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Evaluation of pesticide monitoring strategies in agricultural streams based on the toxic-unit concept — Experiences from long-term measurements

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HIGHLIGHTS

- Pesticide concentrations in Swedish streams rarely exceed European Uniform Principles.
- A risk for aquatic ecosystem structure and function can nonetheless be anticipated.
- Time-proportional weekly samples inform about the long-term average exposure pattern.
- Flow proportional event-triggered samples capture peak exposure and duration.

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ABSTRACT

The European Water Framework Directive requires surface water bodies to have a good chemical and ecological status. Although relatively few pesticides are included in the list of priority pollutants, they pose, due to their intrinsic biological activity, a significant risk for the integrity of aquatic ecosystems. In this context, the pesticide (up to 128 pesticides including some transformation products) exposure pattern in four agricultural streams and two rivers was determined from 2002 to 2011 under the umbrella of the Swedish national monitoring program employing time-proportional and grab sampling strategies, respectively. After transforming the measured pesticide concentrations into toxic units, the European Uniform Principles for algae (chronic), invertebrates and fish (both acute), which are partly employed as benchmark for pesticide regulation, were only occasionally (<2%) exceeded. Moreover, this evaluation showed no long-term trends over the years. However, recent publications suggested that those thresholds are not protective for ecosystem structure and function, indicating a risk of up to 20% and 35% of the samples from the agricultural streams and the rivers, respectively. Moreover, the monitoring data show a continuous but rather low toxic potential of pesticides for all three trophic levels throughout the year, which suggests pesticides as an evolutionary force in agriculturally impacted aquatic ecosystems. However, the flow-triggered sampling, which was implemented as an additional sampling strategy in one of the agricultural streams starting in 2006, displayed an up to 7-fold underestimation of the maximum concentration in terms of toxic units for daphnids and fish during run-off events. The present study thus underpins that the optimal sampling design for pesticide monitoring strongly depends on its overall purpose. If the long-term exposure pattern is of concern a time-proportional composite sampling strategy is recommended, while for an assessment of peak exposures a flow-event-triggered high-resolution sampling strategy is superior.

1. Introduction

Surface water bodies are subjected to a multitude of stressors that may affect their chemical as well as their ecological status. Among such stressors, the millennium ecosystem assessment (MEA, 2005) identified anthropogenic toxicants as a major threat. Metals, personal care products, pharmaceuticals and many other substances of daily domestic and industrial use are continuously released from point sources, such as wastewater treatment plants (Daughton and Ternes, 1999). Pesticides

Abbreviations: EC, effective concentration; EU, European Union; LOD, limit of detection; TU, toxic units; UP, Uniform Principle; WFD, Water Framework Directive.

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(i.e. herbicides, fungicides, insecticides), however, enter aquatic ecosystems mainly via diffuse sources such as drainage, spray drift and/or surface run-off resulting in complex exposure dynamics triggered by the high temporal variability in rainfall events and timing of pesticide applications (Schulz, 2004). Due to their intrinsic biological activity, pesticides can adversely affect individual organisms (e.g. algae, macrophytes, invertebrates and fish; Matthiessen et al., 1995), aquatic communities (Schulz and Liess, 1999) as well as fundamental ecosystem functions such as leaf litter decomposition and gross primary production (Peters et al., 2013).

Chemical contamination and resultant ecotoxicological effects of pesticide pollution conflict with the objectives of the European Water Framework Directive (WFD) that aims at a good ecological and chemical status of surface water bodies by 2015 to also secure "the drinking water supply" for Europe (European Commission, 2000). Although streams with catchments less than 10 km^2 do not fall under the WFD, they closely reflect human activity and are thus particularly vulnerable to pesticide exposure (Kreuger, 1998; Rabiet et al., 2010; Leu et al., 2004; Liess et al., 1999). Moreover, the pattern of pesticide exposure in small streams feeds into downstream larger catchments. Hence, understanding the exposure pattern in small catchments facilitates risk mitigation measures that aim at reducing pesticide losses from the agricultural landscape, such as natural or constructed wetlands trapping pesticides upstream (Schulz and Peall, 2001; Stang et al., 2013; Tournebize et al., 2013).

For the characterisation of the chemical status of surface water bodies, the WFD suggests taking a grab water sample for chemical analysis of "priority pollutants" and "other pollutants" each single and every third month, respectively, and that the sampling frequency should "take account of the variability in parameters resulting from both natural and anthropogenic conditions" (European Commission, 2000). This approach may deliver sensible results for wastewater recipients with low water renewal rates that are rather stable in their chemical composition (Hollender et al., 2009; Castiglioni et al., 2006). However, such a sampling strategy seems inappropriate to capture the exposure of ecosystems to pesticide contamination, considering that peak concentrations occur stochastically, i.e. following major rainfall events or after application (Schulz, 2004). Indeed, recent studies indicate that (weekly and monthly) grab samples substantially underestimate the (maximum) pesticide exposure triggered by transport losses across the land–water interface (Xing et al., 2013; Stehle et al., 2013).

The Swedish pesticide-monitoring program (2002–2011), which is detailed in Adielsson and Kreuger (2007), provides insights into the pesticide exposure pattern in four agricultural streams and two rivers, representative of agricultural areas with different cropping patterns and soil types in southern Sweden. For this purpose, weekly time-proportional composite samples (agricultural streams) and grab samples (rivers) are collected during the summer season and analysed for their pesticide concentrations. These results are supplemented by data collected during the winter season from two of the streams during later years and also by data using a flow-event-triggered (i.e. a sampling strategy initiated by an increase in flow) sampling strategy implemented from 2006 in one of the streams. Hence, this paper aims to assess long-term trends of pesticide exposure in Swedish agricultural streams normalised to their potential effects for algae (chronic), invertebrates, and fish (both acute) using the toxic unit approach (TU defined in Section 2.2; Sprague, 1971). This procedure allowed for a direct comparison of these results with the Uniform Principles (UPs) of the European Union, which are required to be lower than 0.1 and 0.01 TUs for algae as well as invertebrates and fish, respectively (European Commission, 2011). Moreover, monitoring strategies for ecosystem exposure to pesticides are critically evaluated.

2. Material and methods

2.1. The Swedish pesticide monitoring program

The Swedish national pesticide monitoring program covers four agricultural streams (i.e. O18, E21, N34, M42; catchment sizes between 8 and 16 km^2) and two rivers (i.e. the rivers Skivarpsån and Vege å; 100 and 500 km^2 catchment size, respectively) (Fig. 1; Adielsson and Kreuger, 2007). These sites are representative of their respective regions (climate, soils and agricultural practices) and are located in agriculturally intensive areas (85–93% and 65–85% arable land in the stream and river catchments, respectively) with autumn- and spring-sown cereals being the dominant crop. Time-proportional composite samples (made up of subsamples taken every ca. 90 min) were collected each week using automated samplers from the four streams during the whole agricultural production period, i.e. from late April/early May until the end of October/November. In the two rivers, single (grab) samples were collected on fixed dates twice a month during May–June and monthly during July–November, which provide information about concentration levels during a brief, although well defined, point in time (a few seconds or minutes). Long-term monitoring data collected from 2002 to 2011 were thus incorporated into the present analysis, resulting in 899 and 178 independent water samples for the streams and rivers, respectively. For the sites M42 and N34 occasional (until 2006) and more regular (2007 onwards) time-proportional biweekly composite samples were considered separately, resulting in 116 independent samples during the winter period. Furthermore, a flow-event-triggered sampling strategy was implemented in 2006 in catchment M42 in parallel with the time-proportional sampling procedure. Flow-based sampling involved the collection of single samples triggered by stream flow velocity, i.e. more samples were collected during storm flow events. Under the flow-event-triggered sampling regime, 91 samples were available.

The automated samplers used to collect water from the streams had a built-in fridge, with water samples stored at +4 °C during the collection period. Water retrieved from the stream was directly diverted, by the sampler, into different bottles and stored in parallel in either plastic or glass bottles – depending on the target pesticide – during the entire collection and transport procedure. Samples were transported to the lab by overnight freight in coolers and immediately extracted and/or stored in a freezer. Subsequent analysis was done by gas chromatography mass spectrometry (GC–MS) and liquid chromatography (tandem) mass spectrometry (LC–MS and LC–MS/MS) for some 100 current-use pesticides. In 2002, 76 pesticides, including a few transformation products, were analysed in our accredited laboratory, increasing gradually to 128 in 2011 (Jansson and Kreuger, 2010). Approximately 90% (by weight) of the pesticides sold in Sweden for agricultural use were included in the analytical program. The limit of detection (LOD) among these pesticides varied between 0.1 ng/L (e.g. chlorpyrifos) and 100 ng/L (e.g. the glyphosate transformation product aminomethylphosphonic acid (AMPA)). The number of substances as well the respective LOD varied over the years as the target compounds in the monitoring program were adjusted for new compounds entering the Swedish market as well as the development of new and more sensitive analytical technology/methodology.

2.2. Calculation of predicted mixture toxicity

For all the samples with pesticide detections above the LOD, the sum of toxic units (ΣTU), which allows for an effect-standardised expression of the exposure, was calculated separately for aquatic primary producers (algae), primary consumers (invertebrates) as well as secondary consumers (fish), as follows (Sprague, 1971):

$$\sum \mathrm{TU} = \sum_{i=1}^{n} \frac{C_i}{\mathrm{EC50_i}}$$

where ΣTU is the summed toxic unit for the pesticides detected in a single water sample, defined as one time-proportional (agricultural streams) or grab (rivers) water sample from one of the monitoring sites. C*i* is the concentration of the pesticide *i* and $EC50_i$ is the concentration where 50% of the test organisms were affected under the exposure to pesticide *i*. Although other species may be more sensitive, the EC50 for algal growth inhibition (chronic), invertebrate immobility (acute),