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Relationships between the psychiatric drug carbamazepine and freshwater macroinvertebrate community structure

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HIGHLIGHTS

- We related stream macroinvertebrate abundance to carbamazepine concentrations.
- Macroinvertebrate richness was positively correlated with carbamazepine.
- Carbamazepine influenced macroinvertebrates through indirect effects on Baetidae.

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ABSTRACT

Pharmaceutical pollutants are commonly detected in surface waters and have the potential to affect non-target organisms. However, there is limited understanding of how these emerging contaminants may affect macroinvertebrate communities. The pharmaceutical carbamazepine is ubiquitous in surface waters around the world and is a pollutant of particular concern due to its recalcitrance and toxicity. To better understand the potential effects of carbamazepine on natural macroinvertebrate communities, we related stream macroinvertebrate abundance to carbamazepine concentrations. Macroinvertebrate and water samples were collected from 19 streams in central Indiana in conjunction with other stream physiochemical characteristics. Structural equation modeling (SEM) was used to relate macroinvertebrate richness to carbamazepine concentrations. Macroinvertebrate richness was positively correlated with increasing concentrations of carbamazepine. From the SEM we infer that carbamazepine influences macroinvertebrate richness through indirect pathways linked to Baetidae abundance. Baetidae abundance influenced ephemeropteran abundance and FBOM percent organic matter, both of which altered macroinvertebrate richness. The pharmaceutical carbamazepine may alter freshwater macroinvertebrate species composition, which could have significant consequences to ecosystem processes.

1. Introduction

The integrity of freshwater ecosystems is dependent on the biodiversity of macroinvertebrates. Macroinvertebrates play key roles in freshwater ecosystems, by cycling nutrients, aerating sediments, and serving as conduits of energy flow in food webs (Covich et al., 1999; Clements and Rohr, 2009). Anthropogenic stressors associated with an increasing human population threaten biodiversity and reduce services provided by freshwater ecosystems (Vörösmarty et al., 2010; Dodds et al., 2013). Freshwater pollutants degrade habitat quality (Schulz et al., 2002; Clements et al., 2013), alter species composition (Muñoz et al., 2009; Beketov et al., 2013), and reduce macroinvertebrate richness, which is related to the pollution tolerance of taxa (Fig. 1; Wogram and Liess, 2001). With the global human population anticipated to reach 9.6 billion in 2050, freshwater ecosystems will experience continued and elevated stressors, mostly from nutrient and organic pollution (Vörösmarty et al., 2010; UN, 2013).

Pollutants such as heavy metals, nutrients and organic contaminants have been detected in freshwater ecosystems for decades (Murray et al., 2010; Larsson et al., 1999). Research has illuminated the source, fate and effects of some of these emerging contaminants (e.g., nutrients Carpenter et al., 1998; pesticides Relyea, 2005; heavy metals Runck, 2007); however, less is understood about pharmaceuticals and personal care products (PPCPs) pollutants (Rosi-Marshall and Royer, 2012; Hughes et al., 2013). Abiotic factors such as pH, dissolved oxygen and temperature have an effect on the fate of PPCPs and macroinvertebrate communities (Muñoz et al., 2009; Ferguson et al., 2013). Additionally, contaminants such as PPCPs influence macroinvertebrate community structure through changes in the habitat quality of freshwater ecosystems (Schulz et al., 2002; Muñoz et al., 2009; Clements et al., 2013). Therefore macroinvertebrate richness and diversity are dependent on the tolerance of the taxa present (Wogram and Liess, 2001). An increase in concentrations of PPCPs leads to habitat degradation, which alters the

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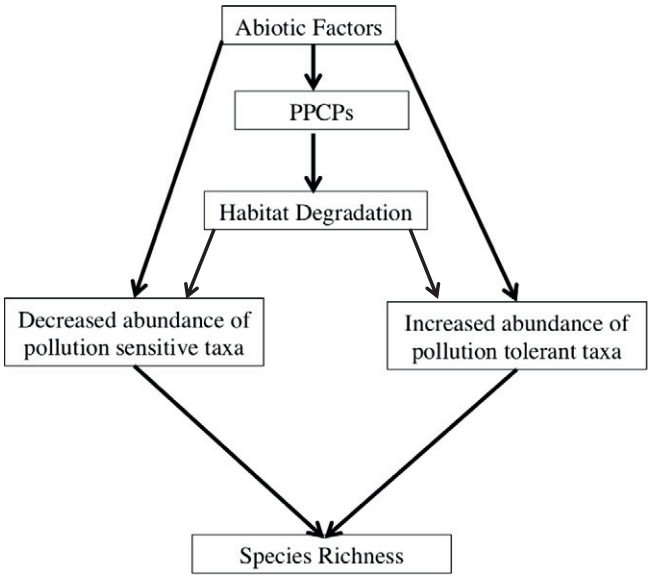

Fig. 1. Conceptual model of potential factors influencing macroinvertebrate community structure.

abundance of pollution sensitive (Ephemeroptera and Trichoptera) and tolerant taxa (Chironomidae and Oligochaeta), thereby changing the macroinvertebrate community.

Pharmaceuticals continuously enter freshwater ecosystems most commonly through effluent from wastewater treatment plants (WWTPs; Rosi-Marshall and Royer, 2012). However, septic tank leaching and agricultural runoff are also substantial contributors (Godfrey et al., 2007; Bunch and Bernot, 2011; Bernot et al., 2013; Du et al., 2014). This chronic exposure to pharmaceuticals has the potential to influence non-target organisms in unintended ways throughout their life cycles (Hughes et al., 2013). Thus, ecosystem-level assessments investigating the influence of pharmaceuticals on aquatic communities and ecosystems are critically needed (Rosi-Marshall and Royer, 2012).

Hundreds of pharmaceutical compounds ranging from antibiotics to hormones are commonly found in surface waters. Recent reviews have highlighted specific pharmaceutical compounds of concern due to their abundance, recalcitrance, and potential for toxicity (Murray et al., 2010). Among these is carbamazepine (5H-dibenz[b,f]azepine-5-carboxamide), which is one of the most commonly detected contaminants globally (Hughes et al., 2013). Worldwide concentrations of carbamazepine range from 0.5 to 11,561 ng/L (Loos et al., 2009; Ferguson et al., 2013) with a global median of 174 ng/L and a detection frequency of 85% (Hughes et al., 2013). Carbamazepine is a psychiatric drug that blocks sodium channels and reduces the firing of neurons and therefore is used to treat epilepsy, bipolar disorder, chronic nerve pain and addiction (Porter and Meldrum, 2012). Global human consumption of carbamazepine is estimated to be 1014 tons per year, with lower usage occurring in the U.S. compared to other countries (35 tons; Zhang et al., 2008). Carbamazepine is recalcitrant in freshwater (half-life = 82 days; Lam et al., 2004) and minimally removed during wastewater treatment (5–26% removal; Miao et al., 2005). Further, carbamazepine has a moderate affinity for binding to sediments (log K_{OW} = 2.25; Löffler et al., 2005). The high usage rates, limited removal from wastewater treatment processes and chemical properties, suggest that freshwater ecosystems are persistently exposed to carbamazepine.

Carbamazepine has limited acute effects on freshwater organisms due to high lethal concentrations (LC50 > 4 mg/L in *Lumbriculus variegatus* and *Chironomus riparius*), above environmental-relevance (Nentwig et al., 2004). However, carbamazepine can have chronic effects on aquatic organisms. Specifically, Oetken et al. (2005) found that sediments with carbamazepine reduced the emergence of *C. riparius* at 0.16 mg/kg dry weight and yielded no emergence at 20 mg/kg dry weight. Further, reduced feeding and hydranth attachment of *Hydra attenuata* has been observed at carbamazepine concentrations of 50 and 25 mg/L, respectively (Quinn et al., 2008). While previous studies have assessed the effects of carbamazepine at concentrations higher than those measured in situ, these studies indicate that exposure to carbamazepine may influence the emergence, feeding, reproductive success and behavior of freshwater invertebrates through altering physiological functions. Therefore, nonlethal concentrations of carbamazepine could adversely affect freshwater macroinvertebrates in natural ecosystems.

The objectives of this study were to quantify the concentrations of carbamazepine in the Upper White River and Mississinewa River watersheds and to determine the influence of carbamazepine on macroinvertebrate community structure. In this study, we use carbamazepine as a surrogate of wastewater input over time due to its persistence in freshwater ecosystems and range of concentrations measured across sites. We hypothesized that carbamazepine would reduce macroinvertebrate richness and change community structure. Specifically, sites with high concentrations of carbamazepine were expected to have lower Ephemeroptera and Trichoptera abundance and higher Oligochaeta and Chironomidae abundance.

2. Materials and methods

Nineteen sites, encompassing a gradient of land use types, were sampled along the Upper White and Mississinewa River watersheds over two weeks in July 2012 (Fig. 2). The Upper White River flows through central Indiana and is 104 km in length (USGS, 2013). The Mississinewa River is 190 km in length and a tributary of the Wabash River running through western Ohio and eastern Indiana. The Upper White and Mississinewa River watersheds are dominated by agricultural land use (75% and 88% of the area, respectively) with relatively low urban development (15% and 1.9% of the area, respectively; IDEM, 2001; Lanthrop et al., 2011). All sites were influenced either by WWTP effluent upstream or septic wastewater to various degrees although only one site (denoted "Down Muncie WWTP"; Table 1) had point WWTP effluent discharge immediately upstream of the collection site (~300 m). At each site, stream physiochemical characteristics were measured as well as primary producer and benthic organic matter biomass and macroinvertebrate diversity and abundance. Additionally, dissolved nutrient and carbamazepine pharmaceutical concentrations were measured.

For pharmaceutical analyses, composite water samples were collected simultaneously at multiple points across the thalweg and filtered in the field, using a 60 mL syringe fitted with a glass fiber filter (pore size = 0.7 μm) into a 1 L amber glass bottle containing the dechlorinating sodium thiosulfate preservative. All samples were immediately placed on ice for transport to the laboratory. Individuals collecting samples did not ingest or apply any of the target pharmaceutical analytes for a minimum of 24 h prior to sampling and individuals wore latex gloves during sample collection. At each sampling event, field blanks and matrix samples were collected to ensure robust chemical analyses. All water samples were transported on ice to the Indiana State Department of Health (ISDH) Chemical Laboratories in Indianapolis, Indiana within 6 h of collection for measurement of pharmaceutical concentrations via solid-phase extraction liquid chromatography tandem mass spectrophotometry (SPE/LC/MS/MS) using an Applied Biosystems triple quad API 4000 equipped with an Agilent 1200 high performance liquid chromatograph. Compounds measured (N = 19) included acetaminophen, caffeine, carbamazepine, cotinine, DEET, gemfibrozil, ibuprofen, lincomycin, naproxen, paraxanthine, sulfadimethoxine, sulfamerazine, sulfamethazine, sulfamethoxazole, sulfathiazole, triclocarban, triclosan, trimethoprim, and tylosin. Detection limits varied for each tested compound and ranged from 0.5 to 25 ng/L (Ferguson et al., 2013; Bernot et al.,