Science of the Total Environment 505 (2015) 615–622

Contents lists available at ScienceDirect

Science of the Total Environment

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

Fate of selected pharmaceutically active compounds during simulated riverbank filtration

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HIGHLIGHTS

- Riverbank filtration (RBF) can remove pharmaceutically active compounds (PhACs).
- The impact of temperature, oxygen and organic matter on PhACs removal was studied.
- Removal mechanisms of PhACs occurring at RBF sites were also investigated.
- Caffeine, E1, E2, and phenazone are impacted by the level of oxygen and humic acid.
- Biodegradation, followed by sorption are the predominant PhACs removal mechanisms.

ARTICLE INFO

Article history:
Received 17 August 2014
Received in revised form 9 October 2014
Accepted 9 October 2014
Available online xxxx

Editor: D. Barcelo

Keywords:
PhACs
RBF
Temperature
Oxygen
Humic acid
Biodegradation

ABSTRACT

The objective of this study was to investigate the effect of temperature, oxygen, and organic matter on the removal of selected pharmaceutically active compounds (PhACs) during simulated riverbank filtration (RBF). The behavior of six PhACs (caffeine, carbamazepine, 17-β estradiol [E2], estrone [E1], gemfibrozil, and phenazone) was evaluated by small flow-through column experiments. Results from our study showed that RBF can be used to treat many of the PhACs found in environmental waters. Local conditions at the RBF site, however, can affect the removal of PhACs and should be investigated. Biodegradation and sorption represented the predominant mechanisms involved during the removal of the selected PhACs. All selected PhACs showed limited and slower removal during the winter. Phenazone was highly impacted by the level of oxygen; complete depletion of phenazone below the analytical limit occurred only under aerobic conditions (dissolved oxygen >8 mg L^{-1}). Caffeine and E2 were highly impacted by the presence of humic acid in the feed water. Caffeine and E2 were depleted below the detection limit in the presence of humic acid regardless of the temperature and the level of oxygen. E1 was impacted by the different environmental conditions and depletion below the detection limit occurred only during the summer under aerobic conditions. Carbamazepine (10%) and gemfibrozil ($<30\%$) showed limited removal regardless of the different levels of temperature, oxygen and humic acid.

1. Introduction

Trace organic compounds (TrOCs) in the environment are receiving significant attention because of their potential impact on aquatic and terrestrial organisms (Madureira et al., 2011; Vajda et al., 2008; Thiele-Bruhn and Beck, 2005), ecosystems, and human health (Pal et al., 2010; Bolong et al., 2009). Due to advances in analytical instrumentation, measurements of TrOCs have shown that personal care products, household chemicals, and pharmaceutically active compounds (PhACs) have dramatically increased in environmental waters during the last few decades (ng L^{-1} to μg L^{-1}) (Luo et al., 2014; Meffe and de Bustamante, 2014; Fatta-Kassinos et al., 2011; Benotti et al., 2009; Focazio et al., 2008; Verliefde et al., 2007; Kolpin et al., 2002; Ternes, 1998). Increased use of these chemicals by humans and for animal consumption, the disposal of wastewater or biosolids from wastewater plants onto land, and the disposal of untreated animal wastes in rural landscapes has led to their frequent detection in wastewater effluents (Luo et al., 2014; Verlicchi et al., 2012; Dickenson et al., 2011; Yu et al., 2006; Heberer, 2002), and in surface and groundwater in both the United States and Europe (Meffe and de Bustamante, 2014; Lapworth et al., 2012; Benotti et al., 2009; Verliefde et al., 2007; Kolpin et al., 2002; Ternes, 1998).

Riverbank filtration (RBF) is a common natural filtration treatment for drinking water. RBF systems consist of a series of abstraction wells in the vicinity of a river or lake. When these wells are pumped, the cone of depression of groundwater that develops around well screen

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http://dx.doi.org/10.1016/j.scitotenv.2014.10.032

zones forces river or lake water to infiltrate into the subsurface towards the abstraction wells (Hoppe-Jones et al., 2010). RBF systems have been operating in some cities along the Rhine and Elbe rivers in Europe for over a century (Ray et al., 2008). RBF provides about 50% of the potable water in the Slovak Republic, 45% in Hungary, 16% in Germany and 5% in The Netherlands (Dash et al., 2008). Such systems have also been providing drinking water to US cities for more than 50 years (Drewes and Khan, 2010; Ray et al., 2008). Many other countries around the world including India, China, Korea, Jordan, and Egypt recently have started to evaluate the feasibility of using RBF for water treatment (Ray and Shamrukh, 2011; Ray, 2008).

RBF can be used as a treatment to remove PhACs (Sudhakaran et al., 2013; Storck et al., 2012; Grünheid et al., 2005; Ray et al., 2002). Hiscock and Grischeck (2002) showed that biodegradation and sorption represented the predominant removal mechanisms of PhACs during RBF. Field studies conducted at bank filtration sites in Europe and in the US (Storck et al., 2012; Patterson et al., 2011; Hoppe-Jones et al., 2010; Storck et al., 2010: Vogel et al., 2005) have revealed the impact of redox conditions, residence time, river flow, and physico-chemical properties of PhACs on their removal (Table SM-1). To further investigate the removal mechanisms and the impact of environmental factors on the removal of selected PhACs, laboratory column studies have been used (Bertelkamp et al., 2014; Banzhaf et al., 2012; Baumgartern et al., 2011; Maeng et al., 2011). Commercial sand has been widely used as packing material during these studies (Bertelkamp et al., 2014; Onesios and Bouwer, 2012; Maeng et al., 2011; Rauch-Williams et al., 2010; Gruenheid et al., 2008).

Many of the previous studies investigated the impact of individual or limited environmental factors on the removal of a limited number of PhACs. For example, Gruenheid et al. (2008) investigated the impact of temperature on three TrOCs; Baumgartern et al., 2011 studied the impact of redox conditions, level of organic and the starting concentrations on the removal of sulfamethoxazole; while Maeng et al. (2011) performed his study only under constant temperature (16 °C). A few studies have attempted to separate sorption and biodegradation such as Onesios and Bouwer (2012) and Maeng et al. (2011). These studies compared the removal of PhACs in the presence of biotic (nonsterile) and abiotic (sterile) packing materials and showed little removal of selected PhACs under abiotic conditions suggesting the limited impact of sorption. It has been established that biodegradation processes are temperature dependent and this can highly impact one of the predominant removal mechanisms occurring during RBF. However, there are few studies focused on the impact of temperature and the results were contrasting (Storck et al., 2012; Hoppe-Jones et al., 2010; Gruenheid et al., 2008). According to Gruenheid et al. (2008) adequate retention times should be allowed during the cold season. Diminished attenuation of PhACs during the cold season was also observed by Hoppe-Jones et al. (2010). On the other hand, Storck et al. (2012) suggested a limited impact of temperature on the removal of PhACs.

Seasonal variability of surface water in most temperate regions of the world can vary from near 0 °C in winter to as high as 35 °C in summer. During soil and aquifer passages, there is some moderation of this extreme temperature variation (Sharma et al., 2012; Storck et al., 2010, 2012; Vogel et al., 2005). For example, at the Flehe Waterworks well field (eastern bank of the Rhine River, Germany) the temperature of the river water fluctuates seasonally between 3 °C and 27 °C and between 7 °C and 21 °C in the infiltrated water approximately 60 m from the bank (Sharma et al., 2012). Oxygen is another key environmental factor that shows seasonal variability (Storck et al., 2010; Vogel et al., 2005). Oxygen of the surface water is consumed by bacteria for organic degradation during soil and aquifer passages. Over a period of approximately 2 years, fluctuations in oxygen were observed at the Platte River where the level of dissolved oxygen ranged between 4.79 and 10.74 mg L^{-1} and 0.16 to 9.85 mg L^{-1} at the river and at the closest well, respectively (Vogel et al., 2005). The highest values were observed during the winter and the lowest during the summer. These fluctuations can negatively impact the removal of PhACs. For example, diclofenac and phenazone are more efficiently removed under aerobic conditions compared to anaerobic conditions (Maeng et al., 2011; Rauch-Williams et al., 2010; Zuehlke et al., 2006). Other PhACs, such as iodinated X-ray contrast agents, are preferentially removed under anaerobic conditions (Heberer et al., 2008; Grünheid et al., 2005).

The level of organic carbon in surface waters, and to a limited extent at RBF sites, can vary between 1 to 2 mg L^{-1} and 20 mg L^{-1} depending on the location and environmental conditions (Storck et al., 2012; Hoppe-Jones et al., 2010; Vogel et al., 2005; Volk et al., 2002). Humic acid (HA) accounts for approximately 50–80% of the dissolved organic matter and 30–40% of the aromatic carbon in natural waters (Rodrigues et al., 2009; Aiken, 1985). Different levels of acetate (Onesios and Bouwer, 2012), and different types of water (river water, river water with synthetic organic matter, secondary effluent; Maeng et al., 2011) have been used to investigate the effect of various amounts and types of organic carbon sources on the removal of PhACs. Limited knowledge exists regarding the impact of HA on the removal of PhACs (Lee et al., 2011; Behera et al., 2010). HA represents approximately 70% of natural organic matter (Mamba et al., 2009). HA contains a variety of functional components including carboxylates and phenolic hydroxyls, and it has a refractory nature (Baraněíková et al., 1997). Due to its complex nature, HA shows a strong tendency to retain organic compounds (Zhang and Zhou, 2005).

Physico-chemical properties of the PhACs can be used to estimate the removal of PhACs during RBF (Bertelkamp et al., 2014; Storck et al., 2012), however local conditions such as level of oxygen, temperature, and the presence of organic matter should be carefully investigated.

The objectives of this study were to investigate the role of (i) temperature near the riverbank—summer vs. winter, (ii) oxygen level, and (iii) level of organic matter on the removal of selected PhACs during simulated RBF. The predominant removal mechanisms (biodegradation vs. sorption) were also investigated.

2. Materials and methods

2.1. Selection criteria

PhACs used in this study were chosen based upon: i) pharmaceutical class: steroids, stimulant, anticonvulsant, ii) toxicity: carcinogenic, mutagenic, iii) physico-chemical properties: hydrophobic vs. hydrophilic, iv) fate in the environment: persistent vs. possible removal, v) impact of environment factors on removal: temperature, level of oxygen and organic matter, and vi) availability of analytical standards and adequate instrumentation.

Carbamazepine has been selected as a control due to its persistence in the environment, while the remaining PhACs (caffeine, estrone [E1], 17-β estradiol [E2], gemfibrozil, and phenazone) were chosen for their behavior under different environmental conditions. Additional information related to the appearance and the environmental fate, as well as to the physico-chemical properties of the selected PhACs, are shown in the Supplementary information (Tables SM-1, SM-2). Among the different physico-chemical properties, the octanol–water partitioning coefficient (K_{ow}) provides an indication of compound mobility and affinity to sorption, and can be used for the preliminary screening of the fate of PhACs. Compounds with log $K_{ow} < 3$ can be classified as hydrophilic, while compounds with log $K_{ow} > 3$ can be classified as hydrophobic (Maeng et al., 2011). Hydrophobic compounds tend to have poor solubility, are more likely to sorb, and consequently have reduced mobility in soil (Bertelkamp et al., 2014). High sorption affinity of hydrophobic compounds occurred especially onto organic matter (Pal et al., 2013). Rogers (1996) predicted the sorption capacity of selected compounds based on the log K_{ow}. In particular, a log $K_{ow} < 2.5$ indicates low sorption potential, $2.5 <$ log $K_{ow} < 4$ indicates medium sorption, and log $K_{ow} > 4$ indicates high sorption potential (Rogers, 1996).