An exponential model based new approach for correcting aqueous concentrations of hydrophobic organic chemicals measured by polyethylene passive samplers

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HIGHLIGHTS

- A new exponential model of non-equilibrium correction for HOCs.
- Linkage of two exposure scenarios based on convection mass transfer principle.
- Established relationships between rate constants or log K_{PEW} and log K_{ow}.
- Incorporating hydrodynamics for optimization of PE sampler configuration.
- The proposed method was validated showing close agreement with alternative method.

GRAPHICAL ABSTRACT
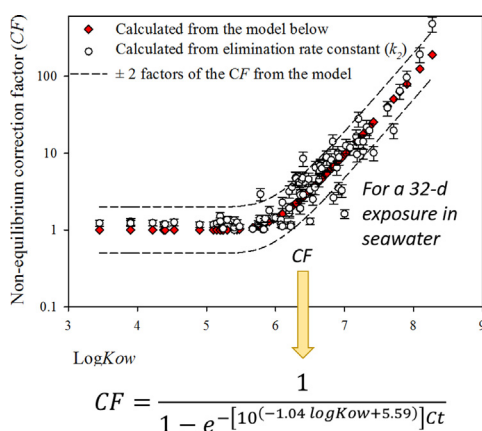
$$CF = \frac{1}{1 - e^{-\left[10^{(-1.04\, logKow + 5.59)}\right]Ct}}$$

ABSTRACT

Although low density polyethylene (PE) passive samplers show promise for the measurement of aqueous phase hydrophobic organic chemicals (HOCs), the lack of a practical and unsophisticated approach to account for non-equilibrium exposure conditions has impeded widespread acceptance and thus application *in situ*. The goal of this study was to develop a streamlined approach based on an exponential model and a convection mass transfer principle for correcting aqueous concentrations for HOCs deduced by PE samplers under non-equilibrium conditions. First, uptake rate constants (k_1), elimination rate constants (k_2), and seawater-PE equilibrium partition coefficients (K_{PEW}s) were determined in laboratory experiments for a diverse suite of HOCs with logK_{ow} range of 3.4–8.3. Linear relationships between log k_2 and logK_{ow}, and between log K_{PEW} and logK_{ow} were established. Second, PE samplers pre-loaded with ^{13}C-labeled performance reference compounds (PRCs) were deployed in the ocean to determine their k_2 *in situ*. By applying boundary layer and convection mass transfer theories, ratio (C) of k_2 values in field and laboratory exposures was estimated. This C value was demonstrated a constant that was only determined by water velocities and widths of PE strips. A generic equation with C and logK_{ow} as parameters was eventually established for extrapolation of non-equilibrium correction factors for the water boundary layer-controlled HOCs. Characterizing the hydrodynamic conditions indicated the sampler configuration and mooring mode should aim at sustaining laminar flow on the PE surface for optimal mass transfer. The PE estimates corrected using this novel approach possessed high accuracy and acceptable precision, and can be suited for a broad spectrum of HOCs. The presented method should facilitate routine utilization of the PE samplers.

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1. Introduction

Low density polyethylene (PE) films have been used to concentrate hydrophobic organic compounds (HOCs) from the aqueous phase (Adams et al., 2007; Booij et al., 1998; Lohmann et al., 2017). The simplest method to estimate freely dissolved HOC concentration (C_{free}) is to allow the polymer and aqueous phases to reach equilibrium, and apply the chemical-specific PE-water partition coefficient (K_{PEW}) to deduce C_{free}. For highly hydrophobic chemicals, however, the extended time needed to achieve equilibrium can be prohibitively lengthy, and thus not practical. Under non-equilibrium conditions, kinetic parameters, such as uptake rate constant (k_1), elimination rate constant (k_2), or sampling rate (R_s), are needed (Booij et al., 2002). Despite the expanding use of passive samplers, standardization and/or widespread acceptance of chemical-specific values for these calibration parameters is limited, and for many HOCs, non-existent (Perron et al., 2013). For example, only K_{PEW} values were able to be measured with cosolvent methods for 41 polychlorinated biphenyls (PCBs), and 26 polyaromatic hydrocarbons (PAHs) (Smedes et al., 2009).

Performance reference compounds (PRCs) preloaded into polymer sorbents, such as PE, have been used to determine the extent of equilibrium achieved, and subsequently to correct aqueous concentrations that would otherwise be underestimated assuming full achievement of equilibrium (Tomaszewski and Luthy, 2008). As it is not feasible to employ a large suite of PRCs, several correction methods utilizing a relatively small subset of PRCs have been introduced. These methods have been based on 1) physicochemical property correlations (e.g. molecular weight, molecular volume or aqueous diffusivity) between PRCs and target HOCs (Booij et al., 2003b; Tomaszewski and Luthy, 2008); 2) the adjustment of exposure by comparing PRC desorption rates measured in the lab vs. in the field (Huckins et al., 2002); 3) quantitative structure–activity relationships (QSARs), e.g. relating extent of equilibrium to the octanol-water partition coefficient (K_{ow}) as a proxy (Booij and Smedes, 2010; Huckins et al., 2006); 4) dissolution rates of a reference material (e.g. gypsum) in a co-deployed flow monitor to estimate water velocity, which in turn is correlated to R_s (O'Brien et al., 2012; O'Brien et al., 2011; O'Brien et al., 2009); and 5) the Fickian diffusion model, which requires to estimate multiple parameters and uses numerical inverse Laplace transform in Matlab (Fernandez et al., 2009a; Fernandez et al., 2012; Fernandez et al., 2009b; Tcaciuc et al., 2015; Thompson et al., 2015). With the exception of diffusion model, the above methods are largely empirical, lacking a substantial theoretical link to the equilibrium, hydrodynamic, and mass transfer principles that are relevant to the uptake and desorption of HOCs, and their PRC surrogates, under field conditions (Booij et al., 2017a).

The most widely used model to describe the kinetics of passive sampling for HOCs is an exponential model as

$$C_{free}(t) = \frac{1}{(1 - e^{-k_2 t})} \times \frac{C_{PE}}{K_{PEW}} \qquad (1)$$

where C_{PE} is the HOC concentration (ng/L) in PE (with K_{pew} units of L/L) and t (d) is exposure time. Herein, we define the non-equilibrium sampling correction factor (CF) as

$$CF = 1 / \left(1 - e^{-k_2 t}\right) \qquad (2)$$

When equilibrium between the passive sampler and water is approached, $CF \to 1$; when it reaches 10% equilibrium (i.e. 90% PRC retained in the PE), $CF = 10$. The PRC desorption rate ($k_2^{f\_PRC}$) in the field is estimated as:

$$k_2^{f\_PRC} = \frac{1}{t} \ln \frac{C_{PRC}^0}{C_{PRC}} \qquad (3)$$

where C_{PRC}^0 is the pre-loaded PRC concentration in the PE sampler at time

zero, and C_{PRC} is the PRC concentration remaining in the PE sampler at time t. Encouragingly, the Fickian diffusion model has demonstrated that this exponential model is suitable for description of the time-dependence profile for water boundary layer-controlled chemicals that are mostly HOCs (Tcaciuc et al., 2015; Thompson et al., 2015). Therefore, application of the exponential model is not only very straightforward but also compliant with the appropriate mechanism.

As a passive sampler is deployed in flowing fluid, e.g. in stirring bath or natural waters, mass transfer is governed by convection that includes both diffusion and advection (Bergman et al., 2011). In the case of laminar flow over a flat plate (e.g. herein the PE film), besides a velocity boundary layer, there are chemical-specific concentration layers developed at the plate-water interface (we neglect temperature boundary layer in this study). The velocity boundary layer is usually thicker than the concentration layers. Hydrodynamic conditions, including flow velocity, significantly control thicknesses of these boundary layers, and further determine mass transfer efficiency, especially for water boundary layer-controlled chemicals (Pintado-Herrera et al., 2016; Stephens et al., 2005). PRCs may not be suitable for some sensitive situations. For example, release of PRCs might be unacceptable in certain systems for water purification and distribution, and in application of passive dosing for some toxicity tests. It is desired to have an approach only employing hydrodynamic parameter without addition of any chemicals for non-equilibrium correction.

In the present study, we investigated a novel approach based on the exponential model and convection mass transfer principle to simplify correction of C_{free} determined by PE passive samplers under non-equilibrium conditions. We first determined values of k_1, k_2 and K_{PEW} ($= k_1 / k_2$) in laboratory calibration experiments and evaluated correlative relationships with widely available chemical parameters (e.g., K_{ow}) for a large suite of HOCs. We then explored the relationships among kinetic parameters under laboratory and field conditions by measuring desorption rate constants (k_2) in situ for selected PRCs. Next, we linked the parameters estimated from laboratory and field measurements to generate a generic non-equilibrium correction equation for water boundary layer-controlled chemicals. We also characterized the hydrodynamic conditions to elucidate convection mass transfer principle in the PE sampling so that we could provide guidance to optimally utilize the PE sampler. Lastly, we evaluated performance of this approach.

2. Theory

For a PE passive sampler deployed in water with the film surface parallel to the prevailing current at velocity U (m/s) (see Fig. 1 for a schematic representation), symmetrical velocity boundary layers develop on either surface of the film (Pijush K. Kundu et al., 2012). In the laminar region, thickness (δ_w, μm) of velocity boundary layer can be estimated as:

$$\delta_w \approx 4.91 \sqrt{\frac{\nu L}{U}} = 4.91 L \ Re^{-\frac{1}{2}} \qquad (4)$$

where ν (m²/s) is the kinematic viscosity of the fluid, L (m) is the downstream distance from the starting point of the boundary layer (i.e. width of the PE strip in the direction of flow), and Re is the Reynolds number ($Re = UL / \nu$). A hypothetical layer of zero-velocity fluid that has the same velocity deficit as the actual boundary layer is known as the displacement thickness δ_w^d ($= 0.35 \ \delta_w$). Convective mass transfer at the PE-water interface develops a compound-specific concentration boundary layer, in which a concentration gradient extends from the PE surface into the water stream. Within the polymer film matrix, mass transfer occurs by molecular diffusion from the PE-water interface to internal layers of the PE film. The concentration boundary layer thickness (δ_c, μm) is:

$$\delta_c \approx \delta_w Sc^{-\frac{1}{3}} = 4.91 L \ Re^{-\frac{1}{2}} Sc^{-\frac{1}{3}} \qquad (5)$$