



Review

A review of long-term pesticide monitoring studies to assess surface water quality trends

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ABSTRACT

Aquatic pesticide pollution from both agricultural and urban pest control is a concern in many parts of the world. Making an accurate assessment of pesticide exposure is the starting point to protecting aquatic ecosystems. This in turn requires the design of an effective monitoring program. Monitoring is also essential to evaluate the efficacy of mitigation measures aimed to curb pesticide pollution. However, empirical evidence for their efficacy can be confounded by additional influencing factors, most prominently variable weather conditions. This review summarizes the experiences gained from long-term (>5 years) pesticide monitoring studies for detecting trends and provides recommendations for their improvement. We reviewed articles published in the scientific literature, with a few complements from selected grey literature, for a total of 20 studies which fulfill our search criteria. Overall, temporal trends of pesticide use and hydrological conditions were the two most common factors influencing aquatic pesticide pollution. Eighteen studies demonstrated observable effects to surface water concentrations from changes in pesticide application rates (e.g., use restriction) and sixteen studies from interannual variability in hydrological conditions during the application period. Accounting for seasonal- and streamflow-related variability in trend analysis is important because the two factors can obscure trends caused by changes in pesticide use or management practices. Other mitigation measures (e.g., buffer strips) were only detectable in four studies where concentrations or loads were reduced by > 45%. Collecting additional agricultural (e.g., pesticide use, mitigation measures) and environmental (e.g., precipitation, stream flow) data, as well as establishing a baseline before the implementation of mitigation measures have been consistently reported as prerequisites to interpret water quality trends from long-term monitoring studies, but have rarely been implemented in the past.

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1.0. Introduction

Inadvertent pollution from both agricultural and urban pesticide (e.g., herbicides, insecticides, and fungicides) use is known to be a threat to the healthy ecological functioning of aquatic environments in many parts of the world since the chemical revolution of the 1940's (Carson, 1964; Spurrier, 1990). Making an accurate assessment of pesticide exposure is the starting point to protecting aquatic ecosystems. This in turn requires the design of an effective monitoring program, which includes sampling and chemical

analysis. Monitoring is also essential to evaluate the effectiveness of mitigation measures (e.g., bans and use restrictions, installation of buffer strips, safe handling procedures, drift reduction sprayers, Integrated Pest Management) aimed to curb pesticide pollution. However, providing empirical evidence for the efficacy of specific measures or entire mitigation programs is challenging because several characteristics and confounding factors (e.g., variability in weather) can strongly influence pollution to surface waters, some being unique to pesticides (Fig. 1). Therefore, statistical analysis of hydrochemical time-series is often required for trend detection and to interpret the factors influencing their presence (or absence).

A number of factors differentiate aquatic pesticide pollution patterns from other pollution types (e.g., nutrients), which makes them especially challenging for long-term monitoring and trend detection. For instance, pesticides include hundreds of different

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active ingredients, which differ in their chemical properties and thus in their environmental behaviour, reaction to specific mitigation measures, and ecotoxicity. Pesticide-use patterns, which are generally crop and region-specific, can also change markedly over time due to changing pest pressure and as compounds get banned and replaced by others (Schreder and Dickey, 2005). Since chemical analyses of pesticides is time-consuming and costly, the compound diversity inherent to pesticide pollution poses a challenge for developing and maintaining a consistent pesticide monitoring program over time (Spycher et al., 2018).

Individual pesticides often exhibit seasonal application patterns, which are reflected in pronounced seasonality of their concentrations in streams (e.g., Adams and Thurman, 1991; Leu et al., 2005; Leu et al., 2010). Furthermore, pesticide transport to surface water is typically triggered by rainfall events (Leu et al., 2004; Doppler et al., 2012) or mishandling during dry periods (Kreuger, 1998), which can cause highly variable concentrations peaks of short duration (i.e., a few hours) in small catchments. From an ecological viewpoint, these concentration peaks are of special concern (Schäfer et al., 2012; Beketov et al., 2013). Therefore, even multi-year data series may only contain a limited number of high-concentration events that can be used for trend analysis (e.g., Lerch et al., 2011a).

The problem of observing a limited number of high-concentrations peaks in surface waters is exacerbated by the strong dependence between the coincidence of pesticide application with precipitation events, particularly with herbicides (Leu et al., 2004; Singer, 2005; Lerch et al., 2011a; Doppler et al., 2012). Local pesticide-use data (i.e., pesticide-type, quantity, location, and timing of application) is often not available and has been shown to play a dominant role in determining pesticide losses (Ryberg and Gilliom, 2015). Furthermore, there are pesticides that degrade slowly in and have a strong affinity to soils, such as pyrethroids. Such pesticides have been shown to be mobilized by rain events in seasons proceeding their application, which further obscures the identification of seasonal trends (Delgado-Moreno et al., 2011; Budd et al., 2020).

Thus, pesticide monitoring in surface waters is challenged by choosing the appropriate sampling strategy to meet both the monitoring objectives and to be able to capture the strong inter-annual variability in concentrations. Key aspects in designing the appropriate sampling strategy is choosing the (sub-)sampling frequency and the factor (i.e., time or flow) controlling this frequency. For composite water samples, the time period in which composite samples are formed is also a key design aspect. The monitoring data can represent significantly different measured quantities depending on the chosen sampling strategy employed. Detecting temporal trends from such data is additionally challenged by the large variety of relevant compounds (Section 2.2) and the need to account for hydrological effects (Section 2.4).

One way of addressing these challenges is by conducting long-term monitoring over several growing seasons or years (i.e., >5 years in this review) with a consistent sampling scheme. Long-term monitoring can help define the range and interannual variability of aquatic pesticide pollution, which provides greater context when comparing pesticide levels from year to year. Long-term monitoring can also help determine the extent that confounding factors affect pesticide transport to surface waters over a range of environmental and agricultural conditions. If consistent patterns are observed over a variety of conditions, more confidence can be made in statements about observed trends.

The current scientific literature has studied the issue of detecting trends from water quality time series (Hirsch et al., 2010; Ryberg and Vecchia, 2013). Lloyd et al. (2014) reviewed statistical techniques used to detect changes in hydrochemistry and provided

a conceptual framework for choosing the appropriate statistical analysis method based on the scientific question being addressed and the structure of the data under analysis. However, to date there is a knowledge gap in how pesticide-specific challenges affect long-term trend detection and which mitigation measures have consistently demonstrated long-term efficacy in such monitoring studies. Therefore, there is a need for a comprehensive review that assembles all the lessons learned from the various long-term pesticide monitoring studies throughout the world, in order to get the most out of existing monitoring programs and enhance the design of future programs. The objectives of this literature review is to answer the following questions:

- How does the studies' design address the issue of confounding factors?
- Which sampling strategy is appropriate to meet monitoring objectives?
- What are metrics used to describe interannual variability in pesticide pollution levels?
- How do the studies statistically account for confounding factors and make annual values more comparable?
- What factors have been commonly associated with long-term aquatic pesticide trends?
- What kind of mitigation measures have been demonstrated to be effective based on the long-term monitoring data?
- What are limitations to existing monitoring programs?

In Section 1.1, we start by discussing a theoretical monitoring design aimed to evaluate the effectiveness of mitigation measures and suggest ways inferences can be drawn if the monitoring is less than ideal. We then provide a general overview of the confounding factors that make interpreting long-term aquatic pesticide pollution data difficult and introduce a causal diagram that maps the interconnectivity of these factors (Fig. 1). Section 2.0 discusses common methods used in the reviewed literature, which includes: sampling strategies, substance selection for chemical analysis, metrics used to describe the interannual variability in pesticide pollution, and the statistical treatment of factors affecting pesticide concentrations. Section 3.0 discusses the specific factors from the reviewed literature observed to affect long-term pesticide trends and the limitations of the monitoring design. In Section 4.0 we conclude with recommendations for future aquatic pesticide monitoring programs. In the Supporting Information we present the methods used for our literature search and provide a table that summarizes the reviewed case studies (Table S2).

1.1. Evaluating effectiveness of mitigation measures

The effectiveness of a specific mitigation measure can be evaluated by monitoring before (i.e., baseline) and after its implementation, while simultaneously monitoring a control. This is known as a Before-After, Control-Impact (BACI) design, which aims to quantify the effect size (i.e., the effectiveness of a mitigation measure) and differentiate environmental changes due to some planned intervention from other factors (Green, 1979; Downes et al., 2002). The Before monitoring forms a baseline and should be long enough to establish an envelope of 'normal' behaviour or variability. Pesticide concentrations in flowing waters tend to exhibit strong seasonality (Kreuger, 1998). Therefore, sampling should cover the full range of seasons and more than one instance of each season should be sampled. This means that baseline sampling would need to span at least two years, but ideally three or more depending on the strength of the interannual variability (Downes et al., 2002). A baseline is important for two reasons. The first is to form a basis to evaluate whether a significant change has

occurred. The second reason is that baseline monitoring can indicate whether there is a pre-existing trend, which may indicate the influence of factors other than the implemented mitigation measure.

The Control-Impact component refers to the simultaneous monitoring of the site being impacted and a control site that is outside the influence of the impact (Downes et al., 2002). In hydrology, the Control-Impact design can be implemented through paired catchment experiments, which provide a logical basis to separate (to some extent) water quality responses from natural or human-induced disturbances (see Neary, 2016 for a review). National databases on catchment characteristics, such as StreamCat by the United States Environmental Protection Agency (Hill et al., 2016), can be useful in finding an appropriate control site. If similar changes are observed at both the control and impact sites after mitigation, then it would be illogical to infer that the changes were due to the mitigation.

Due to the inherent costs and difficulties of conducting a BACI design in long-term environmental experiments at the catchment-scale, all long-term pesticide studies we reviewed lack one or more of the BACI elements (i.e., the Before or Control). Thus, long-term pesticide studies are observational studies by nature, which are empirical investigations that monitor and collect data on key status indicators (e.g., in-stream concentrations) to elucidate trends, but lack a baseline or experimental controls (Rosenbaum, 2002). Observational studies are potentially useful because they allow us to document progress toward policy goals and can indicate if more action is needed. However, without a baseline and/or an experimental control it can be difficult to isolate for factors contributing to cause-and-effect relationships. For instance, peak pesticide concentrations in surface waters often coincide with rainfall events due to the runoff generated from fields of pesticide application (Leu et al., 2004; Doppler et al., 2012). Therefore, drier annual weather conditions (i.e., lower frequency and intensity of rainfall events) could lead to less runoff, resulting in lower pesticide concentrations in surface waters. If the coincidence of rainfall events and pesticide application was the only relationship governing the transport of pesticides to surface waters, the main cause of pesticide loss reduction would be the prevailing (drier) weather conditions. In this case, it would be incorrect to conclude that any mitigation measure implemented during the same time period was effective.

In the absence of a BACI-type design, Runge et al. (2019) recommends the use of causal inference methods on observational time-series to identify and quantify causal interdependencies of the underlying system. Such methods often require large high-dimensional datasets, which makes them less suitable for long-term pesticide monitoring programs. Ryberg et al. (2020) provides an example of such an effort by applying structural equation models to infer major causal factors driving long-term atrazine and deethylatrazine concentration trends in conterminous U.S. streams, which turned out to be corn acreage, moisture supply, and tile drainage. Downes et al. (2002) has proposed a less stringent level-of-evidence approach that takes into account nine causal criteria in order to lower the inference uncertainty (Table 1). Using the level-of-evidence approach provides a practical framework to interpret data from observational studies and can help to elucidate the effectiveness of specific mitigation measures from other factors. However, it is important to note that none of the criteria by themselves can establish definite causality. Instead, various sorts of correlative evidence can collectively build a robust case to infer causality. Hill (1965), who was first to formalize these nine types of evidence, argued against demanding that any particular criterion be met and that there is no formal way to weigh some criteria more heavily than others.

1.2. Factors affecting the evaluation of aquatic pesticide pollution

Accounting for factors that affect aquatic pesticide pollution is important for two reasons. The first is to make year-to-year pesticide pollution levels (more) comparable. The second is to make an accurate evaluation of the effectiveness of specific mitigation measures. To better understand the observational case studies in this review (See Table S2) we explicitly mapped the main factors (ignoring minor feedbacks for clarity) that affect pesticide concentrations in surface waters with a focus on agricultural pesticide use (Fig. 1). We would expect a causal diagram for non-agricultural pesticide use to be similar to Fig. 1; however, the anthropogenic factors such as farming practices and crop types could be replaced by urban pesticide use practices and the farmyard source pathway could be replaced by urban hardscapes and landscapes. Having this visual tool allows us to evaluate the levels of the evidence (Table 1) and hypothesize plausible explanations that could explain changes in observed pesticide levels.

Fig. 1 divides the factors into two broad categories: (1) environmental factors and (2) anthropogenic factors. In this context, a confounding factor is one that can disguise trends caused by changes in pesticide use or the effect of mitigation measures. The main confounding environmental factor that can affect nearly all others is the weather (e.g., precipitation, evapotranspiration (ET), temperature, and wind). The weather can influence which organisms are likely to thrive, including both pests and beneficial predators, which subsequently affects which pesticide products are applied and their dosage. The weather also drives the transport of pesticides from their site of application to surface water (Larson et al., 1998).

An anthropogenic factor that influences aquatic pesticide levels is the changing of pesticide use patterns over time. This includes the switching of products due to changes in pest pressure (also to avoid resistance; Hawkins et al., 2019) or crops. Furthermore, pesticide registration, which is the permission granted by authorities to allow the sale (pricing and taxation) and use of specific products, can change the pesticides available on the market. This ultimately determines which pesticides will be used and exposed to the environment.

Additionally, farmers may adopt mitigation measures against point and diffuse pesticide losses either voluntarily or with monetary compensation. Agricultural point sources have been frequently found to originate from farmyards (Neumann et al., 2002). Measures that target point sources include courses on proper pesticide disposal and handling, cleaning of spraying equipment, and restrictions on aesthetic farmyard pesticide use (Kreuger, 1998). A common measure to limit diffuse losses are to install buffer strips, which are vegetated spray-free zones between the fields and waterways, designed to reduce pesticide spray drift, runoff and erosion inputs into surface waters (Reichenberger et al., 2007).

There are two general analysis methods to treat confounding factors in order to reveal potential trends caused by changes in pesticide use or mitigation measures: 1) stratification, and 2) multivariate regression analysis. Both methods require confounding factors to be identified and monitored during the study period (Braga et al., 2012). Stratification is the process in which subgroups or strata are formed based on the value of the confounder and compared within their respective strata (e.g., years are categorized by their total annual rainfall). Stratification is useful if there are only one or two confounders and if there are several years of data. Multivariate regression analysis uses a mathematical model that estimates the associations between a number of independent variables (e.g., river flow, seasonal pesticide use) and one dependent variable (i.e., pesticide concentration in surface water). The drawbacks of regression analysis are that

Table 1
The causal criteria in decreasing order of importance. The criteria can be used when a correlation is observed between a mitigation measure and the decrease of in-stream pesticide concentrations, to help decide whether there is a case for inferring the effectiveness of a mitigation measure (Adapted from Downes et al., 2002).

Causal criterion	Description
Strength of association	Relative to other mitigation measures, there is a large decrease in pesticide concentrations associated with this particular mitigation measure.
Consistency of association	The association has been observed repeatedly in different places, circumstances and times.
Specificity of association	The association is commonly limited to particular substances, locales (e.g., countries, regions), and seasons.
Temporality	Whether or not a significant decrease in pesticide concentration always follows the implementation of the mitigation measure. Note: Pesticides that degrade slowly in and have a strong affinity to soils (e.g., pyrethroids) could show a significant delay in response to the implementation of mitigation measures.
Dose-response relation	Whether there is a larger decrease in pesticide concentrations when the mitigation measure level is increased (e.g., dimensions of buffer strips).
Physicochemical plausibility	There is a physically and/or chemically plausible explanation for causality, even if there is no current evidence for the mechanism.
Coherence	A cause-and-effect interpretation should not seriously conflict with known literature or physicochemical nature of pesticides.
Experimental evidence	An experiment where implementation of the mitigation measure shows evidence of changed pesticide concentrations.
Analogy	In some cases, changes of pesticide concentrations may be argued by analogy because they may behave in similar ways.

the interpretation of the results may be inaccurate if assumptions of the mathematical models are not satisfied. An objective of this review is to see which confounding factors were commonly dealt with and the methods used to account for them. This will be discussed further in Section 2.4.

2.0. Methods from case studies

2.1. Sampling strategies

The choice between sampling strategies depends strongly on the monitoring objectives. For the monitoring of aquatic pesticide levels three sampling strategies were common to the reviewed studies: 1) grab sampling, 2) time-proportional sampling, and 3) flow-proportional sampling. Bundschuh et al. (2014) compared all three sampling strategies and found that occasional grab sampling during periods without rainfall is not a sensible option because it can substantially underestimate the peak pesticide exposure triggered by transport losses across the land-water interface. Time-proportional composite sampling strategy is recommended for assessing the ecotoxicological risks because this strategy reflects concentrations levels that aquatic organisms actually experience.

However, time-proportional sampling may underestimate the maximum acute exposure because sampling over a constant time interval can cause the sample to be diluted with low flow or baseflow aliquots with little or no pesticides. Therefore, if peak exposures are of concern an event triggered sampling strategy is recommended (Oelsner et al., 2017). Flow-proportional sampling provides concentrations, which can be useful for calculating loads and loss rates (if quantity of pesticide application is known). However, it can be challenging to implement because sampling is driven by unpredictable weather conditions. One way of making flow-proportional sampling more practical is to conduct time-proportional sampling and to weight the composite sample on flow measurements (e.g., Daouk et al., 2019).

The main issue, irrespective of the sampling strategy, is whether the sampling frequency is high enough to capture the short-duration pesticide concentration dynamics, which can be less than a few hours in small headwater catchments (Leu et al., 2004; Doppler et al., 2012). Furthermore, there are constraints from the cost and labour of chemical analysis. Therefore, samples are usually combined to form a composite sample for chemical analysis. How composite samples are formed will depend on the objectives of the pesticide exposure monitoring. For instance, 14-day composite

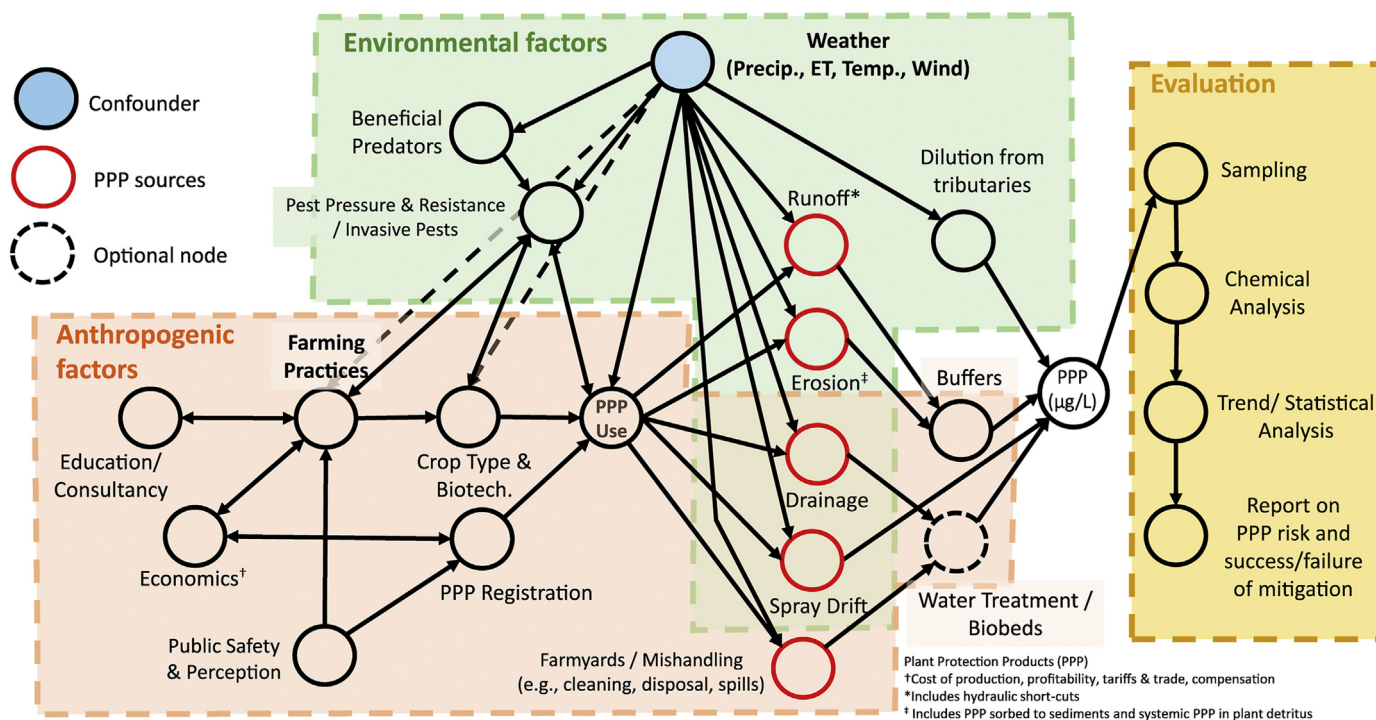


Fig. 1. Causal diagram of factors affecting evaluation of in-stream pesticide monitoring.

samples would be adequate to assess chronic exposure. However, if the objective is to assess acute exposure, composite samples would need to be 3.5-days or less (Spycher et al., 2018).

A promising alternative to the aforementioned active sampling strategies is the use of passive samplers, which require no technical facilities or power supply and can be deployed flexibly both temporarily and spatially (Bundschuh et al., 2014). There are however several shortcomings that confound the level of confidence associated with the data obtained from passive samplers, such as the optimal duration of sampler deployment, possible influence of seasons and biofouling, implications of other non-target water quality parameters (e.g., dissolved organic matter, nutrients), and chemical properties of compounds on their sorption rate (Miège et al., 2012). For these reasons, none of the long-term aquatic pesticide studies we reviewed used passive samplers for their monitoring programs. Nevertheless, the use of passive samplers to monitor aquatic pesticide pollution is an area of active research (e.g., Moschet et al., 2015; Lao et al., 2016; Liao et al., 2017; Xue et al., 2017; Curchod et al., 2020).

All studies focused their sampling over the plant-growing season, which starts between March–May and ends between September–October (in the Northern hemisphere). Kreuger and Nilsson (2001) extended their sampling to the off-season months (i.e., October to November) and observed substantial pesticide losses in 1992, suggesting that sampling is required in late fall and early winter for a more comprehensive assessment. Sampling in the off-season is especially important in regions where most rainfall events occur in the winter months (e.g., California), which can lead to a delay between the time of application and increased concentrations in surface waters (Wang et al., 2017).

2.2. Limitations of substance selection for chemical analysis

A recurring theme from this review is the uncertainty and possible underestimation of the aquatic pesticide exposure because

the suite of analytes were limited. Without a comprehensive chemical analysis over time (e.g., Spycher et al., 2018), the possibility remains that some unscreened substances may be present in quantities that are harmful to aquatic organisms. Daouk et al. (2019) recommends collecting additional information, such as pesticide use (i.e., application and registration) to help narrow down target screening and to keep costs manageable. Luo et al. (2018) developed the Surface Water Prioritization (SWMP) model to prioritize the monitoring of specific pesticides and geographic locations by incorporating pesticide use data, physicochemical properties, aquatic toxicity, and watershed morphology.

Additionally, improvements in chemical analytics are likely to occur over the course of a long-term monitoring program, which can potentially lead to different statements about the chemical status of rivers (Wahlin and Grimvall, 2008). Stenrød (2015) and Lindström et al. (2015) noted that limits of quantification lowered over the course of their studies, which can replace pesticides that were once below the detection limit with quantified concentration values. In the Charmilles catchment, the ecotoxicological risk increased as of 2013 after nicosulfuron (water quality criteria for chronic exposure 0.0087 µg/L; Annex 2 – RS 814.201; WPO, 1998) was included in the chemical analysis (Daouk et al., 2019), which also suggests that the ecotoxicological risk could have been underestimated prior to its inclusion.

Thus, there are two reasons that the chemical status of rivers could change due to improvements in analytical methods. First, is from finding newly included substances at relevant concentrations that were previously excluded (e.g., nicosulfuron in Charmilles; Daouk et al., 2019). Second, is from the lowering of the limit of detection over time. Substances that were once below the detection limit could be replaced with quantified (albeit low) concentrations. If the detected substance is toxic at low concentrations (such as pyrethroids e.g., cypermethrin), this could increase the quantified risk of exposure to aquatic organisms. Conversely, the exposure risk could be lowered as limits of quantification (LOQ) decrease and

substances continue to be very low or nondetectable. For instance, cases that previously replaced values below the LOQ with half the LOQ value may now be replaced by actual concentrations that are less than half the LOQ, lowering the exposure risk. Despite the inappropriateness and criticism of substituting censored pesticide monitoring data, it still commonly occurs. Instead, there are more appropriate methods to analyze censored pesticide data for trends (e.g., Helsel, 2012; Therneau, 2013; Wang et al., 2016; Lee, 2020). Furthermore, van Leeuwen and Vermeire (2007) recommends conducting a sensitivity analysis with a range of values between zero and LOQ instead of replacing concentrations below LOQs with a single value. In this way improved analytics should result in a smaller range of uncertainty rather than inconsistent results. Nonetheless, pesticides that are currently known to be toxic at concentrations below or around the limit of detection for many analytical methods (e.g., neonicotinoids and pyrethroids; Boye et al., 2019), will drive the need for improved method detection limits and have the potential to play a larger role in future risk assessments.

Additionally, some pesticides are difficult to detect analytically. For instance, glyphosate requires a separate and costly analytical method (Ibáñez et al., 2005; Boye et al., 2019). For this reason, glyphosate is often excluded from the suite of substances being analyzed (Moschet et al., 2014; Stone et al., 2014). This data gap can lead to the potential underestimation of the exposure risk and will be discussed further in Section 3.3: Toxic tradeoffs.

Consistent sampling and laboratory practices are critical to the interpretation of long-term environmental trends. Wahlin and Grimvall (2008) have found strong evidence that long-term trends in measured nutrient concentrations can be more extensively influenced by changes in sampling and laboratory practices than by actual changes in the state of the environment. This raises important concerns regarding quality assurances in environmental monitoring and laboratory analysis. However, it is important to note that consistency should not come at the expense of improvements in basic monitoring design. It is of little use for a monitoring program to continue in the same way, if it is known to be unfit-for-purpose. Therefore, Downes et al. (2002) recommends that the design of new monitoring programs should consider prior experience, which is subject to critical review, and that improvements in design are favoured over adherence to heuristic traditions.

2.3. Metrics to describe the interannual variability in pesticide pollution

A variety of different metrics and statistical methods have been used by the reviewed studies to evaluate for pesticide trends in surface waters. A common approach is to take the measured pesticide concentrations, calculate a time-weighted annual average value, then sum the values for all detected pesticides (Kreuger and Nilsson, 2001; Hermosin et al., 2013). An issue with this approach is that interannual pesticide concentrations can vary considerably over the years, often denoted by short-term peaks in concentration over the application period and surrounded by frequent low or nondetect values. This can skew the mean and underestimate short-term acute exposure. Thus, the use of box-plots is helpful to depict the interannual distribution (i.e., median, upper and lower quartiles, 10th and 90th percentiles, and outliers) of total pesticides. In particular, several studies (Schreder and Dickey, 2005; Phillips et al., 2007; Todd and Struger, 2014) used box-plots to show the interannual variability of pesticide concentrations and a clear reduction in concentrations before and after the ban of specific pesticide products. Censored values are typically set to any single value lower than the reporting limit, with the box-plot distribution below the reporting limit blanked out (Helsel, 2012).

Richards and Baker (1993) displayed concentration time-series practically through a concentration exceedancy curve (CEC). To plot a CEC, samples are first sorted by decreasing concentrations, allotting a duration of time for each sample. For grab samples, the time duration allotted to each sample is equal to half the time between it and the preceding sample, plus half that between it and the following sample. It is important to have a sufficiently short duration of time between samples to create a useful CEC plot. Richards and Baker (1993) stated that a majority of their time intervals did not exceed 2 days, and that longer intervals (<7 days) were typically associated with low-flow periods with low pesticide concentrations. After time allotment, concentrations are plotted against cumulative time, expressed as a percentage of entire observation period. These cumulative frequency plots display the percentage of time a given pesticide exceeds a particular concentration (e.g., Environmental Quality Standard), which can be compared annually for concentration exceedance trends.

Annual pesticide loads are another important metric for evaluating water quality trends. Pesticide loads can be calculated if measurements of flow are taken concurrently with sampling. In the small Charmilles stream, a clear reduction in annual pesticides loads from 2008 to 2013 was observed, whereas the interannual concentrations were more erratic due to interannual variability in river discharge (Daouk et al., 2019). This decreasing trend in loads, was linked to substantially reduced pesticide wash off after rain events due to the installation of grass strips between vine rows. This example shows us how pesticide loads can be a useful metric in evaluating the effectiveness of mitigation measures and that analyzing concentrations alone, which showed no clear trends, would not have led to the same conclusion.

Additionally, the variability in annual pesticide use can be treated by normalizing annual pesticide loads with the total amount of pesticides applied annually. This equates to an annual pesticide loss rate. Comparing annual loss rates is one way to evaluate whether measures other than changing annual pesticide application rates had an effect. For instance, Singer (2005) showed that pesticide losses to Lake Greifensee in Switzerland were mainly related to the coincidence of pesticide application and rain events (i.e., timing, quantity, and intensity). There was no evidence that the implemented pesticide loss-reduction measures (e.g., sprayer inspections, buffer strips) were affecting loss rates, which suggests that restricting the quantities of pesticide use was the main mitigation measure that reduced pesticide loads to Lake Greifensee (Singer, 2005). Similarly, Leu et al. (2010) found close relationships between herbicide loss rates and catchment metrics for fast flow during the application periods for six streams in the US and Switzerland.

Accurate pesticide use data (i.e., location, timing, and quantity of specific pesticide application) is also critical for the interpretation of monitoring results for patterns and trends, but may be difficult to obtain. Lerch et al., (2011a) used corn planting progress as a surrogate for the timing of pesticide application, which showed promising results when combined with streamflow and degradation rates for predicting atrazine loads. Schreder and Dickey (2005) used annual sales of pesticides as a substitute for pesticide use data. Using such proxy data can be useful if the area under study is large enough so that statistical downscaling is meaningful or for simple agronomic systems with limited crop diversity (i.e., monocropping) where a few herbicides dominate.

Stenrød (2015) extended their analyses by assessing ecotoxicological risk, which combines the exposure assessment with an ecological effects assessment (van Leeuwen and Vermeire, 2007). An effect assessment estimates the relationship between the exposure level of a substance and the severity of an effect to an organism. The effects assessment can be used to establish the

threshold of allowable concentrations in the environment, e.g., forming the basis for Environmental Quality Standards. Since different substances vary in their dose-response relationship with differing aquatic organisms, a long-term aquatic pesticide monitoring program would require the analysis of a large spectrum of pesticides to conduct an accurate ecotoxicological assessment (Spycher et al., 2018). For instance, 96 active ingredients and 19 metabolites were analyzed in 6 small Norwegian catchments, which allowed Stenrød (2015) to evaluate water quality trends regarding mixture toxicity. To account for this, Stenrød (2015) calculated a summed monthly relative cumulative risk value, or cumulative risk for short. Cumulative risk is the sum of the ratios between the measured environmental concentration and its Environmental Quality Standard (EQS; EC, 2011), which was based on the most sensitive aquatic test species for the active ingredient of each pesticide. From her cumulative risk assessment, she observed both a reduction in the detection frequency and concentrations for in-stream pesticides in catchments growing heavily sprayed potato and vegetable crops, while catchments mainly comprised of cereal production showed no significant reduction in the environmental pesticide loads. In general, Stenrød (2015) concluded that the presence of in-stream pesticides can be mainly explained by pesticide use on nearby land areas and the prevailing weather conditions.

2.4. Treatment of factors affecting pesticide trends

Most studies included some treatment of factors such as river flow, seasonality, and/or pesticide use when comparing aquatic pesticide pollution levels from year to year. As already mentioned, Singer (2005) accounted for changes in annual pesticide use by calculating and comparing annual loss rates. However, a few long-term studies were observational in nature (Cerejeira et al., 2003; Schreder and Dickey, 2005), meaning that the study mainly focused on observing whether pesticide concentration trends were taking place rather than attempting to determine the precise cause of the trend (e.g., the effectiveness of mitigation measure other than restricting use). For those studies explicit treatment of factors was unnecessary.

Several authors accounted for river flow by calculating flow-weighted average concentration (Bodo, 1991; Richards and Baker, 1993; Lerch et al., 2011a, 2011b). Whereas others (Power et al., 1999; Phillips et al., 2007; Todd and Struger, 2014) noted that no flow adjustment was needed because their analyses showed no correlation between flows and concentrations. Power et al. (1999) found that lindane was an exception and that its concentrations correlated with flow rates in the River Thames, which they believed were due to its chemical properties.

Several studies treated seasonality in their trend analysis by introducing stratification to nonparametric tests. For example, Bodo (1991) used the seasonal Mann-Kendall test (Hirsch et al., 1982) and Phillips et al. (2007) used a seasonal step-trend analysis (Helsel and Hirsch, 1992). Seasonal stratification is common in the analyses of pesticide time-series because peak concentrations in agricultural settings typically occur seasonally within the spring and summer months when planting and pesticide application, particularly herbicides, take place (see Table 2). It should be noted that certain pesticides, which degrade slowly in and have a strong affinity to soils (e.g., diazinon, fipronil, pyrethroids), that are applied in regions where rain events dominate in the winter months (e.g., California) have shown to be delayed in their transport to surface waters relative to their time of application (Budd et al., 2015, 2020; Wang et al., 2017). This fact does not undermine the importance of evaluating seasonality in the analyses of pesticide time-series, but highlights the fact that the seasonality of

pesticide application and peak surface water concentrations do not always coincide.

Researchers from the USGS created a parametric regression model specifically designed for analysing pesticide concentration trends treating both seasonal- and streamflow-related variability, which they called SEAWAVE-Q (Vecchia et al., 2008, 2009). Ryberg and Gilliom (2015) used SEAWAVE-Q to analyze pesticide trends in major rivers throughout the US from 1992 to 2010, where they found concentration trends mostly agreeing with pesticide use trends. Sullivan et al. (2009) compared SEAWAVE-Q with and without streamflow adjustment to the nonparametric seasonal Kendall test (SEAKAN) by analyzing 10 years of pesticide concentrations in the US Corn Belt streams. They favoured the SEAWAVE-Q method because it required substantially fewer measurements than the flow-adjustment procedure for SEAKAN and found that including flow-adjustment was an important part of trend analysis because changing flow conditions could alter or disguise trends caused by changes in pesticide use or management practices.

To the best of our knowledge, process-based models have yet to be used to evaluate long-term pesticide monitoring data. A more flexible alternative for treating confounders is the use of process based catchment-scale hydrological pesticide transport models, such as the one developed by Ammann et al. (2020) for the Ossingen catchment in Switzerland. Such a model could provide process-based estimates of pesticide concentrations in surface water. It can be used to simulate the situation before and after the implementation of a mitigation measure (e.g., 50% reduction in pesticide use) and can therefore be used to simulate the counterfactual assuming that no measures were taken. This type of modelling could help fill the gap from missing baseline monitoring by calculating pesticide concentrations using historic meteorological forcings. In essence, this would be using a conceptual hydrological model for quantitative counterfactual thinking (Ferraro, 2009), which attempts to answer the question “does the intervention (i.e., mitigation measure) work better than no intervention at all?” Using counterfactual thinking to develop various model scenarios allows one to estimate the expected effect size from introducing mitigation measures and to assess the potential conditions necessary to meet water quality objectives.

Wang et al. (2019) proposes to supplement physical and statistical models used to analyze aquatic pesticide pollution data with machine learning methods (e.g., Random Forests), which are tools that can extract important trends from data. Machine learning methods could be used to conduct meta-analyses that compile data from many different monitoring programs across different regions to identify potential relationships between the fate and transport of pesticides in the aquatic environment, the effectiveness of specific mitigation measures, and a large number of current and historical factors at the given sites (e.g., land use, demographics, geomorphological and hydrological attributes). Machine learning methods have the advantage of relying on few assumptions; however, they are notably more difficult to interpret (Rudin, 2019). Therefore, machine learning methods can be used as an initial screening tool to identify the factors that influence aquatic pesticide pollution the most. Afterwards, physical and statistical models can be applied considering these factors to expand upon limited (spatial and temporal) monitoring data and to gain a better mechanistic understanding of the processes governing aquatic pesticide fate and transport.

3.0. Factors associated with pesticide trends and limitations of monitoring design

Several common factors have been associated with long-term aquatic pesticide pollution from the reviewed studies (Table 2).

The two most common factors were pesticide application rates (18 studies), which includes bans and restricted use of specific products, and hydrology (16 studies), particularly post-application rainfall-runoff events. Fourteen studies have recognized or statistically treated for seasonal patterns in aquatic pesticide pollution, which is primarily due to increases in pesticide use during the plant

growing season in predominantly agricultural catchments or seasonal pest pressure in predominantly urban catchments. Ten studies discussed the chemical properties of pesticides (e.g., sorption, persistence, volatility, photolysis) to partly explain observed differences in concentration patterns between different substances and why long-term trends were detectable for some pesticides and

Table 2

Factors associated with pesticide concentrations in long-term surface water monitoring studies.

Reference(s)	Pesticide application rates	Hydrology	Seasonality	Chemical properties	Mitigation ^a
Bodo (1991)	✓	✓	✓		
Richards and Baker (1993)	✓	✓	✓	✓	
Kreuger (1998), Kreuger and Nilsson (2001)	✓	✓	✓	✓	✓
Power et al. (1999)	✓	✓	✓	✓	
Cerejeira et al. (2003)			✓		
Schreder and Dickey (2005)	✓				
Singer (2005)	✓	✓			
Phillips et al. (2007)	✓		✓		
Vryzas et al. (2009)	✓	✓	✓		
Leu et al., (2010)	✓	✓	✓	✓	
Lerch et al. (2011a, 2011b, 2015)	✓	✓	✓	✓	
Hermosin et al. (2013)	✓	✓	✓	✓	✓
Todd and Struger (2014)	✓				
Budd et al. (2015)	✓	✓		✓	
Ryberg and Gilliom (2015)	✓	✓	✓	✓	
Stenrød (2015)	✓	✓			
Wang et al. (2016, 2017)	✓	✓	✓	✓	
Carazon-Rojas et al. (2018)		✓	✓		
Daouk et al. (2019)	✓	✓			✓
Budd et al. (2020)	✓	✓	✓	✓	✓

^aOther than changes in pesticide use.

not for others. Only four studies specifically attributed mitigation measures (other than limiting pesticide use) to curbing aquatic pesticide pollution.

A notable exception comes from a study conducted in Costa Rica (Carazo-Rojas et al., 2018), where crop growing seasons and pesticide application extend throughout the year. In this case, pesticide application patterns were not a good predictor of aquatic pesticide concentrations. Higher pesticide application rates (mainly fungicides) throughout the rainiest months were associated with lower aquatic pesticide concentrations, suggesting a dilution effect. Tropical environments prove to be an exceptional agro-ecosystem, where the occurrence of aquatic pesticide pollution may be more related to environmental factors that govern the fate and transport of pesticides (e.g., rainfall events, soil properties, adsorption, runoff, leaching, and degradation) rather than the anthropogenic factor of pesticide application rates.

Furthermore, the timing of peak concentrations in surface water may not necessarily coincide with seasonal pesticide application patterns. There can be a delay of several months between pesticide application and peak concentrations in regions where rainfall events occur with greater frequency in the winter months (e.g., California). This delay is particularly prominent for those pesticides (e.g., diazinon, fipronil, pyrethroids) that degrade slowly in and have a strong affinity to soils (Budd et al., 2015, 2020; Wang et al., 2017). Wang et al. (2017) found that the diazinon application rates from the preceding year was better at explaining the variance in exceedance frequency compared to the current year's application rates, which suggests that the physiochemical properties of diazinon and the prevailing weather conditions in California may cause a significant delay in diazinon transport to surface waters.

A few other less commonly noted factors shown to be associated with aquatic pesticide pollution include: catchment size, soil type, catchment flashiness, population density, crop prices, and transboundary pesticide sources from neighbouring countries. Although these factors relate more to spatial differences, rather than temporal trends, they provide important insights into observed pesticide patterns through inter-catchment comparisons. Richards and Baker (1993) observed the tendency for peak observed concentrations to increase as watershed size decreased, which they theorized was due to the greater mixing and dilution in larger watersheds that receive water from various tributaries. Richards and Baker (1993), Lerch et al. (2015), and Stenrød (2015) noted that the greater proportion of fine-grained soil types in the near-surface could lead to less pesticide sorption and more rapid transport to streams. Similarly, Leu et al. (2010) observed an increasing risk for herbicide losses with the flashiness of the catchment. Todd and Struger (2014) found significant relationships between population density or urban land cover and the concentrations of urban-use insecticides in surface water. Bodo (1991) linked a decline in atrazine concentrations with a drop in corn prices, illustrating a direct connection between economics, crop selection, and pesticides use (or non-use). Vryzas et al. (2009) found evidence of transboundary aquatic pesticide pollution sources in three Greek rivers that border Bulgaria, which suggested the clandestine use of banned substances (i.e., DDT and γ -HCH) by their neighbour.

3.1. Identifying urban pesticide sources

Understanding the main source and pathways of aquatic pesticide pollution can help with the development of targeted mitigation measures. A major source of pesticide pollution to surface water comes from agricultural pesticide use. However, a few long-term studies also highlight the importance of urban pesticide use as a source (Phillips et al., 2007; Ryberg et al., 2010; Todd and Struger, 2014; Budd et al., 2020). Specific pesticides that are registered for

non-agricultural use can be particularly useful as tracers to identify urban pesticide sources. For instance, Todd and Struger (2014) used the ratio of the active ingredients in products sold for urban use and compared them to the observed concentration ratios in streams and found them to be somewhat similar, suggesting an urban source. In catchments with both agricultural and nonagricultural pesticide use, Ryberg and Gilliom (2015), found that concentration trends could be explained by a combination of agricultural-use trends and concentration trends in urban streams. It is important to note that long-term aquatic pesticide monitoring programs may be inadequate for the purpose of identifying pesticide sources because they typically lack the high-frequency temporal resolution necessary for the analysis of source dynamics (e.g., Peter et al., 2020).

3.2. Effective mitigation measures

A majority of the long-term studies we reviewed attributed a reduction in pesticide use (including bans or use restrictions) as the main factor linked to reductions in aquatic pesticide concentrations (Table 2). Restricting or banning the use of a pesticide is a particularly powerful mitigation measure that directly affects the quantity of that pesticide available for transport to surface waters. However, the benefits of an outright ban can be obscured if the pesticide is simply replaced by another (Section 3.3) or if it can persist in groundwater, which can be a long-term source of pesticides to surface waters even decades after a ban (Törnquist et al., 2007; Larsson et al., 2014). Furthermore, the effectiveness of pesticide use restrictions can be unclear because the quantity of pesticides that are ultimately applied is influenced by a number of other factors, such as pest pressure and weather conditions.

The moderate effects of potentially effective mitigation measures (other than use restrictions) were often indistinguishable against the background of interannual variability in surface water concentrations. Nonetheless, numerous short-term (i.e., <3 years) studies have shown that specific mitigation strategies (e.g., grassed buffer strips, spray drift reduction, better handling practices) are effective to varying degrees at reducing pesticide losses to surface water (Reichenberger et al., 2007).

Although a decrease in pesticide pollution is expected after bans or policies on restricted use, there are a number of cases where declining trends in pesticide concentrations were observed before such measures were put into place (e.g., Power et al., 1999; Philipps et al., 2007; Todd and Struger, 2014). The presence of a decreasing trend before a ban puts into question their effectiveness and indicates the presence of other factors that could be contributing to a decreasing trend. It also emphasizes the importance of sampling before the implementation of mitigation measures in order to establish a baseline. Todd and Struger (2014) speculated that the decreasing trend before the ban could be related to increased public awareness due to bans in neighbouring provinces that potentially led to voluntary reductions in pesticide use. Similarly, Wang et al. (2017) concluded that a downward diazinon-use trend from 1994 to 1998, which occurred before introducing regulatory stimulus, could have resulted from changing pest pressures, economy, or market forces.

Only one study by Singer (2005) specified a water quality objective to be met through the implementation of mitigation measures, which was to reduce pesticide loads in Lake Greifensee, Switzerland by 50% from 1993 to 2003. All other studies did not state meeting specific water quality objectives. Singer (2005) analyzed pesticide loads within Lake Greifensee from 1993 to 2003, concluding that none of the mitigation measures (e.g., 3 m wide buffer strips along water courses, regulated crop rotation, field sprayer inspections, soil erosion measures), except restrictions

on the allowable quantity of pesticide use led to detectable trends in load reduction. This is consistent with [Lerch et al. \(2011b\)](#), who concluded that best management practices (i.e., grassed waterways, Conservation Reserve Programs, terraces) implemented in the Goodwater Creek catchment from 1992 to 2006 were either ineffective and/or insufficient in their areal extent to achieve meaningful reductions in herbicide transport. There are currently no long-term studies that have attributed buffers to reducing long-term aquatic pesticide pollution. However, this does not mean that they are ineffective, since there are numerous studies that have demonstrated their short-term efficacy ([Reichenberger et al., 2007](#)).

In the Charmilles stream, annual pesticide loads decreased by 60% (5.2–2.1 kg/year) between 2008 and 2015 ([Daouk et al., 2019](#)). This decrease in loads was linked to the installation of grass strips between vine rows in 2009–2010, which appeared to have reduced peak flows following rain events. However, [Daouk et al. \(2019\)](#) concluded that establishing precise quantitative relationships between specific mitigation measures and observations was difficult because several measures (e.g., washing stations, better storage) were implemented simultaneously by varying degrees in addition to other confounding factors (e.g., interannual variability in precipitation).

In the Vemmenhög catchment (Sweden), numerous mitigation measures were implemented to reduce aquatic pesticide pollution in late-1994 and from 1997 to 1999 ([Kreuger and Nilsson, 2001](#)). In late 1994, a meeting was held with farmers, where information was shared on sources of pesticide contamination, reduction strategies, and safe pesticide use. Afterwards, free anonymous consultations were offered to farmers where they were given site-specific advice, such as safe storage of pesticides, best practices for filling and cleaning of sprayers, and appropriate parking grounds for sprayers. Additionally, restricting aesthetic herbicide spraying on farmyards and other areas with low organic matter was discussed. These initial measures reduced annual average pesticide concentrations by about 65%, which [Kreuger \(1998\)](#) suggests may be mainly attributed to the reducing farmyard point sources and aesthetic herbicide use. In 1997, new legislation was introduced requiring spray-free buffer zones and compulsory record keeping of pesticide applications. From 1998 to 1999, a program was introduced that provided small and mid-sized farmers economical compensation over a 5-year period for complying to risk reduction measures, such as spray-free buffer zones, safe filling and cleaning areas (e.g., biobeds), sprayer inspections, licensing and training courses, which contributed to an additional 25% reduction in total annual average pesticide concentrations. Combined, these mitigation measures resulted in a 90% cumulative reduction of total annual average pesticide concentrations in surface water between 1992 and 2000 ([Kreuger and Nilsson, 2001](#)).

[Hermosin et al. \(2013\)](#) associated a decreasing trend in mean herbicide levels from 2002 to 2010 in the Guadalquivir river of southern Spain to regulations (changes in authorized products) and actions (courses and technical workshops on pesticide management practices). Surface water concentrations of diuron decreased by 99% (2.36 µg/L to 0.3 µg/L) from 2003 to 2010 and terbuthylazine decreased by 78% (0.89 µg/L to 0.20 µg/L) from 2008 to 2010. Although substantial decreases were observed, it is unclear what the relative contribution of regulations and actions were to this decrease. Similarly, [Budd et al. \(2020\)](#) attributed a decreasing trend in aquatic bifenthrin concentrations from 2008 to 2018 in Northern California to the adoption of regulations and licensing applied to professional pest control operators that limited their application of pyrethroids to structures.

The simultaneous implementation of several mitigation measures is common to national action plans aimed at curbing aquatic

pesticide pollution. Along with the implementation of measures is the surface water monitoring program to gauge the progress towards water quality objectives. Such monitoring programs are not designed to evaluate the effectiveness of individual measures. Instead the evaluation of individual mitigation measures would require an experimental approach, such as the BACI design ([Downes et al., 2002](#)). Nonetheless, these four studies ([Kreuger and Nilsson, 2001](#); [Hermosin et al., 2013](#); [Daouk et al., 2019](#); [Budd et al., 2020](#)) demonstrated that mitigation measures, other than pesticide use restrictions, have the potential to produce detectable long-term reductions in pesticide concentrations or loads. In all four studies, a reduction of greater than 45% led to conclusions that the implemented mitigation measures were the causal criteria. Thus, relying on the strength of association and temporality within the levels-of-evidence approach ([Table 1](#)).

3.3. Toxic tradeoffs

Toxic tradeoffs refers to the scenario where banned or restricted pesticides are replaced by others, which may not necessarily lead to improvements to the aquatic environment. For instance, [Power et al. \(1999\)](#) observed declining atrazine herbicide concentrations in the Thames Estuary between 1988 and 1997. After atrazine was placed on the UK Red List (i.e., banned) in August 1993, atrazine concentrations continued to decrease significantly while the concentrations of simazine stabilized and showed no further declines from 1994 to 1997. This suggests that the atrazine ban led to the increased use of simazine as a substitute. Therefore, there may have been little improvement to the cumulative toxicity in the Thames Estuary after the atrazine ban because simazine has similar toxic effects to atrazine ([Cheremisinoff and Rosenfeld, 2010](#)).

Similarly, the net effect on aquatic organisms may not necessarily improve if a banned pesticide is replaced with one that is more toxic to aquatic organisms. For example, in the Charmilles catchment, several substances replaced atrazine after its ban in 2012, one of which was nicosulfuron. Nicosulfuron requires lower application rates compared to atrazine because of its greater effectiveness. However, it has an EQS value approximately 100 times lower than atrazine and can contribute significantly to the overall ecotoxicological risk ([Daouk et al., 2019](#)). Furthermore, substitution of one pesticide with another may lead to an increase in surface water concentrations due to its differing chemical properties (e.g., sorption, degradation half-lives). For instance, [Richards and Baker \(1993\)](#) attributed a higher time-weighted mean concentration for atrazine compared to alachlor due to its greater mobility and relative half-life. Therefore, the dosage, ecotoxicity, and chemical properties are critical factors to include when assessing the replacement of one pesticide with another.

Another example of a toxic tradeoff occurred in the US after the federally mandated phaseout of insecticides diazinon and chlorpyrifos in 2001 ([Schreder and Dicky, 2005](#); [Phillips et al., 2007](#); [Ryberg et al., 2010](#)). Following the 2001 phaseout, [Schreder and Dickey \(2005\)](#) observed a significant increase of the carbaryl concentrations in two northwestern US creeks. [Phillips et al. \(2007\)](#) extended the analysis to 20 sites throughout the US and did not detect significant changes in carbaryl concentrations in the north-eastern and midwestern US in response to the phaseout. From 2000 to 2008, [Ryberg et al. \(2010\)](#) found that trends for carbaryl were mostly nonsignificant and mixed (upward and downward in a few locations), and instead detected significant upward trends for fipronil and its degradation products throughout the US, indicating that fipronil was the more popular substitute for organophosphate insecticides during that period.

Three conclusions come from synthesizing the findings from these studies. Firstly, the toxic tradeoff [Schreder and Dicky \(2005\)](#)

observed seemed to be localized to the northwestern US and not generalizable across the entire US. Indicating a strong spatial preference for the use of specific pesticide products and the importance of site selection in the design of monitoring programs. Secondly, analysis of different (overlapping) time periods can result in very different trends. This is illustrated by comparing the significant carbaryl upward trend in Thornton Creek from 1996 to 2003 (Schreder and Dickey, 2005), followed by a downward trend from 2000 to 2008 (Ryberg et al., 2010). Significant downward trends were observed when the intervention (e.g., pesticide ban or mitigation measure) occurred within the time period as opposed to the beginning of the time period, which indicates the importance of including a baseline in the trend analysis. Finally, greater evidence indicated that fipronil was a more widespread substitute than carbaryl throughout the US from 2000 to 2008, which would have been missed from only analyzing diazinon, chlorpyrifos, and carbaryl. This stresses the importance of having a sufficient selection of substances for chemical analysis so that accurate statements can be made regarding national scale water quality trends.

Besides explicitly measured toxic tradeoffs, there can also be hidden toxic tradeoffs due to limited sampling and chemical analytics. With any kind of substitution, the important aspect for monitoring is that the substitute is also analyzed. Otherwise, there might only be an apparent improvement in water quality. For instance, Kreuger and Nilsson (2001) noted that glyphosate use doubled in the Vemmenhög catchment after the implementation of mitigation measures in 1994. However, glyphosate concentrations were not reflected in the monitoring results from 1992 to 2000. Therefore, the apparent improvement to water quality in their study may have been less if glyphosate was analyzed.

Another hidden toxic tradeoff is if banned pesticides are replaced by others that preferentially enter other parts of the environment (e.g., atmosphere, groundwater, sediments) that can evade detection if unmonitored. Although, our review focuses on pesticides in surface water, it is important to mention general pesticide pollution here because hidden toxic tradeoffs can be a total environmental issue. For instance, the herbicide prosulfocarb is a popular substitute for triazine herbicides (Devault et al., 2019). In Vavihill, Sweden, Kreuger and Lindström (2019) detected prosulfocarb at high frequencies in precipitation (>55% of samples from 2012 to 2015) and high quantities of atmospheric deposition (>70 $\mu\text{g}/\text{m}^2 \cdot \text{year}$ from 2012 to 2015). Prosulfocarb has the tendency to contaminate areas surrounding the targeted application due to its volatilization potential followed by vapour drift. There have been reports in Denmark and France of non-targeted produce (e.g., autumn apples) that exceeded maximum prosulfocarb residue limits, which makes it a potential human health hazard (Devault et al., 2019). Thus, this type of hidden toxic tradeoff can lead to the appearance of improved surface water quality at the detriment of other environmental compartments, which would be concealed unless monitored.

4.0. Conclusions

The importance of collecting accurate pesticide use data has been unanimous in all the reviewed studies. Data on pesticide use includes the location, timing, and quantity of the specific pesticide products used. Such data can indicate which substances to include in the chemical analysis and reduce the uncertainty when interpreting monitoring results for aquatic pesticide trends. Although there is a need to have a standard set of analytes for chemical analyses to make results more comparable from year to year, there is also a need to make updates as pesticide use changes to guard against potential toxic tradeoffs. In many cases accurate pesticide use data cannot be obtained, which has led to the use of proxies,

such as crop planting progress (Lerch et al., 2011a) and pesticide sales (Schreder and Dickey, 2005).

Collecting data on the implementation of mitigation measures is also critical to evaluate their overall effectiveness. This includes the timing, spatial extent, and magnitude of the specific measures that were implemented. However, this data can also be difficult to obtain. Several studies have collected such data and were able to demonstrate long-term reductions in aquatic pesticide pollution from mitigation measures (Kreuger and Nilsson, 2001; Hermosin et al., 2013; Daouk et al., 2019; Budd et al., 2020). It may however be difficult to separate the effects from an individual mitigation measure since several were implemented simultaneously.

When it comes to choosing the appropriate sampling method for surface water, we emphasize the need to sample at a high enough frequency to capture the short-duration concentration dynamics typical of streams in headwater catchments. This can be met by either a time- or flow-proportional sampling strategy, where the former is better at providing long-term exposure patterns relevant to organisms and the latter has the benefit of being able to derive loads and potentially loss rates (if quantity of pesticide application is known). It is also important to consider the periods in which subsamples are mixed to form composite samples. 14-day composites are suitable to assess water quality objectives for chronic exposure. However, composite samples would need to be 3.5-day or less to assess for acute exposure. Additional sampling of other environmental compartments (e.g., atmosphere and groundwater) and the periodic analysis of highly used but costly-to-analyze substances (e.g., glyphosate) could potentially identify some hidden toxic tradeoffs.

Statistical analysis of long-term pesticide trends in surface water should account for seasonality and make some adjustment for streamflow either through stratification (e.g., seasonal Mann-Kendall test; Hirsch et al., 1982) or a multivariate regression analysis (e.g., SEAWAVE-Q; Vecchia et al., 2009) because these two factors can obscure trends caused by changes in pesticide use or management practices.

Long-term monitoring studies consistently show that reducing aquatic pesticide pollution can be linked to the ban or restricted use of specific pesticide products. However, several studies have observed the presence of a decreasing trend prior to a ban, which indicates the presence of other influencing factors and the importance of baseline sampling to identify pre-existing trends. Nonetheless, updating and enforcing pesticide registration as the science of pesticides advances appears to be a key way to curb future pesticide pollution.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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