Science of the Total Environment 634 (2018) 448–458

Contents lists available at ScienceDirect

Science of the Total Environment

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

Urbanization gradient of selected pharmaceuticals in surface water at a watershed scale

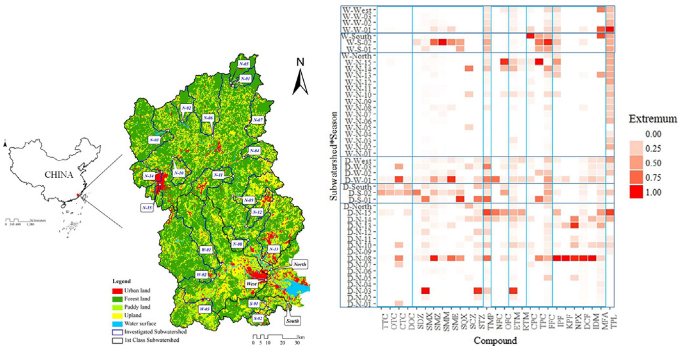
Bing Hong [a,b,1], Qiaoying Lin [a,b,1], Shen Yu [a,*], Yongshan Chen [a], Yuemin Chen [a], Penchi Chiang [c]

[a] CAS Key Laboratory of Urban Environment and Health, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, China
[b] University of Chinese Academy of Sciences, Beijing, China
[c] National Taiwan University, Taipei, China

HIGHLIGHTS

- Instream pharmaceutical loads along a subwatershed-based urbanization gradient.
- 27 out of 33 selected compounds in 3 categories were quantified in surface water.
- Urban land use in subwatersheds was highly correlated to instream pharmaceuticals.
- Evident seasonality of level and number of instream pharmaceuticals was observed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 February 2018
Received in revised form 30 March 2018
Accepted 31 March 2018
Available online xxxx

Editor: Jay Gan

Keywords:
Pharmaceutical residues
Surface water
Seasonality

ABSTRACT

Ubiquitous detection of pharmaceuticals in the aquatic environment around the world raises a great public concern. Aquatic residuals of pharmaceuticals have been assumed to relate to land use patterns and various human activities within a catchment or watershed. This study generated a gradient of human activity in the Jiulong River watershed, southeastern China by urban land use percentage in 20 research subwatersheds. Thirty-three compounds from three-category pharmaceuticals [26 compounds of 5 antibiotic groups, 6 compounds of non-steroidal anti-inflammatory drugs (NSAIDs), and 1 compound of respiratory system drugs (RSDs)] were quantified in stream water before the research subwatershed confluences with two sampling events in dry and wet seasons. In total, 27 out of the 33 pharmaceutical compounds of interest were found in stream waters. Seasonality of instream pharmaceuticals was observed, with less compounds and lower concentrations in the wet season sampling event than in the dry season one. Urban land use in the research subwatershed was identified as the main factor influencing in stream pharmaceutical concentrations and composition regardless of season. Rural land uses

---

Abbreviations: Tetracyclines (TCs), Tetracycline (TTC), Oxytetracycline (OTC), Chlortetracycline (CTC), Doxycycline (DOC); Sulfonamides (SAs), Sulfadiazine (SDZ), Sulfamethoxazole (SMX), Sulfamethazine (SMZ), Sulfamerazine (SMR), Sulfamonomethoxine (SMM), Sulfaquinoxaline (SQX), Sulfadimethoxine (SDM), Sulfameter (SME), Sulfaclozine (SCZ), Sulfathiazole (STZ), Synergist: Trimethoprim (TMP); Fluoroquinolones (FQs), Norfloxacin (NFC), Ofloxacin (OFC), Ciprofloxacin (CFC), Enrofloxacin (EFC), Difloxacin (DFC); Macrolides (MLs), Erythromycin-H2O (ETM), Roxithromycin (RTM), Tylosin (TLS); Chloramphenicols (CPs), Chloramphenicol (CPC), Thiamphenicol (TPC), Florfenicol (FFC); Non-steroidal anti-inflammatory drugs (NSAIDs), Naproxen (NPX), Ketoprofen (KPF), Diclofenac (DCF), Ibuprofen (IPF), Indomethacin (IDM), Mefenamic acid (MFA); Respiratory system drug (RSD), Theophylline (TPL); Standards, D$_4$ sulfamethazine (D$_4$-SMZ), D$_8$ ofloxacin (D$_8$-OFC), Erythromycin (*N* dimethyl ^{13}C) (^{13}C-ETM), D$_5$ chloramphenicol (D$_5$-CPC), D$_3$ mecoprop (D$_3$-MCP), ^{13}C phenacetin (^{13}C-PNC), D$_5$ Atrazine (D$_5$-ATZ), methyl D$_3$ benzeneamide D$_4$ (D$_7$-DEET), D$_6$ gemfibrozil (D$_6$-GFZ); SPE, Solid phase extraction; DEM, Digital elevation map; QA/QC, Quality assurance and quality control; LOD, Limit of detection; S/N, Signal-to-noise; LOQ, Limit of quantification; One-way ANOVA, One-way analysis of variance; NMDS, Non-metric multidimensional scaling; WWTP, Wastewater Treatment Plant.

* Corresponding author at: 1799 Jimei Road, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China.
E-mail address: syu@iue.ac.cn. (S. Yu).

[1] Note: Hong and Lin equally contribute this study.

https://doi.org/10.1016/j.scitotenv.2018.03.392

Land use pattern
Jiulong River

contributed a mixture of human and veterinary pharmaceuticals possibly from agricultural application of manure and sewage sludge and aquaculture in the research subwatersheds. Erythromycin in both sampling events showed medium to high risks to aquatic organisms. Results of this study suggest that urban pharmaceutical management, such as a strict prescription regulations and high-efficient removal of pharmaceuticals in wastewater treatment, is critical in reducing aquatic pharmaceutical loads.

1. Introduction

Large amounts of pharmaceutical compounds have been widely used as human and veterinary medicines and growth promoters in bee-keeping, livestock production, and aquaculture (Kümmerer, 2009) over decades. China produced approximately two million tons of active pharmaceutical ingredients in 2011, which doubled the production of 2003, accounting for over 20% of worldwide production (Liu and Wong, 2013). It was estimated that China consumed over 162,000 tons of antibiotics in 2013 of which approximately 48% was human medication (Zhang et al., 2015). An estimate indicated that Chinese daily dosage per thousand persons of antibiotics was approximately 6 times greater than residents in UK, USA, Canada, and European countries in 2013 (Zhang et al., 2015).

Given a huge variation of pharmaceutical uptake efficiency among various organisms, a considerable amount of pharmaceutical residuals has been assumably discharged into the aquatic environment (Kümmerer, 2009). Pharmaceutical compounds have been ubiquitously detected in natural ecosystems (Chen et al., 2013; Lapworth et al., 2012; Li et al., 2016; Luo et al., 2011; Peng et al., 2014; Tran et al., 2014; Wu et al., 2014; Xu et al., 2007) besides wastewaters from households, hospitals, livestock farms, aquacultural ponds, and pharmaceutical manufactures (Jiang et al., 2013; Luo et al., 2011; Sim et al., 2011; Xi et al., 2015; Zhu et al., 2013), In total, 94 pharmaceutical compounds, consisting of over 75% antibiotics, were reported at least once in surface waters and sediments in China mostly at a level of ng L^{-1} or ng g^{-1}, comparable to the rest world (Bu et al., 2013). Environmental residuals of pharmaceutical compounds are defined as a group of emerging micro-pollutants (Boxall et al., 2012; Daughton, 2004; Daughton and Ternes, 1999; Field et al., 2006) according to their ecosystem impacts on antibiotic resistance, endocrine disruption, and microbial community structure and function (Oaks et al., 2004; Peng et al., 2008; Pruden et al., 2006; Xi et al., 2015; Su et al., 2017; Zhang et al., 2015; Zhu et al., 2017).

Although most pharmaceuticals, such as antibiotics, are related to natural products (Li and Vederas, 2009), their escalating concentrations in the aquatic environment are anthropogenically caused. Pharmaceutical residues in the aquatic environment have been assumed in relation to the catchment land use patterns (Davis et al., 2006; Kemper, 2008; Li et al., 2016). A number of anthropogenic sources (or endmembers) of pharmaceutical residues in the aquatic environment has been identified, including above-mentioned wastewater discharges and the effluents from wastewater treatment plants (Arlos et al., 2014; Fairbairn et al., 2016; Hanamoto et al., 2018). However, few studies have linked the pharmaceutical residues in stream water to specific anthropogenic activities, such as urbanization or animal farming and agricultural production except implications (Yu et al., 2013; Fairbairn et al., 2016). Hanamoto et al. (2018) found that instream loadings of 12 WWTPs-derived pharmaceuticals could be predicted by human population in the catchments. However, Veach and Bernot (2011) found comparable concentrations of 12 pharmaceutical compounds in stream water between agricultural and urban influenced sites in an Indiana watershed, USA. The source-sink relationship between pharmaceutical residues in surface water and anthropogenic activity in the catchment needs further clarifications, which will be helpful to understand bio-physico-chemical behaviors and ecological effects of pharmaceutical residuals in the aquatic environment.

Objectives of this study were to explore responses of instream pharmaceutical concentrations to land use patterns in subwatersheds along a gradient of urban land use composition during dry and wet seasons. Based on existing research, it was hypothesized that concentration and composition of instream pharmaceuticals would be associated with the land use patterns in subwatersheds relating to human activities, such as human medication uses in urban areas and animal farming uses and agricultural application of pharmaceutical contaminated sludge/composts in rural areas. Seasonality, dry and wet seasons, might also differentiate instream pharmaceutical interactions with human activity in subwatershed due to dilution effects of seasonal precipitation (Fairbairn et al., 2016). Our previous study found 330 compounds of 9 pharmaceutical categories were detected in surface sediments from the coastal tidal section of the Jiulong River (Chen et al., 2013). Other studies indicated approximately 1.8 million pigs were farmed in the Jiulong River watershed (Zhang et al., 2012), and the swine wastewater discharges elevated instream antibiotic concentrations (Jiang et al., 2013; Zhang et al., 2011). This study selected 20 research subwatersheds among the 3 Class I subwatersheds (the main tributaries draining through) in the Jiulong River watershed in southeastern China (Fig. 1). The 20 research subwatersheds formed a gradient of urban land use composition in the subwatershed. Two seasonal sampling events of stream water were conducted above the confluences of the 23 subwatersheds (20 research subwatersheds and 3 Class I subwatersheds) to the main river during the dry season (November 2014) and the wet season (June 2015). The pharmaceutical compounds of interest in this study included 3 categories, i.e. 26 compounds of five-group antibiotics, 6 compounds of non-steroidal anti-inflammatory drugs (NSAIDs), and 1 compound of respiratory system drugs.

2. Materials and methods

2.1. Study watershed and sampling

The 258-km long Jiulong River drains the 2nd largest watershed in Fujian Province, China (24°13′-25°51′ N, 116°47′-118°02′ E). There are three Class I tributary confluences meeting in its estuary, namely the North Stream, the West Stream, and the South Stream. The watershed covers 14,741 km^2 and hosts two regional cities, Longyan and Zhangzhou, with a population over 10.5 million (Fig. 1). The monsoon climate brings annual precipitation of 1716 mm (2014) and 2114 mm (2015) in the upper catchment (Longyan) and 1578 mm (2014) and 1824 mm (2015) in the lower catchment (Zhangzhou) (Fig. S1 in the Supplementary information).

The Jiulong River watershed is divided into 197 minimal subwatersheds according to the digital elevation map (DEM) using an ArcGIS (Ver. 10 for Windows). Five land use types in the watershed, i.e. forest land, upland, paddy land, urban land, and water surface, were identified using LandSat ETM+ images (August 2014) using the ArcGIS with field validations (Fig. 1). Briefly, the forest land is coved by mature and full canopy forests; upland is a rain-fed and irrigated cultivated field with crops, vegetables, orchards, nursery plants, and grasses; paddy land referred to irrigated rice paddy land and other aquatic plants; urban land was covered by impervious surfaces; and water surface included streams, lakes and ponds, and reservoirs. The minimal subwatersheds were grouped by a cluster analysis with parameters of land use composition (%) and 20 research subwatersheds were