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Risk assessment of three fluoroquinolone antibiotics in the groundwater recharge system

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ABSTRACT

Three fluoroquinolone antibiotics agents (FQs) in groundwater and reclaimed water have been investigated in Changzhou and Beijing, China. The occurrence of ofloxacin (OFL), enrofloxacin (ENR) and norfloxacin (NOR) is in nanograms per liter and has 100% frequency. The concentration order of FQs in reclaimed water is NOR > OFL > ENR, whilst the order in groundwater is NOR > ENR > OFL. And then the single and mixture adsorption-desorption have been studied and showed that (i) silty clay loam has higher sorption capacity than loamy sand, (ii) competitive adsorption exists when the three selected FQs coexist, (iii) ENR has a significantly priority sorption to NOR, whilst OFL has a least sorption among the mixture, (iv) there is no significant difference between the desorption results of mixture and the individual compound in relatively low concentration, (v) the formed chemical bonds and the irreversible combination of adsorption point are the significant influential factors for explaining desorption hysteresis of the selected FQs. Based on the above study, transport model and risk quotient have been performed, and the calculated risk quotient reveals that: (i) the selected FQs risk order in reclaimed water is OFL > ENR > NOR, (ii) in groundwater, OFL and ENR pose a higher risk than NOR no matter whether considering the long time groundwater recharge. This study will help policy makers to decide which FQs need to be covered in the priority substance lists defined in legislative frameworks.

1. Introduction

Fluoroquinolone antibiotics agents (FQs) are one of the ubiquitous antibiotics for human health care and veterinary applications for antibacterial properties or as growth promoters. Large portions of FQs enter into the environment transported by human and animal excrement. With their extensive use, an increasing concentration of FQs has been detected in soil and water environment in the recent decades. In 2002, the reported articles showed that the presence concentration of FQs in wastewaters and streams of United States and Europe was in the range of nano- to micro-grams per liter (Campagnolo et al., 2002; Golet et al., 2002, 2003; Hartmann et al., 1999; Kolpin et al., 2002). Although these substances increase year by year in surface water, there has been less concern on their fate from surface water to soil, their potential effects on groundwater or even ecology system. Disturbingly, during the year of 2014 in China, the detected concentration of antibiotics in drinking water is up to a dozen nanogram per liter (Ye and Zhang, 2015). Their potential effects are mainly shown as follows: gastrointestinal intolerance, dysfunction of the central nervous system, skin allergic, phototoxicity, liver toxicity, cartilage toxicity (Klecak et al., 1997; Traynor et al., 2000; Zhang et al., 2003). Considering their potential impacts on human health and ecosystem, increasing significant concerns have been paid on FQs pollution and their fate in water and soil environment.

There is usually more than one type of FQs in the aquatic environment. From the surveys of 20 antibiotics in reclaimed water and groundwater in the fifteen cities of China, FQs were the dominant antibiotics pollutants with a higher concentration than any other types of antibiotics in northern China, especially OFL, NOR, ENR, which have a concentration range of n.d ~ 1.12×10^3 ng/L, n.d ~ 703 ng/L, n.d ~ 49.0 ng/L, respectively (Ma et al., 2015). However, it is extremely difficult to understand and master the compounds fate of FQs in the "real" surface water and wastewater treatment processes owing to the complicated influential factors, let alone in soil/groundwater. FQs have a low mobility, high partitioning and low biodegradation rates in loamy sand soils (Golet et al., 2002). From the reported literature review, photolysis and adsorption-desorption are the most influence transport factors of FQs in soil, and further influence the occurrence of FQs in groundwater. Zhang (2013) have studied the photolysis of FQs and revealed that photolysis was the main degradation way of

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enoxacin and lomefloxacin. Nowara et al. (1997) have studied the adsorption of ciprofloxacin to soil and pure clay minerals which indicated that ciprofloxacin (CIP) was easily sorbed to soil, especially to pure clay minerals, and the results showed that cation bridging was the major mechanism responsible for FQs sorption. Gu and Karthikeyan (2005) have studied clay minerals like hydrous oxides of aluminum (HAO) and iron (HFO) and concluded that HAO and HFO were the important mineral components of environmental particles, which accounted for up to 50.0% of the total soil mass and sorbed more than 90.0% FQs in highly weathered soils. Compared with the above investigations of single FQ, the coexistence of FQs would bring more complicated sorption mechanism and then influence groundwater quality (Bonin and Simpson, 2007; Li and Werth, 2001). Therefore, it is necessary to investigate the effects of interactions of different FQs on soil, and further obtain influence mechanism and occurrence of FQs in groundwater.

The objective of this study is to investigate adsorption and desorption of FQs onto soil, explore their fate and occurrence in soil and groundwater, and further assess the FQs risk in groundwater. In the present study, the occurrence of OFL, ENR and NOR in reclaimed water and groundwater has been studied. Adsorption-desorption of the single and coexistence of OFL, ENR and NOR onto soil has been investigated, and then a transport model has been used to predict the risk of groundwater contamination.

2. Material and methods

2.1. Chemicals and Reagents

HPLC-grade methanol, HPLC-grade acetonitrile and LC/MS formic acid were purchased from Merck KGaA (Germany), J.T.Baker (USA) and Fisher Scientific (Pittsburgh, PA, USA), respectively, while OFL (99.0%), NOR (99.1%), ENR (99.0%) were purchased from Dr. Ehrenstorfer GmbH, Germany (Augsburg, Germany). The properties of OFL, NOR and ENR were listed in Table S1. Ultrapure water was prepared with the Milli-Q unit (Millipore, USA).

2.2. Site description and sample preparation

In order to obtain the occurrence of OFL, ENR and NOR in reclaimed water and groundwater, Beijing and Changzhou were selected to studied. All reclaimed water samples were collected from the reclaimed water treatment plant (RWTP) outlets or the effluent of WWTP, whilst groundwater samples were collected from

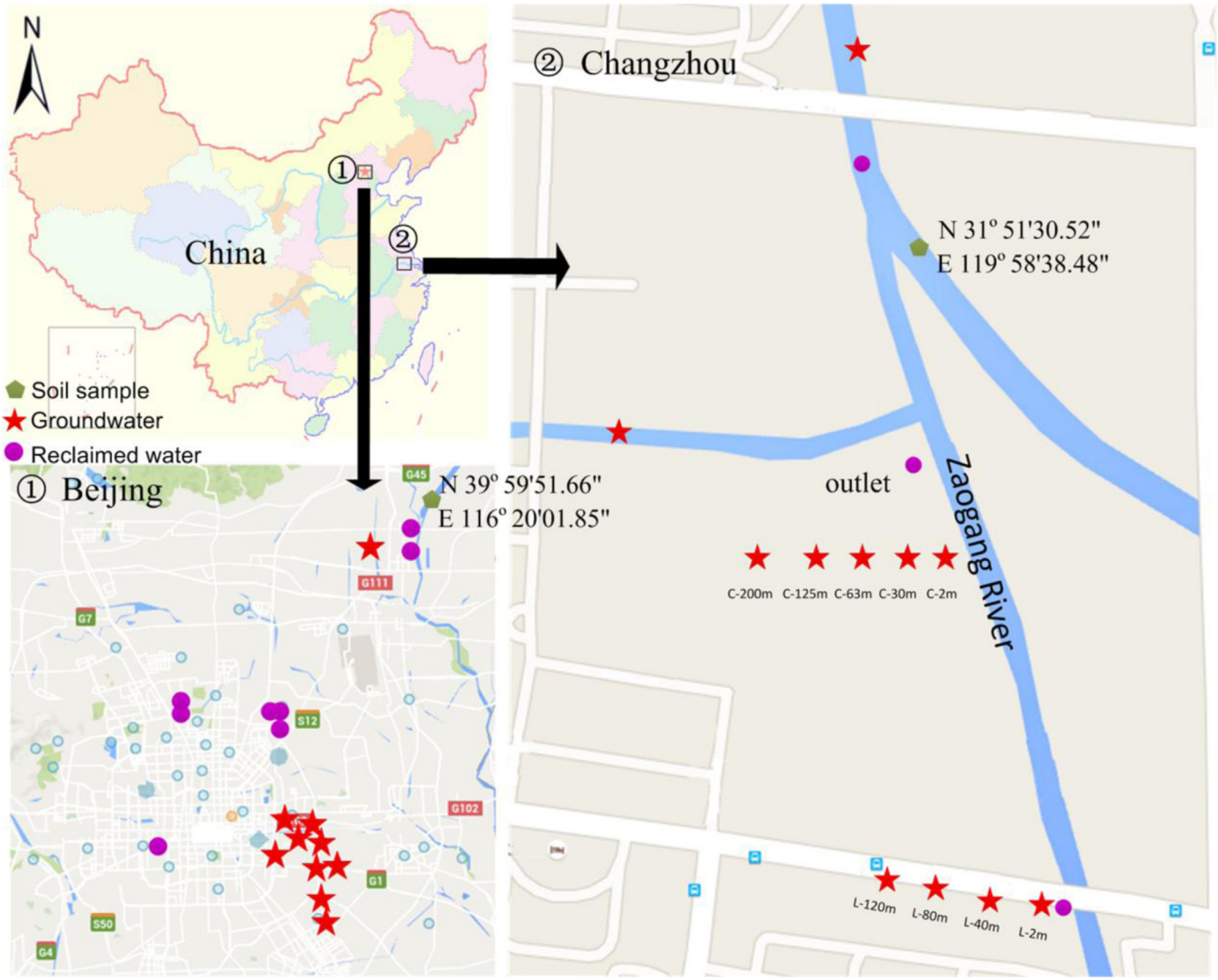

Fig. 1. Map with the location of the sampling points.