



## Levels of endocrine disrupting compounds in South China Sea

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### ABSTRACT

The occurrence of estrogens in the aquatic environment has become a major concern worldwide because of their strong endocrine disrupting potency. In this study, concentrations of four estrogenic compounds, estrone (E1), 17 $\beta$ -estradiol (E2), 17 $\alpha$ -ethynylestradiol (EE2), estriol (E3) were determined with liquid chromatography-tandem mass spectrometry analyses in surface water from South China Sea, and distributions and potential risks of their estrogenic activity were assessed. The estrogenic compounds E1, E2 and E3 were detected in most of the samples, with their concentrations up to 11.16, 3.71 and 21.63 ng L<sup>-1</sup>. However, EE2 was only detected in 3 samples. Causality analysis, EEQ values from chemical analysis identified E2 as the main responsible compounds. Based on the EEQ values in the surface water, high estrogenic risks were in the coastal water, and low estrogenic risks in the open sea.

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### 1. Introduction

In recent years, it has been shown that certain environmental contaminants, present at trace concentrations, can have dramatic effects on the endocrine systems of organisms (Jobling et al., 1998). These compounds are collectively known as endocrine-disrupting compounds. Most EDCs are synthetic organic chemicals being introduced to the environment by anthropogenic inputs (Ashton et al., 2004; Petrovic et al., 2001; Rhind et al., 2010). Man-made estrogens such as 17 $\alpha$ -ethynylestradiol (EE2), are highly potent and persistent, being unaltered by sewage treatment (Ternes et al., 1999). However, EDCs can also be naturally occurring in the environment. For example, the natural female hormones estrone (E1) and 17 $\beta$ -estradiol (E2) are both excreted by women or animals, are therefore ubiquitous in aquatic environments receiving sewage inputs (Desbrow et al., 1998; Ashton et al., 2004). These natural hormones display the greatest estrogenic potency compared to synthetic chemicals like as plastifiers, paints and industrial chemicals (Hanselman et al., 2006). Similarly, natural estrogens are also sufficiently stable to survive many conventional water treatment process. Studies have shown that EDCs can be absorbed from water into the aquatic organisms (Depledge and Billinghamurst, 1999; Rhind et al., 2010). Once these compounds entering the aquatic environment may pose a severe threat to the ecosystem. It may cause adverse biological effects compromised immune function, sexual dysfunction, cancers and cardiovascular disorders (Depledge and Billinghamurst, 1999; Rhind, 2008). Therefore, it is

important to monitor these estrogenic compounds in aquatic environments in order to protect the ecosystem.

In China, some works pertaining to investigation of estrogenic disrupting compounds in surface waters have been developed for several years. Wang et al. (2011) conducted an extensive survey of estrogens of 23 source water from six main river systems found E1, E2, E3, EE2 ranging from 0.86 to 2.98 ng L<sup>-1</sup>, nd-1.78 ng L<sup>-1</sup>, nd-4.37 ng L<sup>-1</sup>, nd-2.59 ng L<sup>-1</sup>, respectively. In three rivers of Tianjin, estrogens were detected in the range from 0.98 to 21.6 ng L<sup>-1</sup> for E1, nd-9.70 ng L<sup>-1</sup> for E2, nd-7.29 ng L<sup>-1</sup> for E3, nd-7.67 ng L<sup>-1</sup> for EE2 (Lei et al., 2009). Moreover, there were higher levels of estrogens in bay surface water. For example, Zhou (2009) surveyed Licun River-Jiaozhou Bay in Shandong province and found the maximum concentrations of 318 ng L<sup>-1</sup> for E1, 185 ng L<sup>-1</sup> for E2, 306 ng L<sup>-1</sup> for E3 and 70 ng L<sup>-1</sup> for EE2. The largest concentration of E2 was up to 60.2 ng L<sup>-1</sup> in Xiamen Bay (Zhang et al., 2012). However, little information is available on estrogens concentration levels in the marginal sea of China.

The southern coastal area of China is the most developed region. About 270 million people live in the coastal sub-regions of South China Sea (Morton and Blackmore, 2001). The Pearl River, Han River and many other rivers that contain industrial and domestic sewage drain into South China Sea. The development of this Economic Zone has resulted in significant stress to South China Sea. Except that there are densely industrial plants along the catchment, it is also an important area for agriculture and aquaculture. There are very populated and a large ongoing population increase in the coastal sub-regions of the South China Sea which increases the pollution load on South China Sea. To date, studies of estrogens in South China Sea focus primarily on the Pearl River system, Estuary

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and adjacent Northern South China Sea (Peng et al., 2007, 2008; Gong et al., 2009; Zhao et al., 2011). So the levels of estrogens in South China Sea were still unclear. The purpose of our study is to investigate the levels of estrogens in surface water in South China Sea. Potential ecological risks to aquatic organisms were assessed based on the data from chemical analysis.

## 2. Materials and methods

### 2.1. Sample collection

Samples were collected from 32 Stations in the wet season (August 2012) along the South China Sea (Fig. 1). Most of sample stations were located in the coastal waters. For all sites, a total of 8 L water was collected as a grab sample.

### 2.2. Materials

Target compounds are steroidal estrogens including three natural estrogens of estrone (E1), 17 $\beta$ -estradiol (E2) and estriol (E3), and one synthetic estrogen of 17 $\alpha$ -ethynylestradiol (EE2). All target compounds are of the highest purity commercially available. E1, E2, E3 and EE2 were purchased from TCI, Japan. 17 $\beta$ -estradiol-d3 (E2-d3) as internal standard and 17 $\alpha$ -ethynylestradiol-d4 (EE2-d4) as surrogate standard, both of them were purchased from Cambridge, USA.

All organic solvents were of HPLC grade. Acetone, methanol and dichloromethane were from Sigma, USA. The solid phase extraction cartridges were obtained from Waters Corporation (Milford, MA, USA). Glass fiber filters (GF/F, 0.7  $\mu$ m) were obtained from Whatman and pyrolyzed at 450  $^{\circ}$ C for 4 h prior to use. Deionized water was prepared with a Milli-Q water purification system (Millipore, Watford).

### 2.3. Sample extraction

All water samples were filtered through 0.7  $\mu$ m GF/F to remove insoluble materials and extracted using HLB solid phase extraction cartridges that had been preconditioned with 5 mL dichloromethane, 5 mL methanol and 5 mL water. Then the cartridges for chemicals analysis were eluted with 6 mL methanol. The eluted analyte were collected, evaporated to dryness with nitrogen stream, and

reconstituted to 1 mL with methanol. Final solutions were filtered through a 0.22  $\mu$ m PTFE membrane filter before instrument analysis.

### 2.4. Instrumental analysis

The target compounds in sample were identified and quantified by liquid chromatography–tandem mass spectrometry (LC–MS/MS, Agilent technologies 6490). A thermo scientific column (100 mm  $\times$  2.1 mm, 3  $\mu$ m, USA) was used for separation of target compounds. Electrospray ionization was used as ionization technique, and all target compounds were analyzed in negative mode. Detailed information on analysis parameters was shown in Table 1. A binary gradient of deionized water and 100% acetonitrile was used. The HPLC gradient used for separation of estrogens is shown in Table 2. Flow rate was held constant at 0.20 mL min $^{-1}$ .

### 2.5. Quality assurance and quality control

All data generated from the analysis were subject to strict quality control procedures. With each set of samples to be analyzed, a solvent blank, a standard and a procedure blank were run in sequence to check for background contamination, peak identification and quantification. In addition, surrogate standards (17 $\beta$ -estradiol-d3) were added to all the samples to monitor matrix effects. The spiking recoveries in samples were at 81–96%. The surrogate recoveries were between 85% and 98%. Detailed information on quality control was shown in Table 3.

## 3. Results and discussion

### 3.1. Estrogenic compounds in surface water

All the target compounds were detected in the surface water of South China Sea. E3 was detected in all the sampling sites, while EE2 was only detected 3 sites. E1 was determined at concentrations ranging between LOQ and 11.16 ng L $^{-1}$  with a median of 1.38 ng L $^{-1}$ . Highest concentrations were detected for E3, ranging between LOQ and 21.63 ng L $^{-1}$  with a median of 4.89 ng L $^{-1}$ . The median concentrations in the decreasing order is E3 > E1 > E2 > EE2. E1, E2, E3 are known as natural estrogens. The results demon-

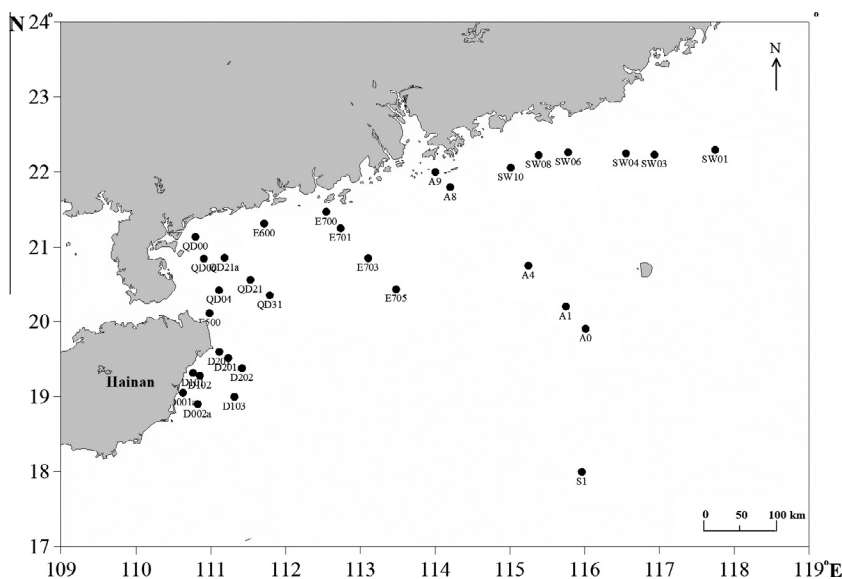


Fig. 1. Sampling sites in South China Sea.

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