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Calibration and field application of passive sampling for episodic exposure to polar organic pesticides in streams

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ABSTRACT

Rainfall-triggered runoff is a major driver of pesticide input in streams. Only few studies have examined the suitability of passive sampling to quantify such episodic exposures. In this study, we used Empore™ styrene-divinylbenzene reverse phase sulfonated disks (SDB disks) and event-driven water samples (EDS) to assess exposure to 15 fungicides and 4 insecticides in 17 streams in a German vineyard area during 4 rainfall events. We also conducted a microcosm experiment to determine the SDB-disk sampling rates and provide a free-software solution to derive sampling rates under time-variable exposure. Sampling rates ranged from 0.26 to 0.77 L d^{-1} and time-weighted average (TWA) concentrations from 0.05 to 2.11 μg/L. The 2 sampling systems were in good agreement and EDS exceeded TWA concentrations on average by a factor of 3. Our study demonstrates that passive sampling is suitable to quantify episodic exposures from polar organic pesticides.

1. Introduction

Large amounts of pesticides including hundreds of different active ingredients are applied worldwide annually and may partly reach surface and groundwaters (Schwarzenbach et al., 2010). Pesticide pollution is consequently of great concern and may result in ecological effects on non-target organisms (Beketov et al., 2013). Beside the diversity of compounds, a major challenge for pesticide monitoring in lotic ecosystems is the variability of concentrations due to the dynamic nature of pesticide input. Runoff-related pesticide input triggered by precipitation events has been identified as a major driver of pesticide input in streams (Bereswill et al., 2012; Leu et al., 2004; Rabiet et al., 2010), and positive relationships between pesticide concentrations and stream discharge have been reported (Rabiet et al., 2010; Taghavi et al., 2010). Moreover, maximum exposure concentrations of pesticides in streams following precipitation have been linked to adverse effects on freshwater communities as well as on essential ecosystem functions (Schäfer et al., 2012). Hence, capturing peak pesticide concentrations during episodic inputs is pivotal for an ecologically relevant characterisation of exposure.

Grab water sampling at individual time points is very likely to miss relevant exposure events unless event-triggered or flow proportional samples are taken (Stehle et al., 2013). While automatic sampling equipment is expensive and requires technical maintenance, event-driven water samplers (EDS) sensu Liess et al. (1996) represent an economic alternative. Nevertheless, EDS require immediate retrieval and sample processing shortly after the rainfall events, to prevent degradation of compounds, which would result in underestimation of the exposure. This renders larger scale applications of this technique laborious.

Passive sampling constitutes an alternative to water sampling (Kot et al., 2000; Vrana et al., 2005) and through concentration of compounds may allow for lower quantification limits compared to extracted water samples. Besides, passive samplers provide an integrated measure of the pesticide concentration during the deployment period and are less logistically constraining for the monitoring of pesticides than repeated grab sampling. Thus, they are becoming popular for characterising field exposure. Semipermeable membrane devices (SPMD; Huckins et al., 2006), Chemcatcher (Sánchez-Bayo et al., 2013; Schäfer et al., 2008b) and Polar Organic Chemical Integrative Samplers (POCIS; Bartelt-Hunt et al., 2011; Thomatou et al., 2011) are among the most used passive samplers for this purpose, although other samplers have also provided with satisfactory results (Assoumani et al., 2013; Hyne

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et al., 2004). However, only few studies examined the suitability of passive sampling for pesticide episodic exposure characterisation (Schäfer et al., 2008b; Shaw and Mueller, 2009). Furthermore, to determine field concentrations after field exposure requires so-called substance-specific sampling rates (i.e. volume of water sampled per unit of time), which allow users to compute time-weighted average (TWA) concentrations from the compound mass in the receiving phase (Gunold et al., 2008). While several calibration studies have been conducted for pharmaceuticals and polar herbicides and insecticides, there is a scarcity of fungicide calibration data.

In this study, we used Empore™ styrene-divinylbenzene reverse phase sulfonated disks (hereafter SDB disks) to assess the exposure to 15 and 4 polar organic fungicides and insecticides, respectively, in 17 streams in a vineyard area in the south–west of Germany. SDB disks were deployed shortly before 4 presumed rainfall events, in concert with EDS. In addition, a 6-day microcosm calibration study was conducted to determine sampling rates of the 19 target pesticides under close-to-natural conditions. Sampling rates were subsequently used to estimate TWA concentrations, which were in turn compared to concentrations from the EDS to evaluate the suitability of SDB disks for capturing episodic exposure. Moreover, we provide a free open source software solution to derive sampling rates under variable exposure in calibration experiments.

2. Material and methods

2.1. Study area and survey design

The study was conducted in 17 streams in the South of the federal state of Rhineland-Palatinate (southwest Germany), which is the largest German vine-growing region characterised by 23,000 ha of vineyards (Statistisches Landesamt RLP, 2011). Fungicides are applied every 10–14 days from end of April to middle August (Bereswill et al., 2012) and are the most used pesticides for grapes (96% of all applications), whereas herbicides (1.5%) and insecticides and acaricides (2.5%) play a minor role (Roßberg, 2010).

A natural conserve, the Palatinate forest, is located upstream of the vineyards and is the source of all streams in the region so that other than vinicultural pesticide input can largely be excluded. The selected streams covered a presumed gradient of fungicide exposure including 4 reference sites without exposure, located in the Palatinate Forest (Supplementary Data Figure S1). This presumed gradient of fungicide exposure was estimated from the proportion of vineyards with respect to the total catchment area, using Corine Land Cover (Büttner and Kosztra, 2007) maps. The sites were monitored for 15 fungicides and 4 insecticides (environmental properties in Supplementary Data Table S1) in 2012 from July to September, and physico-chemical variables at the sampling location were also measured (Supplementary Data Table S2). Pesticides were selected based on: (i) information on exposure from a previous pesticide study in the region (Bereswill et al., 2012) and (ii) spraying recommendations from local authorities. The monitoring was based on precipitation information and both passive samplers and EDS were deployed 1–2 days preceding forecasted precipitation events (>10 mm/day; Supplementary Data Table S3). Samplers were retrieved within 2 days after precipitation events (except for the fourth precipitation event, were samplers were retrieved after 5 days due to logistic constraints).

2.2. Passive samplers

All solvents used were HPLC grade (Carl Roth, Karlsruhe, Germany). Before deployment, SDB disks (47 mm diameter; Sigma–Aldrich Chemie GmbH, Schnelldorf, Germany) were conditioned for each 30 min in methanol and in ultrapure water under gentle rotation (100 rpm) in a shaker. Subsequently, they were placed between 2 stainless steel sheets (2 mm thickness), one of them presenting a 40 mm diameter circular opening (Vermeirssen et al., 2012; Supplementary Data Figure S2) and kept submerged in ultrapure water until field deployment. The whole device was fixed in duplicate (2 disks) with a single metal stake in the stream bed with the disks facing the riverbanks, to protect the disks from damage from water-transported materials. Upon retrieval, the disks were rolled up and stored in 7 mL acetone at −21 °C. Each disk was extracted for 30 min under gentle rotation in a shaker (100 rpm). Acetone was quantitatively moved to a new vial and concentrated to 0.5 mL in a nitrogen stream, while the disk was extracted a second time in the vial with 7 mL of methanol. These 2 extractions were deemed sufficient as a third extraction with methanol yielded only negligible concentrations (Supplementary Data Table S4). The 2 extracts were combined and passed through a 0.45 μm PTFE membrane in a polypropylene housing (Altmann Analytik Gmbh & Co. KG, Munich, Germany). Then the solvent was evaporated to dryness under a gentle stream of nitrogen and the analytes were retrieved in 1 mL methanol LC-MS grade. The extracts were analysed using liquid chromatography-high resolution mass spectrometry (LC-HRMS; see Section 2.5). The concentrations reported for the passive samplers (both calibration and field data) were adjusted for matrix effects and to the recovery for each pesticide (Supplementary Data Table S4, mean recovery: 77% ± 8 RSD). Recovery was determined by testing the loss of the analyte in an extraction procedure without disks: reduction of acetone containing a known concentration of the pesticides, methanol addition, mixture filtration and make up in 1 mL methanol.

2.3. Calibration of SDB disks, modelling of sampling rates and calculation of TWA concentrations

To assess the sampling rates of the disks for the target analytes, a microcosm experiment was performed using 4 artificial channels (50 L each) made from stainless steel (Supplementary Data Figure S3) and were run with stream water at 0.15–0.2 m/s in a circular flow (velocities adjusted to median of sampled streams). The microcosms were situated on a field station in a distance of 5 m to a stream to mimic field conditions. The water temperatures ranged from 10 to 16 °C due to daily variation and were representative of the temperature in the streams during deployment. Each channel was spiked with 30 mL of a pesticide mixture in methanol containing 66.7 mg/L of each target analyte (99% purity; Sigma–Aldrich Chemie GmbH, Schnelldorf, Germany) to obtain an initial concentration of approximately 40 μg/L per microcosm. Although this concentration was higher than field concentrations, we chose this calibration concentration to: (i) facilitate detection in SDB disk extracts for short calibration periods and (ii) overlay any possible effects from the river water used in the calibration experiment. Besides, the sampling rate gives the extracted volume of water per unit of exposure time (L/d) and is generally independent from the water concentration level (Booij et al., 2007; Vrana et al., 2005). Hence, the higher calibration concentrations in our experiment did not affect the relevance of the derived sampling rates for field conditions. At the start of the experiment 6 disks were submerged in each channel. On each day after exposure, 1 disk was retrieved from each microcosm in concert with a water sample. Disks were extracted and analysed as described above, while water samples were centrifuged 1 min at 10,000 rpm and directly analysed into LC-HRMS (see Section 2.5). At this step matrix effects were also considered for both SDB disk and water samples (Supplementary Data Table S4). The uptake in the samplers was modelled by optimising a one-compartment first-order kinetic model with respect to the measured mass of pesticide accumulated in the disk m_{sorb} and the concentration of the respective pesticide in the water C_W.

$$\frac{dm_{sorb}}{dt} = k_{WS} \cdot C_W - k_{SW} \cdot m_{sorb} \quad (1)$$

where the rate constants for the transfer from water to sampler (k_{WS}) and from sampler to water (k_{SW}) were used from the best fit model. Briefly, the optimisation relied on the Flexible Modelling Environment package to create a function calculating the model residuals, which are then minimised using the Levenberg–Marquardt algorithm (Ranke et al., 2013; for details see computer code in Supplementary Data). Once the parameters were obtained, Equation (1) was solved using (i) $C_W = 1$ μg/L, as this value is a realistic field concentration during episodic exposures and it does not affect the calculation of sampling rates, (ii) the obtained parameters and (iii) the exposure time for the respective sampler t. Then, C_W (here C_{TWA}), t and m_{sorb} were used to estimate the sampling rate R_S (L/day; Gunold et al., 2008; Kingston et al., 2000):

$$R_s = m_{sorb}/C_{TWA}t \quad (2)$$

Finally, the sampling rate and the mass absorbed in the disks during field deployment were used to calculate the C_{TWA} for each individual compound, using $t = 2$ days as an approximation, as pesticide concentration is assumed to rapidly decrease after the peak of flow (Leu et al., 2004; Taghavi et al., 2010; Wittmer et al., 2010). The modelling was done in R (R Development Core Team, 2012) with the additional packages "mkin" (Ranke et al., 2013) and "kinfit" (Ranke and Lindenberger, 2012) and deSolve (Soetaert et al., 2010). The algorithm, which allows the assessment of sampling rates under time-variable exposure and is available in the Supplementary Data, can be adapted for different compounds and calibration conditions by modifying the input parameters.

2.4. Event-driven water sampling

The sampling system consisted of 2 1-L brown glass bottles that were fixed to a steel bar and placed in the stream with the bottle opening approximately 10 and 20 cm above the normal water level (Supplementary Data Figure S4; Liess et al., 1996; Schulz, 2001). Bottle lids were fixed 1 cm above the opening to prevent rainfall to enter the bottle and dilute the sample. Stream water samples were retrieved after the 4 monitored rain events, stored in a fridge and solid-phase-extracted within 24 h after retrieval. When the 2 bottles were filled, the lowest one was discarded as the peak concentration of pesticides occur simultaneously to the increase in water level (Rabiet et al., 2010; Taghavi et al., 2010). Due to loss of samplers and fixing the bottles too high above the water level, the number of EDS