Concentrations, fluxes and field calibration of passive water samplers for pesticides and hazard-based risk assessment

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HIGHLIGHTS

- Chemcatcher® C_{18}, POCIS-HLB, silicone rubber were evaluated for 124 pesticides.
- *In situ* sampling rates, passive sampler-water partition coefficients were assessed.
- Good agreement between pesticide levels derived by passive and active sampling.
- Additional 38 pesticides were detected using passive sampling (*vs* active sampling).
- The risk quotient of 1 was exceeded on a number of occasions.

GRAPHICAL ABSTRACT
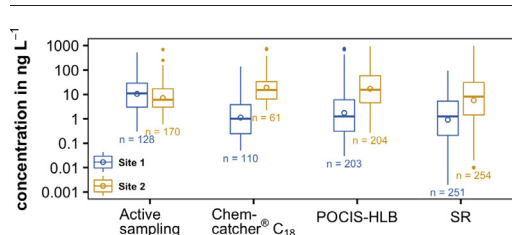
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ABSTRACT

Three passive sampler types including Chemcatcher® C_{18}, polar organic chemical integrative sampler-hydrophilic–lipophilic balance (POCIS-HLB) and silicone rubber (SR) based on polydimethylsiloxane (PDMS) were evaluated for 124 legacy and current used pesticides at two sampling locations in southern Sweden over a period of 6 weeks and compared to time-proportional composite active sampling. In addition, an *in situ* calibration was performed resulting in median *in situ* sampling rates (R_S, L day^{-1}) of 0.01 for Chemcatcher® C_{18}, 0.03 for POCIS-HLB, and 0.18 for SR, and median *in situ* passive sampler-water partition coefficients (log K_{PW}, L kg^{-1}) of 2.76 for Chemcatcher® C_{18}, 3.87 for POCIS-HLB, and 2.64 for SR. Deisopropylatrazine D_5 showed to be suitable as a performance reference compound (PRC) for SR. There was a good agreement between the pesticide concentrations using passive and active sampling. However, the three passive samplers detected 38 pesticides (including 9 priority substances from the EU Water Framework Directive (WFD) and 2 pyrethriods) which were not detected by the active sampler. The most frequently detected pesticides with a detection frequency of >90% for both sites were atrazine, 2,6-dichlorobenzamide, bentazone, chloridazon, isoproturon, and propiconazole. The annual average environmental quality standard (AA-EQS) for inland surface waters of the EU WFD and the risk quotient (RQ) of 1 was exceeded on a number of occasions indicating potential risk for the aquatic environment.

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1. Introduction

The application and number of pesticides used has increased exponentially to improve agricultural production for the increasing human population (Köhler and Triebskorn, 2013). As a consequence, monitoring methods have to be continuously adjusted to measure both legacy

and current used pesticides (Robles-Molina et al., 2014). In particular, monitoring methods need to be able to detect pesticides below or near water quality objectives or environmental quality standards (EQS) set by national or international legislation such as EU Water Framework Directive (WFD) (The European Parliament and of the Council, 2013). In addition, concentrations of pesticides in freshwater streams strongly fluctuate over time, depending mainly on precipitation and pesticide use (Kreuger, 1998). Time-weighted average (TWA) concentrations are preferable for assessing the risk to aquatic organisms and the environment, however, conventional methods for regular monitoring programmes for pesticides in freshwater streams mainly rely on grab sampling which may not fully account for temporal variations (Bundschuh et al., 2014).

Passive sampling is an alternative sampling strategy which provides TWA concentrations with minimal infrastructure and high sensitivity due to extraction of contaminants from large volumes of water (Vrana et al., 2005; Harman et al., 2012). However, passive sampling is associated with uncertainties in calculating accurate TWA concentrations, limited uptake capacity of the media and influence of environmental conditions (e.g., water temperature, dissolved organic carbon (DOC), pH, water flow rate, biofouling) (Li et al., 2011; Harman et al., 2012). Performance reference compounds (PRCs), analytically non-interfering compounds, can be added to passive samplers prior to deployment to compensate for the effect of environmental variables (Booij and Smedes, 2010). The application of passive samplers for pesticides have been described in the literature using Chemcatcher® Empore™ disk (Gunold et al., 2008; Schäfer et al., 2008; Fernández et al., 2014; Moschet et al., 2015), polar organic chemical integrative sampler (POCIS) (Alvarez et al., 2004; Fox et al., 2010; Morin et al., 2012; Fauvelle et al., 2012; Ibrahim et al., 2013; Assoumani et al., 2013; Zhang et al., 2016; Criquet et al., 2017; Van Metre et al., 2017), silicone rubber (Wille et al., 2011; Emelogu et al., 2013; Martin et al., 2016), and other passive sampler devices (Vrana et al., 2005; Allan et al., 2009; Page et al., 2014; Guibal et al., 2017a). However, there is a lack of studies investigating the application of passive samplers for multiple pesticides with a wide range of different physicochemical properties (e.g., octanol-water partition coefficient (K_{OW})). Ultimately, more studies are needed to compare active and passive samplers in the field to prove if passive samplers can be an alternative monitoring tool to assess concentrations, fluxes and risks of pesticides at agricultural-impacted sites.

The aim of this study was to evaluate different passive sampler types (i.e., Chemcatcher® C_{18}, POCIS-hydrophilic–lipophilic balance (HLB), and SR) for 124 legacy and current used pesticides and applied at two monitoring stations at fresh water streams equipped with time-proportional composite active samplers. The specific objectives included i) to compare in situ sampling rates (R_S) and passive sampler-water partition coefficients (K_{PW}) with those obtained under laboratory conditions (Ahrens et al., 2015), ii) to determine pesticide concentrations and fluxes at the two monitoring stations to assess the performance of three passive samplers in comparison to active sampling, iii) to perform a risk assessment based on measured pesticide concentrations and toxicity data, and iv) to evaluate implications for future monitoring programmes using passive sampling techniques.

2. Materials and methods

2.1. Chemicals and materials

The target analytes included 124 legacy and current used pesticides including herbicides, insecticides, and fungicides which were obtained from Teknolab AB (Kungsbacka, Sweden, for details see supplementary text). Internal standards (IS) fenoprop (2,4,5-TP), clothianidin-D_3, ethion, and terbuthylazine-D_5 were purchased from Teknolab AB (Kungsbacka, Sweden). In addition, 11 isotopically labeled performance reference compounds (PRCs) including 3,5–6-D_3-phenoxy (MCPA D_3),

acetamiprid D_3 (N-methyl D_3), deisopropylatrazine D_5 (ethylamino D_5), diflufenican D_3 (3-trifluoromethylphenoxy-2,4,6 D_3), diuron D_6 (dimethyl D_6), β-endosulfan D_4, imidacloprid D_4 (imidazolidin-4,4,5,5 D_4), chlorfenvinphos (ethyl) D_{10}, γ-hexachlorocyclohexane (HCH) D_6, simazine D_{10}, and terbutryn D_5 (ethyl D_5) were purchased from Dr. Ehrenstorfer (Augsburg, Germany).

Passive sampler canisters, spider carriers, holders, canisters, and polyethersulfone (PES) membranes were purchased from Environmental Sampling Technologies (EST, pore size 0.1 μm), Inc. (St. Joseph, MO, USA). Chemcatcher® C_{18} were purchased from Supelco (St Paul, MN, USA, Ø 47 mm, surface area (a_p) = 35 cm^2, sorbent mass (m_p) = 0.58 g, volume (V_p) = 1.7 cm^3), POCIS-HLB were purchased from EST (St. Joseph, MO, USA, 220 mg Oasis HLB sorbent (particle Ø 29.4 μm, a_p = 1.78×10^6 cm^2), and SR based on polydimethylsiloxane were purchased from Altec (Bude, England, 25 mm × 914 mm, 0.5 mm thick, surface area (a_p) = 457 cm^2, m_p = 15.6 g, V_p = 22.9 cm^3).

2.2. Sampling

The performance of the three passive sampler types was investigated at the two monitoring stations (i.e., site 1 and site 2) in southern Sweden from July 8 to August 19, 2013, which are included in the national pesticide monitoring programme of Sweden (Bundschuh et al., 2014). Site 1 and site 2 have a catchment area of 14 km^2 and 8 km^2, respectively, and are mainly characterized by agricultural activities (85% and 92%, respectively). The average annual water flow was 15,540 m^3 for site 1 (median flow of 2900 m^3 d^{-1} during the sampling period) and 5744 m^3 for site 2 (median flow of 92 m^3 d^{-1} during the sampling period). During the exposure of the passive samplers, time-proportional composite active samples (subsamples taken every ~90 min, ISCO©, NE, USA) were collected every week (in the following referred to as active sampling). At site 2, passive samplers were deployed 1 km further downstream of the active sampling point because of low water concentrations at the active sampling site. Three different passive sampler types were used for the field application including Chemcatcher® C_{18}, POCIS-HLB and SR. Before deployment, SRs were equilibrated for 48 h in a solution of methanol/water (20/80, v/v) spiked with a PRC mixture (c = 0.9 μg L^{-1}) (see Section 2.1). The preparation of the passive samplers Chemcatcher® C_{18}, POCIS-HLB and SR is described in the supplementary text and elsewhere (Ahrens et al., 2016). The passive samplers Chemcatcher® C_{18} ($n = 2 \times 6$), POCIS-HLB ($n = 2 \times 6$) and SR ($n = 2 \times 6$) were deployed in duplicates in stainless steel canisters for one week (7 days) at both sampling locations and covered a sampling period of six weeks total (July 8 to August 19, 2013). In addition, passive samplers Chemcatcher® C_{18} ($n = 2 \times 4$), POCIS-HLB ($n = 2 \times 4$) and SR ($n = 2 \times 4$) were deployed in duplicates for 7, 14, 28 and 42 days, respectively, at site 1 to investigate the uptake profiles of pesticides under field conditions. For comparison of passive and active sampling techniques, the concentrations of pesticides were measured using 7-day composite water samplers.

2.3. Sample extraction and instrumental analysis

The extraction and instrumental analysis is based on the methods described in the supplementary text and elsewhere (Ahrens et al., 2015). Prior to extraction, all passive samplers were spiked with an IS mixture (see Section 2.1). For pesticides analysed by gas chromatography–mass spectrometry (GC–MS), the SR stripes were extracted by Soxhlet extraction using 300 mL petroleum ether/acetone (50/50, v/v) for 19 h, POCIS-HLB was extracted by solid-phase extraction (SPE) using 5 mL ethyl acetate for the elution, and Chemcatcher® C_{18} was sonicated twice using 5 mL of ethyl acetate and 3 mL of ethyl acetate for each 10 min. The extracts were concentrated to 0.5 mL by gentle nitrogen blow-down and the solvent was exchanged to cyclohexane/acetone (90/10, v/v). For pesticides analysed by liquid chromatography–tandem mass spectrometry (LC-MS/MS), the extraction of the SR stripes