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Developing and applying a site-specific multimedia fate model to address ecological risk of oxytetracycline discharged with aquaculture effluent in coastal waters off Jangheung, Korea

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ABSTRACT

The overuse of oxytetracycline (OTC) in aquaculture has become a problem because of its chronic toxic effects on marine ecosystems. The present study assessed the ecological risk of OTC in the coastal waters near the Jangheung Flatfish Farm using a site-specific multimedia fate model to analyze exposure. Before the model was applied, its performance was validated by comparing it with field data. The coastal waters in the testbed were sampled and analyzed using liquid chromatography-tandem mass spectrometry (LC-MS/MS) followed by solid-phase extraction (SPE). The concentrations of OTC measured varied from 7.05 to 95.39 ng/L. The results of validating the models showed that the site-specific multimedia fate model performed better (root mean square error (RMSE): 24.217, index of agreement (IOA): 0.739) than conventional fugacity approaches. This result demonstrated the utility of this model in supporting effective future management of aquaculture effluent. The results of probabilistic risk assessment indicated that OTC from aquaculture effluent did not cause adverse effects, even in a maximum-use scenario.

1. Introduction

The presence of antibiotics in the marine environment has become a problem because of their propensity to induce microbial resistance and the attendant risk of reducing the efficacy of some antibiotics. Many studies have addressed the occurrence, fate, and effects of antibiotics on terrestrial and freshwater ecosystems (Kim et al., 2010; Wu et al., 2014); however, few studies have been conducted on marine ecosystems (Gaw et al., 2014), even though most antibiotics enter coastal waters. The studies that have monitored concentrations of antibiotics in marine environments have found that observed concentrations varied from a few ng/L to µg/L levels that were far less than lethal concentrations (Pereira et al., 2016; Wahlberg et al., 2011; Zhang et al., 2013; Zou et al., 2011). However, most antibiotics are designed to interact actively at low concentrations, so even at those concentrations, they may cause chronic, sublethal effects, including genotoxic responses (Botelho et al., 2015), changes in biochemical responses (Bossus et al., 2014), and reduced feeding rates (Sole et al., 2010).

Whereas a few studies have addressed the adverse effects of antibiotics in the marine environment, none have adequately assessed the risk of point-source pollution. Most antibiotics used for human consumption, agriculture, and manufacturing are eventually released into wastewater treatment plants, and some leak into soil, landfills, and groundwater before entering marine environments (Gaw et al., 2015). However, aquaculture effluents, which contain uneaten food pellets that include high levels of antibiotics, are introduced into the marine environment without any treatment along the way. In South Korea, the aquaculture industry is overcrowded, and the amount of antibiotics used in aquaculture continues to increase; according to a monitoring report from the Animal and Plant Quarantine Agency (QIA), the sales volume of antibiotics to fisheries was about 213 t in 2013 (QIA, 2015). However, there are no guidelines regulating antibiotic use in Korea; therefore, an Ecological Risk Assessment (ERA) was needed to provide scientific evidences with which to set guidelines.

For this reason, the present study conducted a regional ERA for point-source oxytetracycline (OTC) contamination. OTC has a high consumption rate in South Korea and its use in domestic fisheries accounts for 80% of total antibiotic use (QIA, 2015). OTC is commonly used in fish farms because of its low cost and broad-spectrum efficacy in treating infections (Ferreira et al., 2007); however, research has reported several side effects, including immunosuppressive effects and liver damage in fish (Bruno, 1989; Rijkers et al., 1980) and growth

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inhibition in crustaceans (Isidori et al., 2005). The present study chose the Jangheung Flatfish Farm, which uses OTC predominantly, as a testbed. The study aimed to investigate the risks of OTC discharged from aquaculture effluent into coastal waters. Exposure-monitoring data regarding an antibiotic is necessary to conduct exposure analysis for an ERA, but no field data exists on antibiotic residues in Korean coastal waters. Therefore, exposure-data prediction using a chemical fate model was used to acquire the data. The study constructed a site-specific multimedia fugacity model (SSMFM) to predict the OTC fate. Because the fish farm discharged the antibiotic sporadically, the Level IV approach, which considers non-equilibrium and unsteady-state conditions, was used. Previous studies using the fugacity approach had distinctive characteristics, some of which needed to differ in the present study. First, to implement the behavior of the aquaculture effluent in the near-field, the fugacity model was coupled with the jet-plume model (JETLAG). Second, most previous studies using the fugacity approach focused on river and lake environments (Jung et al., 2014; Kong et al., 2014; Zhang et al., 2014), so their governing equations were not appropriate for the marine environment without the application of adjusted constants and equations that considered chemical interactions in the marine environment, including the salting-out effect. Third, the present study further adjusted the fugacity model to be site-specific by dividing the modeled region into several small grids (500 m × 500 m) (Liu et al., 2015; Song and Xu, 2011). In addition, to better reflect the testbed environment, the study used environmental properties, meteorological, and hydrological data for the Jangheung region instead of default values. Fourth, the coastal water in the testbed was sampled and analyzed, and each model was validated using the input data corresponding to the sampling time. This validation approach enabled accurate comparisons rather than those using monitoring data from previous studies.

2. Methods

2.1. Site-specific multimedia fugacity model

The model consisted of three bulk compartments: atmosphere, seawater, and sediment. The atmospheric compartment included the gas phase and aerosols. The seawater compartment included water, suspended sediment, and fish. The sediment compartment included solid sediment and pore water. All compartments were treated as homogeneous boxes. Mass-balance equations were created for each compartment and included transport processes between the compartments, inputs into and outputs from the system, and degradation processes. Kinetic processes between phases of the same compartment (e.g., air and aerosol) were disregarded.

Seawater properties (e.g., bathymetry, water temperature, and salinity) were obtained from the Ocean Data in Grid Framework system which was operated by the Ministry of Oceans and Fisheries. The hydrological data such as current speed and direction were obtained from the real time database of North-East Asian Regional Global Ocean Observing System (NEAR-GOOS) and the modeled data of Korea Hydrographic and Oceanographic Agency (KHOA). The meteorological data were available from the meteorological stations located near the Goheung. As hydrolysis and photolysis is the main degradation pathways for OTC in the aquatic environment, both degradation rate constants were investigated for this study (Xuan et al., 2010; Zaranyika et al., 2015).

The size of each grid was 500 m × 500 m, and the overall modeling region was 17.5 km^2 and had 70 cells. The depth of each grid varied from 2 to 14 m. Given the shallow depth, a 2-dimensional fugacity model was applied to take into account only the advection and dispersion movements in the x and y directions. The governing equation of the fugacity level IV is

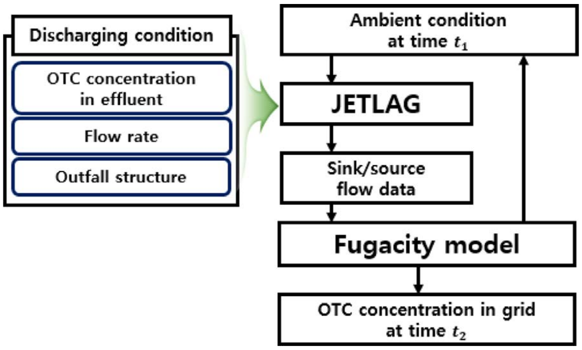

Fig. 1. Overall framework for JETLAG and fugacity model coupling (modified from Zhao, 2015).

$$\frac{\partial f_C}{\partial t} + \frac{\partial u_C f_C}{\partial x} + \frac{\partial v_C f_C}{\partial y} = \frac{\partial}{\partial x}\left(Ex_C \frac{\partial f_C}{\partial x}\right) + \frac{\partial}{\partial y}\left(Ey_C \frac{\partial f_C}{\partial y}\right) + S + \frac{\sum_{M=1,M\neq L}^{N} (f_M D_{M,C} - f_C D_{C,M})}{\Delta Z_c} - k_C f_c \tag{1}$$

where f is fugacity, Z is fugacity capacity, C is the environmental compartment, u and v is the velocity of the current, Ex and Ey is the dispersion coefficient, S is the source term from the JETLAG, D is the transport coefficient, and k is the kinetic constant of decay reactions. The mass-balance equations were formulated by differential equations for each compartment. To solve the equation, this governing equation was discretized for each time step of length 1 min. The solution integrated the differential equations for small time steps, assuming that the fugacity within these steps was constant. Thus, a fugacity change was obtained that could be added to the fugacity at time t to obtain the fugacity at time t + Δt.

The near-field JETLAG model was integrated into the fugacity model using a dynamic coupling method introduced by Choi and Lee (2007). As shown in Fig. 1, a series of entrainment sinks and the diluted source flow, which were obtained from the JETLAG, were introduced into the fugacity model. The ambient conditions which are required for the JETLAG were provided by the fugacity model at each time step. If the JETLAG calculates the amount of sink and source flow from the effluent, these values were used as input for the fugacity model, and then the change in ambient conditions was obtained and used as ambient data for the JETLAG for the next time step. This iterative process involving the JETLAG and fugacity models continued until the plume reached the terminal level.

2.2. Field sampling and OTC quantification

The study selected 7 sites in the coastal region near the Jangheung Flatfish Farm as sampling sites (Fig. 2). Table S1 described the detailed information for sampling sites. The depth was measured with a rope to ensure that each sample was taken at the depth of 1 m. The water samples were transported in sterilized, 4-liter water-collection bottles that were coated with polyethylene. To suppress microbial activity, 0.02 M of sodium azide was added. Then, to maintain the water samples at 4 ± 2 °C, all samples were refrigerated.

The OTC in the seawater samples was quantified using solid-phase extraction (SPE) followed by liquid chromatography-tandem mass spectrometry (LC-MS/MS) with a triple quadrupole and a standard source electrospray ionization (ESI) source. The overall sample-preparation and quantification methods were modified from the US EPA 1694 method. Prior to extraction, 80 mg/L of sodium thiosulfate anhydrous was added, and the pH of each seawater sample was adjusted to 2.5 ± 0.5 using an HCl solution (1 M). SPE experiments were conducted using 200-mg Oasis hydrophilic lipophilic balanced (HLB) cartridges (Waters; Milford, MA, USA), which were preconditioned with 20 ml of methanol, 6 ml of Milli-Q water, and 6 ml of pH 2 ± 0.5 Milli-