Dealing with flow effects on the uptake of polar compounds by passive samplers

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Passive sampling of polar contaminants in aquatic environments is commonly undertaken using the Polar Organic Chemical Integrative Sampler (POCIS) or the Chemcatcher. Many studies have shown that the sampling rates (R_s) of contaminants increase with increasing water flow velocities (v), and could reach a maximum $R_{s(max)}$ at high v (several dm s^{-1} and beyond).[1, 2] *In situ* v are often within the range where flow effects on R_s can persist, and it has thus been concluded that the transfer of most contaminants is (at least partially) under water boundary layer (WBL) control both for the POCIS and Chemcatcher.[1]

Two methods have been proposed to account for the effects of v on R_s. The first method adapted the performance reference compounds (PRC) approach for the POCIS.[1] Although several studies indeed showed that higher R_s are associated with higher dissipation rates of some PRCs, this method has not proven to be fully quantitative.[1] The current application of this method for POCIS takes into account the overall mass transfer coefficient (MTC) of the PRC selected, including its transport within the sorbent, which i) is governed by various interaction types (e.g., π-π, dipole-dipole, H-bonding and ionic interactions) depending on the analyte considered, and ii) is often anisotropic. The second method uses passive flow monitors (PFMs) to measure time averaged *in situ* v from the mass loss rate of calcium sulfate casts. An empirical relationship between the PFM derived v and R_s is established in the laboratory, and is then applied for field exposed PFMs and passive samplers to obtain *in situ* R_s.[1]

A more thorough understanding of the effect of transport through the WBL on R_s of polar compounds can be obtained by considering that the overall resistance to mass transfer ($1/k_o$) equals the sum of the resistances for transport through the WBL, the membrane, and the sorbent:[3]

$$\frac{1}{k_o} = \frac{A}{R_s} = \frac{1}{k_w} + \frac{1}{K_{mw}k_m} + \frac{1}{K_{sw}k_s} \qquad (1)$$

When transport through the membrane is only via the pore space, eq 1 becomes:

$$\frac{1}{k_o} = \frac{\delta}{D_w} + \frac{d\theta^2}{\phi D_w} + \frac{1}{K_{sw}k_s} \qquad (2)$$

Where k_o is the overall MTC, k_w, k_m, k_s are the MTC for the WBL, the membrane, and the sorbent respectively, A is the exposure surface area of the device, and K_{mw}, K_{sw} are the sorption coefficients of the membrane and the sorbent. δ and d are WBL and membrane thicknesses, D_w is the contaminant diffusion coefficient in water, θ is the tortuosity, and ϕ is the membrane porosity.

During the last International Passive Sampling Workshop (Prague, September 2016), several options were identified to deal with flow effects on R_s: i) increasing the membrane resistance, ii) accepting and quantifying the larger uncertainties associated to low flow conditions, iii) establishing empirical relationships between R_s and v, iv) taking k_w explicitly into account during laboratory calibrations and in field exposures. These options are discussed below.

i) increasing the membrane resistance (second term in eq 1 and 2) reduces the relative importance of k_w, and shifts the occurrence of flow effect to a lower v. Thus, laboratory calibrations will be applicable for a wider range of flow conditions. This approach was chosen for the development of the diffusive gradient in thin films for organics which employs a 0.8 mm hydrogel membrane.[4] Considering a typical WBL thickness between 10 to 500 µm, $(1 < k_w < 50$ µm s$^{-1})$, 2 mm thick diffusion layers would decrease flow effects on R_s to less than 20% for all environments (eq 2, adopting θ and ϕ =1). Increasing the resistance to diffusion implies smaller R_s, which may or may not be problematic, depending on the analytical detection limits and the concentration of the analytes.

ii) accepting larger uncertainties at low flow conditions may be a relevant option when differences between R_s under quiescent and fully turbulent conditions are smaller than a chosen value. The available evidence shows that these differences amount to a factor of 2 or more for most compounds.[1] This implies that calibrations should be carried out over a range of v, to determine the smallest flow rate at which the R_s reduction is smaller than a given value. However, if such laborious calibrations are to be done, then flow-R_s relationships in the first place for field use may as well be established with little extra effort. Differences in R_s between quiescent and turbulent conditions have been used by Poulier et al. for determining confidence intervals for the application of POCIS for the regulatory monitoring of polar pesticides.[5]

iii) empirical relationships between R_s and v were used by Li et al.,[2]

$$R_s = cv^n \qquad (3)$$

Where c and n are laboratory-determined fitting parameters. Although this model gave an accurate description of analyte accumulation by POCIS at v between 3 and 37 cm s^{-1}, it cannot handle the nonzero R_s that are observed at zero flow, nor a limiting R_s value at infinite v.

iv) taking k_w explicitly into account. The co-deployment of two devices with different d can give an estimation of δ. Otherwise, the MTC of the WBL can be directly measured in the laboratory and *in situ*, using alabaster dissolution rates, or the dissipation rates of PRCs from nonpolar samplers.[3] Knowledge of k_w for the laboratory calibration studies allows quantifying the limiting sampling rate $R_{s(max)}$ at high v.

$$\frac{1}{R_{s(\max)}} = \frac{1}{AK_{mw}k_m} + \frac{1}{AK_{sw}k_s} \qquad (4)$$

By also measuring the *in situ* k_w, the in situ R_s can be obtained from

$$\frac{1}{R_{s(insitu)}} = \frac{1}{R_{s(\max)}} + \frac{1}{Ak_w} \qquad (5)$$

In brief, it needs to be recognized that monitoring organic chemicals using passive sampling relies on balancing considerations related to sensitivity (i.e., rapid uptake rates) and accuracy (i.e., compensating for flow effects on R_s) to provide a best estimate of time integrative concentrations of the chemicals of interest. In recognition of the effect of v on R_s we offer a series of approaches with the aim to decrease uncertainties. Arguably, none of the proposed techniques provides a universal solution for the wide range of applications nor is it likely that the development of novel passive samplers will overcome the issues discussed. Hence, we propose the application of at least one or ideally a combination of the approaches discussed above to improve confidence in results.

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