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Changes in the adsorption of bisphenol A, 17 α-ethinyl estradiol, and phenanthrene on marine sediment in Hong Kong in relation to the simulated sediment organic matter decomposition

Ying-heng Fei[1, 2], Baoshan Xing[3], Xiao-yan Li[1]*

[1] Department of Civil Engineering, The University of Hong Kong, Hong Kong, China

[2] Water Science Research Center, Guangzhou Institute of Advanced Technology, Chinese Academy of Sciences, Guangzhou, China

[3] Department of Plant, Soil and Insect Sciences, University of Massachusetts, Amherst, MA, USA

(*Corresponding author: phone: 852-28592659; fax: 852-28595337; e-mail: xlia@hkucc.hku.hk)

Abstract

Marine sediment with an input of particulate organic matter was incubated to simulate the early aging process. On the sediment after various incubation periods, adsorption and desorption tests were conducted for three selected organic micropollutants: bisphenol A (BPA), 17α-ethinyl estradiol (EE2), and phenanthrene (Phe). The results showed significant sediment organic matter (SOM) decomposition during the incubation, and the SOM decay and transformation had a profound impact on the adsorption of organic compounds by the sediment. An increasing-delay-increasing pattern of change was observed for the SOM

normalized partition coefficients of EE2 and Phe. This change was accordant to the transformation of SOM from labile organics into active biomass and its microbial products, and finally into more condensed and humic-like substances. Comparison between the 3 model micropollutants indicates that the chemical adsorption behaviors were mostly affected by their hydrophobic properties.

Capsule:

The early aging process of sediment organic matter led to an increasing-delay- increasing pattern of change for the adsorption of hydrophobic organic pollutants by marine sediment.

Key words: adsorption; endocrine disrupting chemicals (EDCs); marine sediment; sediment organic matter (SOM); SOM decomposition

1 Introduction

Sediment adsorption plays an important role in the fate of environmental pollutants in the aquatic system. Sediment organic matter (SOM) has been shown to be the most important component in the adsorption of hydrophobic organic pollutants (Chiou et al., 1979). The adsorption of organic pollutants by SOM often has a stronger affinity compared to the adsorption by mineral fractions, especially in SOM-rich soil or sediment (Cornelissen et al., 2005; Voice and Weber, 1983; Zhao et al., 2010). A partition mechanism has been adopted for nonionic organic adsorption by SOM (Chiou et al., 1979; Wang and Keller, 2009) in which the partition coefficient, K_d, is used to quantify the adsorption capacity. The amount of SOM in sediment has been shown to greatly influence the partition coefficients of environmental contaminants on marine sediment (Gao et al., 1998; Xu et al., 2008).

Moreover, researchers have found that the adsorption of organic contaminants by sediment is affected not only by the SOM content, but also by the chemical property of the SOM (Cornelissen et al., 2005; Weber et al., 1999). Xing and Pignatello (1997) proposed that various types of SOM in aged sediment could be compared to rubbery or/and glassy polymers in explaining the sediment adsorption behaviors. Their dual model implying the impact of SOM quality on the adsorption behaviors of sediment was supported by later studies (e.g. Ran et al., 2007; Sun et al., 2010; Yang et al., 2010).

However, accounting for organic decomposition in sediment, the adsorption of pollutants onto marine sediment with a rich organic input from particulate organic matter can be more complicated. Under natural conditions, major fractions of labile SOM are biologically mineralized within a few months, while more refractory fractions can be rather stable in sediment (deBruyn and Gobas, 2004). Organic decomposition transforms SOM from less stable organics into humic substances (Farnet et al., 2009; Plaza et al, 2009), which would fundamentally affecting the adsorption behavior and capacity of the sediment (Fei et al., 2011; Fei and Li, 2013). Prior studies have predicted the enrichment of chemicals in sediment during SOM mineralization by theoretical analysis (Gobas and MacLean, 2003; Johnson et al., 2001). However, few experimental studies have been conducted to prove the influence of SOM degradation and transformation on the adsorption of environmental micropollutants by the sediment. There is also a need to investigate the dynamic process of SOM decomposition and its effect on sediment adsorption. Such an issue is of great importance for estuary or marine areas such as Hong Kong and the Pearl River Delta in South China, where the sediment receives a high SOM input, e.g. from stormwater runoff, sewage discharge and mariculture activities (Wang et al., 2010). In our previous studies (Fei et al., 2011; Fei and Li, 2013), laboratory experiments were conducted to simulate the aging and decomposition of SOM in artificial sediment, with flour powder as the fresh SOM input. With the SOM decay

during the sediment incubation, the adsorption of chemicals, including bisphenal A (BPA), nonylphenol and tetracyclines, by the sediment was found to change significantly.

In the present study, the influence of SOM decomposition on the sediment adsorption behavior was further investigated with following major modifications: (1) instead of artificial sediment made of sand and clay, actual marine sediment was used for the experimental study; (2) instead of flour powder (carbohydrate), fish food was selected as a better SOM to provide a mixture of various particulate organic compounds; (3) three different chemicals were selected as model micropollutants with different chemical structures and hydrophobic properties. Based on the experimental results, sound theoretical analysis was conducted and more comprehensive understanding was obtained. In addition, a conceptual model was proposed to describe the dynamic change of chemical adsorption by the sediment in connection to the SOM decomposition and transformation.

2 Materials and Methods

2.1 Sediment samples and sediment incubation

Natural sediment was collected from depths 0 to 20 cm below the sediment surface at a site ($22^{o}18.400/114^{o}06.500$) in Victoria Harbour, Hong Kong, and the sample was stored under $4^{o}C$ before use. After removing shells and gravels, the marine sediment was air-dried, ground and homogenized, and dry sediment that passed through a 200 μm sieve was collected. The organic content in the raw sediment was around 6.4%. Fish food was added as a fresh SOM input into the sediment. Dried and ground fish food pellets (Hikari Lionhead, Japan) were thoroughly mixed into the sediment at a dry weight ratio of 10%. The fish food as the fresh SOM input was mostly insoluble, and its dry mass consisted of >61% of proteins, >8% of lipids, <7% of fibers, <14% of other carbohydrates, and <10% of ashes, according to the product information.

The sediment with a high SOM input was incubated in water to simulate the natural decay and aging process. The sediment was placed into 30 separate glass dishes, each dish being 6 cm in diameter and 1 cm in depth, and the sediment dishes were then placed on the bottom of a large water tank. The tank was filled with 20 L of saline water made with reef salt at a salinity of 10‰, which is close to the average salinity level in Deep Bay, Hong Kong, where a large amount of SOM is received from Pearl River (Xu et al., 2010). The water in the tank was circulated and aerated to ensure a dissolved oxygen (DO) level of 5 mg/L or higher in the water over the sediment. The saline water was replaced weekly and the water temperature varied between 22-24^{o}C. Throughout the sediment incubation process, 4 dishes of the incubated sediment were retrieved each time after different incubation periods (0, 15, 33, 54, 75, 96, and 125 d). The incubated sediment samples were then air-dried and ground gently before SOM analysis and the subsequent adsorption tests.

2.2 Sediment characterization

The SOM content in a sediment sample was measured by means of LOI-550 (loss on ignition at 550^{o}C) (Beaudoin, 2003). As a simple and reliable measurement, the LOI results have been to be consistent with the element-based organic carbon analysis (Fei et al., 2011). In brief, the sediment sample was first dried in an oven at 105^{o}C for 1 h. After cooling and weighing, the dry solids was placed in a muffle oven and heated to 550^{o}C for 15 min, followed by cooling and weight measurement. The loss of weight after ignition was determined as the amount of SOM in the sediment. The fraction of organic matter, f_{OM}, in the raw or incubated sediment was calculated accordingly.

Humic substances were extracted from the sediment samples following the method previously employed by Droussi et al. (2009). Briefly, humic matter was extracted by 0.1M KOH for 7 times, the combined extract solution was precipitated by 6M H_2SO_4, and the precipitate was then dissolved in 0.05M $NaHCO_3$ (pH=8.0) for analysis. Fluorescence

excitation and emission matrix (FEEM) was obtained by a fluorescence spectrophotometer (F-7000, Hitachi, Japan) for the emission wavelength ranging 300-600 nm with the excitation wavelength ranging 250-500 nm (Plaza et al., 2009). The absorbance at 465 nm (E_4) and 665 nm (E_6) of the humic solution was determined by a UV-VIS spectrophotometer (Lambda 12, Perkin Elmer, USA), and the E_4/E_6 ratio was then calculated accordingly.

2.3 Model micropollutants

Endocrine disrupting chemicals (EDCs) have attracted public attention in recent years due to the chronic harm they cause to the reproduction of organisms in the ecosystem (e.g. Colborn et al., 1993; Collins, 2008). Two typical EDCs, BPA and 17 α-ethinyl estradiol (EE2) were selected as the model chemicals for the sediment adsorption study. Another typical non-polar organic contaminant, phenanthrene (Phe), which also has been indicated with potential estrogenic activities in human colons (Van de Wiele et al., 2005), was selected as well. Table 1 summarizes the chemical properties of the model compounds, including their water solubility S_w and octanol-water partition coefficient K_{ow} values.

The chemicals were of analytical purity, with BPA (> 99%) purchased from Aldrich (USA), EE2 (> 98%) from Sigma (USA), and Phe (> 98%) from Aldrich (USA). All of the other chemicals and solvents used in the study were of analytical grade or better and were obtained from Sigma-Aldrich (USA). BPA, EE2, and Phe were prepared in a background solution consisting of 0.01 M $CaCl_2$ for a basic ionic strength and 200 mg/L of NaN_3 for the inhibition of microbial activities during the adsorption tests (Xing and Pan, 2010). The chemical solutions were prepared just before the adsorption experiment, and the solution pH was 7.5.

2.4 Adsorption experiments

Adsorption tests were conducted to determine the isotherms of adsorption of the model compounds on the sediment, using 11-mL or 40-mL screw-cap vials with Teflon-lined septa (Xing and Pan, 2010; Xing and Pignatello, 1997). Briefly, a pre-determined amount of sediment was placed in a series of vials, into which a model micropollutant solution of different concentrations was subsequently added. The initial concentrations of BPA, EE2 and Phe were in the ranges of 10-50 mg/L, 0.5-5 mg/L, and 0.1-0.5 mg/L, respectively. The vials, which had nearly no headspace, were placed in a temperature-controlled shaking incubator (Polyscience, USA) at 25^{o}C and were rotated at the rate of 130 rpm. Upon completion of the adsorption test, the sediment mixture from each vial was centrifuged at 4000 rpm for 5 min to separate the liquid from the sediment, and the pollutant concentration in the aqueous phase was measured using a high-performance liquid chromatography (HPLC).

The dry sediment/aqueous ratios were 0.7 g/10 mL, 0.3 g/10 mL, and 5 mg/40 mL for the BPA, EE2, and Phe, respectively. The pH level of the solutions during the adsorption tests was around 7.5. Our preliminary tests showed that the adsorption equilibrium could be achieved in 24 hr for BPA or EE2 and in 72 hr for Phe. Losses of 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 in the liquid phase.

After the adsorption experiment being completed, a desorption test was conducted on the same sediment. For the desorption of BPA, the aqueous solution was replaced by 10 mL of the clean background solution, and the sample vials were placed in the shaking incubator (Polyscience, USA) at 25^{o}C. After 48 hr, the sediment and solution were separated as previously described, and the BPA concentration in the liquid phase was measured by the HPLC. For EE2 desorption, due to the HPLC detection limit, only half (5 mL) of the liquid

was replaced with the clean solution, with the other half (5 mL) remaining in the vial. The great hydrophobicity of Phe made its desorption into water extremely difficult. Sodium dodecyl benzene sulfonate (SDBS), a surfactant often used in soil extraction (Zhao et al., 2010), was therefore dosed (5 mL) into the sediment mixture at 10,000 mg/L for Phe desorption.

2.5 Chemical analysis

The BPA, EE2, and Phe concentrations in water were measured by an HPLC (Waters 2695) with a C18 column (5 μm, 2.1×150 mm) for separation and a photodiode array detector (Waters 2996) for quantification. For BPA and EE2, the mobile phase was a mixture of Milli-Q water and acetonitrile (50:50, v/v). The flow rate was set at 0.5 mL/min, and the sample injection volumes were 10 μL for BPA and 50 μL for EE2. Under this chromatographic condition, the BPA peak appeared at around 6 min and the EE2 peak at around 8 min. The area of the peak detected at a wavelength of 225 nm was used to quantify the amount of the chemical detected (Mnif et al., 2012). The limits of detection and quantification (LOD and LOQ) were 0.03 and 0.1 mg/L for BPA and 0.1 and 0.3 mg/L for EE2. For Phe, the HPLC program was optimized by using acetonitrile as the mobile phase at a flow rate of 0.5 mL/min. The Phe peak was obtained at around 7 min by detection at 250 nm **(**Zhao et al., 2010**)**. Setting the injection volume at 10 μL, the LOD and LOQ were 0.05 and 0.15 mg/L, respectively. The HPLC chromatographs for the chemical detections are shown in the Supplementary Material (SI).

2.6 Data analysis

The results obtained in the sediment adsorption and desorption tests were used to determine the adsorption and desorption isotherms. The isotherm data were arranged to fit the

following linear partition model (Eq. 1) and the Freundlich model (Eq. 2) (Voice and Weber, 1983):

$$q_e = K_d C_e \quad (1)$$

$$q_e = K_F C_e^{1/n} \quad (2)$$

where C_e and q_e are the equilibrium concentrations of the chemical in the aqueous phase and sediment, respectively; K_d is the partition coefficient in the linear model; K_F and *1/n* are the affinity coefficient and curvature index, respectively, in the Freundlich equation. Microsoft Excel 2010 was used for data analysis and curve fitting. Furthermore, K_d for partition is normalized by the SOM content (f_{OM}) to obtain the organic matter normalized partition coefficient K_{OM} (Eq. 3), i.e.

$$K_{OM} = \frac{K_d}{f_{OM}} \quad (3)$$

Based on the comparison between the adsorption and desorption tests for a chemical by the sediment, an hysteresis index (*HI*) can be calculated as follows (Wu and Sun, 2010),

$$HI = \frac{K_{d(D)} - K_{d(A)}}{K_{d(A)}} \quad (4)$$

where $K_{d(D)}$ and $K_{d(A)}$ stand for the chemical partition coefficients obtained from the desorption and adsorption tests, respectively. The *HI* value signifies the irreversibility of an adsorption process, with $HI = 0$ representing completely reversible adsorption and a higher *HI* value indicating more irreversible adsorption.

3 Results and Discussion

3.1 SOM degradation and transformation

The loaded SOM, fish food pallets, degradation was well observed during the sediment incubation. The organic content in the sediment fell by 47% over 4 months (Fig. 1). The SOM decomposition could be well fitted by multi-fractional first-order kinetic equations (please refer to SI). SOM decay occurred more rapidly in the first month with a reduction of around 40% of the initial f_{OM}. SOM reduction became much slower in the following 3 months. Along with the SOM degradation, fresh SOM would be rapidly transformed into biomasses and their metabolic products (Fei et al., 2011). Subsequent to SOM biodegradation, biomass and microbial intermediate products would undergo further decay to form more condensed geo-polymers such as fulvic acid, humic acid, and humin (Farnet et al., 2009; Plaza et al., 2009).

Analysis on humic substances confirmed the humificiation-like process within the sediment aging process. As shown in Fig 2., the FEEM features a primary peak at the excitation/emission wavelength pair of 370/470 nm, and a secondary peak at around 450/540 nm. The E_4/E_6 ratio decreased significantly, as shown in Fig 3, indicating the accumulation of aromatic contents and the condensation of the acidic humic substances in the sediment samples (Droussi et al., 2009). Based on previous studies on organic incubation or composting (e.g. Droussi et al., 2009; Guo et al., 2013), the elemental ratios of N/C, H/C, and O/C would be increased during the organic matter decomposition process. The condensation and humification process in sediment would change SOM into more humic-like matter eventually with more carboxyl groups, alkyl carbon, and non-lignin aromatic structures (Farnet et al., 2009).

3.2 Adsorption and desorption of BPA

Batch adsorption tests were conducted with the model chemical compounds to characterize the change in the adsorption properties of the sediment after various periods of incubation. The isotherms of BPA adsorption by the sediment fit well with either the linear partition model or the Freundlich model ($R^2 \geq 0.98$) (Table 2 and Fig. 4). Chiou et al. (1979) suggested that the adsorption of hydrophobic organic contaminants on soil or sediment could be accurately described by the linear model with a partition coefficient indicating adsorption capacity. Mathematically, the linear model can be considered a special case of the Freundlich isotherm model when the curvature index *1/n* in the Freundlich equation is close to 1 (Voice and Weber, 1983). To allow simple and direct comparisons, the linear isotherm model and related partition coefficients were used in most of the following analysis and discussion to mathematically compare adsorption capacity between sediment samples after different incubation periods.

For BPA, the partition coefficient K_d of the sediment cooperated with fish food pallets increased by 8 times than the raw sediment (Table 2). The affinity coefficient in the Freundlich model, K_F, showed more than 3 times of increase. It has been widely demonstrated that a higher SOM content would lead to a higher adsorption affinity (e.g. Fei et al., 2013; Sun et al., 2010; and Xu et al., 2008). Besides, the curvature index, *1/n*, also increased from 0.71 to more than 0.97. For the raw sediment, the curved adsorption isotherm has been commonly reported by others (e.g. Cornelissen et al., 2005; Gao et al., 1998; Voice and Weber, 1983; etc.), and the linearity of the sorption isotherm is usually negatively related with the SOM maturity (Cornelissen and Gustafsson, 2004).

For the SOM loaded and incubated sediment, K_d decreased by 69% from 35 to about 11 L/kg after 4 months of incubation. Most of the K_d decrease occurred in the first month, accounting for a 54% decrease from the initial value. K_d fell by another 15% in the following

3 months. It is apparent that the loaded SOM influenced the adsorption capacity, and the degradation of fresh SOM was the main cause of K_d reduction, as the K_d decreases observed correlated well with f_{OM} reduction during the sediment incubation process. This is accordant to our previous findings (Fei et al., 2011; Fei and Li, 2013). However, at the end of the incubation, when the f_{OM} of the humified sediment was only 20% more than that of the raw sediment without the SOM input, the K_d was still more than doubled. The change of adsorption was not only influenced by the quantity, but also by the property. The curvature index *1/n* in the Freundlich model for BPA adsorption also decreased from 0.97 to 0.89, showing a more curved adsorption isotherm after SOM decay. This change is consistent with previous findings showing that the pattern of chemical adsorption by organic materials becomes more curved after organic decomposition (Hur et al., 2011; Plaza et al., 2009).

The desorption experiment showed that the desorption-based partition coefficient for BPA also decreased by 56% for the incubated sediment, which was still higher than the raw sediment (Table 2). Moreover, desorption hysteresis was found for BPA desorption from the sediment. Hysteresis is a result of partially irreversible adsorption, and the *HI* value has been used to quantify the irreversibility of chemical adsorption (Wu and Sun, 2010). The BPA desorption results indicated that *HI* increased continuously and significantly for the incubated sediment. The *HI* change also correlated well with the transformation of SOM during incubation, as chemical adsorption by condensed SOM is theoretically stronger, and chemical desorption by more condensed SOM is harder than that by less condensed SOM (Gunasekara and Xing, 2003).

3.3 Adsorption and desorption of EE2

Similar to BPA, the isotherm of EE2 adsorption by the incubated sediment also fits well with the linear partition model ($R^2 \geq 0.95$) for the sediment samples after various incubation periods (Fig. 4), whilst the curvature index *1/n* in the Freundlich model is close to 1 (Table 2).

The fresh SOM into the sediment increased the adsorption affinity as well as the isotherm linearity (Table 2, raw sediment and 0 day sediment). The fish food pellets with rich contents of proteins and lipids apparently enhanced the adsorption capacity of the sediment and changed the shape of its adsorption isotherm.

For the change of adsorption along with the incubation time, K_d initially decreased, but recovered in the later phase. Within the first 2 months of sediment incubation, the K_d value decreased by 43%, which correlated well with the rapid f_{OM} reduction in the sediment. K_d then began to increase after about 2 months of sediment incubation and eventually reached 73% of its initial value. In the later phase of sediment incubation, a large portion of the SOM would have been transformed from simple hydrocarbons and fresh biomass to more humic-like substances with more carboxylic and aromatic groups (Farnet et al., 2009). Such SOM transformation is more favorable to the adsorption of EE2 molecules by the incubated sediment, probably through π-π bonds and hydrogen bonds (Yamamoto et al., 2003).

As the desorption K_d values obtained were lower than the corresponding adsorption K_d values, the desorption HI could not be derived for EE2. Consistent with the change in the adsorption isotherm, the K_d value determined for the desorption of EE2 also decreased initially before reversing direction and increasing (Table 2). The K_d decrease was most significant in the first month, which correlated well with the rapid f_{OM} reduction observed.

3.4 Adsorption of Phe

A much greater amount of adsorption by the sediment was observed for Phe (Table 2). Comparison between the raw sediment with SOM added sediment demonstrated that the SOM addition greatly enhanced the sorption capacity to the sediment, as the K_d value increased from 132.5 to 4430 kg/L. The *1/n* values for Phe were higher than 1 for some of the aged sediment. This might be contributed to multilayer adsorption, as the sediment surface would be modified by the Phe adsorption, leading to more and stronger adsorption. In

comparison to BPA and EE2, the partition coefficient of Phe showed a lower degree of change during the sediment incubation. Its K_d value initially increased by 11% before decreasing from 5612 on 15 day to 4686 L/Kg on 54 day (Table 2). The adsorption then began to recover, eventually reaching to a level of around 5000 L/kg. It has been reported that the sorption of Phe on SOM is mainly driven by hydrophobic effects (Wang et al., 2011). The hydrophobic carbon content (the sum of alkyl and aromatic carbon content) was expected to increase in the later phase of SOM decay in the incubated sediment (Hur et al., 2011), which would lead to more and stronger nonspecific Phe bindings by the sediment for adsorption.

The strong degree of Phe adsorption by the sediment meant the surfactant SDBS had to be used for the desorption tests. As a result, the partition coefficients of the desorption isotherms were much lower than those of the adsorption isotherms and hence could not be compared with the latter. Nonetheless, an increasing trend in desorption K_d became apparent as the sediment incubation progressed, which also indicated stronger Phe adsorption by the incubated sediment.

Data fitting with the Frunelich model showed the isotherm of Phe adsorption by the incubated sediment became more non-linear in the later phase of sediment incubation (Table 2). The curvature index *1/n* increased from 1.02 at the beginning of the incubation period to more than 1.50 by the end. A value of $1/n > 1$ often indicates easier and stronger partitioning at higher concentrations (Voice and Weber, 1983). It is apparent that the SOM was converted to more condensed and humic-like materials with a strong binding affinity to Phe (Grathwol, 1990; Plaza et al., 2009).

3.5 K_{OM} for BPA, EE2, and Phe

SOM in sediment is believed to be the main adsorbent for chemical adsorption (e.g. Sun et al., 2010; Wu and Sun, 2010; Xu et al., 2008). SOM normalized K_d was determined for the model compounds (Fig. 5) using the K_d values and f_{OM}. The average LogK_{OM} values were 2.2,

2.9, and 4.7 for BPA, EE2, and Phe, respectively. In other words, among the selected contaminants, BPA was in all instances adsorbed the least and Phe was adsorbed the most by the SOM after various periods of incubation. This is consistent with the common understanding that the adsorption or partition of hydrophobic contaminants correlates strongly with the hydrophobicity of the chemical molecules (Chiou et al., 1979; Voice and Weber, 1983). In comparison to EE2 and Phe, BPA has a much lower K_{ow} and a much higher S_w value (Table 1), which probably gives rise to its weak affinity with sediment organics and hence its lowest level of adsorption by the sediment. Karickhoff et al. (1979) developed the following relationship between the adsorption coefficient and the adsorbate hydrophobicity,

$$\text{Log}\, K_{oc} = \text{Log}\, K_{ow} - 0.21. \quad (5)$$

Based on this correlation, the LogK_{oc} values of the studied chemicals could be calculated as 2.0, 3.9, and 4.4 for BPA, EE2, and Phe, respectively. Comparison between the experimental K_{OM} and the predicted values, a disagreement for EE2 can be found, as the K_{OM} determined for EE2 was lower than expected. This result might have been affected by other factors, besides the hydrophobic properties, such as the molecular size and structure of the chemicals (Sun et al., 2010). For instance, the molecular size of EE2 is larger than that of BPA, which would be an impediment for EE2 molecules accessing some adsorption sites. This could be one of the more likely reasons for the difference in K_{OM} between EE2 and Phe being greater than that predicted from the K_{ow} values alone.

The K_{OM} values were found to undergo various changes rather than staying constant during the sediment incubation period. A general trend of increasing-delay-increasing could be used to characterize the K_{OM} values for EE2 and Phe. Despite the great difference in values, the K_{OM} for BPA, EE2, and Phe increased sharply within the first 15 days of incubation (Fig. 5). This correlates well with the period when the microbial activity increased greatly in the

sediment, as indicated by the rapid SOM degradation (Fig. 1) in the present work and observed in our previous studies (Fei et al., 2011).

Afterwards, there was a slight decrease in K_{OM} for BPA and EE2, followed by a rather stable pattern of values over a long period (d 33-75). During this period, SOM decomposition became slower (Fig. 1), with biomass decay in the sediment (Fei et al., 2011). According to the analysis of humic substances (Fig. 2), the humification process was in progress, though not dramatically yet. The decrease of active biomass possibly caused the decrease of K_{OM} for BPA and EE2. However, the inconspicuous transformation of SOM fractions might offset this lose and keep the K_{OM} stable for a period.

Subsequently, biodegradable SOM was exhausted and biomass decay became more important, when humic-like substances accumulated remarkably in the sediment (Fig. 2).. The SOM was further converted into more condensed humic-like substances with more aromatic, phenolic, carboxyl and other functional groups (Farnet et al., 2009) with higher chemical adsorption capacities to hydrophobic chemicals (Gunasekara and Xing, 2003; Hur et al., 2011). Owing to the SOM degradation and humification, K_{OM} increased by 111% and 38% for Phe and EE2, respectively (Fig. 5). Thus, SOM input and decomposition in the sediment had a profound impact on its adsorption behavior and capacity.

Noticeably, K_{OM} of BPA did not increase at the end, but decreased by 42% (Fig. 5). The different 'increasing' levels were found to be well consistent with the chemical hydrophobicity, following the sequence of BPA<EE2<Phe. This result was similar to that obtained by Sun et al. (2012), which reported that the adsorption of BPA, EE2, and Phe decreased, insignificant changed, and increased, respectively. For the reason that Phe might be much more dependent on the hydrophobic interactions than BPA (Sun et al., 2012), the changes in the polarity and accumulation of aromatic structures of SOM would bring much more significant effect on the increased hydrophobic adsorption to Phe. For relatively

hydrophilic molecules like BPA, however, the shifted SOM structure might not be able to make positive impact. As for the differences among chemicals with varied chemical properties, a conceptual model is presented in SI, which would help explain the possible changing process of sediment adsorption in relation to SOM decomposition.

4 Conclusions

- Fresh SOM (fish food pellets) in marine sediment was decomposed during a 4-month incubation. Extraction and analysis of humic-like substances suggest a humification-like process during the sediment and SOM incubation.
- The adsorption behaviors of the 3 model micropollutants (BPA, EE2 and Phe) was significantly influenced by the SOM decomposition. The K_d for BPA and EE2 decreased by 70% and 28%, respectively, while for Phe increased by 11%.
- Generally, a 3-stage change for K_{OM} could be summarized. K_{OM} of the model chemicals all increased at the beginning. After a period of delaying, it continued to increase for EE2 and Phe. For BPA, which was less hydrophobic, the K_{OM} decreased eventually.

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Table 1 - Chemical properties of the selected micropollutants: BPA, EE2, and Phe (Sun et al., 2011).

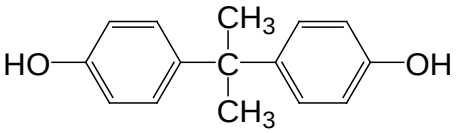
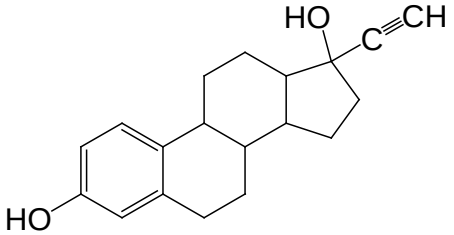
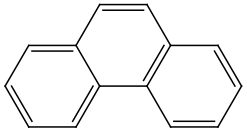
	BPA	EE2	Phe
Molecular structure			
Molecular diameter (Å)	4.3	6.0	5.6
Water solubility, S_W (mg/L)	380	7.6	1.12
Octanol-water distribution coefficient, LogK_{ow}	2.20	4.15	4.57

Table 2 - Summary of the adsorption and desorption isotherms of BPA, EE2, and Phe for the sediment after various periods of incubation.

Chemicals	Incubation time (d)	Adsorption					Desorption		
		Linear model		Freundlich model			Linear model		Hysteresis index
		K_d (L/kg)	R^2	Log K_F	*1/n*	R^2	K_d (L/kg)	R^2	(HI, %)
BPA	Raw sediment	4.15±0.15	0.99	1.07±0.022	0.71±0.021	1.00	6.71±0.53	0.97	61.69
	0	34.88±0.76	0.99	1.56±0.021	0.97±0.019	1.00	41.07±0.93	0.99	17.75
	15	26.69±0.86	0.98	1.49±0.043	0.94±0.042	0.99	33.17±1.75	0.97	24.28
	33	16.07±0.29	0.99	1.26±0.029	0.94±0.031	1.00	24.71±1.29	0.97	53.76
	54	12.93±0.34	0.99	1.25±0.024	0.89±0.024	1.00	19.20±0.45	0.99	48.49
	75	12.31±0.21	1.00	1.18±0.022	0.92±0.017	1.00	19.67±1.38	0.95	59.79
	96	13.54±0.31	0.99	1.22±0.031	0.92±0.032	1.00	22.41±1.47	0.96	65.51
	125	10.60±0.17	0.99	1.16±0.018	0.89±0.02	1.00	18.08±1.70	0.92	70.57
EE2	Raw sediment	25.27±0.98	0.97	1.48±0.009	0.77±0.022	0.99	9.83±0.95	0.89	-
	0	100.08±3.74	0.95	2.02±0.018	1.02±0.079	0.97	45.18±3.12	0.85	-
	15	89.94±2.67	0.97	1.95±0.020	1.12±0.072	0.98	45.49±1.69	0.96	-
	33	61.40±1.94	0.96	1.81±0.019	0.99±0.074	0.97	25.53±1.21	0.93	-
	54	57.49±1.39	0.98	1.75±0.012	1.07±0.049	0.99	22.28±1.99	0.76	-
	75	59.82±1.81	0.97	1.82±0.022	0.91±0.063	0.97	23.77±2.09	0.76	-
	96	63.02±1.53	0.98	1.82±0.019	1.00±0.055	0.98	27.30±1.73	0.87	-
	125	73.05±2.63	0.98	1.80±0.027	1.33±0.11	0.96	26.95±1.98	0.84	-
Phe	Raw sediment	132.5±3.3	0.98	1.98±0.038	1.13±0.049	0.99	6.47±0.74	0.92	-

0	4430±168	0.95	3.66±0.19	1.02±0.18	0.93	36.00±1.49	0.98	-
15	5612±66	1.00	3.84±0.039	1.08±0.029	1.00	-	-	-
33	4962±158	0.98	3.95±0.12	1.24±0.10	0.98	36.49±2.28	0.97	-
54	4686±178	0.99	4.17±0.056	1.47±0.057	1.00	-	-	-
75	4731±182	0.99	4.20±0.068	1.49±0.057	1.00	47.58±1.83	0.96	-
96	4988±312	0.98	4.95±0.27	2.16±0.25	0.97	-	-	-
125	4916±264	0.95	4.27±0.24	1.54±0.22	0.95	51.59±4.47	0.95	-

“-”: invalid or not determined.

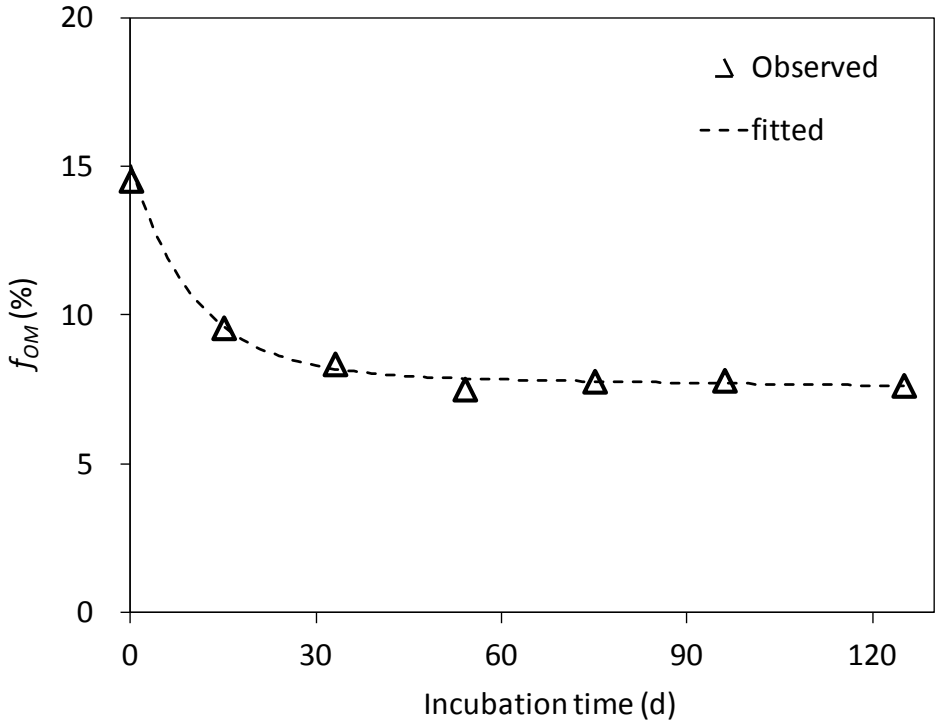


Fig. 1 - SOM reduction during the sediment incubation.

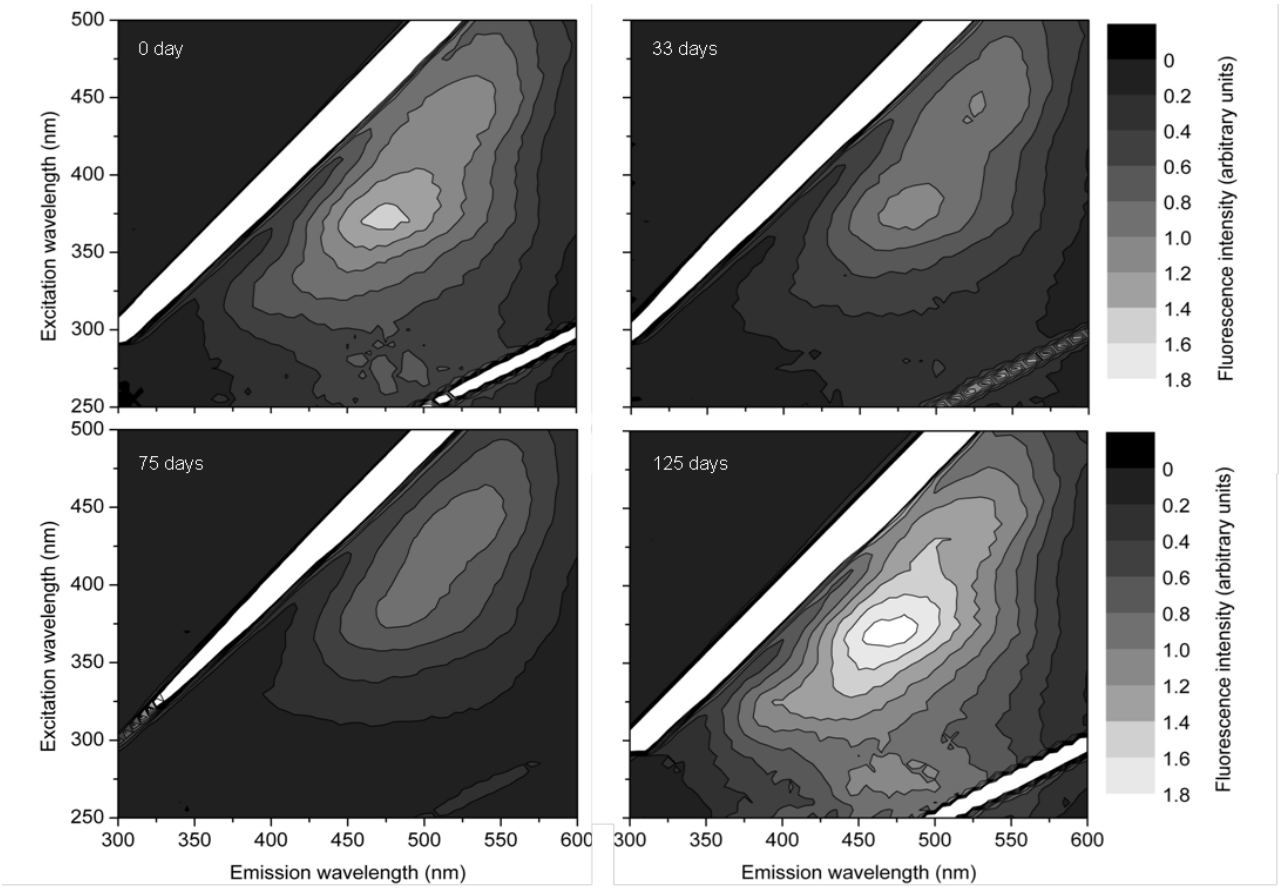


Fig. 2- FEEM of the humic substances extracted from the sediment samples after different incubation periods.

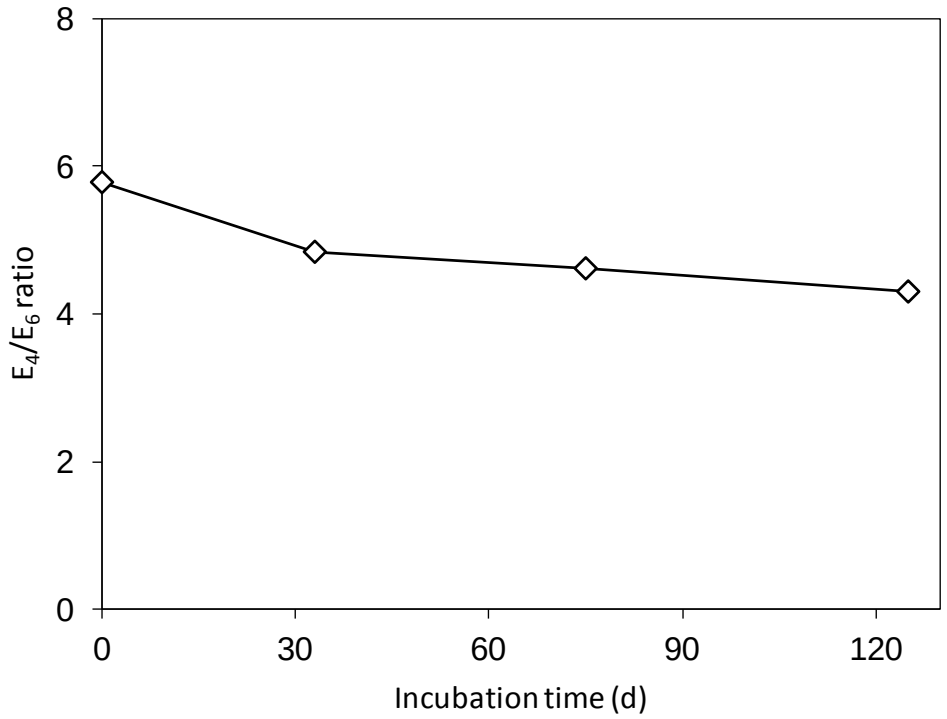


Fig. 3- E_4/E_6 ratio of the humic substances extracted from the sediment samples after different periods of sediment incubation.

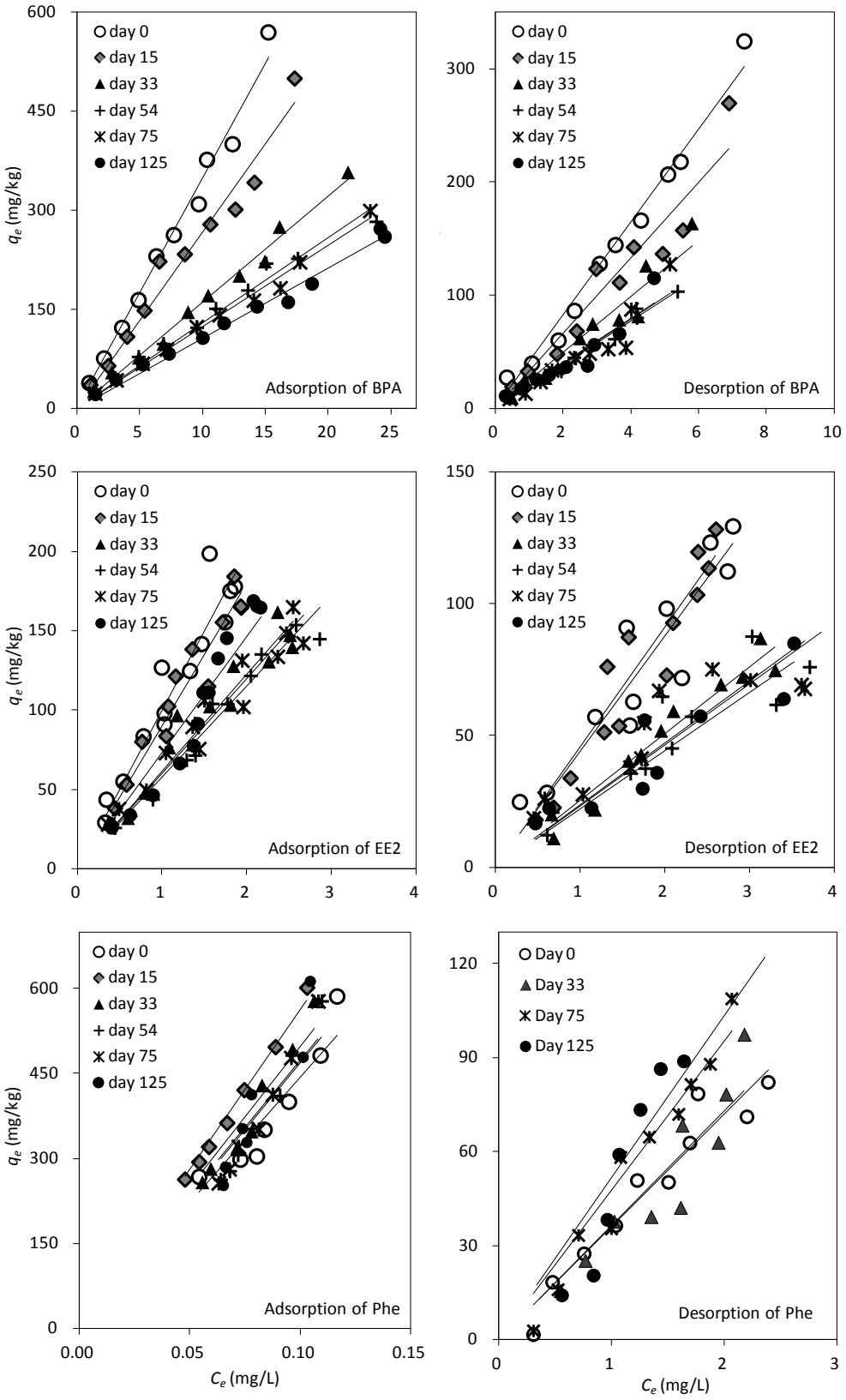


Fig. 4 - Isotherms of the adsorption and desorption of BPA, EE2, and Phe for the sediment samples after different periods of incubation.

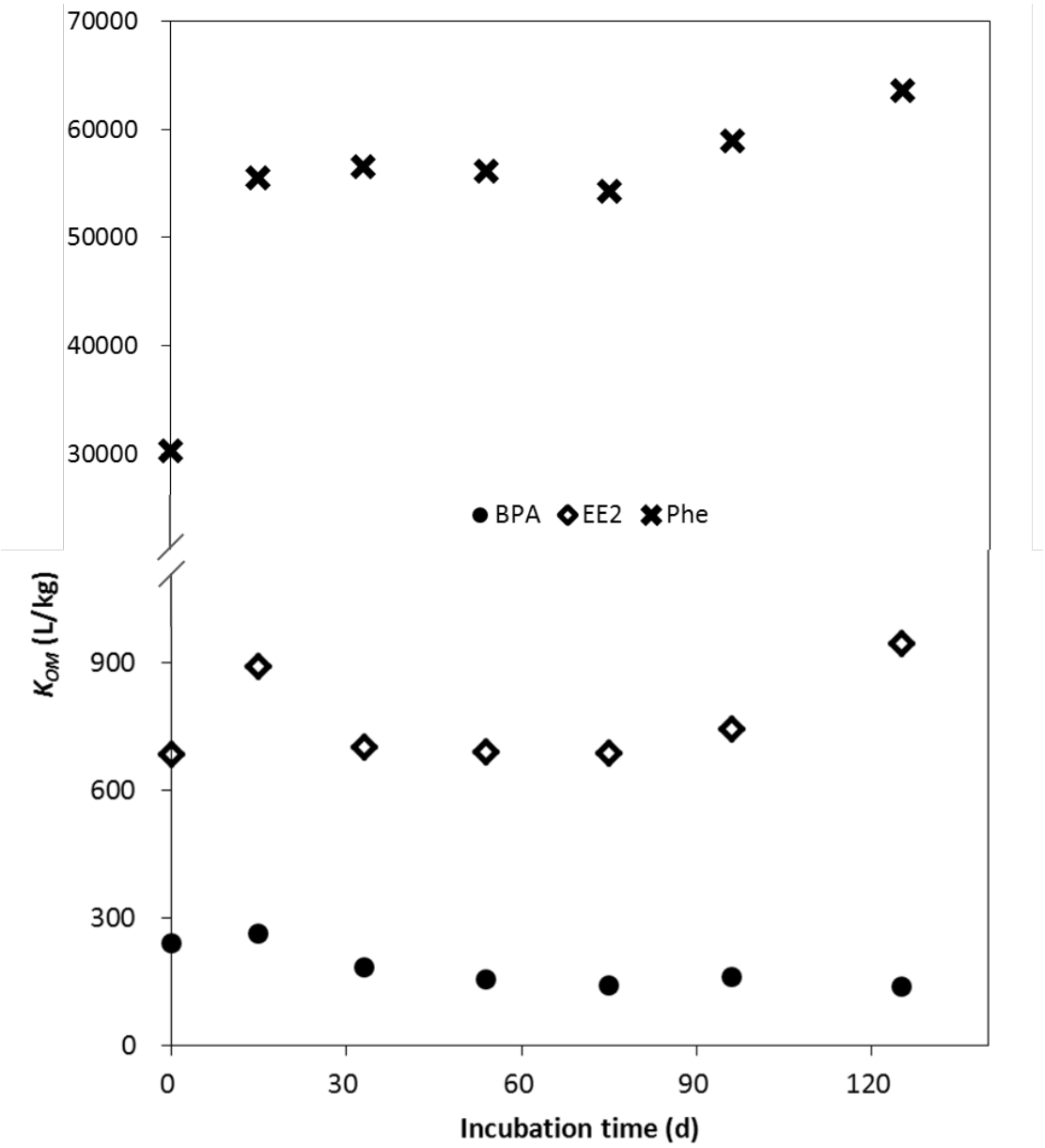


Fig. 5 - Changes in the K_{OM} values of BPA, EE2, and Phe with the sediment incubation time.

Supplementary Material

Changes in the adsorption of bisphenol A, 17 α-ethinyl estradiol, and phenanthrene on marine sediment in Hong Kong in relation to the simulated sediment organic matter decomposition

Ying-heng Fei[1, 2], Baoshan Xing[3], Xiao-yan Li[1]*

[1] Department of Civil Engineering, The University of Hong Kong, Hong Kong, China

[2] Water Science Research Center, Guangzhou Institute of Advanced Technology, Chinese Academy of Sciences, Guangzhou, China

[3] Department of Plant, Soil and Insect Sciences, University of Massachusetts, Amherst, MA, USA

(*Corresponding author: phone: 852-28592659; fax: 852-28595337; e-mail: xlia@hkucc.hku.hk)

The following supplementary materials are included:

(1) HPLC chromatograph for BPA, EE2 and Phe detection.

(2) A conceptual model for SOM decay in sediment and its effect on adsorption capacity.

(1) HPLC chromatograph for BPA, EE2 and Phe detection

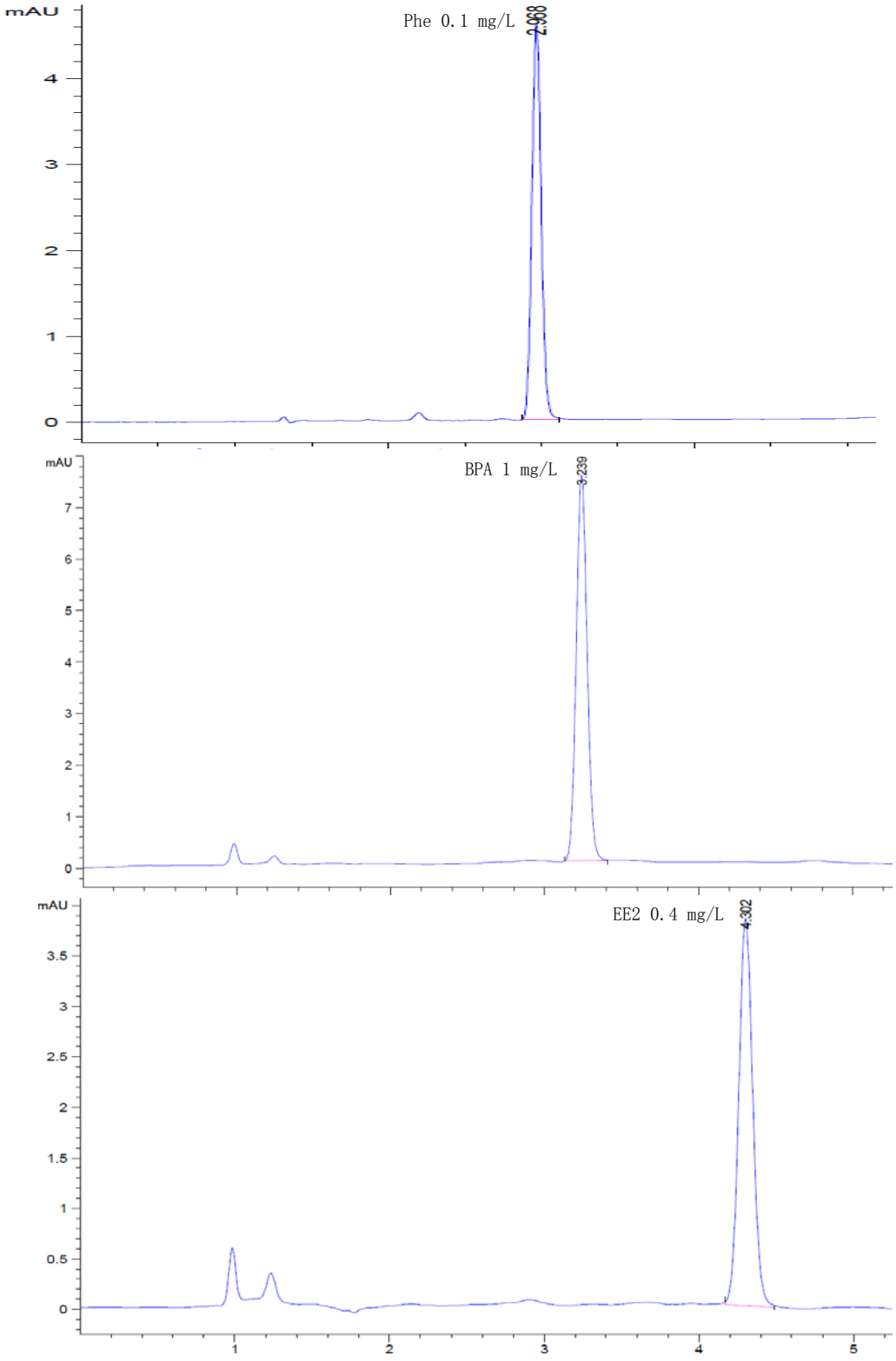


Fig. S1 - HPLC chromatograph for BPA, EE2 and Phe detection.

(2) A conceptual model for SOM decay in sediment and its effect on adsorption capacity

The lab results reveal that fresh particulate matter deposited into sediment may not behave as a stable entity for the transport of pollutants in the environment. SOM will undergo various forms of degradation and diagenesis, and the aging process will alter the chemical adsorption capacity of the sediment. However, in conventional chemical partition modeling concerning SOM, a simple model of $K_d = f_{OM} K_{OM}$ is often used, in which all SOM contents are grouped into the f_{OM} fraction with a single K_{OM} value. This study shows that such a simplified approach cannot be employed to describe the dynamics of SOM degradation and the resulting changes in adsorption capacity. It may be necessary to adopt a multi-fractional approach to describe SOM transformation and its effect on sediment adsorption.

SOM input into sediment consists of multiple components in terms of biodegradability, ranging from readily biodegradable organic matter to less degradable, refractory and non-degradable organics (deBruyn and Gobas, 2004). Hence, the f_{OM} fraction can be written as the sum of the finer individual SOM fractions, i.e.

$$f_{OM} = \sum_{i=1}^{n} f_{OM_i} \qquad \text{(S1)}$$

where i signifies the i^{th} SOM fraction. The fraction f_{OM1} represents the most readily biodegradable organic fraction, and as the i value increases, the SOM fraction becomes less degradable.

In this experimental study, initial f_{OM} in the sediment was around 15%, including 5% of raw organic in the Harbour sediment and 10% of fish food (SOM) added into the sediment. Most of the raw SOM in the natural sediment could be considered refractory, while feeds in the fish farms are usually believed to be predominated by labile organic matters (deBruyn and

Gobas, 2004). For the loaded fish food pallets that contains about 70% of proteins and lipids, and 30% of fibers and other carbohydrates, based on the product information, the fast- and slow-decomposing fractions with a ratio of 7:3 might be assumed (Jamu and Piedrahita, 2002; Arndt et al., 2013). Hence, the initial f_{OM} could be approximated into 3 components with a ratio of 7:3:5.

Assuming first-order kinetics for the degradation of different organic components in sediment, the fraction-based SOM reduction dynamics may be described by the following simplified form:

$$f_{OM}^{t} = \sum_{i=1}^{n} f_{OM_i}^{0} e^{-k_i t} \tag{S2}$$

where $f_{OM}{}^{t}$ is the overall SOM content after period t, $f_{OMi}{}^{0}$ stands for the i^{th} fraction of fresh SOM on day 0, and k_i is the rate constant of organic degradation for the i^{th} SOM fraction. Using the best fit for the SOM reduction results reported in Fig. S1 as an example, the following expression can be obtained for SOM degradation during sediment incubation:

$$f_{OM}^{t} = 0.07e^{-0.096t} + 0.03e^{-0.0011t} + 0.05e^{-0t} \tag{S3}$$

This fitting result is comparable to organic decomposition rates observed by others. For instance, it has been reported that rapid and slow organic decay occur in the order of several per cents and tenths of a per cent per day in marine sediment, respectively, while recalcitrant organic substances in sediment can decay at the rate of 0.1% per year or lower (deBruyn and Gobas, 2004).

In relation to the SOM fractions, there should be a K_{OM} value for the adsorption of a given chemical pollutant by a particular f_{OM} fraction. Thus, the SOM-based partition coefficient may be written as

$$K_d = \sum_{i=1}^{n} f_{OM_i} K_{OM_i} \tag{S4}$$

Furthermore, the overall K_{OM} value, or K_d/f_{OM}, can be calculated by

$$K_{OM} = \sum_{i=1}^{n} \frac{f_{OM_i}}{f_{OM}} K_{OM_i} \quad \text{(S5)}$$

For each fraction, the fractional coeffeicnet, K_{OMi}, is a constant, as for that unchanged chemical composition and structure is assumed for each subdivided fraction. Hence, the change of SOM during organic composition was achieved by the alteration among different fractions, instead of the chemical transformation inside each fraction. When SOM undergoes humification, many SOM fractions, particularly the readily biodegradable fractions, i.e. f_{OM1}, f_{OM2} or f_{OM3}…, will reduce over time. Thus, there could be a shift in the f_{OMi} profile during the sediment aging process. The f_{OMi} for lower i SOM fractions will decrease significantly, and the f_{OMi} for the higher i fractions will hardly decrease and may even increase. As a result, the f_{OMi}/f_{OM} ratio will decrease greatly for lower i fractions and will increase considerably for higher i fractions. In the present study, after 120 d of incubation the fractional ratio of f_{OM} shifted to 0:2.5:5. As we can find out that, not only the SOM content decreased from 15% to 7.6%, and also the SOM fraction distribution was altered from f_{OM1} dominated to f_{OM3} dominated.

The change in the f_{OMi} profile during sediment aging will affect the chemical adsorption capacity of the sediment. In comparison to more hydrophilic and biodegradable SOM, more condensed humic-like SOM bring about more and stronger adsorption (Sun et al., 2010; Weber et al., 1999). Thus, for hydrophobic micropollutants typically found in sediment, K_{OMi} values for lower i SOM fractions are generally lower than those for higher i fractions. If the difference is only marginal for a particular chemical, i.e. $K_{OMi} \approx K_{OMj}$ ($i < j$), Eq. S5 suggests that the change in the f_{OMi} profile resulted from the SOM degradation will cause little change in the overall K_{OM} value of the sediment. This is likely to have been the case for hydrophilic chemicals, i.e. BPA observed in this study. However, SOM decay and reduction would still

lead to a continuous decrease in the K_d value of BPA in the sediment. If the difference is significant, i.e. $K_{OMi} < K_{OMj}$ ($i < j$), the change in the f_{OMi} profile will result in a general increase in the overall K_{OM} value, which is likely to have been the case for EE2 and Phe observed here. If the difference is rather great, i.e. $K_{OMi} << K_{OMj}$ ($i < j$), the change in the f_{OMi} profile would lead to a greater increase in K_{OM}. Moreover, the overall K_d value may not decrease but increase with the SOM decay and f_{OM} reduction, as displayed by both Phe and EE2 in the later phase of sediment incubation.

The model proposed here is basically a conceptual description for the analysis of experimental observations on the change in chemical adsorption by sediment in relation to SOM degradation. The great complexity of sediment and the dynamic changes in SOM components mean determining f_{OMi} fractions and corresponding K_{OMi} values is extremely difficult, if not impossible. To quantitatively validate it to a mathematical model, the SOM fractionation as well as the determination of the assigned fractional K_{OM} need to be further discussed, and the dynamic change of each fraction need to be carefully monitored. This would be a follow-up study in the future. Nonetheless, the model and its underlying mechanism provide a sound basis for predicting the impact of organic deposition and SOM decomposition on the adsorption of environmental pollutants in marine sediment.

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