



# Predicting bioaccessibility of contaminants of emerging concern in marine sediments using chemical methods

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## Abstract

**Purpose** A comparison was made between three chemical methods to predict bioaccessibility of triclosan (TCS), bisphenol A (BPA), and 17 $\alpha$ -ethynylestradiol (EE2) in marine sediments, involving an exchangeable (E) value, butanol extractions, and hydroxypropyl- $\beta$ -cyclodextrin ( $\beta$ -HPCD) extractions.

**Materials and methods** A 60-day batch experiment was undertaken where the aqueous phase was analyzed by GC-MS/MS. The bioaccessibility study based on the *E* value model involved monitoring stable isotopes exchanging with the bioaccessible phase, while this exchangeability was also estimated with sediment extractions with butanol and  $\beta$ -HPCD, respectively.

**Results and discussion** Based on the *E* value method, TCS was readily exchangeable for up to 7 days, while after this period become virtually non-exchangeable (not detected in aqueous phase). This trend was also evident for butanol and  $\beta$ -HPCD extractions, suggesting TCS was strongly complexed with the matrix. For BPA and EE2, the fraction considered exchangeable was higher after 14 days and the extraction efficiency was slightly higher for the butanol treatment.

**Conclusions** Chemical methods to predict bioaccessibility in marine sediments have demonstrated differences between selected contaminants, but agreement between methods. Triclosan shows the highest affinity with tested sediments, some exchangeability in the first days of interaction of *E* value experiment as well as observed for extraction methods. However, the highest capacity to be extracted from already-sorbed phase was observed for BPA, showed in both extraction methods, and confirming its mobility and bioaccessibility in sediments over the time.

**Keywords** Emerging contaminant · Isotopic exchangeability · Sediment · Sorption bioaccessible

## 1 Introduction

The marine environment is exposed to the input of organic contaminants originating from anthropogenic sources, such as urban and industrial effluents, which can impact biological organisms even at very low concentrations (e.g., part per

trillion). The potential risks of these contaminants can be strongly influenced by bioavailability, contamination concentrations, as well as exposure pathway and duration (Fent 2006). Marine organisms can be exposed to these contaminants through sediment, the water column, and trophic chain (Morcilo et al. 1997; Campillo et al. 2004; Harmsen 2007), and the accumulation/uptake can occur through active and/or passive mechanisms (Dafforn et al. 2012).

Sorption and desorption of hydrophobic contaminants has been considered to be a major factor controlling the transport and fate of contaminants into the aquatic system and are determined by chemical, physical, and biological process (NRC 2003). In this sense, sorption studies can generate important information about the mobility and distribution of contaminants, being considered as a key process for influencing bioavailability (Cunha et al. 2012; Sun et al. 2012). The partitioning coefficient ( $K_d$ ) is the ratio between the concentration of a contaminant present in the solid phase and in the

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aqueous phase, when the adsorption equilibrium has been reached (OECD 2000). However, behavior and distribution of contaminants in aquatic systems can be very complex, particularly in marine environments due to variation in ecological and hydrodynamic profiles (Bayen et al. 2013). Also, chemical parameters specific to the marine environment are important in affecting the sorption of hydrophobic contaminants to organic carbon. For example, salinity can increase the tendency of non-polar organic contaminants to leave the aqueous phase (“salting out”) (Scharzenbach et al. 2003).

For organic contaminants, the release of previously sorbed contaminants can have many implications, such as the sediment acting as a long-term source of these contaminants, since desorption can be kinetically slower than sorption (Williams and Kookana 2010). This long-term release of contaminants back into solution, where it is considerably more bioaccessible, may result in a significant exposure to aquatic organisms (Karnjanapiboonwong et al. 2010). Contaminants of emerging concern (CECs), including pharmaceuticals and personal care products (PPCPs) and endocrine disruptors (EDCs), are commonly investigated in the water column close to submarine outfalls of wastewater treatment plants (WWTPS) or stormwater discharges (Sanchez-Brunete et al. 2010; Boehler et al. 2017) where can be continuously released.

Triclosan (TCS) is commonly used as an antimicrobial agent in personal care and household products and in the textile and plastic industry. This contaminant is typically added to products at concentrations between 0.1 and 0.3% by product weight. This contaminant is transported to municipal wastewater treatment plants (WWTPs) and discharged into the aquatic system. Under estuarine conditions, TCS can be rapidly accumulated into sediments (Cantwell et al. 2010). Bisphenol A (BPA) is a compound used in many industrial process and because of this, widespread application can be found in many environmental compartments as result of leaching of products containing this contaminant. In the environment, this contaminant has a half-life time of 2.5 to 4 days and is commonly associated with organic matter despite its water solubility (Flint et al. 2012). 17 $\alpha$ -Ethinylestradiol (EE2) is a potent synthetic estrogen used as an oral contraceptive and is released into the aquatic environment at sub-ng L<sup>-1</sup> concentrations following incomplete removal in WWTPs. Due to its physicochemical properties, these contaminants have a tendency to be associated with organic matter (Ding et al. 2015) and accumulates in sediments and aquatic organisms (Ying and Kookana 2003; Dhillon et al. 2015; Ebele et al. 2017).

The study of the bioaccessible fraction of a contaminant associated with solids in the environment can be also estimated using a number of chemical extraction approaches, mainly involving non-exhaustive methods to predict the labile (accessible) fraction that can be readily released, as would occur when chemical/physical conditions of the environment

change (Reid et al. 2000; Williams and Kookana 2010; Cui et al. 2013; He et al. 2017). This prediction, as well as the exposure of organisms to a contaminant, where bioavailable fraction is verified, figures out as important investigations for characterizing ecological risk of contaminants in aquatic systems (Harmsen 2007; Ortega-Calvo et al. 2015). The exchangeable (E) value has been used to estimate bioaccessible fractions of contaminants since it corresponds with the freely exchangeable portion, existing between aqueous and sediment phases (Hamon et al. 2002; Williams and Kookana 2010; Delgado-Moreno and Gan 2013). In this case, the exchangeable pool of a contaminant can be considered as the sum of sorption and desorption occurring in the interface between two phases. Studies involving partial chemical extraction techniques such as hydroxypropyl- $\beta$ -cyclodextrin ( $\beta$ -HPCD) and butanol can also be predictive of bioaccessibility mimicking the uptake obtained in bioassays (Reid et al. 2000; Cui et al. 2013; Corrotea et al. 2016). Cyclodextrins are a class of oligosaccharides with circular structures with a hydrophobic organic cavity in the center surrounded by a hydrophilic outer shell (Song et al. 2011; Cui et al. 2013). This apolar cavity allows the formation of a complex between a cyclodextrin molecule and low-polarity organic contaminant (Swindell and Reid 2007). Contaminants that are readily released, or labile, from solids can be accessed when cyclodextrin is introduced into a sediment and water system. The mild solvent *n*-butanol can also be applied in bioavailability tests with satisfactory results in terms of representativeness in bioaccessibility prediction (Liste and Alexander 2002; Song et al. 2011).

In this study, we investigated three contaminants of environmental concern: triclosan (TCS), bisphenol A (BPA), and 17 $\alpha$ -ethinylestradiol (EE2) (Table 1-SI) and assessed their bioaccessibility following long-term sorption (60 days) under laboratory conditions, comparing extraction of sediments using three chemical methods: the *E* value, butanol, and hydroxypropyl- $\beta$ -cyclodextrin ( $\beta$ -HPCD).

## 2 Materials and methods

### 2.1 Chemicals

Triclosan (5-chloro-2-(2,4-dichloro-phenoxy)-phenol—CAS 3380-34-5), bisphenol A (4,4'-dihydroxy-2,2-diphenylpropane—CAS 80-05-7), and 17- $\alpha$  ethinylestradiol (EE2) all had purity >98% and CAS 57-63-6 98.0% were purchased from Sigma-Aldrich (NSW, Australia). The stable isotopes triclosan d<sub>3</sub> (TCS d<sub>3</sub>), bisphenol A d<sub>16</sub> (BPA d<sub>16</sub>), and 17 $\alpha$ -ethinylestradiol <sup>13</sup>C<sub>2</sub> (EE2 <sup>13</sup>C<sub>2</sub>) were purchased from ScyVac Pty Ltd. (NSW, Australia). Acetonitrile, dichloromethane, methanol, and acetic acid are all of HPLC or higher grade (Thermo Fisher Scientific; Victoria, Australia). Primary

secondary amine (PSA) and C18 (octadecyl) dispersive salts, pyridine, BSTFA (*N,O*-Bis(trimethylsilyl)trifluoroacetamide) with 1% TMCS, butanol, and hydroxypropyl- $\beta$ -cyclodextrin ( $\beta$ -HPCD) were purchased from Sigma-Aldrich (NSW, Australia).

## 2.2 Sediment samples and materials preparation

Sediment samples were obtained from a single sampling campaign proceeded on September 2013 at Barker Inlet (34.74681 S; 138.4832 E) from a depth of 3.4 m. Barker Inlet is located 15 km north of Adelaide, South Australia, and receives effluents from Bolivar WWTP (Fernandes et al. 2011). Samples were transported to the laboratory in the dark and on ice. Sediments were sieved (2-mm mesh), homogenized for 24 h using a rotation mixer, and stored at 4 °C. Sub-samples were used for organic carbon and percentage of fines determination (silt and clay) as well as a portion for chemical analysis using QuEChERS method (described in detail in [Supplementary Material-SM](#)) to check the bulk concentration of investigated contaminants, where no detection levels were detected in sediment extracts. Sediment composition, measured by pipette (four fractions) and combustion methods, was total carbon (1.8%); organic carbon (0.5%); total nitrogen (0.023%); CaCO<sub>3</sub> (10.9%); clay (0.9%); silt (0.4%); sand (83.8%); and total fines (1.3%).

All glassware used for the sorption experiments were washed using a neutral detergent, rinsed with tap water followed by 18.2 M $\Omega$  cm ultrapure water (Milli-Q®, Millipore), wrapped in aluminum foil and heated to 350 °C for 3 h. Contaminant standards were prepared in methanol from a stock solution of 1 g L<sup>-1</sup> and were kept at -18 °C in the dark and renewed after 1 month of preparation.

## 2.3 Sorption experiment setup

Batch sorption methods were based on OECD methodology (OECD 2000). Initially, 2 g of wet sediments was weighed in glass tubes with PTFE-lined lids, followed by addition of 10 mL of artificial seawater spiked with the contaminants, and left for 24-h equilibrium within an end over end rotating shaker. The sediment was shaken in contact with the aqueous phase to check the equilibrium between phases. Sorption was assessed using 10 different concentrations for each target contaminant in a range of 5 to 1000  $\mu$ g L<sup>-1</sup>. The concentration of sorbed contaminant in sediments was indirectly measured based on the difference between the amount initially added into the testing tubes and the final amount measured in solution after the sorption period using linear (Eq. (1)), Freundlich (Eq. (2)), and Langmuir (Eq. (3)) isotherms as follows:

$$K_d = \frac{C_{\text{sed}}}{C_{\text{aq}}} \quad (1)$$

where  $K_d$  is the partitioning coefficient,  $C_{\text{sed}}$  is the estimated concentration of contaminant in sediment (ng g<sup>-1</sup>), and  $C_{\text{aq}}$  is the concentration of contaminant in seawater (ng mL<sup>-1</sup>).

$$C_{\text{sed}} = K_f x C_{\text{aq}}^{1/n} \quad (2)$$

where  $K_f$  is the Freundlich partitioning coefficient (log intercept) and  $1/n$  is the Freundlich exponent (1/slope). If  $n = 1$ , sorption is constant with the increase of concentration;  $n < 1$ , sorption decreases with the increase of concentration;  $n > 1$ , sorption increases with the increase of concentration.

$$C_{\text{sed}} = \frac{(K_L x C_{\text{aq}} x b_L)}{1 + K_L x C_{\text{aq}}} \quad (3)$$

where  $K_L$  is the Langmuir partitioning coefficient and  $b_L$  is the maximum adsorption (ng g<sup>-1</sup>).

Adsorption kinetics were also checked overtime (0, 4, 8, 16, 24, 48, and 72 h), using the equilibrium concentration. The interactions between unlabeled and labeled analytes were also checked after 24 h of interaction as well as the differences in sorption when sodium azide (NaN<sub>3</sub>) 0.1% was added in to the system. Theoretical sediment:solution ratio was verified considering Eq. (4):

$$K_d = \frac{(V_w(C_o - C_i))}{M_{\text{sed}} x C_i} \quad (4)$$

where  $V_w$  is the volume of seawater,  $C_o$  is the initial concentration of analyte in spike seawater,  $C_i$  is the final concentration of analyte in seawater, and  $M_{\text{sed}}$  is the mass of sediment.

The sorption of TCS was assessed alone and in a mixture with EE2 and BPA to check sorption behavior in the presence of additional contaminants. Experiments were conducted in triplicate, with controls including unspiked sediments and spiked seawater without sediments. All experiments were conducted using prepared artificial seawater 31 psu (Morrison and Chapman 1990) pH 8 at 22  $\pm$  1 °C.

## 2.4 Bioaccessibility study

Bioaccessibility was estimated using an isotope exchange ( $E$  value) method and butanol and  $\beta$ -HPCD extractions. Experiments were conducted over 60 days with sampling at 0, 1, 3, 7, 14, 30, 45, and 60 days. Samples were kept in the dark at constant temperature (22 °C  $\pm$  1), shaking on a flat-bed orbital shaker at 115 rpm.

The concentrations of CECs in seawater used in this experiment were: 250 ng mL<sup>-1</sup> for TCS; 150 ng mL<sup>-1</sup> for BPA; and 100 ng mL<sup>-1</sup> EE2, determined according to equilibrium concentrations reached in sorption studies. A spiking solution of the respective contaminants was prepared in artificial seawater containing 0.1% NaN<sub>3</sub> for inhibiting microbial degradation, with 4 mL of this spiking solution added to scintillation flasks

containing 1 g of previously weighed wet sediments. Scintillation vials were shaken for 72 h to attain equilibrium of contaminants between solution and sediment before commencing time 0 sampling.

For the *E* value method, an isotope solution was prepared as the unlabeled contaminants with  $2.5 \mu\text{g mL}^{-1}$  TCS  $d_3$  and  $1.25 \mu\text{g mL}^{-1}$  for BPA  $d_{16}$  and EE2  $^{13}\text{C}_2$ . Following the 72-h equilibration period and for each sampling period, 1 mL of this isotope solution was added to the scintillation vials. After spiking isotopes to the sediment/solution mixture, tubes were shaken in an orbital shaker for a further 72 h prior to analysis. For the butanol extraction, 7 mL butanol was added following the removal of the aqueous phase from the scintillation vial after sediment settling. For the  $\beta$ -HPCD extraction, a 50-mM  $\beta$ -HPCD was prepared and 1 mL of this was added to the scintillation vial containing sediment and aqueous phase. Following the addition of butanol and  $\beta$ -HPCD to the scintillation vials, shaking for an extra 24 h was required.

An aliquot of 1 mL was removed from the scintillation vials for all extraction methods following this shaking period, filtered through a glass fiber filter ( $0.7 \mu\text{m}$ ), and kept in the freezer at  $-18 \text{ }^\circ\text{C}$ . Contaminants were extracted from this solution using solvent exchange with 0.1% acetic acid in dichloromethane, which was separated from the aqueous phase and passed through a column of activated sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) and florisil. Recoveries were above 60% for all contaminants (RSD < 20%). Dichloromethane extracts were then dried under a gentle  $\text{N}_2$  stream and derivatized for gas chromatograph tandem mass spectrometry (GC-MS/MS) analysis by adding  $0.4 \mu\text{L}$  of pyridine and  $0.1 \mu\text{L}$  of solution BSTFA + TCMS in a vial and heating in a thermal block at  $60 \text{ }^\circ\text{C}$  for 30 min. After this period, extracts were cooled to room temperature and injected for analysis within 48 h of derivatization.

## 2.5 Analytical system and quality control

A GC-MS/MS triple quadrupole (Agilent Technologies) operating on SIM mode (selective-ion mode) was used for CEC determination along with a selective precursor-product ion transition, operating in MRM (multiple reaction monitoring) mode. The column used was HP-5 ms Agilent 19091S-433 ( $30 \text{ m} \times 250 \mu\text{m} \times 0.24 \mu\text{m}$  film thickness) using helium ( $1 \text{ mL min}^{-1}$ ) as the carrier gas. The injector temperature was  $250 \text{ }^\circ\text{C}$  and operated in splitless mode with  $1 \mu\text{L}$  of injection volume. The oven program was  $130 \text{ }^\circ\text{C}$  (0.5 min), then  $40 \text{ }^\circ\text{C min}^{-1}$  until  $240 \text{ }^\circ\text{C}$  and  $5 \text{ }^\circ\text{C min}^{-1}$  until  $280 \text{ }^\circ\text{C}$  (3.75 min). The total running time was 15 min.

During the experiments, matrix and method blanks were considered for quantification. For injections, quality control was checked using QC standards between samples throughout and calibration curves in the beginning and end of each sample list daily. Linearity of curves was checked for each

contaminant in the range of 1 to  $1000 \text{ ng mL}^{-1}$  with correlation factors ( $R^2$ ) above 0.99. Matrix effects were checked in both systems, and no relevant effect (> 10%) was verified for seawater. Further details of GC-MS/MS analysis are summarized in the Supplementary Material (Tables 2 and 3-SM). Comparison between prediction methods and contaminants was verified using one-way ANOVA with a confidence level of 95% ( $p = 0.05$ ).

## 3 Results and discussion

### 3.1 Sorption of contaminants

Isotherm models obtained from the batch experiments are summarized in Table 1 and Fig. 1. Results from sediment equilibrium over 72-h interaction as well as theoretical determination of sediment:solution ratio are present in Fig. 1-SM. Considering the higher sorption capacity of TCS ( $K_d = 40$ ), the optimal mass of sediment was 0.1 g for 5 mL seawater (1:50), while for EE2 ( $K_d = 2.9$ ) and BPA ( $K_d = 2.7$ ), the optimum amount was around 2.5 g (1:2). Thus, a compromise sediment:solution ratio of 1:5 was chosen for the experiments.

For the linear mode,  $K_{oc}$  values for each contaminant were checked based on the content of organic carbon from tested sediment (0.5%). Following this model, the ratio  $C_{aq}/C_s$  can decrease with increase of concentration for BPA and EE2. Those contaminants (BPA and EE2), due to the presence a plateau, the sorption using the tested sediment is considered the sorption limit. For TCS, sorption in the mixture of contaminants and alone had demonstrated similar results as observed in Table 1. The high slope at the beginning of the curve for TCS may indicate a high affinity with sediment (Fig. 1), beside the fact that the pH of experiment ( $\sim 8$ ) was close to TCS pKa (7.8), where the anionic form of this contaminant was dominant, and sorption capacity can decrease due to repulsive electrostatic interactions with a negatively charged sediment surface, as well as a higher water solubility (Lin et al. 2011). The sorption behavior of TCS in the mixture and individually demonstrates there was no effect on  $K_F$  (0.34) based on the Freundlich isotherms and demonstrates a higher interaction with organic matter (Cunha et al. 2012), when compared with that of BPA and EE2 (0.21). Freundlich isotherm was previously indicated as a better sorption model for TCS in sediments (Xu et al. 2009; Huang et al. 2015). However, linear equation is also discussed (Wu et al. 2003). In the same way, Sun et al. (2012) investigated sorption of BPA and EE2 in river sediments and also concluded that the Freundlich isotherm was the best model to explain the sorption of these contaminants. The same result was also observed for BPA in sediments (Tian et al. 2009; Ding et al. 2015).

In this sense, contaminant sorption could be explained based on Freundlich isotherms and follow the order TCS >

**Table 1** Isotherm parameters for all target contaminants

	Linear			Freundlich			Langmuir		
	$K_d$	$K_{oc}$	$R^2$	$K_f$	$N$	$R^2$	$K_L$	$b_L$	$R^2$
TCS	40	8000	0.8792	0.34	1.38	0.67785	-4E-01	116	-0.0168
TCS mix	38	7600	0.8253	0.34	1.40	0.68759	-2E-02	112	-2.086E-4
BPA	2.7	540	0.056	0.21	2.49	0.89055	-2E-01	75	-0.024
EE2	2.9	580	0.5101	0.21	2.40	0.8897	-1E+00	99	-0.0538

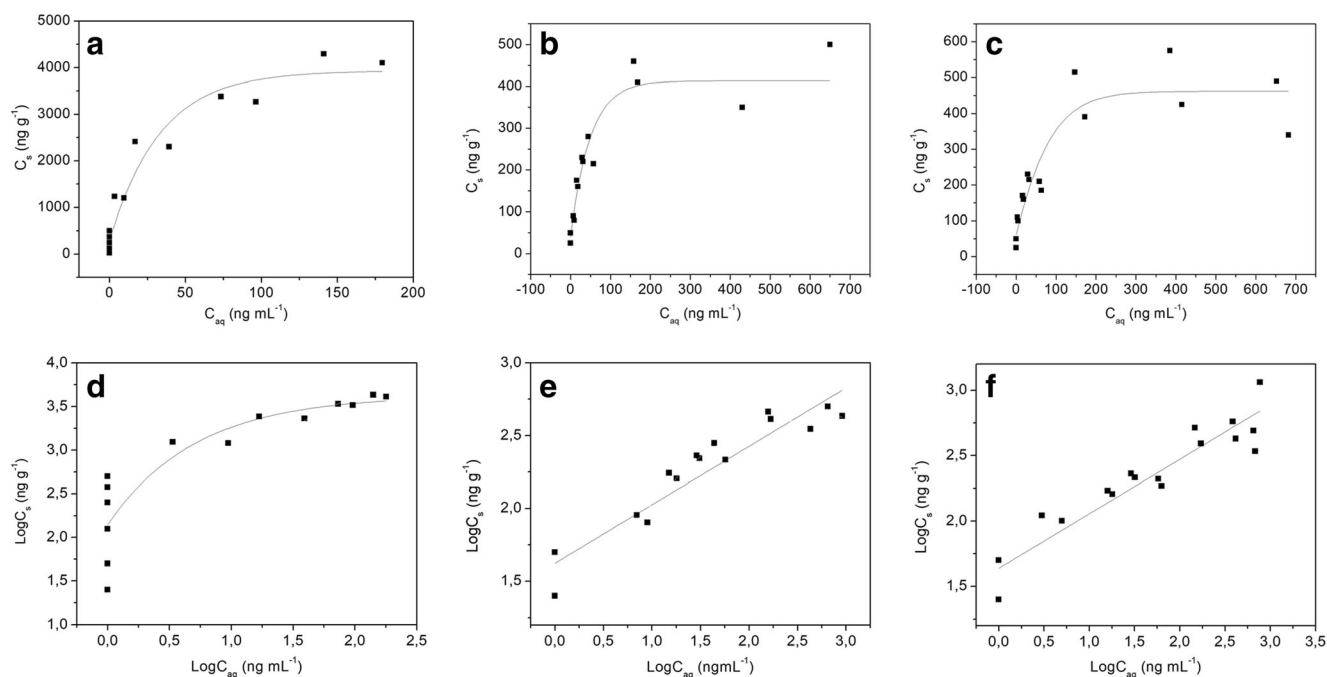
BPA > EE2 for tested sediments. A non-linearity observed in Freundlich curve (based on  $n$  values) can be observed, once values for all contaminants were not equal to 1, indicating a concentration dependence in the adsorption process (Xu et al. 2009). According to Lu et al. (2003), the behavior of contaminants with reversible sorption was better described by a linear isotherm while irreversible sorption usually follows the Langmuir model. As none of the investigated contaminants could be explained using this model, these conditions used in the present study could indicate all contaminants can be desorbed from sediments.

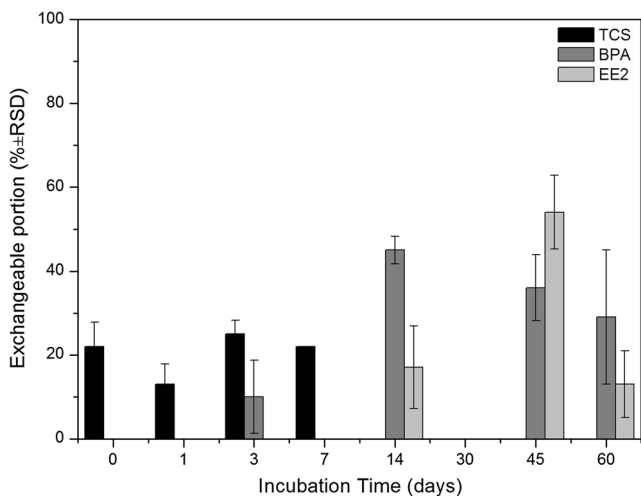
Although the high correlation between sorption affinity and  $K_{ow}$  for those contaminants is associated with hydrophobic partitioning process, other sorption processes can be involved (Lee et al. 2003). For example, sorption isotherms involving TCS at high concentrations depend on organic matter, pH, and clay content of studied sediments (Lin et al. 2011). Yu et al. (2004) report that estrogen (including EE2) sorption onto soil samples is affected not only by hydrophobic interactions but also by hydrogen and covalent bonds. In a sorption study

assessing BPA, EE2, and nonylphenol (NP) in soils, Li et al. (2010) noted that affinity of BPA was higher than that of EE2 based on the Freundlich model. In marine sediments with relatively high (6%) organic carbon content, Robinson and Hellou (2009) observed the opposite, with EE2 sorption greater than that of BPA. In the present study, the sorption of these two contaminants was similar ( $K_d = 2.7$  and  $2.9$  for BPA and EE2, respectively) and had an affinity to sediments below the observed for TCS ( $K_d = 40$ ).

### 3.2 Bioaccessibility

The bioaccessibility assessment was undertaken as a comparison between the  $E$  value, butanol, and  $\beta$ -HPCD extractions. The results from the  $E$  value experiments (%) for TCS, BPA, and EE2 analyzed by GC-MS/MS are shown in Fig. 2 and for extraction methods in Fig. 3. Controls indicated that there was little biodegradation of the contaminants over 60 days (in details in SM).

**Fig. 1** Linear and Freundlich isotherms for TCS (a, d), BPA (b, e), and EE2 (c, f), respectively

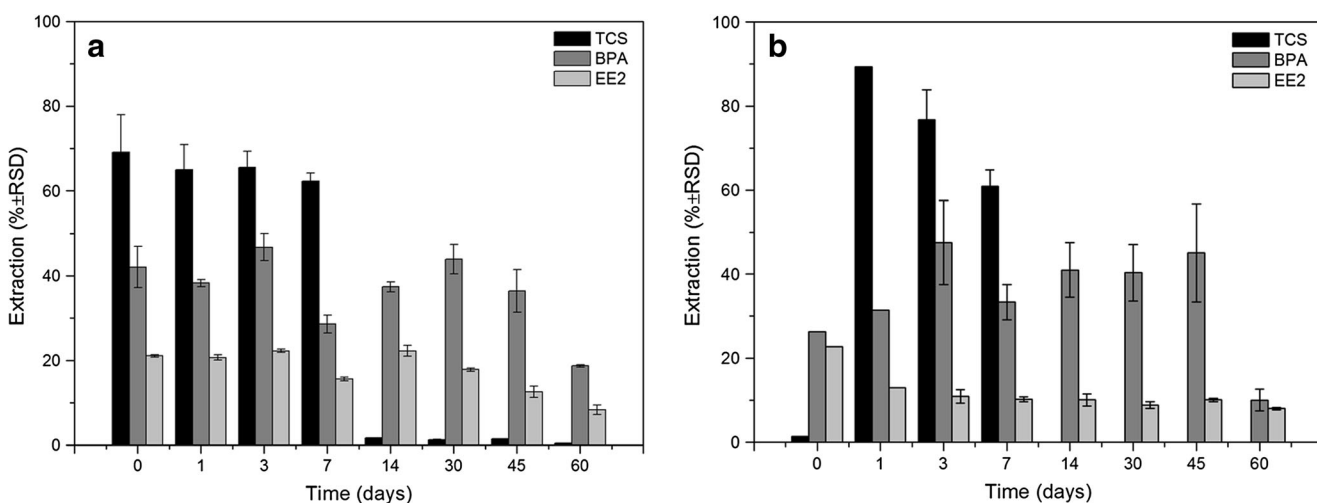


**Fig. 2** *E* value results (% of exchangeable portion ± RSD) for TCS, BPA, and EE2 over 60-day experiment

*E* values measured for all three contaminants were variable over the time. For TCS, the highest exchangeable percentage (25% ± 7.4) occurred after 72 h. However, due to variability (RSD) of measurements, there is no significant difference compared with 0 h. The *E* value of TCS indicated a fraction of it (< 25%) that was exchangeable with solution until day 7 (Fig. 2). After this period, the *E* value for TCS could not be determined, since it was below LOQ in solution for the following sampling days. This may be explained by the rate of desorption being kinetically slower than that of sorption, causing an apparent irreversibility of sorption that can be affected by time (Limousin et al. 2007; Williams and Kookana 2010). According to Lin et al. (2011), TCS sorption to soils is highly irreversible due to its low water solubility and high interfacial tension. Huang et al. (2015) have reported a higher  $K_d$  for TCS desorption than that observed for adsorption indicating the low desorption capacity of this contaminants in sediments. This sorption capacity can also indicate a low mobility in

sediments (Karnjanapiboonwong et al. 2010). This irreversible sorption behavior was also demonstrated for butanol and β-HPCD extractions of TCS, where this compound was not detected in extraction solutions after 7 days of incubation (Fig. 3).

In contrast to TCS, the *E* value of BPA and EE2 could not be determined up until day 7 of incubation, except for BPA where 10 ± 8% was observed to be exchangeable after 72 h of shaking (Fig. 2). These non-detected levels in initial days reported for BPA and EE2 could be related with the detection limits of GC-MS/MS and quantification in aqueous phase, where *E* value could not be estimated. For EE2, the exchangeable fraction was observed on days 14 (17 ± 9%), 45 (54 ± 8%), and 60 (13 ± 8%), consistent with the slower desorption of these contaminants from sediment particles (Robinson and Hellou 2009). For the chemical extractions, the pattern was similar for BPA and EE2 over time, with a greater fraction of BPA in the bioaccessible fraction. Bisphenol A has two phenolic functional groups which can be adsorbed within the hydrophobic cavity of β-HPCD (Kono et al. 2013). This complexing agent was investigated to predict bioavailability of polycyclic aromatic hydrocarbons (PAHs) (Reid et al. 2000; Cuypers et al. 2002), and for chlorobenzenes—CB (Song et al. 2011). Song et al. (2011) pointed out butanol extraction shows better results than β-HPCD and was better correlated with earthworm-accumulated CBs. The addition of a small amount of isotope in the binary system has shown that the exchangeability equilibrium was not reached at the same time for tested contaminants, once BPA bioavailable portion could be observed on days 45 and 60. This can indicate a slow desorption rate comparing with the other contaminants. According to Tian et al. (2009), BPA is primarily sorbed to sediment mineral surfaces, where physical adsorption involves Van de Waals forces and hydrophobic bonding. This association with minerals can be exposed to exchange with solution.



**Fig. 3** Butanol and β-HPCD results (% of extractable portion) for TCS, BPA, and EE2 over 60-day experiment analyzed by GC-MS/MS

The estimation of bioaccessibility can depend on the method used and is contaminant specific (Song et al. 2011) where the mobility is determined by sorption/desorption rate as well as degradation rate (Martínez-Hernández et al. 2014). The availability of these organic contaminants can be also directly related with the content of organic matter in sediment samples (Cunha et al. 2012). Most of literature includes studies with more hydrophobic contaminants, and the assessment of bioavailability/bioaccessibility involving less hydrophobic contaminants (as emerging concern contaminants) with multiple functional groups is relatively new. Considering the constant input rate of these contaminants, it can be observed that bioaccessibility for organisms can be reached in different moments. In this sense, the constant release of these contaminants can lead to continuous exposures to organisms, especially for BPA.

Considering the results from the three tested methods, a similar pattern of exchange/extraction through 60 days is observed when each contaminant is taken into account. However, the difference between them is significant ( $p < 0.05$ ) in bioaccessibility prediction. For exchangeable (E) value, the equilibrium exchangeability presents a limitation in detection of tested levels in the aqueous phase as well as the disadvantage of higher costs by using labeled isotopes. Meanwhile, this method can be considered as reliable, easy to use with the advantage of representing only freely labile fraction in exchangeable pool. For direct analysis by GC-MS/MS, the butanol method is the most straightforward, with better reproducibility if comparing with  $\beta$ -HPCD, in addition to being less expensive and laborious, once no solvent exchange step is necessary.

## 4 Conclusions

The sorption extent of tested marine sediment in the batch experiment has follow the order: TCS > BPA > EE2. The use of three different chemical methods to predict bioaccessibility had demonstrated, after a few days, that TCS is likely to become more irreversibly bound to sediments and less likely to: (a) be available over a new input and (b) less likely to be degraded meaning increasing residues in sediments near WWTP outfalls. With a constant input of WWTP effluents, it suggests long-term studies looking at the time effect on multiple addition of TCS are required. For BPA and EE2, chemical extractions indicate that binding to sediment does not necessarily reduce the bioaccessible burden of such contaminants because a large fraction can be re-released from sediments. In general aspects, the three prediction methods tested seemed to be in agreement, confirming mobility and bioaccessibility of these contaminants in sediments over the time. These obtained results can be important in the comprehension of the complex behavior pathways of these contaminants in the marine environment, providing complementary

information for bioaccessibility prediction accessed using chemical methods. Further studies involving uptake by aquatic organisms and passive sampling devices (as SPME polymeric fibers) can be considered to validate methodology of bioaccessibility/bioavailability prediction.

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