Herrmann *et al.*
Environmental Sciences Europe (2023) 35:90
https://doi.org/10.1186/s12302-023-00795-4

Environmental Sciences Europe

RESEARCH **Open Access**

Large monitoring datasets reveal high probabilities for intermittent occurrences of pesticides in European running waters

Larissa Z. Herrmann[1], Sascha Bub[1], Jakob Wolfram[1], Sebastian Stehle[1], Lara L. Petschick[1] and Ralf Schulz[1,2*]

Abstract

Many studies have investigated short-term peak concentrations of pesticides in surface waters resulting from agricultural uses. However, we lack information to what extent pesticides reoccur over medium (> 4 days) and longer time periods (> 10 days). We use here large-scale pesticide monitoring data from across Europe (~ 15 mil. measurements, i.e., quantified concentrations in water at > 17,000 sites for 474 pesticide compounds) to evaluate the degree to which pesticides were not only detected once, but in sequences of a compound repeatedly quantified in the same area (0.015 km^2) within 4–30 days. Reoccurrence was observed at ~ 18% of sites for > 76% of compounds, ~ 40% of which not a priori considered to chronically expose aquatic ecosystems. We calculated a probability of reoccurrence (POR) over medium-term (4–7 days) and long-term (8–30 days) time periods for ~ 360 pesticides. Relative PORs (ratio between long-term and medium-term POR) revealed three occurrence patterns: ephemeral, intermittent and permanent. While fungicides dominated intermittently occurring substances, aligning with application strategies and physico-chemical properties, neonicotinoids and legacy pesticides were among substances permanently occurring. The results of this study shed new light on previously underestimated longer-term occurrence of many pesticides in aquatic environments (35% of investigated substances occurring intermittently or permanently were previously not considered to pollute the aquatic environment chronically), entailing new challenges for chronic risk assessments and the evaluation of pesticide effects on aquatic biodiversity.

Keywords Environmental monitoring, Chronic exposure, Pesticide reoccurrence, Pesticides

Background

Pesticides are considered an important chemical threat to aquatic ecosystems [38, 44, 65, 71] with a number of studies that have shown concentrations to exceed regulatory threshold levels, implying risks for aquatic organisms [13, 28, 38, 42, 63, 71, 77]. Assessing aquatic pesticide exposure is, therefore, vital to identify ecotoxicologically relevant effects on a large scale.

Determining and evaluating these effects requires knowledge about the exposure regimens to which aquatic ecosystems are subjected (acute or chronic). In the ecological risk assessment of pesticides there is no uniform and generally accepted threshold criterion for chronic exposure, due to different life-spans of assessed species groups (i.e., aquatic invertebrates, fish, algae or aquatic plants). However, durations of > 30 days have sometimes been mentioned [25]. Particularly in the case of aquatic invertebrates, much shorter time periods are already considered relevant in a chronic context. Standard laboratory tests exceeding 96 h represent, i.e., (sub-)chronic conditions and *Daphnia* reproduction tests employed

---

*Correspondence:
Ralf Schulz
r.schulz@rptu.de
[1] iES Landau, Institute for Environmental Sciences, RPTU Kaiserslautern-Landau, Fortstrasse 7, 76829 Landau, Germany
[2] Eusserthal Ecosystem Research Station, RPTU Kaiserslautern Landau, Birkenthalstrasse 13, 76857 Eusserthal, Germany

worldwide to assess chronic toxicity, last 28 days [25]. For algae, chronic test durations are even shorter. We, therefore, here consider time periods exceeding 96 h as chronically relevant from an ecotoxicity perspective. Although multiple different thresholds for the assessment of chronic effects are considered for different standard test species groups (i.e., aquatic invertebrates, algae or aquatic plant and fish), 96 h or 4 days is assumed as an absolute minimum for the consideration of chronic exposure.

To assess chronically relevant exposure, data in suitable temporal-spatial resolution are necessary to determine reoccurring environmental concentrations. Governmental monitoring programs often employ regular sampling regimes with repeated pesticide measurements conducted, e.g., at weekly or monthly intervals [12, 20, 77] to an extent, which allows for the evaluation of time series. Many of the resulting data are accessible via large data bases and can be used to assess whether pesticides reoccur over periods of time exceeding the usual acute time frame of 96 h.

Studies in peer-reviewed literature often measure pesticides at fixed time intervals, but are, however, frequently constrained to rather short periods of time. Their data, therefore, do not necessarily allow for the derivation of time series, which is necessary for the evaluation of sustained or chronic exposure (e.g., [27, 47, 72]). Previous evaluations of pesticides in European surface waters—monitored over longer time periods—are either limited to single countries (e.g., [36, 44]) or are meta-analyses of peer-reviewed or specifically collected exposure data (e.g., [14, 19, 47, 63]).

In addition, many recent studies emphasized short-term peak exposure [37, 38], which is considered an important factor particularly for the (acute) effects of insecticides on the aquatic fauna. Fungicides are, however, considered as rather persistent in water in comparison to other pesticide types [80] and—often prophylactically—applied at comparably high application rates, as fungal pests require long-term treatment [51, 69]. Similar conditions are relevant for neonicotinoids [62]. Relatively few monitoring studies have investigated longer-term aqueous-phase exposure of aquatic ecosystems to pesticides [36, 44] in a way that would retrospectively allow for the evaluation of chronic environmental risks. Chronic pesticide risk evaluations are, however, regularly done based on sediment concentrations (e.g., [48, 55, 61, 76]), due to pesticides' longer residence times in sediment phases [13, 21, 49].

The present study assesses pesticide reoccurrence based on a large aqueous-phase pesticide monitoring dataset from the European Union (EU), containing ~ 15 mil. Measurements, i.e., quantified concentrations in water at > 17,000 sites for 474 pesticide compounds. Analysis was based on occurrences, considered here as the categorization whether a pesticide was measured above the detection limit—hence detected—or remained below the analytical sensitivity threshold (limit of detection or LOD). The study has three main objectives: *(1)* illustrate the extent of the phenomenon of reoccurrence of pesticides in European surface waters for time periods of 4 to 30 days, *(2)* evaluate trends of subsequent concentrations of reoccurring pesticides, i.e., whether subsequent concentrations are lower than the initial ones or whether reoccurrence provides an indication of permanent exposure and *(3)* evaluate how the probability of reoccurrence (POR) of a pesticide after 4–7 days relates to the POR after 8–30 days.

Methods

Monitoring data

Data on pesticide measurements in surface waters were downloaded in July 2022 from two European databases, the EU Waterbase ([24, 75]; from here on referred to as "WB") and the NORMAN EMPODAT Database of Chemical Occurrence Data ([60]; from here on referred to as "NORMAN"), and one national database, the Water Framework Directive Monitoring Data Germany ([20]; from here-on referred to as "WFD-DE"). The WFD-DE was included to account for the sparse coverage of Germany within NORMAN and WB (see Additional file 1: Figure SI-1). The downloaded data sets comprised 60 million (WB), 6.5 million (NORMAN), and 3.8 mil. (WFD-DE) raw data entries, respectively. These data were thoroughly harmonized and error checked (see Additional file 1: Figure SI-2 and Methods), resulting in a combined data set which comprises pesticide monitoring data for 40 European countries with varying coverage (< 50 datapoints in e.g., Greece or Turkey compared > 1 mil. datapoints in, e.g., Germany or France; see also Additional file 1: Figure SI-1) for more than 40 years (1978–2021). The data describe 14,967,874 pesticide measurements from > 17,000 sampling sites at rivers or streams ($n = 14{,}040{,}012$), of which 52% relate to herbicides, 38% to insecticides and 10% to fungicides (for more detailed descriptive statistics, see Additional file 1: Table SI-1). A measurement was considered quantified if the respective data source stated so, or, in case no explicit statement was present, if the reported concentration was greater than or equal to the reported limit of quantification (LOQ).

The processed data (~15 mil. measurements) were attributed with specific to the catchment area regarding hydrography (Strahler order, catchment size [km^2], catchment area [km^2]; [23]), agricultural land use (croptype, e.g., orchards, cereals, vineyards) in close proximity (point locations of the monitoring data intersected with the land-use raster data) to the sampling site [29]. Furthermore, physico-chemical properties ($DT_{50,soil}$ [days], $DT_{50,water}$ [days], $DT_{50,water/sediment}$ [days], vapor pressure [mPa], Henry coefficient H [-], aqueous solubility S [mg/L], k_{OC} [-], k_{OW} [-], total polarizable surface area [Å]; [68]), approval status [22] and approved applications [11] have been attributed to the data. Measurements were binned into a hexagonal hierarchical spatial index (H3, zoom-level 10, corresponding to 0.015 km^2; H3 hexagon diameter; 150 m; [9, 66] to account for deviations in coordinate accuracy, e.g., due to different rounding in the three data sources.

Consecutive measurements and pesticide PORs

Whenever two measurements of the same pesticide at the same location (defined by their H3 index) within 1–40 days were reported in the combined data set, these measurements were considered a pair, regardless of whether the measurement yielded a quantified concentration or not. Acknowledging that a measurement can be part of multiple pairs, the dataset detailed 13,187,219 pairs, whereof 9,813,492 (74%) consisted of two quantified concentrations. Likewise, measurements were considered triples if three of the same pesticide at the same location were reported within 1–40 days in total (and a minimum of one day between measurements; see Additional file 1: Figure SI-3 for the illustration of an exemplary time series). According to this definition, the dataset contained 10,156,250 triples, whereof 7,844,495 (77%) consisted exclusively of quantified concentrations. The time frame of 1–40 days to identify consecutive measurements (i.e., pairs or triples) was chosen to reflect typical ecotoxicological test durations (chronic test designs for many aquatic invertebrates range from 96 h up to several weeks). Consecutive measurements were further divided into temporal categories according to typical monitoring intervals derived from the distribution of durations between measurements (1–3, 4–7, 8–14, 15–30 and 31–40 days; see Additional file 1: Figure SI-4).

PORs were calculated per substance (Eq. 1) based on measurement pairs of 4–7 days intervals (medium-term; $n = 241{,}895$) and triples of 8–30 days intervals, with the additional constraint in the latter case, that the middle measurement took place approximately in the middle of the interval between the first and last measurement accounting for a triple (long-term; $n = 177{,}992$; $n = 34{,}496$ or 9.69% of concentration pairs also appear as part of concentration triples, hence contributing to long-term POR calculations; see also Additional file 1: Figure SI-2). The analysis was limited to a maximum of 30 days due to the availability of data with respective sequences (see Additional file 1: Figure SI-4) and due to the calculation of PORs, which centers around the assumption of continuous exposure, which becomes less maintainable with increasing time intervals. The POR, thus, forms a measure that describes by what probability a pesticide is repeatedly quantified at fixed locations (i.e., reoccurs in the dataset as a quantified concentration) after medium or long terms. Pesticides with a high POR are more likely to reoccur in concentrations above their quantification limit than those with a smaller POR. To avoid introducing interpretation bias through overestimating the influence of substances with few overall occurrences, only substances having more than 50 pairs and triples (medium-term: $n = 358$, long-term: $n = 365$) were considered.

Calculation of POR per substance

$$\mathrm{POR}_{\mathrm{S,medium\text{-}term}} = \frac{\mathrm{n}_{\mathrm{S}[\mathit{pairs}\,4-7\mathit{d}]}}{\mathrm{N}_{\mathrm{S}[\mathit{pairs}\,4-7\mathit{d}]}};\ \mathrm{POR}_{\mathrm{S,long\text{-}term}} = \frac{\mathrm{n}_{\mathrm{S}[\mathit{triples}\,8-30\mathit{d}]}}{\mathrm{N}_{\mathrm{S}[\mathit{triples}\,8-30\mathit{d}]}} \tag{1}$$

n = number of quantified concentrations with given constraints, S = substance, N = total number of concentrations with given constraints

Statistical analysis

Differences between physico-chemical parameters, chemical classifications (e.g., pyrethroids, neonicotinoids), hydrological properties and application schemes were assessed by comparing group means using student's *t*-tests (in case of variance homogeneity) and Kruskal–Wallis tests (in case of heterogenous variances). These analyses were conducted for the two different POR metrics ($POR_{medium\text{-}term}$ based on concentration pairs and $POR_{long\text{-}term}$ based on triples), both individually and in comparison (relation between $POR_{long\text{-}term}$ and $POR_{medium\text{-}term}$). Concentrations making up pairs and triples were further analyzed by linear regression to evaluate to what extent concentrations of consecutive measurements relate to each other. An α-level of 0.05 was taken as level of significance for all statistical tests. Normality was assessed visually and through statistical testing (e.g., histograms, Anderson–Darling test). Homogeneity of variances was tested using f-statistics. Statistical analyses were conducted using R (R base: Ver. 4.2.2, 64-bit, Windows 11; [54]) and Python (Ver. 3.10.7, 64-bit, Windows 11; [70]). Geostatistical analyses were conducted using QGIS (Ver. 3.26.3, 64-bit, Windows 11; [53]).

Results and discussion

Concentration sequences and probabilities of reoccurrence

The majority of measurements ($n=474$; 88.8%) of 534 pesticide compounds yielded quantified concentrations, spread over 17,638 sites (93.2% of all sites). From these measurements, 9.8 mil. concentration pairs and 7.8 mil. concentration triples could be derived. Linear relationships between consecutive concentrations of concentration pairs and triples show that concentration levels are regularly present within the same order of magnitude (median $R^2=81.4\%$ of linear correlation of consecutive concentration pairs and triples) at situation-specific levels. Figure 1 shows the linear relationships of concentrations in concentration pairs for twelve pesticides, indicative for the patterns found for most pesticides (median $R^2=81.3\%$, 84.4% and 81.4% of concentration pairs and triples between the first two and the first and last concentration, respectively; see Additional file 1: Figure SI-5 for a linear regression across all substances). Despite challenges regarding data quality (i.e., quantification status of a measurement, see SI

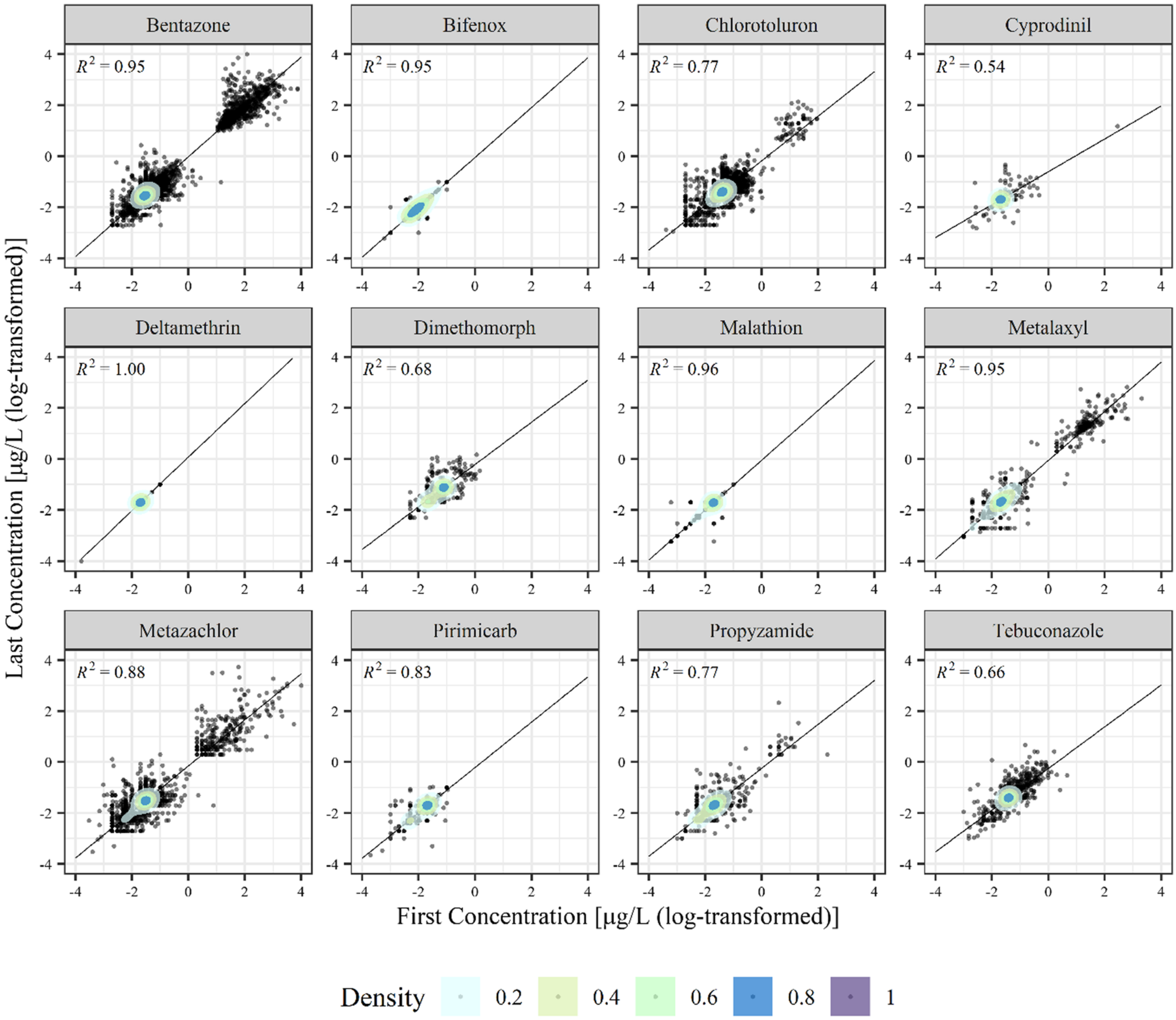

Fig. 1 Correlations of 1st and last concentrations of concentration triples for twelve pesticides on $\log_{10}$-transformed axes. Density clouds illustrate the accumulation of data. Linear regression models were fitted for the relation between 1st and last concentrations with respective R^2 displayed accordingly. Displayed substances were chosen based on their relevance for the POR calculation ($n=12$ currently approved substances frequently occurring in the triple dataset and depicting representative distributions among PORs)

Methods and Results for detailed descriptions), linear relations between subsequent, quantified measurements suggest a permanent presence of pesticides in European rivers and streams. This suggests a potential for sustained stress for aquatic ecosystems, which have been demonstrated to be affected negatively when exposed to both constant and pulsed concentrations of pesticides (e.g., [2, 8, 79]. For instance, chronic exposure to chlorotoluron (at concentrations starting from 80 µg/L) has been demonstrated to constantly decrease algal biomass [74], chronic exposure to metazachlor (a mixture herbicide containing metolachlor and alachlor) to negatively affect reproduction and survival of aquatic invertebrates (*Daphnia magna*; determined lowest observed effect concentration [LOEC] of 10 µg/L; [39]). Our results hence indicate the probability of potential detected risks for aquatic organisms, ecosystems and ecosystem functions to reoccur due to the similarity in the range of subsequent concentration values used for the calculation of PORs, thereby extending risk considerations to a temporal dimension.

Herbicides make up 46% ($n_{\text{medium-term}} = 165$, $n_{\text{long-term}} = 169$) of substances for which medium- and long-term PORs were calculated, followed by insecticides with 29% ($n_{\text{medium-term}} = 104$, $n_{\text{long-term}} = 106$) and fungicides with 25% ($n_{\text{medium-term}} = 89$, $n_{\text{long-term}} = 90$; see also Additional file 1: Table SI-2). Differences in the number of substances between pesticide groups not only depend on the predictability of their POR, but also reflect on their inclusion in monitoring campaigns as well as their detectability (as can be seen in e.g., [26, 28]), sampling frequency and strategies (e.g., flow-event-triggered or composite samples, [78]). POR were overall calculated for 358 (medium-term) and 365 substances (long-term), respectively. Medium-term reoccurrence was hereby indicated for 47.2% of pairs (quantified pairs derived for 62.6%, $n = 11{,}846$ of all sites), spread over 11% of all sites ($n = 2122$; 17.9% of sites with pairs) and 80% of substances ($n = 428$), while long-term reoccurrence was shown for 61.7% of triples (derived for 48.3%, $n = 9140$ of all sites), distributed across 6% of all sites ($n = 1256$; 13.7% of sites with triples) and 76% of all substances ($n = 406$; see Additional file 1: Table SI-2 for a further descriptive overview and Additional file 1: Table SI-3 for a list of all substances with respective PORs). Based on the proportion of sites contributing to reoccurrence, the phenomenon is relevant for 14–18% of Europe, however, it has to be taken into account, that reoccurrence can only be assessed based on monitoring data allowing for the derivation of time series. Our assessment can, therefore, be regarded as conservative, as pesticide reoccurrence could potentially affect more sites, if they were more narrowly assessed.

Pesticide occurrence patterns

Intermittent, ephemeral and permanent occurrence patterns of pesticides were derived based on the relation between medium- and long-term POR of the 326 pesticides for which PORs were calculated (Fig. 2). Medium-term POR of fungicides tend to be low ($\text{POR}_{\text{medium-term}}$ of < 50% for 80.9% of fungicides), whereas $\text{POR}_{\text{medium-term}}$ of herbicides and insecticides are relatively evenly distributed across all possible values (see Additional file 1: Figure SI-6 I). All pesticide types contain a considerable number of substances with long-term POR > 50% ($n = 268$, 82.2% of all substances in Fig. 2 with 47.4% herbicides, 26.7% insecticides and 25.7% fungicides; see also Additional file 1: Figure SI-6 II), while 39.6% of substances in Fig. 2 show long-term PORs of > 85% ($n = 129$ with 40.3% herbicides, 31.8% insecticides and 27.9% fungicides; see Additional file 1: Figure SI-6 II). This observation suggests that all pesticide types contain substances that are regularly found in in consecutive measurements taking place between 8 and 30 days with the largest proportion (almost half of all fungicides with PORs) of pesticides reoccurring long-term belonging to fungicides. Proportions of concentration pairs upon which medium-term reoccurrence is calculated also account for the calculation basis of long-term POR (see Eq. 1 and further discussion below). From an ecosystem perspective, repeated, long-term reoccurrence of fungicides potentially results in chronic exposure of non-target species, which likely bares risks for the individual and the community (e.g., [3, 35]).

Substance spectra differ by 39 substances for which $\text{POR}_{\text{long-term}}$ were calculated, but no $\text{POR}_{\text{medium-term}}$ were obtained, and 31 substances yielded $\text{POR}_{\text{medium-term}}$ but no $\text{POR}_{\text{long-term}}$. Pesticides were categorized into four groups, represented by the quadrants of Fig. 2. Three of these groups are of particular interest: *(I)* medium-term and long-term POR are both < 50%, ephemeral, *(II)* medium-term POR < 50% and long-term POR ≥ 50%, intermittent, and *(III)* medium-term and long-term POR both ≥ 50%, permanent.

Quadrant III in Fig. 2 contains pesticides ($n = 123$) that exert a high POR, regardless of whether medium-term or long-term POR are considered. This temporal invariance suggests to conclude that certain pesticides occur permanently at fixed locations: no matter after which time the pesticide is sampled again, the probability to find it in a quantifiable concentration is high. This group of pesticides with permanent occurrence is important for herbicides (46% of all herbicides) and insecticides (44% of all insecticides), but less important for fungicides (20% of all fungicides). Notably, the percentage of legacy substances (i.e., pesticides no longer approved to be used in the EU, e.g., thiamethoxam, endosulfan, chlorpyrifos, lindane)

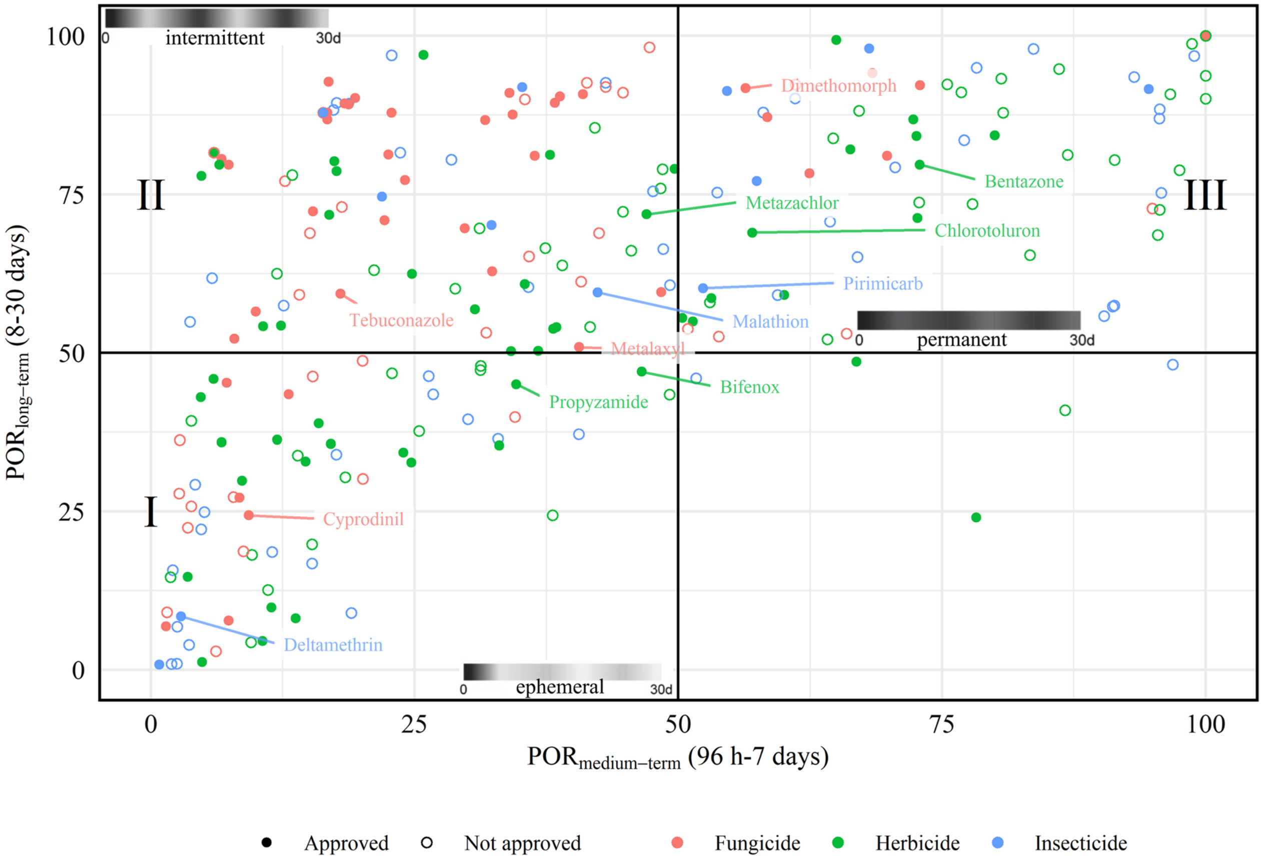

Fig. 2 Medium-term (4–7 days) vs. long-term (8–30 days) POR grouped by pesticide types (red = fungicides, green = herbicides, blue = insecticides). Filled data points indicate pesticides currently approved in the EU ($n = 111$), not filled indicate not approved ($n = 148$, $n = 67$ unknown and not displayed)

is higher in this group (67.4%) compared to the overall percentage of non-approved pesticides in the dataset (57.2%).

Most neonicotinoids belong to the permanent category in quadrant III ($n = 3$, i.e., thiamethoxam, chlothianidin, acetamiprid). Neonicotinoids display a tendency to expose aquatic ecosystems chronically [7, 16, 32, 50], hence exerting chronic risks to aquatic or riparian non-target organisms [32, 56, 59, 62], partly entering waterbodies over multiple months post application [40]. Most neonicotinoid substances ($n = 3$, thiamethoxam, chlothianidin, acetamiprid) are located in Fig. 2 III, indicating permanent occurrence, while thiacloprid is found in Fig. 2 II, rather indicating intermittent occurrence. Imidacloprid is the sole neonicotinoid insecticide located in Fig. 2 I, which would, contrary to the knowledge on neonicotinoids (e.g., high active substance content in seed coatings widely used [30] and persistent environmental behavior [16, 32], indicate a low likelihood of chronically exposing aquatic ecosystems (low medium- & long-term POR). Various global studies [1, 46, 57, 62, 73] nevertheless highlighted the frequent detection of especially imidacloprid, suggesting that sampling strategies are potentially especially relevant for the derivation of PORs of these substances.

Quadrant I in Fig. 2 contains pesticides ($n = 88$) that show an ephemeral pattern of occurrence: after such a pesticide is found with a quantified concentration at a specific site, the likelihood to find it again at the same site after a medium (4–7 days) or long-term (8–30 days) time period is rather low. About one-quarter to one-third of the pesticides follow this ephemeral pattern (26% of fungicides, 25% of herbicides and 33% of insecticides) and can, therefore, be characterized as occurring only ephemerally or sporadically at fixed monitoring locations. There appears to be one characteristic of these pesticides that might promote their ephemeral occurrence pattern: a relatively high percentage of them is used only in single applications instead of application sequences (69.2% of approved pesticides compared to 40.9% of approved pesticides in other groups). Among the pesticides in this group are pyrethroid insecticides like deltamethrin, which have been shown to be the largest contributors to the total applied toxicity for aquatic invertebrates in Germany [10]. A high amount of applied toxicity combined with sporadic occurrences in the aquatic environment due to situational applications means that the total amount of toxicity per occurrence is potentially very high, as it distributes among fewer cases, making these pyrethroids especially prone to exerting acute risks to aquatic environments. Several studies have indeed shown that reported pyrethroid concentrations regularly exceed acute regulatory thresholds (e.g., [41, 43, 64, 77]).

Quadrant II in Fig. 2 contains pesticides ($n=108$) that show an interesting combination of medium-term and long-term POR: their medium-term POR is rather low (<50%), i.e., they tend to be not found again within 4–7 days after an initial quantification, whereas their long-term POR is rather high (>50%), i.e., they tend to be quantified at least twice between 8 and 30 days after an initial quantification. In combination, this indicates an intermittent occurrence of these pesticides. More generally, pesticides located in Fig. 2 II are neither unanimously characterized by pseudo-persistent (continuous input into surface waters, inducing ongoing pollution, [17, 52]) nor by strictly transient behavior. Fungicides express such an intermittent pattern of occurrence particularly often. While 29% of the considered herbicides and 23% of insecticides are associated with this pattern, it applies to more than half of the fungicides (55%). Fungicides ($n=45.4\%$ of pesticide types in Fig. 2 II) are characterized by overall higher environmental aquatic persistence compared to other pesticide types (e.g., insecticides; [80]). In combination with their frequently prophylactic application at comparably high rates [51, 69] with frequently occurring minimum time periods between applications of i.e., 7–14 days [11], these characteristics can enhance the intermittent occurrence profile of fungicides observed in our analysis. While intermittent occurrence of a substance (e.g., a fungicide), does not unanimously allow conclusions to be drawn regarding chronic stresses (since ecotoxicological testing of chronic risks requires uninterrupted exposure; [25]), they at the same time do not allow narrowing conclusions down to potential acute risks. The date differences chosen to determine intermittent occurrence (4–7 days in case of medium-term and 8–30 days in case of long-term PORs) are short enough to assume constant stress to a certain extent, hence delivering a proxy for estimating a pesticide's probability to exert chronic stress in an aquatic ecosystem. The prominent presence of fungicides in the category of intermittently occurring pesticides raises the question, whether field concentrations of fungicides in aquatic environments should not be generally evaluated on a chronic basis (i.e., by comparing them to chronic ecotoxicological risk thresholds as done by e.g., [80]). Aquatic fungi, a species group specifically prone to negative effects through the exposure to fungicides [15, 31], are fundamental for the functioning of aquatic ecosystems [31], which means that the improvement of their protection should be a focus of the further development of environmental exposure and risk assessment.

Quadrant III in Fig. 2 is particularly relevant for potential chronic or repeated risks to aquatic environments, emphasizing the need to analyze pesticide risks through integration of the concepts of reoccurring exposure and environmental persistence (see also the following chapter). This implies frequent sampling at closely succeeding time intervals, enabling the derivation of reliable time series to assess substance PORs. Despite the distinction between intermittently and permanently occurring pesticides (Fig. 2 II and III), both substance categories are potentially relevant in the assessment of (chronic) ecotoxicological risks; while permanently occurring pesticides could exert constant stress to aquatic ecosystems, intermittent exposure is not necessarily less harmful. Ecosystems require different time periods to recover from damages inflicted by, e.g., pesticides and while it may be possible for a variety of ecosystems to recover between exposure events, having ecosystems in a consistent state of recovery is not necessarily desirable, because these ecosystems can, therefore, be rendered more vulnerable to other stressors [45]. All three categories are, therefore, relevant for the future evaluation of pesticide exposure and the associated ecotoxicological risks for aquatic ecosystems. It should be noted, that due to the skewedness of the data available for this study (most frequent sampling period monthly; see figure SI-4), PORs are likely to even be underestimated in the present analysis.

Drivers of POR distribution

Fungicides categorized as intermittently and permanently occurring are applied significantly more frequently (Fig. 2 II and III; maximum per year: 3.4 & 3, respectively; maximum per use: 2) compared to those ephemerally occurring (Fig. 2 I; maximum per year: 2.1; maximum per use: 1.5). Insecticides applied at highest maximum rates per year and use are, however, found in Fig. 2 I (2.3 and 1.8 respectively), followed by Fig. 2 II (1.7 each) and III (1.8 and 1.4 respectively), highlighting the importance of peak exposure events in connection with insecticide application and monitoring. Depending on weather conditions during pesticide application (e.g., rainfall causing runoff, drought causing increased soil porosity and resulting drainage or leaching or strong wind increasing drift), their usage can potentially have a stronger influence on their reoccurrence in adjacent water bodies than their physico-chemical properties and be a major influencing factor for toxicity towards aquatic non-target organisms [71]. This especially holds true in case of fungicides, where no significant physico-chemical property differences were distinguishable between POR categories, while application schemes of this pesticide types were shown to influence their tendency to occur intermittently or permanently.

Pesticide physico-chemical properties (i.e., water solubility, $DT_{50,soil}$, vapor pressure, Henry coefficient) differed significantly among the compounds in the three quadrants (I–III in Fig. 2, see SI results for detailed results description), indicating their role for PORs. Pesticides in Fig. 2 II (intermittently occurring) expressed significantly lower volatility (vapor pressure and Henry coefficient) than pesticides in Fig. 2 I (ephemerally occurring; vapor pressure) and III (permanently occurring; vapor pressure and Henry coefficient). This pattern appears to be mainly influenced by insecticides (Henry coefficient) and herbicides (Henry coefficient and vapor pressure), with fungicides not exhibiting these significant differences (see Additional file 1: Figure SI-7). Lower volatility indicates a tendency of pesticides to remain in the aquatic environment for longer timespans, increasing their potential to occur intermittently or even permanently. However, fungicide PORs were not subject to this trend and physico-chemical properties of a subset of pesticides (e.g., tebuconazole, cyprodinil, the insecticide deltamethrin) furthermore suggest that environmental behavior disagrees with relative POR categorizations, indicating further drivers (e.g., sampling approach, application strategies) influencing POR. Also, laboratory-based physico-chemical properties have been shown to not fully align with pesticide environmental behavior (e.g., DT_{50} [4]), indicating additional parameters being relevant for pesticide PORs (i.e., agricultural application practices).

Relative PORs of a majority of fungicides indicated intermittent occurrence, an observation in line with physico-chemical properties of the fungicides found in Fig. 2 II (median values: $\log_{10}\text{-}k_{OC} = 3.03$, $DT_{50,water} = 5.11$ days, $DT_{50,sediment/water} = 34$ days, solubility = 8.01 mg/L), which indicate a tendency to sorb to e.g., sediments while being released therefrom rather slowly, followed by moderate dissolution and dissipation or transformation beyond the time-spans relevant for long-term POR (≥ 8 days). Along with repeated applications (maximum of ten times, on average three applications per year; [11]), this environmental behavior, likely contributes to fungicides occurring intermittently in aquatic environments, in turn potentially causing negative effects to a variety of organisms (e.g., to *Gammarus fossarum* by tebuconazole, [81] or azoxystrobin, [34], both found in Fig. 2 II). Substance-specific physico-chemical parameters and pesticide application regulations hence are determining factors influencing the distribution of pesticide PORs, underlining the distinction of intermittently occurring pesticides (i.e., mainly fungicides with lower volatility, soil half-life and solubility) from ephemerally and permanently occurring substances.

Disparities between POR as novel measure for the reoccurrence of pesticides in aquatic environments and knowledge about the environmental behavior (i.e., physico-chemical properties) of chemicals have to be taken into account when interpreting these results. Out of 159 pesticides not considered persistent according to aquatic half-life ($DT_{50} < 40$ days; [67]), 30.8% ($n = 49$) were found to occur permanently (for 8–30 days). Contrarily, 41.5% ($n = 66$) of pesticides—45.4% of which ($n = 30$) fungicides—occurring intermittently are not considered persistent. While the review or verification of environmental persistence of pesticide was not within the scope of this work, it can be assumed, that persistence is an influential factor for reoccurrence below the limit considered in regulation (≥ 40 days in water).

The observation of pesticides found to occur intermittently, which are not considered to be persistent in water, can be explained by application regimes, while that of pesticides occurring permanently while not being categorized as persistent opens the question, whether basing decisions regarding the safety of a chemical on laboratory-derived proxies of environmental behavior—as it is currently implemented—is sufficient. Environmental behavior has been shown to deviate from laboratory-derived physico-chemical properties [4] and conventional biodegradation test procedures, which were designed a number of years ago for soluble, nonvolatile, single-constituent test substances do no longer represent the large spectrum of manufactured chemical substances ([18], see SI Results for further elaborations). In addition, because persistence has the potential to increase a substance's toxicity, which is crucial for compounds that are present in the environment permanently, there are calls for more cautious considerations of persistence in chemical evaluation and regulation [58].

Study limitations

The chosen terminology used to describe the presence of a pesticide in the aquatic environment as (re-)occurring depends on the sensitivity of the analytical method. We, therefore, emphasized the inspection and incorporation of quality parameters (e.g., LOD) into our analysis. This limitation in mind, we decided to base pesticide POR solely on the binary evaluation whether a pesticide occurred, hence was quantified as opposed to incorporating continuous concentration data, due to the similarity of subsequent measurements and a major proportion of the data identified as quantified, which gives a similar calculation basis for both approaches. Studying successive environmental concentrations of pesticides is, however, a subject for future research in the field of pesticide exposure evaluation.

Subsequent occurrences of different pesticides with concentration values within the same order of magnitude can further indicate the probability of potential risks to aquatic organisms to reoccur also. Depending on the pesticides' modes of action, subsequent occurrences of various pesticides may also enhance the risks encountered by aquatic organisms, which points to an essential point for future research.

Finally, while physico-chemical properties can only reflect POR to a limited extent (e.g., by providing information to a pesticide's tendency to be bind to or be released from sediment), their evaluation with focus on and in combination with application regimens, weather events and further spatio-temporal factors will be valuable subjects of further research in this area.

Conclusion

Analyzing pesticide exposure based on publicly available monitoring databases provides new, comprehensive insights into pesticide environmental reoccurrence in aquatic ecosystems on a continental scale, highlighting chronic exposure potentials of various substances across pesticide groups. Established POR categories partially aligned with expectations based on previous knowledge about substance properties (e.g., neonicotinoids found as permanently occurring due to their persistent environmental behavior), while especially fungicides highlighted the existence of a novel category between ephemeral and permanent pesticide occurrence. These substances occur to a large extent intermittently, while also tending to (pseudo)-persistent behavior (due to e.g., application strategies). This category has previously not been described separately from per-se persistent or pseudo-persistent substances. Environmental behavior and potential ecotoxicological impacts of these substances are therefore sensible targets for further investigation.

The findings of this study are in line with recommendations in peer-reviewed literature for improving and updating the current environmental risk assessment to prospectively estimate risks based on holistically assessed exposure scenarios (e.g., [5, 6, 18, 33, 38]). We presented a number of pesticides, previously not known to contaminate the aquatic environment at (sub-)chronic intervals, to occur intermittently or permanently at 17% of sites contained in the European monitoring databases. Further research (e.g., investigation of potential non-parametric relationships between PORs and environmental, geographical and substance-specific properties) based on and regular updates of the data used in this study are, however, necessary to aid in completing the picture of pesticide exposure patterns in aquatic ecosystems.

Abbreviations

WB	EU waterbase
EU	European Union
H3	Hierarchical spatial index
LOQ	Limit of quantification
LOEC	Lowest observed effect concentration
NORMAN	NORMAN EMPODAT database of chemical occurrence
POR	Probability of reoccurrence
WFD-DE	Water framework directive monitoring data Germany

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s12302-023-00795-4.

Additional file 1. Supporting Methods: Additional methodological details regarding database pre-processing and data quality assessment. Supporting Results: Additional results regarding database pre-processing and data quality assessment. **Figure SI-1.** Map displaying data coverage of the three opensource databases used in this study. CORINE Land Cover (Heymann 1993) data were used to display agriculturally used land-types across Europe. **Figure SI-2.** Data processing flowchart illustrating the pipeline of data streamlining and preparation for the derivation of concentration pairs and triples and the subsequent calculation of pesticide PORs. **Figure SI-3.** Exemplary visualization of the derivation of concentration sequences for the calculation of pesticides PORs. **Figure SI-4.** Density distribution of sampling intervals discovered in the data used for our analysis of substances with n > 100. **Figure SI-5.** Comparison of subsequent concentrations based on concentration triples (I: 1st and 2nd concentration, II: 1st and 3rd concentration) on $\log_{10}$-transformed axes. Points are overlayed with density clouds demonstrating the concentration of data. Linear regression models were fitted for the relation between 1st and 2nd (I) and 1st and 3rd (II) concentrations with respective R^2 displayed accordingly. **Figure SI-6.** Histograms of POR distribution categorized by pesticide types (red = fungicides, green = herbicides, blue = insecticides) for concentration pairs (A) and triples (B). Concentration pairs (indicating medium-term reoccurrence) exhibit a skewedness towards POR < 50% while POR calculated based on concentration triples (indicating long-term reoccurrence) tend to be more right-skewed. **Figure SI-7.** Boxplots of distributions of ($\log_{10}$-transformed) vapor pressure across POR categories (I) assigned in Fig. 2 (main text), grouped by pesticide types (II). Levels of significance for differences in mean values are denoted as: *: $p < 0.05$, **: $p < 0.01$, ***: $p < 0.005$. **Table SI-1.** Descriptive statistics of databases used and created in the course of this study. **Table SI-2.** Descriptive statistics of pesticide reoccurrences derived from concentration pairs and triples. **Table SI-3.** Pesticides with at least one POR ($POR_{medium\text{-}term}$ or $POR_{long\text{-}term}$), respective pesticide type and POR category.

Additional file 2. Dataset of processed pesticide monitoring data used for the analyses.

Acknowledgements

Larissa Zoë Herrmann would like to thank the DBU (Deutsche Bundesstiftung Umwelt) for funding her doctoral research by a doctoral fellowship (grant 20021/734).

Author contributions

LZH, SS, SB, JW, LLP and RS designed the research. LZH and JW researched and analyzed the data. LZH and SB wrote the manuscript. LZH prepared the figures and tables. All authors reviewed and edited the manuscript. All authors have given approval to the final version of the manuscript.

Funding
Open Access funding enabled and organized by Projekt DEAL. The DBU, *Deutsche Bundesstiftung Umwelt*, provides funding for Larissa Z. Herrmann and Lara L. Petschick (grants 20021/734 and 20019/593, respectively). This work was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation), grant number 326210499/GRK2360.

Availability of data and materials
The databases EU Waterbase and NORMAN, supporting the conclusions of this article are available in the original, openly accessible repositories: EU Waterbase and WISE Freshwater Information System for Europe, https://www.eea.europa.eu/en/datahub/datahubitem-view/fbf3717c-cd7b-4785-933a-d0cf510542e1 and NORMAN Empodat Chemical Occurrence Database, https://www.norman-network.com/nds/common/. The gathered and processed data used for the evaluations made in this paper are available as Additional file 2: rds file. Table SI-5 is furthermore available as.csv file. The datasets generated during the current study beyond the two mentioned files are available from the corresponding author upon reasonable request.

Declarations

Ethics approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

Competing interests
S.B. and R.S. are employees of the RPTU Kaiserslautern-Landau and also work as part-time consultants in the field of ecotoxicology and environmental risk assessment. The authors declare no other competing interests.

Received: 3 August 2023 Accepted: 7 October 2023

References

1. Anderson JC, Dubetz C, Palace VP (2015) Neonicotinoids in the Canadian aquatic environment: a literature review on current use products with a focus on fate, exposure, and biological effects. Sci Total Environ 505:409–422
2. Ashauer R, Boxall ABA, Brown CD (2007) Modeling combined effects of pulsed exposure to carbaryl and chlorpyrifos on *Gammarus pulex*. Environ Sci Technol 41(15):5535–5541. https://doi.org/10.1021/es070283w
3. Baudy P, Zubrod JP, Konschak M, Röder N, Nguyen TH, Schreiner VC, Baschien C, Schulz R, Bundschuh M (2021) Environmentally relevant fungicide levels modify fungal community composition and interactions but not functioning. Environ Pollut 285:117234. https://doi.org/10.1016/j.envpol.2021.117234
4. Beulke S, Brown C (2001) Evaluation of methods to derive pesticide degradation parameters for regulatory modelling. Biol Fertil Soils 33(6):558–564. https://doi.org/10.1007/s003740100364
5. Birch H, Dechesne A, Knudsmark Sjøholm K, Mayer P (2023) Biodegradation of chemicals tested in mixtures and individually: mixture effects on biodegradation kinetics and microbial composition. Biodegradation 34(2):139–153. https://doi.org/10.1007/s10532-022-10009-y
6. Boethling R, Fenner K, Howard P, Klecka G, Madsen T, Snape JR, Whelan MJ (2009) Environmental persistence of organic pollutants: guidance for development and review of POP risk profiles. Integr Environ Assess Manag 5(4):539–556. https://doi.org/10.1897/IEAM_2008-090.1
7. Borsuah JF, Messer TL, Snow DD, Comfort SD, Mittelstet AR (2020) Literature review: global neonicotinoid insecticide occurrence in aquatic environments. WATER 12(12):3388
8. Boxall ABA, Fogg LA, Ashauer R, Bowles T, Sinclair CJ, Colyer A, Brain RA (2013) Effects of repeated pulsed herbicide exposures on the growth of aquatic macrophytes. Environ Toxicol Chem 32(1):193–200. https://doi.org/10.1002/etc.2040
9. Brodsky I (2018) H3: uber's hexagonal hierarchical spatial index. Uber Technologies, Inc.
10. Bub S, Wolfram J, Petschick LL, Stehle S, Schulz R (2023) Trends of total applied pesticide toxicity in German agriculture. Environ Sci Technol 57(1):852–861. https://doi.org/10.1021/acs.est.2c07251
11. Bundesamt für Verbraucherschutz und Lebensmittelsicherheit (BVL). Verzeichnis zugelassener Pflanzenschutzmittel. https://apps2.bvl.bund.de/psm/jsp/index.jsp (Accessed May 17, 2023).
12. Bundschuh M, Goedkoop W, Kreuger J (2014) Evaluation of pesticide monitoring strategies in agricultural streams based on the toxic-unit concept—experiences from long-term measurements. Sci Total Environ 484:84. https://doi.org/10.1016/j.scitotenv.2014.03.015
13. Ccanccapa A, Masiá A, Navarro-Ortega A, Picó Y, Barceló D (2016) Pesticides in the Ebro river basin: occurrence and risk assessment. Environ Pollut 211:414–424. https://doi.org/10.1016/j.envpol.2015.12.059
14. Chow R, Scheidegger R, Doppler T, Dietzel A, Fenicia F, Stamm C (2020) A review of long-term pesticide monitoring studies to assess surface water quality trends. Water Res X 9:100064. https://doi.org/10.1016/j.wroa.2020.100064
15. Cornejo A, Pérez J, Alonso A, López-Rojo N, Monroy S, Boyero L (2020) A common fungicide impairs stream ecosystem functioning through effects on aquatic hyphomycetes and detritivorous caddisflies. J Environ Manage 263:110425. https://doi.org/10.1016/j.jenvman.2020.110425
16. Craddock HA, Huang D, Turner PC, Quirós-Alcalá L, Payne-Sturges DC (2019) Trends in neonicotinoid pesticide residues in food and water in the United States, 1999–2015. Environ Health 18(1):7. https://doi.org/10.1186/s12940-018-0441-7
17. Daughton CG (2003) Cradle-to-cradle stewardship of drugs for minimizing their environmental disposition while promoting human health. I. Rationale for and avenues toward a green pharmacy. Environ Health Perspect 111(5):757–774. https://doi.org/10.1289/ehp.5947
18. Davenport R, Curtis-Jackson P, Dalkmann P, Davies J, Fenner K, Hand L, McDonough K, Ott A, Ortega-Calvo JJ, Parsons JR, Schäffer A, Sweetlove C, Trapp S, Wang N, Redman A (2022) Scientific concepts and methods for moving persistence assessments into the 21st century. Integr Environ Assess Manag 18(6):1454–1487. https://doi.org/10.1002/ieam.4575
19. de Souza RM, Seibert D, Quesada HB, de Jesus Bassetti F, Fagundes-Klen MR, Bergamasco R (2020) Occurrence, impacts and general aspects of pesticides in surface water: a review. Proc Safety Environ Prot 135:22–37. https://doi.org/10.1016/j.psep.2019.12.035
20. European Parliament and Council (2000) Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. WFD. In Official Journal of the European Union (OJ L 327). https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32000L0060. Accessed 3 Jan 2022
21. Eissa F, Al-Sisi M, Ghanem K (2022) Occurrence and ecotoxicological risk assessment of pesticides in sediments of the rosetta branch, Nile River, Egypt. J Environ Sci 118:21–31. https://doi.org/10.1016/j.jes.2021.08.047
22. European Commission. EU pesticides database (v.2.1) search active substances, safeners and synergists. https://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/active-substances/?event=search.as. Accessed 1 Mar 2022
23. European Environment Agency (2012) EEA catchments and rivers network system. ECRINS v11. https://doi.org/10.2800/51667
24. European Environment Agency (2021) Waterbase—water quality ICM. https://www.eea.europa.eu/data-and-maps/data/waterbase-water-quality-icm-2. Accessed 17 May 2023
25. European Food Safety Authority (EFSA) (2013) Guidance on tiered risk assessment for plant protection products for aquatic organisms in edge-of-field surface waters. EFSA J. https://doi.org/10.2903/j.efsa.2013.3290
26. Finizio A, Azimonti G, Villa S (2011) Occurrence of pesticides in surface water bodies: a critical analysis of the Italian national pesticide survey programs. J Environ Monit 13(1):49–57. https://doi.org/10.1039/c0em00192a
27. Golfinopoulos SK, Nikolaou AD, Kostopoulou MN, Xilourgidis NK, Vagi MC, Lekkas DT (2003) Organochlorine pesticides in the surface waters of Northern Greece. Chemosphere 50(4):507–516. https://doi.org/10.1016/s0045-6535(02)00480-0
28. Halbach K, Möder M, Schrader S, Liebmann L, Schäfer RB, Schneeweiss A, Schreiner VC, Vormeier P, Weisner O, Liess M, Reemtsma T (2021) Small streams-large concentrations? Pesticide monitoring in small

agricultural streams in Germany during dry weather and rainfall. Water Res 203:117535. https://doi.org/10.1016/j.watres.2021.117535
29. Heymann Y (1993) CORINE land cover guide technique; environnement, sécurité nucléaire et protection civile 12585. Office des publ. officiellles des Communautés Européennes, Luxembourg
30. Hladik ML, Kolpin DW (2016) First national-scale reconnaissance of neonicotinoid insecticides in streams across the USA. Environ Chem 13(1):12. https://doi.org/10.1071/EN15061
31. Ittner LD, Junghans M, Werner I (2018) Aquatic fungi: a disregarded trophic level in ecological risk assessment of organic fungicides. Front Environ Sci. https://doi.org/10.3389/fenvs.2018.00105
32. Klingelhöfer D, Braun M, Brüggmann D, Groneberg DA (2022) Neonicotinoids: a critical assessment of the global research landscape of the most extensively used insecticide. Environ Res 213:113727. https://doi.org/10.1016/j.envres.2022.113727
33. Knäbel A, Stehle S, Schäfer RB, Schulz R (2012) Regulatory FOCUS surface water models fail to predict insecticide concentrations in the field. Environ Sci Technol 46(15):8397–8404. https://doi.org/10.1021/es301649w
34. Konschak M, Zubrod JP, Baudy P, Fink P, Kenngott KGJ, Englert D, Röder N, Ogbeide C, Schulz R, Bundschuh M (2021) Chronic effects of the strobilurin fungicide azoxystrobin in the leaf shredder *Gammarus fossarum* (Crustacea; Amphipoda) via two effect pathways. Ecotoxicol Environ Saf 209:111848. https://doi.org/10.1016/j.ecoenv.2020.111848
35. Konschak M, Zubrod JP, Baudy P, Fink P, Pietz S, Duque ATS, Bakanov N, Schulz R, Bundschuh M (2021) Mixture effects of a fungicide and an antibiotic: assessment and prediction using a decomposer-detritivore system. Aquat Toxicol 232:105762. https://doi.org/10.1016/j.aquatox.2021.105762
36. Konstantinou IK, Hela DG, Albanis TA (2006) The status of pesticide pollution in surface waters (rivers and lakes) of Greece. Part I. Review on occurrence and levels. Environ Pollut 141(3):555–570. https://doi.org/10.1016/j.envpol.2005.07.024
37. La Cecilia D, Dax A, Ehmann H, Koster M, Singer H, Stamm C (2021) Continuous high-frequency pesticide monitoring to observe the unexpected and the overlooked. Water Res X 13:100125
38. Liess M, Liebmann L, Vormeier P, Weisner O, Altenburger R, Borchardt D, Brack W, Chatzinotas A, Escher B, Foit K, Gunold R, Henz S, Hitzfeld KL, Schmitt-Jansen M, Kamjunke N, Kaske O, Knillmann S, Krauss M, Küster E, Link M, Lück M, Möder M, Müller A, Paschke A, Schäfer RB, Schneeweiss A, Schreiner VC, Schulze T, Schüürmann G, von Tümpling W, Weitere M, Wogram J, Reemtsma T (2021) Pesticides are the dominant stressors for vulnerable insects in lowland streams. Water Res 201:117262. https://doi.org/10.1016/j.watres.2021.117262
39. Liu H, Ye W, Zhan X, Liu W (2006) A comparative study of rac- and S-metolachlor toxicity to *Daphnia magna*. Ecotoxicol Environ Safety 63(3):451–455
40. Main AR, Headley JV, Peru KM, Michel NL, Cessna AJ, Morrissey CA (2014) Widespread use and frequent detection of neonicotinoid insecticides in wetlands of Canada's Prairie Pothole Region. PLoS ONE 9(3):e92821. https://doi.org/10.1371/journal.pone.0092821
41. Major KM, Brander SM (2020) The ecological and evolutionary implications of pyrethroid exposure: a new perspective on aquatic ecotoxicity. In: Eljarrat Ethel (ed) Pyrethroid insecticides. Springer, Cham
42. Malaj E, von der Ohe PC, Grote M, Kühne R, Mondy CP, Usseglio-Polatera P, Brack W, Schäfer RB (2014) Organic chemicals jeopardize the health of freshwater ecosystems on the continental scale. Proc Natl Acad Sci USA 111(26):9549–9554. https://doi.org/10.1073/pnas.1321082111
43. Massei R, Busch W, Wolschke H, Schinkel L, Bitsch M, Schulze T, Krauss M, Brack W (2018) Screening of pesticide and biocide patterns as risk drivers in sediments of major European river mouths: ubiquitous or river basin-specific contamination? Environ Sci Technol 52(4):2251–2260. https://doi.org/10.1021/acs.est.7b04355
44. McKnight US, Rasmussen JJ, Kronvang B, Binning PJ, Bjerg PL (2015) Sources occurrence and predicted aquatic impact of legacy and contemporary pesticides in streams. Environ Pollut 200:64–76. https://doi.org/10.1016/j.envpol.2015.02.015
45. Mebane CA (2022) The capacity of freshwater ecosystems to recover from exceedences of aquatic life criteria. Environ Toxicol Chem 41(12):2887–2910. https://doi.org/10.1002/etc.5471
46. Morrissey CA, Mineau P, Devries JH, Sanchez-Bayo F, Liess M, Cavallaro MC, Liber K (2015) Neonicotinoid contamination of global surface waters and associated risk to aquatic invertebrates: a review. Environ Int 74:291–303
47. Norman JE, Mahler BJ, Nowell LH, van Metre PC, Sandstrom MW, Corbin MA, Qian Y, Pankow JF, Luo W, Fitzgerald NB, Asher WE, McWhirter KJ (2020) Daily stream samples reveal highly complex pesticide occurrence and potential toxicity to aquatic life. Sci Total Environ 715:136795. https://doi.org/10.1016/j.scitotenv.2020.136795
48. Palma P, Köck-Schulmeyer M, Alvarenga P, Ledo L, de Alda ML, Barceló D (2015) Occurrence and potential risk of currently used pesticides in sediments of the alqueva reservoir (Guadiana Basin). Environ Sci Pollut Res Int 22(10):7665–7675. https://doi.org/10.1007/s11356-015-4390-1
49. Peris A, Barbieri MV, Postigo C, Rambla-Alegre M, López de Alda M, Eljarrat E (2022) Pesticides in sediments of the Ebro river delta cultivated area (NE Spain): occurrence and risk assessment for aquatic organisms. Environ Pollut 305:119239. https://doi.org/10.1016/j.envpol.2022.119239
50. Pietrzak D, Kania J, Kmiecik E, Malina G, Wątor K (2020) Fate of selected neonicotinoid insecticides in soil-water systems: current state of the art and knowledge gaps. Chemosphere 255:126981
51. PNPM Handbooks. Fungicide Theory of Use and Mode of Action. https://pnwhandbooks.org/plantdisease/pesticide-articles/fungicide-theory-use-mode-action (Accessed May 17, 2023).
52. Primost JE, Marino DJG, Aparicio VC, Costa JL, Carriquiriborde P (2017) Glyphosate and AMPA, "pseudo-persistent" pollutants under real-world agricultural management practices in the mesopotamic pampas agroecosystem, Argentina. Environ Pollut 229:771–779. https://doi.org/10.1016/j.envpol.2017.06.006
53. QGIS Development Team. QGIS Geographic Information System, 2022.
54. R Core Team (2010) R. A language and environment for statistical computing: reference index. R Foundation for Statistical Computing, Vienna
55. Rasmussen JJ, Wiberg-Larsen P, Baattrup-Pedersen A, Cedergreen N, McKnight US, Kreuger J, Jacobsen D, Kristensen EA, Friberg N (2015) The legacy of pesticide pollution: an overlooked factor in current risk assessments of freshwater systems. Water Res 84:25
56. Roodt AP, Huszarik M, Entling MH, Schulz R (2023) Aquatic-terrestrial transfer of neonicotinoid insecticides in riparian food webs. J Hazard Mater 455:131635
57. Sánchez-Bayo F, Goka K, Hayasaka D (2016) Contamination of the aquatic environment with neonicotinoids and its implication for ecosystems. Front Environ Sci. https://doi.org/10.3389/fenvs.2016.00071
58. Scheringer M (2023) Innovate beyond PFAS. Science 381(6655):251. https://doi.org/10.1126/science.adj7475
59. Schmidt TS, Miller JL, Mahler BJ, van Metre PC, Nowell LH, Sandstrom MW, Carlisle DM, Moran PW, Bradley PM (2022) Ecological consequences of neonicotinoid mixtures in streams. Sci Adv 8(15):8182. https://doi.org/10.1126/sciadv.abj8182
60. Slobodnik J (2022) NORMAN EMPODAT database—chemical occurrence data; NORMAN Network
61. Stehle S, Bline A, Bub S, Petschick LL, Wolfram J, Schulz R (2019) Aquatic pesticide exposure in the U.S. as a result of non-agricultural uses. Environ Int 133:105234. https://doi.org/10.1016/j.envint.2019.105234
62. Stehle S, Ovcharova V, Wolfram J, Bub S, Herrmann LZ, Petschick LL, Schulz R (2023) Neonicotinoid insecticides in global agricultural surface waters—exposure, risks and regulatory challenges. Sci Total Environ 867:161383
63. Stehle S, Schulz R (2015) Agricultural insecticides threaten surface waters at the global scale. Proc Natl Acad Sci USA 112(18):5750–5755. https://doi.org/10.1073/pnas.1500232112
64. Stehle S, Schulz R (2015) Pesticide authorization in the EU-environment unprotected? Environ Sci Pollut Res Int 22(24):19632–19647. https://doi.org/10.1007/s11356-015-5148-5
65. Stevanovic M, Gasic S (2019) Herbicides in surface water bodies—behaviour, effects on aquatic organisms and risk assessment. Pesticidi i fitomedicina 34(3–4):157–172. https://doi.org/10.2298/PIF1904157S
66. Uber Technologies, Inc. H3: Hexagonal hierarchical geospatial indexing system. https://h3geo.org/ (Accessed May 17, 2023).
67. Umweltbundesamt (UBA). Protecting the sources of our drinking water - The criteria for identifying Persistent, Mobile and Toxic (PMT) substances, and very Persistent and very Mobile (vPvM) substances under EU REACH Regulation (EC) No 1907/2006. Texte 2019, 127/2019 (127). https://www.umweltbundesamt.de/sites/default/files/medien/1410/publikationen/

2019-11-29_texte_127-2019_protecting-sources-drinking-water-pmt.pdf (Accessed July 26, 2023).
68. University of Hertfordshire. PPDB: Pesticide Properties DataBase (Accessed September 22, 2022).
69. van den Berg F, van den Bosch F, Paveley ND (2013) Optimal fungicide application timings for disease control are also an effective anti-resistance strategy: a case study for *Zymoseptoria tritici* (Mycosphaerella graminicola) on wheat. Phytopathology 103(12):1209–1219. https://doi.org/10.1094/PHYTO-03-13-0061-R
70. van Rossum G, Drake FL (2009) Python 3 reference manual. CreateSpace, Scotts Valley
71. Vormeier P, Schreiner VC, Liebmann L, Link M, Schäfer RB, Schneeweiss A, Weisner O, Liess M (2023) Temporal scales of pesticide exposure and risks in German small streams. Sci Total Environ 871:162105. https://doi.org/10.1016/j.scitotenv.2023.162105
72. Vryzas Z, Vassiliou G, Alexoudis C, Papadopoulou-Mourkidou E (2009) Spatial and temporal distribution of pesticide residues in surface waters in Northeastern Greece. Water Res 43(1):1–10. https://doi.org/10.1016/j.watres.2008.09.021
73. Warne MSJ, Turner RDR, Davis AM, Smith R, Huang A (2022) Temporal variation of imidacloprid concentration and risk in waterways discharging to the great barrier reef and potential causes. Sci Total Environ 823:153556. https://doi.org/10.1016/j.scitotenv.2022.153556
74. Weber D, Weyman G, Fruhmann T, Gagniarre M, Minten B, Memmert U (2019) Time-variable exposure experiments in conjunction with higher tier population and effect modeling to assess the risk of chlorotoluron to green algae. Environ Toxicol Chem 38(11):2520–2534. https://doi.org/10.1002/etc.4544
75. WISE Freshwater. Surface water chemical status. https://water.europa.eu/freshwater/europe-freshwater/water-framework-directive/surface-water-chemical-status-pressures (Accessed May 17, 2023).
76. Wolfand JM, Seller C, Bell CD, Cho Y-M, Oetjen K, Hogue TS, Luthy RG (2019) Occurrence of urban-use pesticides and management with enhanced stormwater control measures at the watershed scale. Environ Sci Technol 53(7):3634–3644
77. Wolfram J, Stehle S, Bub S, Petschick LL, Schulz R (2021) Water quality and ecological risks in European surface waters—monitoring improves while water quality decreases. Environ Int 152:106479. https://doi.org/10.1016/j.envint.2021.106479
78. Xing Z, Chow L, Rees H, Meng F, Li S, Ernst B, Benoy G, Zha T, Hewitt LM (2013) Influences of sampling methodologies on pesticide-residue detection in stream water. Arch Environ Contam Toxicol 64(2):208–218. https://doi.org/10.1007/s00244-012-9833-9
79. Zafar MI, Belgers JDM, van Wijngaarden RPA, Matser A, van den Brink PJ (2012) Ecological impacts of time-variable exposure regimes to the fungicide azoxystrobin on freshwater communities in outdoor microcosms. Ecotoxicology 21(4):1024–1038. https://doi.org/10.1007/s10646-012-0856-9
80. Zubrod JP, Bundschuh M, Arts G, Brühl CA, Imfeld G, Knäbel A, Payraudeau S, Rasmussen JJ, Rohr J, Scharmüller A, Smalling K, Stehle S, Schulz R, Schäfer RB (2019) Fungicides: an overlooked pesticide class? Environ Sci Technol 53(7):3347–3365. https://doi.org/10.1021/acs.est.8b04392
81. Zubrod JP, Bundschuh M, Schulz R (2010) Effects of subchronic fungicide exposure on the energy processing of *Gammarus fossarum* (Crustacea; Amphipoda). Ecotoxicol Environ Safety 73(7):1674–1680

Publisher's Note