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Equilibrium sampling informs tissue residue and sediment remediation for pyrethroid insecticides in mariculture: A laboratory demonstration

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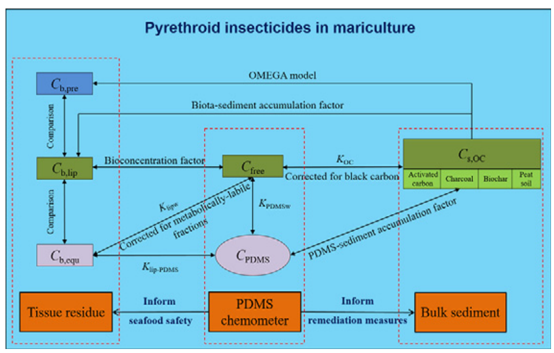
HIGHLIGHTS

- Equilibrium sampling senses reduced bioavailability of sediment-associated pyrethroids by biochar amendment.
- Equilibrium sampling translates freely-dissolved concentrations of pyrethroids into seafood tissue residues.
- Equilibrium sampling alerts for seafood safety and guides sediment remediation in mariculture.

GRAPHICAL ABSTRACT



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ABSTRACT

Mariculture product safety in relation to sediment quality has attracted increasing attention because of the accumulation of potentially hazardous chemicals, including pyrethroid insecticides, in sediment. Passive sampling has been widely used to assess the bioavailability of sediment-associated hydrophobic organic contaminants and predict their body residue in benthic organisms. Therefore, in this study, we introduced polydimethylsiloxane (PDMS) polymer as a biomimetic "chemometer" for freely-dissolved concentrations (C_{free}) to assess the efficacy of different carbon sorbents in reducing the bioavailability of pyrethroids in the process of sediment remediation. Black carbon (BC)-based materials (e.g., charcoal, biochar, and activated carbon) showed the advantageous sorption capacity over humic substance-based peat soil based on both C_{free} and tissue residue in exposed clams. Of the tested BC-type materials, biochar appeared to be an ideal one in the remediation of pyrethroid-contaminated sediment. The predictive value of the PDMS chemometer approach to informing tissue residue was confirmed by a good agreement between the measured lipid-normalized concentrations of pyrethroids in clams and the lipid-based equilibrium concentrations calculated from C_{free} via lipid-water partition coefficients. The quantitative inter-compartmental relationship underlying the laboratory system of sediment-pore water-PDMS-biota was also cross-validated by a mechanistically-based bioaccumulation model, thus confirming the validity of C_{free} as a predictive intermediate to alert for tissue residue and guide sediment remediation. The present study revealed a great promise of sensing C_{free} by polymer-based equilibrium sampling in predicting tissue residue of chemicals applied in mariculture against regulatory guidelines, and, in turn, informing remediation measures when needs arise. In situ demonstration is warranted in the future to ascertain the field applicability of this approach in real mariculture systems.

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1. Introduction

There has been a sharp increase in demand for seafood products, including finfish and shellfish, for their high protein content since the 20th century, particularly in the past 50 years. To meet such a great demand, mariculture has undergone unprecedented growth, evolving as a significant contributor. However, in order to enhance the seafood production, the overwhelming majority of the world's aquaculture systems continue to intensify cultivation methods such as the heavy application of pesticides (Sapkota et al., 2008). These methods put forward a number of potential food safety and human health concerns associated with maricultured seafood products.

As an emerging class of insecticides, pyrethroids have been used worldwide to replace the traditional ones (e.g., organochlorines and organophosphorus) for pest control due to their relatively lower environmental persistence (Li et al., 2017; Ye et al. 2017b). Upon application in the aquatic environment, pyrethroids tend to bind rapidly to the particulate phase in water due to their high hydrophobicity, resulting in the accumulation in sediment (Hill, 1989; Solomon et al., 2001; Booij et al., 2015; Joyce et al., 2016). Compared with the half-life of organochlorine pesticide (several years) in surface soil (Toan et al., 2009), anaerobic half-life of pyrethroids in soil ranged from 33 to 425 days (Feo et al., 2010), which makes the latter an attractive replacement of traditional pesticides. In mariculture, they have been increasingly used as a treatment against the infestation caused by the parasitic sea lice (Geest et al., 2014). Continuous consumption of these pesticides for such practices result in "pseudo-persistence" and, consequently, accumulation of these chemicals in the mariculture environment and seafood products.

The accumulation and toxicity of pyrethroids in non-target aquatic organisms (Edwardsa et al., 1986) would have strong implications for the quality of seafood products and subsequent health risks of human consumers. For example, Rawn et al. (2010) detected cypermethrin in Canadian farmed salmon samples with concentrations ranging from 0.30 to 6.5 ng/g fresh weight. Pyrethroids pose cumulative risks to fish (Xiao et al., 2016; Corcellas et al., 2015; Tu et al., 2014), and they were even detected in marine mammals (Alonso et al., 2012; Aznar-Alemany et al., 2017). A recent wastewater-based sewage epidemiology study (Rousis et al., 2017) has revealed elevated human exposure to permethrin, cypermethrin, and cyfluthrin in Florence with exceedance of their respective acceptable daily intake. Increased pyrethroid exposure has been associated with the elevated gonadotropins levels and earlier pubertal development in Chinese boys (Ye et al., 2017b). The epidemiological findings have been further evidenced by in vivo mechanistic investigations in male mice (Ye et al., 2017a). Several countries have established the maximum residue level (MRL) for pyrethroids in aquatic products. The MRLs of deltamethrin and cypermethrin were set at 30 μg/kg for salmoniformes and 10 μg/kg for other fish and aquatic organisms in the "positive list system" enacted by Japan (Umetsu, 2006), and at 10 and 50 μg/kg, respectively, by European Union (http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32001R2162&from=EN). The relevant regulatory guideline of deltamethrin (30 μg/kg in fish muscle) has also been established in China (http://www.moa.gov.cn/zwllm/tzgg/gg/200302/t20030226_59300.htm; in Chinese). Therefore, understanding the fate of pyrethroids in the mariculture environment is essential for seafood safety assessment and remediation efforts.

The fate of pyrethroids, like other hydrophobic organic contaminants (HOCs) in the aquatic environment, is governed by the quantitative sediment-water-biota relationship, where the freely dissolved concentration in sediment pore water (C_{free}) is a central mediator driving the bioaccumulation process from the bulk sediment to the exposed aquatic organisms (Mayer et al., 2014; Peijnenburg et al., 2014; Li et al., 2016). The equilibrium sampling technique using polymers (e.g., polydimethylsiloxane or PDMS) has been established to measure C_{free} for a broad spectrum of HOCs based on their concentrations on PDMS (C_{PDMS}) and PDMS-water partition coefficient (K_{PDMSw}) (Hunter et al., 2008; Mayer et al., 2014). The PDMS-based technique further demonstrated its utility as a quantitative "chemometer" to assess the lipid-based equilibrium concentrations as the thermodynamic potential for bioaccumulation of sediment-associated HOCs in benthic species from C_{PDMS} multiplied by the lipid-PDMS partition coefficient ($K_{lip\text{-}PDMS}$) (Lydy et al., 2014). Passive samplers have been deployed in a PCB-contaminated sediment as a surrogate for benthic organisms to assess their predictability for bioaccumulation (Figueiredo et al., 2017). Our previous study also demonstrated the quantitative utility of C_{free} to link back to the total chemical burden and mixture effect in sediment as well as tissue residue in benthic species (Li et al., 2016). This approach generally applies to metabolically-inert chemicals; however, its applicability to less persistent chemicals such as pyrethroids remains to be tested with a correction for the metabolically-labile fraction. From bulk sediment to pore water, C_{free} depends largely on the sorptive capacity of the solid phase, especially the organic carbon (OC) content. In general, the OC-normalized concentration ($C_{s,oc}$) and OC-water partition coefficient (K_{oc}) is used to predict the partitioning of HOCs between sediment and pore water.

However, the heterogeneous compositions of carbon sorbents in sediment, particularly the presence of black carbon (BC) with a stronger sorption effect, would largely modify the bioavailable fraction of sediment-associated HOCs (Amymarie and Gschwend, 2002; Jonker and Koelmans, 2002; Jager et al., 2003; Kraaij et al., 2003; Lohmann et al., 2005). This has implications for remediation practices where carbon sorbents with high sorptive capacity are used for sediment capping in order to reduce C_{free} and hence the bioavailability of contaminants from bulk sediment (Ghosh et al., 2011). Understanding the modulating effect of carbon sorbents on the contaminant bioavailability is key for remediating, for example, pyrethroid-impacted sediment in maricultural environment, in alleviation of seafood tissue residue of these chemical hazards in benthic organisms.

In the current study, we employed PDMS-based equilibrium sampling in an in vivo contact bioassay with spiked sediment in the presence of carbon sorbents to assess the bioavailability and bioaccumulation of pyrethroids to typical seafood species (*Venerupis philippinaram*). We further elucidated the inter-compartmental relationship in the amended sediment-porewater-PDMS-biota partitioning system by cross-validation with a predictive bioaccumulation model (Optimal Modeling for Ecotoxicological Applications, OMEGA). With such a quantitative insight (the overall quantitative framework of the study illustrated in Fig. 1), our central aim was to enhance the practical utility of equilibrium sampling to alert for tissue residue of hazardous chemicals in seafood products, and inform risk-based decision-making on remedial actions. Such an approach would circumvent the need to measure contaminant concentrations in tissue and sediment, thus providing an efficient means of monitoring seafood safety in maricultural environment.

2. Materials and methods

2.1. Chemicals and materials

Four pyrethroids including fenpropathrin (FN), permethrin (PERM), bifenthrin (BF) and lambda-cyhalothrin (LCY) were purchased from ChemService (West Chester, PA). These four pyrethroids were selected for their high detection frequency (Li et al., 2017) and widespread occurrence in the environment due to their wide use for pest control in aquaculture and as insecticides in agriculture (Garcia-Rodriguez et al., 2012; Alonso et al., 2012; Aznar-Alemany et al., 2017). Although classified into two types based on their modes of toxic action, pyrethroids share similar physicochemical properties and hence similar environmental behavior of these chemicals (Li et al., 2017; Li et al., 2014a).

The stock standard solutions were prepared in acetone and kept at −18 °C. The surrogate 4, 4′-dibromooctafluorobiphenyl (DBOFB) and