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Sources and transport of contaminants of emerging concern: A two-year study of occurrence and spatiotemporal variation in a mixed land use watershed

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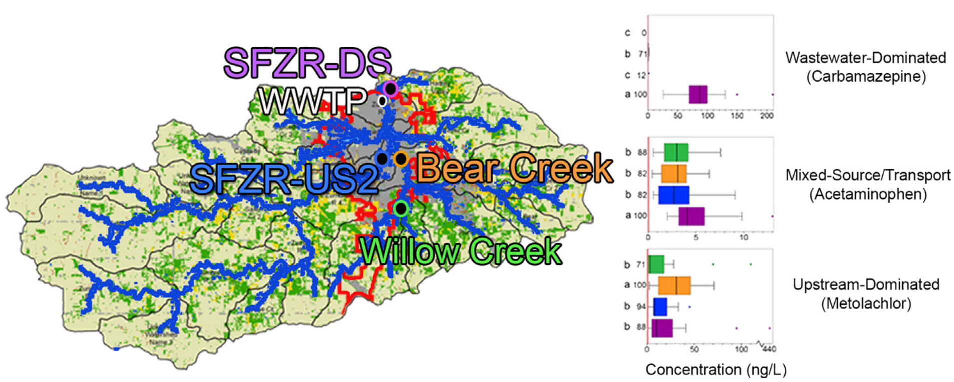
HIGHLIGHTS

- 26 CECs measured in 68 water samples from 4 sites in 2011–2012
- Some PPCPs and agricultural herbicides were ubiquitously detected.
- Land use and seasonality affected the instream concentrations and loading of CECs.
- Wastewater, agricultural/upstream, and mixed-source influences were evident.
- Understanding land use and temporal factors will enhance CEC monitoring and mitigation.

GRAPHICAL ABSTRACT



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ABSTRACT

The occurrence and spatiotemporal variation of 26 contaminants of emerging concern (CECs) were evaluated in 68 water samples in 2011–2012 in the Zumbro River watershed, Minnesota, U.S.A. Samples were collected across a range of seasonal/hydrological conditions from four stream sites that varied in associated land use and presence of an upstream wastewater treatment plant (WWTP). Selected CECs included human/veterinary pharmaceuticals, personal care products, pesticides, phytoestrogens, and commercial/industrial compounds. Detection frequencies and concentrations varied, with atrazine, metolachlor, acetaminophen, caffeine, DEET, and trimethoprim detected in more than 70% of samples, acetochlor, mecoprop, carbamazepine, and daidzein detected in 30%-50% of samples, and 4-nonylphenol, cotinine, sulfamethoxazole, erythromycin, tylosin, and carbaryl detected in 10%–30% of samples. The remaining target CECs were not detected in water samples. Three land

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Pesticide
Fate transport
Agricultural
Urban
Endocrine disrupting compound (EDC)

use-associated trends were observed for the detected CECs. Carbamazepine, 4-nonylphenol, erythromycin, sulfamethoxazole, tylosin, and carbaryl profiles were WWTP-dominated, as demonstrated by more consistent loading and significantly greater concentrations downstream of the WWTP and during low-flow seasons. In contrast, acetaminophen, trimethoprim, DEET, caffeine, cotinine, and mecoprop patterns demonstrated both seasonally-variable non-WWTP-associated and continual WWTP-associated influences. Surface water studies of CECs often target areas near WWTPs. This study suggests that several CECs often characterized as effluent-associated have additional important sources such as septic systems or land-applied biosolids. Finally, agricultural herbicide (atrazine, acetochlor, and metolachlor) profiles were strongly influenced by agricultural land use and seasonal application-runoff, evident by significantly greater concentrations and loadings at upstream sites and in early summer when application and precipitation rates are greatest. Our results indicate that CEC monitoring studies should consider a range of land uses, seasonality, and transport pathways in relation to concentrations and loadings. This knowledge can augment CEC monitoring programs to result in more accurate source, occurrence, and ecological risk characterizations, more precisely targeted mitigation initiatives, and ultimately, enhanced environmental decision-making.

1. Introduction

Over the past two decades, enhanced awareness of ecotoxicological issues and the refinement of analytical techniques have resulted in the identification and assessment of numerous contaminants of emerging concern (CEC) in freshwater ecosystems. These CECs include, but are not limited to, natural and synthetic hormones, veterinary pharmaceuticals, pesticides, human pharmaceuticals and personal care products (PPCP), and other industrial/commercial compounds (Kolpin et al., 2002; Petrie et al., 2014). Numerous agricultural, residential, commercial, and industrial sources contribute CECs to surface waters (Kolpin et al., 2002; Boxall et al., 2004; Kolpin et al., 2004). CECs are detected throughout the environment and biota worldwide, even in remote, "pristine" areas and in treated drinking water (Benotti et al., 2009). Several authors have reviewed potential CEC effects (Petrie et al., 2014; Boxall et al., 2004; Kaplan, 2013), which include endocrine disruption and associated biological fitness issues in aquatic systems (Petrie et al., 2014) and human populations (Damstra, 2002), induction of antibiotic resistance (Boxall et al., 2004), and direct aquatic toxicity (Petrie et al., 2014).

Despite recent advances, knowledge of the environmental sources, fate and transport of many CECs remains limited (Boxall et al., 2004; Veach and Bernot, 2011; Luo et al., 2011; Sengupta et al., 2014; Vidal-Dorsch et al., 2012; Diamond et al., 2011). Longitudinal studies have reported in-stream transport of many persistent and labile CECs across kilometer-scale distances (Sengupta et al., 2014; Massey et al., 2010). Spatial concentration differences have been linked to land uses and wastewater treatment plant (WWTP) influences (Kolpin et al., 2002; Kolpin et al., 2004; Veach and Bernot, 2011; Vidal-Dorsch et al., 2012; Barber et al., 2006; Velicu and Suri, 2009; Shala and Foster, 2010). Reports have explained temporal concentration increases of PPCPs in cold or low-flow conditions by reduced degradation, dilution, and/or increased usage at these times (Musolff et al., 2009; Osorio et al., 2012; Bernot et al., 2013). Other researchers have explained elevated concentrations of certain PPCPs in high-flow spring conditions by lower temperatures and increased WWTP flow, reducing hydraulic retention times and removal efficiencies (Conley et al., 2008). Finally, increased concentrations and detection frequencies of agricultural herbicides and veterinary pharmaceuticals in spring and summer have been explained by increased usage and runoff transport (Bernot et al., 2013; Hua et al., 2006; Gómez et al., 2012). Overall, variation of CECs is dependent on physicochemical, societal, and/or environmental variables such as temperature, sunlight, precipitation, chemical use, source proximity, flow, dissolved oxygen, specific conductance, pH, solubility, sorption, photodegradability, biodegradability, and wastewater treatment processes (Veach and Bernot, 2011; Vidal-Dorsch et al., 2012; Conley et al., 2008; Hua et al., 2006). Environmental systems are complex, and these processes are not easily modeled or extrapolated from one site to another (Sengupta et al., 2014; Musolff et al., 2009; Barber et al., 2013; Brooks et al., 2009; Acuña et al., 2014; Brown et al., 2009; Writer et al., 2011). Limited sampling periods or sample sizes may inhibit trend assessments (Vidal-Dorsch et al., 2012; Johnson, 2010; Alvarez et al., 2014). In addition, although significant temporal trends are often identified at a particular site, the associations of CEC concentrations with flow, temperature, or season are often unclear, insignificant, or inconsistent within or between study areas (Veach and Bernot, 2011; Luo et al., 2011; Shala and Foster, 2010; Musolff et al., 2009; Osorio et al., 2012; Bernot et al., 2013; Conley et al., 2008; Hua et al., 2006; Alvarez et al., 2014). A greater understanding of spatiotemporal patterns in CEC concentration and loading is necessary to characterize CEC sources, fate/transport, and ultimately, risk and improve predictability from site to site (Vidal-Dorsch et al., 2012; Bernot et al., 2013).

Three related studies have recently been completed on the inland South Fork of the Zumbro River (SFZR), the area also targeted in this work. A principal components analysis of concentrations of 10 CECs identified a primary agricultural source for herbicides and a primary urban wastewater source for some PPCPs (e.g., carbamazepine, erythromycin, and DEET); nevertheless this study was unable to clarify the sources of acetaminophen or caffeine (Karpuzcu et al., 2014). Another study performed an analysis of instream mass balances for 16 CECs across seven seasonal events and showed that the measured WWTP effluent and upstream sources accounted for the majority of CEC loadings, and demonstrated the proportional contributions of these sources, to the mouth of the catchment (Fairbairn et al., 2016). Finally, a study of eight CECs detected in bed sediments found that observed instream sediment-water distribution coefficients were typically greater than values predicted with traditional K_{ow}-based methods due to non-hydrophobic interactions between hydrophilic or moderately hydrophobic CECs and the low organic carbon sediments (Fairbairn et al., 2015). This study also found that highly variable instream sediment-water distributions could be a result of CEC-specific seasonality and/or lability in the water column.

To complement previous studies in the SFZR area, the current research analyzed 26 CECs in 68 water samples collected from four instream sites over two years to investigate the seasonal/hydrologic and land use drivers of instream concentration and loading variations. We hypothesized that CEC concentrations and loadings would be affected by seasonal/temporal factors, compound type/usage, and land uses in this mixed-use watershed. This study provides new information on how land use, seasonal/hydrologic factors, and CEC characteristics affect spatiotemporal patterns. This knowledge of CEC sources and seasonality is useful for developing sampling regimes, predicting sources, and assessing ecological risks of CECs based on land use and other watershed and contaminant characteristics.