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Endocrine disrupting compounds reduction and water quality improvement in reclaimed municipal wastewater: A field-scale study along Jialu River in North China

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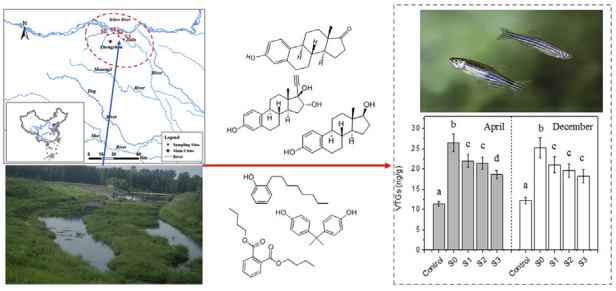
HIGHLIGHTS

- COD and NH_3-N could be effectively removed through the ecological purification.
- The natural EDCs could be effectively eliminated in 18.5 km-scale restored river.
- The synthetic EDCs were difficult to remove through purification of restored river.
- The bioassays *in vitro* showed that purified water had no direct estrogenic activity.
- The purified water still had the estrogenic activity to fish after 21-day exposure.

GRAPHICAL ABSTRACT



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ABSTRACT

Several ecological restoration projects have been constructed along urban rivers in North China to purify reclaimed municipal wastewater and improve the water quality of urban rivers. These projects attempt to address several environmental issues, including treating water contamination that is not fully remediated through standard wastewater treatment. This study investigated the efficiency of reducing endocrine disrupting compounds (EDCs) and estrogenic activity in reclaimed municipal wastewater along an 18.5 km field-scale ecological restoration project in Jialu River. The river only receives reclaimed municipal wastewater without natural effluent in North China. Data show that the chemical oxygen demand (COD) and ammonia nitrogen (NH_3-N) of reclaimed municipal effluent improved when compared to the Chinese surface water standard, and natural estrogens, such as estrone (E1) and estradiol (E2), were effectively removed during ecological restoration purification processes. The estradiol activity based on measured EDCs concentrations (ΣEEQ_{EDC}) was less than 0.01 ng/L after the ecological purification of restoration river; however, synthetic endocrine disrupting compounds in reclaimed municipal wastewater, such as octylphenol (OP), bisphenol A (BPA), and dibutyl phthalate (DBP), were difficult to eliminate. The bioassays of MDA-kb2 cells and recombinant yeast *in vitro* showed

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no direct androgen response and estrogen effect in reclaimed municipal effluent after the purification processes. However, a chorionic long-term (21d) exposure *in vivo* test showed that exposure to the reclaimed municipal effluents, even after river purification, still significantly induced yolk protein vitellogenin (Vtg) in male zebrafish, leading to abnormal expression of testosterone (T) and E2. This indicates continued potent estrogenic activity to aquatic organisms, even after treatment and purification.

1. Introduction

Closely associated with accelerating urbanization and industrial growth, river pollution is a major problem for Chinese cities, especially for urban rivers in North China. Municipal wastewater reclamation and reuse is an effective way to mitigate both water resource shortages and some elements contributing to water contamination(Cao et al., 2009). Many urban rivers in North China do not have a natural water base flow (they are not fed by upland water or supplemented by groundwater), and been filled with municipal wastewater.

Effluents from municipal wastewater plants (MWPs) are discharged into urban rivers as landscape water after secondary bio-treatment or chlorinated secondary bio-treatment (Sun et al., 2014; Wang et al., 2014a). To further improve water quality of reclaimed municipal wastewater and improve the river's ecosystem, some urban river ecosystems have been constructed, with the goal of enhancing the capacity to purify reclaimed municipal wastewater and improve river water quality (Sheng et al., 2012, 2013; Avila et al., 2013). The advanced purification of reclaimed municipal wastewater using ecologically restored rivers has gained attention in China, because these treatment environments require less time, space, and cost compared with other technologies. Purification of reclaimed municipal wastewater in ecological restored rivers has been studied, but few studies have reported on their effectiveness. Sheng et al. (2013) reported that a 23 km river remediation project decreased COD from 250 mg/L to 50 mg/L, and decreased NH_3-N from 27 mg/L to 4 mg/L in the Shijin River in North China. A separate field-scale experiment removed 70% COD in an ecologically restored urban river in Guangzhou in South China (Sheng et al., 2012, 2013; Avila et al., 2013).

EDCs are natural and synthetic chemicals, with the potential to negatively affect human and wildlife endocrine systems. EDCs have been found in surface water, groundwater, and drinking water (Jürgens et al., 2002). When present in wastewater at extremely low concentrations (measured at ng/L), traditional MWP treatment methods do not effectively remove EDCs (Murk et al., 2002). As such, municipal wastewater has been confirmed as a major source of EDCs in urban rivers.

EDCs at ng/L-levels in aquatic environments are biologically active concentrations, and may disrupt endocrine activity in wildlife (Williams et al., 2003). These effects have been observed in mammals, birds, reptiles, fish, and mollusks from Europe, North America, and other areas, and deformations vary from subtle changes to permanent alterations, including changed sexual behavior, and feminized and masculinized sex organs (Vos et al., 2000). For example, male common carp (*Cyprinus carpio*) collected from the effluent channel below the St. Paul, Minnesota (United States) metropolitan sewage treatment plant experienced disruptive endocrine effects (Vos et al., 2000), and intersex was seen at a high rate in roaches (*Rutilus rutilus*) in a wild river in the United Kingdom (Jobling et al., 1998). Another study investigated the purification potential of River Aire and River Thames (United Kingdom), downstream of MWPs, in the spring, summer, and winter. The study found that concentration of estrone (E1) and estradiol (E2) and dissolved organic carbon from December to April was much higher than during August (Jürgens et al., 2002), indicating that the river's purification capacity in the winter was not as good as during other months.

Jialu River, a typical urban river in North China, receives only Wulongkou MWP effluent, without any natural upland water. The water quality in the upper stream of the Jialu River has historically been less than the V level of the Chinese surface water standard (Chenqiao section, (N 34° 52′ 09.1″, E 113° 43′ 30.3″)). The first objective of this study was to evaluate water quality improvements and the river's ability to remove COD, NH_3-N and other pollutants during the coldest months of a year. The second objective was to evaluate the efficiency of EDCs removal and estrogenic activity reduction through river purification. The third objective was to compare the *in vitro* and *in vivo* endocrine disrupting effects of river water.

2. Material and methods

2.1. The field-scale ecological restoration project along the Jialu River

The Jialu River is a small branch of Huai River, located in Zhengzhou City, in the Henan Province of China (Fig. 1). The regional climate is monsoon: hot and rainy in summer (470 mm rainfall), and cold and dry in winter (42 mm rainfall). The Jialu River only receives effluent from WLK MWP, which treats all municipal wastewater for 4-million people in south Zhengzhou City. Channel widths in the upper reaches of the Jialu River range from 120 to 170 m and channel depth ranged from 1.5 to 3.0 m, and the river receives approximately 150–200 kilotons of WLK MWP effluent daily. From 2009 to 2011, an ecological restoration project (Studies and pilot practices of key technique of ecological purification of industrial and urban life-hood wastewaters, the National Water Pollution Control and Treatment Science and Technology Major Project, 2009ZX07210-001) was constructed at approximately 18.5 km scale (a near nature wetland from Shijiahe section to Chenqiao section) to further purify the MWPs effluent and restore the Jialu River's aquatic ecology. In general, the original ecosystem of Jialu River had been destroyed before, and a new near nature wetland was rebuilt in this river. The river channel was also widened from 30–60 m–120m–170 m. Many kinds of aquatic plants, such as Acorus calamus L., Ceratophyllum demersum L., *Cyperus imbricatus* Retz., and *Scirpus tabernaemontani Vahl*, were planted in river. Three rubber dams and a solar aerator were set up at the Chenqiao section and were used to add the DO in river. The project site is located between S0 (Shijiahe section, the first rubber dam, N 34° 52′ 13.5″, E″ 113° 34′ 02.1″) and S3 (Chenqiao section, N 34° 52′ 09.1″, E 113° 43′ 30.3″). Approximately 7.7 km of the river lies between S0 and S1 (the second rubber dam, N 34° 52′ 12.2″, E″ 113° 36′ 04.2″); approximately 4.0 km lies between S1 and S2 (the third rubber dam, N 34° 52′ 13.1, E" 113° 41′ 24.4″); and approximately 6.8 km lies between S2 and S3 (Fig. 1). Based on 30 years of