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Occurrence and risk assessment of pharmaceuticals and personal care products and endocrine disrupting chemicals in reclaimed water and receiving groundwater in China

Zhen Li [a], Xi Xiang [a], Miao Li [a], Yeping Ma [a], Jihua Wang [b,**], Xiang Liu [a,*]

[a] School of Environment, Tsinghua University, Beijing 100084, China
[b] Life Science and Technology College, Harbin Normal University, Harbin 150080, China

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ABSTRACT

Groundwater recharge using reclaimed water is considered a promising method to alleviate groundwater depletion. However, pollutants in reclaimed water could be recharged into groundwater during this process, thereby posing a risk to groundwater and human health. In this study, 12 cities in northern China were selected for reclaimed water and groundwater sampling. Analysis of the samples revealed the presence of nine pharmaceutical and personal care products (PPCPs) and five endocrine disrupting compounds (EDCs). In reclaimed water, all the PPCPs and EDCs were found, with sulpiride (SP) and estriol (E3) being most frequently detected. In groundwater samples, only ketoprofen (KP), mefenamic acid (MA), nalidixic acid (NA) and SP were detected among PPCPs, while bisphenol-A (BPA) was dominant among the target EDCs. The risk quotients (RQs) of all target PPCPs and EDCs except 17α-ethinyl estradiol (EE2) and E3 were below 1 in groundwater samples, indicating that EE2 and E3 deserve priority preferential treatment before recharging.

1. Introduction

PPCPs are emerging environmental pollutants that have attracted a great deal of public attention (Kwon and Rodriguez, 2014; Ngoc et al., 2014; Padhye et al., 2014). In this study, in order to better discuss EDCs, they were separated. There are several direct and indirect pathways through which PPCPs and EDCs can be introduced into aqueous environments. Wastewater treatment plants (WWTPs) are insufficient to remove PPCPs and EDCs and have been identified as primary sources of those pollutions in aquatic systems (Barnes et al., 2008). However, the likelihoods of contamination with PPCPs and EDCs in the groundwater as a result of discharge of reclaimed water depend on several factors, the most important being physico-chemical properties of pollutants, the type of wastewater treatment technology implemented and climatic conditions (e.g., rainfall, temperature and level of sunlight).

Methods of groundwater recharge using reclaimed water have been rapidly developed around the world to replenish decreasing groundwater resources and declining water tables. In China, 0.69×10^8 m^3 of reclaimed water was recharged into groundwater during 2007 (Guo et al., 2012), and this process was especially common in northern China owing to water shortage. In Beijing city, 18×10^6 m^3/y of wastewater was treated as reclaimed water from 2008 (Zheng et al., 2015).

Many studies have focused on the concentration of pollutants in influent and effluent of WWTPs (Guerra et al., 2014; Kosma et al., 2014; Sun et al., 2014) and their impact on surface water (Al-Odaini et al., 2013; Tran et al., 2014). However, a few studies (Cabeza et al., 2012; Estevez et al., 2012; Karnjanapiboonwong et al., 2011; Lapworth et al., 2012; Ngoc et al., 2014; Stuart et al., 2014a; Teijon et al., 2010) have reported the occurrence of PPCPs and EDCs in reclaimed water and receiving groundwater. Moreover, the national distribution of PPCPs and EDCs in reclaimed water and receiving groundwater has rarely been reported.

Thus, in this study, we conducted a detailed investigation of nine PPCPs and five EDCs (bezafibrate (BF), clofibric acid (CA), carbamazepine (CBZ), caffeine (CF), indomethacine (IM), ketoprofen (KP), mefenamic acid (MA), nalidixic acid (NA), SP, BPA, EE2, estrone (E1), 17β-estradiol (E2) and E3) to gain insight into their occurrence in reclaimed water and receiving groundwater in

* Corresponding author. Tel.: +86 010 62772485; fax: +86 010 62785685.
** Corresponding author. Tel.: +86 0451 88060780; fax: +86 0451 88060780
E-mail addresses: wangjihua333@hotmail.com (J. Wang), x.liu@tsinghua.edu.cn (X. Liu).

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China. To explore the spatial variation of the occurrences and concentrations of PPCPs and EDCs in reclaimed water and receiving groundwater, 12 cities in northern China were selected as targets for reclaimed water and groundwater sampling.

2. Materials and methods

2.1. Site description

Twelve representative cities were selected from northern China. Water samples (12 reclaimed water samples and 12 groundwater samples) were collected from April 2013 to July 2013 from 12 cities in 11 provinces in China (Table 1 and Fig. 1). All reclaimed water was recharged through surface infiltration by rivers or lakes.

Owing to costs and other environment conditions, for each city only one typical reclaimed water recharge site for groundwater supplement was selected. If no reclaimed water was available, the effluent of a domestic WWTP was selected as an alternative. In addition, groundwater that had been influenced by reclaimed water was sampled. Groundwater sampling sites should be not too far from the recharge site of reclaimed water and the recharge sites were not lined with concrete and retained a natural permeability. The groundwater samples were collected from unconfined aquifers.

2.2. Sampling and analysis

The methods used for sampling and analysis of PPCPs and EDCs were based on those reported by Sui et al. (2011) and Li et al. (2013a). All samples were collected (1000 mL for reclaimed water and groundwater, respectively) in prewashed amber glass bottles, kept in a cooler, and transported to the laboratory.

PPCPs and EDCs in the samples were concentrated and purified prior to analysis. All samples were filtered through 0.45 μm glass filter membranes (Whatman, UK) and acidified to pH 7 for PPCPs and pH 3 with 1 M of HCl for EDCs. Next, 1 L of acidified sample was introduced to an Oasis HLB cartridge (Waters, 6 mL × 200 mg) that had been previously activated. The HLB was then eluted with 5 mL water–methanol (19:1, v/v) for PPCPs or 5 mL dichloromethane/acetone solution and 5 mL of methanol for EDCs. The EDCs extract was subsequently purified through a silica gel column (Waters, Sep-Pak Plus) and then evaporated under a gentle nitrogen stream and re-dissolved.

The concentrations of selected PPCPs and EDCs were determined using an Acquity UPLC system (Waters Corporation, USA) coupled to a Quattro Premier XE tandem quadruple mass spectrometer (Waters, USA) equipped with an electrospray ionization source. The MS/MS parameters of selected PPCPs and EDCs and the limits of detection/quantification (LOD/LOQ) are shown in Table S2.

2.3. Chemicals

The physicochemical properties of the nine targeted PPCPs and five EDCs are shown in Table S1. Standards of the target compounds were purchased from Sigma-Aldrich (Steinheim, Germany) and Dr. Ehrenstorfer (Augsburg, Germany). Stock solutions of individual compounds were prepared in methanol, and a mixture standard solution was prepared by diluting the stock solutions before each analytical run. All solutions were stored at 4 °C in the dark until analysis.

2.4. RQ and ecotoxicological risk assessment

Ecotoxicological risk was assessed based on the RQ value, which is expressed as the ratio between the measured environmental concentration (MEC) and the predicted no-effect concentration (PNEC) of an individual compound (Santos et al., 2007a). Worst case assumptions refer to cases in which the highest concentration of the target compound is detected. Therefore, the MEC corresponded to the highest measured concentration detected in groundwater samples (Gros et al., 2010; Santos et al., 2007b), while the PNEC was estimated using the acute half maximal effective concentration (EC_{50}) or half maximal lethal concentration (LC_{50}) divided by a default assessment factor (Damasio et al., 2011). For each PPCP or EDC, estimations were made based on toxicity data obtained from the Estimations Programs Interface for Windows (EPI) (US Environmental Protection Agency (USEPA), 2012) for three different representative trophic levels of the ecosystem, fish, invertebrates and algae. PNEC was estimated from the acute toxicity test results (Eq. (2)) (Ferrari et al., 2004; Ginebreda et al., 2010).

$$RQ = \text{exposure/toxicity} = MEC/PNEC \quad (1)$$

where,

$$PNEC = (EC_{50} \text{ or } LC_{50})/1000 \quad (2)$$

Table 1
Description of sampling locations in China.

Samples	City	Treatment technology	Groundwater depth (m)	Distance (km)[a]	Daily recharge quantity (10^4 m^2)	Matrix
BJ	Beijing	MBR[b]	30	5.4	10	Sandy clay
BT	Baotou	BAF[c]	6	0.45	0.46	Sandy soil
CZ	Changzhou	AA/O[d]	5	0.02	10	Loam
HF	Hefei	Coagulation-filter-disinfection	15	0.4	8	Loam
JN	Jinan	AA/O	28	0.4	18	Loam
NT	Nantong	Improved SBR[e]	5	0.3	10	Silt and sandy loam
NY	Nanyang	AA/O	20	0.03	1	Sandy soil
SY	Shenyang	MBR	60	0.66	20	Loam
TJ	Tianjin	Improved UASB[f]	10	0.5	2.38	Loam and sandy loam
TY	Taiyuan	AA/O	10	0.4	4.76	Sandy loam soil
XA	Xi'an	ORBAL[g]	70	1	10	Loam
XN	Xining	Carrousel Oxidation Ditch	10	0.6		Sandy clay

[a] Distance between the sampling locations of reclaimed water and groundwater.
[b] Membrane bioreactor.
[c] Biological aerated filter.
[d] Anaerobic-anoxic-oxic.
[e] Sequencing batch reactor.
[f] Upflow anaerobic sludge blanket.
[g] Orbal oxidation ditch.