Science of the Total Environment 642 (2018) 914–924

Contents lists available at ScienceDirect

Science of the Total Environment

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

Fate of five pharmaceuticals under different infiltration conditions for managed aquifer recharge

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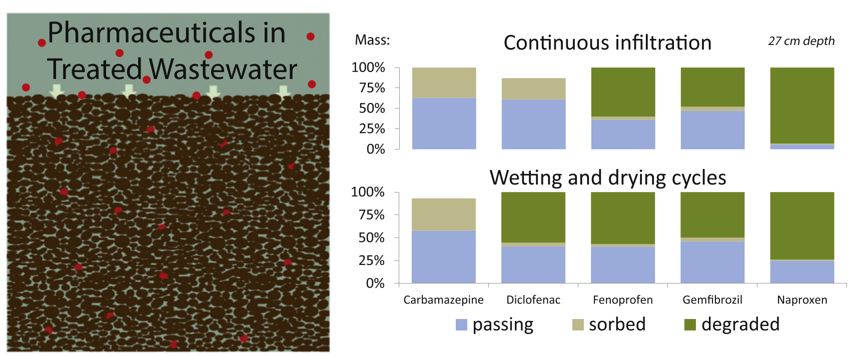
HIGHLIGHTS

- Treated wastewater containing pharmaceuticals was infiltrated in column experiments.
- A mass balance of water-phase and sorbed pharmaceuticals is presented.
- Up to 92% of carbamazepine and up to 32% of diclofenac sorbed to the soil.
- No significant degradation of diclofenac was found for continuous infiltration.
- Cyclic compared to continuous infiltration resulted in equal or better degradation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 20 March 2018
Received in revised form 9 June 2018
Accepted 10 June 2018
Available online xxxx

Editor: D. Barcelo

Keywords:
Wetting and drying cycles
Continuous infiltration
Column experiments
Extraction
Sorption
Degradation

ABSTRACT

Infiltration of treated wastewater (TWW) to recharge depleted aquifers, often referred to as managed aquifer recharge, is a solution to replenish groundwater resources in regions facing water scarcity. We present a mass balance approach to infer the amounts of five pharmaceuticals (carbamazepine, diclofenac, fenoprofen, gemfibrozil, and naproxen) degraded in column experiments based on concentrations of pharmaceuticals in the aqueous and solid (sorbed) phases. Column experiments were conducted under three different conditions: continuous infiltration, wetting and drying cycles, and wetting and drying cycles with elevated concentrations of antibiotics (which may reduce microbially aided degradation of other compounds). A mass balance comparing pharmaceutical mass in the water phase over the 16-month duration of the experiments to mass sorbed to the soil was used to infer the mass of pharmaceuticals degraded. Results show sorption as the main attenuation mechanism for carbamazepine. About half of the mass of diclofenac was degraded with wetting and drying cycles, but no significant degradation was found for continuous infiltration, while 32% of infiltrated mass sorbed. Fenoprofen was degraded in the shallow and aerobic part of the soil, but degradation appeared to cease beyond 27 cm depth. Gemfibrozil attenuated through a combination of degradation and sorption, with slight increases in attenuation with depth from both mechanisms. Naproxen degraded progressively with depth, resulting in attenuation of >90% of the mass. In the column with elevated concentrations of antibiotics, the antibiotics attenuated to about 50% or less of inflow concentrations by 27 cm depth and within this zone, less degradation of the other compounds was observed.

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https://doi.org/10.1016/j.scitotenv.2018.06.120
0048-9697/

1. Introduction

Water scarcity and increasing water demand are problems facing many countries worldwide, especially in arid and semi-arid regions. Managed aquifer recharge (MAR) is a socially and economically valuable set of techniques employed to recharge aquifers using excess water sources (Tuinhof and Heederik, 2002; Dillon et al., 2009; Damigos et al., 2017; San-Sebastián-Sauto et al., 2018), such as treated wastewater (TWW), while attenuating trace organic compounds (TrOCs) contained in the source water (Maeng et al., 2011a). MAR techniques include riverbank filtration (RBF), to remove TrOC mass prior to drinking water production (Tufenkji et al., 2002; Eckert and Irmscher, 2006; Storck et al., 2010), as well as soil aquifer treatment (SAT), where TWW is infiltrated from constructed basins, often resulting in attenuation of emerging anthropogenic contaminants (Amy and Drewes, 2007; Laws et al., 2011; Valhondo et al., 2015). Many studies have investigated the occurrence of pharmaceuticals and other TrOCs in groundwater receiving infiltrated TWW (Drewes et al., 2003; Amy and Drewes, 2007; Bekele et al., 2011; Patterson et al., 2011). Concentrations generally decrease with distance from the infiltration source, but understanding the attenuation mechanism(s) is critical. Numerous studies have utilized tracer methods combined with monitoring pharmaceutical breakthrough (Matamoros et al., 2008; Rauch-Williams et al., 2010; Hoppe-Jones et al., 2012; Burke et al., 2013; Durán-Álvarez et al., 2015) while other studies have included transport modeling (Greskowiak et al., 2006; Nham et al., 2015; Hamann et al., 2016) or compared biotic with abiotic experiments (Lin et al., 2010; Lin and Gan, 2011; Maeng et al., 2011b; D'Alessio et al., 2015; Martínez-Hernández et al., 2015; Zemann et al., 2016).

However, few studies have quantified the mass of pharmaceuticals into a system and the mass remaining in the soil after some time period. Banzhaf et al. (2012) performed column experiments lasting 71 days and extracted pharmaceuticals from the soil afterwards, finding sorption of almost half of the infiltrated carbamazepine (an anti-epileptic medication) but <3% of infiltrated diclofenac (a nonsteroidal anti-inflammatory drug). In a field-based study of soils from several field sites irrigated with TWW, Kinney et al. (2006) found accumulation of carbamazepine in all soils exceeding infiltrated mass monitored over a six-month time period (additional irrigation also occurred before the monitored period), suggesting that the compound is recalcitrant. No accumulation was found for other pharmaceutical compounds, including gemfibrozil. Accumulation exceeding the six-month infiltrated mass of the antibiotic sulfamethoxazole was observed by Kinney et al. (2006), while Banzhaf et al. (2012) found degradation of sulfamethoxazole where nitrate reducing conditions are present. In MAR applications, the fate of pharmaceuticals has been studied extensively (Maeng et al., 2011a; Hoppe-Jones et al., 2012; D'Alessio et al., 2015; Nham et al., 2015; Valhondo et al., 2015; Hamann et al., 2016), but mass balance approaches are not common.

The aim of this study is to determine the fate of pharmaceutical compounds by quantifying both the water (dissolved) and solid (sorbed) phase mass, under conditions of continuous infiltration, wetting and drying cycles, and wetting and drying cycles with elevated water-phase concentrations of antibiotics. Continuous infiltration was conducted as a reference (with more consistent redox conditions) to wetting and drying cycles, which are commonly used in the field (Goren et al., 2014). An infiltration water with higher concentrations of antibiotics was used to evaluate the possibility that antibiotics commonly present in the environment might reduce microbial degradation of other compounds. Oxidation-reduction potential (ORP) was measured in the column with wetting and drying cycles to observe changes in redox conditions with this infiltration mode.

Research on the fate of pharmaceuticals in MAR has shown that concentrations of pharmaceuticals generally decrease along the infiltration flowpath, with sorption and degradation playing roles that vary by compound (Maeng et al., 2011a). In soils with low organic matter content, sorption typically plays less of a role than in organic-rich soils (Chefetz et al., 2008). Meanwhile, several studies have shown that some pharmaceuticals (and other TrOCs), including diclofenac, gemfibrozil, and naproxen, are degraded better when biodegradable organic carbon (BDOC) concentrations are low, with bacteria becoming less selective in utilization of carbon sources (Rauch-Williams et al., 2010; Hoppe-Jones et al., 2012; Alidina et al., 2014b). Moreover, some recent studies have found better degradation for certain compounds (e.g. diclofenac and sulfamethoxazole) under oxic conditions (Bertelkamp et al., 2016; Müller et al., 2017). However, with the presence of other contaminants (e.g. nitrate) that are better degraded with high BDOC concentrations, reducing conditions are also important. Valhondo et al. (2015, 2018) investigated adding an organic carbon-rich layer at the top of infiltration basins, making conditions more reducing. Others have proposed and demonstrated the concept of sequential managed aquifer recharge technology, in which an aeration step follows initial infiltration with higher BDOC conditions and/or microbial activity, with the aeration step typically resulting in similar or better degradation of TrOCs compared to without aeration (Regnery et al., 2016; Hellauer et al., 2017a; Hellauer et al., 2017b). This sequential technique may be applicable to combining RBF (step 1), in which wetting and drying cycles are not practical, with extraction, aeration, and reinfiltration in a SAT basin (Regnery et al., 2016). In SAT, infiltration is often conducted in wetting and drying cycles (Drewes et al., 2003; Goren et al., 2014). He et al. (2016) found better degradation of some compounds, such as sulfamethoxazole, with wetting and drying cycles compared to continuous infiltration, but did not find a difference for many other compounds (e.g. diclofenac, fenoprofen, gemfibrozil, and naproxen).

For the current study, an organic-rich natural soil from a possible future MAR site in Greece was used. With this soil, column experiments were conducted and secondary TWW of mostly domestic urban origin was used as inflow water. As sorption is a key process to be quantified, a soil with high organic content was chosen as it is expected to increase sorption and retardation of pharmaceuticals (Chefetz et al., 2008; Hebig et al., 2017). This study focuses on the pharmaceuticals carbamazepine, diclofenac, gemfibrozil, and naproxen, which are each commonly found in TWW at concentrations up to ~5–20 μg/L, as well as fenoprofen which is found at lower concentrations (up to ~0.04 μg/L) (Verlicchi et al., 2012). Many studies of the environmental fate of carbamazepine have found the compound to be recalcitrant (Maeng et al., 2011a), although one study found some degradation with an organic-rich soil (Banzhaf et al., 2012), while both sorption and degradation of the four remaining compounds have been reported (Maeng et al., 2011a, 2011b; Fang et al., 2012). Sampling of the inflow water and soil pore water at depths of 12, 27, and 72 cm was conducted during the experiments, with the sampling results and measurement of the volume of infiltrated water allowing for calculation of the mass of each pharmaceutical passing each sampling port in the water phase. When the experiments ended, the pharmaceutical compounds were extracted from soil samples to obtain the mass sorbed to the soil. The mass sorbed was then compared to the mass attenuated (i.e., mass that left the water phase) at each sampling point to infer the quantity of mass degraded.

2. Materials and methods

2.1. Soil and inflow water

The experimental soil is classified as a rendzina soil (Zvorykin and Saul, 1948) and was obtained from open, non-agricultural grassland approximately 12 km northeast of Athens, Greece, immediately west of the Dimosio Dasos Rapentosas wildlife refuge, at a possible future MAR site. Disturbed soil samples were collected and packaged in plastic-coated aluminum bags. The soil is a loamy sand and contains 2.6% organic carbon and 0.2% nitrogen (analyses described in the Supplementary Information (SI)). The soil contains pristine (not decayed)