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Adsorption and desorption behaviors of selected endocrine disrupting chemicals in simulated gastrointestinal fluids

Ying-heng Fei [a,c], Kenneth M.Y. Leung [b], Xiao-yan Li [a,*]

[a] Environmental Engineering Research Centre, Department of Civil Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong, China
[b] The Swire Institute of Marine Science and School of Biological Sciences, The University of Hong Kong, Pokfulam Road, Hong Kong, China
[c] Guangzhou Institute of Advanced Technology, Chinese Academy of Sciences, Guangzhou, China

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ABSTRACT

An *in vitro* technique using simulated gastrointestinal (GI) fluids was applied to investigate the desorption of selected endocrine disrupting chemicals (EDCs), i.e. bisphenol A (BPA) and 17 α-ethinylestradiol (EE2), from the marine sediment in the digestive environment. The results show that the GI fluids suppressed chemical adsorption and greatly increased the desorption of BPA and EE2 from the sediment. Pepsin in the gastric fluid would compete for the adsorption sites with the adsorbates, and bile salts in the intestinal fluid had a solubilization effect on the chemicals. The amount of chemical release from the sediment in different fluids followed intestinal (fed) > intestinal (fasted) > gastric > saline water. During the dynamic desorption tests, 62% and 21% of sediment-bound BPA and EE2, respectively, could be released into the simulated GI fluids. The enhanced desorption of EDCs from sediment in the digestive system would make the pollutants more bioavailable in the ecosystem.

1. Introduction

Water pollution by emerging environmental contaminants has caused increasing public concerns in recent years. Many emerging pollutants are endocrine disrupting chemicals (EDCs) that would interfere with biological reproduction and upset the ecosystem. Due to the incomplete removal by conventional wastewater treatment, significant inputs of EDCs from the wastewater discharge and/or sludge disposal has been reported (Wang et al., 2010; Ying et al., 2008). Upon entering the natural system, adsorption of the chemical pollutants by soil and sediment may play a crucial role in the fate and transport of the pollutants in the environment (Weber et al., 1991). Pollutants can accumulate to a rather high level in the sediment (Kueh and Lam, 2008; Lai et al., 2000). With the rapid and extensive binding of hydrophobic contaminants onto the sediment matter, marine sediment has been considered as an important sink of EDCs and other emerging contaminants (Kawakami et al., 2007; Fei et al., 2011).

It is believed that adsorption would reduce the bioavailability of organic pollutants, as only the free or unbound fraction of pollutants is considered to be bioavailable to organisms and food chain (Dewitt et al., 1992). Research showed that chemical adsorption by sediment would reduce the mortality of organisms in the water–sediment system (Gourlay et al., 2005), and exposure to the overlaying water of the sediment with immobilized pollutants is therefore less harmful. However, desorption of the adsorbed chemicals from the sediment will greatly increase the bioavailability and ecotoxicity effect of the chemicals (Chai et al., 2008). Although chemical molecules adsorbed by condensed sediment can be hardly desorbed into water (Cornelissen et al., 2005), ingestion by benthic organisms of the sediment with adsorbed chemicals can be a more significant pathway to introduce the chemicals into the food chain (Shaw, 2009). Therefore, release of chemical pollutants from the sediment into the digestive fluids can be an important process for the chemical compounds to become bioavailable in the ecosystem, bringing about hazards to the environment and human health.

Instead of *in vivo* experiments on living organisms, *in vitro* gastrointestinal (GI) fluids have been used in batch tests to assess the potential bioavailability of pollutants from soil and other solid media (Rodriguez and Basta, 1999; Holman et al., 2002; Wang et al., 2011). A number of chemical desorption and dissolution studies has been conducted on the release of polycyclic aromatic hydrocarbons (PAHs) from soils and carbon nanotubes in the simulated digestive fluids (Holman et al., 2002; Tao et al., 2011; Wang et al., 2011). However, little is known about the potential desorption and release of EDCs from contaminated sediment in the digestive system. In the present study, the technique using

* Corresponding author. Tel.: +852 28592659; fax: +852 28595337.
E-mail address: xlia@hkucc.hku.hk (X.-y. Li).

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in vitro GI fluids was employed to investigate the desorption behavior of EDCs from marine sediment in the simulated digestive environment in comparison to that in saline water. Two typical EDCs, bisphenol A (BPA) and 17 α-ethinyl estradiol (EE2), were selected as the model chemicals for the experimental study, focusing on the release of the chemicals from polluted marine sediment in the simulated GI fluids.

2. Materials and methods

2.1. Marine sediment

Natural marine sediment was collected from a sampling site (22°18.400/114°06.500) in Victoria Harbour, Hong Kong (Fig. 1). The surface sediment was collected from the site 0 to 20 cm below the sediment surface. The sediment sample was stored below 4 °C in a refrigerator. Before use, shells and gravels were removed, and the sediment was air-dried and homogenized gently with a mortar and pestle. The dry sediment was the ground, and the powder passed through a 600-μm sieve was collected for the experimental use.

2.2. Model chemicals

Two typical EDCs, BPA and EE2, were chosen as the model pollutants for the sediment adsorption and desorption tests. Both the chemicals in a solid form were supplied by Sigma–Aldrich with an analytical purity (>99%). The water solubility values (S_w) of BPA and EE2 are 380 mg/L and 7.6 mg/L, respectively (Sun et al., 2011), and their octanol–water partition coefficients ($\log K_{ow}$) are 3.3 and 4.2, respectively (according to the material safety data sheet (MSDS) from the supplier). Stock solutions were made in acetonitrile that were kept in a refrigerator at 4 °C.

2.3. Environmental and gastrointestinal (GI) fluids

Simulated GI fluids were prepared for the adsorption and desorption experiments based on the methods described in literature (Wang et al., 2011). The gastrointestinal composition included ions (for ionic strength), pepsin and bile slats, as summarized in Table 1. Pepsin was added to simulate proteins in the gastric fluid, and bile salts consisting of sodium cholate and sodium deoxycholate were used for the organic salts in intestinal fluids. For comparison, a background fluid was prepared as a control, a low pH background fluid was made to have a pH (pH = 2) similar to the simulated gastric fluid, and saline water was used to simulate the marine environment. The background ionic strength was provided by 0.01 M $CaCl_2$ in water solution, and the saline water had an extremely high ionic strength from 30 g/L of NaCl. HCl was used to adjust the solution pH to pH 2. The intestinal fluid was prepared for two conditions, a fasted condition with a low concentration of bile salts (500 mg/L) and a fed condition with a high bile salt content (5000 mg/L). To avoid organic degradation during the adsorption and desorption tests, 200 mg/L of NaN_3 was added in all working solutions to inhibit microbial activities.

Table 1
Chemical compositions of the simulated environmental and gastrointestinal (GI) fluids.

Fluids	Ionic strength	Pepsin[a]	Bile salts[b]	pH
Background	0.01 M $CaCl_2$	–	–	7.5
Saline water	30 g/L NaCl	–	–	7.5
Background pH = 2	0.01 M $CaCl_2$	–	–	2.0
Gastric fluid	0.1 M NaCl	800 mg/L	–	2.0
Intestinal fluid (fasted)	0.12 M NaCl + 0.02 M Na_2CO_3	–	500 mg/L	7.5
Intestinal fluid (fed)	0.12 M NaCl + 0.02 M Na_2CO_3	–	5000 mg/L	7.5

[a] Pepsin:>250 units/mg solid (sigma, USA).
[b] Bile salts: 50% sodium cholate ($C_{24}H_{39}NaO_5$, >99%, Sigma–Aldrich) and 50% sodium deoxycholate ($C_{24}H_{39}NaO_4$, >97%, Sigma–Aldrich).

2.4. Batch adsorption tests

Batch adsorption tests were carried out to determine the isotherms of adsorption of the model EDCs by the marine sediment in different fluids, including the background solution, saline water

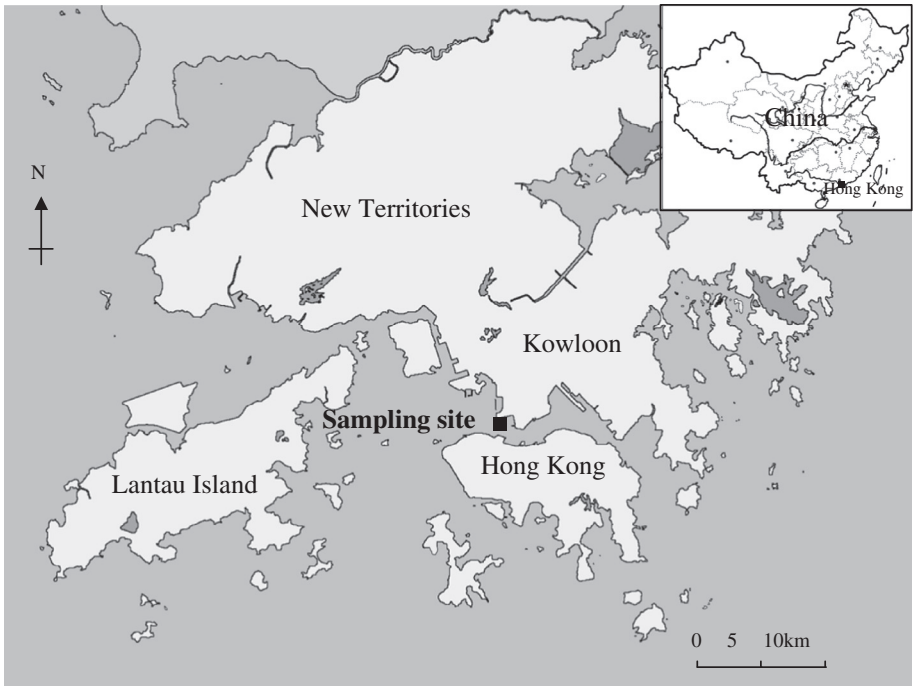

Fig. 1. The sediment sampling site in Victoria Harbour, Hong Kong.

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