Environmental Pollution 211 (2016) 58–66

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Partitions and vertical profiles of 9 endocrine disrupting chemicals in an estuarine environment: Effect of tide, particle size and salinity☆

Lihua Yang [a, b], Qiao Cheng [a], Li Lin [c], Xiaowei Wang [a], Baowei Chen [a], Tiangang Luan [a, *], Nora F.Y. Tam [b, **]

[a] MOE Key Laboratory of Aquatic Product Safety, School of Marine Sciences, Sun Yat-Sen University, Guangzhou, 510275, China
[b] Department of Biology & Chemistry, City University of Hong Kong, Kowloon, Hong Kong, China
[c] MOE Key Laboratory of Aquatic Product Safety, School of Life Sciences, Sun Yat-Sen University, Guangzhou, 510275, China

ARTICLE INFO

Article history:
Received 22 September 2015
Received in revised form
16 December 2015
Accepted 17 December 2015
Available online xxx

Keywords:
Endocrine disrupting chemicals
Humen estuary
Vertical distribution
Partition coefficient

ABSTRACT

Phenolic endocrine disrupting chemicals (EDCs) in an estuarine water column in a depth profile of five water layers (0.05 D, 0.20 D, 0.60 D, 0.80 D and 0.90 D, D = Depth, 10.7 ± 0.7 m) and their corresponding environmental parameters (tide, salinity and particle size) were investigated over a year. Water sample from each layer was further separated into three fractions, which were dissolved, coarse (SPM-D, $\Phi \geq 2.7$ μm) and fine (SPM-F, 2.7 μm > $\Phi \geq 0.7$ μm) suspended particulate matters. Most of EDCs in the water column were presented in the dissolved fraction. Vertical profiles of salinity fluctuations showed that the upper water layer was most influenced by upstream flow. Estriol (E_3), mestranol (Mes) and 17α-ethynylestradiol (EE_2) concentrations were significantly higher in ebb tide than in flood tide, indicating that EDCs mainly came from terrestrial source, the upstream flow. Dissolved EDCs also exhibited high levels in the surface layer (0.05 D) due to the upstream source and atmosphere deposition, followed by the bottom layer (0.90 D) owing to the re-suspension of EDCs-containing sediment. Compared to the dissolved phase, the contents of BPA, Mes and EE_2 in the solid phase were affected by particle size and exhibited a trend of SPM-F > SPM-D > sediment. On the other hand, the concentrations of octylphenol (OP) and *t*-nonylphenol (NP), the degradation products from common nonionic surfactants, in sediment were higher than those in suspended particles, and NP concentration was higher in flood tide than that in ebb tide. For both SPM-D and SPM-F, their corresponding EDCs concentrations were negatively related to SPM concentrations due to particle concentration effect (PCE). Owing to the "salting-out effect", salinity pushed EDCs from dissolved fraction to particulate or sedimentary phase.

1. Introduction

Endocrine disrupting chemicals (EDCs), important groups of emerging organic contaminants, have attracted more attentions in recent years. Industrial compounds octylphenol (OP), *t*-nonylphenol (NP), bisphenol A (BPA) and propylparaben (PP), synthetic hormones mestranol (Mes) and 17α-ethynylestradiol (EE_2), natural steroids 17β-estradiol (E_2), estrone (E_1) and estriol (E_3) are some key chemicals within EDCs groups. OP and NP are biodegradation products of alkylphenol polyethoxylates (APEOs), common nonionic surfactants (Isobe et al., 2006; Kolpin et al., 2002; Lye et al., 1999), BPA is a common plasticizer used in the formulation of polycarbonate- and epoxy resins-based consumer goods (Selvaraj et al., 2014). PP is widely used as a preservative in cosmetic and food products (Fang et al., 2013; Meyer et al., 2007). Mes and EE_2 are oral bio-active estrogens derived from natural hormone estradiol (E_2), which are the most common medications for humans, livestock, and aquaculture (Aris et al., 2014; Kolpin et al., 2002; Lai et al., 2000). Additionally to E_2, E_1 and E_3 are steroids discharged by natural processes of human and animals which exert hormonal actions, and can also be used as the transformation products of EE_2 (Aris et al., 2014; Ying and Kookana, 2003). The total excretion of steroids by humans and animals in China was estimated to be 3069 t/yr (Zhang et al., 2014a). Exposure to these exogenous EDCs, even at low concentrations (ng/L), could have

☆ This paper has been recommended for acceptance by Klaus Kummerer.
* Corresponding author.
** Corresponding author.
E-mail addresses: cesltg@mail.sysu.edu.cn (T. Luan), bhntam@cityu.edu.hk (N.F.Y. Tam).

http://dx.doi.org/10.1016/j.envpol.2015.12.034
0269-7491/

endocrine-like effects on the exposed organism, and their offspring might also suffer drastic repercussions (Aris et al., 2014; Jobling et al., 1998; Yang et al., 2008).

The occurrence of OP, NP, BPA, E_1, E_2 and EE_2 have been widely reported in the scale from ng/L (ng/g) to μg/L (μg/g) in municipal sewage, river water and sediment, estuarine and marine water and sediment, or even wild life around the world (Isobe et al., 2001; Kolpin et al., 2002; Lye et al., 1999; Staniszewska et al., 2014; Yang et al., 2014). Suspended particles in aquatic environments provide a crucial link for chemical constituents between water columns, bed sediments and food chains (Turner and Millward, 2002). Different sizes of particles exhibited varied compositions of inorganic materials, organic matters and microorganisms (Turner and Millward, 2002; Volkman and Tanoue, 2002), leading to the varied abilities of EDCs adsorption (Sun et al., 2012). The association of EDCs with aquatic particles was one of the most important processes controlling the fate of EDCs in rivers and coastal environments (Isobe et al., 2001). Higher partition coefficient values were found between dissolved fraction and suspended particle matters (SPM) than between dissolved fraction and sediments (Arditsoglou and Voutsa, 2012). Adsorption of EDCs to suspended particles or sediments were influenced by the organic carbon (OC) content of the sorbents (Gong et al., 2012; Guo et al., 2012; Navarro et al., 2009; Zhang et al., 2014b) and the solubility of the compounds (Navarro et al., 2009).

The sorption of EDCs onto suspended particles or sediments generally increases with increasing salinity because the solubility of neutral (hydrophobic) compounds inversely depends on the concentration of dissolved salt (Turner and Millward, 2002). Lai et al. (2000) reported that the sorption of estrogens such as E_1, E_2, E_3, EE_2 and Mes onto sediment increased with the addition of sodium chloride (NaCl) to reverse osmosis water, and to saline water. The increase in salinity also enhanced the adsorption of E_2 on various adsorbents, including granular activated carbon, chitin, chitosan, ion exchange resin and a carbonaceous adsorbent (Zhang and Zhou, 2005). However, salinity effects are not always positive. Xu et al. (2008) observed that a reduction in salinity would increase the sorption of BPA on sediment. The effect of salinity on the sorption of E_1 on various adsorbents was insignificant (Zhang and Zhou, 2005). All these reported effects of salinity on EDCs occurrences and partitions were based on laboratory batch experiments, relatively less on natural field environments.

Estuaries between continents and oceans are critical interfaces in the exchange processes of biogeochemically relevant materials including pollutants between the land and the sea (Goni et al., 2009). Lai et al. (2000) found that EDCs were more likely to be deposited or adsorbed on sediments in estuarine areas. Estuaries in the Pearl River Delta (PRD) area in South China, which is currently classified as a highly polluted region, are likely to receive and retain all the organic contaminants from the upstream Pearl River with some discharge into the South China Sea. Typical phenolic EDCs such as OP, NP, BPA, E_1 and E_2 have been detected in surface water and surface sediment from the upstream Pearl River and its estuary, and even in sedimentary cores of the adjacent sea (Chen et al., 2005; Gong et al., 2011, 2009; Peng et al., 2007; Zhao et al., 2009). The occurrence of OP, NP and BPA has also been detected in the bile of wild carps and algal samples collected in this aquatic ecosystem (Yang et al., 2014). However, most of the previous studies focused on total concentrations, few examined the partitioning of EDCs in different compartments in the estuary and their controlling factors. So far, only one preliminary investigation reporting the relationships of EDCs with dissolved and with particulate organic carbon in the Pearl River (Gong et al., 2012).

The present study therefore aimed to: 1) comprehensively investigate the spatial, temporal, vertical and tidal variations of EDCs in different environmental matrices; 2) study the partitioning behaviors of EDCs between the solid phase (sediment, fine and coarse SPMs) and the dissolved phase; 3) elucidate the relationships between concentrations and partitions of each EDCs in different matrixes and their associated effects of particle properties and salinity. In this study, Humen estuary, the largest and most polluted estuary, was chosen as an estuarine environment in the PRD area, and the representative 9 phenolic EDCs belong to the three typical kinds of natural, synthetic and industrial compounds were selected. Water, suspended particles and sediment samples were collected from Humen estuary seasonally in a year through four cruise ships.

2. Materials and methods

2.1. Chemicals and standards

Standards (purity > 99%) shown in Table S1 were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany), Aldrich Chemistry Corporation (Milwaukee, WI), or Supelco (Bellefonte, PA). Internal standards including NP-d_4, E_1-d_4 and EE_2-d_4 were purchased from Sigma–Aldrich (St. Louis, MO, USA). Derivatization regent *N,O*-Bis (trimethylsilyl) trifluoroacetamide (BSTFA) with 1% of trimethylchlorosilane (TMCS) was obtained from Supelco (Supelco Park, PA). HPLC grade acetone and methanol were obtained from Sigma–Aldrich (St. Louis, MO, USA) and pyridine (AR) was from Guangzhou chemical reagent factory (Guangzhou, China).

2.2. Site description and sample collection

Humen estuary situated in the PRD area, South China was a tidal-dominant estuary (Fig. 1). The sampling site (22°48′35.9″N, 113°36′40.5″E) was located 1.5 km from the coastline, away from

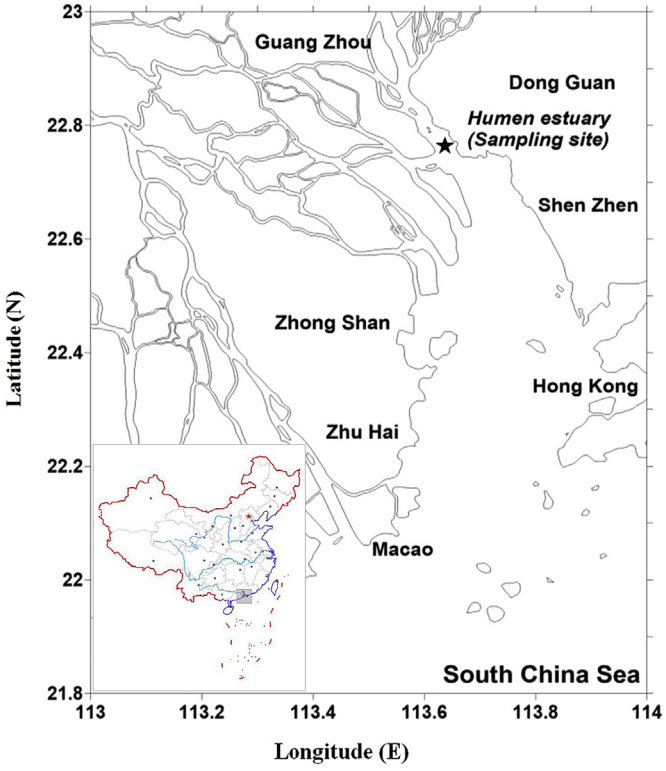

Fig. 1. The sketch map of showing the geographical location of the sampling site (★).