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Adsorption and Desorption Behaviours of Selected Endocrine Disrupting Chemicals in Simulated Gastrointestinal Fluids

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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).

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 *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 ($22^o18.400/114^o06.500$) in Victoria Harbour, Hong Kong (Figure 1). The surface sediment was collected from the site 0 to 20 cm below the sediment surface. The sediment sample was stored below 4^oC 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 oragnic 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.

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 and GI fluids. The tests were performed following the batch equilibration procedures, using 11-mL screw-cap vials with Teflon-lined septa (Sun et al., 2010; Xing and Pignatello, 1997). Briefly, a pre-determined amount of the sediment was placed into each of a series of the test vials. The solution of BPA or EE2 at a certain concentration was then added to fill the vials with no headspace. The vials were placed in a temperature-controlled shaking incubator (Polyscience, USA) for 24 hr at 25°C and a rotating rate of 130 rpm. Upon completion of the adsorption test, the sediment mixture from each vial was centrifuged to separate the liquid from the sediment, and the concentration of BPA or EE2 in the aqueous phase was measured using a high-performance liquid chromatograph (HPLC).

The dry sediment/aqueous ratios were 0.8 g/10 mL and 0.5 g/10 mL for the tests on BPA and EE2, respectively, and the initial concentrations were in the ranges of 5-50 mg/L and 0.5-8 mg/L for BPA and EE2, respectively. Preliminary tests showed that the adsorption of both chemicals by the sediment could reach equilibrium in less than 24 hr. Losses of the chemicals attributable to glass wall adsorption or other causes were found to be less than 3%. Thus, the amount of the chemical adsorbed by the sediment in each test vial could be determined by the difference between the initial and final concentrations of the chemical in the liquid phase.

2.5 Desorption tests

Desorption experiments were conducted on the model EDCs for their desorption behaviors in different fluids. Prior to desorption, the chemical was spiked into the sediment by adsorption in saline water, following the same procedure as described for the batch adsorption tests. For

each chemical, either BPA or EE2, the spiking concentration was varied to have three initial concentrations, about $0.01S_w$, $0.03S_w$ and $0.1S_w$, in the sediment.

After adsorption for 7 d, the sediment mixture from each vial was centrifuged. The supernatant liquid was measured for the chemical concentration. Accordingly, the amount of the chemical adsorbed by the sediment was determined, which was the initial content of the sediment-bound chemical for the desorption test. The sediment was then placed in the vial and the supernatant was replaced by clean saline water or a simulated GI fluid for desorption. The vials were placed in the shaking incubator at 25°C and a rotation rate of 130 rpm for 48 hr. Upon completion, the mixture was again centrifuged, and the concentration of the chemical dissolved in the supernatant was measured and subsequently the amount of chemical desorption into the fluid was determined.

2.6 Desorption and release of model EDCs in the simulated digestion process

To assess the potential release of EDCs from the sediment in the digestive system, a more dynamic desorption experiment was carried out for a simulated digestion process (Wang et al., 2011). The sediment was firstly spiked with either BPA or EE2 in saline water for 7 days for chemical adsorption. The initial spiking concentrations were 5-50 mg/L and 0.5-8 mg/L for BPA and EE2, respectively. To result in a detectable level of chemical concentrations after a shorter period of desorption, high solid (sediment)/liquid ratios were used for the tests, which were set as 1 g/10 mL for BPA and 0.7 g/10 mL for EE2.

After the chemical spiking and adsorption, the sediment with the adsorbed EDC was separated from the solution by centrifugation. The vial with sediment was then filled with 10 mL clean gastric fluid and placed in the shaking incubator 37°C for 2 hr to determine the chemical desorption in a gut-like environment. Afterward, the supernatant was separated from the sediment, and the concentration of the chemical dissolved in the gastric fluid was measured. The vial with sediment was then filled with the intestinal fluid, and the subsequent desorption of the

residual chemical from the sediment was conducted at 37°C for 4 hr to test the chemical release in the simulated intestinal environment. The desorption test in the intestinal fluids was conducted for both the fasted or fed conditions.

2.7 Chemical analysis

The concentration of model EDCs, either BPA or EE2, in water was measured by a HPLC (Waters 2695) with a C18 column (5 µm, 2.1×150 mm) for separation and a photodiode array detector (Waters 2996) for detection and quantification. The mobile phase was a mixture of acetonitrile and water (50:50, v/v), and the flow rate was 1.0 ml/min. Under this chromatographic condition, the baseline separation could be obtained within 8 min. The peak area at the wavelength of 225 nm was used for BPA and EE2 quantification. The limits of detection and quantification were about 0.03 mg/L and 0.1 mg/L for BPA, 0.1 mg/L and 0.3 mg/L for EE2, respectively.

2.8 Data analysis

All of the data collected from the experiments were processed by Microsoft Excel 2010, SPSS 13.0 and Origin 8.0. For both adsorption or desorption, the isotherms were fitted by the linear partition model as follows,

$$q_e = K_d C_e \tag{Eq. 1}$$

where q_e and C_e are the equilibrium concentrations of the chemical in the solid phase and bulk solution, respectively, and K_d is the partition coefficient (Chiou, 2002). K_d indicates the potential distribution of a chemical between the solid and aquatic phases. A lower K_d suggests more dissolution of the chemical in the solution, while a higher K_d signifies more adsorption of the chemical onto the sediment. The K_d values for BPA or EE2 in different fluids were compared by the Student's t-test using a statistical software, SPSS 13.0. A p value less than 0.05 indicates

statistical significance for the comparison between different groups that were marked by letters superscripted to the K_d values in the result tables.

Moreover, the hysteresis phenomenon was characterized for EDC desorption from the sediment using the following hysteresis index (*HI*) (Wu and Sun, 2010),

$$HI = \frac{K_{d(D)} - D_{d(A)}}{D_{d(A)}} \qquad \text{(Eq. 2)}$$

where $K_{d(D)}$ and $K_{d(A)}$ are the partition coefficients of a chemical obtained from the desorption and adsorption tests, respectively. *HI* indicates the irreversibility of the adsorption process, with *HI* = 0 for completely reversible adsorption and a higher *HI* value for more irreversible adsorption. No hysteresis could be reported if $K_{d(D)} < K_{d(A)}$ or *HI* < 0.

3. Results and Discussion

3.1 Adsorption of BPA and EE2 on the marine sediment in GI fluids

The adsorption of the model EDCs onto the marine sediment in different fluids was investigated and compared in terms of the adsorption isotherm. In the concentration ranges tested, the adsorption of BPA and EE2 by the sediment can be well fitted by the linear partition model (Figure 2). The partition coefficients, K_d, were obtained for the adsorption of the model EDCs in different sediment-fluid systems (Table 2). Curved adsorption isotherms have been reported for chemical pollutants in a wider concentration range in some other studies (Cornelissen et al., 2005; Sun et al., 2011; Xu et al., 2008). However, the linear partition model usually can describe the isotherm very well for most environmental adsorption cases (Chiou, 2002). The linear isotherm is in fact considered as a special form of the curvilinear adsorption models, especially for the low chemical concentration range.

As indicated by the K_d values, the adsorption of BPA and EE2 by the sediment in saline water was higher than that in the background environment. The enhancement of chemical adsorption by the salt content was apparently caused by an effect called 'salting out', which is

mainly attributable to a reduced chemical activity at a higher ion strength (Means, 1995). Similar results on the effect of salinity on chemical adsorption have been reported by others (Lai et al., 2000; Tian et al., 2009; Xu et al., 2008). Compared to adsorption in the background solution, the K_d values of the two EDC compounds were considerably higher in the acidic fluid at pH = 2. It has been reported that the solubility (S_w) of BPA and EE2 decreased at a lower pH (Shareef et al., 2006; Xu et al., 2008) and the hydrophobic effect played an important role in the adsorption of BPA and EE2 (Pan et al., 2008). Thus, an acidic solution is more favorable to the adsorption of these EDCs by marine sediment, which is consistent with other experimental findings (Pan et al., 2008).

In the simulated gastric fluid, the K_d value for the sediment adsorption of BPA and EE2 were lower than that in the background solution at a similar pH level (pH = 2). It has been suggested that the strong π-π interaction is the dominant mechanism for the adsorption of BPA and EE2, which serve as π-donors with their –OH substituted benzene rings (Sun et al., 2010; 2011). However, the presence of proteins such as pepsin would reduce the strength of π-π bonding for chemical adsorption, as the aromatic surface of proteins would compete with the concerned chemical substances for the binding sites (Matsuura et al., 2006). Such a competition might be the main cause for the decreased adsorption of BPA and EE2 by sediment in the gastric fluid. Similar observations have been reported for the effect of gastric fluids on the adsorption of other organic pollutants, such as phenanthrene (Wang et al., 2011). Compared to BPA, the influence of the gastric fluid on EE2 adsorption by the sediment appeared to be more significant, likely due to that EE2 might have a weaker π-π interaction with the sediment as it consists of one less benzene ring than BPA.

In the simulated intestinal fluids, adsorption of BPA and EE2 by the sediment increased slightly for the fasted condition and decreased greatly for the fed condition. The intestinal fluid under the fed condition had a much higher content of organic salts, bile salts, than that under the fasted condition. A surfactant-like phenomenon has been suggested for bile salts that would

increase the dissolution of adsorbates (Amundson et al., 2008). It was reported that the solubility of PAHs in water could increase by more than 30 times by bile salts, which largely reduced the PAH adsorption by carbon nanotubes (Wang et al., 2011). Apparently, for the fed condition with much more bile salts (5000 mg/L), the chemical dissolution effect became dominate that weakened the adsorption of BPA and EE2. Such a dissolution effect was more significant for BPA than EE2.

The adsorption isotherms suggest that both BPA and EE2 had more adsorption by the marine sediment in saline water than in the GI fluids, following the order of saline water > gastric > intestinal (fasted) > intestinal (fed). Based on the K_d values, the adsorption of BPA was 19%, 24% and 54% lower in the gastric, intestinal (fasted) and intestinal (fed) fluids than in saline water, respectively. These reductions in adsorption in the respective GI fluids were even more significant for EE2, as by 29%, 46% and 47% compared to its adsorption in saline water. The largely reduced adsorption of the model EDCs in GI fluids suggests a high potential of desorption of the chemicals from the sediment in GI system.

3.2 Desorption of BPA and EE2 from the sediment in GI fluids

The desorption behaviors of the model EDCs were investigated at several concentration levels. After the chemical spiking and adsorption equilibrium in saline water, the initially q_e in sediment varied in 10-100 mg/kg for BPA and in 5-50 mg/kg for EE2. The desorption isotherms and the resulting K_d values for the chemicals in different fluids were summarized in Figure 3 and Table 3. Besides, the *HI* was also calculated for the chemical in a fluid based on the difference between the adsorption K_d and desorption K_d values.

As shown by the desorption isotherms, the desorption K_d of BPA was highest in saline water, followed by that in the gastric fluid and then in the intestinal fluids. For instance, for the low initial q_e tests, the desorption K_d of BPA in the gastric fluid was 11% lower than that in saline water. Under the fed condition, the desorption K_d in intestinal fluid was only half of that in the

saline water. Similar K_d comparisons were observed for the medium and high BPA q_e groups. The same results were also obtained for the desorption of EE2 from the sediment in different fluids. As K_d signifies the chemical distribution between the solid phase and the bulk solution (Chiou, 2002), a significantly lower desorption K_d indicates that more pollutant molecules would dissolve from the solid phase into the liquid phase. Thus, desorption of the model EDCs from the sediment appeared to be much easier and more significant in the GI fluids than that in saline water. As indicated by Ahrens *et al.* (2001) on other hydrophobic organic contaminants, GI proteins and bile salts in the digestive system would facilitate the desorption of chemicals.

Hysteresis has been commonly found for sediment adsorption of environmental pollutants in saline water (Wu and Sun, 2010), which suggests that chemical adsorption by sediment in seawater may not fully reversible. In Figure 3, the desorption hysteresis was indicated by the desorption data points above the lines of adsorption isotherms. For both BPA and EE2, the *HI* values obtained in the gastric fluid were lower than those in saline water in the concentration levels tested (Table 3). The lower degree of desorption hysteresis in the gastric fluid suggests a higher proportion of reversible adsorption in the gastric fluid than in saline water. In the intestinal fluids, either fasted or fed, no hysteresis was observed (with negative *HI* values), as the desorption K_d values in the fluids were lower than the adsorption K_d in saline water. Thus, complete reversible adsorption and desorption appeared to be possible for the EDCs in the simulated intestinal environment. In comparison, the degree of desorption from the sediment in the different fluids follows the order of intestinal fluid (fed) > intestinal fluid (fasted) > gastric fluid > saline water.

In relation to the desorption K_d values, the amounts of the model EDCs released from the sediment in the bulk solutions differed accordingly (Figure 4). After the equilibrium of desorption, the chemical concentrations were all higher in GI fluids than in saline water. For BPA, the desorption equilibrium concentrations in gastric, intestinal (fasted) and intestinal (fed) fluids were 5-18%, 16-22% and 56-79% more than that in saline water, respectively, while for

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EE2, these were 7-36%, 56-62% and 164-186%, respectively. This is consistent with the report that biomolecules such as pepsin and bile salts could enhance the desorption of hydrophobic organic compounds (Wang et al., 2011). The enhanced chemical release would increase the bioavailability and related health risk of the sediment-bound contaminants. Moreover, the difference between the desorption in GI fluids and saline water appeared to be larger for more hydrophobic chemicals, based on the comparison between BPA and EE2,

3.3 Release of BPA and EE2 from marine sediment into the GI fluids

To evaluate the release of chemical compounds during the digestion process, a more dynamic desorption test was conducted on the model EDCs adsorbed on the sediment through the GI fluids in a short period of time. The initial BPA and EE2 contents adsorbed by the sediment ranged in 21-202 and 27-216 mg/kg, respectively. Note that the chemical release in the simulated digestion system might not reach the equilibrium, as the duration of the desorption test was only 2 hr in the gastric fluid and then 4 hr in the intestinal fluid. However, fast desorption would occur in a short period, e.g. 1 hr (Ahrens et al., 2001; Wang et al., 2011), and the fraction of fast desorption is important to the prediction of the bioavailability of sediment-bound chemical pollutants (Chai et al., 2008).

The results shows that about 36% of the sediment-adsorbed BPA could dissolve into the simulated gastric fluid, and 21-26% more dissolved into the simulated intestine fluid under the fasted or fed condition (Figure 5). As a more hydrophobic chemical with a higher molecular weight, desorption of EE2 from the sediment was supposed to be more difficult (Ran et al., 2003). However, there was still 20-21% in total of the sediment-bound EE2 that could release into the GI fluids. It is believed that pepsin and bile salts in GI liquid would function as digestive surfactants to facilitate the mobilization and release of sediment-bound contaminants (Ahrens et al., 2001; Wang et al., 2011). For both BPA and EE2, most of the desorption took place in the gastric fluid, as most of the loosely-adsorbed or loosely-bound fractions would be mobilized in

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the first step of the desorption test. Afterward, the strong solubilization effect of bile salts in the intestinal fluid, especially under the fed condition, still could dissolve the sediment-bound chemicals to a certain extent. The much enhanced release of sediment-bound EDCs and similar pollutants in the digestive fluids would greatly increase their bioavailability and health risk of in the aquatic system.

4. Conclusions

- Adsorption of BPA and EE2 onto marine sediment is influenced by the ionic strength, pH and co-existing chemicals in the bulk solution. Generally, a higher ionic strength and lower pH would enhance the chemical adsorption, while the presence of pepsin and bile salts in the GI fluids suppresses the adsorption. According to the partition coefficients, adsorption of BPA and EE2 by marine sediment in different fluids followed the order of saline water > gastric fluid > intestinal fluid (fasted) > intestinal fluid (fed).

- GI fluids with pepsin and bile salts can greatly enhance the desorption of BPA and EE2 from the sediment. The amount of chemical release from the sediment was in the order of intestinal fluid (fed) > intestinal fluid (fasted) > gastric fluid > saline water. According to the dynamic desorption tests for the digestion process, 62% of sediment-bound BPA and 21% of sediment-bound EE2 could be released rapidly into the simulated GI fluids. The enhanced dissolution of EDCs from the sediment in the digestive system would increase the bioavailability of the chemicals in the ecosystem.

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Table and figure captions

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

Table 2. Partition coefficients for the adsorption of model EDCs on the marine sediment in different fluids.

Table 3. Partition coefficients and hysteresis values for the desorption of model EDCs from the marine sediment in different fluids.

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

Figure 2. Linear partition isotherms for the adsorption of BPA (top) and EE2 (bottom) on marine sediment in different fluids.

Figure 3. Comparison between the adsorption in saline water and desorption in different fluids for BPA (top) and EE2 (bottom) (dashed line: adsorption isotherm for the chemical spiking).

Figure 4. Comparison of the equilibrium concentrations of BPA (top) and EE2 (bottom) after desorption from the marine sediment in different fluids.

Figure 5. Rapid release of the sediment-sorbed BPA and EE2 in the simulated GI fluids in comparison to the amount remained on the sediment (left: concentrations; right: normalized fractions).

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

Fluids	Ionic strength	Pepsin[*]	Bile salts[**]	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$_2$CO$_3$	-	500 mg/L	7.5
Intestinal fluid (fed)	0.12 M NaCl + 0.02 M Na$_2$CO$_3$	-	5000 mg/L	7.5

[*]Pepsin: >250 units/mg solid (Sigma, USA).

[**]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)

Table 2. Partition coefficients for the adsorption of model EDCs on the marine sediment in different fluids.

Fluids	BPA		EE2	
	K_d (L/kg) [*]	R^2	K_d (L/kg) [*]	R^2
Background	2.38±0.09[a]	0.99	13.49±0.74[a]	0.95
Saline water	3.17±0.08[b]	1.00	25.25±1.44[b]	0.94
Background pH=2	2.77±0.06[c]	1.00	26.06±1.82[b]	0.92
Gastric fluid	2.57±0.07[d]	0.99	17.90±1.09[c]	0.93
Intestinal fluid (fasted)	2.41±0.07[a]	1.00	13.71±0.54[a]	0.97
Intestinal fluid (fed)	1.45±0.04[e]	0.99	13.32±0.21[a]	1.00

[*] Values with different letters are significantly different.

Table 3. Partition coefficients and hysteresis values for the desorption of model EDCs from the marine sediment in different fluids.

Fluids	BPA			EE2		
	Initial q_e (mg/kg)	K_d (L/kg)[*]	HI[**]	Initial q_e (mg/kg)	K_d (L/kg)[*]	HI[**]
Saline water	10	2.82 ± 0.10^a	0.19	5	37.09 ± 6.01^a	0.89
Gastric fluid		2.50 ± 0.44^{ab}	0.05		27.67 ± 6.28^{ab}	0.41
Intestinal fluid (fasted)		2.27 ± 0.09^b	-		17.52 ± 6.67^b	-
Intestinal fluid (fed)		1.43 ± 0.08^c	-		7.20 ± 3.95^c	
Saline water	20	1.99 ± 0.06^a	0.31	25	30.89 ± 8.5^a	0.23
Gastric fluid		1.55 ± 0.04^b	0.02		26.70 ± 2.68^a	0.06
Intestinal fluid (fasted)		1.52 ± 0.24^b	-		16.63 ± 3.30^b	-
Intestinal fluid (fed)		0.60 ± 0.08^c	-		6.80 ± 1.17^c	-
Saline water	100	2.07 ± 0.02^a	0.82	50	31.10 ± 2.95^a	0.88
Gastric fluid		1.87 ± 0.06^b	0.65		29.54 ± 1.22^a	0.78
Intestinal fluid (fasted)		1.67 ± 0.11^c	0.47		11.76 ± 1.58^b	-
Intestinal fluid (fed)		1.04 ± 0.09^d	-		7.10 ± 0.06^c	-

[*] Values with different letters are significantly different.

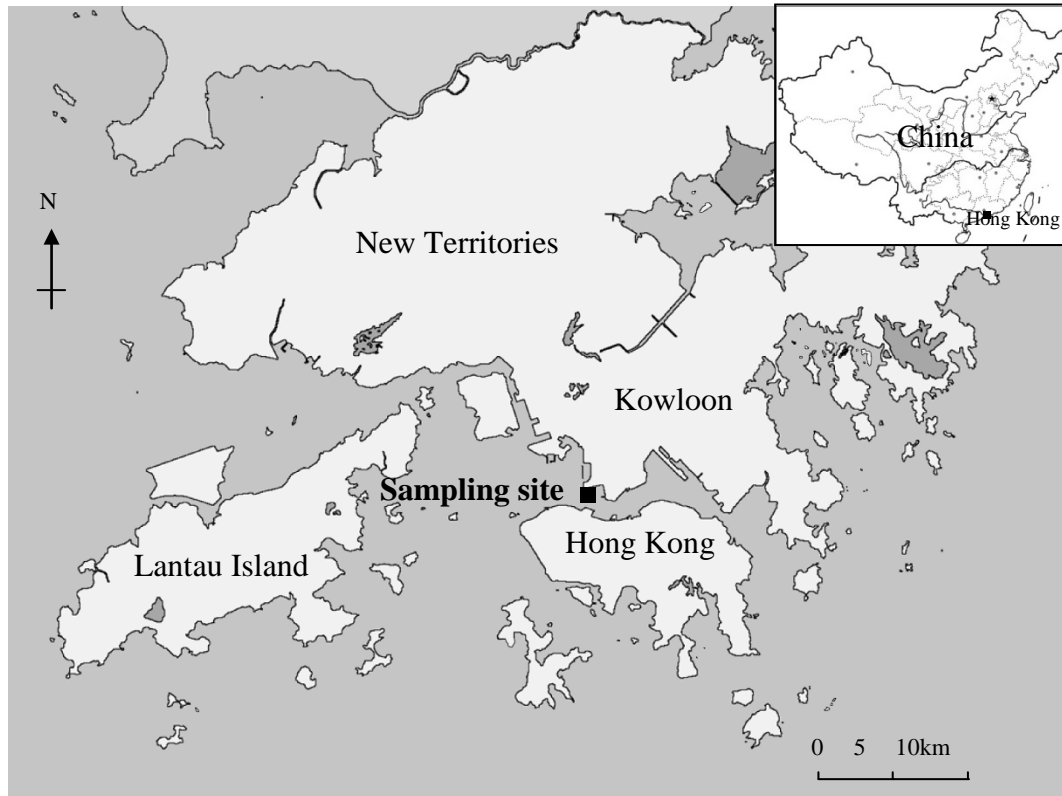[**] No desorption hysteresis was observed for negative HI values.

Figure 1. The sediment sampling site in Victoria Harbour, Hong Kong.
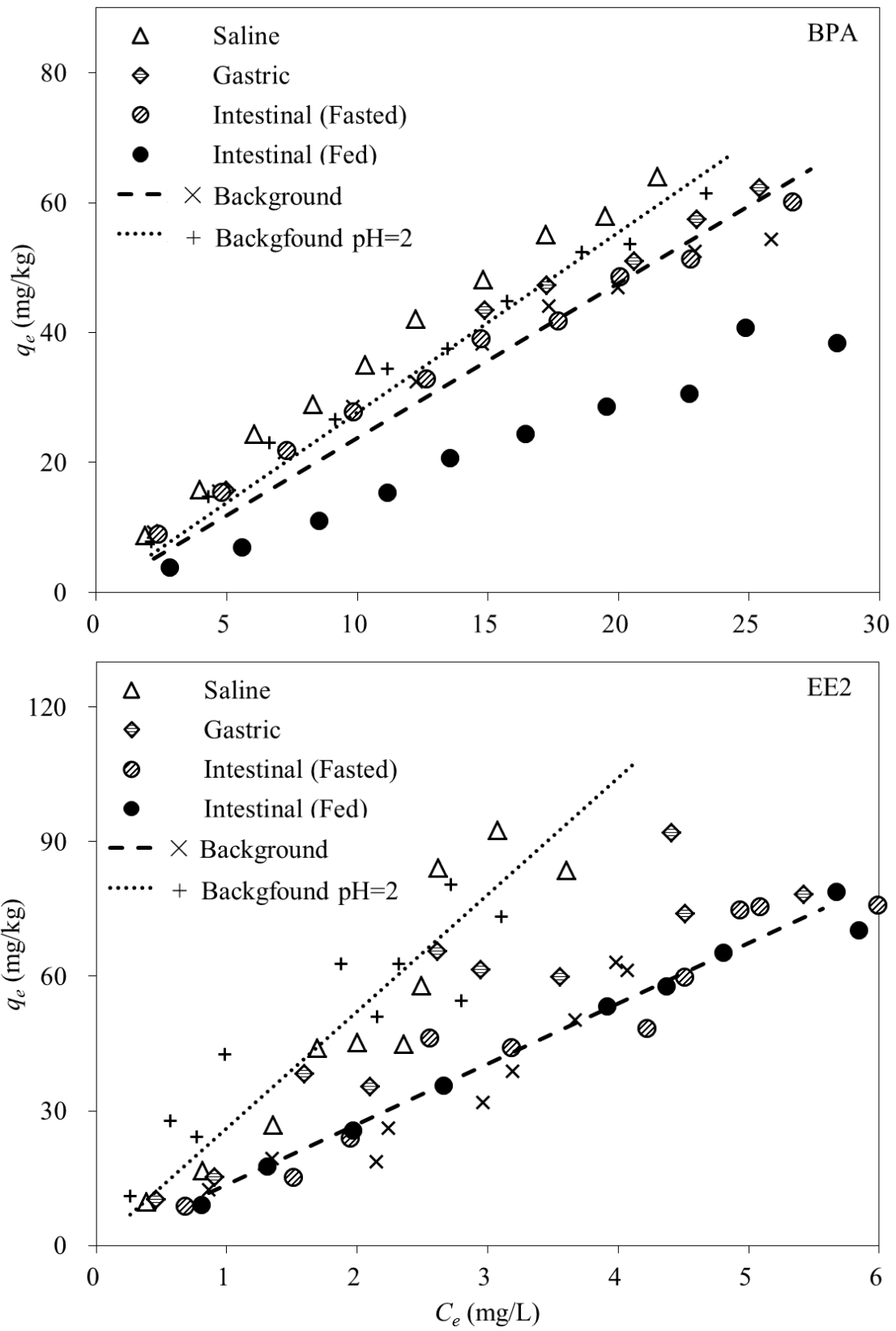
Figure 2. Linear partition isotherms for the adsorption of BPA (top) and EE2 (bottom) on marine
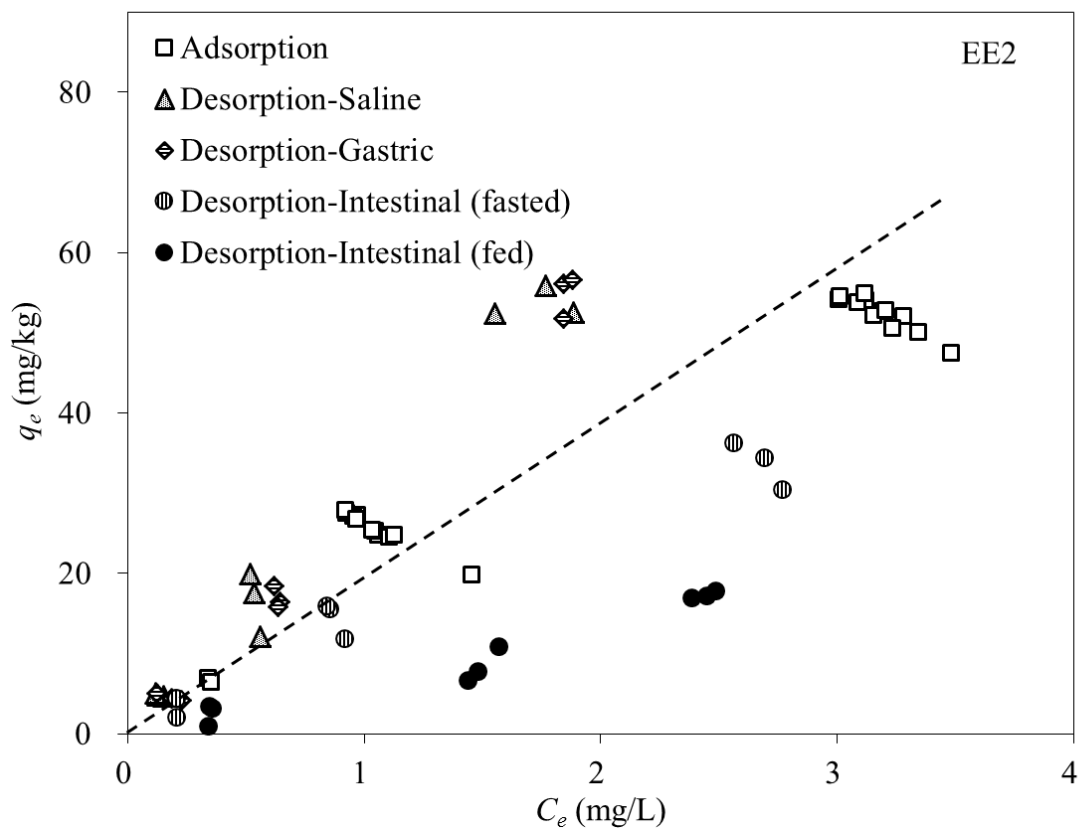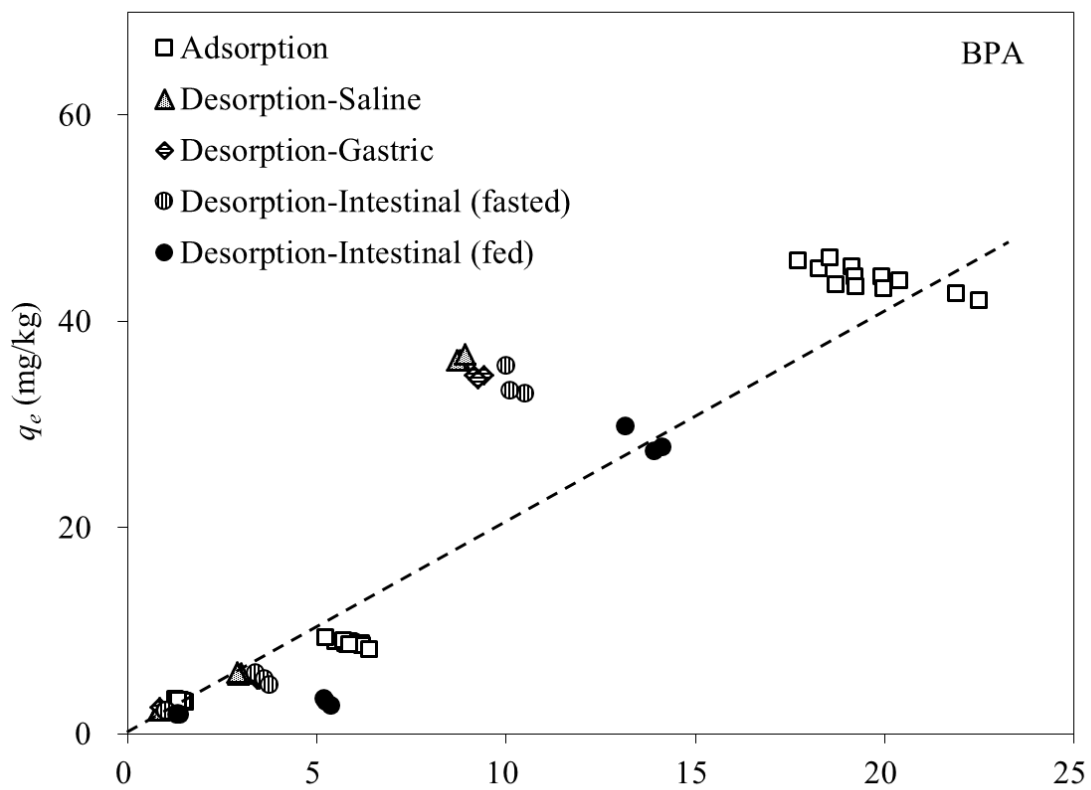
sediment in different fluids.

Figure 3. Comparison between the adsorption in saline water and desorption in different fluids

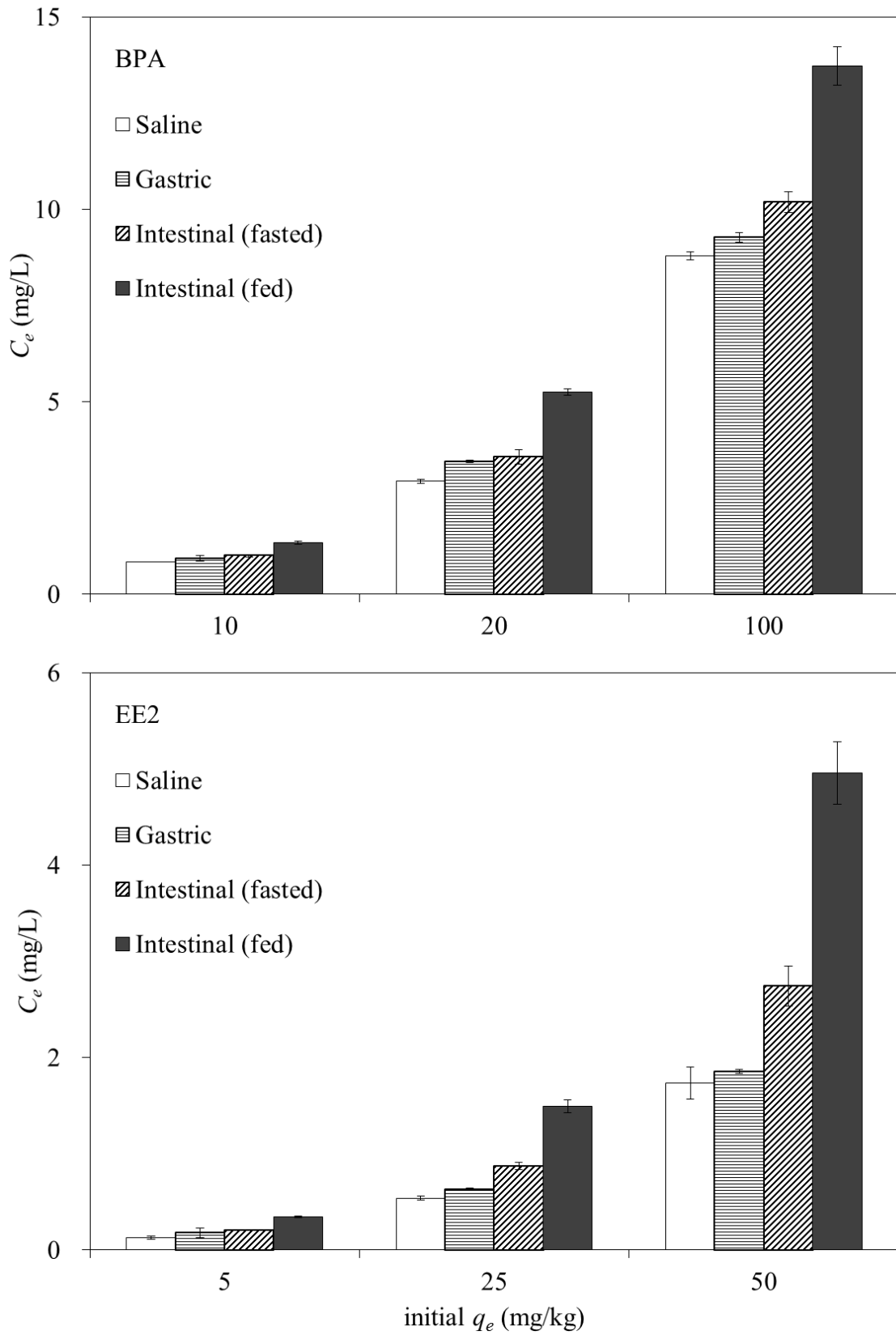for BPA (top) and EE2 (bottom) (dashed line: adsorption isotherm for the chemical spiking).

Figure 4. Comparison of the equilibrium concentrations of BPA (top) and EE2 (bottom) after

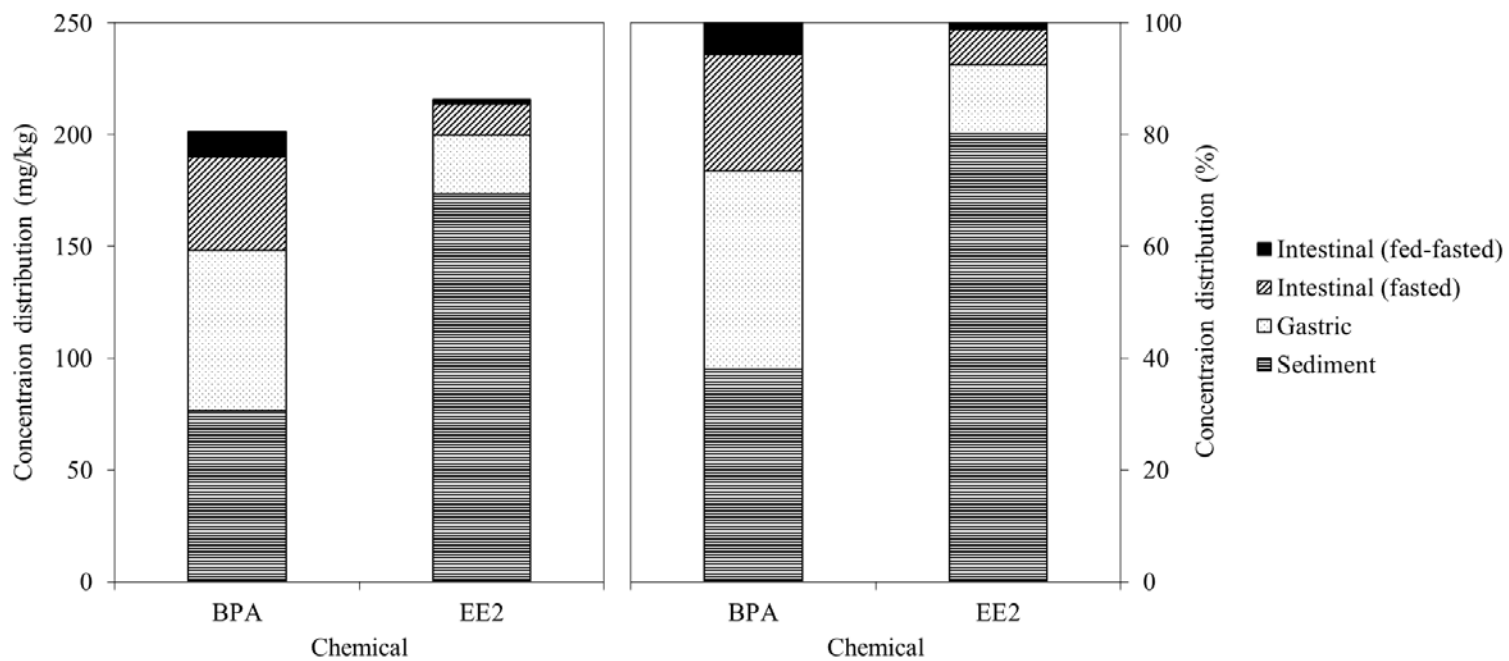desorption from the marine sediment in different fluids.

Figure 5. Rapid release of the sediment-sorbed BPA and EE2 in the simulated GI fluids in comparison to the amount remained on the sediment (left: concentrations; right: normalized fractions).