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Method to account for the effect of hydrodynamics on polar organic compound uptake by passive samplers

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Abstract

Mass transfer coefficients of the water boundary layer ($k_w$) were measured using alabaster dissolution kinetics in a diffusion cell that was operated at stirring rates between 90 and 600 min$^{-1}$, aiming to provide a more robust characterisation of the effect of hydrodynamics on the uptake of polar compounds by passive samplers, as compared with characterisations in terms of stirring rates and water flow velocities. The measured $k_w$ helped to quantitatively understand calcium sulphate transport through a poly(ethersulfone) membrane and two water boundary layers (at both sides of the membrane). Alabaster based $k_w$ were used to understand atrazine transport in the diffusion cell, allowing the conclusion that atrazine transport in the membrane is via the pore space, rather than via the polymer matrix. The merits of measuring alabaster dissolution rates for passive sampler calibration and application in the field is discussed. We propose that passive sampler calibrations be carried out under controlled $k_w$ conditions, rather than under controlled stirring rates or flow velocities. This would facilitate the interpretation of passive sampler calibration studies and the translation of laboratory based water sampling rates to flow conditions that apply in the field.
Key words: Analytical chemistry, Organic contaminants, Passive sampler, Calibration, Water boundary layer, Mass transfer

Running head: Accounting for hydrodynamics in passive sampling

INTRODUCTION

Passive samplers of polar organic chemicals are frequently used for monitoring concentration levels of these compounds in environmental waters. These samplers include the polar organic chemical integrative sampler (POCIS) [1], the polar version of the Chemcatcher [2], the cellulose/isooctane/dodecanol sampling device (CIDS) [3], and the diffusive gradients in thin films for organics (o-DGT) [4], among others. These devices typically consist of a sorption phase that is covered by a microporous membrane made of poly(ethersulfone) (PES) or poly(sulfone) for POCIS and Chemcatcher, cellulose for CIDS, or an overlay of agarose gel and PES for o-DGT. Commonly used sorption phases are granular poly(divinylbenzene-co-N-vinylpyrrolidone) or a mixture of sorbents (activated carbon - poly(styrene-co-divinylbenzene) - polystyrene) for POCIS, poly(styrene-co-divinylbenzene) for Chemcatchers, granular poly(divinylbenzene-co-N-vinylpyrrolidone) suspended in agarose gel for o-DGT, or a mixture of 1-dodecanol and 2,2,4-trimethylpentane for CIDS. Chemicals of interest diffuse from bulk water through the water boundary layer (WBL), into the membrane, and further into the sorption phase. Despite their apparent simplicity, our knowledge of mass transport towards and within these samplers is rather limited. Harman et al. [5] reviewed the calibration and use of POCIS and concluded that the effect of water flow velocity, temperature, pH, ionic strength, biofouling, and compound properties on the uptake rates by POCIS are poorly understood, and that mechanistic models are needed to increase our understanding of this sampler.
The common approach to calibrate the uptake kinetics of polar compounds by passive samplers is to expose the samplers to contaminated water and to monitor the depletion rate of the water [6,7] and/or the accumulation rate of the sampler [8–10]. Flow conditions are reported sometimes as average flow velocities \( U \) at some distance from the sampler surface [9,11–13], and sometimes as stirring rates of a magnetic or overhead stirring device [4,8]. In other studies, flow is qualitatively characterized as “turbulent” or “quiescent” [1,14]. Uptake rates of many polar chemicals are often found to be higher at higher flow rates, but it is difficult to apply this observation to field-exposed samplers, because stirring rates obtained in the laboratory and qualitative characteristics like “turbulent” versus “quiescent” cannot be easily linked to flow velocities in the field. In addition, these characterizations of water flow do not provide a sound basis for developing mechanistic models for passive sampler - water exchange. The options for the use of average flow velocities in passive sampler calibration studies are better, but some challenges exist. First, it is not always clear from the literature reports if \( U \) was calculated (e.g., from pumping rates and cross-sectional areas of the exposure system), or measured using a current meter. Second, uptake rates may also depend on the direction of the flow relative to the sampler surface and on the turbulence intensity, which may both be different in the field and in the laboratory.

Mass transport rates can be conveniently parameterised using mass transfer coefficients (MTCs), which are the proportionality constants \( k_i \) between the steady state flux \( j_i \) - amount per unit surface area per unit time) through a phase \( i \) and the concentration difference over this phase \( \Delta C_i \)

\[
j_i = k_i \cdot \Delta C_i
\]

(1)

Uptake of chemicals by passive samplers involves transport through the WBL, through the membrane, and into the sorption phase, where each transport step can be characterized by an MTC, if steady state conditions apply. Under the assumption that the MTCs are independent of time, and that local sorption equilibrium exists at the interfaces, the relative importance of mass transport through the WBL, the membrane and the sorption phase can be evaluated from [15–17]
\[
\frac{1}{k_o} = \frac{1}{k_w} + \frac{1}{k_m K_{mw}} + \frac{1}{k_s K_{sw}}
\]  
(2)

where \( K_{mw} \) is the membrane-water partition coefficient of the chemical of interest, \( K_{sw} \) is its sorbent-water partition coefficient, \( k_w, k_m, k_s \) are the MTCs of the WBL, the membrane and the sorption phase, and \( k_o \) is the overall MTC that relates the flux to the effective concentration difference between water and sorbent.

\[ j = k_o \left( C_w - \frac{C_s}{K_{sw}} \right) \]  
(3)

In passive sampling research it is common practice to express compound accumulation as an equivalent water sampling rate \((R_s)\), which is related to \( k_o \) by

\[ R_s = k_o A \]  
(4)

where \( A \) is the surface area of the sampler. Hence, \( k_o \) can be interpreted as a surface area normalised sampling rate, with units of \( \text{L dm}^{-2} \text{d}^{-1} \) or \( \text{µm s}^{-1} \), for example.

Equation 2 expresses that the overall transport resistance \((1/k_o)\) equals the sum of the transport resistances of the WBL, the membrane and the sorption phase. In studies on uptake rates by the diffusive gradients in thin films sampler (DGT) it was shown that plotting the overall transport resistance as a function of the membrane thickness allowed estimation of the WBL resistance [18–20], and below we demonstrate that manipulation of the WBL resistance allows to measure the membrane resistance, using a similar approach.

The use of MTCs is convenient, because they can often be experimentally determined and require no knowledge of transport mechanisms on the molecular level or the structure of the membrane. A limitation is that their use relies on the assumption that they are independent of time, which is not always the case at the initial stages of passive sampler exposures [21,22]. In addition, transport within the sorption compartment can be expected to be fairly complicated due to the existence of different pore space domains, nonlinear sorption isotherms, and the mixed occurrence of
absorption by the sorbent polymer and adsorption to the polymer surface [23]. Still, equation 2 may be a valuable tool to gain more insight into the mechanisms of solute transfer to passive samplers because it allows for separating the effects of transport through the WBL, the membrane, and the sorbent. For example, the product \( k_m K_{mw} \) can be experimentally determined in membrane permeation experiments (i.e., without a sorbent) by measuring \( k_o \) at known values of \( k_w \). The obtained value may in turn be used to evaluate the sorbent term \( (k_s K_{sw}) \) by studying the \( k_o \) of solute uptake by intact passive samplers as a function of \( k_w \). Equation 2 also provides a basis for comparing laboratory calibration studies for passive samplers, because it allows for separating the effects of flow, which are exposure specific, and the effects of sampler layout and compound properties. Knowledge of the value of \( k_w \) is therefore crucial in this respect.

A number of methods exist for estimating \( k_w \). Stephens et al. [24] adopted an equation for mass transfer to a flat plate under laminar flow

\[ k_w = \frac{0.664 D_w}{L} \left( \frac{\nu}{D_w} \right)^{1/3} \left( \frac{UL}{\nu} \right)^{1/2} \]  

(5)

where \( D_w \) is the diffusion coefficient in water, \( \nu \) is the kinematic viscosity of water, \( U \) is the flow velocity, and \( L \) is the length of the plate. Taking \( L \) to be the sampler diameter, these authors could predict the sampling rates of four polar compounds by C18 and sulfonated poly(styrene-co-divinylbenzene) extraction disks within a factor of 2, assuming that the uptake was fully WBL controlled. Adopting a length scale \( L = 10 \text{ cm} \), and \( D_w = 5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \), equation 5 predicts \( k_w \) values between 1 and 60 \( \mu \text{m s}^{-1} \), at flow velocities between 0.05 and 200 cm s\(^{-1}\). A similar range of \( k_w \) values (1 - 50 \( \mu \text{m s}^{-1} \)) was suggested by Lohmann [25]. Experimental values of \( k_w \) can be obtained by measuring the limiting current for some electrochemical reactions (e.g., reduction of hexacyanoferrate(III)) on an electrode surface [26–28], or by studying the dissolution kinetics of benzoic acid that is coated on the surface of interest [29–31].
The alabaster dissolution rate method is an alternative method for obtaining $k_w$ in the laboratory and in the field [32–34]. Alabaster is a natural deposit of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), which can be purchased from sculpture supply shops. The method relies on the assumption that the dissolution process is rate limited by transport through the WBL, rather than by solvation from the crystal lattice. The evolution of the mass loss ($\Delta m$) of a dissolving alabaster plate is then given by

$$\Delta m = V C_w^* \left[1 - \exp\left(-\frac{k_w A t}{V}\right)\right] \quad (6)$$

where $C_w^*$ is the alabaster solubility (mass per volume units), $V$ is the water volume, $t$ is time, and $A$ is the surface area of the plate. Rearranging equation 6 yields $k_w$ as a function of the observed mass loss

$$k_w = -\frac{V}{A t} \ln \left(1 - \frac{\Delta m}{V C_w^*}\right) \quad (7)$$

For $k_w$ measurements in the field (i.e., very large water volumes), equation 7 reduces to

$$V \rightarrow \infty : \quad k_w = \frac{\Delta m}{A t C_w^*} \quad (8)$$

since $\ln(1-x) \rightarrow -x$ when $x \rightarrow 0$. It should be noted that $C_w^*$ is the alabaster solubility in the exposure medium, i.e., background concentrations of calcium and sulphate should be taken into account [35].

For the present study we chose to assess the merits of alabaster dissolution rate measurements by also studying the mass transfer rates in a diffusion cell that consisted of two stirred compartments with equal volume ($V$), which were separated by a PES membrane with surface area $A$.

With identical hydrodynamic conditions at both sides of the membrane, $k_o$ is given by

$$\frac{1}{k_o} = \frac{2}{k_w} + \frac{1}{k_m K_{mw}} \quad (9)$$

The factor 2 in equation 9 emerges because in this system there is a WBL at both sides of the membrane.

Plotting $1/k_o$ as a function of $1/k_w$ (as determined from the alabaster dissolution method) then should yield a straight line with slope 2 and intercept $1/(k_m K_{mw})$. 
When the background concentrations in both compartments equal zero, the evolution of concentrations in the donor compartment \( (C_1) \) and the acceptor department \( (C_2) \) is given by

\[
\begin{align*}
C_1 &= \frac{C_0}{2} \left[ 1 + \exp \left( -\frac{2k_o At}{V} \right) \right] \\
C_2 &= \frac{C_0}{2} \left[ 1 - \exp \left( -\frac{2k_o At}{V} \right) \right]
\end{align*}
\]

(10)

(11)

where \( C_0 \) is the concentration in the donor compartment at \( t = 0 \). Estimates of \( k_o \) and \( C_0 \) can be obtained by curve fitting of equations 10 and 11 to all experimental \( C_1 \) and \( C_2 \) data. Alternatively, these parameters can be obtained for each individual sampling time by elimination:

\[
C_0 = C_1 + C_2
\]

(12)

\[
k_o = -\frac{V}{2At} \ln \left( \frac{C_1 - C_2}{C_1 + C_2} \right)
\]

(13)

The purpose of the present work was to assess the performance of the alabaster dissolution rate method for calibrating the hydrodynamics of calibration setups for passive samplers of polar chemicals. This method was chosen because it can also be applied for passive sampler exposures in the environment. Membrane permeation experiments were carried out to check consistency with the alabaster dissolution measurements.

**METHODS**

**Diffusion cell**

The diffusion cell was made of 6 mm thick polyacrylate, and consisted of two 1-L compartments that were separated by an impermeable wall with a 5 cm wide opening, in which a membrane or an alabaster plate could be mounted (Supplemental Data, S1). The diameter of the exposed alabaster and membrane surface was 4.0 cm. Both cells were stirred with an overhead stirrer (IKA RW20) with speed detector and regulator. The 4-blade (2.5 × 1.0 cm) stirring shaft was positioned 5 mm above the bottom.
The effect of stirrer height on the $k_0$ of sodium chloride at 400 min$^{-1}$ was found to be insignificant (CV=3% for six stirrer heights in the range 3-20 mm above the bottom). The diffusion cell was placed in a temperature controlled water bath. Experiments were carried out at a temperature of $21.0 \pm 1.5$ °C.

Poly(ethersulfone) membranes (PAL Life sciences, Supor-200, 47 mm diameter, 145 µm nominal thickness, 0.2 µm nominal pore size) were conditioned overnight in demineralised water before use.

**Chemicals**

KCl (Sigma-Aldrich, ACS reagent) was pre-combusted 16 h at 500 °C. NaCl (BDH, AnalaR NORMAPUR) and CaSO$_4$·2H$_2$O (Merck, MSURE) were used as received. White, translucent, alabaster was purchased from a local sculpture supplies shop, and was shaped into 1 cm thick, 4 cm diameter slices that were pre-weighted and mounted in a poly(oxymethylene) holder that was clamped vertically in the compartment separation wall (Supplemental Data, S1).

**Conductivity measurements**

Electrolyte concentrations were determined using a Greisinger GMH3430 conductivity meter. The cell constant was calibrated using 0.01 and 0.1 m KCl solutions [36]. Calibration functions were obtained by fitting measured conductivities ($\kappa$) to the electrolyte’s concentration (5-12 levels over the range 0.01- 1 g L$^{-1}$) according to

$$\kappa - \kappa_0 = aC - bC^{3/2} + dC^2$$  \hspace{1cm} (14)

where $\kappa_0$ is the background conductivity of the deionized water after equilibration with atmospheric CO$_2$ and $a$, $b$, $d$ are fitting parameters. Calibration solutions were prepared by mass (g kg$^{-1}$ solution).

Concentrations were converted to g L$^{-1}$ using solution densities that were calculated from the apparent molar volumes and the Redlich-Meyer limiting slopes at 25 °C, as outlined by Millero [37]. Solution densities of the most concentrated solutions (2.5 g L$^{-1}$ CaSO$_4$·2H$_2$O) were only 0.2% higher than those of pure water, indicating that the effect of dissolved electrolytes on the solution density can be neglected.
for future studies. Because the inverse function of equation 14 is not easily obtained, experimental concentrations were obtained recursively from

\[ C_{i+1} = \frac{\kappa - \kappa_0}{a - b \sqrt{C_i + d C_i}} \]  

(15)

where new estimates of the concentration \( C_{i+1} \) were calculated from previous values \( C_i \) until a constant value was obtained (Supplemental Data, S2).

**Permeation experiments**

Permeation experiments with electrolytes were conducted by filling both compartments with equal masses of deionized water, followed by a 30-min period to allow atmospheric CO\(_2\) to equilibrate with the water. At \( t = 0 \), a spike solution in water was added to the donor compartment and an equal water mass was added simultaneously to the receptor compartment. Conductivities were measured at 5 min time intervals during the first hour, followed by a 30-60 min intervals (during office hours). Concentrations were chosen so as to obtain a conductivity just below 200 \( \mu \)S cm\(^{-1}\) in the donor compartment, in order to have all conductivity readings on the same scale of the instrument. Control experiments were carried out before and after each permeation experiment, as a check on equipment failure (e.g., membrane rupture, leaking O-ring). These experiments involved monitoring the permeation of a 1 g L\(^{-1}\) NaCl solution for 1 h at fixed times at a stirring rate of 400 min\(^{-1}\). The \( k_o \) for these control experiments showed a coefficient of variation of 3%, and corrective measures were taken when \( k_o \) deviated more than 9% from the average (replacement of the membrane or the O-ring).

Permeation rates of atrazine were studied by spiking a water volume of 1040 mL with 36 ng mL\(^{-1}\) atrazine. This spiked water and an equal volume of ultrapure water were added simultaneously to the compartments. Six to eight water samples (10 mL) were taken to monitor the evolution of concentrations over a time period of 55 to 160 h. After addition of internal standard (110 ng atrazine-d5) the water samples were extracted using solid phase extraction columns filled with 0.2 g Oasis HLB on a
vacuum manifold (Baker SPE-12G), followed by drying under vacuum (~ 20 min). Columns were eluted
with methanol. Extracts were evaporated to dryness under a stream of nitrogen, and the residue was
redissolved in 50 µL ethyl-acetate. After addition of an injection internal standard (50 µL anthracene-d10
solution in 2,2,4-trimethylpentane) the samples were analysed by GC/MS in selective ion monitoring
mode (m/z = 200 and 205).

**Alabaster solubility and dissolution rates**

Alabaster solubility was determined by incubating pre-weighed alabaster pieces (size ~2 cm) in
200 mL water in a closed glass vessel for 24 h under continuous stirring (400 min⁻¹), at temperatures of 4
and 20 °C, and NaCl background concentrations of 0 and approximately 36 g kg⁻¹. Solubilities of pure
CaSO₄·2H₂O were calculated as outlined elsewhere [35].

MTCs of the WBL were measured by mounting a pre-weighed alabaster plate (40 mm diameter
and ~ 1 cm thickness) in the wall of one of the compartments (Supplemental Data, S1). The position of
the alabaster surface was the same as the position of the membrane during the permeation
experiments. Alabaster mass losses were determined after drying the plates at 60 °C for 30 min, followed
by cooling in ambient air. Mass loss rates ranged from about 30 - 300 mg h⁻¹ at stirring rates between 0
and 600 min⁻¹.

At very high mass transfer rates, the solvation of ions from the crystal lattice may become rate
limiting. To investigate this, two experiments were carried out, in which an alabaster plate was
positioned under a tap water jet that hit the surface at a right angle, with velocities of 3 and 8 m s⁻¹.

**Hydraulic permeability**

The hydraulic permeability of the membranes was determined by filling both compartments of
the diffusion cell to just above the top of the membrane (850 mL) followed by the addition of 350 mL
water to one compartment, and monitoring the water levels in both compartments over time. Hydraulic
permeation was modelled using Darcy’s law, which relates the water flux through the membrane \( q = \frac{k \Delta p}{\mu d} = -k \frac{\Delta h}{d} \) (16)

where \( \mu \) is the dynamic viscosity of the water, \( d \) is the membrane thickness (145 \( \mu \)m), \( k \) is the permeability of the membrane \((m^2)\), and \( K = k \rho g / \mu \) is the hydraulic conductivity \((m \text{s}^{-1})\), with \( \rho \) the density of the water and \( g \) the acceleration of gravity. The difference in water levels \( \Delta h \) is then governed by

\[
\Delta h = \Delta h_0 \exp \left( -\frac{2K A_m}{d A_s} t \right)
\]

(17)

where \( t \) is time, \( \Delta h_0 \) is the water level difference at \( t = 0 \), \( A_m \) is the surface area of the membrane \((12.6 \text{ cm}^2)\), and \( A_s \) is the cross sectional area of the compartments \((1.1 \text{ dm}^2)\).

**RESULTS AND DISCUSSION**

*Alabaster dissolution*

Experimental alabaster solubilities were in good agreement with the values that were calculated from O’Brien et al. [35]. Ratios of measured/calculated solubilities \((1.028 \pm 0.016, n = 6)\) showed no systematic trend with temperature \((4 \text{ and } 21 ^\circ \text{C})\) or NaCl background concentrations \((0 \text{ and } 36 \text{ g kg}^{-1})\) (Supplemental Data, S3). The slightly higher experimental solubilities may be related to the presence of water soluble impurities that were co-precipitated during alabaster deposition. Although the correction factor is rather close to 1, it may be higher or lower for other alabaster batches, depending on the deposit.

Measured \( k_w \) increased from 2.7 \( \mu \text{m s}^{-1} \) at 0 \( \text{min}^{-1} \) to 27 \( \mu \text{m s}^{-1} \) at 600 \( \text{min}^{-1} \) (Figure 1). Method repeatability was about 6% at stirring rates of 200, 400, and 600 \( \text{min}^{-1} \) (two experimenters, \( n = 3 \) for each stirring rate) and 12% at 0 \( \text{min}^{-1} \) (one experimenter, \( n = 4 \)) (Supplemental Data, S4). Between 90 and 600
min^-1, $k_w$ increased with stirring rate to the power 0.74, but attained a value of 2.7 ± 0.3 µm s^-1 in the absence of forced convection (Figure 1 and Supplemental Data, S4).

The nonzero value of $k_w$ under unstirred conditions may be explained by the free convection currents that result from the greater density of the saturated calcium sulphate solution near the alabaster surface, relative to the density of the bulk water (~ 0.0021 g cm^-3 difference). The observed $k_w$ is close to the value of 3.0 µm s^-1 that is calculated from the Churchill-Chu equation for free convection heat and mass transfer near vertical plates (Supplemental Data, S5). Incropera et al. [38] proposed to model the effect of free convection on the total MTC by

$$ (k_w)^n = (k_{w,free})^n ± (k_{w,forced})^n $$

(18)

where the minus sign applies for opposing flows (forced flow opposite to the direction of free convection) and the plus sign applies for assisting and transverse flows, and $n = 3$ to 4. Adopting a conservative value of $n = 3$, the effect of free convection on $k_w$ is estimated to be less than 10% when $k_w$ is larger than 1.5 times $k_{w,free}$, indicating that this method is limited to the measurement of $k_w$ values larger than 4 µm s^{-1}.

The highest dissolution rates were obtained for the experiments in which an alabaster plate was positioned under a tap water jet that hit the surface at a right angle, with velocities of 3 and 8 m s^{-1}. The resulting $k_w$'s (120 and 300 µm s^{-1}, respectively) gave no reason to believe that solvation kinetics was a rate limiting factor at the stirring rates that were used.

**Electrolyte permeation**

The permeation experiments were carried out to investigate if alabaster dissolution rate measurements help to understand mass transfer through membranes and (ultimately) mass transfer to passive samplers. At the initial stages of this study, the overall MTCs ($k_o$) of calcium sulphate were estimated from equations 10 and 11 using nonlinear least squares, but it was observed that the residual errors showed systematic deviations (Supplemental Data, S6). The high accuracy of the conductivity
measurements allowed \( k_o \) to be estimated for individual points in time (equation 13). In most cases, \( k_o \) increased with time during the first half day, after which it attained a constant value (Figure 2), although one occurrence of decreasing values was also observed. We have no definite explanation for the cause of this effect, but we speculate that it is related to an initial difference in hydrostatic pressure between the compartments that induces a water flow across the membrane. As time goes by, this water flow causes the pressure difference to decrease, which in turn causes the flow to fade out. Results of the hydraulic permeation experiments indicated that differences in water height decrease with a first order rate constant of 0.36 h\(^{-1}\), which corresponds to a hydraulic conductivity of \( K = 0.060 \, \mu m \, s^{-1} \) (Supplemental Data, S7). This implies that an initially 1 mm higher water level in the acceptor compartment generates a 0.43 \( \mu m \, s^{-1} \) water flow into the donor compartment, and hence reduces \( k_o \) by the same value. The initial values of \( k_o \) were on average 0.25 \( \mu m \, s^{-1} \) smaller than the plateau value (range 0.14 to 0.42 \( \mu m \, s^{-1} \)), which can then be explained by assuming a 0.6 mm difference in water level. This difference may be caused by a slight tilt of the diffusion cell support, by small asymmetries in the dimensions of the two compartments, or by the volume of the conductivity sensor (3 to 10 cm\(^3\), depending on the immersion depth). The results of the hydraulic permeation experiments indicated that water level equilibration takes place with half-life time of 2 h, which is in accordance with the time needed for \( k_o \) to attain a constant value (Figure 2). We therefore adopted the plateau values (\( t > 24 \) h) as the best available estimates of \( k_o \). The relative standard deviations of these plateau values ranged from 0.1 to 0.8%.

Permeation experiments at 90 and 400 min\(^{-1}\) were carried out in duplicate, and differences between the duplicates were 2.0 and 3.5%, respectively.

Increasing the stirring rate from 90 to 600 min\(^{-1}\) causes an increase of \( k_o \) by a factor of 1.7 (Figure 3). The conductivity of the membrane \((k_mK_{mw})\) for calcium sulphate transport can be estimated from the measured values of \( k_o \) and \( k_w \) by
\[
\frac{1}{k_{m}K_{mw}} = \frac{1}{k_{o}} - \frac{2}{k_{w}}
\]  

(19)

which yielded a value of \(4.3 \pm 0.3 \, \mu m \, s^{-1}\). It may appear in Figure 3 that the membrane conductivity is higher (\(4.6 \, \mu m \, s^{-1}\)) at 90 min\(^{-1}\), but it should be noted that the accuracy of this estimate is lower than at higher stirring rates. For example, an error in \(k_{o}\) and \(k_{w}\) of 5\% results in an error in \(k_{m}K_{mw}\) of 13\% at 90 min\(^{-1}\) and 7\% at 600 min\(^{-1}\), while all estimates deviated less than 10\% from the average.

A more insightful visualisation of the data can be obtained by plotting the overall transport resistance (\(1/k_{o}\)) as a function of the WBL resistance (\(1/k_{w}\)), as shown in Figure 4. In this case, there is a mechanistic relationship between the dependent variable (\(1/k_{o}\)) and independent variable (\(1/k_{w}\)) via equation 19, in contrast with the representation in Figure 3, where the relationship with the independent variable (stirring rate) is empirical.

The expectation value of \(k_{m}K_{mw}\) for solutes that are only transported via the water filled pores of the membrane can be estimated from the mass transport equations for porous media [39]

\[
k_{m}K_{mw} = \frac{\phi D_{w}}{d \tau^2}
\]  

(20)

where \(\phi\) is the porosity, \(d\) is the membrane thickness and \(\tau\) is the tortuosity (length of the diffusion path divided by the thickness of the membrane; some authors use the name “tortuosity factor” for \(\tau^2\)).

Adopting \(\phi = 0.7\), \(D_{w}= 800 \, \mu m^2 \, s^{-1}\), \(d = 145 \, \mu m\), and \(\tau = 1\) yields a value of \(k_{m}K_{mw} = 3.9 \, \mu m \, s^{-1}\), which is 11\% smaller than the experimental value of \(4.3 \pm 0.3 \, \mu m \, s^{-1}\). In the absence of accurate values for \(\phi\) and \(\tau\) this can be considered to be a satisfactory correspondence. It should also be noted that the manufacturer lists a “typical thickness” of 145 \(\mu m\) for PES membranes with a nominal pore size of 0.2 \(\mu m\), and specifies that the actual thickness could range between 130 and 163 \(\mu m\). This means that a specific membrane could have a thickness that is 10\% lower or 12\% higher than the nominal thickness.

*Atrazine permeation*
Overall MTCs of atrazine were estimated by nonlinear least squares regression (equations 10 and 11), and ranged from 1.3 μm s⁻¹ at 90 min⁻¹ to 2.3 μm s⁻¹ at 600 min⁻¹. Recoveries were 83 ± 8 % (estimated C₀ relative to the concentration that was calculated from the spiked amount). Residual errors were about 0.6 ng mL⁻¹ (~ 4% of the average concentrations). Atrazine amounts detected in the membrane were 1.0 ± 0.5 % of the amounts in the water (n = 6), which yields a tentative PES-water sorption coefficient of 130 L kg⁻¹. Experiments at 90, 400, and 600 min⁻¹ were repeated 3 months later by a second experimenter, who obtained kₒ estimates that were 8 - 22 % lower. A data summary is given in the Supplemental Data (S4).

The kₔ obtained from alabaster dissolution can be used for other compounds after accounting for differences in diffusion coefficient. Although exact kₔ - Dₐ relationships are only available for a limited number of flow configurations, it is widely accepted to take kₔ to be proportional to the 2/3 power of the diffusion coefficient [24,40–43]. It then follows that the kₐ of compound i (kₐ,i) can be estimated from the alabaster based value (kₐ,CaSO₄) and the respective diffusion coefficients (Dₐ,i and Dₐ,CaSO₄) from

\[ k_{a,i} = k_{a,CaSO₄} \left( \frac{D_{a,i}}{D_{a,CaSO₄}} \right)^{2/3} \]  

The aqueous diffusion coefficient of atrazine is reported to be 560 μm² s⁻¹ at 20 °C [44]. With Dₐ,CaSO₄ = 800 μm² s⁻¹ this implies that the kₐ of atrazine is a factor of 1.26 lower than the kₐ of calcium sulphate.

Values of 1/ kₒ for atrazine permeation increase linearly with 1/ kₐ with a slope of 2 and an intercept 1/(kₐ,Kₐₐ), in accordance with equation 9 (Figure 5).

The membrane conductivity (Kₐₐ) obtained by experimenter 1 was 3.2 μm s⁻¹. The standard error of the mean (SEM) was 0.26 μm s⁻¹ (n = 4). Estimates of Kₐₐ from experimenter 2 were lower (2.5 μm s⁻¹) and showed a smaller scatter (SEM : 0.07 μm s⁻¹, n = 4). Experimental values were 19% higher (experimenter 1) and 7% lower (experimenter 2) than the theoretical value obtained from equation 20.
(adopting $\phi = 0.7, D_w = 560 \mu m^2 s^{-1}, d = 145 \mu m, \text{ and } \tau = 1$), which can be considered to be a satisfactory agreement. Transport through the polymer matrix cannot be completely excluded, but is not likely to be important, in view of the low PES-water sorption coefficients and the fact that the membrane conductivity was in good agreement with equation 20.

The data from this experiment suggest that atrazine transport through the PES membrane is through the pore space, rather than through the polymer matrix. But more importantly, this approach allows to assess data quality through the uncertainty in the intercept of $1/k_o$ vs. $1/k_w$ and through the deviation of individual measurements from the theoretical slope. Such assessments are not possible when empirical relationships between sampling rates and flow rates or stirring rates are used.

**IMPLICATIONS FOR PASSIVE SAMPLING CALIBRATION AND APPLICATION**

The present study demonstrates the merits of measuring $k_w$ using alabaster dissolution rates for quantifying the mass transfer resistance of PES membranes, albeit for one organic compound only. Yet, we expect that this method may also be used to improve our understanding of the uptake rates of polar organic compounds by passive samplers for several reasons. First, this method allows to separate the effects of flow from the effects of membrane and sorption phase on the uptake rates. This facilitates comparability of passive sampler calibrations between laboratories, because flow conditions are laboratory specific, while the transport resistances of membrane and sorbent are sampler/compound specific. Second, the quantification of $k_w$ may help strengthening the theoretical framework for interpreting sampling rates. Presently reported sampling rates are often difficult to interpret in terms of transport resistances of the WBL, the membrane, and the sorbent, because these sampling rates reflect the combined effects of transport through all of these phases. It can be expected that improved knowledge of the importance of the separate transport steps helps to improve passive sampler design. Improved mechanistic understanding of the uptake kinetics is also much needed for estimating the
Accounting for hydrodynamics in passive sampling

uncertainties in passive sampler based monitoring, which in turn is indispensable for the application of
passive samplers in a regulatory context. Third, the alabaster dissolution rate method may help in
translating the results of laboratory calibrations to field conditions. Laboratory calibrations obtained
under defined stirring rates are obviously difficult to apply in the field. But also the use of (measured)
flow velocities has its difficulties, because exposures in laboratory and field may differ in the
presence/absence of protective cages and in the angle of incidence of the incoming water. More robust
sampling rate estimates for field exposures may be obtained through equation 2, by combining the WBL
resistance that is measured in the field, with compound/sampler specific transport resistances of
membrane and sorption phase that are obtained in the laboratory. This improvement can be achieved
with relatively little effort, because quantification of $k_w$ requires the determination of a mass loss of a
few hundred milligrams, which can be achieved after a 1 to 5 hour exposure time, depending on the
flow.

A number of caveats for the proposed method should be mentioned as well. First, this method is
limited to the measurement of $k_w$ values > 4 $\mu$m s$^{-1}$ (flow velocities > 2.4 cm s$^{-1}$, based on equation 5)
because free convection currents that are generated by the alabaster dissolution itself cannot be
neglected at lower values. An alternative could be to obtain $k_w$ from the dissipation of performance
reference compounds from nonpolar passive samplers, provided that the sampler-water partition
coefficients (including their temperature dependence) are as accurately known as the solubility of
calcium sulphate. This is a challenge on its own. Calibrating the dissipation kinetics from nonpolar
passive samplers against the dissolution kinetics of alabaster may permit the quantification of $k_w$ values <
4 $\mu$m s$^{-1}$. Second, alabaster solubility is a critical parameter in the $k_w$ measurement, which is close to, but
likely always different from the solubility of pure calcium sulphate. The solubility of alabaster should
therefore be calibrated against the literature values for each new batch of alabaster, preferably at
different temperatures, as outlined above. Third, when applying this method in connection with passive
samplers, the membrane/sorbent envelope of sub-millimetre thickness is replaced by an alabaster plate of 4-10 mm thickness. This may have an effect on the hydrodynamical conditions at the alabaster surface, and some additional experiments may be needed to investigate the effect of plate thickness on $k_w$. Forth, upper and lower limits exist for the permissible alabaster exposure time. The mass loss should be sufficiently large to be measured accurately. After exploring various drying techniques we selected drying for 30 min at 60 °C, followed by cooling in ambient air. This procedure yielded a precision of about 1 mg for 4 cm diameter plates. We therefore recommend a minimum mass loss of 200 mg for this plate diameter. For the upper mass loss limit, it should be considered that the alabaster surface recedes as a result of the dissolution process and may become increasingly shielded from the flow. We suggest a maximum mass loss of 1.5 g for a 4 cm diameter plate, which corresponds to a surface recession of 0.5 mm. However, a smaller mass loss in the range 200-400 mg is sufficiently accurate and extends the life time of the plate.

Summarising, the measurement of $k_w$ using dissolution rates of flat alabaster plates is not a full solution for all flow related challenges with passive sampler calibration and application, but may be helpful for strengthening the mechanistic basis of models for polar compound uptake by passive samplers.

**Supplemental Data** - The Supplemental Data are available on the Wiley Online Library

**Acknowledgment** - We thank Joanne Beerda and Hamidreza Sharifan for their participation in this study.

**Data availability** - The raw data are provided in the Supplemental Data.
REFERENCES


**Figures**

**Figure 1.** Mass transfer coefficients ($k_w$) of the water boundary layer obtained from alabaster dissolution rates as a function of stirring speed ($f$) at 0 min$^{-1}$ (open circles) and 90 to 600 min$^{-1}$ (filled circles). The drawn line represents the forced convection component ($k_w = 0.23 f^{0.74}$), and equation 18 is shown as a dashed line.

**Figure 2.** Time dependency of the overall mass transfer coefficient ($k_o$) of calcium sulphate for a permeation experiment at a stirring rate of 400 min$^{-1}$. The drawn line is shown as a guide for the eye.
Figure 3. Overall mass transfer coefficients ($k_o$) for calcium sulphate permeation (circles) and estimates of $k_mK_{mw}$ (asterisks) as a function of stirring rate. The horizontal line represents the average $k_mK_{mw}$. The curved line ($k_o= 0.53 f^{0.28}$) is shown as a guide for the eye.

Figure 4. Overall mass transfer resistance ($1/k_o$) for calcium sulphate permeation. The drawn line represents the model equation $1/k_o = 1/(k_mK_{mw}) + 2/k_w$. 
Figure 5. Overall mass transfer resistance (1/k_o) for atrazine permeation measured by experimenters 1 (asterisks) and 2 (circles). The drawn lines represent the model equation 1/k_o = 1/(k_mK_{mw}) + 2/k_w.
Supplemental data

Method to account for the effect of hydrodynamics on polar organic compound uptake by passive samplers

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S1 Diagram of the experimental setup  
S2 Calculation of electrolyte concentrations from conductivity  
S3 Experimental alabaster solubilities  
S4. Data summary of dissolution and permeation kinetics  
Alabaster dissolution rates  
Calcium sulphate permeation rates  
Atrazine permeation rates  
S5. Mass transfer coefficients for alabaster dissolution under conditions of free convection  
S6. Model fit and residual errors of nonlinear least squares estimation  
S7 Hydraulic permeation experiments  
References
**S1 Diagram of the experimental setup**

![Diagram of the experimental setup](image)

**Figure S1-1.** Schematic drawing of the setup for measuring permeation rates (left) and alabaster dissolution rates (right): overview (top) and expanded view of the opening in the separation wall between the compartments (bottom).

**S2 Calculation of electrolyte concentrations from conductivity**

The conductivity ($\kappa$) of the electrolyte solutions was modelled as a function of concentration using

$$\kappa - \kappa_0 = a C - b C^{3/2} + d C^2 \quad (S2-1)$$

Because the inverse of this equation is not readily available, eq. S2-1 was rearranged to

$$C = \frac{\kappa - \kappa_0}{a - b C^{1/2} + d C} \quad (S2-2)$$

A first estimate of $C$ can be obtained by setting $C = 0$ at the right hand side of eq. S2-2

$$C_{i=1} = \frac{\kappa - \kappa_0}{a} \quad (S2-3)$$

This value is used at the right hand side of eq. S2-2 to obtain a better estimate of $C$

$$C_{i=2} = \frac{\kappa - \kappa_0}{a - b C_{i=1}^{1/2} + d C_{i=1}} \quad (S2-4)$$

This process is repeated until the change in subsequent concentration estimates is sufficiently small.
Below follows a sample calculation.
During one of the permeation experiments with calcium sulphate, the conductivity reading was 192.0 µS cm⁻¹, and the conductivity-concentration relationship was

\[ \kappa = 0.80 + 1448.3 \ C - 738.6 \ C^{3/2} + 193.1 \ C^2 \]  \hspace{1cm} (S2-5)

with \( \kappa \) in µS cm⁻¹ and \( C \) in g L⁻¹. From eq. S2-3, the first concentration estimate is

\[ C_{i=1} = \frac{\kappa - \kappa_0}{\alpha} = \frac{192.0 - 0.8}{1448.3} = 0.1320 \text{ g L}^{-1} \]  \hspace{1cm} (S2-6)

Subsequently better estimates are obtained from eq S2-4

\[ C_{i=2} = \frac{192.00 - 0.80}{1448.3 - 138.6 \times (0.1320)^{1/2} + 193.1 \times 0.1320} = 0.1586 \text{ g L}^{-1} \]

\[ C_{i=3} = \frac{192.00 - 0.80}{1448.3 - 138.6 \times (0.1586)^{1/2} + 193.1 \times 0.1586} = 0.1614 \text{ g L}^{-1} \]  \hspace{1cm} (S2-7)

\[ C_{i=4} = \frac{192.00 - 0.80}{1448.3 - 138.6 \times (0.1614)^{1/2} + 193.1 \times 0.1614} = 0.1617 \text{ g L}^{-1} \]

\[ C_{i=5} = \frac{192.00 - 0.80}{1448.3 - 138.6 \times (0.1617)^{1/2} + 193.1 \times 0.1617} = 0.1617 \text{ g L}^{-1} \]

### S3 Experimental alabaster solubilities

**Table S3-1.** Experimental solubilities of alabaster compared with literature values of CaSO₄·2H₂O

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>[NaCl] (g kg⁻¹ sln.)</th>
<th>C_{\text{experimental}} (g L⁻¹)</th>
<th>C_{\text{literature}} (g L⁻¹)</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.6</td>
<td>0</td>
<td>2.65</td>
<td>2.55</td>
<td>1.038</td>
</tr>
<tr>
<td>21.9</td>
<td>0</td>
<td>2.59</td>
<td>2.56</td>
<td>1.009</td>
</tr>
<tr>
<td>3.7</td>
<td>0</td>
<td>2.32</td>
<td>2.25</td>
<td>1.032</td>
</tr>
<tr>
<td>22.4</td>
<td>35.1</td>
<td>6.54</td>
<td>6.48</td>
<td>1.009</td>
</tr>
<tr>
<td>21.4</td>
<td>37.9</td>
<td>6.92</td>
<td>6.63</td>
<td>1.043</td>
</tr>
<tr>
<td>4.0</td>
<td>35.0</td>
<td>6.12</td>
<td>5.87</td>
<td>1.042</td>
</tr>
</tbody>
</table>

\(^{a}\) O’Brien et al. [1]
S4. Data summary of dissolution and permeation kinetics

Alabaster dissolution rates

Table S4-1. Experimental details of experiments to determine the mass transfer coefficients ($k_w$) of the water boundary layer, using alabaster dissolution rates. $t$ = exposure time, $\Delta m$ = alabaster mass loss, temp. = temperature, $\Delta$ = calculated recession of the alabaster surface due to dissolution (adopting an alabaster density of 2.3 g cm$^{-3}$)

<table>
<thead>
<tr>
<th>experimenter</th>
<th>stirring rate (min$^{-1}$)</th>
<th>$k_w$ (µm s$^{-1}$)</th>
<th>$t$ (h)</th>
<th>$\Delta m$ (g)</th>
<th>temp. (°C)</th>
<th>$\Delta$ (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0</td>
<td>3.0</td>
<td>18.6</td>
<td>0.59</td>
<td>21.7</td>
<td>0.20</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>2.8</td>
<td>7.0</td>
<td>0.24</td>
<td>22.6</td>
<td>0.08</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>2.3</td>
<td>5.0</td>
<td>0.13</td>
<td>22.6</td>
<td>0.04</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>2.5</td>
<td>4.8</td>
<td>0.14</td>
<td>21.8</td>
<td>0.05</td>
</tr>
<tr>
<td>2</td>
<td>90</td>
<td>6.4</td>
<td>8.5</td>
<td>0.57</td>
<td>20.8</td>
<td>0.20</td>
</tr>
<tr>
<td>2</td>
<td>200</td>
<td>11.0</td>
<td>5.3</td>
<td>0.61</td>
<td>20.1</td>
<td>0.21</td>
</tr>
<tr>
<td>2</td>
<td>200</td>
<td>11.8</td>
<td>5.0</td>
<td>0.62</td>
<td>21.1</td>
<td>0.21</td>
</tr>
<tr>
<td>1</td>
<td>200</td>
<td>12.2</td>
<td>21.6</td>
<td>1.82</td>
<td>19.5</td>
<td>0.63</td>
</tr>
<tr>
<td>2</td>
<td>400</td>
<td>17.7</td>
<td>3.3</td>
<td>0.61</td>
<td>20.3</td>
<td>0.21</td>
</tr>
<tr>
<td>2</td>
<td>400</td>
<td>19.5</td>
<td>3.1</td>
<td>0.62</td>
<td>20.5</td>
<td>0.21</td>
</tr>
<tr>
<td>1</td>
<td>400</td>
<td>17.8</td>
<td>25.2</td>
<td>2.28</td>
<td>20.2</td>
<td>0.79</td>
</tr>
<tr>
<td>2</td>
<td>600</td>
<td>24.4</td>
<td>2.6</td>
<td>0.65</td>
<td>20.4</td>
<td>0.22</td>
</tr>
<tr>
<td>2</td>
<td>600</td>
<td>27.8</td>
<td>2.2</td>
<td>0.64</td>
<td>21.0</td>
<td>0.22</td>
</tr>
<tr>
<td>1</td>
<td>600</td>
<td>27.3</td>
<td>6.5</td>
<td>1.45</td>
<td>20.0</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Calcium sulphate permeation rates

Table S4-2. Experimental details of calcium sulphate permeation experiments. $C_0$ = estimated initial concentration in the donor compartment, mass balance = estimated $C_0$ relative to the concentration calculated from the spiked amount, $k_o$ = overall mass transfer coefficient, temp. = temperature.

<table>
<thead>
<tr>
<th>experimenter</th>
<th>stirring rate (RPM)</th>
<th>temp. (°C)</th>
<th>$C_0$ (g L$^{-1}$)</th>
<th>mass balance (%)</th>
<th>$k_o$ (µm s$^{-1}$)</th>
<th>residual error (g L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>90</td>
<td>20.0</td>
<td>0.161</td>
<td>101</td>
<td>1.908 ± 0.011</td>
<td>0.0003</td>
</tr>
<tr>
<td>4</td>
<td>90</td>
<td>19.7</td>
<td>0.159</td>
<td>100</td>
<td>1.870 ± 0.006</td>
<td>0.0003</td>
</tr>
<tr>
<td>1</td>
<td>200</td>
<td>19.9</td>
<td>0.164</td>
<td>101</td>
<td>2.385 ± 0.004</td>
<td>0.0001</td>
</tr>
<tr>
<td>1</td>
<td>400</td>
<td>19.7</td>
<td>1.018</td>
<td>102</td>
<td>2.942 ± 0.024</td>
<td>0.0007</td>
</tr>
<tr>
<td>1</td>
<td>400</td>
<td>20.0</td>
<td>0.168</td>
<td>101</td>
<td>2.842 ± 0.009</td>
<td>0.0001</td>
</tr>
<tr>
<td>1</td>
<td>600</td>
<td>20.6</td>
<td>0.163</td>
<td>101</td>
<td>3.212 ± 0.004</td>
<td>0.0001</td>
</tr>
</tbody>
</table>
**Atrazine permeation rates**

Table S4-3. Experimental details of atrazine permeation experiments. \( C_0 = \) estimated initial concentration in the donor compartment, mass balance = estimated \( C_0 \) relative to the concentration calculated from the spiked amount, \( k_o = \) overall mass transfer coefficient, temp. = temperature.

<table>
<thead>
<tr>
<th>experimenter</th>
<th>stirring rate (RPM)</th>
<th>temp. (°C)</th>
<th>( C_0 ) (ng mL(^{-1}))</th>
<th>mass balance (%)</th>
<th>( k_o ) (( \mu )m s(^{-1}))</th>
<th>residual error (ng mL(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>90</td>
<td>22</td>
<td>34.5</td>
<td>90</td>
<td>1.54 ± 0.07</td>
<td>0.6</td>
</tr>
<tr>
<td>2</td>
<td>90</td>
<td>20</td>
<td>36.7</td>
<td>93</td>
<td>1.24 ± 0.04</td>
<td>0.7</td>
</tr>
<tr>
<td>2</td>
<td>200</td>
<td>20</td>
<td>34.0</td>
<td>85</td>
<td>1.62 ± 0.04</td>
<td>0.6</td>
</tr>
<tr>
<td>1</td>
<td>400</td>
<td>22</td>
<td>2.7</td>
<td>71</td>
<td>2.37 ± 0.24</td>
<td>0.1</td>
</tr>
<tr>
<td>1</td>
<td>400</td>
<td>22</td>
<td>33.6</td>
<td>88</td>
<td>1.92 ± 0.05</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>400</td>
<td>20</td>
<td>26.7</td>
<td>68</td>
<td>1.78 ± 0.14</td>
<td>1.0</td>
</tr>
<tr>
<td>1</td>
<td>600</td>
<td>23</td>
<td>31.7</td>
<td>83</td>
<td>2.36 ± 0.09</td>
<td>0.6</td>
</tr>
<tr>
<td>2</td>
<td>600</td>
<td>20</td>
<td>35.0</td>
<td>89</td>
<td>2.18 ± 0.10</td>
<td>0.9</td>
</tr>
</tbody>
</table>

**S5. Mass transfer coefficients for alabaster dissolution under conditions of free convection**

Churchill and Chu [2] showed that mass transfer rates for a vertical plate under conditions of free convection \( (k_{w,\text{free}}) \) can be modelled as

\[
Sh = \frac{k_{w,\text{free}} L}{D_w} = 0.68 + \frac{0.670Ra^{1/4}}{1 + \left(\frac{0.492}{Sc}\right)^{9/16}}^{4/9} \tag{S5-1}
\]

where \( k_{w,\text{free}} \) is the mass transfer coefficient for free convection, \( L \) is the length of the plate, \( D_w \) is the diffusion coefficient of the solute, \( Ra \) is the Rayleigh number and \( Sc \) the Schmidt number

\[
Sc = \frac{\nu}{D_w} \tag{S5-2}
\]

\[
Ra = \frac{gL^3 \Delta \rho}{\nu D \rho} \tag{S5-3}
\]

where \( \nu \) is the kinematic viscosity of the fluid, \( g \) is the acceleration of gravity, \( \Delta \rho \) the density difference over the boundary layer, and \( \rho \) the density of the water.

Solvent and solute properties were evaluated at 22 °C (the temperature during the free-convection experiments), and \( k_{w,\text{free}} \) was calculated from eq. S5-1 as follows.

Density of saturated (2.57 g L\(^{-1}\)) calcium sulphate solution [3]: \( \rho = 0.9999 \text{ g cm}^{-3} \)

Density of water [4]: \( \rho = 0.9978 \text{ g cm}^{-3} \)

Dynamic viscosity of water [5]: \( \eta = 0.9547 \text{ mPa s} \)

Kinematic viscosity \( \nu = \eta/\rho = 0.955\cdot10^{-6} \text{ m}^2 \text{ s}^{-1} \)

Diffusion coefficient of calcium sulphate was calculated by interpolation of \( \log D_w \) vs. \( 1/T \), using the salt diffusion coefficients from Li and Gregory [6], which yielded \( D_w = 847 \mu \text{m}^2 \text{ s}^{-1} \)

The length of the plate was taken to be its surface area divided by its diameter: \( 12.6/4.0 = 3.1 \text{ cm} \)

Inserting these values yields \( Sc = 1127 \), \( Ra = 7.6\cdot10^8 \), \( Sh = 111 \), \( k_{w,\text{free}} = 3.0 \mu \text{m s}^{-1} \)
S6. Model fit and residual errors of nonlinear least squares estimation

![Figure S6-1](image)

Figure S6-1. Results of the nonlinear least squares estimation using eqs. 10 and 11, using data from a calcium sulphate permeation experiment at 400 min$^{-1}$. Left panel: concentrations and model fit. Right panel: residual errors.

S7 Hydraulic permeation experiments

The difference in water height between the two compartments followed an exponential decrease with time, with a first order rate constant of 0.36 h$^{-1}$, in accordance with eq. 17 (Fig. S7-1). This rate constant corresponds to a hydraulic conductivity of $K = 0.060 \mu$m s$^{-1}$, and a membrane permeability of $k = 6.2 \times 10^{-15}$ m$^2$ (eq. 16).

![Figure S7-1](image)

Figure S7-1. Difference in water height as a function of time in the diffusion cell, following the addition of 0.85 L water to one compartment and 1.20 L water to the other. The drawn line represents the model fit (eq. 17).
References


