Electronic Supplementary Material

Passive sampling of organic contaminants across the water-sediment interface of an urban stream

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Contents

ESM1.A. Instrumental analysis

Table ESM1.A-1 Overview on methods used for instrumental analysis by LC/MS. *CAL*: calibration. *ESI*: electrospray ionization. *IS*: isotope-labeled internal standard. *IV*: injection volume. *NPW*: NANOpure™ water. *MS*: mass spectrometric.

	Substance Screening	***Field application***
Sample type	passive sampler (PS) extracts	PS extracts
Instrument	QExactive+	QExactive+
MS scans	FullMS + Top5 data-dependent (DD) MS2	FullMS + Top5 DD MS2
Mass resolution	MS1: 140'000 MS2: 17'500	MS1: 140'000 MS2: 17'500
ESI	pos/neg separate	pos/neg separate
Mass range (m/z)	100 to 1‘000	100 to 1‘000
IV [µL]	20	100
Column	XBridge C18, 2.1x50 mm, 3.5 µm, Waters, USA	Atlantis T3, 3 x 150 mm, 3 µm, Waters, USA
Eluents	*A*: MeOH, 0.1V% FA, *B*: NPW, 0.1V% FA	*A*: MeOH, 0.1V% FA, *B*: NPW, 0.1V% FA
Chrom. gradient	No. | Time | A% | B% | C% | D% | µL/min	No. | Time | A% | B% | C% | D% | µL/min
	0 | 0.00 | 90.0 | 10.0 | 0.0 | 0.0 | 200 1 | 4.00 | 50.0 | 50.0 | 0.0 | 0.0 | 200 2 | 17.00 | 5.0 | 95.0 | 0.0 | 0.0 | 200 3 | 25.00 | 5.0 | 95.0 | 0.0 | 0.0 | 200 4 | 25.10 | 90.0 | 10.0 | 0.0 | 0.0 | 200 5 | 29.00 | 90.0 | 10.0 | 0.0 | 0.0 | 200	0 | 0.00 | 95.0 | 5.0 | 0.0 | 0.0 | 300 1 | 1.50 | 95.0 | 5.0 | 0.0 | 0.0 | 300 2 | 17.50 | 5.0 | 95.0 | 0.0 | 0.0 | 300 3 | 25.50 | 5.0 | 95.0 | 0.0 | 0.0 | 300 4 | 26.00 | 95.0 | 5.0 | 0.0 | 0.0 | 300 5 | 31.00 | 95.0 | 5.0 | 0.0 | 0.0 | 300
Detection	0.5 to 24.5 min	0.5 to 28 min
CAL levels	0, 1, 5, 10, 50, 100, 500, 1'000 xray: x10, PFC: x1/10	0, 0.5, 1, 5, 10, 20, 50, 100, 200, 500, 1'000 xray: x10, PFC: x1/10
Concentration unit	ng/mL	ng/mL
IS [ng] on column	4 ng, xray: x10, PFC: x0.1	10 ng, xray: x10, PFC: x0.1

Table ESM.A-1 Overview on methods used for instrumental analysis by LC/MS (continued).

	Uptake experiment	***Uptake experiment***
Sample type	PS extracts	water samples (grab)
Instrument	QExactive	QExactive
MS scans	FullMS + Top5 DD MS2	FullMS + Top5 DD MS2
Mass resolution	MS1: 140'000 MS2: 17'500	MS1: 140'000 MS2: 17'500
ESI	pos/neg separate	pos/neg separate
Mass range (m/z)	100 to 1000	100 to 1000
IV [µL]	20	100
Column	Atlantis T3, 3 x 150 mm, 3 µm, Waters, USA	Atlantis T3, 3 x 150 mm, 3 µm, Waters, USA
Eluents	*A*: MeOH, 0.1V% FA, *B*: NPW, 0.1V% FA	*A*: MeOH, 0.1V% FA, *B*: NPW, 0.1V% FA
Chrom. gradient	No. | Time | A% | B% | C% | D% | µL/min	No. | Time | A% | B% | C% | D% | µL/min
	0 | 0.00 | 95.0 | 5.0 | 0.0 | 0.0 | 300 1 | 1.50 | 95.0 | 5.0 | 0.0 | 0.0 | 300 2 | 17.50 | 5.0 | 95.0 | 0.0 | 0.0 | 300 3 | 25.00 | 5.0 | 95.0 | 0.0 | 0.0 | 300 4 | 25.50 | 95.0 | 5.0 | 0.0 | 0.0 | 300 5 | 29.50 | 95.0 | 5.0 | 0.0 | 0.0 | 300	0 | 0.00 | 95.0 | 5.0 | 0.0 | 0.0 | 300 1 | 1.50 | 95.0 | 5.0 | 0.0 | 0.0 | 300 2 | 17.50 | 5.0 | 95.0 | 0.0 | 0.0 | 300 3 | 25.00 | 5.0 | 95.0 | 0.0 | 0.0 | 300 4 | 25.50 | 95.0 | 5.0 | 0.0 | 0.0 | 300 5 | 29.50 | 95.0 | 5.0 | 0.0 | 0.0 | 300
Detection	0.5 to 27 min	0.5 to 27 min
CAL levels	0, 1, 5, 10, 50, 100, 500, 1'000	0, 5, 10, 50, 100, 250, 500, 750, 1'000, 10'000
Concentration unit	ng/mL	ng/L
IS [ng] on column	2 ng	0.5 ng

ESM1.B. Schemes of the setups used for the uptake experiments

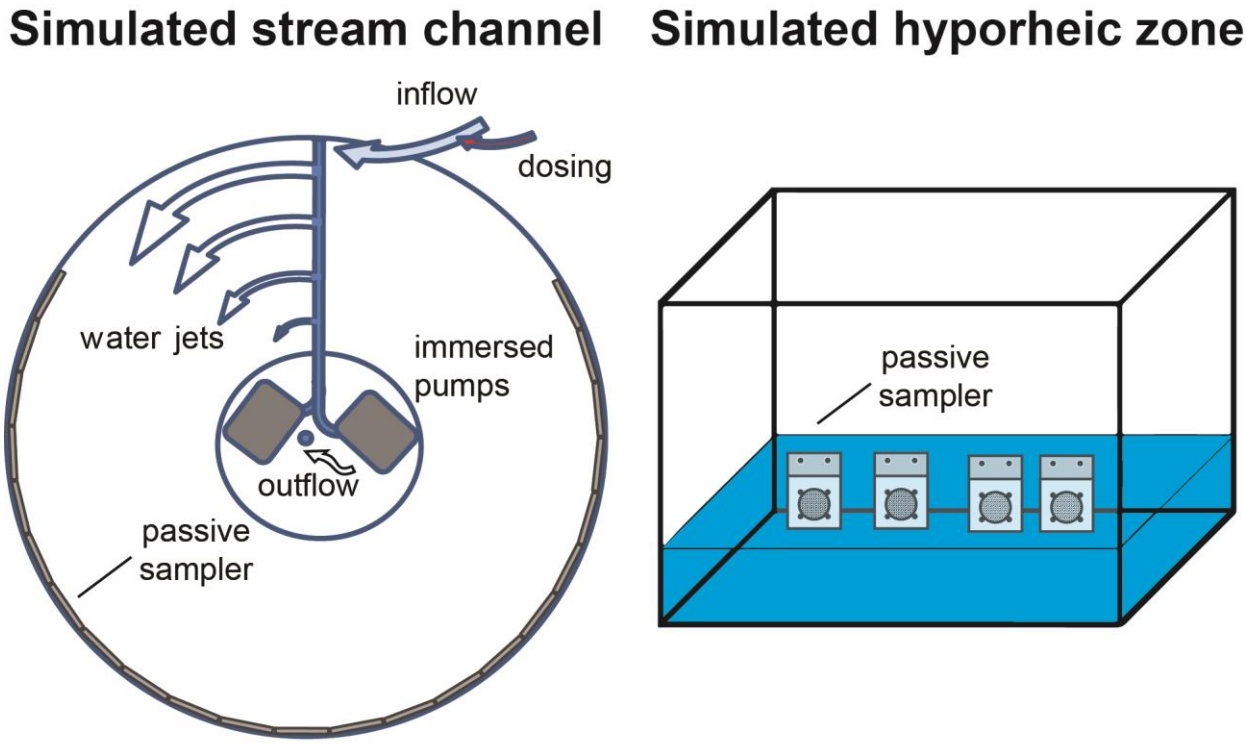


Fig. ESM1.B-1 Scheme of the experimental setups used in the uptake experiments.

ESM1.C. Flow velocity in the circular flume

In the circular flume, 25 passive sampler positions were available during the uptake experiment. To expose passive samplers (presented as numbers in Table S3) to about the same water flow velocity, they were rotated every 24 h three positions counter-clockwise (see Table S3). The flow velocity was measured daily at the start of position 1, between all positions and directly after position 25 using a handheld flowmeter (model MiniAir2, Schildknecht, Switzerland). Flow velocities per sampler ranged from 0.12 to 0.16 m s^{-1} (mean: 0.13 m s^{-1}). After sampler retrieval, empty positions were immediately occupied with dummy samplers.

Table ESM1.C-2 PS positions in the circular flume over the course of the uptake experiments.
Grey level: retrieval after 2 (white), 6 (grey) and 14 days (black).

Days	Hours	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
0	0	18	23	24	57	1	2	7	8	13	14	19	20	3	4	9	10	15	16	21	22	5	6	11	12	17
1	24	11	12	17	18	23	24	57	1	2	7	8	13	14	19	20	3	4	9	10	15	16	21	22	5	6
2	48	22	5	6	11	12	17	18	23	24	57	retrieval								3	4	9	10	15	16	21
3	72	15	16	21	22	5	6	11	12	17	18	23	24	57									3	4	9	10
4	96	4	9	10	15	16	21	22	5	6	11	12	17	18	23	24	57									3
5	120			3	4	9	10	15	16	21	22	5	6	11	12	17	18	23	24	57						
6	144						retrieval								5	6	11	12	17	18	23	24	57			
7	168																	5	6	11	12	17	18	23	24	57
8	192	23	24	57																	5	6	11	12	17	18
9	216	12	17	18	23	24	57																	5	6	11
10	240	5	6	11	12	17	18	23	24	57																
11	264				5	6	11	12	17	18	23	24	57													
12	288							5	6	11	12	17	18	23	24	57										
13	312										5	6	11	12	17	18	23	24	57							
14	336													retrieval												

ESM1.D. Photographs of the setups used for the uptake experiments

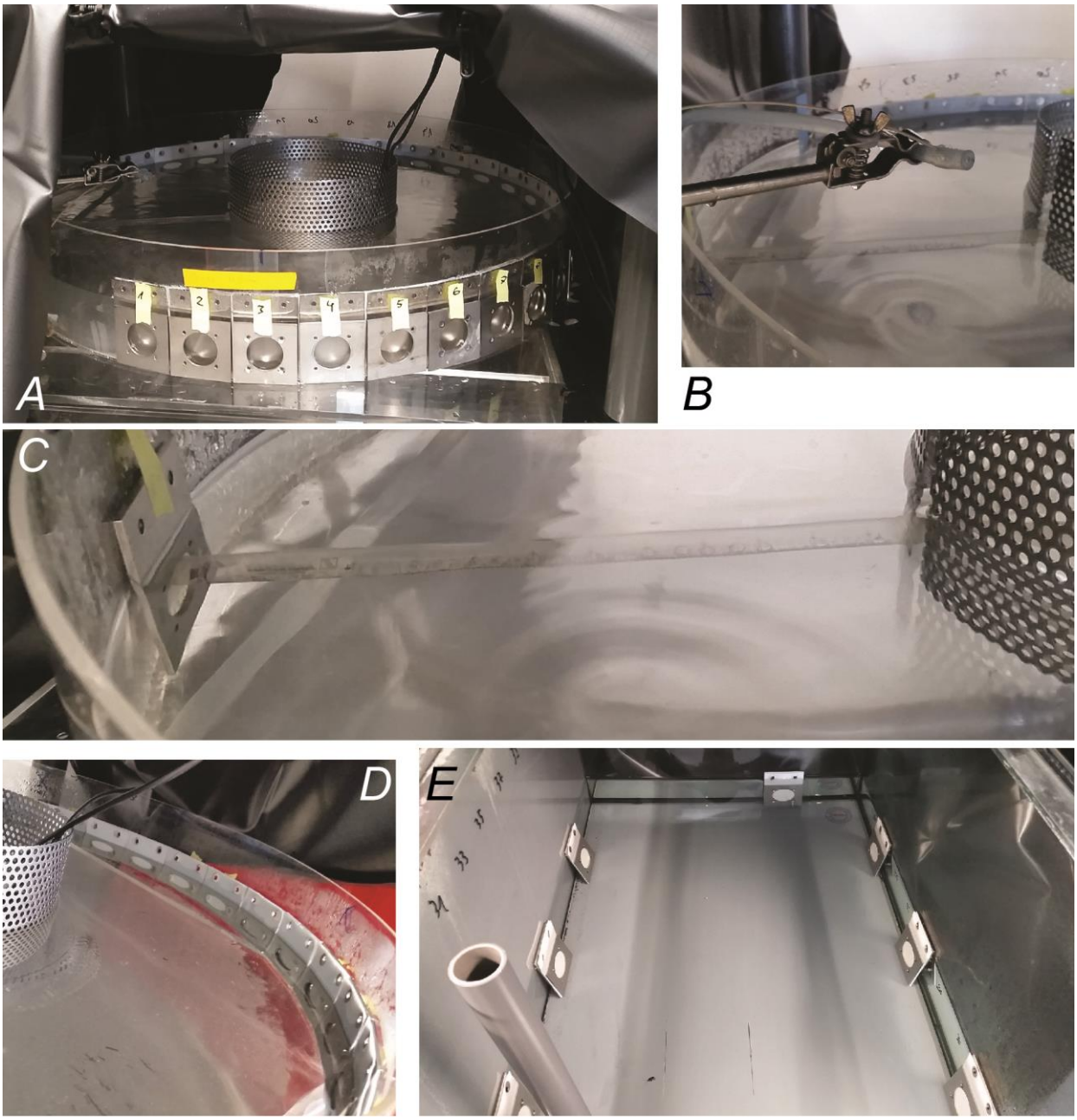


Fig. ESM1.D-2 Photographs of the setups used in the uptake experiments. *A*: circular flume. *B*: outflow of dosing solution into *A*. *C*: pipette with drillings connected to two immersed pumps for inducing water jets in *A*. *D*: positioning of passive samplers along the inner wall of *A*. *E*: aquarium.

ESM1.E. Correlation between Rs, $logD_{OW}$ and speciation

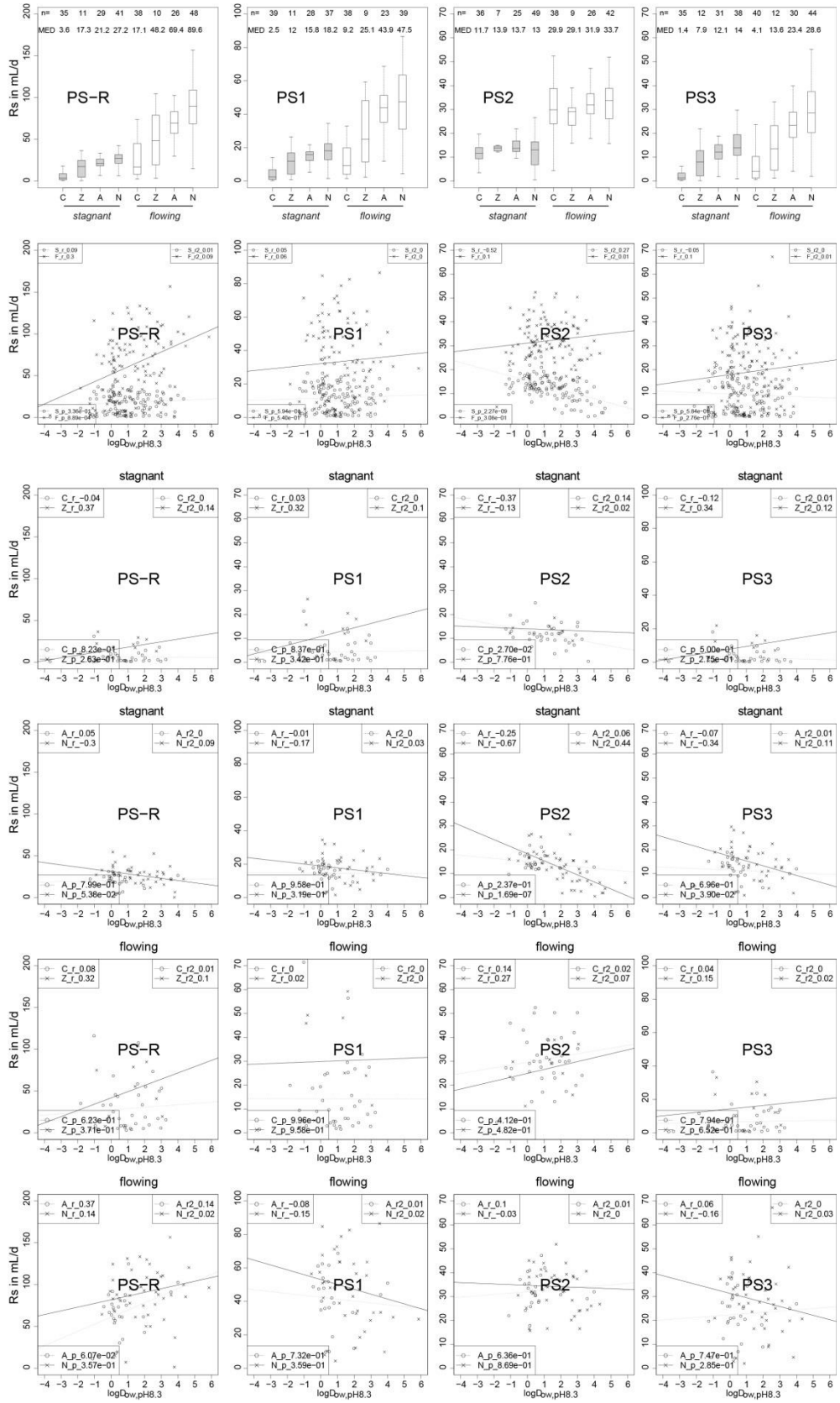


Fig. ESM1.E-3 Correlations between sampling rate (Rs) and substance properties for four different passive sampler configurations (PS-R, PS1, PS2 and PS3). *Top row*: Rs versus substance speciation summarized as boxplots (median, interquartile range). *Second row*: Rs versus $logD_{OW,pH8.3}$ (no distinction of speciation). *Rows 3 and 4*: Rs (stagnant) versus $logD_{OW,pH8.3}$ (distinction of speciation). *Rows 5 and 6*: Rs (flowing) versus $logD_{OW,pH8.3}$ (distinction of speciation).

ESM1.F. Correlation between ΔRs, speciation and $logD_{OW}$

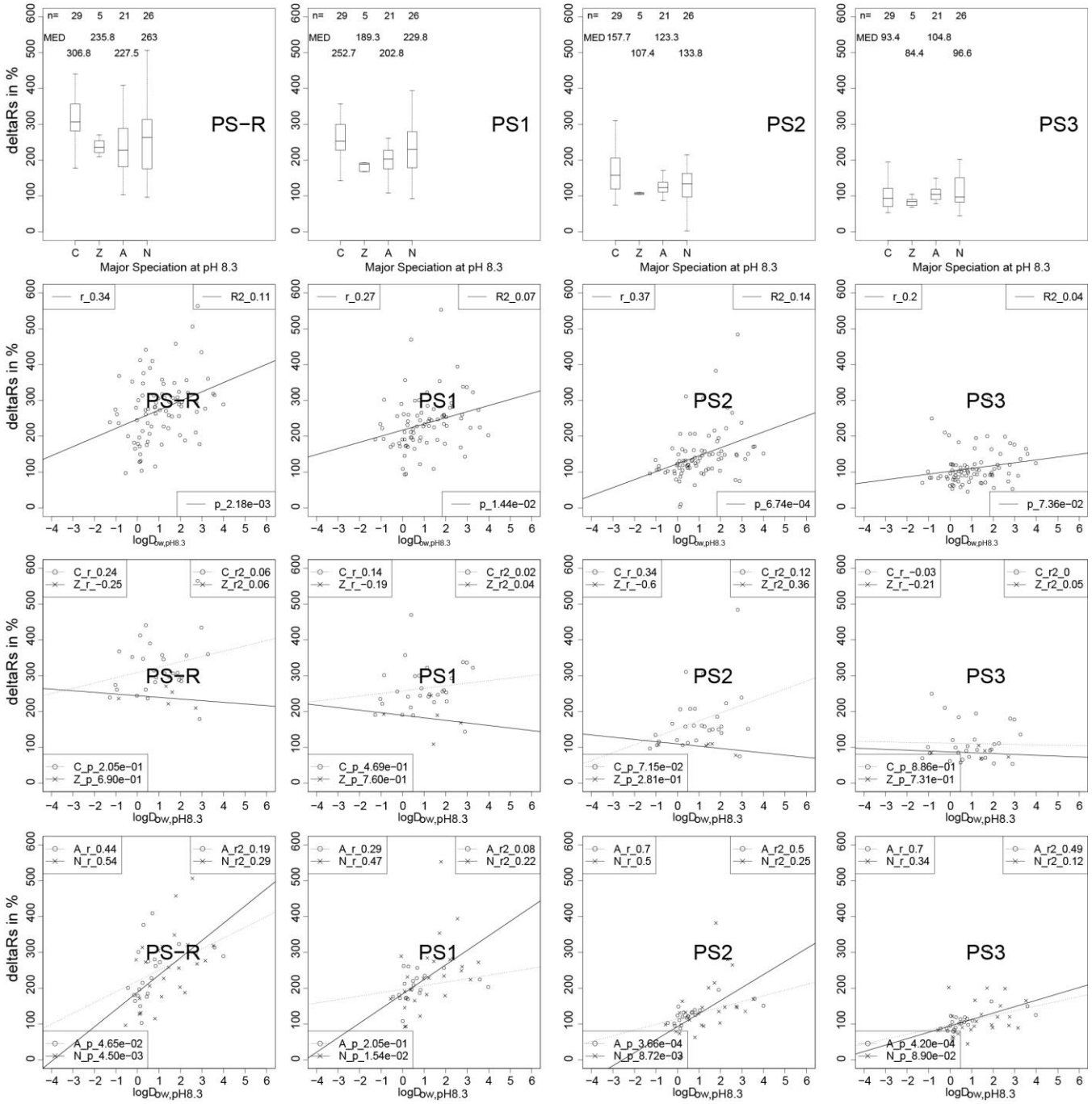


Fig. ESM1.F-4 Correlation between ΔRs (sensitivity of PS uptake towards water flow velocity) and substance properties. *Top row*: ΔRs versus substance speciation. *Second row*: ΔRs versus $logD_{OW,pH8.3}$ (no distinction of speciation). *Rows 3 and 4*: ΔRs versus $logD_{OW,pH8.3}$ (distinction of speciation).

ESM1.G. Linear regression of experimental Rs at stagnant and flowing conditions with correlated errors

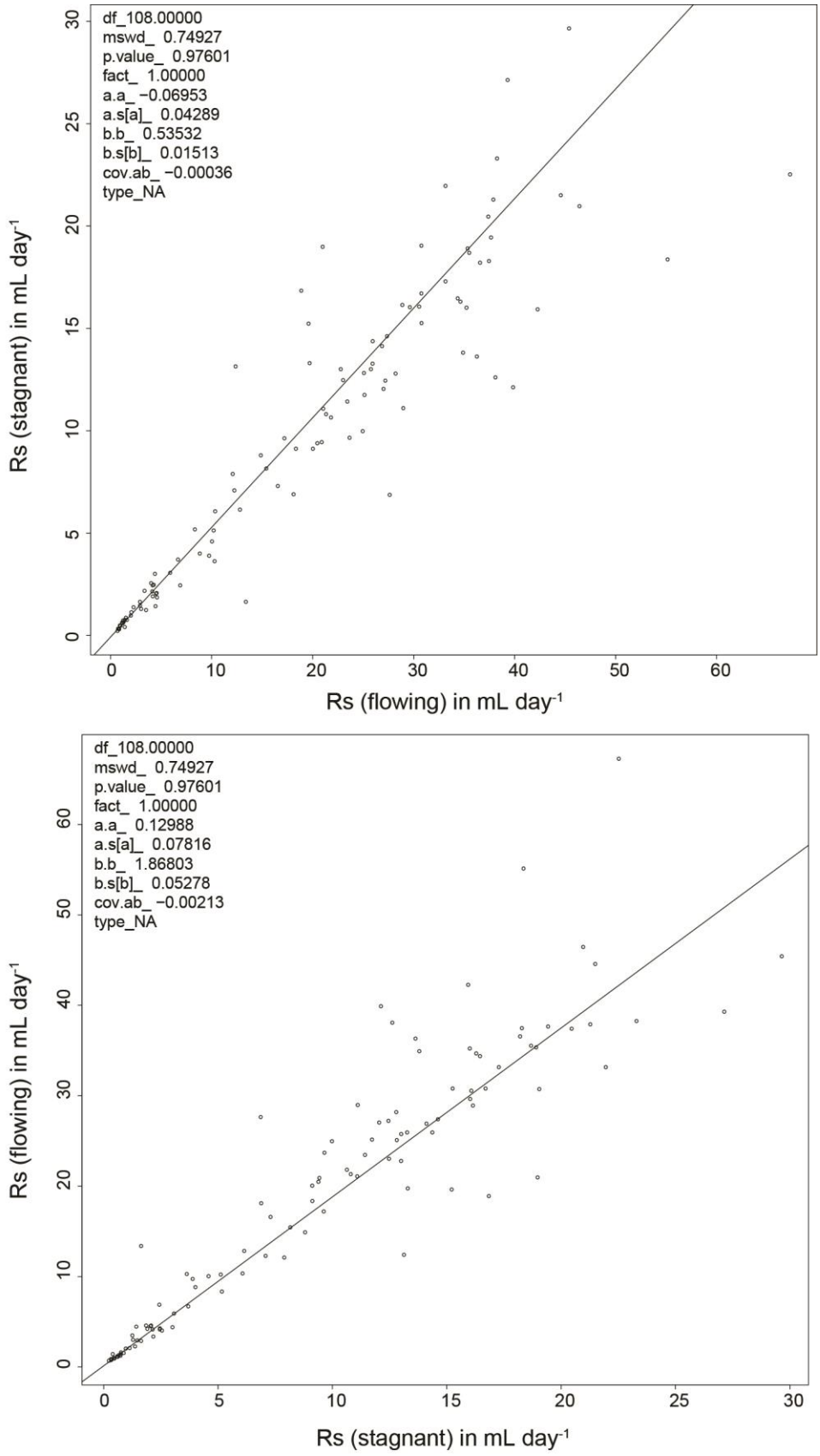


Fig. ESM1.G-5 Linear regression of experimental sampling rates (Rs) at stagnant and flowing conditions considering the correlated errors with the 'York' approach (alpha = 0.05) in the IsoplotR R package (v2.6).

ESM1.H. Installation of PS in the sediment of an urban stream

For the installation of sediment passive samplers, a hollow steel sleeve (Fig. ESM1.H-6, *3*) was slid onto a wooden tip (Fig. ESM1.H-6, *2*) and the latter was placed onto the sediment surface. A hammering cap (Fig. ESM1.H-6, *4*) was placed on top of the steel sleeve to receive hammer blows from a large hammer. Once the sleeve reached the desired depth, passive samplers mounted on a holding device (Fig. ESM1.H-6, *1*) were slid into the sleeve. Finally, the sleeve was slowly pulled out, allowing sediment around the holder to collapse.

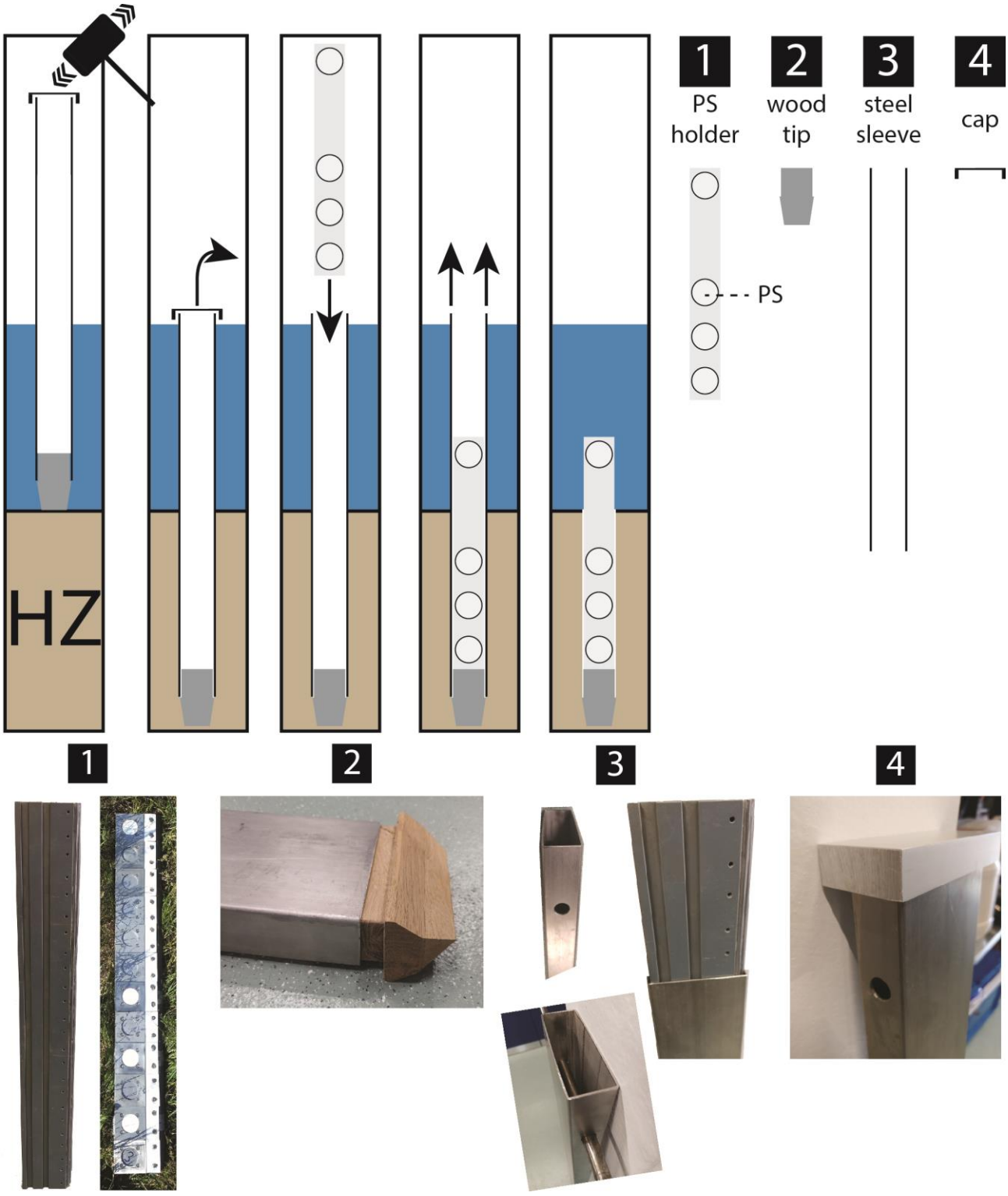


Fig. ESM1.H-6 Field installation of passive samplers in the sediment of an urban stream.

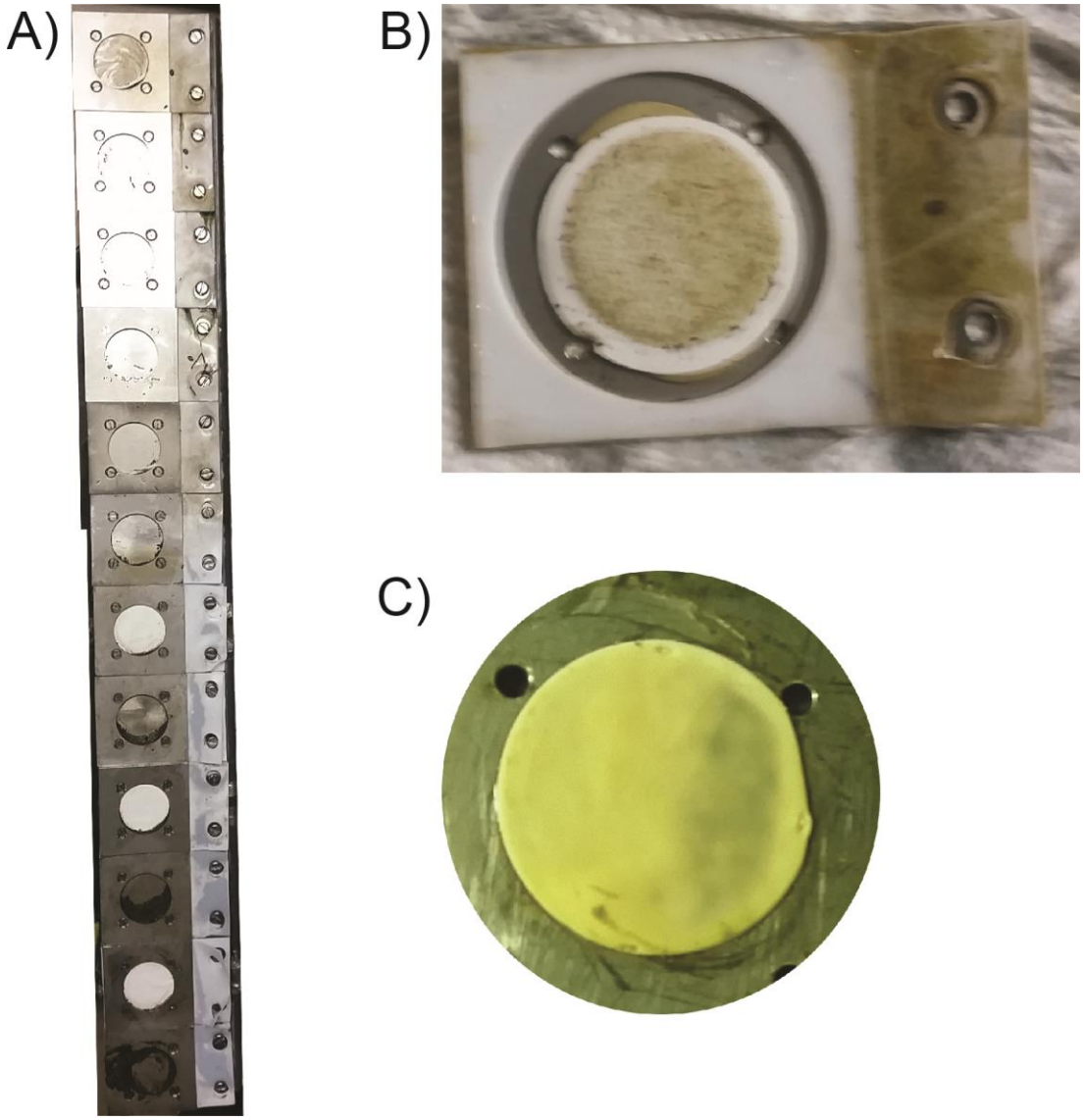


Fig. ESM1.H-7 Visual appearance of passive samplers after field installation. *A*: entire holder 1. *B*: uptake of water matrix constituents into surface water passive sampler. *C*: SDB-RPS disk retrieved from sediment passive sampler showing some discoloration.

ESM1.I. Comparison of passive sampling against active sampling

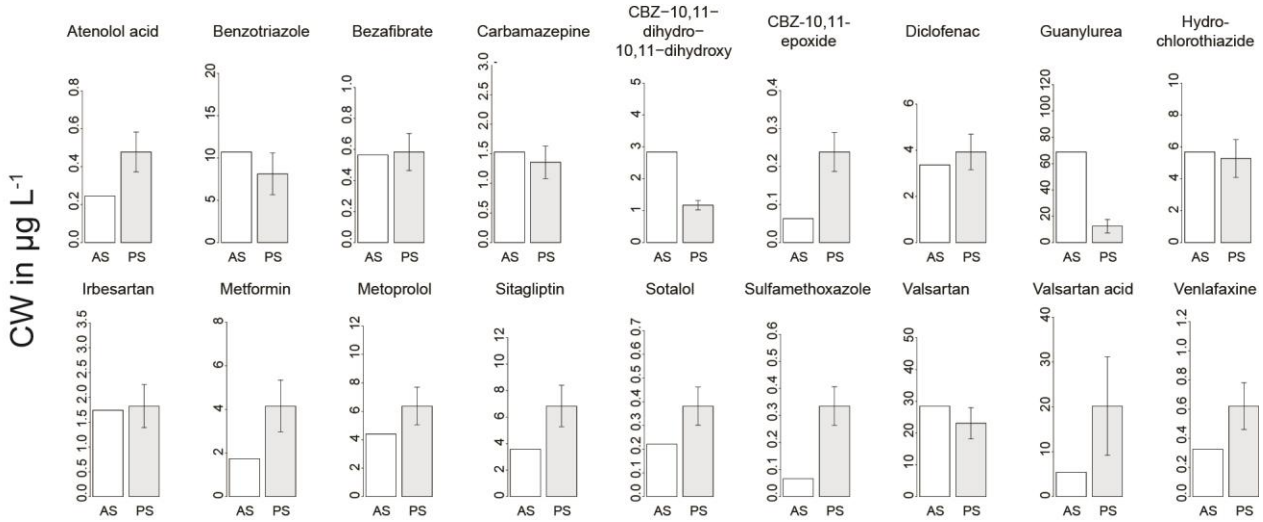


Fig. ESM1.I-8 Comparison of OC concentrations in surface water (CW) obtained by active sampling (AS) and passive sampling (PS in PS3 configuration). *Active sampling*: mean CW over 48 consecutive hourly samples taken between June 14 and June 17, 2016 (Jaeger et al., 2019). *Passive sampling*: 11-day TWA concentration ± SD between June 5 and June 16, 2016. *Please note* that not only the sampling periods differed, but also the sampling locations (autosamplers were installed approx. 120 m upstream of the passive samplers).

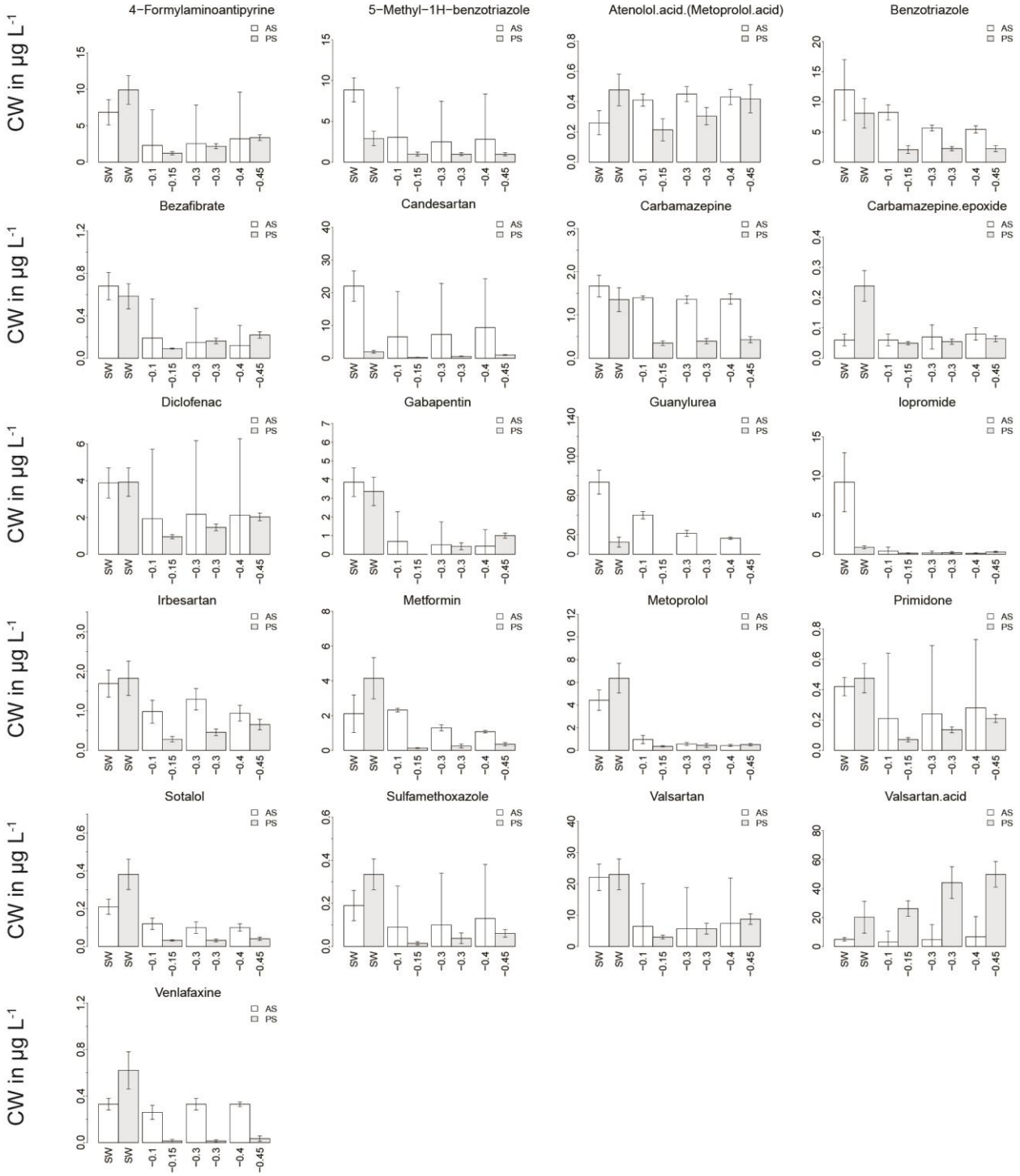


Fig. ESM1.I-9 Comparison of OC concentrations (CW) in surface water (SW) and hyporheic pore water (-0.1 to 0.45 m sediment depth) obtained by active sampling (AS) and passive sampling (PS in PS3 configuration). *Active sampling*: median ± 1 IQR for 17 hourly consecutive samples taken between June 15 and June 16, 2016 (Schaper et al., 2019). *Passive sampling*: 11-day TWA concentration ± SD between June 5 and June 16, 2016. *Please note* that sampling periods and sampling locations differed (active sampling was performed approx. 50 m downstream of the passive samplers).

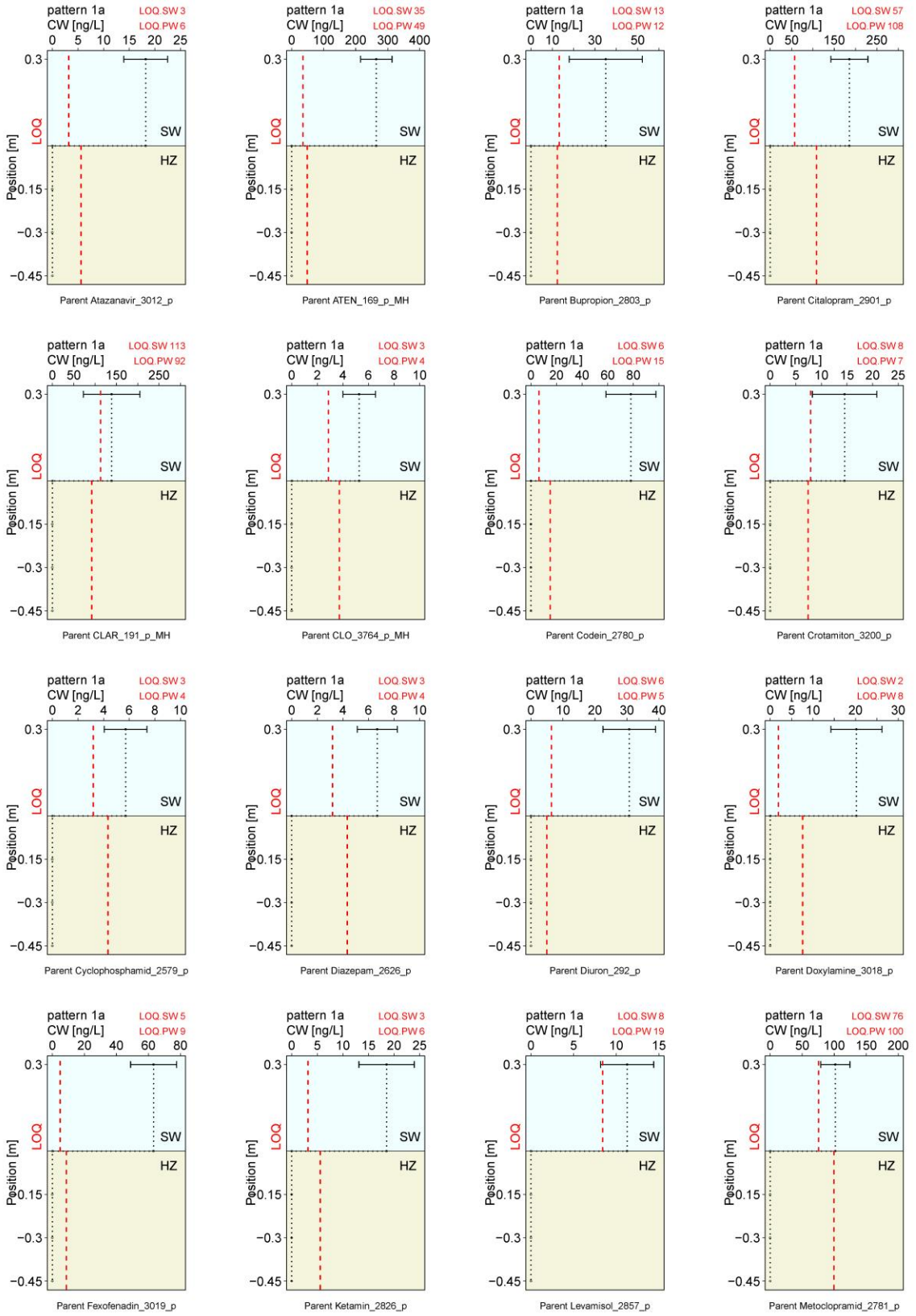


Fig. ESM1.J-10 Fate of OC across the water-sediment interface of an urban stream sorted by pattern (1a to 1d, 2 and 3) and within a pattern by compound type, i.e. parent compounds before transformation products (TP). *Red dashed lines*: limit of quantification in the respective compartment in ng L^{-1} (value in top margin). *Black dotted line*: linear interpolation between mean concentrations (standard deviation as error bars). Concentrations below LOQ are plotted at 0 ng/L.

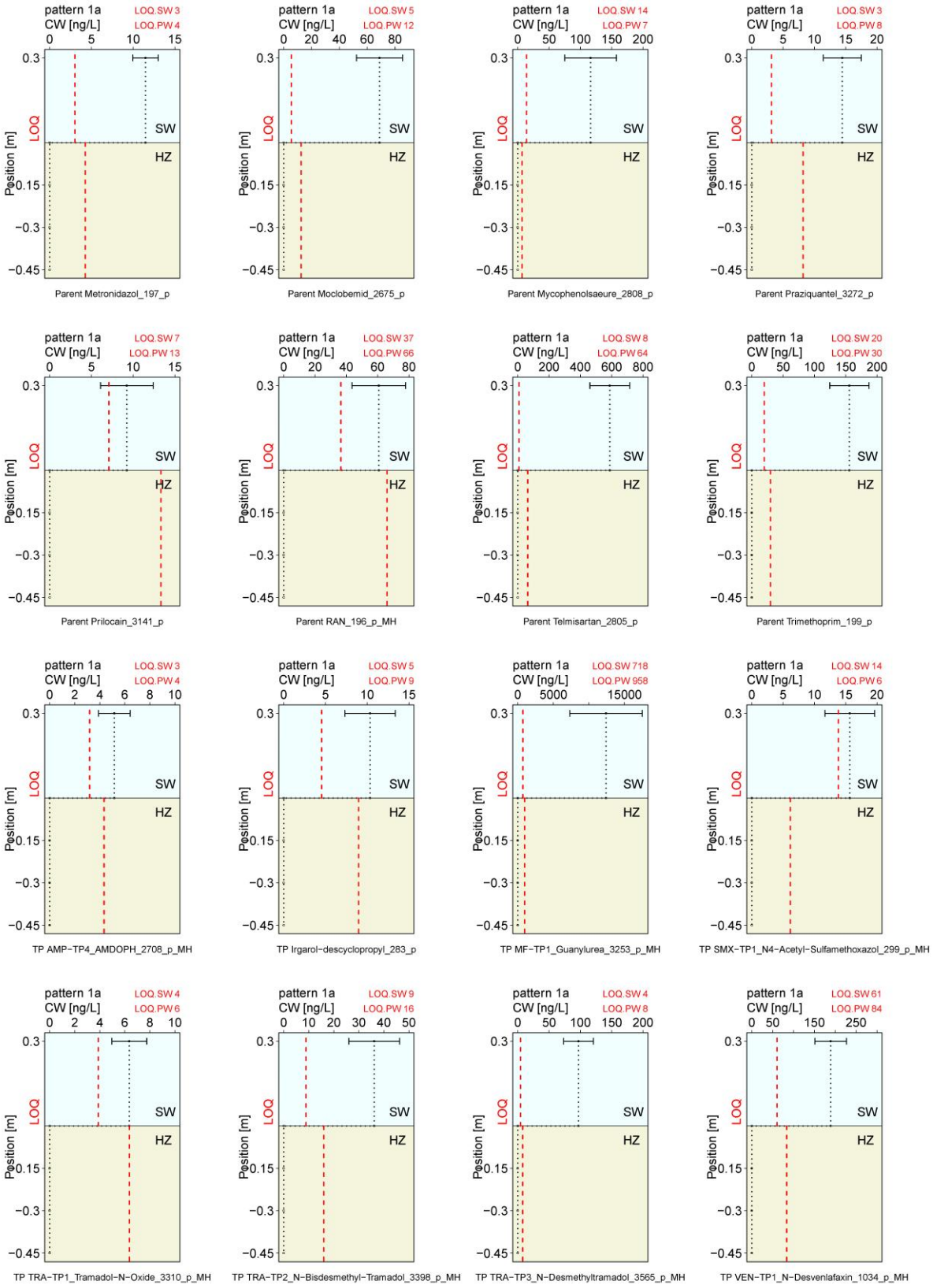


Fig. ESM1.J-10 (*continued, a*) Fate of OC across the water-sediment interface of an urban stream.

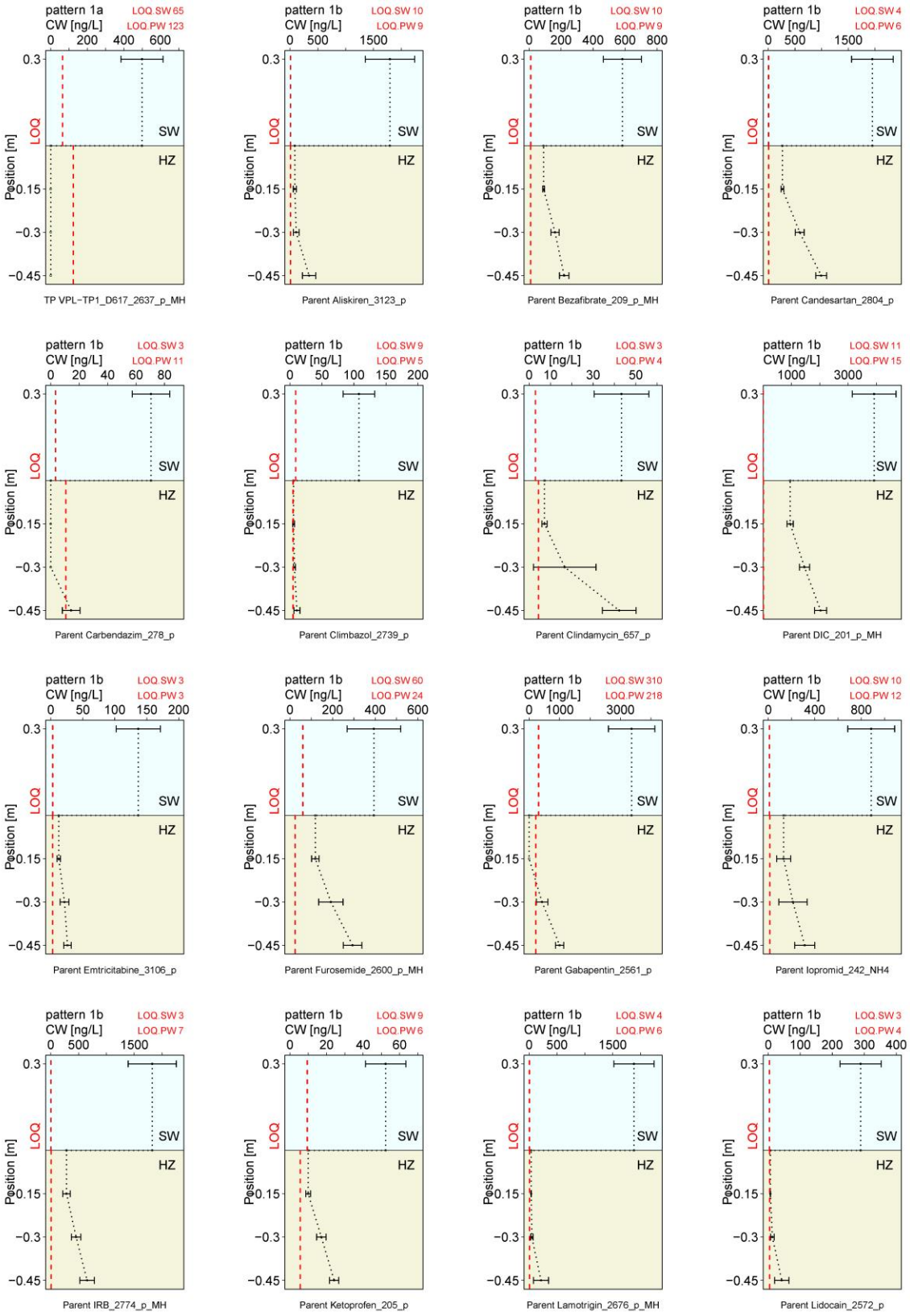


Fig. ESM1.J-10 (*continued, b*) Fate of OC across the water-sediment interface of an urban stream.

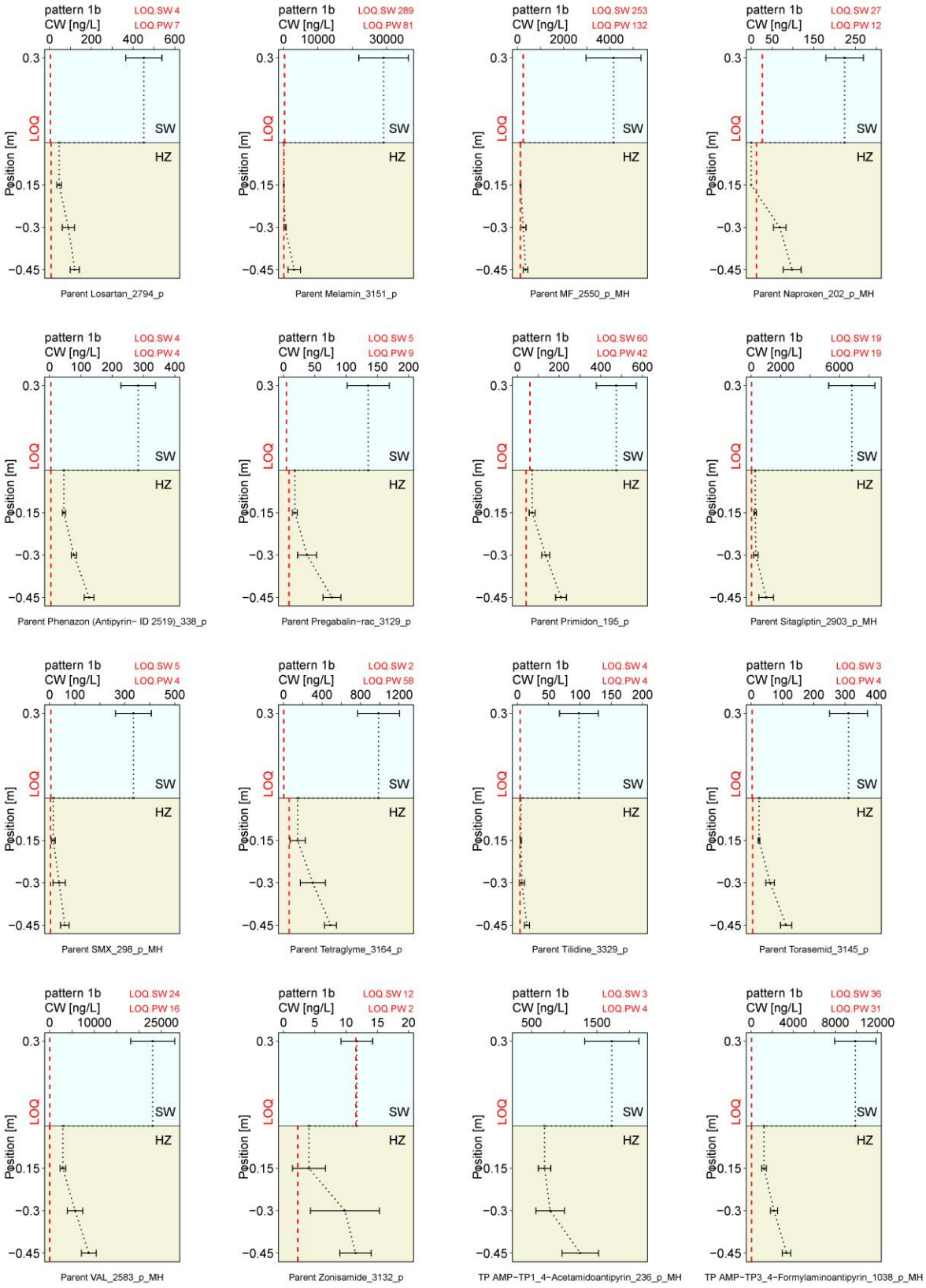


Fig. ESM1.J-10 (*continued, c*) Fate of OC across the water-sediment interface of an urban stream.

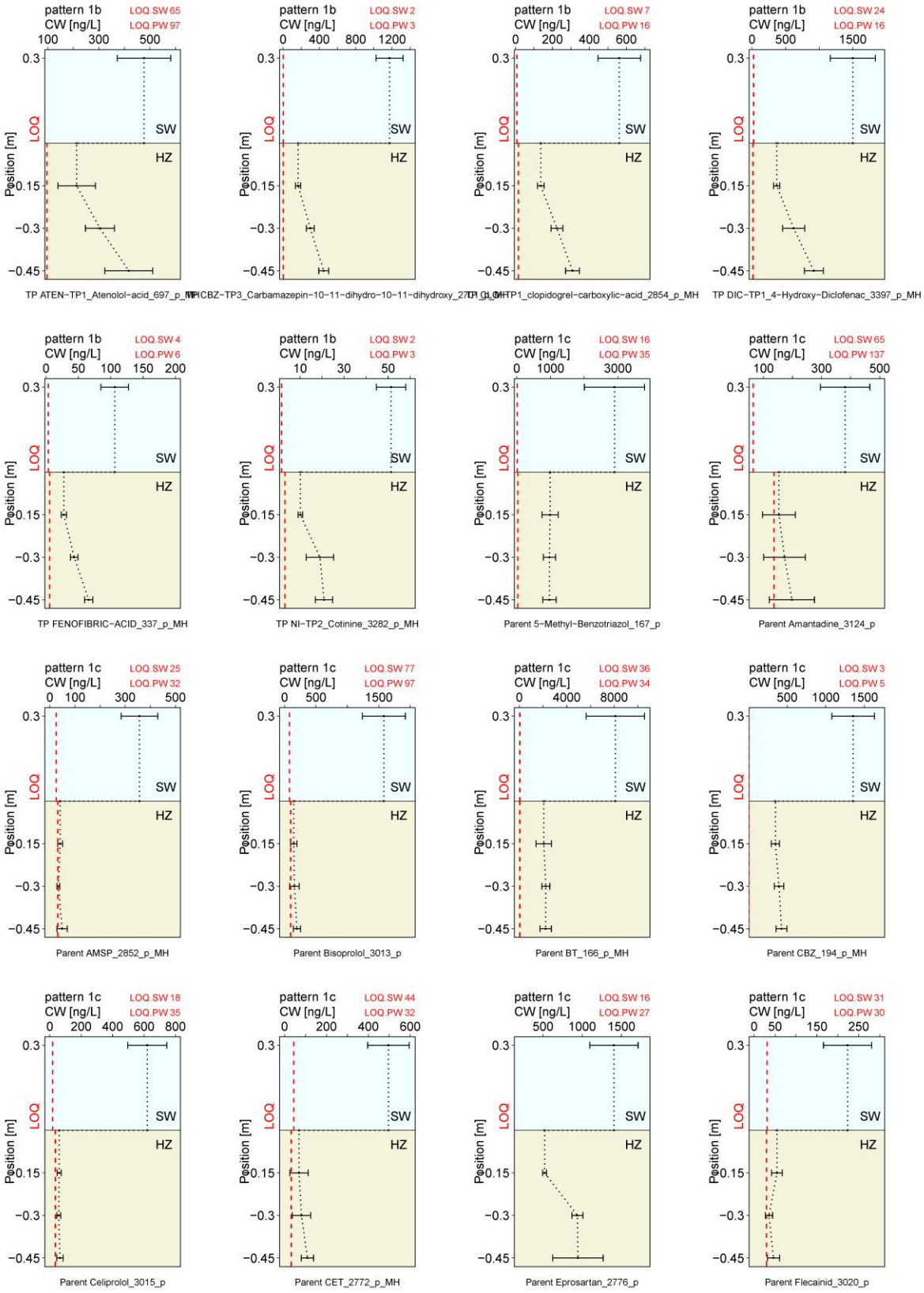


Fig. ESM1.J-10 (*continued, d*) Fate of OC across the water-sediment interface of an urban stream.

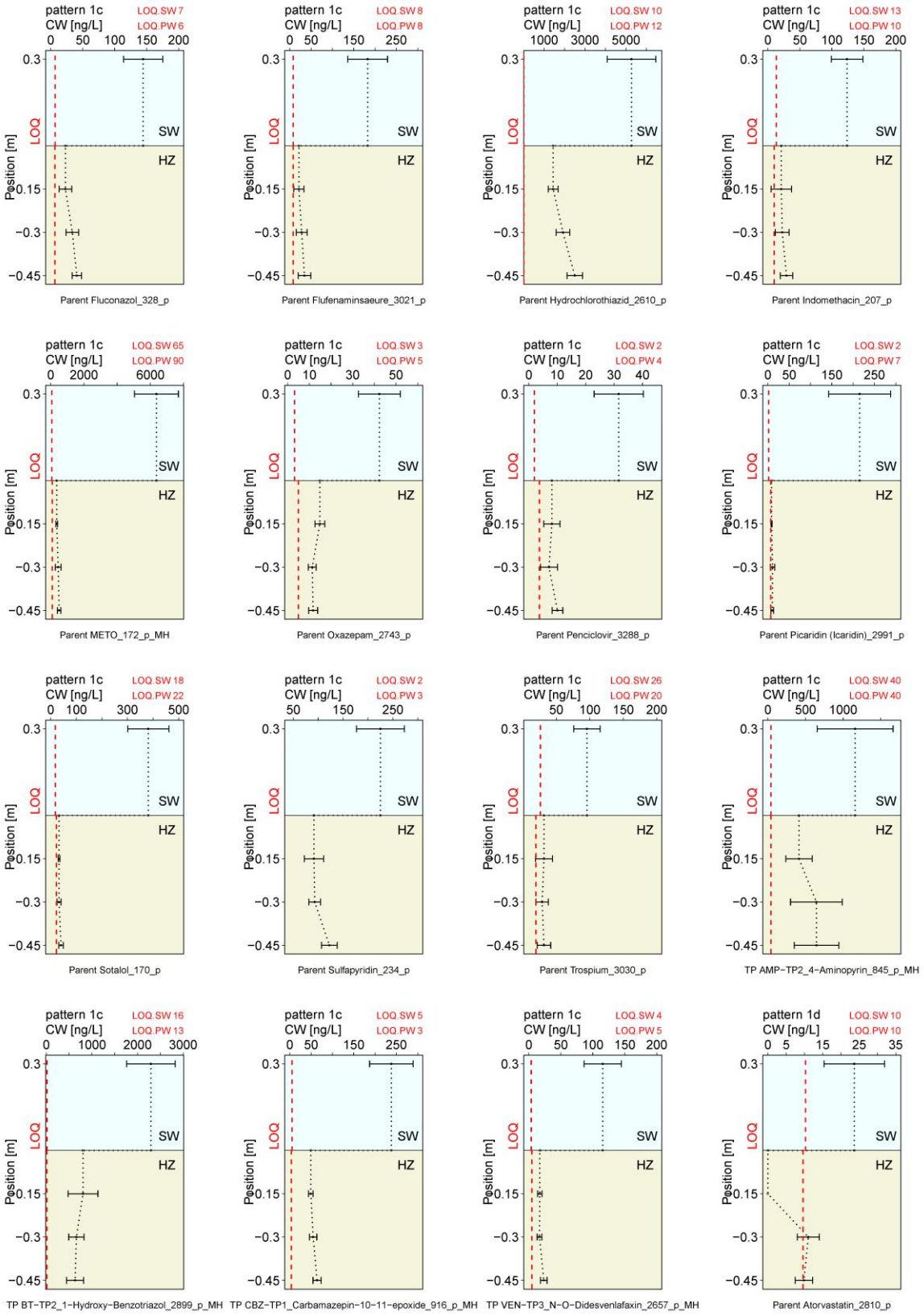


Fig. ESM1.J-10 (*continued, e*) Fate of OC across the water-sediment interface of an urban stream.

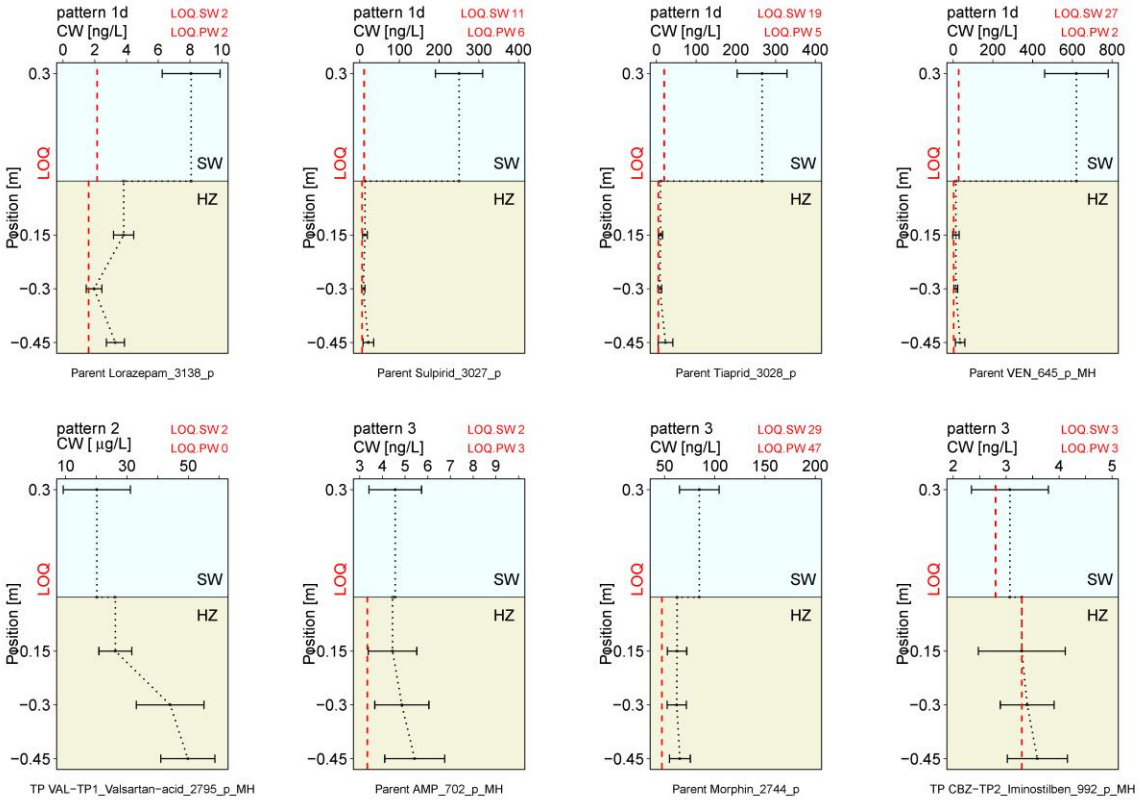


Fig. ESM1.J-10 (*continued, f*) Fate of OC across the water-sediment interface of an urban stream.

ESM1.K. Compound Discoverer 2.1 – Workflow details

The Compound Discoverer 2.1 (Thermo Scientific, USA) workflow is presented in Fig. ESM1.K-11. Detailed parameter settings are shown in Table ESM1.K-3.

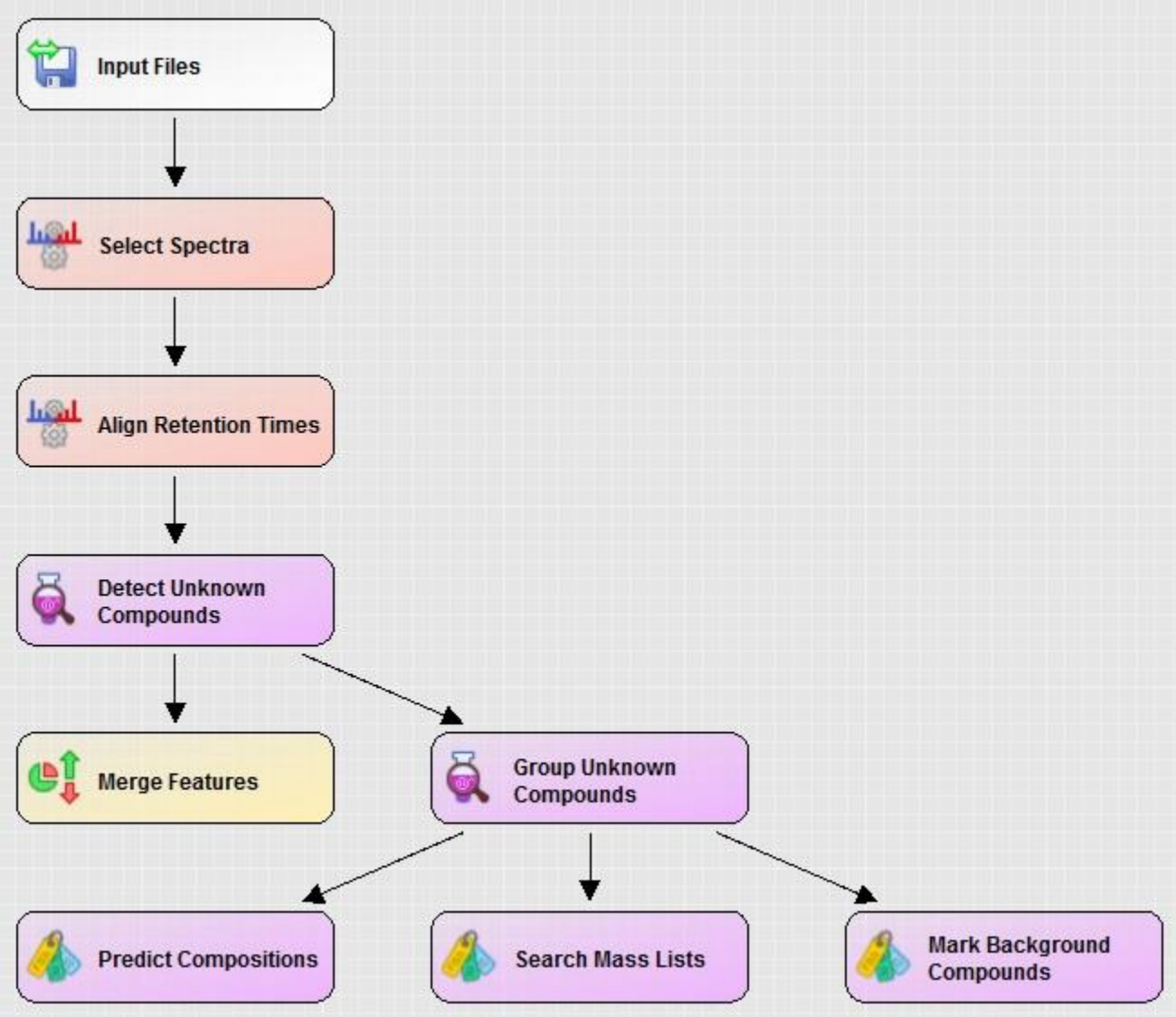


Fig. ESM1.K-11 Compound Discoverer 2.1 workflow scheme.

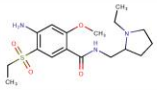
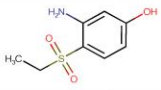
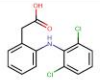
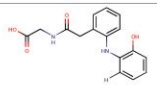
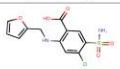
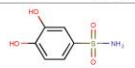
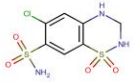
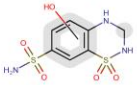
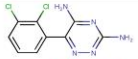
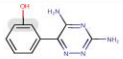
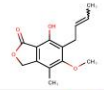
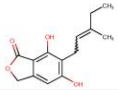
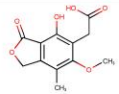
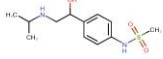
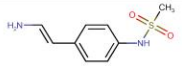
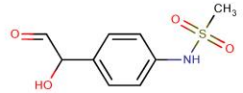
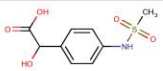
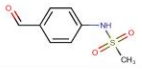
Table ESM1.K-3 Compound Discoverer 2.1 workflow parameters.

Processing Node	**Applied Parameter Settings**
Select Spectra	Presettings
	Polarity mode: + (pos batch), - (neg batch)
	Unrecognized Polarity Replacements: + (pos batch), - (neg batch)
Align Retention Times	Alignment Model: Adaptive curve
	Maximum Shift: 2 min
	Mass Tolerance: 5 ppm
Detect Unknown Compounds	Mass Tolerance: 5 ppm
	Intensity Tolerance: 30%
	S/N Threshold: 3
	Min Peak Intensity: 10000*
	Preferred ions: pos ESI mode: [2M+H]+1; [M+2H]+2; [M+DMSO+H]+1; [M+H]+1; [M+K]+1; [M+Na]+1; [M+NH4]+1; neg ESI mode: [2M-H]-1; [M+Cl]-1; [M+FA-H]-1; [M-2H]-2; [M-H]-1
	Min Element Counts: C H
	Max Element Counts: C90 H190 Br3 Cl4 F6 I3 K2 N10 Na2 O23 P3 S5
Group Unknown Compounds	Mass Tolerance: 5 ppm
	RT Toerance: 0.75 min
	Preferred ions: pos ESI mode: [2M+H]+1; [M+2H]+2; [M+DMSO+H]+1; [M+H]+1; [M+K]+1; [M+Na]+1; [M+NH4]+1; neg ESI mode: [2M-H]-1; [M+Cl]-1; [M+FA-H]-1; [M-2H]-2; [M-H]-1
Mark Background Compounds	Max. Sample/Blanks: 3
	Max. Blank/Samples: 0
	Hide Background: FALSE
Search Mass Lists	Consider Retention Time: True
	RT tolerance: 2
	Mass Tolerance: 5 ppm
Predict Compositions	Mass Tolerance: 5 ppm
	Min. Element Counts: C H
	Max Element Counts: C90 H190 Br3 Cl4 F6 I3 K2 N10 Na2 O23 P3 S5
	Min. RDBE: 0
	Max. RDBE: 40
	Min. H/C: 0.1
	Max H/C: 3.5
	Max. # Candidates: 10
	Intensity Tolerance: 30%
	Intensity Threshold: 0.1%
	S/N Threshold: 3
	Use Dynamic Recalibration: True
	Use Fragments Matching: True
	Mass Tolerance: 10 ppm
	S/N Threshold: 3

* since contaminant concentrations were particularly high in the investigated stream, contaminants were enriched in the receiving phases of the passive samplers, and because we were particularly interested in the most relevant (abundant) transformation products, we kept the default threshold of 10’000.

ESM1.L. Suspect screening for further transformation products

Table ESM1.L-4 Details on suspect transformation products in field passive sampler extracts.

											ESI mode supporting suspected compound							likely not impossible not sufficient diagnostic evidence
											ESI.pos			ESI.neg				
Parent	Structure.Parent	Transformation	Structure.TP	Const.Isomer	Name	Source	Mol.formula	Exact.mass	TP.logDOW.pH3	RT (exp/predicted/parent)	FISh [%]	Sfit [%]	pattern	FISh	Sfit	pattern	Further evaluation	Final status
Amisulpride		ether to OH amide to H			AMSP-deme-deCONRH	PPS	C8H11N1O3S1	201.0460	0.19	9.5/13.3/9.6	2.4	72	≠ 1a	3.9	75	1a	MS1: good LC (neg) MS2: M-H- of TP, no diagnostic fragment	no diagnostic MS2 fragment(s)
Diclofenac		Cl to OH Cl to H RCO2 to glycine conjugtae			DIC-disclox-clXh-glyc	MPS	C16H16N2O4	295.0167	1.56	8.9/16.6/19.5	27.3	90	1a	no mS2	0	1a	MS1: good LC (pos), MS2: 11 annotated MS2 fragments, probably some diagnostic	not detected in neg ESI mode (against expectations)
Furosemide		Cl to H all other groups to OH			FUR-clXh-disnhox	PPS	C6H7N1O4S1	189.0096	-0.03	8.3/12.8/15.2	no MS2	0	1a	7.7	78	1a	MS1: good LC (neg), MS2: M-H- of TP, no diagnostic fragment	no diagnostic MS2 fragment(s)
Hydrochlorothiazide		Cl to H hydroxylation			HCTZ-clXh-oh	MPS	C7H9N3O5S2	278.9984	-1.48	7.2/9.4/9.3	1.4	0	1a	2.2	79	1a	MS1: good LC (neg), MS2: M-H- of TP, no diagnostic fragment	no diagnostic MS2 fragment(s)
Lamotrigine		Cl to OH Cl to H			LTG-disclox-clXh	MPS	C9H9N5O1	203.0807	-2.26	10.7/7.5/11.9	1.4	91	1a	0	0	≠ 1a	MS1: good LC (pos), MS2: 3 annotated fragments (unspecific or M+H+ of TP)	no diagnostic MS2 fragment(s)
Mycophenolic acid		decarboxylation deethylation or 2x demethylation			MPA-deco2-deet	MPS	C14H16O4	248.1049	3.72	12.3/21.8/17.8	21.4/13.7	73	1a	bad LC (MS1) no MS2	NA	≠ 1a	MS1: good LC (pos), MS2: 25 annotated fragments (probably some diagnostic)	not impossible but rather uncommon
		carboxylic acid side chain: C7 to C2			MPA-C2	PPS	C12H12O6	252.0634	1.70	14.2/16.9/17.8	6.3	97	1a	0	83	≠ 1a	MS1: good LC (pos), MS2: 13 annotated MS2 fragments (but low FISh score). MS1 peak in neg mode but not confirmed by MS2 (FISh=0)	not confirmed in neg ESI mode (FISh=0)
Sotalol		deisopropylation dehydration			Sot-deipr-deh2o	MPS	C9H12N2O2S1	212.0619	-2.89	13.5/6/7.5	1.1	53	1a	different RT			MS1: bad LC (pos), MS2: 2 annotated (rather unspecific) MS2 fragments	bad LC, MS2 fragments rather unspecific
		sec. amine to aldehyde			Sot-disnCHO	PPS	C9H11N1O4S1	229.0409	-0.89	13.8/10.8/7.5	3.0	76	1a	3.7	70	1a	pos: MS1: good LC, MS2: 7 annotated MS2 fragments (likely diagnostic). neg: MS1: good LC, MS2: 1 annotated MS2 fragment (not the molecular parent ion)	The most likely TP candidate: found in both ionization modes following pattern 1a with a high isotopic pattern match and (probably) diagnostic MS2 fragments. However, both FISh score were low (<4%).
		sec. amine to carboxylic acid			Sot-TP1.intermediate	Stadlmair et al., 2019	C9H11NO5S	245.0358	-0.98	NA/10.6/7.5	pos/neg: compound detected (MS1) but no chromatographic peak, no MS2 scans							proposed in Stadlmair et al., 2019 but not detected in the present study
		sec. amine to carboxylic acid decarobxylation alcohol to aldehyde			Sot-TP1	Stadlmair et al., 2019	C8H9NO3S	199.0303	0.06	NA/13.0/7.5	pos/neg: no compound detected in CD at proposed exact mass							

References

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