

Time integrative passive sampling of very hydrophilic chemicals in wastewater influent

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SI1 Materials and methods

Materials. Methanol and acetone were purchased from Merck (Germany) and were of chromatography quality. Water was purified through a Milli-Q system (Millipore, 0.22 μm filtered, 18.2 $\text{m}\Omega\text{ cm}^{-1}$). Regenerated cellulose (RC) filters (0.2 mm pore size) were purchased from Agilent Technologies and used to filter the samples. Acesulfame, ethyl sulphate, methamphetamine, benzoylecgonine, acesulfame D4, ethyl sulphate D5, methamphetamine D9 and benzoylecgonine D3 were purchased from Novachem (Heidelberg West, Australia). A stock solution of 1000 $\mu\text{g mL}^{-1}$ (native) and 100 $\mu\text{g mL}^{-1}$ (isotopically labelled) was prepared and stored at $-20\text{ }^{\circ}\text{C}$.

Deployment. The sampler was deployed over 31 days in the influent of a municipal wastewater treatment plant in Queensland, Australia. Location of sampling was after influent screening and grit removal processes within the WWTP. Analytical triplicates 1.5 mL were taken from the sampling port with a syringe each day for the first 7 days of deployment, followed by days: 11, 15, 17, 21, 24, 28 and 31. The exact volume extracted from G-TIPS was replaced with clean milliQ-water via the sampling port. Concurrent to the deployment of the passive sampler, on each day, a refrigerated auto sampler collected a 24 h composite sample (250 mL) in time-proportional mode with 15 min intervals for the entire 31-day period.

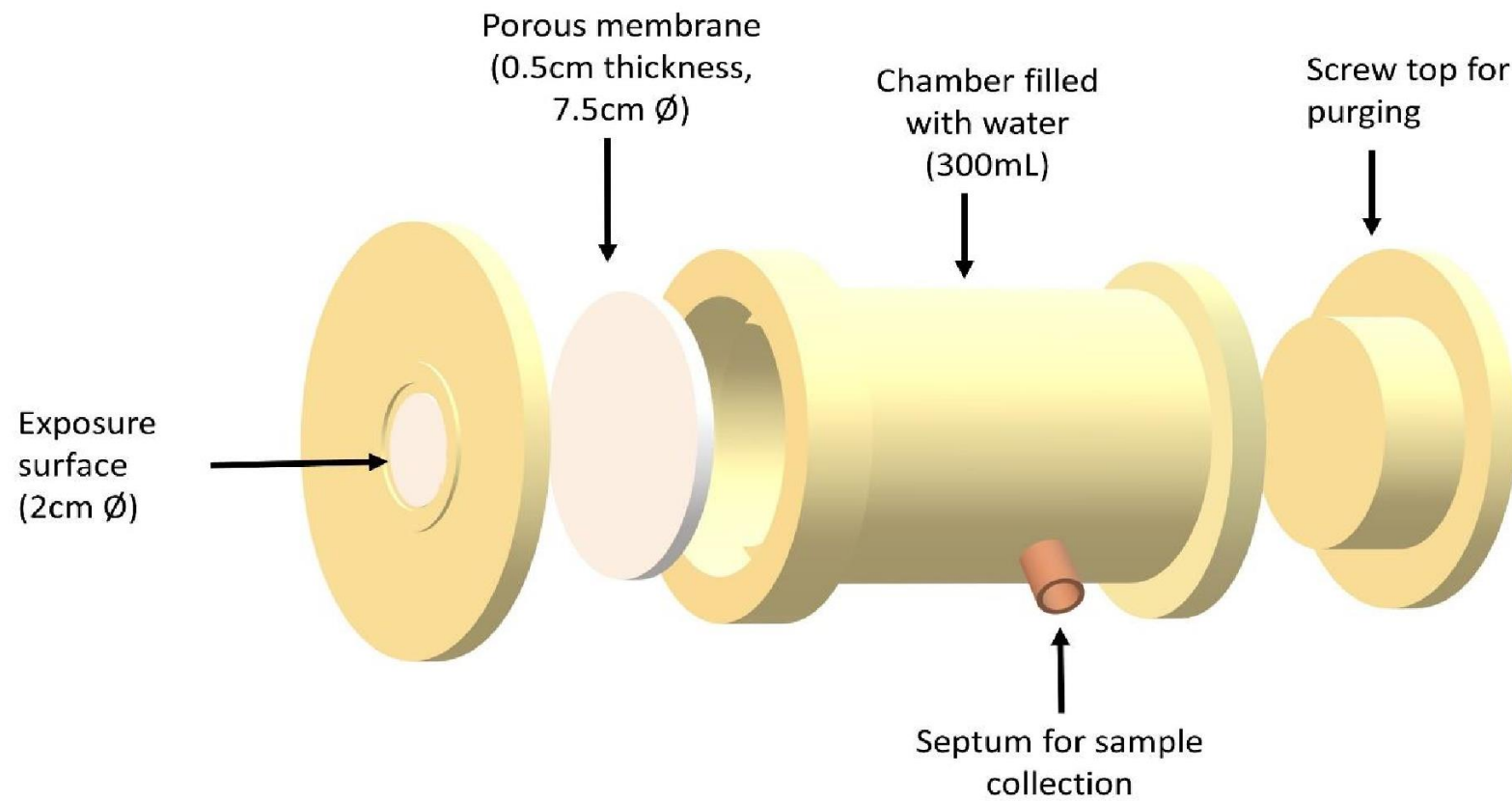
Analysis. Aliquots of the samples collected from G-TIPS and the 24 h composite samples (1 mL) were filtered using an RC 0.2 μm Agilent filter on the day of collection (within an hour of sampling) and spiked with isotopically labelled standards (10 μL of a 1 ppm stock solution) prior to direct injection analysis on LC-MS/MS. All samples were stored at $-20\text{ }^{\circ}\text{C}$ until analysis. Samples were analysed using Liquid Chromatography (LC) (Shimadzu, Nexera HPLC system, Kyoto, Japan) coupled with tandem electrospray ionization (ESI) mass spectrometry (MS/MS) (SCIEX API 5500 QTRAP[®] Mass Spectrometers, Ontario, Canada). To quantify the target analytes the isotopic ratio between native and labelled was used. An eight-point calibration (0.1-100 ng mL^{-1}) was used to calculate the concentrations in the samples. Data was processed with MultiQuant[™] and Analyst Software (Sciex).

Quality assurance and quality control (QA/QC). Samples were collected from the sampler prior to deployment (time 0), and were considered as a field blanks. Two additional blanks were taken from a sample bottle brought into the field during the sampling period. None of the analytes of interest were detectable in the time 0/field blank samples. Results from the

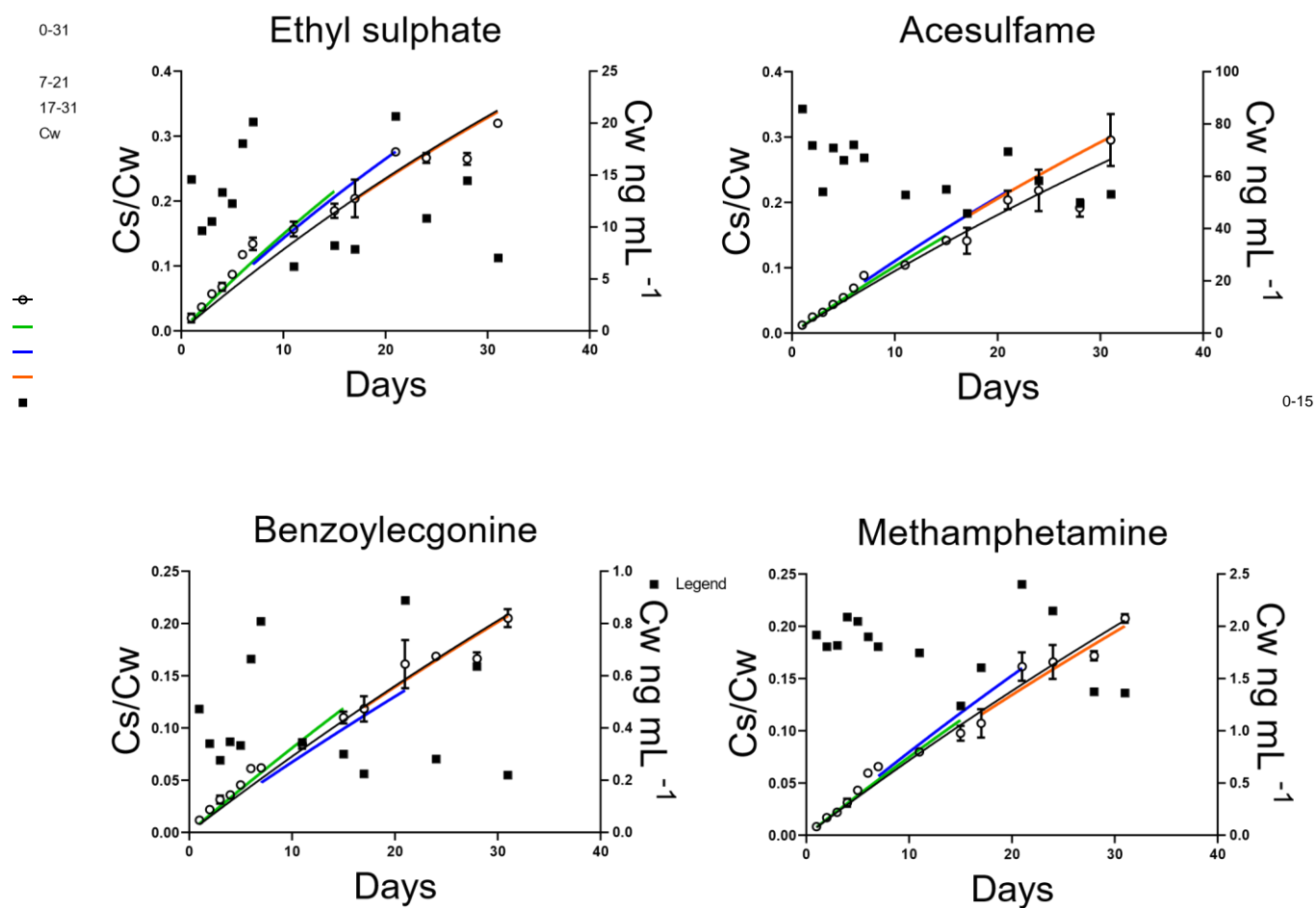
analysis of triplicate G-TIPS samples showed low percent coefficient of variation (%CV) within the sampler <16% (with the exception of day one for EtS at 35%).

Analytical method detection limits (LODs) were calculated as three times the standard deviation of the 0.1 or 0.5 ng mL⁻¹ calibration standard from 5x injections. Limits of quantification (LOQs) were calculated as three times the LOD. LODs ranged from 0.003 to 0.15 ng mL⁻¹ for benzoylecgonine and acesulfame (table 1).

Our laboratory uses well-established quantitation methods for drugs, and routinely participates in passive sampling inter-laboratory studies and the EU wastewater based drug monitoring inter-laboratory comparison study SCORE^{1,2}.



SI3: Calculated sampling rates (Eq3) for the four different sampling duration sections (Rs_{0-15} , Rs_{7-21} , Rs_{17-31} and Rs_{0-31}). On the left y-axis the product of C_w/C_s (circles), on the right y-axis are the concentrations of the raw wastewater ng mL^{-1} (squares) determined from the composite 24h auto samplers and on the x-axis the time in days.



SI4: concentration of analytes in wastewater derived from 24h composite samples

Days	EtS (ng mL ⁻¹)	ACS (ng mL ⁻¹)	BZE (ng mL ⁻¹)	Meth (ng mL ⁻¹)
1	14.6	85.6	0.5	1.9
2	9.6	71.9	0.3	1.8
3	10.5	54.0	0.3	1.8
4	13.3	70.9	0.3	2.1
5	12.3	66.1	0.3	2.0
6	18.0	72.1	0.7	1.9
7	20.1	67.0	0.8	1.8
11	6.2	52.9	0.3	1.7
15	8.2	55.0	0.3	1.2
17	7.8	45.8	0.2	1.6
21	20.6	69.5	0.9	2.4
24	10.8	58.4	0.3	2.1
28	14.5	49.6	0.6	1.4
31	7.0	53.1	0.2	1.4

SI5: Explanation of theory used to predict sampling rates with the chemical diffusivity through water.

One of the reasons porous polyethylene is useful as a diffusive barrier is that water-filled pores in PE have similar properties to stagnant water. The molecules diffusing from the sampled aqueous phase across the porous polyethylene membrane to the receiving aqueous phase pass several barriers to mass transfer. Besides the membrane pores water boundary layers (WBL) can form on both sides of the membrane. The overall resistance to mass transfer can be expressed a sum of resistances of individual barriers in series:

$$\frac{1}{k_o} = \frac{1}{k_{w,ext}} + \frac{1}{k_{PE}} + \frac{1}{k_{w,int}} \quad (1)$$

Where k_o is the overall mass transfer coefficients, $k_{w,ext}$ and $k_{w,int}$ are resistances of the WBL on external and internal side of the PE membrane, respectively. The mass transfer in PE controls the uptake of sampled compounds when the WBL resistances are negligible, i.e. when

$$\frac{1}{k_{PE}} \gg \frac{1}{k_{w,ext}} + \frac{1}{k_{w,int}} \quad (2)$$

To assure this, water on both sides of PE membrane should be stirred to minimise the thickness of WBL or creation of undesired concentration gradients in liquid phases at both sides of PE membrane surface. We assume that the compounds pass the membrane via the water-filled pores and due to their very hydrophilic character they do not interact with the polymer matrix of PE. In such case, k_{PE} can be estimated as ³:

$$k_{PE} = \frac{\phi D_w}{\theta \delta_{PE}} \quad (3)$$

where ϕ is the porosity, θ the tortuosity of the diffusion pathways within the PE membrane and δ_{PE} is the PE membrane thickness.

D_w values can be estimated, e.g. using the Wilke-Chang equation⁴:

$$D = 7.4 \times 10^{-8} \frac{(xM)^{0.5} T}{\eta V^{0.6}} \quad (4)$$

or the Hayduk-Laudie equation⁵:

$$D = \frac{13.26 \times 10^{-5}}{\eta^{1.4} V^{0.589}} \quad (5)$$

where x is the solvent association parameter (2.6 for water), M (g mol⁻¹) is molar mass of water, T (K) is the thermodynamic temperature, η (cP) is viscosity of water and V (cm³ mol⁻¹) is molar volume of the diffusing compound at its normal boiling point.

Estimated D_w at 23°C.

Compound	Molar mass	Molar volume	Wilke-Chang $D \times 10^6$ $\text{cm}^2 \text{s}^{-1}$	Hayduk-Laudie $D \times 10^6$ $\text{cm}^2 \text{s}^{-1}$
Acesulfame	201.242	111.18	9.54	8.98
Ethyl sulphate	125.99	83.99	11.29	10.6
Methamphetamine	149.23	165.81	7.51	7.1
Benzoylecgonine	289.33	222.56	6.29	5.97

The porosity is known from the manufacture and is 35%.

The theoretical tortuosity for a randomly oriented cylindrical pore network can be determined as follows^{6,7}.

The diffusion flux along the pore aligned in direction "R" of the liquid flux is given as $F = -D \frac{dC}{dR}$.

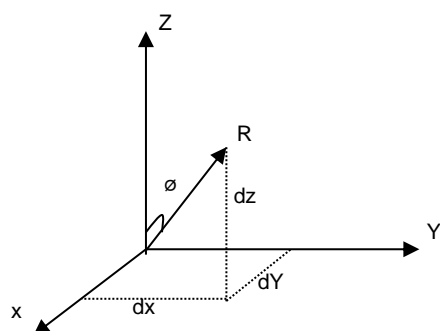
Assuming that the pore axis is at an angle ϕ from the "z" axis, or the direction of net liquid flow.

Hence $dz = dR \cos \phi$. (6)

Additionally, the component of flux in the z direction is given as

$F_z = -D \cos \phi \frac{dC}{dR}$, where F_z is the z component of the flux. (7)

Combining 6 and 7, we get $F_z = -D \cos^2 \phi \frac{dC}{dR}$, thus tortuosity is represented as $1/\cos^2 \phi$



For a randomly oriented pore and for a very large sample, the "average value" of distance \overline{dR} can be equated to

$$\overline{dR \cos \phi} = \overline{dz} = \overline{dx} = \overline{dy}$$

Also since $dr^2 = dz^2 + dx^2 + dy^2$. Combining we get the averaged values, $\overline{dr^2} = 3 \overline{\cos^2 \phi} \overline{dr^2}$. Or $\overline{\cos^2 \phi} = \frac{1}{3}$.

Thus tortuosity for a randomly oriented pore equals 3.0.

The sampling rate can be estimated as $R_s = k_{PE} A$:

$$R_s = k_{PE} A = \frac{\phi D_w A}{\theta \delta_{PE}}$$

where A is the surface area of sampler in contact with sampled water (30.19 cm^2), $\delta_{PE}=0.5 \text{ cm}$, $\phi=0.35$ and $\theta=3$ the estimated R_s values are:

Compound	R_s (mL/day) (Wilke-Chang)	R_s (mL/day) (Hayduk-Laudie)
Acesulfame	5.81	5.47
Ethyl sulphate	6.87	6.45
Methamphetamine	4.57	4.32
Benzoylecgonine	3.83	3.63

SI6: Calculated partition coefficients from unpublished work showing no interaction with the PE membrane as partition coefficients are close to 1 or no chemicals were detected in the PE membrane (a).

Compound	K_{mw} (mL g ⁻¹)
Acesulfame	a
Codeine	1.19 ± 0.12
Ibuprofen	1.06 ± 0.11
Naproxen	0.68 ± 0.02
Paracetamol	a

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