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# Possible effect of submarine groundwater discharge on the pollution of coastal water: Occurrence, source, and risks of endocrine disrupting chemicals in coastal groundwater and adjacent seawater influenced by reclaimed water irrigation

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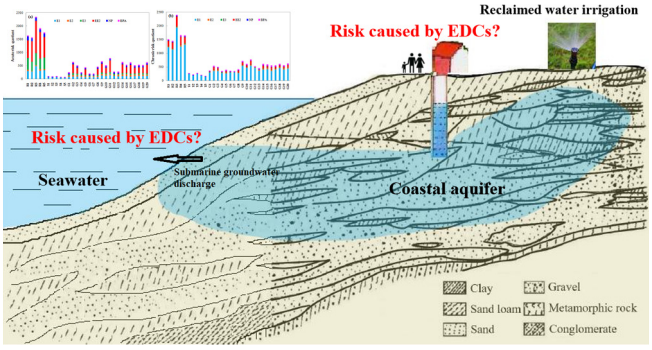
## HIGHLIGHTS

- Total concentrations of EDCs in groundwater were in the range of 46.3–66.5 ng/L.
- Ecological risks posed by EDCs in groundwater and seawater were very high.
- Estrone averagely contributed to 65.2% of total estradiol equivalent concentration.
- Reclaimed water was proved to be the main source of EDCs in coastal groundwater.
- 82% of EDCs was discharged into Laizhou Bay through submarine groundwater discharge.

## GRAPHICAL ABSTRACT

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## ABSTRACT

This study investigated occurrence, source, and risks of endocrine disrupting chemicals (EDCs) in coastal groundwater and adjacent seawater influenced by reclaimed water irrigation in a typical coastal region of China. All target EDCs were detected in coastal groundwater and reclaimed water while only estrone, bisphenol A (BPA), and nonylphenol were detected in seawater. Concentrations of BPA that was the predominant EDC in coastal groundwater ranged from 35.9 to 52.9 ng/L and estradiol was easy to accumulate in groundwater under reclaimed water irrigation. Concentrations of all target EDCs in seawater ranged from 18.9 to 30.9 ng/L, much lower than those in groundwater. Ecological risks posed by EDCs in groundwater and seawater were very high. Estrone contributed to 51.3%–62.9% of total acute risk quotients for seawater while detected 17-α-ethynylestradiol contributed to 41.1%–56.2% of total acute risk quotients for groundwater. Estradiol equivalent concentrations of target EDCs in groundwater/seawater were in the range of (3.5–7.6)/(1.4–2.3) ng/L while non-cancer risks posed by EDCs in groundwater/seawater were acceptable. Dual-isotope analysis illustrated that reclaimed water was the main source of EDCs in coastal groundwater. About 82% of EDCs was discharged into the Laizhou Bay through the submarine groundwater discharge based on the flux analysis. The pollution of the coastal groundwater through reclaimed water irrigation subsequently led to EDCs pollution of the adjacent seawater through the submarine groundwater discharge. Therefore, effective control of EDCs in

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reclaimed water for irrigation will be beneficial to control EDCs in groundwater and seawater of the coastal regions.



## 1. Introduction

Endocrine disrupting chemicals (EDCs) are regarded to pose potential health threats since they can disturb hormone biosynthesis and metabolism or cause a deviation from normal homeostatic control/reproduction (Nowak et al., 2019). Among these EDCs, natural estrogens including estrone (E1), estradiol (E2), and estriol (E3), the synthetic estrogen 17-α-ethynylestradiol (EE2), bisphenol A (BPA), and nonylphenol (NP) have attracted global attention due to their negative effects on ecosystem and human health (Balabanič et al., 2011; Nowak et al., 2019; Zbucka-Kretowska et al., 2018). BPA as plastic additive has been widely used in the production of polycarbonate plastic and other plastics (Usman and Ahmad, 2016). NP, common biodegradation product of non-ionic surfactant nonylphenol polyethoxylates (NPEOs) widely used in the world (Lu et al., 2007, 2008, 2009), has shown estrogenic activity and possessed many isomers with a phenol group and a linear or branched carbon chain of nine carbon atoms (Lu et al., 2007). Steroidal estrogens (including E1, E2, and E3) are essential natural EDCs existing in human and animal bodies while EE2 is synthesized and used for birth control (An et al., 2018; Damkjaer et al., 2018; Oliveira et al., 2016). EDCs have been widely detected in various environmental matrices (An et al., 2018; Damkjaer et al., 2018; Pignotti and Dinelli, 2018; Rhind et al., 2013) and foodstuffs (He et al., 2015; Lu et al., 2015) to have potential exposure to humans.

Irrigation for agriculture is one important pathway of water usage and approximately 60% of global freshwater withdrawals have been used for irrigation (USGS , 2005). Reclaimed water is an alternative water resource widely used for irrigation due to increasing shortage of freshwater resources (Gonzales-Gustavson et al., 2019; Wu et al., 2010). However, reclaimed water might become an important pollution source of emerging contaminants including EDCs for food crops and groundwater (Gonzales-Gustavson et al., 2019; Li et al., 2015; Wu et al., 2010).

Groundwater is an important water resource in the world, especially in coastal zone. Coastal groundwater is generally influenced by various factors such as seawater/saltwater intrusion and agricultural/industrial activities (Mahlknecht et al., 2017; Wen et al., 2019) while the submarine groundwater discharge is the main delivery pathway of nutrients to coastal bays (Wu et al., 2013; Zhang et al., 2016). EDCs have been widely detected in groundwater and exerted potential health risks to human beings (Bartelt-Hunt et al., 2011; Gottschall et al., 2013; Li et al., 2015). Therefore, it is important to discuss whether reclaimed water irrigation has important influences on groundwater quality since reclaimed water usually contains EDCs and other emerging contaminants with unexpected relatively high concentrations. Furthermore, seawater near the reclaimed water irrigation area or polluted coastal groundwater might also be influenced to exert potential risks.

This study investigated occurrence and risks of EDCs in coastal groundwater and adjacent seawater of a typical coastal region in China influenced by the intensive reclaimed water irrigation. The possible effect of submarine groundwater discharge on the pollution of coastal waters was also discussed. The final objective of this study was to gain initial information regarding the effects of reclaimed water irrigation on occurrence of EDCs in coastal groundwater and adjacent seawater of North China.

## 2. Materials and methods

### 2.1. Study area and sampling strategy

Laizhou Bay is a coastal region with extensive human activities (Wen et al., 2019). Laizhou Bay is one of the most important bays for marine fishery. Groundwater is an important water resource for Laizhou Bay region and it is directly used as drinking water by the residents (Wen et al., 2019). Reclaimed water has become a common irrigation approach in Laizhou Bay area with rapid urbanization and reclaimed water supply can be controlled by machines at the roadside in Laizhou City.

To investigate the EDCs pollution in coastal groundwater and adjacent seawater influenced by reclaimed water irrigation in Laizhou Bay area, 20 groundwater water samples (G1-G20), 5 reclaimed water samples (R1-R5), and 5 seawater samples (S1−S5) were collected in May of 2018 (Fig. 1a). Shallow groundwater samples with volume of 1 L were collected from the wells used by the residents living in the study area and reclaimed water samples were directly collected from the reclaimed water pipes. Seawater samples were collected below the water surface with a depth of 0.5 m and the sampling sites were approximately 100 m away the shoreside. Pre-clean amber glass bottles were rinsed by groundwater, seawater, or reclaimed water several times before storing water samples.

### 2.2. Standards, reagents, sample pretreatment, and instrumental analysis

Standards including estrone (E1, purity>98%), 17-β-estradiol (E2, purity>97%), estriol (E3, purity of 98%), 17-α-ethynylestradiol (EE2, purity>98%), 4-n-nonylphenol (4-n-NP, purity>98%), and bisphenol A (BPA, purity>99%) were purchased from Sigma-Aldrich (St. Louis MO, USA). Isotope dilution standards (IDS) including estrone-D4 (E1-D4, purity of 99%) and bisphenol A-D16 (BPA-D16, 98 atom% D) were purchased from Sigma-Aldrich (St. Louis MO, USA). The N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA, purity>98%) and trimethylchlorosilane (TMCS, purity> 98%) were purchased from Alfa Aesar (Ward Hill, MA). Standards were individually dissolved in acetonitrile with concentrations of 1 g/L. Methylene chloride and acetonitrile were HPLC grade and obtained from Merck (Germany).

All water samples were placed on ice, transported back to the laboratory as soon as possible, stored in refrigerator at 4 °C, and extracted using liquid-liquid extraction (LLE) method within 24 h of sampling. Nitrate concentrations and compositions of stable isotopes $\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$ were determined according to Wu et al. (2019). The LLE process included the following steps. The entire 1-L water sample was poured into a pre-cleaned 2-L Teflon separatory funnel. The sample bottle was rinsed twice by 30 mL nanopure water each time, with addition of the rinsates into the separatory funnel. Immediately 10 μL of mixed isotope internal standards (concentration of 5 mg/L) was added in water sample. A 30 mL of methylene chloride was added to the separatory funnel, followed by shaking for 10 min. The extracts were collected into a 100 mL flask after shaking. This extraction procedure was repeated twice and all extracts were combined. The methylene chloride

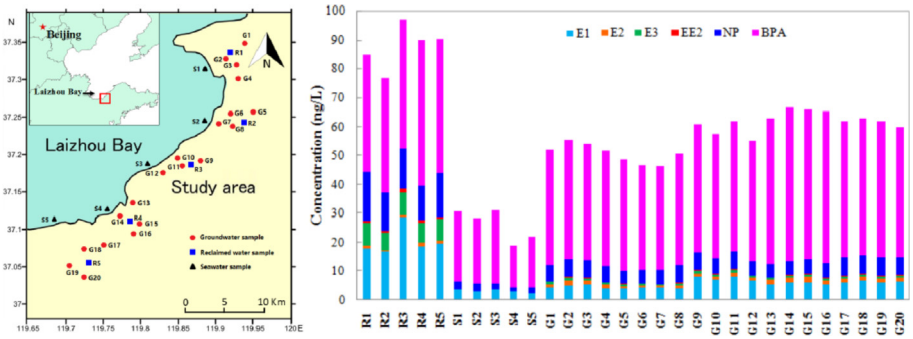


**Fig. 1.** Sampling map and concentrations of target EDCs in reclaimed water (R1-R5), seawater (S1−S5), and coastal groundwater (G1-G20).

extract was concentrated to about 1.5 mL in a water bath (50 °C), and then passed through anhydrous sodium sulphate to remove water. The solution was concentrated to nearly dry using nitrogen evaporator. Then 100 μL of methylene chloride and 50 μL of BSTFA (99%) -TMCS (1%) were added to the dried samples. The vials were sealed and heated at 70 °C for 2 h. The derivatised samples were cool down to room temperature prior to analysis by GC/MS.

Agilent 7820 A GC system (Palo Alto, CA, USA) coupled to a M7 single quadrupole MS system (Persee Co., Beijing, China), equipping with a 30 m DB-5MS column (0.25 mm I.D, Agilent J&W Scientific, Palo Alto, CA, USA) was used to analyze EDCs in water samples. The injection volume for the extract sample was 1 μL and measured in splitless mode with helium (purity>99.999%, 1.0 mL/min) as a carrier gas. The temperature program for column oven began at 50 °C and kept for 1min, then increased to 120 °C at a rate of 20 °C/min and kept for 3 min, continually increased to 280 °C at rate of 8 °C/min, and finally kept for 10 min. The total runtime was 37.5 min, including a solvent delay time of 14 min. The temperatures of the injector, transfer line and ion source were held at 280 °C, 250 °C and 230 °C, respectively. The confirmation and identification of target EDCs were based on their retention time and selected ion. Quantitative ions for 4-n-NP, BPA-D16, BPA, E1-D4, E1, E2, E3, and EE2 were *m/z* 179, *m/z* 368, *m/z* 357, *m/z* 346, *m/z* 342, *m/z* 416, *m/z* 311, and *m/z* 368, respectively. Qualitative ions for 4-n-NP, BPA-D16, BPA, E1-D4, E1, E2, E3, and EE2 were *m/z* 292/220, *m/z* 386/217, *m/z* 358/372, *m/z* 220/261, *m/z* 218/257, *m/z* 285/129, *m/z* 386/504, and *m/z* 285/207, respectively. Two purewater blanks were extracted for each analysis assay and no target EDCs were detected. Two purewater samples spiked by 5 μL of mixed solution of EDCs (concentration of 5 mg/L) were extracted for every 5 real water samples to assure quality control. The recoveries of target EDCs ranged from 86.6% to 116.0% while the RSD values were in the range of 0.1%−6.3% to meet the quality-control requirements.

### 2.3. Ecological risks, estradiol equivalent concentrations, and health risks of EDCs in water

Risk quotient (*RQ*) is generally used to evaluate ecological risk of emerging contaminants including EDCs in water (Li et al., 2015; Liu et al., 2017; Lu et al., 2018). *RQs* of EDCs were calculated according to the followings (Lu et al., 2018):

$$RQ_A = \frac{MEC}{PNEC_A},\quad PNEC_A = \frac{EC50/LC50}{1000}$$

$$RQ_C = \frac{MEC}{PNEC_C},\quad PNEC_C = \frac{NOEC}{AF}$$

where *MEC* is the measured concentration of the individual target EDC in water; *PNEC* is the predicted no-effect concentration of the individual target EDC; *EC50/LC50* is the half maximal effective/lethal concentration of the individual target EDC and *EC50/LC50* can be obtained through ECOTOX database (https://cfpub.epa.gov/ecotox/search.cfm) and checked by the corresponding source references; *NOEC* is no observable effect concentration of the individual target EDC; *AF* that is assessment factor can be set as 100, 50, and 10 if *NOEC* was obtained from the species standing for 1, 2, or at least 3 trophic levels (Lu et al., 2018); $RQ_A/RQ_C$ is risk quotient calculated by $PNEC_A/PNEC_C$ to illustrate the potential short-term/long-term ecological risk posed by EDCs in water. Ecological risks can be classified into 4 levels including high (RQ > 1), medium (0.1 < RQ ≤ 1), low (0.01 < RQ ≤ 0.1), and insignificant (RQ < 0.01) (Liu et al., 2017; Lu et al., 2018). *PNEC* values of target EDCs were shown in Table 1.

Estradiol equivalent concentration (*EEQ*) of target EDCs in water was determined by the following equation (Liu et al., 2017; Sun et al., 2008):

$$EEQ = \sum EEQ_i = \sum EEF_i \times MEC_i$$

where $EEQ_i$ is the estradiol equivalent concentration of the individual target EDC; $EEF_i$ is estradiol equivalency factor of the individual target EDC. *EEF* values of E1, E2, E3, EE2, NP, and BPA were 0.63, 1.00, 0.297, 2.2, $6.9 \times 10^{-4}$, and $3.8 \times 10^{-4}$, respectively (Canesi et al., 2007; Drewes et al., 2005; Sun et al., 2008; Zhao et al., 2011).

Groundwater has provided over 50% of drinking water in the world (Zektser and Lorne, 2004) and it is also important water resource for residential use in the study area. Therefore, it is important to evaluate the health risks posed by EDCs in groundwater. Although some EDCs have been proved to cause carcinogenic effects (Song et al., 2018), no carcinogenic potency factors of target EDCs are recommended. Therefore, this study evaluated non-cancer risks of EDCs and hazard quotient (*HQ*) was adopted. Non-cancer risks of EDCs in groundwater were caused through two pathways including dermal contact ($HQ_{dermal}$) and oral intake ($HQ_{oral}$) while those in seawater and reclaimed water were only caused through dermal contact. Calculation of *HQs* for adults/teenagers/children/infants and parameters used in model referred to Wu et al. (2019). The reference dose (*RfD*) through oral exposure pathway was $5.00 \times 10^{-5}$ mg/(kg·day) for E1 and E2 (Song et al., 2018) while it was $8.00 \times 10^{-2}$/$1.00 \times 10^{-2}$/$6.48 \times 10^{-2}$/$6.00 \times 10^{-3}$ mg/(kg·day) for E3/EE2/NP/BPA calculated by the equation (Lu et al., 2018). Non-cancer risks of EDCs were not acceptable when *HQ* was greater than 1.0 (Lu et al., 2018; Wu et al., 2019).

### 2.4. The analysis of annual inflow flux of EDCs of Laizhou Bay

The annual inflow flux of EDCs was calculated by multiplying

**Table 1**
*PNEC* (predicted no effect concentration) values of target EDCs.

| Antibiotics | *EC50/LC50* (μg/L) | Species/cells | Reference | AF | $PNEC_A$ (ng/L) |
|---|---|---|---|---|---|
| Estrone (E1) | 0.060 | Rainbow trout | Thorpe et al. (2003) | 1000 | 0.060 |
| 17β-estradiol (E2) | 0.025 | Fish | Brian et al. (2005) | 1000 | 0.025 |
| Estriol (E3) | 0.017 | MVLN cells | Gutendorf and Westendorf (2001) | 1000 | 0.017 |
| 17α-ethynylestradiol (EE2) | 0.0009 | Fish | Brian et al. (2005) | 1000 | 0.0009 |
| 4-n-nonylphenol (4-n-NP) | 0.12 | Boreal toad tadpoles | Bridges et al. (2002) | 1000 | 0.12 |
| Bisphenol A (BPA) | 1.02 | *Haliotis diversicolor supertexta* | Liu et al. (2011) | 1000 | 1.02 |
| Antibiotics | *NOEC* (μg/L) | Species | Reference | AF | $PNEC_C$ (ng/L) |
| Estrone (E1) | 0.00074 | Rainbow trout | Thorpe et al. (2003) | 50 | 0.0148 |
| 17β-estradiol (E2) | 0.0004 | *Oryzias latipes* | Metcalfe et al. (2001) | 10 | 0.04 |
| Estriol (E3) | 0.05 | *Oryzias latipes* | Lei et al. (2014) | 100 | 0.50 |
| 17α-ethynylestradiol (EE2) | 0.00003 | *Oryzias latipes* | Metcalfe et al. (2001) | 10 | 0.003 |
| 4-n-nonylphenol (4-n-NP) | 0.01 | *Tigriopus japonicus* | Marcial et al. (2003) | 10 | 1 |
| Bisphenol A (BPA) | 0.01 | *Tigriopus japonicus* | Marcial et al. (2003) | 10 | 1 |

the concentration of EDCs with corresponding water discharge. The annual discharge of groundwater in Laizhou Bay area was $1514.75 \times 10^8$ $m^{-3}$ $y^{-1}$ (Zhang et al., 2016). The annual discharge of rivers and sewage into Laizhou Bay was $321.89 \times 10^8$ and $2 \times 10^8$ $m^{-3}$ $y^{-1}$, respectively (reported by Ministry of Water Resources). The mean concentrations of EDCs of the reclaimed water and groundwater were used for the calculation of EDC flux of the sewage discharge and groundwater discharge, separately. Since the concentrations of EDCs in groundwater are comparable with those in river waters, concentrations of EDCs in the groundwater were also used for the calculation of EDC flux of river discharge.

## 3. Results and discussion

### 3.1. Occurrence and distribution of target EDCs in coastal groundwater, seawater, and reclaimed water

All target EDCs were detected in reclaimed water for irrigation while several steroid hormones including E2, E3, and EE2 were not detected in all seawater samples (Fig. 1b). Total concentrations of target EDCs in reclaimed water ranged from 76.8 to 90.3 ng/L while those in seawater were in the range of 18.9–30.9 ng/L. Concentrations of steroidal estrogens in seawater of this study were lower than those in Kuwait coastal areas (Saeed et al., 2017) while concentrations of phenolic EDCs in seawater of the study area were much lower than those previously reported (Diehl et al., 2012; Ko et al., 2007). BPA accounted for approximately 45.9%–55.9% of total target EDCs in reclaimed water while E1 and NP averagely contributed to 22.9% and 16.4% of target EDCs in reclaimed water. BPA/E1/NP averagely accounted for 79.6%/11.8%/8.6% of target EDCs in seawater.

Except EE2 that was detected in 70.0% of coastal groundwater samples, the remaining target EDCs were detected in all coastal groundwater. Total concentrations of target EDCs in groundwater were in the range of 46.3–66.5 ng/L (Fig. 1b). The concentrations of EDCs in coastal groundwater of the study area were comparable with those previously reported (Li et al., 2015). Concentrations of BPA ranged from 35.9 (G7) to 52.9 (G14) ng/L, being the predominant EDC in groundwater. Similar to reclaimed water and seawater of the study area, E1 and NP served as the second and third endocrine disrupting chemical in coastal groundwater with the average/maximal concentration of 5.6/8.1 and 5.6/6.6 ng/L, respectively. Concentrations of E1, E3, EE2, and NP in groundwater were significantly lower than those in reclaimed water while concentrations of BPA in groundwater were comparable with those in reclaimed water. Interestingly, concentrations of E2 in groundwater were higher than those of reclaimed water for neighboring irrigation, exhibiting that E2 might be easier to accumulate in groundwater under reclaimed water irrigation. Higher concentrations of EDCs in reclaimed water illustrated that reclaimed water might become an important source of EDCs for groundwater through different pathways including irrigation. Concentrations of target EDCs in coastal groundwater were significantly higher than those in seawater nearby, suggesting coastal groundwater might be a potential source of EDCs in seawater since possible exchange behaviors such as submarine groundwater discharge often exist in coastal regions.

### 3.2. Ecological risks of target EDCs in reclaimed water, seawater, and coastal groundwater

Short-term and long-term ecological risks of target EDCs in various water samples were calculated using *PNEC* determined by *LC50/EC50* and *PNEC* determined by *NOEC*, respectively (Fig. 2). The average/maximal $RQ_A$ of EDCs in reclaimed water reached 1847.8/

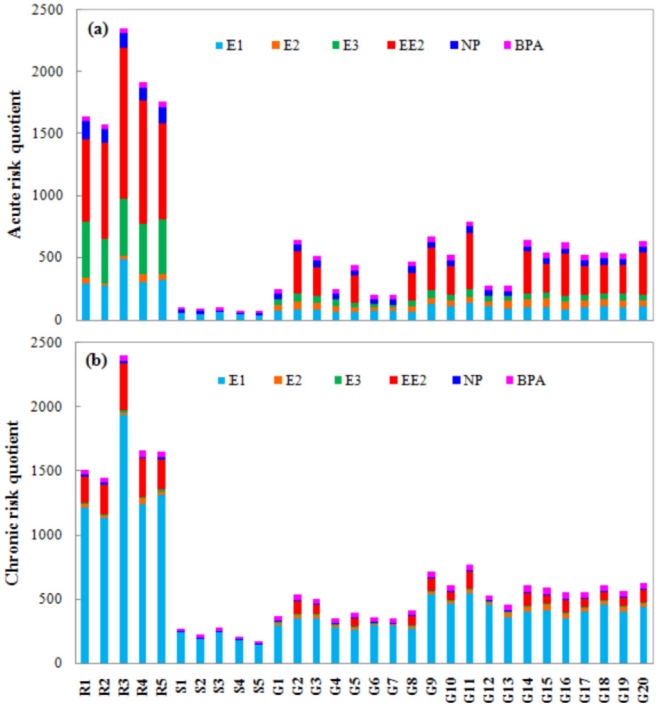


**Fig. 2.** Short-term (a) and long-term (b) ecological risks of EDCs in reclaimed water, seawater, and coastal groundwater.

2354.5, much higher than that in seawater and coastal groundwater (Fig. 2a). EE2/E3/E1 in reclaimed water averagely contributed to 47.7%/22.9%/18.1% of total acute risk quotients. $RQ_A$ of EDCs in seawater ranged from 71.4 to 106.3 with a mean value of 89.3. E1 that was the predominant risk contributor in seawater averagely contributed to 56.5% of total acute risk quotients, and then followed by BPA and NP. $RQ_A$ values of target EDCs in coastal groundwater ranged from 200.1 to 791.0, much lower than those in reclaimed water but significantly higher than those in seawater. Similar to reclaimed water, EE2 in coastal groundwater was the predominate risk contributor to averagely account for 33.5% of total acute risk quotient (Fig. 2a). E1 in groundwater contributed to 13.3%–40.5% of total acute risk quotients while E2, E3, NP, and BPA averagely contributed to 10.4%–11.9% of total risk quotients.

$RQ_C$ values of EDCs in reclaimed water ranged from 1445.7 to 2397.9 while those in seawater were in the range of 168.3–277.2 (Fig. 2b). $RQ_C$ values of EDCs in coastal groundwater ranged from 349.7 to 766.3 with a mean value of 521.8 (Fig. 2b). Completely different form acute risks, E1 was the predominant chronic ecological risk contributor for all water samples with proportions greater than 63.8%. EE2 served as the second chronic risk contributor for reclaimed water and groundwater while BPA was the second risk contributor for seawater. All risk quotients were much greater than 1.0, suggesting that EDCs in waters of the study area exerted very high ecological risks. High ecological risks posed by EDCs in seawater might cause potential serious threat to the organisms in the coastal regions and marine.

*EEQs* of target EDCs in water samples showed significant variation (Fig. 3). *EEQs* of target EDCs in reclaimed water and seawater were in the range of 14.4–23.6 and 1.4–2.3 ng/L, respectively. *EEQs* of E1 in reclaimed water ranged from 10.6 to 18.1 ng/L, averagely accounting for 71.9% of total *EEQs*. Accordingly, E1 contributed to over 99.3% of total *EEQs* in seawater. *EEQs* of target EDCs in coastal groundwater ranged from 3.5 to 7.6 ng/L (Fig. 3). The average *EEQ* in coastal groundwater was much lower than that in reclaimed water. *EEQs* of E1 in coastal groundwater were in the range of 2.5–5.1 ng/L, averagely accounting for 65.2% of total EEQs. E2 served as the second contributor for estrogenic equivalents with average *EEQ* of 1.3 ng/L while EE2 detected in groundwater also contributed to 6.8%–11.5% of total *EEQs*. *EEQs* of E3 in coastal groundwater accounted for 3.2%–6.7% of total *EEQs* while BPA and NP only contributed to less than 0.5% of total *EEQs*. Aquatic organisms such as fish are very sensitive to pollution of EDCs and feminization of male fish occurs at estradiol concentration of 1.0 ng/L (Hansen et al., 1998). *EEQs* of EDCs in all water samples were greater than 1.0 ng/L, illustrating high potential feminization risks of EDCs to aquatic organisms in the study area, especially the coastal regions and adjacent marine.

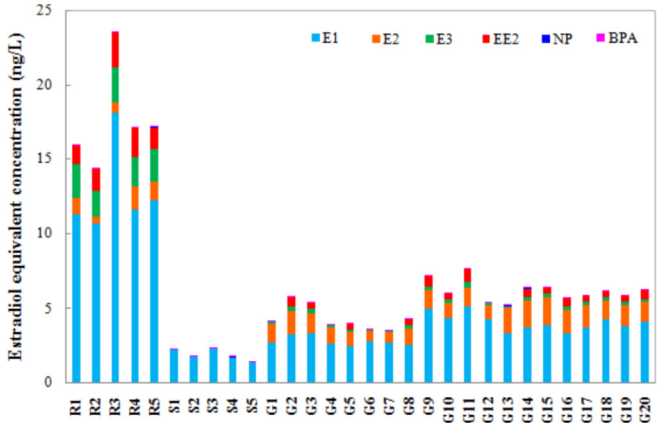


**Fig. 3.** Estradiol equivalent concentrations of target EDCs in reclaimed water, seawater, and coastal groundwater.

### 3.3. Potential health risks of target EDCs in reclaimed water, seawater, and coastal groundwater

Non-cancer risks of target EDCs in reclaimed water ranged from $1.8 \times 10^{-5}$ (R2) for male adults to $1.1 \times 10^{-4}$ (R3) for children while those in seawater ranged from $2.4 \times 10^{-6}$ (S5) for male adults to $1.5 \times 10^{-5}$ (S3) for children (Fig. 4a). E1 was the predominant risk contributor in reclaimed water and seawater through dermal contact pathway while E3 and EE2 in reclaimed water posed lower non-cancer risks for humans than the other EDCs. Non-cancer risks of EDCs in reclaimed water and seawater for different groups followed the order of children > infants > female adults > female teenagers > male teenagers > male adults. Therefore, young people, especially children and infants, should pay attention to potential health risks of EDCs in seawater.

Non-cancer risks of target EDCs in coastal groundwater ranged from $3.2 \times 10^{-3}$ (G5) for male adults to $3.3 \times 10^{-2}$ (G11) for infants (Fig. 4b). Non-cancer risks of EDCs through oral intake accounted for 99.8%–99.9% of total risks. *HQs* posed by E1 in coastal groundwater through oral intake ranged from $2.5 \times 10^{-3}$ (G5) for male adults to $2.7 \times 10^{-2}$ (G11) for infants, accounting for 71.2%–84.4% of total *HQs*. *HQs* posed by E2/BPA in coastal groundwater through oral intake were in the range of ($4.4 \times 10^{-4}$-$6.3 \times 10^{-3}$)/($1.9 \times 10^{-4}$-$1.5 \times 10^{-3}$), covering (11.2%–22.9%)/(3.8%–6.3%) of total *HQs*. *HQs* of EDCs for coastal groundwater were generally 1215–3861 times those for seawater. Non-cancer risks posed by EDCs in coastal groundwater for different groups followed the order of infants > children > female teenagers > male teenagers > female adults > male adults. Infants and children deserve more attention

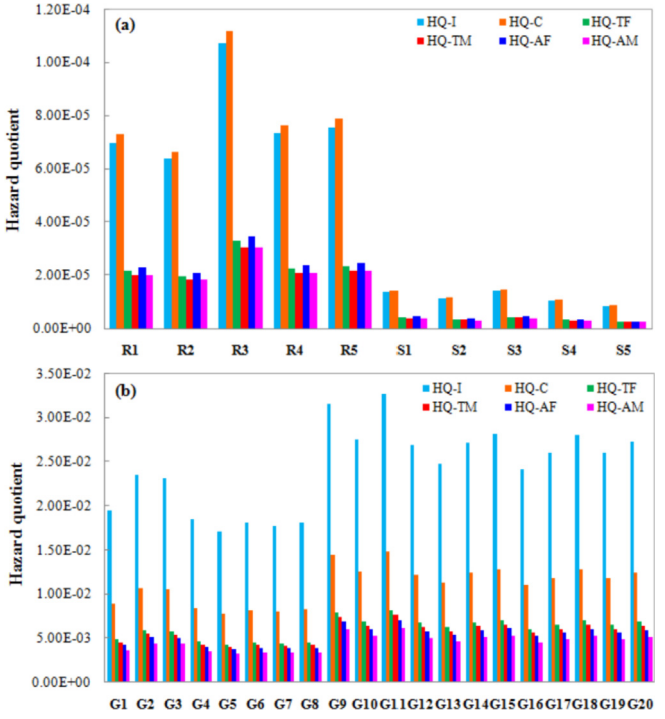


**Fig. 4.** Non-cancer risks of target EDCs in reclaimed water and seawater (a) as well as coastal groundwater (b). *HQ* means hazard quotient; I and C refer to infants and children, respectively; TF and TM stand for female and male teenagers, respectively; AF and AM refer to female and male adults, respectively.

since they are more sensitive to groundwater pollution.

Non-cancer risks are generally acceptable when *HQs*<1 (Wen et al., 2019; Wu et al., 2019). Therefore, non-cancer risks posed by EDCs in waters collected from the study area were acceptable for infants, children, teenagers, and adults since all *HQs* were less than 1.0. EDCs in aquatic environments generally caused higher ecological risks than health risks based on the risk assessment results.

### 3.4. Possible sources of EDCs in coastal groundwater and adjacent coastal seawater

Dual isotopes are generally used to determine the possible sources of nitrate in groundwater (Wu et al., 2019). Therefore, dual isotopes might be good indicators to determine the possible sources of EDCs if they are strongly positively correlated with nitrate in groundwater. Correlation analysis showed that E1 and BPA were significantly positively correlated with nitrate in groundwater at $p < 0.01$ (Fig. 5a). Thus, it was reasonable to assume that EDCs especially E1 and BPA in coastal groundwater of this study might originate from the same or similar sources of nitrate. Dual-isotope analysis illustrated that reclaimed water (sewage) was the main source of groundwater nitrate for all sampling sites (Fig. 5b), which suggested that reclaimed water irrigation might also be the important source of EDCs in groundwater of the study area. Meanwhile, the adjacent seawater could be polluted by EDCs through the submarine groundwater discharge when the coastal aquifer was polluted by EDCs through the intensive reclaimed water irrigation. According to the EDC flux analysis (Fig. 6), the groundwater discharge was the main pollution pathway of EDCs for the Laizhou Bay seawater. The annual flux of EDCs through the submarine groundwater discharge was 6656.6 kg, much higher than that of the river discharge (1414.5 kg). About 82% of EDCs was discharged into the Laizhou Bay through the submarine groundwater discharge. Previous observation has shown that the submarine groundwater discharge is the main delivery pathway of nutrients to coastal bays including Laizhou Bay (Wu et al., 2013; Zhang et al., 2016). Since the coastal aquifer was mainly contaminated by the reclaimed water, the main pollution mechanism of EDCs in the coastal water was proposed as a two-step process (Fig. 7). The coastal aquifer was firstly contaminated by EDCs through the reclaimed water usage and then the EDCs were discharged into the coastal waters through the submarine groundwater discharge, which subsequently led to possible ecological risk on the coastal waters. Therefore, efficient control of EDCs in reclaimed water for irrigation would be beneficial to control EDCs in coastal groundwater and seawaters.

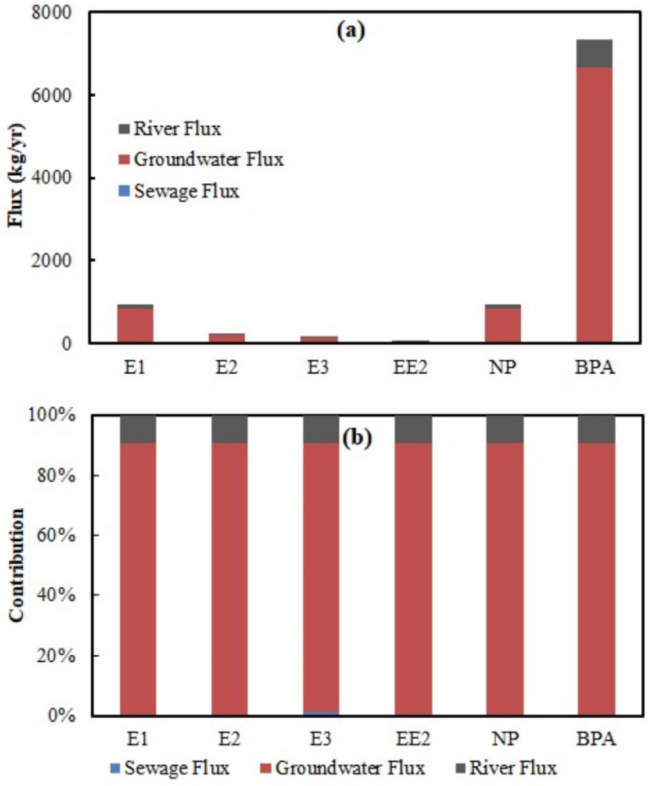


**Fig. 6.** Inflow flux of EDCs in Laizhou Bay (a) and contribution of EDCs (b).

## 4. Conclusions

Occurrence and risks of EDCs in coastal groundwater and adjacent seawater influenced by reclaimed water irrigation was investigated. BPA was the predominant endocrine disrupting chemical in coastal groundwater and E2 concentrations in groundwater were higher than those in reclaimed water. Concentrations of EDCs in seawater were much lower than those in coastal groundwater, suggesting that coastal groundwater containing EDCs with relatively high concentrations might become a potential pollution source for marine through interaction between groundwater and seawater. EDCs in coastal groundwater and seawater posed very high ecological risks in both long and short term. EE2/E1 was the predominate risk contributor for total acute risk quotient of groundwater/seawater while E1 was the main chronic ecological

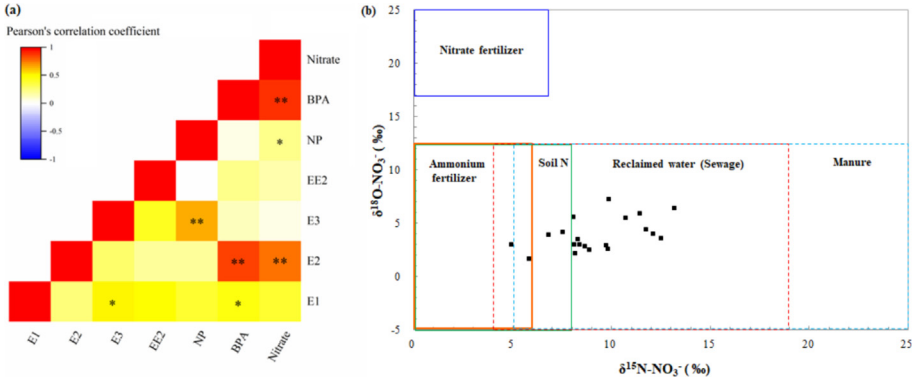


**Fig. 5.** Heatmap of Pearson's correlation matrix among target EDCs (a) and source apportionment of EDCs based on dual isotope model (b). Signals * and ** refer to significance level at $p < 0.0$ and $p < 0.01$, respectively.

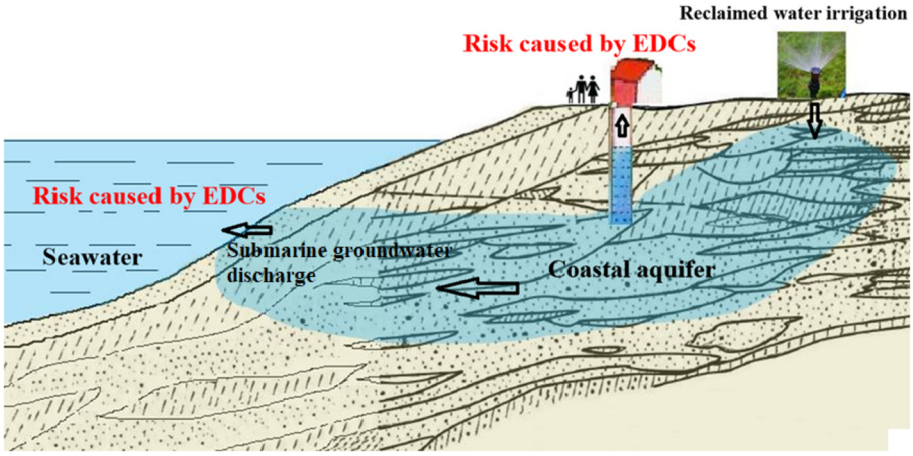


**Fig. 7.** Proposed mechanism of EDCs pollution through reclaimed water irrigation in coastal groundwater and adjacent seawater.

risk contributor for groundwater and seawater. *EEQs* of target EDCs in seawater and coastal groundwater were much lower than those in reclaimed water. Non-cancer risks posed by EDCs in coastal groundwater and seawater were acceptable. BPA and E1 were significantly positively correlated with nitrate in groundwater so that dual-isotope analysis was used to identify that reclaimed water (sewage) was the main source of EDCs for all coastal groundwater samples. More than 80% of EDCs was discharged into the Laizhou Bay through the submarine groundwater discharge based on the flux analysis. EDCs contaminated the coastal aquifer through the reclaimed water usage and entered the coastal waters through the submarine groundwater discharge to subsequently pose possible ecological risks. Therefore, it is necessary to control EDCs in reclaimed water so as to prevent/alleviate EDCs in groundwater and adjacent seawater of the coastal regions.

## Author contributions section

Jian Lu: Original draft preparation, Conceptualization, Methodology, Software, Writing- Reviewing and Editing. Jun Wu: Validation, Methodology, Conceptualization, Writing- Reviewing and Editing, Software, Supervision. Cui Zhang: Investigation, Data curation. Yuxuan Zhang: Investigation, Data curation.

## Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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