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Three Reasons Why the Water Framework Directive (WFD) Fails to Identify Pesticide Risks

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Abstract

The Water Framework Directive (WFD) demands that good status is to be achieved for all European water bodies. While governmental monitoring under the WFD mostly concludes a good status with regard to pesticide pollution, numerous scientific studies have demonstrated widespread negative ecological impacts of pesticide exposure in surface waters. To identify reasons for this discrepancy, we analysed pesticide concentrations measured in a monitoring campaign of 91 agricultural streams in 2018 and 2019 using methodologies that exceed the requirements of the WFD. This included a sampling strategy that takes into account the periodic occurrence of pesticides and a different analyte spectrum designed to reflect current pesticide use. We found that regulatory acceptable concentrations (RACs)

were exceeded for 39 different pesticides at 81% of monitoring sites. In comparison, WFD-compliant monitoring of the same sites would have detected only eleven pesticides as exceeding the WFD-based environmental quality standards (EQS) at 35% of monitoring sites. We suggest three reasons for this underestimation of pesticide risk under the WFD-compliant monitoring: (1) The sampling approach - the timing and site selection are unable to adequately capture the periodic occurrence of pesticides and investigate surface waters particularly susceptible to pesticide risks; (2) the measuring method - a too narrow analyte spectrum (6% of pesticides currently approved in Germany) and insufficient analytical capacities result in risk drivers being overlooked; (3) the assessment method for measured concentrations - the protectivity and availability of regulatory thresholds are not sufficient to ensure a good ecological status. We therefore propose practical and legal refinements to improve the WFD's monitoring and assessment strategy in order to gain a more realistic picture of pesticide surface water pollution. This will enable more rapid identification of risk drivers and suitable risk management measures to ultimately improve the status of European surface waters.

Keywords: Water quality, Agriculture, Freshwater ecosystem, Pesticide monitoring, Ecological risk

1 Introduction

Since its implementation in the year 2000, the Water Framework Directive (WFD, 2000/60/EG) has served as the legal basis for EU member states to protect their surface waters (European Union, 2000). It requires member states to achieve and maintain a good status of all lentic and lotic waters. To have good status, a surface water must exhibit both a good chemical and a good ecological status. However, the latest results on the status of European surface waters submitted by the member states reveal that at least 35% of surface waters fail to achieve a good chemical status and 51% show an insufficient ecological status (moderate, poor or bad) (EEA, 2018).

The drivers made responsible for this poor status mainly include the occurrence of ubiquitous, persistent, bioaccumulative and toxic substances (uPBTs), morphological degradation and high nutrient

loads (BMUB/UBA, 2016; EEA, 2018). Pesticides, on the contrary, are broadly represented in the WFD list of analytes but cause only 0.4% of surface waters to fail to achieve a good chemical status according to the monitoring data from the 2nd river basin management plan (Mohaupt et al., 2020). This contradicts numerous studies which observed that pesticides frequently exceed regulatory acceptable concentrations (RACs) (Stehle and Schulz, 2015b; Szöcs et al., 2017) and even pose a greater threat to European surface water ecology than any other pollutant class (Malaj et al., 2014; Wolfram et al., 2021). Pesticides have been shown to impair surface water fauna and flora within Europe (Beketov et al., 2013; Larras et al., 2017; Liess et al., 2021a; Liess and Ohe, 2005; Schäfer et al., 2011), but also worldwide, for example in Africa (Ganatra et al., 2021), Australia (Burgert et al., 2011; Wood et al., 2019) and North and South America (Chiu et al., 2016; Hunt et al., 2017). These contrasting results suggest that the current monitoring and assessment methods used in compliance with the WFD result in an underestimation of the actual pesticide risk.

The WFD surface water monitoring strategy focuses on larger rivers while catchments are surveyed less frequently if <100 km² or only in exceptional cases if <10 km² (Szöcs et al., 2017; Wick et al., 2019). The chemical and ecological status of European small streams is therefore largely unknown. This is problematic because small headwater streams play a decisive role in large-scale overall ecological condition and biodiversity, as they make up two thirds of the entire river network (BfN, 2021; Meyer et al., 2007). Small stream ecosystems are considered biodiversity hotspots, offering diversified habitats for numerous animal, plant, algae and fungi species, and act as recolonization sources for impaired downstream reaches (Liess and Ohe, 2005; Orlinskiy et al., 2015). Such streams have also been shown to be particularly susceptible to agricultural diffuse pesticide pollution, often being located in direct proximity to agricultural fields while lacking the capacity of larger waters to dilute pesticide inputs (Schulz, 2004; Stehle and Schulz, 2015b; Szöcs et al., 2017). These inputs are mostly due to rainfall-induced surface runoff transporting pesticide residues from fields into adjacent streams, resulting in short-term concentration peaks (Liess et al., 1999). For these reasons, there is growing global concern about the chemical and ecological quality of small rivers, which is also reflected in more recent

monitoring programmes focusing on small streams such as the Regional Stream Quality Assessment (RSQA) in the US (<https://webapps.usgs.gov/RSQA/#/>) or the NAWA SPEZ in Switzerland (<https://www.eawag.ch/en/research/water-for-ecosystem/pollutants/nawaspez/>).

Among other objectives, the German National Action Plan (NAP) for the Sustainable Use of Plant Protection Products addressed this blind spot in WFD monitoring, specifically requiring representative monitoring of small surface waters in agricultural catchments with an area of <10 km² (BMEL, 2013). Consequently, a uniquely comprehensive monitoring campaign of 124 small streams designed to adequately characterise pesticide pollution was carried out in 2018 and 2019 throughout Germany, Central Europe (see project homepage under www.ufz.de/kgm). Apart from the focus on small streams, its strategy comprised (i) event-driven sampling (EDS) to capture transient pesticide peak concentrations in addition to WFD-compliant regular grab sampling, (ii) an analyte spectrum based on current pesticide use statistics, which differs from the WFD pesticide analytes, and (iii) the consideration of additional pesticide surface water thresholds beyond those listed for the purposes of the WFD. On the basis of this stream monitoring, Liess et al. (2021a) confirmed the frequent occurrence of pesticides in ecologically harmful concentrations generally exceeding regulatory thresholds. Additionally, they linked ecological status to pesticide pressure and proposed protective pesticide thresholds relying on field observations. Further, Halbach et al. (2021) quantified the periodic occurrence of pesticides following rain events in these streams and compared measured concentrations with those recorded during the routine WFD monitoring of two German federal states. The present study now uses this stream monitoring data to evaluate the WFD's pesticide monitoring strategy. Therefore, we compared the results of the surface water assessment of our refined stream monitoring approach against a WFD-compliant approach of the same monitoring sites. In this way, we aim to evaluate the WFD's ability to detect pesticide risks in surface waters, identify reasons for divergent results where they exist, and propose refinements to improve the WFD's pesticide monitoring strategy.

2 Material and methods

2.1 Pesticide monitoring under the WFD – the current situation

Under the WFD, EU member states monitor three different categories of sites: (i) Surveillance monitoring sites, where all the WFD quality elements (ecological, hydromorphological, chemical and physico-chemical) are normally assessed. In Germany, the extensive surveillance monitoring network comprises about 260 sites mostly located in larger rivers. (ii) Operational monitoring sites are more abundant (>13,000 in Germany), but require a limited monitoring effort restricted to the assessment of quality elements known to react most sensitively in a water body. This operational monitoring therefore depends on the locally specific pressure situation. (iii) Investigative monitoring sites to locate and assess causes of water pollution that make a surface water fail to achieve a good status (Arle et al., 2016).

The WFD monitoring of pesticides is involved in both the chemical and the ecological status assessment. To classify a surface water's chemical status, all EU member states regularly measure 45 priority substances (PS) or substance groups listed in the WFD and implemented in German law by the Surface Water Ordinance (BGBI, 2016 Annex 8). The list of PS contains 23 pesticides (see supplementary information - SI Table 1). As part of the ecological classification, each EU member state is also obliged to identify pollutants of regional or local importance, the river basin-specific pollutants (RBSP). In Germany, the list of RBSP comprises 67 substances, 44 of which are pesticides (BGBI, 2016 Annex 6). Both PS and RBSP are assigned legally binding environmental quality standards (EQS) reflecting concentration levels below which it is assumed that the aquatic environment and human health are protected. If a single PS or RBSP exceeds an EQS, the chemical status is classified as "not good" or the ecological status is downgraded to less than "good" (at most "moderate"), respectively. In contrast to PS, RBSP must be monitored if "discharged in significant quantities". Monitoring frequencies are legally defined in that PS are measured twelve times per year at least once every three years (operational monitoring) or six years (surveillance monitoring), while RBSP require monitoring four to 13 times per

year at least once every three years (operational monitoring) or six years (surveillance monitoring) (BGBI, 2016 Annex 10).

2.2 Monitoring design used in this study

The information on stream water pesticide concentrations was collected as part of a Germany-wide monitoring campaign of 124 small lowland streams in 2018 and 2019. The monitoring strategy was described in detail by Liess et al. (2021a) and only a short summary is provided here.

This study focused on a subset of the complete monitoring dataset by considering lowland streams (i) within agricultural catchments, i.e. those with > 20% agricultural land cover within the catchment (Copernicus Land Monitoring Service, 2019) and (ii) where rainfall event-driven sampling (EDS, see below) could be carried out. This subset comprised 91 agricultural streams, of which ten were monitored in both 2018 and 2019. These ten streams are analysed individually for each year, as weather conditions and/or crop types in the catchments differed between the years. The hydrological catchments of these small streams were mostly <30 km² (mean = 19 km²) with an agricultural land cover ranging from 22% to 100% (mean = 75%). Although the selection of agricultural stream monitoring sites and respective catchments showed a higher percentage of agricultural land cover than average German small stream catchments, we estimate the level of pesticide pollution to be representative for German agricultural streams in general (see SI – Representativity analysis). Urban land cover accounted for less than 5% in the majority of stream catchments (see SI Figures 1 & 2).

The streams were sampled from the beginning of April to mid-July, covering the intense application period of pesticides in early summer (Szöcs et al., 2017; Weisner et al., 2021). The samplings were carried out in two different ways: (i) Grab samples (n = 450) were taken on a regular, three-week cycle comparable to the monthly samplings performed under the WFD. Grab sampling was thus carried out irrespective of weather and discharge conditions. (ii) Additionally, the streams were sampled directly after rainfall assumed to cause surface runoff (EDS, n = 312) using automatic sampling devices collecting

time-integrated composite samples triggered by a significant water level increase (for details see SI). In total, an average of 4.5 grab samples and 3.1 EDS samples was collected per site.

All water samples were cooled below 4°C during sampling and transport and analysed within four days for 75 pesticides and 33 pesticide metabolites using LC-MS/MS (see SI for substance list and Halbach et al., 2021 for the analytical method). The selection of pesticide analytes was compiled from a prior study by Wick et al. (2019), taking into account (i) a pesticide's current use statistics in relation to its toxicity, (ii) measured concentrations in previous monitoring programmes and (iii) its compatibility with a multi-substance method for chemical analysis. The selected analyte spectrum overlapped with the list of PS and RBSP for two and 22 pesticides, respectively (see SI Table 2). Pyrethroid insecticides and the herbicide Glyphosate are expected potential risk drivers for aquatic ecosystems that were omitted due to analytical limitations. Nonetheless, we consider that the analyte spectrum covered the majority of ecotoxicologically relevant pesticides at the time.

2.3 Pesticide surface water thresholds

We applied three different types of pesticide surface water thresholds to assess the ecological relevance of measured concentrations: the WFD-based EQS, the regulatory acceptable concentrations (RAC) derived during the authorisation of plant protection products containing the pesticides (UBA, 2019) and the field-based acceptable concentrations (AC_{field}) (Liess et al., 2021a).

The EQS values were taken from the list of PS and German RBSP according to the Surface Water Ordinance (BGBI, 2016 Annex 6/8). To account for the duration of exposure, there are two different EQS under the WFD: (i) the annual average-EQS (AA-EQS) covering long-term effects normally derived on the basis of chronic toxicity data, and (ii) maximum acceptable concentration-EQS (MAC-EQS), which covers short-term effects normally derived on the basis of acute toxicity data (European Commission, 2018). AA-EQS are therefore used to assess time-averaged, long-term concentration levels, while MAC-EQS are used to assess short-term peak concentrations. AA-EQS were available for 24 pesticides (three insecticides, three fungicides, 18 herbicides) and MAC-EQS were available for ten of these 24 pesticides

(two insecticides, one fungicide, seven herbicides). When comparing MAC-EQS to the RAC and AC_{field} , we also considered pesticides that are listed as RBSP in other EU member states (see SI Table 2, EEA, 2021) and/or were not included in the stream monitoring analyte spectrum (see SI Table 3).

The RACs as thresholds derived within the environmental risk assessment of plant protection products were obtained from UBA (2019). As each plant protection product containing a specific pesticide (= active ingredient) requires (re-)authorisation prior to use, RACs were available for all pesticides analysed ($n = 75$, eleven insecticides, 25 fungicides, 39 herbicides). The metabolites Methiocarb sulfoxide and Prothioconazole-desthio are also assigned a RAC due to their elevated ecotoxicological potential. The RACs applied in this study reflect the regulatory status when monitoring was carried out in 2018 and 2019. Individual RACs may have been adjusted in the meantime as the plant protection products may have been reauthorised taking new scientific knowledge into account. Both RAC and MAC-EQS assess concentration maxima but originate from different legal frameworks and differ in terms of the definition of the protection goal and the precise derivation approach. If a MAC-EQS is exceeded then counteractive measures must be initiated, while compliance with RACs is not legally required.

The AC_{field} was derived on the basis of field observations by Liess et al. (2021a) by linking a stream's peak exposure to its ecological status as reflected by the invertebrate community. This threshold aims for 95% of streams to show a good or high ecological status in terms of the invertebrate-based indicator $SPEAR_{\text{pesticides}}$, which responds specifically to pesticide pressure. An AC_{field} was only assigned to the 22 pesticides (eleven insecticides, eight fungicides, three herbicides) for which freshwater invertebrates were considered the most sensitive organism group according to UBA (2019) (referred to in this article as primarily invertebrate-toxic pesticides from here). In contrast to the EQS or RAC, this threshold incorporates other environmental stresses present in the field that interact with pesticide toxicity (e.g. other pesticides, nutrients, temperature or competition). All thresholds are listed in SI Table 2.

2.4 Evaluation of risk indicated by threshold exceedances

Exceedances of the RAC, MAC-EQS and AC_{field} were determined by comparing the measured concentration c_i of pesticide or pesticide metabolite i to the relevant threshold. A threshold exceedance is indicated by a risk quotient (RQ) greater than 1:

$$RQ = \frac{c_i}{Threshold_i} \quad (\text{Eq. 1})$$

To determine exceedances for the AA-EQS, the average of all measured concentrations of the pesticide i is divided by the threshold:

$$RQ_{AA-EQS} = \frac{\text{mean } c_i}{AA-EQS_i} \quad (\text{Eq. 2})$$

In the WFD-compliant assessment, the monthly sampled concentrations are commonly averaged over an entire year and then compared to the AA-EQS (LAWA-AO, 2019). Since the stream samples of this study were taken only during the period of intense pesticide application, our averaging period only ranged from April to July. This limited averaging period may result in a higher risk than if considering the year as a whole, which would include months with no or reduced pesticide application, particularly in winter (Weisner et al., 2021). However, unlike in practice, the WFD guidance document also explicitly advises that averaging periods should be shorter than a year when episodic exposure is known, which will also be discussed below (see chapter 3.1) (European Commission, 2018). Therefore, we also considered a best-case scenario including hypothetical measurements in which no pesticides were detected in the months when no samplings took place and calculated annual average concentrations following the German guidance (see SI and LAWA-AO, 2019).

All calculations were performed using the statistical software R (version 3.5.1) and all plots were created using the R package “ggplot2” (version 3.2.0) (R Core Team, 2018; Wickham, 2009).

3 Results and discussion

3.1 Reason #1 – Sampling pesticides

Here we discuss the time and sites to sample surface waters for pesticides. Firstly, the WFD sampling frequencies and intervals must be regarded as unsuitable with respect to the seasonal application of pesticides and their event-related input. The rainfall event-driven sampling (EDS) used in our refined monitoring approach captured on average 8.3 times higher pesticide concentration peaks (95th percentile) compared to common grab sampling as performed under the WFD (see Figure 1 and SI Table 2) (Halbach et al., 2021; Liess et al., 2021a). For the metabolites analysed, EDS concentration peaks exceeded the relevant grab sample concentration on average by a factor of 3.8. EDS detected higher total pesticide concentrations compared to grab sampling in 80% of streams (n = 81). As a consequence, EDS increased the probability that an exceedance of the maximum acceptable concentration environmental quality standard (MAC-EQS) would be detected by a factor of four: respective exceedances were identified in 3% (n = 16) of grab samples and 12% (n = 35) of EDS samples. Restricting our analysis to grab sampling caused 16 of the 30 streams with MAC-EQS exceedances to go unnoticed. EDS was thus indispensable to adequately monitor pesticide toxicity peaks as shown in multiple studies (Bundschuh et al., 2014; Lorenz et al., 2017; Rasmussen et al., 2017). It is these peak concentrations that were shown to determine the ecological status of a surface water (Liess et al., 2021a; Ohe et al., 2011; Schäfer et al., 2012). By investigating the concentration differences depending on weather conditions, Szöcs et al. (2017) and Halbach et al. (2021) confirmed the periodic occurrence of pesticides in surface waters on runoff-relevant days. However, WFD-compliant grab sampling following a regular schedule coincided with such runoff-relevant days in only 7% of samplings, minimizing the likelihood of capturing relevant concentration peaks (rainfall >10 mm/d). Norman et al. (2020) and Spycher et al. (2018) found that regular grab sampling needed to be performed at a high frequency of 12 – 24 hours to capture transient peaks adequately. For optimal cost benefit, we therefore recommend supplementing the usual grab sampling with EDS sampling during the main period of pesticide

application and following rainfall events. This can also be performed with less elaborate methods than automated sampling devices, for example simple bottle samplers (Liess and Ohe, 2005).

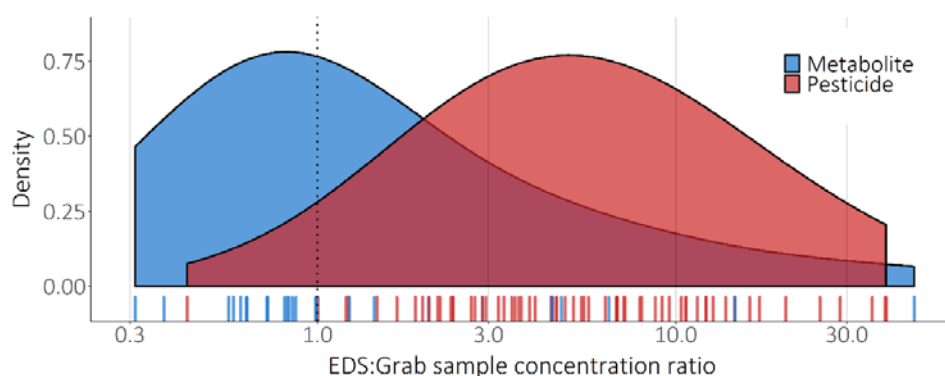


Figure 1: Smoothed distribution of ratios of measured concentration peaks (95th percentile) from event-driven sampling (EDS) and grab sampling for monitored pesticides (red, n = 63 substances) and pesticide metabolites (blue, n = 25) on a logarithmic scale. Vertical lines at the bottom show the single, compound-specific ratios. Pesticides and metabolites not shown revealed 95th percentiles of 0 in EDS (n = 3), grab samples (n = 8) or both (n = 9, see SI Table 2).

The monthly WFD samplings also cover periods outside the growing season when no relevant pesticide inputs are expected. Accordingly, the assessment of chronic exposure through compliance with annual average-EQS (AA-EQS) involves averaging all monthly measurements for the entire year (LAWA-AO, 2019). However, pesticide application frequencies peaking in April-May (Weisner et al., 2021) were shown to directly relate to measured toxicity peaks in streams in April-June (Liess et al., 1999; Spycher et al., 2018). The current AA-EQS assessment under the WFD thus causes a downscaling of time-averaged concentrations which conceals exceedances of AA-EQS. This is in contrast to the WFD guidance explicitly stating that “when the exposure pattern for a substance is known to be episodic e.g. many pesticides, the averaging period may be a shorter period than a year” (European Commission, 2018). So far, this guidance has been disregarded in practical implementation. The scheduling of sampling and the corresponding averaging period for the AA-EQS assessment thus need to account for the substance-specific, periodic occurrence of pesticides. For larger rivers, the timing of sampling may be of less relevance as pesticide exposure may occur in flattened peaks as inputs from different tributaries arrive successively.

Secondly, the selection of sampling sites currently monitored under the WFD is biased, resulting in unrepresentative estimations of the status of surface waters and contributing to the underestimation of pesticide risk. Wolfram et al. (2021) estimated a median catchment area of 238 km² of European surface waters monitored under the WFD, while the median catchment area of the natural river network is less than 20 km². Small streams are thus underrepresented in the WFD monitoring site selection while being particularly susceptible to pesticide pollution (Lorenz et al., 2017; Schulz, 2004; Stehle and Schulz, 2015b; Szöcs et al., 2017). This especially concerns small waters with catchments of <10 km², which are completely omitted from regular WFD monitoring and are not required to achieve good status despite making up approximately two thirds of the entire river network (BfN, 2021). For these, we observed the same concerning level of pesticide pollution: the number of RAC exceedances detected between streams with catchments of >10 km² (n = 65) and <10 km² was comparable (n = 36, Wilcoxon rank sum test, p = 0.6). We therefore recommend that the current monitoring performed in the context of the WFD be shifted more towards small water bodies (30-100 km²) and even include smaller waters with catchments of <10 km².

3.2 Reason #2 – Measuring pesticide contamination

In this section, we discuss issues related to the chemical analysis following water sampling. Firstly, we found the spectrum of pesticide analytes to be measured under the WFD to be outdated and inconsistent. All 108 pesticides and metabolites detected in this study were chosen on the basis of their expected environmental relevance (see chapter 2.2). However, only 24 of the 75 detected pesticides are subject to mandatory monitoring under the WFD and assigned an EQS (two priority substances (PS) and 22 river basin-specific pollutants (RBSP), see SI Table 2). Accordingly, WFD-compliant monitoring of the 101 streams identified eleven pesticides that exceeded their EQS if only grab samples were counted, or 16 if EDS were included. We also found that pesticides not listed in the WFD occurred in ecologically relevant concentrations, with 31 pesticides and one metabolite (grab samples only) or 37 pesticides and two metabolites (EDS included) exceeding the regulatory acceptable concentrations (RACs, see SI Table 2). For Aclonifen and Metazachlor, the EQS but not the RAC was exceeded. By contrast, 31 RAC

exceeding pesticides were identified that would have gone unnoticed in WFD monitoring (see SI Figure 4). Of the ten pesticides most frequently found in concentrations exceeding their RAC, only three are included in the WFD spectrum of analytes. None of the four pesticides that most frequently caused RAC exceedances - Thiacloprid, Clothianidin, Methiocarb and Fipronil ($\Sigma = 54\%$ of RAC exceedances) - are listed as a PS or RBSP. These results are supported by Tsaoulas et al. (2016) who identified 71 pesticides that required monitoring based on a multi-criteria prioritisation in a large Greek river basin while only small fractions of 13 and 6 pesticides were PS and RBPS, respectively. Accordingly, Moschet et al. (2014) found that when measurements were restricted to pesticides listed as PS in a Swiss stream monitoring campaign, 80% of threshold exceedances remained undetected.

This significantly influences the status classification of surface waters. WFD-compliant pesticide monitoring would yield a good status for 65% ($n = 66$) of the streams investigated in this study (see Figure 2). Only in 12% ($n = 12$) of streams, more than one pesticide exceeding the EQS would have been detected. By including EDS samples and RACs to assess additional pesticide analytes, only 19% ($n = 19$) of streams were found to achieve good status with respect to pesticides. Almost two thirds of the streams (64%, $n = 65$) exhibited at least two RAC-exceeding pesticides. WFD-compliant monitoring and assessment therefore failed to detect the unacceptable pesticide risk (RAC exceedance) for 57% of agricultural streams and 72% of the pesticides. Consequently, the list of analytes to be monitored under the WFD by far does not include the majority of environmentally relevant pesticides.

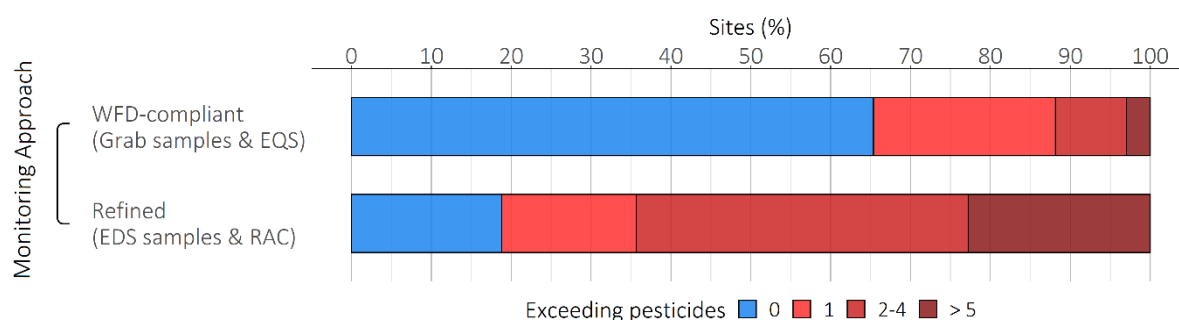


Figure 2: Fraction of sites with good status (blue = no threshold exceedance) and failing to achieve good status (shades of red = threshold exceedances) due to pesticides depending on the type of assessment. The WFD-compliant assessment is limited to

grab samples and pesticides with an assigned EQS and found 65% of agricultural streams to have a good status with respect to pesticides. When EDS samples and a wider spectrum of pesticides were included, only 19% of streams were found to have a good status with respect to pesticides.

At the same time, we found that approximately three quarters ($n = 49$) of pesticides considered under the WFD were no longer approved for use in Germany (EU Pesticides Database of the European Commission, as of July 2021). In contrast, of the 301 different pesticides currently approved for use in Germany, only 6% ($n=18$) are subject to mandatory analysis under the WFD. Previous investigations have already emphasized that prioritization, monitoring and assessment mostly cover long-known substances while those of emerging concern remain disregarded (Brack et al., 2017; Heiss and Küster, 2015). Thiacloprid, for example, was responsible for 25% of RAC exceedances showing the highest rate of exceedances in our study. Thiacloprid, along with other neonicotinoids, was placed on the so-called Watch List, which brings together candidates for an updated list of PS, in 2015. In 2020, however, its use for plant protection was banned across the EU (European Commission, 2020). Not yet listed as a PS, Thiacloprid has probably already peaked in terms of environmental relevance. In the stream monitoring campaign, Clothianidin, Methiocarb and Fipronil were also often measured in concentrations exceeding the RAC. These substances have not been monitored under the WFD and were also banned for plant protection in recent years. Nevertheless, substitutes (e.g. anthranilic diamides like Chlorantraniliprole (Schmidt-Jeffris and Nault, 2016)) will fill the emerging gap, and if the aim is to avoid unexpected ecological consequences environmental concentrations must be monitored directly when a compound is used in significant amounts. The list of WFD pesticide analytes and the corresponding EQS must therefore respond more rapidly to the continuously changing spectrum of pesticides applied and relevant in the environment. The Watch List needs to be updated before the candidate substance's environmental relevance peaks. This could be achieved by monitoring a wide range of pesticides in a representative selection of agricultural surface waters and through regular dialogue with pesticide regulators familiar with the dynamics of the current-use pesticide spectrum. For now, we recommend that environmental authorities in charge of monitoring extend the mandatory analyte spectrum to include pesticides currently used (e.g. on the basis of sales quantities as published by the BVL for

Germany) or identified as drivers of risk in this study (see SI Table 2). To classify measured concentrations when EQS are not available, we suggest using the AC_{field} (for invertebrate toxic pesticides, Liess et al., 2021a) and the RAC (for pesticides primarily affecting other organism groups, UBA, 2019) to assess concentration maxima. The Swiss Ecotox Centre has also derived chronic and acute quality standards for many pesticides not assigned an AA- or MAC-EQS following the official guidance (Oekotoxzentrum, 2021), that may not provide sufficient protection, though (see Reason #3 below).

Furthermore, the spectrum of RBSP to be measured by an EU member state involves two deficiencies: (i) Increasing the monitoring effort and extending the RBSP spectrum involves additional costs for monitoring and possible risk mitigation measures. By providing less monitoring data, the obligation to initiate such measures can be circumvented, thus penalising ambitions to protect the environment. (ii) Under the WFD, RBSP are monitored in a certain surface water if they were considered beforehand to be “discharged in significant quantities”. Whether an RBSP is “discharged in significant quantities” in a specific water body and needs to be integrated in routine WFD monitoring is difficult to evaluate reliably as long as the RBSP is not measured. Monitoring capacities for almost 10,000 WFD water bodies in Germany alone are limited and do not allow all pollutants “discharged in significant quantities” to be precisely identified in advance. Meanwhile, continuous changes in agricultural use and pesticide application schemes make it more difficult to monitor relevant RBSP (Arle et al., 2016). Moreover, the WFD does not define what “significant quantities” are, with the result that different interpretations prevail in the EU member states. We therefore support the integration of RBSP monitoring into the chemical status assessment as proposed by Brack et al. (2017). The separate assessment of PS for chemical status and RBSP for determining ecological status unjustifiably implies different monitoring intensities and complicates the interpretation of the effect of chemicals on the ecological status. The proposed integration would also have the positive side effect of harmonizing monitoring ambitions, as all EU member states would monitor the same list of RBSP assigned harmonized EQS. To take into account regional differences in pollution patterns and risk drivers, EU member states might omit analytes of negligible concern for their region or river basin. Such a negligible concern would have to be

convincingly demonstrated on a regular basis by representative measurements, pesticide sales and application quantities or exposure modelling.

In addition to the insufficient analyte spectrum, analytical capacities hinder measuring the pesticide contamination. Several pesticides are so toxic for aquatic organisms that their acceptable concentrations in the water phase are below common analytical limits of detection. This partly concerns legacy compounds like Heptachlor and Dichlorvos, but also current-use neonicotinoid and pyrethroid insecticides. The AA-EQS for Imidacloprid and Cypermethrin, for example, are only 2 ng/L and 80 pg/L – concentrations too low to be quantified by the commissioned laboratories in the WFD monitoring (Jarosch, 2018; Moschet et al., 2014; Rösch et al., 2019; Weißbach and Stricker, 2020). EQS exceedances may therefore remain unmeasured, raising the question of how to adequately monitor such toxic compounds and whether their use is generally justifiable when the resulting risk cannot be reliably assessed.

3.3 Reason #3 – Assessing pesticide effects

Here, we address the assessment of potential ecological consequences of measured concentrations by applying regulatory thresholds. Firstly, we raise concerns regarding the capacity of current regulatory thresholds to adequately assess pesticide risk. We compared the absolute values of MAC-EQS (including other member states' RBSP) with the German RACs and the field-based acceptable concentrations (AC_{field} , Liess et al., 2021a), all of which aim to assess acute pesticide risks. RAC and MAC-EQS values differed for 29 of the 31 analysed pesticides that are assigned both thresholds, but were on average comparable (log-transformed paired t-test, $p = 0.4$). All four pesticides that are assigned MAC-EQS and AC_{field} values, Imidacloprid, Dimethoate, Pirimicarb and Ethofumesate, exhibit a MAC-EQS greater than the respective AC_{field} by a mean factor of 16 (geometric mean, min = 2.4, max = 195, see Figure 3). The RAC exceeded the corresponding AC_{field} values for 90% ($n = 20$) of compared pesticides. RACs were significantly higher than AC_{field} values (log-transformed paired t-test, $p < 0.001$) by a mean factor of 4.2 (geometric mean, $n = 22$, min = 0.04, max = 56.5). Consequently, applying the mostly lower AC_{field}

classified more streams as being at risk than the EQS or RAC, showing 96% (n = 97) of agricultural streams as failing to achieve good status (see SI Figure 4).

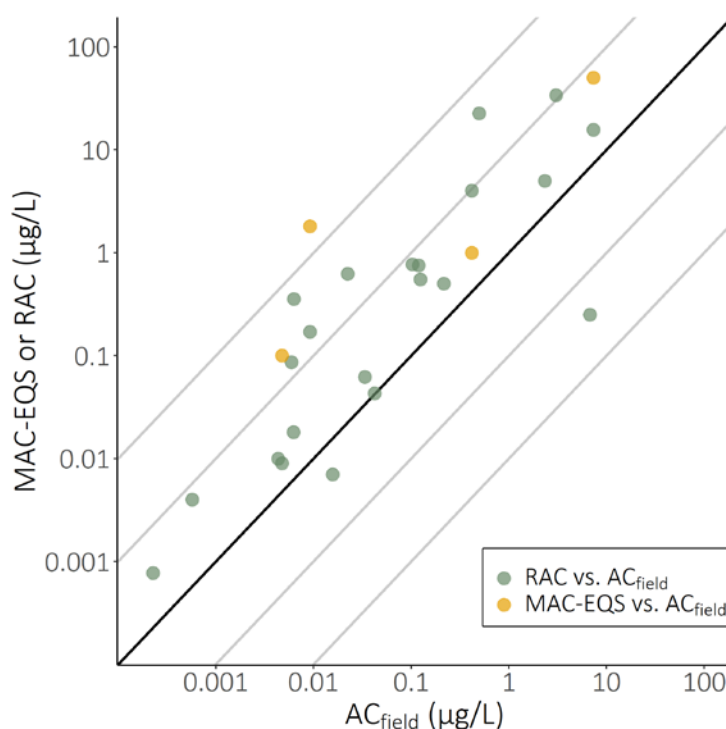


Figure 3: Comparison of the acceptable concentrations for pesticides derived from field observations (AC_{field} , Liess et al., 2021a) with those provided in the WFD (maximum acceptable concentration environmental quality standard - MAC-EQS) or from pesticide risk assessment (regulatory acceptable concentration - RAC). Each dot represents one pesticide for which the AC_{field} and either the MAC-EQS (orange) or the RAC (olive) is available. A dot on the black bisectrix indicates equal values for the AC_{field} and the MAC-EQS/RAC. Dots above or below the black bisectrix indicate a lower or higher AC_{field} compared to the MAC-EQS/RAC, respectively. Grey lines indicate value differences in orders of magnitude. The average deviation from the AC_{field} was 16 for the four MAC-EQS and 4.2 for the 22 RACs (geometric mean).

The general comparability of absolute values of MAC-EQS and RAC and the divergence from the AC_{field} are largely due to the differing assessment factors (AFs) applied in the respective threshold derivation. MAC-EQS and RAC rely on comparable or partly equal AFs aiming to account for the uncertainties relating to the transferability of effects from artificial test systems to the field. To extrapolate from acute toxicity tests to the field for invertebrates for example, the guidance for the derivation of MAC-EQS and RAC propose AFs of 100 (EFSA, 2013; European Commission, 2018). While AFs of MAC-EQS and RAC are generally based on estimations derived from artificial test systems, the AF determined for the AC_{field} is

calibrated to pesticide effects observed in the field. Following this approach, Liess et al. (2021a) determined an AF for acute toxicity tests of almost 2,000 required to protect vulnerable species in the field, resulting in the mostly lower AC_{field} values. This insufficiency of current AFs is supported by several other studies relating pesticide concentrations to effects on invertebrates under field conditions. Significant shifts in stream invertebrate communities were demonstrated at concentrations of one 100th of the concentration causing 50% of organisms to display effects in acute toxicity tests (Knillmann et al., 2018; Liess and Ohe, 2005; Münze et al., 2017; Ohe et al., 2011). Schäfer et al. (2012) found that the relative abundance of sensitive species decreased by 27% - 61% with an AF of 100 and estimated that an AF of 1,000 - 10,000 was required to avoid pesticide-related effects. In addition, the richness of invertebrate families was found to decrease in the field when concentration maxima exceeded levels equalling one tenth of regulatory thresholds (Beketov et al., 2013; Stehle and Schulz, 2015a). In contrast to these field investigations, an AF of ten to 100 was estimated as sufficient to extrapolate from single species acute toxicity tests to multi-species micro- and mesocosms (Brock and van Wijngaarden, 2012; van Wijngaarden et al., 2015). These test systems, however, fail to realistically represent environmental conditions and to account for factors that increase the sensitivity of organisms in the field. These include the joint toxicity of co-occurring pesticides (Weisner et al., 2021), additional environmental stress (Beermann et al., 2018), complex trophic interactions leading to indirect effects (Miller et al., 2020), delayed effects appearing after the runtime of the test (Rasmussen et al., 2017), sequential pesticide exposure (Wiberg-Larsen et al., 2020) and the insensitivity of commonly studied biological metrics (Liess and Beketov, 2011).

All these investigations indicate that regulatory thresholds are too high to protect aquatic ecosystems. This inadequacy of regulatory thresholds is also supported by an extreme variability between EQS for a single RBSP in different EU member states (when national RBSP overlap) with divergences amounting to as much as a factor of 100,000 despite a common guideline for the derivation of thresholds (Arle et al., 2016). This is despite an absence of evidence that effect thresholds vary by such magnitude across geographic regions. Instead, this underlines the regulatory uncertainty when predicting effect

thresholds from experimental data. Further efforts are therefore needed to validate regulatory thresholds based on field observations – also for AA-EQS and considering groups of organisms other than invertebrates. For many pesticides, algae, plants or fish are the first organism groups to show effects (Leblanc, 1984) but still lack a suitable bioindicator for pesticide stress, which is required to validate the relevant regulatory thresholds and AFs.

Besides the question whether EQS are protective enough, we raise concerns regarding the availability of MAC-EQS to assess concentration maxima. For the 24 pesticides to be analysed both under the WFD in Germany and in our study, only ten are assigned a MAC-EQS. However, the remaining fourteen pesticides also showed a periodically increased occurrence following rain events (mean EDS:Grab sample concentration ratio = 9.5, Figure 1). The guideline theoretically requires that exposure duration be taken into account, since “exposure may also occur intermittently for short periods e.g. coinciding with storm events” (European Commission, 2018), but once again, the implementation has so far disregarded this requirement.

In conclusion, there is strong evidence that compliance with current regulatory thresholds does not ensure a good ecological status in the field. We therefore recommend the use of AC_{field} values validated by field observations for invertebrate-toxic pesticides. However, a field-based validation of MAC-EQS for pesticides primarily affecting organism groups other than invertebrates as well as AA-EQS in general is lacking. The comparability of status assessments throughout the EU and the coherence of initiation of risk-reducing strategies requires an EU-wide harmonization of EQS for pesticides and other RBSP. Furthermore, there is no logical reason to separately define divergent pesticide thresholds for acceptable concentration maxima, as for the RAC under Regulation (EC) No 1107/2009 and the EQS under the WFD. Following the recommendations of Brack et al. (2017) and Schäfer et al. (2019), coexisting legal frameworks should thus be more interconnected where their scopes overlap in order to harmonize protection goals.

3.4 Our findings in the light of EU-wide results

Even if pesticide risk drivers are expected to vary locally due to differing cropping patterns and pest pressures, pesticide pressure and related ecological risks were found to be comparable for surface waters across European regions despite differences in agricultural use intensities (Schreiner et al., 2021; Stehle and Schulz, 2015b; Wolfram et al., 2021). We thus assume that our findings quantifying pesticide risk are generally transferable to other regions beyond our German study area. However, our results differ distinctly from EU-wide WFD-compliant assessments. By applying the RAC, we found 81% of the streams investigated to be at risk due to pesticides (see Figure 2). RACs were exceeded in 38% (n = 38) of streams by herbicides and in 75% (n = 76) of streams by insecticides. An EU-wide assessment of WFD monitoring data covering the period 2007 to 2017 found only 5% to 15% and 3% to 8% of surface waters failing to achieve a good status due to herbicides and insecticides, respectively (Mohaupt et al., 2020). This discrepancy is partly rooted in our focus on surface waters in the agricultural landscape. More importantly, we conclude that the discrepancy in results is due to the issues associated with the WFD monitoring strategy as outlined above, which apply to all EU member states.

4 Conclusions

- WFD sampling, chemical analysis and assessment of measured concentrations are insufficient to identify pesticide risks in surface waters. As a consequence, the chemical status of surface waters is overestimated and the contribution of pesticides to the ecological status is underestimated under the WFD.
- We propose legal and practical adjustments that would enable refined and more realistic WFD pesticide monitoring. This will (i) help explain and narrow the gap between the chemical and ecological status of surface water bodies also requiring the consideration of suitable ecological indicators that respond to pesticide pressure and (ii) implement an adequate pesticide post-registration monitoring that enables a shift in the prospective pesticide risk assessment from non-validated exposure and effect predictions to actual environmental exposure and protective

thresholds. As shown in this study, current governmental monitoring under the WFD is only of very limited use for such validation as critical pesticides and threatened surface waters remain undetected. Following the polluter pays principle, the European Parliament has already suggested in the plant protection products regulation that the additional costs for specific pesticide monitoring could be (co-)financed by plant protection product manufacturers.

- Early identification of risk drivers and immediate feedback to pesticide regulators is key to reducing the proportion of surface waters that fail to achieve a good chemical and ecological status. 20 years after the implementation of the WFD, the failure to come closer to meeting the envisaged good status for European surface water bodies underlines the necessity to substantially improve the monitoring and assessment strategy.

Additional resources

Supplementary information is available in the document “SI.docx” including considered pesticides and related thresholds, analytical methods and more detailed results. A visualisation of the distribution of measured pesticide concentrations in agricultural streams during the stream monitoring is provided by the exposure classifier (<https://www.ufz.de/kgm/index.php?en=48130>). All raw data is publicly available by Liess et al. (2021b).

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