

# Modelling and field application of the Chemcatcher passive sampler calibration data for the monitoring of hydrophobic organic pollutants in water

Branislav Vrana <sup>a,\*</sup>, Graham A. Mills <sup>b</sup>, Michiel Kotterman <sup>c</sup>, Pim Leonards <sup>c</sup>,  
Kees Booij <sup>d</sup>, Richard Greenwood <sup>a</sup>

<sup>a</sup> School of Biological Sciences, University of Portsmouth, King Henry Building, King Henry I Street, Portsmouth PO1 2DY, United Kingdom

<sup>b</sup> School of Pharmacy and Biomedical Sciences, University of Portsmouth, St Michael's Building,  
White Swan Road, Portsmouth PO1 2DT, United Kingdom

<sup>c</sup> Netherlands Institute for Fisheries Research, P.O. Box 68, Haringkade 1, 1970 AB IJmuiden, The Netherlands

<sup>d</sup> Royal Netherlands Institute for Sea Research, P.O. Box 59, 1790 AB Texel, The Netherlands

Received 16 December 2005; received in revised form 28 March 2006; accepted 12 April 2006

*The exchange kinetics of hydrophobic organic pollutants between passive sampler and water were modelled to enable the measurement of time weighted average concentrations of pollutants. The applicability of the model was tested in a field study.*

## Abstract

Passive sampling of dissolved pollutants in water has been gaining acceptance for environmental monitoring. Previously, an integrative passive sampler consisting of a C<sub>18</sub> Empore<sup>®</sup> disk receiving phase saturated with *n*-octanol and fitted with low density polyethylene membrane, was developed and calibrated for the measurement of time weighted average (TWA) concentrations of hydrophobic pollutants in water. In this study, the exchange kinetics were modelled to obtain a better understanding of the mechanism of the accumulation process and to enable the measurement of TWA concentrations of hydrophobic pollutants in the field. An empirical relationship that enables the calculation of *in situ* sampling rates of chemicals using performance reference compounds was derived and its application was demonstrated in a field study in which TWA aqueous concentrations estimated from sampler data for target analytes were compared with TWA concentrations obtained from spot samples of water collected regularly during the sampler deployment period.

© 2006 Elsevier Ltd. All rights reserved.

**Keywords:** Chemcatcher; Hydrophobic organic pollutants; Passive sampling; Water monitoring

## 1. Introduction

Passive sampling of organic pollutants in water has been gaining acceptance for environmental monitoring. A range of passive sampling devices has been developed for monitoring organic pollutants in water. These include the lipid-filled

semi-permeable membrane device (SPMD; Huckins et al., 1993) and the membrane enclosed sorptive coating (MESCO; Vrana et al., 2001) for non-polar compounds and the polar organic chemical integrative sampler (POCIS; Alvarez et al., 2004) for polar compounds. The design and field performance of a wide range of passive samplers suitable for monitoring organic pollutants have recently been reviewed (Namiesnik et al., 2005; Stuer-Lauridsen, 2005; Vrana et al., 2005a).

We previously developed a passive sampling device (Chemcatcher) for the measurement of time weighted average (TWA) concentrations of pollutants in aquatic environments

\* Corresponding author. Present address: Water Research Institute, Nabr. arm. gen. L. Svobodu 7, 81249 Bratislava, Slovakia. Tel.: +421259343401.

E-mail address: [branovrana@googlemail.com](mailto:branovrana@googlemail.com) (B. Vrana).

(Kingston et al., 2000; Vrana et al., 2005b). The sampler is based on the diffusion of target compounds through a membrane and the subsequent accumulation of these pollutants in a sorbent-receiving phase. Accumulation rates and selectivity are regulated by the choice of both the membrane and a receiving phase material. One of the prototypes was designed for the sampling of non-polar organic compounds with log octanol/water partition coefficient (log  $K_{OW}$ ) values greater than three (Kingston et al., 2000). This system used a 47 mm C<sub>18</sub> Empore<sup>®</sup> disk as the receiving phase and a low density polyethylene (LDPE) membrane. The C<sub>18</sub> Empore<sup>®</sup> disk has a high affinity and capacity for the sampled pollutants.

Despite the wide application of passive samplers, calibration data that relate absorbed amounts of chemicals to their aqueous concentrations are rare. As a result, field measurements using passive samplers are primarily reported in terms of absorbed amounts of chemicals, and only occasionally are the absorbed amounts translated into actual aqueous concentrations. To enable measurement of TWA water concentrations of non-polar organic pollutants, we calibrated the Chemcatcher sampler in a flow-through tank under controlled conditions. The calibration experiments were designed to characterize the effect of physicochemical properties (compound hydrophobicity), temperature and hydrodynamics on kinetic and thermodynamic parameters characterising the exchange of analytes between the sampler and water. The calibration data have been reported recently (Vrana et al., 2006).

In this study, the exchange kinetics of analytes between the sampler and water was modelled to obtain further insight into the mechanism of the accumulation process and to enable the measurement of TWA concentrations of non-polar priority pollutants in the field. An empirical relationship that enables the calculation of *in situ* sampling rates of non-polar chemicals using performance reference compounds (PRCs) was derived. Its application was demonstrated in a field study in which sampler data were compared with spot samples of water, collected regularly during the sampler deployment.

### 1.1. Theory

The theory of steady-state mass transfer of an analyte from water to the Chemcatcher passive sampler has been described (Vrana et al., 2006). The amount of the chemical accumulated from water in the receiving phase of the sampler with constant analyte concentration can be described by the equation:

$$m_D = m_{D0} + (C_W K_{DW} V_D - m_{D0}) \left[ 1 - \exp\left(-\frac{k_o A}{K_{DW} V_D}\right) t \right] \quad (1)$$

where  $m_D$  [kg] is the mass of analyte in the receiving phase,  $m_{D0}$  [kg] is the analyte mass in the receiving phase at the start of exposure,  $C_W$  [kg m<sup>-3</sup>] represents the water concentration during the deployment period,  $K_{DW}$  is the receiving phase/water distribution coefficient,  $V_D$  [m<sup>3</sup>] is the volume of the receiving phase,  $k_o$  [m s<sup>-1</sup>] is the overall mass transfer coefficient,  $A$  [m<sup>2</sup>] is the membrane surface area, and  $t$  [s] equals time.

The overall mass transfer coefficient  $k_o$  is affected by the diffusion of analytes in the individual layers; i.e. aqueous boundary layer and LDPE membrane as well as by their partitioning into the membrane and receiving phase. The contribution of the receiving phase to the overall resistance is considered to be negligible (Vrana et al., 2005b). From theory (Scheuplein, 1968; Flynn and Yalkowsky, 1972), the overall mass transfer resistance to the uptake of a chemical is given by the sum of particular barrier resistances to mass transfer. The overall resistance ( $1/k_o$ ) is then given by:

$$\frac{1}{k_o} = \frac{1}{k_W} + \frac{1}{k_M K_{MW}} = \frac{\delta_W}{D_W} + \frac{\delta_M}{D_M K_{MW}} \quad (2)$$

where  $k_W$  and  $k_M$  are mass transfer coefficients in the aqueous boundary layer and the membrane, respectively. Eq. (2) shows that resistance to mass transfer increases with the increasing thickness of the barrier  $\delta$  and decreases in the diffusion and partition coefficients  $D$  and  $K$ , respectively.

The coefficient in the exponential function (Eq. (1)) is referred to as the overall exchange rate constant  $k_e$ .

$$k_e = \frac{k_o A}{K_{DW} V_D} \quad (3)$$

In the initial uptake phase, pollutant uptake is linear or integrative. For practical applications, Eq. (1) can be reduced and rewritten:

$$m_D = m_{D0} + C_W R_S t \quad (4)$$

where  $R_S$  [m<sup>3</sup> s<sup>-1</sup>] is the sampling rate of the device, and represents the equivalent water volume sampled per unit of time.

$$R_S = k_o A = k_e K_{DW} V_D \quad (5)$$

Adding chemical standards called PRCs to the receiving phase of the passive sampler prior to exposure has been suggested as a means to calibrate the exchange rates *in situ* (Booij et al., 1998; Huckins et al., 2002a). The use of PRCs can be justified providing that analyte uptake and offload kinetics are governed by the same mass transfer law, and obey first order exchange kinetics. When PRCs are used that are not present in water ( $C_W = 0$ ) and isotropic exchange kinetics applies, Eq. (1) reduces to:

$$m_D = m_{D0} \exp(-k_e t) \quad (6)$$

## 2. Materials and methods

### 2.1. Physicochemical properties of chemicals

Preferred or selected values of physicochemical properties, including octanol/water partition coefficients (log  $K_{OW}$ ) and aqueous solubilities ( $S$ ) were taken from Mackay et al. (1992a,b) and have been summarized previously (Vrana et al., 2006). Values of  $D_W$  were estimated using Hayduk and Laudie equation (Tucker and Nelken, 1982). The distribution coefficient between the receiving phase of the sampler and water log  $K_{DW}$  can be described by a linear empirical function of log  $K_{OW}$  (Vrana et al., 2006):

$$\log K_{DW} = 1.382 \log K_{OW} - 1.77 \quad (R = 0.97, s = 0.13, n = 31) \quad (7)$$

Download English Version:

<https://daneshyari.com/en/article/4427858>

Download Persian Version:

<https://daneshyari.com/article/4427858>

[Daneshyari.com](https://daneshyari.com)