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Spatial and seasonal variations of occurrences and concentrations of endocrine disrupting chemicals in unconfined and confined aquifers recharged by reclaimed water: A field study along the Chaobai River, Beijing

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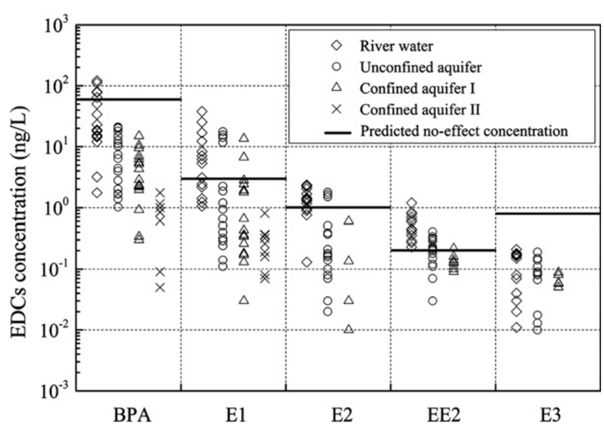
HIGHLIGHTS

- ► Five selected endocrine disrupting chemicals (EDCs) were detected in groundwater.
- ► Occurrences and concentrations of EDCs decreased with increasing depths of aquifers.
- ► Occurrences and concentrations of EDCs declined with increasing distance to river.
- ► Dry season without recharging resulted in a significant drop of EDC concentrations.
- ► Two most frequently detected compounds in groundwater were bisphenol A and estrone.

GRAPHICAL ABSTRACT



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ABSTRACT

A field study on the spatial and seasonal variations of occurrences and concentrations of five selected endocrine disrupting chemicals (EDCs), namely, estrone, 17β-estradiol, 17α-ethinyl estradiol, estriol, and bisphenol A, was conducted in Beijing, where reclaimed water is used to recharge groundwater through the permeable bed of the Chaobai River. This study collected 64 surface water samples from the Wenyu and the Chaobai Rivers and 51 groundwater samples from the unconfined aquifer (UA) and two underlying confined aquifers (CA I and CA II) at depths of 30, 50 and 80 m, respectively. EDCs were detected in 100.0%, 94.4% and 40.0% of groundwater samples from the UA, CA I and CA II, respectively, at concentrations which decreased by 1–2 orders of magnitude with depth. The occurrences and concentrations of EDCs in groundwater also decreased with the increasing distance to the river bank. In one monitoring section with seasonal wetting and drying, the occurrences and concentrations of EDCs dropped significantly during the dry season (December to March) without recharging. These results indicate that improving the removal of EDCs in reclaimed water and optimizing the management of the recharging operation could reduce the risks of endocrine disrupting chemicals.

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1. Introduction

There have been many studies on the occurrence, concentration, transport and fate of endocrine disrupting chemicals (EDCs) in aquatic environments during the past few decades. Specifically, EDCs in groundwater have been intensively studied in the following sites: artificial aquifer recharge sites (Diaz-Cruz and Barcelo, 2008), sewage disposal sites (Cajthaml et al., 2009; Stanford et al., 2010), septic tank sites (Sulleabhain et al., 2009), obsolete landfill sites (Kuch et al., 2010), urban aquatic environments (Musolff et al., 2010), animal feed operation sites (Steiner et al., 2010; Zhao et al., 2010), wastewater lagoons (Bartelt-Hunt et al., 2011), municipal biosolid reuse fields (Giudice and Young, 2011), farms using reclaimed water for irrigation (Mahjoub et al., 2011), infiltration galleries (Mansilha et al., 2011), and bank filtration sites (Wolz et al., 2011). In the aforementioned sites, a large amount of sewage, reclaimed water and river water containing sewage effluents, or septic tank effluents, have infiltrated groundwater. Based on the previous researches, it is possible to obtain basic fundamental data of occurrences and concentrations of EDCs in groundwater. However, it is difficult to capture their spatial and seasonal variations, mainly due to limited monitoring wells and few sampling campaigns from a single aquifer.

Most previous studies have focused on unconfined aquifers, perhaps because it was considered that confined aquifers should be protected by the overlying aquiclude. Other constraints have been the high limit of quantification (LOQ) of EDCs and often poor reproducibility and variable detection limits (Katz and Griffin, 2008; Zhou et al., 2010; LaFleur and Schug, 2011). Furthermore, the seasonal variation of occurrences and concentrations of EDCs has not been well documented in the aquifer with seasonal wetting and drying.

Therefore, the objective of this research is to explore the spatial and seasonal variations of the occurrences and concentrations of EDCs in unconfined and confined aquifers recharged by reclaimed water along the Chaobai River, Beijing. We measured steroid estrogens and endocrine disrupting phenolic compounds (Bisphenol A, BPA) which are of particular concern compared to other classes of EDCs found in wastewater and reclaimed water (De Alda and Barcelo, 2001; Lagana et al., 2001; Joss et al., 2005, 2006; Kim et al., 2007; Fernandez et al., 2008; Sumpter and Johnson, 2008; Xu et al., 2008; Stalter et al., 2011; Yi et al., 2011). Steroid estrogens, including estrone (E1), 17β-estradiol (E2), 17α-ethinyl estradiol (EE2), and estriol (E3), have relatively high endocrine disrupting capabilities at very low concentrations (Table S1). BPA, widely used in food packaging, was proposed as one of the most suitable reclaimed water markers in groundwater because of its high concentration in reclaimed water, high resistance to biodegradation and high migratory aptitude (Musolff et al., 2010; Li et al., 2013). These five compounds vary in physico-chemical properties (Table S1). Their octanol–water partition coefficient ($\log K_{OW}$) is in the order: EE2 > E2 > E1 > BPA > E3, which indicates that E3 is the most mobile and EE2 is the least. In addition, their biodegradability was in the order: BPA > EE2 > E2 (Ying and Kookana, 2005). E1 and E3 were reported to be the biodegradation products of E2 and EE2 (Li et al., 2013). Thus, these five compounds are considered to represent EDCs with different physico-chemical properties and biodegradability.

2. Materials and methods

2.1. Site description

The study area is located in the northeast of Beijing (N 40°10′, E116°41′), and a map showing a section of the Chaobai River is depicted in Fig. 1c. The Wenyu River water, mainly composed of wastewater treatment plant effluent, is further treated in a membrane bio-reactor (MBR) to produce reclaimed water. Then the reclaimed water is introduced to the Chaobai River (Fig. 1b), where there is no water from upstream. Reclaimed water, about 38,000,000 m^3/year, is released at MP 2 and feeds into the river body among MP 2, MP 8 and MP 10. The river water is managed by two sluices (at MP 8 and MP 10) and a dam (near MP 5) to control water levels and to separate reaches of the river (Fig. 1c). The intake area is separated by the dam. The reclaimed water, released at MP 2 all year around, flows into the area among MP 2, MP 5 and MP 8. The river water near MP 5 is pumped into the area among the dam, MP 9 and MP 10 only from April to November. Thus, river water in the latter area extends to the zone near MW 4 from April to November (the wet season) and shrinks back to the zone between MP 9 and MP 10 from December to March of the following year (the dry season). Thus, groundwater near the Sluice 2 is only recharged by reclaimed water in the wet season. Hence, a cycle of wetting and drying is formed and the time–length ratio of the wet and the dry seasons is 2:1. The recharge project has run for nearly 4 years since 2007. Besides, some water containing treated and untreated municipal water from nearby factories and villages also flows into the area near the Sluice 2.

The intake area is located in the alluvial fan of the Chaobai River. The geological condition of the study area is shown in Fig. 1d and summarized as follows. Generally, the vertical profile is composed of three aquifers (sand and gravel) and two impervious layers (silt and clay) with different depths. The first aquifer is mainly composed of cobble and boulder with a buried depth of 0–40 m. Groundwater in this layer is partly dewatered due to overexploitation. The second aquifer mainly consists of gravel and rubble with a buried depth of 40–70 m. The permeability coefficient is 100–400 m^3/d, and the water yield of a single well is greater than 10,000 m^3/d. The third aquifer is buried at a depth of 70–250 m, and is mainly composed of sandy gravel and coarse sand. In this aquifer, the water content is abundant, the water permeability coefficient is 60–100 m^3/d, and the water yield of a single well is greater than 5000 m^3/d. The uppermost aquifer (UA) is unconfined and therefore vulnerable to pollution. The piezometric heads of the latter two aquifers are 5–50 m above their elevation, which indicates that the two impervious layers (mainly silty clay) buried between the three aquifer layers act as aquicludes. Therefore, the second and third aquifers are considered confined aquifers (CA I and CA II, respectively).

As demonstrated in Fig. 1, Tables S2 and S3, eleven river water monitoring points (MP 1–11) and eleven groundwater monitoring well groups (MW 1–4, 13–15, 22, 23, 26 and 32) in three water quality monitoring sections (MS I, II and III) form a monitoring network in the study area. The distance to the source of the reclaimed water of MP 1–9 is from 0 to 7.2 km (Table S2). Since the water bodies between MP 1–10 and MP 11 are not connected, the reclaimed water has no influence on the river water at MP 11. Thus, MP 11 acts as a control point of the river water in the study area. MW 1, MW 2, MW 3, MW 4, MW 13, MW 14, MW 15, MW 22, MW 23, MW 26 and MW 32 are about 10, 20, 30, 20, 380, 170, 20, 20, 100, 200 and 810 m to the river bank, respectively. Each well group (except MW 4 and MW 26) consists of three wells with depths of 30, 50, and 80 m connected to UA, CA I and CA II, respectively. MW 4, as well as MW 26, include two wells with depths of 30 and 50 m connected to UA and CA I, respectively. The information for the river water monitoring points and the groundwater monitoring wells is summarized in Tables S2 and S3, respectively.

2.2. Sampling

We collected 64 river water samples and 51 groundwater samples between April 2011 and March 2012. Among the 64 river water samples, 44 samples were collected in the wet season (at MP 1–11 in April, June, August and October 2011), and 20 samples were collected in the dry season (at MP 1–9 and MP 11 in December 2011 and March 2012). Among the 51 groundwater samples, 20 samples were collected in the wet season (at MS II and III in November 2011) and 31 samples were collected in the dry season (at MS I, II and III in March 2012). Since the groundwater samples were collected from the monitoring wells with different distances to the river bank and aquifers with different depths,