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Occurrences and regional distributions of 20 antibiotics in water bodies during groundwater recharge

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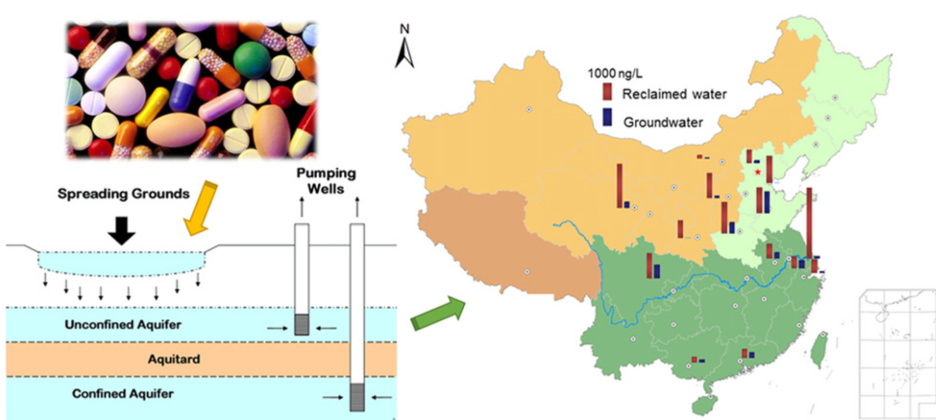
HIGHLIGHTS

- Antibiotic pollution was investigated nationwide in China.
- Regional differences in antibiotics pollution were observed.
- SMZ, OFL and ERY were the top three antibiotics with high ecotoxicological risk.

GRAPHICAL ABSTRACT



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ABSTRACT

To develop a better understanding of the pollution conditions of antibiotics during the groundwater recharge process, a nation-wide survey was conducted across China for the first time. Overall, 15 recharge sites employing reclaimed water located in different humid, semi-humid and semi-arid regions were selected for analysis of the presence of the 20 most commonly used antibiotics, including tetracyclines (TCs), fluoroquinolones (FQNs), sulfonamides (SAs) and macrolides. All types of antibiotics were detected at concentrations of 212–4035 ng/L in reclaimed water and 19–1270 ng/L in groundwater. FQNs were the predominant antibiotics in reclaimed water samples (38%), followed by SAs (34%). In the SAs group, sulfamethoxazole (SMZ) and sulfamonomethoxine together with trimethoprim accounted for 78% of the total, while ofloxacin (OFL) and norfloxacin accounted for 90% of the FQNs, and doxycycline and oxytetracycline accounted for 82% of the TCs. The concentrations in groundwater were generally 1–2 orders of magnitude lower than in reclaimed water. The three most common antibiotics were OFL, erythromycin (ERY) and SMZ. Similar occurrences of different group antibiotics might be evidence of the influence of groundwater recharge by reclaimed water. FQNs were predominant in northern China, while SAs were predominant in the south. Ecotoxicological risk assessment showed that SMZ, ERY and OFL had the top three hazard quotient values, indicating they should receive preferential treatment before recharging. Overall, these results provide a theoretical basis for development of a recharge standard in China.

Abbreviations: TCs, tetracyclines; FQNs, fluoroquinolones; SAs, sulfonamides; SMZ, sulfamethoxazole; OFL, ofloxacin; ERY, erythromycin.

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1. Introduction

Groundwater is the most important source of water in China, especially in the north, which contains many arid and semi-arid climate zones. According to a study released by the State Council in China, 400 out of 657 cities use groundwater for drinking water in northern China, and 65% of all drinking water in this region originates from groundwater. The large-scale overuse of groundwater has led to a serious shortage of groundwater, resulting in investigation of the potential for groundwater recharge using reclaimed water. Owing to the extremely high water quality required for direct aquifer injection, studies have investigated the use of surface percolation to recharge aquifers with reclaimed water. However, during recharge, certain contaminants that pose risks to the environment and human health may also enter groundwater systems. Indeed, many contaminants, including antibiotics, hormones, and polycyclic aromatic hydrocarbons have been detected in groundwater, especially in areas disturbed by anthropogenic activity.

Antibiotics have been extensively used during the past few decades; however, 70% of these are excreted unchanged into wastewater on average (Kümmerer, 2009). Their frequent use and continual input has led to accumulation of antibiotics in the environment (Gao et al., 2012). The amount of human antibiotics used by the general population is greater than that used in hospitals (Thomas et al., 2007); thus, wastewater treatment plants (WWTPs) have become hotspots of antibiotics. Additionally, veterinary antibiotics can enter the environment through manufacturing plants, process effluents, overland flow runoff, and transport from fields to which agricultural waste has been applied (Heberer, 2002). WWTPs play important roles in gathering and eliminating of antibiotics. Unfortunately, many existing water treatment units that employ flocculation, sedimentation and active sludge treatment, as well as some advanced systems that use disinfection and ultrafiltration do not effectively remove antibiotics (Peng et al., 2006); therefore, they are still released into aquatic systems at levels as high as tens to thousands of nanograms per liter (Jiang et al., 2013; Manzetti and Ghisi, 2014; Verlicchi et al., 2012; Zhang et al., 2013). In cases of bank filtration, contaminated river water can flow into groundwater systems, resulting in their contamination.

In this investigation, typical groundwater recharge sites in 15 cities across China were investigated and basic information was collected. In addition, samples of reclaimed water and groundwater were collected to detect the concentrations of 20 antibiotics to obtain a general understanding of antibiotic pollution in groundwater throughout China. High risk antibiotics that require treatment before discharge were then screened by the risk quotient method. The results presented herein provide a theoretical basis for development of a guideline for antibiotic controls during groundwater recharge projects.

2. Materials and methods

2.1. Sampling sites

Fifteen typical cities in China that use reclaimed water for groundwater recharge were selected owing to their different climatic and geological conditions. For the climate parameter, temperature and precipitation were considered. Locations and detailed information regarding the sites are shown in Fig. 1 and Table 1. Cities C1–C4 were located in Region 1, which is semi-humid, while C12–C15 were located in Region 3, which is semi-arid. Both of these regions are in northern China. Cities C5–C11 were located in Region 2, which is humid and has a relatively higher annual precipitation and temperature. In each city, satisfactory sampling sites were selected based on the presence of reclaimed water reused as a groundwater replenishment source through infiltration by rivers or lakes, available groundwater monitoring wells, and river and lake beds that were not lined with concrete and retained a natural permeability.

2.2. Chemicals

Twenty antibiotics were selected for this study based on known antibiotics use in China. These antibiotics could be classified into four groups, tetracyclines group (TCs), including tetracycline (TC), chlortetracycline (CTC), doxycycline (DO) and oxytetracycline (OTC); fluoroquinolones group (FQNs), including ciprofloxacin (CIP), OFL, norfloxacin (NOR), enrofloxacin (ENR), lomefloxacin (LOM), and difloxacin (DIF); sulfonamides group (SAs), including trimethoprim (TMP), sulfadiazine (SD), sulfamerazine (SM1), sulfamethazine (SM2), sulfisoxazole (SIZ), SMZ, sulfamonomethoxine (SMM), sulfachlorpyridazine (SCP) and sulfathiazole (STZ); and macrolides group (MCs), including ERY and azithromycin (AZM). Since TMP is usually used as a SA drug synergist, it was categorized into the SAs group. The properties of targeted antibiotics are listed in Table 2. All antibiotics standards were purchased from Dr Ehrenstorfer (Augsburg, Germany). The chemicals were of >98% purity and used directly in experiments. Standard antibiotic-mix stock solutions with concentrations up to 500 mg/L were prepared in methanol (HPLC grade) and stored in the dark at −20 °C before use. Working solutions with different concentrations were prepared by diluting the stock solutions before each analytical run.

2.3. Sample collection and processing

All samples were collected between April and early July of 2013. Reclaimed water samples were collected from the outlet of reclaimed water treatment plants and groundwater samples were collected from monitoring wells. Duplicate samples (1 L each) for detection of antibiotics were collected into brown glass bottles. Samples were pretreated immediately upon arrival in the laboratory.

2.4. Quantification of antibiotics

Analytical procedures for the 20 antibiotics in reclaimed and groundwater samples were optimized based on EPA Method 1694 (EPA, 2007), with some modifications. Briefly, water samples were filtered through a muffle furnace-burned glass fiber filter (47 mm in diameter with a 0.7 μm pore size) (Whatman, USA). Next, 500 mg Na_2EDTA was added to the filtrate to complex divalent cations and the pH value was then adjusted to 3 with HCL (6 mol/L). An antibiotic mix standard solution was then spiked into one of the duplicate filtrates to monitor the pretreatment loss. Solid phase extraction (SPE) was conducted using the Supelco Visiprep SPE system (Supelco, USA), and oasis hydrophilic–lipophilic balance (HLB) cartridges (6 mL/500 mg, Waters, UK) were used to gather antibiotics. The cartridges were pretreated with 5 mL methanol followed by 3 × 5 mL ultrapure water, after which samples were passed through at a loading rate of 1–2 mL min^{-1}. After all samples were loaded, the HLB cartridges were washed with 10 mL ultrapure water and then lyophilized (Labconco Freeze Dry System, USA) for at least 8 h before being eluted with 2 mL of methanol three times. The final eluate was collected into a glass tube and evaporated to dryness using a pressure gas blowing concentrator (Anpel, China). Next, 1 mL methanol containing 100 ng of each internal standard substance was added to redissolve the target antibiotics. Here, sulfamethoxazole (SMZ)-$^{13}C_6$, CIP-$^{13}C_3^{15}N$, erythromycin (ERY)-$^{13}C_2$ and d_3-thiabendazole were selected for calibration of SAs, FQNs, MCs and TCs group antibiotics according to the EPA method (EPA, 2007).

Experiments were performed on an ultraperformance liquid chromatography system and tandem mass spectrophotometer (Waters, UK) equipped with a Waters Acquity UPLC BEH C18 column (2.1 × 50 mm, particle size 1.7 μm). Mass analysis was carried out on a Quattro Premier XE tandem quadrupole mass spectrometer operating in positive ion electrospray mode (ESI(+)) (Waters, USA). The procedure was described in detail in the Supplementary Information.