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Bioaccumulation and trophic transfer of pharmaceuticals in food webs from a large freshwater lake☆

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Pharmaceuticals are increasingly detected in environmental matrices, but information on their trophic transfer in aquatic food webs is insufficient. This study investigated the bioaccumulation and trophic transfer of 23 pharmaceuticals in Taihu Lake, China. Pharmaceutical concentrations were analyzed in surface water, sediments and 14 aquatic species, including plankton, invertebrates and fish collected from the lake. The median concentrations of the detected pharmaceuticals ranged from not detected (ND) to 49 ng/L in water, ND to 49 ng/g dry weight (dw) in sediments, and from ND to 130 ng/g dw in biota. Higher concentrations of pharmaceuticals were found in zoobenthos relative to plankton, shrimp and fish muscle. In fish tissues, the observed pharmaceutical contents in the liver and brain were generally higher than those in the gills and muscle. Both bioaccumulation factors (median BAFs: 19–2008 L/kg) and biota–sediment accumulation factors (median BSAFs: 0.0010–0.037) indicated a low bioaccumulation potential for the target pharmaceuticals. For eight of the most frequently detected pharmaceuticals in food webs, the trophic magnification factors (TMFs) were analyzed from two different regions of Taihu Lake. The TMFs for roxithromycin, propranolol, diclofenac, ibuprofen, ofloxacin, norfloxacin, ciprofloxacin and tetracycline in the two food webs ranged from 0.28 to 1.25, suggesting that none of these pharmaceuticals experienced trophic magnification. In addition, the pharmaceutical TMFs did not differ significantly between the two regions in Taihu Lake.

1. Introduction

Pharmaceuticals have been identified as emerging contaminants due to the possible threats to ecological environments (Liu and Wong, 2013). Several hundred thousand tons of pharmacologically active substances are estimated to be used yearly to treat human and animal diseases (Zenker et al., 2014). After administration, pharmaceuticals and their excreted metabolites are subsequently released to municipal and onsite wastewater treatment systems or farm wastewater treatment facilities (Conn et al., 2006; Du et al., 2014b). Due to the incomplete removal during these treatment processes, a wide range of pharmaceuticals have been detected in aquatic environments globally, primarily in municipal wastewater effluent, agricultural runoff, ground and surface waters, and even drinking water (Bu et al., 2013; Liu and Wong, 2013). Typically, pharmaceuticals are found at low concentrations ranging from ng/L to μg/L levels in surface water (Klosterhaus et al., 2013; Liu et al., 2015; Tang et al., 2015; Subedi et al., 2012). However, pharmaceuticals have been observed to be pseudo-persistent due to their continuous loading into aquatic systems via effluent discharges (Brooks et al., 2006). As a result, organisms inhabiting aquatic ecosystems may be subjected to chronic pharmaceutical exposure.

A better understanding of pharmaceutical distribution in water, sediment and biota could facilitate evaluation of their transport mechanisms and ultimate fates in aquatic environments. A range of field investigations have been performed to determine pharmaceutical concentrations in aquatic organisms and to evaluate pollution levels (Du et al., 2014a, 2015; Li et al., 2012b; Liu et al., 2015). Research on the tissue distribution of pharmaceuticals in

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organisms might be more informative for better understanding and assessment of the physiological/biological adverse effects of pharmaceuticals in terms of toxicokinetic and toxicodynamic processes (Tanoue et al., 2015). However, only limited research has studied the tissue distribution of pharmaceuticals in wild fish (Brooks et al., 2005; Ramirez et al., 2009; Schultz et al., 2010; Subedi et al., 2012; Tanoue et al., 2015; Huang et al., 2013; Zhao et al., 2015b).

Aquatic sediments act as an important sink for pharmaceuticals and might also be important sources of pharmaceutical contamination in some aquatic food webs (Li et al., 2012b; Schultz et al., 2010; Xu et al., 2014). Benthic invertebrates are often exposed to sediment contaminated with pharmaceuticals via ingestion of sediment particles. These organisms are highly important components of the food web in aquatic environments and contribute significantly to fish diets (Grabicova et al., 2015). The biota-sediment accumulation factor (BSAF) is a useful parameter for understanding the partitioning of pharmaceutical contamination from sediment to benthic organisms. Thus, investigation into the BSAFs of pharmaceuticals in benthic organisms will improve our understanding how pharmaceuticals enter the aquatic food web. However, field-based BSAF data for pharmaceuticals are still unavailable.

The extent of biomagnification for a given contaminant in a food web can be quantified by establishing the trophic magnification factor (TMF). The TMF is determined from the slope of a regression of the logarithmically transformed normalized contaminant concentrations against trophic levels (TLs) of the organisms (Fisk et al., 2001; Borgå et al., 2012). Compared with other bioaccumulation metrics such as the bioconcentration factor (BCF), bioaccumulation factor (BAF) and BSAF, the TMF is potentially more robust to errors because it is not prone to uncertainty in measurement of chemical concentrations in abiotic media (McLeod et al., 2015). So far, studies on TMFs have primarily focused on nonionic organic chemicals and metals (Borgå et al., 2012); less is known regarding the trophic transfer of ionizable organic chemicals. To date, few studies have investigated the trophic transfer of pharmaceuticals in aquatic food webs (Du et al., 2014a; Xie et al., 2015). A recent study in the North Bosque River conducted by Du et al. (2014a) found a slightly positive (non-significant) slope between carbamazepine (CBZ) concentrations and TLs and a significant and negative slope for diphenhydramine. In a food web studied in Taihu Lake, propranolol (PRP) concentrations decreased significantly with increasing TLs, whereas slightly positive (non-significant) slopes in the regression between concentrations and TLs were observed for both roxithromycin (RTM) and diclofenac (DCF) (Xie et al., 2015). The results of these studies suggested that none of the above mentioned pharmaceuticals underwent trophic magnification. However, it should be noted that TMFs were only calculated for a total of five pharmaceuticals in the North Bosque River and Taihu Lake food web studies. Clearly, additional field-based studies are needed for thorough assessment of the TMFs of other pharmaceuticals.

Taihu Lake is located in the heart of Yangtze River Delta, one of the most economically developed regions in China. As the second largest freshwater lake in China, it is an indispensable drinking water, fishing and tourism resource for the surrounding regions. Unfortunately, many studies have shown evidence of Taihu Lake as a significant sink for organic pollutants, including pharmaceuticals from the surrounding runoffs (Xie et al., 2015; Xu et al., 2014; Yan et al., 2014). Our group carried out preliminary research on bioaccumulation of eight pharmaceuticals in biota in this lake and found an absence of biomagnification of pharmaceuticals in the food web (Xie et al., 2015). However, significant differences in environmental conditions between different lake regions that could mask the biomagnifications of pharmaceuticals were not considered in this prior work. The northern region of the lake (e.g., Meiliang Bay) is eutrophic and characterized by the dominance of phytoplankton with fewer submerged macrophytes, whereas the eastern region of the lake is dominated by submerged macrophytes with fewer occurrences of algal blooms (Mao et al., 2014). In addition, high degrees of spatial heterogeneity for pharmaceutical concentrations in water and sediments have been observed in Taihu Lake (Xie et al., 2015; Xu et al., 2014). Concentrations of contaminants (e.g., Hg and organochlorines) in biota at the base of the food web are relatively dilute in systems with more nutrients and higher primary productivity (Karimi et al., 2007; Borgå et al., 2012). Thus, it is likely that the magnitude of biomagnification of contaminants through food webs are also related to the chemical or physical conditions of lakes. Recent model studies revealed that field TMFs were sensitive to concentration gradients and species migration patterns, especially for chemicals that are subject to a low degree of biomagnification or trophic dilution (Kim et al., 2016; McLeod et al., 2015). Taking these previous findings and regional variability in Taihu Lake into account, it is important to determine whether pharmaceutical food web biomagnification assessed by TMF is consistent spatially and temporally in the food webs. This will not only improve the understanding of pharmaceutical biomagnification but also broad the understanding of TMFs variability in general.

The aim of the current study was to investigate the bioaccumulation and trophic transfer of 23 multi-class pharmaceuticals, selected according to their frequent occurrences in aquatic ecosystems (Bu et al., 2013; Liu and Wong, 2013; Verlicchi et al., 2012; Hughes et al., 2012), as well as to their ecological risk to aquatic organisms (Chen et al., 2015; Godoy et al., 2015; Huang et al., 2013; Li et al., 2012b). The target pharmaceuticals included ten antibiotics of RTM, erythromycin (ETM), ofloxacin (OFC), norfloxacin (NFC), ciprofloxacin (CFC), tetracycline (TC), chloramphenicol (CAP), sulfamethoxazole (SMX), sulfamerazine (SMZ) and sulfadiazine (SDZ), four non-steroidal anti-inflammatory drugs of ibuprofen (IPF), DCF, naproxen (NPX) and indomethacin (IMC), three lipid regulators of clofibric acid (CA), gemfibrozil (GFB) and bezafibrate (BZB), two steroid estrogens of 17β-estradiol (E2) and 17α-ethynylestradiol (EE2), one non-selective β-adrenoceptor blocker PRP, one antiepileptic drug CBZ, one antifungal drug ketoconazole (KTC) and one antidepressant sertraline (SER). Additionally, the current study assessed whether the transfer behavior of pharmaceuticals was consistent across two food webs sampled from lake regions with different environmental conditions.

2. Materials and methods

2.1. Sampling sites, sample collection and food web description

Taihu Lake is a large shallow freshwater lake, with an area of approximately 2250 km^2 and an average depth of 1.9 m. A total of sixteen sites were spatially distributed throughout Taihu Lake (Fig. 1). These sites were located in Gonghu Bay (S1-S3), Meiliang Bay (S4-S6), Zhushan Bay (S7 and S8), the West Coast (S9 and S10), South Coast (S11 and S12), East Coast (S14-S16) and Lake Centre (S13). Sampling was carried out in December 2014. Surface water ($n = 64$), sediment ($n = 64$), phytoplankton (mainly *Chlorophyta, Bacillariophyta and Cyanophyta*) [pooled samples (p) = 64], zooplankton (mainly *Copepoda, Cladocera, and Rotifers*) ($p = 64$), three types of zoobenthos [mussel (*Anodonta*) ($n = 35$), snail (*Bellamya* sp.) ($n = 195$) and bivalve (*Corbiculidae*) ($n = 146$)], two types of shrimp [white shrimp (*Exopalaemon modestus*) ($n = 213$) and Taihu shrimp (*Macrobranchium nipponense*) ($n = 254$)] and seven fish species [silver carp (*Hypophtha lmichthys molitrix*) ($n = 24$), common carp (*Cyprinus carpio*) ($n = 27$), crucian carp (*Carassius auratus*) ($n = 43$), lake anchovy (*Coilia ectenes*) ($n = 78$), whitebait