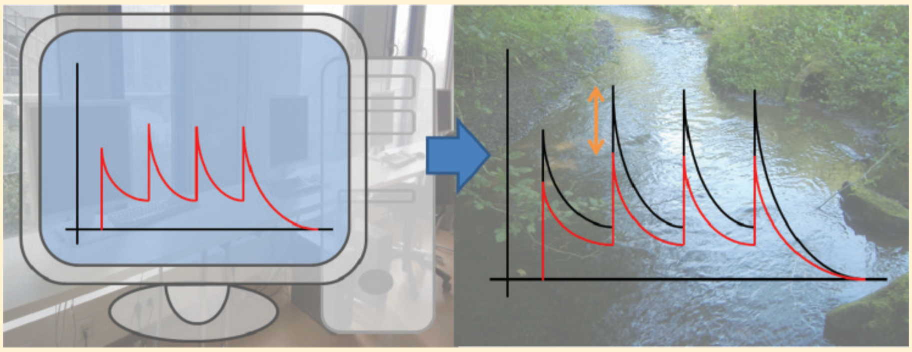
Supporting Information



ABSTRACT: FOCUS models are used in European regulatory risk assessment to predict the frequency and magnitude of individual pesticide surface water concentrations. A recent study showed that these models are not protective in the prediction of insecticide concentrations in surface waters and sediments. Since fungicides differ with regard to their physicochemical properties, application patterns, and entry routes, we compared a larger data set of 417 measured field concentrations (MFC) of agricultural fungicides in surface waters and sediments from 56 studies to the respective predicted environmental concentrations (PEC) calculated with FOCUS step 1–4. Although the fraction of the underestimation of fungicide MFC values was generally lower than that obtained for insecticides, 12% of step 3 and 23% of step 4 PECs were exceeded by surface water MFCs. Taking only the 90th percentile concentration of every substance and only E.U. studies into account (E.U. studies: $n = 327$; 90th percentile + E.U. studies: $n = 136$), a maximum of 25% of the step 3 and 43% of the step 4 PECs were exceeded by surface water MFCs, which is an even worse outcome than that obtained for insecticides. Our results demonstrate that FOCUS predictions are neither protective nor appropriate for predicting fungicide concentrations in the field in the context of European pesticide risk assessment.

INTRODUCTION

Fungal diseases are an important factor in modern agriculture, where it is common to plant the same strains of high-yield crops, which results in the reduction in the variety of resistance genes.[1] In addition, the spread of fungal diseases may be accelerated by climate change.[1] For this reason, fungicides are considered indispensable in food production today and may become even more important in the future. Nearly half (49% based on total active ingredient) of the pesticides used in the European Union (E.U.) are fungicides that are mainly used in vineyards.[2] Because fungicides are mainly used as precautionary agents to prevent the spread of diseases, these compounds are sprayed repeatedly throughout the growing season, which consequently leads to a considerable diversity in the fungicides applied to agricultural areas.[3] The application of fungicides to these areas can result in their transport to adjacent nontarget surface water systems.[4] When fungicides enter aquatic environments, they may pose a substantial threat to the ecological integrity of surface waters. Some fungicides act on constitutive cell processes, such as energy production or cell division, which are not specific to fungi and are consequently toxic to a wide range of organisms.[5] Nevertheless, the effects of fungicides have received little attention in the past compared with insecticides and herbicides.[3] Although there is little knowledge on the exact impact of fungicides on aquatic organisms and communities, there is evidence that fungicides have a high impact on amphibians.[6,7] To minimize the risk to nontarget organisms, the E.U. prescribes an ecotoxicological risk assessment within the registration procedure of pesticides, which consists of an effect and an exposure assessment (i.e., E.U. Directive 1107/2009).[8] The exposure assessment relies on modeling because no field monitoring data are available when a compound is assessed for the first time. In the E.U., the tiered modeling approach of the FOrum for the Co-ordination of pesticide fate models and their USe (FOCUS) is used to determine the

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Table 1. Description and Source of FOCUS Input Parameters

category	relevant FOCUS step	parameter	source
physicochemical fungicide properties[a]	step 1−3	K_{OC}, DT_{50}, water solubility, etc.	Footprint Pesticide Property Database[19] according to FOCUS[9]
application data[b]	step 1−4	application rate, number and interval of applications, application timing	E.U. registration documents according to GAP[20] U.S. Registration Eligibility Decision (RED) documents[21] producer product labeling
scenario	step 2	northern or southern Europe	selected according to field study information
	step 3	D1−D6, R1−R4[c]	selected according to field study information
cultivated crops	step 1−3	maize, cereals, fruit crops, etc.	selected according to field study information
water body	step 3	ditch, stream	selected according to field study information
mitigation option[b]	step 4	no-spray buffer zone, vegetated filter strip	E.U. registration documents according to GAP[20] U.S. Registration Eligibility Decision (RED) documents[21] producer product labeling

[a]All fungicide parameters used for FOCUS modeling are given in Table S4 (SI). [b]For field studies conducted in the E.U., information was obtained from E.U. registration documents or the product labels designed by the producer. For field studies conducted in Australia, information was obtained from product labels designed by the producer, which were approved by the Australian Pesticides and Veterinary Medicines Authority. For field studies conducted elsewhere, information was obtained from US RED documents. Only spray application was used for FOCUS calculations. [c]D1−D6 are the standard drainage scenarios implemented in FOCUS step 3 for different locations in Europe, and R1−R4 are the standard runoff scenarios.

predicted environmental concentration (PEC) in surface waters and sediments.[9] The FOCUS modeling approach consists of four different tiers named FOCUS step 1 to step 4. The FOCUS surface water working group claims that the highest step 3 PEC_{sw} (PEC in surface water) estimates from the 10 scenarios are likely to represent at least a 90th percentile worst-case for surface water exposures resulting from agricultural pesticide use within the European Union. A detailed description of the different steps and models is provided elsewhere.[9,10] In the fungicide risk assessment, step 1 and step 2 PECs play a smaller role compared to steps 3 and 4. Of the 54 fungicides approved under the E.U. Directive 1107/2009[8] (for which the European Food Safety Authority risk assessment was publicly available), the risk assessment for 45 substances was based on PECs calculated with FOCUS. For 28 (62%) of these fungicide compounds, the exposure estimation was based on the FOCUS step 3 (12 of 28 compounds) or step 4 (16 of 28 compounds) PEC calculations. In an earlier study, we showed that the FOCUS modeling approach is not protective for the prediction of insecticide concentrations in the field.[10] We found that 31% of the measured insecticide concentrations were underpredicted by the step 4 PECs and that the model is less protective for hydrophobic insecticides, such as pyrethroids, compared to other insecticide classes. However, because insecticides are used in different application scenarios, have different physicochemical properties, and different prevailing routes of entry, the results are not transferable to other pesticide groups.[11,12]

To the best of our knowledge, no study had compared a large amount of fungicide field exposure data across a wide range of situations using the PECs derived from the complete FOCUS modeling approach. Hence, the aim of this study was to evaluate the FOCUS predictions for fungicides using concentrations that were measured through field monitoring studies. In detail, we used 482 fungicide concentrations (384 from E.U.) extracted from 56 field studies (40 from E.U.) to test whether the FOCUS surface water approach predicts the 90th percentile worst-case concentrations for a representative sample (see Supporting Information (SI) for details on representativeness of field sampling sites) of fungicide concentrations in agricultural surface water bodies in Europe.

MATERIALS AND METHODS

Derivation of Measured Fungicide Concentrations. To identify field studies that reported measured fungicide concentrations in lotic and lentic surface water bodies, such as streams, ditches, and ponds, a literature review was performed in multiple literature databases (i.e., ISI Web of Science, BIOSIS Previews, CAB Abstracts). Only studies containing fungicide concentrations that the authors claimed resulted from agricultural nonpoint-source pollution (i.e., spray drift, edge-of-field runoff and drainage) were selected from the databases. Further criteria for the selection of field studies were comparably small water body size or catchments smaller than 1000 km^2 (not all studies met these criteria, see SI) and the presence of agricultural land in the surrounding area. Studies that report concentrations that, despite the author's claims, might have been influenced by point-sources are marked in Table S1 in the SI section. With the exception of imazalil and thiabendazole, which are only used for dipping and waxing fruits, and eight active ingredients, which were banned but are still detectable in the environment due to high persistence, all of the detected substances were considered. In addition, fungicide concentrations measured in rice paddies were not considered in this analysis because there is no corresponding FOCUS scenario available. This resulted in a data set of 56 field studies covering 46 active ingredients (SI Tables S1 and S2). The selected field studies were conducted in Europe (n = 40), the United States (n = 9), Canada (n = 4), and Australia (n = 3) and published between 1996 and 2012, with the majority of studies published after 2000 (approximately 90%). Available field study conditions are given in SI Table S3. From the selected field studies, all of the fungicide concentrations measured during independent events in surface waters and sediments were extracted instead of only using the maximum measured concentrations, which might rather result in a data set biased toward worst-case conditions. If multiple fungicide concentrations per active ingredient were reported in one field study, then only those peak concentrations that originated from different entry events (i.e., measured after different precipitation or application events or in different seasons)[13] were selected. Therefore, multiple fungicide concentrations in one publication can be regarded as independent even though some of these peak values might be lower than others.

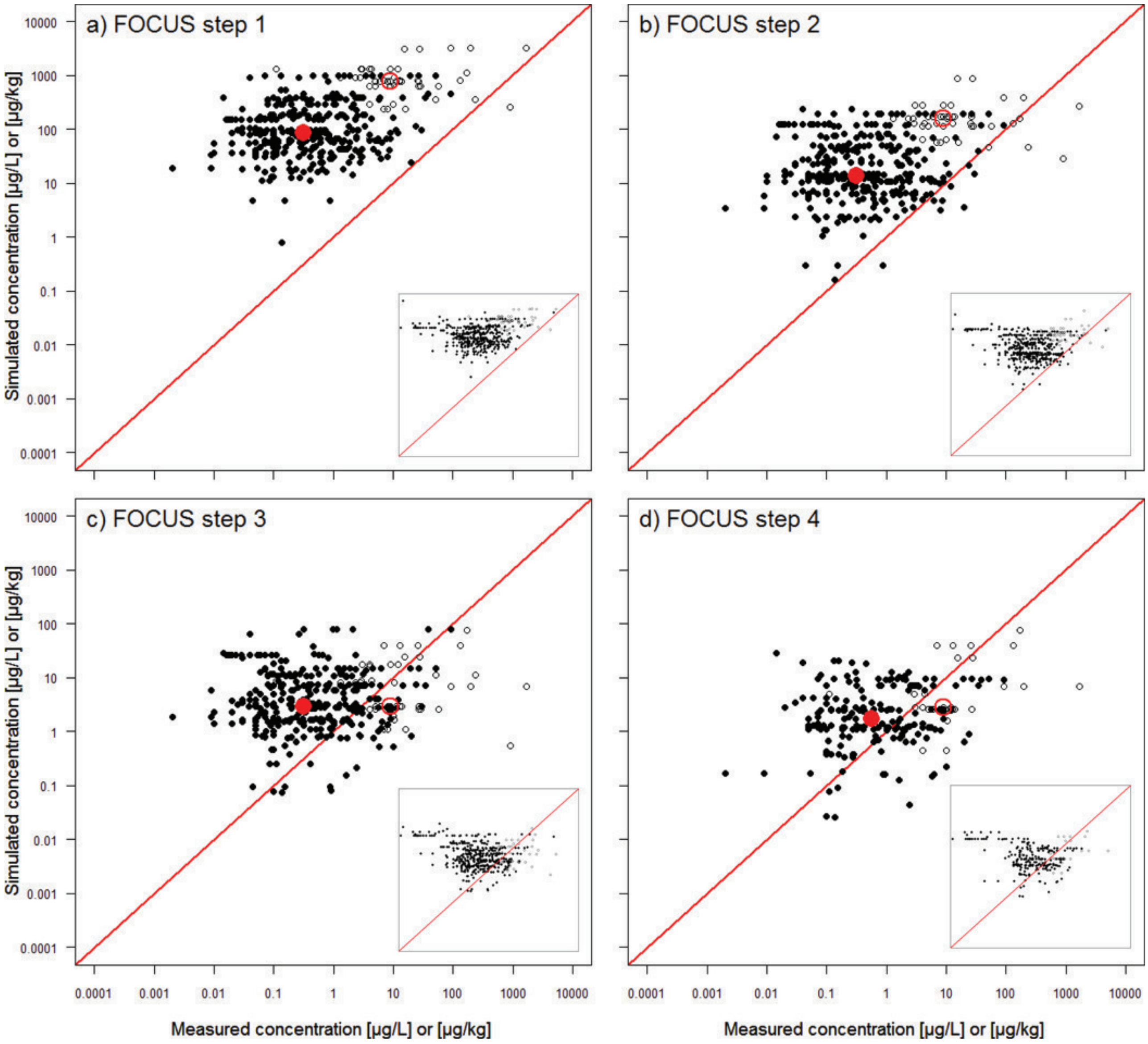

Figure 1. Relationship between simulated and measured fungicide concentrations from E.U. studies for FOCUS steps 1−4. Black dots = water (step 1−3: *n* = 327; step 4: *n* = 187); white dots = sediment (step 1−3: *n* = 57; step 4: *n* = 37); large red dot = overall median surface water concentration, large red circle = overall median sediment concentration. Small figures = respective data for E.U. plus rest of the world (water: step 1−3: *n* = 417, step 4: *n* = 223; sediment: step 1−3: *n* = 65, step 4: *n* = 38). The 45° line denotes identity between PEC and MFC. The simulated concentrations are displayed on the *y*-axis such that the MFC underestimations are plotted below the 45° line.

FOCUS Calculations. The selected measured field concentrations (MFC) were compared to the respective PECs calculated using the tiered FOCUS surface water approach (Steps 1−4) in accordance with E.U. Directive 1107/2009. FOCUS steps 1−2 model version 1.1[9] was used to calculate the tier 1 and tier 2 PECs in surface water and sediment, respectively. FOCUS step 3 simulations were performed with MACRO version 4.3b,[14] PRZM version 3.2.1b,[15] and TOXSWA version 2.1.3.[16] These different models are integrated into the SWASH shell version 3.1.2.[9] Step 4 calculations were performed when applicable using SWAN version 1.1.3[17] according to FOCUS[18] taking mitigation options into account. Step 4 calculations were only performed if the application restrictions for the respective substances are mandatory. The FOCUS calculations rely on several input parameters related to the pesticide, application, crop type, climate, and landscape,[9] as detailed in Table 1. Scenario selection was mainly based on climatic conditions relevant for the respective field study, cultivated crops (crops are associated with particular scenarios), and fungicide input pathway. If no crop type was specified in a field study, then the crops commonly grown in the specific study region and for which the use of the particular fungicide was permitted were selected. If several crops were cultivated in an agricultural area where a field study was conducted, then multiple FOCUS PEC calculations were performed (SI Table S4). For most of the selected studies, it was not possible to define only one climate scenario that represented the respective conditions. In such cases, step 1 and 2 calculations were performed for northern and southern Europe and for all relevant drainage and runoff

Table 2. Overpredictions and Underpredictions from FOCUS Step 1−4 Simulations for Agricultural Fungicides[b] Measured in Europe[a]

	surface water			sediment		
FOCUS tiers	*n* (*n* world)	overprediction PEC > MFC, % (% world)	underprediction PEC < MFC, % (% world)	*n* (*n* world)	overprediction PEC > MFC, % (% world)	underprediction PEC < MFC, % (% world)
step 1	327 (417)	100 (100)	0 (0)	57 (65)	98 (98)	2 (2)
step 2	327 (417)	98 (98)	2 (2)	57 (65)	89 (91)	11 (9)
step 3	327 (417)	85 (88)	15 (12)	57 (65)	33 (35)	67 (65)
step 4	187 (223)	72 (77)	28 (23)	37 (38)	24 (26)	76 (74)

[a]The number in brackets shows the percentages of overpredictions and underpredictions of the concentrations measured in field studies conducted worldwide (including the E.U. data). [b]PEC = predicted environmental concentration; MFC = measured field concentration.

scenarios in FOCUS step 3 (Table 1 and SI Table S4). Taking all crop-scenario combinations into account, a total of approximately 600 step 1 and 600 step 2 calculations and approximately 2000 step 3 and 4 calculations were conducted during this study.

Data Analysis. The MFCs were compared to the calculated PECs, and the amount of overpredictions and underpredictions were identified. If multiple PECs were calculated because of different crop-scenario combinations, then the maximum PECs were compared to the respective measured concentrations. In addition to the comparison of the global data, we also calculated the ratios of MFCs and PECs only for concentrations extracted from the field studies conducted in the E.U. Due to the claim made by the FOCUS working group, we also analyzed the amount of overpredicitions and underpredictions by comparing only the 90th percentile of all measured surface water concentrations of every substance analyzed in each study with the respective PECs. The relationship between step 3 and step 4 PECs and MFCs measured during an event-related sampling (for both all concentrations and only for the 90th percentile concentrations) were analyzed using linear regression. The effects of different fungicide substance classes (e.g., triazole, strobilurin, and morpholine) on the ratio of simulated to measured concentration were analyzed by single-factor analysis of variance (ANOVA) followed by Tukey's honestly significant differences (HSD) post hoc test for pairwise multiple comparisons. The PEC to MFC ratio used in ANOVA was transformed ($\ln[x]$) prior to the statistical analysis to satisfy the assumptions of normally distributed residuals and homogeneity of variance. To test whether the ratios of the PEC_{sw} to the MFC in surface water (MFC_{sw}) for different substance classes are significantly smaller than 1 (which indicates that the MFCs were significantly underestimated), we performed a one-sample *t* test for all FOCUS steps using a 95% confidence interval. All of the statistical analyses and graphics were made with the open-source software package R (www.r-project.org), version 2.14.1.[22]

■ RESULTS

Figure 1 shows the relationship between PECs and MFCs in surface water (E.U. step 1−3: n = 327, step 4: n = 187) and sediment (E.U. step 1−3: n = 57, step 4: n = 37; Table 2) for all results from the E.U. Examples of FOCUS input data and results are given in Table 3. A comparison of FOCUS step 1 PECs and E.U. MFCs showed that all of the water MFCs were overpredicted by the PECs with a median PEC to MFC factor that is greater than 300. Only 2% of the simulated E.U. sediment concentrations underestimated the real concentrations. In FOCUS step 2 assessments, most of the PECs in surface water and sediment (PEC_{sed}) were higher than the E.U. field concentrations (Figure 1b, Table 2). However, 2% of the water and 11% of the sediment predictions underestimated the respective MFCs by up to 30-fold, whereas the median water and sediment concentrations exhibited a general 50- and 20-fold overestimation, respectively (Figure 1b, Table 2). Most (85%) of the simulated water concentrations resulting from step 3 were greater than the detected E.U. field concentrations with a median PEC to MFC factor of 10. However, 15% of the PEC_{sw} values underestimated the fungicide field concentrations in surface water (by more than a factor of 10 in 2% of the cases). In addition, most of the E.U. sediment field concentrations were underestimated by the step 3 PEC_{sed} (67%) by up to more than 1600-fold with a median PEC to MFC factor that was smaller than 1. In the step 4 calculations, 28% and 76% of the simulated water and sediment concentrations underestimated the E.U. MFCs (Figure 1d, Table 2). In addition, 4% of all PEC_{sw} values and 14% of all PEC_{sed} values underestimated the field concentrations by more than a factor of 10. In addition, Figure 1 clearly shows that there is no obvious relationship between the simulated and measured fungicide E.U concentrations for all FOCUS steps. We also found that the underestimation rates for the E.U. MFCs were similar for FOCUS step 1 and 2 to those for the

Table 3. Examples of FOCUS Input Data and Respective Calculated and Measured Surface Water Concentrations

	Bereswill et al. 2012[25]	Rabiet et al. 2010[26]
substance	myclobutanil	tebuconazole
scenario[a]	R1	R1, R2, R3, R4
crop, country	vine, Germany	vine, France
water body	stream	stream
number of applications	4	3
interval between applications [d]	10	14
application amount [g a.i./ha]	48	100
application method	airblast	airblast
application window [Julian days]	152 − 212	152 - 210
MFC_{max} [μg/l]	4.7	6.5
PEC_{max} step 3 [μg/l]	0.75[c]	1.5
mitigation option	15 m no spray buffer	5 m no spray buffer
PEC_{max} step 4 [μg/l]	0.75[c]	1.1
PNEC[b] [μg/l]	4	1
% of all used MFC > PNEC	13	23

[a]R1−R4 are the standard runoff scenarios implemented in FOCUS step 3 for different locations in Europe. [b]Predicted no effect concentration used in the aquatic risk assessment (relevant end point/safety factor)[19] [c]The step 3 and step 4 PECs are similar because a spray buffer was used as step 4 mitigation option, whereas runoff was the major input pathway.

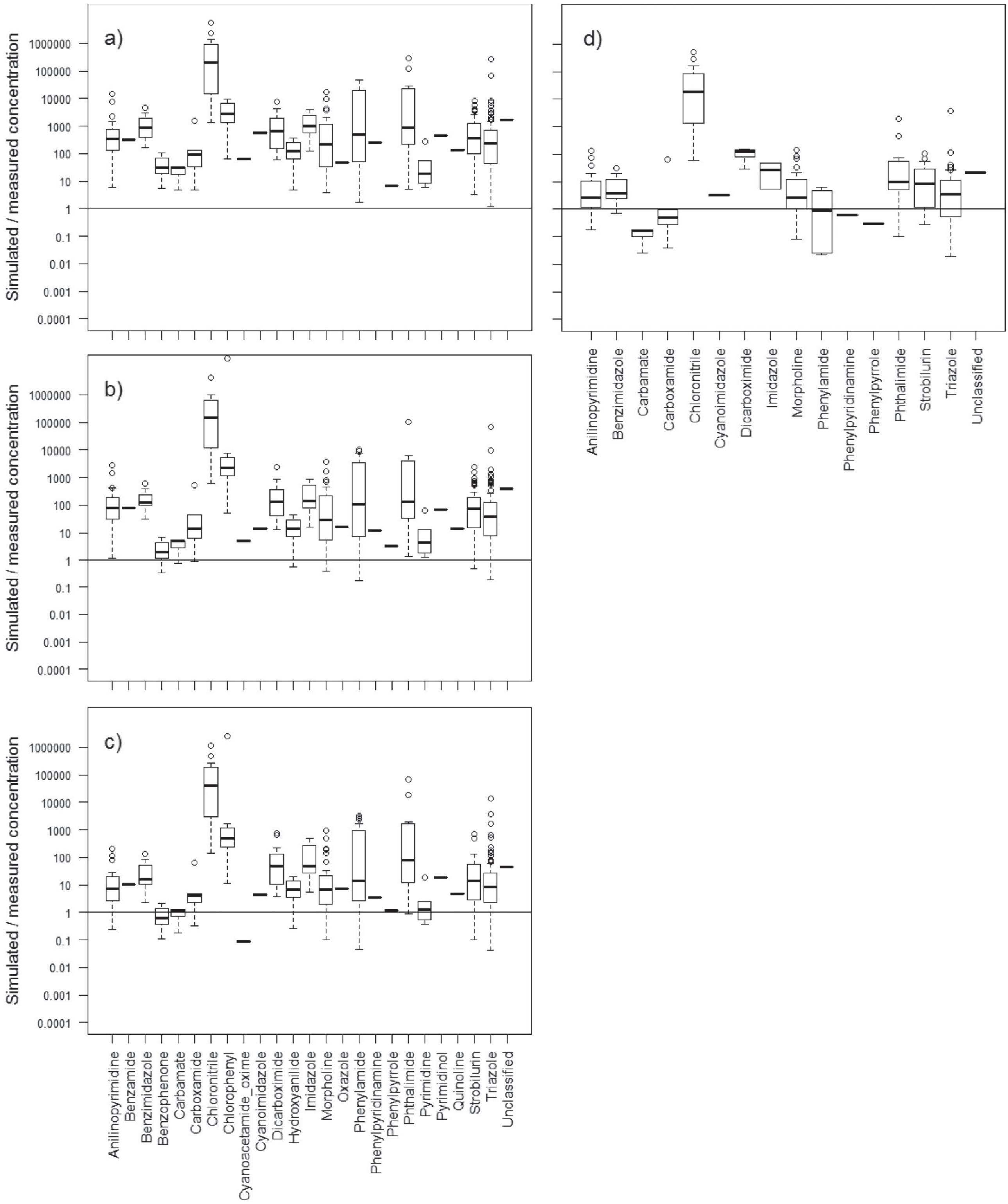

Figure 2. Boxplots of simulated to measured concentration ratios in the water phase for different fungicide classes for all FOCUS steps; (a) FOCUS step 1, (b) FOCUS step 2, (c) FOCUS step 3, and (d) FOCUS step 4.

complete data set in surface waters (world data: step 1−3: *n* = 417; step 4: *n* = 223; Table 2) and for step 1 in sediments (world data: step 1−3: *n* = 65; step 4: *n* = 38). Nevertheless, the fraction of MFC underprediction for E.U. studies is higher for step 3 (15 and 67% instead of 12 and 65%) and step 4 (28 and 76% instead of 23 and 74%) water and sediment calculations than for the complete data set (Table 2). Furthermore, the evaluation of only the 90th percentile value of all measured surface water concentrations of each substance analyzed in each study revealed that the fraction of underprediction for step 3 and 4 are 19 and 36%, respectively, considering all studies (step 3: $n = 197$, step 4: $n = 97$) and 25 and 43% when the data set is restricted to the E.U. data (step 3: $n = 136$, step 4: $n = 82$). The results of the linear regression between step 3 and step 4 PECs and those MFCs, which were sampled by an event related sampling showed, that there is a very weak (maximum $r^2 = 0.08$), yet due to the large n, significant relationship for EU and world data (see SI Figure S4 for further details).

Figure 2 shows that there are differences in the ratios of PEC to MFC for different substance classes. Chloronitril and chlorophenyl fungicides exhibited significantly higher ($p < 0.05$) PEC to MFC ratios and thus higher overestimation rates than most of the other fungicide classes in all FOCUS steps. Details of significant differences in the PEC to MFC ratio for different fungicide classes are given in Tables S5−S8 in the SI section. Furthermore, only carbamate fungicides exhibited significantly lower PEC_{sw} to MFC_{sw} ratios in FOCUS step 4 than 1 ($n = 3$; mean $=0.13$; $t = -17.3$; $p = 0.003$).

■ DISCUSSION

Protectiveness of FOCUS Predictions. The fact that the degree of conservatism decreases from FOCUS step 1 to step 4 is clearly visible in our data. More realistic model assumptions resulted in lower PECs, and consequently, the percentage of fungicide MFCs that exceed the PECs increased from 0% for step 1 to 28% for step 4 in surface water and from 2% for step 1 to 76% for step 4 in sediment (E.U. data, Figure 1, Table 2). The increase in the MFC underpredictions from step 1 to step 4 was also shown in an earlier study for insecticide concentrations in surface waters and sediments.[10]

In general, a criterion is needed to decide whether the model outcomes are valid.[23] The FOCUS surface water working group claims that the FOCUS scenarios “provide a mechanism for assessing pesticide PECs in surface water and sediment with an acceptable degree of uncertainty” and that the highest PEC_{sw} estimates from the 10 scenarios would represent at least the 90th percentile for surface water exposures.[9] These criteria appear to be subjective to a certain extent and also the European Food Safety Authority states that the level of protection achieved by the current FOCUS surface water exposure assessment methodology is unknown.[24] Nevertheless, taking the ±10% exceedance value as a quality threshold, the results of the present study on fungicides clearly support the conclusion, which was previously reached for insecticides, that the degree of uncertainty is not acceptable. Even if the fraction of E.U. MFC_{sw} underprediction is lower than the one calculated for insecticides (33.3% for step 3; 50% for step 4),[10] 15% of the step 3 PEC_{sw} and 28% of the step 4 PEC_{sw} underestimated the E.U. fungicide MFCs (Table 2). This finding is substantial because FOCUS step 3 and 4 are the most realistic standard tiers available in European regulatory exposure modeling and are used for the risk assessment of 62% of the fungicides registered in the European Union. Thus, because values that are lower than the actual surface water concentrations are considered in the regulatory risk assessment, fungicides might exhibit unacceptable ecological effects in the field, as has been previously shown for insecticides.[10] This fact can be illustrated using myclobutanil as an example (Table 3). The measured field concentration of myclobutanil exceeds the calculated step 3 and step 4 PEC_{sw} values and the respective PNEC (PNEC: relevant aquatic end point/safety factor). Although the PEC indicates that there is no risk for aquatic organisms, the actual MFC_{sw} shows that the risk is underestimated. The underestimation of the MFC is also shown for tebuconazole (Table 3), although in this case the calculated PEC exceeds the PNEC. In addition, 13% and 23% of all considered myclobutanil and tebuconazole MFC_{sw} values exceed the relevant PNEC (Table 3).

In contrast to insecticides, fungicides are used at comparably high application rates and multiple applications per season, which can lead to a more continuous entry of fungicides into surface water bodies than that observed with insecticides.[25] Static fixed-interval and fixed-station monitoring tends to underpredict the contamination of surface water bodies with insecticides because it is not possible to detect the short peak concentrations, which leads to arbitrarily high amounts of nondetects.[12] The situation for fungicides is different. With an almost continuous exposure throughout the season, static fixed sampling intervals may lead to the detection of concentrations lower than the maximum peak concentration instead of nondetects.[26] Because nearly half (46%) of the MFC_{sw} values used in this study were not measured by an event-related sampling, we also compared the calculated PECs to the 90th percentile concentrations of every substance’s MFCs from each study. This was done to exclude particularly low water-phase concentrations and to increase the chance that measured concentrations are peak concentrations. The 90th percentile criterion was also claimed by the FOCUS surface water working group to be valid for FOCUS predictions.[9] The fraction of the MFC_{sw} underprediction is higher for the 90th percentile concentrations compared with the complete data (19% and 36% underprediction for step 3 and 4, respectively; SI Figure S5). The fact that the FOCUS predictions are not protective for fungicide concentrations in surface water, clearly confirms the urgent need for extensive model improvement.

In response to the results obtained for insecticides,[27,28] it was argued that the FOCUS modeling approach is only valid for the pesticide registration process in the E.U. because the agricultural and climatic settings are specific for European countries (but see also[13,29]). This statement, however, is not relevant for FOCUS steps 1 and 2 because these steps are not specific to any climate, crop, topography, or soil type.[9] Nevertheless, most (78%) of the measured fungicide concentrations used in this study were extracted from scientific studies conducted in European countries (40 out of 56 studies). However, the comparison of the steps 1 and 2 PEC_{sw} to MFC_{sw} values that were derived only from E.U. studies showed that the amount of MFC underprediction is equal to that obtained for the global data in surface water (Table 2, Figure 1). This finding is in contrast to the results of the comparison of the step 3 and step 4 PECs to MFC values, which showed that 13% in step 3 and 27% in step 4 of the field water concentrations were underestimated when only E.U. data are used (this number is higher than the average for the global data: 12% and 23% underestimation for step 3 and 4, respectively; Table 2). Furthermore, of the 48 substances considered in this analysis 42 are approved under the E.U. Directive 1107/2009, and for 85% of these substances for which the risk assessment was publicly available, the PECs were calculated with FOCUS. This result clearly indicates that the FOCUS model is even less protective for fungicide field concentrations typical for conditions in Europe, as was demonstrated for insecticides.[10,29]

In addition to model inaccuracies, the underestimation of MFCs might also be a result of farmers' malpractice, for example the nonadherence to spray buffer zones. But this would only explain a theoretical maximum of 13% (i.e., difference between 28% and 15% underestimation in step 4 and step 3, respectively) of the cases in which step 4 underestimates respective $\mathrm{MFC}_{\mathrm{sw}}$, since step 3 does not consider mitigation options.

The underestimation of the actual pesticide concentration was also described by Jung et al.[30] using an environmental exposure model (KOIEM) to predict insecticide concentrations in water bodies in Korea. These researchers compared the average measured deltamethrin concentrations with the PECs and found that the calculated PECs for ditches underestimated the real concentrations with a median factor of approximately 3. Most important, they found that estimated maximum concentrations predicted by KOIEM were higher than those obtained from FOCUS and GENEEC, which indicates that the underestimation obtained with FOCUS could even be worse.

Only a few other published studies have compared predicted environmental pesticide concentrations and field data; however, most of these studies have either not analyzed fungicides or studied only a very limited number of cases ($n < 5$).[31−33] However, this is the first study that has evaluated the FOCUS approach using a larger number of fungicide concentrations from several field studies, most of which were conducted in the E.U.

Quality of FOCUS Predictions. Predicted pesticide concentrations used in aquatic risk assessment should provide some degree of realistic estimates of field concentrations, i.e., there should ideally be a close relationship between measured and predicted concentrations. The results of our study show that there are only very few matches between predicted and measured fungicide concentrations, most likely due to coincidence. If a difference of ±10% is regarded as adequate,[9,34] then less than 7% of the step 4 $\mathrm{PEC}_{\mathrm{sw}}$ matched the $\mathrm{MFC}_{\mathrm{sw}}$. Even when the performance threshold was set at ±30% to account for uncertainties in the field studies, almost all predictions, i.e., 94% of all step 3 and 92% of all step 4 PECs, did not match the MFCs in surface water and sediment.

Furthermore, Figure 1 shows that there is no positive relationship in terms of a statistically significant slope with a value greater than 0, e.g., in a linear regression model between predicted and measured concentrations. The same was shown for insecticides.[10,13] In response to the results obtained for insecticides,[10] Reichenberger[27] criticized that one modeled data point was plotted against several measured data points and claimed that only the maximum measured concentration should be used to evaluate the linear relationship (see also[13]). Even if the fungicide concentrations considered here were measured either during different seasons or originated from clearly distinguishable entry events, it cannot be ensured that they are absolute peak concentrations. For this reason, we additionally analyzed the relationship between step 3 and step 4 PECs and MFCs which were measured during an event related sampling. To further increase the robustness of this analysis, we also used the 90th percentile MFCs for every substance per study for the examination of the relationship between step 3 and step 4 PECs and event-related MFCs. The results for this analysis (SI Figure S4) showed, that there is still a very week (maximum $r^2 = 0.08$, 90th percentile MFCs + only E.U. data), yet due to the large n, significant linear relationship for the E.U. data. This result underlines the importance of the inherent model restrictions. Even if there might be uncertainties in the field data, the plot of observed data against model predictions should show at least a positive trend for the data points. Because the FOCUS working group claims that the model predicts environmental concentrations with an acceptable degree of uncertainty,[9] one would expect that the data correspond more or less to the line of perfect agreement or at least runs parallel above (considering the claimed worst-case conditions[9]) the 45° line shown in Figures 1 and SI S4. Nevertheless, the complete absence of a relationship between predicted and measured fungicide data provides evidence that the model is not at all suitable for predicting pesticide concentrations in surface waters. Bach and Hollis[28] also questioned the quality of the FOCUS models, although their argument was not based on any empirical evidence.

Kirchner et al.[23] stated that a model is valid if it is adequate for a specific purpose, rather than absolute truth in every respect. Assuming that the only purpose of the FOCUS approach is to be protective and not to lead to underestimations of the real contamination in the field, then FOCUS steps 1 and 2 might achieve this aim, but step 3 and step 4 predictions are unacceptable in their present form. Possible reasons for the low quality of the FOCUS predictions, such as the too-simplified integration of upstream catchment, translation of runoff fluxes from PRZM to TOXSWA, and the impossibility of a simultaneous calculation for drainage and runoff entries, are described elsewhere.[10,28] Another shortcoming, which seems to be particularly relevant for fungicides, is that not all relevant entry pathways are included in the FOCUS modeling approach. It has for instance been shown that the wash-off from paved edge-of-field farm pathways in vineyards, on which the fungicides dropped during the turn of the spraying machines, is a highly relevant entry pathway into aquatic ecosystems.[25,35] Nevertheless, vineyards are only relevant in 10 of the 56 field studies considered here.

Factors Influencing PEC to MFC Ratio. As was shown for insecticides,[10] the PECs for low fungicide field concentrations in the water-phase are higher than the MFCs in all FOCUS steps (Figure 1). The reason for this discrepancy is that, as described above, the MFCs were compared to maximum $\mathrm{PEC}_{\mathrm{sw}}$ values, and several of the MFCs were plotted against one PEC, although the latter most likely did not represent the peak concentrations. This explanation is supported by SI Figure S4, which shows that, for the field concentrations measured during an event-related sampling regime, the overestimation, especially for low water-phase field concentrations, appears to be less compared to the complete data set (Figure 1).

In addition, only 48% of the 261 $\mathrm{MFC}_{\mathrm{sw}}$ values less than 0.5 μg/L and 64% of the 156 fungicide concentrations greater than 0.5 μg/L were obtained via an event-related sampling approach. This suggests that the actual fungicide field concentrations are higher than the $\mathrm{MFC}_{\mathrm{sw}}$ values presented in the published studies and thus used here, but these were not detected due to the lack of consistent use of event-related sampling. Consequently, the real amount of FOCUS underpredictions might be even worse.

As was described above, we considered only those field studies that reported agricultural nonpoint-source fungicide entries from comparably small catchments as the input pathway for the extraction of MFCs. Bach et al.[36] concluded that the contribution of point-sources to the total river load is more relevant in larger catchments, whereas, in small catchments, point-sources are often excluded by the selection of monitoring sites. Even if it is never entirely excludable that the MFCs were influenced by point-sources, we tried to identify those studies in which this uncertainty still needs to be considered or in which the relevant surface water bodies are most likely not comparable to the FOUCS water bodies in terms of size or flow conditions (SI Table S1). Excluding these studies would result in an underprediction of 13.8% and 26% in surface water for step 3 and step 4 and thus even higher values than those obtained for the complete data set (Table 2). This result highlights that MFCs increase if ascertained nonpoint-sources are considered, as has been also shown for insecticides.[29] Nevertheless, this might also be an effect of the water body size, since it influences, on the one hand, the likelihood of point-source-related pesticide entries within the catchment, and on the other hand, the dilution of pesticides once they have entered a water body.

Generally, there are differences between the field situation and the FOCUS surface water scenarios that might influence the PEC to MFC ratios. In most cases, the actual water bodies are larger than the FOCUS water bodies, which results in an overestimation of the actual field concentrations. In consequence, this fact implies that the underprediction of MFCs might be even higher considering only surface water bodies, which are smaller than those considered in this study. In addition, the size of the adjacent field (or upstream catchment) and the time between application and first rainfall influences the amount of pesticides entering the water body due to runoff or drainage. The FOCUS models use a pesticide application timer to minimize the influence of the users' choice of application date on the FOCUS results and to select application dates within a user-defined application window depending on the precipitation amounts. A shorter time between application and precipitation and a higher precipitation amount than the one used in the FOCUS approach can lead to the underestimation of the MFC. Other aspects, such as the too-simplified integration of the upstream catchment (a constant additional pesticide loading of 20% for the stream scenario only) have been discussed already elsewhere.[10]

In contrast to insecticides,[10] we found only small differences in the ratios of PEC_{sw} to MFC_{sw} between different fungicide substance classes for all FOCUS steps. Chloronitril and chlorophenol fungicides exhibited significantly higher ratios than most of the other fungicide classes in all FOCUS steps (Figure 2). The reason for this is that chloronitril (e.g., chlorothalonil) and chlorophenol (e.g., dicloran and quintozene) fungicides were measured at relatively low concentrations but the predicted concentrations were comparatively high due to high application rates. In addition, only the PEC_{sw} to MFC_{sw} ratio for carbamate fungicides in step 4 were significantly lower than 1 because all of the MFC_{sw} were underpredicted by the respective PECs. Nevertheless, no general conclusion should be derived from this finding because the sample size is rather low ($n = 3$).

In summary, our study clearly demonstrates the need for a further targeted analysis of parameters and processes of the FOCUS exposure models. As the goal of predicting the 90th percentile worst-case concentrations for a representative sample is not achieved by the FOCUS approach, our data suggest that the model is not able to predict fungicide concentrations with an "acceptable degree of uncertainty". A maximum of 25% of the MFC_{sw} (90th percentile concentration, only studies conducted in Europe, excluding studies that might be influenced by point-sources) were underpredicted by FOCUS step 3 and a maximum of 43% (90th percentile concentration, E.U. data) of the MFC_{sw} were underpredicted by FOCUS step 4, which is the most realistic tier available in the European risk assessment. Furthermore, no obvious relationship between measured and predicted fungicide concentrations was found for all FOCUS steps.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional tables and figures with information on selected field studies and modeling input parameters. Results from a GIS analysis on the representativeness of field sampling sites for Europe. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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Supporting Information for:

Fungicide Field Concentrations Exceed FOCUS Surface Water Predictions: Urgent Need of a Model Improvement

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35 pages

8 tables

5 figures

1 text

Table S1. Field studies (n = 56) selected for comparison between measured and simulated fungicide concentrations (n = 482) in agricultural surface waters and analytical methods.

Reference	Country	Fungicide compounds	Detections Water/ sediment	Substance class	Entry pathway	Analytical method	LOD /LOQ (µg/L or µg/kg)	Analytical recovery (%)
Angelidis et al. 1996[1*]	Greece	captan	2 / 3	phthalimide	nonpoint source	GC/FTD	0.05/-[a]; 0.6/-[b]	-
Arnold et al. 2004[2]	USA	chlorothalonil	1 / 0	chloronitrile	runoff	GC/ELCD	-	-
Battaglin et al. 2011[3*]	USA	azoxystrobin	1 / 0	strobilurin	nonpoint source	GC/MS	-	140-517[a]
		chorothalonil	1 / 0	chloronitrile	nonpoint source	GC/MS	-	44-128[a]
		metalaxyl	1 / 0	phenylamide	nonpoint source	GC/MS	-	-
		myclobutanil	1 / 0	triazole	nonpoint source	GC/MS	-	101-230[a]
		propiconazole	1 / 0	triazole	nonpoint source	GC/MS	-	27-162[a]
		pyraclostrobin	1 / 0	strobilurin	nonpoint source	GC/MS	-	162-508[a]
		tebuconazole	1 / 0	triazole	nonpoint source	GC/MS	-	81-138[a]
		tetraconazole	1 / 0	triazole	nonpoint source	GC/MS	-	-
		trifloxystrobin	1 / 0	strobilurin	nonpoint source	GC/MS	-	81-161[a]
Belden et al. 2012[4]	USA	propiconazole	0 / 1	triazole	runoff	GC/MS	-/4[b]	-
		pyraclostrobin	0 / 1	strobilurin	runoff	GC/MS	-/5[b]	-
Berenzen et al. 2005[5]	Germany	azoxystrobin	12 / 0	strobilurin	runoff	GC/ECD, GC-MS	0.05/-[a]	97-99[a]
		epoxiconazole	9 / 0	triazole	runoff	GC/ECD, GC-MS	0.05/-[a]	97-99[a]
		kresoxim-methyl	4 / 0	strobilurin	runoff	GC/ECD, GC-MS	0.05/-[a]	97-99[a]
		tebuconazole	8 / 0	triazole	runoff	GC/ECD, GC-MS	0.05/-[a]	97-99[a]
Bereswill et al. 2012[6]	Germany	azoxystrobin	3 / 0	strobilurin	runoff	GC/NPD/ECD	0.01-0.07/-[a]	-
		boscalid	3 / 0	carboxamide	runoff	GC/NPD/ECD	0.01-0.07/-[a]	-
		cyazofamid	1 / 0	cyanoimidazole	runoff	GC/NPD/ECD	0.01-0.07/-[a]	-
		cyprodinil	2 / 0	anilinopyrimidine	runoff	GC/NPD/ECD	0.01-0.07/-[a]	-
		dimethomorph	3 / 0	morpholine	runoff	GC/NPD/ECD	0.01-0.07/-[a]	-
		famoxadone	1 / 0	oxazole	runoff	GC/NPD/ECD	0.01-0.07/-[a]	-
		fenhexamid	3 / 0	hydroxyanilide	runoff	GC/NPD/ECD	0.01-0.07/-[a]	-
		fludioxonil	1 / 0	phenylpyrrole	runoff	GC/NPD/ECD	0.01-0.07/-[a]	-
		folpet	3 / 0	phthalimide	runoff	GC/NPD/ECD	0.1-0.6/-[a]	-
		iprovalicarb	3 / 0	carbamate	runoff	GC/NPD/ECD	0.01-0.07/-[a]	-
		kresoxim-methyl	3 / 0	strobilurin	runoff	GC/NPD/ECD	0.01-0.07/-[a]	-
		metalaxyl-M	3 / 0	phenylamide	runoff	GC/NPD/ECD	0.01-0.07/-[a]	-
		metrafenone	3 / 0	benzophenone	runoff	GC/NPD/ECD	0.01-0.07/-[a]	-
		myclobutanil	3 / 0	triazole	runoff	GC/NPD/ECD	0.01-0.07/-[a]	-
		penconazole	2 / 0	triazole	runoff	GC/NPD/ECD	0.01-0.07/-[a]	-
		pyrimethanil	3 / 0	anilinopyrimidine	runoff	GC/NPD/ECD	0.01-0.07/-[a]	-
		quinoxyfen	3 / 0	quinoline	runoff	GC/NPD/ECD	0.01-0.07/-[a]	-

LOD: limit of Detection; LOQ: Limit of Quantification, [a]: surface water; [b]: sediment

* Not excludable that point sources were within the examined catchment or water body may not be representative for FOCUS surface water bodies

Table S1. (continued)

Reference		Fungicide compounds	Detections Water/ sediment	Substance class	Entry pathway	Analytical method	LOD /LOQ (µg/L or µg/kg)	Analytical recovery (%)
		spiroxamine	2 / 0	morpholine	runoff	GC/NPD/ECD	0.01-0.07/-[a]	-
		tebuconazole	1 / 0	triazole	runoff	GC/NPD/ECD	0.01-0.07/-[a]	-
		trifloxystrobin	1 / 0	strobilurin	runoff	GC/NPD/ECD	0.01-0.07/-[a]	-
Bermudez-Couso et al. 2007[7]	Spain	metalaxyl	0 / 2	phenylamide	nonpoint source	GC/MS	-	81-97[b]
		penconazole	0 / 3	triazole	nonpoint source	GC/MS	-	81-97[b]
		cyprodinil	0 / 13	anilinopyrimidine	nonpoint source	GC/MS	-	81-97[b]
		procymidone	0 / 9	dicarboximide	nonpoint source	GC/MS	-	81-97[b]
		fludioxonil	0 / 6	phenylpyrrole	nonpoint source	GC/MS	-	81-97[b]
Daniels et al. 2000[8*]	England	fenpropimorph	0 / 2	morpholine	nonpoint source	GC/MS; GC/NPD	0.5/-[b]	-
Dorigo et al. 2007[9]	France	azoxystrobin	2 / 0	strobilurin	runoff	GC/MS; HPLC/MS/MS	-	-
		oxadixyl	2 / 0	phenylamide	runoff	GC/MS; HPLC/MS/MS	-	-
		tebuconazole	1 / 0	triazole	runoff	GC/MS; HPLC/MS/MS	-	-
Furtula et al. 2006[10]	Canada	metalaxyl	3 / 0	phenylamide	nonpoint source	GC/MS	0.0021/-[a]	-
Ganzelmeier et al. 2011[11]	Germany	captan	6 / 0	phthalimide	spray drift	LC/MS/MS; GC/MS	0.01/-[a]	72-100[a]
		cyprodinil	1 / 0	anilinopyrimidine	spray drift	LC/MS/MS; GC/MS	0.01/-[a]	72-100[a]
		trifloxystrobin	4 / 0	strobilurin	spray drift	LC/MS/MS; GC/MS	0.01/-[a]	72-100[a]
		fluquinconazole	1 / 0	triazole	spray drift	LC/MS/MS; GC/MS	0.01/-[a]	72-100[a]
		pyrimethanil	1 / 0	anilinopyrimidine	spray drift	LC/MS/MS; GC/MS	0.01/-[a]	72-100[a]
		penconazole	6 / 0	triazole	spray drift	LC/MS/MS; GC/MS	0.01/-[a]	72-100[a]
Graves et al. 2004[12]	USA	metalaxyl	1 / 0	phenylamide	runoff	GC/ECD; GC/NPD	-	-
Griffini et al. 1997[13*]	Italy	procymidone	1 / 0	dicarboximide	nonpoint source	GC/ITDMS	0.005-0.03/-[a]	-
Haarstadt et al. 2005[14]	Norway	fenpropimorph	1 / 0	morpholine	runoff	GC/NP-EC	-	-
		metalaxyl	1 / 0	phenylamide	runoff	GC/NP-EC	-	-
		propiconazole	1 / 0	triazole	runoff	GC/NP-EC	-	-
Johnson et al. 2000[15]	USA	chlorothalonil	1 / 0	chloronitrile	runoff	GC/MS	-	-
Karaouzas et al. 2011[16*]	Greece	triadimenol	1 / 2	triazole	nonpoint source	GC/MS	-	-
		penconazole	5 / 1	triazole	nonpoint source	GC/MS	-	-
Kern et al. 2011[17]	Switzerland	azoxystrobin	3 / 0	strobilurin	runoff	LC/MS/MS	0.0003/0.001[a]	-
		epoxiconazole	3 / 0	triazole	runoff	LC/MS/MS	0.0006/0.002[a]	-
		spiroxamine	3 / 0	morpholine	runoff	LC/MS/MS	0.0003/0.001[a]	-
Kreuger 1998[18]	Sweden	fenpropimorph	3 / 0	morpholine	runoff, drainage	GC/MS	-/0.1-0.5[a]	75-100[a]
		prochloraz	1 / 0	imidazole	runoff, drainage	GC/MS	-/0.1-0.5[a]	75-100[a]
		propiconazole	3 / 0	triazole	runoff, drainage	GC/MS	-/0.1-0.5[a]	75-100[a]
		triadimenol	1 / 0	triazole	runoff, drainage	GC/MS	-/0.1-0.5[a]	75-100[a]

LOD: limit of Detection; LOQ: Limit of Quantification, [a]: surface water; [b]: sediment

* Not excludable that point sources were within the examined catchment or water body may not be representative for FOCUS surface water bodies

Table S1. (continued)

Reference	**Country**	**Fungicide compounds**	**Detections Water/ sediment**	**Substance class**	**Entry pathway**	**Analytical method**	**LOD /LOQ (µg/L or µg/kg)**	**Analytical recovery (%)**
Kronvang et al. 2003[19]	Denmark	fenpropimorph	0 / 1	morpholine	nonpoint source	GC/MS	0.01/-[b]	72
		prochloraz	0 / 1	imidazole	nonpoint source	GC/MS	0.05/-[b]	92
		propiconazole	0 / 1	triazole	nonpoint source	GC/MS	0.02/-[b]	117
Kuo et al 2012[20]	Canada	captan	1 / 0	phthalimide	runoff	GC/ECD, GC/MS	0.00001-0.0125/-[a]	376[a]
		chlorothalonil	1 / 0	chloronitrile	runoff	GC/ECD, GC/MS	0.00001-0.0125/-[a]	213.5[a]
		flutriafol	1 / 0	triazole	runoff	GC/ECD, GC/MS	0.00001-0.0125/-[a]	-
		quintozene	1 / 0	chlorophenyl	runoff	GC/ECD, GC/MS	0.00001-0.0125/-[a]	238[a]
Lehotay et al 1998[21]*	USA	chlorothalonil	19 / 0	chloronitrile	nonpoint source	GC/ITMS	0.005/-[a]	87-116[a]
Liess and Von der Ohe 2005[22]	Germany	kresoxim-methyl	1 / 0	strobilurin	nonpoint source	GC/ECD, GC/MS	0.05/-[a]	-
		epoxiconazole	1 / 0	triazole	nonpoint source	GC/ECD, GC/MS	0.05/-[a]	-
		azoxystrobin	1 / 0	strobilurin	nonpoint source	GC/ECD, GC/MS	0.05/-[a]	-
		propiconazole	1 / 0	triazole	nonpoint source	GC/ECD, GC/MS	0.05/-[a]	-
		fenpropimorph	1 / 0	morpholine	nonpoint source	GC/ECD, GC/MS	0.05/-[a]	-
		tebuconazole	1 / 0	triazole	nonpoint source	GC/ECD, GC/MS	0.05/-[a]	-
Long et al 1998[23]*	England	flutriafol	2 / 1	triazole	nonpoint source	GC/MS, GC/NPD	-/0.01[a]; -/0.5[b]	-
		propiconazole	1 / 5	triazole	nonpoint source	GC/MS, GC/NPD	-/0.01[a]; -/0.5[b]	-
Ludvigsen and Lode 2001[24]	Norway	metalaxyl	1 / 0	phenylamide	nonpoint source	GC/MS	0.05/-[a]	-
		propiconazole	1 / 0	triazole	nonpoint source	GC/MS	0.05/-[a]	-
		fenpropimorph	1 / 0	morpholine	nonpoint source	GC/MS	0.02/-[a]	-
		fluazinam	1 / 0	phenylpyridinamine	nonpoint source	GC/MS	0.02/-[a]	-
		prochloraz	1 / 0	imidazole	nonpoint source	GC/MS	0.05/-[a]	-
		iprodione	1 / 0	dicarboximide	nonpoint source	GC/MS	0.02/-[a]	-
Maillard et al. 2011[25]	France	cymoxanil	1 / 0	cyanoacetamide oxime	runoff	LC/MS/MS	0.02/0.05[a]	70[a]
		carbendazim	1 / 0	benzimidazole	runoff	LC/MS/MS	0.02/0.05[a]	80[a]
		dimethomorph	1 / 0	morpholine	runoff	LC/MS/MS	0.02/0.05[a]	76[a]
		kresoxim-methyl	1 / 0	strobilurin	runoff	LC/MS/MS	0.03/0.1[a]	81[a]
		metalaxyl	1 / 0	phenylamide	runoff	LC/MS/MS	0.02/0.05[a]	86[a]
Merli et al. 2010[26]	Italy	quinoxyfen	0 / 4	quinoline	nonpoint source	HPLC/MS	0.54/ -[b]	77-109[b]
Miles and Pfeuffer 1997[27]*	USA	metalaxyl	1 / 0	phenylamide	nonpoint source	-	0.06-1.5/ -[a]	-
Morin et al. 2010[28]	France	azoxystrobin	1 / 0	strobilurin	nonpoint source	LC/MS/MS	-/0.025[a]	-
		tebuconazole	2 / 0	triazole	nonpoint source	LC/MS/MS	-/0.04[a]	-
		dimethomorph	2 / 0	morpholine	nonpoint source	LC/MS/MS	-/0.04[a]	-
		procymidone	2 / 0	dicarboximide	nonpoint source	LC/MS/MS	-/0.08[a]	-

LOD: limit of Detection; LOQ: Limit of Quantification, [a]: surface water; [b]: sediment

* Not excludable that point sources were within the examined catchment or water body may not be representative for FOCUS surface water bodies

Table S1. (continued)

Reference	Country	Fungicide compounds	Detections Water/ sediment	Substance class	Entry pathway	Analytical method	LOD /LOQ (µg/L or µg/kg)	Analytical recovery (%)
Neumann et al. 2002[29]	Germany	azoxystrobin	1 / 0	strobilurin	runoff	GC/NPD, GC/MS	0.1-0.5/-[a]	-
		epoxiconazole	2 / 0	triazole	runoff	GC/NPD, GC/MS	0.1-0.5/-[a]	-
		fenpropimorph	1 / 0	morpholine	runoff	GC/NPD, GC/MS	0.1-0.5/-[a]	-
		propiconazole	1 / 0	triazole	runoff	GC/NPD, GC/MS	0.1-0.5/-[a]	-
Neumann et al. 2003[30]	Germany	azoxystrobin	3 / 0	strobilurin	nonpoint source	GC/MS	0.1-0.5/-[a]	-
		epoxiconazole	2 / 0	triazole	nonpoint source	GC/MS	0.1-0.5/-[a]	-
		fenpropimorph	2 / 0	morpholine	nonpoint source	GC/MS	0.1-0.5/-[a]	-
		propiconazole	4 / 0	triazole	nonpoint source	GC/MS	0.1-0.5/-[a]	-
Oliver et al. 2012[31]	Australia	fenarimol	3 / 0	pyrimidine	runoff	HPLC	0.08/-[a]	-
		bupirimate	1 / 0	pyrimidinol	runoff	GC/MS	0.33/-[a]	-
		penconazole	2 / 0	triazole	runoff	GC/MS	0.04/-[a]	-
		procymidone	3 / 0	dicarboximide	runoff	GC/MS	0.02/-[a]	-
		propiconazole	1 / 0	triazole	runoff	GC/MS	0.04/-[a]	-
Pacioni et al. 2009[32]	Italy	iprodione	1 / 0	dicarboximide	nonpoint source	SPE/HPLC	-	72-101[a]
		procymidone	2 / 0	dicarboximide	nonpoint source	SPE/HPLC	-	72-101[a]
		dicloran	2 / 0	chlorophenyl	nonpoint source	SPE/HPLC	-	72-101[a]
Pesce et al. 2008[33]*	France	oxadixyl	1 / 0	phenylamide	nonpoint source	HPLC, GC/MS, CPG	-	-
		procymidone	1 / 0	dicarboximide	nonpoint source	HPLC, GC/MS, CPG	-	-
Piscart et al. 2011[34]	France	tebuconazole	1 / 0	triazole	nonpoint source	LC/MS/MS	-	-
		procymidone	1 / 0	dicarboximide	nonpoint source	LC/MS/MS	-	-
Polard et al. 2011[35]	France	tebuconazole	3 / 0	triazole	runoff	GC/MS	0.01/-[a]	-
		cyproconazole	2 / 0	triazole	runoff	GC/MS	0.01/-[a]	-
		epoxiconazole	3 / 0	triazole	runoff	GC/MS	0.01/-[a]	-
		flusilazole	2 / 0	triazole	runoff	GC/MS	0.01/-[a]	-
Rabiet et al. 2010[36]	France	azoxystrobin	6 / 0	strobilurin	runoff	LC/MS/MS	-/0.02-0.08[a]	80-107[a]
		tebuconazole	6 / 0	triazole	runoff	LC/MS/MS	-/0.02-0.08[a]	80-107[a]
		dimethomorph	7 / 0	morpholine	runoff	LC/MS/MS	-/0.02-0.08[a]	80-107[a]
		carbendazim	6 / 0	benzimidazole	runoff	LC/MS/MS	-/0.02-0.08[a]	80-107[a]
		procymidone	7 / 0	dicarboximide	runoff	LC/MS/MS	-/0.02-0.08[a]	80-107[a]
Rasmussen et al. 2011[37]	Denmark	azoxystrobin	1 / 0	Strobilurin	runoff	GC/MS, LC/MS	0.01-0.1/-[a]	85-110[a]
		tebuconazole	1 / 0	triazole	runoff	GC/MS, LC/MS	0.01-0.1/-[a]	85-110[a]
		propiconazole	1 / 0	triazole	runoff	GC/MS, LC/MS	0.01-0.1/-[a]	85-110[a]
		dimethomorph	1 / 0	morpholine	runoff	GC/MS, LC/MS	0.01-0.1/-[a]	85-110[a]
		boscalid	1 / 0	carboxamide	runoff	GC/MS, LC/MS	0.01-0.1/-[a]	85-110[a]
Readman et al. 1997[38]*	France	dicloran	1 / 0	chlorophenyl	nonpoint source	GC/NPD, GC/ECD	0.0003-0.02/-[a]	-

LOD: limit of Detection; LOQ: Limit of Quantification, [a]: surface water; [b]: sediment

* Not excludable that point sources were within the examined catchment or water body may not be representative for FOCUS surface water bodies

Table S1. (continued)

Reference	Country	Fungicide compounds	Detections Water/ sediment	Substance class	Entry pathway	Analytical method	LOD /LOQ (µg/L or µg/kg)	Analytical recovery (%)
Reilly et al. 2012[39]	USA	boscalid	1 / 0	carboxamide	nonpoint source	GC/EI-MS	0.0009-0.0.012/-[a]	85-104[a]
		azoxystrobin	1 / 0	strobilurin	nonpoint source	GC/IT-MS	0.0009-0.0.012/-[a]	85-104[a]
		chlorothalonil	1 / 0	chloronitrile	nonpoint source	GC/IT-MS	0.0009-0.0.012/-[a]	85-104[a]
		pyraclostrobin	1 / 0	strobilurin	nonpoint source	GC/IT-MS	0.0009-0.0.012/-[a]	85-104[a]
		cyprodinil	1 / 0	anilinopyrimidine	nonpoint source	GC/IT-MS	0.0009-0.0.012/-[a]	85-104[a]
		zoxamide	1 / 0	benzamide	nonpoint source	GC/IT-MS	0.0009-0.0.012/-[a]	85-104[a]
Ruggieri et al. 2005[40]	Italy	dicloran	13 / 0	chlorophenyl	nonpoint source	HPLC	-	75-80[a]
		iprodione	1 / 0	dicarboximide	nonpoint source	HPLC	-	81-85[a]
Sancho et al 2004[41*]	Spain	carbendazim	1 / 0	benzimidazole	nonpoint source	LC/MS/MS	0.0001-0.0005/-[a]	70-120[a]
Schäfer et al. 2007[42]	France	fenpropidin	1 / 0	unclassified	runoff	GC/MS	-	-
		tebuconazole	1 / 0	triazole	runoff	GC/MS	-	-
Schäfer et al. 2008[43]	France	fenpropidin	0 / 2	unclassified	runoff	GC/MS	-/0.125[b]	-
		tebuconazole	0 / 1	triazole	runoff	GC/MS	-/0.125[b]	-
Schäfer et al 2011[44]	Australia	azoxystrobin	1 / 0	strobilurin	runoff	GC/NPD, LC/MS/MS	-/0.002[a]	-
		boscalid	1 / 0	carboxamide	runoff	GC/NPD, LC/MS/MS	-/0.004[a]	-
		difenconazole	1 / 0	triazole	runoff	GC/NPD, LC/MS/MS	-/0.004[a]	-
		dimethomorph	1 / 0	morpholine	runoff	GC/NPD, LC/MS/MS	-/0.002[a]	-
		fenarimol	1 / 0	pyrimidine	runoff	GC/NPD, LC/MS/MS	-/0.2[a]	-
		iprodione	1 / 0	dicarboximide	runoff	GC/NPD, LC/MS/MS	-/0.2[a]	-
		metalaxyl	1 / 0	phenylamide	runoff	GC/NPD, LC/MS/MS	-/0.002[a]	-
		myclobutanil	1 / 0	triazole	runoff	GC/NPD, LC/MS/MS	-/0.004[a]	-
		oxadixyl	1 / 0	phenylamide	runoff	GC/NPD, LC/MS/MS	-/0.004[a]	-
		penconazole	1 / 0	triazole	runoff	GC/NPD, LC/MS/MS	-/0.002[a]	-
		prochloraz	1 / 0	imidazole	runoff	GC/NPD, LC/MS/MS	-/0.004[a]	-
		procymidone	1 / 0	dicarboximide	runoff	GC/NPD, LC/MS/MS	-/0.5[a]	-
		propiconazole	1 / 0	triazole	runoff	GC/NPD, LC/MS/MS	-/0.01[a]	-
		pyraclostrobin	1 / 0	strobilurin	runoff	GC/NPD, LC/MS/MS	-/0.002[a]	-
		pyrimethanil	1 / 0	anilinopyrimidine	runoff	GC/NPD, LC/MS/MS	-/0.002[a]	-
		tebuconazole	1 / 0	triazole	runoff	GC/NPD, LC/MS/MS	-/0.01[a]	-
		tetraconazole	1 / 0	triazole	runoff	GC/NPD, LC/MS/MS	-/0.004[a]	-
		triadimenol	1 / 0	triazole	runoff	GC/NPD, LC/MS/MS	-/0.01[a]	-
		trifloxystrobin	1 / 0	strobilurin	runoff	GC/NPD, LC/MS/MS	-/0.002[a]	-

LOD: limit of Detection; LOQ: Limit of Quantification, [a]: surface water; [b]: sediment

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Table S1. (continued)

Reference	Country	Fungicide compounds	Detections Water/ sediment	Substance class	Entry pathway	Analytical method	LOD /LOQ (µg/L or µg/kg)	Analytical recovery (%)
Schlichting et al. 2001[45]	Germany	cyprodinil	1 / 0	anilinopyrimidine	nonpoint source	-	-	-
		penconazole	1 / 0	triazole	nonpoint source	-	-	-
		pyrimethanil	1 / 0	anilinopyrimidine	nonpoint source	-	-	-
		triadimenol	1 / 0	triazole	nonpoint source	-	-	-
Scott et al. 2002[46]	USA	chlorothalonil	1 / 0	chloronitrile	runoff	GC/MS	0.0004/-[a]	-
Süss et al. 2006[47]	Germany	carbendazim	9 / 0	benzimidazole	spray drift	GC/MS, LC/MS/MS	-/0.05[a]	70-110[a]
		cyprodinil	7 / 0	anilinopyrimidine	spray drift	GC/MS, LC/MS/MS	-/0.05[a]	70-110[a]
		fluquinconazole	8/ 0	triazole	spray drift	GC/MS, LC/MS/MS	-/0.05[a]	70-110[a]
		kresoxim-methyl	3 / 0	strobilurin	spray drift	GC/MS, LC/MS/MS	-/0.05[a]	70-110[a]
		myclobutanil	4 / 0	triazole	spray drift	GC/MS, LC/MS/MS	-/0.05[a]	70-110[a]
		penconazole	7 / 0	triazole	spray drift	GC/MS, LC/MS/MS	-/0.05[a]	70-110[a]
		pyrimethanil	11 / 0	anilinopyrimidine	spray drift	GC/MS, LC/MS/MS	-/0.05[a]	70-110[a]
Taghavi et al. 2010[48]	France	tebuconazole	1 / 0	triazole	runoff	GC/MS	0.005-0.01/-[a]	92-102[a]
		epoxiconazole	1 / 0	triazole	runoff	GC/MS	0.005-0.01/-[a]	92-102[a]
		flusilazole	1 / 0	triazole	runoff	GC/MS	0.005-0.01/-[a]	92-102[a]
Taghavi et al. 2011[49]	France	fenpropimorph	1 / 0	morpholine	runoff	GC/MS	0.001-0.003/-[a]	-
		flusilazole	1 / 0	triazole	runoff	GC/MS	0.001-0.003/-[a]	-
		cyproconazole	1 / 0	triazole	runoff	GC/MS	0.001-0.003/-[a]	-
		tebuconazole	1 / 0	triazole	runoff	GC/MS	0.001-0.003/-[a]	-
		epoxiconazole	1 / 0	triazole	runoff	GC/MS	0.001-0.003/-[a]	-
Turnbull et al. 1997[50]	England	fenpropimorph	2 / 0	morpholine	runoff	-	-	-
Villeneuve et al. 2011[51]	France	azoxystrobin	1 / 0	strobilurin	nonpoint source	LC/MS/MS	-	-
		tebuconazole	1 / 0	triazole	nonpoint source	LC/MS/MS	-	-
		dimethomorph	1 / 0	morpholine	nonpoint source	LC/MS/MS	-	-
		procymidone	1 / 0	dicarboximide	nonpoint source	LC/MS/MS	-	-
Vioque-Fernandez et al. 2007[52]	Spain	folpet	1 / 0	phthalimide	nonpoint source	GC/MS/MS, GC/ECD	-	-
Vyrzas et al. 2011[53]	Greece	bitertanol	1 / 0	triazole	drainage	GC/MS/MS	-	-
		difenconazole	1 / 0	triazole	drainage	GC/MS/MS	-	-
		fenarimol	1 / 0	pyrimidine	drainage	GC/MS/MS	-	-
		flutriafol	1 / 0	triazole	drainage	GC/MS/MS	-	-
		propiconazole	1 / 0	triazole	drainage	GC/MS/MS	-	-
Wan et al. 2006[54*]	Canada	chlorothalonil	1 / 0	chloronitrile	runoff	GC/ECD, GC/MS	0.01/-[a]	105[a]
		metalaxyl	2 / 0	phenylamide	runoff	GC/ECD, GC/MS	0.25/-[a]	93[a]

LOD: limit of Detection; LOQ: Limit of Quantification, [a]: surface water; [b]: sediment

* Not excludable that point sources were within the examined catchment or water body may not be representative for FOCUS surface water bodies

Table S1. (continued)

Reference	Country	Fungicide compounds	Detections Water/ sediment	Substance class	Entry pathway	Analytical method	LOD /LOQ (µg/L or µg/kg)	Analytical recovery (%)
Wightwick et al 2012[55]	Australia	azoxystrobin	1 / 0	strobilurin	runoff, spray drift	LC/MS/MS	-/0.002-0.004[a]	-
		chlorothalonil	0 / 1	chloronitrile	runoff, spray drift	GC/NPD	-/50[b]	-
		cyproconazole	1 / 0	triazole	runoff, spray drift	LC/MS/MS	-/0.01[a]	-
		difenconazole	1 / 0	triazole	runoff, spray drift	LC/MS/MS	-/0.002-0.004[a]	-
		iprodione	1 / 0	dicarboximide	runoff, spray drift	GC/NPD	-/0.2[a]	-
		metalaxyl	1 / 1	phenylamide	runoff, spray drift	LC/MS/MS	-/0.002-0.004[a],-/1-5[b]	-
		myclobutanil	0 / 1	triazole	runoff, spray drift	LC/MS/MS	-/1-5[b]	-
		pyraclostrobin	0 / 1	strobilurin	runoff, spray drift	LC/MS/MS	-/1-5[b]	-
		pyrimethanil	1 / 1	anilinopyrimidine	runoff, spray drift	LC/MS/MS	-/0.002-0.004[a],-/1-5[b]	-
		trifloxystrobin	0 / 1	strobilurin	runoff, spray drift	LC/MS/MS	-/1-5[b]	-
Woudneh et al. 2009[56]	Canada	captan	1 / 0	phthalimide	nonpoint source	HRGC/HRMS	0.057-0.505/-[a]	-
		chlorothalonil	4 / 0	chloronitrile	nonpoint source	HRGC/HRMS	0.055/-[a]	-
		tebuconazole	1 / 0	triazole	nonpoint source	HRGC/HRMS	0.38-0.67/-[a]	-

LOD: limit of Detection; LOQ: Limit of Quantification, [a]: surface water; [b]: sediment

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Table S2. Fungicide parameters used for FOCUS modeling. Physicochemical data were taken from the FOOTPRINT pesticide database.[57]

Substance	Substance-class	Molar mass (g/mol)	Saturated vapour pressure (Pa)[a]	Solubility in water (mg/L)[b]	KOC (L/kg)	Freundlich exponent	Half-life time water (d)[c]		Half-life time soil (d)	Half-life time sediment (d)[d]	
							value	note		value	note
azoxystrobin*	Strobilurin	403.4	1.10E-10	6.7	589	0.85	46	water phase only	70	205	system
bitertanol*	Triazole	337.42	1.36E-09	3.8	2461	0.88	27	water phase only	23	39.2	system
boscalid*	Carboxamide	343.21	7.20E-07	4.6	772	0.864	1000	default	200	1000	default
bupirimate*	Pyrimidinol	316.42	5.70E-05	13.6	1882	0.94	6.2	water phase only	79	42.5	system
captan*	Phthalimide	300.61	4.20E-06	5.2	200	0.9	0.6	water phase only	0.8	1	system
carbendazim*	Benzimidazole	191.21	9.00E-05	8	350	0.967	7.9	water phase only	40	33.7	system
chlorothalonil*	Chloronitrile	265.91	7.60E-05	0.81	850	0.64	0.1	water phase only	22	0.1	system
cyazofamid*	Cyanoimidazole	324.78	1.33E-05	0.114	1338	0.96	6.2	water phase only	10	14	system
cymoxanil*	Cyanoacetamide oxime	198.18	1.50E-04	780	43.6	0.86	0.3	water phase only	0.7	0.3	system
cyproconazole*	Triazole	291.78	2.60E-05	93	364	0.862	1000	default	142	1000	system
cyprodinil*	Anilinopyrimidine	225.29	5.10E-04	13	2277	0.888	12.5	water phase only	37	142	system
dicloran	Chlorophenyl	207.01	2.61E-04	6.4	1000	0.739	2.94	water phase only	401	3.84	system
difenconazole*	Triazole	406.26	3.33E-08	15	3760	0.87	3	water phase only	130	1053	system
dimethomorph*	Morpholine	387.86	9.85E-07	28.95	348	0.84	10	water phase only	57	38	system
epoxiconazole*	Triazole	329.76	1.00E-05	7.1	1073	0.836	65.8	water phase only	354	119.8	system
famoxadone*	Oxazole	374.39	6.40E-07	0.11	3740	0.77	0.1	water phase only	6	0.7	system
fenarimol	Pyrimidine	331.2	6.50E-05	13.7	760	0.87	4	water phase only	250	1000	default
fenhexamid*	Hydroxyanilide	302.2	4.00E-07	20	475	0.9	17	water phase only	1	7	system
fenpropidin*	Unclassified	273.46	1.70E-02	530	3808	0.71	1.8	water phase only	90	34	system
fenpropimorph*	Morpholine	303.48	3.90E-03	4.32	4382	1.05	2.65	water phase only	35	38	system
fluazinam*	Phenylpyridinamine	465.14	7.50E-03	0.135	16430	0.65	2.7	water phase only	11	3.1	system
fludioxonil*	Phenylpyrrole	248.19	3.90E-07	1.8	145600	1	2	water phase only	164	575	system
fluquinconazole*	Triazole	376.17	6.40E-09	1.15	870	0.891	3.5	water phase only	350	13.7	system
flusilazole*	Triazole	315.39	3.87E-05	41.9	1664	0.9	1	water phase only	300	365	system
flutriafol*	Triazole	301.29	4.00E-07	95	205	0.906	36	water phase only	1358	1000	default
folpet*	Phthalimide	296.56	2.10E-05	0.8	304	0.9	0.02	water phase only	4.7	0.02	system
iprodione*	Dicarboximide	330.17	5.00E-07	12.2	700	0.93	30	water phase only	84	30	system
iprovalicarb*	Carbamate	320.43	7.90E-08	17.8	106	0.9	54	water phase only	15.5	181	system
kresoxim-methyl*	Strobilurin	313.35	2.30E-06	2	308	0.975	0.85	water phase only	16	1.3	system
metalaxyl*	Phenylamide	279.33	7.50E-04	7100	171	0.98	56	water phase only	42	56	system

[a] measured at 25 °C, [b] measured at 20 °C, [c] water phase only DT_{50} from water sediment study, [d] total system DT_{50} from water sediment study

*Substances are approved under the EU Directive 1107/2009

Table S2. (continued)

Substance	Substance-class	Molar mass (g/mol)	Saturated vapour pressure (Pa)[a]	Solubility in water (mg/L)[b]	KOC (L/kg)	Freundlich exponent	Half-life time water (d)[c]		Half-life time soil (d)	Half-life time sediment (d)[d]	
							value	note		value	note
metalaxyl-M*	Phenylamide	279.33	3.30E-03	26000	660	0.93	47.5	water phase only	39	47.5	system
metrafenone*	Benzophenone	409.3	1.53E-04	0.492	7061	0.91	3.9	water phase only	250.6	9.3	system
myclobutanil*	Triazole	288.78	1.98E-04	132	500	0.88	12	water phase only	560	626	system
oxadixyl	Phenylamide	278.3	3.30E-06	3400	36	0.9	25	water phase only	75	21	system
penconazole*	Triazole	284.18	3.66E-04	73	2205	0.816	2	water phase only	197	853	system
prochloraz*	Imidazole	376.7	1.50E-04	26.5	500	0.81	2	water phase only	120	359	system
procymidone	Dicarboximide	284.14	2.30E-05	2.46	378	0.9	0.8	water phase only	7	1.4	system
propiconazole*	Triazole	342.22	5.60E-05	150	1221	0.81	6	water phase only	214	636	system
pyraclostrobin*	Strobilurin	387.8	2.60E-08	1.9	9304	0.83	2	water phase only	32	28	system
pyrimethanil*	Anilinopyrimidine	199.11	1.10E-03	121	301	0.868	16.5	water phase only	55	80	system
quinoxyfen*	Quinoline	308.13	1.20E-05	0.047	22929	0.9	5	water phase only	97	127	system
quintozene	Chlorophenyl	295.3	1.27E-02	0.44	4498	0.9	1000	default	210	1000	default
spiroxamine*	Morpholine	297.5	3.50E-03	405	14567	0.821	0.8	water phase only	25	66.2	system
tebuconazole*	Triazole	307.82	1.30E-06	36	769	0.84	42.6	water phase only	62	365	system
tetraconazole*	Triazole	372.15	1.80E-04	156.6	1152	0.92	2	water phase only	61	340	system
triadimenol*	Triazole	295.76	5.00E-07	72	750	0.89	53	water phase only	250	91	system
trifloxystrobin*	Strobilurin	408.37	3.40E-06	0.61	2377	0.96	1.1	water phase only	7	2.4	system
zoxamide*	Benzamide	336.64	1.30E-05	0.681	1224	0.9	3	water phase only	60	5.8	system

[a] measured at 25 °C, [b] measured at 20 °C, [c] water phase only DT_{50} from water sediment study, [d] total system DT_{50} from water sediment study

* Substances are approved under the EU Directive 1107/2009

Table S3. Water body and application characteristics.

	Water body				
Reference	Field size (ha)	Width (m)	Depth (m)	Flow[a]	Time between application and first rain (d)
Angelidis et al. 1996[1]	na	na	na	na	na
Arnold et al. 2004[2]	na	na	na	na	na
Battaglin et al. 2011[3]	na	na	na	na	na
Belden et al. 2012[4]	na	na	na	na	na
Berenzen et al. 2005[5]	0-25	na	na	10-80 L/s	3
Bereswill et al. 2012[6]	na	0.4-2.4	0.03-0.13	0.01-0.14 m/s	na
Bermudez-Couso et al. 2007[7]	14.31-105.82	na	na	na	na
Daniels et al. 2000[8]	na	na	na	na	na
Dorigo et al. 2007[9]	20-620	na	na	na	na
Futula et al. 2006[10]	na	na	na	na	na
Ganzelmeier et al. 2011[11]	na	na	na	na	na
Graves et al. 2004[12]	na	na	na	na	na
Griffini et al. 1997[13]	na	na	na	na	na
Haarstadt and Braskerud 2005[14]	0.1	na	na	na	na
Johnson et al. 2000[15]	na	5	0.5	na	na
Karaouzas et al. 2011[16]	na	na	na	na	na
Kern et al. 2011[17]	na	na	na	1 m^3/s	na
Kreuger 1998[18]	na	na	na	na	na
Kronvang et al. 2003[19]	na	na	na	na	na
Kuo et al. 2012[20]	na	na	na	na	na
Lehotay et al. 1998[21]	na	na	na	na	na
Liess and Von der Ohe 2005[22]	na	0.5-2.5	0.04-0.6	0.02-0.5 m/s	na
Long et al. 1998[23]	na	na	na	na	na
Ludvigsen and Lode 2001[24]	na	na	na	na	na
Maillard et al. 2011[25]	na	na	na	0.3 m^3/h	na
Merli et al. 2010[26]	na	na	na	na	na
Miles and Pfeuffer 1997[27]	na	na	na	na	na
Morin et al. 2010[28]	57-670	na	na	na	na
Neumann et al. 2002[29]	na	na	na	10-300 L/s	na
Neumann et al. 2003[30]	na	0.5	na	na	na
Oliver et al. 2012[31]	4-34.6	na	na	na	na
Pacioni et al. 2010[32]	na	na	na	na	na
Pesce et al. 2008[33]	na	na	na	na	na
Piscart et al. 2011[34]	na	na	na	na	na
Polard et al. 2011[35]	na	na	na	4.3-16 m^3/s	na
Rabiet et al. 2011[36]	na	na	na	0.005-0.11 m^3/s	na
Rasmussen et al. 2011[37]	na	na	na	na	na
Readman et al. 1997[38]	na	na	na	na	na
Reilly et al. 2012[39]	na	na	na	na	na
Ruggieri et al. 2005[40]	na	na	na	na	na
Sancho et al. 2004[41]	na	na	na	na	na
Schäfer et al. 2007[42]	na	max 5	max 0.8	na	na

a Flow is either given as discharge or flow velocity

na: not available

Table S3. (continued)

Reference	Field size (ha)	Water body				Time between application and first rain (d)
		Width (m)	Depth (m)	Flow[a]		
Schäfer et al. 2008[43]	na	max 5	max 0.8	na		na
Schäfer et al. 2011[44]	na	1-25	0.1-0.9	na		na
Schlichting et al. 2001[45]	600	na	na	3.1 m³/s		na
Scott et al. 2002[46]	na	na	na	na		na
Süß et al. 2006[47]	na	2.9-4	0.1-0.89	na		na
Taghavi et al. 2010[48]	na	na	na	na		na
Taghavi et al. 2011[49+]	na	na	na	na		na
Turnbull et al. 1997[50]	5.16	na	na	na		49-51
Villeneuve et al. 2011[51]	na	na	na	0.021-0.088 m³/s		na
Vioque-Fernandez et al. 2007[52]	na	na	na	na		na
Vryzas et al. 2011[53]	na	na	na	na		na
Wan et al. 2006[54]	na	na	na	na		na
Wightwick et al. 2012[55]	na	1-25	0.1-0.9	na		na
Woudneh et al. 2009[56]	na	na	na	na		na

a Flow is either given as discharge or flow velocity

na: not available

Table S4. FOCUS parameters used for modeling

Reference	Substance	Scenario[a]	Crop	Number of applications	Intervall between applications (d)	Application amount (g a.i./ha)	Application window (julien days)
Angelidis et al. 1996[1]	captan	R2, R3, R4	pome stone fruit	4	7	2500	91-142
Arnold et al. 2004[2]	chlorothalonil	R1, R2, R3	potatoes	5	7	1962	91-142
Battaglin et al. 2011[3]	azoxystrobin	R3, R4	soybean	1	na	280	152-196
	chlorothalonil	R3, R4	soybean	2	14	2018	152-196
	metalaxyl	R3, R4	soybean	1	na	1403	152-182
	myclobutanil	R3, R4	soybean	8	7	70	121-200
	propiconazole	R3, R4	soybean	2	7	126	152-189
	pyraclostrobin	R3, R4	soybean	2	7	420	152-189
	tebuconazole	R3, R4	soybean	3	10	123	152-202
	tetraconazole	R3, R4	soybean	2	21	114	152-203
	trifloxystrobin	R3, R4	soybean	3	10	140	152-202
Belden et al. 2012[4]	propiconazole	R1, R2, R3	winter cereals	2	7	126	61-98
	pyraclostrobin	R1, R2, R3	winter cereals	2	10	224	61-101
Berenzen et al. 2005[5]	azoxystrobin	R1	winter cereals	2	14	250	135-186
	epoxiconazole	R1	winter cereals, sugar beet	2	21	125	135-186; 105-156
	kresoxim-methyl	R1	winter cereals	2	21	125	135-186
	tebuconazole	R1	winter cereals	2	21	250	135-186
Bereswill et al. 2012[6]	azoxystrobin	R1	vines	1	na	220	166-196
	boscalid	R1	vines	1	na	600	166-196
	cyazofamid	R1	vines	8	12	80	121-235
	cyprodinil	R1	vines	4	6	225	152-200
	dimethomorph	R1	vines	5	10	300	121-191
	famoxadone	R1	vines	1	na	270	166-196
	fenhexamid	R1	vines	1	na	180	166-196
	fludioxonil	R1	vines	2	21	250	152-203
	folpet	R1	vines	8	7	1500	135-214
	iprovalicarb	R1	vines	1	na	90	166-196
	kresoxim-methyl	R1	vines	3	8	100; 120; 150	152-198

[a] D1 - D6 are the standard drainage scenarios implemented in FOCUS step 3 for different locations in Europe, and R1 - R4 are the standard runoff scenarios.

Table S4. (continued)

Reference	Substance	Scenario[a]	Crop	Number of applications	Intervall between applications (d)	Application amount (g a.i./ha)	Application window (julien days)
	metalaxyl-M	R1	vines	1	na	120	166-196
	metrafenone	R1	vines	8	12	10	121-235
	myclobutanil	R1	vines	4	10	48	152-212
	penconazole	R1	vines	4	10	25	152-212
	pyrimethanil	R1	vines	1	na	600	166-196
	quinoxyfen	R1	vines	7	10	50	121-211
	spiroxamine	R1	vines	1	na	300	166-196
	tebuconazole	R1	vines	3	14	100	152-210
	trifloxystrobin	R1	vines	4	7	187.5	152-203
Bermudez-Couso et al. 2007[7]	metalaxyl	R2, R3, R4	vines	3	14	200	70-128
	penconazole	R2, R3, R4	vines	3	7	40	130-174
	cyprodinil	R2, R3, R4	vines	4	6	225	196-244
	procymidone	R2, R3, R4	vines	2	7	750	152-189
	fludioxonil	R2, R3, R4	vines	2	21	250	196-247
Daniels et al. 2000[8]	fenpropimorph	D1, D2, D4, D5, R1	sugarbeet, winter cereals, spring cereals	1-2	28	750	91-149, 121-179, 121-151
Dorigo et al. 2007[9]	azoxystrobin	R1, R2, R3, R4	vines	2	14	250	121-165
	oxadixyl	R1, R2, R3, R4	vines	3	15	200	121-181
	tebuconazole	R1, R2, R3, R4	vines	3	14	100	121-179
Futula et al. 2006[10]	metalaxyl	D3, D4, R1	potatoes, leafy vegetables, bulb vegetables	4	7-14	202-216	74-146
Ganzelmeier et al. 2011[11]	captan	D3, D4, D5, R1	pome stone fruit	8	7	1250	91-170
	cyprodinil	D3, D4, D5, R1	pome stone fruit	4	6	225	91-139
	trifloxystrobin	D3, D4, D5, R1	pome stone fruit	6	7	75	121-186
	fluquinconazole	D3, D4, D5, R1	pome stone fruit	2	21	125	91-142
	pyrimethanil	D3, D4, D5, R1	pome stone fruit	5	7	400-600	91-149
	penconazole	D3, D4, D5, R1	pome stone fruit	4	10	25	91-151

[a] D1 - D6 are the standard drainage scenarios implemented in FOCUS step 3 for different locations in Europe, and R1 - R4 are the standard runoff scenarios.

Table S4. (continued)

Reference	Substance	Scenario[a]	Crop	Number of applications	Intervall between applications (d)	Application amount (g a.i./ha)	Application window (julien days)
Graves et al. 2004[12]	metalaxyl	D6, R4	citrus	3	90	2240	91-301
Griffini et al. 1997[13]	procymidone	D4, D5, R1	pome stone fruit	2	7	750	121-158
Haarstadt and Braskerud 2005[14]	fenpropimorph	R1	sugarbeet	1	na	750	91-121
	metalaxyl	R1	potatoes	3	14	200	91-149
	propiconazole	R1	sugarbeet	2	21	250	91-142
Johnson et al. 2000[15]	chlorothalonil	R3, R4	soybeans	2	14	2016	91-145
Karaouzas et al. 2011[16]	triadimenol	R4	citrus, olives	4	21	62.5	152-245
	penconazole	R4	citrus, olives	3	7	40	152-196
Kern et al. 2011[17]	azoxystrobin	R1, R3, R4	winter cereals	2	14	250	60-104
	epoxiconazole	R1, R3, R4	winter cereals, sugar beet	2	21	125	60-111, 91-142
Kreuger 1998[18]	fenpropimorph	D1, D2, D4, D5, R1	winter cereals, spring cereals	2	28	270	91-149, 121-179
	propiconazole	D1, D2, D4, D5, R1	winter cereals, spring cereals	2	21	90	91-142, 121-172
	prochloraz	D1, D2, D4, D5, R1	winter cereals, spring cereals	2	10	540	105-145, 135-175
	triadimenol	D1, D2, D4, D5, R1	winter cereals, spring cereals	2	28	125	108-166, 136-194
Kronvang et al 2003[19]	fenpropimorph	D1, D2, D4, D5 R1	winter cereals, spring cereals, sugar beet	1-2	28	750	91-149, 121-179
	prochloraz	D1, D2, D4, D5 R1	winter cereals, spring cereals	2	10	540	105-145, 135-175
	propiconazole	D1, D2, D4, D5 R1	winter cereals, spring cereals, sugar beet	2	21	250	91-142, 121-172
Kuo et al. 2012[20]	chlorothalonil	R1, R2, R3, R4	root vegetables, bulb vegetables, fruiting vegetables	2-8	5-7	1261-2522	91-131, 91-142
	captan	R1, R2, R3, R4	pome stone fruit	8	1	4483	91-128
	flutriafol	R1, R2, R3, R4	pome stone fruit	4	14	107	91-163
	quintozene	R1, R2, R3 , R4	potatoes, leafy vegetables	1	na	28000	91-121
Lehotay et al. 1998[21]	chlorothalonil	R2, R3, R4	maize, soybean	2-7	7-14	1680	91-156, 91-135
Liess and Von der Ohe 2005[22]	kresoxim-methyl	R1	winter cereals	2	21	125	91-142

[a] D1 - D6 are the standard drainage scenarios implemented in FOCUS step 3 for different locations in Europe, and R1 - R4 are the standard runoff scenarios.

Table S4. (continued)

Reference	Substance	Scenario[a]	Crop	Number of applications	Intervall between applications (d)	Application amount (g a.i./ha)	Application window (julien days)
	epoxiconazole	R1	winter cereals, sugar beet	2	21	125	91-142, 121-172
	azoxystrobin	R1	winter cereals	2	14	250	91-135
	propiconazole	R1	winter cereals, sugar beet	2	14	250	91-135, 121-165
	fenpropimorph	R1	winter cereals, sugar beet	1-2	28	750	91-149, 121-151
	tebuconazole	R1	winter cereals	2	21	250	91-142
Long et al. 1998[23]	flutriafol	D1, D2, D4, D5, R1	winter cereals, spring cereals	1	na	125	91-121
	propiconazole	D1, D2, D4, D5, R1	winter cereals, spring cereals, sugar beet	2	21	250	91-142, 121-172
Ludvigsen and Lode 2001[24]	metalaxyl	D1, D2, D4, D5, R1	winter cereals, spring cereals	3	14	200	91-149, 121-179
	propiconazole	D1, D2, D4, D5, R1	winter cereals, spring cereals	2	21	250	91-142, 121-172
	fenpropimorph	D1, D2, D4, D5, R1	winter cereals, spring cereals	2	28	750	91-149, 121-179
	fluazinam	D1, D2, D4, D5, R1	winter cereals, spring cereals	8	7	200	121-200, 165-244
	prochloraz	D1, D2, D4, D5, R1	winter cereals, spring cereals	2	10	540	105-145, 135-175
	iprodione	D1, D2, D4, D5, R1	winter cereals, spring cereals	1	na	500	74-104, 91-121
Maillard et al. 2011[25]	cymoxanil	R1	vines	8	7	175	121-200
	carbendazim	R1	vines	3	21	374	141-213
	dimethomorph	R1	vines	5	10	300	121-191
	kresoxim-methyl	R1	vines	3	8	100-150	121-167
	metalaxyl	R1	vines	4	14	300	121-193
Merli et al. 2010[26]	quinoxyfen	D6, R2, R3, R4	vines	7	21	20-77.5	91-247
Miles and Pfeuffer 1997[27]	metalaxyl	D6, R2, R3, R4	citrus, bulb vegetables, fruiting vegetables, leafy vegetables	3-4	10-90	202-2242	60-270, 60-132, 60-120
Morin et al. 2010[28]	azoxystrobin	R1, R2, R3, R4	vines	2	14	250	121-165

[a] D1 - D6 are the standard drainage scenarios implemented in FOCUS step 3 for different locations in Europe, and R1 - R4 are the standard runoff scenarios.

Table S4. (continued)

Reference	Substance	Scenario[a]	Crop	Number of applications	Intervall between applications (d)	Application amount (g a.i./ha)	Application window (julien days)
	tebuconazole	R1, R2, R3, R4	vines	3	14	100	121-179
	dimethomorph	R1, R2, R3, R4	vines	5	10	300	121-191
	procymidone	R1, R2, R3, R4	vines	2	7	750	121-158
Neumann et al. 2002[29]	azoxystrobin	R1	winter cereals	2	14	250	91-135
	epoxiconazole	R1	winter cereals, sugar beet	2	21	125	91-142, 121-172
	fenpropimorph	R1	winter cereals, sugar beet	1-2	28	750	91-151, 121-179
	propiconazole	R1	winter cereals, sugarbeet	2	21	250	91- 142, 121-172
Neumann et al. 2003[30]	azoxystrobin	D1, D2, D4, D5, R1	winter cereals, spring cereals	2	14	250	91-135, 105-149
	epoxiconazole	D1, D2, D4, D5, R1	winter cereals, spring cereals, sugar beet	2	21	250	91- 142, 121-172
	fenpropimorph	D1, D2, D4, D5, R1	winter cereals, spring cereals, sugar beet	1-2	28	750	91-149, 91-179, 121-151
	propiconazole	D1, D2, D4, D5, R1	winter cereals, spring cereals, sugar beet	2	21	250	91-142, 121-172
Oliver et al. 2012[31]	fenarimol	R2, R3, R4	pome stone fruit	4	14	54	121-193
	bupirimate	R2, R3, R4	pome stone fruit	8	10	225	91-191
	penconazole	R2, R3, R4	pome stone fruit	5	10	50	74-144
	procymidone	R2, R3, R4	pome stone fruit	1	na	375	152-182
	propiconazole	R2, R3, R4	pome stone fruit	5	7	160	121-179
Pacioni et al. 20103[32]	procymidone	D6, R2, R3, R4	root vegetables	2	7	750	105-142
	dicloran	D6, R2, R3, R4	fruiting vegetables	3	20	1000	105-175
	iprodione	D6, R2, R3, R4	root vegetables, leafy vegetables	3-4	14-28	750	105-219, 105-163
Pesce et al. 2008[33]	oxadixyl	R1, R3, R4	winter cereals	3	15	200	60-120
	procymidone	R1, R3, R4	winter cereals	2	7	750	60-97
Piscart et al. 2011[34]	tebuconazole	R1, R2, R3, R4	vines	3	14	100	152-210
	procymidone	R1, R2, R3, R4	vines	2	7	750	152-189
Polard et al. 2011[35]	tebuconazole	R3, R4	winter cereals	2	21	250	74-125
	cyproconazole	R3, R4	winter cereals	2	28	100	74-132

[a] D1 - D6 are the standard drainage scenarios implemented in FOCUS step 3 for different locations in Europe, and R1 - R4 are the standard runoff scenarios.

Table S4. (continued)

Reference	Substance	Scenario[a]	Crop	Number of applications	Intervall between applications (d)	Application amount (g a.i./ha)	Application window (julien days)
	epoxiconazole	R3, R4	winter cereals	2	21	125	74-125
	flusilazole	R3, R4	winter cereals, maize	2-3	21-28	160-200	60-146, 74-125
Rabiet et al. 2011[36]	azoxystrobin	R1, R3, R4	winter cereals	2	28	750	121-179
	tebuconazole	R1, R2, R3, R4	vines	3	14	100	152-210
	dimethomorph	R1, R2, R3, R4	vines	5	10	300	121-191
	carbendazim	R1, R3, R4	winter cereals	2	14	100	121-165
	procymidone	R1, R2, R3, R4	vines	2	7	750	121-158
Rasmussen et al. 2011[37]	azoxystrobin	R1	winter cereals	2	21	125	60-111
	propiconazole	R1	winter cereals	2	21	250	60-111
	tebuconazole	R1	winter cereals	2	21	250	60-111
	dimethomorph	R1	winter cereals	8	7	180	60-139
	boscalid	R1	oil seed rape winter	2	28	250	91-149
Readman et al. 1997[38]	dicloran	R2, R3, R4	fruiting vegetables	3	20	1000	60-130
Reilly et al. 2012[39]	chlorothalonil	D3, D4, D6, R1, R2,R3	potatoes	6	10	1960	91-171
	pyraclostrobin	D3, D4, D6, R1, R2,R3	potatoes	6	7	219	91-156
	azoxystrobin	D3, D4, D6, R1, R2,R3	potatoes	2	7	280	91-128
	boscalid	D3, D4, D6, R1, R2,R3	potatoes	2	14	490	91-135
	cyprodinil	D3, D4, D6, R1, R2,R3	potatoes	4	7	368	91-142
	zoxamide	D3, D4, D6, R1, R2,R3	potatoes	6	7	190	91-156
Ruggieri et al. 2005[40]	dicloran	D6, R2, R3, R4	fruiting vegetables	3	20	1000	105-175
	iprodione	D6, R2, R3, R4	root vegetables, leafy vegetables	3-4	14-28	750	105-219
Sancho et al. 2004[41]	carbendazim	R2, R3, R4	pome stone fruit	4	7	1962	135-186
Schäfer et al. 2007[42]	fenpropidin	R1	winter cereals	2	21	750	60-111
	tebuconazole	R1	winter cereals	2	21	250	60-111

[a] D1 - D6 are the standard drainage scenarios implemented in FOCUS step 3 for different locations in Europe, and R1 - R4 are the standard runoff scenarios.

Table S4. (continued)

Reference	Substance	Scenario[a]	Crop	Number of applications	Intervall between applications (d)	Application amount (g a.i./ha)	Application window (julien days)
Schäfer et al. 2008[43]	fenpropidin	R1	winter cereals	2	21	750	60-111
	tebuconazole	R1	winter cereals	2	21	250	60-111
Schäfer et al. 2011[44]	azoxystrobin	D6, R2, R3, R4	vines, pome stone fruit, potatoes, fruiting vegetables	3	7-14	150-200	135-185, 152-210, 152-196, 121-165
	boscalid	D6, R2, R3	potatoes, fruiting vegetables	2	10	75	121-161
	difenoconazole	D6, R2, R3, R4	root vegetables, potatoes, fruiting vegetables, pome stone fruit	2-4	7-10	70-125	91-131, 91-142
	dimethomorph	D6, R2, R3, R4	bulb vegetables, potatoes	2-4	7	180	152-189, 152-203
	fenarimol	D6, R2, R3, R4	pome stone fruit, vines	3-4	14	36-54	121-193, 121-179
	iprodione	D6, R2, R3, R4	vines, pome stone fruit, potatoes, fruiting vegetables	3-5	10-14	375-500	135-185, 135-195, 121-207, 91-163
	metalaxyl	D6, R2, R3, R4	vines, bulb vegetables, potatoes	4-8	7	200-225	91-142, 60-139, 91-170
	myclobutanil	R2, R3, R4	pome stone fruit	8	7	48	91-170
	oxadixyl	D6, R2, R3, R4	bulb vegetables, vines	2	7	200	152-189, 121-185
	penconazole	D6, R2, R3, R4	pome stone fruit, vines	3-5	10-14	25-50	74-144, 91-149
	prochloraz	R2, R3, R4	pome stone fruit	2	21	393	91-142
	procymidone	D6, R2, R3, R4	vines, pome stone fruit, potatoes, bulb vegetables	1-2	14-70	375-1000	152-182, 91-135, 60-160
	propiconazole	R2, R3, R4	pome stone fruit	5	7	100-160	121-179
	pyraclostrobin	D6, R2, R3, R4	potatoes, fruiting vegetables, pome stone fruit	2	7-30	150	152-189, 121-161, 121-181
	pyrimethanil	D6, R2, R3, R4	vines	2	7	800	152-189
	tebuconazole	D6, R2, R3, R4	vines	5	14	129	91-177
	tetraconazole	D6, R2, R3, R4	vines	3	10	18	91-149
	triadimenol	D6, R2, R3, R4	leafy vegetables, fruiting vegetables, vines	3-8	5-10	37.5-100	91-191, 91-136, 91-141
	trifloxystrobin	D6, R2, R3, R4	pome stone fruit, vines	3	10-14	50-75	91-141, 135-193
Schlichting et al. 2001[45]	cyprodinil	D1, D2, D3, D4, D5, R1	winter cereals, pome stone fruit	1-4	0-6	225-750	60-90, 121-169

[a] D1 - D6 are the standard drainage scenarios implemented in FOCUS step 3 for different locations in Europe, and R1 - R4 are the standard runoff scenarios.

Table S4. (continued)

Reference	Substance	Scenario[a]	Crop	Number of applications	Intervall between applications (d)	Application amount (g a.i./ha)	Application window (julien days)
	penconazole	D3, D4, D5, R1	pome stone fruit	4	10	25	121-181
	pyrimethanil	D3, D4, D5, R1	pome stone fruit	5	7	400-600	91-149
	triadimenol	D1, D2, D3, D4, D5, R1	winter cereals	2	14	125	105-149
Scott et al. 2002[46]	chlorothalonil	R2, R3, R4	fruiting vegetables, potatoes	5-6	7-10	1261-1962	74-132, 74-154
Süß et al. 2006[47]	carbendazim	D3, D4, D5, R1	pome stone fruit	3	21	374	141-213
	cyprodinil	D3, D4, D5, R1	pome stone fruit	4	6	225	141-189
	fluquinconazole	D3, D4, D5, R1	pome stone fruit	2	21	125	141-192
	kresoxim-methyl	D3, D4, D5, R1	pome stone fruit	4	7	100-125	105-156
	myclobutanil	D3, D4, D5, R1	pome stone fruit	4	10	48	105-165
	penconazole	D3, D4, D5, R1	pome stone fruit	4	10	250	152-212
	pyrimethanil	D3, D4, D5, R1	pome stone fruit	5	7	400-600	105-163
	triadimenol	D3, D4, D5, R1	pome stone fruit	4	21	62.5	83-176
Taghavi et al. 2010[48]	tebuconazole	R3, R4, D6	winter cereals	2	21	250	152-203
	epoxiconazole	R3, R4, D6	winter cereals	2	21	125	105-156
	flusilazole	R3, R4, D6	winter cereals	3	28	160	152-211
Taghavi et al. 2011[49]	flusilazole	R3, R4	winter cereals	3	28	160	60-146
	cyproconazole	R3, R4	winter cereals	2	28	100	60-118
	tebuconazole	R3, R4	winter cereals	2	21	250	60-111
	epoxiconazole	R3, R4	winter cereals	2	21	125	60-111
Turnbull et al. 1997[50]	fenpropimorph	R1	winter cereals	1	na	750	60-90
Villeneuve et al. 2011[51]	azoxystrobin	R1, R2, R3, R4	vines	2	14	250	152-196
	tebuconazole	R1, R2, R3, R4	vines	3	14	100	152-210
	dimethomorph	R1, R2, R3, R4	vines	5	10	300	152-222
	procymidone	R1, R2, R3, R4	vines	2	7	750	152-189
Vioque-Fernandez et al. 2007[52]	folpet	R2, R3, R4	vines	8	7	1500	105-184
Vryzas et al. 2011[53]	bitertanol	D6, R4, R3	winter cereals	1	na	130	305-335

[a] D1 - D6 are the standard drainage scenarios implemented in FOCUS step 3 for different locations in Europe, and R1 - R4 are the standard runoff scenarios.

Table S4. (continued)

Reference	Substance	Scenario[a]	Crop	Number of applications	Intervall between applications (d)	Application amount (g/ha)	Application window (julien days)
	difenconazole	D6, R4, R3	winter cereals	1	na	12	305-335
	fenarimol	R3, R4	sunflower	3	7	72	152-196
	flutriafol	D6, R4, R3	winter cereals	1	na	125	91-121
	propiconazole	D6, R4, R3	winter cereals, sugar beet	2	7	250	91-128
Wan et al. 2006[54]	chlorothalonil	R1	pome stone fruit, potatoes, root vegetables, bulb vegetables	5-8	7-10	1261-3474	121-191, 74-154, 74-153, 74-146
	metalaxyl	R1	potatoes, leafy vegetables, bulb vegetables	4	7-14	202-216	74-146, 74-125
Wightwick et al. 2012[55]	azoxystrobin	D6, R2, R3, R4	vines, pome stone fruit, potatoes, fruiting vegetables	3	7-14	150-200	135-185, 152-210, 152-196, 121-165
	chlorothalonil	D6, R2, R3, R4	vines, pome stone fruit, leafy vegetables, root vegetables, bulb vegetables	8	7-14	1150-2500	91-170, 91-219
	cyproconazole	D6, R2, R3	potatoes	8	7	25	105-184
	difenoconazole	D6, R2, R3, R4	root vegetables, potatoes, fruiting vegetables, pome stone fruit	2-4	7-10	70-125	91-131, 91-142
	iprodione	D6, R2, R3, R4	vines, pome stone fruit, potatoes, fruiting vegetables	3-5	10-14	375-500	135-185, 135-195, 121-207, 91-163
	metalaxyl	D6, R2, R3, R4	vines, bulb vegetables, potatoes	4-8	7	200-225	91-142, 60-139, 91-170
	myclobutanil	R2, R3, R4	pome stone fruit	8	7	48	91-170
	pyraclostrobin	D6, R2, R3, R4	potatoes, fruiting vegetables, pome stone fruit	2	7-30	150	152-189, 121-161, 121-181
	pyrimethanil	D6, R2, R3, R4	vines	2	7	800	152-189
	trifloxystrobin	D6, R2, R3, R4	pome stone fruit, vines	3	10-14	50-75	91-141, 135-193
Woudneh et al. 2009[56]	captan	D2, D3, D4, D6, R1, R2, R3, R4	field beans	8	3	2802	121-172
	chlorothalonil	D2, D3, D4, D6, R1, R2, R3, R4	field beans, root vegetables, maize, bulb vegetables, potatoes	3-8	5-10	1681-3363	121-171, 91-170
	tebuconazole	D2, D3, D4, D6, R1, R2, R3, R4	maize, bulb vegetables	4	7-14	191	91-142, 91-163

[a] D1 - D6 are the standard drainage scenarios implemented in FOCUS step 3 for different locations in Europe, and R1 - R4 are the standard runoff scenarios.

Text S1. GIS Analysis on the representativeness of sampling sites within Europe

First, we tested if the empirical study sites were situated within the distribution of the FOCUS scenarios.[58] Therefore, we used the ArcMap GIS files from the FOCUS surface water working group in which they intersected climate conditions, soil patterns and land use to show the distribution of all drainage and runoff scenarios (details are given in FOCUS 2001[58]). We identified and georeferenced 49 different sampling points from the studies conducted in the European Union. We decided to take a 10 km buffer around each sampling point to account for uncertainties in georeferencing (because sampling points were not exactly described or could not be related to concentrations) and especially because the used climate and soil data do have the same resolution (10 x 10 km) and can therefore not exactly be allocated to raster grid cells. Subsequently, the sampling points were plotted together with the distribution of FOCUS scenarios. For every sampling point we screened if the coordinates of the sampling points were situated within the area that is covered by the FOCUS scenarios. The results are shown in Figure S1: 42 (86%) of the 49 sampling points are located within the distribution of the FOCUS scenarios. Except D1 and R2, which cover only small areas of Europe (0.8 and 0.7%), at least one sampling point lies within every scenario distribution. In summary, we conclude that with respect to the FOCUS scenario classification the used study sampling points cover at least 31.4% (32.9% for all FOCUS scenarios[58]) of all agricultural land in the European Union (or even more as 14% of the sampling sites are not located within the FOCUS scenario distribution and thus represent even areas which are not necessarily covered by FOCUS).

In a second step we identified those areas in Europe for which the prevailing climate and soil conditions at the specific sampling points are appropriate. The analysis of the representativeness of the sampling sites was based on several data sets that cover all areas of Europe. In general, we used the datasets and methods described in the FOCUS report.[58] The climate data were provided by the FOCUS working group (Dr John Hollis). Relevant soil attributes that characterize Soil Typological Units within the 1:1,000,000 scale were taken from the Soil Geographic Database of Europe. In addition, relevant crops were also identified through the Soil Typological Units (STU) at the 1:1,000,000 scale from the Soil Geographical Database of Europe.[59]

Initially, relevant soil properties (soil, texture class, parent material, water management, water regime), land use, and relevant climate data (average spring and autumn temperature, average annual precipitation and average annual groundwater recharge) corresponding to each sampling point were identified using the ArcView GIS software. Corresponding average annual precipitation, average annual recharge and average spring and autumn temperature were ranked in categories as described in the FOCUS report (FOCUS 2001).

The distribution of the conditions at the specific sampling points within Europe was then mapped with ArcView GIS by intersecting relevant climate data, soil patterns and land use. This was done for average annual precipitation and average annual recharge separately as these are the driving factors for either surface runoff or drainage, respectively.

The results are shown in Figure S2 and Figure S3. The conditions at the field sampling sites represent 9.1% for average annual precipitation and 11.9% for average annual recharge of the land across Europe.

The field sampling sites are related to specific soil attributes or land uses while the FOCUS scenarios are designed to represent wider areas and include several optional representations of environmental parameters within one soil attribute. For this reason, we believe that a coverage of 10% of all land across Europe, in comparison to the 33% covered by the FOCUS scenarios, shows that the used field sampling sites gives a representative sample for the evaluation of the FOCUS surface water approach. The 10% can be considered a high coverage given the fact that the MFCs stem from discrete sites distributed all over Europe and not from model sites selected particularly for their representativeness (as the FOCUS scenarios). In comparison, the FOCUS working group states that it is estimated that a favorable risk assessment for any single drainage or runoff scenario should protect a significant area (at least >5%) of relevant European agriculture and thus should be adequate for achieving Annex 1 listing.[58]

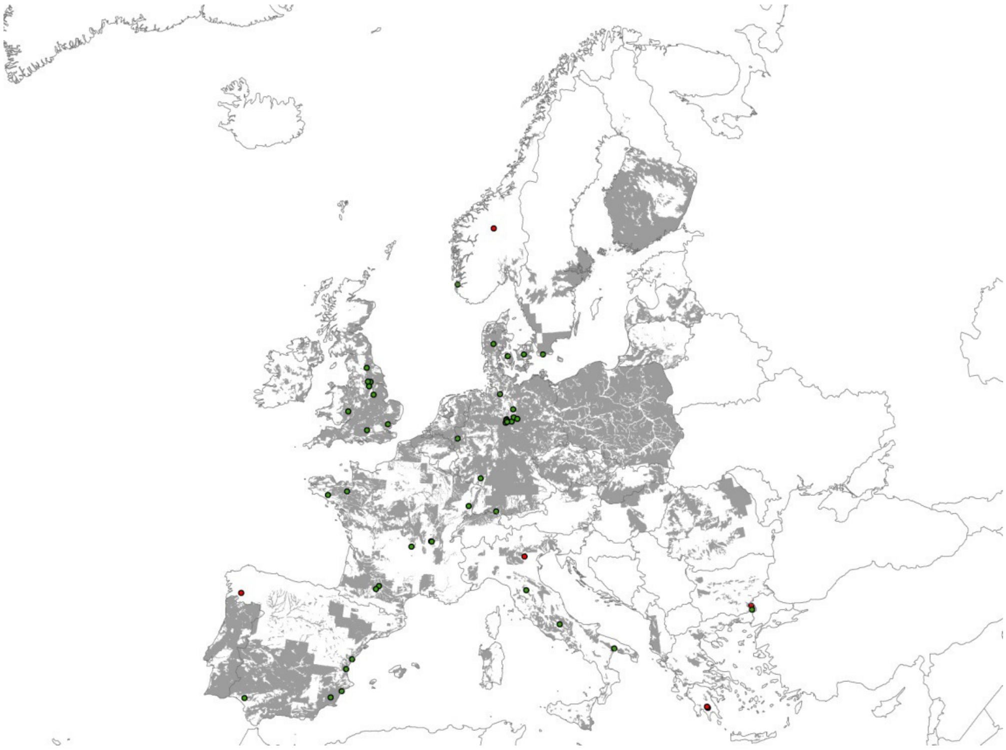


Figure S1. Distribution of the FOCUS surface water scenarios within Europe and actual sampling points of the field studies used in our analysis. Green points: Sampling points are covered by the distribution of the FOCUS scenarios. Red points: Sampling points are not covered by the distribution of the FOCUS scenarios.

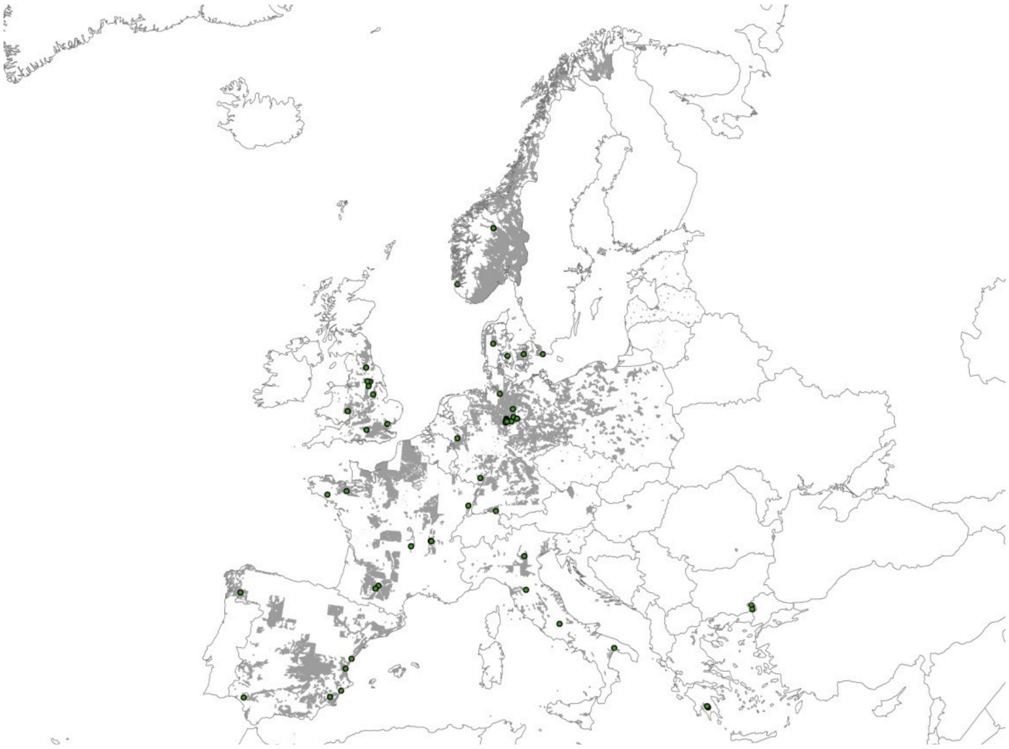


Figure S2. Distribution of the areas represented by climate and soil conditions of the field sampling sites in relation to drainage. The points mark the locations of the sampling stations. All grey areas are the areas represented by the sampling points.

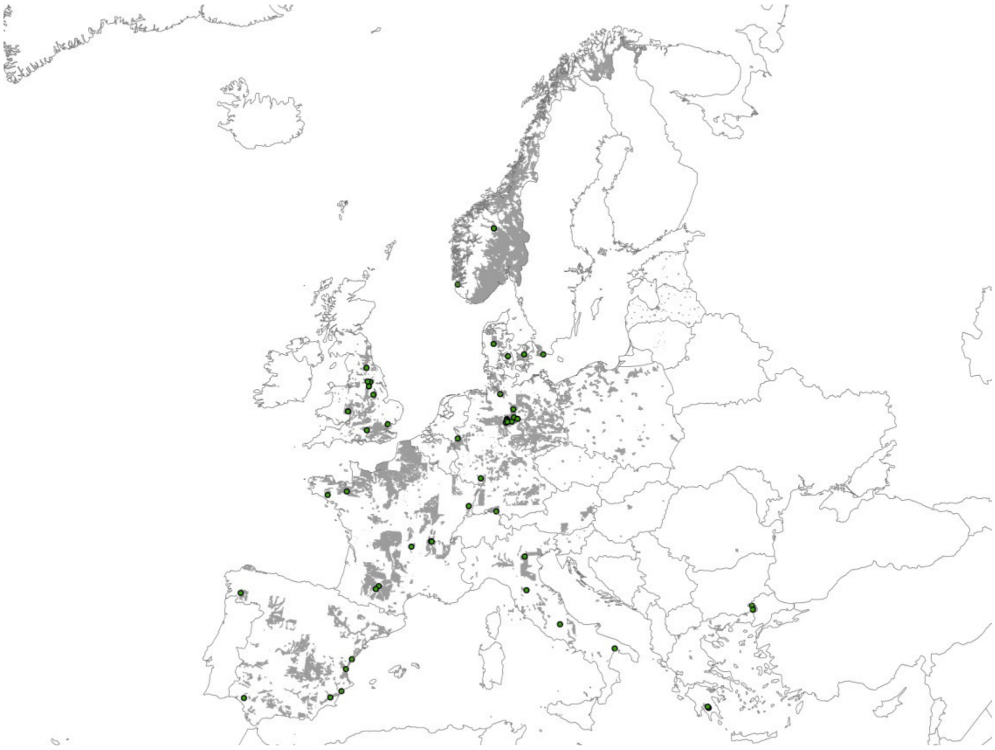
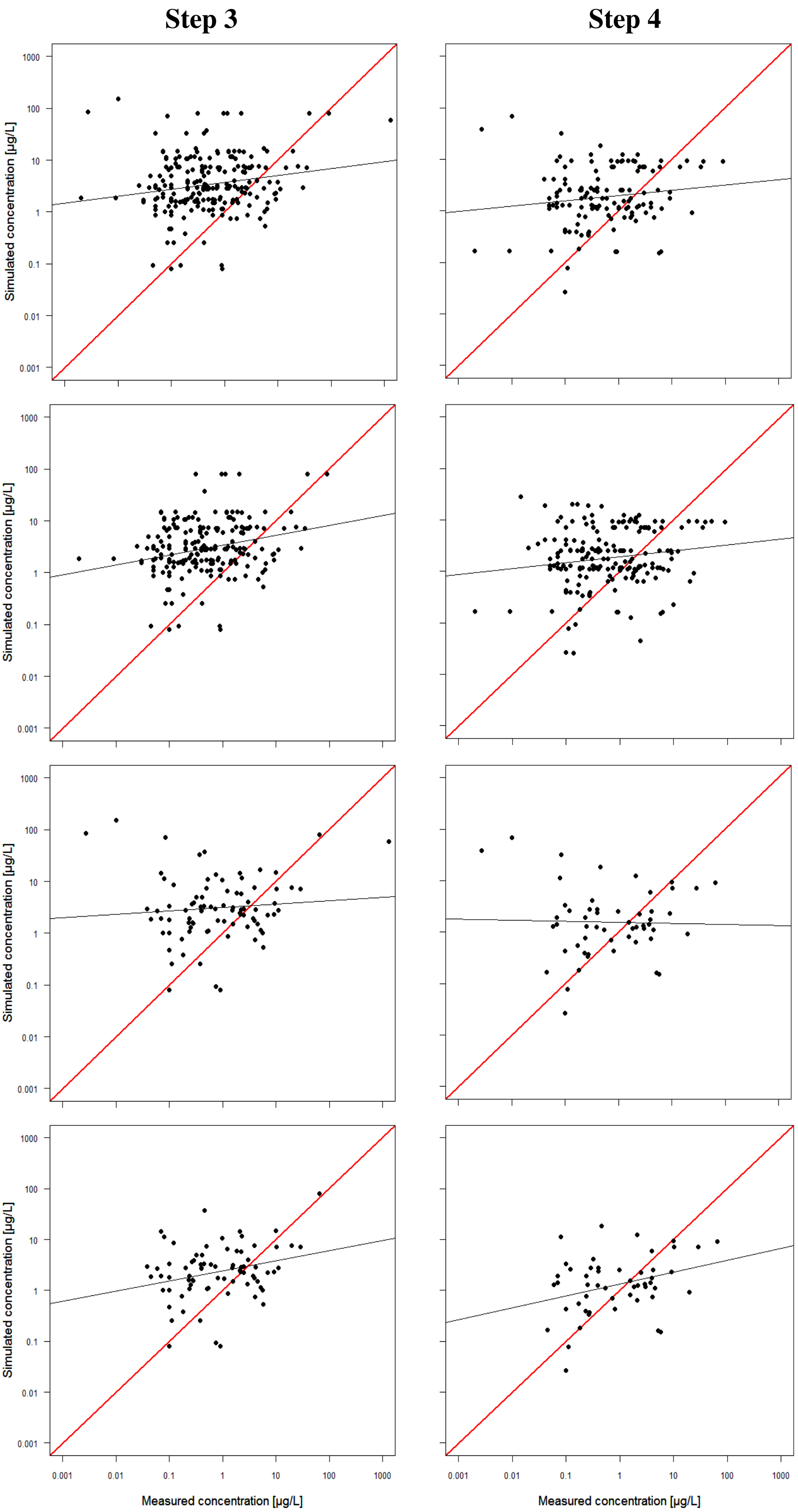


Figure S3. Distribution of the areas represented by climate and soil conditions of the field sampling sites in relation to surface runoff. The points mark the locations of the sampling stations. All grey areas are the areas represented by the sampling points.



World

Step 3:
n=225; r²=0.03,
p=0.005**

Step 4:
n=134; r²=0.01,
p=0.09*

EU

Step 3:
n=209; r²=0.07,
p<0.001***

Step 4:
n=131; r²=0.02,
p=0.03*

World 90th percentile

Step 3:
n=86; r²= 0.004,
p=0.4

Step 4:
n=54; r²= 0.02,
p=0.9

EU 90th percentile

Step 3:
n=76; r²=0.06,
p=0.02*

Step 4:
n=51; r²=0.08,
p=0.02*

Figure S4. Relationship between event-related measured (MFC) and respective predicted (PEC) step 3 and step 4 concentrations of all world (including EU) and only EU concentrations and for the 90th percentile concentration of all event-sampled concentrations per substance per study. The 45° line denotes identity between PEC and MFC. The simulated concentrations are displayed on the y-axis such that the MFC underestimations are plotted below the 45° line. Asterisks indicates significance (Linear regression; *** p< 0.001; ** p < 0.01; * p < 0.05).

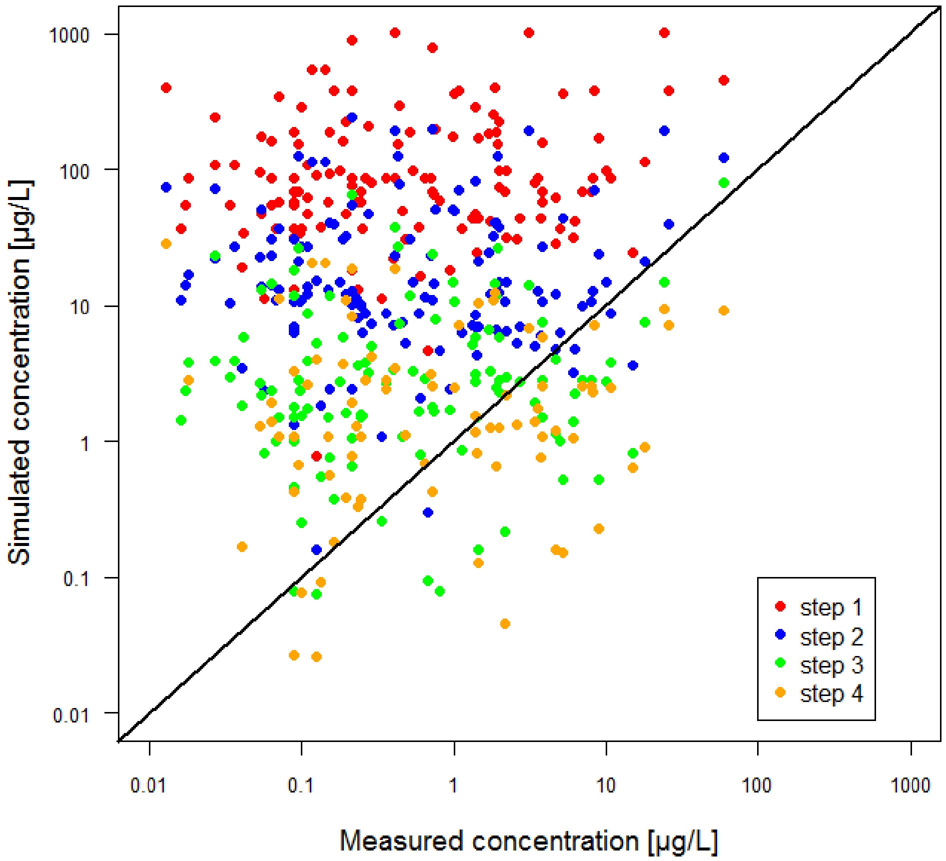


Figure S5. Relationship between simulated and the 90th percentile of all measured water concentrations in each single publication for FOCUS step 1 – 4 (only E.U. data). The 45° line denotes identity between PEC and MFC. The simulated concentrations are displayed on the y-axis such that the MFC underestimations are plotted below the 45° line.

Table S5. P-values of differences in simulated to measured concentration ratios in the water phase for different fungicides for FOCUS step 1, (ANOVA, Tukey`s HSD post hoc test). Bold characters indicate significant difference ($p < 0.05$).

	Anilinopyrimidine	Benzamide	Benzimidazole	Benzophenone	Carbamate	Carboxamide	Chloronitrile	Chlorophenyl	Cyanoacetamide_oxime	Cyanoimidazole	Dicarboximide	Hydroxyanilide	Imidazole	Morpholine	Oxazole	Phenylamide	Phenylpyridinamine	Phenylpyrrole	Phthalimide	Pyrimidine	Pyrimidinol	Quinoline	Strobilurin	Triazole	Unclassified
Anilinopyrimidine	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Benzamide	1.0000	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Benzimidazole	0.9996	1.0000	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Benzophenone	0.9435	1.0000	0.5779	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Carbamate	0.7765	1.0000	0.3216	1.0000	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Carboxamide	0.9982	1.0000	0.7930	1.0000	1.0000	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Chloronitrile	**0.0000**	0.4658	**0.0000**	**0.0000**	**0.0000**	**0.0000**	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Chlorophenyl	0.0567	1.0000	0.9578	**0.0426**	**0.0128**	**0.0355**	**0.0000**	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cyanoacetamide_oxime	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	0.0828	0.9823	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cyanoimidazole	1.0000	1.0000	1.0000	0.9999	0.9993	1.0000	0.6748	1.0000	1.0000	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Dicarboximide	1.0000	1.0000	1.0000	0.7282	0.4578	0.9181	**0.0000**	0.5913	1.0000	1.0000	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Hydroxyanilide	0.9998	1.0000	0.9527	1.0000	1.0000	1.0000	**0.0000**	0.2639	1.0000	1.0000	0.9869	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Imidazole	1.0000	1.0000	1.0000	0.9495	0.8448	0.9980	**0.0203**	1.0000	1.0000	1.0000	1.0000	0.9987	-	-	-	-	-	-	-	-	-	-	-	-	-
Morpholine	1.0000	1.0000	0.8795	0.9950	0.9488	1.0000	**0.0000**	**0.0025**	1.0000	1.0000	0.9776	1.0000	1.0000	-	-	-	-	-	-	-	-	-	-	-	-
Oxazole	1.0000	1.0000	0.9999	1.0000	1.0000	1.0000	0.0538	0.9594	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	-	-	-	-	-	-	-	-	-	-	-
Phenylamide	1.0000	1.0000	1.0000	0.7300	0.4626	0.9212	**0.0000**	0.7062	1.0000	1.0000	1.0000	0.9864	1.0000	0.9834	1.0000	-	-	-	-	-	-	-	-	-	-
Phenylpyridinamine	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	0.3894	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	-	-	-	-	-	-	-	-	-
Phenylpyrrole	0.9812	0.9999	0.8640	1.0000	1.0000	1.0000	**0.0015**	0.3880	1.0000	0.9990	0.9221	1.0000	0.9579	0.9966	1.0000	0.9198	1.0000	-	-	-	-	-	-	-	-
Phthalimide	0.9704	1.0000	1.0000	0.3773	0.1793	0.5475	**0.0000**	0.9998	0.9998	1.0000	1.0000	0.8469	1.0000	0.5677	0.9990	1.0000	1.0000	0.7613	-	-	-	-	-	-	-
Pyrimidine	0.6930	1.0000	0.1912	1.0000	1.0000	1.0000	**0.0000**	**0.0018**	1.0000	0.9999	0.3071	1.0000	0.8727	0.9415	1.0000	0.3205	1.0000	1.0000	0.0860	-	-	-	-	-	-
Pyrimidinol	1.0000	1.0000	1.0000	1.0000	0.9997	1.0000	0.6095	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	0.9995	1.0000	1.0000	-	-	-	-	-
Quinoline	1.0000	1.0000	0.9997	1.0000	1.0000	1.0000	**0.0000**	0.7234	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	0.9952	1.0000	1.0000	-	-	-	-
Strobilurin	1.0000	1.0000	0.9847	0.9602	0.8133	0.9993	**0.0000**	**0.0056**	1.0000	1.0000	0.9996	0.9999	1.0000	1.0000	1.0000	0.9997	1.0000	0.9868	0.8165	0.7299	1.0000	1.0000	-	-	-
Triazole	1.0000	1.0000	0.5918	0.9940	0.9392	1.0000	**0.0000**	**0.0001**	1.0000	1.0000	0.7975	1.0000	1.0000	1.0000	1.0000	0.8630	1.0000	0.9966	0.2562	0.9191	1.0000	1.0000	1.0000	-	-
Unclassified	1.0000	1.0000	1.0000	0.9923	0.9727	0.9998	0.9480	1.0000	1.0000	1.0000	1.0000	0.9998	1.0000	1.0000	1.0000	1.0000	1.0000	0.9795	1.0000	0.9868	1.0000	1.0000	1.0000	1.0000	-

Table S6. P-values of differences in simulated to measured concentration ratios in the water phase for different fungicides for FOCUS step 2, (ANOVA, Tukey`s HSD post hoc test). Bold characters indicate significant difference ($p < 0.05$).

	Anilinopyrimidine	Benzamide	Benzimidazole	Benzophenone	Carbamate	Carboxamide	Chloronitrile	Chlorophenyl	Cyanoacetamide_oxime	Cyanoimidazole	Dicarboximide	Hydroxyanilide	Imidazole	Morpholine	Oxazole	Phenylamide	Phenylpyridinamine	Phenylpyrrole	Phthalimide	Pyrimidine	Pyrimidinol	Quinoline	Strobilurin	Triazole	Unclassified
Anilinopyrimidine	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Benzamide	1.0000	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Benzimidazole	1.0000	1.0000	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Benzophenone	0.3809	0.9978	0.1440	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Carbamate	0.6838	0.9998	0.3480	1.0000	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Carboxamide	0.9990	1.0000	0.9278	0.9982	1.0000	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Chloronitrile	**0.0000**	0.2104	**0.0000**	**0.0000**	**0.0000**	**0.0000**	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Chlorophenyl	**0.0000**	0.9975	**0.0201**	**0.0000**	**0.0001**	**0.0003**	**0.0001**	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cyanoacetamide_oxime	1.0000	1.0000	0.9988	1.0000	1.0000	1.0000	**0.0031**	0.4439	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cyanoimidazole	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	**0.0187**	0.7901	1.0000	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Dicarboximide	1.0000	1.0000	1.0000	0.1191	0.3072	0.8989	**0.0000**	**0.0056**	0.9987	1.0000	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Hydroxyanilide	0.9873	1.0000	0.8596	1.0000	1.0000	1.0000	**0.0000**	**0.0034**	1.0000	1.0000	0.8352	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Imidazole	1.0000	1.0000	1.0000	0.6990	0.8787	0.9998	**0.0003**	0.8623	0.9999	1.0000	1.0000	0.9949	-	-	-	-	-	-	-	-	-	-	-	-	-
Morpholine	0.9995	1.0000	0.8300	0.8185	0.9683	1.0000	**0.0000**	**0.0000**	1.0000	1.0000	0.6614	1.0000	1.0000	-	-	-	-	-	-	-	-	-	-	-	-
Oxazole	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	**0.0230**	0.8250	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	-	-	-	-	-	-	-	-	-	-	-
Phenylamide	1.0000	1.0000	1.0000	0.2312	0.4918	0.9831	**0.0000**	**0.0020**	0.9997	1.0000	1.0000	0.9405	1.0000	0.9682	1.0000	-	-	-	-	-	-	-	-	-	-
Phenylpyridinamine	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	**0.0146**	0.7459	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	-	-	-	-	-	-	-	-	-
Phenylpyrrole	0.9995	1.0000	0.9917	1.0000	1.0000	1.0000	**0.0012**	0.2876	1.0000	1.0000	0.9910	1.0000	0.9989	1.0000	1.0000	0.9972	1.0000	-	-	-	-	-	-	-	-
Phthalimide	0.9922	1.0000	1.0000	0.0580	0.1688	0.6940	**0.0000**	0.2450	0.9922	0.9999	1.0000	0.6399	1.0000	0.4026	1.0000	1.0000	0.9998	0.9659	-	-	-	-	-	-	-
Pyrimidine	0.7834	1.0000	0.3889	1.0000	1.0000	1.0000	**0.0000**	**0.0000**	1.0000	1.0000	0.3235	1.0000	0.9635	0.9959	1.0000	0.5670	1.0000	1.0000	0.1684	-	-	-	-	-	-
Pyrimidinol	1.0000	1.0000	1.0000	0.9988	0.9999	1.0000	0.1777	0.9955	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	-	-	-	-	-
Quinoline	0.9999	1.0000	0.9915	1.0000	1.0000	1.0000	**0.0000**	**0.0247**	1.0000	1.0000	0.9891	1.0000	0.9999	1.0000	1.0000	0.9986	1.0000	1.0000	0.9341	1.0000	1.0000	-	-	-	-
Strobilurin	1.0000	1.0000	0.9950	0.4956	0.7960	0.9999	**0.0000**	**0.0000**	1.0000	1.0000	0.9767	0.9969	1.0000	1.0000	1.0000	1.0000	1.0000	0.9999	0.8197	0.8882	1.0000	1.0000	-	-	-
Triazole	0.9981	1.0000	0.7068	0.7125	0.9318	1.0000	**0.0000**	**0.0000**	1.0000	1.0000	0.4060	0.9999	1.0000	1.0000	1.0000	0.9282	1.0000	1.0000	0.2539	0.9826	1.0000	1.0000	1.0000	-	-
Unclassified	1.0000	1.0000	1.0000	0.8756	0.9504	0.9998	0.7331	1.0000	0.9995	1.0000	1.0000	0.9964	1.0000	1.0000	1.0000	1.0000	1.0000	0.9974	1.0000	0.9882	1.0000	0.9998	1.0000	1.0000	-

Table S7. P-values of differences in simulated to measured concentration ratios in the water phase for different fungicides for FOCUS step 3, (ANOVA, Tukey`s HSD post hoc test). Bold characters indicate significant difference ($p < 0.05$).

	Anilinopyrimidine	Benzamide	Benzimidazole	Benzophenone	Carbamate	Carboxamide	Chloronitrile	Chlorophenyl	Cyanoacetamide_oxime	Cyanoimidazole	Dicarboximide	Hydroxyanilide	Imidazole	Morpholine	Oxazole	Phenylamide	Phenylpyridinamine	Phenylpyrrole	Phthalimide	Pyrimidine	Pyrimidinol	Quinoline	Strobilurin	Triazole	Unclassified
Anilinopyrimidine	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Benzamide	1.0000	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Benzimidazole	0.9975	1.0000	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Benzophenone	0.9543	1.0000	0.5432	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Carbamate	0.9840	1.0000	0.6763	1.0000	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Carboxamide	1.0000	1.0000	0.9968	0.9999	1.0000	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Chloronitrile	**0.0000**	0.1090	**0.0000**	**0.0000**	0.0000	**0.0000**	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Chlorophenyl	**0.0000**	0.9910	**0.0054**	**0.0002**	**0.0004**	**0.0009**	**0.0000**	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cyanoacetamide_oxime	0.9580	0.9984	0.7529	1.0000	1.0000	0.9971	**0.0000**	**0.0286**	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cyanoimidazole	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	**0.0332**	0.9186	0.9999	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Dicarboximide	0.2551	1.0000	1.0000	0.1337	0.2088	0.7095	**0.0000**	0.0922	0.4595	1.0000	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Hydroxyanilide	1.0000	1.0000	0.9998	1.0000	1.0000	1.0000	**0.0000**	**0.0479**	0.9995	1.0000	0.9581	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Imidazole	0.9992	1.0000	1.0000	0.6467	0.7432	0.9953	0.0017	0.9930	0.6892	1.0000	1.0000	0.9985	-	-	-	-	-	-	-	-	-	-	-	-	-
Morpholine	1.0000	1.0000	0.9896	0.9680	0.9899	1.0000	**0.0000**	**0.0000**	0.9664	1.0000	0.1451	1.0000	0.9983	-	-	-	-	-	-	-	-	-	-	-	-
Oxazole	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	0.0689	0.9747	0.9995	1.0000	1.0000	1.0000	1.0000	1.0000	-	-	-	-	-	-	-	-	-	-	-
Phenylamide	0.9940	1.0000	1.0000	0.5109	0.6465	0.9953	**0.0000**	**0.0029**	0.7417	1.0000	1.0000	0.9997	1.0000	0.9773	1.0000	-	-	-	-	-	-	-	-	-	-
Phenylpyridinamine	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	**0.0238**	0.8792	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	-	-	-	-	-	-	-	-	-
Phenylpyrrole	1.0000	1.0000	0.9999	1.0000	1.0000	1.0000	**0.0034**	0.5350	1.0000	1.0000	0.9957	1.0000	0.9990	1.0000	1.0000	0.9999	1.0000	-	-	-	-	-	-	-	-
Phthalimide	**0.0135**	1.0000	0.8237	**0.0193**	**0.0346**	0.1658	**0.0000**	0.9883	0.1949	0.9991	0.9997	0.5908	1.0000	**0.0063**	0.9999	0.7834	0.9977	0.9324	-	-	-	-	-	-	-
Pyrimidine	0.9996	1.0000	0.8444	1.0000	1.0000	1.0000	**0.0000**	**0.0001**	1.0000	1.0000	0.2533	1.0000	0.9077	0.9999	1.0000	0.8146	1.0000	1.0000	**0.0319**	-	-	-	-	-	-
Pyrimidinol	1.0000	1.0000	1.0000	0.9996	0.9999	1.0000	0.2093	0.9990	0.9923	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	-	-	-	-	-
Quinoline	1.0000	1.0000	1.0000	0.9999	1.0000	1.0000	**0.0000**	0.1141	0.9975	1.0000	0.9940	1.0000	0.9999	1.0000	1.0000	1.0000	1.0000	1.0000	0.7966	1.0000	1.0000	-	-	-	-
Strobilurin	1.0000	1.0000	1.0000	0.7641	0.8697	1.0000	**0.0000**	**0.0000**	0.8785	1.0000	0.5950	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	**0.0462**	0.9705	1.0000	1.0000	-	-	-
Triazole	1.0000	1.0000	0.9901	0.9152	0.9661	1.0000	**0.0000**	**0.0000**	0.9437	1.0000	**0.0484**	1.0000	0.9992	1.0000	1.0000	0.9722	1.0000	1.0000	**0.0017**	0.9981	1.0000	1.0000	1.0000	-	-
Unclassified	1.0000	1.0000	1.0000	0.9888	0.9945	1.0000	0.4799	1.0000	0.9499	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	0.9997	1.0000	1.0000	1.0000	1.0000	-

Table S8. P-values of differences in simulated to measured concentration ratios in the water phase for different fungicides for FOCUS step 4, (ANOVA, Tukey`s HSD post hoc test). Bold characters indicate significant difference ($p < 0.05$).

	Anilinopyrimidine	Benzimidazole	Carbamate	Carboxamide	Chloronitrile	Cyanoimidazole	Dicarboximide	Imidazole	Morpholine	Phenylamide	Phenylpyridinamine	Phenylpyrrole	Phthalimide	Strobilurin	Triazole	Unclassified
Anilinopyrimidine	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Benzimidazole	1.0000	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Carbamate	0.2841	0.1897	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Carboxamide	0.9905	0.9536	0.9911	-	-	-	-	-	-	-	-	-	-	-	-	-
Chloronitrile	**0.0000**	**0.0000**	0.0000	**0.0000**	-	-	-	-	-	-	-	-	-	-	-	-
Cyanoimidazole	1.0000	1.0000	0.9860	1.0000	**0.0205**	-	-	-	-	-	-	-	-	-	-	-
Dicarboximide	0.4872	0.7298	**0.0109**	0.1767	**0.0191**	0.9947	-	-	-	-	-	-	-	-	-	-
Imidazole	0.9997	1.0000	0.3551	0.9439	**0.0044**	1.0000	1.0000	-	-	-	-	-	-	-	-	-
Morpholine	1.0000	1.0000	0.2637	0.9878	**0.0000**	1.0000	0.4832	0.9998	-	-	-	-	-	-	-	-
Phenylamide	0.7745	0.6048	0.9995	1.0000	**0.0000**	1.0000	0.0503	0.7871	0.7429	-	-	-	-	-	-	-
Phenylpyridinamine	1.0000	0.9999	1.0000	1.0000	**0.0011**	1.0000	0.8200	0.9967	1.0000	1.0000	-	-	-	-	-	-
Phenylpyrrole	0.9992	0.9968	1.0000	1.0000	**0.0003**	1.0000	0.6316	0.9776	0.9991	1.0000	1.0000	-	-	-	-	-
Phthalimide	0.8784	0.9956	**0.0288**	0.4675	**0.0000**	1.0000	0.9945	1.0000	0.8684	0.1107	0.9904	0.9401	-	-	-	-
Strobilurin	1.0000	1.0000	0.1292	0.8952	**0.0000**	1.0000	0.8026	1.0000	1.0000	0.4503	0.9997	0.9937	0.9993	-	-	-
Triazole	1.0000	0.9999	0.3137	0.9956	**0.0000**	1.0000	0.3433	0.9989	1.0000	0.8141	1.0000	0.9996	0.6024	0.9972	-	-
Unclassified	1.0000	1.0000	0.6722	0.9884	0.2425	1.0000	1.0000	1.0000	1.0000	0.9481	0.9983	0.9887	1.0000	1.0000	0.9999	-

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Response to Comment on “Fungicide Field Concentrations Exceed FOCUS Surface Water Predictions: Urgent Need of Model Improvement”

It is no surprise that our paper,[1] that seriously questions the current regulatory exposure assessment and thus a fundamental part of the European pesticide registration procedure, raises criticism. In this context we acknowledge the fact that Reichenberger also mentioned the option of the FOCUS statement of concern to be questionable. We are pleased to respond to these comments, since we indeed are fully convinced that our data indicate great concern and points to some entirely unacceptable weaknesses of the FOCUS approach which urgently need to be addressed in order to establish an appropriate exposure assessment in Europe.

As a matter of fact, FOCUS is used in most European countries (e.g., Sweden, Denmark, France, Spain) in the national registration procedure in addition to being a prerequisite for E.U.[2] Annex I listing in the national registration procedure. FOCUS is thus not at all irrelevant and its importance is even bigger when one considers the fact, that Annex I listing is an important driver leading ultimately also to national registrations of pesticides in the member states. To our knowledge there is not a single case, where a pesticide received Annex I listing but was never registered in any E.U. member state.

The main point made by Reichenberger is the fact that we did not include any fungicide concentrations measured in the field at levels below the maximum and particularly that we excluded nondetects. We have made the rationale for this approach very clear and used by the way the exactly same approach in our previous study on insecticides,[3] on which Reichenberger also commented, but obviously did not criticize the omission of nondetects. The FOCUS statement “the highest $\mathrm{PEC_{sw}}$ estimates from the 10 scenarios are likely to represent at least a 90th percentile worst-case for surface water exposure resulting from agricultural pesticide use within the European Union”[4] contains a very important aspect, that we would like to highlight here: The phrase “...at least a 90th percentile worst-case...” clearly points out that the maximum PEC derived from FOCUS is not representing the 90th percentile of all possible situations in European agriculture, it rather refers to the “worst-case” situation. This is from a precautionary point of view and from the rationale behind the environmental risk assessment (ERA) of chemicals (to compare the ± highest possible PEC with the ± lowest effect) absolutely logic. In other words, it does not make sense to look at concentrations, which are not likely to be among the highest and particularly not at those that were not detected (see below). Maximum peak concentrations of pesticides occur in the field only during rather short periods of time and their presence is spatially scattered as well. It is thus extremely difficult to sample these transient peak concentrations (which at the same time also should have been present during worst-case conditions) properly and even more difficult to preserve samples correctly in order to be indeed able to find and quantify the target molecules at the end. This all leads to a situation, in which a nondetect from a field study tells us not much more than that there was nothing detected and a concentration from a nonevent sampling nothing about the maximum peak: The former does not mean that there was no contamination and it does definitely not mean that there will never be a contamination event. The point made by Reichenberger that the nondetection of one compound in a sample containing a second compound thus indicates no or low risk for this first compound is not valid. Moreover, including nondetects in the analysis of pesticide monitoring data for short-term pesticide contamination peaks, and thus those concentrations relevant from a risk assessment point of view, will lead to a bias. Their number may in addition even increase further when time periods of low input probability or compounds not even used in the area during time of sampling were included in the analysis. In many field studies the selection of substances to be analyzed is not based on the actual application but aligns for example on substances which are usually applied to the respective crops. Given this fact, it is neither feasible nor valid to test the hypothesis if the regulatory exposure assessment is sufficiently conservative (i.e., MFC < PEC), as no reliable information needed to verify or falsify this hypothesis can be generated based on nondetects. Most importantly this “dilution” bias is from a risk assessment point of view really dangerous as it leads to false negative reports and thus to an underestimation of a risk, which is in fact there. For further discussion on this, please refer to Stehle et al. 2013.[5]

However, as described in our study all concentrations measured (i.e., those detected and quantified) during independent events in surface waters and sediments which were reported in the respective field study were extracted. For studies in which only maximum measured concentrations were reported, only those concentrations could exclusively be used, which is the case in three of the four examples[6−8] used by Reichenberger. In the other study mentioned[9] the fungicide measured in Finland was only reported as time-weighted-average concentration and was therefore not considered in our analysis.

Furthermore, Reichenberger criticizes the definition of the 90th percentile concentration and suggests to use a method which is almost identical to the one used by us:

(1) For each combination of sampling site and substance, we added all measured independent peak concentrations reported in the respective field study. See above why it is neither feasible nor valid to include nondetects.

(2) For a given substance, we took the 90th percentile of these concentration data points across all sampling sites and sampling events per study. It is not meaningful to

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use the 90th percentile of all concentrations (measured in different studies) per substance because different crops or climate conditions are relevant.

(3) For a given concentration, FOCUS step 3 calculations were conducted for crops and scenarios relevant for the respective study area.

(4) We compared the 90th percentile field concentration with the highest PEC_{sw}.

We agree with Reichenberger that for some studies only a few numbers of concentrations are reported and that in these cases the 90th percentile concentration is uncertain but this is for the reasons provided above similar for studies with a higher number of concentrations. Nevertheless, the only plausible alternative is to use only the maximum concentration which would result in a higher amount (more than 10%) of underpredictions than for the 90th percentile field concentration. Furthermore, as described in our study,[1] there are reasons why the actual fungicide field concentrations might be higher than the measured ones presented in the studies. Consequently, the real amount of FOCUS underpredictions might be even worse.

Overall, we are convinced that the used methodology is appropriate for the evaluation of the protectiveness of the FOCUS modeling approach.

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Notes

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Appendix II

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Runoff of veterinary pharmaceuticals from arable and grassland—A comparison between predictions from model simulations and experimental studies

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ABSTRACT

Veterinary pharmaceuticals (VPs) are routinely used in livestock breeding. As a consequence, high concentrations of such VPs can be found in liquid manure, which is often applied to arable crops and grassland. From the soil, the VPs may enter surface water bodies via edge-of-field runoff, representing a potential risk to aquatic ecosystems. In the present study, the worst-case runoff predictions obtained by the FOCUS step 3 modeling approach, which is recommended for environmental-risk assessment of VPs in Europe, were compared with fate data obtained from experimental plot studies involving both arable and grassland plots. Five VPs were selected comprising three sulfonamides (sulfadiazine, sulfadimidine, sulfamethoxazole) and two benzimidazoles (flubendazole, fenbendazole). The respective concentrations in runoff were initially estimated using literature data for model parameterization. Subsequently, the scenarios were parameterized specifically for each experimental plot study performed, enabling a direct comparison of the model performance with the close-to-field relevant situation.

Generally, substantial variations between the predicted and measured concentrations of VPs in the runoff were uncovered. Although the FOCUS prediction suggested higher concentrations than were actually measured in 65% of the cases, the runoff concentrations of VPs were underestimated in the remaining 35%. This frequent underestimation of runoff concentrations was primarily observed for the grassland plots (85% of the underestimated situations), whereas the FOCUS predictions largely overestimated the measured concentrations for the arable plots. More strikingly, when involving a difference between the measured and predicted concentrations of 10% as a validity criterion for the model, only one (out of a total of 17) runoff concentration among the five VPs (i.e., sulfadimidine) assessed in the seven scenarios fell within this tolerance margin. Thus, these results demonstrate the substantial uncertainties related to the use of the FOCUS surface water modeling approach for the prediction of VPs introduced with manure and their environmental risk.

1. Introduction

Pharmaceuticals are of paramount importance for the wellbeing of humans and domestic animals, as well as for the efficiency of productive livestock (Boxall et al., 2003). However, they are not completely metabolized by the treated organism and thus are excreted (Zuccato et al., 2006). As a result, pharmaceuticals are discharged to wastewater treatment plants and may accumulate in the aquatic environment because most treatment systems are not designed to remove organic micro-pollutants, such as pharmaceuticals (Ternes 2007). In addition, these substances can also be absorbed into sewage sludge, which is – similar to the manure from livestock or poultry production – applied in a number of countries as a fertilizer to agricultural fields in the form of slurry or biosolids (Topp et al., 2010). Comparable to pesticides (Schulz, 2004), human and veterinary pharmaceuticals (VPs) can be mobilized from these fields during heavy precipitation and may enter surface water bodies via edge-of-field runoff (Kemper 2008). Although the research focused mainly on the remobilization of antibiotics, this phenomenon was reported for various classes of pharmaceuticals, with peak concentrations directly following the rainfall event (e.g., Davis et al., 2006; Kreuzig et al., 2005; Kuchta and Cessna, 2009; Topp et al., 2008). According to the

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environmental risk-assessment approach for VPs (e.g., EMEA, 2008), these peak concentrations indicate the potential for certain antimicrobials, antibiotics, and even fragrances to affect the integrity of aquatic ecosystems (Giudice and Young, 2011; Langdon et al., 2010). In addition to these peak exposures, the continuous introduction of VPs from the field application of, for instance, manure (Kuchta et al., 2009) may be of concern for the development of antibiotic-resistant bacterial strains (Kemper, 2008).

With the intention of managing the environmental impact associated with the administration of VPs, the European Medicine Agency provided a guideline (EMEA, 2008) to support the European directive 92/18/EC (1992) and complement the VICH guidelines (2000, 2004). In these guidelines, simulation models are suggested to obtain a refined predicted environmental concentration (PEC) for surface water, while a first estimation of the PEC is obtained by dividing the PEC in the porewater by three (EMEA, 2008). With certain exceptions, the available simulation models do well in representing the environmental conditions relevant for contamination by VPs in Europe (Schneider et al., 2007). However, little is known regarding how well the model output, i.e., the PEC or the concentrations in runoff water that may be a surrogate for the PEC, represents the situation in the field. To the best of the authors' knowledge, only one study, namely, Larsbo et al. (2008), addressed this question. These authors demonstrated that the MACRO-model, which is part of the FOCUS model family, although not particularly recommended for the calculation of runoff-induced PECs by the EMEA (2008), may very well represent the runoff-induced peak concentration for the sulfonamide antibiotic sulfadimidine on a small scale. However, for larger catchments, this model may not be optimal, as it ignores the infiltration of water into the soil during runoff. This publication is limited to one particular substance which, at the same time, exhibits comparable hydrophilic properties (Table 1) and may hence be susceptible to runoff-induced transportation (Sabourin et al., 2009).

In this context, the present study aims at comparing the worst-case predictions for runoff concentrations obtained by the FOCUS step 3 modeling approach, which is recommended for environmental risk assessment of VPs in Europe (EMEA, 2008) with fate data obtained from experimental plot studies (Kreuzig et al., 2004, 2005). Using five VPs exhibiting a broad range of physicochemical properties comprising three sulfonamide antibiotics (i.e., sulfadiazine, sulfadimidine, sulfamethoxazole) and two benzimidazole anthelmintics (i.e., flubendazole, fenbendazole; Table 1), we hypothesized that due to worst-case assumptions, the FOCUS step 3 predictions will overestimate the overall runoff concentrations if performed as recommended in the risk assessment for VPs. At the same time, it was also hypothesized that substantial differences between the predicted and measured concentrations will be detected even if the modeling scenarios are parameterized specifically for each experimental study because scenarios and modeling conditions were not built to represent the runoff of VPs via application of manure.

2. Materials and methods

2.1. Chemicals

The investigated sulfonamide (i.e., sulfadiazine, sulfadimidine, sulfamethoxazole) and benzimidazole (i.e., flubendazole, fenbendazole) VPs are used in the therapies of intensively reared animals against bacterial infection (Lamshoft et al., 2007) and endoparasites, such as nematodes and cestodes worms (Balizs 1999), respectively. The amount of each of the VPs added to 20 kg of liquid manure prior to its aging, which was applied to each experimental plot and represented 50% of the maximum nitrogen content that is accepted by the German Ordinance Concerning Fertilizers (170 kg N ha^{-1} a^{-1}) (Kluge and Embert 1996), was 1 g of active substance (Kreuzig et al., 2005). The concentration of each of the VPs within

Table 1

Chemical properties of the VPs assessed during the present study, which have also been used as input parameters for the FOCUS modeling.

Substance parameters	Unit	Sulfadiazine	Sulfadimidine	Sulfamethoxazole	Flubendazole	Fenbendazole
Molar mass[a,b]	g mol^{-1}	250.28	278.33	253.25	313.28	299.35
Saturated vapour pressure (at 25 °C)[a,c,d]	Pa	5.73×10^{-6}	4.85×10^{-6}	9.24×10^{-6}	1.33×10^{-3}	1.33×10^{-4}
Molar enthalpy of vaporization[e]	J mol^{-1}	95000	95000	95000	95000	95000
Solubility in water (at 20 °C)[a,d,f]	mg L^{-1}	130	1500	610	33.76	0.01
Molar enthalpy of dissolution[e]	J mol^{-1}	27000	27000	27000	27000	27000
Diffusion coefficient in water[e]	m^2 d^{-1}	4.30×10^{-5}	4.30×10^{-5}	4.30×10^{-5}	4.30×10^{-5}	4.30×10^{-5}
Diffusion coefficient in air[e]	m^2 d^{-1}	0.43	0.43	0.43	0.43	0.43
K_{OC}[a,g]	L kg^{-1}	81	127	1531	7427	46
Freundlich exponent[h]	–	0.9	0.9	0.9	0.9	0.9
Reference concentration in liquid phase[e]	g m^{-3}	1	1	1	1	1
Factor for the uptake by plant roots in soil[i]	–	0	0	0	0	0
Wash-off factor from crop[i]	mm^{-1}	0	0	0	0	0
Half-life water (at 20 °C)[a,d,j]	d	5.5	1000	37.5	60	37.5
Half-life soil (at 20 °C)[a,d]	d	75	18.6	75	120	75
Half-life sediment (at 20 °C)[a,d,j]	d	5.5	1000	338	542	338
Half-life crop (at 20 °C)[i]	d	1000	1000	1000	1000	1000
Activation energy[e]	J mol^{-1}	65400	65400	65400	65400	65400
Exponent[e]	K^{-1}	0.09	0.09	0.09	0.09	0.09
Q10 factor[e]	–	2.58	2.58	2.58	2.58	2.58

[a] University of Hertfordshire (2013).
[b] Thienpont et al. (1978).
[c] Neely and Blau (1985).
[d] EPISUITE (2012).
[e] Default, FOCUS (2001).
[f] Arbeitsgemeinschaft für die Reinhaltung der Elbe (2003).
[g] Kreuzig et al. (2004).
[h] Selected according to FOCUS (2001).
[i] Required by EMEA (2008).
[j] No value available; hence worst case value were used.

Table 2
Properties of the liquid manure, that is the aging duration of the VPs in the manure and their concentration at the time of manure application to the experimental plots, together with the characteristics of the run-off event given the run-off volume, the associated particle transport as well as the percentage loss of the VPs. Data have been abstracted from Kreuzig et al. (2004, 2005).

Experimental plot	A1	A2	A3	A4	A5	A6	G1	G2
Liquid manure properties								
Aging duration (d)	6.0	–	7.0	0.0	0.0	0.0	9.0	9.0
Sulfadiazine (g 20 kg^{-1})	0.5	–	0.4	0.9	0.8	0.4	0.2	0.4
Sulfadimidine (g 20 kg^{-1})	0.7	–	0.4	1.0	–	–	0.4	–
Sulfamethoxazole (g 20 kg^{-1})	0.6	–	0.3	1.0	–	–	0.3	–
Flubendazole (g 20 kg^{-1})	–	0.8	–	–	–	–	–	–
Fenbendazole (g 20 kg^{-1})	–	0.7	–	–	–	–	–	–
Run-off characteristics								
Run-off volume (L)	73	130	66	99	128	57	252	106
Particle transport (g)	406	417	301	386	206	268	64	491
Sulfadiazine loss (%)	2.5	–	0.1	0.1	0.2	0.8	27.6	14.4
Sulfadimidine loss (%)	1.2	–	0.2	0.1	–	–	15.8	–
Sulfamethoxazole loss (%)	1.6	–	0.2	0.1	–	–	13.3	–
Flubendazole loss (%)	–	0.06[a]	–	–	–	–	–	–
Fenbendazole loss (%)	–	0.06[a]	–	–	–	–	–	–

[a] Mainly particle bound transport.

the manure was quantified directly prior to its application (Table 2; Kreuzig et al., 2005).

2.2. Experimental plot studies

A detailed description of the plot study and the analytical procedures can be found in Kreuzig et al. (2004, 2005) from which the experimental fate data for this study have been obtained. Therefore, the present study provides only a brief overview of the experimental procedure.

The experiments were performed near Adenstedt in the southeast of Lower Saxony, Germany. The soil is a clayey silt luvisol with an organic carbon content of 1.6%. The slope of the plots was between 7.7 and 8.2% on arable land and 9.0% on grassland. The runoff of the VPs was assessed in two series of plot studies: in April 2003, four plots (three plots in arable land (A1, A2 & A3) and one plot in grassland (G1)) and in September 2003, another four plots (three plots in arable land (A4, A5 & A6) and one plot in grassland (G2)) were tested. The area of each plot was 4 × 2 m, and the edges of the plots were enclosed with tin walls.

For the manure preparation, 1 g of each of sulfonamide or benzimidazole was distributed homogeneously in 20 kg of liquid bovine manure. The bovine manure had a dry matter content of 12% and an organic matter content of 36%. The average measured pH was 7.5 and the oxygen consumption ranged between 6.8 and 13.6 mg L^{-1} h^{-1}. Although rather at the upper limits, the resulting concentration approached the levels of liquid manure (Kreuzig et al., 2005). The fortified manures were stored between zero and nine days prior to application (Table 2). The actual residue levels determined in the manure directly before application to the test plots are given in Table 2. A total of 20 kg of manure was applied to each plot.

Immediately after the application of the liquid manure spiked with the VPs of interest (see Table 2 for concentrations), the manure was incorporated into the upper soil layer in the arable plots (i.e., the upper 15 cm) but not in the grassland plots, which followed the general practice of the local farmers. Subsequently, a two-hour rain event of constant intensity was simulated using a swing-nozzle sprinkler (Kainz and Eicher, 1990). By moving the nozzle, the water was evenly distributed over the entire plot area at an intensity of 50 mm h^{-1}. A tin funnel on the lower end of the experimental plots directed the runoff into vessels in order to quantify the amount of runoff. In addition, the VPs were quantified in the water phase by high performance liquid chromatography following solid phase extraction (Kreuzig et al., 2005). In total, 17 individual peak concentrations measured in the different plots (13 on arable land, 4 on grassland with an unequal number of applied substances on each test plot, Table 3) were considered for the comparison between the predicted and measured concentrations of VPs in the runoff.

2.3. FOCUS modeling

The concentrations of the VPs in the runoff water were predicted using the FOCUS surface water step 3 modeling approach. PRZM version 3.1.1 (Carsel et al., 1998) and TOXSWA version 3.3.1 (Adriaanse and Beltman, 2009) were used for model estimations. These models are integrated into the SWASH shell version 3.1 (FOCUS, 2001). Two different types of calculations were performed for each of the five VPs. Within the first model exercise, the calculations were conducted as recommended for the exposure assessment of veterinary medicinal products in Europe (EMEA, 2008). In this context, it is further recommended to perform FOCUS step 3 calculations assuming that the release of the VPs into the environment is initiated with the application of the manure originating from intensively reared animals – animals that are housed and treated with VPs indoors – along with the drilling of cereals in autumn. Thus, this scenario ignores the potential release of the VPs during grazing on the grassland. Moreover, the calculations for all substances were performed involving the climate and soil scenario R1 located in Weiherbach, Germany (FOCUS, 2001), assuming one manure application to winter cereals. To meet the requirements of manure application with the drilling of cereals, an application window of 30 days prior to the emergence day of the winter cereals at location R1 was selected for the PEC calculations (13 October–12 November). In addition, granular application and an incorporation depth of 15 cm, as recommended by EMEA (2008), were chosen. For all substances, an application rate of 1250 g ha^{-1} was used. This application rate is equivalent to the concentrations of the VP in the spiked manure prior to its aging (i.e., 1 g per 20 kg of manure).

In addition to the calculations performed as recommended by EMEA (2008), in the second model exercise, FOCUS step 3 calculations were also conducted by adapting a portion of the input data to the site-specific plot conditions. The application window for plots A1, A2, A3 and G1, which were treated in April 2003, was set at April 1 to 30, while for the remaining plots (i.e., A4, A5, A6 and G2), the selected application window was between September 1 and 30 because the manure was applied in September

Table 3
Application rates used within the site specific FOCUS modeling.

Plot	Substance	Application rate (g a.i. ha^{-1})
A1	Sulfadiazine	625
	Sulfadimidine	875
	Sulfamethoxazole	750
A2	Flubendazole	1000
	Fenbendazole	875
A3	Sulfadiazine	500
	Sulfadimidine	500
	Sulfamethoxazole	375
A4	Sulfadiazine	1125
	Sulfadimidine	1250
	Sulfamethoxazole	1250
A5	Sulfadiazine	1000
A6	Sulfadiazine	500
G1	Sulfadiazine	250
	Sulfadimidine	500
	Sulfamethoxazole	375
G2	Sulfadiazine	500

of the same year. The FOCUS crop scenarios for "winter cereals" and "grass/alfalfa" were selected for the arable (A) and grassland (G) plots, respectively. To further improve the comparability between the FOCUS model scenarios and the field conditions, the amount of precipitation causing the relevant runoff event was set to 50 mm. The FOCUS step 3 modeling approach does not allow for the consideration of precipitation events above an amount of 2 mm within the first two days after application. Therefore, the implications of the 50 mm precipitation in the runoff concentration of each VP could only be modeled on day three, at the earliest. To avoid degradation in soil between the application and relevant runoff event, each VP's half-life in the soil was set to 1000 days. Thus, the field situation was reflected as realistically as possible in the model, subject to the model's restrictions. Furthermore, the application rates were adapted to the actual substance concentrations that remained following the aging of the manure prior to the field application (Table 2). The application rates used for the site-specific modeling are given in Table 3. For the plots located in the arable land (A1–A6), the calculations were conducted based on scenario R1 using granular application and an incorporation depth of 15 cm. For the plots located in grassland (G1 and G2), it was not possible to use the R1 climate and soil scenario because the FOCUS surface water scenarios assume no cultivation of "grass or alfalfa" in this climatic region (FOCUS, 2001). Therefore, the calculations for the grassland plots were conducted for all other available runoff scenarios, while the predicted runoff concentrations detailed in Table 4 represent the worst-case estimates from all of the model outputs. In accordance with the procedure employed during the plot experiments, the incorporation depth of the manure was set at zero for both G1 and G2 (see also Table 3). All further parameters involved in the FOCUS modeling – particularly the VP-specific characteristics – can be abstracted from Table 1.

3. Results and discussion

The application of the liquid manure to both the arable and grassland plots resulted during the rain event in VP-specific concentrations in the runoff water (Table 4), ultimately leading to VP losses from the plots of from 2.5 to 27.6% of the total applied amount (cf., Popova et al., 2013). Such a substantial difference between the two types of land use, in terms of the relative loss of the VPs, can mainly be explained by the fact that the manure was

Table 4

Measured and predicted run-off concentrations as well as the ratio between both of each of the VPs assessed during the present study. Concentrations are given in $\mu g\,L^{-1}$.

	Sulfadiazine	Sulfadimidine	Sulfamethoxazole	Flubendazole	Fenbendazole
FOCUS scenarios for agricultural land					
Predicted run-off concentration	167.8	165.0	38.1	10.3	105.4
Average measured run-off concentration from all relevant experimental plots[a]	145.2 (6–543; 7)	97 (10–251; 4)	77 (9–158; 4)	0.5[b]	0.16[b]
Site specific FOCUS scenarios for agricultural land					
A1					
Measured run-off concentration	171.0	115.0	131.0	–	–
Predicted run-off concentration	90.3	116.5	22.7	–	–
Factor between measured and predicted run-off concentration	1.9	0.99	5.77	–	–
A2					
Measured run-off concentration	–	–	–	0.5	0.16
Predicted run-off concentration	–	–	–	12.7	66.4
Factor between measured and predicted run-off concentration	–	–	–	0.04	0.002
A3					
Measured run-off concentration	6.0	12.0	9.0	–	–
Predicted run-off concentration	72	65.6	10.9	–	–
Factor between measured and predicted run-off concentration	0.08	0.18	0.8	–	–
A4					
Measured run-off concentration	9.0	10.0	10.0	–	–
Predicted run-off concentration	153.1	164.2	38.4	–	–
Factor between measured and predicted run-off concentration	0.06	0.06	0.3	–	–
A5					
Measured run-off concentration	12.5	–	–	–	–
Predicted run-off concentration	136	–	–	–	–
Factor between measured and predicted run-off concentration	0.09	–	–	–	–
A6					
Measured run-off concentration	56.0	–	–	–	–
Predicted run-off concentration	67.9	–	–	–	–
Factor between measured and predicted run-off concentration	0.8	–	–	–	–
Side specific FOCUS scenarios for grassland					
G1					
Measured run-off concentration	219.0	251.0	158.0	–	–
Predicted run-off concentration	20.3	43.3	11	–	–
Factor between measured and predicted run-off concentration	10.8	5.8	14.4	–	–
G2					
Measured run-off concentration	543.0	–	–	–	–
Predicted run-off concentration	22.8	–	–	–	–
Factor between measured and predicted run-off concentration	23.8	–	–	–	–

[a] In brackets: range of concentrations and number of measurements.

[b] Only one measurement.

incorporated into the soil following its application to the arable plots, but not for the grassland. This procedure may have induced a co-transport of the liquid manure containing the VPs together with the particles mobilized from the top layer of the soil during the rainfall (e.g., Schulz et al., 1998). At the same time, a substantially higher mass loss of sulfonamides relative to benzimidazoles was observed, which may be explained by the generally high mobility of the sulfonamide antibiotics, as well as their water solubility (Table 1) (Bialk-Bielinska et al., 2012). Similarly, Sabourin et al. (2009) explained the substantial mass loss of five out of the eleven pharmaceutical and personal care products they quantified during runoff events following the application of dewatered biosolids to the agricultural fields by the compounds' absorptivity. These data thus suggest that both the management practice following the manure application, as well as the physico-chemical properties of the VPs trigger their loss via edge-of-field runoff.

As hypothesized the present study also revealed that the overall predicted runoff concentrations obtained on the basis of the FOCUS step 3 modeling approach (Table 4) are much higher than the measurements for four of the five VPs applied during the plot experiments, if performed as recommended for the risk assessment for VPs on arable land (see for insecticides and fungicides Knäbel et al., 2012, 2014). Specifically, four of the five overall predicted runoff concentrations are higher than the average of all the measured concentrations of each substance during the relevant plot experiment. Only the overall predicted concentration for sulfamethoxazole was lower than its average measured runoff concentration. This high level of protection, which is generated by the overall predicted runoff concentrations, may be primarily explained by the fact that the application rate for each VP corresponded to its initial (spiked) concentration and not its concentration after aging.

However, this overprediction is reduced if the FOCUS scenario is parameterized to the site- and hence, the situation-specific conditions (Table 4). Nonetheless, the predictions of the site-specific FOCUS modeling approach were higher than the measured concentrations (up to a factor of 415) for most of the cases (65%). However, in 35% of the cases, the measured concentrations in the runoff are underestimated by up to 24-fold by the model output. This frequent underestimation of the runoff concentrations was mainly (85% of the underestimated situations) observed for the grassland plots, whereas the FOCUS predictions overestimated the concentrations in the runoff from the arable plots. Specifically, this finding means that only two of the 13 runoff concentrations in the arable land plots were underestimated by the model predictions; for sulfadiazine and sulfamethoxazole in arable land plot A1, the concentrations were underestimated by a factor of two and six, respectively. In the grassland plots, however, the site-specific FOCUS model output underestimated the sulfonamide concentrations in all cases (Table 4). This phenomenon may be partly explained by the overestimation of the infiltration rate during the runoff causing an underestimation of the runoff-induced translocation *inter alia* VPs (Jones and Mangels, 2002). Therefore, considering the general substantial overestimation of the runoff concentrations generated by the models that were parameterized for the site-specific situations during the arable land plot experiments (up to 415-fold; Table 4), the reliability of the predictions generated by the FOCUS step 3 models are questionable—irrespective of the partly high level of protectiveness with regard to the risk assessment associated with their predictions.

Moreover, these concerns are further underpinned by the fact that the predictions of the site-specific modeling, in which the most important scenario conditions (e.g., precipitation, application scheme) were adapted to the field situation, exhibited no improved accuracy.

Similarly, by accepting a difference between the measured and predicted concentrations of 10%, which is suggested as a validity criterion for the models (FOCUS, 2001; U.S. EPA, 1988), only one runoff concentration of the 17 cases (i.e., sulfadimidine, A1) fell within this tolerance margin. This discrepancy may be explained by the deviation in the soil conditions that significantly influence the chemicals' fate and behavior. Although the soil conditions were not adapted during the site-specific FOCUS modeling, the soil characteristics of the R1 scenario, which formed the basis for the prediction of the concentrations in the runoff from the arable land, is very similar to the soil at the study site. For instance, the organic carbon content that is crucial for the sorption of chemicals is 1.2% and 1.6% for the soil of the R1 scenario and the field soil, respectively (Kreuzig et al., 2005). In addition, silt is the main component in both soils, followed by clay, while the amount of sand is exactly the same (i.e., 5%). Therefore, it is not likely that the differences in the soil characteristics contributed substantially to the large deviation between the measured and predicted concentrations of the VPs in the surface runoff. More importantly, the FOCUS modeling approach was not designed to estimate the runoff of VPs after the application of manure, a fact that likely substantially contributed to the detected differences between the predicted and measured concentrations. In addition, the FOCUS modeling approach aims at the prediction of the fate of pesticides, which are applied as formulations directly to the soil surface but are not bound to other organic material, such as manure, which explains the large overestimation of the actual VP concentrations in certain cases. Altogether, these observations confirm our second hypothesis, namely that there are substantial differences between the predicted and measured VP concentrations in the runoff. Therefore, the present study calls for a more targeted analysis questioning, for instance, the representativeness of the FOCUS modeling approach for substances applied to agricultural fields in combination with organic-enriched matrices (i.e., manure) and the analysis of the sensitivity of important input parameters.

Nevertheless, the results from this study – due to the rather small sample size and the use of spatially closely related experimental plots – can only give a first indication of the uncertainties associated with the use of the FOCUS modeling approach for the prediction of VPs in surface water, especially because only one soil type was included in the experimental field study. Similar observations have recently been reported for the PECs of insecticides derived from FOCUS models, which have also been parameterized for the local and, hence, site-specific conditions (Knäbel et al., 2012), highlighting the general rather than arbitrary mismatch between the model output and the field/experimental data. This raises concerns about the suitability of the FOCUS modeling approaches for reliable risk assessment, which aims to ensure the balance between societal benefits and the protection of the environment (FOCUS, 2001).

Irrespective of the discrepancies revealed between the modeling output and the experimental data used during the course of the present study, a considerable amount of the VPs applied together with the liquid manure onto the arable and grassland plots is retained in the soil, where they may be degraded over time (Kemper, 2008). From there, these VPs may also be washed into adjacent surface water bodies during subsequent rainfall events. However, this path may not be considered to be of major importance because Stoob et al. (2007) demonstrated that the loss of VPs to streams is close to zero two weeks after the application of the manure to a grassland. It also seems feasible that the VPs are transported to the groundwater bodies, potentially contaminating human drinking-water resources (Heberer, 2002a) or are taken up by the agricultural crops (Bassil et al., 2013). In this context, the health risks for humans can be reduced or even eliminated by treating the drinking water with, for instance, ozone prior to use (Heberer, 2002b), and a recent review suggested only a limited health risk for humans associated with the consumption of crops grown on agricultural fields treated with liquid manure (Prosser and Sibley, 2015). Nonetheless, the risk associated with the application of manure, particularly the risks associated with the VPs in the manure, to arable fields and grasslands cannot be excluded. To reduce these risks further, an extended aging (storage) of the manure prior to its application to the field may be sensible, as this would further reduce the VPs' concentrations (Kreuzig et al., 2005).

4. Conclusions

The results of this study provide a first indication of the uncertainties associated with the use of the FOCUS modeling approach to predict the runoff of VPs from agricultural land. The high discrepancies between the predicted and measured runoff-concentrations might be primarily caused by the fact that the FOCUS approach was not built to predict the runoff of VPs, especially via the application of manure. Nevertheless, there is a need for the further targeted evaluation of the FOCUS predictions for other commonly used VPs and soil types. These findings is ultimately call for careful interpretation, a critical evaluation, and the development of methods that can be used for the exposure assessment of VPs during their registration.

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Appendix III

- Knäbel, A.; Scheringer, M.; Schulz, R. (2016) Aquatic exposure predictions of insecticide field concentrations using a multimedia mass-balance model. *Environmental Science and Technology*, DOI: 10.1021/acs.est.5b05721.
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Aquatic Exposure Predictions of Insecticide Field Concentrations Using a Multimedia Mass-Balance Model

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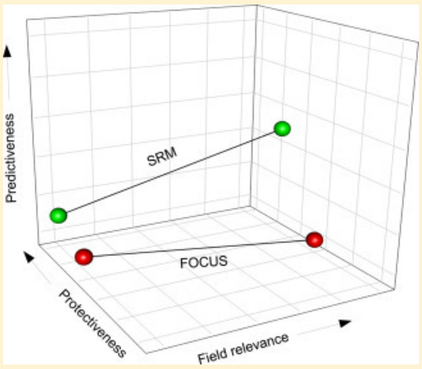
Ⓢ *Supporting Information*

ABSTRACT: Highly complex process-driven mechanistic fate and transport models and multimedia mass balance models can be used for the exposure prediction of pesticides in different environmental compartments. Generally, both types of models differ in spatial and temporal resolution. Process-driven mechanistic fate models are very complex, and calculations are time-intensive. This type of model is currently used within the European regulatory pesticide registration (FOCUS). Multimedia mass-balance models require fewer input parameters to calculate concentration ranges and the partitioning between different environmental media. In this study, we used the fugacity-based small-region model (SRM) to calculate predicted environmental concentrations (PEC) for 466 cases of insecticide field concentrations measured in European surface waters. We were able to show that the PECs of the multimedia model are more protective in comparison to FOCUS. In addition, our results show that the multimedia model results have a higher predictive power to simulate varying field concentrations at a higher level of field relevance. The adaptation of the model scenario to actual field conditions suggests that the performance of the SRM increases when worst-case conditions are replaced by real field data. Therefore, this study shows that a less complex modeling approach than that used in the regulatory risk assessment exhibits a higher level of protectiveness and predictiveness and that there is a need to develop and evaluate new ecologically relevant scenarios in the context of pesticide exposure modeling.



INTRODUCTION

The use of pesticides on agricultural cropland seems to be indispensable in modern agriculture to prevent and control pest-caused yield losses.[1] The application of pesticides to agricultural areas often results in transport to adjacent nontarget environments. In particular, surface-water systems are likely to receive agricultural pesticide input.[2−4] Several studies have shown that especially insecticides pose a substantial threat to the ecological integrity of aquatic ecosystems.[2,3,5,6] In the European Union (EU), the registration procedure (i.e., EU Directive 1107/2009)[7] for the authorization of pesticides prescribes an environmental risk assessment (ERA) that consists of effect and exposure assessment to prevent effects in nontarget ecosystems. The exposure assessment relies on a computer simulation approach of the Forum for the Coordination of Pesticide Fate Models and their Use (FOCUS), which is used to calculate the predicted environmental concentration (PEC) in surface-water bodies adjacent to agricultural fields. The FOCUS approach consists of several mechanistic fate and transport models of different complexity arranged in four different tiers (step 1 to step 4).[8] A detailed description of the different steps and scenarios is provided elsewhere.[8,9] Generally, the FOCUS modeling approach is very complex and time-intensive, and the application has to be highly regulated within the risk assessment to minimize influence of the user running the model. The FOCUS working group claims that the highest step-3 PEC values from 10 representative scenarios are likely to represent at least the 90th percentile worst-case field concentration.[8] This protection goal shows that the main aim of the modeling approach is not to represent local field conditions as accurately as possible but to provide scenarios that represent the range of realistic worst-case conditions (in some cases, this range can be several orders of magnitude) to make sure that the overall ERA of pesticides is protective. In two earlier studies, we have shown that the protection goal of the FOCUS approach was not achieved for fungicide and insecticide field concentrations. In detail, we found that 23% and 15% of the measured insecticide and fungicide field concentrations (MFC), respectively, were underpredicted by the step-3 PECs calculated with FOCUS (PEC_{FOCUS}) when applied exactly as it is done within the regulatory risk assessment for pesticides.[9,10] That means that the FOCUS model is not protective in estimating actual

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pesticide concentrations measured in surface water. Furthermore, even when the scenarios were adapted to the field conditions to overcome the generalizing nature of the standard scenarios, the study on insecticides[9] revealed that there is no relationship between predicted and measured pesticide concentrations, which shows that also the predictiveness of the FOCUS modeling approach is questionable.

Beside the highly complex process-driven mechanistic fate and transport models used in the FOCUS surface-water modeling approach, there are also other environmental fate models, such as multimedia mass-balance models, which are a well-established technique in the risk assessment of organic chemicals.[11] Mackay and Paterson[12,13] introduced four types of multimedia mass-balance models with different levels of complexity in 1982. Compared to the FOCUS approach, these models have a different spatial and temporal resolution and employ different mathematical methods.[14] Multimedia mass-balance models describe a system of different environmental compartments with exchange processes between the compartments and chemical and biological degradation in every compartment simultaneously. For these models, "the power lies in demonstrating the connections among different factors that determine the chemical concentrations and the rates of transport and transformation of chemicals in the environment."[15] The most important advantage is that the use of multimedia models is less time-consuming because of the efficient mathematical treatment, relatively low computing effort, and small set of input data needed. One model publicly available is the small-region model (SRM) that is part of the small models.[16,17] The SRM is a four-box level-III fugacity model that consists of tropospheric air, soil, water, and sediment. The substance-specific input data required by the SRM are the Henry's law constant, the octanol−water partition coefficient, and the degradation half-lives for every compartment. Furthermore, scenario-specific input data are needed that describe the compartment sizes (i.e., volume) and specify the model processes (e.g., wind speed, precipitation amount, and concentration of atmospheric aerosols and particles in water). The model estimates the concentration of a chemical in a box as the combination of the total emission rate, the available volume, and the losses by degradation and outflow under the steady-state assumption, which means that the model is not dynamic because conditions are constant with time. The capacity of an environmental compartment is described by the fugacity capacity that is determined by the chemical partition coefficients. In addition, the model system includes outflow with moving air and water. All losses, outflow, and degradation are combined in an overall removal rate constant.[17]

The aim of this study is to evaluate the predictions of the SRM at two different levels of field relevance (i.e., two levels of realism of scenarios and input parameters) for insecticide field concentrations compared to predicitions of the FOCUS approach. Specifically, we conducted SRM calculations for a representative set of 466 measured insecticide concentrations extracted from 64 field studies performed in the EU and compared the results from the SRM to those calculated with the FOCUS surface-water approach regarding both protectiveness and predictiveness at two different levels of realism of scenario assumptions (cf. the TOC art).

■ MATERIALS AND METHODS

Selection of Measured Insecticide Concentrations. Studies that reported MFCs in lotic and lentic surface-water bodies, such as streams, ditches, and ponds, were identified by Stehle and Schulz.[2] They conducted a comprehensive literature search in multiple databases for the most important insecticide substances and selected all peer-reviewed studies that reported measured insecticide concentrations that resulted from agricultural nonpoint-source pollution. From these field studies, Stehle and Schulz[2] extracted all concentrations of the selected substances that were measured during independent events in surface water and sediment. Therefore, multiple insecticide concentrations reported in one publication can be regarded as independent (cf. ref 10). In total, Stehle and Schulz were able to compile 11 300 MFCs from field studies conducted worldwide. In the present study, we selected from the complete data set of Stehle and Schulz[2] all concentrations that were measured in Europe (see also ref 3). Further criteria for the selection of field studies were (i) comparably small water-body size or catchments smaller than 10 000 km^2 and (ii) the presence of agricultural land in the surrounding area (within approximately 50 m of field sampling site, cf.[10]). Not all MFCs met these criteria. Studies that reported concentrations that are not definitely from agricultural nonpoint sources or were measured in water bodies for which the catchment size could not be exactly determined were included in one analysis but are marked in Table S1 (SI); further analyses excluding these values were also conducted. In addition, all studies in which the insecticide concentrations were measured in rice paddies or were influenced by entries from rice paddies were not considered in this analysis because there is no corresponding FOCUS scenario. This resulted in a data set of 64 studies and 466 MFCs published between 1978 and 2012, covering 21 active ingredients. The selected field studies and the available study information are given in Table S1.

Overview of Model Calculations. The MFCs were compared to concentrations predicted with the fugacity-based small-region model.[16] This model is designed for nonionizing organic compounds and is not specific for pesticides. In addition, PECs were calculated using the tiered FOCUS surface-water approach[8] as it is applied in the official EU regulatory risk assessment of pesticides[7] (see ref 9 for details of the approach). All physicochemical substance properties were taken from the Pesticide Property Database.[18] Application data (application rate, number and interval of applications, and application timing) for every substance were taken from the official EU registration documents according to the Good Agricultural Practice.[19] For substances for which no registration document was publicly available (fenvalerate, parathion-methyl, azinphos-methyl, and endosulfan), application data were taken from UNEP (parathion-methyl and endosulfan) or WHO monographs (fenvalerate and azinphos-methyl). Nevertheless, these documents are based on official EU documents as well.

In addition to the standard calculations, in which the 10 standard scenarios applied in the EU regulatory risk assessment of pesticides were used, model calculations were also performed by adapting the model input data and scenarios to actual field conditions; these calculations were designated as "realistic" calculations (cf. ref 9) and have a higher field relevance than the standard calculations. The higher field relevance is important to overcome the generalizing nature of the standard scenarios, which are used to achieve the claimed level of protectiveness (90th percentile criterion).

SRM Calculations. PEC calculations were conducted with the small-region model (PEC_{SRM}) that belongs to the Small Models LEVEL-III Version 2.0.[16,17] These models can be used

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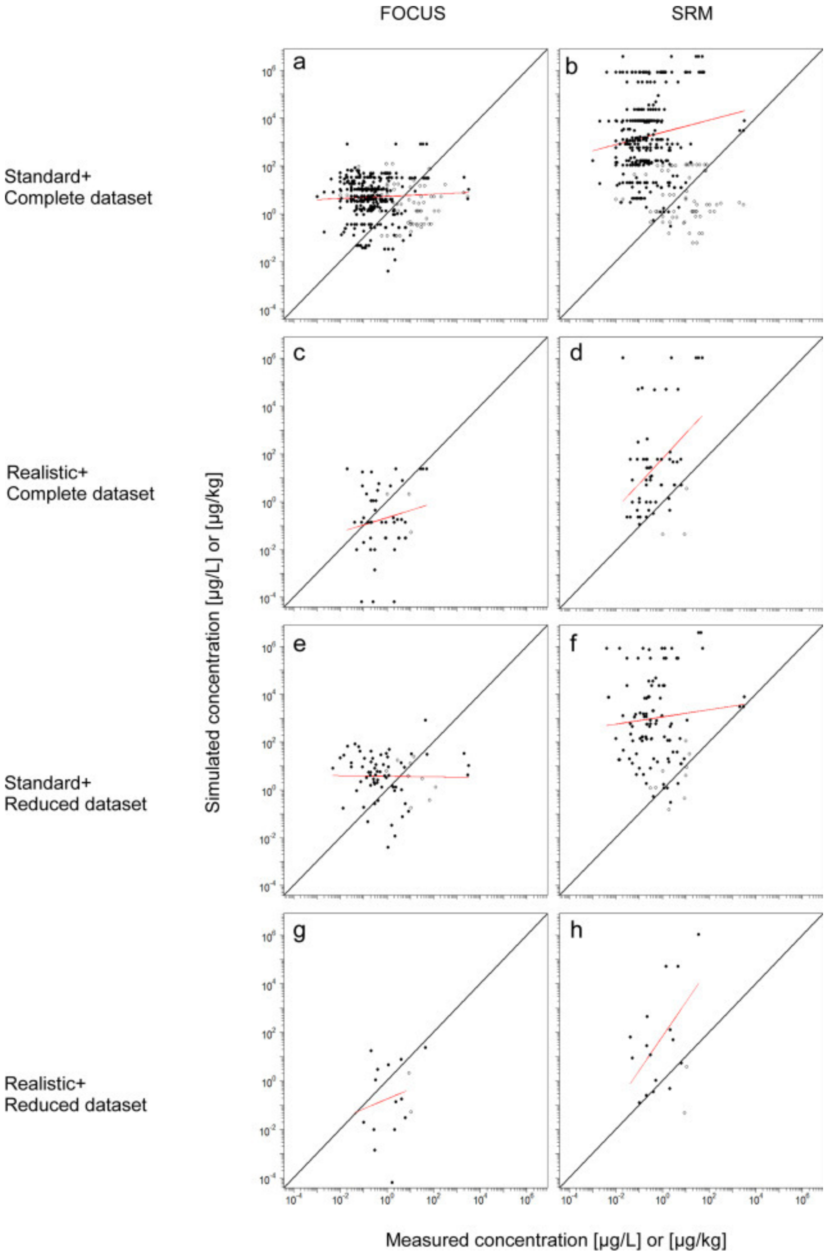

Figure 1. Relationship between simulated (FOCUS step 3 and SRM) and measured insecticide concentrations (complete data set and reduced data set of 90th percentile value per substance and study that are definitely of agricultural origin). Black dots = water (complete data set: (a) FOCUS step 3 and (b) SRM: $n = 397$, (c) step 3 realistic: $n = 47$, (d) SRM realistic: $n = 63$; reduced data set: (e) FOCUS step 3 and (f) SRM: $n = 66$, (g) step 3 realistic: $n = 14$, (h) SRM realistic: $n = 16$). White dots = sediment (FOCUS step 3 and SRM: $n = 69$; step 3 realistic and SRM realistic: $n = 3$); the 45° line denotes identity between PEC and MFC. The red lines show linear regression between simulated and measured concentrations (complete data set: FOCUS step 3: $r^2 = 0.002$, $p = 0.3$; FOCUS step 3 realistic: $r^2 = 0.006$, $p = 0.3$; SRM: $r^2 = 0.018$, $p = 0.004$; SRM realistic: $r^2 = 0.15$, $p < 0.001$; reduced data set: FOCUS step-3: $r^2 < 0.001$, $p = 0.9$; FOCUS step 3 realistic: $r^2 = 0.04$, $p = 0.5$; SRM: $r^2 = 0.001$, $p = 0.4$; SRM realistic: $r^2 = 0.31$, $p = 0.03$). The simulated concentrations are displayed on the *y*-axis, such that the MFC underestimations are plotted below the 45° line.

to provide estimates of chemical concentrations in air, water, soil, and sediment in a region of interest.[17] Beside the scenario description (dimensions of environmental compartments), only the overall emission rate of the chemical and its phase partitioning and degradation properties are needed as model input.[16] For the predictions, the SRM was scaled to the proportion of the landscape and water-body conditions of the FOCUS stream, pond, and ditch scenarios in three different SRM runs.[8] In addition, the model was parametrized to the climate and soil conditions of the ten runoff and drainage step-3 FOCUS surface-water scenarios (R1-R4 and D1-D6[8]). This was done to make the model outcome comparable to the predictions of the FOCUS model because the realistic worst-case FOCUS scenarios used in the regulatory risk assessment are intended to constitute a representative sample (33%) of the European agriculture. The scenario input parameters are given in Table S2. For each MFC several calculations were conducted with the parametrization for all water body and climate scenario combinations (30 possible combinations) that are relevant for the respective field sampling site. Details on scenario selection is described elsewhere.[9,10] In the SRM, the application rate is considered as emission rate to different compartments (soil, air,

Table 1. Over- and Underpredictions for FOCUS step 3 and SRM Standard and Realistic Calculations[a]

	total			surface water			sediment		
SRM	*n*	overprediction PEC > MFC, %	underprediction PEC < MFC, %	*n*	overprediction PEC > MFC, %	underprediction PEC < MFC, %	*n*	overprediction PEC > MFC, %	underprediction PEC < MFC, %
FOCUS step 3	466	81	19	397	89	11	69	39	61
FOCUS step 3 realistic	50	36	64	47	36	64	3	33	67
SRM	466	91	9	397	99	1	69	45	55
SRM realistic	66	88	12	63	92	8	3	0	100

[a] PEC = predicted environmental concentration; MFC = measured field concentration.

water, and sediment) in mol h^{-1}. To account for the fact that the application of pesticides does not take place directly on the soil surface and that spray-drift can occur during application, we split total emission rates into emission to soil and emission to air, while interception by plants was not considered. The percentage of emission to soil and air from the total emission rate were based on the BBA drift values[20] also used in the FOCUS surface-water approach. Therefore, emission to air was calculated as the total emission rate multiplied by the FOCUS drift value for the respective crop-water body combination. Overall, approximately 750 SRM calculations were conducted in this study. In addition, SRM realistic calculations were conducted for MFCs (n = 66) from studies for which enough information on the actual field condition was provided in the respective publication. These calculations were performed using all available realistic field information regarding insecticide use patterns, climate and soil conditions, landscape, and water-body characteristics.

FOCUS Calculations. PEC_{FOCUS} values were derived from FOCUS step 1 to step 4 calculations. Details on calculations and scenario crop selection are described elsewhere.[9,10] FOCUS steps 1 and 2, model version 2.1,[8] FOCUS_MACRO version 5.5.4,[21] FOCUS_SW PRZM version 3.1.1,[22] and FOCUS_TOXSWA version 3.3.1[23] were used for step-1−3 PEC calculations. Step-4 calculations were conducted when applicable[9,10] using SWAN version 1.1.3[24] according to FOCUS.[25] A total of 280 step-1 and step-2 calculations, approximately 750 step-3, and 800 step-4 calculations were performed for this study. Step-4 PECs are only available for 365 of 466 MFCs, and no step-4 calculations were conducted for carbamate insecticides because no application restrictions are available. Nevertheless, this study almost exclusively focuses on the FOCUS step-3 results because this is the most important step within the environmental risk assessment for fungicides and insecticides.[9,10]

Step-3 realistic PECs were taken from Knäbel et al.[9] for all measured concentrations from studies that were also considered in the earlier study (n = 34). Further step-3 realistic calculations were conducted for MFCs (n = 16) for which enough information on the actual field condition was provided in the respective publication. An exact description of the adaptations and methods for the calculation of FOCUS step-3 realistic PECs is given elsewhere.[9] Overall, a total of 50 step-3 realistic PECs were used in this study.

Data Analysis. The MFCs were compared to the calculated SRM and step 3 FOCUS PECs in the same way as in the earlier study on insecticides,[9] and the extent of over- and underprediction was determined. When multiple PECs were calculated because of different crop−scenario combinations, the maximum PECs were compared to the respective MFCs. More important than the PEC-MFC comparison for the complete data set is a reduced data set of MFCs. This data set consists of the 90th percentile value of all MFCs per substance and study that are definitely of agricultural origin. The reduced data set is composed of n = 66 concentrations and was also used for the comparison with the respective PECs. We used the 90th percentile value of the MFCs because it was claimed by the FOCUS group that the highest PEC estimates from the ten scenarios would represent at least the 90th percentile surface-water exposure.[8]

The effect of different insecticide substance classes (i.e., organophosphate, carbamate, organochlorine, pyrethroid, and neonicotinoid) on the ratio of simulated to measured concentrations (PEC divided by MFC; $ratio_{S/M}$) was analyzed by a single-factor analysis of variance (ANOVA) test followed by Tukey's honestly significant differences (HSD) post hoc test for pairwise multiple comparisons. Furthermore, a multiple linear regression analysis was conducted with the $ratio_{S/M}$ as the dependent variable to identify interactions between different independent variables. The independent variables investigated in the analysis were K_{OC}, catchment size, and sampling interval. First, a main effect model was used to test all individual independent variables, followed by models containing all relevant interactions. Automated model building was used to identify the best-fit linear model containing variables and interactions with the highest explanatory power. The model building started with the most complex model, including all variables and interactions, and used a stepwise backward method with Akaike's information criterion (AIC) as the goodness-of-fit measure. All data were transformed ($\ln[x]$) prior to statistical analysis to satisfy the assumption of normally distributed residuals. The models were also checked for heteroscedasticity and outliers (leverage plots and Cook's distance). In addition, the relationship between PEC_{SRM} and PEC_{FOCUS} (for FOCUS steps 1−4) was also determined using linear regression. All of the statistical analyses and graphics were made with the open-source software package R (www.r-project.org), version 3.1.0.[26]

RESULTS

Measured and simulated concentrations are compared in Figure 1 for both models for the standard and realistic case and for the complete and reduced data set. Important features of these results are

(i) The FOCUS model underpredicts substantial fractions of the measured data (11% for the complete data set to 26% for the more reliable reduced data set, Figure 1a and g, Table 1). Linear regression does not show a significant relationship in any of the cases.

(ii) The SRM underpredicts a much smaller fraction of the data (maximum of 2% for the reduced data set, Figure 1f), and there is a weak significant positive relationship between model results and field data for the complete data set (Figure 1b).

(iii) The higher field relevance of the realistic calculations results in a higher frequency of MFC underprediction for FOCUS (64%, complete data set, Figure 1c) and SRM (8%, complete data set, Figure 1d) and a significant relationship between SRM model results and field data for the reduced data set.

Already in the earlier analysis, Knäbel et al. found that the performance of the FOCUS model was low.[9] This is confirmed by the present analysis (Figure 1, left panels). The SRM (Figure 1, right panels) shows a better performance, but it is important to note in this context that a close agreement cannot be expected due to possible inaccuracies in the field data and the lack of site-specific conditions (i.e., actual emission rate and compartment size) in the model scenarios.

Furthermore, it was detected that pyrethroids had significantly lower PEC-to-MFC ratios (PEC divided by MFC; $\text{ratio}_{S/M}$) than all other substance classes for FOCUS calculations (Figure S2) and that there is a significant negative relationship between the $\text{ratios}_{S/M}$ and the substance K_{OC} for SRM and FOCUS predictions (Figure S5 and S7).

■ DISCUSSION

Protectiveness of Exposure Estimates. The fact that the FOCUS modeling approach is not protective in estimating insecticide field concentrations, already shown in a previous study,[9] is confirmed by the results of this analysis. Compared to the earlier study we used a data set of field concentrations for the evaluation that is by more than 500% greater and relies exclusively on insecticide concentrations measured in Europe arising from various field situations. Considering the calculated standard step-3 $\text{PEC}_{\text{FOCUS}}$ and only the reduced data set of the 90th percentile value of MFCs that are definitely from agricultural nonpoint sources (n = 66), up to 26% of the MFCs were underpredicted by the step-3 $\text{PEC}_{\text{FOCUS}}$ values for surface water. This finding is substantial because the reduced data set has a higher relevance for the evaluation of the FOCUS approach as it represents peak concentrations stemming from nonpoint-source entries also predicted within the FOCUS approach, taking into account the 90th-percentile protection goal claimed by the FOCUS surface-water group. This means that more than 25% of the values considered in the regulatory risk assessment of insecticides underestimate the actual field concentrations, which is similar to the 23% underprediction frequency that was shown in the earlier study on insecticides[9] and implies that unacceptable ecological effects in the field are possible (see also ref 2). This fact is even more important considering that the used insecticide field concentrations most likely underestimate actual exposure levels due to the fact that it is extremely unlikely to measure short-term insecticide peaks in the field because the application is episodic, and the resulting exposure is strongly related to runoff events.[2,27]

Compared to the result of the FOCUS calculations, the PEC values from the SRM generally overestimate the corresponding MFCs by several orders of magnitude (Figure 1b). Only 1% of all PECs calculated with SRM underpredicted the respective surface-water field concentrations. Even for the reduced data set, the frequency of underprediction increased only slightly to 2%. This means that the SRM exposure predictions are much more protective than the predictions of the regulatory FOCUS step-3 approach. The most important reason for the generally higher PEC_{SRM} might be that within the SRM model the total amount of the applied substance is available for the partitioning between the different compartments within the system because the model does not capture several processes that might limit the transfer of chemical to surface water. This includes, for example, plant interception (up to 90% depending on crop and growth stage)[8] and photodegradation (depending on environmental conditions and chemical structure) on the soil surface, which may generally result in lower chemical amounts available for the surface-water entry within the system. Nevertheless, there are indications that within the FOCUS approach especially the extent of plant interception is overestimated for some crops.[28] Di Guardo et al.[29] stated that in reality, the transfer process of pesticides from soil to surface water may only depend on a mixing layer of a few centimeters of soil from which the pesticide can be extracted. During a rainfall event, a relevant amount of the substance can be moved downward, such that the chemical is not available for runoff. This might even be increased by the presence of cracks and macropores, which are not considered in the SRM modeling scenario. Nevertheless, there are several reasons why it is likely that measured concentrations are still lower than the actual peak concentrations.[10,27,30]

Di Guardo et al.[29] compared herbicide runoff measured in two different basins with concentrations predicted with a fugacity model. They showed that the model has a tendency to overestimate actual measured concentrations and concluded that the worst-case scenario results in concentrations "protective for the environment". In our study, the frequency of MFC_{SW} underprediction by PEC_{SRM} is even lower than that from the $\text{PEC}_{\text{FOCUS}}$ calculated with the very conservative FOCUS steps 1 and 2 (Table S3), especially for the reduced data set (frequency of underprediction: step 1, 14%; step 2, 23%; Table S5). Mackay et al.[31] stated that it is unlikely for exposure models to be universally valid, but they may produce results that are deemed to be reliable with a level of accuracy that depends on the nature of the chemical, the environment, and regulatory requirements. Regarding only the aspect of the regulatory requirements, the FOCUS approach failed to meet the demanded protection goal, while the SRM showed a very high level of protectiveness. In terms of accuracy of the model results, the standard SRM calculations do not show a better performance than the FOCUS predictions because the standard SRM PECs generally overestimate the MFCs by up to several orders of magnitude (this is different for the realistic PECs; see below).

The evaluation of the realistic simulations in which the standard scenarios were adapted to the respective study conditions showed that the extent of underprediction is higher than for the standard calculations. For FOCUS step-3 realistic calculations, the frequency of MFC underprediction is more than three times the frequency of the step-3 standard calculations (64%; Table 1) and even higher than that shown in the earlier insecticide study (43%).[9] The frequency of MFC underprediction by realistic PEC_{SRM} values is also higher than for the standard SRM calculations, but there is only a small difference between standard and realistic calculations (8% instead of 1%, Table 1). This fact demonstrates that the substitution of the worst-case assumptions included in the step-3 standard scenarios, to which the SRM model was also parametrized, by real-world field data generally results in lower PECs. Nevertheless, the frequency of MFC underestimation by PECs calculated with the SRM realistic scenarios remains

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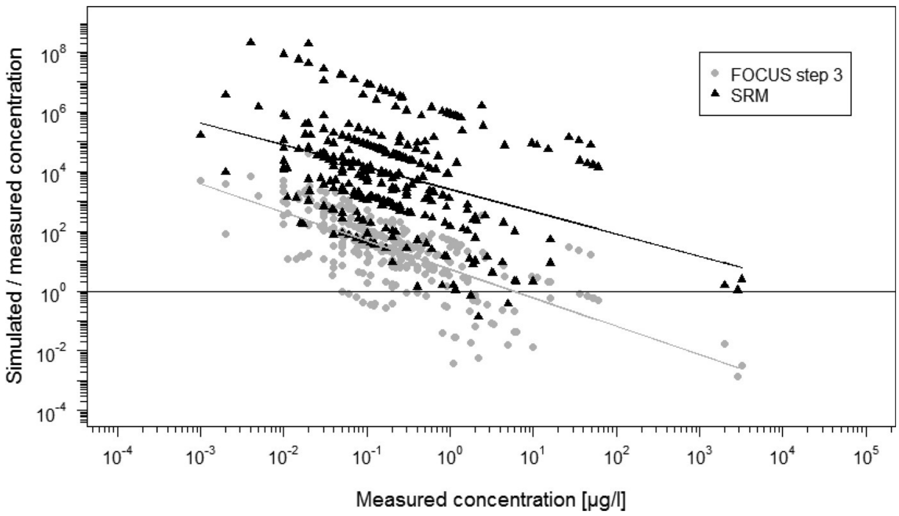

Figure 2. Relationship between the simulated-to-measured concentration ratios and the measured concentration for FOCUS step 3 (gray dots, n = 397) and SRM (black triangles, n = 397). The lines are the respective regression lines (FOCUS step 3: $p < 0.001$, $r^2 = 0.15$; SRM: $p < 0.001$, $r^2 = 0.51$).

within the range of 10%, which is often used as a quality criterion for model evaluations and can therefore still be claimed as protective.

Predictiveness of Exposure Estimates. As stated before, the model simulations should be reliable with a degree of accuracy that depends on the nature of the chemical[31] and therefore provides some degree of realistic estimates of field concentrations. This means that there should be some kind of relationship between PEC and MFC to fulfill the requirement of predictiveness. However, the results of this study confirm the observation made earlier[9,10] that the quality of FOCUS predictions, regarding a relationship between measured and predicted insecticide concentrations, is not sufficient even if the FOCUS working group does not aim at an accurate prediction of actual field concentrations. Figure 1a shows that there is no positive relationship in terms of a statistically significant slope with a value greater than 0 between MFCs and PEC_{FOCUS} values for the complete data set. The same has been shown for insecticides[9,30] and fungicides.[10] In addition, only a very weak significant relationship between MFCs and PEC_{FOCUS} values with a maximum r^2 of 0.096 was found for organochlorine insecticides when the linear relationship was determined for individual substance classes (Figure S8). Even if there might be uncertainties in the field data used, a valid model should show at least a positive trend between predicted and measured data, especially for peak concentrations. However, also no significant relationship was found between the MFC and the respective PEC_{FOCUS} (p = 0.9) for the reduced data set. This result underlines the importance of the inherent FOCUS model limitations.

Also for the SRM predictions, only a very weak but significant linear relationship was found for surface water MFCs and PECs calculated with SRM standard ($p = 0.004$; $r^2 = 0.018$); there was no significant relationship for the reduced data set. Regarding the individual substance classes, only for organochlorine insecticides was a considerable significant relationship between PEC_{SRM} and MFCs detected ($p > 0.001$; $r^2 = 0.24$; Figure S9); this might be due to the fact that for several MFCs, the same PEC is applicable (cf. ref 30). Nevertheless, Figure 2 shows that the relationship between the $ratio_{S/M}$ and the measured concentrations has a slightly higher elasticity (log–log scale) for FOCUS step 3 than for the SRM calculations (FOCUS step 3: $\beta_1 = -0.96$, SRM: $\beta_1 = -0.74$; Figure 2). This underpins the fact that the predictiveness of the FOCUS calculations is worse compared to the SRM calculations because for a perfect model the relationship should be a horizontal regression line with an elasticity of zero. In addition, from the regression equations (Figure 2) for the log–log model, it follows that the FOCUS model tends to underpredict measured concentrations above 2 μg/L, whereas the SRM only underpredicts measured concentrations of ≥8000 μg/L.

In addition, as shown in the earlier insecticide study,[9] the relationship between realistic PEC_{FOCUS} and MFC was not improved compared to the standard calculations. However, for the SRM results, there is a significant relationship between realistic PEC_{SRM} and MFCs of the reduced data set ($p = 0.03$, $r^2 = 0.31$), which clearly shows that the SRM's predictiveness increases with a higher field relevance (i.e., an increase in realism of input parameters and scenario). In most of the cases, the adaptations made are related to emission rate and emission compartment and also to the compartment volume, of which all three belong to the most influential parameters of a multicompartment model. This higher predictiveness is important in the context of ERA because it means that a relatively simple multimedia mass-balance model serves the purpose better than the FOCUS models do, which has been shown in this study for the first time. Furthermore, Figure 1h shows that for the SRM realistic calculations, some points directly lie along the 45° line. The distance of the data-points to the 45° line is lower when only concentrations are considered that were measured by an event-related sampling. Even if the data set is rather small for this evaluation, this result indicates that there is a need for the development of more realistic exposure scenarios because a higher field relevance resulted in a higher predictive performance of the SRM model.

Factors Influencing the PEC-to-MFC Ratio. As was shown in the earlier study,[9] the protectiveness of the FOCUS modeling approach is not similar for all substance classes. The results of this study, with a much larger sample size, confirm that the FOCUS approach is less protective for highly toxic pyrethroids, even when neonicotinoids as an additional substance class are included. This result is remarkable because pyrethroids generally have a low water solubility and consequently high K_{OC} values, which leads to a rapid and strong sorption to soil and sediment, which should reduce both the entry into surface water and the concentration within the water column after the entry into the water body. Therefore, we tested whether exclusion of sorption to sediment had an impact, but neither the extent of underestimation of MFCs by step-3 PEC_{FOCUS} nor the $ratio_{S/M}$ for different substance classes changed. Possible reasons for the significantly lower $ratio_{S/M}$ for pyrethroids, like the overestimation of pesticide downward movement in soil in the PRZM model, are discussed elsewhere.[9] Also for the SRM, the lowest $ratio_{S/M}$ was found for pyrethroids, but almost no underprediction occurred even for this insecticide class (see above).

Therefore, we analyzed the relationship between the $ratio_{S/M}$ and the substance K_{OC} value. A significant negative linear relationship was found for all FOCUS steps, which shows that the chance that MFCs are underestimated by the respective PECs increases with increasing K_{OC} values (also shown in the multiple regression analysis; Figure S10 and S11). This result confirms the fact that especially highly hydrophobic pyrethroids are underpredicted by the PEC_{FOCUS} results. Overall, the MFC underestimation depends on a variety of factors including substance properties and environmental parameters. In addition, Stehle and Schulz[2,3] showed that the frequency of regulatory threshold level exceedances by MFCs is significantly higher for pyrethroids compared to those of organophosphorus and organochlorine insecticides.

In conclusion, this study has shown that a much simpler model than the regulatory FOCUS surface-water approach is more appropriate for the prediction of insecticide concentrations in surface waters in the context of ERA. In particular, the results of the SRM realistic calculations indicate that the SRM might estimate insecticide concentrations with an acceptable degree of uncertainty if the model is parametrized in a more realistic way than the FOCUS standard scenarios. In addition, it is important for exposure models that model assumptions, setup, and results are transparent and confirmable to ensure the confidence of different stakeholders and the general public in the ERA. Thus, the simplicity and transparency of both input parameters and process descriptions of the SRM can result in a higher level of acceptance than for the complex FOCUS approach. In addition, Di Guardo and Hermens[32] concluded that for an improvement of the exposure assessment, the current environmental scenarios should be improved to describe realistic conditions and that more evaluation data sets should be made publicly available. Furthermore, this study confirmed that the FOCUS modeling approach is neither appropriate nor protective in predicting insecticide field concentrations measured in surface waters.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b05721.

> Tables showing field studies (n = 64) selected for comparison between measured and simulated insecticide concentrations in agricultural surface waters and analytical methods and input parameters used for the calculations with the SRM model. Figures showing the relationship between simulated and measured insecticide concentrations, over- and underpredictions from FOCUS step 1−4 simulations, box-plots of simulated and measured concentration ratios, the relationship between simulated and measured concentration ratios, results of multiple linear regression analyses, relationships between simulated and measured insecticide concentrations, two-way interactions among logarithmic K_{OC}, and relationship between concentrations calculated with FOCUS and SRM. (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Supporting Information for:

Exposure Predictions of Insecticide Field Concentrations Using a Multimedia Mass-Balance Model

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23 pages
12 figures
7 tables

Table S1. Field studies (n = 64) selected for comparison between measured and simulated insecticide concentrations in agricultural surface waters and analytical methods.

Reference	Country	Field size	Water body width (m)	Water body depth (m)	Flow	Time between application and first rain	Insecticide compounds	Detections water/ sediment	Entry pathway	Analytical method	LOD /LOQ (µg/L or µg/kg)	Analytical recovery (%)
1 Albanis and Hela 1998	Greece	na	na	na	19.4 m³/sec	na	Parathion-methyl	2 / 0	nonpoint source	GC/FTD	na/0.005	87.3
							Carbofuran	2 / 0	nonpoint source	GC/FTD	na/0.005	93.6
2 Altmayer et al. 2003	Germany	na	na	na	na	na	Parathion-methyl	13 / 0	runoff	GC/NPD; GC/ECD	na/na	na
3 Bacigalupo and Meroni 2007	Italy	na	na	na	na	na	Carbofuran	11 / 0	runoff, spray drift, nonpoint source	TR-FIA	na/na	-
4 Berenzen et al. 2005	Germany	na	na	na	10-80 l/s	na	Parathion-ethyl	3 / 0	runoff	GC/ECD	na/0.05	97-99
*5 Botta et al. 2012	France	na	na	na	na	na	Imidacloprid	1 / 0	nonpoint source	na	na/0.05-0.005	na
6 Cappiello et al. 2002	Italy	na	na	na	na	na	Azinphos-methyl	1 / 0	runoff	LC/MS	na/na	92.6-100.3
							Parathion-ethyl	1 / 0	runoff	LC/MS	na/na	92.6-100.3
							Parathion-methyl	1 / 0	runoff	LC/MS	na/na	92.6-100.3
7 Capri et al. 2005	Italy	11000 m²	2.5-3.3	0.7	0.0017 m/s	na	Chlorpyrifos	4 / 0	runoff, spray drift	GC/NPD	na/0.05	87.8
8 Carter and Capri 2004	Italy, Spain	na	na	na	na	na	Chlorpyrifos	8 / 1	runoff, spray drift, nonpoint source	na	na/na	na
*9 Chevre et al. 2008	Switzerland	na	na	na	670 l/s	na	Diazinon	1 / 0	nonpoint source	GC/MS	na/0.01	na
10 Crossland et al. 1982	France	1.3-3 ha	0.25-12	5-50	0.4-0.5 m/s	na	Cypermethrin	20 / 0	spray drift	GLC/EC	0.01/na	na
11 Curini et al. 2001	Italy	na	na	na	na	na	Malathion	5 / 0	runoff, nonpoint	HPLC/MS	0,008-0,029/na	90-92
							Carbofuran	3 / 0	runoff, nonpoint	HPLC/MS	0,008-0,029/na	94
*12 Damasio et al. 2008	Spain	na	na	na	0.1-12 m³/s	na	Chlorpyrifos	1 / 0	nonpoint source	GC/MS	< 0,01/na	na
							Diazinon	2 / 0	nonpoint source	GC/MS	< 0,01/na	na
13 Daniels et al. 2000	UK	na	na	na	na	na	Permethrin	0 / 4	nonpoint source	GC/MS; GC/NPD	na/0.5	na
14 Fagotti et al. 2005	Italy	na	na	na	na	na	Endosulfan	2 / 0	nonpoint source	GC/MS	na/na	na
*15 Fatta et al. 2007	Cyprus	na	na	na	na	na	Parathion-ethyl	3 / 0	nonpoint source	GC/ECD; GC/FTP	0.005/0.01	94
*16 Friberg et al. 2003	Denmark	na	0.49-4.82	0.03-0.48	0-0.3 m/s	na	Lambda-Cyhalothrin	0 / 1	nonpoint source	GC/MS	na/na	na
17 Ganzelmeier et al. 2012	Germany	na	na	na	na	na	Imidacloprid	1 / 0	spray drift	LC/MS/MS; GC/MS	na/0.01	72-100
							Thiacloprid	1 / 0	spray drift	LC/MS/MS; GC/MS	na/0.01	72-100
18 Gomez-Gomez et al. 1995	Spain	na	na	na	na	na	Parathion-ethyl	2 / 0	nonpoint source	GC/NPD	0.1/na	91.8-103.4
*19 Hela et al. 2000	Greece	na	na	na	na	na	Parathion-methyl	1 / 0	nonpoint source	GC/FTD; GC/MS	0.001/na	78.7-93.7
20 Höcker et al. 1998	Germany	na	na	na	na	na	Imidacloprid		nonpoint source	HPLC	na/na	na
21 House et al. 1991	UK	na	na	na	na	na	Cypermethrin	1 / 1	nonpoint source	GLC/ECD; GLC/MS	na/0.01; na/1	89; 67-97
							Deltamethrin	0 / 3	nonpoint source	GLC/ECD; GLC/MS	na/1	67-97
							Fenvalerate	0 / 5	nonpoint source	GLC/ECD; GLC/MS	na/1	67-97
							Permethrin-cis	3 / 0	nonpoint source	GLC/ECD; GLC/MS	na/0.01	123
							Permethrin-trans	0 / 1	nonpoint source	GLC/ECD; GLC/MS	na/1	67-97

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* Not excludable that point sources were within the examined catchment or water body may not be representative for FOCUS surface water bodies

Table S1. (continued)

Reference	Country	Field size	Water body width (m)	Water body depth (m)	Flow	Time between application and first rain	Insecticide compounds	Detections water/ sediment	Entry pathway	Analytical method	LOD /LOQ (µg/L or µg/kg)	Analytical recovery (%)
22 House et al. 1992	UK	na	na	na	na	na	Parathion-ethyl	0 / 3	nonpoint source	GC/ECD; GC/FTP; GC/MS	na/0.1	na
23 Jimenez et al. 1997	Spain	na	na	na	na	na	Azinphos-methyl	2 / 0	nonpoint source	GC/NPD	0.07/0.22	different
							Malathion	1 / 0	nonpoint source	GC/NPD	0.001/0.005	different
							Cypermethrin	1 / 0	nonpoint source	GC/ECD	0.15/0.5	different
							Permethrin	1 / 0	nonpoint source	GC/ECD	0.37/1.24	different
*24 Kanzari et al. 2012	France	na	na	na	1-1000 m³/s	na	Endosulfan (beta)	0 / 1	nonpoint source	GC/MS	0,006-0,06/na	90-105
							Endosulfan (alpha)	0 / 1	nonpoint source	GC/MS	0,006-0,06/na	90-105
							Chlorpyrifos	0 / 5	nonpoint source	GC/MS	0,006-0,01/na	90-105
*25 Karaouzas et al. 2011	Greece	na	na	na	na	na	Malathion	1 / 1	runoff	GC/MS	na/na	na
26 Kreuger 1998	Sweden	na	na	na	na	na	Cyfluthrin	2 / 0	nonpoint source	GC/MS	na/0.2	90-102
*27 Kreuger and Brink 1988	Sweden	na	na	na	na	na	Endosulfan	1 / 0	nonpoint source	GC/MS	na/0.1	na
							Permethrin	1 / 0	nonpoint source	GC/MS	0.1-0.6/na	na
28 Kreuger et al. 1999	Sweden	na	na	na	na	na	Fenvalerate	0 / 4	nonpoint source	GC/MS	na/5	71-115
							Permethrin	1 / 3	nonpoint source	GC/MS	na/0.5; na/2	71-115
*29 Kronvang et al. 2003	Denmark	na	na	na	na	na	Cypermethrin-alpha	0 / 1	nonpoint source	GC/MS	10/na	103
							Deltamethrin	0 / 1	nonpoint source	GC/MS	10/na	106
							Esfenvalerate	0 / 1	nonpoint source	GC/MS	5-10/na	109
							Lambda-Cyhalothrin	0 / 1	nonpoint source	GC/MS	5/na	75
30 Lambropoulou et al. 2000	Greece	na	na	na	na	na	Malathion	1 / 0	nonpoint source	GC/FTD; GC/MS	na/0.02	86.2-119.7
							Parathion-ethyl	1 / 0	nonpoint source	GC/FTD; GC/MS	na/0.05	86.2-119.7
							Parathion-methyl	1 / 0	nonpoint source	GC/FTD; GC/MS	na/0.05	86.2-119.7
31 Liess and Von der Ohe 2005	Germany	na	0.5-2.5	0.04-0.6	0.02-0.5 m/s	na	Parathion-ethyl	11 / 0	runoff	GC/ECD, GC/MS	na/0.05	na
32 Liess et al. 1999	Germany	na	na	na	10 l/s	1-2	Parathion-ethyl	10 / 2	runoff	GC/ECD, GC/MS	na/0.02; na/1	na
							Fenvalerate	7 / 1	runoff	GC/ECD, GC/MS	na/0.1; na/5	na
*33 Long et al. 1998	UK	na	na	na	na	na	Diazinon	2 / 5	nonpoint source	GC/MS; GC/NPD	na/0.01; na/0.5	na
							Malathion	2 / 5	nonpoint source	GC/MS; GC/NPD	na/0.01; na/0.5	na
							Parathion-ethyl	1 / 4	nonpoint source	GC/MS; GC/NPD	na/0.01; na/0.5	na
							Cypermethrin	0 / 1	nonpoint source	GC/MS; GC/NPD	na/0.5	na
							Fenvalerate	0 / 4	nonpoint source	GC/MS; GC/NPD	na/0.5	na
							Permethrin	0 / 4	nonpoint source	GC/MS; GC/NPD	na/0.5	na

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Table S1. (continued)

Reference	Country	Field size	Water body width (m)	Water body depth (m)	Flow	Time between application and first rain	Insecticide compounds	Detections water/ sediment	Entry pathway	Analytical method	LOD /LOQ (µg/L or µg/kg)	Analytical recovery (%)
*35 Melluso et al. 1994	Italy	na	na	na	na	na	Endosulfan	0 / 2	nonpoint source	GC/ECD; GC/NPD; GC/FID	0.0003/na	65-70
							Malathion	0 / 1	nonpoint source	GC/ECD; GC/NPD; GC/FID	0.24/na	65-70
							Parathion-methyl	0 / 1	nonpoint source	GC/ECD; GC/NPD; GC/FID	0.09/na	65-70
*36 Molto et al. 1991	Spain	na	na	na	na	na	Diazinon	1 / 0	nonpoint source	GC/ECD	0.001/na	89.1
*37 Monteoliva and Augustin 1985	Spain	na	na	na	na	na	Parathion-methyl	82 / 0	nonpoint source	GC/ECD	na/na	na
38 Neamtu et al. 2010	Romania	na	na	na	na	na	Endosulfan	4 / 0	nonpoint source	GC/MS	0.001/na	80-114
*39 Neumann et al. 2002	Germany	na	na	na	10-300 l/s	na	Parathion-ethyl	2 / 0	runoff	GC/NPD; GC/MS	na/0.1	na
							Fenvalerate	1 / 0	runoff	GC/NPD; GC/MS	na/0.1	na
*40 Papadopoulou-Mourkidou et al. 2004a	Greece	na	na	na	na	na	Parathion-ethyl	2 / 0	runoff	GC/MS	0.001-0.01/0.005-0.01	na
							Carbofuran	8 / 0	runoff	GC/MS	0.001-0.01/0.005-0.01	na
*41 Papadopoulou-Mourkidou et al. 2004b	Greece	na	na	na	na	na	Carbofuran	8 / 0	runoff	GC/MS	0.001-0.01/0.005-0.01	na
*42 Perez-Trujillo et al. 2002	Spain	na	na	na	na	na	Endosulfan (alpha)	1 / 0	nonpoint source	GC/MS	0.006/na	87.4-103.4
*43 Planas et al. 1997	Spain	na	na	na	na	na	Chlopyrifos	1 / 0	nonpoint source	GC/ECD, GC/MS	0.005-0.05/na	40-100
							Diazinon	1 / 0	nonpoint source	GC/ECD, GC/MS	0.005-0.05/na	40-100
							Parathion-methyl	2 / 0	nonpoint source	GC/ECD, GC/MS	0.005-0.05/na	40-100
*44 Provini et al. 1991	Italy	na	na	na	9.9-15.2 m³/s	na	Diazinon	3 / 0	nonpoint source	GC/NPD; GC/ECD	0.005/na	na
							Parathion-methyl	1 / 0	nonpoint source	GC/NPD; GC/ECD	0.005/na	na
45 Sancho et al. 2004	Spain	na	na	na	na	na	Carbofuran	1 / 0	nonpoint source	LC/MS-MS	0.0001-0.0005/na	70-120
46 Schäfer et al. 2007	France	na	1-4.5	0.15-0.6	0.1-0.73 m/s	na	Endosulfan (alpha)	1 / 0	runoff	GC/MS	na/na	na
							Carbofuran	1 / 0	runoff	GC/MS	na/na	na
47 Schäfer et al. 2008	France	na	max 5	max 0.8	na	na	Endosulfan	0 / 1	runoff	GC/MS	na/3.7-48	50-100
48 Schäfer et al. 2008a	France	na	max 5	max 0.8	na	na	Carbofuran	8 / 0	runoff	GC/MS	na/0.025	na
49 Schlichtig et al. 2001	Germany	na	na	na	3.1 m³/s	na	Imidacloprid	1 / 0	nonpoint source	HPLC; GC/MS	na/na	na
50 Schulz 2005	Germany	na	1.3-4.9	0.23-0.72	0.21-0.5 m/s	na	Parathion-ethyl	1 / 0	runoff	GC/ECD, GC/MS	na/0.01	na
							Fenvalerate	1 / 0	runoff	GC/ECD, GC/MS	na/0.05	na
51 Sturm et al. 2000	Germany	na	na	na	na	na	Parathion-ethyl	5 / 0	runoff	GC/ECD, GC/MS	na/0.05	na
52 Süss et al. 2003	Germany	na	2.5	0.63	na	na	Parathion-ethyl	1 / 0	spray drift	GC/MS; LC/MS/MS	na/na	na
53 Süss et al. 2006	Germany	na	2.9-4	0.2-0.89	na	na	Parathion-ethyl	1 / 0	spray drift	GC/MS; LC/MS/MS	0.05/na	80-85
							Cyfluthrin-beta	1 / 0	spray drift	GC/MS; LC/MS/MS	0.1/na	na
							Imidacloprid	2 / 0	spray drift	GC/MS; LC/MS/MS	0.05/na	75-85
							Thiacloprid	2 / 0	spray drift	GC/MS; LC/MS/MS	na/na	60-115
54 Turnbull et al. 1995	UK	5.16 ha	na	na	na	1	Deltamethrin	3 / 0	runoff	GC/ECD	na/na	na

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Table S1. (continued)

Reference	Country	Field size	Water body width (m)	Water body depth (m)	Flow	Time between application and first rain	Insecticide compounds	Detections water/ sediment	Entry pathway	Analytical method	LOD /LOQ (µg/L or µg/kg)	Analytical recovery (%)
55 Turnbull et al. 1997	UK	5.16 ha	na	na	na	19-21	Chlorpyrifos	2 / 0	runoff	GC/ECD	na/na	na
*56 Vassilakis et al. 1998	Greece	na	na	na	na	na	Endosulfan (alpha)	1 / 0	nonpoint source	GC/ECD; GC/NPD; GC/MS; HPLC	na/0.001	93.8
*57 Belmonte Vega et al. 2005	Spain	na	na	na	na	na	Acetamiprid	1 / 0	nonpoint source	LC/ESI/MS	0.01/0.025	98.5-99.4
							Imidacloprid	1 / 0	nonpoint source	LC/ESI/MS	0.025/0.05	99.4-101
*58 Veljanoska-Sarafiloska et al. 2011	Macedonia	na	na	na	na	na	Endosulfan	2 / 2	nonpoint source	GC/ECD	0.002/0.005; 0.2/0.5	90-91
*59 Vryzas et al. 2009	Greece	na	na	na	na	na	Diazinon	1 / 0	nonpoint source	GC/EI/MS	na/na	na
							Malathion	7 / 0	nonpoint source	GC/EI/MS	na/na	na
							Carbofuran	9 / 0	nonpoint source	GC/EI/MS	na/na	na
							Bifenthrin	3 / 0	nonpoint source	GC/EI/MS	na/na	na
60 Vryzas et al. 2011	Greece	na	na	na	na	na	Endosulfan	4 / 0	nonpoint source	GC/MS/MS	na/na	na
							Chlorpyrifos	5 / 0	nonpoint source	GC/MS/MS	na/na	na
							Diazinon	5 / 0	nonpoint source	GC/MS/MS	na/na	na
							Carbofuran	4 / 0	nonpoint source	GC/MS/MS	na/na	na
							Bifenthrin	5 / 0	nonpoint source	GC/MS/MS	na/na	na
							Cypermethrin	3 / 0	nonpoint source	GC/MS/MS	na/na	na
							Lambda-Cyhalothrin	4 / 0	nonpoint source	GC/MS/MS	na/na	na
*61 Wegman and Greve 1978	Netherland	na	na	na	na	na	Endosulfan	23 / 0	nonpoint source	GC/ECD	na/0.1	na
62 Williams et al. 1995	UK	na	na	na	na	>15	Carbofuran	5 / 0	runoff	GC/MS; HPLC	na/0.02	na
63 Wittmer et al. 2010	Switzerland	na	na	na	<28 m³/s	na	Diazinon	5 / 0	runoff	LC/MS/MS	0.002-0.01/na	na
64 Yildrim and Özcan 2007	Turkey	na	na	na	na	na	Endosulfan	15 / 0	nonpoint source	GC/ECD	na/na	98

* Not excludable that point sources were within the examined catchment or water body may not be representative for FOCUS surface water bodies

Table S2. Input parameters used for the calculations with the SRM model.

		Value	Note
Bulk Environmental Properties	Temperature (°C)	25	chemical data are mostly available for 25 °C
	Total Surface Area (m^2)	10100 m^2 ditch/stream, 4500 m^2 pond	
	Fraction of area covered by water	0.0099 ditch/stream, 0.2 pond	
	Fraction of area covered by soil	0.9901 ditch/stream, 0.8 pond	
	Height of the air compartment (m)	1000	not considered in FOCUS
	Depth of water compartment (m)	1 m pond; 0.3 m ditch /stream	
	Depth of soil compartment (m)	0.05	taken from PEC soil calculation
	Depth of sediment compartment (m)	0.05	
	Wind speed (m/h)	18000	3-5 m/s
	Water residence time (days)	50 d pond; 5 d ditch; 0.1 d stream	
Environmental Subcompartment Properties	Volume fraction of aerosols in air	2.00E-011	not considered in FOCUS
	Volume fraction of particles in water	1.50E-005	
	Volume fraction of air in soil	0.2	not considered in FOCUS
	Volume fraction of water in soil	R1: 33.8%, R2: 36%, R3: 37%, R4: 26%, D1: 47%, D2: 52%, D3: 48%, D4:42%, D5: 41%, D6: 45%	R scenarios: field capacity; D scenarios: saturated water content
	Volume fraction of water in sediments	0.68	
	Density of water (kg/m^3)	1000	
	Density of aerosols (kg/m^3)	2400	not considered in FOCUS
	Density of soil solids (kg/m^3)	D1: 1350, D2: 1200, D3: 1350, D4: 1480, D5: 1550, D6: 1430, R1: 1350, R2: 1150, R3: 1460, R4: 1520	
	Density of particles in water (kg/m^3)	2400	not considered in FOCUS
	Density of particles in sediment (kg/m^3)	800	
	Fraction of OC in particles in water	0.05	
	Fraction of OC in soil solids	D1: 2%; D2: 3.3%, D3: 2.3%; D4: 1.4%; D5: 2.1%; D6: 1.2%; R1: 1.2%; R2: 4%; R3: 1%; R4: 0.6%	
	Fraction of OC in sediment solids	0.05	

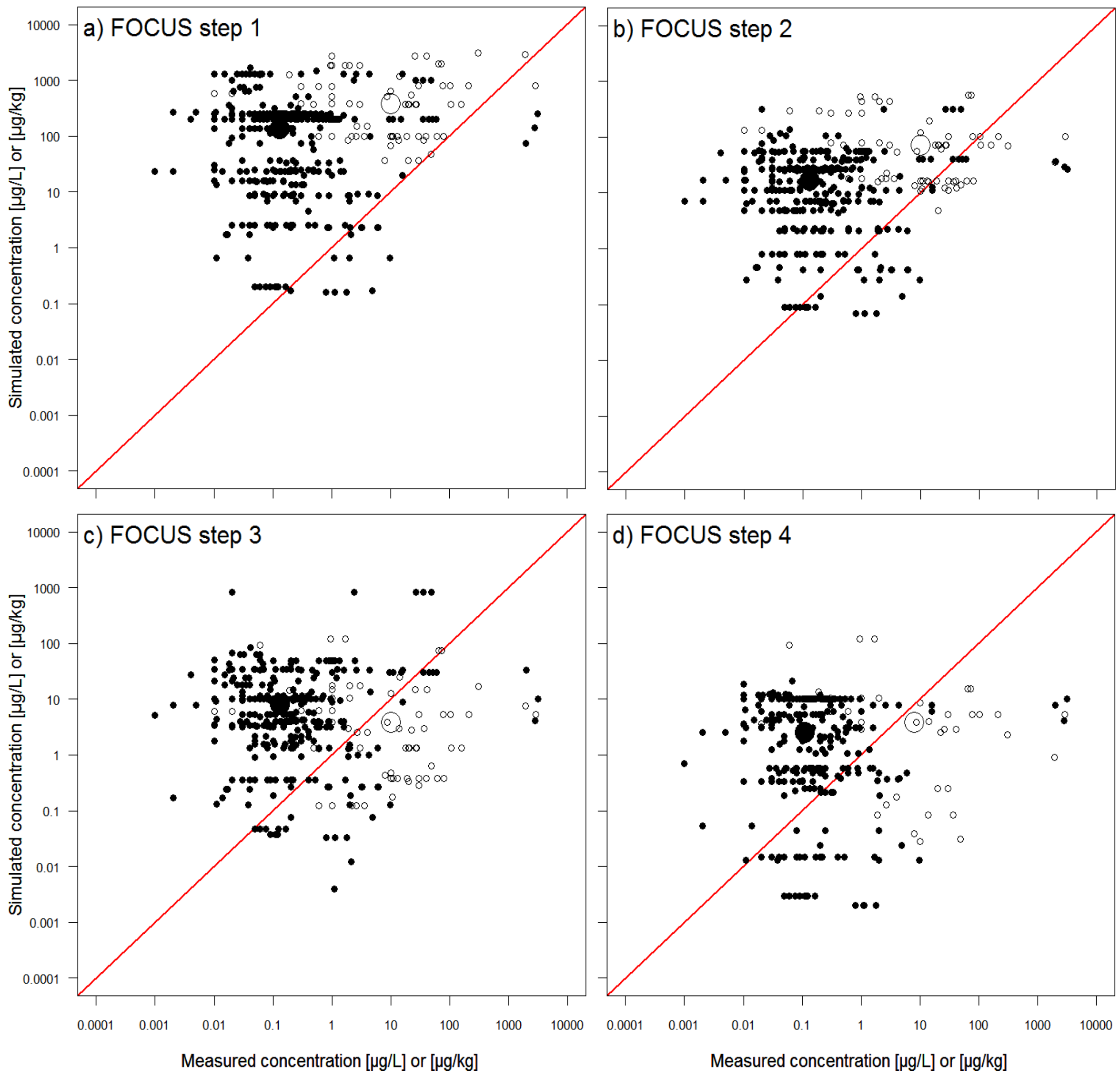

Figure S1. Relationship between simulated and measured insecticide concentrations from E.U. studies for FOCUS steps 1-4. Black dots = water (step 1-3: n = 397; step 4: n = 322); white dots = sediment (step 1-3: n = 69; step 4: n = 43); large dot = overall median surface water concentration, large circle = overall median sediment concentration. The 45° line denotes identity between PEC and MFC. The simulated concentrations are displayed on the y-axis such that the MFC underestimations are plotted below the 45° line.

Table S3. Over- and underpredictions from FOCUS step 1-4 simulations for agricultural insecticides measured in Europe (complete dataset).

	surface water			sediment		
FOCUS tiers	n	overprediction PEC > MFC, %	underprediction PEC < MFC, %	n	overprediction PEC > MFC, %	underprediction PEC < MFC, %
Step 1	397	96	4	69	97	3
Step 2	397	91	9	69	74	26
Step 3	397	89	11*	69	39	61
Step 4	322	80	20	43	42	58

[a] PEC = predicted environmental concentration; MFC = measured field concentration; *one concentration was exactly predicted

Table S4. Over- and underpredictions from FOCUS step 1-4 standard, FOCUS step 3 realistic, SRM standard, and SRM realistic simulations for agricultural insecticides currently approved under EC regulation 1107/2009 measured in Europe

	surface water			sediment		
FOCUS tiers	n	overprediction PEC > MFC, %	underprediction PEC < MFC, %	n	overprediction PEC > MFC, %	underprediction PEC < MFC, %
Step 1	102	97	3	34	94	6
Step 2	102	93	7	34	71	29
Step 3	102	91	9	34	35	65
Step 3 realistic	17	35	65	3	33	67
Step 4	75	71	29	9	33	67
SRM	102	99	1	34	36	74
SRM realistic	28	92	8	3	0	100

[a] PEC = predicted environmental concentration; MFC = measured field concentration

Table S5. Over- and underpredictions from FOCUS step 1-4 standard, FOCUS step 3 realistic, SRM standard, and SRM realistic simulations for the 90th percentile concentration per substance and study and only for insecticide concentrations which are definitely agricultural origin

	surface water		
FOCUS tiers	n	overprediction PEC > MFC, %	underprediction PEC < MFC, %
Step 1	66	86	14
Step 2	66	77	23
Step 3	66	74	26
Step 3 realistic	14	40	60
Step 4	51	67	33
SRM	66	98	2
SRM realistic	16	81	19

[a] PEC = predicted environmental concentration; MFC = measured field concentration

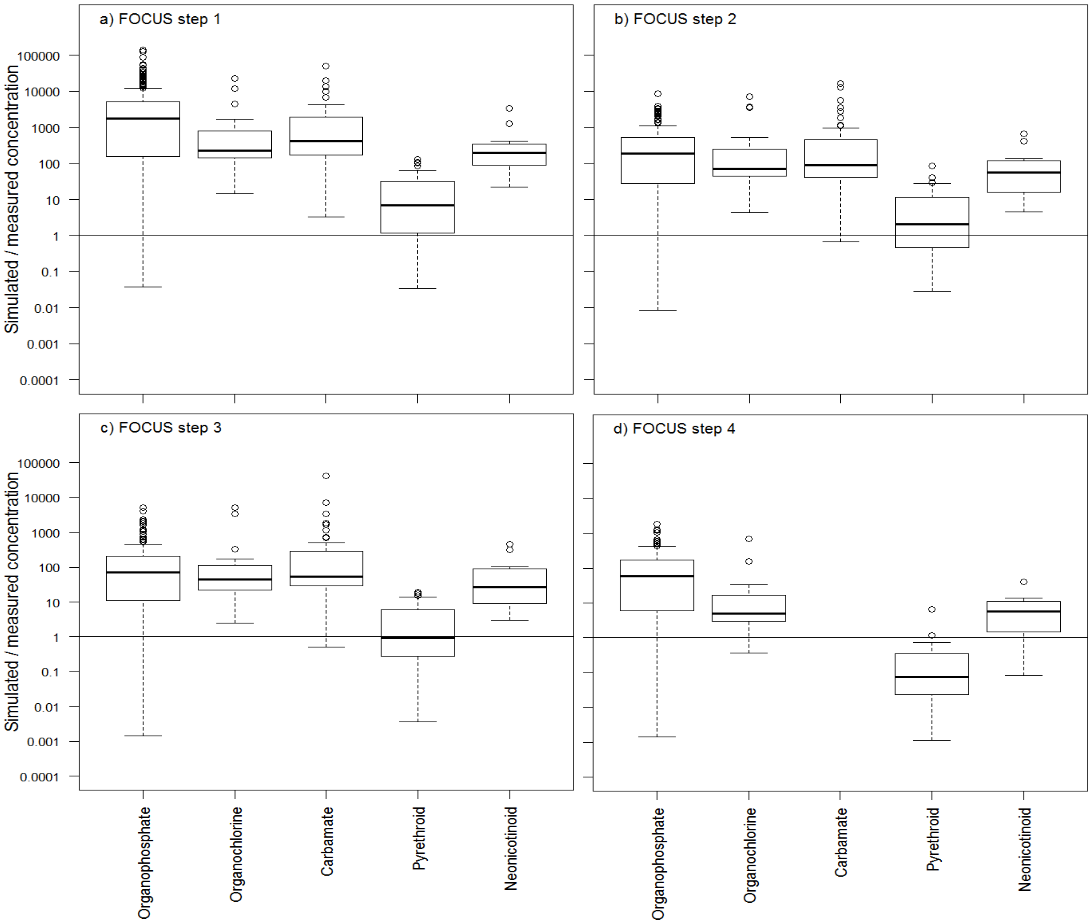

Figure S2. Boxplots of simulated to measured concentration ratios in the water phase for different insecticide classes for all FOCUS steps. No step 4 calculations has been conducted for carbamate insecticides. (Step 1-3: pyrethroids: n = 58; neonicotinoids: n = 15; organochlorines: n = 54; organophosphate: n = 210, carbamate: n = 60; Step 4: pyrethroids: n = 43; neonicotinoids: n = 15; organochlorines: n = 54; organophosphates: n = 210).

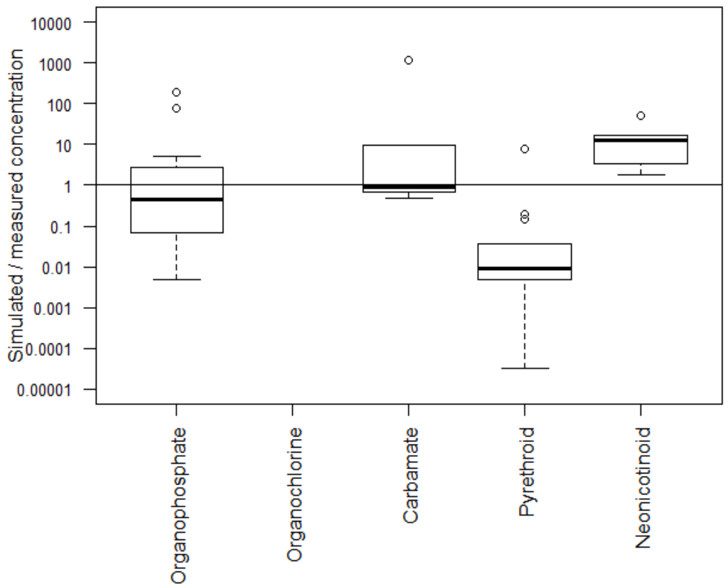

Figure S3. Boxplots of simulated to measured concentration ratios in the water phase for different insecticide classes for FOCUS step 3 realistic calculations. No calculations has been conducted for organochlorine insecticides. (pyrethroids: n = 13; neonicotinoids: n = 5; organophosphates: n = 24; carbamates: n = 5).

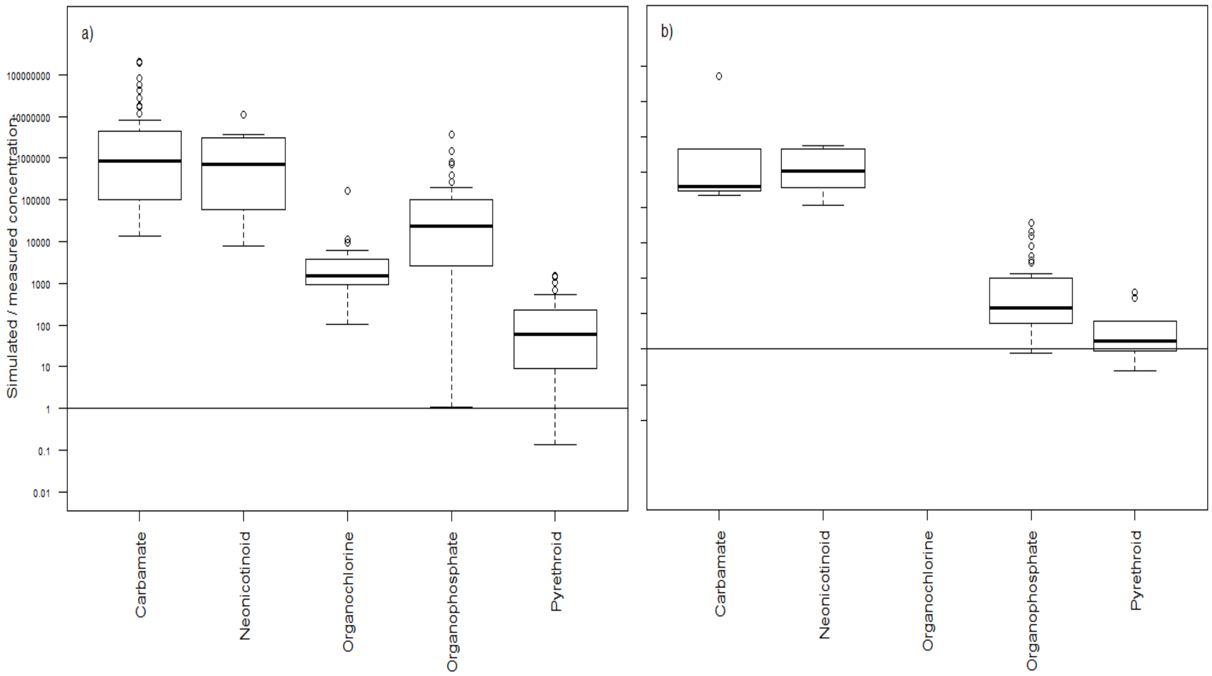

Figure S4. Boxplots of simulated to measured concentration ratios in the water phase for different insecticide classes for a) SRM standard and b) SRM realistic. No SRM realistic calculations has been conducted for organochlorine insecticides. (SRM standard: pyrethroids: n = 58, neonicotinoids: n = 54, organochlorines: n = 54, organophosphates: n = 210, carbamates: n = 60; SRM realistic: pyrethroids: n = 13, neonicotinoids: n = 5, organophosphates: n = 40, carbamates: n = 5)

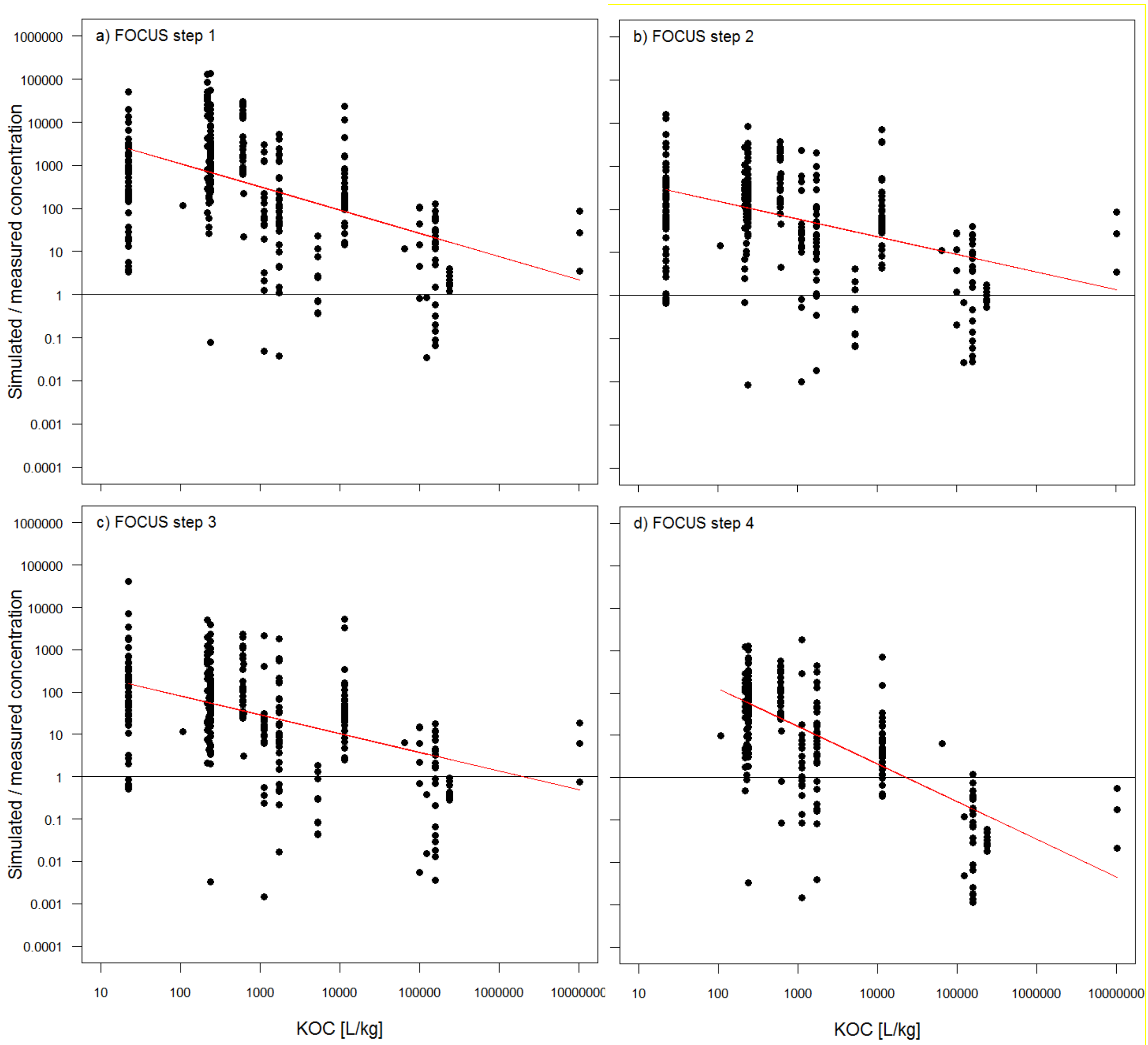

Figure S5. Relationship between simulated to measured concentration ratios in the water phase and substances K_{OC} for all FOCUS steps. Red lines shows linear regression between simulated to measured concentration ratios and substance K_{OC} (Step 1: $p < 0.001$; $r^2 = 0.25$; Step 2:$p < 0.001$; $r^2 = 0.19$; Step 3: $p < 0.001$; $r^2 = 0.21$, Step 4:$p < 0.001$; $r^2 = 0.49$).

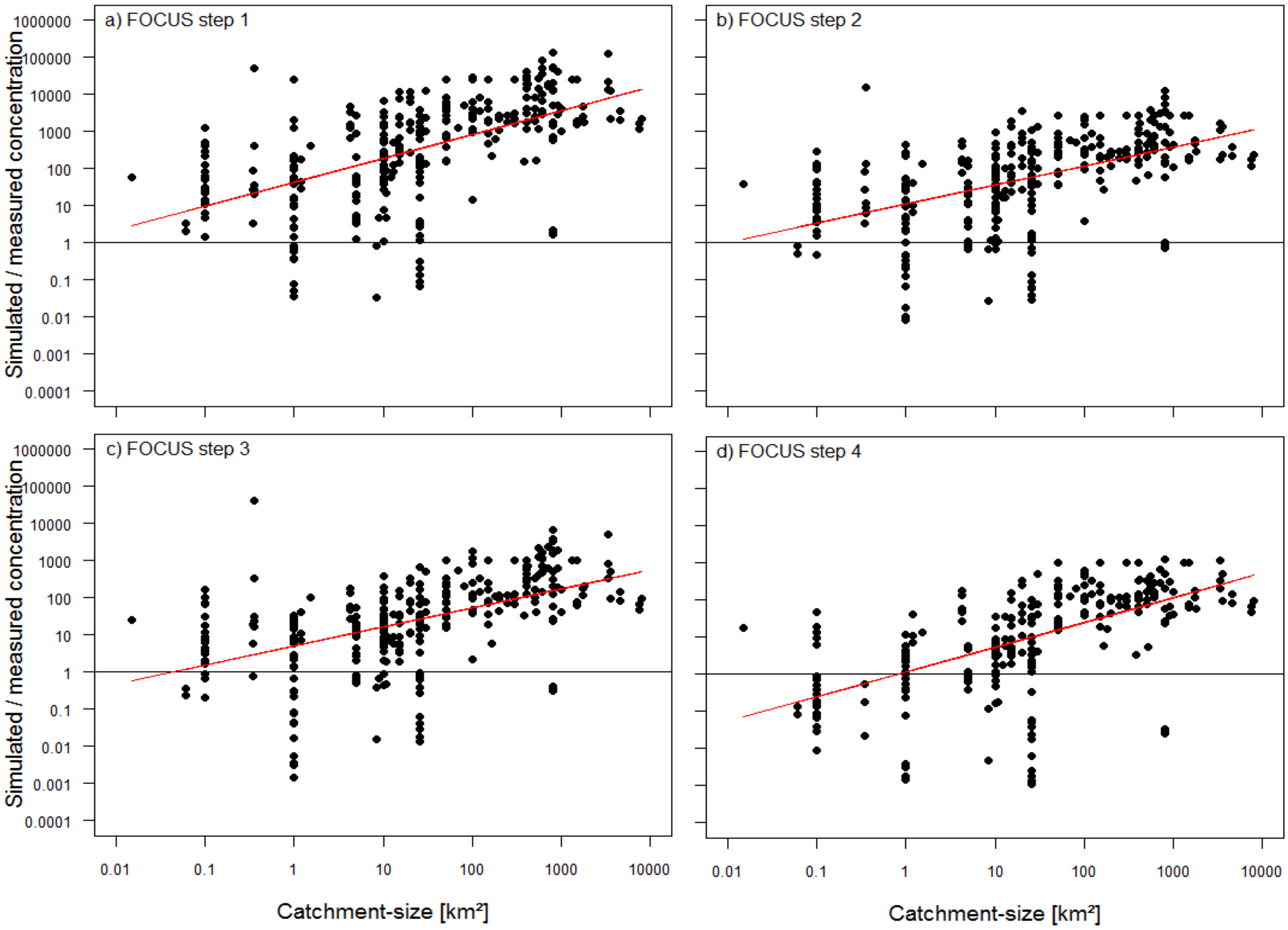

Figure S6. Relationship between simulated to measured concentration ratios in the water phase and catchment-size for all FOCUS steps Red lines shows linear regression between simulated to measured concentration ratios and catchment-size (step 1-3: n = 341; step 4: n = 282; Step 1: $p < 0.001$, $r^2 = 0.34$; Step 2: $p < 0.001$, $r^2 = 0.29$; Step 3: $p < 0.001$, $r^2 = 0.28$; Step 2: $p < 0.001$, $r^2 = 0.37$).

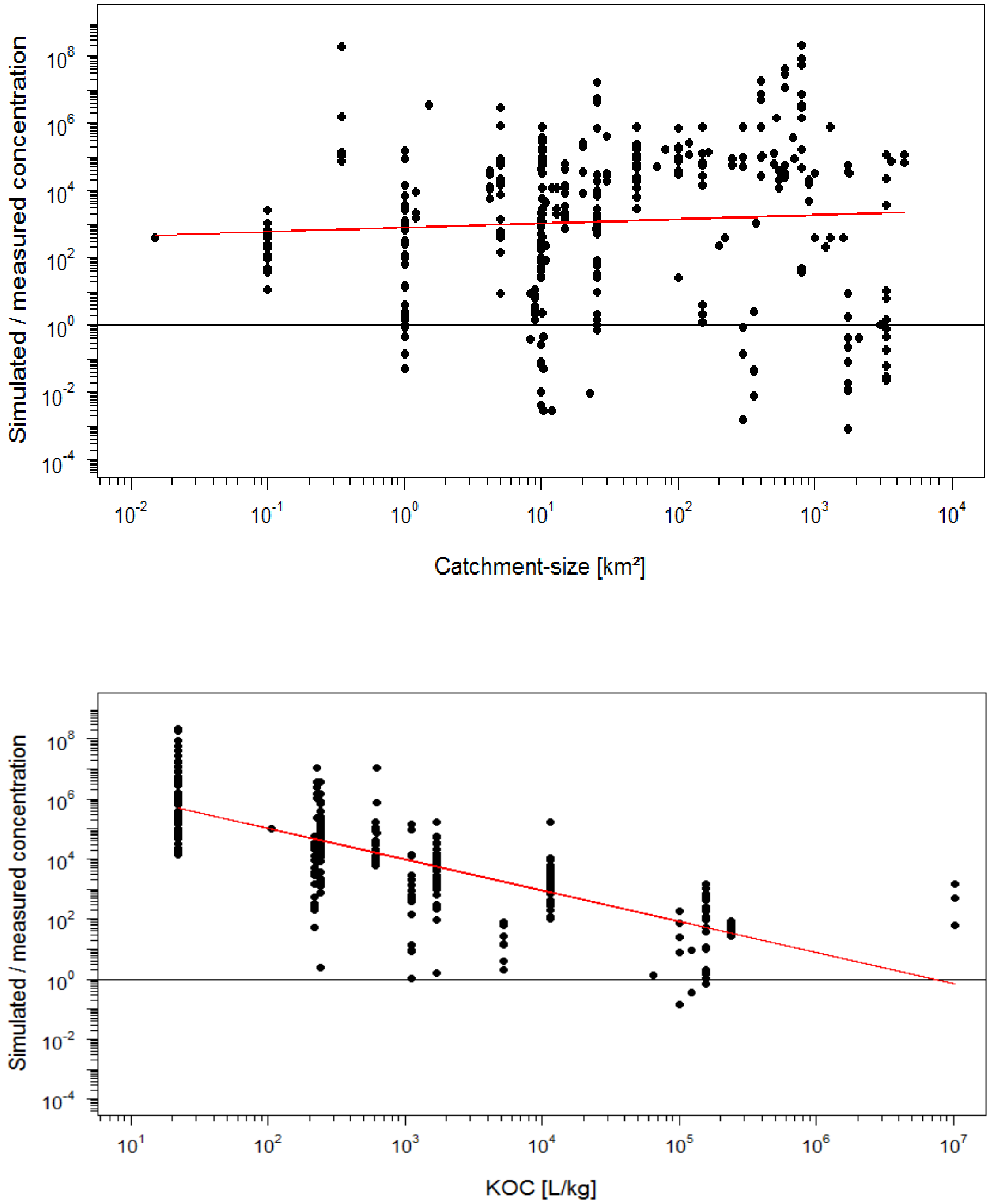

Figure S7. Relationship between simulated to measured concentration ratios in the water phase and a) catchment size b) substances K_{OC} and for concentrations calculated with SRM. (K_{OC}: $p < 0.001$; $r^2 = 0.55$, Catchment size: $p = 0.2246$, $r^2 = 0.001$)

Table S6. Results of multiple linear regression analyses (main effect model and full model including interactions) for predicting logarithmic water phase step 3 PEC_{FOCUS} to MFC ratio.

	Multiple R2	Predictors	Estimate (B)	Std.Error (SE B)	beta	T-value	P-value	
Main effect model	0.3986	Intercept	4.67391	0.44492		10.505	< 0.001	***
		log(Catchment-size)	0.16322	0.06641	0.1739713	2.458	0.01	*
		log(KOC)	-0.34711	0.05016	-0.3566973	-6.92	< 0.001	***
		log(Sampling-interval)	0.19467	0.04955	0.2608133	3.928	< 0.001	***
Interaction (both directions)	0.4964	Intercept	3.09546	0.49092		6.305	< 0.001	***
		log(Catchment-size)	1.22556	0.20718	1.30625545	5.915	< 0.001	***
		log(KOC)	-0.18041	0.05627	-0.18539563	-3.206	0.002	**
		log(Sampling-interval)	-0.02814	0.16389	-0.03770158	-0.172	0.864	
		log(Catchment-size) x log(KOC)	-0.1536	0.02844	-0.1637124	-5.401	< 0.001	***
		log(KOC) x log(Sampling interval)	0.03231	0.02273	0.03319774	1.421	0.156	

Table S7. Results of multiple linear regression analyses (main effect model and full model including interactions) for predicting logarithmic water phase PEC_{SRM} to MFC ratio.

	Multiple R2	Predictors	Estimate (B)	Std.Error (SE B)	beta	T-value	P-value	
Main effect model	0.5889	Intercept	14.50841	0.51476		28.185	< 0.001	***
		log(Catchment-size)	0.05605	0.07683	0.04269254	0.73	0.5	
		log(KOC)	-0.8839	0.05803	-0.64912956	-15.231	< 0.001	***
		log(Sampling-interval)	0.22649	0.05733	0.21686072	3.951	< 0.001	***
Interaction (both directions)	0.6551	Intercept	13.821702	0.686877		20.123	< 0.001	***
		log(Catchment-size)	0.787015	0.268323	0.59947477	2.933	0.004	**
		log(KOC)	-0.860983	0.091265	-0.63230113	-9.434	< 0.001	***
		log(Sampling-interval)	0.459555	0.232508	0.44001732	1.977	0.05	*
		log(Catchment-size) x log(KOC)	-0.106461	0.034619	-0.08109174	-3.075	< 0.001	***
		log(Catchment-size) x log(Sampling-interval)	-0.0761	0.067986	-0.05588753	-1.119	0.3	
		log(KOC) x log(Sampling interval)	-0.035771	0.030387	-0.03425023	-1.177	0.2	
		log(Catchment-size) x log(KOC) x log(Sampling-interval)	0.013839	0.009777	0.01054139	1.416	0.2	

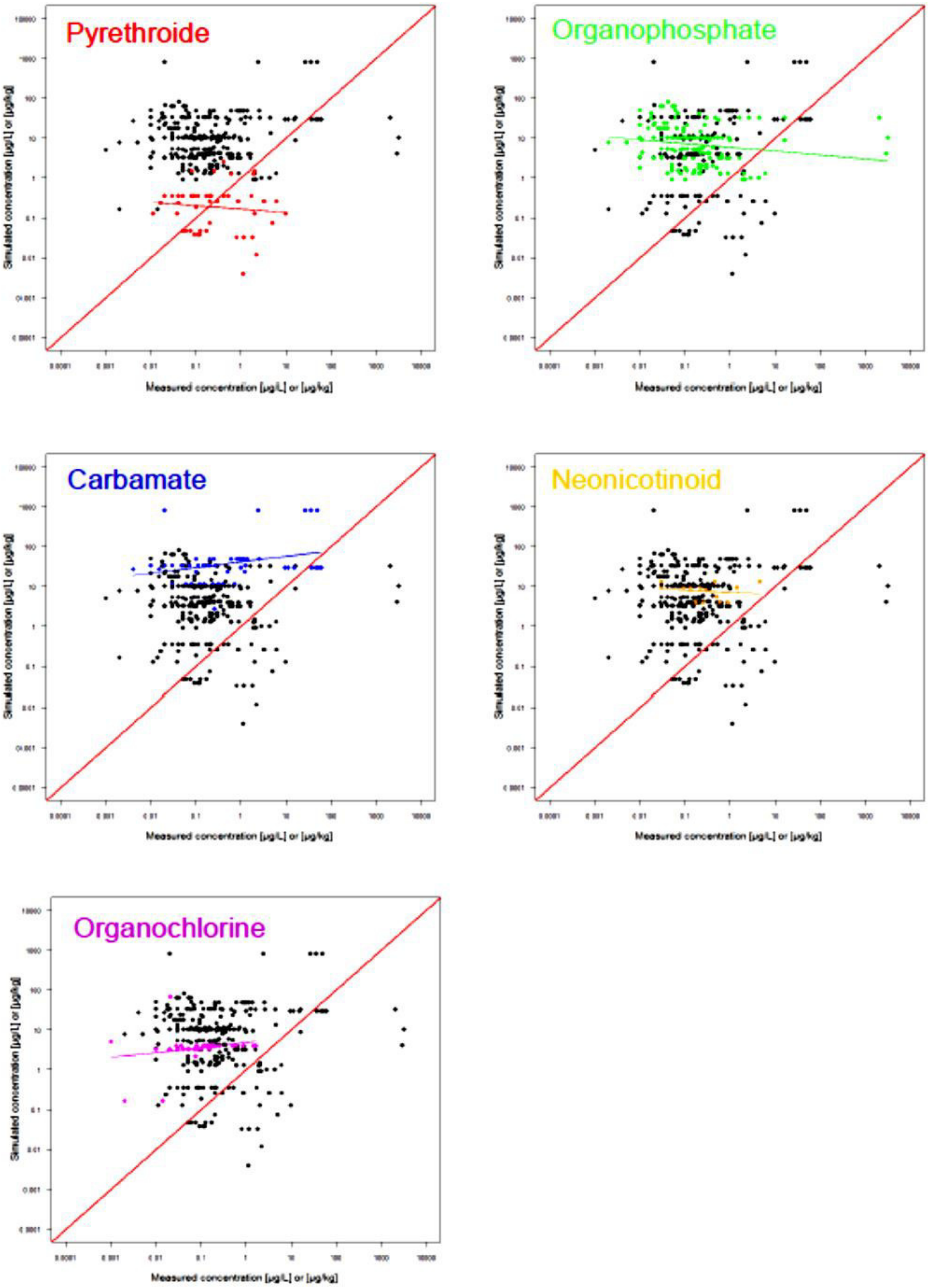

Figure S8. Relationship between simulated and measured insecticide concentrations from E.U. studies for FOCUS step 3 standard calculations for individual substance classes (pyrethroids: n = 58; neonicotinoids: n = 15; organochlorines: n = 54; organophosphate: n = 210, carbamate: n = 60). The 45° line denotes identity between PEC and MFC. Coloured lines shows linear regression between simulated and measured concentration (pyrethroide: $p = 0.4$, $r^2 = 0.014$; organophosphate: $p = 0.009$, $r^2 = 0.032$; carbamate: $p = 0.016$, $r^2 = 0.096$; neonicotinoid: $p = 0.6$, $r^2 = 0.018$; organochlorine: $p = 0.07$; $r^2 = 0.064$).The simulated concentrations are displayed on the y-axis such that the MFC underestimations are plotted below the 45° line.

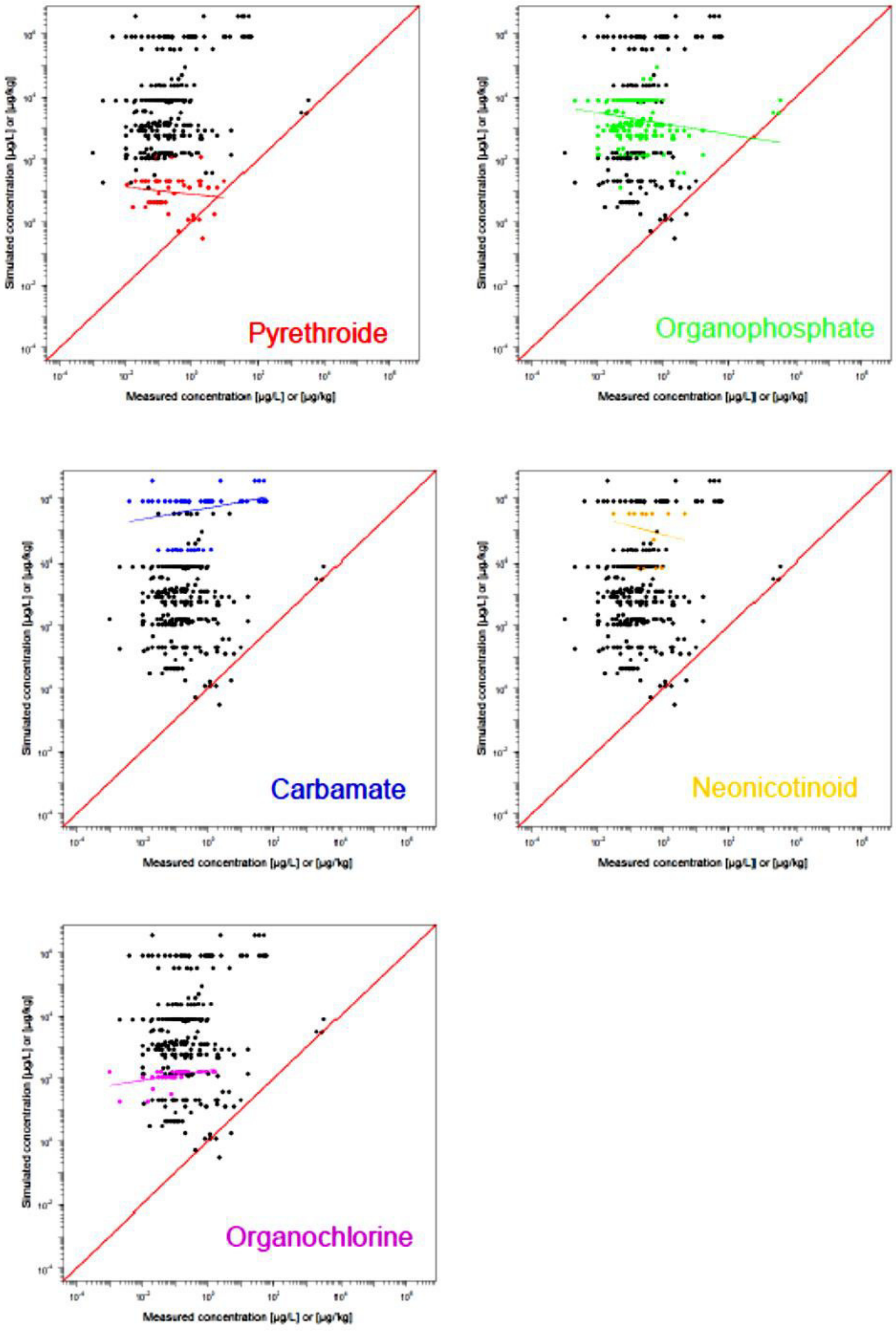

Figure S9. Relationship between simulated and measured insecticide concentrations from E.U. studies for SRM standard calculations for individual substance classes (pyrethroids: n = 58; neonicotinoids: n = 15; organochlorines: n = 54; organophosphate: n = 210, carbamate: n = 60). The 45° line denotes identity between PEC and MFC. Coloured lines shows linear regression between simulated and measured concentration (pyrethroide: $p = 0.22$, $r^2 = 0.003$; organophosphate: $p = 0.002$, $r^2 = 0.046$; carbamate: $p = 0.08$, $r^2 = 0.031$; neonicotinoid: $p = 0.5$, $r^2 = 0.05$; organochlorine: $p < 0.001$; $r^2 = 0.024$).The simulated concentrations are displayed on the y-axis such that the MFC underestimations are plotted below the 45° line.

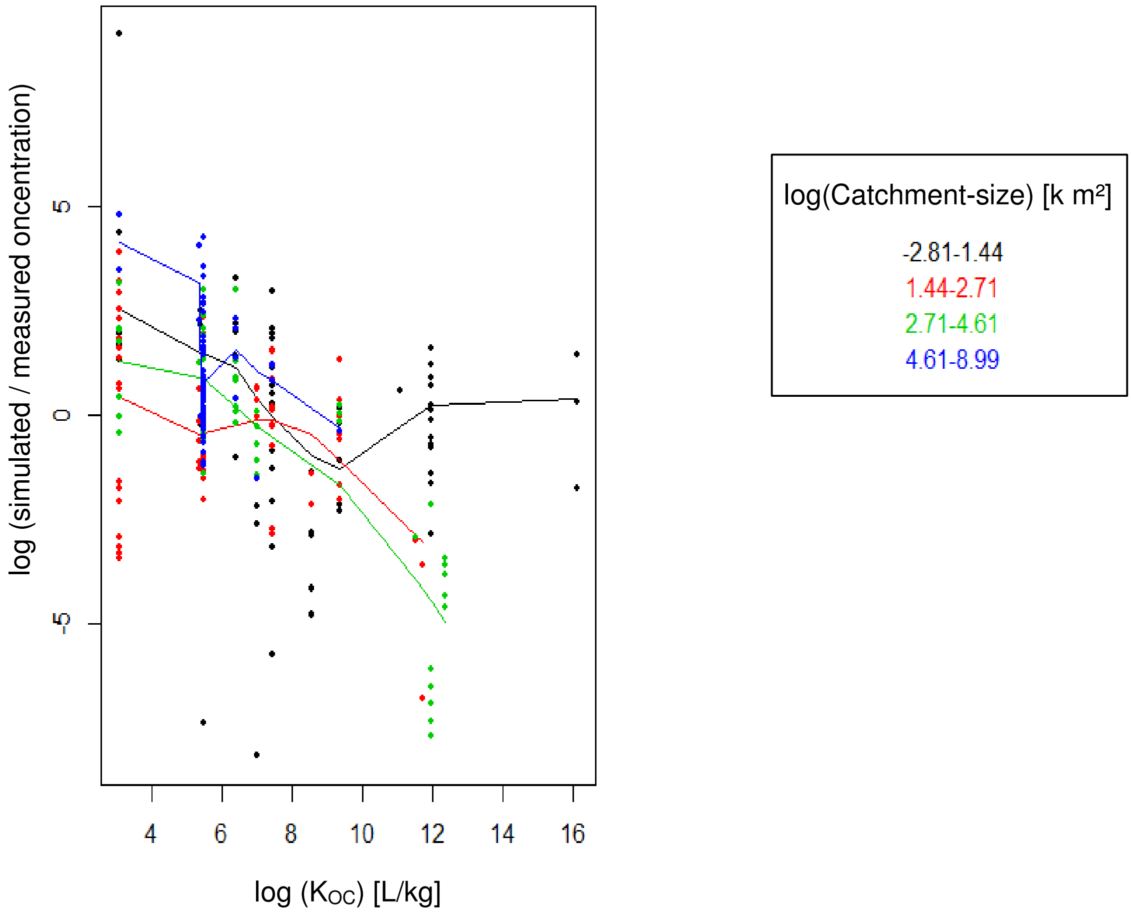

Figure S10. Two-way interaction among logarithmic KOC, logarithmic field study catchment-size (different colours indicates different catchment-sizes) versus logarithmic FOCUS step 3 predicted to measured concentration ratio.

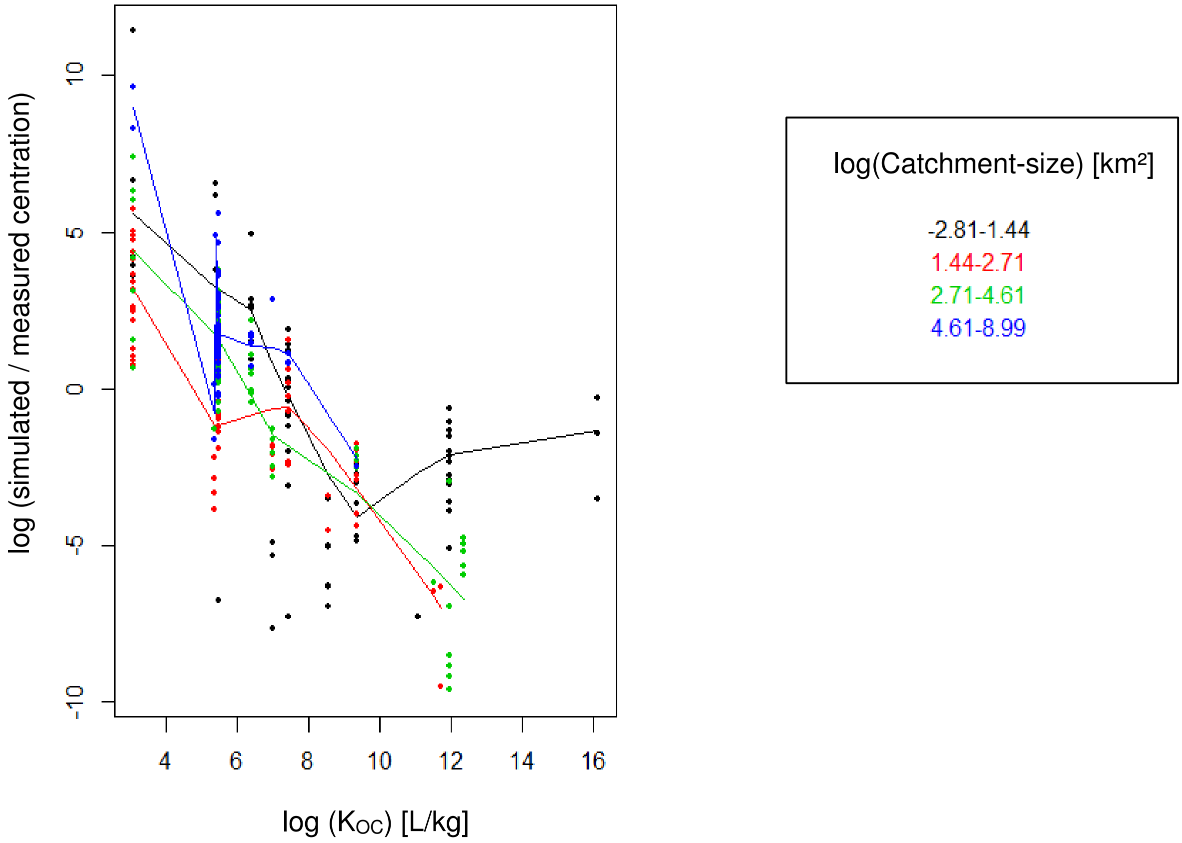

Figure S11. Two-way interaction among logarithmic KOC, logarithmic field study catchment-size (different colours indicates different catchment-sizes) versus logarithmic SRM predicted to measured concentration ratio.

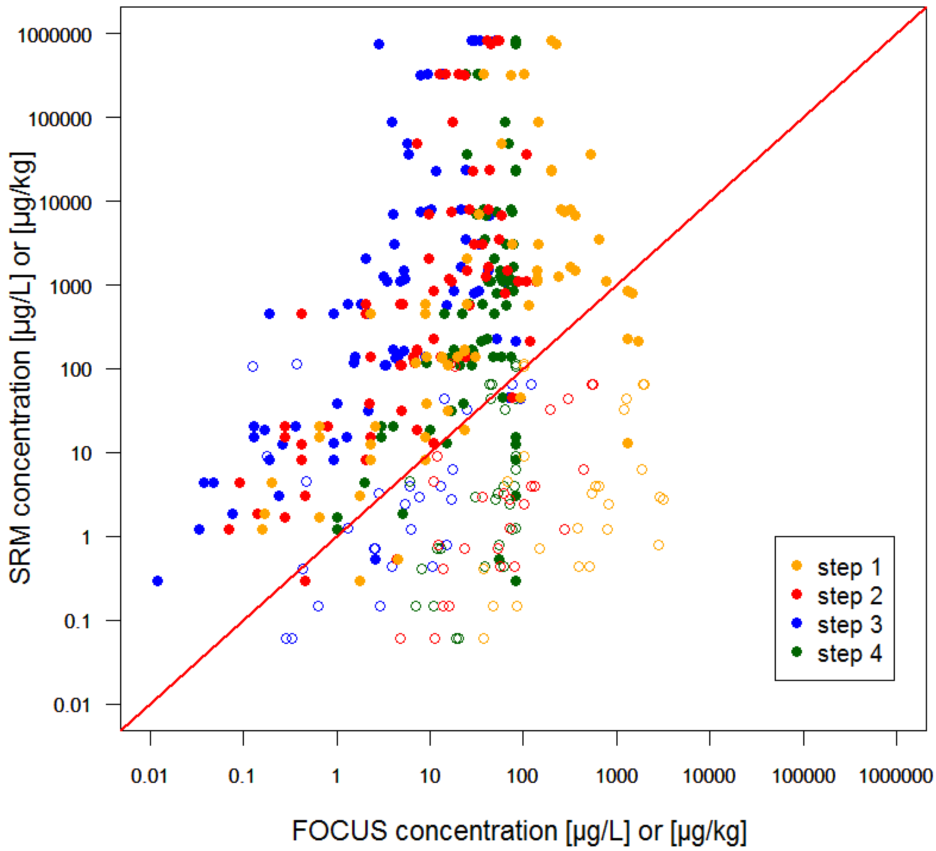

Figure S12. Relationship between concentrations calculated with FOCUS and SRM for all (n = 60) from E.U. studies for the Small region model adapted to the field study conditions. Coloured dots = water (step 1-3: n = 397; step 4: n = 322); coloured circles = sediment (step 1-3: n = 69; step 4: n = 43). The 45° line denotes identity between calculated concentrations. Linear regression: Step1: $p < 0.001$, $r^2 = 0.5346$; Step2: $p < 0.001$, $r^2 = 0.6587$; Step3: $p < 0.001$, $r^2 = 0.651$; Step4: $p < 0.001$, $r^2 = 0.597$.

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Appendix IV

- Stehle, S.; Knäbel, A.; Schulz, R. (2013) Probabilistic Risk Assessment of Insecticide Concentrations in Agricultural Surface Waters: A Critical Appraisal. *Environmental Monitoring and Assessment*, 185, 6295-6310.
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Probabilistic risk assessment of insecticide concentrations in agricultural surface waters: a critical appraisal

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Abstract Due to the specific modes of action and application patterns of agricultural insecticides, the insecticide exposure of agricultural surface waters is characterized by infrequent and short-term insecticide concentration peaks of high ecotoxicological relevance with implications for both monitoring and risk assessment. Here, we apply several fixed-interval strategies and an event-based sampling strategy to two generalized and two realistic insecticide exposure patterns for typical agricultural streams derived from FOCUS exposure modeling using Monte Carlo simulations. Sampling based on regular intervals was found to be inadequate for the detection of transient insecticide concentrations, whereas event-triggered sampling successfully detected all exposure incidences at substantially lower analytical costs. Our study proves that probabilistic risk assessment (PRA) concepts in their present forms are not appropriate for a thorough evaluation of insecticide exposure. Despite claims that the PRA approach uses all available data to assess exposure and enhances risk assessment realism, we demonstrate that this concept is severely biased by the amount of insecticide concentrations below detection limits and therefore by the sampling designs. Moreover, actual insecticide exposure is of almost no relevance for PRA threshold level exceedance frequencies and consequential risk assessment outcomes. Therefore, we propose a concept that features a field-relevant ecological risk analysis of agricultural insecticide surface water exposure. Our study quantifies for the first time the environmental and economic consequences of inappropriate monitoring and risk assessment concepts used for the evaluation of short-term peak surface water pollutants such as insecticides.

Keywords Insecticides · Surface water exposure · Monitoring · Risk assessment

Introduction

Insecticide surface water exposure and consequences for monitoring

Due to their global use and intentional release into the environment, agricultural pesticides have been shown to regularly enter aquatic ecosystems (Schwarzenbach et al. 2006; Schulz 2004). In general, pesticides are characterized by a complex input dynamic, i.e., their release into surface waters is usually coupled to rain events and seasonal use, which results in a discontinuous and complex exposure pattern (Götz et al. 2010; Rabiet et al. 2010). Herbicides and fungicides have relatively slow modes of action and thus must persist in the environment for longer time periods to act against their respective pests. Therefore, these

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pesticides are used at comparably high application rates with several consecutive applications per season. In contrast, insecticides often show fast modes of action (Yu 2008) and thus do not need to persist in the environment to be effective against target organisms. This, in combination with the fact that their intrinsic toxicities are often very high (Schäfer et al. 2011; Schulz 2004), leads to discrete insecticide applications at comparably low rates. Concerning exposure and associated risks for aquatic ecosystems, these low application rates, accompanied by short field half lives and high K_{OC} values, result in infrequent and very short-term (i.e., a few hours) exposure events (Spurlock et al. 2005; Kreuger 1995). However, even in surface waters, which may be considered high-risk sites, a single transient insecticide surface water concentration can cause substantial adverse ecological effects (Schulz 2001b; Schulz and Liess 1999; Schulz 2004). When focusing on the ecological risk of agricultural insecticides use, particularly small headwater streams (e.g., catchment areas <100 km^2) may be at risk of pollution, as they have close proximities and huge connectivities with surrounding agricultural areas and limited dilution potentials (Karaouzas et al. 2011; Schulz 2004). All of these specific characteristics and watershed scale effects have to be taken into account when insecticide exposure and risk are evaluated using monitoring data. Static fixed-interval and fixed-station governmental monitoring programs are rather unspecific (Holvoet et al. 2007; House 1994) and tend to emphasize the importance of regularly occurring chemical stressors, such as nutrients and herbicides. They may thus underrate the exposure and risk of rare but potentially toxic contaminants such as insecticides. To overcome these serious shortcomings, Liess and Schulz (2000) and Schulz (2004) noted that the very specific insecticide exposure dynamics, which are driven mainly by distinct rainfall-, irrigation-, and application-related short-term entry events, need to be monitored using an event-triggered sampling design. This is in accordance with Strobl and Robillard (2008), who stated that sampling strategies have to be primarily oriented toward the expected variability of the quality of the water being examined.

Insecticide risk assessment approaches

During regulatory pesticide registration procedures, exposure models are used to predict environmental concentrations, which are subsequently compared to regulatory acceptable concentrations (RACs) using deterministic or probabilistic approaches (U.S. EPA 2011; DG SANCO 2002). However, when a pesticide has been in use, instead of modeling environmental concentrations, actual measured values from monitoring programs can be used for a deterministic or probabilistic risk evaluation. The deterministic risk assessment (DRA) of insecticide monitoring data (e.g., Iwafune et al. 2011; Jergentz et al. 2005; Karaouzas et al. 2011) is performed by comparing a point estimate of exposure to a threshold level within a hazard quotient (HQ) approach. This risk evaluation concept is rather simplified and not conclusive, as usually only the highest exposure incidence is assessed, whereas the full range of insecticide concentrations remains unconsidered (Solomon et al. 2000).

In contrast, probabilistic risk assessment (PRA) approaches focus on the frequencies or likelihoods of insecticide exposure incidences to exceed a specific threshold level (e.g., the RAC) by incorporating both variability and uncertainty into risk estimates. In detail, compilations of insecticide concentrations are used to derive a cumulative frequency distribution, which intentionally includes monitoring values below the limit of detection (LOD) (Solomon et al. 2000). Such PRA methods rapidly gained acceptance and have been used for the ecological risk assessment of insecticide surface water concentrations by several researchers (e.g., Giddings et al. 2000; Hall 2003) and regulatory agencies (e.g., Starner et al. 2011; Spurlock 2002) over the past decade. However, despite being more comprehensive, concerns were raised that probabilistic monitoring data evaluation approaches may yield misleading results if inappropriate data are included (Hart 2001). Here, we evaluate whether PRA methods are adequate for a thorough risk assessment of insecticide monitoring data by applying these to generalized and realistic insecticide exposure data.

The following three objectives were addressed:

(a) The derivation of two generalized and two realistic insecticide exposure patterns for small agricultural surface waters and their verification using real-world field studies
(b) The implications of insecticide exposure pattern characteristics for different sampling strategies commonly used in monitoring campaigns
(c) The consequences arising from insecticide exposure patterns in agricultural surface waters for

their environmental risk assessment using monitoring data and PRA, DRA, and relevance-driven risk assessment (RRA) concepts

Materials and methods

Derivation of a typical model insecticide and selection of real insecticides

A typical “model insecticide” was specified that typifies the median physicochemical properties, application rates, acute ecotoxicity, and LOD of all synthetic insecticide compounds (n=50, comprising 20 insecticide classes) currently listed on Annex I of the 91/414/EEC EU Pesticide Directive (DG SANCO 2008) (see Table S1 in electronic supplementary material (ESM) for all model insecticide parameters). Therefore, median values of physicochemical properties retrieved from the Footprint pesticide properties database (PPDB 2011) and official pesticide registration documents for all 50 synthetic insecticide compounds were calculated. In addition, the organophosphorous insecticide malathion, the neonicotinoid acetamiprid, and the pyrethroid deltamethrin were selected as examples of real insecticide compounds. These three compounds cover the three most important insecticide classes (Wirtz et al. 2009), are currently approved for and highly used in European (DG SANCO 2008) and US agriculture (Gianessi and Reigner 2006), and cover a wide range of physicochemical properties and application rates (see Table S1, ESM), which are important in determining the pesticide exposures of surface water systems (FOCUS 2001).

We derived a conservative RAC for the model insecticide and the three real compounds by calculating Tier I Uniform Principle (UP) criteria, which are commonly used for the ecotoxicological evaluation of insecticide monitoring data (e.g., Schäfer et al. 2012). In detail, the median EC_{50} (*Daphnia magna*) value retrieved from the Footprint pesticide properties database (PPDB 2011) for the 50 insecticide compounds listed on Annex I and the actual toxicity values for the three real insecticide compounds were divided by a safety factor of 100 (DG SANCO 2002; Table S1, ESM). The RAC, which is defined as part of the legal pesticide registration procedure, describes a concentration level that must not be exceeded to exclude adverse environmental effects (Brock et al. 2006). In addition, a representative LOD for the model insecticide was obtained by calculating the median value of all detection limits for insecticide compounds (n=22) analyzed in the USGS NAWQA monitoring campaign (Gilliom et al. 2006). This median LOD was in good accordance with LOD values typically observed for different insecticide compounds in monitoring campaigns (e.g., Pichon et al. 1998; Lepom et al. 2009). As no LOD values were available in the work of Gilliom et al. (2006) for deltamethrin and acetamiprid, the calculated median value was also used for these insecticides, whereas the actual LOD reported by Gilliom et al. (2006) was used for malathion (Table S1, ESM).

FOCUS simulations

Two generalized and two realistic insecticide exposure patterns were simulated for arable and permanent crops using the standardized forum for the coordination of pesticide fate models and their use (FOCUS) modeling approach for surface waters in Europe, which considers all non-point source entry routes (i.e., spray drift, runoff, drainage) potentially resulting in the exposure of surface waters to insecticides (FOCUS 2001). Predicted environmental concentrations (PECs) induced by spray drift during pesticide application or rainfall events were calculated using the FOCUS step 3 “realistic worst-case” surface water scenarios (FOCUS 2001) and the physicochemical properties of the model and the three real insecticides (Table S1, ESM). For arable crops, model and realistic insecticide PECs were simulated for eight model years using four out of six drainage scenarios (D1, D2, D4, and D5) and all runoff scenarios (R1–R4). Drainage scenarios D3 and D6 were excluded because no streams are associated with these scenarios. Concerning permanent crops, PECs were simulated for six model years using all available FOCUS stream scenarios, i.e., D4, D5, and R1–R4. We focused here on small streams (e.g., catchment areas <100 km^2), as these are by far the most abundant streams in Europe (European Environment Agency 2007) and the USA (Allan and Castillo 2007) and they are the most vulnerable to agricultural non-point source pollution (Schulz 2004; Karaouzas et al. 2011). In addition, the PECs calculated by FOCUS for streams included pesticide exposure from a 20-ha field in the upstream catchment, considerably increasing the field relevance and realism of the exposure simulations (FOCUS 2001).

For arable crops, winter cereals were selected as crops in the four drainage scenarios, and maize was selected in the four runoff scenarios, while pomes (apples) were chosen for the FOCUS drainage and runoff scenarios for permanent crops. The selection of all crops was based on (a) their importance for European agriculture in terms of cultivated area, as cereals and maize are the two most important arable crops and pomes are the second most important permanent crop (Eurostat 2007); (b) their importance in terms of insecticide use in European agriculture, as cereals, maize, and pomes require the highest volumes of insecticide among arable and permanent crops, respectively (European Commission 2000); and (c) the associations of crops and scenarios, as winter cereal is the only crop selectable for all drainage scenarios, maize is the most important arable crop available for all runoff scenarios, and most FOCUS scenarios for permanent crops are available for pomes (FOCUS 2001). The model insecticide application rates for winter cereals, maize, and pomes were extracted from Eurostat (2007) for the years 1992 to 2003 (see Table S1, ESM). However, as the amount of insecticides applied to cereals was only specified as <0.1 kg a.i./ha for each year, a conservative average of 0.09 kg a.i./ha was used for FOCUS calculations. With regard to malathion and acetamiprid, application rates for the different crops were obtained from official EU and US EPA pesticide registration documents, while those for deltamethrin were obtained from the official product label. The model insecticide was applied three times per growing season to winter cereals and maize and six times to pomes in each scenario. For malathion, acetamiprid, and deltamethrin, one application to winter cereals and maize (in total, three applications per season) and two to pomes (in total, six applications per season) were simulated. All insecticide application dates, intervals, and numbers were selected to be representative for real agricultural insecticide use (Ewald and Aebischer 2000; Schulz and Liess 1999; Süss et al. 2006).

Data aggregation, derivation, and verification of generalized and realistic insecticide exposure patterns

The results of the FOCUS calculations were combined into two generalized insecticide exposure patterns using the model insecticide results for arable and permanent crops to generate representative insecticide exposure patterns not influenced by individual compound properties. In addition, we synthesized two realistic insecticide exposure patterns using FOCUS simulation results for the application of the three real compounds to arable and permanent crops. In detail, the average application dates, the average number of days with PECs > LOD per year, the associated exposure durations (hourly resolution), and the average concentration heights, as well as the average exposure dates relative to the application dates, were calculated from the respective scenarios and model years for arable and permanent crops. Subsequently, we merged all these data into four synthesis graphics to create generalized and realistic annual insecticide exposure patterns for arable and permanent crops and a typical agricultural stream. Furthermore, ecotoxicological evaluations of these insecticide exposure profiles were performed by comparing aggregated concentrations to the RACs of the model insecticide and real compounds.

Evaluation of different sampling strategies

We reviewed 56 US governmental monitoring reports and compiled information on typical sampling strategies most frequently used for regulatory insecticide monitoring (see Table S2 in ESM). As a result, 97 % of the 2,775 measured insecticide concentrations were sampled using one of the following six sampling intervals: event-based sampling, daily, 3.5 days, weekly, 14 days, and monthly. Subsequently, these sampling intervals were applied to the generalized and realistic insecticide exposure patterns synthesized from FOCUS stream scenarios using Monte Carlo simulations (Crawford 2004). A program written in R (www.r-project.org; version 2.11.1 (R 2011)) was used to randomly sample from the population of model insecticide concentrations using the fixed monthly, 14 days, weekly, and 3.5-day sampling intervals. The date of the first sample in the first sampling period (e.g., first month, first week, etc.) to be taken in the model year was selected randomly using the R-function "sample()" (sampling of a random number with replacement). Subsequent samples were drawn at approximately fixed intervals. The exact intervals were allowed to vary randomly within a specified amount of time to simulate the variability inherent in water quality sampling programs because of logistic restrictions. The variations ranged from 1 day for weekly sampling up to 3 days for monthly sampling (14-day interval: ±2 days;

3.5-day interval: random sequence of 3- or 4-day intervals). A total of 100,000 Monte Carlo simulations were run for each of these sampling strategies, and the mean, minimum, and maximum numbers of insecticide detections per model year were computed. In addition, we considered the average exposure durations simulated by FOCUS for the model and realistic insecticide concentrations in the evaluation of all fixed interval sampling strategies.

In contrast, event-based sampling (Liess and Schulz 2000; Harmel et al. 2003) followed no fixed intervals but was triggered in a twofold manner: (a) spray drift-related pesticide entries were sampled manually during pesticide application (e.g., Schulz 2001a; Dabrowski et al. 2006), and (b) a runoff sample was taken by an automatic water sampler (e.g., Harmel et al. 2003; Jergentz et al. 2005) if a rainfall intensity of 15 mm/day occurred, which denotes a typical threshold level for moderate to heavy precipitation events leading to erosion events on agricultural land (Boardman et al. 1990; Bocheva et al. 2009). This rainfall intensity was also used as a trigger value for event-related runoff sampling in pesticide monitoring campaigns (Pedersen et al. 2006). We extracted the number of days exceeding 15 mm of irrigation or rainfall from FOCUS climate documents (FOCUS 2001) for each of the runoff and drainage scenarios for arable and permanent crops (see Table S3 in ESM) and subsequently applied the average number to the generalized and realistic yearly insecticide exposure patterns. Consequently, simulated event-driven runoff samples originated from the population of post-rainfall data points simulated by FOCUS.

For the overall evaluation of sampling strategies, we assumed that the two typical agricultural streams located in arable and permanent crop agri-environments were monitored within one sampling campaign. To facilitate an economic evaluation of all sampling strategies, we determined total costs of \$300 per sample, which is composed of \$200 of analytical cost per sample and \$100 in additional costs for sample collection and preparation, travel costs, and equipment/supplies (California EPA 2006). However, no costs for the monitoring plan, data evaluation, quality assurance, or the reporting of monitoring results were included in this amount. For event-triggered sampling, in addition to \$300 per sample, yearly costs of \$1,500 were assumed, comprising \$10,000 in acquisition costs for the automatic water sampler and \$5,000 in maintenance charges over an expected service life of 10 years.

The field relevance of the simulated insecticide monitoring results was compared to real-world insecticide monitoring studies. We reviewed and compiled field studies reporting insecticide concentrations in small agricultural streams located in the same geographic regions as those covered by the FOCUS simulations used here (i.e., D1, D2, D4, D5 and R1–R4, see above) and compared these real-world sampling results to findings from Monte Carlo simulations conducted in this study.

Risk assessment procedures

Monitoring results derived from Monte Carlo simulations applied to generalized and realistic insecticide exposure patterns were subsequently evaluated using the following three risk assessment procedures:

(a) DRA, i.e., comparison of a single maximum exposure value to an RAC within an HQ approach
(b) PRA, i.e., comparing the cumulative frequency distribution of all monitoring data, including values below the LOD, to the RAC to achieve RAC-exceedance percentages. Given the fact that at least six concentrations > LOD are considered necessary to characterize a concentration frequency distribution (Giddings et al. 2000) and that the total number of insecticide exposure incidences are actually known in our study, we did not create centile ranks of concentrations and use regression analyses for the calculation of RAC-exceedance probabilities (e.g., Solomon et al. 2000), but rather we calculated PRA results by dividing the number of insecticide concentrations > RAC detected by a given sampling strategy by the amount of samples taken
(c) RRA, defined as the comparison of all insecticide concentrations > LOD to the RAC

Although it is not a typical practice, we performed the risk assessments not separately for each of the three realistic insecticide compounds but for all insecticide concentrations normalized by their RACs (i.e., normalization using HQ). This procedure does not bias risk assessment outcomes, yet it overcomes the restrictions of the small number of concentrations of individual real insecticide compounds available for exemplary risk assessments.

Results and discussion

Generalized and realistic insecticide exposure patterns in small agricultural streams

The generalized exposure patterns simulated for arable and permanent crops and a typical agricultural stream revealed the occurrence of 11 and 16 distinct model insecticide concentrations above the LOD, respectively (Fig. 1a, b, see Table S4 in ESM for detailed FOCUS scenario results). Considering the mean simulated model insecticide surface water exposure durations of 10.7 h in arable and 12.7 h in permanent crop scenarios, insecticide concentrations were detectable during only 1.3 % (117.7 h/year) and 2.3 % (203.2 h/year) of the time, respectively. Correspondingly, no concentrations were observed during the remainder of the model year, i.e., for 354 (arable crops) and 349 (permanent crops) out of 365 days. For real insecticides, applications resulted in six (0.62 % of the time; mean exposure duration, 9.1 h) and nine (0.97 % of the time; mean exposure duration, 9.7 h) individual surface water concentrations for arable and permanent crop scenarios, respectively (Fig. 1c, d; Table S5, ESM). Again, no concentrations were observed during most of the days of the model year, i.e., for 359 (arable crops) and 356 (permanent crops) out of 365 days. In contrast to the model insecticide results, which also indicated exposure incidences in October and November, simulations using real insecticide compounds resulted only in surface water exposures within the respective insecticide application periods, i.e., May to July for arable crops and June to August for permanent crops (Fig. 1). Generally, the highest concentrations for the model and real insecticides occurred via spray drift entries, while the subsequent exposure incidences due to drainage and runoff entries led to lower concentrations. However, nine out

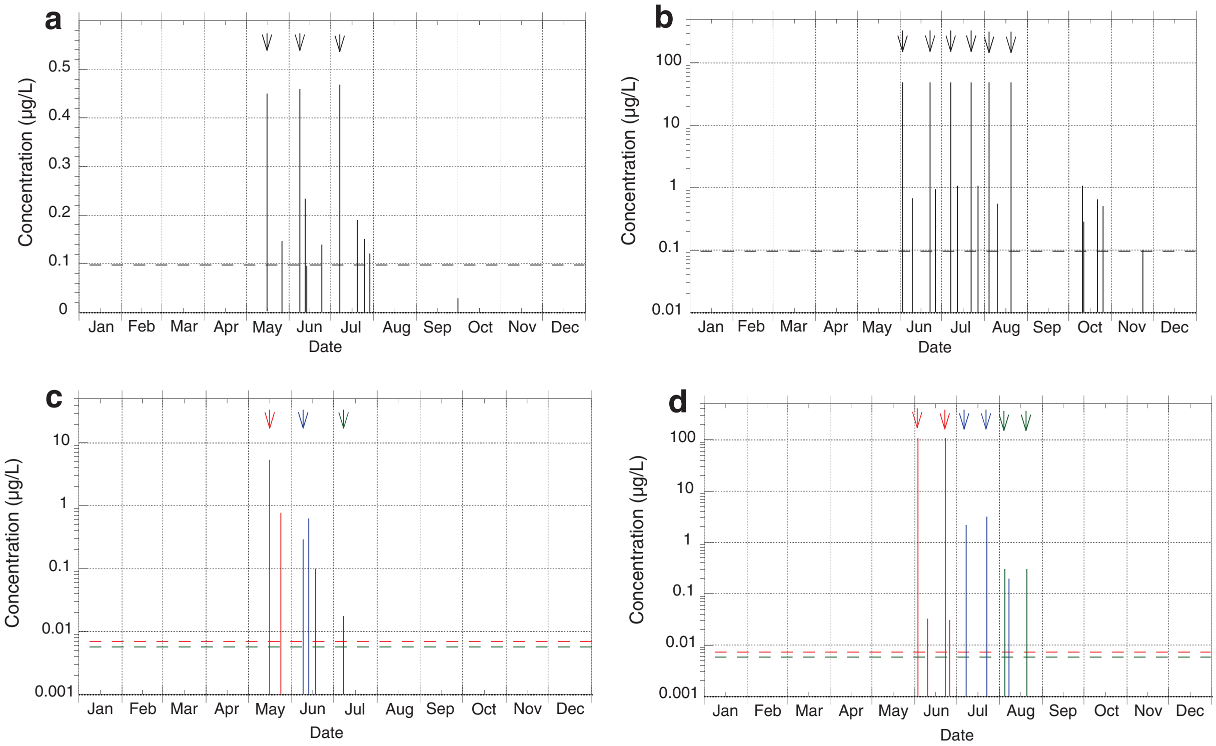

Fig. 1 Generalized (**a**, **b**) and realistic (**c**, **d**) insecticide (*red bars* malathion; *blue bars* acetamiprid; *green bars* deltamethrin) exposure profiles in a stream receiving agricultural non-point source pollution as synthesized from respective FOCUS surface water scenarios (see Table S4 and Table S5 in ESM for detailed FOCUS scenario results). **a**, **c** Arable crops with three insecticide applications (*arrows above bars*, application dates 16.5.; 9.6.; 7.7.); **b**, **d** six applications to permanent crops (application dates: 3.6.; 23.6.; 7.7.; 22.7.; 4.8.; 20.8.). The *dashed horizontal lines* indicate the RAC for the model insecticide (*black dashed line* in **a** and **b**, RAC=0.0995 µg/L) and the *red* (malathion, RAC=0.007 µg/L) and *green* (deltamethrin, RAC=0.0056 µg/L) *dashed horizontal lines* indicate the RAC for the real insecticides. The RAC for acetamiprid (498 µg/L) is not shown here

of 11 and 15 out of 16 model insecticide concentrations, as well as three out of six and six of nine real insecticide concentrations, exceeded their particular RACs in arable and permanent crop scenarios, respectively (Fig. 1).

The FOCUS model is currently used for regulatory pesticide surface water exposure predictions in the EU. Although a broad generalization of modeled insecticide concentration patterns for the variety of all real-world situations is challenging, recent reports (Ashauer and Brown 2007; Brock et al. 2008) confirmed that FOCUS predictions adequately reproduce the general pattern of pesticide surface water exposure, as comparisons between measured and simulated data showed broad correspondences with respect to overall concentration patterns, peak intervals, and decreases in peak concentration heights for successive pesticide exposure events. However, the frequency of insecticide concentration peaks in the field is potentially even lower than that calculated by FOCUS. Numerous field investigations in small agricultural streams showed, on average, a maximum of five insecticide inputs associated with one insecticide application period (e.g., Liess et al. 1999; Williams et al. 1995; Jergentz et al. 2005; Barra et al. 1995; Schulz et al. 1998). In addition to exposure frequencies, the mean exposure durations of 9.1 to 12.7 h are most likely overrated by FOCUS simulations, as various field studies clearly demonstrated a rapid decrease of insecticide concentrations to below the LOD within 3 to 4 h following inputs to small agricultural streams (Kreuger 1995; Spurlock et al. 2005; Crossland et al. 1982). These overestimations are due to several realistic worst-case assumptions, which determine simulated pesticide exposure in surface waters within the FOCUS modeling (FOCUS 2001). However, although the overall characteristics (i.e., the occurrence of few discrete insecticide concentrations) are comparable, a comparison of the simulated insecticide exposure patterns (Fig. 1) to those described in real-world monitoring studies confirms that there is a higher degree of realism for the realistic (Fig. 1c, d) compared to the generalized insecticide exposure profiles (Fig. 1a, b). Therefore, we focus in subsequent chapters on the realistic insecticide exposure patterns. Nevertheless, the generalized exposure patterns derived using a model insecticide, which is unbiased by physicochemical properties or application rates of individual compounds, clearly indicate that the occurrence of few, transient short-term peak concentration incidences in small agricultural streams is a specific exposure feature typical for all modern insecticides.

Despite their rare occurrences, the high intrinsic acute toxicity potentials of insecticides, accompanied by their fast modes of action (Yu 2008), lead to a higher ecotoxicological risk for aquatic ecosystems compared to herbicides and fungicides (Schäfer et al. 2011). The few available field studies on aquatic insecticide effects measured under normal farming practices (Table 1) indicate that insecticide concentrations > RAC indeed led to severe ecological effects (e.g., changes in community structure or function, changes in invertebrate dynamics, fish kills) in the affected aquatic ecosystems. Transferred to results concerning the realistic simulated exposure patterns (Fig. 1), this means that, although only very few insecticide exposure incidences are expected to occur in agricultural surface waters, these in fact constitute a high ecological risk (Table 2). It follows that there are urgent needs to adequately address these low-frequency/high-risk insecticide exposure patterns in monitoring campaigns and risk assessment concepts. Although one can argue that the Tier I UP criteria denote rather conservative RACs and other toxicity thresholds (e.g., those derived from species sensitivity distributions or mesocosm data) would presumably result in more realistic and less stringent RACs, evidence exists that the occurrence of insecticide concentrations well below (i.e., 1/10 to 1/100) their respective Tier I UP criteria already leads to unacceptable effects in stream ecosystems (Schäfer et al. 2012). It follows that the evaluation of the observed (Table 1) and simulated (Table 2) insecticide field concentrations using less stringent RACs would potentially result in substantial underestimations of ecological risks.

Implications for monitoring

All fixed-interval sampling regimes (i.e., monthly, 14 days, weekly, 3.5 days, daily) detected less than 50 % of the concentrations simulated for the realistic insecticide exposure patterns, as shown in Fig. 1c, d, resulting in peak detection errors of 60 to 100 % for the two typical agricultural streams (Table 3; see Table S6 in ESM for individual results for arable and permanent crops). The same holds true if the detection frequencies of RAC-exceeding concentrations are considered (Table 5), indicating that fixed-interval monitoring programs are unbiased with respect to time but seriously biased with respect to risk when highly

Table 1 Field studies reporting effects caused by insecticide exposure of small agricultural surface waters (adapted from Schulz (2004)) and related hazard quotients based on RAC

Insecticide	Observed field concentration (μg/L)	RAC[a] (μg/L)	HQ[b] (RAC[a])	Observed effect size and endpoint	Species	Source
Azinphos-methyl	0.87	0.011	**79**	46 % in situ mortality	*Chironomus* spec.	Schulz et al. (2001)
Chlorpyrifos	1.3	0.001	**1,300**	46 % in situ mortality	*Chironomus* spec.	Moore et al. (2002)
Cypermethrin	0.03	0.003	**10**	90 % abundance reduction	Various invertebrate species	Shires and Bennett (1985)
Endosulfan	1.44	4.4	0.33	Die-off	Various fish species	Finley et al. (1999)
Fenvalerate	0.11	0.0003	**367**	55 % in situ mortality	Shrimp (*P. pugio*)	Baughman et al. (1989)
Parathion-ethyl	6	0.025	**240**	100 % mortality	Various invertebrate species	Schulz and Liess (1999)

RAC regulatory acceptable concentration, *HQs* hazard quotients

[a] The Uniform Principle criterion was calculated by dividing the respective median LC50 (*D. magna*) values for the respective insecticide by a safety factor of 100 (see DG SANCO (2002) for details) and subsequently used here as the regulatory acceptable concentration

[b] Hazard quotients were calculated by dividing the observed insecticide concentrations by the RACs. HQs>1 are displayed in bold

Table 2 Simulated insecticide field concentrations, hazard quotients based on the RAC, and related expected effects in agricultural surface waters

Insecticide	Simulated field concentration (μg/L)	RAC[a] (μg/L)	HQ[b] (RAC[a])	Expected effect size	Date	Crop
Malathion	5.47	0.007	**782**	Very strong	16.5.	Arable
Malathion	0.729	0.007	**104**	Very strong	24.5.	Arable
Acetamiprid	0.29	498	0.0006	No effects	9.6.	Arable
Acetamiprid	0.65	498	0.0013	No effects	13.6.	Arable
Acetamiprid	0.1	498	0.0002	No effects	18.6.	Arable
Deltamethrin	0.018	0.0056	**3.23**	Strong	7.7.	Arable
Malathion	104.8	0.007	**14,976**	Extreme	3.6.	Permanent
Malathion	0.034	0.007	**4.83**	Strong	10.6.	Permanent
Malathion	105.4	0.007	**15,059**	Extreme	23.6.	Permanent
Malathion	0.032	0.007	**4.6**	Strong	27.6.	Permanent
Acetamiprid	2.28	498	0.0046	No effects	7.7.	Permanent
Acetamiprid	3.22	498	0.0065	No effects	22.7.	Permanent
Acetamiprid	0.199	498	0.0004	No effects	7.8.	Permanent
Deltamethrin	0.29	0.0056	**51.9**	Strong	4.8.	Permanent
Deltamethrin	0.29	0.0056	**51.9**	Strong	20.8.	Permanent

Insecticide exposure data were derived from realistic exposure patterns simulated by FOCUS exposure modeling (see Fig. 1c, d) for three real insecticide compounds

RAC regulatory acceptable concentration, *HQs* hazard quotients

[a] The Uniform Principle criterion was calculated by dividing the median LC50 (*D. magna*) values for the respective insecticides by a safety factor of 100 (see DG SANCO (2002) for details) and subsequently used here as the regulatory acceptable concentration

[b] Hazard quotients were calculated by dividing the simulated insecticide concentrations by the RACs. HQs>1 are displayed in bold

Table 3 Effectiveness and costs associated with different sampling strategies

Interval (no. of samples[a])	Mean[d] no. of detects (peak detection error[e] (%))	Mean[d] no. of non-detects	Percentage of non-detects	Costs per detection ($)	Total costs per year ($)
Monthly (24)	0 (100)	24	100	n/a	7,200
14 days (52)	0 (100)	52	100	n/a	15,600
Weekly (104)	1 (93.3)	103	99	31,200	31,200
3.5 days (208)	2 (86.6)	206	99	31,200	62,400
Daily[b] (730)	6 (60)	724	99.2	36,500	219,000
Event[c] (40)	15 (0)	25	62.5	1,000	15,000

Values were calculated and combined by applying Monte Carlo simulations to realistic insecticide exposure patterns synthesized from FOCUS exposure model calculations (Fig. 1c, d) for two typical agricultural streams located in arable and permanent crop agri-environments

[a] No. of samples refers to two typical agricultural streams, where one is located in arable and one in permanent crop agri-environments (see Table S6 in ESM for detailed results separated by crops)

[b] Despite the fact that one sample per day was taken, only two out of six (arable crops) and four out of nine (permanent crops) insecticide concentrations (total: six out of 15) were detected due to the respective mean exposure durations simulated by FOCUS

[c] Eighteen (arable crops) and 22 (permanent crops) samples (total 40) were considered to be taken by event-triggered sampling assuming three (arable crops) and six (permanent crops) spray events plus 15 (arable crops) and 16 (permanent crops) insecticide entry events potentially occurring due to 15 mm/day irrigation or rainfall as extracted from FOCUS climate documents (see Table S3, ESM) for the respective scenarios used here

[d] The minimum and maximum no. of detects calculated by Monte Carlo simulations were (min/max): monthly (0/1); 14 days (0/1); weekly (0/2); 3.5 days (0/2) in the case of arable crops and (min/max): monthly (0/1); 14 days (0/2); weekly (0/3); 3.5 days (0/3) in the case of permanent crops

[e] Defined as the percentage of non-detected insecticide concentrations out of all concentrations available. Calculated as follows: ((Total concentrations available−concentrations detected)/Total concentrations available)×100

transient but very toxic insecticide concentrations are to be evaluated. However, with higher temporal resolutions of fixed-interval sampling strategies, the mean number of non-detects increased considerably in parallel with the increasing mean number of detections and decreasing peak detection errors. All sampling strategies based on fixed intervals resulted in high percentages of non-detects (99 to 100 %; Table 3), which compares well with findings from the generalized insecticide exposure pattern (Table S7, ESM) and from real-world monitoring studies (97.9 % non-detects in regular sampling programs, Table 4). This further confirms that fixed-interval sampling schemes are generally inappropriate for insecticide exposure assessment irrespective of particular insecticide properties and application schemes. This is alarming considering that small streams are those aquatic habitats most likely to be exposed to agricultural non-point source insecticide pollution (Schulz 2004) and that governmental monitoring predominantly relies on fixed-interval sampling (Holvoet et al. 2007; House 1994; see also Table S2, ESM). Our results further demonstrate that even the employment of a more flexible and sophisticated fixed-interval sampling strategy (i.e., increasing the sampling frequency from monthly to weekly or daily during insecticide application periods) would not improve insecticide monitoring results (Table 3), but only substantially increase monitoring program costs (see below).

In contrast, event-based sampling detected all insecticide concentrations with a peak detection error of 0 % (Table 3) and therefore also detected all RAC-exceedance incidences (Table 5). Thorough field monitoring of the typical low-frequency/high-risk insecticide exposure pattern thus inevitably requires an event-controlled sampling design. This is of particular importance because 50 % (arable crops) and 66.6 % (permanent crops) of the simulated realistic insecticide concentrations exceeded their RACs (Fig. 1), which underlines the high risk to aquatic communities (Table 2). Regarding the sampling of spray drift events, we acknowledge that this is a challenging approach, with both implications for logistics and manpower requirements, especially when targeting on the landscape level. However, the consideration of insecticide application recommendations as released by official

Table 4 Number of samples with insecticide concentrations < LOD (non-detects) extracted from real-world monitoring studies conducted in small agricultural surface waters

Reference	Region/ FOCUS scenario	No. of insecticides analyzed	Total no. of samples	No. (%) of non-detects	Sampling regime	Total program costs (costs per detection) ($)
Kreuger and Brink (1988)	Sweden; D1	5	378	361 (95.5)	14 days–monthly	113,400 (6,671)
Crawford (2004)	Ohio, USA; D1, D4	1	3,956	3,818 (96.5)	Event–3.5 days^a; weekly–14 days^b	1,186,800 (8,600)
Turnbull et al. (1995)	UK; D2	1	10	7 (70)	Event	4,500 (1,500)
Gregoire et al. (2010)	France; D4, R1	1	41	37 (90.2)	Event	13,800 (3,450)
Schäfer et al. (2007)	France; D5	4	16	5 (31.3)	Event	6,300 (573)
Sturm et al. (2000)	Germany; R1	4	85	78 (91.8)	Event	27,000 (4,500)
Tauler et al. (2001)	Portugal; R2, R4	3	256	230 (89.8)	Monthly^a	76,800 (2,954)
Wilson and Foos (2006)	Florida, USA; R3	14	789	783 (99.2)	Daily	236,700 (39,450)
Senseman et al. (1997)	Arkansas, USA; R3	3	485	484 (99.7)	Regular intervals	145,500 (145,500)
Carter and Capri (2004)	Italy, Spain; R3, R4	1	4,640	4,611 (99.4)	n/a	1,392,000 (48,000)
Aguilar et al. (1999)	Spain; R4	2	20	20 (100)	Monthly^a	6,000 (n/a)
Total		27	10,676	10,434 (97.4)		3,208,800 (13,260)

All FOCUS scenarios used for the syntheses of generalized and realistic exposure patterns (Fig. 1) were covered by these field studies

n/a no information available

[a] Sampling interval during application period

[b] Sampling interval during non-application period

extension services in the planning of monitoring programs for a particular study area, as well as the cooperation with local farmers, could provide a targeted approach for the effective sampling of spray drift-related exposure events. The necessity of employing event-based sampling for the detection of insecticides in the field has also been recognized in the scientific literature (e.g., Schulz et al. 1998; Liess and Schulz 2000; Schulz 2004). This study quantifies the general implications for the first time.

In addition to the fact that the information obtained for water quality management must be questioned when insecticide contamination is monitored using fixed-interval sampling, a cost–benefit analysis also highlights the deficiencies of this approach. As shown in Table 3, costs were more than a factor of 30 higher for positive detections by fixed-interval sampling compared to event-based sampling. Again, the economic analyses of both real-world monitoring studies (Table 4) and simulation results (Table 3) support this conclusion, as on average \$14,549 and \$32,966, respectively, had to be spent to detect one insecticide concentration > LOD in the field using fixed intervals, whereas only \$2,506 and \$1,000, respectively, were spent in the case of event sampling. Excepting monthly sampling, which did not detect any exposure incidences, the simulated total yearly surveillance costs were also substantially lower for event-based than for fixed-interval sampling strategies (Table 3).

Generally, water quality monitoring targets are characterized by multiple objectives and need multi-objective optimization (Kollat and Reed 2006). These objectives are usually conflicting and optimality must be defined in the context of objectives trade-offs, often by finding Pareto-optimal solutions, i.e., the improvement in one objective (e.g., an increased number of insecticide detections through more frequent sampling) is accompanied by disadvantages for another objective (e.g., higher monitoring costs) (Kollat and Reed 2006). However, in contrast to fixed-interval sampling, these trade-offs do not exist for event-based sampling of insecticide concentrations in small streams, as this approach results in a maximum of information (i.e., detection of all insecticide concentrations) at a minimum cost (Table 3). Overall, these findings may become increasingly relevant considering the extent of

Table 5 Risk assessment results for deterministic, probabilistic, and relevance-driven data evaluation approaches

Interval (no. of samples)	Mean[a] no. of RAC-exceeding concentrations detected (%)	Deterministic risk assessment: comparison of peak concentration to RAC	Probabilistic risk assessment based on RAC exceedance frequencies[c] (%)	Relevance-driven risk assessment: no. of relevant concentrations > RAC
Monthly (24)	0 (0)	n/a[b]	0	n/a[b]
14 days (52)	0 (0)	n/a[b]	0	n/a[b]
Weekly (104)	1 (11.1)	1 of 1	0.96	1 of 1
3.5 days (208)	2 (22.2)	1 of 1	0.96	1 of 2
Daily (730)	4 (44.4)	1 of 1	0.55	4 of 6
Event (40)	9 (100)	1 of 1	22.5	**9 of 15**
Theoretical concept		Based on the highest concentration	Based on all concentrations, including non-detects	Based on relevant concentrations, i.e., those > LOD

Data were combined from realistic insecticide exposure patterns for typical streams located in arable and permanent crop agroecosystems (Fig. 1c, d; Table 3). The actual ecological risks of insecticide concentrations can only be obtained by the relevance-driven evaluation of insecticide concentrations detected by event-triggered sampling (bold, see text for details)

DRA deterministic risk assessment, *PRA* probabilistic risk assessment, *RRA* relevance-driven data evaluation approaches, *RAC* regulatory acceptable concentration

[a] Mean no. of insecticide concentrations > RAC refers to 100,000 Monte Carlo simulations applied to a realistic insecticide exposure pattern considering mean exposure durations of 9.1 h (arable crops) and 9.4 h (permanent crops) (see Fig. 1 and Table 3 for details).

[b] No risk assessment results are available for monthly and 14-day sampling because no concentrations > LOD were detected

[c] Calculated by dividing the number of insecticide concentrations > RAC for each sampling interval by the amount of samples taken

the current economic crisis in the EU and the US and the associated budget restrictions in the governmental sector (Marshall 2008).

Implications for risk assessment

In the DRA approach, only the highest insecticide concentration is compared to the RAC. As a result, all monitoring findings derived from sampling strategies with one concentration > RAC indicate a risk independent of the actual number of RAC exceedances (Table 5). Overall, the deterministic concept ignores the temporal characteristics of exposure and therefore ignores the risks resulting from repeated insecticide concentrations caused by consecutive spray drift and runoff events that are relevant in terms of adverse ecological effects (Ashauer et al. 2006; Table 2). However, if DRA is perceived only as a risk screening tool, that is if one HQ>1 indicates unacceptable risk (e.g., Iwafune et al. 2011; Karaouzas et al. 2011), and subsequent risk mitigation measures are implemented, this concept may be protective. Nevertheless, DRA appears unsuitable for a realistic and thorough retrospective risk assessment of highly variable insecticide exposure.

The PRA concept uses all data points of insecticide monitoring programs to estimate ecological risks in terms of threshold level exceedance frequencies (Solomon et al. 2000; Hall 2003). Therefore, all risk estimates based on fixed-interval sampling regimes indicated extremely low RAC exceedance frequencies (Table 5) and, consequently, low ecological risks (see Table S8 in ESM for risk assessment results separated for arable and permanent crops and Table S9 in ESM for model insecticide risk assessment results). For instance, 99 to 100 % of samples taken at fixed intervals were below the LOD (Table 3), corresponding to RAC exceedance frequencies between 0 and 0.96 % (Table 5). In contrast, the application of an event-based sampling strategy and subsequent probabilistic data evaluation to the identical insecticide exposure data results in a completely different ecological risk assessment outcome, with 22.5 % of the samples exceeding RACs (Fig. 2a; Table 5). This large discrepancy in the outcomes of PRA clearly shows that, in contrast to DRA and RRA results (see below), the RAC exceedance probability depends, in the case of insecticides, almost exclusively on the amount of samples taken and not on the actual concentrations present in surface waters. An increase of a

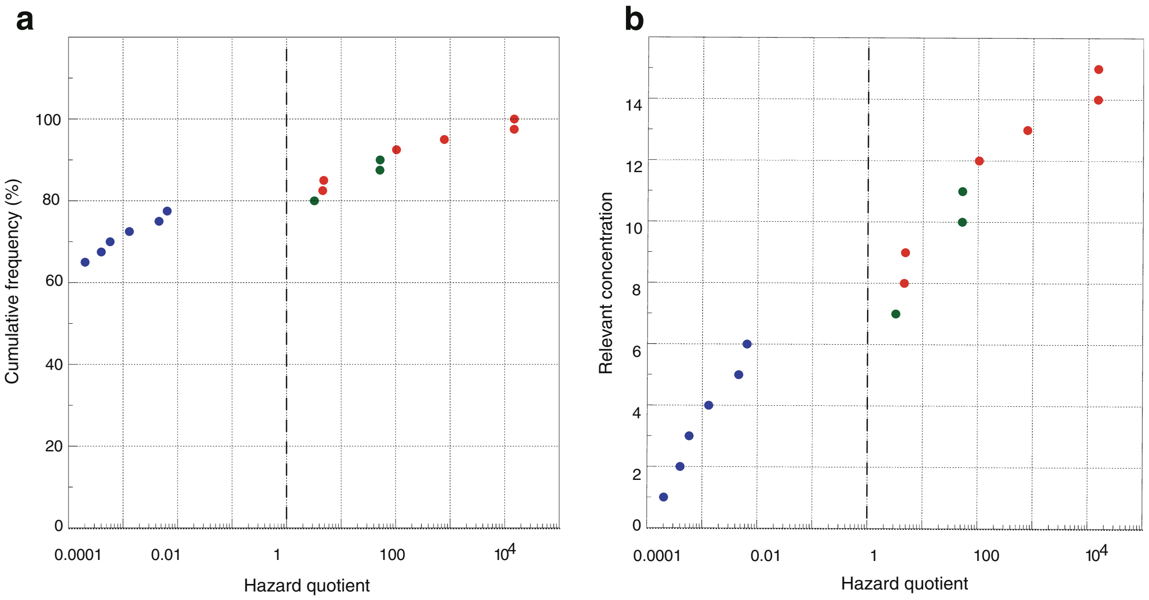

Fig. 2 Exemplary risk assessment results using probabilistic (**a**) and relevance-driven (**b**) insecticide monitoring data evaluation approaches. Concentrations were normalized by calculating hazard quotients and result from realistic insecticide exposure patterns for two typical agricultural streams located in arable and permanent crop agri-environments (see Fig. 1c, d, data taken from Tables 2, 3, and 5) constructed using event-triggered sampling. In Fig. 2a, 62.5 % of all (n=40) concentrations were below the LOD, resulting in an RAC (*vertical dashed line*) exceedance probability of 22.5 % (i.e., 9 out of 40 samples > RAC). In contrast, the relevance-driven risk assessment (**b**) assesses only insecticide concentrations > LOD, i.e., those which are of ecological relevance. As a result, a high ecological risk is indicated, as nine out of 15 concentrations exceeded their RACs

regular sampling frequency (e.g., from weekly to daily) disproportionally increases the number of non-detects (Table 3) and therefore results in a greater arbitrary decrease in the threshold level exceedance rate, even though a greater number of insecticide concentrations > RAC were detected (Table 5). In conclusion, if no considerations are made as to how accurate and complete available insecticide monitoring data are, PRA creates a false sense of certainty and protection. Overall, our simulated risk assessment results clearly demonstrate that a probabilistic evaluation of monitoring data including concentrations < LOD is unsuitable for contaminants characterized by a low frequency and extreme short-term peak exposure pattern such as insecticides. Although the PRA approach uses more information (data) compared to DRA, it introduces “new uncertainties” (Verdonck et al. 2007) into insecticide ecological risk assessment in that outcomes rely substantially on available input data, which, in turn, are ultimately determined by the methods (i.e., sampling intervals) used to acquire these data. This is alarming because PRA is already used for insecticide risk assessment for regulatory purposes. Presumably, no risk management options would be considered based on PRA applied to the data used here (Table 5), despite the fact that nine insecticide concentrations above mandatory threshold levels occurred in the field (Fig. 1) and potentially led to severe ecological effects (Tables 1 and 2), indicating that risk mitigation measures (e.g., no-spray buffer zones, constructed wetlands) would be strongly advisable (Stehle et al. 2011).

Relevance-driven risk assessment evaluates the actual, existing, and therefore potentially relevant insecticide contamination of an agricultural stream by comparing each detected concentration to the RAC within an HQ. It follows that RRA focuses on all insecticide exposure characteristics that are pertinent for adverse ecological effects, that is, the number of exposure incidences, concentration, and toxicity levels (Fig. 1). The hazard of insecticide exposure in small streams can therefore be quantified in terms of incidence frequencies and given ecotoxicological relevance (height of HQs) (Fig. 2b). This information also allows the RRA to rank surface water sites according to their insecticide exposure-related risks (e.g., Table S8, ESM), which, however, is not fully possible for either deterministic or probabilistic approaches. Based on RRA outcomes, complementary and unbiased insecticide risk management decisions can be made. However, sampling is also a critical factor for relevance-driven risk assessment, as fixed-interval measurements led to inaccurate risk assessment results, with non-conformance increasing with larger sampling intervals (Table 5).

Overall, our results demonstrate that the RRA approach, which focuses on insecticide concentrations actually present, is appropriate for the specific low-frequency/high-risk insecticide exposure patterns in small streams. The combination of event-related insecticide monitoring with such a relevance-driven data evaluation concept constitutes a risk assessment approach that is not biased by methodological artifacts but is only driven by exposure features relevant for aquatic ecosystems.

Conclusions

Insecticide concentrations have very high toxic potentials and thus pose a great threat to the ecological integrities of agricultural surface waters. It is therefore important that monitoring programs accurately detect insecticide exposure incidences. Due to the very transient natures of insecticide exposures, this inevitably requires an event-based sampling design. Traditionally operated fixed-interval sampling regimes fail to accurately depict the typical low-frequency/high-risk exposure patterns of insecticides. As a consequence, risk assessment must be further improved for insecticides by considering the generation and interpretation of monitoring data. PRA concepts in particular potentially underestimate risks, as these do not address the substantial uncertainties arising from the extremely high variabilities of insecticide exposure data. An important paradigm for a realistic insecticide risk assessment must therefore be to focus on the environmental relevance of insecticide exposure, i.e., on the actually present and thus relevant ecological impacts of insecticides. Ultimately, the RRA concept demonstrated here for insecticides implies a general change of the focus of pesticide risk assessment from generalizations across all pesticide groups (herbicides, insecticides, fungicides) to an assessment accounting for pesticide property- and application-specific exposure assessment and from rigid reliance on occurrence probabilities to relevance-driven analyses that elucidate the actual ecological risks in the field.

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Electronic Supplementary Material

Probabilistic Risk Assessment of Insecticide Concentrations in Agricultural Surface Waters: A Critical Appraisal

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Table S1 Parameters for the model insecticide and three real insecticides used for FOCUS calculations and the derivations of generalized and realistic insecticide exposure patterns. The parameters for the model insecticide were synthesized from all synthetic insecticide compounds (n = 50) currently listed on Annex I of the 91/414/EEC EU pesticide directive (DG SANCO 2008)

Parameter	**Unit**	**Model insecticide**	**Malathion**	**Acetamiprid**	**Deltamethrin**
Insecticide class[a]		-	OP	Neo	Pyr
Molar mass	g/mol	351.68	330.36	222.67	505.2
Vapor pressure	Pa	9.3×10^{-7}	0.0031	1.73×10^{-7}	1.24×10^{-8}
Solubility	mg/L	1.13	148	2,950	0.0002
K_{OC}	ml/g	3,916	1,800	200	10,240,000
Freundlich isotherm (1/n)		0.95	0.94	0.9	1.1
DT_{50} water	d	5.85	0.4	4.7	17
DT_{50} soil	d	18	0.17	3	13
DT_{50} sediment	d	24.5	0.4	42.3	65
Application rates for cereals	kg/ha	0.09	1.12	0.05	0.005625
Application rates for maize	kg/ha	0.099	1.12	0.07	0.0075
Application rates for permanent crops (pomes)	kg/ha	0.792	1.8	0.055	0.00875
LOD		0.0095	0.014	0.0095	0.0095
48-h EC_{50} (*Daphnia magna*)	µg/L	9.95	0.7	49,800	0.56
Tier I UP criterion (RAC)	µg/L	0.0995	0.007	498	0.0056

[a] OP: organophosphorous insecticide; Neo: neonicotinoid; Pyr: pyrethroid.

Table S2 Sampling intervals extracted from 56 US governmental monitoring reports. In total, 3,049 insecticide surface water concentrations were reported (time span: 1976 – 2008), with sampling interval information available for 2,775 insecticide concentrations. Bold sampling intervals denote common sampling strategies applied to generalized and realistic insecticide exposure patterns within the present study

Sampling interval	**No. of concentrations (percentages) measured by a specific sampling interval**
Yearly	7 (0.25%)
Biannual (180 d)	12 (0.43%)
90 d	8 (0.29%)
60 d	18 (0.65%)
Monthly (30 d)	427 (15.4%)
21 d	13 (0.47%)
14-d	408 (14.7%)
Weekly	766 (27.6%)
3.5- or 4-d	202 (7.3%)
2-d	25 (0.9%)
Daily	370 (13.3%)
Event	519 (18.7%)
n/a[a]	274

[a] No information available.

Table S3 Number of irrigation and rainfall events exceeding 15 mm per day for the different runoff and drainage scenarios and crop combinations. Values were extracted from FOCUS climate documents (FOCUS 2001)

Scenario	**Crop**	**No. of irrigation and rainfall events > 15 mm/day per year**
D1	Winter cereals	6
D2	Winter cereals	5
D4	Winter cereals	6
D5	Winter cereals	4
R1	Maize	8
R2	Maize	33
R3	Maize	24
R4	Maize	32
Mean (arable crops)		**15**
D4	Pomes	6
D5	Pomes	4
R1	Pomes	8
R2	Pomes	33
R3	Pomes	15
R4	Pomes	30
Mean (permanent crops)		**16**

Table S4 Detailed results of FOCUS step 3 calculations for the model insecticide used to derive a generalized insecticide concentration pattern (see Materials and Methods for details)

Scenario[a]	**Location**	**Application dates**	**No. of exposure events (route of entries**[b]**)**	**Days (percentage) with concentration > LOD**[c]
Arable crops (3 applications)				
D1	Sweden	25.04.; 14.05.; 17.06.	3 (3 s)	3 (0.8%)
D2	UK	07.05.; 11.05.; 02.06.	3 (3 s)	10 (2.7%)
D4	Denmark	25.04.; 05.05.; 01.06.	3 (3 s)	3 (0.8%)
D5	France	25.04.; 11.05.; 31.05.	3 (3 s)	3 (0.8%)
R1	Germany	01.06.; 11.07.; 20.08.	26 (3 s; 23 r)	26 (7.1%)
R2	Portugal	04.06.; 16.07.; 05.08.	4 (3 s; 1 r)	4 (1.1%)
R3	Italy	02.06.; 06.07.; 01.08.	15 (3 s; 12 r)	15 (4.1%)
R4	France	01.06.; 03.07.; 07.08.	19 (3 s; 16 r)	20 (5.5%)
Permanent crops (6 applications)				
D4	Denmark	01.06.; 04.07.; 18.07.; 01.08.; 13.08.; 27.08.	11 (6 s; 5 d)	11 (3%)
D5	France	09.06.; 09.07.; 21.07.; 04.08; 17.08.; 29.08.	6 (6 s)	12 (3.3%)
R1	Germany	01.06.; 18.06.; 30.06.; 12.07.; 27.07.; 20.08.	10 (6 s; 4 r)	10 (2.7%)
R2	Portugal	02.06.; 14.06.; 06.07.; 18.07.; 30.07.; 11.08.	16 (6 s; 10 r)	18 (4.9%)
R3	Italy	01.06.; 18.06.; 01.07.; 26.07.; 07.08.; 19.08.	15 (6 s; 9 r)	23 (6.3%)
R4	France	01.06.; 15.06.; 27.06.; 09.07.; 25.07.; 11.08.	22 (6 s; 16 r)	23 (4.9%)

[a] Arable crops: winter cereals in D scenarios and maize in R scenarios. Permanent crops: pomes (apples) in D and R scenarios.

[b] Routes of entry: s: spray drift; r: rainfall- or irrigation-induced runoff; d: drainage.

[c] Limit of detection.

Table S5 Detailed results of FOCUS step 3 calculations for three real insecticide compounds used to derive a realistic insecticide concentration pattern (see Materials and Methods for details)

Scenario[a]	**Location**	**Insecticide**	**Application dates**	**No. of exposure events (route of entries**[b]**)**	**Sum**[c] **of days (percentage) with concentration > LOD**[d]
			Arable crops (3 applications)		
D1	Sweden	Malathion	25.04.	1 (1 s)	3 (0.82)
		Acetamiprid	14.05.	1 (1 s)	
		Deltamethrin	17.06.	1 (1 s)	
D2	UK	Malathion	07.05.	1 (1 s)	14 (3.8%)
		Acetamiprid	11.05.	3 (1 s; 2 d)	
		Deltamethrin	02.06.	1 (1 s)	
D4	Denmark	Malathion	25.04.	1 (1 s)	3 (0.82)
		Acetamiprid	05.05.	1 (1 s)	
		Deltamethrin	01.06.	1 (1 s)	
D5	France	Malathion	25.04.	1 (1 s)	3 (0.82)
		Acetamiprid	11.05.	1 (1 s)	
		Deltamethrin	31.05.	1 (1 s)	
R1	Germany	Malathion	01.06.	1 (1 s)	4 (1.1%)
		Acetamiprid	11.07.	2 (1 s; 1 r)	
		Deltamethrin	20.08.	1 (1 s)	
R2	Portugal	Malathion	04.06.	1 (1 s)	3 (0.82)
		Acetamiprid	16.07.	1 (1 s)	
		Deltamethrin	05.08.	1 (1 s)	
R3	Italy	Malathion	02.06.	1 (1 s)	6 (1.6%)
		Acetamiprid	06.07.	4 (1 s; 3 r)	
		Deltamethrin	01.08.	1 (1 s)	
R4	France	Malathion	01.06.	2 (1 s; 1 r)	7 (1.9%)
		Acetamiprid	03.07.	4 (1 s; 3 r)	
		Deltamethrin	07.08.	1 (1 s)	
			Permanent crops (6 applications)		
D4	Denmark	Malathion	01.06.; 04.07.	2 (2 s)	6 (1.6%)
		Acetamiprid	18.07.; 01.08.	2 (2 s)	
		Deltamethrin	13.08.; 27.08.	2 (2 s)	
D5	France	Malathion	09.06.; 09.07.	2 (2 s)	8 (2.2%)
		Acetamiprid	21.07.; 04.08.	2 (2 s)	
		Deltamethrin	17.08.; 29.08.	2 (2 s)	
R1	Germany	Malathion	01.06.; 18.06.	3 (2 s; 1 r)	9 (2.5%)
		Acetamiprid	30.06.; 12.07.	4 (2 s; 2 r)	
		Deltamethrin	27.07.; 20.08.	2 (2 s)	
R2	Portugal	Malathion	02.06.; 14.06.	2 (2 s)	8 (2.2%)
		Acetamiprid	06.07.; 18.07.	2 (2 s)	
		Deltamethrin	30.07.; 11.08.	2 (2 s)	
R3	Italy	Malathion	01.06.; 18.06.	3 (2 s; 1 r)	11 (3%)
		Acetamiprid	01.07.; 26.07.	4 (2 s; 2 r)	
		Deltamethrin	07.08.; 19.08.	2 (2 s)	
R4	France	Malathion	01.06.; 15.06.	5 (2 s; 3 r)	13 (3.6%)
		Acetamiprid	27.06.; 09.07.	6 (2 s; 4 r)	
		Deltamethrin	25.07.; 11.08.	2 (2 s)	

[a] Arable crops: winter cereals in D scenarios and maize in R scenarios. Permanent crops: pomes (apples) in D and R scenarios.

[b] Routes of entry: s: spray drift; r: rainfall- or irrigation-induced runoff; d: drainage.

[c] Sum of all days (and percentages) with concentration > LOD for all three insecticide compounds.

[c] Limit of detection.

Table S6 Implications for monitoring: Detailed results for the real insecticides. Mean number of detects and non-detects of insecticides resulting from different sampling strategies, costs per one detection, and total costs per year. Data are shown separately for the two streams located in arable crop (3 applications; 6 concentrations > LOD; mean exposure duration: 9.1 h) and permanent crop (6 applications; 9 concentrations > LOD; mean exposure duration: 9.4 h) agri-environments. Values were calculated by applying Monte Carlo simulations to realistic insecticide exposure patterns for arable and permanent crops synthesized from FOCUS exposure model calculations (Fig. 1c and Fig. 1d)

Interval (No. of samples)	Mean[a] no. of detects (peak detection error[b] (%))	Mean[a] no. of non-detects	Percentage of non-detects	Costs per detection ($)	Total costs per year ($)
Arable crops					
Monthly (12)	0 (100)	12	100%	n/a	3,600
14-d (26)	0 (100)	26	100%	n/a	7,800
Weekly (52)	0 (100)	52	100%	n/a	15,600
3.5-d (104)	1 (83.3)	103	99%	31,200	31,200
Daily[c] (365)	2 (66.7)	363	99.5%	54,750	109,500
Event[d] (18)	6 (0)	12	66.7%	1,150	6,900
Permanent crops					
Monthly (12)	0 (100)	12	100%	n/a	3,600
14-d (26)	0 (100)	26	100%	n/a	7,800
Weekly (52)	1 (88.9)	51	98.1%	15,600	15,600
3.5-d (104)	1 (88.9)	103	99%	31,200	31,200
Daily[c] (365)	4 (55.6)	361	98.9%	27,375	109,500
Event[d] (22)	9 (0)	13	59.1%	900	8,100

[a] The minimum and maximum no. of detects calculated by Monte Carlo simulations were (Min / Max): monthly (0 / 1); 14-d (0 / 1); weekly (0 / 2); 3.5-d (0 / 2) in the case of arable crops and (Min / Max): monthly (0 / 1); 14-d (0 / 2); weekly (0 / 3); 3.5-d (0 / 3) in the case of permanent crops.

[b] Defined as percentage of non-detected insecticide concentrations out of all concentrations available. Calculated as follows: ((Total concentrations available – concentrations detected) / Total concentrations available) x 100.

[c] Despite the fact that one sample per day was taken, only 2 out of 6 (arable crops) and 4 out of 9 (permanent crops) insecticide concentrations were detected, due to the respective mean exposure durations simulated by FOCUS.

[d] Totals of 18 (arable crops) and 22 (permanent crops) samples were considered as taken by event-triggered sampling, assuming three (arable crops) and six (permanent crops) spray events plus 15 (arable crops) and 16 (permanent crops) insecticide entry events potentially occurring due to 15 mm/day irrigation or rainfall, as extracted from FOCUS climate documents (see Table S3) for the respective scenarios used here.

Table S7 Implications for monitoring: Detailed results for the model insecticide. Mean number of detects and non-detects of insecticide concentrations resulting from different sampling strategies, costs per one detection, and total costs per year. Data are shown separately for the two streams located in arable crop (3 applications; 11 concentrations > LOD; mean exposure duration: 10.7 h) and permanent crop (6 applications; 16 concentrations > LOD; mean exposure duration: 12.7 h) agri-environments. Values were calculated by applying Monte Carlo simulations to the generalized model insecticide exposure patterns for arable and permanent crops synthesized from FOCUS exposure model calculations (Fig. 1a and Fig. 1b)

Interval (No. of samples)	Mean[a] no. of detects (peak detection error[b] (%))	Mean[a] no. of non-detects	Percentage of non-detects	Costs per detection ($)	Total costs per year ($)
Arable crops					
Monthly (12)	0 (100)	12	100%	n/a	3,600
14-d (26)	0 (100)	26	100%	n/a	7,800
Weekly (52)	1 (90.9)	51	98.1%	15,600	15,600
3.5-d (104)	1 (90.9)	103	99%	31,200	31,200
Daily[c] (365)	5 (54.5)	360	98.6%	21,900	109,500
Event[d] (18)	11 (0)	7	38.9%	627	6,900
Permanent crops					
Monthly (12)	0 (100)	12	100%	n/a	3,600
14-d (26)	1 (93.8)	25	96.2%	7,800	7,800
Weekly (52)	1 (93.8)	51	98.1%	15,600	15,600
3.5-d (104)	1 (93.8)	103	99%	31,200	31,200
Daily[c] (365)	8 (50)	357	97.8%	13,688	109,500
Event[d] (22)	16 (0)	6	27.3%	506	8,100

The minimum and maximum no. of detects calculated by Monte Carlo were (Min / Max): monthly (0 / 1); 14-d (0 / 3); weekly (0 / 3); 3.5-d (0 / 4) in the case of arable crops and (Min / Max): monthly (0 / 3); 14-d (0 / 4); weekly (0 / 5); 3.5-d (0 / 4) in the case of permanent crops.

[b] Defined as percentage of non-detected insecticide concentrations out of all concentrations available. Calculated as follows: ((Total concentrations available – concentrations detected) / Total concentrations available) x 100.

[c] Despite the fact that one sample per day was taken, only 5 out of 11 (arable crops) and 8 out of 16 (permanent crops) insecticide concentrations were detected due to the respective mean exposure durations simulated by FOCUS.

[d] Totals of 18 (arable crops) and 22 (permanent crops) samples were considered as taken by event-triggered sampling assuming three (arable crops) and six (permanent crops) spray events plus 15 (arable crops) and 16 (permanent crops) insecticide entry events potentially occurring due to 15 mm/day irrigation or rainfall, as extracted from FOCUS climate documents (see Table S3) for the respective scenarios used here.

Table S8 Implications for risk assessment: Detailed results for the real insecticides. Risk assessment results for deterministic (DRA), probabilistic (PRA), and relevance-driven (RRA) data evaluation approaches based on mean numbers and percentages of realistic insecticide exposure incidences and concentrations > RAC detected by different sampling strategies. Data are separately shown for two typical streams located in arable (3 out of 6 concentrations > RAC) and permanent crop (6 out of 9 concentrations > RAC) agroecosystems. A profound risk assessment result (bold) can only be obtained by the relevance-driven evaluation of insecticide concentrations detected by event-triggered sampling (see text for details)

Interval (No of samples)	Mean[a] no. of RAC[b]-exceeding concentrations detected (percentages)	Deterministic risk assessment: Comparison of peak concentration to the RAC[b]	Probabilistic risk assessment based on RAC[b] exceedance frequencies[c]	Relevance-driven risk assessment: No. of relevant concentrations > RAC[b]
Arable crops				
Monthly (12)	0 (0%)	n/a[d]	0%	n/a
14-d (26)	0 (0%)	n/a[d]	0%	n/a
Weekly (52)	0 (0%)	n/a[d]	0%	n/a
3.5-d (104)	1 (33.3%)	1 of 1	0.96%	1 of 1
Daily (365)	1 (33.3%)	1 of 1	0.27%	1 of 2
Event (18)	3 (100%)	1 of 1	16.6%	**3 of 6**
Permanent crops				
Monthly (12)	0 (0%)	n/a[d]	0%	n/a
14-d (26)	0 (0%)	n/a[d]	0%	n/a
Weekly (52)	1 (16.6%)	1 of 1	1.9%	1 of 1
3.5-d (104)	1 (16.6%)	1 of 1	0.96%	1 of 1
Daily (365)	3 (50%)	1 of 1	0.82%	3 of 4
Event (22)	6 (100%)	1 of 1	27.3%	**6 of 9**
Theoretical concept		Based on highest concentration	Based on all concentrations, including non-detects	Based on relevant concentrations, i.e., those > LOD

[a] Mean nos. of insecticide concentrations > RAC refer to 100,000 Monte Carlo simulations applied to a realistic insecticide exposure pattern with mean exposure durations of 9.1 hours (arable crops) and 9.4 hours (permanent crops).

[b] Regulatory Acceptable Concentration (RAC).

[c] Calculated by dividing the number of insecticide concentrations > RAC for each sampling interval by the amount of samples taken.

[d] No risk assessment results are available for monthly, 14-d, and weekly sampling intervals for arable crops or for monthly and 14-d sampling intervals for permanent crops because no concentrations > LOD were detected.

Table S9 Implications for risk assessment: Detailed results for the model insecticide. Risk assessment results for deterministic (DRA), probabilistic (PRA), and relevance-driven (RRA) data evaluation approaches based on mean numbers and percentages of model insecticide exposure incidences and concentrations > RAC detected by different sampling strategies. Data are separately shown for two typical streams located in arable (9 out of 11 concentrations > RAC) and permanent crop (15 out of 16 concentrations > RAC) agroecosystems. A profound risk assessment result (bold) can only be obtained by the relevance-driven evaluation of insecticide concentrations detected by event-triggered sampling (see text for details)

Interval (No. of samples)	Mean[a] no. of RAC[b]-exceeding concentrations detected (percentages)	Deterministic risk assessment: Comparison of peak concentration to the RAC[b]	Probabilistic risk assessment based on RAC[b] exceedance frequencies[c]	Relevance-driven risk assessment: No. of relevant concentrations > RAC[b]
Arable crops				
Monthly (12)	0 (0%)	n/a[d]	0%	n/a
14-d (26)	0 (0%)	n/a[d]	0%	n/a
Weekly (52)	1 (11.1%)	1 of 1	1.9%	1 of 1
3.5-d (104)	1 (33.3%)	1 of 1	0.96%	1 of 1
Daily (365)	4 (44.4%)	1 of 1	1.1%	4 of 5
Event (18)	9 (100%)	1 of 1	50%	**9 of 11**
Permanent crops				
Monthly (12)	0 (0%)	n/a[d]	0%	n/a
14-d (26)	1 (6.7%)	1 of 1	3.8%	1 of 1
Weekly (52)	1 (6.7%)	1 of 1	1.9%	1 of 1
3.5-d (104)	1 (6.7%)	1 of 1	0.96%	1 of 1
Daily (365)	8 (53.3%)	1 of 1	2.2%	8 of 8
Event (22)	15 (100%)	1 of 1	68.2%	**15 of 16**
Theoretical concept		Based on highest concentration	Based on all concentrations, including non-detects	Based on relevant concentrations, i.e., those > LOD

[a] Mean nos. of insecticide concentrations > RAC refer to 100,000 Monte Carlo simulations applied to generalized insecticide exposure patterns with mean exposure durations of 10.7 hours (arable crops) and 12.7 hours (permanent crops).

[b] Regulatory Acceptable Concentration (RAC).

[c] Calculated by dividing the number of insecticide concentrations > RAC for each sampling interval by the amount of samples taken.

[d] No data are available for monthly and 14-d sampling intervals for arable crops or for monthly sampling intervals for permanent crops because no concentrations > LOD were detected.

References

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