



Sediment–water distribution of contaminants of emerging concern in a mixed use watershed



David J. Fairbairn^{a,*}, M. Ekrem Karpuzcu^a, William A. Arnold^b, Brian L. Barber^c, Elizabeth F. Kaufenberg^a, William C. Koskinen^d, Paige J. Novak^b, Pamela J. Rice^d, Deborah L. Swackhamer^a

^a University of Minnesota, Water Resources Center, 1985 Buford Ave., St Paul, MN 55108, United States

^b University of Minnesota, Civil, Environmental, and Geo-Engineering, 500 Pillsbury Drive SE, Minneapolis, MN 55455, United States

^c University of Minnesota, Department of Soil, Water, and Climate, 1902 Dudley Ave, Saint Paul, MN 55108, United States

^d United States Department of Agriculture, Agricultural Research Service, 1991 Upper Buford Circle, University of Minnesota, Saint Paul, MN 55108, United States

HIGHLIGHTS

- Sediment–water distributions of CECs were not governed by hydrophobic partitioning.
- Water concentrations exhibited seasonal variation; sediment concentrations did not.
- Spatial variations correlated with land use for many CECs in water and/or sediment.
- Hydrophobicity and persistence affected predictability of distribution coefficients.

ARTICLE INFO

Article history:

Received 6 September 2014

Received in revised form 13 October 2014

Accepted 13 October 2014

Available online 7 November 2014

Editor: Damia Barcelo

Keywords:

Sediment
Surface water
CEC
Agriculture
PPCP
Urban

ABSTRACT

This study evaluated the occurrence and distribution of 15 contaminants of emerging concern (CECs) in stream water and sediments in the Zumbro River watershed in Minnesota and compared these with sub-watershed land uses. Sixty pairs of sediment and water samples were collected across all seasons from four stream sites for over two years and analyzed for selected personal care products, pesticides, human and veterinary medications, and phytoestrogens. Spatial and temporal analyses indicate that pharmaceuticals and personal care products (urban/residential CECs) are significantly elevated in water and/or sediment at sites with greater population density (>100 people/km²) and percentage of developed land use (>8% of subwatershed area) than those with less population density and land area under development. Significant spatial variations of agricultural pesticides in water and sediment were detectable, even though all sites had a high percentage of agricultural land use. Seasonality in CEC concentration was observed in water but not in sediment, although sediment concentrations of three CECs did vary between years. Average measured non-equilibrium distribution coefficients exceeded equilibrium hydrophobic partitioning-based predictions for 5 of the 7 detected CECs by at least an order of magnitude. Agreement of measured and predicted distribution coefficients improved with increasing hydrophobicity and in-stream persistence. The more polar and degradable CECs showed greater variability in measured distributions across different sampling events. Our results confirm that CECs are present in urban and agricultural stream sediments, including those CECs that would typically be thought of as non-sorptive based on their log K_{ow} values. These results and the observed patterns of sediment and water distributions augment existing information to improve prediction of CEC fate and transport, leading to more accurate assessments of exposure and risk to surface water ecosystems.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Contaminants of emerging concern (CECs) are widely found in the environment and include natural/synthetic hormones, pharmaceuticals

and personal care products (PPCPs), veterinary medicines, industrial/household products, pesticides, and other chemical and physical agents (Caliman and Gavrilescu, 2009; Kolpin et al., 2002). CECs are not commonly subject to environmental monitoring or regulations, but they have potential adverse effects on human and ecosystem health (USGS, 2011), which include endocrine disruption in aquatic systems (Caliman and Gavrilescu, 2009) and human populations (Damstra, 2002), induction of antibiotic resistance (Pharmaceuticals in the Environment,

* Corresponding author at: 520 Lafayette Rd, St. Paul, MN 55101, United States. Tel.: +1 651 757 2659.

E-mail address: david.fairbairn@state.mn.us (D.J. Fairbairn).

2004), and direct aquatic toxicity (Richardson et al., 2005). Numerous sources of CECs to surface water ecosystems include concentrated animal feeding operations (CAFOs) (Tolls, 2001), row crops (Gilliom et al., 2006), lawns and golf courses (Gilliom et al., 2006), industry (Kolpin et al., 2002), roads (Zhang et al., 2009), landfills (Heberer, 2002), land-applied sludge or biosolids (Kinney et al., 2006), and wastewater treatment system effluent (Heberer, 2002; Drillia et al., 2005). National and international reviews of CEC occurrence in surface waters are available (Caliman and Gavrilescu, 2009; Heberer, 2002) with far fewer reports of CECs in river sediments (Lei et al., 2009; Xue et al., 2005; Lee et al., 2008; Kim and Carlson, 2007).

Sorption is a dynamic process that occurs primarily through hydrophobic interactions or attractive force and is related to the physico-chemical properties of the sediment and the sorbate (Karickhoff, 1984). Observed empirical relationships between the soil organic carbon–water partition coefficient (K_{oc}) and the octanol–water partition coefficient (K_{ow}) for neutral hydrophobic organic contaminants (HOCs) are often able to predict the overall solid–water distribution coefficient (K_d) within an order of magnitude (Doucette, 2000). Although HOC sorption has been studied extensively, relatively little information is available on sorption of hydrophilic and moderately hydrophobic contaminants, including many CECs (Yamamoto et al., 2003). Sorption of polar/ionizable compounds is influenced strongly by non-hydrophobic interactions when relevant mineral or soil organic matter components are present (Tolls, 2001; Yamamoto et al., 2003; Schenzel et al., 2012; Nguyen et al., 2005; MacKay and Vasudevan, 2012; Karickhoff, 1981). For these compounds, K_d is often poorly predicted by K_{ow} and K_{oc} relationships, with non-hydrophobic interactions driving sorption for compounds with relevant functionalities (e.g., amine, carboxylic acid, or hydroxyl groups). Models are being developed for sorption of such compounds (Nguyen et al., 2005; MacKay and Vasudevan, 2012; Smaraweera et al., 2014).

Few studies have analyzed CECs in water and sediment samples collected at the same time and place (Kim and Carlson, 2007; Kim and Carlson, 2006; Yang et al., 2010; Massey et al., 2010; Tomasek et al., 2012). Measured in-stream K_d values for low- K_{ow} antibiotics and natural hormones exceeded K_{ow} -based predictions by at least an order of magnitude (Lei et al., 2009; Kim and Carlson, 2007; Massey et al., 2010). In contrast, hydrophobic synthetic hormones ($\log K_{ow} > 4$) agreed more closely with predictions (Lei et al., 2009). Similarly, the distributions of neutral CECs with $\log K_{ow} > 2$ (e.g., carbamazepine (Scheytt et al., 2005; Yamamoto et al., 2009) and atrazine (Wauchope and Myers, 1985)) have been well-predicted by K_{ow} - K_{oc} relationships. Wide “within-compound” spatial and temporal variations in K_d , often up to three orders of magnitude, have been observed for individual CECs across field sampling events (Kim and Carlson, 2006; Boxall et al., 2003). It has been suggested that this variation is due to non-hydrophobic interactions, hydrologic factors, chemical usage variations, and variable attenuation rates between aqueous and sediment-bound fractions (Tolls, 2001; Kim and Carlson, 2007; Yamamoto et al., 2003; Kim and Carlson, 2006; Massey et al., 2010; Yamamoto et al., 2009). Laboratory studies have corroborated both the within-compound variations and the deviation from K_{ow} -based predictions (up to 4 orders of magnitude) for many low- K_{ow} CECs (Yamamoto et al., 2009; Davis et al., 2006; Yamamoto et al., 2005). Nevertheless, most field studies of sediment–water distribution of CECs have analyzed only a few pairs of samples or sampling periods. Thus, there is little available information on the spatial–temporal variation of sediment concentrations and sediment–water distributions in the environment.

The objectives of this study were to assess the occurrence, distribution, and spatial–temporal variation of CECs measured in stream water and sediments of a mixed-use watershed and to evaluate the use of equilibrium partition coefficients to predict non-equilibrium sediment–water distribution of CECs in streams. Understanding CEC sediment–water distributions and variation is important because these processes influence the fate and bioavailability of CECs, thus

affecting the sediment's function as a CEC source or sink (Xue et al., 2005). In addition, CEC presence in the sediment will influence benthic organisms' exposures to CECs as well as the development of antimicrobial resistance (Pharmaceuticals in the Environment, 2004). The results of this study will ultimately enhance future CEC research, predictive methods, and effective targeting of monitoring, management, and mitigation solutions.

2. Methods

2.1. Study area and CECs of interest

The South Fork of the Zumbro River (SFZR) watershed (Fig. 1) in southeastern Minnesota contains a gradient of land uses across its subwatersheds. This provides a unique opportunity to study CECs from both agricultural and urban sources. Four sampling sites in four subwatersheds were chosen to reflect different types and extents of land uses, different human and animal populations, and use of septic systems versus a city sanitary sewer system (see Fig. 1 and Table 1).

A detailed land use and hydrologic characterization was conducted by McGhie Betts, Inc. (Rochester, MN) (discussed in Karpuzcu et al. (2014)). Pertinent information is presented in Table 1, and was used to categorize sites as being primarily agricultural or urban/residential for categorical data analysis and interpretation.

Fifteen CECs were selected based on surface water occurrences reported in the literature (Kolpin et al., 2002; Lee et al., 2004), chemical usage patterns (Pharmaceuticals in the Environment, 2004; Lee et al., 2008; Keefe et al., 2009; VanRyswyk and Tollefson, 2008), potential effects (Pharmaceuticals in the Environment, 2004; Combalbert and Hernandez-Raquet, 2010), and land-use associations (Kolpin et al., 2002; Lee et al., 2008). The suite includes three agricultural herbicides, one veterinary antibiotic, five urban/residential PPCPs, and six mixed use compounds (pesticides, phytoestrogens, and antibiotics) (Table 2).

2.2. Sample collection, processing, and analysis

Sampling periods (four in 2011 and five in 2012) were chosen to reflect a variety of seasonal, flow, and land use conditions. In the late summer (August–September), fall (October–November), and winter (January–February) periods, low flows were expected to result in enhanced CEC signals associated with sanitary sewers and with reduced contributions from runoff. During spring melt (March), CECs associated with land-applied manure and other terrestrial components were expected to be transported with snowmelt runoff. During early summer (May–June), runoff of row crop herbicides was expected to be associated with precipitation events.

Two sampling days occurred one week apart for all sites in early summer, late summer, and fall periods. Prior to use, all field, laboratory, and storage equipment was cleaned with CEC-free soap and distilled water, triple rinsed with ultrapure water, methanol-rinsed, and (for glassware and metals) heated to 400 °C for 3 h. Sediment samples were collected from the top 5 cm of multiple areas across the width of the stream using a stainless steel scoop. The samples were deposited into cleaned 1-L glass jars. The jars were sealed with Teflon-lined lids and transported on ice to the storage facility, where they were frozen (–18 °C) until processing. Water samples were collected a few minutes prior to sediment samples by submerging a clean amber glass or stainless steel container into the stream to a depth of 10–20 cm. Water samples were sealed with Teflon-lined or stainless steel lids and transported on ice to the laboratory. Water samples were refrigerated at 4 °C until processing, which was initiated with 72 h of collection. Corollary physical and chemical data were acquired using *in situ* sondes (YSI Inc., Yellow Springs, OH, USA; Hach Hydromet, Loveland, CO, USA), YSI flowmeters, and existing USGS monitoring stations.

Water samples (2 L) were filtered through 0.7 µm glass-fiber filters, spiked with a surrogate standard (metazachlor, which is not approved

Download English Version:

<https://daneshyari.com/en/article/6328200>

Download Persian Version:

<https://daneshyari.com/article/6328200>

[Daneshyari.com](https://daneshyari.com)