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Effect of housing geometry on the performance of ChemcatcherTM passive sampler for the monitoring of hydrophobic organic pollutants in water

Short communication

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The effect of passive sampler geometry on accumulation kinetics of organic pollutants from water was evaluated.

Abstract

Passive sampling of pollutants in water has been gaining acceptance for environmental monitoring. Previously, an integrative passive sampler (the ChemcatcherTM) was developed and calibrated for the measurement of time weighted average concentrations of hydrophobic pollutants in water. Effects of physicochemical properties and environmental variables (water temperature and turbulence) on kinetic and thermodynamic parameters characterising the exchange of analytes between the sampler and water have been published. In this study, the effect of modification in sampler housing geometry on these calibration parameters was studied. The results obtained for polycyclic aromatic hydrocarbons show that reducing the depth of the cavity in the sampler body geometry increased the exchange kinetics by approximately twofold, whilst having no effect on the correlation when the sampler body geometry is modified.

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1. Introduction

Passive sampling devices are gaining acceptance as tools that can be used in monitoring programmes to measure concentrations of pollutants dissolved in water (Vrana et al., 2005a). One of these, the Chemcatcher[™] passive sampler, was developed to measure time weighted average (TWA) concentrations of a range pollutants (including non-polar organic, polar organic and metals) in aquatic environments (Kingston et al., 2000). The sampler is based on the diffusion of

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compounds through a membrane and their subsequent accumulation in a sorbent receiving phase. The prototype designed to sample non-polar organic compounds (log octanol/water partition coefficient (log K_{OW}) greater than four) has a C₁₈ Empore[®] disk saturated with *n*-octanol as the receiving phase and this is overlaid with a low density polyethylene (LDPE) membrane (Vrana et al., 2005b). The sampler has been calibrated for the measurement of TWA concentrations of hydrophobic pollutants in water (Vrana et al., 2006). In the calibration experiments the effect of physicochemical properties (e.g. compound hydrophobicity), water temperature and hydrodynamics on kinetic and thermodynamic parameters characterising the exchange of analytes between the sampler

and water were investigated. It was found that the rate of uptake of test analytes from water to the sampler receiving phase is related to the rate at which they offload to the water. This enables the use of off-loading rates of performance reference compounds (PRCs) preloaded on to the receiving phase to be used to adjust uptake rates for the effects of temperature and hydrodynamic conditions in the field. The calibration procedures and data have been reported (Vrana et al., 2006, 2007).

The rate of diffusion from the bulk water to the receiving phase is proportional to the surface area over which diffusion takes place and inversely proportional to the diffusion path length. Therefore, the physical dimensions of the sampler body will significantly affect the sampling rate for different analytes. The body of the ChemcatcherTM was optimised in terms of both materials of construction and geometry. PTFE was selected for the sampler body as it has a low sorption capacity for most environmental pollutants (Kingston et al., 2000; Vrana et al., 2005b, 2006, 2007). The housing was constructed to fit a 47 mm Empore[®] disk receiving phase, having an active sampling area of 17.5 cm².

Uptake kinetics of many hydrophobic analytes have been shown to be controlled by diffusion in the aqueous boundary layer at the surface of the LDPE membrane (Vrana et al., 2006). The resistance to mass transfer of the boundary layer depends on hydrodynamic conditions in the vicinity of the membrane, and these are significantly affected by the sampler geometry. The membrane and receiving phase of the first generation ChemcatcherTM (old design) were located inside a 20 mm deep depression in the front of the sampler body. This well effectively buffers the effect of fluctuating flow on sampler performance. It effectively reduces convective transport of analytes to the sampler membrane, thus reducing sampling rates (i.e. the rate at which the sampler accumulates chemicals). The depth of cavity in the Chemcatcher[™] body (new design) was reduced to 7 mm (Fig. 1) in order to increase sampling rates; this is particularly important for hydrophobic



Fig. 1. Views of the old (left) and the new (right) designs of the ChemcatcherTM sampler body.

chemicals that are present in only low dissolved concentrations in the aquatic environment.

The aim of this study was to compare the performance of the old and new designs in monitoring hydrophobic organic pollutants and to determine whether calibration data obtained with the old design could be used for the new design. The uptake kinetics of polycyclic aromatic hydrocarbons (PAHs) to and release kinetics of PRCs from the new design were measured in a flow-through system under conditions identical to those used by Vrana et al. (2006) with the old design.

2. Theory

Mass transfer of an analyte from water to the ChemcatcherTM sampler has been described (Vrana et al., 2006), and accumulation of a chemical in the receiving phase of the sampler from water can be described by:

$$m_{\rm D}(t) = m_{\rm D0} + (C_{\rm W}K_{\rm DW}V_{\rm D} - m_{\rm D0})[1 - \exp(-k_{\rm e}t)]$$
(1)

where $m_{\rm D}$ [kg] is the mass of analyte in the receiving phase, $m_{\rm D0}$ [kg] is the analyte mass in the receiving phase at the start of exposure, $C_{\rm W}$ [kg m⁻³] is the concentration in the water during the deployment period, $K_{\rm DW}$ is the receiving phase/ water distribution coefficient, $V_{\rm D}$ [m³] is the volume of the receiving phase, $k_{\rm e}$ [s⁻¹] is the exchange rate constant and t [s] equals time.

The initial uptake phase is approximately linear or integrative. Here the amount of a chemical in the receiving phase is directly proportional to the product of the concentration in the surrounding water (C_W) and the exposure time (t). Eq. (1) can be rewritten as:

$$m_{\rm D}(t) = m_{\rm D0} + C_{\rm W} R_{\rm S} t \tag{2}$$

where $R_{\rm S}$ is the substance specific sampling rate (L day⁻¹), which can be determined experimentally. When PRCs are used and exchange kinetics are isotropic, Eq. (1) reduces to a single parameter equation:

$$m_{\rm D}(t) = m_{\rm D0} \exp(-k_{\rm e} t) \tag{3}$$

where the amount of PRC added to the sampler (m_{D0}) is known.

Mass transfer is affected by the diffusion of analytes in the individual layers (i.e. aqueous boundary layer, diffusion limiting membrane and the receiving phase) and by their partitioning into the LDPE membrane and receiving phase. Compounds with log $K_{OW} > 4$ are accumulated in the ChemcatcherTM under aqueous boundary layer control (Vrana et al., 2006), and their uptake kinetics is therefore sensitive to changes in the boundary layer thickness, and this depends on hydrodynamic conditions at the sampling surface. For compounds with log $K_{OW} > 4$, the kinetic performance characteristics of the ChemcatcherTM are likely to be highly dependent on the geometry of the sampler body. The new design effectively decreases the thickness of the boundary layer and

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