Supporting Information

Time weighted average concentration monitoring based on thin film solid phase microextraction

Fardin Ahmadi[a], Chris Sparham[b], Ezel Boyacı[a], Janusz Pawliszyn[a]*

[a]*Department of Chemistry, University of Waterloo, 200 University Avenue West, Waterloo, Ontario, N2L 3G1, Canada.*

[b]*Unilever, Safety & Environmental Assurance Centre, Colworth Science Park, Sharnbrook, Bedford, MK44 1LQ, UK.*

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Number of tables: 5

MATERIALS AND METHODS

Chemicals and Materials. All chemicals and reagents utilized in this study were obtained at the highest available purity (>99%) and used without further purification. The standards octylmethoxycinnamate (OMC), benzophenone-1 (Ben-1), benzophenone-2 (Ben-2), benzophenone-3 (Ben-3), benzophenone-4 (Ben-4), 2-phenylbenzimidazole-5-sulfonic acid (PBSA), octocrylene (OCR), butylmethoxydibenzoylmethane (BM-DBM), triclosan (TCS), and triclocarban (TCC), as well as HPLC-grade solvents acetonitrile (ACN), methanol, isopropyl alcohol (IPA), ethyl acetate, formic acid (LC-MS grade), sodium hydroxide, sodium hydrogen carbonate, and ammonium formate (HPLC grade) were purchased from Sigma (Oakville, ON, Canada). Ultrapure water was obtained from a Barnstead nanopure water purification system with 18.2 MΩ.cm resistivity. The internal standard (IS) 2-hydroxy-4-methoxybenzophenone-2',3',4',5',6'-d5 (Ben-3-d_5) was obtained from CDN isotopes (Pointe-Claire, QC, Canada). Oasis HLB (hydrophilic lipophilic balanced) polymeric reversed-phase particles (30 µm in diameter) were purchased from Waters (ON, Canada), C18 (5 µm in diameter) particles were supplied by Supelco, and Chromabond Easy polystyrene-divinylbenzene-weak anion exchange (PS-DVB-WAX, Macherey-Nagel) particles were obtained from VWR International (Mississauga, Canada). Polyacrylonitrile (PAN), obtained from Sigma-Aldrich (Oakville, ON, Canada), was dissolved in N, N-dimethylformamide, also obtained from Sigma-Aldrich, (Oakville, ON, Canada), and used as a biocompatible glue(to prevent fouling of the coating in complex matrices[1]) for the immobilisation of functional particles to the blades. Coated blades

consisting of either HLB, PS-DVB-WAX, or C18 particles were prepared as reported by Mirnaghi et al.[2] The digital conductivity meter used for measuring limiting ionic conductance was obtained from VWR (ON, Canada).

Individual stock solutions were prepared either in methanol (Ben-1, Ben-2, Ben-3, Ben-4, TCS, TCC, OCR, OMC and BM-DBM), or in ultrapure water with the addition of a few drops of 2 M sodium hydrogen carbonate (in the case of PBSA) at a 2 $mgmL^{-1}$ concentration. Mixed standard solutions were prepared at a 100 μgmL^{-1} concentration and stored at 4 °C. Instrument calibration standards were prepared daily in methanol/water (50/50, v/v).

Instrumentation. A Shimadzu (LC-10 AD-vp) high-performance liquid chromatograph (HPLC) and an Applied Biosystems API 4000 triple quadrupole mass spectrometer (equipped with TurboIonSpray source) were used for separation and quantitative analysis of analytes. The chromatographic column used was a Waters Symmetry Shield RP18 with dimensions of 2.1mm × 50 mm, and a 3.5 µm particle diameter. Sample volumes of 20 µL of both standards and extracted analytes were injected into the LC-MS/MS system using an HTC PAL autosampler from Leap Technologies (HTC Analytics, NC). Two different chromatography methods were used for negative and positive mode. In positive mode, mobile phase A consisted of ACN/water (50/50, v/v), with a 10 mM ammonium formate buffer with the pH adjusted to 3.2 with formic acid, while mobile phase B consisted of IPA with 0.1% formic acid. The applied chromatographic gradient was started at 10% of B and kept at this

composition for 2.2 min, then linearly increased to 50% of B within the next 2 min, where it was held for an additional 2 min. Finally, within the next 1 min, the gradient was returned to 10% of B and held for an additional 1 min at the same composition (total cycle was 8.2 min). This method prevented carry-over for hydrophobic compounds.[3] In negative mode, the mobile phase consisted of solvent A (water) and solvent B (ACN), both containing 1 mM acetic acid (HOAc). The applied chromatographic gradient was started at 10% of B and kept at this composition for 2.2 min, then linearly increased to 100% of B within the next 2 min, where it was held for an additional 2 min. Finally, within the next 1 min, the gradient was returned to 10% of B and kept for an additional 1 min at the same composition (total cycle was 8.2 min). Ionization efficiency was improved by using acetic acid in negative mode, as acetate has a high basicity function in the gas phase.[4] After each injection, the autosampler system was cleaned by washing the syringe and injector port with two separate washing solutions. Washing solvent A was composed of ACN/IPA(50/50, v/v), and washing solvent B was methanol. MS/MS analyses were performed in positive and negative modes in separate runs under multiple reaction monitoring (MRM) conditions. A summary of the MS/MS parameters is given in Table S2.

Aqueous standard generation. In order to prepare a robust and reliable standard aqueous generation of UV filters and biocides, a careful investigation into the physical-chemical properties of each analyte was required. Parameters studied included solubility in water, physical state (liquid or solid), polarity, and molecular weight. Some of the relevant properties of the analytes under study are summarized in Table S1. A permeation tube consisting of polytetrafluoroethylene (PTFE) with 0.25 mm thickness was used for standard generation of OCR and OMC (liquid state). Cellulose acetate dialysis membranes with 100-500 Da and 500-1000 Da MWCO were used for Ben-1, Ben-2, Ben-3 and TCS, TCC, BM-DBM, respectively. A stainless steel porous frit (0.5µm) coated with epoxy glue was used for Ben-4 and PBSA. The system consisted of a permeation chamber, mixing chamber, and sampling chamber. Water was filled into an 18 L polypropylene reservoir, and delivered by a Series 200 Perkin Elmer pump (Shelton, Connecticut, USA) at 3 $mLmin^{-1}$ to the permeation chamber (capacity is about 1000mL). The permeation chamber has an inlet for introduction of fresh water that is close to the bottom of the chamber and outlet (close to the top) and connected to the mixing chamber. The key part of the standard generation system is the permeation chamber, which consists of dialysis membranes, a permeation tube, and a porous frit coated by epoxy glue. The mixing chamber was used to ensure that the resulting solution was homogeneous, and the sampling chamber was used for SPME optimization and passive sampler evaluation. The entirety of the aqueous standard generator system was covered with aluminum foil so as to prevent any photodegradation of analytes. The system generated a steady state concentration after an initial induction period of 1 week for all compounds, and showed variations in concentrations of less than 20% within a three-month period. Room temperature was kept at 24±1 °C, and new water was allowed to

reach room temperature before being added to the system. Average concentrations of individual analytes were 375, 138, 12, 380, 118, 3.26, 0.25, 0.08, 1.2, and 0.12 $ngmL^{-1}$ for PBSA, Ben-1, Ben-3, Ben-4, Ben-2, TCS, OCR, OMC, TCC, and BM-DBM, respectively.[5]

SPME procedure using TF-SPME. TF-SPME method development included selection of a suitable coating, desorption solvent, desorption time, and preconditioning time. For selection of the best extraction phase, three different coating types were evaluated, namely, C18, HLB, and WAX-PS-DVB coated blades. Prior to extraction, the coatings were preconditioned in MeOH/H_2O (50/50, v/v) for 30 min. Conditioned coatings were placed in the sampling chamber of the aqueous standard generator system for an extraction time of 180 min. Following extraction, to find the best solvent for desorption of the analytes, four desorption solvents were tested simultaneously. After extractions for 180 min in the aqueous standard generator system, first and second desorption were performed with a range of desorption solvents. MeOH/ACN/IPA (50/25/25, v/v/v), MeOH/ACN/H_2O (40/40/20, v/v/v), ACN/H_2O(50/50, v/v), and MeOH/H_2O(80/20, v/v), were studied to find the most appropriate desorption solvent. This step was performed in a 2 mL amber vial containing 1800 µL of desorption solvent using vortex agitation at 1500 rpm. The desorption step was followed with a second desorption to evaluate the carryover in each extraction phase/desorption solvent pair. The amounts of extracted analytes were determined in the LC-MS/MS method described above, using instrument

calibration solutions prepared in MeOH/H_2O(50/50, v/v) in a range of 0.1 to 100 $ngmL^{-1}$.A summary of the experimental conditions is given in Table S3.

Grab sampling procedure. Two different spot sampling approaches were used. SPME analysis of a sample taken to the laboratory in a bottle and equilibrium on-site passive sampling[6,7]with open bed TF-SPME were selected to compare concentrations for non-polar and polar analytes, respectively. Equilibrium concentrations of the analytes in water were calculated with equation S1.

$$C_0 = \frac{n}{K_{fs}S_a} = \frac{n}{B_c} \quad \text{(S1)}$$

Where C_0 is the equilibrium concentration, B_c is the blade constant, which is the product of the distribution coefficient of the analytes and the active surface area of the solid coating, and n is the amount of extracted analyte at equilibrium. On-site equilibrium spot sampling with TF-SPME was performed every month in parallel to the longer-term deployment of the retracted sampler. Three HLB TF-SPME were exposed directly into the river at the sampling point for 10 days. After extraction, the devices were wrapped individually in aluminum foil and transported to the lab in an insulated box containing dry ice. In addition, three spot samples were taken in a bottle at the sampling location at days 1, 3, and 5 of the sampler deployment. Samples were taken in 1 L amber glass bottles previously washed with acetone, methanol, and ultrapure water. Upon collection of the samples, sodium azide (0.2 gL^{-1}) and ascorbic acid (0.05 gL^{-1}) were added to the sample bottles to inhibit microbial degradation of analytes. The bottles were transferred to the laboratory on ice and analyzed immediately. Spot samples were analyzed in triplicate in a 500 mL amber bottle and quantified by external SPME calibration technique, using C18 TF-SPME as

extraction phase. Extraction time was set at 120 min with 800 rpm of agitation. External SPME calibration was constructed in a range of 10.0 to 1000.0 ng mL^{-1}. Moreover, it should be noted that loss of analyte onto the glassware was shown to be negligible.

Blank samples. Two types of blank samples were prepared and considered in all steps, including preparation, assembling, transportation, storage, deployment, and retrieval (Standard ISO-5667). The procedural blank sampler was used to evaluate if any possible contamination occurred during preparation, assembling, loading of the calibrant, storage, transportation, processing, and analysis. Another blank sampler was used as a field blank by exposing it to ambient air during deployment and retrieval of samplers. Both samplers were stored at -20 °C until processing. In addition, procedural and field blank samples related to these samples were analyzed, and none of the analytes under the study were detected. For the in-field trial for the open bed TF-SPME TWA samplers, nine thin film samplers were loaded with the calibrant and transported to the sampling location on dry ice. Upon arrival, samplers were placed individually in copper meshes to prevent biofouling, then subsequently placed in plastic cages before deployment.

RESULTS AND DISCUSSION

Selection of the coating and desorption solvent. Selection of the coating and desorption solvent. In order to find the optimum SPME coating for the extraction of the analytes of interest, three different extractive phases (i.e., WAX-PS-DVB, C18, and HLB) were prepared in blade format and evaluated. Evaluations of coating and desorption solvent were performed simultaneously by considering the extraction capability, observed carryover in each coating, and potential application for TWA sampling. The results indicated that the MeOH/ACN/IPA (50/25/25, v/v/v) yielded the best recovery and the lowest carryover (less than 4%) in comparison to other desorption solvents. HLB and C18 extractive phases showed enhanced extraction abilities for hydrophilic and hydrophobic compounds, respectively. The WAX-PS-DVB coating was not considered for further studies, as the extraction efficacies for most of the analytes were low and carryover was high in comparison with C18 and HLB coatings. The obtained results for the coating and desorption solvent optimization experiments are shown in Table S4 A-J.

Desorption time was also optimized, where 15 and 30 min were found as optimum desorption times for HLB and C18 coatings, respectively, using vortex agitation at 1500 rpm (Figure S2).

After selection of the extraction phases and desorption solution, the necessity of performing a preconditioning step for the extraction phases was evaluated in two experiments. In the first experiment, prior to extraction, the extraction phases were conditioned in MeOH/H2O (50/50, v/v) for 30 min. In the second experiment, extraction was performed directly with dry coating without preconditioning. The

obtained results for extraction with HLB coated blades revealed no significant difference in extraction efficiencies between conditioned and non-conditioned coatings. Conversely, the extraction efficiencies of the C18 coated blades were affected by presence or absence of a conditioning step, revealing higher recoveries when the conditioning step was used. (Data not shown). Therefore, the C18 coating was preconditioned for 30 min in MeOH/H2O (50/50, v/v) before extractions.

Loading of the calibrant on open bed TF-SPME. C18 was used as a coating in the TWA passive sampler in open bed configuration. The initial loading of the calibrant (Ben-3-d5) was optimized and subsequently used for evaluation and on-site sampling. The amount of calibrant on the coating should be sufficient to be detected by the instrument after sampling. Loading was performed by extraction from an aqueous solution composed of 100 ng mL^{-1} of the calibrant in a 2mL amber vial for 60 min at 1500 rpm agitation. The amount of loaded calibrant was calculated after desorption and analysis by the instrument, and quantified by external calibration. The relative standard deviation of the loading procedure was less than 7% (Figure S7).

Calculation of diffusion coefficients for uncharged and charged molecules. The diffusion coefficients for uncharged and charged organic molecules are calculated with the following equations:

$$D_{w=}\frac{1.326\times10^{-4}}{\eta w^{1.14}V^{0.589}} \quad \text{(S2)}$$

$$D_W = \frac{RT}{F^2}\left(\frac{\frac{1}{n^+}+\frac{1}{n^-}}{\frac{1}{\lambda_+^\circ}+\frac{1}{\lambda_-^\circ}}\right) \quad \text{(S3)}$$

Where D_W is the liquid-phase diffusion coefficient at infinite dilution, cm^2s^{-1};R is the universal gas constant, 8.314 J (mol· K)$^{-1}$; T is the absolute temperature, K (273 ◦C); n^+ is cation valence and n– anion valence; F is Faraday's constant, 96,500 Ceq^{-1}; $\lambda\circ^+$is the limiting positive ionic conductance, cm2· Seq^{-1}, and $\lambda\circ^-$the limiting negative ionic conductance, cm^2· Seq^{-1}.Limiting ionic conductance values of Ben-4 and PBSA were obtained by the conductivity method, and measured at 30 and 25cm^2· Seq^{-1}, respectively.[8]

Determination of distribution coefficient. The extraction time profiles of the hydrophobic analytes (TCS, TCC, OMS, OCR and BM-DBM) for the TF-SPME C18 coating were investigated in the aqueous standard generator system. TF-SPME coated samplers were placed in the sampling chamber at 800 rpm from 30-7230 min in triplicate. Equilibrium time was defined as the time when the extracted amount was statistically constant. The distribution coefficient was obtained based on equation S4:

$$K_{fs}V_f = \frac{n}{c_0} \quad \text{(S4)}$$

When the amount of extracted analyte at equilibrium and the initial concentration are known. The volume of the thin film blade coatings was calculated based on the length (l = 20 mm) and thickness (b = 200μm) of the coating, and the width (w = 2.5 mm) and depth (d = 0.7 mm) of the blades, using the following equation[9]:

$$Vf = 2[lb(w + 2b)] + 2[lb(d + 2b)] + [b(\text{d+2b})(\text{w+2b})] \quad \text{(S5)}$$

Limit of detection of the TWA samplers. The equation for SPME is written in equation S6, and can be simplified to equation S7 when $V_s >> K_{fs}V_f$ in the aqueous standard generator system.

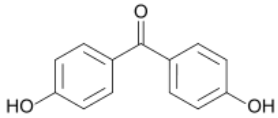
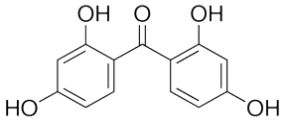
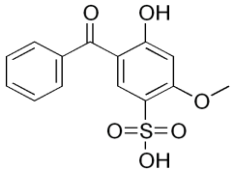
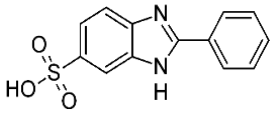
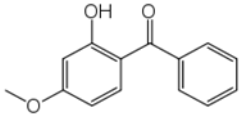
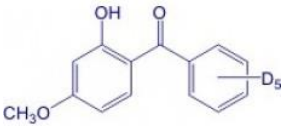
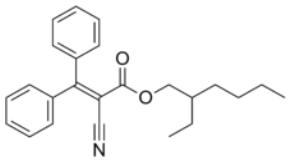
$$n = \frac{K_{fs}V_f C_0 V_s}{K_{fs}V_f + V_s} \quad \text{(S6)}$$

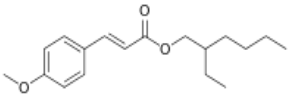
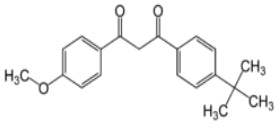
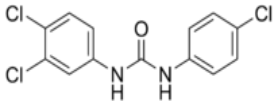
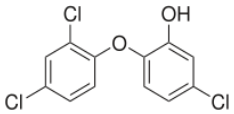
$$n = K_{fs}V_f C_0 \quad \text{(S7)}$$

Equation S7 was used for calculation of the LOD of the passive sampler when n (absolute instrument detection limit) and the blade constant were known. The absolute instrument detection limit was obtained by multiplying instrument detection limit in volume of injection. For the retracted device, equation 1 was used for calculating the limit of detection when sampling time, diffusion path, and absolute instrument detection limit were known. The sampling time and diffusion path and inner diameter of the sampler were 90 days and 10.0 mm, 0.79 mm, respectively.

Limit of detection of the grab samplers. The limit of detection for the equilibrium on-site passive sampler with HLB TF-SPME was calculated based on instrument absolute limit of detection (ng) and blade constant by using equation S1. For bottle grab sampling, S/N=3 was used for calculating the limit of detection of the external calibration SPME method. Limits of detection for both procedures are shown in Table S5.

Table S1. Physical-chemical properties of UV blockers and biocide compounds

Compound	Chemical Structure[e]	Log P	pKa	Water solubility (mg/L)	TWA Sampler
Ben-1		2.9[b]	7.53[b]	236[b]	Retracted device
Ben-2		2.1[b]	6.98[b]	399[b]	Retracted device
Ben-4		0.37[a]	-0.7[b]	250000[a]	Retracted device
PBSA		1.03[b]	-0.87[b]	23600[d]	Retracted device
Ben-3		3.8[b]	7.56[b]	68.6[a]	Retracted device Open bed
Ben 3-d5		nd	nd	nd	Calibrant
OCR		6.4[a]	na	0.001[c]	Open bed

Compound	Chemical Structure	Log P	pKa	Water solubility (mg/L)	TWA Sampler
OMC		5.8[a]	na	0.003[c]	Open bed
BM-DBM		4.5[a]	9.74[b]	0.008[c]	Open bed
TCC		4.9[b]	12.77[b]	0.0237[b]	Open bed
TCS		4.76[a]	8.14[b]	10[a]	Open bed

nd; no data

na; not applicable

[a] Experimental values, from database of physicochemical properties. Syracuse Research Corporation:

http://www.syrres.com/esc/physdemo.htm, accessed on Oct, 2015

[b] Software-calculated value, from SciFinder Scholar Database 2006: ttp://www.cas.org/products/sfacad/

[c]Unilever internal report (2013). UV – filters Partition coefficient (n-octanol/water): slow stirring method and water solubility (column generator method)

[d]Estimated value, from database of Royal Society of Chemistry's databases; Chemspider: http://www.chemspider.com, accessed on Oct,2015

[e]Chemical structure, from database of Royal Society of Chemistry's databases; Chemspider: http://www.chemspider.com, accessed on Oct,2015

Table S2. Mass spectrometry conditions for the analytes: Optimized ionization source values

Negative mode: ion source gas 1 (GS1) = +40, ion source gas 2 (GS2) = +40, curtain gas = +50, collision gas = 10, spray ionization voltage = -4500 V, and temperature = 500◦C.
Positive mode: Negative mode: ion source gas 1 (GS1) = +40, ion source gas 2 (GS2) = +60, curtain gas = +50, collision gas = 10, spray ionization voltage = 5500 V, and temperature = 500◦C.
*DP=Declutteringpotential,EP= entrance potential, CE=Collision energy, and CXP=Collision cell exit potential

Compound	Q1 mass (amu)	Q3 mass (amu)	*CE (V)	*CXP (V)	*DP (V)	*FP (V)	Ionization mode
TCS	287	35	-58	-58	-32	-32	Negative
Ben-2	245	109	-72	-72	-31	-31	Negative
TCC	315	162	-69	-69	-22	-22	Negative
Ben-4	307	227	-96	-96	-32	-32	Negative
PBSA	273	193	-84	-84	-36	-36	Negative
Ben-1	213	169	-85	-85	-29	-29	Negative
OCR	362	232	39	5	5	16	Positive
BM-DBM	311	135	55	8	8	24	Positive
BM-DBM	311	177	55	8	8	15	Positive
Ben-3	229	151	70	6	6	11	Positive
Ben 3-d5	234	151	73	10	10	11	Positive
Ben 3-d5	234	110	40	10	10	15	Positive
OMC	291	161	37	4	4	11	Positive

Table S3. Summary of experimental conditions used throughout the evaluation of coatings and desorption solvents

1) Preconditioning conditions		2) Rinsing conditions	
Time	30 min	Time	5 sec
Agitation	1500 rpm	Agitation	1500 rpm
Solvent	50/50 (MeOH/H_2O)	Solvent	H_2O
Volume	1800 µL	Volume	1800 µL
3) Desorption conditions		4) Reconstitution	
Time	30 min	Time	2 min
Agitation	1500 rpm	Agitation	1500 rpm
Volume	1800 µL	Volume	300 µL
Desorption solvent	50:25:25 (MeOH/ACN/IPA)	Desorption solvent	50/50 (MeOH/H_2O)

Table S4 (A).Evaluation of various blades in terms of extraction amount and carryover of TCS

Coating	Solvent type	1st desorption ng	RSD %	2nd desorption ng	Carry over %
HLB	A	195.1	4.3	30.7	13.6
	B	243.1	9.3	42.6	14.9
	C	54.0	1.6	37.7	41.1
	D	98.5	12.5	60.9	38.2
C18	A	211.2	11.8	7.5	3.4
	B	133.7	12.3	1.6	1.2
	C	147.4	13.3	5.7	3.8
	D	122.2	12.9	5.4	4.2
PS-DVB	A	30.3	3.4	14.1	31.7
	B	23.9	16.8	8.8	26.8
	C	24.7	10.3	13.0	34.5
	D	45.6	10.0	17.6	27.9

A: (50/25/25) MeOH/IPA/ACN
B: (40/40/20) MeOH/ACN/H_2O
C: (50/50) ACN/H_2O
D: (80/20) MeOH/H_2O

Table S4 (B).Evaluation of various blades in terms of extraction amount and carryover of Ben-2

Coating	Solvent type	1st desorption ng	RSD %	2nd desorption ng	Carry over %
HLB	A	954.0	6.7	14.8	1.3
	B	897.6	4.4	136.6	13.2
	C	385.3	1.5	104.0	21.3
	D	553.8	5.8	170.3	23.5
C18	A	97.4	4.9	2.2	2.2
	B	77.4	9.2	3.1	3.9
	C	64.0	8.8	1.0	1.6
	D	44.5	2.8	1.2	2.7
PS-DVB	A	124.2	8.5	9.0	6.7
	B	119.9	11.3	12.3	9.3
	C	146.1	11.5	20.0	12.1
	D	72.0	7.7	5.4	6.9

Table S4 (C).Evaluation of various blades in terms of extraction amount and carryover of TCC

Coating	Solvent type	1st desorption ng	RSD %	2nd desorption ng	Carry over %
HLB	A	44.4	4.5	20.7	31.8
	B	46.0	5.8	20.9	31.3
	C	6.8	12.7	4.7	40.9
	D	10.1	11.7	13.9	57.8
C18	A	40.4	13.4	0.4	1.0
	B	19.8	12.3	0.2	1.5
	C	19.8	11.9	0.3	1.5
	D	18.6	6.0	0.2	1.2
PS-DVB	A	5.4	12.6	2.6	32.2
	B	2.5	11.3	0.7	21.6
	C	2.1	12.7	0.8	27.0
	D	2.7	13.3	1.3	32.3

Table S4 (D).Evaluationofvarious blades in terms of extraction amount and carryover of Ben-4

Coating	Solvent type	1st desorption ng	RSD %	2nd desorption ng	Carry over %
HLB	A	57.9	9.5	1.5	2.5
	B	53.2	12.8	0.6	1.2
	C	23.2	6.3	0.9	3.7
	D	31.8	8.9	1.9	5.7
C18	A	8.3	0.9	1.0	10.7
	B	2.2	0.4	1.0	32.8
	C	2.2	8.1	0.6	21.9
	D	3.0	12.8	2.0	39.3
PS-DVB	A	19.2	8.5	3.3	14.6
	B	28.7	11.4	2.3	7.4
	C	22.9	6.8	1.9	7.8
	D	27.2	10.8	1.1	4.0

Table S4 (E).Evaluation of various blades in terms of extraction amount and carryover of PBSA

Coating	Solvent type	1st desorption ng	RSD %	2nd desorption ng	Carry over %
HLB	A	12.6	8.1	0.5	3.8
	B	11.8	9.2	0.6	4.8
	C	6.7	5.1	0.9	11.8
	D	7.8	7.2	1.9	19.6
C18	A	6.8	5.2	0.9	11.7
	B	5.3	3.7	1.3	19.7
	C	5.3	6.1	0.6	10.2
	D	4.8	8.1	1.5	23.8
PS-DVB	A	4.6	5.9	1.8	28.1
	B	4.8	9.1	1.7	26.2
	C	4.9	8.1	1.9	27.9
	D	5.1	9.1	1.1	17.7

Table S4 (F).Evaluation of various blades in terms of extraction amount and carryover of Ben-1

Coating	Solvent type	1st desorption ng	RSD %	2nd desorption ng	Carry over %
HLB	A	857.4	10.4	30.2	3.4
	B	750.6	1.9	104.7	12.2
	C	216.0	7.6	84.0	28.0
	D	565.2	9.4	169.0	23.0
C18	A	198.3	8.6	5.8	2.8
	B	19.3	4.1	0.5	2.5
	C	110.3	9.3	2.2	2.0
	D	124.2	8.9	1.5	1.2
PS-DVB	A	131.2	7.7	12.8	8.9
	B	111.9	11.6	15.7	12.3
	C	102.5	10.2	22.3	17.9
	D	86.8	4.5	9.3	9.7

Table S4 (G).Evaluationofvarious blades in terms of extraction amount and carryover of OCR

Coating	Solvent type	1st desorption ng	RSD %	2nd desorption ng	Carry over %
HLB	A	12.0	7.4	4.9	28.9
	B	7.1	16.1	15.3	68.3
	C	2.2	9.3	1.3	36.7
	D	3.7	11.5	1.8	33.0
C18	A	11.1	11.2	0.3	2.6
	B	5.7	12.0	0.3	4.4
	C	6.2	10.3	1.1	15.0
	D	3.4	13.2	1.3	27.3
PS-DVB	A	4.6	12.9	1.7	26.7
	B	1.7	0.7	0.6	27.0
	C	0.9	3.0	0.6	40.8
	D	2.0	3.5	0.0	1.8

Table S4 (H).Evaluationofvarious blades in terms of extraction amount and carryover of BM-DBM

Coating	Solvent type	1st desorption ng	RSD %	2nd desorption ng	Carry over %
HLB	A	2.8	10.0	0.1	4.0
	B	2.0	10.1	2.1	52.0
	C	0.6	7.7	0.8	57.9
	D	0.8	5.5	1.7	68.4
C18	A	7.9	4.7	0.5	5.7
	B	5.9	7.9	0.7	10.1
	C	1.6	7.0	0.6	28.1
	D	2.3	5.0	0.9	27.6
PS-DVB	A	1.9	3.3	1.9	50.6
	B	0.7	8.2	0.6	44.4
	C	0.6	10.0	0.7	53.3
	D	0.9	12.5	0.4	30.7

Table S4 (I).Evaluation ofvarious blades in terms of extraction amount and carryover of OMC

Coating	Solvent type	1st desorption ng	RSD %	2nd desorption ng	Carry over %
HLB	A	5.8	13.9	1.9	25.0
	B	2.8	10.4	1.6	36.2
	C	8.6	6.9	3.7	30.1
	D	1.5	6.0	0.8	35.1
C18	A	12.1	7.0	0.4	3.2
	B	1.9	9.8	0.6	23.2
	C	7.6	1.7	4.5	5.9
	D	2.5	7.9	0.2	8.2
PS-DVB	A	10.1	8.3	1.9	16.0
	B	7.6	7.1	0.8	9.2
	C	0.6	2.0	0.3	31.2
	D	1.5	7.3	0.1	3.4

Table S4 (J).Evaluation of various blades in terms of extraction amount and carryover of Ben-3

Coating	Solvent type	1st desorption ng	RSD %	2nd desorption ng	Carry over %
HLB	A	652.1	1.8	23.0	3.4
	B	748.2	6.9	98.5	11.6
	C	189.8	6.7	94.5	33.2
	D	607.1	8.0	197.8	24.6
C18	A	540.0	7.5	23.3	4.1
	B	106.7	7.4	2.6	2.4
	C	311.4	2.1	7.2	2.3
	D	279.6	5.5	10.6	3.6
PS-DVB	A	61.4	7.6	16.8	21.5
	B	57.9	4.2	10.2	15.0
	C	32.7	7.3	16.5	33.5
	D	52.3	7.5	11.4	17.9

Table S5. Limits of detection of the TWA sampler, grab samplers, and instrument

	LOD of TWA samplers and grab samplers (ngL^{-1})				
	Ben-1	Ben-4	PBSA	Ben-2	Ben-3
Thin filmretracted device(HLB)	700	800	160	130	500
On-site equilibrium sampling	1.0	250	100	0.50	1.0
Instrument	500	2500	500	100	1000

	LOD of TWA samplers and grab samplers (ngL^{-1})					
	OCR	Ben-3	OMC	TCS	TCC	BM-DBM
Open bed TWA sampler (C18)	0.20	0.50	0.04	0.20	0.10	0.01
External calibration SPME	20	10	20	10	0.1	3
Instrument	1000	1000	500	100	1	160

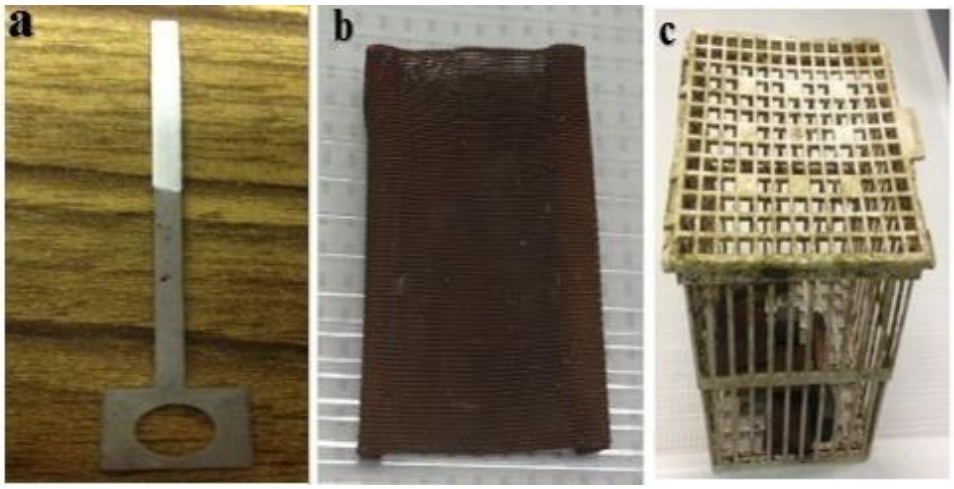


Figure S1. Thin-film passive samplers: (a) C18 thin-film sampler, (b) copper bag, (c) samplers' cage

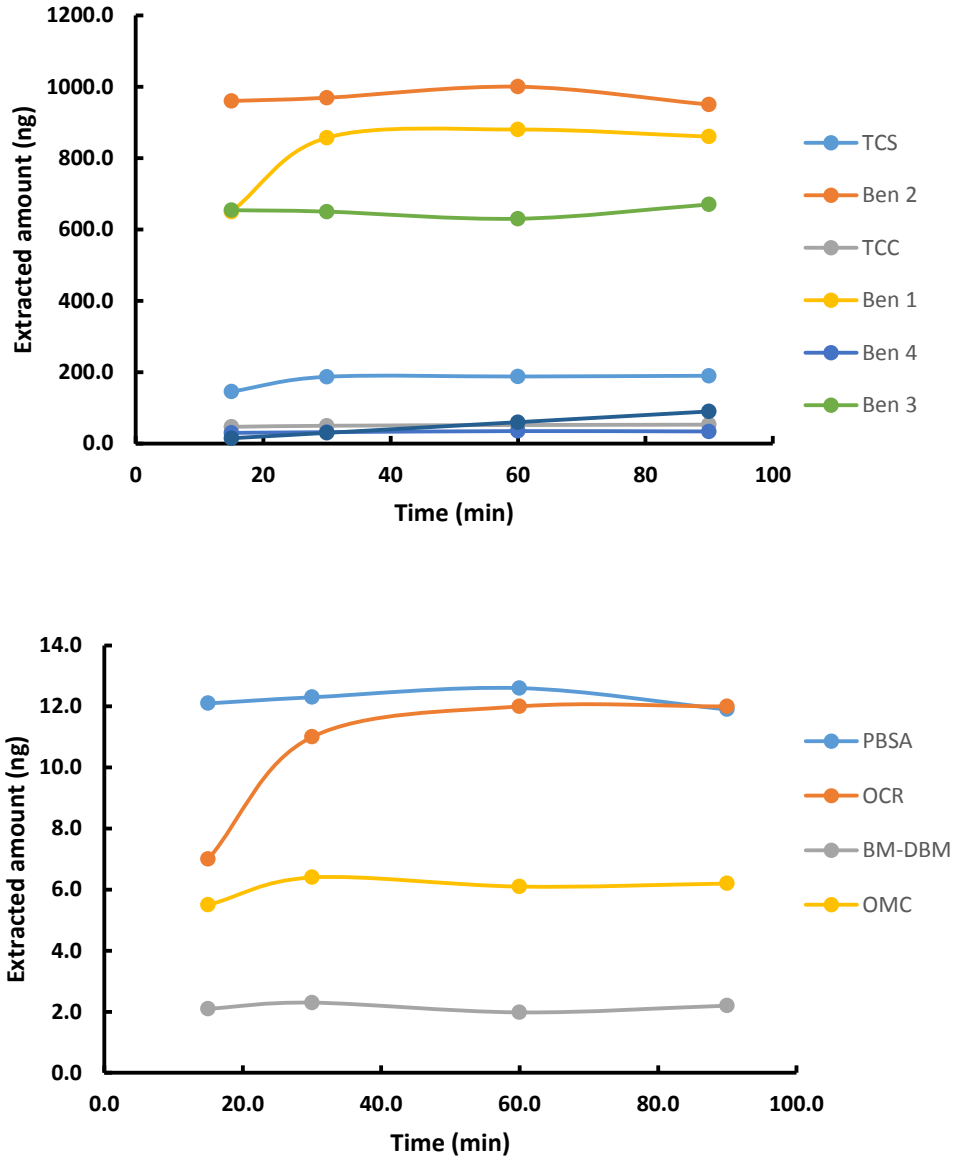


Figure S2. Desorption time profile for analytes under study, extraction from aqueous standard generator system

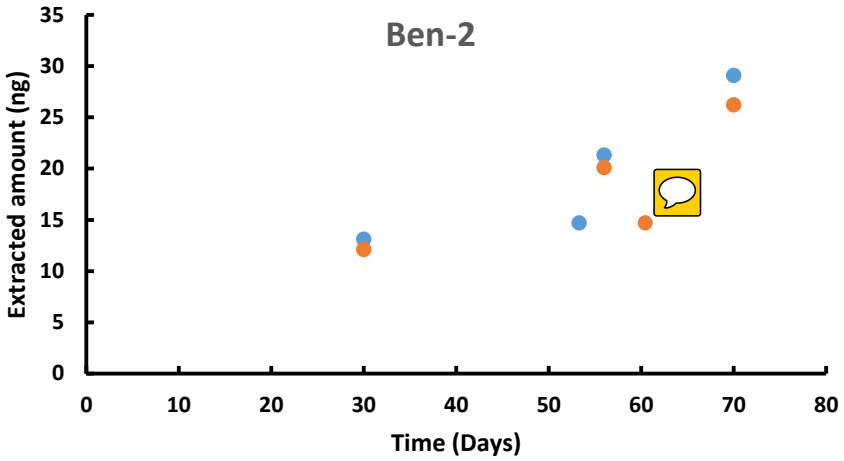
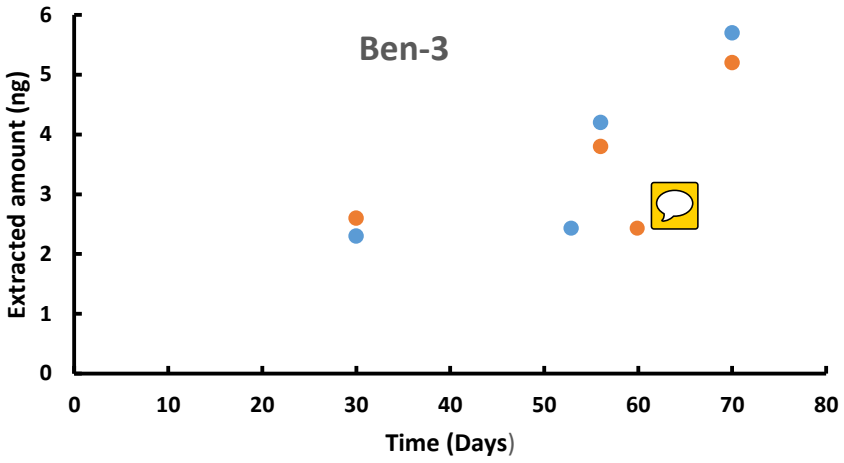
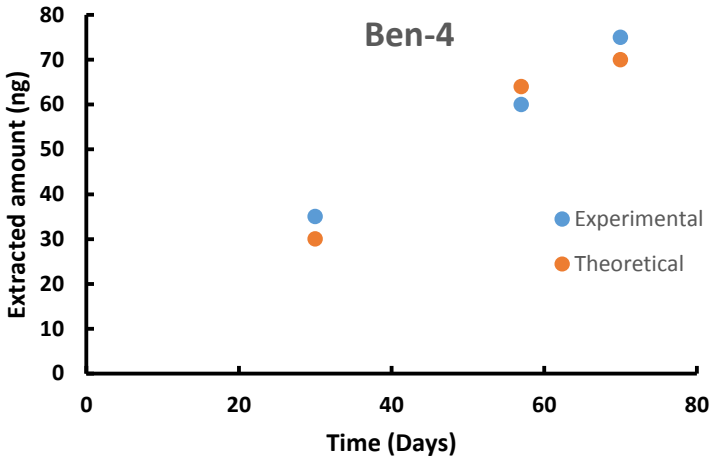


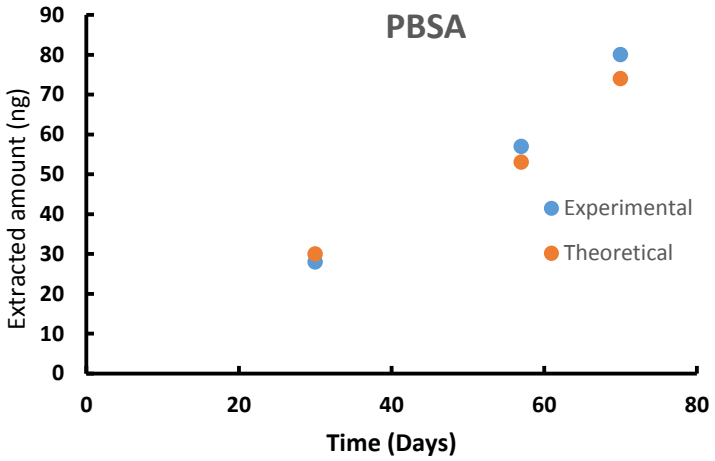
Figure S3. TWA concentration of Ben-2 using retracted TF-SPME (diffusion path: 10 mm and analyte concentration in the aqueous standard generator system:118 $ngmL^{-1}$)



FigureS4. TWA concentration of Ben-3 using retracted TF-SPME (diffusion path: 10 mm and analyte concentration in the aqueous standard generator system: 28 $ngmL^{-1}$)



FigureS5. TWA concentration of Ben-4 using retracted TF-SPME (diffusion path: 10 mm and analyte concentration in the aqueous standard generator system: 459 $ngmL^{-1}$)



FigureS6. TWA concentration of PBSA using retracted TF-SPME (diffusion path: 10 mm and analyte concentration in the aqueous standard generator system: 377 ngmL^{-1})

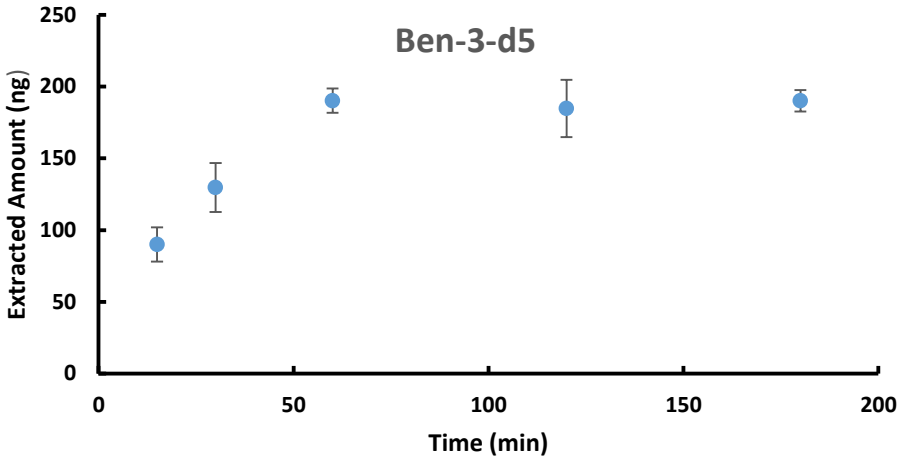


Figure S7. Extraction time profile of Ben-3-d5 (n=3)

Figure S8. Coordination of the sampling location

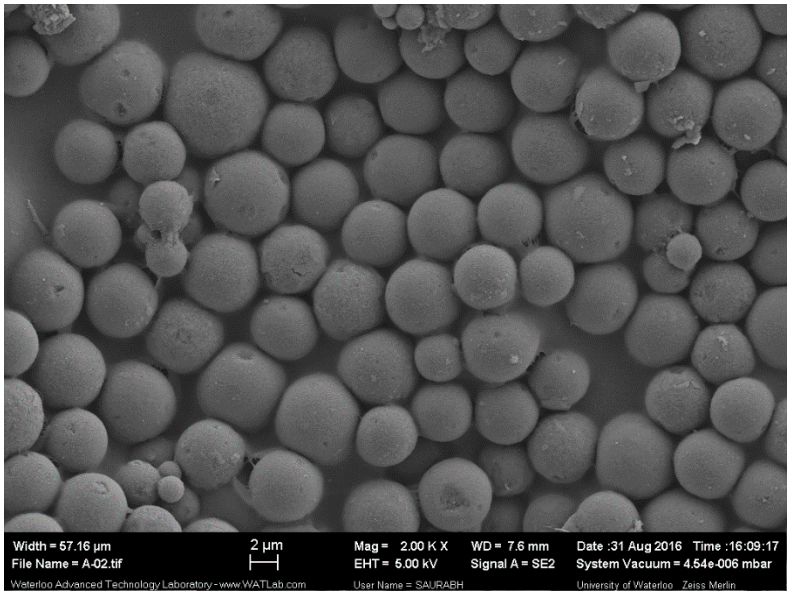


Figure S9. SEM image of the morphology of the C18 coating after 5 days sampling (x 2000 magnification)

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