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Occurrence and risk assessment of antibiotics in surface water and groundwater from different depths of aquifers: A case study at Jianghan Plain, central China

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ABSTRACT

The occurrence of 14 antibiotics (fluoroquinolones, tetracyclines, macrolides and sulfonamides) in groundwater and surface water at Jianghan Plain was investigated during three seasons. The total concentrations of target compounds in the water samples were higher in spring than those in summer and winter. Erythromycin was the predominant antibiotic in surface water samples with an average value of 1.60 μg/L, 0.772 μg/L and 0.546 μg/L respectively in spring, summer and winter. In groundwater samples, fluoroquinolones and tetracyclines accounted for the dominant proportion of total antibiotic residues. The vertical distributions of total antibiotics in groundwater samples from three different depths boreholes (10 m, 25 m, and 50 m) exhibited irregular fluctuations. Consistently decreasing of antibiotic residues with increasing of depth was observed in four (G01, G02, G03 and G05) groundwater sampling sites over three seasons. However, at the sampling sites G07 and G08, the pronounced high concentrations of total antibiotic residues were detected in water samples from 50 m deep boreholes instead of those at upper aquifer in winter sampling campaign, with the total concentrations of 0.201 μg/L and 0.100 μg/L respectively. The environmental risks posed by the 14 antibiotics were assessed by using the methods of risk quotient and mixture risk quotient for algae, daphnids and fish in surface water and groundwater. The results suggested that algae might be the aquatic organism most sensitive to the antibiotics, with the highest risk levels posed by erythromycin in surface water and by ciprofloxacin in groundwater among the 14 antibiotics. In addition, the comparison between detected antibiotics in groundwater samples and the reported effective concentrations of antibiotics on denitrification by denitrifying bacteria, indicating this biogeochemical process driven by microorganisms won't be inhibitory influenced by the antibiotic residues in groundwater.

1. Introduction

Antibiotics have been widely used for decades not only as human and animal medicines, but as growth promoters in the livestock and aquaculture industry. The expired antibiotic drugs, the scrap antibiotic materials in the pharmaceutical process and the unabsorbed antibiotics in human and animal excreta (Bu et al., 2013; Heuer et al., 2008; Kümmerer, 2009; Phillips et al., 2010) are collected in the wastewater and introduced to the wastewater treatment plants (WWTPs), where antibiotics cannot be completely removed by the treatment facilities (Chang et al., 2010; Li et al., 2013a; Michael et al., 2013; Zhou et al., 2013). The residual antibiotics are thus continuously discharged into the environment, especially into surface water and groundwater due to their water solubility and degradation resistant characteristics (Bound and Voulvoulis, 2004; Noedler et al., 2012; Tang et al., 2015; Wei et al., 2011).

Antibiotics contamination of surface water have been reported in case studies of the effluent of WWTPs, river and lake water and reservoir water, with the values of concentrations ranging from nano- to milli-grams per liter (Al Aukidy et al., 2012; Cheng et al., 2014; De Liguoro et al., 2012; Deng et al., 2016; Jiang et al., 2011; Lopez-Serna et al., 2012; Peng et al., 2014; Zuccato et al., 2010). As for the investigation of antibiotics in groundwater, the detected samples were generally collected from the wells for municipal or agricultural supply (Fram and Belitz, 2011; Gottschall et al., 2012; Hu et al., 2010; Lapworth et al., 2012; Tong et al., 2014). In the study of Gottschall

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et al. (2012), pharmaceutical concentration levels of 10–19 ng/L were studied using groundwater samples collected at 2 m deep below the soil surface. Hu et al. (2010) found the highest ciprofloxacin residue with the value above 40 ng/L in groundwater samples from 40 m deep. Up till now, few systematic work has been done on the vertical distribution of antibiotics in the aquifers.

According to the results of studying the bioaccumulation of pharmaceuticals in the aquatic organisms (Brozinski et al., 2013; Edwards et al., 2009; Gao et al., 2012; Li et al., 2012), the target accumulation positions of fish were concentrated on the brain and liver tissues (Grabicova et al., 2014; Liu et al., 2015). The ongoing extensive use of antibiotics by human and livestock and poultry industry would result in their continuous introduction into the environment, and when the rate of compound depuration and degradation cannot offset the rate of accumulation (Lombardo et al., 2014), the ecosystems and human health would be in high risks (Pinheiro et al., 2013). The environment effects of individual contaminant to the aquatic organisms can be assessed by using the risk quotient approach (Shi et al., 2014; Yan et al., 2013). In addition, the water environment is usually contaminated by multiple compounds, considering the probability of risk underestimations by ignoring the possible mixture effects, the mixture risk toxicity concepts were proposed by Backhaus and Faust (2012), and applied to estimate the mixture risk of several compounds to different trophic levels in aquatic environment (Backhaus and Karlsson, 2014; Liu et al., 2015).

In this study, fourteen antibiotics in the aquatic environment were investigated by collecting groundwater and surface water samples in three seasons (spring, summer, and winter) at Jianghan Plain. There are three objectives of this study: (1) to understand the occurrence, especially the seasonal variation of selected 14 antibiotics in different water matrices during different seasons; (2) to investigate the vertical distribution of antibiotics in aquifers by detecting the antibiotic residues in groundwater samples from a multi-level monitoring well field with boreholes at three different depths (10 m, 25 m, and 50 m); and (3) to assess the aquatic environmental risks of individual compound and the mixture of the 14 antibiotics by employing two risk quotient approaches. Organisms in three trophic levels (algae, daphnids, and fish) were selected as references to evaluate the ecological risk in surface water and groundwater of the study area.

2. Materials and analysis

2.1. Chemicals and standards

Fourteen antibiotic standards were obtained from Dr. Ehrenstorfer (Augsburg, Germany) and classified into four groups, fluoroquinolones (FQs), including ofloxacin (OFL), enrofloxacin (ENR), lomefloxacin (LMX), ciprofloxacin (CIP) and norfloxacin (NOR); tetracyclines (TCs), including clorotetracycline (CTC), oxytetracycline (OTC) and tetracycline (TC); macrolides (MLs), including roxithromycin (ROX), clarithromycin (CAM) and erythromycin (EYR); sulfonamides (SAs), including sulfamethazine (SM-2), sulfamethoxazole (SMZ) and sulfadiazine (SDZ). The internal standard was simatone, which was the product of Accu-Standard Inc. (United States). Individual stock solutions of antibiotic standards and internal standard were prepared in methanol, and stored in the dark at −20 °C, different concentrations of working mixtures were prepared by diluting the stock solutions. All chemicals and solvents used were of HPLC grade, ultrapure water was prepared with a Milli-Q water purification system (18.2 MΩ cm^{-1}).

2.2. Study sites and sampling

The study was conducted on the surface water and groundwater in Shahu County of Jianghan Plain, central China. The detailed sampling sites were displayed in Fig. 1. Jianghan Plain is one of the major bases of agriculture and aquaculture production in China, including paddy, cotton, meat and fish. Livestock farms and aquaculture ponds were scattered distributed in the sampling area, and the livestock breeding wastewater were discharged into the ditches, besides, the bottom of some fishponds were below the local groundwater table, which is averagely 0.5–3.5 m below the land surface (Gan et al., 2014). Water samples were collected in April 2014 (spring), August 2014 (summer) and December 2014 (winter), respectively. It rained heavily and continually during the first sampling campaign in April. All the groundwater sampling sites (G01–G13) have multilevel boreholes with sampling ports at the deep of 10, 25 and 50 m below the land surface (b.l.s.). The surface water samples (R01-R08) were collected from two tributaries of the Yangtze River flow from west to east, named Tongshun River (TSR, R01-R04) and Dongjing River (DJR, R05 and R06); and another two rainfall-dependent rivulets, Kuige Rivulet (KGR, R07) and Lvfeng Rivulet (LFR, R08). All of these surface water bodies receive discharge from domestic sewage and/or industries wastewater. In the first sampling campaign, groundwater samples were collected from seven multilevel sampling boreholes (G03, G07, G08, G10, G11, G12, and G13) and four surface water samples (R02, R03, R05, and R07), while in the second and third sampling campaign, all of 13 (G01–G13) groundwater sampling boreholes and 8 (R01–R08) surface water were sampled.

2.3. Sample extraction and analysis

Solid phase extraction (SPE) and high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) were used to extract and analyze water samples, the detailed information about the methods were described in our previous publication (Yao et al., 2015). Briefly, before conducting the SPE operation, water samples were filtered through 0.45 µm glass fiber filter, adjusted to pH=4.0 and Na_2-EDTA was added as chelant. The SPE was performed by using Oasis hydrophilic-liphophilic balance (HLB) cartridge (200 mg, 6 mL, Waters, Milford MA, USA). Before loading the pretreated water samples, cartridges were activated with 6 mL of methanol and 6 mL of ultra-pure water. When water samples were finished passing through the cartridges, 6 mL of ultra-pure water were used to wash out the chelating agent on the solid phase, vacuum dried for 10 min, and eluted HLB cartridge with 12 mL of methanol. Eluent was evaporated to near dryness by using nitrogen, added 100 ng of internal standard simatone, and re-dissolved up to 1 mL with solution of methanol-0.1% formic acid (v/v, 1/1) and stored at −4 °C.

Antibiotics were detected by HPLC-MS/MS system consisting of the Agilent of auto-sampler (1200 series), binary pump (1260 series), thermostated column compartment (1200 series), variable wavelength detector (1260 series), triple quadrupole (6400 series) and an electro-

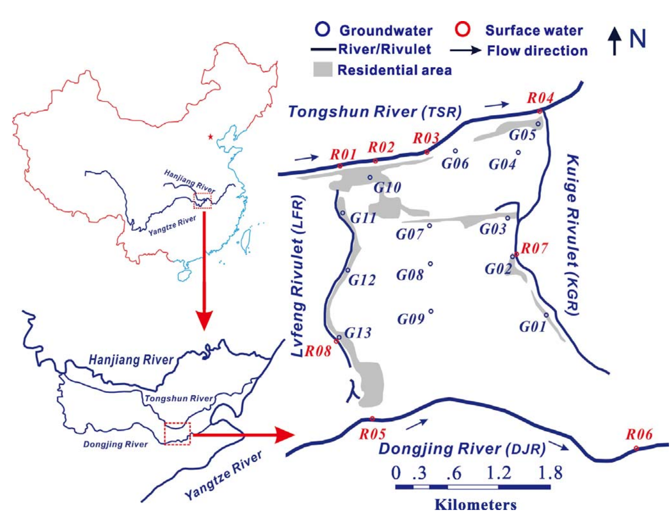

Fig. 1. Sampling sites in the study area.