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Applicability of PDMS in measuring HOCs in aquaculture

Applicability of equilibrium sampling in informing tissue residues and dietary risks of legacy and current-use organic chemicals in aquaculture

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Accepted Article

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Abstract: Equilibrium sampling based on silicone polydimethylsiloxane (PDMS) has been used to determine the concentrations of freely dissolved hydrophobic organic compounds (HOCs) and assess the thermodynamic potentials for bioaccumulation of these compounds in the aquatic environment. This allows the use of PDMS-based sampling techniques in assisting conventional sampling and extraction methods for the determination of the concentrations of HOCs in aquaculture products. This study presented an *ex-situ* demonstration of how well PDMS can inform the tissue residues and dietary risks of legacy or current-use organic chemicals in the aquaculture species from the farm ponds in Eastern China. For legacy contaminants such as polybrominated diphenyl ethers (PBDEs, n=10), a good agreement between the predicted concentrations based on PDMS and the measured lipid-normalized concentrations was observed for 60% of the studied biota, including both pelagic and benthic species. For pesticides currently used, such as pyrethroid (PE, n=4) and organophosphate pesticides (OPPs, n=7), the measured tissue residues were consistently higher than those predicted by PDMS, possibly caused by the continuous input from surroundings. For the organochlorine pesticides (OCPs, n=5), the only detected chemical (β -HCH) was also underestimated. Adjusted by ingestion rates of aquaculture products and toxicology data, the target hazard quotients (THQs) of these chemicals predicted from PDMS were generally comparable to those derived from measured concentrations in tissue due to the predominance of PBDEs. Overall, PDMS-based equilibrium sampling offered an alternative approach for the

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prediction of the tissue residues and dietary risks of PBDEs. Moreover, it should be applied with caution for PEs, OPPs and OCPs. Improving the application of PDMS for these chemicals in farm ponds warrants future study.

Keywords: PDMS, porewater, bioavailability, aquaculture environment

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1. INTRODUCTION

Aquaculture production has risen significantly since the 1990s to meet the growing demand for high-quality protein in China. As reported by Wang et al. (2015), culturing ponds accounted for approximately half of the total production. Accompanied the rapid development of the intensive aquaculture industry, a variety of contaminants have been identified in aquaculture products. This included pyrethroid insecticides, which was used to replace the legacy persistent pesticides in aquaculture (Corcellas et al., 2015; Mimbs et al., 2016; Han et al., 2017; Li et al., 2017). Organophosphorus pesticides (Henríquez-Hernández et al., 2017) have also been found in aquaculture environment due to atmospheric deposition, agricultural application and surface runoff (Melymuk et al., 2014). Moreover, legacy persistent chemicals such as organochlorine pesticides (Yu et al., 2011) and polybrominated diphenyl ethers (Yu et al., 2011) have been detected due to their historical application and environmental persistency (Da et al., 2019). Therefore,

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these compounds are ubiquitous in the environment, especially in sediment and porewater as a result of their relatively high hydrophobicity (Lamoureux and Brownawell, 1999).

The chemicals retained in sediment could be released into the water column under some unexpected changes of environment and hydraulic turbulence (Josefsson et al., 2010).

Consequently, aquaculture organisms can ingest and accumulate these HOCs from aquaculture environment. This would ultimately lead to a potential risk to human health through consumption of these products.

On account of people's concern on food safety, the routine monitoring of HOCs in aquaculture environment has become increasingly vital. However, the conventional methods are complicated, time consuming, costly, and provide bulk burden of the contaminants in different matrices. It was demonstrated that the residues and risks of the HOCs in aquatic organism were greatly correlated to the bioavailable concentrations (that is, freely dissolved concentrations), rather than the bulk burden (Hawthorne et al., 2007). Equilibrium passive samplers, such as low-density polyethylene (LDPE) and silicone polydimethylsiloxane (PDMS) (Posada-Ureta et al., 2017), are well-known for their advantages in simplicity of extraction procedures (Isetun et al., 2004) and provision of bioavailable concentrations of HOCs in different environmental matrices. Among the different equilibrium passive samplers, PDMS is extensively used due to its non-toxicity, high hydrophobicity and non-reactivity to most organic chemicals (Seethapathy and Górecki, 2012).

Currently PDMS is applied broadly in assisting the traditional monitoring techniques to measure the bioavailable concentrations of HOCs in different environmental matrices, including overlying water (Xue et al., 2020), sediment porewater (Trimble et al., 2008; Lu

et al., 2011) and biota (Jahnke et al., 2009; Jahnke et al., 2014b). In the water-sediment-biota system, the bioavailable concentrations in water or porewater, which is generally freely dissolved concentrations, is the main contributor driving the bioaccumulation processes in aquatic environment (Mayer et al., 2014; Peijnenburg et al., 2014; Li et al., 2016). Therefore, it is critical to determine whether PDMS is practicable in predicting tissue residues of HOCs in aquaculture products with a comparable lipid content to the biota reported previously (Jahnke et al., 2009) based on bioavailable concentrations and ultimately assisting in monitoring and inspecting the quality of the aquaculture products. Theoretically, PDMS was applicable in predicting the thermodynamic potential of HOCs in biota due to its similar characteristics to membrane (Naeimi et al., 2013). Hunter et al. (2008), Jahnke et al. (2008) and Heltsley et al. (2005) have confirmed the linear regression between the body burdens of HOCs and their concentrations partitioned into polymers, which suggested the possible application of PDMS in predicting the residues of HOCs in Chironomidae, vegetable oil, and fish tissue, respectively. PDMS devices have also been established as a tool to link the concentrations of polycyclic aromatic hydrocarbons (PAHs) and PEs on the silicone with the tissue residues in the biota from Taihu lake (Li et al., 2016) and Yangshan Port (Li et al., 2018) in our previous study.

However, it is noted that the previous applications were primarily in natural environment rather than artificial system (*e.g.* aquaculture ponds) which might be significantly affected by human activities. Specifically, aquaculture farm ponds were usually built within small-scale (1,000-10,000 m² with depth of 1-1.5 m) in crop field without connecting channels with natural waterbody. The environmental parameters and

concentrations of the HOCs in the artificial ponds would fluctuate consequently if heavy precipitation occurred or contaminated surface runoffs were introduced (Dong, 2014). Therefore, it is necessary to extend the application of PDMS into predicting body loads of HOCs in aquaculture products in artificial farm ponds with limited environmental capacity. It would play a significant role in the traditional method of the food inspection programs.

Notably, the aquaculture products ingested the chemicals through exposing to feed, water and sediment. The concentration of studied HOCs in the fish feed were strictly regulated (SAMR, 2017) and limited investigation has been reported on the residues of these chemicals in fish feed. Since aquaculture products, mostly benthic species in the present study, inhabit in pond sediment, we assumed that a considerable proportion of HOCs in these organisms could have originated from the sediment and porewater in which hydrophobic chemicals were highly retained (Oziolor et al., 2018). Therefore, it is crucial to quantify the bioavailable concentrations of HOCs ($n_{PBDEs}=10$, $n_{OCPs}=5$, $n_{OPPs}=7$ and $n_{PEs}=4$) in the porewater of culturing pond. Based on the bioavailable fraction in the silicone, the body burdens of the HOCs in biota and the corresponding dietary risk could be estimated (Li et al., 2018; Razzaghi et al., 2018). The possibility of applying the passive sampler in aquaculture environment could be confirmed through comparing the measured concentrations using traditional method and the corresponding dietary risks with the results from PDMS-based predictions. Overall, this study provided a comprehensive investigation regarding the feasibility of applying PDMS passive samplers to assist the routine inspection of the aquaculture products from farming ponds.

2. METHODOLOGY

2.1 Field sampling

Pond culture is popular among the aquaculture industry in China. Numerous farm ponds in China are located in Eastern China, including the provinces of Shanghai, Jiangsu, Anhui, Zhejiang and Shandong, etc. The residents of these provinces have great desire towards aquaculture foodstuffs (Cao et al., 2007; Jia et al., 2016). Therefore, ensuring the environmental quality of aquaculture ponds and products is vital for people in Eastern China. The samples were collected from the farm ponds in Shanghai (S1-S8), Zhejiang (S9-S13), Jiangsu (S14, S15), Anhui (S16), Shandong (S17) and Fujian (S18-S21) (**Figure 1**). The aquaculture products, including fish, crab, shrimp, shellfish and turtle, along with sediments, were collected from May to November in 2017. Each species (including fish and turtle) with similar sizes was sampled in triplicate (n=3) from the corresponding ponds randomly and processed within two days. For crab, shrimp and shellfish, the edible tissue of each species was mixed, and then distributed into triplicate (n=3). The lipid fractions of biota samples were measured and removed according to our previous protocol (Li et al., 2018). More information on the studied farm ponds and collected species are given in **Table S1** and **Figure S1** in the Supplemental Data. For ethical concerns, the animals were sacrificed through anaesthesia with eugenol (1:10000) (Shanghai Reagent, China).

2.2 Chemicals and exhaustive solvent extraction

Methanol, ethyl acetate, acetone, dichloromethane, hexane, anhydrous sodium sulfate, silica gel and copper disks were purchased from Sinopharm, China. The silicone

(SSPM823-005) was obtained from Specialty Silicone Products Inc. in Ballston Spa, NY, US. The standard solutions of PBDEs (BDE-17, BDE-28, BDE-47, BDE-66, BDE-71, BDE-85, BDE-99, BDE-100, BDE-153 and BDE-154), PEs (cyhalothrin, bifenthrin, permethrin, and fenpropathrin) and OPPs (dimethoate, methyl parathion, malathion, chlorpyrifos, quinalphos, triazophos and phosalone) were purchased from the National Institute of Metrology, China, while OCPs, including hexachlorocyclohexane isomers (HCHs), hexachlorobenzene (HCBz), heptachlor epoxide (HE), dichlorodiphenyldichloroethane (p,p-DDD), dichlorodiphenyldichloroethylene (p,p-DDE), were provided by Dr. Ehrenstorfer, Germany. The extraction procedures of PBDEs, PEs, OPPs and OCPs in biota are briefly summarized in **Table S2** and more details could be found in our previous investigations (Li et al., 2015; Li et al., 2018). All processed samples were kept at -20 °C prior to the chemical analysis.

2.3 Determination of bioavailable concentrations in porewater

The experimental protocols were established in our previous studies (Li et al., 2013; Li et al., 2016). In brief, PDMS with a diameter of 16 mm, a thickness of 0.127 mm and a weight of 24.8 mg was rinsed and sonicated with hexane/acetone (V:V=1:1) for 15 min twice to remove the interferences. The prepared silicone was reserved in methanol/water (V:V=1:1) solution prior to use. Sediment samples from the central point in each sampling pond were prepared in triplicate in amber bottles (n=3), mixed with mercuric chloride (0.15% of the sediment dry weight) and covered by deionized water. Subsequently, one piece of the silicone sheet was placed into each replicate after being rinsed with pure water and dried in air. The water content in the system was kept between 60% and 70%. Mercuric chloride was added to suppress the activities of microbes in

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order to minimize the degradation of HOCs in the system. The bottles were then placed into an incubator at 20 °C and shaken at a rate of 200 rpm for 28 days (Hunter et al., 2009; Jia et al., 2012; Li et al., 2013). The duration of the experiment was determined according to the content of organic carbon (OC) in the sediment (Table S1), with reference to our previous research (Li et al., 2013). After the exposure, the silicone was rinsed with pure water and desiccated at room temperature. A mixed solvent of hexane/acetone (V:V=1:1) was added to extract the targets in the silicone twice (Jia et al., 2012; Li et al., 2013; Jia and Gan, 2014; Li et al., 2016). The extracts were finally concentrated to 1 mL prior to the instrumental analysis.

2.4 Instrumental analysis and quality control

The target chemicals (PBDEs, PEs, OCPs, and OPPs) were measured using an Agilent gas chromatography-mass spectrometry (GC-MS) system (7890A/5975C) coupled with a column of DB-5MS (30 m×0.25 mm×0.25 μm). More details regarding the instrumental parameters are listed in **Table S3**.

The concentrations which yielded a signal to noise ratio of 3 were defined as the method detection limits (MDLs, **Table S4**). The observed concentrations in aquaculture products and porewater were reported in the format of arithmetic mean (n=3) with standard deviations. The procedural blanks (n=3) were prepared and processed along with biota and sediment-silicones. The blanks were subtracted from the analysis if the concentrations of analytes were above the MDLs. The recoveries were measured by spiking 5, 50 and 200 ng/g d.w. of the compounds into the biota samples prior to the pretreatment. The recoveries were measured using the measured concentration after

spiking minus the initial concentration before spiking, then divided by the spiked concentration. As given in **Table S4**, the recoveries of the studied chemicals ranged from 75% to 115%.

2.5 Data analysis

The freely dissolved concentration of HOCs in porewater (C_{PW}) could be quantified by the following equation (Mayer et al., 2003):

$$C_{PW} = C_{PDMS} / K_{PDMS} \quad (1)$$

where C_{PDMS} ($\text{ng} \cdot \text{g}^{-1}$) is the concentration of HOCs partitioned into PDMS and K_{PDMS} (Kg/L) is the partition coefficient of the target chemical between PDMS and water.

Considering the similar functional structure of PDMS polymer and biomembrane, the residues of HOCs in biota could be predicted using the following equation (Leslie et al., 2002; Sinko et al., 2017; Li et al., 2018):

$$C_{PRE} = K_{LP} \times C_{PDMS} \quad (2)$$

where C_{PRE} is the residue of HOCs in biota predicted using PDMS with the unit of $\text{ng} \cdot \text{g}^{-1}$ on a lipid weight basis and PRE stands for predicted values. K_{LP} is the partition coefficient of each chemical between lipid and PDMS, derived from the difference of intercepts of $\log BCF = a \times \log K_{OW} + b$ and $\log K_{PDMS} = a' \times \log K_{OW} + b'$ (see **Section S1** for details). The $\log K_{LP}$ of PEs was determined to be 0.03 in our previous investigations (Li et al., 2016; Li et al., 2018), while the $\log K_{LP}$ values of PBDEs, OPPs and OCPs in the

present study were derived as 1.32, 0.13 and 1.43 respectively. More details of K_{OW} , K_{PDMS} , C_{PW} , C_{PDMS} , and C_{PRE} are given in **Tables S5-S11**.

3. RESULTS AND DISCUSSION

3.1 Concentrations in porewater

Bioavailable concentration (freely dissolved concentration) of HOCs in porewater was of great importance in the evaluation of the partitioning behavior of HOCs between sediment and aquaculture organisms, mostly benthos and demersal fish in the present study. As indicated in **Figure S2** and **Table S6**, the mean C_{PW} of OPPs was 65 ± 55 (1.3 - 170) $\mu\text{g}\cdot\text{L}^{-1}$, which was significantly higher than the levels of OCPs (only β -HCH detected in the present study), PEs and PBDEs, with mean concentrations and ranges of 245 ± 187 (0.33 - 820), 7.7 ± 3.3 (2.2 - 14) and 0.71 ± 0.50 (0.15 - 2.2) $\text{ng}\cdot\text{L}^{-1}$, respectively. The C_{PW} of different chemicals diminished significantly with their rising hydrophobicity in the present study, which suggested low bioavailability of the chemicals with super high hydrophobicity (*e.g.*, PBDEs). This result was similar to Jia et al.'s (2012) finding that super hydrophobic PBDEs were anticipated to sorb on organic matter in sediment or dissolved organic carbon in water, resulting in low bioavailability of these compounds.

It is noted that no significant spatial pattern was detected for PBDEs, PEs and OCPs (**Table S6**, p values >0.05 , T-Test), which indicated similar contamination scenarios of these chemicals in the farm ponds from different provinces in Eastern China. However, the measured bioavailable concentrations for OPPs in porewater in the farm ponds from Shanghai, Shandong and Fujian were significantly higher than those detected in Jiangsu, Zhejiang and Anhui (p values <0.05 , T-Test). This might be related to the introduction of

OPP used by surrounding agriculture or widespread use of these pesticides to control parasites during culturing process in these areas.

As compared in **Figure 2**, the bioavailable concentrations of PBDEs were lower than those observed in US (Jia et al., 2012; Khairy and Lohmann, 2017) and the offshore areas in Xiamen, China (Li et al., 2010). In the meantime, the present bioavailable PBDEs concentrations were higher than those in the Dutch coast (Booij et al., 2002). PEs exhibited lower concentration in the present study than that found in the urban creeks in US (Bondarenko et al., 2007), indicating different application scenarios of PEs in these regions. OCPs levels in the studied porewater were higher than those found in Daliao River estuary of Bohai Sea in China, which was near the industrial zone in the northeast of China (Tan et al., 2009). OCPs in the porewater may have originated from historical applications in agriculture in Eastern China. The data of OPPs were not included in **Figure 2** due to its limited data availability in porewater.

3.2 Applicability domain of equilibrium sampling

PDMS provided a robust benchmark of the bioavailable fraction of non-polar HOCs in sediment (Li et al., 2016). However, the question remained whether the silicone could serve as a tool to quantify the tissue residues of HOCs in aquaculture species. The comparison between the measured concentrations (C_{BIO}) in different aquaculture products using conventional methods and predicted ones (C_{PRE}) based upon PDMS were therefore indicated in **Figure 3**. We assumed a fair prediction if the ratio of $C_{\text{BIO}}/C_{\text{PRE}}$ fell between 0.5 and 2.0, highlighted by gray shade, for chemicals whose hydrophobicity spanned several orders of magnitude (Jahnke et al., 2014a). The estimations based on PDMS

(C_{PRE}) were in good agreement with the measured residues of PBDEs (C_{BIO}) for both benthos and fishes generally (T-Test, p value=0.84>0.05), which covered approximately 60% of the samples ($n=42$). Specifically, the prediction performed well for crab (Chinese mitten crab), shrimp species (white shrimp, giant river prawn and Australia lobster), shellfish (triangle mussel), turtle (freshwater turtle) and fish species (snakehead, sturgeon, bighead carp, crucian carp, sand fish and striped bass). However, it should be highlighted that the silicone overestimated the body burdens of PBDEs in topmouth culter, bighead carp and grass carp. This could be explained by these organisms lived in the middle or top layer of the farm ponds and ingested less PBDEs from porewater, therefore should be verified by applying the silicone in the overlying water in the future.

PDMS generally underestimated tissue residues for PEs by the factors ranging from 1.6 to 57 (mean=18±17), which was different from our previous laboratory demonstration where equilibrium reached between aquaculture species and PE-spiked sediments (Li et al., 2018). This discrepancy highlighted the need to consider the continuous input for current-use chemicals in the field application of equilibrium sampling in aquaculture environment or other purpose-built aquatic systems. PEs are widely used to control pests and diseases throughout the culturing process or growth cycle of surrounding crops. Therefore, the body residues of PEs in farmed organisms would rise with increased environmental exposure. The continuous input of PEs during the culturing made the chemical hard to achieve equilibrium among different environmental matrices, which led to the delayed response of PDMS to the fresh input by reason of the relatively lower environmental persistence of PEs (Laskowski, 2002; Morgan et al., 2018). The underestimation with the factor of 57 occurred in topmouth culter, which was one of the

pelagic species, rather than the benthic species. Aquaculture products that inhabited in the middle or top layer of the pond may have ingested more freshly imported contaminants.

Similarly, as shown in **Figure 3(c)**, PDMS underestimated OPPs with a factor of 5.4 ± 5.9 . Some OPPs with low toxic are still extensively applied in the removal of weeds in aquaculture ponds or surrounding farmlands. As shown in **Figure 3(d)**, PDMS underestimated OCPs, particularly β -HCH in the present study (Table S11), as well. The underestimation factors ranged from 0.86 to 18 with a mean value of 5.6. Other OCPs were hardly detected, as the studied OCPs have been banned from use in the agricultural field since 1989 in China. The applicability of PDMS in predicting OCP residues in aquaculture products should be re-evaluated based on more OCP individuals in the future.

The findings based on artificial ecosystem (aquaculture ponds in the present study) were different from those reported in natural environments in previous investigations, such as Lake Ången in Sweden (Jahnke et al., 2014a), Tai Lake (Li et al., 2016) and Yangshan Port in China (Li et al., 2018), which suggested that the boundary conditions of equilibrium passive sampling should be highly noted when PDMS was applied to sense the bioavailability and predicted the body residues of HOCs in artificial systems. Specifically, in artificial ecosystems such as culture ponds, the body burden prediction of current-use pesticides based on PDMS seemed unreliable, due to the particularity of the artificial ecosystem and the non-equilibrium chemicals in the system. The regular pesticides used in culturing or those introduced along with surface runoff from the surrounding agriculture accounted the pond as not a steady-state system and resulted in the deviation in predicting body residues of pesticides based on thermodynamic potential. PDMS performed well for those chemicals in steady state with no additional input

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(PBDE in this article) during the culturing process in the present small-scale farm ponds. These results enriched the practical application of PDMS in artificial ecosystems (i.e. aquaculture ponds) which have not been involved in the previous researches. However, it is necessary to carry out an in-situ investigation based on the silicone to quantify the bioavailable concentrations of these current-use pesticides (e.g., PEs and OPPs) in both porewater and overlying water. In addition, a time-weighted type passive sampling approach is also critical to capture fresh input variability. These would finally improve the accuracy of body residues of these chemicals in the future.

3.3 Comparison of directly measured and PDMS-based dietary risk

Humans are exposed to HOCs through several pathways, among which dietary intake was well documented and highly associated with human health. Non-cancer risk through daily consumption of aquaculture products could be assessed by the target hazard quotients (THQs) proposed by the USEPA. The THQs based upon the ratio of the daily intake to the reference doses (RfDs) are plotted and compared in **Figure 4**. If $THQs > 1$, the consumption of farmed aquatic products could cause health risks. More details on THQs calculation are given in **Tables S12-S13**.

Generally, the THQs calculated according to conventional method and PDMS would be below 1. This suggested no significant dietary risk for human beings from the consumption of these foodstuffs. As shown in **Figure 4(a)**, the predicted risks of crab, shrimp and fish were comparable to those risks derived from traditional monitoring program (T-Test, p values=0.89 for crab, 0.14 for shrimp and 0.79 for fish). The fair estimation of the risks based on PDMS was possibly a result of good prediction for

PBDEs using the silicone and high contribution of PBDEs to the total THQs (**Tables S12-S13**). High contribution of PBDEs to total THQs was generally caused by the higher toxicity (Table S5) and tissue residues than those of the current-use pesticides (Table S7). Comparing to PBDEs, the contribution of the current-use pesticides (PEs and OPPs) to total THQs could be ignored (Tables S12-S13) as their toxicity and residues in aquaculture products was several magnitudes lower. Therefore, for the current-use pesticides, both risk values estimated from directly measured and PDMS predicted could be disregarded in this study, although the former was higher than latter (Table S7). Hence, if highly hydrophobic and toxic chemicals were the dominant contaminants in aquaculture ponds without fresh input, risk derived from PDMS was reliable. In other cases, the prediction of risk based on PDMS should be used with caution.

As shown in **Figure 4(a)**, the dietary risks by consuming crab and fish were comparable (T-Test, $p=0.67>0.05$), but was significantly higher (t-test, p value= $0.03<0.05$) than that by consuming shrimp. This might be closely related to people consuming shrimps at a lower rate (**Figure 4(c)**). Although the total concentrations of the studied HOCs in crabs was lower than those in fish (**Figure 4(b)**), the dietary risks were not significantly different. This was primarily caused by the comparable ingestion rates, detection frequencies and concentrations of the highly toxic congeners, such as BDE-99 and triazophos (**Tables S6, S8 and S11**). Similar patterns were observed for the risk estimated based on PDMS.

Therefore, the silicone was an alternative tool to estimate the dietary risk of very hydrophobic HOCs (*eg.* PBDEs) without external input in this semi-closed environment. However, the equilibrium-based PDMS was demonstrated to be not reliable enough to

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predict the tissue residues and the corresponding dietary risks of the current-use chemicals (such as PEs and OPPs in the present study) in aquaculture products from farm ponds, due to continuous input of the chemicals. Therefore, confirming the application of PDMS for current-use chemicals in the present or similar artificial systems warrants future study. The in-situ application of the silicone in both porewater and overlying water and quantification of fresh input variability should be considered in the prediction comprehensively.

4. CONCLUSION

The bioavailable concentrations of the studied HOCs, namely, PBDEs, PEs, OCPs and OPPs, in porewater were highly dependent on their hydrophobicity and could be determined by PDMS. The comparison between traditionally measured and PDMS predicted concentrations and risks suggested that the PDMS performed well for predicting the tissue residues and risks of HOCs in aquaculture products if those chemicals were persistent and in steady state with no additional input during the culturing. The silicone underestimated the concentration of current-use chemicals such as PEs and OPPs in aquaculture environment, possibly due to continuous input of such chemicals during culturing and from surrounding agriculture. Therefore, it is requisite to extend the PDMS from ex-situ application to periodical in-situ deployment in the overlying water to provide the bioavailable concentrations of HOCs to finally determine the input of HOCs from surroundings and correct PDMS-predicted residues and risks of these compounds in aquaculture products in the future.

Overall, the present research extended the application of PDMS from natural environment to artificial environment, specifically in culturing ponds in Eastern China. It was confirmed that PDMS could be used as a supplementary tool to the traditional monitoring programs for quality control of aquaculture products, if the estimation of PDMS for current-use chemicals was improved. Due to the differences between the small-scale farm ponds and natural environment, the application of PDMS in farm ponds (receiving fresh input surrounded and with small environmental capacity) and natural environment (relatively constant concentration of HOCs and large environmental capacity) should be considered separately.

Supplemental Data—The Supplemental Data are available on the Wiley Online Library at DOI: 10.1002/etc.xxxx.

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Figure 1 Descriptive map of the sampling aquaculture farm ponds in Eastern China.

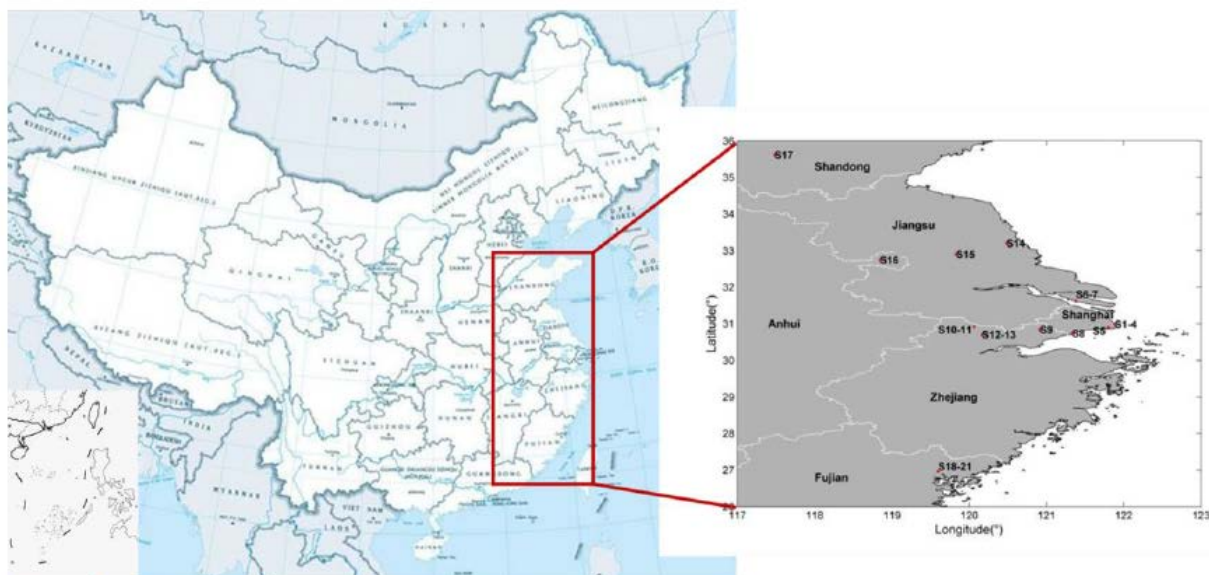


Figure 1

Figure 2 Comparisons of the observed bioavailable concentrations in the present study and other regions for PBDEs (Booij et al., 2002; Li et al., 2010; Jia et al., 2012; Khairy and Lohmann, 2017), PEs (Bondarenko et al., 2007) and OCPs (Xue et al., 2006; Li et al., 2010). The data regarding OPPs in porewater were not included in the figure due to limited data availability.

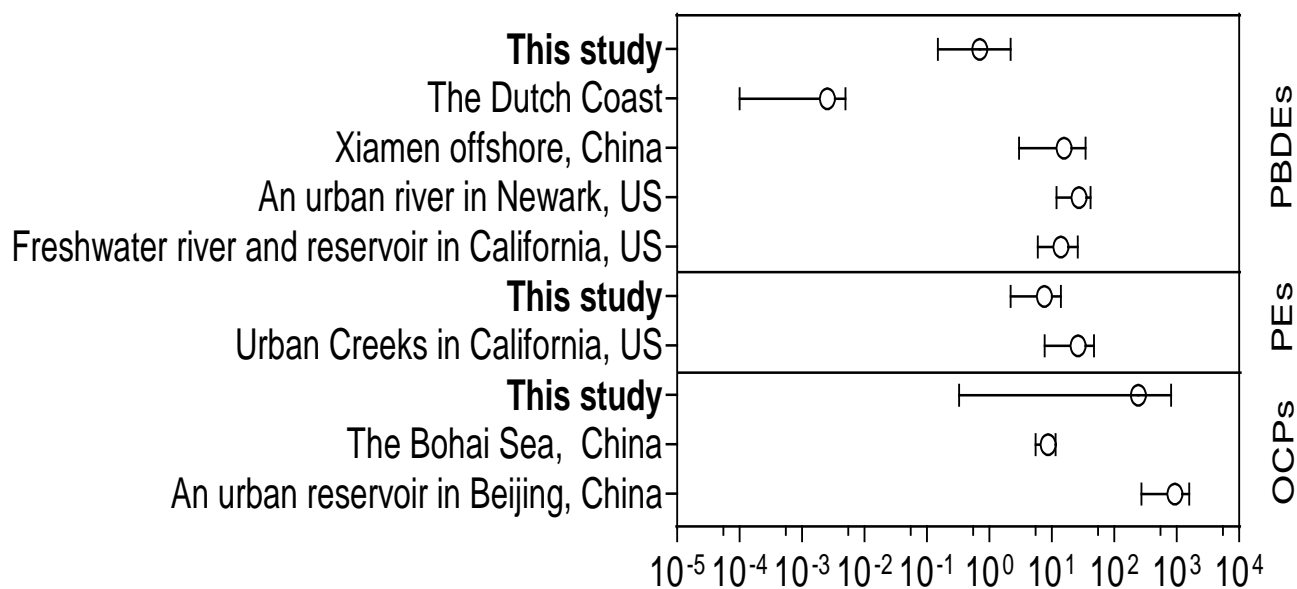


Figure 3 Estimation of the body residues based on PDMS for different aquaculture species in different farm ponds. C_{BIO} is the measured concentration normalized by lipid fraction. C_{PRE} represents the body burdens (lipid fraction normalized) estimated based on the freely dissolved concentrations in porewater quantified by PDMS (Eq. 2). The gray shaded area highlighted the ratio of $C_{\text{BIO}}/C_{\text{PRE}}$ between 0.5 and 2.0. All the raw data of C_{BIO} and C_{PRE} are given in **Tables S7 and S11**.

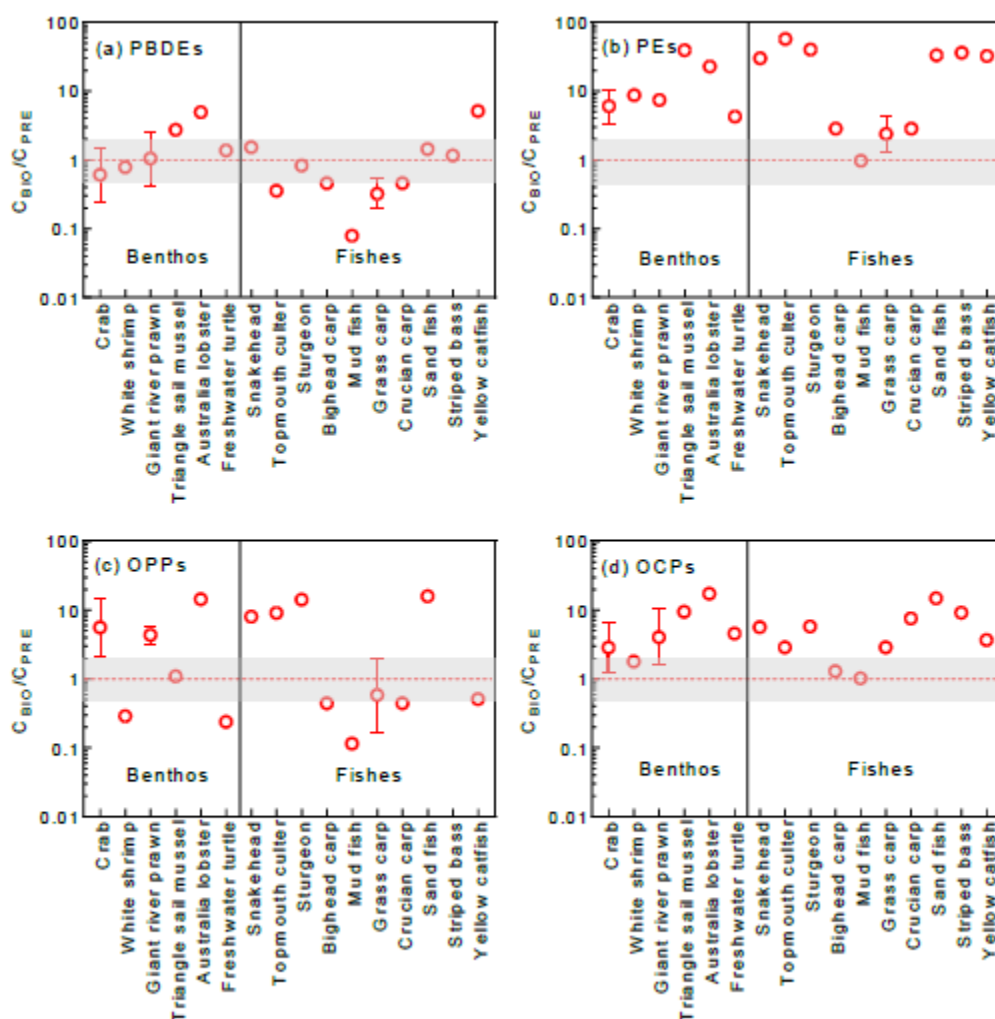


Figure 3

Figure 4 Comparison between the measured and predicted dietary risk (a), tissue residues on a wet weight basis (b) and the corresponding daily ingestion rates (c). The data of ingestion rates were collected from our previous research (Li et al., 2019) and the observed tissue residues could be found in **Tables S7** through **S11**. Note, due to the data availability of RfD, only some of the chemicals were considered in the risk estimation. Specifically, the risks of BDE-28, BDE-71, BDE-154 and bifenthrin were not included. The raw data on the calculated risk could be found in **Tables S12-S13**.

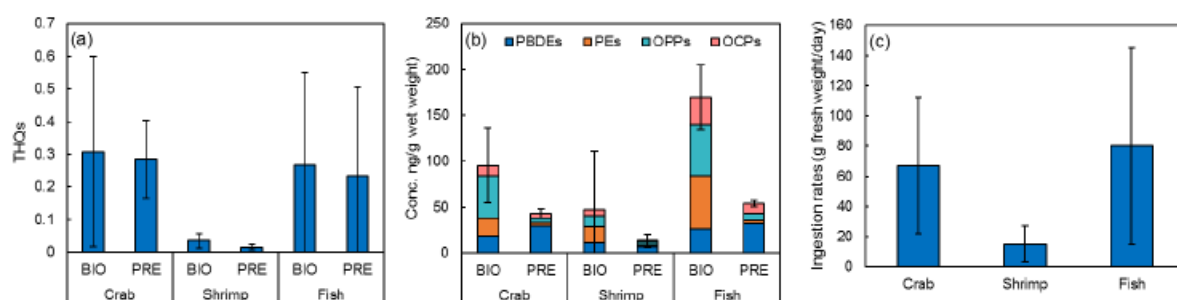


Figure 4.