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Effect of runoff discharge on the environmental levels of 13 veterinary antibiotics: A case study of Han River and Kyungahn Stream, South Korea

Younghee Kim [a,*], Kee-Bong Lee [a], Kyungho Choi [b]

[a] Graduate School of Venture, Hoseo University, Seoul 137-867, South Korea
[b] School of Public Health, Seoul National University, Seoul 151-742, South Korea

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ABSTRACT

In this study, the effect of heavy monsoon rains on the environmental levels of 13 veterinary pharmaceuticals was investigated. Kyungahn Stream has an annual average flow rate (AVF) of 4.2 m^3/s and receives runoffs from agricultural areas and livestock farms scattered in the upper stream area, and Han River has an AVF of 845 m^3/s with four sewage treatment plants with individual capacities of >1 million m^3/day.
Grab samples collected in three different rain seasons, before, during, and after rain, were analyzed. Kyungahn Stream and Han River showed completely different patterns of environmental levels of pharmaceuticals: the former had higher detection rates and concentrations of the pharmaceuticals during and after rainy season, implying direct influence by rainfalls, whereas in the latter, higher detection rates were observed before rain (1236 ng/L of oxytetracycline (OTC), 2093 ng/L of tetracycline (TC), and 793 ng/L of chlorotetracycline (ChTC) as the highest values).

1. Introduction

Extreme events of drought and flood have been increasing recently worldwide. South Korea has a clearly divided rainy season, and most rainfalls are converged on summer, called "Jangma".

Hirsch et al. (1999), Kolpin et al. (2002), and Heberer (2002) issued pharmaceuticals in the environment earlier, which has currently become a worldwide concern, and their occurrence has been studied in many other countries. The study of veterinary pharmaceuticals was conducted in discharge characteristics from the application of manure or sludge on arable land (Lapen et al., 2008; Gielen et al., 2009; Edwards et al., 2009; Ramaswamy et al., 2010; Walters et al., 2010) and the influence of rainfall on their transport to water from soils was also investigated (Topp et al., 2008; Blackwell et al., 2009; Kim et al., 2010; Sabourin et al., 2009).

The environmental prevalence of veterinary pharmaceuticals is characterized by a large variety of usage, administration methods, discharge pathways, and metabolisms of parent compounds in animal body (Capleton et al., 2006), and hence their concentrations in the environment are likely to be even more variable. In general, the detection rate and concentration of human pharmaceuticals in the environment depend on the amounts of annual usage. Anti-inflammatory drugs such as ibuprofen, acetaminophen, clofibric acid, and diclofenac are the most widely used over-the-counter drugs, which are frequently detected in aquatic environments (Scheytt et al., 2001; Kim et al., 2007; Choi et al., 2008b).

However, the environmental levels of veterinary pharmaceuticals are generally higher in soil than water: concentrations in soil were as high as 900 and 52 μg/kg for tetracyclines and ciprofloxacin, respectively, but the corresponding maximum concentrations in water were only 0.4 and 0.4 μg/L (Kemper, 2008). Sometimes, environmental concentration can be affected by physicochemical characteristics of the pharmaceutical itself (Mompelat et al., 2009) and hydrological condition of receiving water (Tamtam et al., 2008; Kolpin et al., 2004). Thus, the environmental level of pharmaceuticals also depends on sampling time (Hua et al., 2006; Choi et al., 2008b).

The runoff from composted arable land is considered as a primary contributor of environmental levels of veterinary pharmaceuticals, and hence it could be affected by rainfall as reported in previous studies. Boyd et al. (2004) showed an increase in the concentrations of ibuprofen and naproxen with cumulative rainfall and Sabourin et al. (2009) reported that pharmaceuticals with log Kow values of ≤2.45 were readily exported from soils by precipitation. Therefore, the effect of rainfall on the transport of pharmaceuticals from agricultural field or livestock farms is of importance, particularly in South Korea, because over one-half of the total annual rainfall occurs in summer, from June to August. In 2014, approximately 65% of the 1173-mm annual rainfall occurred in summer in South Korea (KMA, 2006) and >30% in August. In addition, intensity of rainfall becomes stronger every year, while the frequency of rain decreases. In this study, samples collected in different rainfall

* Corresponding author.
E-mail addresses: Yhkim514@hoseo.edu (Y. Kim), Kblee5910@naver.com (K.-B. Lee), kyungho@snu.ac.kr (K. Choi).

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seasons were investigated to study the influence of runoffs on environmental concentration of pharmaceuticals.

2. Materials and methods

2.1. Site description

Han River has a watershed area of 34,305 km^2 (KMOE, 2006), and is divided into North Han River, South Han River (the upstream of Han River), the main stream of Han River (Han River Seoul), and other small tributaries (Fig. 1).

Han River is an important drinking water source for >20 million people, approximately 50% of the South Korean population. Approximately 600,000 cows, 3 million pigs, and 15 million chickens were raised in the area, and 16% of the study area comprised arable land as of 2003 (KMOE, 2006). Kyungahn Stream is one of the tributaries of Han River, which flows into the upstream of Han River Seoul. A total of approximately 0.38 million people live around its 561-km^2 watershed area, and 7255 cows, 92,645 pigs, and 1,533,852 chickens were raised in the 136-km^2 agricultural area in its upstream watershed as of 2006 (KHRBEO, 2007). Its stream flow closely depends on precipitation, and is easily depleted during dry season, from December to April. Most rainfall in rainy season increases the flow rate by up to hundreds of times compared with that in drought conditions (Fig. 2).

2.2. Selection of target compounds

A total of 13 widely used antibiotics were selected based on their annual usage and detection frequency in South Korean rivers obtained from the literature (Tables 1 and 2). Tetracyclines are the most frequently used antibiotics with a more likelihood of reaching the environment (Kim et al., 2008). Sulfonamides, which are not as frequently used as tetracyclines, are also reported in the surface waters of South Korea (Choi et al., 2008a, 2008b; KNIER, 2006). In particular, sulfamethoxazole is recognized to be associated with high environmental risk in a previous study (Kim et al., 2007). Virginiamycin and carbadox are also not used in high volumes, but their excretion rates are high, thereby increasing their potential to reach the environment (Kim et al., 2008). In addition, they are mostly prescribed for pigs and chickens, which are the prevalent livestock in the study area.

2.3. Sample collection

A total of 96 samples were collected from 33 sampling sites: nine in the main stream of Han River, five in North Han River, six (five after rainy season) in the upstream (south) part of Han River, and 13 (12 during and after rainy seasons) in Kyungahn Stream (Fig. 1). A total of 33 grab samples were collected before rainy season (May 25–31), which could be due to the accumulation of pharmaceuticals because of low flow rate, 32 samples during the rainy season (August 2–10), which could show immediate export from arable land or farms, and 31 samples after the rainy season (September 20–29) (Fig. 2). The sampling sites were scattered too widely to collect samples in a day, and hence sampling was conducted for 4 days for each sampling season, 1 day each for main stream of Han River, North Han River, upstream part of Han River, and Kyungahn Stream.

2.4. Analytical methods

Slightly modified analytical methods of Choi et al. (2008b) were used in this study. Briefly, a sample volume of 1000 mL was prepared by adding simeton (CAS no. 673-04-1, $C_8H_{15}N_5O$, Sigma-Aldrich Ltd.) as the internal standard and Na_2 ethylenediaminetetraacetic acid (EDTA) (Junsei Chemical Co., Japan) to increase the recovery rate. The samples were filtered with ashless filter paper (5C; Advantec, Toyo Roshi Kaisa, Tokyo, Japan) before solid-phase extraction to eliminate suspended particles, if present.

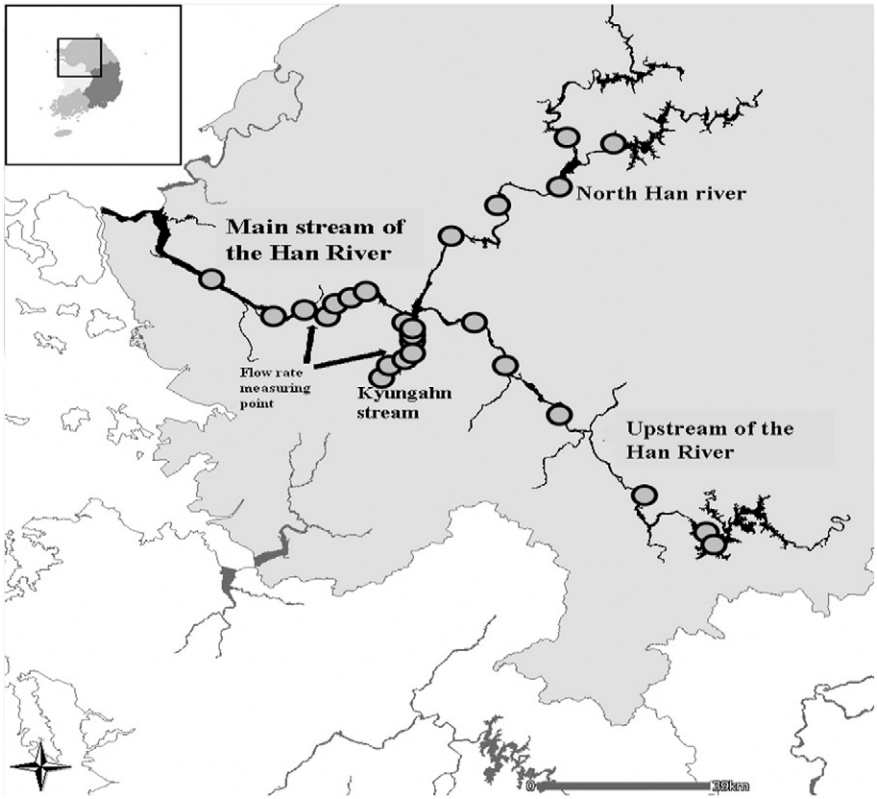

Fig. 1. Study area and sampling sites.