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Human and veterinary pharmaceuticals in the marine environment including fish farms in Korea

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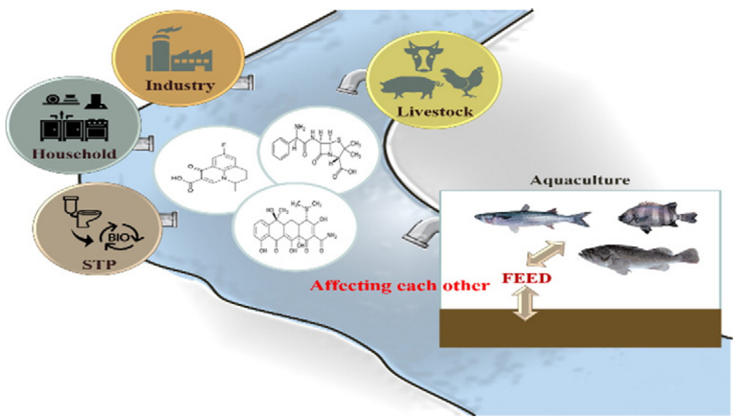
HIGHLIGHTS

- Human and veterinary pharmaceuticals in the marine environment were investigated.
- Different occurrence and distribution pattern were observed according to sites.
- Antibiotics especially fish drugs were predominant in fish farm area.
- Terrestrial origin pharmaceuticals were dominant in coastal area.

GRAPHICAL ABSTRACT



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ABSTRACT

The occurrence trends and effects of 30 human and veterinary pharmaceuticals, including antibiotics, anthelmintics, anti-inflammatory drugs, and β-blockers, in the marine environment, with a focus on seawater, sediment, cultured fish, and their feed collected from coastal and fish farm areas in the southern sea of Korea, were investigated. The concentrations of total pharmaceuticals in coastal area seawater (mean: 533 ng/L) were higher than those in fish farm seawater (mean: 300 ng/L), while the opposite trend (coastal area: 136 ng/g dry wt < fish farm area; 195 ng/g dry wt) was observed for sediment samples. Regarding cultured fish, the concentration of total pharmaceuticals in fish muscle (mean: 5.08 ng/g wet wt) was lower than that in organs (mean: 14.1 ng/g wet wt). However, not all compounds were present at higher concentrations in organs. Characteristic distribution patterns of pharmaceuticals were observed according to sample types and sampling sites based on the predominance of various antibiotics in fish farms (including cultured fish and feed) and the predominance of pharmaceuticals of terrestrial origin (human and livestock) in coastal areas. Pharmaceuticals used as fish drugs, such as sulfadiazine, erythromycin, and trimethoprim, were commonly detected in fish farm media (seawater, sediment, and cultured fish), which might contaminate fish farm media.

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1. Introduction

As industry has developed, >260,000 chemicals have been distributed globally. Among them, 40,000 are used and over 400 are newly produced every year in Korea (Lee et al., 2011). Among these chemicals, pharmaceuticals are commonly used to relieve symptoms and treat human, animal, and plant diseases. With an aging population and increase in chronic diseases, the pharmaceutical market is rapidly growing worldwide. Generally, many group of pharmaceuticals such as antibiotics, anthelmintics, nonsteroidal anti-inflammatory drugs (NSAIDs), β-blockers, and stimulants etc. are used depending on their pharmacological action and each of the pharmaceuticals has a specific physiological function. Most of pharmaceuticals are well biodegradable in the body of humans or animals, but several pharmaceuticals have relatively long biological half-life such as carbamazepine (26–65 h), acetaminophen (2 − 3 h), and sulfamethoxazole (10 h) (Smith and Pappagallo, 2012). These compounds enter the aquatic environment after their ingestion and subsequent excretion in a metabolized or non-metabolized form (Boleda et al., 2013). According to the Korean Ministry of Health & Welfare and Health Insurance Review & Assessment service, the defined daily dose of annual Korean antibiotic usage in 2003 was 22.97/1000 people/day, which is the sixth highest among the Organization for Economic Cooperation and Development members (KFDA, 2006). Moreover, Korea used more veterinary pharmaceuticals for meat production (0.72 kg/ton meat production) than other countries (USA, 0.24 kg/ton; Japan, 0.36 kg/ton; Denmark, 0.04 kg/ton; Sweden, 0.03 kg/ton) in 2003 (MAFRA, 2010). In addition, about 13% of veterinary pharmaceuticals used in Korea in 2008 were used in fisheries (Agricultural Food Information, 2008).

Similarly, large amounts of used pharmaceuticals are introduced into the aquatic environment through direct waste and sewage discharge. Many studies have examined the occurrence and fate of pharmaceuticals in rivers. Most of these have been near wastewater treatment plants (WWTP) or water intake stations (Boleda et al., 2013; Gros et al., 2006; Locatelli et al., 2011; López-Serna et al., 2010; Yan et al., 2013), while few have investigated marine environments, such as coastal zone seawater (Claessens et al., 2013; Gomez et al., 2012; Lalumera et al., 2004; Meador et al., 2016; Scott et al., 2015; Zhang et al., 2013) or biota (Gomez et al., 2012; Lalumera et al., 2004), focusing on a few antibiotics, although contaminated river water ultimately flows into the sea.

In fish farms, some pharmaceuticals (especially antibiotics such as fluoroquinolones and tetracyclines) have been used mainly for therapeutic purposes and are put directly into the water or mixed with fish feed to prevent infectious diseases (Burridge et al., 2010; Cabello et al., 2013; Rico et al., 2013). Therefore, contamination of the fish farm environment by pharmaceuticals in the southern coast of Korea, where over 70% of aquaculture sites (Ministry of oceans and fisheries, Korea, 2016) are concentrated, including seawater, sediment, cultured fish, and their feed, must be considered because waste pharmaceuticals in fish farms could contaminate fish and seafood, and might contribute to human exposure by ingesting contaminated fish and seafood. To ensure human food safety, the European Union (EU) and other regulatory authorities worldwide have established tolerance concentrations for veterinary pharmaceuticals as maximum residue limits (MRLs) (Cañada-Cañada et al., 2009). Since 1989, MRLs for veterinary pharmaceutical residues in animal products entering the human food chain have been established for over 140 compounds, including antibiotics and some anthelmintics in fish, which are regulated in Korea (MFDS, 2014). The majority of studies of pharmaceuticals in the marine environment have focused on regulated pharmaceuticals in fish, especially antibiotics (Potter et al., 2007). Studies of pharmaceutical contamination of the marine environment, such as seawater and marine sediment, are limited (Afonso-Olivares et al., 2013; Borecka et al., 2015; Claessens et al., 2013; Lolić et al., 2015; Long et al., 2013; Zhang et al., 2013). Therefore, this study investigated the concentrations and characteristic occurrence of various pharmaceuticals in the marine environment including coastal area and fish farms. Seawater and sediment (especially cultured fish and their feed in fish farms) were collected, and the occurrence and distribution of pharmaceuticals on the marine environment were examined.

2. Materials and methods

2.1. Chemicals and material

In this study, 16 antibiotics (enrofloxacin, ciprofloxacin, ofloxacin, norfloxacin, sulfamethazine, sulfamonomethoxine, sulfachloropyridazine, sulfamethoxazole, sulfadiazine, sulfathiazole, sulfamerazine, erythromycin, spiramycin, lincomycin, trimethoprim), seven anthelmintics (albendazole, flubendazole, thiabendazole, fenbendazole, fenbendazole-SO, fenbendazole-SO_2, praziquantel), and seven “others” (atenolol, metoprolol, propranolol, acetaminophen, caffeine, carbamazepine, crotamiton) were analyzed in seawater, sediment, cultured fish, and their feed. Table 1 gives specific information on the target compounds according to the pharmaceutical group and these were selected by the pharmaceutical usage in Korea, the species that have maximum residue limits (MRLs) in food (livestock and seafood) and detection frequency of other matrixes in previous domestic studies. Standards for all 30 target compounds were purchased from Sigma-Aldrich (St. Louis, MO, USA). Norfloxacin-d_5, ciprofloxacin-d_8, enrofloxacin-d_5, sulfamethazine-$^{13}C_6$, sulfamethoxazole-$^{13}C_6$, and fenbendazole-d_3 were used as internal standards (ISs) and all standard solutions were diluted in HPLC-grade methanol and stored in amber vials at 3–5 °C. Ammonium formate, formic acid, disodium hydrogen phosphate, and citric acid were purchased from Wako (Osaka, Japan) and ammonium hydroxide was obtained from Junsei (Tokyo, Japan). Acetonitrile, Milli-Q water, and methanol were purchased from J.T. Baker (Phillipsburg, NJ, USA).

2.2. Sample collection

A sampling campaign was conducted from March to June 2012. Sampling areas included the southern sea of Korea, nine sampling points in coastal areas (S1–S9), and three fish farms culturing black rockfish (*Sebastes schlegelii*) (A), gray mullet (*Mugil cephalus*) (B), and red seabream (*Pagrus major*) (C) (Fig. 1).

Two sewage treatment plants (STPs) were located near the coastal sampling areas, and three sampling sites (S2, S3, and S8) were located near the discharge point of treated sewage. The surface (0.5 m below the surface seawater layer) and deep (0.5 m above the surface sediment

Table 1
Target compounds in this study.

Compound	
Antibiotic	**Anthelmintic**
Fluoroquinolones	Albendazole
Enrofloxacin	Flubendazole
Ciprofloxacin	Thiabendazole
Ofloxacin	Fenbendazole
Norfloxacin	Fenbendazole-SO
Sulfonamides	Fenbendazole-SO_2
Sulfamethazine	Praziquantel
Sulfamonomethoxine	**Others**
Sulfadimethoxine	*β-blockers*
Sulfachloropyridazine	Atenolol
Sulfamethoxazole	Metoprolol
Sulfadiazine	Propranolol
Sulfathiazole	*Anti-inflammatory drug*
Sulfamerazine	Acetaminophen
Macrolides	*Stimulant*
Erythromycin	Caffeine
Spiramycin	*Anti-seizure*
Other antibiotics	Carbamazepine
Lincomycin	*Scabicide*
Trimethoprim	Crotamiton