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Seasonal variation, flux estimation, and source analysis of dissolved emerging organic contaminants in the Yangtze Estuary, China

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ABSTRACT

The occurrence and seasonal variation of 24 dissolved emerging organic contaminants in the Yangtze Estuary were studied, including 12 non-antibiotic pharmaceuticals, seven sulfonamides, two macrolides and three chloramphenicols. Sulfadiazine, erythromycin, thiamphenicol and paracetamol were the primary contaminants in sulfonamides, macrolides, chloramphenicols and non-antibiotic pharmaceutical groups, respectively. Compared to the concentrations at Datong, chloramphenicols at Xuliujing were significantly higher in autumn and winter, while macrolides were lower in spring. Based on the flux estimation, approximately 37.1 tons of sulfonamides, 17.4 tons of macrolides, 79.2 tons of chloramphenicols and 14.1 tons of non-antibiotic pharmaceuticals were discharged into the Yangtze Estuary from June 2013 to May 2014. However, the total flux from the Huangpu River only represented 5% of the total. The pharmaceutical sources were speculated on by analyzing the seasonal variations in pharmaceutical concentrations and fluxes at various sites. Both environmental and social factors might affect the fluxes.

1. Introduction

As a significant class of emerging organic contaminants (EOCs) in the aquatic environment, pharmaceuticals are becoming a growing concern. EOCs are broadly regarded as newly generated or detected chemicals that are not commonly monitored and do not have environmental protection laws and regulations (Ternes et al., 2015). EOCs and their transformation products have potential adverse effects on aquatic organisms and human health even at low concentrations via induction of resistance genes in harmful micro-organisms (Mohapatra et al., 2014; Cheng et al., 2016; Gabarrón et al., 2016; Hurtado et al., 2016; Zhou et al., 2016).

Generally, massive pollution load from land-based sources accumulates in the estuarine environment via river runoff. To date, a number of studies have focused on the environmental fate of pharmaceuticals in estuarine systems and reported on pharmaceuticals released into coastal environments, and the environmental behavior of pharmaceuticals in estuarine and coast has become a research hotspot (Stewart et al., 2014; Birch et al., 2015; Boix et al., 2016; Zhao et al., 2016). These data are still limited, especially for seasonal variation and flux estimates of dissolved pharmaceuticals in the Yangtze River, which is the largest river in Asia and the fourth largest in the world in terms of both water and sediment discharge. The freshwater discharge of the Yangtze Estuary has annual and seasonal variations (Wang et al., 2010). The high water level period of the Yangtze River Basin is from July to September, while the low water level period is from December to February. The flow discharge into the East China Sea is recorded by the Datong Gauge Station located at the tidal limit, with an average annual flow discharge of 28,587 m^3/s from 1950 to 2002 (Yang et al., 2015). The Yangtze Basin covers one-fifth of the total land area of China, with a population of approximately 400 million. In the past several decades, the Yangtze River has received a high load of pharmaceutical contaminants from the discharge of municipal sewage, agricultural runoff, industrial wastewater and other human activities (Bu et al., 2013; Chen and Zhou, 2014; Yan et al., 2015). Moreover, a great deal of untreated municipal sewage is a primary source of pharmaceuticals (Nodler et al., 2014; Chen et al., 2015). Eventually, most of these pharmaceutical contaminants accumulate in the Yangtze estuarine system. Considering the mass production and use of pharmaceuticals with incomplete treatment in sewage treatment plants, some pharmaceuticals exhibit pseudo-persistent when release rates are higher than transformation and removal rates (Zhou et al., 2009; Stuart et al., 2012).

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Due to the large area and high discharge of the Yangtze Estuary, the transport process of pharmaceutical compounds to the Yangtze Estuary and East China Sea may have a potential impact on the aquatic ecosystem even at low concentrations (Yang et al., 2011). However, information about seasonal variation and comprehensive flux data for pharmaceuticals discharged into the Yangtze Estuary is still lacking. Therefore, 24 pharmaceuticals that have been detected in the environment were selected in this study, including three groups of antibiotics (sulfonamides, macrolides and chloramphenicols) and 12 non-antibiotic pharmaceuticals. The objectives are the following: (1) to investigate the seasonal variation of pharmaceuticals in two typical sections of the main water channel of the Yangtze River, as well as Wusongkou, where the Huangpu River meets the Yangtze River; (2) to study the transport process and sources of these pharmaceuticals; and (3) to estimate the annual fluxes discharged from the Yangtze Estuary to the coastal zone of the East China Sea.

2. Experimental section

2.1. Sampling

Water samples were collected from Datong, Xuliujing and Wusongkou (Fig. 1). Datong is the tidal limit of the Yangtze Estuary, while Xuliujing is the bifurcation node of the North and South Branch of the Yangtze Estuary, which is influenced by the tide. Wusongkou is the confluence of the Huangpu River and the Yangtze River. The Huangpu River is a main river in Shanghai and the last tributary of the Yangtze River before it meets the sea. From June 2013 to May 2014, sampling was conducted twice in each season at Xuliujing and Wusongkou during the ebb tide phase, and once in each season in Datong section. Ten-L water samples were collected in amber glass bottles that were precleaned with acetone and ultrapure water. The samples were cooled with ice bags and transported to the lab within several hours. The properties of water samples were measured immediately once transported to the laboratory and stored under cool conditions before treatment. Detailed properties of water sampling sites at Datong, Xuliujing and Wusongkou are shown in Table S1, including location, temperature, pH, dissolved organic carbon, salinity and dissolved oxygen.

2.2. Chemicals and analytical methods

Twenty-four pharmaceutical standards and stable isotope-labeled internal standards were purchased from Dr. Ehrenstorfer (GmbH, Germany); detailed physicochemical properties are shown in Table S2, e.g., CAS number, molecular mass and formula, *n*-octanol/water partition coefficient (K_{ow}), pK_a and solubility.

The water samples were filtered through 0.7-μm glass fiber filters, concentrated by solid-phase extraction (SPE) and analyzed by a Waters Acquity™ UHPLC-MS/MS system; quality control procedures were conducted. Detailed preparation and detection methods are presented in the Supporting Information.

2.3. Estimation of pharmaceutical fluxes into the Yangtze Estuary

Eq. (1) is the second choice of the Oslo-Paris (OSPAR) Convention (Littlewood, 1995). Mean daily flux is calculated and converted to the measuring period in this method. Only a large variability in the target concentration and runoff discharge over a sampling period will introduce substantial systematic errors. This method can lead to good estimation results when there is no correlative relationship between concentration and runoff discharge (Ullrich and Volk, 2010). Pharmaceutical contaminants, as man-made emissions, had no significant correlation between the bulk concentrations of Yangtze River Estuary and instantaneous discharges near the estuary area, with the more obvious characteristics of point source. Therefore, Eq. (1) was selected to estimate pharmaceutical fluxes at Datong and Xuliujing in this study.

$$F = K\frac{1}{N}\sum_{i=0}^{N} cQ \tag{1}$$

where F is the seasonal flux (tons/quarter); K is a conversion factor for the period of record (K = 91d/quarter ∗ 24 h/d ∗ 3600 s/h ∗ 10^{-9} = 0.0079 s/quarter for one season); c is mean concentration

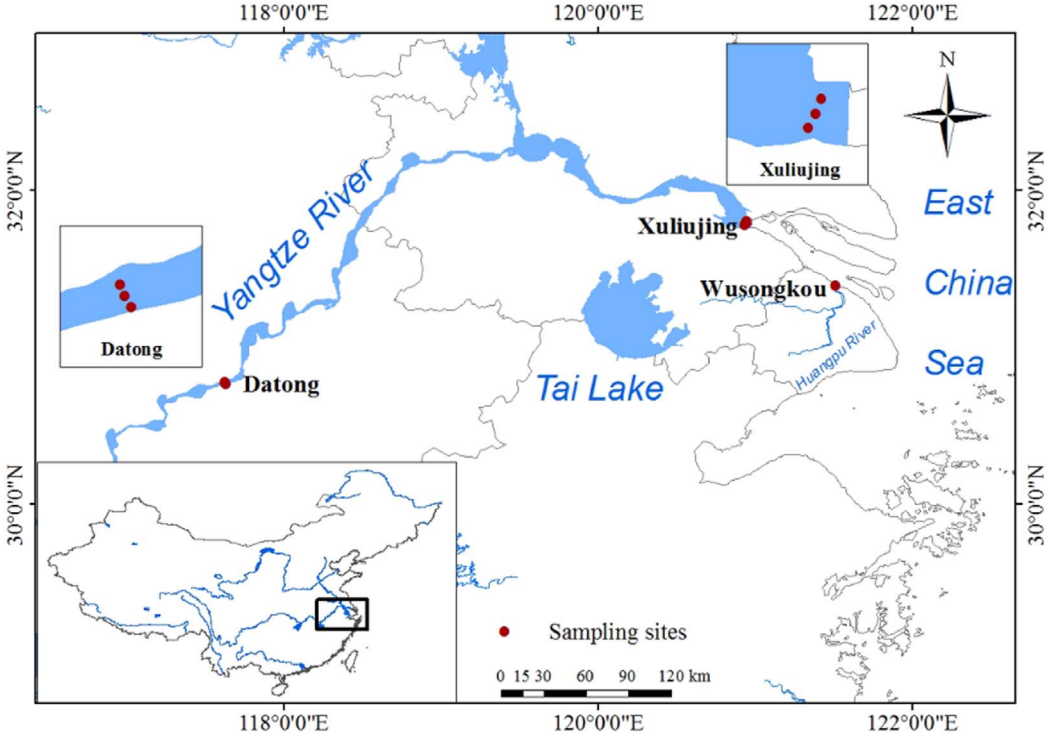

Fig. 1. Sampling sites in the Yangtze Estuary, China.