Supporting information

Persistent organic pollutants in stream water – influence of hydrological conditions and landscape type

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Table S1. Sampling seasons (SC=snow-covered, SprFl=spring flood, SF=snow-free) and dates, as well as determined bulk concentrations of PCDD/F_{17}, PCB_7, HCB, total organic carbon (TOC), suspended particulate matter (SPM), and pH; na = not available. Triplicate samples were taken for site D2 during the spring flood 2008; these values are given as average ± standard deviations.

Season	Site	Date	PCDD/F_{17} (pg m^{-3})	PCB_7 (ng m^{-3})	HCB (ng m^{-3})	TOC (mg L^{-1})	SPM (mg L^{-1})	pH
SC	C2	2008.03.10	35	na	3.3	11.0	14.7	5.4
SC	C13	2008.03.11	107	na	4.6	20.8	51.4	5.9
SC	C4	2008.03.12	118	na	6.0	36.0	7.7	4.3
SC	C16	2008.03.28	52	na	4.2	7.1	22.4	6.7
SC	D1	2008.03.29	45	na	6.8	5.4	8.8	7.0
SC	D2	2008.03.30	60	na	8.2	2.9	2.7	6.9
SC	D3	2008.04.03	4649	na	17	4.4	13.4	6.8
SprFl	C4	2008.05.02	807	na	9.7	18.1	7.8	4.3
SprFl	C2	2008.05.03	739	na	7.4	26.1	14.2	4.5
SprFl	C13	2008.05.06	261	na	7.9	17.7	63.2	5.0
SprFl	C16	2008.05.07	475	na	21	15.4	430.8	5.7
SprFl	D1	2008.05.15	396	na	14	7.6	37.8	6.8
SprFl	D2	2008.05.16	160	na	9.7	7.8	9.3	6.9
SprFl	D3	2008.05.20	180	na	9.4	6.7	7.4	6.8
SprFl	D2	2008.05.21	92		8.5	7.9	7.6	6.8
SprFl	D2	2008.05.21	±	na	±	±	±	±
SprFl	D2	2008.05.21	44		0.5	0.2	1.0	0.1
SF	C2	2008.11.04	*	*	*	18.6	18.5	na
SF	C13	2008.11.06	405	13	5.4	19.7	27.2	na
SF	C4	2008.11.07	172	9.7	3.3	37.9	10.6	na
SF	C16	2008.11.14	136	13	6.4	11.8	33.1	na
SF	D3	2008.11.24	395	16	8.3	4.4	2.5	na
SF	D2	2008.12.03	109	8.4	7.1	3.2	1.5	na
SF	D1	2008.12.04	68	3.4	5.7	5.1	5.6	na
SC	C2	2009.03.17	123	2.2	3.0	10.5	21.3	5.6
SC	C4	2009.03.18	136	3.8	3.1	27.8	18.6	4.6
SC	C13	2009.03.18	164	3.4	4.6	12.5	41.0	5.9
SC	C16	2009.03.19	151	3.9	3.3	4.2	30.0	6.8
SC	D3	2009.03.30	253	9.8	8.2	3.0	2.9	6.7
SC	D1	2009.03.31	111	4.0	5.9	4.2	5.2	6.9
SC	D2	2009.04.01	85	1.8	6.7	2.4	0.9	7.0
SC	C16	2009.04.15	204	4.3	5.1	11.2	62.8	6.6
SprFl	C16	2009.04.27	707	13	9.3	21.0	325.7	6.0
SprFl	C2	2009.05.02	300	3.3	4.4	25.8	10.7	4.6
SprFl	C4	2009.05.03	361	4.2	5.0	15.6	5.3	4.4
SprFl	C16	2009.05.03	834	13	14	15.8	696.0	5.9
SprFl	C13	2009.05.04	152	3.1	4.1	21.9	13.8	5.1
SprFl	C16	2009.05.08	471	11	9.7	15.6	344.0	6.0
SprFl	D2	2009.05.11	185	6.9	8.2	8.0	12.7	6.9
SprFl	D1	2009.05.12	177	3.9	7.2	9.9	25.9	6.7
SprFl	C16	2009.05.13	233	5.7	6.1	12.8	129.3	6.4
SprFl	D3	2009.05.14	492	23	10	8.9	19.1	6.9
SF	C2	2009.11.09	25	na	4.5	16.3	19.8	5.2
SF	C4	2009.11.10	44	na	4.0	39.7	11.4	4.4
SF	C13	2009.11.10	50	na	9.4	18.0	25.5	5.8
SF	C16	2009.11.19	148	na	10	17.0	42.4	6.4

*PUF sample, i.e. dissolved concentrations, missing due to spilled sample.

POP flux calculations for sites C2 and C4

Daily POP fluxes were calculated for sites C2 and C4 as the product of estimated dissolved and particulate contaminant concentrations and daily water flow. First, water runoff was calculated by multiplying flows ($m^3 s^{-1}$) by 86 400 s d^{-1} to obtain daily flows, and dividing by catchment area (470 000 m^2 for subcatchment C7 for which daily flow was measured; runoff was assumed equal for all Krycklan subcatchments) to obtain runoff in m d^{-1}. This was multiplied by 1000 mm m^{-1} to produce runoff in mm d^{-1}.

Site-specific linear regressions predicting contaminant concentration as a function of runoff were produced for sites C2 and C4. Separate regressions were created for dissolved and particulate contaminant fractions at each site. Daily POP concentrations (e.g. in ng m^{-3}) for sites C2 and C4 were then estimated based on daily runoff and the site-specific regression parameters. The daily POP concentrations were transformed into daily POP fluxes by multiplying with daily water flow. Daily flux estimates were then summed to derive monthly and annual values.

Table S2. Average and standard deviation of TOC, SPM and pH for the seven sampling sites during the three different hydrological seasons.

	Snow-covered							Spring flood							Snow-free					
	TOC		SPM		pH		*n*	TOC		SPM		pH		*n*	TOC		SPM		pH	*n*[1]
	Ave.	STD	Ave.	STD	Ave.	STD		Ave.	STD	Ave.	STD	Ave.	STD		Ave.	STD	Ave.	STD	Ave.	
C2	10.7	0.4	18.0	4.7	5.5	0.13	*2*	25.9	0.3	12.4	2.5	4.6	0.10	*2*	17.4	1.6	19.1	0.9	5.2	*2 (1)*
C4	31.9	5.8	13.2	7.7	4.5	0.19	*2*	16.8	1.7	6.6	1.7	4.3	0.06	*2*	38.8	1.3	11.0	0.6	4.4	*2 (1)*
C13	24.2	5.9	46.2	7.4	5.9	0.04	*2*	19.8	3.0	39	35	5.1	0.07	*2*	18.8	1.2	26.4	1.2	5.8	*2 (1)*
C16[2]	5.7	2.1	26.2	5.4	6.8	0.08	*2*	16.1	3.0	385	206	6.0	0.25	*5*	14.4	3.6	37.7	6.5	6.4	*2 (1)*
D1	4.8	0.9	7.0	1.3	6.9	0.07	*2*	8.7	1.6	31.9	8.4	6.7	0.02	*2*	5.1		5.6			*1 (0)*
D2	2.7	0.3	1.8	1.2	6.9	0.07	*2*	7.9	0.1	8.9	2.4	6.8	0.07	*5*	3.2		1.5			*1 (0)*
D3	3.7	1.0	8.2	7.4	6.8	0.03	*2*	7.8	1.6	13.2	8.3	6.9	0.03	*2*	4.4		2.5			*1 (0)*

[1] *n* within parenthesis denotes the number of samples for pH when different from TOC and SPM.

[2] Sample from 2009.04.15 not included in snow-covered average due to being influenced by spring flood.

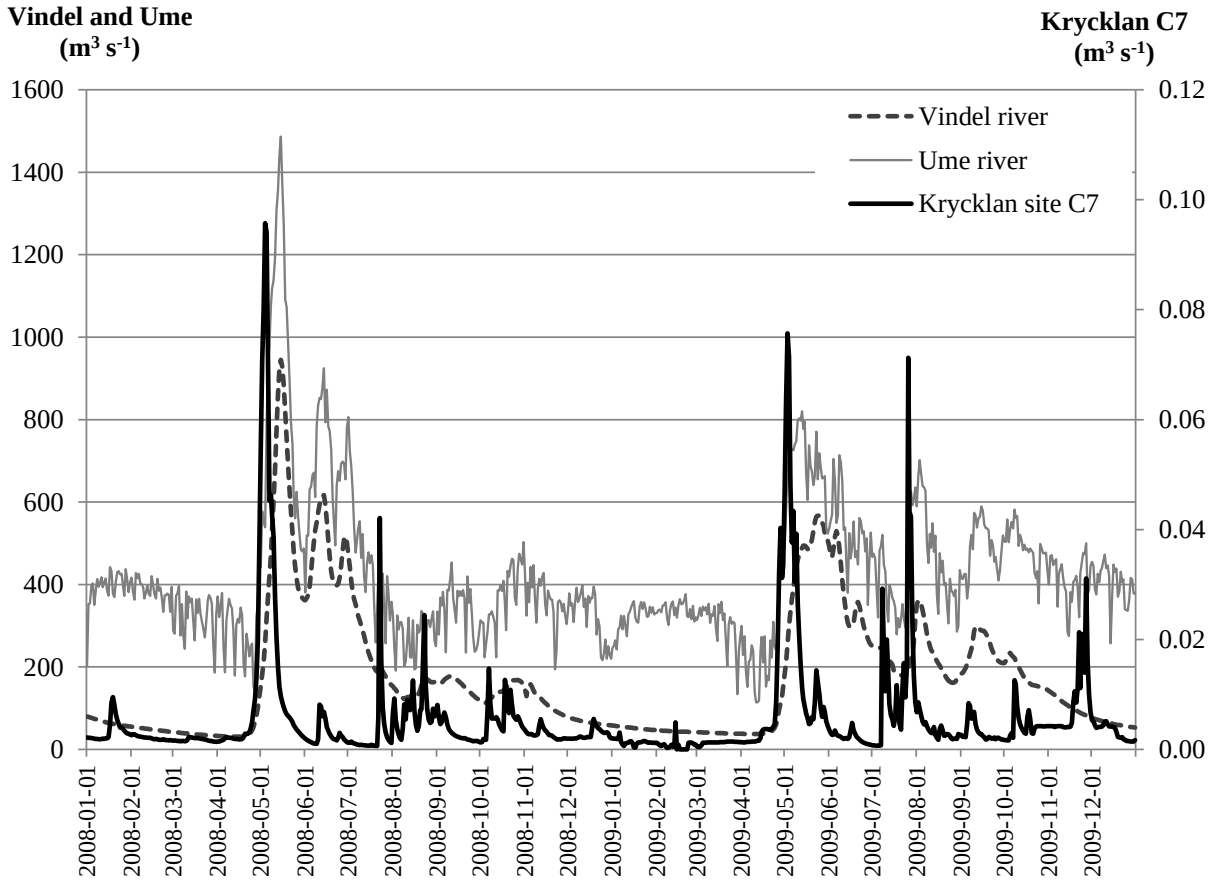
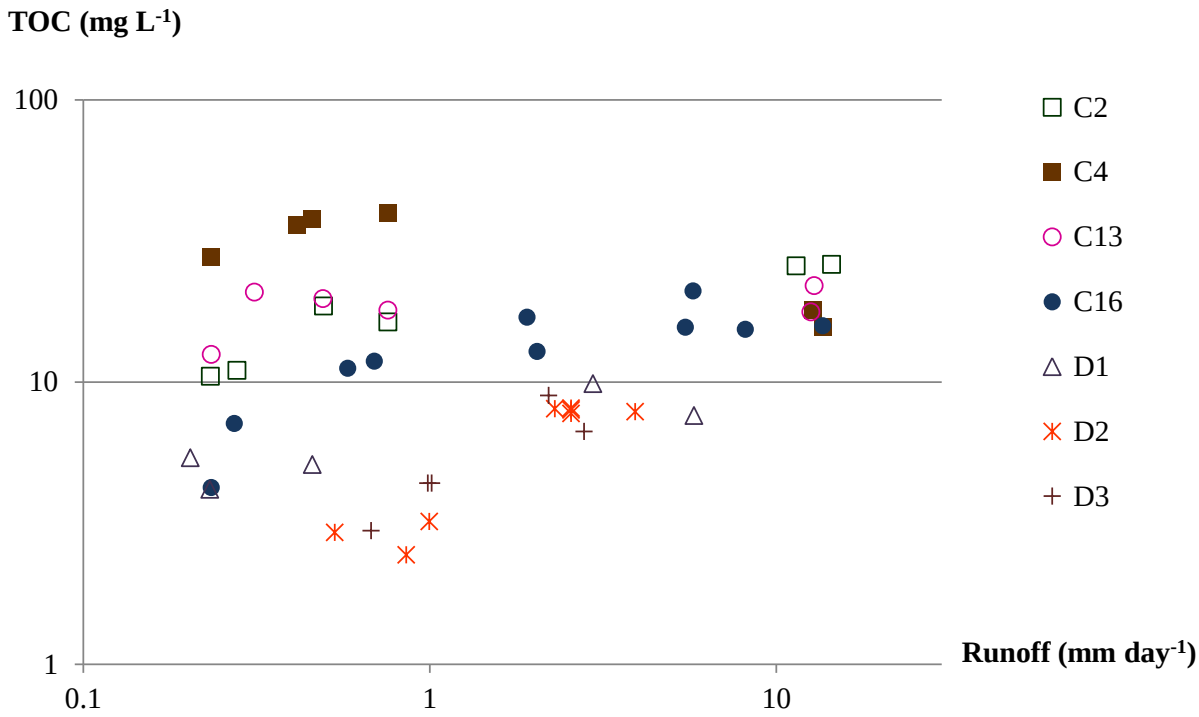


Figure S1. Water flow for Krycklan (Site C7), Ume River (Stornorrfors) and Vindel River (Granåker) during 2008-2009.

a)



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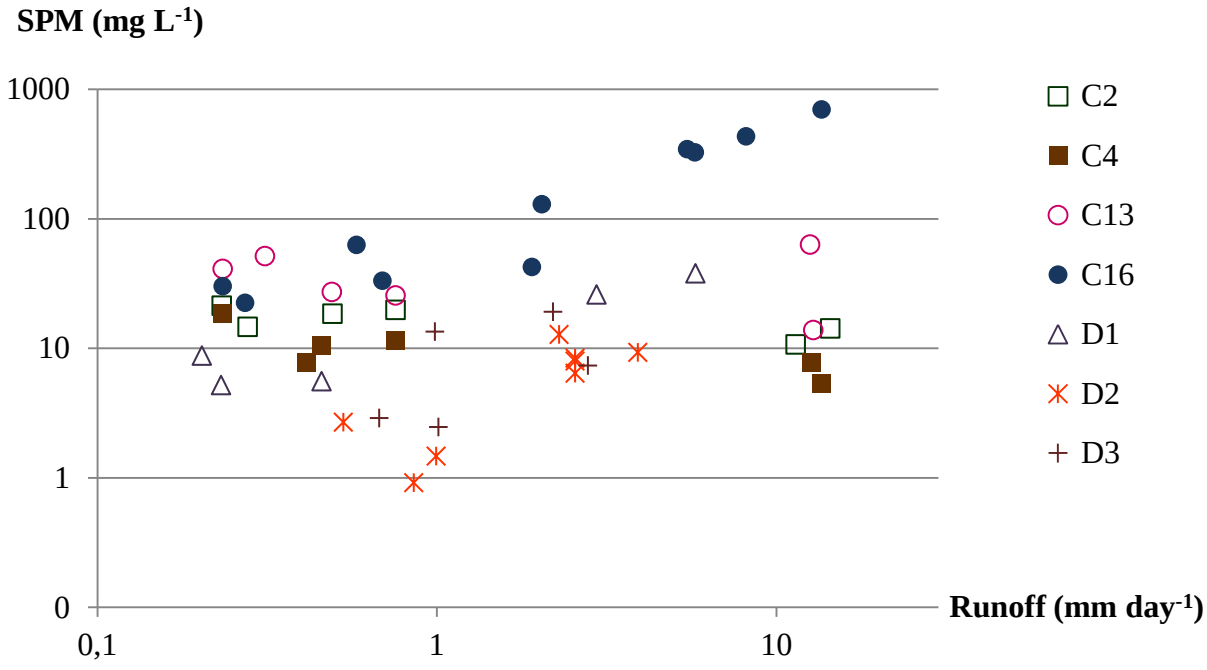
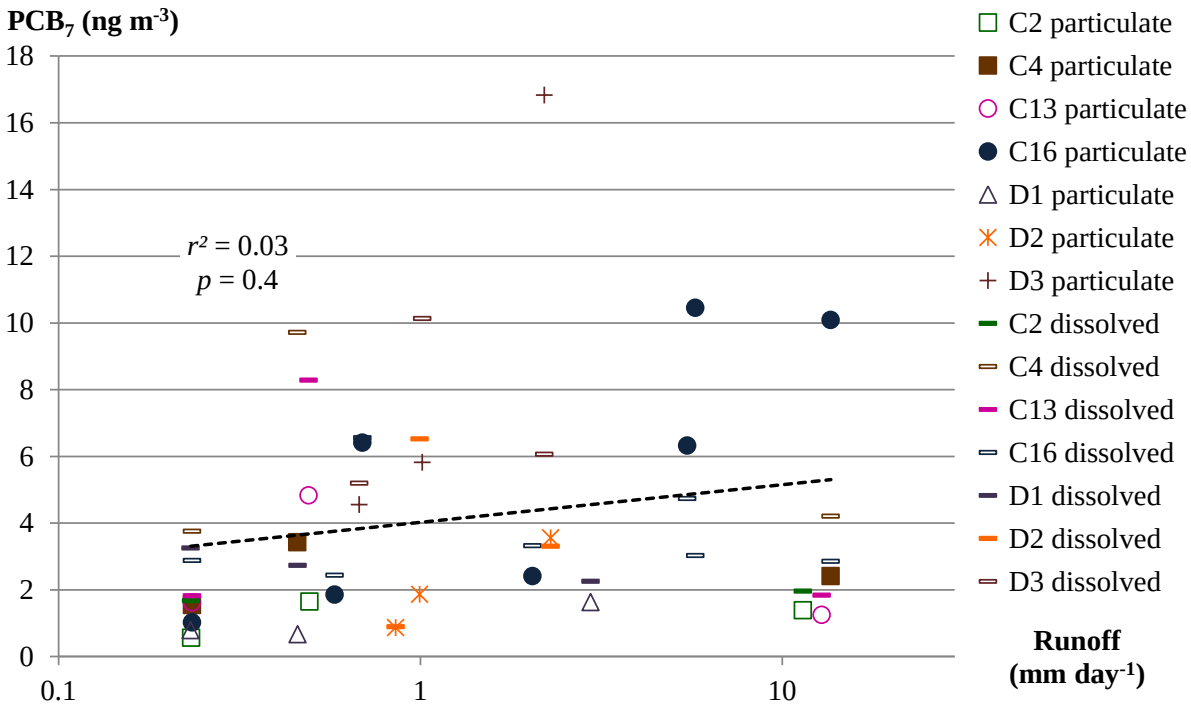


Figure S2. Concentrations of *a)* TOC and *b)* SPM for the seven sampling sites as a function of runoff.

a)



b)

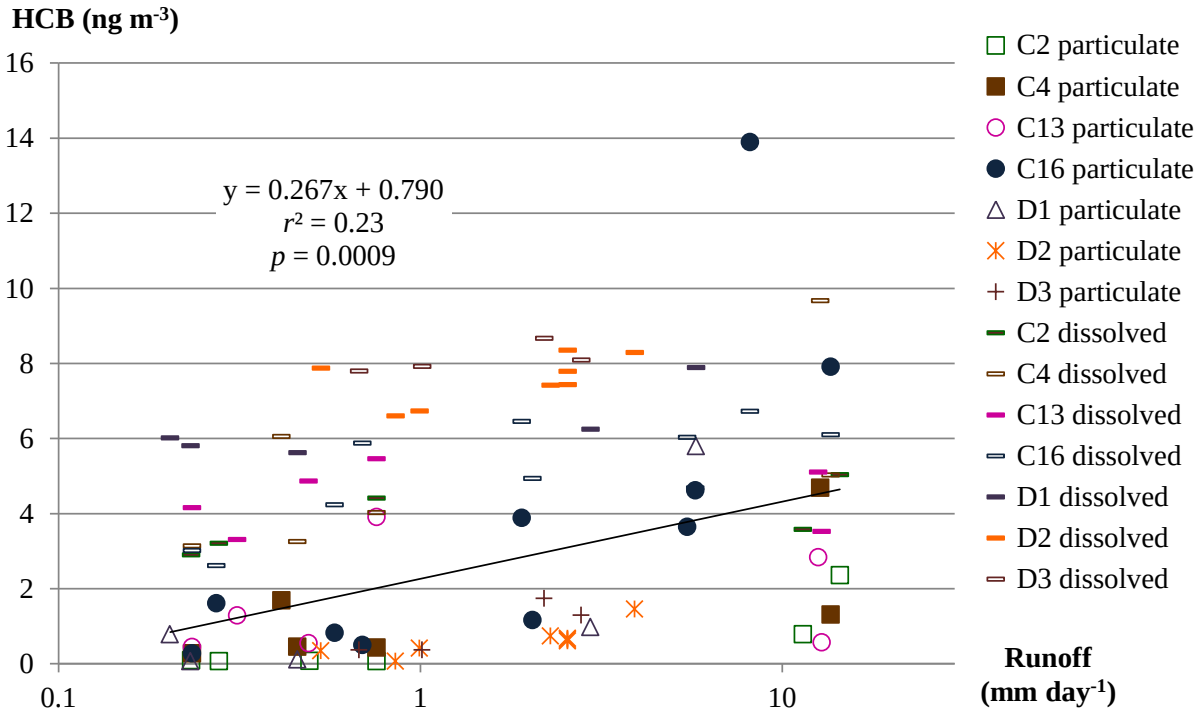


Figure S3. Concentrations of particulate and dissolved *a)* PCB_7 and *b)* HCB at the seven sampling sites as a function of runoff, and the linear regression for the particulate fraction (not significant for PCB_7 or for the dissolved fraction for PCB_7 or HCB).

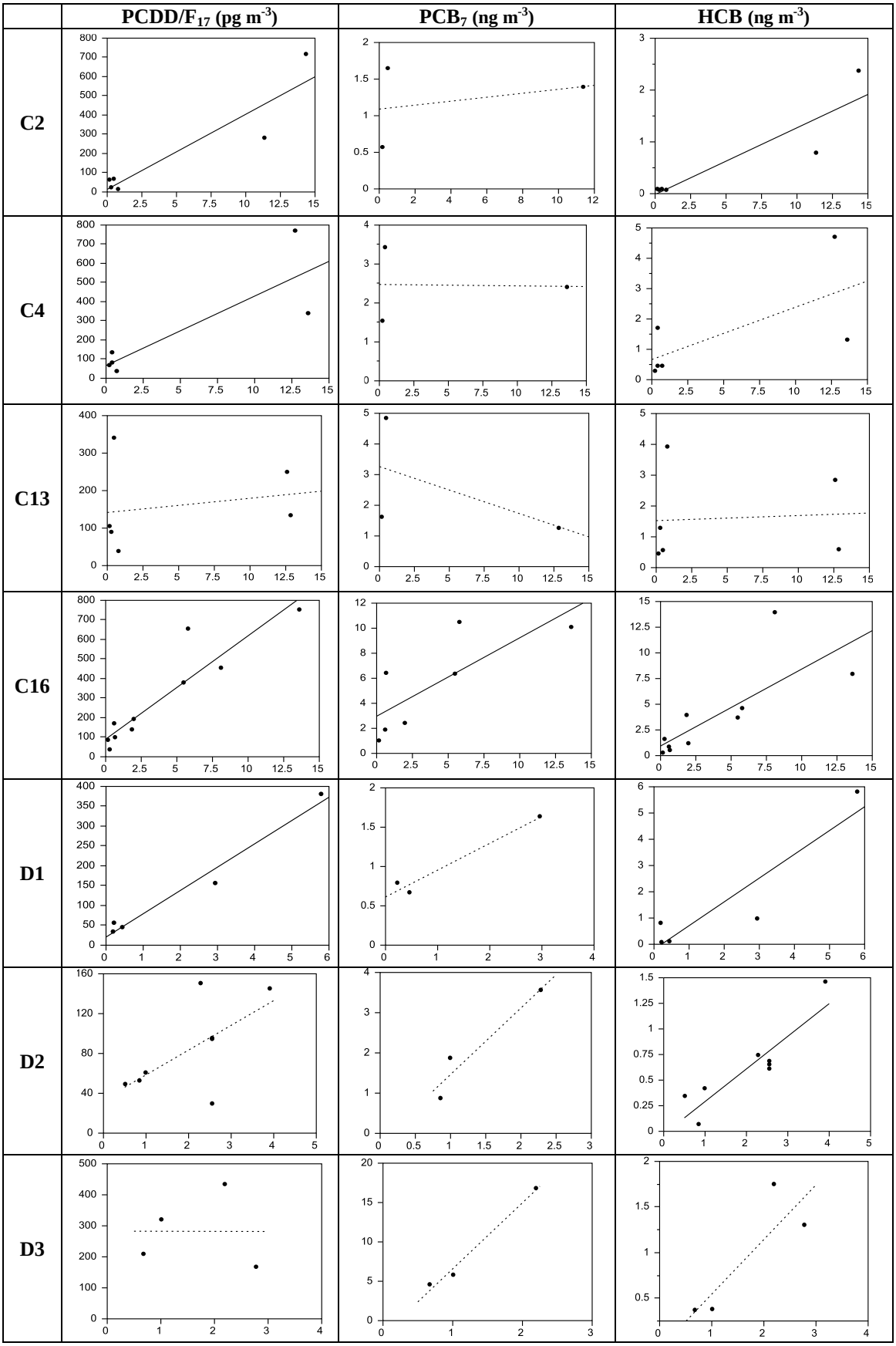


Figure S4. Particulate POP concentrations versus runoff (mm day^{-1}) for the seven sampling sites. Parameters for significant regressions are available in Table S3; not significant regressions (p>0.05) marked with dashed lines.

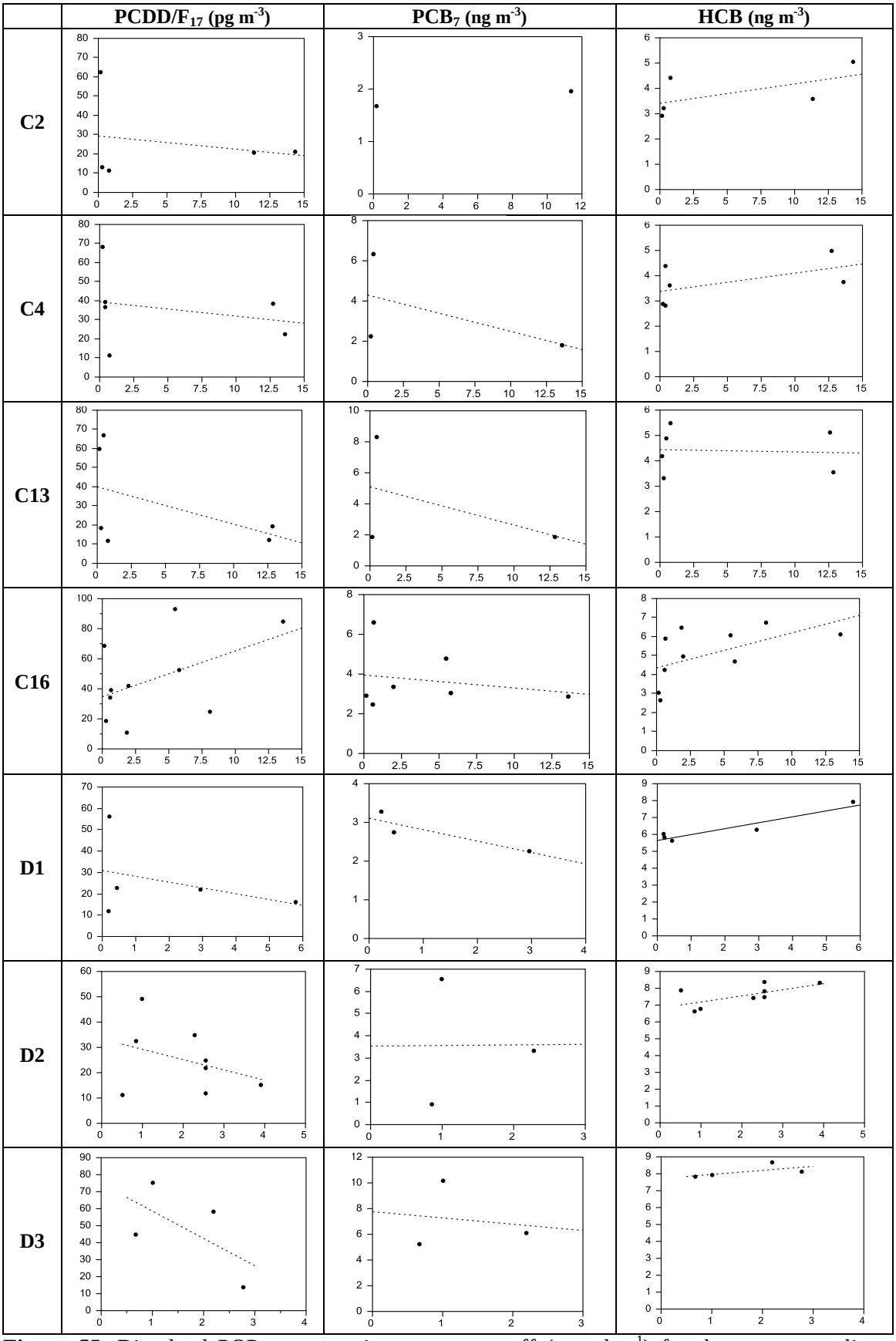
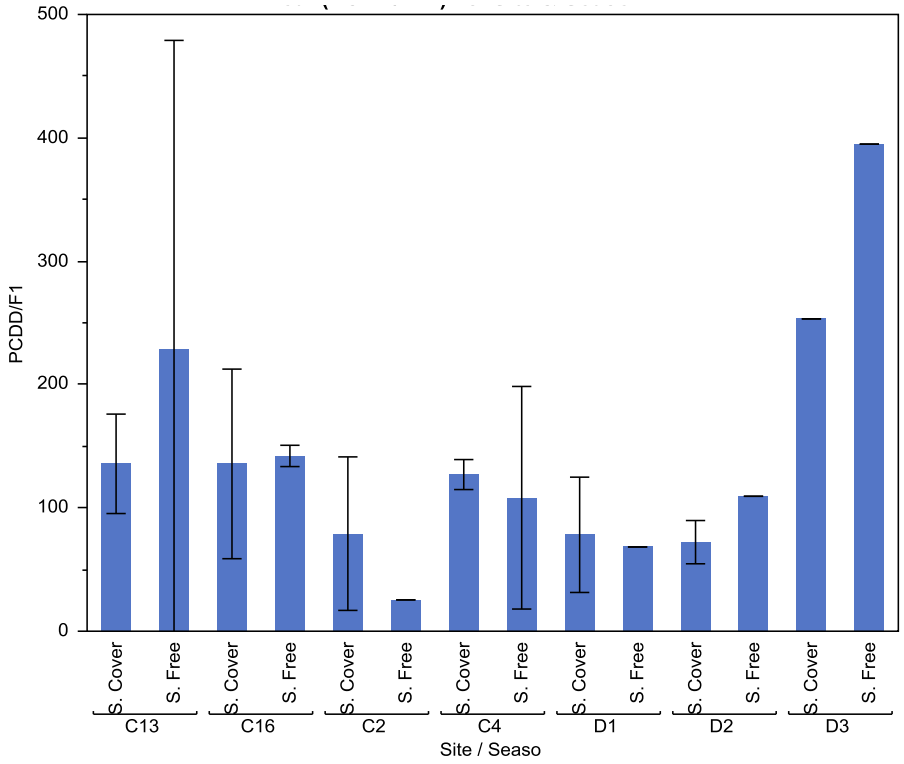


Figure S5. Dissolved POP concentrations versus runoff (mm day^{-1}) for the seven sampling sites. Parameters for significant regressions are available in Table S3; not significant regressions (p>0.05) marked with dashed lines.

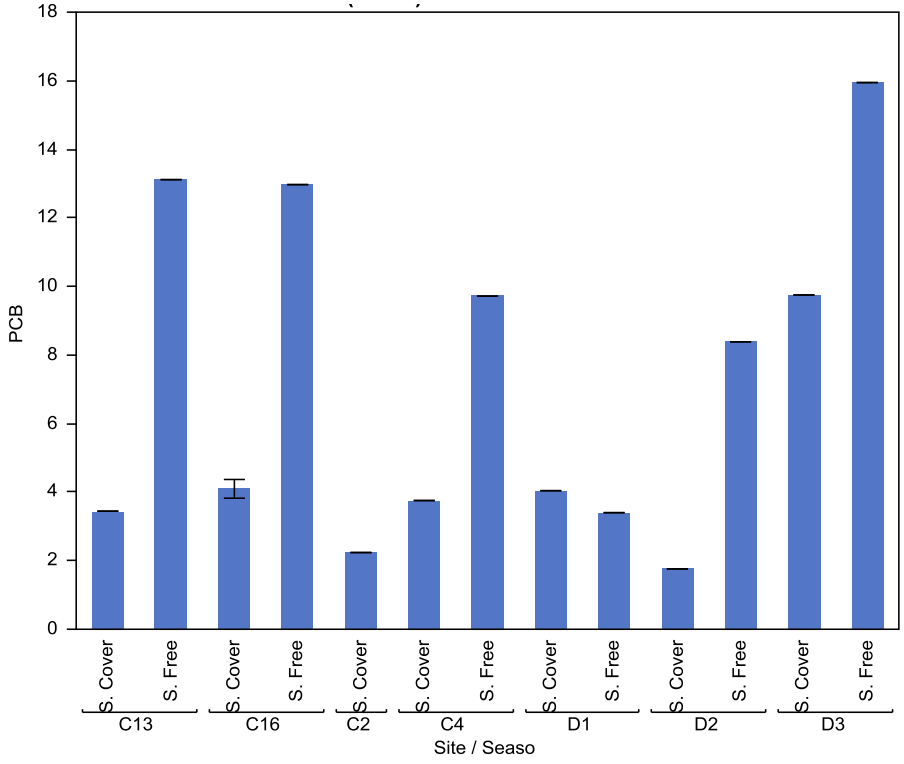
Table S3. Parameters for significant linear regressions (y=a+bx) of different POPs on runoff (from Figures S4-S5).

Site	***y***	**Fraction**	***a***	***b***	***p***	r^2	***n***
C2	$PCDD/F_{17}$	Part	13.8	39.0	0.009	0.85	6
C2	HCB	Part	-0.02	0.13	0.012	0.83	6
C4	$PCDD/F_{17}$	Part	66.3	36.3	0.034	0.72	6
C16	$PCDD/F_{17}$	Part	89.8	52.9	0.000	0.85	10
C16	PCB_7	Part	3.0	0.63	0.040	0.60	7
C16	HCB	Part	0.94	0.75	0.009	0.59	10
D1	$PCDD/F_{17}$	Part	20.5	58.7	0.002	0.97	5
D1	HCB	Part	-0.20	0.91	0.026	0.85	5
D2	HCB	Part	-0.03	0.32	0.002	0.82	8
D1	HCB	Diss	5.64	0.35	0.016	0.89	5

a)


PCDD/F1
500
400
300
200
100
0
S. Cover
S. Free
C13
C16
C2
C4
D1
D2
D3
Site / Seaso

b)


PCB
18
16
14
12
10
8
6
4
2
0
S. Cover
S. Free
C13
C16
C2
C4
D1
D2
D3
Site / Seaso

c)

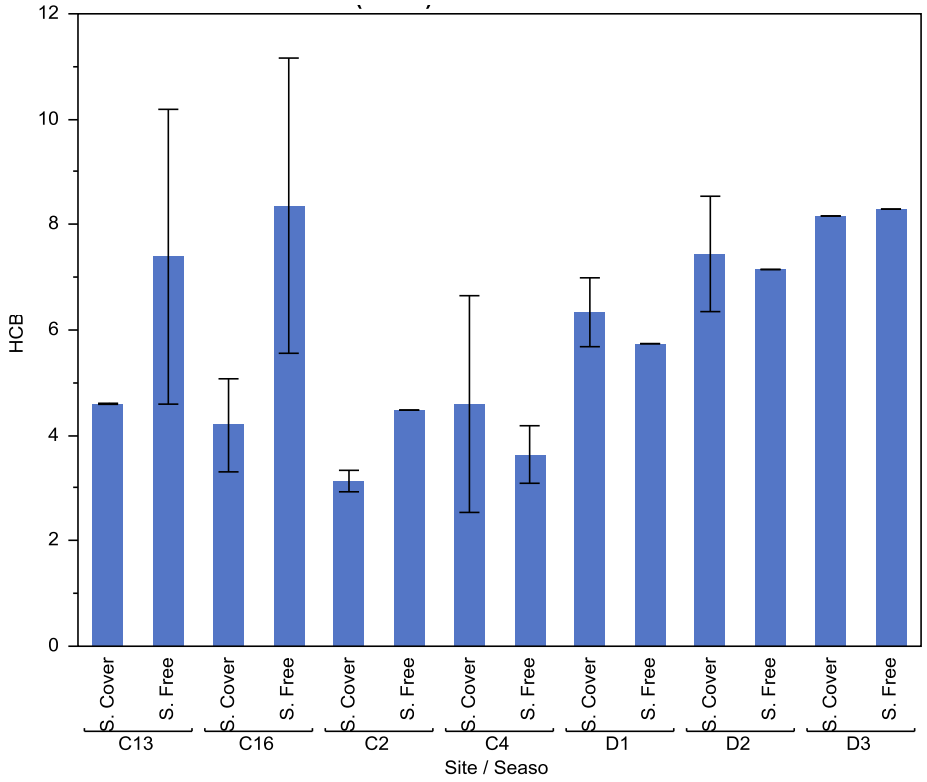
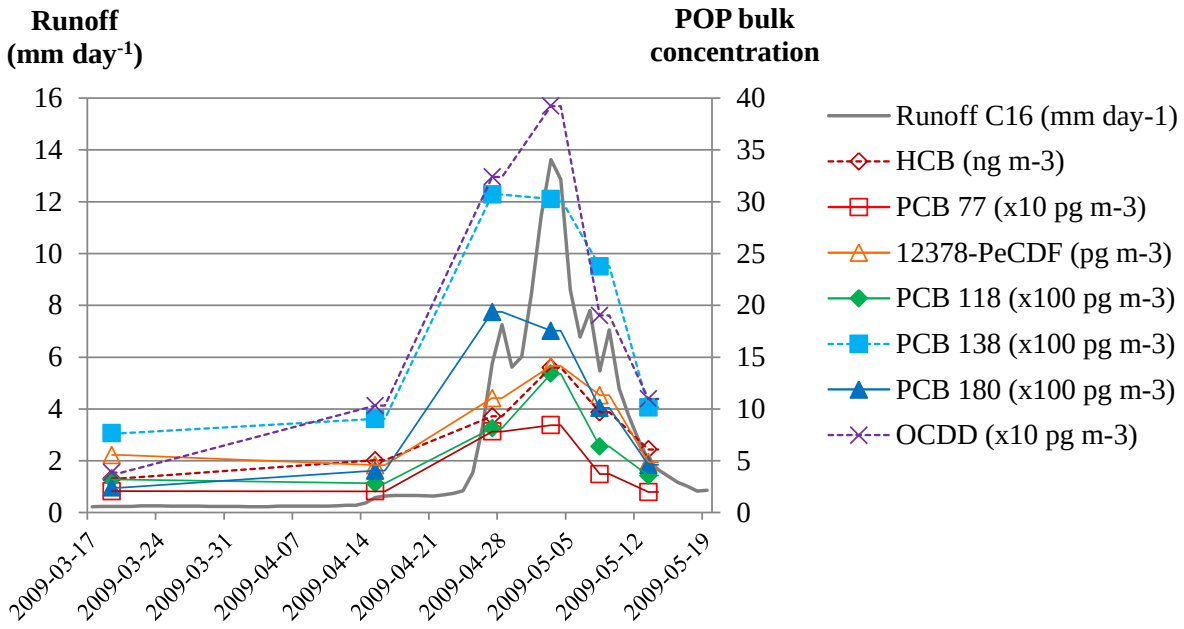
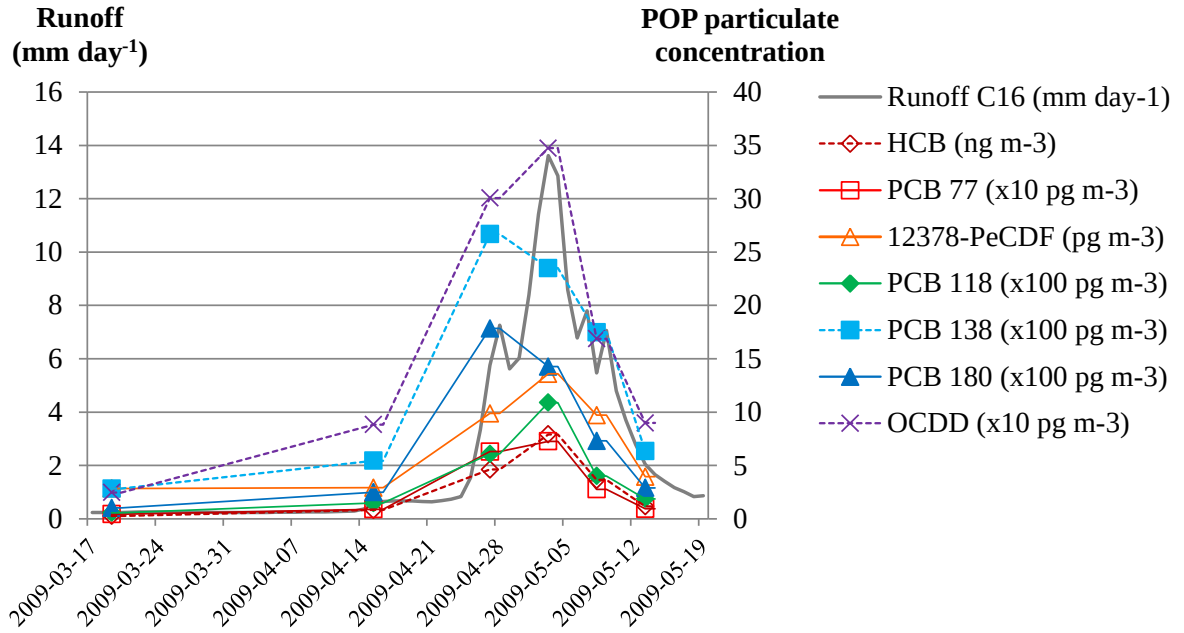


Figure S6. Comparisons of *a)* PCDD/F_{17} (pg m^{-3}) *b)* PCB_7 (ng m^{-3}) and *c)* HCB (ng m^{-3}) bulk concentrations between the snow-covered and the snow-free season at the seven sampling sites. Error bars denote 1 standard deviation (*n*=2 or 3; if error bars are not present, *n*=1).

a)


Runoff (mm day-1)
POP bulk concentration
16
14
12
10
8
6
4
2
0
40
35
30
25
20
15
10
5
0
2009-03-17
2009-03-24
2009-03-31
2009-04-07
2009-04-14
2009-04-21
2009-04-28
2009-05-05
2009-05-12
2009-05-19
Runoff C16 (mm day-1)
HCB (ng m-3)
PCB 77 (x10 pg m-3)
12378-PeCDF (pg m-3)
PCB 118 (x100 pg m-3)
PCB 138 (x100 pg m-3)
PCB 180 (x100 pg m-3)
OCDD (x10 pg m-3)

b)


Runoff (mm day-1)
POP particulate concentration
16
14
12
10
8
6
4
2
0
40
35
30
25
20
15
10
5
0
2009-03-17
2009-03-24
2009-03-31
2009-04-07
2009-04-14
2009-04-21
2009-04-28
2009-05-05
2009-05-12
2009-05-19
Runoff C16 (mm day-1)
HCB (ng m-3)
PCB 77 (x10 pg m-3)
12378-PeCDF (pg m-3)
PCB 118 (x100 pg m-3)
PCB 138 (x100 pg m-3)
PCB 180 (x100 pg m-3)
OCDD (x10 pg m-3)

c)

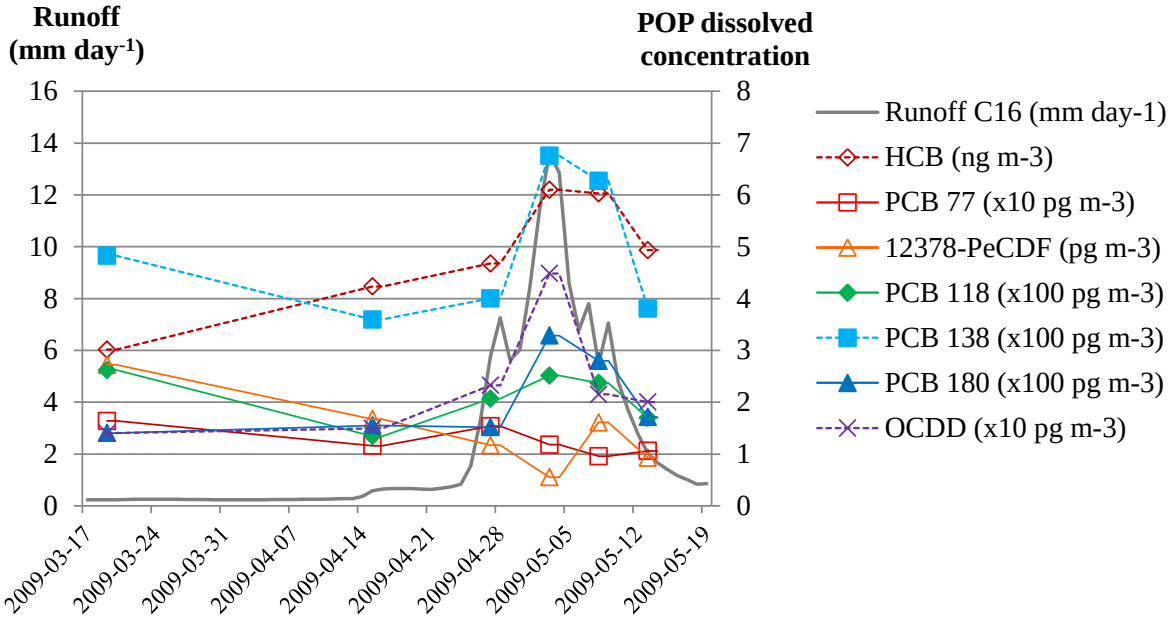


Figure S7. The concentration of different POPs in the *a)* bulk (particulate+dissolved) phase, *b)* particulate phase and *c)* dissolved phase in water at site C16 during spring flood 2009. The plotted POPs had no or a few non-detects and were selected to cover a wide range of K_{OW} values (log K_{OW} 5.5-8.3).

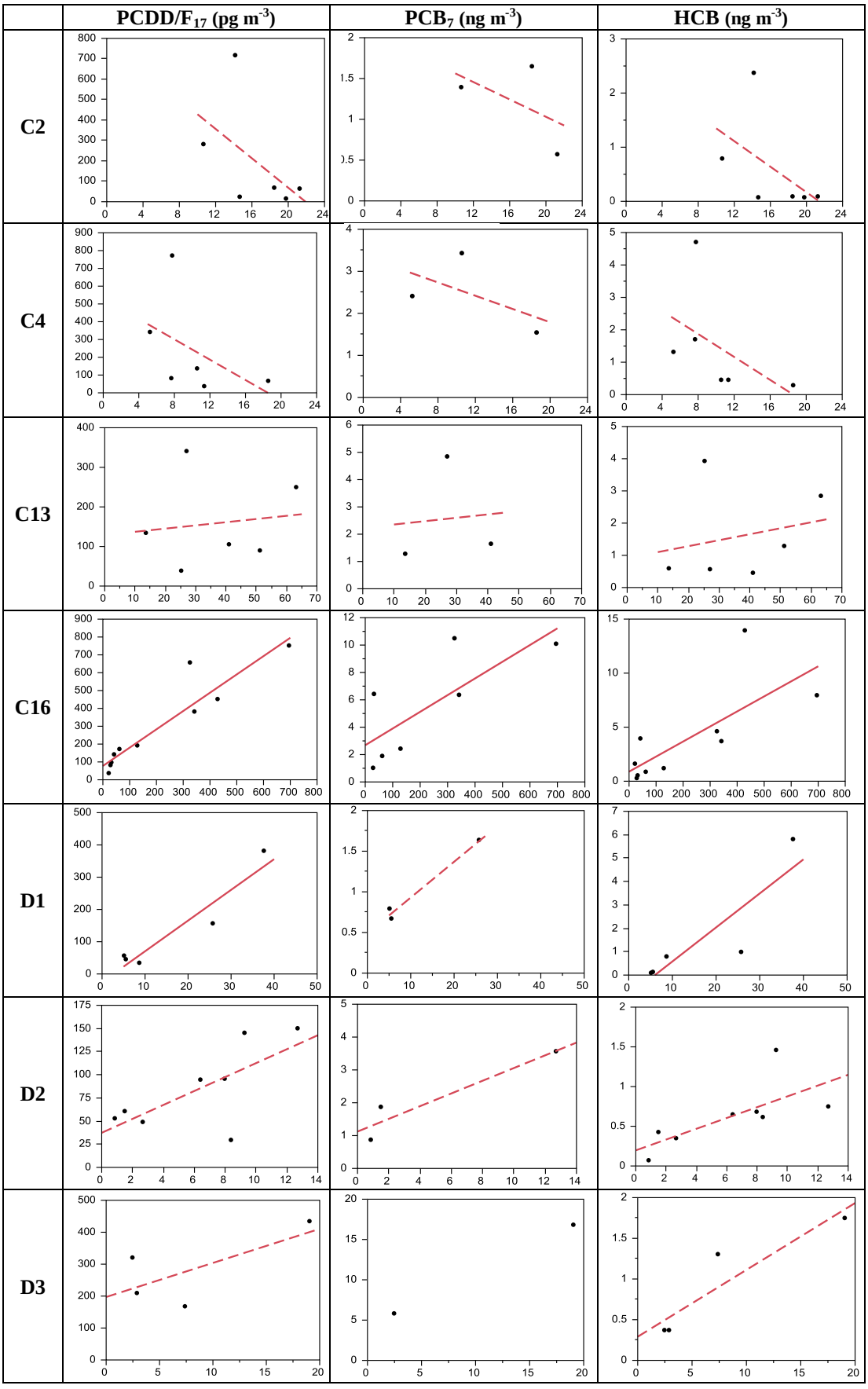


Figure S8. Regressions of particulate POP concentration vs. SPM. Parameters for significant regressions are available in Table S4; not significant regressions (p>0.05) marked with dashed lines.

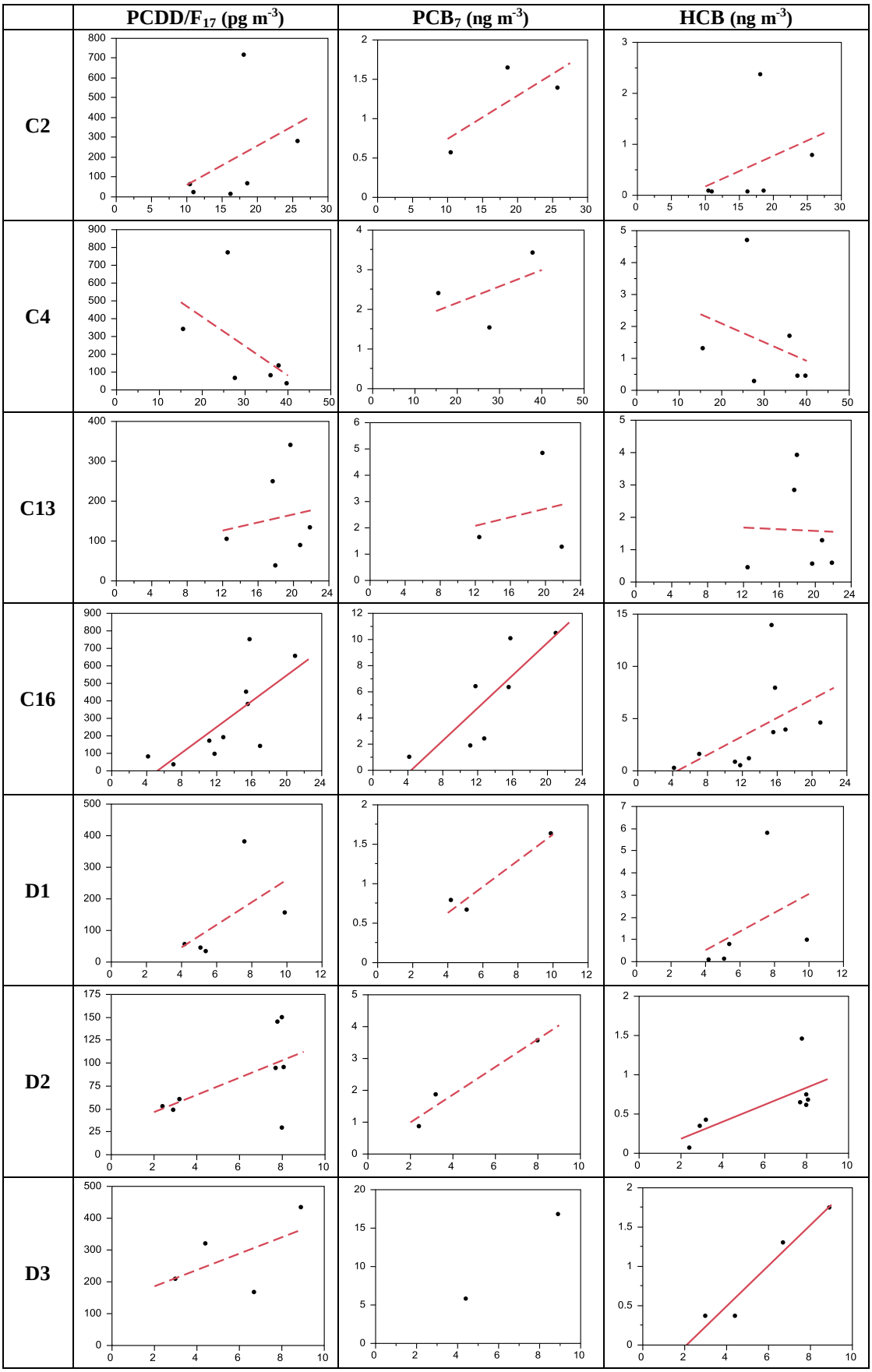


Figure S9. Regressions of particulate POP concentration vs. TOC. Parameters for significant regressions are available in Table S4; not significant regressions (p>0.05) marked with dashed lines.

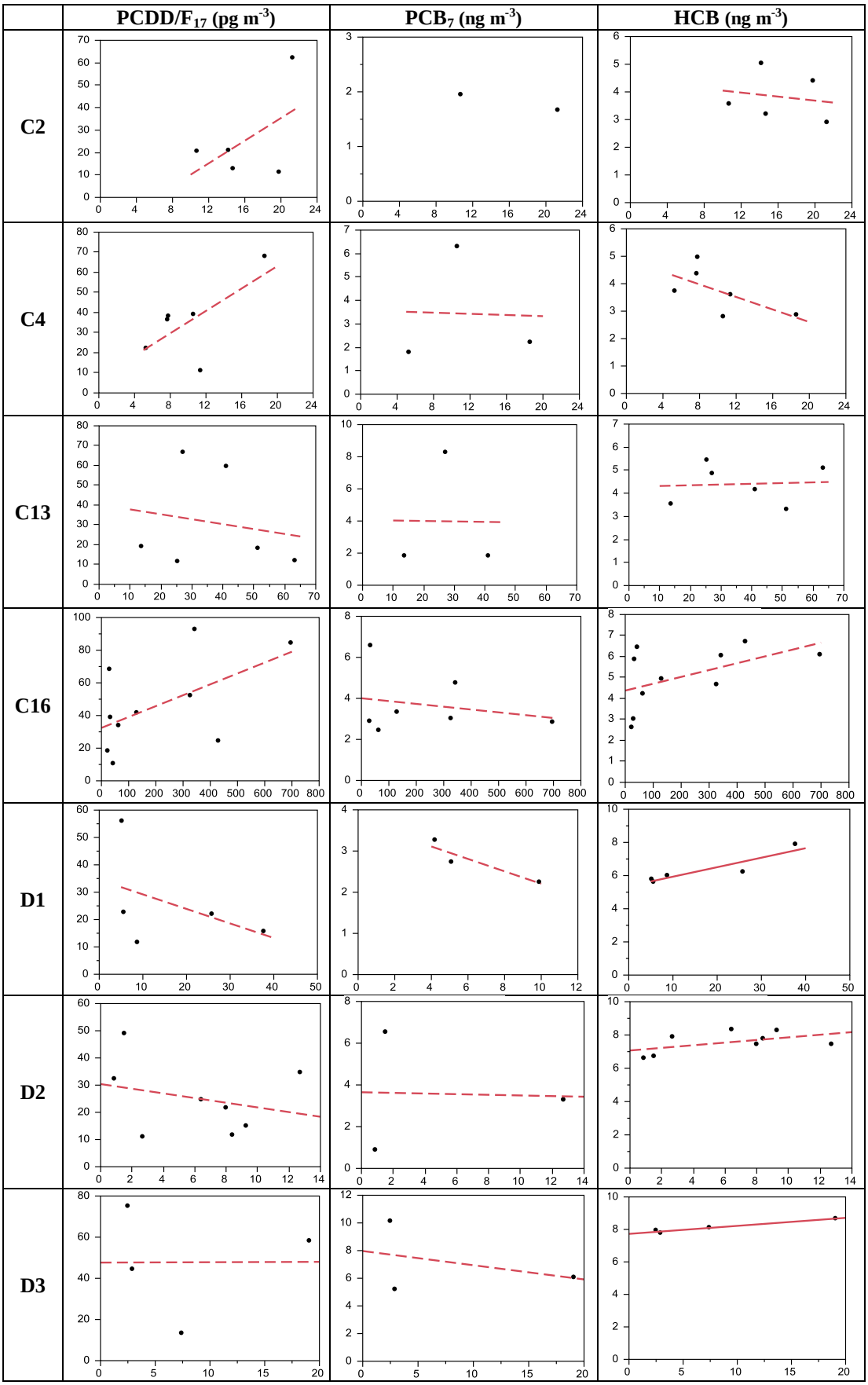


Figure S10. Regressions of dissolved POP concentration vs. SPM. Parameters for significant regressions are available in Table S4; not significant regressions (p>0.05) marked with dashed lines.

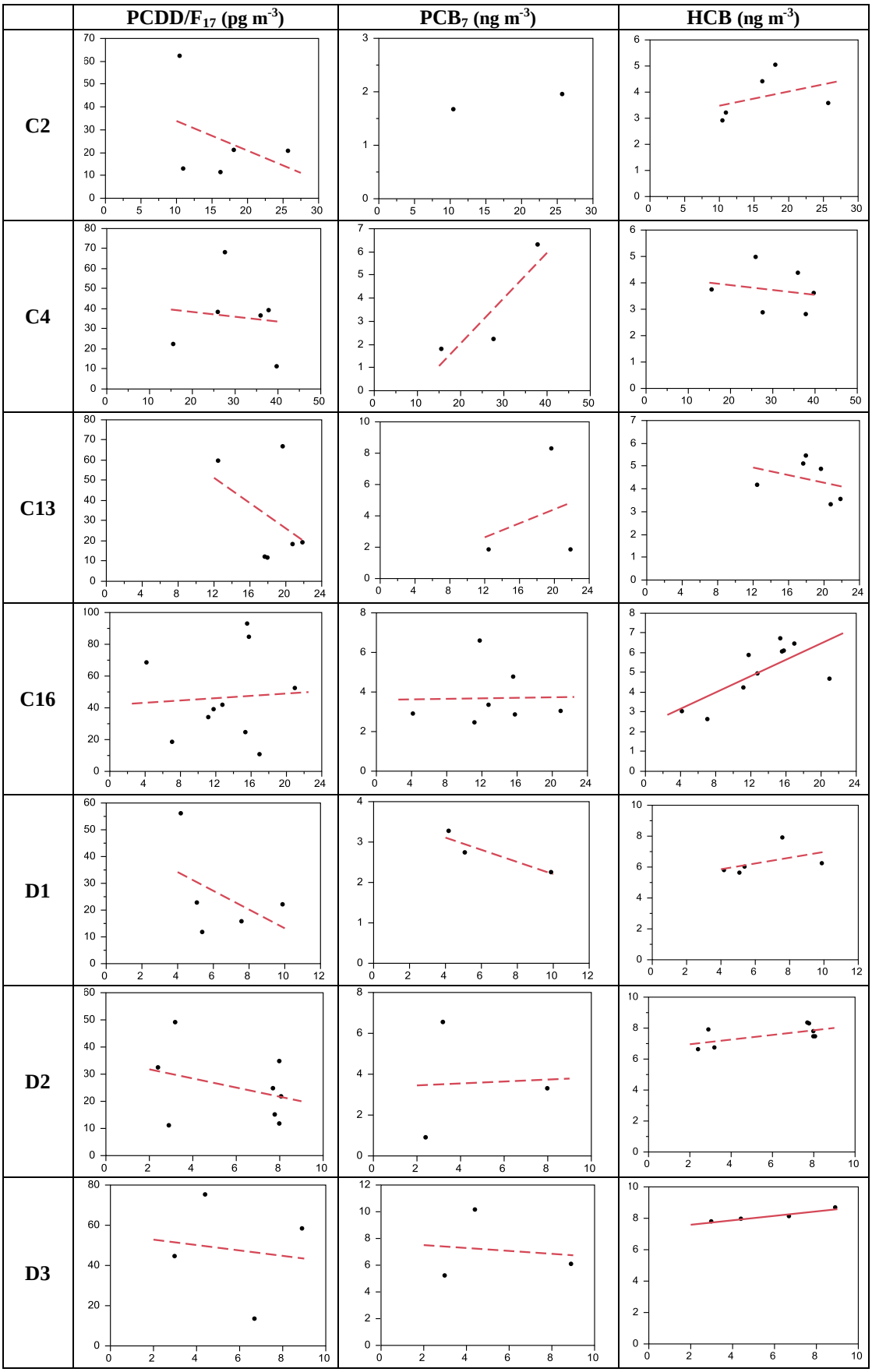


Figure S11. Regressions of dissolved POP concentration vs. TOC. Parameters for significant regressions are available in Table S4; not significant regressions (p>0.05) marked with dashed lines.

Table S4. Parameters for significant linear regressions (y=a+bx) of different POPs on SPM and TOC (from Figures S8-S11).

	Site	***y***	**Fraction**	***a***	***b***	***p***	r^2	***n***
SPM	C16	$PCDD/F_{17}$	Bulk	110	1.1	0.0001	0.88	10
	D1	$PCDD/F_{17}$	Bulk	9.7	9.0	0.024	0.86	5
	C16	$PCDD/F_{17}$	Particulate	77	1.0	0.0001	0.87	10
	D1	$PCDD/F_{17}$	Particulate	-25	9.5	0.014	0.90	5
	C16	PCB_7	Particulate	2.7	0.012	0.044	0.69	7
	C16	HCB	Bulk	5.3	0.017	0.013	0.56	10
	D1	HCB	Bulk	4.5	0.20	0.043	0.79	5
	D3	HCB	Bulk	8.0	0.13	0.035	0.93	4
	C16	HCB	Particulate	0.89	0.014	0.013	0.56	10
	D1	HCB	Particulate	-0.87	0.15	0.049	0.77	5
	D1	HCB	Dissolved	5.4	0.057	0.029	0.84	4
	D3	HCB	Dissolved	7.7	0.049	0.012	0.98	4
TOC	C16	$PCDD/F_{17}$	Bulk	-151	37.3	0.029	0.47	10
	C16	$PCDD/F_{17}$	Particulate	-192	36.9	0.019	0.52	10
	C16	PCB7	Particulate	-2.7	0.62	0.020	0.59	7
	D2	HCB	Bulk	6.6	0.26	0.049	0.50	8
	D3	HCB	Bulk	6.8	0.40	0.016	0.97	4
	D2	HCB	Particulate	-0.032	0.11	0.048	0.50	8
	D3	HCB	Particulate	-0.54	0.26	0.028	0.94	4
	C16	HCB	Dissolved	2.3	0.21	0.021	0.50	10
	D3	HCB	Dissolved	7.3	0.14	0.049	0.90	4

Table S5. *p*-values of linear regressions of particulate concentration of different compounds on SPM and TOC at C16; n=10; $p < 0.05$ indicates significant (positive) regressions, marked in bold. For the dissolved concentrations, only OCDD and PCB 169 had significant (positive) regressions, both with SPM (p=0.011 and 0.008, respectively).

		SPM	TOC
PCDD/F_{17}	2378-TeCDD	**0.011**	*0.775*
	12378-PeCDD	**0.001**	*0.059*
	123478-HxCDD	**0.002**	*0.111*
	123678-HxCDD	**0.000**	**0.049**
	123789-HxCDD	**0.000**	**0.017**
	1234678-HpCDD	**0.000**	**0.012**
	OCDD	**0.000**	**0.018**
	2378-TeCDF	**0.011**	*0.066*
	12378-PeCDF	**0.001**	*0.057*
	23478-PeCDF	**0.004**	**0.016**
	123478-HxCDF	**0.001**	**0.032**
	123678-HxCDF	**0.000**	**0.021**
	234678-HxCDF	**0.003**	**0.015**
	123789-HxCDF	**0.033**	*0.185*
	1234678-HpCDF	**0.000**	**0.014**
	1234789-HpCDF	**0.001**	**0.016**
	OCDF	**0.000**	**0.036**
non-*ortho* PCBs	PCB77	**0.008**	**0.034**
	PCB81	*0.076*	*0.092*
	PCB126	**0.000**	**0.042**
	PCB169	**0.000**	*0.114*
mono-*ortho* PCBs	PCB105	**0.011**	**0.028**
	PCB114	**0.039**	*0.107*
	PCB118	**0.026**	*0.091*
	PCB123	*0.221*	*0.134*
	PCB156	*0.647*	*0.091*
	PCB157	*0.148*	**0.036**
	PCB128/167	*0.987*	*0.520*
	PCB189	*0.599*	*0.398*
PCBs with ≥2 Cl in *ortho* positions	PCB28	*0.374*	*0.311*
	PCB52	*0.812*	*0.628*
	PCB101	*0.716*	*0.542*
	PCB138	*0.174*	**0.021**
	PCB153	*0.072*	**0.027**
	PCB180	*0.899*	*0.088*

Table S6. Average ratios between bulk concentrations of POPs in C4 and C2 during different hydrological seasons. The number is always >1, demonstrating that concentrations were higher in C4.

	PCDD/F$_{17}$	**PCB$_7$**	**HCB**
Snow-covered	2.4	2.7	13.1
Spring flood	2.2	2.1	6.2
Snow-free	1.1	1.8	1.8
***n* (per season)**	*2*	*1*	*2*

Table S7. Calculations for site-specific retention of POPs in forest and mires.

Site characteristics:

	C2	C4
Area (m^2)	129900	190000
Forest	100%	55.9%
Mire	0%	44.1%
Forest (m^2)	129870	106210
Mire (m^2)	0	83790

Deposition to open areas = mires (Bergknut et al. 2011):

PCDD/F_{17} using glass fibre thimble (GFT) sampler:	10	pg m^{-2} day^{-2}
PCDD/F_{17} using amberlite (AMB) sampler:	39	pg m^{-2} day^{-2}
PCB_7 using AMB sampler:	3.9	ng m^{-2} day^{-2}

Deposition to forested areas, assumed to be 4 times higher (Bergknut et al. 2011):

PCDD/F_{17} using glass fibre thimble (GFT) sampler:	41	pg m^{-2} day^{-2}
PCDD/F_{17} using amberlite (AMB) sampler:	156	pg m^{-2} day^{-2}
PCB_7 using AMB sampler:	16	ng m^{-2} day^{-2}

Yearly deposition (µg $year^{-1}$):

	C2			C4		
	Total	*Forest*	*Mire*	*Total*	*Forest*	*Mire*
PCDD/F_{17} using GFT sampler:	1958	1958	0	1917	1601	316
PCDD/F_{17} using AMB sampler:	7395	7395	0	7240	6048	1193
PCB_7 using AMB sampler:	735056	735056	0	719703	601142	118561

Yearly export by streams (µg $year^{-1}$):

	C2	C4
PCDD/F_{17}:	11	19
PCB_7:	147	423

Retention = (deposition - export)/deposition (%):

	C2	C4
PCDD/F_{17} using GFT sampler:	99.5	99.0
PCDD/F_{17} using AMB sampler:	99.9	99.7
PCB_7 using AMB sampler:	100.0	99.9

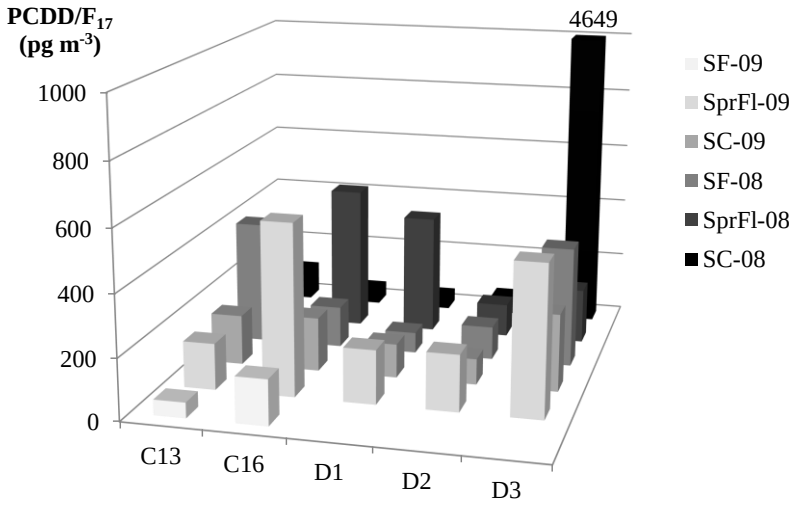
Retention in mire, assuming retention in C2 corresponds to retention in forest:
$Retention_{Mire}$ = ($Retention_{C4}$ - $Retention_{C2}$ × $Percentage_{Forest, C4}$)/$Percentage_{Mire, C4}$ (%)

PCDD/F_{17} using GFT sampler:	98.4
PCDD/F_{17} using AMB sampler:	99.6
PCB_7 using AMB sampler:	99.9

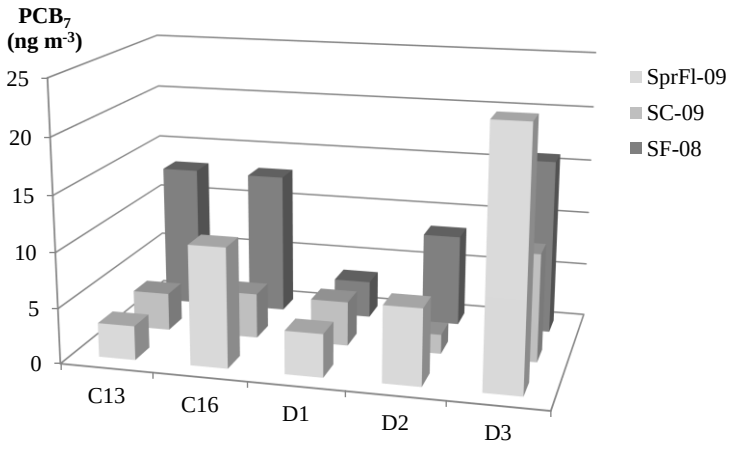
Export = 100 - retention (%):

	Mire	Forest (=C2)	Ratio mire/forest
PCDD/F_{17} using GFT sampler:	1.6	0.5	2.9
PCDD/F_{17} using AMB sampler:	0.4	0.2	2.8
PCB_7 using AMB sampler:	0.1	0.0	5.5

a)



b)



c)

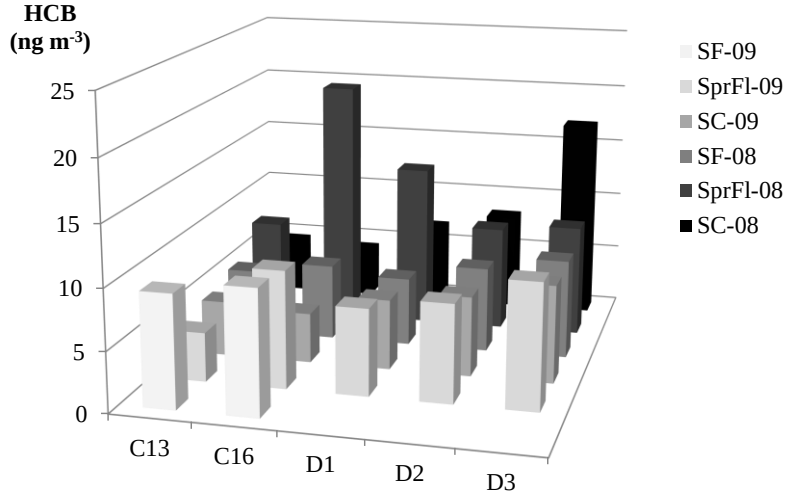
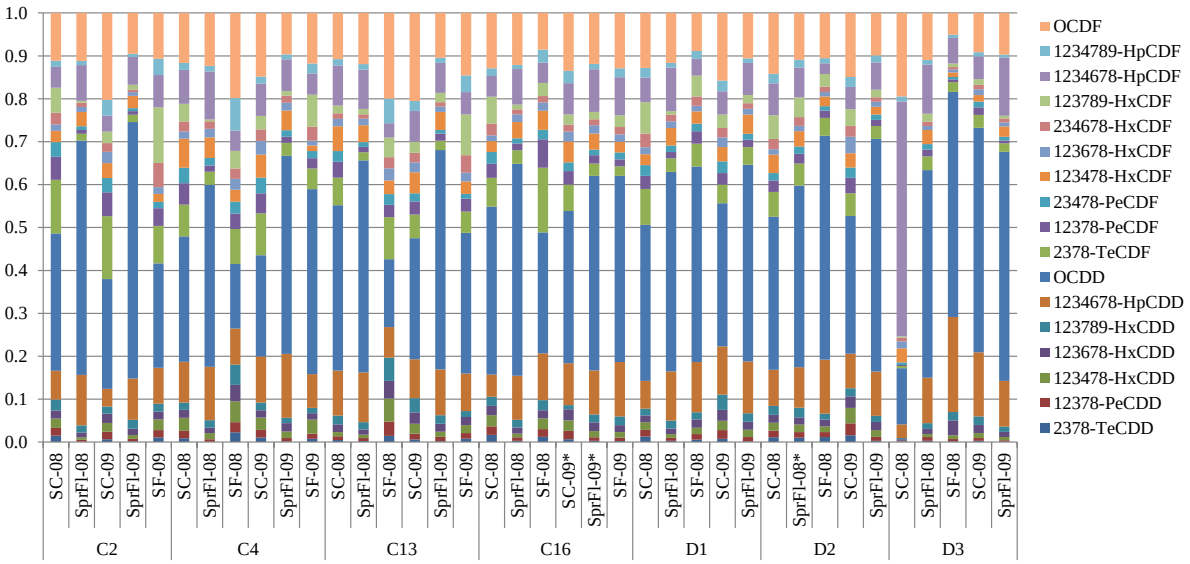


Figure S12. Bulk concentrations of *a)* $PCDD/F_{17}$ (pg m^{-3}), *b)* PCB_7 (ng m^{-3}) and *c)* HCB (ng m^{-3}) at the seven sampling sites during different hydrological seasons (SF: snow-free; SprFl: spring flood; SC: snow-covered; -08: year 2008; -09: year 2009).

a)



b)

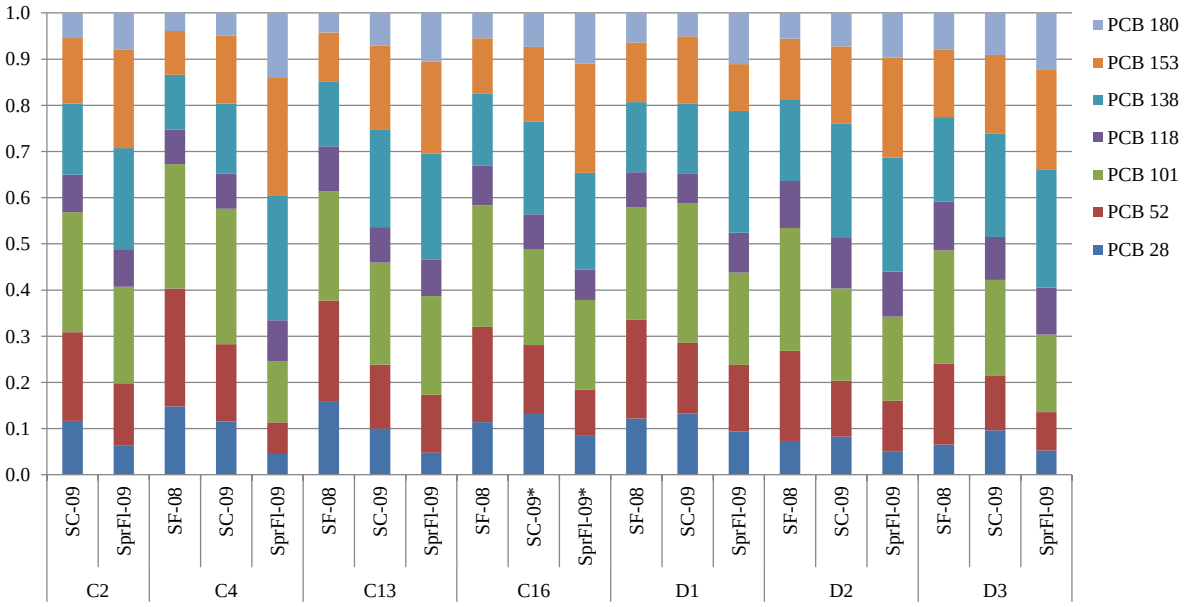


Figure S13. Congener patterns of *a)* PCDD/F_{17} and *b)* PCB_7 at the seven different sampling sites during different hydrological seasons (SF: snow-free; SprFl: spring flood; SC: snow-covered; -08: year 2008; -09: year 2009). * denotes an average value when several samplings were performed at a site during one season.

Table S8. The percentage of HpCDD and OCDD of total PCDD/F_{17} concentrations at the different sites. Numbers are average and standard deviation (SD) of samples in snow-covered + snow-free (SC + SF) seasons, or spring flood (SprFl) season. The deviating high-level SC-08 sample from D3 is not included; its fraction of HpCDD+OCDD was 16%.

Site	**SC + SF**		**SprFl**	
	Average ± SD	***n***	**Average ± SD**	***n***
C2	34 ± 5%	3	68 ± 2%	2
C4	37 ± 11%	4	58 ± 4%	2
C13	38 ± 11%	4	61 ± 0.5%	2
C16	46 ± 7%	4	58 ± 3 %	2
D1	48 ± 8%	3	58 ± 0.1%	2
D2	50 ± 13%	3	58 ± 9%	2
D3	71 ± 5%	2	61 ± 4%	2