Science of the Total Environment 485–486 (2014) 193–204

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Simulation of the fate of selected pharmaceuticals and personal care products in a highly impacted reach of a Canadian watershed

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HIGHLIGHTS

- Simulation of trace contaminant fate and transport was successful using WASP 7.5.
- Flow-driven processes greatly influenced the behavior of contaminants.
- In-stream photolysis and biodegradation were also important mechanisms.
- Carbamazepine behaved differently and acted as a tracer contaminant.

ARTICLE INFO

Article history:
Received 20 February 2014
Received in revised form 19 March 2014
Accepted 19 March 2014
Available online 12 April 2014

Editor: D. Barcelo

Keywords:
Water quality model
Antiandrogens
Pharmaceuticals
Endocrine disruption
Sewage
Wastewater treatment

ABSTRACT

Municipal wastewater treatment plants (WWTPs) dispose of numerous trace organic contaminants in the receiving waters that can impact biological function in aquatic organisms. However, the complex nature of WWTP effluent mixtures and a wide variety of potential mechanisms that can alter physiological and reproductive development of aquatic organisms make it difficult to assess the linkages and severity of the effects associated with trace organic contaminants. This paper describes a surface water quality modeling exercise that was performed to understand the relevant contaminant fate and transport processes necessary to accurately predict the concentrations of trace organic compounds present in the aquatic environment. The target compounds modeled include a known antiandrogenic personal care product (triclosan) and selected pharmaceuticals (venlafaxine, naproxen, and carbamazepine). The WASP 7.5 model was adapted and calibrated to reflect approximately ten kilometers of reach of the Grand River watershed that is highly influenced by a major urban WWTP. Simulation of the fate and transport of the target compounds revealed that flow-driven transport processes (advection and dispersion) greatly influenced the behavior of the target contaminants in the aquatic environment. However, fate mechanisms such as photolysis and biodegradation can play an important role in the attenuation of some compounds. The exception was carbamazepine where it was shown to act as a conservative tracer compound for wastewater specific contaminants in the water phase. The calibrated water quality model can now be employed in a number of future applications. Prediction of fate and transport of other trace organic contaminants across the watershed and assessment of the performance of WWTP infrastructure upgrades in the removal of these compounds are just a few examples.

1. Introduction

Concerns for effluent quality have expanded beyond traditional pollutants, such as biological oxygen demand and nutrients, to include trace organic contaminants that can alter responses in aquatic organisms at very low concentrations (Corcoran et al., 2010; Daughton and Ternes, 1999). Trace organic contaminants in wastewater treatment plant (WWTP) effluents collectively include pharmaceuticals, endocrine disrupting compounds, and personal care products (Daughton and Ternes, 1999; Kolpin et al., 2002; Ternes et al., 2004). The effects of these compounds on aquatic species can be broad or highly specific depending on their mechanism of action (Daughton and Ternes, 1999).

In the Grand River watershed in southern Ontario, pharmaceuticals ranging from anti-inflammatory drugs to antidepressants have been detected in its water (Arlos, 2013; Lissemore et al., 2006; Tanna et al., 2013; Metcalfe et al., 2010) and biota (Wang et al., 2011; Togunde et al., 2012). A variety of effects have also been reported in fish downstream of WWTP effluents in this watershed, including changes in gene expression (Ings et al., 2011), physiology

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http://dx.doi.org/10.1016/j.scitotenv.2014.03.092
0048-9697/

(Ings et al., 2012), population endpoints (Tetreault et al., 2011), and community assemblages (Tetreault et al., 2013). Very high incidences of intersex (ova-testis) have been additionally observed in several species of fish immediately downstream of Kitchener WWTP (KWWTP), a major WWTP outfall in the watershed (Tetreault et al., 2011; Tanna et al., 2013). The endocrine disruption in fish has been linked to a diverse array of pharmaceuticals, endocrine disrupting compounds, and personal care products found in WWTP effluent mixtures (Corcoran et al., 2010; Daughton and Ternes, 1999). Intersex, in particular, has been primarily associated with the presence of natural and synthetic female receptor agonists (estrogens) (Jobling et al., 2006; Nash et al., 2004). However, male hormone receptor antagonists (antiandrogens) such as triclosan have also been reported to contribute in endocrine disruption in fish (Hill et al., 2010; Rostkowski et al., 2011). High concentrations of triclosan have already been observed in several WWTP effluents in the watershed, including KWWTP (Arlos, 2013). Furthermore, KWWTP effluent was also found to be estrogenic (Tanna et al., 2013). The combined effects of both antiandrogenic and estrogenic compounds found in municipal WWTP effluents may likely explain the expression of endocrine effects in wild fish (Grover et al., 2011; Jobling et al., 2009). This hypothesis, however, has not yet been substantiated. Endocrine active contaminants are usually present at very low levels in surface waters and environmental monitoring of these compounds is very challenging (Fenlon et al., 2010).

Mathematical models can be employed to understand and predict the behavior of contaminants in aquatic ecosystems (Martin and McCutcheon, 1999; Chapra, 1997; Ji, 2008), especially when environmental data are limited. The application of a fate and transport model would enhance our ability to understand the distribution of selected trace organic contaminants within a watershed. The prediction of their fate and transport could also serve as a supplemental tool in assessing the exposure of aquatic ecosystems to these compounds. In the current study, the Water Quality Simulation Program (WASP) 7.5 developed by the United States Environmental Protection Agency was employed to predict the fate and understand the processes responsible for the spatial and temporal distributions of an antiandrogenic personal care product (triclosan) and three selected pharmaceuticals (naproxen, venlafaxine, and carbamazepine) that have been frequently detected in the area downstream of KWWTP (Fig. 1). This area is one of most highly contaminated and impacted reaches in the watershed. The KWWTP is also scheduled to undergo significant infrastructure improvements, thus making this an ideal location for the modeling study.

2. Modeling approach

A stepwise approach to transport and fate modeling was completed starting with the definition of boundary conditions, simulation of tracer contaminant and solid transport, and the addition of significant fate mechanisms necessary to accurately predict the concentrations of target compounds. The approach taken is described subsequently.

2.1. Target compounds

The compounds modeled in this study were the antiandrogen, triclosan, and the pharmaceuticals, carbamazepine, naproxen, and venlafaxine. The target compounds have been frequently detected in the watershed in prior sampling events (Arlos, 2013; Tanna et al., 2013; Wang et al., 2011). The compounds studied have slight to moderate hydrophobicity as suggested by the octanol–water partitioning coefficients (log K_{ow}) listed in Table 1. They are also less likely to volatilize in the atmosphere due to their relatively low Henry's law constants. These properties suggest the likely affinity of these compounds to the water phase.

2.2. Model description

The WASP model is a public domain model that can simulate flow in unsteady and non-uniform cases as well as contaminant fate and transport in up to three dimensions. WASP has been used to simulate a variety of organic contaminants including the fate and transport of persistent compounds such as polychlorinated biphenyls (PCBs) and the pesticide atrazine (Rygwelski et al., 1999; Vuksanovic et al., 1996). WASP utilizes a "box" model approach for modeling contaminants in surface waters. The Saint-Venant equations (continuity and momentum) are employed when simulating water quality along one-dimensional unsteady flow channels. One-dimensional transport is often assumed in river water quality modeling since longitudinal movement in rivers is more significant than vertical and transverse movements (Ji, 2008).

2.3. Site selection and segmentation

The reach modeled in this study included a portion of the river that has been found to be affected by the KWWTP discharge. Historically poor water quality conditions such as low dissolved oxygen levels, high ammonia concentrations (Anderson, 2012; Cooke, 2006) and the presence of a variety of trace organic contaminants (Arlos, 2013; Tanna et al., 2013) have been observed. This area has also been found to have a high incidence of intersex in wild fish (Tanna et al., 2013; Tetreault et al., 2011). A Grand River watershed modeling exercise conducted by Hosseini et al. (2012) identified this area as having the highest risk of exposure to trace organic contaminants resulting from municipal WWTP effluent discharge.

The total length of the modeled reach was approximately 10 km and started immediately below the Manheim Dam (~3 km upstream of the KWWTP outfall) and ended at the confluence of the Grand and Speed Rivers (~7 km downstream of the KWWTP outfall) (Fig. 1). The reach was discretized into ten segments and the average dimensions of the segments are shown in the Supplementary data (Table S1). WASP treats each segment as being completely mixed, so that the areas known to have incomplete mixing conditions (e.g., downstream of effluent discharge and streams inputs such as Schneider Creek) were more finely segmented (Fig. 1).

2.4. Boundary conditions

There were three locations in the reach that required the definition of boundary conditions: the upstream site (G49), the KWWTP outfall, and Schneider Creek. There are numerous wastewater treatment plant outfalls above the study area and these were considered as part of the input at the upstream sites. The KWWTP outfall was considered as an extra segment acting as a tributary discharging into the Grand River. It also served as the major point source for chloride and the target contaminants. Schneider Creek was a major source for chloride but not for target contaminants. It was assumed that there were no significant groundwater contributions in the study area based on an initial site investigation.

Definition of the boundary conditions required data on (1) flow inputs and (2) concentrations of the tracer substance (chloride) and the target compounds. Daily flows for the Grand River, KWWTP, and Schneider Creek (2009–2012); the seasonal chloride data set for G49 and Schneider Creek (2009–2012); and a constant chloride concentration (average value of 430 ng/L, $n = 6$) discharged from the KWWTP were used to simulate chloride transport. A summary of the chloride dataset is presented in the Supplementary data (Table S2). Unlike the chloride dataset, only limited information was available for the target organic compounds. Hence, the simulation of these substances was only conducted for a period of five months to be consistent with a sampling regime that had been completed previously (Arlos, 2013).