Science of the Total Environment 640–641 (2018) 671–677

Contents lists available at ScienceDirect

Science of the Total Environment

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

Removal of selected pharmaceuticals and personal care products in reclaimed water during simulated managed aquifer recharge

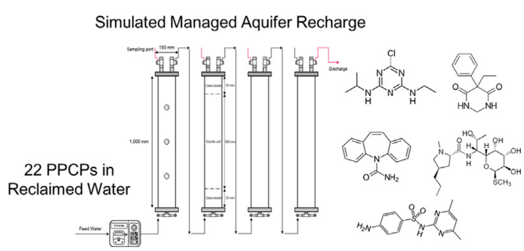
Soohyung Park, Wontae Lee *

Department of Environmental Engineering, Kumoh National Institute of Technology, Gumi, South Korea

HIGHLIGHTS

- Per monitoring of 22 PPCPs at a WRF in Korea, 15 substances were detected.
- Atenolol, propranolol and trimethoprim were removed >80% through MAR.
- Atrazine, carbamazepine, lincomycin and primidone were not readily removed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 February 2018
Received in revised form 28 April 2018
Accepted 18 May 2018
Available online xxxx

Keywords:
Pharmaceuticals
Personal care products
Water reclamation
Water reuse
Managed aquifer recharge

ABSTRACT

This study investigated the removal of selected pharmaceuticals and personal care products (PPCPs) in a simulated managed aquifer recharge (MAR) system. The PPCPs included antibiotic, antiepileptic, antihypertensive, anti-inflammatory, and antilipidemic drugs, contrast media, herbicides, and stimulants. We first monitored the occurrence and fate of 22 PPCPs at a water reclamation facility (WRF) in Korea, and found carbamazepine and primidone were not readily removed (below 25% removal in average) by the WRF. This reclaimed water passed through a laboratory-scale soil column set-up at 0.5 m/d over one year, simulating MAR system. Atenolol, propranolol, and trimethoprim exhibited higher removal rates (>80%) than other PPCPs through the simulated MAR, while atrazine, carbamazepine, lincomycin, primidone, and sulfamethazine were not readily removed, exhibiting removal rates below 20%. It can be efficient to monitor and manage these recalcitrant compounds at MAR systems to improve water quality.

1. Introduction

Approximately 12,000 pharmaceuticals and personal care products (PPCPs) have been distributed for human use worldwide. PPCPs include a variety of chemical substances, including human and veterinary drugs, disinfectants or fragrances in personal care products such as lotions, lipsticks, hair sprays/dyes, body cleaning products, and sun-screens (Balmer et al., 2005; Gago-Ferrero et al., 2011), and household chemicals (Boxall et al., 2012; Bu et al., 2013; Lin et al., 2016). After their use in hospitals, households, and industries, residual PPCPs can enter the aquatic environment via wastewater treatment systems and/or water reclamation facilities (WRFs) (Tran et al., 2014a, 2018). PPCPs have been detected in waste and reclaimed waters at ng/L to μg/L levels (Pedrouzo et al., 2007; Tran and Gin, 2017; Yang et al., 2011).

The presence of PPCPs in reclaimed water has received great attention owing to their potentially adverse influences on human health and ecosystems (Tran et al., 2014a; Tran and Gin, 2017; Yang et al., 2011). PPCPs are potentially hazardous to the aquatic ecosystem, and can cause endocrine disruption and other severe side effects resulting from the specific biological effects they were developed to induce (Clara et al., 2005; Nakada et al., 2007; Tran and Gin, 2017; Tran et al., 2014b; Vulliet et al., 2011). Wastewater can be reclaimed and reused through various engineering techniques and natural or passive treatment processes. Most WRFs employ multiple barrier approaches, including activated sludge processes, media and/or membrane filtration,

* Corresponding author.
E-mail address: wtlee@kumoh.ac.kr (W. Lee).

https://doi.org/10.1016/j.scitotenv.2018.05.221

and disinfection (Page et al., 2010a, 2010b). However, the removal of PPCPs by WRFs is reportedly inefficient (Nakada et al., 2006; Santos et al., 2007; Tran et al., 2018) and depends on compound-specific properties as well as factors related to WRFs, such as the types of treatment processes or age of sludge (Tran et al., 2013, 2018).

Water reuse can be facilitated by purposefully recharging reclaimed water into aquifers for natural treatment prior to recovery and reuse. This artificial recharge is called "managed aquifer recharge (MAR)", and is a natural water treatment process that induces the flow of water the soil. MAR provides a natural buffer, provides a residence time that can facilitate the removal of biodegradable organic matters and pathogens, improves the quality of the treated wastewater, including PPCPs, and reduces the cost of seasonal peak demands (Dillon et al., 2008; Levantesi et al., 2010; Page et al., 2010a, 2010b).

MAR has not yet been applied for water reuse in Korea, although this technology has been studied and applied in other countries, such as the United States and Australia. PPCPs are an ideal group of compounds for assessing the removal mechanisms of emerging contaminants by MAR owing to their varied chemical properties. The occurrence of PPCPs in wastewater can be related to local production, and the fate of these compounds in WRF and MAR can differ from that observed in other countries. Though previous studies have elucidated the removal characteristics of several PPCPs in MAR, few have systematically evaluated the relationship between the removals of PPCPs and operational conditions with respect to the PPCPs' properties. This study addresses these questions by monitoring the removals of 22 PPCPs in a full-scale water reclamation facility in Korea and a laboratory-scale MAR.

2. Materials and methods

2.1. Laboratory-scale soil column set-up and operation

MAR was simulated using a laboratory-scale soil column set-up, which consisted of four 1000-mm acrylic glass columns in series with an inner diameter of 150 mm. The columns were filled with native alluvial material (diameter < 2 mm). The porosity was 0.4, and the permeability coefficient was 0.013 cm/s. The system was positioned in a temperature-controlled room at 20 °C, and feed water was injected into the soil column system by a peristaltic pump at 0.5 m/day (volumetric flow rate of 6.13 mL/min) upward flow, considering the typical residence time of water in MAR systems (Racz et al., 2012). To eliminate the effect of varying hydraulic recharge conditions, the experiment ran at a fixed flow rate over the whole experimental period (from September 2016 through August 2017). The columns were initially saturated with ambient groundwater and subsequently rinsed with the final effluent. The initial increase in electrical conductivity was used as a tracer for determining the hydromechanical properties of the columns. The soil columns were kept saturated at all times.

2.2. WRF and feed water to MAR

The simulated MAR system was fed with the final effluent of a WRF in an industrial complex in Gumi, Korea, which had a capacity of 50,000 m^3/d and received wastewater from the surrounding industrial complex. The WRF consisted of primary treatment followed by a biological process, coagulation/filtration, and UV disinfection. Prior to MAR test, concentrations of target PPCPs in the influent, biological process, coagulation/filtration process, and effluent were monitored for the 12-month period (sampled every other month) from January to December 2015. The final effluent of the facility was collected and used as the feed water for the laboratory-scale MAR from September 2016 through August 2017. The feed water was filtered through glass fiber filters with a pore size of 0.7 μm after collection.

2.3. Target PPCPs

Among the diverse array of PPCPs, we selected 22 compounds that are common in aquatic systems, and the physical and chemical properties of these target compounds are presented in the supplementary material (Table A.1). The compounds were selected to represent different antibiotics, such as chlortetracycline, lincomycin, oxytetracycline, sulfachloropyridazine, sulfamethazine, sulfamethoxazole, sulfathiazole, tetracycline, and trimethoprim; antiepileptics, such as carbamazepine and primidone; antihypertensive drugs, such as atenolol, metoprolol, and propranolol; anti-inflammatory drugs, such as acetaminophen, diclofenac, ibuprofen, and naproxen; antilipidemics, such as gemfibrozil; contrast media, such as iopromide; herbicides, such as atrazine; and stimulants, such as caffeine. These compounds were listed among the 30 most frequently detected organic wastewater contaminants reported by the United States Geological Survey (Kolpin et al., 2002). Atenolol, carbamazepine, gemfibrozil, ibuprofen, and sulfamethoxazole were among the top ten high-priority pharmaceuticals identified in a European PPCP assessment (Global Water Research Coalition, 2008).

2.4. Determination of water quality parameters and target PPCPs

All samples were filtered through membrane filters (0.4 μm, Whatman, USA) to remove any particulate materials, and stored at 4 °C in the dark. All water samples were extracted within one week for further analysis if necessary. DOC was measured by a TOC analyzer (TOC-VCPH, Shimadzu, Japan) using the non-purgeable organic carbon method. Ultraviolet absorbance at 254 nm (UVA_{254}) was measure at 254 nm wavelength by a UV spectrophotometer (Hach, USA). Electrical conductivity (EC) was measured using a conductivity meter (ThermoFisher, USA).

A highly sensitive analytical method was developed and validated for determining the levels of PPCPs in wastewater. The PPCPs were separated and detected using LC-MS/MS methods based on the direct injection of a sample into the chromatograph (Tran et al., 2016; Tran and Gin, 2017; Vymazal et al., 2017). A 1290 High-Performance Liquid Chromatograph tandem with a 6490 Triple Quad Mass Spectrophotometer (LC/MS-MS) (Agilent 1200 series rapid-resolution liquid chromatograph (Waldbronn, Germany), triple quadrupole 6490 Mass) was used in the electrospray ionization (ESI; positive/negative) mode. ESI separation was conducted on an Eclipse C18 analytical column (100 × 2.1 mm, 3.5 μm particle size, Agilent). The mobile phase for material separation contained de-ionized water (solvent a) and acetonitrile/methanol (4:1, V/V) (solvent b). Both solvents A and B were added with 0.1% formic acid, and the fractions of solvents A and B were changed over time to efficiently separate the target material. Analytical conditions for the LC/MS-MS are summarized in the supplementary material (Table A.2). Limit of quantification (LOQ) for PPCPs was 1 ng/L, except naproxen (20 ng/L). All standards were of high purity grade (>99%) and purchased from Sigma-Aldrich (USA).

3. Results and discussion

3.1. Removal of target PPCPs by the WRF

The target compounds were selected to represent different PPCPs, such as antihypertensive drugs (such as atenolol), stimulants (such as caffeine), antilipidemics (such as gemfibrozil), antibiotics (such as sulfamethoxazole), and antiepileptics (such as carbamazepine and primidone). Seven of the twenty-two target compounds were detected at every sampling campaign of the WRF for the 12-month period from January to December 2015, and they were listed in Table 1. Table 1 summarizes the average, minimum, and maximum concentrations of the target PPCPs in the influent and biological process, coagulation/filtration, and UV disinfection effluents.