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# Pesticide impact on aquatic invertebrates identified with Chemcatcher® passive samplers and the SPEAR$_{pesticides}$ index

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## HIGHLIGHTS

- The membrane-covered Chemcatcher® reliably detects pesticide pollution.
- We estimate peak concentrations from time-weighted average concentrations.
- The SPEAR$_{pesticides}$ index reveals ecological effects of pesticide pollution.
- Carbofuran is shown to have adverse effects on stream macroinvertebrates.

## GRAPHICAL ABSTRACT


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## ABSTRACT

Pesticides negatively affect biodiversity and ecosystem function in aquatic environments. In the present study, we investigated the effects of pesticides on stream macroinvertebrates at 19 sites in a rural area dominated by forest cover and arable land in Central Germany. Pesticide exposure was quantified with Chemcatcher® passive samplers equipped with a diffusion-limiting membrane. Ecological effects on macroinvertebrate communities and on the ecosystem function detritus breakdown were identified using the indicator system SPEAR$_{pesticides}$ and the leaf litter degradation rates, respectively. A decrease in the abundance of pesticide-vulnerable taxa and a reduction in leaf litter decomposition rates were observed at sites contaminated with the banned insecticide Carbofuran (Toxic Units ≥ −2.8), confirming the effect thresholds from previous studies. The results show that Chemcatcher® passive samplers with a diffusion-limiting membrane reliably detect ecologically relevant pesticide pollution, and we

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suggest Chemcatcher® passive samplers and $SPEAR_{pesticides}$ as a promising combination to assess pesticide exposure and effects in rivers and streams.



## 1. Introduction

Freshwater ecosystems are affected by a multitude of human activities leading to catchment disturbance and water pollution, with pesticides, nutrients, polycyclic aromatic hydrocarbons (PAH), and brominated flame retardants being the most important contaminants (Malaj et al., 2014; Sarriquet et al., 2006; UNEP, 2010; Vörösmarty et al., 2010). Surface water pollution leads to adverse effects on the benthic fauna (Liess and von der Ohe, 2005; Ippolito et al., 2015) and on ecosystem functions (Bowmer, 2013; Peters et al., 2013). Field studies on pesticide exposure and community-level effects that include more than one waterbody have been performed by Liess and von der Ohe (2005) and by Schäfer et al. (2012), but such studies are generally rare (Beketov and Liess, 2012). This scarcity of investigations stems from the challenging nature of pesticide exposure assessment at the ecosystem level. Edge-of-field runoff, the dominant non-point source entry route for pesticides into surface waters, occurs in pulses and leads to short-term contamination (Liess and Schulz, 1999; Wauchope, 1978). Furthermore, pesticide loads in running waters are subject to (i) the pesticide amounts applied to fields, (ii) the timing and intensity of rain, (iii) the pesticide-specific octanol-water partition coefficient $K_{OW}$ (Bach et al., 2000; Burgoa and Wauchope, 1995; Kreuger and Törnqvist, 1998; Neumann et al., 2002; Schulz, 2004), and (iv) the heterogeneous soil hydrology at the catchment level (Doppler et al., 2012; Freitas et al., 2008; Leu et al., 2004).

In an attempt to reduce the cost and complexity of surface water monitoring, a range of passive samplers has been introduced recently (Greenwood et al., 2007a). These samplers can be deployed for an integrative sampling of pesticides in the water phase, providing less variable data in much shorter times and at much lower monetary expenses (Allan et al., 2009; Gunold et al., 2008; Kot et al., 2000; Kreuger, 1998; Schäfer et al., 2008b, 2011; Shaw and Mueller, 2009; Stephens et al., 2005; Vrana et al., 2005). However, passive samplers have rarely been used to capture short-term pollution events, such as pesticide input via edge-of-field runoff (Fernandez et al., 2014; Greenwood et al., 2007a).

In addition to metal species, most passive samplers are designed to monitor non-polar organic compounds (Lohmann et al., 2012; Schulze et al., 2011; Vrana et al., 2005). However, many currently used pesticides are polar and semi-polar compounds (Jansson and Kreuger, 2010). The Chemcatcher® passive sampler, hereafter referred to as Chemcatcher, is one of two passive samplers designed to monitor polar organic compounds in surface waters and can be configured with or without a diffusion-limiting membrane overlaying the receiving sorbent phase (Greenwood et al., 2007b; Schäfer et al., 2008a; Stephens et al., 2005). Comparing these two Chemcatcher configurations in a mesocosm experiment, Schäfer et al. (2008a) proposed the use of 'naked' receiving sorbent phases, i.e., Chemcatchers without a diffusion-limiting membrane, when monitoring short-term contaminations. Moreover, Schäfer et al. (2008b) reported community-level responses using 'naked' receiving sorbent phases in the only field study with Chemcatchers using an ecological endpoint (macroinvertebrate community structure; $SPEAR_{pesticides}$).

Chemcatchers without protecting membranes have a shorter response time, i.e., the analyte uptake commences instantly after exposure. However, for exposure periods longer than a week at ambient temperatures above approx. 10 °C, considerable biofouling occurs directly on the receiving phase, which can alter the uptake characteristics of the sampler. Another problem can arise through a larger influence of (changing) hydrodynamic conditions on the exchange surface of the sampler. From their uptake simulation study, Shaw and Mueller (2009) concluded that Chemcatchers should be exposed with a membrane, as they predict time-weighted average concentrations closely when deployed beyond the lag period of several hours.

At the beginning of our study, a newly designed Chemcatcher body became available (Greenwood et al., 2007b; Lobpreis et al., 2008) in which the depth of the cavity at the 'sampler face' is reduced from 20 to 5 mm to increase sampling rates (decrease the sampler response time). With this new sampler design, the use of a diffusion-limiting membrane appeared advisable (i) to balance the samplers' sensitivity (short response time) with a reduction in the impact of hydrodynamics on the sampling rates (comparable results) and (ii) to extend the time of exposure until pesticides reach the distribution equilibrium between the water and the receiving phase. This last reason is evident based on the evaluation of time-weighted average concentrations ($c_{TWA}$) using sampling rates because this approach requires linear uptake kinetics throughout exposure. On the basis of the performance of Chemcatchers without a diffusion-limiting membrane (Gunold et al., 2008; Stephens et al., 2005), the advanced properties of the latest Chemcatcher version, and the suggestion by Shaw and Mueller (2009) to use a diffusion-limiting membrane, we hypothesised that Chemcatchers equipped with a diffusion-limiting membrane are also capable of detecting ecologically relevant pesticide concentrations.

The stressor specific $SPEAR_{pesticides}$ index reliably uncovers community-level responses to pesticide stress (Liess et al., 2008; Liess and von der Ohe, 2005; Schäfer et al., 2007, 2008b, 2012; Schletterer et al., 2010; von der Ohe and Goedkoop, 2013). Complementary to structural integrity (e.g., macroinvertebrate community composition), the inclusion of functional integrity (e.g., ecosystem processes) into the assessment of stream ecosystem health has been suggested repeatedly (Bunn and Davies, 2000; Gessner and Chauvet, 2002; Rasmussen et al., 2012a; Woodward et al., 2012). We chose the $SPEAR_{pesticides}$ index and the shredder feeding guild (Cummins, 1973) for the evaluation of the pesticide impact and the ecosystem function 'leaf litter degradation', respectively. Using ecosystem-level endpoints (USEPA, 2003), the present study sought to establish the 'shielded' Chemcatcher, i.e., the membrane-equipped version, as a reliable alternative pesticide monitoring tool for future investigations into the effects of pesticides on aquatic biota.

## 2. Materials and methods

### 2.1. Study area

The present study was conducted in the Bode river catchment in Central Germany (SI Fig. S1). The area is part of the TERENO Harz/Central German Lowland Observatory (TERENO, 2011). The sampling sites were located in rural areas of the Harz and Börde regions dominated by forest and arable land. The potential for pesticide contamination of the investigated rivers was classified as low to medium in a previous study (Kattwinkel et al., 2011). The most important crops are cereal (wheat, barley, rye; approx. 60%) and rapeseed (approx. 20%; STALA, 2011).

In total, the samples were taken from 19 sites in 6 perennial rivers (Bode, 6 sites; Eine, 2; Mulde, 1; Selke, 5; Wipper, 3; Ziethe, 2) exposed to diffuse pesticide input from adjacent agricultural fields. The streams were of Strahler stream orders 1 to 5 and were between 5 and 10 m wide, except for the Mulde, with a width of approx. 40 m. Any neighbouring sampling sites along the same water body were at least