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Effect of dissolved organic matter on pre-equilibrium passive sampling: A predictive QSAR modeling study

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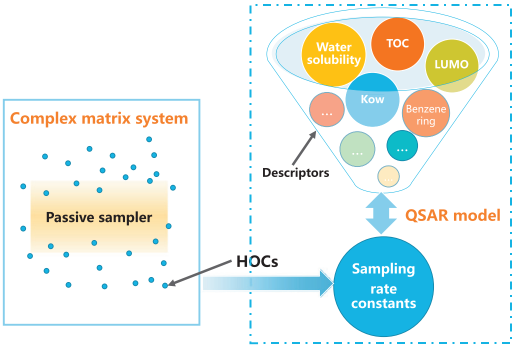
HIGHLIGHTS

- A flow-through system was set up to obtain desorption rate constants in various complex matrices.
- Passive sampling rate constants significantly increased as the concentration of DOM increased.
- A QSAR model was proposed to predict passive sampling rate constants.

GRAPHICAL ABSTRACT



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ABSTRACT

Pre-equilibrium passive sampling is a simple and promising technique for studying sampling kinetics, which is crucial to determine the distribution, transfer and fate of hydrophobic organic compounds (HOCs) in environmental water and organisms. Environmental water samples contain complex matrices that complicate the traditional calibration process for obtaining the accurate rate constants. This study proposed a QSAR model to predict the sampling rate constants of HOCs (polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and pesticides) in aqueous systems containing complex matrices. A homemade flow-through system was established to simulate an actual aqueous environment containing dissolved organic matter (DOM) i.e. humic acid (HA) and (2-Hydroxypropyl)-β-cyclodextrin (β-HPCD)), and to obtain the experimental rate constants. Then, a quantitative structure-activity relationship (QSAR) model using Genetic Algorithm-Multiple Linear Regression (GA-MLR) was found to correlate the experimental rate constants to the system state including physicochemical parameters of the HOCs and DOM which were calculated and selected as descriptors by Density Functional Theory (DFT) and Chem 3D. The experimental results showed that the rate constants significantly increased as the concentration of DOM increased, and the enhancement factors of 70-fold and 34-fold were observed for the HOCs in HA and β-HPCD, respectively. The established QSAR model was validated as credible ($R^2_{Adj.} = 0.862$) and predictable ($Q^2 = 0.835$) in estimating the rate constants of HOCs for complex aqueous sampling, and a probable mechanism was developed by comparison to the reported theoretical study.

Main finding of the work: The present study established a QSAR model of passive sampling rate constants and calibrated the effect of DOM on the sampling kinetics.

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1. Introduction

Passive sampling, a relatively new approach in the analysis of hydrophobic organic compounds (HOCs), has been widely used in environmental monitoring for water and air (Baz-Lomba et al., 2017; Feng et al., 2016; Guo et al., 2017; O'Brien et al., 2011; Vrana et al., 2014; Xue et al., 2017). Although it can largely overcome obstacles in traditional sampling processes, a few technical shortcomings should not be ignored. There are two modes of passive sampling. One is equilibrium extraction, that has been validated to monitor free concentrations accurately but requires long sampling times, which greatly limits application to labile compounds (Zhang et al., 2011). Moreover, it is impractical to achieve real-time monitoring in highly dynamic systems, since analyte concentrations always change rapidly and the equilibrium state is fleeting. Therefore, for analysis of highly dynamic chemical changes in real environmental water and living systems, another mode, pre-equilibrium extraction that also known as kinetic passive sampling (Allan et al., 2006), is a better choice.

When applying pre-equilibrium extraction, sampling kinetics are of great importance because potential environmental factors such as temperature, salt, velocity, biofouling and dissolved organic matter (DOM) have a strong impact on the mass transfer kinetics of pollutants. All of these factors can be easily calibrated by considering parameters like diffusivity, viscosity, distribution coefficient in the system, except for the DOM. The effect of DOM can only be measured by semi-empirical equations because some related parameters remain unavailable (i.e. lability factor, diffusion coefficient of complex matrix, etc.). In recent years, although pre-equilibrium passive sampling has been reported for an extensive range of applications to measure organic compounds in complex matrix systems such as food (Lin et al., 2016; Ziółkowska et al., 2016), semisolid organization (Shiota et al., 2011; Xu et al., 2016) and environmental water (Mirasole et al., 2016), knowledge of the effect of complex matrices on the sampling kinetics is still very limited. Ter Laak et al. (2009b) first investigated the facilitation of the mass transfer of HOCs by DOM, and presented an expression to correct the mass transfer coefficient in complex matrices for passive samplers. Hereafter, a series of studies have given evidence to the influence of complex matrices on uptake kinetics of passive samplers, and new models have been proposed and demonstrated in the laboratory (Gilbert et al., 2014; Jiang et al., 2015a; Zielińska et al., 2012). In the existing reports, preloading passive samplers with performance reference compounds (PRC) was the only effective approach to calibrate the effect of complex matrices (Cui et al., 2013; Lin et al., 2017). This method was based on an isotropic process between the uptake of target compounds into the sampler and the desorption of PRC from the sampler. Despite the reliability and accuracy, application limitations were that not all PRC for the targeted compounds were available and that most PRC were very expensive. To overcome this limitation, Ouyang et al. (2009) proposed a one-calibrant kinetic calibration in which the desorption of a single PRC was used to calibrate all extracted analytes. However, this method could only be applied to water samples without any complex matrix.

Based on the above considerations, a relatively simple, fast empirical method based on essential parameters for HOCs and/or the exposure system, should be more applicable to environmental water. Therefore, we do a new attempt to construct a quantitative structure-activity relationship (QSAR) model to correlate the kinetic rate constants to the properties of analytes and the sample matrices. QSAR models are widely reported to be used in drug design (Ramsay and Di Giovanni, 2017; Tong et al., 2017), chemical engineering design (Fourches et al., 2015; Gonfa et al., 2016) and environmental studies (Shi et al., 2017; Tian et al., 2017). A QSAR model, which represents internal relationships between physical properties, environmental behavior, ecological toxicological parameters and the molecular structure of HOCs, is here investigated to study environmental indicators. It can incorporate the relevant environmental data for HOCs, sharply reduce experimental costs and decrease the number of necessary experiments or even eliminate them altogether.

In the present study, the effect of complex matrices on the passive sampling kinetics was first investigated. Solid phase microextraction was selected as the passive sampler and a homemade flow-through system was established to model a real aqueous environment containing a complex matrix. The flow system effectively solves problems of traditional sampling methods, in which (a) HOCs might sorb to the wall stiffly due to high hydrophobicity, causing low concentration of HOCs in water; (b) the concentrations and states of the matrix are labile; or (c) long times are required to reach equilibrium. The rate constants of 19 HOCs in complex matrices containing humic acid (HA) and (2-Hydroxypropyl)-β-cyclodextrin (β-HPCD) were acquired. The relative structural and physicochemical parameters of the HOCs and complex matrix were calculated and selected as descriptors by Density Functional Theory (DFT) and Chem 3D. Genetic Algorithm-Multiple Linear Regression (GA-MLR) was used to establish a QSAR model which correlate the rate constants to the system state including the above-mentioned descriptors. Using the obtained QSAR model, the probable mechanism of the sampling kinetics can be further interpreted, and the relationship between rate constants and the system states can be clearly understood.

2. Materials and methods

2.1. Chemicals and instrument

Nineteen solid HOCs (Table S1) were divided into two groups. One was the polycyclic aromatic hydrocarbons (PAHs), which included naphthalene, acenaphthene, phenanthrene, fluorene, pyrene, chrysene, benzo[*k*]fluoranthene, benzo[*a*]pyrene and dibenz[*a*,*h*]anthracene. The other was the polychlorinated biphenyls (PCBs)/pesticides group, containing PCB-1, 3, 9, 11, 18, 77, pentachlorobenzene (penta-CB), hexachlorobenzene (hexa-CB), Aldrin-D and DDT. The PAHs and two complex matrices, humic acid (HA, fulvic acid ≥ 90%) and (2-Hydroxypropyl)-β-cyclodextrin (β-HPCD), were purchased from Sigma-Aldrich (Shanghai, China), while the PCBs/pesticides were purchased from J&K Scientific, Ltd. (Shanghai, China). The polydimethylsiloxane (PDMS) tubing (i.d. 310 μm, o.d. 640 μm) was purchased from PermSelect (Ann Arbor, MI, USA), and the stainless steel wire (diameter of 480 μm) was purchased from Vita Needle Co. (Needham, MA, USA).

An Agilent 7890 GC coupled to 5977A MS (Agilent technologies, CA, USA) was used for quantification purposes. The GC was equipped with a split/splitless injector and an HP-5MS (30 m × 0.25 mm I.D. × 0.25 μm thickness) fused-silica column. The injector temperature was set at 280 °C, while the oven temperature was programmed from 80 °C to 280 °C at a rate of 20 $°C\ min^{-1}$ and then held for 10 min at 280 °C. Chromatographic separation was performed with helium as the carrier gas. A Selected Ion Mode (SIM) was used for all compounds, whose selected ion values are listed in Table S1. A GERSTEL Multi-Purpose System (MPS) was applied for the automation process (GERSTEL, Mülheim a der Ruhr, Germany). The correlation coefficients of calibration curves with GC-MS analysis were higher than 0.99 for all the HOCs. Internal standards were injected periodically to ensure the stability of the instrument.

2.2. Fiber preparation

Stainless steel wires with a core diameter of 480 μm were cut into pieces 4 cm long, sonicated in acetone and deionized water for 15 min each to remove impurities, and dried at room temperature. A piece of carefully cut PDMS tubing with an inner and outer diameter of 320 μm and 650 μm, respectively (1.0 cm), was used as the passive sampler. A swell-shrink method was applied since the inner diameter of PDMS tubing (320 μm) was smaller than the diameter of steel wire (480 μm). Briefly, the PDMS tubing was coated onto the end of the steel wire