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Simultaneous attenuation of pharmaceuticals, organic matter, and nutrients in wastewater effluent through managed aquifer recharge: Batch and column studies

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HIGHLIGHTS

- We tested the removal of soil and aquifer contaminants in batch and column studies.
- A comparison of pollutant attenuation was made between the natural and baked sands.
- Neutral and cationic pharmaceuticals were more eliminated than anionic ones were.
- The removal rates of most of the target contaminants increased under biotic conditions.
- Biodegradation improves the removal of emerging pollutants in managed aquifer recharge.

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ABSTRACT

Batch and column experiments were conducted to evaluate the removal of organic matter, nutrients, and pharmaceuticals and to identify the removal mechanisms of the target contaminants. The sands used in the experiments were obtained from the Youngsan River located in South Korea. Neutral and cationic pharmaceuticals (iopromide, estrone, and trimethoprim) were removed with efficiencies greater than 80% from different sand media during experiments, due to the effect of sorption between sand and pharmaceuticals. However, the anionic pharmaceuticals (sulfamethoxazole, ketoprofen, ibuprofen, and diclofenac) were more effectively removed by natural sand, compared to baked sand. These observations were mainly attributed to biodegradation under natural conditions of surface organic matter and ATP concentrations. The removal of organic matter and nitrogen was also found to increase under biotic conditions. Therefore, it is indicated that biodegradation plays an important role and act as major mechanisms for the removal of organic matter, nutrients, and selected pharmaceuticals during sand passage and the managed aquifer recharge, which is an effective treatment method for removing target contaminants. However, the low removal efficiencies of pharmaceuticals (e.g., carbamazepine and sulfamethoxazole) require additional processes (e.g., AOPs, NF and RO membrane), a long residence time, and long travel distance for increasing the removal efficiencies.

1. Introduction

Surface water has been used as a source of drinking water around the world. However, there has been growing concern over the water shortage and aquatic pollution caused by algal bloom, industrialization, urbanization, and climate change. The use of surface water results in public health concerns regarding nutrients, dissolved organic carbons (DOC), dissolved ions and metals. Although pharmaceuticals are detected at a very low concentration (in units of ng/L or μg/L range) in the aquatic environment, the presence of pharmaceuticals may lead to critical health concerns (Chon et al., 2012). The major route for the occurrence of pharmaceuticals in an aquatic system is through excretion in feces and

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urine discharged into wastewater treatment plants (Ying et al., 2009). Non-point sources (e.g., floods) in farmland can carry pharmaceuticals such as veterinary antibiotics to a river or groundwater (Maeng et al., 2011a). Recently, some researchers showed the fate of pharmaceuticals in drinking water treatment plants and in an aquatic environment (Mompelat et al., 2009). The increasing use of pharmaceuticals for human and veterinary purposes has increased the detection of these pharmaceuticals in aquatic environments (Heberer, 2002). Pharmaceuticals in water cannot be effectively removed by conventional coagulation, flocculation, and sedimentation processes. Oxidation or membrane processes can effectively remove the pharmaceuticals. NF and RO membrane systems have especially been known to be effective processes for the removal of pharmaceuticals at drinking water treatment plants, but at a high cost. Therefore, managed aquifer recharge (MAR), a cost-effective and robust system, has been widely adopted for the removal of pharmaceuticals (Maeng et al., 2011a, 2011b). MAR is a natural and sustainable water treatment that uses all types of water sources. It boasts several environmental benefits, such as the recovery of the ground water level, the storage of water resources, and the improvement of the water quality. The MAR system includes a variety of processes, such as riverbank filtration (RBF), soil aquifer treatment (SAT), and artificial recharge (AR) (Dillon, 2005). The MAR system is deemed to be eco-friendly and economically efficient, and it not only effectively improves water quality but also offers low operational/maintenance costs (O/M costs) and energy use without any chemicals (Sudhakaran et al., 2013). During the process, a variety of contaminants are removed by diverse reduction mechanisms, such as dispersion, filtration, biodegradation, adsorption, precipitation, ion exchange, and mixing with groundwater in the aquifer, the most common of which is biodegradation (Maeng et al., 2011b; Ray et al., 2002). Using a variety of mechanisms, many previous studies have demonstrated that the improvements in quality obtained by the MAR systems may allow for significant reductions in particulates, pathogen turbidity, and natural organic matters (Drewes et al., 2002; Kuehn and Mueller, 2000; Rauch-Williams et al., 2010). South Korea is one country that has generally adopted the RBF process. In the 2000s, the Korean government built a RBF system to remove target contaminants (Ann et al., 2005; Lee et al., 2009). Though many pharmaceuticals are frequently detected in surface water, few studies examining the removal of pharmaceuticals have studied RBF systems in South Korea (Kim et al., 2007, 2014).

Recent studies have attempted to examine the removal of pharmaceuticals from wastewater and surface water using the MAR system (Bertelkamp et al., 2014; Maeng et al., 2011a). However, few studies have investigated (i) the use of demineralized water containing sodium azide (NaN_3) to maintain abiotic experimental conditions during soil passage, (ii) the removal of pharmaceuticals by the MAR system using field water (wastewater and surface water) spiked with pharmaceuticals and (iii) the measurement of DOC removal with only selected pharmaceuticals removal.

In this study, baked sand media was used to maintain abiotic conditions to investigate the removal of pharmaceuticals by sorption. Batch and column experiments were performed using real-field wastewater not spiked with pharmaceuticals in the feed water. Feed water was filtered through 0.45 μm filter before use to reduce the effect of microorganisms. Chemical oxygen demand (COD), total nitrogen (TN), and total phosphorous (TP) concentrations were measured simultaneously with pharmaceuticals concentrations.

Therefore, the primary objective of this study was to investigate the ability of the MAR system to attenuate target contaminants and pharmaceuticals using real-field wastewater not spiked the pharmaceuticals in South Korea. The specific aims were: (i) to investigate the ability of MAR system to attenuate organic matter, nutrients (i.e., nitrogen and phosphate), and 11 pharmaceuticals selected from different sand media (with different organic matter characteristics) during sand passage; and (ii) to investigate the mechanisms for removing pharmaceuticals with regards to the physicochemical properties of the pharmaceuticals and the biodegradation from different sand media.

2. Materials and methods

2.1. Sample preparations

The sand samples used in the experiment were collected from Jangsung-gun, Jeollanam-do near Youngsan River basin, Korea for using batch and column experiment. Sands were collected along the edge of the river, air-dried, sieved, and then stored at room temperature without light. The sand sieved methods were adapted from Oh et al. (2013). Sand was baked to prevent biodegradation and influencing soil organic matter by muffle furnace at 550 °C for 24 h. All experiments were performed to use grain size (0.8–1.25 mm) natural sand and baked sand.

Batch and column experiments were used for secondary effluents of the Damyang Wastewater Treatment Plant (can be removed from both rainwater and sewage) in Jeollanam-do; the effluents were used for feed water. Influent water was used after 0.45 μm filtration during batch and column experiments for removal of microorganisms in the influent water. All experiments were collected the samples to investigate the removal of pharmaceuticals, organic matter, and nutrients. The bulk analysis parameters (DOC, COD, specific UV absorbance (SUVA), total nitrogen (TN), nitrate, nitrite, ammonium, total phosphorus (TP), and phosphate) were investigated during test and the samples for the analysis of pharmaceuticals were also collected during the experiments.

2.2. Chemicals

Table 1 shows the physicochemical properties of the selected compounds. Eleven pharmaceuticals were target compounds commonly detected in municipal wastewater. Iopromide, acetaminophen, carbamazepine and estrone were neutral pharmaceuticals. Most neutral pharmaceuticals showed that the pK_a value was over 10. Atenolol and trimethoprim were cationic pharmaceuticals, and the pK_a value was around 7–9. Clofibric acid, sulfamethoxazole, ketoprofen, ibuprofen, and diclofenac were anionic pharmaceuticals, and the pK_a value was around 1–5. According to Maeng et al. (2011a), a chemical with a log D value of less than 1 (hydrophilic compound) cannot sorb onto organic compounds or biodegrade, which is in contrast to a chemical with a log D value of equal to or greater than 3 (hydrophobic compound), which can significantly biodegrade or sorb onto soil organic matter. Iopromide was purchased from United States Pharmacopeia; acetraminophen, carbamazepine, estrone, atenolol, trimethoprim, clofibric acid, sulfamethoxazole, ketoprofen, ibuprofen, diclofenac were obtained from Sigma–Aldrich. All of 11 selected pharmaceuticals were used to standard solution for analysis of feed and effluent solution.

For a quantitative and qualitative analysis of pharmaceuticals in LC–MS/MS, nine surrogates were prepared. Each pharmaceuticals surrogate had a similar chemical structure. Nine surrogate standards including non-deuterated compounds (dihydrocarbamazepine, cloprop) were purchased from Sigma–Aldrich and deuterated compounds (iopromide-d_3, acetaminophen-d_4, estrone-d_4, atenolol-d_7, trimethoprim-d_9, sulfamethoxazole-d_4, and ibuprofen-d_3) obtained from Toronto Research Chemicals. The purity of surrogate standards used in this study was ≥97%. In addition, surrogate standards (10 mg L^{-1}) were prepared in