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Pesticides from wastewater treatment plant effluents affect invertebrate communities

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HIGHLIGHTS

- Pesticides released from WWTPs affected structure and function of invertebrates.
- The strongest ecological effects were attributed to neonicotinoid insecticides.
- Neonicotinoid concentrations occasionally exceeded regulatory thresholds.
- Strong ecological effects were also apparent below regulatory thresholds.

GRAPHICAL ABSTRACT

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ABSTRACT

We quantified pesticide contamination and its ecological impact up- and downstream of seven wastewater treatment plants (WWTPs) in rural and suburban areas of central Germany. During two sampling campaigns, time-weighted average pesticide concentrations (c_{TWA}) were obtained using Chemcatcher® passive samplers; pesticide peak concentrations were quantified with event-driven samplers. At downstream sites, receiving waters were additionally grab sampled for five selected pharmaceuticals. Ecological effects on macroinvertebrate structure and ecosystem function were assessed using the biological indicator system $\mathrm{SPEAR}_{\mathrm{pesticides}}$ (SPEcies At Risk) and leaf litter breakdown rates, respectively. WWTP effluents substantially increased insecticide and fungicide concentrations in receiving waters; in many cases, treated wastewater was the exclusive source for the neonicotinoid insecticides acetamiprid and imidacloprid in the investigated streams. During the ten weeks of the investigation, five out of the seven WWTPs increased in-stream pesticide toxicity by a factor of three. As a consequence, at downstream sites, SPEAR values and leaf litter degradation rates were reduced by 40% and 53%, respectively. The reduced leaf litter breakdown was related to changes in the macroinvertebrate communities described by $\mathrm{SPEAR}_{\mathrm{pesticides}}$ and not to altered microbial activity. Neonicotinoids showed the highest ecological relevance for the composition of invertebrate communities, occasionally exceeding the Regulatory

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Acceptable Concentrations (RACs). In general, considerable ecological effects of insecticides were observed above and below regulatory thresholds. Fungicides, herbicides and pharmaceuticals contributed only marginally to acute toxicity. We conclude that pesticide retention of WWTPs needs to be improved.

1. Introduction

Pesticide contamination of surface waters is known to affect the structure (Liess and von der Ohe, 2005) and biodiversity of invertebrate communities (Beketov et al., 2013). Pesticides are intended to protect agricultural production from pest organisms; however, their residues reach far beyond their target areas via atmospheric, overland, subsurface, and groundwater routes (Groenendijk et al., 1994). Surface runoff and wastewater effluents are among the most important entry pathways for pesticides into aquatic environments (Holvoet et al., 2007; Köck-Schulmeyer et al., 2013; Liess et al., 1999). Pesticide input from farmyards into sewage systems mainly originates from field sprayer filling and cleaning activities on paved surfaces, the direct disposal of unused product residues, accidental spillages, and non-agricultural uses (Bach et al., 2000; Kreuger, 1998). Pesticide residues from non-agricultural uses found in sewage systems have origins in, for example, grass management activities (e.g., golf courses, parks), industrial vegetation control (e.g., highways, railroads) and pest control in private homes and gardens (Barceló and Hennion, 2003).

The impact of diffuse (non-point) pesticide pollution on aquatic macroinvertebrates has been studied frequently (e.g., Kuzmanović et al., 2016; Liess et al., 2008; Münze et al., 2015; Orlinskiy et al., 2015). In contrast, the majority of studies investigating the environmental impact of wastewater treatment plants (WWTPs) have focused on the quantification of pesticides (Barco-Bonilla et al., 2010; Peschka et al., 2006), the effects of nutrients (Grantham et al., 2012; Gücker et al., 2006; Spänhoff et al., 2007), emerging water contaminants (De Castro-Català et al., 2015; Muñoz et al., 2009; Neale et al., 2017), and differing flow conditions, i.e., the dilution potential of receiving waters (Burdon et al., 2016; Englert et al., 2013; Kolpin et al., 2004). Most investigations that have examined ecological effects on aquatic macroinvertebrates have focused on a single taxon (e.g., Bundschuh et al., 2011; Köck-Schulmeyer et al., 2013).

To our knowledge, only two studies have linked pesticides in WWTP effluents to ecological effects on whole stream macroinvertebrate assemblages. Bunzel et al. (2013) employed the modelled pesticide runoff potential, and Ashauer (2016) used measured micropollutant mixtures from a single WWTP to explain changes in community composition. Expanding on those investigations, we measured the in-stream concentrations of pesticides up- and downstream of seven WWTPs. This allowed us to pinpoint the contribution of wastewater-borne pesticides to alterations in macroinvertebrate community structure.

The aim of our investigation was (1) to assess WWTP-related pesticide pollution in receiving waters with a focus on insecticides, and (2) to link contamination levels to effects on macroinvertebrate community structure and function. Pesticides were quantified using both passive and event-driven samplers. Effects on the composition of the macroinvertebrate community (structural endpoint) were assessed with the biological indicator $SPEAR_{pesticides}$ (Liess and von der Ohe, 2005). In addition, leaf litter degradation (functional endpoint) was included in our study because structural approaches in the assessment of stream health are ideally complemented by functional measures (Woodward et al., 2012). For this, we calculated the breakdown rate, *k*, and analysed the shredder-feeding guild (Cummins, 1973). We hypothesised that pesticides discharged with WWTP effluents affect the structure of the macroinvertebrate community and leaf litter degradation in receiving waters.

2. Materials and methods

2.1. Study area

The present study was conducted in the Bode River catchment in Sachsen-Anhalt, Germany (Fig. 1). This region is part of the TERENO Harz/Central German Lowland Observatory (Wollschläger et al., 2017). The most important crops in the area are cereals (wheat, barley, rye) and rapeseed (STALA, 2014), and the potential for pesticide contamination via agricultural field runoff is low to medium (Kattwinkel et al., 2011). We selected seven rural/suburban WWTPs in agricultural catchment areas (Ballenstedt, Biesenrode, Blankenburg/Harz, Hoym, Osterwieck, Stapelburg, and Straßberg; Fig. 1). They were characterised by a tertiary treatment level (including nitrification, denitrification, and phosphorous removal; LAU, 2012), a zero probability of stormwater overflow into receiving waters (i.e., the absence of a combined sewer overflow; Tibbetts, 2005), and receiving waters with a structural quality class that is typical for streams within agriculturally dominated landscapes in Germany (3 = 'moderately altered' and 4 = 'considerably altered'; classification according to LAWA, 2000). The Hoym and Straßberg WWTPs shared the same receiving water (Selke River); however, these sites were approximately 50 km apart and were therefore treated as independent sampling sites. The GPS coordinates of the effluent discharge points were obtained from the Sachsen-Anhalt State Office of Environmental Protection (LAU, 2012). The streams' structural quality classes were identified using a GIS data shapefile provided by the Sachsen-Anhalt State Agency for Flood Protection and Water Management (LHW). Information on the presence of combined sewer overflows was obtained from the individual WWTPs. Data on the number of farmyards connected to the sewage systems were not available. All receiving waters were perennial rivers and streams of the orders 1 and 3 according to Strahler (1954), with widths of 1.1 m to 6.0 m and depths of 0.1 m to 0.25 m at the sampling sites. The mean stream flow velocity during the investigation period ranged from 0.04 m s^{-1} to 0.19 m s^{-1}. Information on the WWTPs and receiving waters is summarised in SI Table 1.

At each WWTP, samples were taken 50 m upstream (serving as control sites) and 50 m downstream of the effluent discharge point in order to enable the mixing of effluent discharge and stream water and to enable ecological effects. At each sampling site, organic pollution by ammonium (NH_4), nitrite (NO_2), nitrate (NO_3), and phosphate (PO_4) was identified using a Spectroquant® Multy colorimeter (Merck KGaA, Darmstadt, Germany). Electrical conductivity (EC) along with pH and total dissolved oxygen (TDO) were recorded using an ExStik® II pH/Conductivity Meter (EC500) and an ExStik® II Dissolved Oxygen Meter (DO600), respectively (Extech Instruments Corp., Nashua, NH, USA). For the biochemical oxygen demand (BOD) and the total organic carbon (TOC), grab samples were analysed by IFB Halle GmbH (Halle Lettin, Germany) and at the UFZ, respectively (SI Tables 2a, b).

2.2. Monitoring of chemical exposure

In total, 88 pesticides frequently found in surface waters (McKnight et al., 2015; Moschet et al., 2014) were included in the chemical analyses: 32 herbicides, four herbicide metabolites, 30 fungicides, one fungicide metabolite, 18 insecticides, two plant growth regulators, and one acaricide (SI Table 3). In addition, we measured five pharmaceuticals that are ubiquitous in WWTP effluents and surface waters (Ginebreda et al., 2010; Pérez and Barceló, 2007): the anti-epileptic drug carbamazepine,