Evaluation of the Availability of Bound Analyte for Passive Sampling in the Presence of Mobile Binding Matrix

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ABSTRACT

Elucidating the availability of the bound analytes for the mass transfer through the diffusion boundary layers (DBLs) adjacent to passive samplers is important for understanding the passive sampling kinetics in complex samples, in which the lability factor of the bound analyte in the DBL is an important parameter. In this study, the mathematical expression of lability factor was deduced by assuming a pseudo-steady state during passive sampling, and the equation indicated that the lability factor was equal to the ratio of normalized concentration gradients between the bound and free analytes. Through the introduction of the mathematical expression of lability factor, the modified effective average diffusion coefficient was proven to be more suitable for describing the passive sampling kinetics in the presence of mobile binding matrixes. Thereafter, the lability factors of the bound polycyclic aromatic hydrocarbons (PAHs) with sodium dodecylsulphate (SDS) micelles as the binding matrixes were figured out according to the improved theory. The lability factors were observed to decrease with larger binding ratios and smaller micelle sizes, and were successfully used to predict the mass transfer efficiencies of PAHs through DBLs. This study would promote the understanding of the availability of bound analytes for passive sampling based on the theoretical improvements and experimental assessments.

Key words: passive sampling kinetics; diffusion boundary layer; mobile binding matrix; lability factor; polycyclic aromatic hydrocarbons; sodium dodecylsulphate

1. Introduction

Passive sampling techniques are very popular for sampling analytes of interest from various complex sample matrixes, such as environmental waters [1], sediments [2] and biological samples [3-8]. For the implementation of passive sampling in complex sample matrixes, it has long been a concern among the scientific community whether the bound analytes are available for passive sampling in complex sample matrixes, which might complicate the passive sampling kinetics and influence the passive sampling efficiency [9-11].

For over a decade, a series of studies revealed that the presence of diverse mobile binding matrixes, such as humic substances [12-17], surfactant micelles [16,17], nanoparticles [18,19], and proteins [9-11,19], could accelerate the mass transfer kinetics through the diffusion boundary layers (DBLs) in the sample matrixes, which was regarded as a “shuttle effect” of the mobile binding matrixes, indicating that the bound analytes also contributed to the overall mass transfer through DBLs adjacent to passive samplers [9-11,15,18,19]. These studies emphasized the importance of full awareness of the effects of binding matrixes, and showed profound influence on the development of calibration methods for passive sampling techniques [11,20].

Several pioneer studies were committed to quantify the effects of the binding matrixes on the mass transfer through DBLs adjacent to solid-phase microextraction (SPME) fibers [9,10,15,18,19]. All these studies agreed that, to make the bound analytes available for the mass transfer through DBLs, the desorption kinetics of analytes from the binding matrixes should be fast when compared to the time scales

65 that the free analytes diffuse through DBLs [9,10,15,18,19]. ter Laak et al. [15] who
66 were cautious about the desorption kinetics, made a remarkable progress by
67 introducing a lability factor in their theoretical model to correct the possibly
68 inefficient desorption of the analytes from the binding matrixes during the time period
69 of the complexes diffusing in DBLs. The lability factor was assigned to range from
70 zero to unity, which at each endpoint value was corresponding to the completely inert
71 and completely labile complexes. When the complexes were completely inert, the
72 bound analytes would not desorb from the binding matrixes during the time period of
73 the complexes diffusing in DBLs, and thus, would not participate in the mass transfer
74 through DBLs. On the contrary, when the complexes were completely labile, the
75 bound analytes would totally participate in the mass transfer through DBLs. In other
76 words, the lability factor also measures the availability of the bound analytes in the
77 mass transfer through DBLs [12,13,18,19]. The model developed by ter Laak et al.
78 [15] coincided well with the experimental results of several completely labile systems
79 developed by van Leeuwen, Town and their colleagues [18,19]. However, the
80 desorption kinetics of analytes from the binding matrixes might not be that fast, as the
81 desorption kinetic coefficients reported by Kopinke et al. were in the range of 0.0017
82 to 1.1 s^{-1} [21]; while the time scales for the free and bound analytes to diffuse through
83 DBLs are probably at second levels or even subsecond levels. Then, the incompletely
84 labile systems might also be common in real situations according to the Damköhler
85 Number [22]. To our knowledge, the availability of any incompletely labile
86 analyte-binding matrix complexes for passive sampling have not been studied yet. In

addition, the lability factor was introduced conceptually, not through rigorous mathematical derivation.

In the present study, the mathematical expression of the lability factor was deduced for the first time. Based on the upgraded interpretation of the lability factors, an effective average diffusion coefficient was used to establish a model to describe the enhanced mass transfer in DBLs. Thereafter, the lability of the polycyclic aromatic hydrocarbon (PAH)-micelle complexes in the DBLs adjacent to SPME fibers under different SDS concentrations and salinities were figured out according to the model. SDS micelles were selected as the binding matrix since SDS micelles are well known as spherical permeable nanoparticles, whose diameters and diffusion coefficients are constant in a certain concentration range and are tunable under different salinities [23,24]. The lability factors of PAHs clarified the availability of the bound PAHs for SPME.

2. Material and methods

2.1. Materials

Phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), and pyrene (PYR) were all purchased from Supelco Inc. (Bellefonte, PA, USA). Stainless steel wires (SSWs, 127 μm in diameter, medical grade) were purchased from Small Parts Inc. (Miami Lakes, FL, USA). Sylgard 184 silicone elastomer base was purchased from Dow Corning Co. (Midland, MI, USA). Polydimethylsiloxane (PDMS) tubing (i.d. 212 μm , o.d. 300 μm) was purchased from Helixmark (Carpinteria, CA, USA).

Sodium dodecylsulphate (SDS) was purchased from Tianjin Fuchen Chemical Reagents Factory (Tianjin, China). Sodium chloride was purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). Epoxy glue was purchased from Henkel Canada Corporation (Mississauga, ON, Canada).

2.2. Preparation of SPME fiber

Custom-made PDMS fibers were prepared as described in ref. [25] without further modification. Briefly, SSWs were cut into pieces of about 3 cm, and cleaned by sonication in acetone and deionized water for 15 min respectively. Before the well-cut PDMS tubing (1.0 cm) were wore on the SSWs, the SSWs were dried in the air at room temperature, and coated with a thin layer of epoxy glue for about 1 cm at one end. The freshly prepared fibers were kept at room temperature for 24 h till the glue was solidified completely. Prior to use, the prepared PDMS fibers were conditioned in nitrogen flow at 250 °C for 15 min.

2.3. Headspace loading of PAHs on SPME fibers and subsequent desorption in pure water or SDS solutions

A Gerstel multipurpose sampler system (Mülheim an der Ruhr, Germany) was used for automatic headspace loading, desorption in pure water or SDS solutions and injection in the gas chromatograph (GC) inlet (Fig. 1). The agitation speed and temperature of the incubator were 250 rpm and 30 °C during both headspace loading and desorption. The custom-made fiber was assembled to the automatic system as described in ref. [25]. Briefly, the custom-made fiber was mounted to a recycled commercial SPME fiber assembly after removing its extraction tip, then the recycled

SPME fiber assembly was assembled to the holder of the automatic system.

A pseudo solution for headspace loading was prepared by adding PAHs (PHE 30.0 mg, ANT 30.0 mg, FLA 60.0 mg, PYR 60.0 mg) in 5 grams of Sylgard 184 silicone elastomer base in a 20 mL sample vial. After the vial was capped and then sealed with Parafilm[®], the pseudo solution equilibrated in the incubator of the automatic system under 30 °C for 72 h prior to use. The duration of headspace loading was 15 min (Fig. 1A). Subsequently, the loaded fiber was desorbed in pure water, or in SDS solutions of different SDS concentrations and salinities, for certain durations (Fig. 1B). Pure water and SDS solutions also equilibrated in the incubator for 15 min at the same time the headspace loading was proceeding. Finally, the fiber was desorbed in the GC inlet (Fig. 1C). The partition coefficients between the PDMS fiber and pure water were determined after the desorption in pure water reached equilibrium.

2.4. Determination of the partition coefficients between the PDMS fiber and the SDS solutions

The partition coefficients between the PDMS fiber and the SDS solutions were determined by equilibrium sampling in serials of solutions at five different PAH concentrations. Since the time to reach equilibrium is the same for desorption and extraction in the same sample matrix [10,11,20], the extraction time was determined according to the desorption kinetics in the SDS solutions (in solutions containing 3 g·L⁻¹ and 5 g·L⁻¹ SDS, the extraction time was 60 min; in other SDS solutions, the extraction time was 30 min; more than 99% extraction equilibrium could be reached in all

the SDS solutions).

2.5. Instrumental analysis

Instrumental analysis was performed on an Agilent 6890N GC coupled to an Agilent 5975 mass spectrometer (Agilent Technologies, CA, USA). A HP-5 MS capillary column (30 m×0.25 mm×0.25 μm, Agilent Technologies, CA, USA) was used for separation. Ultra-pure helium was employed as the carrier gas. The inlet temperature was 250 °C, and the oven temperature program was as follows: the column temperature was initially kept at 60 °C for 0.5 min, ramped to 250 °C at a rate of 20 °C ·min⁻¹, and held for 2 min; then ramped to 280 °C at a rate of 20 °C·min⁻¹, held for 1.5 min. The total run time was 15.0 min. Ions selected for quantification were as follows: PHE *m/z* 178.0; ANT *m/z* 178.0; FLA *m/z* 202.0; PYR *m/z* 202.0.

3. Mass transfer model building

3.1. Mathematical expression of the lability factor

Considering the simplest situation, i.e. supposing a planar configuration of the passive sampler, the following mathematical derivation is based on a planar DBL. For a cylinder SPME fiber, if the thickness of the DBL is far smaller than the radius of the fiber, the DBL adjacent to the SPME fiber can be treated planar as well. Generally, the thickness of a DBL would be declined by increasing the flow rate of the water.

For a planar DBL, the continuity equations for the free and bound analytes in the aqueous phase are:

$$\frac{\partial C_f(x,t)}{\partial t} = D_f \frac{\partial^2 C_f(x,t)}{\partial x^2} - k_a C_{bm} C_f(x,t) + k_d C_b(x,t) \quad (1)$$

$$\frac{\partial C_b(x,t)}{\partial t} = D_b \frac{\partial^2 C_b(x,t)}{\partial x^2} + k_a C_{bm} C_f(x,t) - k_d C_b(x,t) \quad (2)$$

where $C_f(x,t)$ and $C_b(x,t)$ are the concentrations of the free analyte and the bound analyte in the aqueous phase at a distance of x away from the surface of the passive sampler at time t . D_f and D_b are the diffusion coefficients of the free analyte and the bound analyte. k_a and k_d are the kinetic coefficients of the analyte binding to and desorbing from the binding matrix. Defining C_{bm}^* , C_f^* , and C_b^* to be the concentrations of binding matrix, free analyte, and bound analyte in the bulk aqueous solution, and supposing concentration of binding matrix in the DBL C_{bm} is equal to C_{bm}^* , and also defining K as the association coefficient, then, we get $K = \frac{k_a}{k_d} = \frac{C_b^*}{C_f^* C_{bm}^*}$.

To solve eqs (1) and (2), a pseudo-steady state is assumed. Since compared to the time scales for the free and bound analytes to diffuse through the DBL (probably subsecond levels), the time to reach the passive sampling equilibrium is quite long (often dozens minutes to hours and even days), then, $\frac{\partial C_f(x,t)}{\partial t} = 0$ and $\frac{\partial C_b(x,t)}{\partial t} = 0$ are true for a time interval which is short compared to the equilibrium time while is long enough compared to the time for the bound and free analytes to diffuse through the DBL.

Based on the pseudo-steady state assumption, the ratio of the normalized concentration gradients of the bound analyte to that of the free analyte across the DBL can be expressed as:

$$\frac{1 - \frac{C_b(0,t)}{C_b^*}}{1 - \frac{C_f(0,t)}{C_f^*}} = \frac{\lambda - \tanh \lambda}{\lambda + \varepsilon K' \tanh \lambda} = \xi \quad (3)$$

where $\lambda = \sqrt{\frac{k_d \delta_0^2}{D_b} (\varepsilon K' + 1)}$, $K' = K C_{bm}^*$, $\varepsilon = \frac{D_b}{D_f}$, δ_0 is the thickness of the DBL.

According to eq. (3), ξ should be a constant dependent on the system. For the details

of solving eqs (1) and (2), refer to Text S1 in the Supplementary Data. Eq. (3) can also be written as:

$$C_{b,x=0} = (1 - \xi)C_b^* + \xi K' C_{f,x=0}, \quad \forall t > 0 \quad (4)$$

According to eq. (4), the bound analyte at the interface of the two phases ($x = 0$) can be subdivided into two fractions, of which $\xi K' C_{f,x=0}$ can be treated as the “fully labile” fraction as it is always in proportion to the free concentration at the same domain; on the contrary, $(1 - \xi)C_b^*$ remains unchanged at both sides of the DBL ($x = 0$ and $x = \delta_0$), thus this portion can be treated as the “inert” fraction that does not contribute to the mass transfer through the DBL. Both the free fraction and the “fully labile” fraction can be treated available for passive sampling. In addition, one can imagine, if the complex is fully inert, there is no concentration gradient through the DBL for the bound analyte, ξ should be zero. On the contrary, if the complex is fully labile, the normalized concentration gradient of bound analyte should be identical to that of the free analyte, that is, the ratio should be unity. Thus, ξ should be the so-called lability factor.

As shown in Fig. 2A, the bound analyte was divided into two fractions, i.e. the brown and the purple lines. The gradients in the DBL were shown in dashed lines.

3.2. A model of mass transfer through DBLs in the presence of mobile binding matrixes

According to eq. (3), the concentration gradient of the bound analyte through a DBL is $\xi K'$ times that of the free analyte. Thus, according to Fick’s first law, the mass flux through a DBL can be expressed as the combinatory diffusion of the bound

analyte and the free analyte:

$$\frac{dn}{dt} = AD_f \frac{C_f^* - C_{f,x=0}}{\delta_0} + AD_b \frac{\xi K' (C_f^* - C_{f,x=0})}{\delta_0} \quad (5)$$

where A is the interface area, $AD_f \frac{C_f^* - C_{f,x=0}}{\delta_0}$ represents the mass flux contributed by the free analyte, and $AD_b \frac{\xi K' (C_f^* - C_{f,x=0})}{\delta_0}$ represents the mass flux contributed by the bound analyte. Since the subdivided “inert” fraction of the bound analyte do not contribute to the mass transfer through the DBL, we define an effective average diffusion coefficient as the weighted average diffusion coefficient of the free analyte and the “labile” fraction of the bound analyte:

$$\overline{D_{eff}} = \frac{D_f f\% + D_b b_l\%}{f\% + b_l\%} = \frac{D_f f\% + D_b b_l\%}{1 - b_i\%} \quad (6)$$

where $f\%$, $b_l\%$ and $b_i\%$ are the percentages of the free analyte, the labile fraction and the inert fraction of the bound analyte, respectively. According to eq. (3), $b_l\% = \xi K' f\%$. Thus, eq. (6) can be written as:

$$\overline{D_{eff}} = \frac{D_f + \xi K' D_b}{1 + \xi K'} \quad (7)$$

This expression was also mentioned in ref. [15], while was not discussed in details.

Then, δ_0 can be calculated according to Levich [26],

$$\delta_0 = \left(\frac{D}{\nu}\right)^{1/3} \delta_c \quad (8)$$

where D , ν and δ_c are the diffusion coefficient, the medium kinematic viscosity, and the thickness of the convective boundary layer, respectively. Combine eq. (7) and eq. (8), and replace δ_0 in eq. (5), eq. (5) can be written as:

$$\frac{dn}{dt} = A \frac{D_f + \xi K' D_b}{\left(\frac{D_f + \xi K' D_b}{(1 + \xi K') \nu}\right)^{1/3} \delta_c} (C_f^* - C_{f,x=0}) \quad (9)$$

Compared with the situation where only the free analyte contributes to the mass transfer through the DBL, i.e. $b_l\% = 0$ or $\xi = 0$, the enhanced mass transfer ratio

can be calculated as follow:

$$R_e = \frac{(\frac{dn}{dt})_{\xi \neq 0}}{(\frac{dn}{dt})_{\xi = 0}} = (1 + \varepsilon \xi K')^{2/3} (1 + \xi K')^{1/3} \quad (10)$$

It should be noted that eq. (10) is applicable for both passive sampling and desorption of analytes from passive samplers. As discussed in Text S2 in the Supplementary Data, the time constants of extraction and desorption were proven the same.

In the previous studies [12,13], the overall weighted average diffusion coefficient was used to calculate the thickness of the DBL:

$$\bar{D} = D_f f\% + D_b b_l\% = \frac{D_f + \xi K' D_b}{1 + K'} \quad (11)$$

Then, the enhanced mass transfer ratio is:

$$R_e = (1 + \varepsilon \xi K')^{2/3} (1 + K')^{1/3} \quad (12)$$

Eq. (12) is equivalent to eq. (10) when $\xi = 1$, i.e. when the complex is fully labile. However, according to eq. (12), when $\xi = 0$, $R_e \neq 1$, which is inconsistent with the assumption that there is no mass transfer enhancement when $\xi = 0$ [15]. On the contrary, eq. (10) could fulfil the assumption. Therefore, eq. (10) could be more suitable for describing the mass transfer through DBLs in the presence of binding matrixes.

Then, according to the present model, the ratio of $\bar{D}_{eff}$ to D_f , the ratio of the thickness of the DBL in the presence of binding matrix δ_0 to that in the absence of binding matrix δ_f , and the enhanced mass transfer ratio are plotted to the lability factor in Fig. 2B.

4. Results and discussion

4.1. Binding of PAHs to SDS micelles

In this study, The partition coefficients between the PDMS fiber and the solutions, K_{fs} were determined as described in the Experimental section. As shown in Table 1, the binding of PAHs to SDS micelles decreased the partition coefficients between the PDMS fiber and the solutions. When SDS micelles presented in the solutions (all above the critical micelle concentration of SDS), the K_{fs} values were dramatically reduced. The percentages of the free PAHs in SDS solutions were calculated according to $f\% = \frac{K_{fs}(SDS\ solution)}{K_{fs}(pure\ water)}$ (Fig. 3). It was shown that the percentages of free PAHs decreased when SDS concentration increased, and the salinity nearly had no influence on the binding of PAHs to SDS micelles. Also, more PAHs were bound when the hydrophobicity increased (the logarithms of octanol-water partition coefficients of PHE, ANT, FLA and PYR are 4.46, 4.54, 5.2 and 5.3, respectively [27]). Then, K' could be calculated according to $K' = \frac{b\%}{f\%} = \frac{1-f\%}{f\%}$, where $b\%$ is the percentage of the bound PAH (Table S1). Also, it could easily obtained $K' = \frac{K_{fs}(SDS\ solution)}{K_{fs}(pure\ water)} - 1$.

4.2. Desorption kinetics of PAHs from PDMS fibers in SDS Solutions

To investigate the influence of SDS micelles on the mass transfer of PAHs through DBLs, the desorption kinetics of PAHs from the PDMS fiber was recorded. Since the time constants of desorption and extraction are the same (Text S2), the influence of SDS micelles on the desorption kinetics should be the same to the sampling kinetics [10,11]. Fig. 4 showed the desorption time profiles of PHE in pure water and different SDS solutions, where “Residue” meant the fraction remained in

the fiber coating after a certain desorption duration. It was shown that the desorption kinetics increased with increasing SDS concentration (Fig. 4A). And the desorption kinetics was faster for SDS solution containing 0.3 M NaCl than those containing 0 M NaCl and 0.6 M NaCl (Fig. 4B). The desorption time profiles of the other three PAHs were shown in Fig. S1. The desorption kinetics of the other PAHs was also influenced by SDS concentration and salinity in the similar modes to PHE (Fig. S1). Then, from the desorption profiles, the desorption kinetic coefficients, k_{fd} were figured out according to eq. (13):

$$Residue = a + be^{-\frac{k_{fd}}{b}t} \quad (13)$$

where $a = \frac{K_{fs}V_f}{K_{fs}V_f + V_s}$, $b = \frac{V_s}{K_{fs}V_f + V_s}$, V_f and V_s were the volumes of the fiber coating and the solution, respectively. For the details of the derivation of eq. (13), refer to Text S2 in the Supplementary Data. The kinetic coefficients were presented in Table 1.

The enhanced ratios of the desorption kinetics in SDS solutions compared to those in pure water were shown in Fig. S2. It was shown that the desorption kinetics was more significantly enhanced when the PAHs were more hydrophobic, which was similar to the result of the previous study [16].

It is notable that the satisfactory intrafiber reproducibility (Table S2) demonstrated that repeated desorption in SDS solutions didn't distort the desorption kinetics from the PDMS fibers, which probably indicated the adsorbing of SDS molecules onto the fiber were ignorable.

4.3. Lability factors of PAHs-micelle complexes in DBLs

It should be noted that eq. (10) is only valid for calculating the lability factors in

planar DBLs (see the deduction process above). For the cylindrical geometry of the PDMS fiber, the thickness of DBL adjacent to its surface should be corrected [15]. However, from the desorption kinetic coefficients in Table 1, it could be estimated that the thicknesses of the DBLs were all less than ten micrometers, which were far smaller than the radius of the PDMS fiber (less than one tenth of the fiber radius). Thus, the DBLs around the PDMS fibers were treated planar.

The diffusion coefficients of PAH molecules and SDS micelles were obtained according to the empirical equations or by referring to the literature (Table 2) [22-24]. With the calculated K' values (Table S2), the diffusion coefficients (Table 2) and the enhanced ratios of the desorption kinetics (Fig. S2), the lability factors of the PAH-SDS micelle complexes could be figured out according to eq. (10) (Fig. 5). It was observed the lability factors generally decreased with increasing SDS concentrations (Fig. 5A), even though the lability factors of PAHs in solution containing 5 g·L⁻¹ SDS were close to those in solution containing 10 g·L⁻¹ SDS (Fig. 5A). In addition, the lability factor of each PAH generally increased with increasing the salinities of the solutions (Fig. 5B). In other words, the lability factor of each PAH decreased with increasing K' and increasing ε . From the availability perspective, when larger fractions were bound with increasing SDS concentration, the availability of the bound PAHs decreased; and when the size of the binding matrixes turned larger with increasing salinity, the availability of the bound PAHs increased.

It was plausible that the dwelling time of the PAH-SDS micelle complexes in the DBLs might decrease with increasing binding ratios or decreasing micelle sizes, since

increasing binding ratios might decrease the thicknesses of DBLs according to eqs (7) and (8), and smaller micelles diffuse faster in DBLs. According to eq. (3), the phenomenon that the lability factor decreased with increasing K' and ε might be a common situation for other incompletely labile systems, since K' and ε appeared with the highest power in the denominator on the right side of eq. (3). A more rigorous mathematical explanation based on eq. (3) was also provided in Text S3 in the Supplementary Data. In addition, by replacing eq. (S24) in eq. (10), it could be concluded that the enhanced mass transfer ratio would increase with increasing K' , or in other words, the enhanced mass transfer ratio would increase with decreasing K_{fs} , which is consistent with the results shown in Table 1.

4.4. Validation of the lability factors

To validate the lability factors derived above are accurate for describing the mass transfer through the DBLs surrounding the PDMS fibers, three sets of calculated residues of PAHs on the PDMS fiber were compared with the detected ones after desorption in SDS solutions for 15 min. The calculations were carried out according to eq. (14),

$$Residue = a + be^{-\frac{(1+\varepsilon\xi K')^{\frac{2}{3}}(1+\xi K')^{\frac{1}{3}}k_{fd}(SDS=0)}{b}}t \quad (14)$$

which was derived from combining eq. (10) and eq. (13). $k_{fd}(SDS = 0)$ is the desorption kinetics coefficient in pure water. As shown in Table 3, if assuming the bound PAHs were completely inert in the DBLs, i.e. the bound PAHs were not available to the mass transfer across the DBLs ($\xi = 0$), the calculated residues were significantly larger than the detected ones. In other words, the mass transfer

efficiencies across the DBLs were underestimated without considering the availability of the bound PAHs for the mass transfer. On the other hand, if simply assuming the bound PAHs were completely labile ($\xi = 1$), the mass transfer efficiencies were overestimated. In contrast, by using the lability factors derived above, the mass transfer efficiencies were well consistent to the experimental results.

5. Conclusions

Lability factor is a very important parameter for measuring the availability of the bound analyte for the mass transfer through DBLs adjacent to passive samplers. In this study, we promoted the understanding of the availability of bound analyte by (a) presenting the mathematical expression of the lability factor; (b) using the effective average diffusion coefficient to make the mass transfer model consistent to the extreme assumption about the completely inert complexes; and (c) for the first time estimating the lability factors of bound PAHs with SDS micelles as the binding matrix, and clarifying the availability of bound PAHs for the mass transfer across the DBLs adjacent to the SPME fiber.

The principles underlying this work could be possibly extrapolated to the systems containing more than one mobile binding matrix, to evaluate the overall availability of the bound analytes for mass transfer through the DBLs.

Acknowledgements

We acknowledge financial support from the projects of NNSFC (21225731,

21377172, 21477166), the NSF of Guangdong Province (S2013030013474).

Appendix A. Supplementary data

Procedure of solving eq. (1) and eq. (2), derivation of eq. (13), deviation from simplifying eq. (3), mathematical explanation of Fig. 5, reproducibility of desorption in SDS solutions, values of K' , $\xi K'$, $\varepsilon \xi K'$, $\varepsilon K'$ and λ , desorption profiles of ANT, FLA and PYR in SDS solutions, and enhanced ratios of the desorption kinetics of the PAHs are available in the supplementary data.

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Figure Captions

Figure 1. The experimental procedures based on the automatic sampler. Headspace loading of PAHs (A), desorption of PAHs in pure water or SDS solutions (B), and thermal desorption of the residual PAHs in GC inlet (C).

Figure 2. The conceptual scheme of the mass transfer through DBLs from aqueous phase to passive sampler (A), plots of $\frac{\delta_0}{\delta_f}$, $\frac{\overline{D_{eff}}}{D_f}$ and R_e to the lability factor, where setting $\varepsilon = 0.1$ and $K' = 100$ (B).

Figure 3. The percentages of the free PAHs in different SDS solutions. Error bars represent the standard errors.

Figure 4. The desorption profiles of PHE from the PDMS fiber in the solutions containing different SDS concentrations (A) and different salinities (B). Error bars represent the standard errors.

Figure 5. The lability of the bound PAHs in DBLs under different SDS concentrations (A) and different salinities (B). Error bars represent the standard errors.

449 **Figure 1.**

450

451

Figure 2.

(A)

(B)

Figure 3.

Figure 4.

(A)

(B)

Figure 5.

(A)

(B)

Table 1. The partition coefficients of PAHs between the PDMS fiber and SDS solutions, K_{fs} (Mean $\pm$ SE), and the desorption kinetic coefficients k_{fd} (Mean $\pm$ SE, min⁻¹) of PAHs from PDMS fiber.

		0 g·L ⁻¹		3 g·L ⁻¹		5 g·L ⁻¹		10 g·L ⁻¹		10 g·L ⁻¹ (0.3 M NaCl)		10 g·L ⁻¹ (0.6 M NaCl)	
log K_{ow} ^a		K_{fs}	k_{fd}	K_{fs}	k_{fd}	K_{fs}	k_{fd}	K_{fs}	k_{fd}	K_{fs}	k_{fd}	K_{fs}	k_{fd}
PHE	4.46	11170 $\pm$	0.0223 $\pm$		0.1016 $\pm$		0.1365 $\pm$		0.4200 $\pm$		0.5483 $\pm$		0.4203 $\pm$
		356	0.0011	853 $\pm$ 42	0.0029	370 $\pm$ 15	0.0134	106 $\pm$ 12	0.0134	83 $\pm$ 2	0.0208	80 $\pm$ 5	0.0280
ANT	4.54	14250 $\pm$	0.0207 $\pm$		0.0997 $\pm$		0.1306 $\pm$		0.3973 $\pm$		0.4295 $\pm$		0.3918 $\pm$
		496	0.0014	631 $\pm$ 28	0.0040	298 $\pm$ 7	0.0091	94 $\pm$ 10	0.0091	69 $\pm$ 2	0.0184	72 $\pm$ 4	0.0249
FLA	5.20	35922 $\pm$	0.0068 $\pm$		0.1177 $\pm$		0.1225 $\pm$		0.4502 $\pm$		0.5640 $\pm$		0.3033 $\pm$
		1394	0.0007	575 $\pm$ 27	0.0047	240 $\pm$ 11	0.0269	53 $\pm$ 4	0.0269	52 $\pm$ 1	0.0293	50 $\pm$ 4	0.0176
PYR	5.30	42957 $\pm$	0.0077 $\pm$		0.1123 $\pm$		0.1315 $\pm$		0.4609 $\pm$		0.4712 $\pm$		0.2949 $\pm$
		2761	0.0011	633 $\pm$ 33	0.0037	265 $\pm$ 7	0.0233	67 $\pm$ 4	0.0233	55 $\pm$ 4	0.0279	46 $\pm$ 3	0.0183

Note: ^a referred to ref. [27].

Table 2. The diffusion coefficients ($\times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$) of PAH molecules D_f and SDS micelles D_b .

	D_f^a	D_b		
		3/5/10 g·L ⁻¹	10 g·L ⁻¹ (0.3 M NaCl)	10 g·L ⁻¹ (0.6 M NaCl)
PHE	6.92			
ANT	6.92			
FLA	6.33	1.59 ^b	0.99 ^c	0.29 ^c
PYR	6.33			

Note: ^a calculated from the empirical equation $D_{iw} = \frac{2.7 \times 10^{-8}}{M_i^{0.71}} (\text{m}^2 \cdot \text{s}^{-1})$, for 25 °C, M_i was the relative molecular weight of each PAH), and corrected with temperature based on the Stokes-Einstein relation;²² ^b calculated based on the Stokes-Einstein relation $D_{iw} = \frac{BT}{6\pi\eta r_i}$, where B is the Boltzmann constant ($1.381 \times 10^{-23} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \cdot \text{K}^{-1}$),²³ η is the dynamic viscosity ($0.797 \times 10^{-3} \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$),²² r_i is the micelle radius at 30 °C (1.75 nm).²⁴ ^c referred to ref. [24].

487 **Table 3.** The calculated and detected residues of the PAHs on the PDMS fiber after desorption in SDS solutions for 15 min. “Inert” represents
 488 the residues calculated without considering the contribution of the bound PAHs to the mass transfer through DBLs, “labile” represents the
 489 residues calculated by assuming the bound PAHs were fully labile in DBLs, “Cal” represents the residues calculated with the lability factors
 490 derived in this study, and “Exp” represents the experimental data.

	3 g·L ⁻¹				5 g·L ⁻¹			
	Inert	Labile	Cal	Exp (n=3)	Inert	Labile	Cal	Exp (n=3)
PHE	71.5%	14.6%	21.8%	27.5 ± 1.0%	71.5%	3.2%	13.9%	13.3 ± 0.4%
ANT	73.3%	5.5%	23.6%	27.2 ± 0.3%	73.3%	1.6%	14.9%	15.1 ± 0.3%
FLA	90.3%	7.3%	18.4%	29.5 ± 0.9%	90.3%	1.2%	16.5%	17.9 ± 0.6%
PYR	89.1%	12.1%	19.9%	24.6 ± 0.6%	89.1%	1.2%	14.6%	16.6 ± 0.5%

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Graphic abstract

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