Environmental risk assessment of the emerging EDCs contaminants in Guan river of Jiangsu in China

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ABSTRACT

The emerging endocrine disrupting chemicals pose high risk and much uncertainty to eco-environment and human health. This study evaluated the risks of NP, E1, E2, and EE2 in Guanhe water in Jiangsu province, China. The highest ΣEEQ values in Guanhe river water were found in the sites S14, S15 and S18 and this can be attributed to the highest concentration of EE2 in the three sites, and the high EEF value of EE2. EE2 and E1 were the main contributors to the ΣRQ value in the Guanhe river water. HED values were in the order of EE2 > E2 > E1 > NP, which implies that EE2 imposes the highest level of health risks, and the risk quotient values were in the order of EE2 > E1 > NP > E2 with ADI values, indicating non-negligible level of health risks to humans. Moreover, our results indicated that the co-exposure to multiple EDCs was considerably larger than exposure to EE2 independently. It should be considered as an alert of the default in assessment on health risk of exposure to EDCs and regardless of its combined effect, all sites in the midstream and downstream were in high risk in Guanhe water, associated with high concentration of EE2 and E1.

INTRODUCTION

The endocrine disrupting chemicals (EDCs) have been detected frequently in aquatic environment (Fang et al., 2016). A wide variety of chemicals have been recognized as EDCs, including nonylphenol (NP), estrone (E1), 17α-estradiol (EE2) and 17β-estradiol (E2), as well as natural and synthetic estrogens (Song and Wen, 2018). They, as emerging environmental pollutants, have received considerable concern due to their ability to interfere with the normal functions of the endocrine system (He and Ye, 2015; Tan et al., 2017) at concentrations as low as ng/L level (Goeppeert et al., 2014) and been identified persistent in the environment (Nohynek et al., 2013). The typical EDCs, NP, E1, E2 and EE2 originate from a wide range of human activities and livestock excreta, including the industry of fine chemical products, the synthesis of steroid hormone drugs, and synthetic androgens (Salgueiro-Gonzalez et al., 2015; You et al., 2015). These EDCs have been detected at a higher frequency of more than 70% in different rivers, such as the River Saale in Germany (Prieto et al., 2011), the rivers Jarama and Manzanares in Spain (Esteban et al., 2014), and the River Yangtze in China (Jiang et al., 2012; Shi et al., 2014). A few studies have reported the environmental risk of SEs, they mainly focused on the sources of SEs deriving from drinking water treatment plants (de Jesus Gaffney et al., 2015), reclaimed water and receiving groundwater (Li et al., 2015), WWTPs and sewage sludge treatment (Martín et al., 2012), surface water (Shi et al., 2014; Yan et al., 2017) and so on. The objectives were to evaluate systematically potential estrogenic activity using estradiol equivalents (EEQ), ecological risk of EDCs by human health risk quotient (RQ) method and Monte Carlo simulation assessment in drinking water sources. The risk-assessment results will enhance the overall understanding of EDCs pollution in the seagoing rivers in order to take some effective measures, e.g., developing water quality criteria, proposing restriction strategies and setting
legislation for management of EDCs, to reduce the pollution of those contaminants.

MATERIALS AND METHODS

Chemicals and reagents

The standard chemicals including nonylphenol (NP), estrone (E1), 17α-estradiol (EE2) and 17β-estradiol (E2) were purchased from Sigma-Aldrich (St. Louis, USA). All the solvents used in this study were of high-performance liquid chromatography (HPLC) grade.

Site setting, investigations and sample collection

The Jiangsu coast, with a length of 954 km, is located in the middle west of the Yellow Sea between the Shandong real-time data from inaccessible areas, and including Lianyungang city, Yancheng city and Nantong city. According to the Jiangsu Coastal Development Plan, the northern coastal city such as Lianyungang, has been endorsed as national strategic cities by China's Central Government since 2009. Guanhe river is one of the major rivers of the seagoing rivers to Yellow river and is the major drinking water source for northern residents in Jiangsu province, China. The variety and complexity of coastal geomorphology, coupled with the long history of human activity and industrial distribution, have shaped the city, which is known as “Golden Coast” of Jiangsu Province. It was reported that about 20 industrial chemical plants were built at the lower reaches of Guanhe river. Sewage outfall, midstream and downstream runoff have introduced pollution into the Guanhe river and EDCs in midstream of Guanhe river have been reported to seriously affect the water quality and pose a high environmental risk to the local aquatic organisms. Its climate changes from northern subtropical belt to warm temperate belt. Monsoon climate is characterized by hot and rainy summers and cold and dry winters. The annual mean temperature of this region is 13.7 to 14.8°C, and multi-year average rainfall amounts to 1037.6 mm. Surface water was collected at eighteen sampling points along Guanhe river (Figure 1) in Mach 2017. Water samples were stored in 2 L precleaned brown glass bottle. Once transported to the laboratory, the water samples were analyzed immediately.

Estrogenic activity and ecological risk assessment

Based on the measured endocrine concentration (MEC) of NP, E1, E2, and EE2 in surface water from the river, the estradiol equivalency factor (EEF), and the estrogenic activity of target EDCs were evaluated by EEQ. The EEQ of the pollutants in surface water was calculated using Equation 1 (Valitalo et al., 2016):

\[ \text{EEQ} = \text{EEF} \times \text{MEC} \quad (1) \]

The EEF values were collected from previous scientific studies and the 95th percentiles of EEFs were used to calculate the EEQ (Sun et al., 2013).

According to the method of environmental risk assessment in the European Union Technological Guidance Document, the ecological risk of EDCs in Guanhe river water can be evaluated based on RQS:

\[ \text{RQS} = \frac{\text{MEC}}{\text{PNEC}} \quad (2) \]

Where MEC is the actual monitored concentration of pollutants (ng/L), PNEC is the predicted no effect concentration (ng/L). According to the common risk ranking criteria to the environment, the ecological risk can be classified into three levels: RQS < 0.1, indicating the lowest risk; 0.1≤RQS <1, indicating medium risk; and RQS> 1, indicating high risk.

Monte Carlo simulation Assessment

The intake dose for water exposure to various EDCs was assumed to be an indicator of chronic exposure condition. The estimated dietary intake (EDI, ng/kg bw/day) for a typical adult was calculated on the basis of Equation (3) which had been detailed elsewhere (Trudel et al., 2011; He and Ye, 2015-2017) and with minor modifications:

\[ \text{EDI} = \sum_{i=1}^{n} \left( \frac{C_{ik} a_k}{\text{bw}} \right) \quad (3) \]

Where \( C_{ik} \) (ng/g) is the concentration of congener i in the sample matrix of water group k, \( a_k \) (g/day) is the amount of daily consumption of water group k, and bw is the body weight. In the study, since the data of water consumption cited were presented in gram per 70 kg bodyweight status (Jin, 2008; He and Ye, 2015), we integrated the body weight into consumption data and fixed it on 70 kg in calculation. Equation (4) was used to estimate the integrated effect of EDCs:

\[ \text{EDI}_{\text{EEQ}} = \sum_{i=1}^{n} \left( \frac{C_{ik} f_i a_k}{\text{bw}} \right) \quad (4) \]

Where \( f_i \) is the EEF value of EDCs.

RESULTS AND DISCUSSION

Estrogenic activity and ecological risk assessment

To determine the potential threat from these estrogenic compounds to the environment, it is necessary to quantify the estrogenic activity of these compounds using biological
methods. The concentration of E2 causing endocrine disrupting effects was set as 1 ng/L by European Commission, indicating that selected EDCs with EEQ larger than 1 would affect the endocrine systems of aquatic organisms in the water (AC01769567, 1996). The average EEQs of selected estrogens in Guanhe river water collected during the nonfrozen seasons was calculated based on the EEF (NP: 4.95; E1: 0.69; E2: 1.00; EE2: 5.11) of target EDCs (Sun et al., 2013). The sum of EEQ for each estrogenic compound (ΣEEQ) in different sampling site ranged from 0.16×10^3 ng/L to 2.35×10^3 ng/L in Guanhe river water (Figure 2A). The sampling sites with ΣEEQ larger than 1 accounted for 56.8% in Guanhe river water. In terms of the different basins of Guanhe river, the percentage of sampling sites with high estrogenic activity (ΣEEQ>1) declined in the following order: midstream > downstream>upstream. The highest ΣEEQ values in Guanhe river water were found in the site S14, S15 and S18, which can be attributed to the highest concentration of EE2 in the three sites (5.35×10^3 ng/L, 9.26×10^3 ng/L, 12.13×10^3 ng/L, respectively in river water) and the high EEF value of EE2. Both NP and EE2 in Guanhe river water were the major contributors to the total estrogenic activity among the sampling sites. Although the concentration levels of E1 in the Guanhe river water were higher (1.30-9.52 ng/L more than 0.19-1.43 in Yangze river China) (Tan et al., 2017), its estrogenic activity was negligible due to the low EEF value. This was consistent with the studies conducted by other researchers (Lu et al., 2010; Jin et al., 2013; Tan et al., 2017). The ecological risk of all selected EDCs in Guanhe river water are shown in Figure
Assessment of the risk to human health

EDCs are emerging contaminants that can alter the endocrine system and act at very low doses (μg/L or ng/L). For the health risk assessment, 95th percentiles were used as ‘reasonable maximum’ values to determine the risks associated with the consumption of river water and fish. The hazard quotients (HQs) calculated as the ratio of simulated concentrations to exposure threshold values (ETV) and public health standards (PHS) values are shown in Table 1. Using reasonable maximum values, the hazard quotients for NP, E1, E2 and EE2 in Guanhe river samples S14-S18 were above 1.4-5.6, respectively, indicating potential health risk. In contrast, the HQs based on EQQ values were below 1 for the S1-S11 samples for NP and E2, and EEQ values were 1.2 and 1.1 for E1 and EE2, respectively indicating acceptable health risks. For the S12 and S13, the HQs were more than 1.4 for all the target chemicals NP, E1, E2 and EE2 and are therefore considered unsafe for a lifetime exposure. Overall, this study indicated acceptable human health risks associated with exposure to NP, E1, E2 and EE2 compounds through the consumption of upstream of Guanhe river water. However, NP, E1, E2 and EE2 in midstream and downstream of Guanhe river water were unacceptably high levels of human health risks. EDCs in drinking water were a little higher than the levels expected to have adverse health effects in China (Liu et al., 2015). Compared with humans, higher hazard quotient values were found for fish. For each compound, the hazard quotient values for humans were in the order of EE2 > NP > E1 > E2, but this was different for fishes, which were in the order of NP > EE2 > E2 > E1. The highest hazard quotient values were found in NP, which were 6×10^-2 for fishes and highest hazard quotient values were found in EE2 (3×10^-3) for humans, indicating a high level of risk. NP does not only possess the highest potency (He and Ye, 2015), but also can bioaccumulate in fish due to its highest log Kow value and longest half-life in the environment (Cao et al., 2010). In comparison with EE2 and NP, natural estrogens E1 and E2 are less potent and have much shorter in half-lives. Therefore, lower risks are generally associated with E1 and E2. Human daily doses from the consumption of water and fish were calculated and the related risk quotient is shown in Table 2. It was found that fish was the major source of exposure. Total human equivalent dose (HED) from fish consumption was about 12 times higher than that from drinking water consumption. For each compound, HED values were in the order of EE2 > E2 > E1 > NP, which implies that EE2 imposes the highest level of health risks. When the risk quotient was calculated as the ratio of total HED to the acceptable daily intake (ADI) for each compound, the obtained risk quotient values were in the order of EE2 > E1 > NP > E2 with ADI values between 2.45×10^-3 and 5.69×10^-2, as well total HQs were the same as the order of ADI values, indicating non-negligible level of health risks to humans. The results of the present study showed the need for continual, long-term monitoring, at different times of year, of the presence of these substances in river water, especially those river water that supply the population with drinking water from Guanhe rivers, as highlighted by points S14, S15, S16, S17 and S18 in this study.

Simulation assessment for human exposure to EDCs

By using Monte Carlo method, we simulated the detected EDCs exposure on different scenarios synchronously and found that the forecasted median (50th percentile), even high (95th percentile) exposures for NP, E1, E2 and EE2 were far below the corresponding tolerable daily intake (TDI) values (Figure 3). The NP and E1 intake dose were lower than the value reported in a Taiwanese population (that is, 38.59 ± 2.93 ng/day and 21.46 ± 1.38 ng/day) (Lu et al., 2015; Liu et al., 2017) and the intake dose of E2 and EE2 was far below the value estimated by another study on a Chinese population (409 and 297 ng/kg bw/day) (Liao et al., 2013; Liu et al., 2017). Individuals differ in water consumption and EDCs concentration, and the different
Table 1: HQs in Guanhe water for humans and fishes.

<table>
<thead>
<tr>
<th>Cumulative Probability (%)</th>
<th>HQs for humans</th>
<th>HQs for fishes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NP  E1 E2 EE2</td>
<td>NP  E1 E2 EE2</td>
</tr>
<tr>
<td>90</td>
<td>$1 \times 10^{-5}$ $2 \times 10^{-6}$ $2 \times 10^{-7}$ $1 \times 10^{-3}$</td>
<td>$2 \times 10^{-3}$ $2 \times 10^{-6}$ $2 \times 10^{-5}$ $3 \times 10^{-3}$</td>
</tr>
<tr>
<td>95</td>
<td>$2 \times 10^{-4}$ $2 \times 10^{-5}$ $2 \times 10^{-6}$ $1 \times 10^{-3}$</td>
<td>$3 \times 10^{-3}$ $3 \times 10^{-6}$ $2 \times 10^{-5}$ $3 \times 10^{-3}$</td>
</tr>
<tr>
<td>99</td>
<td>$3 \times 10^{-4}$ $4 \times 10^{-5}$ $3 \times 10^{-6}$ $2 \times 10^{-3}$</td>
<td>$5 \times 10^{-2}$ $3 \times 10^{-6}$ $3 \times 10^{-5}$ $4 \times 10^{-3}$</td>
</tr>
<tr>
<td>99.9</td>
<td>$4 \times 10^{-4}$ $5 \times 10^{-5}$ $4 \times 10^{-6}$ $3 \times 10^{-3}$</td>
<td>$6 \times 10^{-2}$ $2 \times 10^{-5}$ $3 \times 10^{-4}$ $5 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Table 2: Hazard index (HDD, HED and ADI, ng/kg, body weight/day) of human exposure calculated from simulated concentrations in Guanhe river water for humans and fishes.

<table>
<thead>
<tr>
<th>Index</th>
<th>EDCs</th>
<th>From fish</th>
<th>From water</th>
<th>Total</th>
<th>HQ total</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDD</td>
<td>NP</td>
<td>$2.86 \times 10^{-4}$</td>
<td>$2.53 \times 10^{-5}$</td>
<td>$3.11 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>E1</td>
<td>$3.19 \times 10^{-4}$</td>
<td>$1.91 \times 10^{-5}$</td>
<td>$3.38 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>E2</td>
<td>$2.35 \times 10^{-4}$</td>
<td>$2.08 \times 10^{-5}$</td>
<td>$2.56 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>EE2</td>
<td>$4.43 \times 10^{-4}$</td>
<td>$3.12 \times 10^{-5}$</td>
<td>$4.74 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NP</td>
<td>$2.54 \times 10^{-6}$</td>
<td>$1.06 \times 10^{-6}$</td>
<td>$3.60 \times 10^{-6}$</td>
<td>NP: $7.73 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>E1</td>
<td>$6.91 \times 10^{-5}$</td>
<td>$1.58 \times 10^{-5}$</td>
<td>$8.49 \times 10^{-5}$</td>
<td>E1: $1.18 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>E2</td>
<td>$3.12 \times 10^{-4}$</td>
<td>$2.61 \times 10^{-5}$</td>
<td>$3.38 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>EE2</td>
<td>$5.38 \times 10^{-4}$</td>
<td>$3.45 \times 10^{-5}$</td>
<td>$5.72 \times 10^{-4}$</td>
<td>E2: $1.34 \times 10^{-2}$</td>
</tr>
<tr>
<td>Total</td>
<td>NP</td>
<td>$2.92 \times 10^{-4}$</td>
<td>$7.75 \times 10^{-5}$</td>
<td>$9.99 \times 10^{-4}$</td>
<td>EE2: 0.58</td>
</tr>
<tr>
<td></td>
<td>E1</td>
<td>$3.52 \times 10^{-2}$</td>
<td>$1.14 \times 10^{-2}$</td>
<td>$4.66 \times 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>E2</td>
<td>$4.63 \times 10^{-2}$</td>
<td>$2.59 \times 10^{-2}$</td>
<td>$7.22 \times 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>EE2</td>
<td>$2.28 \times 10^{-2}$</td>
<td>$2.45 \times 10^{-3}$</td>
<td>$2.53 \times 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$5.69 \times 10^{-2}$</td>
<td>$4.12 \times 10^{-2}$</td>
<td>$9.81 \times 10^{-1}$</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3: The overlaid distributions of ΣEEQs and E2 exposure in population of Guanhe river basin. The vertical bars represented the medians of the forecasted values.

value of $C_k$ and $a_k$ would apparently result in various EDI values. If the mean or 95th percentile concentration of EDCs and water consumption were available for exposure calculation merely, the result derived of equations is going against the fact and reflect special exposure scenarios (50th or 95th percentile) only. In fact, the majority of EDCs
Conclusion

Due to their ubiquity in the environment and endocrine disruptive activity, the potential impact of EDCs on public health is a reason for concern. This study evaluated the risks of NP, E1, E2, and EE2 in Guanhe water in distribution point water from Guanhe river Jiangsu province, China. The highest $\Sigma$EEQ values in Guanhe river water were found in the site S14, S15 and S18, and this can be attributed to the highest concentration of EE2 in the three sites and the high $\Sigma$RQ value in the Guanhe river water. For each compound, HED values were in the order of EE2 > E2 > E1 > NP, which implies that EE2 imposed the highest level of health risks, and the obtained risk quotient values were in the order of EE2 > E1 > NP > E2 with ADI values, indicating non-negligible level of health risks to humans. Moreover, our results indicated that the co-exposure to multiple EDCs was considerably larger than the exposure to E2 independently. It should be considered as an alert of the default in assessment on health risk of exposure to EDCs and regardless of its combined effect, all sites in the midstream and downstream were in high risk in Guanhe river water, associated with the high concentration of EE2 and E1 in the river water. Therefore, we can develop water quality criteria, proposing restriction strategies and setting legislation for management of EDCs, to reduce the pollution of those contaminants.

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