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Fate of veterinary antibiotics in riverine soils: evaluation of applicability in riverbank filtration

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ABSTRACT

Riverbank filtration, which is an induced bank infiltration method in managed aquifer recharge, is an eco-friendly and economical water treatment method to remove the diverse contaminants in water. One of the primary water environmental concerns today is related to the removal of organic micropollutants, such as veterinary antibiotics (VAs). In this study, we performed batch-scale and column experiments using diverse regional areas of soils and pretreated soils (natural, sterilized, and baked soils) in order to identify the removal mechanisms of the three representative soil VAs. Results from the experiments showed that tetracycline and erythromycin were removed in soils by sorption with an electric attractive force between soil particles and compounds, regardless of soil properties. Sulfathiazole was influenced by microbial activities and sorption with soil organic matter. This study shows that the fate of representative VAs in soil and riverbank/bed filtration system is effective treatment method to remove VAs.

Keywords: Managed aquifer recharge; Riverbank filtration; Veterinary antibiotics; Sorption; Biodegradation

1. Introduction

There have been a variety of attempts to solve and manage global water shortages and pollution. One mechanism gaining favor in many countries is recharging the water in aquifers using managed aquifer recharge (MAR) [1]. MAR is a natural sustainable water treatment that uses all types of water sources. Its environmental benefits include the subsequent recovery of groundwater levels, storage of water resources, and improving water quality. A MAR system includes a variety of processes and is categorized by method, with riverbank/bed filtration (RBF) being a common technique.

RBF is an induced bank infiltration method. It is considered to be eco-friendly and provides not only effective water quality improvement, but also low operational/maintenance (O/M) cost and energy use without chemicals [2]. During the RBF process, a variety of contaminants are removed by diverse reduction mechanisms, including dispersion, filtration, biodegradation, adsorption, precipitation, ion exchange, and mixing with groundwater in the aquifer. The main removal mechanisms are sorption and biodegradation [3]. Many previous studies have demonstrated that the quality improvements obtained by RBF may allow for significant reductions in turbidity and natural

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organic matter [4,5]. One of the primary water environmental concerns related to drinking water is the potential presence of low concentrations of organic micropollutants, such as pesticides, pharmaceutical active compounds, and veterinary antibiotics (VAs) [6]. Consequently, RBF has been examined in many studies as a method to reduce their presence.

Numerous types of VAs are used for livestock to treat disease and maintain livestock health. After administration, VAs are excreted and released into the soil and groundwater and migrate to surface waters via urine and feces [7,8]. As a result, accumulated VAs in the environment can cause ecosystem disturbance, persistence, and the appearance of super bacteria that have a strong resistance to particular antibiotics.

VAs are used more widely in Korea compared to other countries because of their intensive use as feed additives for promoting livestock growth [9,10]. The government has introduced regulations to reduce the sale and use of VAs, and consequently their usage has been declining. VAs have been prohibited from being used as feed additives since 2012; however, they can still enter the environment through livestock manure from the increasing use of self-prophylactic antibiotic treatment. Therefore, since the problems of VA use continue to occur, experiments using RBF are needed in order to document the effective removal of VAs.

The aim of this study is to confirm and compare the fate and removal efficiencies of representative VAs in Korea, which were tetracycline, erythromycin, and sulfathiazole, in RBF using different properties of riverside soils.

2. Material and methods

2.1. Veterinary antibiotics

Three VAs were selected as representative of the major groups of VAs most often used in South Korea: tetracycline as an example of the tetracycline group, erythromycin as an example of macrolides, and sulfathiazole as an example of sulfonamides (all from Sigma Aldrich). They differ significantly in their physicochemical properties (Table 1). In addition, three surrogate standards—minocycline, josamycin, and sulfadiazine—having similar molecular weight and chemical properties were also obtained from Sigma Aldrich. Stock solutions of mixed and single VAs (50 mg/L) and surrogate (10 mg/L) were prepared in deionized water to obtain solutions of 500 μg/L and 1 mg/L, respectively, for each experiment.

2.2. Soil

The soil samples used in the experiment were from four regional areas. Soil samples were collected from Jangsung-gun (JS) and Hampyeong-gun (HP), Jeollanam-do near Youngsan River basin; Gwangju-si (GJ), Kyounggi-do near Kyoungan Stream; and Haman-gun (HA), Gyeongsangnam-do near Nakdong River basin. Surface soil (0–50 cm) was sampled from the riversides. These soils were air dried and sieved (<2 mm mesh), then stored at room temperature without light. The sand sieved methods were adapted from Oh [11]. The particle size distributions of four soils are shown in Fig. 1. HP soil had finer sand particles than other soil.

The soil was sterilized and baked to prevent biodegradation and any influence from soil organic matter (SOM) by using an autoclave and muffle furnace at 121 and 550°C for 30 min and 24 h, respectively. All experiments were performed to obtain natural, sterilized, and baked soil with a grain size of 0.8–1.25 mm.

2.3. Batch experiment

Batch experiments investigate the main removal mechanisms of VAs by comparing removal efficiency between different soil types and influencing competitive adsorption effectiveness. The batch reactors consisted of amber 100 mL bottles containing 75 mL of artificial water and 10 g of soil. Batch reactors were used for two types of experiments: different soil conditions (natural, sterilized, and baked soil) and regional areas (JS, HP, GJ, and HA soil). Control samples, which do not include soils, were also prepared. All reactors were stirred in a shaking incubator at 150 rpm and maintained at a temperature of 25°C for a 30-d hydraulic retention time.

2.4. Column experiment

Column experiments investigate the fate of VAs using different soil types in water. From the respective storage tank, the inflowing water was pumped through the column with a peristaltic pump from bottom to top to prevent problems from gas accumulation in the column. The two fixed bed columns had dimensions of 30 mm diameter and 300 mm length. Before inserting the sediment into the column, the sediment was dried and sieved to remove grain sizes of >2 mm and thus allow adequate packing of the column. Packed columns were operated as a continuous liquid flow system at a flow rate of 1.3 mL/min using peristaltic pump (Cartridge pump 7519-20; Masterflex, USA). Effluents were

Table 1
Summary of all VAs studied with their properties

Compound	Type	MW	pK_a[a]	log K_{ow}[b]	K_d (L/kg)
Tetracycline	Tetracyclines	444.43	pK_{a1}: 3.3 (H_4TC^+) pK_{a2}: 7.68 (H_3TC) pK_{a3}: 9.3 (H_2TC^-)	−1.37	1,140–1,620[c]
Erythromycin	Macrolides	733.93	8.8	3.06	N.A[d] (cf. macrolide: 8.3–240)
Sulfathiazole	Sulfonamides	255.32	pK_{a1}: 2 ($-NH_3^+$) pK_{a2}: 7.24 ($-SO_2NH-$)	0.05	0.6–4.9[e]

[a] Values calculated with ACD/Labs pK_a dB v. 12 program.

[b] pH-dependent octanol–water coefficient; values calculated with ACD/Labs log D v. 12 program at zero ionic strength.

[c] Sithole and Guy, 1987.

[d] Thiele-Bruhn, 1989.

[e] Langhammer and Tolls, 2001.

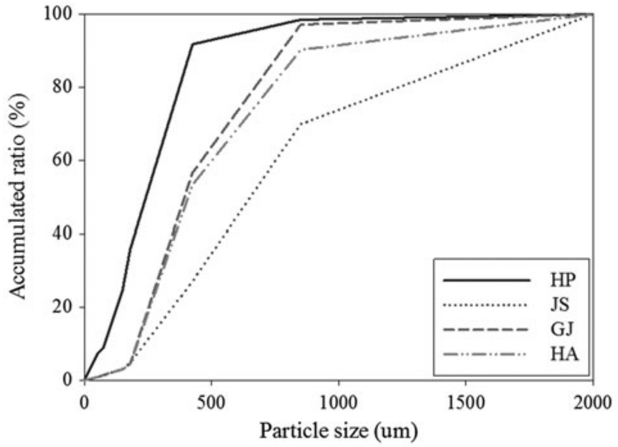

Fig. 1. Accumulated ratio of particle size of HP, JS, GJ, and HA soils.

sampled at desired time intervals using a sampling collector to measure VA concentration. The residence time for the column setup was 11 h, which was determined by a tracer study using 0.01 mM NaCl solution at a hydraulic loading rate of 0.64 m/d [12]. Column experiments were performed in the dark in order to avoid photodegradation of the VAs, and operating temperatures were kept between 16 and 18℃ for 60 d. At the end of the experiment, all columns were dismantled to collect sand samples for the analysis of sand dissolved organic carbon and the active microbial biomass (AMB) associated with the sand.

2.5. Analytic methodologies

2.5.1. Soil samples

The concentration of SOM was quantified using a combustion type total organic carbon analyzer (SSM-5000A; Shimadzu, Japan). Adenosine triphosphate (ATP) was used to determine the AMB associated with the sand [13]. The ATP extraction methods and materials were adapted from Magic-Knezev and van der Kooij [14].

2.5.2. Veterinary antibiotics

VAs were analyzed by liquid chromatography (LC) (Alliance 2695; Waters) involving triple-quadrupole tandem mass spectrometry (Micromass; Waters, UK). The methods used for solid phase extraction and LC-tandem mass spectrometry were adapted from Bui and Choi [15] and Vanderford and Snyder [16] with a few modifications.

3. Results and discussion

3.1. Removal mechanisms of VAs

The main removal mechanisms of contaminants in RBF are adsorption to soil and organic matter and biodegradation by microbial activities. In order to identify the predominant removal mechanisms of the three VAs, batch experiments were taken using HP soil. Soils were pretreated under three different conditions: natural, which retains organic matter and microorganism; sterilized, which contains organic matter without microorganisms; and baked, which does not contain organic matter or microorganisms.

Removal efficiencies of tetracycline using natural, sterilized, and baked soil are shown in Fig. 2(a). Removal efficiencies were similar among all three types (natural 85 ± 2.9%; sterilized 86 ± 0.3%; baked soil 87 ± 0.2%) after 30 d. Thus, the sorption process was the predominant removal mechanism of tetracycline in the soil. Most soil surfaces carry a net negative charge. Since changing the pH leads to protonation or de-protonation of VAs, the physicochemical properties

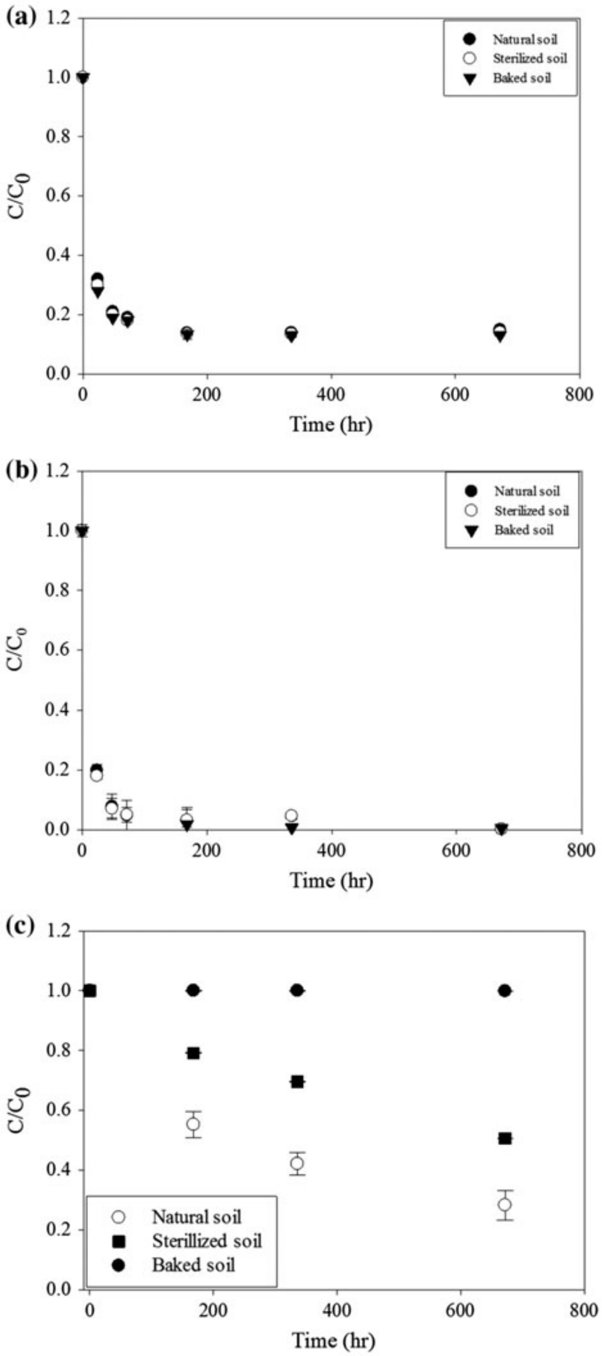

Fig. 2. Removal rate of (a) tetracycline, (b) erythromycin, and (c) sulfathiazole in natural, sterilized, and baked soil ($n = 3$).

and their sorption behaviors of the VAs should have changed. Tetracycline was found to have diverse pK_a values (3.3, 7.68, and 9.3, respectively), with the dominant form (H_4TC^+, H_3TC, and H_2TC^-, respectively) depending on pH. Thus, tetracycline was adsorbed by the electric attractive force with the soil surface because it had a positive charge at pH 6.65. Generally, tetracycline has a high distribution coefficient (K_d) value, so the sorption capability of tetracycline is high in soil [17]. In addition, HP soil includes many multivalent metal cations, such as Ca^{2+}, Al^{3+}, and Fe^{3+}, as noted from the X-ray fluorescence (XRF) data. These cations (Ca^{2+}, Al^{3+}, and Fe^{3+}) tend to bind with tetracycline, which binds divalent and trivalent metal cations due to the presence of two ketone groups [18].

The removal efficiencies of erythromycin using natural, sterilized, and baked soil are shown in Fig. 2(b). Removal efficiencies were similar among natural soil (99 ± 0.2%), sterilized soil (99 ± 0.2%), and baked soil (99 ± 0.1%) after 30 d and reached an equilibrium state in a short time. The results indicated that although erythromycin was influenced by microbial activities, SOM and microbial activities did not have a remarkable influence on its removal. Thus, adsorption occurred between the soil particles and erythromycin. Since the pK_a value of erythromycin is 8.8, it has positive charge at pH 6.65. Therefore, erythromycin was sorbed by electric attractive force with the soil surface, which had a net negative charge. In addition, molecular weight and hydrophobicity generally influence sorptivity. Erythromycin has a large molecular weight and hydrophobicity ($\log K_{ow} > 3$) so that these could be increased to sorb onto soil. In addition, Kim et al. [19] demonstrated that erythromycin is readily adsorbed by soil particles, especially clay, allowing the rate of degradation to be enhanced.

The removal efficiencies of sulfathiazole using natural, sterilized, and baked soil are shown in Fig. 2(c). Removal efficiency was 0% in baked soil, indicating that soil adsorption did not affect its removal mechanism. Thus, to determine the effect of SOM and microbial activities, an additional experiment was performed using sterilized soil. Results for natural and sterilized soil showed removal efficiencies of sulfathiazole were 71 ± 5% and 51 ± 0.1%, respectively, after 30 d. Sulfathiazole was therefore affected by microbial activities and adsorption to SOM to influence removal efficiency. The sorption capability of sulfathiazole with soil has been reported to be very low because it has a low distribution coefficient (K_d) [20]. In addition, removal of sulfathiazole is influenced by organic matter content because organic matter plays a role as a sorbent and generates a Van der Waals attraction force between the organic matter and the sulfathiazole [17].

3.2. 3-Mixed VAs interference effect experiment

In order to investigate the interference effect among VAs when they are dissipated in soil, batch experiment was taken using JS soil with solutions included mixed and single compound. Fig. 3 showed the removal efficiencies of tetracycline, erythromycin, and sulfathiazole between 3-mix and single solutions using JS soil.

As a result, all VAs showed the similar removal trend in the soil. The removal efficiency of tetracycline, which was mixed other compounds, was approximately 90% in the soil. Likewise, tetracycline, which was dissolved alone, was removed about 90% in both soils. In case of erythromycin, the removal efficiency of erythromycin, which was mixed with other compounds, was over 99% in the soil. Similarly, erythromycin, which was dissolved without others, was dissipated over 99% in the soil. The concentrations of sulfathiazole in mixed and single compound solution were decreased 50% in JS soil. To conclude, selected VAs did not affect its dissipation each other while they are reacted with soil during the experiments. Thus, based on this result, the long-term column experiments were performed using solution of mixed compounds solution.

3.3. VAs removal by a batch-scale experiment

To confirm the removal of three VAs in soils from RBF sites, batch-scale experiments were performed using the JS, HP, GJ, and HA soils. As shown in Table 2, the concentration of tetracycline decreased by over 85% in the four soils during the 30 d incubation. Although the soils had different physicochemical properties, tetracycline was almost completely removed in a short time. Thus, the results showed that tetracycline can be readily removed by adsorption to soil with an attractive force, regardless of the soil properties.

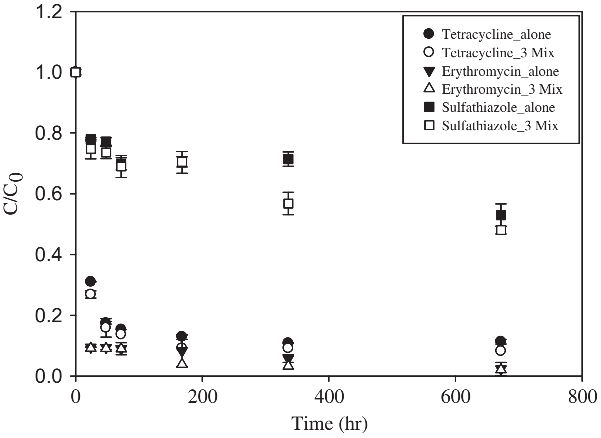

Fig. 3. Comparing the removal efficiencies of tetracycline, erythromycin, and sulfathiazole between 3-mixed and single solution in batch experiment (*n* = 3).

As shown in Table 2, the removal efficiencies of erythromycin were over 96% in the four soils during the 30 d, indicating that adsorption to soil was the main factor of dissipation for erythromycin. In addition, the removal efficiency in HP soil was greater than for the others. Based on a batch experiment, we suggest that silt and clay could be used to enhance the degradation of erythromycin.

Concentration of sulfathiazole decreased 72% in HP soil, 51% in JS soil, 33% in GJ soil, and 17% in HA soil during the 30 d. These results clearly showed that sulfathiazole was influenced by biodegradation and soil properties, such as the amount of SOM. Table 3 shows SOM and ATP concentrations from the four soil types. After the batch experiment, SOM and ATP, respectively, were 57.35 μg/g and 52.16 ng ATP/cm^3 (HP), 25.93 μg/g and 41.30 ng ATP/cm^3 (JS), 19.84 μg/g and 34.12 ng ATP/cm^3 (GJ), and 17.23 μg/g and 22.16 ng ATP/cm^3 (HA). The amount of organic matter and microbial activity were found to be the major influencing factors of removal efficiency in all these soils. Therefore, even though sulfathiazole cannot adsorb to soil particles with high mobility, it should be removed in an RBF system by adsorption to organic matter and biodegradation.

3.4. VAs removal experiment by a column scale experiment

Fig. 4 shows the removal efficiencies of tetracycline, erythromycin, and sulfathiazole in four different soils by a column experiment. The removal efficiencies of tetracycline and erythromycin were over 99% in the four soils. Two VAs persisted and were degraded in the soil by adsorption to soil particles and organic matter caused by a large distribution coefficient and electric attractive force.

The removal efficiencies of sulfathiazole were 43% in HP, 19% in JS, 15% in GJ, and 13% in HA soil over a period of 60 d. The HP soil column system showed high SOM and ATP concentrations compared to the JS, GJ, and HA soil column systems (data not shown).

Table 2
Removal efficiencies of tetracycline, erythromycin, and sulfathiazole in four different soils by batch experiment (*n* = 3)

	HA	GJ	JS	HP
Erythromycin	96 (±2)%	97 (±2)%	98 (±2)%	99 (±1)%
Tetracycline	99 (±1)%	99 (±1)%	89 (±2)%	85 (±2)%
Sulfathiazole	17 (±2)%	33 (±3)%	51 (±2)%	72 (±2)%

Table 3
Sand characteristics for batch experiment (*n* = 3)

	SOM (μg/g)		ATP (ng ATP/cm^3)	
	Influent	Effluent	Influent	Effluent
HP	56.89 (±2.56)	57.35 (±2.25)	45.75 (±3.33)	52.16 (±2.70)
JS	24.79 (±1.84)	25.93 (±1.76)	34.94 (±2.66)	41.30 (±2.82)
GJ	18.32 (±2.95)	19.84 (±2.05)	23.29 (±1.64)	34.12 (±1.97)
HA	16.61 (±5.96)	17.23 (±1.66)	16.02 (±4.25)	22.16 (±1.75)

Notes: The errors indicate the standard deviation calculated from triplicate samples.

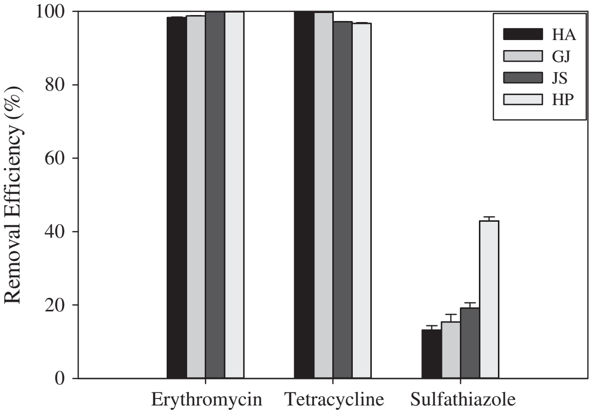

Fig. 4. Removal efficiencies of erythromycin, tetracycline, and sulfathiazole in four different soils by column experiment (*n* = 3).

The different removal efficiencies among the four soils resulted from their soil properties. Furthermore, based on previous batch experiment results, our findings indicated that dissipation of sulfathiazole is influenced by sorption with SOM and microbial activities. Lee et al. [21] demonstrated that sulfonamides, including sulfathiazole, have high mobility characteristic in soil, and therefore a large quantity of sulfathiazole discharges through in an early stage. With time, emissions of sulfathiazole become more stable and dissipation increases via biodegradation. Thus, in our study, although the removal efficiencies of sulfathiazole were less than those of the batch experiments, our findings indicate that this compound could be removed by organic matter and microbial activity.

4. Conclusions

We performed batch-scale experiments and long-term column experiments using soils from diverse regional areas in Korea to confirm the fate and removal efficiencies of three selected VAs and to evaluate the applicability for RBF systems. Tetracycline was predominantly removed in soils by adsorption with electric attractive forces between soil particles and the compound, regardless of soil properties. Erythromycin was readily removed in soils by adsorption with electric attractive forces between the soil particles and the compound, regardless of soil properties but influenced by hydrophobicity. Sulfathiazole was not effectively removed in the soil compared to tetracycline and erythromycin. Adsorption to soil particles did not occur because sulfathiazole has a low distribution coefficient with low sorption capacity. However, the results of the batch and column experiments showed that although removal rates of sulfathiazole differed depending on the soil properties, it was influenced by microbial activities and adsorption to SOM. Thus, sulfathiazole should dissipate in the presence of high levels of SOM and a long residence time in an RBF system.

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