Chemosphere 184 (2017) 137–147

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Occurrence, distribution, and risk assessment of antibiotics in the surface water of Poyang Lake, the largest freshwater lake in China

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HIGHLIGHTS

- Eighteen antibiotics were detected in the surface water of Poyang Lake.
- Sulfadiazine, oxytetracycline, and doxycycline have relatively higher concentrations in the lake.
- Dilution effect of the water flow on the antibiotic levels exists in Poyang Lake during the flood season.
- Sulfadiazine and sulfadimidine presented the main ecological risk factors to Poyang Lake.

ARTICLE INFO

Article history:
Received 18 February 2017
Received in revised form
24 May 2017
Accepted 26 May 2017
Available online 29 May 2017

Handling Editor: Klaus Kümmerer

Keywords:
Antibiotics
Poyang Lake
Sulfonamides
Occurrence
Risk assessment
Water flow

ABSTRACT

SPE–UPLC–MS/MS was used to investigate the occurrence of 18 target antibiotics in the surface water of Poyang Lake over different seasons of 2014–2015. The maximum concentrations of sulfadiazine, oxytetracycline, and doxycycline were 56.2, 48.7, and 39.7 ng/L, respectively. Compared with those in the other lakes or surface waters, the surface water of Poyang Lake contained moderate or below-average levels of antibiotics. The significantly lower concentrations ($P < 0.01$) of roxithromycin in June 2015 likely resulted from the dilution effect of water flow during the flood season. Antibiotic concentrations were higher in site P3-1 than in other sites ($P < 0.01$), whereas those in other sites (P1-1, P2-1, P5-1, P6-1, P7-1, P13-1, P16-1, P17-1, P18-1) were not significantly different ($P > 0.05$). Given that tetracyclines and sulfonamides are common veterinary medicines, the high concentrations of oxytetracycline, doxycycline, and sulfadiazine in site P3-1 might be closely related to agricultural production in the surrounding areas. The risk assessment of the main antibiotic contaminants revealed that the majority of the risk quotients of the target antibiotics were below 0.01, thereby indicating the minimal risk of these antibiotics to organisms at three different trophic levels. Sulfadimidine and sulfadiazine were identified as the main antibiotics that contribute to ecological risk in Poyang Lake, and that the daphnid is the main model organism exposed to these risks. This study provides important data for antibiotic pollution control and environmental protection in the study area and enriches environmental monitoring data on a global scale.

1. Introduction

The occurrence and persistence of antibiotics in the water environment have attracted widespread attention (Fram and Belitz, 2011; Bu et al., 2013) given the close link of antibiotics with antimicrobial resistance (Reardon, 2014) and their toxicity to organisms on different trophic levels (Yang et al., 2013; Johansson et al., 2014;

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http://dx.doi.org/10.1016/j.chemosphere.2017.05.148
0045-6535/

Gorokhova et al., 2015). China is the largest producer and consumer of antibiotics in the world (Richardson et al., 2005). In 2013, 92,700 t of the 36 most frequently detected antibiotic contaminants was consumed in China (Zhang et al., 2015a). Humans and animals excrete approximately 54,000 t of antibiotics. Moreover, 53,800 t of antibiotics enter the receiving environment after various wastewater treatment processes (Zhang et al., 2015a). These data suggest that more than half of the antibiotics used by humans and animals are excreted, and that the removal efficiencies of wastewater treatment plants (WWTPs) are negligible. Studies have also reported that activated sludge in WWTPs exhibit low removal efficiencies for antibiotics (Homem and Santos, 2011; Aukidy et al., 2012).

In China, most surveys on pharmaceuticals and personal care products in various environmental matrices were conducted after 2005 (Luo et al., 2011; Jia et al., 2012; Zhang et al., 2013; Bai et al., 2014). These surveys showed that antibiotic contaminants are present in natural surface waters at ng/L levels (Yan et al., 2013) and in WWTPs, aquaculture waters, and hospital wastewaters at ng/L–μg/L levels (Zhang and Li, 2011). These results imply that these water bodies are potential sources of antibiotic contaminants of natural surface water. To date, most internationally conducted studies on antibiotic contamination in aquatic environments have mainly focused on rivers (Jiang et al., 2011), WWTPs (Jia et al., 2012; Verlicchi and Zambello, 2015), aquaculture waters (Le and Munekage, 2004), hospital wastewaters (Verlicchi et al., 2012; Rodriguez–Mozaz et al., 2015), coastal waters (Na et al., 2011), and groundwater (Tong et al., 2014). Tap water contamination by macrolides in Madrid (Valcarcel et al., 2011) and by fluoroquinolones in Guangzhou and Macao, China has been reported (Yiruhan et al., 2010). However, although some lakes serve as drinking water sources, the antibiotic contamination of large lakes has received considerably less attention. Tang et al. (2014) reported the occurrence of five kinds of sulfonamide (SA) antibiotics in Chao Lake in China. They found that sulfamethoxazole (SMX) is present in the lake at average and maximum concentrations of 2.1–19.3 and 137.9 ng/L, respectively. Lei et al. (2015) reported that ciprofloxacin is present at a median concentration of 39.22 ng/L and dominates the surface water of Bosten Lake, Xinjiang, China. Sulphamethoxazole is present in water samples from the shore of Maumee Bay, Lake Erie, USA, at 211 ng/L (Wu et al., 2008). The maximum concentration of SMX in the middle of Lake Geneva is 130 ng/L (Chèvre, 2014). A national reconnaissance of 139 streams in the USA showed that the maximum detected concentrations of oxytetracycline (OTC), sulfadimidine (SMZ), and roxithromycin (RTM) are 340, 220, and 180 ng/L, respectively (Kolpin et al., 2002). A study that monitored the veterinary medicines in water bodies in the UK reported that OTC and sulfadiazine (SD) are present at maximum concentrations of 4490 and 4130 ng/L, respectively, in the surface water environment (Boxall et al., 2005). The environmental toxicity and risk assessment of antibiotics have attracted attention, as the monitoring studies and reports on antibiotic contamination increase (Kosma et al., 2014). International organizations, such as the European Medicines Evaluation Agency, US Food and Drug Administration, and European Commission, have developed and implemented various environmental risk assessment guidelines (Gheorghe et al., 2016), which provide beneficial references for the ecological risk assessment (ERA) of antibiotics.

Poyang Lake is the largest freshwater lake in China and is one of the two largest lakes connected to the Yangtze River. Poyang Lake is an overflow lake that accepts and releases water and is an internationally important wetland with numerous environmental regulatory functions and ecological benefits (Cui and Zhao, 2004). In the past 30 years, especially after 2004, the water quality of Poyang Lake has significantly degraded because of the annual increases in pollution loads from nonpoint, industrial, agricultural, and urban sources (Wang et al., 2013). Consequently, many studies have focused on eutrophication (Wang et al., 2015), heavy metal pollution (Xie et al., 2016), and algal toxin pollution (Zhang et al., 2015b) in Poyang Lake. To our knowledge, however, no study has addressed the presence of antibiotic contaminants in Poyang Lake. The present study is the first to investigate the occurrence and distribution of five antibiotic classes in the surface water of Poyang Lake. The concentrations of 18 antibiotics were investigated over different seasons. The sources and the temporal and spatial distributions of target antibiotics in Poyang Lake were analyzed. The influences of water flow on the temporal distribution of antibiotics were also investigated. The risk assessment of target antibiotics in Poyang Lake was conducted based on risk quotients (RQs). This study provides important data for trace contaminant management and environmental protection in the study area and enriches the global monitoring database for emerging contaminants. Furthermore, our investigation revealed that the excessive or illegal use of antibiotics remains a regional practice in agriculture despite the implementation of regulatory policies for antibiotic use in fish breeding and poultry raising in China. This phenomenon may be closely related with the high detection frequencies of antibiotics in fish ponds and in Poyang Lake. This study reflects environmental antibiotic contamination in China and provides references for similar regions in the world.

2. Materials and methods

2.1. Chemicals and standards

Antibiotic standards of tetracycline (TC) antibiotics included TC, chlortetracycline (CTC), OTC, and doxycycline (DC). SA antibiotics included SD, sulfapyridine, SMX, sulfathiazole (STZ), and SMZ. Quinolone antibiotics (QUs) included difloxacin, ofloxacin, norfloxacin, enoxacin, ciprofloxacin (CFX), and enrofloxacin. ML antibiotics included RTM and erythromycin (ETM). Lincosamide antibiotics included lincomycin (LCM). Demeclocycline, sulfamerazine–D_4, CFX–D_8, and ETM–^{13}C–D_3 were used as internal standards for TCs, SAs, QUs, MLs, and LCMs. All compounds were purchased from Dr. Ehrenstorfer (Germany). Antibiotic selection depended on the types of antibiotic detected in the Yangtze River Estuary, which lies in the lower reaches of Poyang Lake (Yan et al., 2013). The basic characteristics of these antibiotics are shown in Table S1.

Separate stock solutions (1000 mg/L) of individual compounds and internal standards were prepared with methanol. A 10 mg/L mixture of working standard that contained each compound was prepared by diluting an aliquot of the stock solution with methanol. All standard solutions were stored at −20 °C. All solvents were of high-performance liquid chromatography grade.

2.2. Sampling sites

The study area was Poyang Lake, the largest freshwater lake in China (Fig. 1). Poyang Lake (28.37°–29.75° N, 115.78°–116.75° E) is located in the northern Jiangxi Province and on the southern bank of the middle and lower reaches of the Yangtze River. Its catchment area and annual runoff are 16.22×10^4 and 152.5 km^3, respectively; correspondingly, the catchment area accounts for 9% and 16.3% of the entire Yangtze River catchment and 97.2% of the catchment area of Jiangxi Province (Gao et al., 2015). Gan, Fu, Xin, Rao, and Xiu River (hereafter referred to as the Five Rivers) are the five main rivers in the Jiangxi Province that flow to Poyang Lake. Hukou is the only exit of Poyang Lake to the Yangtze River (Fig. 1). Poyang Lake is a typical large shallow lake with an average water depth of 7.38 m and mean