Water Research xxx (2016) 1–11

Contents lists available at ScienceDirect

Water Research

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

The distribution dynamics and desorption behaviour of mobile pharmaceuticals and caffeine to combined sewer sediments

M. Hajj-Mohamad [a, b, *], H. Darwano [c], S. Vo Duy [c], S. Sauvé [c], M. Prévost [b], H.P.H. Arp [d], S. Dorner [a]

[a] Canada Research Chair in Source Water Protection, Department of Civil, Geological and Mining Engineering, Polytechnique Montréal, C.P. 6079, Succursale Centre-ville, Montréal, QC, H3C 3A7, Canada
[b] NSERC Industrial Chair in Drinking Water Treatment, Department of Civil, Geological and Mining Engineering, Polytechnique Montréal, C.P. 6079, Succursale Centre-ville, Montréal, QC, H3C 3A7, Canada
[c] Department of Chemistry, Université de Montréal, C.P. 6128, Succursale Centre-ville, Montreal, Qc, H3C 3J7, Canada
[d] Norwegian Geotechnical Institute (NGI), P.O. Box 3930 Ullevål Stadion, N-0806, Oslo, Norway

ARTICLE INFO

Article history:
Received 24 February 2016
Received in revised form
19 October 2016
Accepted 21 October 2016
Available online xxx

Keywords:
Emerging contaminants
Anthropogenic tracers
Suspended solids
Settled sediment
Stormwater
Batch equilibrium

ABSTRACT

Pharmaceuticals are discharged to the environment from wastewater resource recovery facilities, sewer overflows, and illicit sewer connections. To understand the fate of pharmaceuticals, there is a need to better understand their sorption dynamics to suspended sediments (SS) and settled sediments (StS) in sewer systems. In this study, such sorption dynamics to both SS and StS were assessed using a batch equilibrium method under both static and dynamic conditions. Experiments were performed with natively occurring and artificially modified concentrations of sewer pharmaceuticals (acetaminophen, theophylline, carbamazepine, and a metabolite of carbamazepine) and caffeine. Differences in apparent distribution coefficients, $K_{d,app}$, between SS and StS were related to differences in their organic carbon (OC) content, and the practice of artificially modifying the concentration. $K_{d,app}$ values of modified contaminant concentrations and high OC sediments were substantially higher. Pseudo-second order desorption rates for these mobile compounds were also quantified. Successive flushing events to simulate the addition of stormwater to sewer networks revealed that aqueous concentrations would not necessarily decrease, because the added water will rapidly return to equilibrium concentrations with the sediments. Sorption and desorption kinetics must be considered in addition to dilution, to avoid underestimating the influence of dilution on concentrations of pharmaceuticals discharged to the environment.

1. Introduction

Many urban regions have combined sewer systems (CSS) that handle both sanitary and stormwater flows within the same network (Even et al., 2007). In addition, “illicit CSS” via sanitary sewer connections to storm sewer networks are frequent (Burian et al., 2000; Hoes et al., 2009). Large quantities of pollutants that settle and accumulate in sewer networks can be resuspended during wet weather events, leading to pulses of contaminants discharged to receiving waters (Wang et al., 2011), and resulting in the degradation of water quality and aquatic habitats (Blumensaat et al., 2012). Accordingly, Combined Sewer Overflows (CSOs) are an important point source of wastewater micropollutants such as mobile pharmaceuticals in aquatic environments (Buerge et al., 2006; Gromaire et al., 2001; Phillips and Chalmers, 2009; Stewart et al., 2014; Zhou and Broodbank, 2014). CSOs have been shown to contribute approximately 10% of the fine particles found in urban river bed sediments (David et al., 2013). Large variations of mobile pharmaceutical concentrations during CSOs have been reported (270–3248 ng caffeine L^{-1}, 4.1–184 ng carbamazepine L^{-1}, non-detected–3591 ng acetaminophen L^{-1}, 57.3–2381 ng theophylline L^{-1}) (Madoux-Humery et al., 2013). One investigation of CSO events showed that the largest fraction of carbamazepine initially originates from sewer deposits, but its main source is from wastewater towards the end of events (Pongmala et al., 2015).

* Corresponding author. Canada Research Chair in Source Water Protection, Department of Civil, Geological and Mining Engineering, Polytechnique Montréal, C.P. 6079, Succursale Centre-ville, Montréal, QC, H3C 3A7, Canada.
E-mail address: mariamhajjm@gmail.com (M. Hajj-Mohamad).

http://dx.doi.org/10.1016/j.watres.2016.10.053
0043-1354/

Sorption is one of the key factors controlling the input, transport, and transformation of pharmaceuticals in an aquatic environment, including within CSS (Scheytt et al., 2005). Resuspension of sewer sediments during wet weather contribute up to 75% of the suspended solids, 10–70% of the *E. coli* and 40–80% of the intestinal enterococci in urban rivers (Passerat et al., 2011). The degree to which pharmaceuticals are released from resuspended CSS sediments is not clear since both stormwater runoff and wastewater can influence sediment resuspension and their pharmaceutical sorption behaviour. Previously, we investigated the occurrence of pharmaceuticals in CSS sediments and their role as both a source and sink of pharmaceuticals in urban water systems (Hajj-Mohamad et al., 2014). Other than this, the few investigations on the occurrence of pharmaceuticals in CSS focused solely on the water column and have seldom considered interactions with sediments (Benotti and Brownawell, 2007; Madoux-Humery et al., 2013; Stewart et al., 2014).

The extent of pharmaceutical sorption to environmental solids is highly variable, partly because pharmaceuticals include a wide variety of substances that can exert different mobility in water in relation to sorption interactions with solids. Several recent reports describe a variety of sorption-desorption behaviours of pharmaceuticals in soils, sediments and sludges (Chefetz et al., 2008; Drillia et al., 2005; Jones et al., 2006; Lin et al., 2010; Navon et al., 2011; Stein et al., 2008; Ternes et al., 2004; Williams et al., 2006; Yamamoto et al., 2005; Yu et al., 2009). In many of these aforementioned studies, environmental media were artificially spiked in the laboratory with pharmaceuticals at the μg L^{-1} range or even higher, which are not representative of the means by which pharmaceuticals come into contact with sediments. A concern is that the sorption behaviour of spiked or artificially added contaminants is not the same as native contaminants, which is a recognized issue with hydrophobic organic contaminants (Arp et al., 2009), but has not been explored with pharmaceuticals.

A challenge with regards to the use of native contaminants in sorption studies rests with methods used to control microbial growth without altering the water/sediment matrix (Cormier, 2014). Sodium azide has been commonly used as a biocide in sorption experiments (e.g. Jiménez et al., 2016). However, sodium azide can react with trace contaminants (Cormier et al., 2015). Irradiation has been proposed to inhibit microbial growth as it does not involve the addition of chemicals, but it could also reduce initial pharmaceutical concentrations in samples and alter organic matter (Wang and Chu, 2016). Thus, studies using native sediments must account for uncertainties related to methods used to control microbial growth.

In this study, the general objective was to illustrate the role of CSS sediments on the fate and transport of pharmaceuticals during wet weather events, using a simple laboratory test system. These tests were done to assess the extent of sorption dynamics for native and artificially added mobile pharmaceuticals in shaken and still batch systems, to simulate changes during water dilution and resuspension events. All experiments were done using actual CSS sediments, to more closely reflect real-world conditions. The specific goals were: (1) to quantify the solid-water distribution coefficient (K_d) and the sorption/desorption kinetics of pharmaceuticals in static and dynamic sewer conditions, simulating the addition of storm water flushing; (2) assess the difference between native and modified (artificially added) contaminated systems; (3) to consider our findings in the context of initial resuspension of settled sewer sediments and their implications for the fate of the targeted compounds during CSOs; and (4) to evaluate selected pharmaceuticals as wastewater tracers in relation to their sorption dynamics.

As such, we selected four mobile pharmaceuticals (acetaminophen, theophylline, carbamazepine, and a metabolite of carbamazepine) and caffeine. To the best of our knowledge, this is the first study investigating the distribution and desorption behaviour of the selected pharmaceuticals in native CSS sediments.

2. Experimental methods

2.1. Chemicals

Acetaminophen (ACE), caffeine (CAF), carbamazepine (CBZ), theophylline (THEO) and the metabolite 10,11-dihydro-10,11-dihydroxycarbamazepine (CBZ-DiOH) were selected as target analytes based on several criteria: (1) their consumption, pharmacokinetic behaviour and occurrence in the environment (Daughton and Ternes, 1999; Heberer, 2002; Viglino et al., 2008); (2) their classification in various groups to cover a wider range of properties and functions; (3) the proposed use of ACE, CAF and CBZ as anthropogenic tracers (e.g., (Benotti and Brownawell, 2007; Daneshvar et al., 2012; Wu et al., 2008); (4) the higher detection of metabolite CBZ-DiOH in wastewater compared to its parent compounds (Hummel et al., 2006; Miao and Metcalfe, 2003); and (5) the importance of CSOs as a primary source of pharmaceuticals including CAF (Musolff et al., 2009).

Table 1 and Tables S1 and S2 in the Electronic Supplementary Information (ESI†) contain literature characteristics, concentration ranges in untreated wastewater and combined sewer overflows and sorption measurements of selected pharmaceuticals. High purity (>97%) analytical standards of acetaminophen, caffeine, theophylline, carbamazepine and 10,11-dihydro-10,11-dihydroxycarbamazepine were purchased from Sigma-Aldrich Canada (Oakville, ON, Canada). Stock solutions (1 mg mL^{-1}) of the standards were prepared by dissolving each compound in methanol and stored at −20 °C. Internal standards of acetaminophen [$^{13}C_2$]-acetaminophen, caffeine (trimethyl-$^{13}C_3$, 99%) and carbamazepine (carbamazepine-d_{10}; 98%) were purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). All solvents, HPLC grade water (H_2O), 0.1% formic acid in H_2O (0.1% FA in H_2O) were purchased from Fisher Scientific (Whitby, ON, Canada). HPLC grade formic acid (FA) (98% pure) was purchased from Sigma-Aldrich (Oakville, ON, Canada). GF-75 glass fiber membrane filters (0.3 μm, 47 mm diameter) were obtained from Sterlitech (Kent, WA, USA).

2.2. CSS sampling and pre-treatment

CSS sediments from the Greater Montreal Region were collected manually with a stainless steel trowel from surface sediment deposits in a CSO collection system. Collected sediments were placed in pre-cleaned glass bottles and covered with aluminum foil to avoid photodegradation. CSS water samples were collected at the same time of sediment sampling in a pre-cleaned 1-L polypropylene bottle at approximately 0.3 m below the water surface, and stored cool in an insulated chest cooler. In the lab, both sediment and water samples were immediately sterilized using gamma radiation (30 kGy, 5.2 h) and then stored at 4 °C. Sediment/water sterilization was confirmed by testing the total concentration of aerobic and anaerobic bacteria after gamma irradiation, using tryptone soybean agar (TSA) at temperature of 30 °C for up to 10 days (Vieira and Nahas, 2005). No bacterial colonies were observed. Although losses of pharmaceuticals could occur following irradiation (Wang and Chu, 2016), measured sediment concentrations following irradiation were not lower than previously measured concentrations without irradiation (Hajj-Mohamad et al., 2014). Prior to the batch experiments, sub-samples were pooled to form composites, homogenized and wet sieved (<1.25 mm) with CSS water (see the next paragraph) in order to remove debris. The pH of

Please cite this article in press as: Hajj-Mohamad, M., et al., The distribution dynamics and desorption behaviour of mobile pharmaceuticals and caffeine to combined sewer sediments, Water Research (2016), http://dx.doi.org/10.1016/j.watres.2016.10.053