

Supplementary Material

Transfer of perfluorooctanesulfonate (PFOS), decabrominated diphenyl ether (BDE-209) and Dechlorane Plus (DP) from biosolid-amended soils to leachate and runoff water

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S.1. Materials and Methods

S1.1. Standards and reagents

Chemicals used as copper fine powder, anhydrous sodium sulphate, sulphuric acid (95 - 97 %) and solvents (dichloromethane -DCM-, hexane, toluene and ethyl acetate) for organic trace analysis were provided from Merck (Darmstadt, Germany). Siliceous earth extrapure, sodium acetate, ammonium acetate, acetic acid, ammonium hydroxide, acetonitrile, methanol, were obtained from Scharlau (Barcelona, Spain).

Oasis WAX cartridges (500 mg, 6 mL) SPE were purchased from Waters (Milford, MA, USA) and EnviCarb cartridges (500 mg, 6 mL) SPE from Sigma-Aldrich (St.Louis, MO, USA)

The analytical standards used in this study are detailed in Table S1.

Table S1.- Analytical standards used in this study.

Native Compounds	Labelled Compounds			Supplier
	Cleanup	Internal	Calibration	
PFAC-MXB				
PFBS (perfluorobutanesulfonate)				
PFHxS (perfluorohexanesulfonate)				
PFOS (perfluorooctanesulfonate)				
PFDS (perfluorodecanesulfonate)				
PFBA (perfluorobutanoic acid)				
PFPeA (perfluoropentanoic acid)				
PFHxA (perfluorohexanoic acid)				
PFHpA (perfluoroheptanoic acid)				
PFOA (perfluorooctanoic acid)	MPFAC-MXA	¹³ C ₉ -PFNA		Wellington Laboratories Inc. (Guelph, Canada)
PFNA (perfluorononanoic acid)				
PFDA (perfluorodecanoic acid)				
PFUdA (perfluoroundecanoic acid)				
PFDoA (perfluorododecanoic acid)				
PFTTrDA (perfluorotridecanoic acid)				
PFTeDA (perfluorotetradecanoic acid)				
PFHxDA (perfluorohexadecanoic acid)				
PFODA (perfluorooctadecanoic acid)				
FOSA (perfluorooctanesulfonamide)			MPFAC-MXA	

N-MeFOSA (N-methyl perfluorooctanesulfonamide)	N-d3-MeFOSA	¹³ C ₉ -PFNA		Wellington Laboratories Inc. (Guelph, Canada)
N-EtFOSA (N-ethyl perfluorooctanesulfonamide)	N-d5-EtFOSA	¹³ C ₉ -PFNA		Wellington Laboratories Inc. (Guelph, Canada)
PBDEs (IUPAC congener numbers: BDE-17, -28, -47, -66, -77, -85, -99, -100, -119, -138, -153, -154, -156, -183, -184, -191, -196, -197, -206, -207, -209)	MBDE-MXE	BDE-CVS-EISS	BDE-CVS-E	Wellington Laboratories Inc. (Guelph, Canada)
DBDPE (decabromodiphenyl ethane)	MDBDPE	BDE-CVS-EISS		Wellington Laboratories Inc. (Guelph, Canada)
<i>anti</i> -DP ^a	¹³ C ₁₀ - <i>anti</i> -DP ^a	BDE-CVS-EISS^b		^a Cambridge Isotope Laboratories. Inc. (Andover, MA, USA)
<i>syn</i> -DP ^a	¹³ C ₁₀ - <i>syn</i> -DP ^a	BDE-CVS-EISS^b		^b Wellington Laboratories Inc. (Guelph, Canada)
Dec 602 (CAS# 31107-44-5) ^c	¹³ C ₁₀ - <i>anti</i> -DP ^a	BDE-CVS-EISS^b		^a Cambridge Isotope Laboratories. Inc. (Andover, MA, USA)
Dec 603 (CAS# 13560-91-4) ^c	¹³ C ₁₀ - <i>anti</i> -DP ^a	BDE-CVS-EISS^b		^b Wellington Laboratories Inc. (Guelph, Canada)
Dec 604 (CAS# 34571-16-9) ^c	¹³ C ₁₀ - <i>anti</i> -DP ^a	BDE-CVS-EISS^b		^c Toronto Research Chemical Inc. (Toronto, ON, Canada)

Table S2.- Physicochemical characterization of the soil used in the experiment.

Parameter	Soil
pH	7.50
EC (1:10) at 25 °C (dS/m)	1.90
Organic C (%)	3.0
Water content 105 °C (%)	<1.0
NO ₃ ⁻ -N (mg/kg)	230
NH ₄ ⁺ -N (mg/kg)	9.7
N Kjeldahl (%)	0.11
Extractable K (%)	0.01
Extractable P (%)	0.11
Mg (%)	0.04
CaCO ₃ , equiv. (%)	<3.0
Ca (%)	0.24
Bulk density (g/cm ³)	1.65
Sand -0.05 < D < 2 mm- (%)	82.2
Silt -0.02 < D < 0.05 mm- (%)	3.8
Silt -0.002 < D < 0.02 mm- (%)	5.6
Clay -0.002 mm- (%)	8.4
Soil Type (USDA)	Loamy sand

(Data obtained from Navarro et al. 2017)

Fig. S1. Sampling dates and rainfall recorded during the experiment.

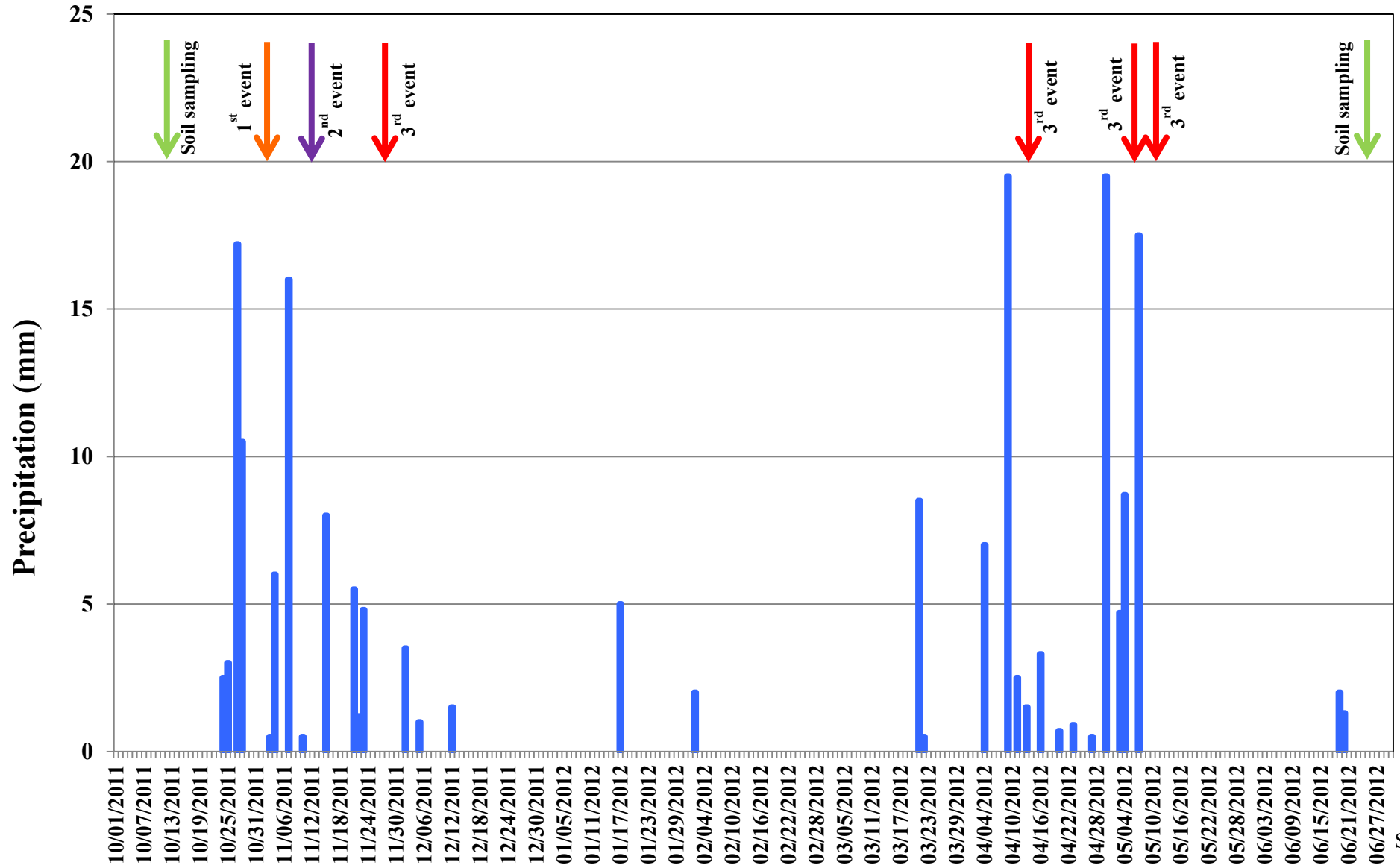


Table S3. Concentrations (ng/g d.w.) of PFASs and HFRs in soils at the beginning (t = 0 days) and the end (t = 293 days) of the experiment.

	CONTROL			T-1			T-2			T-3			T-4		
	t = 0	t = final		t = 0	t = final		t = 0	t = final		t = 0	t = final		t = 0	t = final	
	< 0.5 m	< 0.5 m	0.5 - 2.5 m	< 0.5 m	< 0.5 m	0.5 - 2.5 m	< 0.5 m	< 0.5 m	0.5 - 2.5 m	< 0.5 m	< 0.5 m	0.5 - 2.5 m	< 0.5 m	< 0.5 m	0.5 - 2.5 m
PFBS	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.35	0.20	N.D.
PFHxS	N.D.	N.D.	N.D.	0.97	2.70	N.D.	1.37	0.72	N.D.	0.82	0.27	N.D.	2.31	1.79	0.11
PFOS	0.11 ^{*A}	0.16 ^{*A}	0.29 ^{*A}	41.81 ^{*B}	84.65 ^{*B}	0.59 ^{*B}	44.96 ^{*B}	36.12 ^{*B}	0.41 ^{*B}	37.98 ^{*B}	30.06 ^{*B}	0.33 ^{*B}	94.32 ^{*B}	47.24 ^{*B}	0.49 ^{*B}
PFHxA	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1.28	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PFHpA	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.36	N.D.
PFOA	N.D.	N.D.	N.D.	0.22	1.13	N.D.	0.15	4.54	0.16	0.27	0.36	0.06	0.33	0.43	N.D.
PFNA	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.49	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PFDA	N.D.	0.10	N.D.	N.D.	0.79	N.D.	0.40	2.56	0.13	0.27	0.42	0.09	0.15	0.29	N.D.
PFUdA	N.D.	N.D.	N.D.	N.D.	0.14	N.D.	N.D.	0.34	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PFDoA	N.D.	N.D.	N.D.	0.12	0.23	N.D.	N.D.	0.40	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Σ PFASs	0.11	0.26	0.29	43.12	89.64	0.59	46.88	46.45	0.70	39.34	31.11	0.48	97.46	50.31	0.60
BDE-17	N.D.	N.D.	N.D.	N.D.	0.001	N.D.	N.D.	0.002	N.D.	N.D.	0.001	N.D.	N.D.	0.002	N.D.
BDE-28	N.D.	0.002	0.002	0.002 ^{*B}	0.005 ^{*B}	0.001 ^{*B}	0.01 ^{*B}	0.01 ^{*B}	0.002 ^{*B}	0.01 ^{*B}	0.01 ^{*B}	0.002 ^{*B}	0.02 ^{*B}	0.02 ^{*B}	0.001 ^{*B}
BDE-47	0.06	0.03	0.03	0.20	0.18	0.04	0.41	0.28	0.04	0.22	0.19	0.03	0.56 ^{*A}	0.46 ^{*A}	0.04
BDE-66	N.D.	N.D.	N.D.	N.D.	N.D.	0.001	N.D.	N.D.	0.001	N.D.	N.D.	0.003	N.D.	N.D.	0.002
BDE-99	0.05	0.06	0.04	0.24 ^{*B}	0.30 ^{*B}	0.10 ^{*B}	0.54 ^{*B}	0.43 ^{*B}	0.10 ^{*B}	0.33 ^{*B}	0.30 ^{*B}	0.10 ^{*B}	0.75 ^{*A,B}	0.72 ^{*A,B}	0.05 ^{*B}
BDE-100	0.01	0.01	0.01	0.05	0.06	0.01	0.10	0.08	0.01	0.05	0.06	0.01	0.14	0.15	0.01
BDE-153	0.02 ^{*A}	0.01 ^{*A}	0.01 ^{*A}	0.05 ^{*B}	0.06 ^{*B}	0.01 ^{*B}	0.09 ^{*B}	0.06 ^{*B}	0.01 ^{*B}	0.05 ^{*B}	0.06 ^{*B}	0.02 ^{*B}	1.09 ^{*B}	0.15 ^{*B}	0.02 ^{*B}
BDE-154	0.01	0.01	0.01	0.04	0.06	0.01	0.08	0.05	0.01	0.04	0.05	0.01	0.19	0.09	0.01
BDE-156	N.D.	N.D.	0.01	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
BDE-183	0.03	0.02	0.02	0.06	0.06	0.02	0.11	0.10	0.02	0.09	0.13	0.02	10.05	0.30	0.03

BDE-184	0.04	0.003	N.D.	N.D.	0.004	0.004	N.D.	0.01	0.004	N.D.	0.03	0.004	N.D.	N.D.	0.004
BDE-196	N.D.	0.04	0.02	0.09	0.08	0.04	0.11	0.15	0.04	0.19	0.20	0.03	2.66	0.08	0.05
BDE-197	N.D.	0.03	0.02	0.05	0.03	0.03	0.06	0.08	0.04	0.07	0.22	0.03	4.25	0.06	0.04
BDE-206	0.19	0.08	0.06	19.92 ^{*B}	22.92 ^{*B}	0.12 ^{*B}	20.42 ^{*B}	9.33 ^{*B}	0.23 ^{*B}	19.54 ^{*B}	3.41 ^{*B}	0.08 ^{*B}	64.19 ^{*B}	16.10 ^{*B}	0.23 ^{*B}
BDE-207	N.D.	0.09	0.06	8.02 ^{*B}	6.33 ^{*B}	0.10 ^{*B}	7.91 ^{*B}	3.19 ^{*B}	0.27 ^{*B}	4.12 ^{*B}	1.63 ^{*B}	0.09 ^{*B}	21.82 ^{*B}	5.82 ^{*B}	0.19 ^{*B}
BDE-209	2.14 ^{*A}	1.97 ^{*A}	0.84 ^{*A}	799.39 ^{*B}	725.34 ^{*B}	4.19 ^{*B}	301.67 ^{*B}	234.84 ^{*B}	8.06 ^{*B}	216.00 ^{*B}	143.85 ^{*B}	2.37 ^{*B}	815.19 ^{*B}	588.76 ^{*B}	5.07 ^{*B}
Σ PBDEs	2.55 ^{*A}	2.36 ^{*A}	1.12 ^{*A}	828.10 ^{*B}	755.42 ^{*B}	4.68 ^{*B}	331.51 ^{*B}	248.60 ^{*B}	8.84 ^{*B}	240.70 ^{*B}	150.14 ^{*B}	2.81 ^{*B}	920.91 ^{*B}	612.71 ^{*B}	5.75 ^{*B}
DBDPE	0.56 ^{*A}	0.30 ^{*A}	0.28 ^{*A}	1.14	0.89	0.96	3.46	0.13	2.15	1.50	1.17	0.95	10.78 ^{*A}	3.73 ^{*A}	6.38 ^{*A}
anti-DP	N.D.	N.D.	N.D.	11.56	13.49	0.03	9.58	6.54	N.D.	8.04	5.37	0.03	16.80	16.02	N.D.
syn-DP	N.D.	N.D.	N.D.	4.73	5.82	0.01	3.56	2.92	N.D.	4.34	2.30	0.01	7.09	7.29	N.D.
Σ DP	N.D.	N.D.	N.D.	16.29 ^{*B}	19.31 ^{*B}	0.04 ^{*B}	13.14 ^{*B}	9.46 ^{*B}	N.D.	12.38 ^{*B}	7.67 ^{*B}	0.04 ^{*B}	23.88 ^{*B}	23.31 ^{*B}	N.D.
<i>f_{syn}</i>	-	-	-	0.29	0.30	0.31	0.27	0.31	-	0.35	0.30	0.36	0.30	0.31	-
Dec 602	N.D.	N.D.	N.D.	0.001	0.002	N.D.	0.001	N.D.	N.D.	N.D.	N.D.	N.D.	0.04	N.D.	N.D.
Dec 603	N.D.	N.D.	N.D.	0.01	N.D.	N.D.	0.005	N.D.	N.D.	0.01	N.D.	N.D.	0.01	N.D.	N.D.
CP	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.001	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

N.D.: not detected. < 0.5 m = area of the top of the tray where fortified biosolid was applied; 0.5 - 2.5 m = remaining surface of the tray without amendment.

PFDS, PFBA, PFPeA, PFTrDA, PFTeDA, PFHxDA, PFOA, FOSA, N-MeFOSA, N-EtFOSA, BDE-77, -85, -119, -138, -191, Dec 604 and Mirex were not detected in any soil sample.

T-1: soil + B-1, T-2: soil + B-2, T-3: soil + B-3, T-4: soil + B-4.

B-1: aerobic-digested MSW compost, B-2: anaerobic-digested thermal drying sludge, B-3: aerobic-digested composted sewage sludge, B-4: anaerobic-digested MSW compost.

^{*A} Data showed statistically significant differences ($p < 0.05$; Mann-Whitney U-test) between treatments. ^{*B} Data showed statistically significant differences ($p < 0.05$; Mann-Whitney U-test) between areas of the tray.

Table S4. Biosolid-amended soil/control soil ratios calculated at the beginning of the experiment (t = 0) for PFASs and HFRs.

	T-1	T-2	T-3	T-4
PFOS	380	409	345	857
ΣPFASs	392	426	358	886
BDE 47	3.24	6.77	3.65	9.16
BDE 99	5.09	11.35	7.03	15.83
BDE 100	4.02	8.69	3.90	11.58
BDE 153	2.95	5.63	3.28	67.3
BDE 154	2.85	5.68	3.27	14.3
BDE 183	1.97	3.72	2.90	340
BDE 206	106	109	104	343
BDE 209	373	141	101	381
ΣPBDEs	325	130	94.4	361
DBDPE	2.03	6.17	2.68	19.2

ΣPFASs: sum of PFBS, PFHxS, PFOS, PFOA, PFDA and PFDoA.

ΣPBDEs: sum of BDE-28, -47, -99, -100, -153, -154, -183, -184, -196, -197, -206, -207 and -209.

Biosolid-amended soil/control soil ratios were not calculated individually for PFBS, PFHxS, PFOA, PFDA, PFDoA, BDE-28, -196, -197, -207, *anti*-DP, *syn*-DP, Dec 602 and Dec 603 because these compounds were not detected in control soil.

Table S5. Concentrations (ng/L) of PFASs in leachate and runoff water in the rainfall events.

	CONTROL		T-1		T-2		T-3		T-4	
	Leachate	Runoff	Leachate	Runoff	Leachate	Runoff	Leachate	Runoff	Leachate	Runoff
1st event										
PFBS	13.51	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
PFHxS	N.D.	N.D.	N.D.	12.54	N.D.	N.D.	N.D.	N.D.	N.D.	6.38
PFOS	5.80	10.76	23.87	219.33	11.66	59.16	6.07	115.29	22.85	415.13
PFOA	22.45	7.06	28.56	8.46	23.78	7.82	25.86	6.03	22.11	8.21
PFNA	5.89	7.36	6.71	5.73	5.47	7.60	7.95	6.00	2.96	4.18
PFDA	N.D.	8.33	N.D.	10.98	N.D.	14.82	ND	10.42	N.D.	10.46
PFUdA	N.D.	N.D.	N.D.	N.D.	N.D.	3.08	ND	1.93	N.D.	1.33
PFDoA	N.D.	N.D.	N.D.	N.D.	N.D.	0.49	ND	0.59	N.D.	0.33
Σ PFASs	47.65	33.51	59.14	257.04	40.91	92.97	39.88	140.26	47.92	446.02
2nd event										
PFBS	6.56	N.D.	14.00	N.D.	13.69	N.D.	15.75	N.D.	52.57	N.D.
PFHxS	N.D.	N.D.	26.84	N.D.	18.26	N.D.	25.63	N.D.	53.37	6.17
PFOS	1.16	5.88	23.42	72.79	5.48	91.96	3.12	79.03	14.72	310.25
PFOA	16.70	2.35	27.14	9.84	23.43	9.99	27.47	2.49	21.53	3.84
PFNA	N.D.	1.90	2.45	4.28	1.62	5.25	1.47	1.25	1.50	1.32
PFDA	0.33	2.36	1.24	15.40	0.40	21.80	0.37	3.66	0.26	5.51
PFUdA	N.D.	N.D.	N.D.	2.15	N.D.	3.44	N.D.	0.47	N.D.	0.86
PFDoA	N.D.	N.D.	N.D.	N.D.	N.D.	0.61	N.D.	N.D.	N.D.	N.D.
Σ PFASs	24.75	12.49	95.09	104.46	62.88	133.05	73.81	86.90	143.95	327.95
3rd event										
PFBS	4.42	N.D.	12.74	N.D.	5.90	N.D.	10.74	N.D.	34.12	N.D.
PFHxS	2.64	N.D.	50.12	3.45	34.87	N.D.	47.35	N.D.	81.66	N.D.

PFOS	9.56	4.13	6.84	33.77	5.70	67.62	3.98	73.65	11.80	93.21
PFOA	10.84	3.80	15.62	5.13	63.59	15.42	51.00	8.31	22.48	5.08
PFNA	N.D.	2.41	N.D.	2.51	1.44	8.56	N.D.	6.66	N.D.	3.69
PFDA	N.D.	1.43	N.D.	1.55	0.97	8.04	N.D.	3.96	N.D.	1.90
PFUdA	N.D.	N.D.	N.D.	N.D.	N.D.	0.97	N.D.	N.D.	N.D.	N.D.
Σ PFASs	27.46	11.77	85.32	46.41	112.47	100.61	113.07	92.58	150.06	103.88

N.D.: not detected.

PFDS, PFBA, PFPeA, PFHxA, PFHpA, PFTTrDA, PFTeDA, PFHxDA, PFODA, FOSA; N-MeFOSA and N-EtFOSA were not detected in any sample.

Table S6. Concentrations (ng/g d.w.) of HFRs in particulate matter of leachate and runoff water in the rainfall events.

	CONTROL		T-1		T-2		T-3		T-4	
	Leachate	Runoff	Leachate	Runoff	Leachate	Runoff	Leachate	Runoff	Leachate	Runoff
1st event										
BDE-17	N.D.	0.002	0.003	0.002	0.01	0.001	N.D.	0.002	0.005	0.001
BDE-28	0.02	0.01	0.02	0.004	0.03	0.004	0.01	0.004	0.02	0.01
BDE-47	0.29	0.13	0.23	0.13	0.98	0.10	0.14	0.11	0.22	0.18
BDE-66	N.D.	0.01	N.D.	0.01	0.02	0.005	N.D.	0.005	0.01	0.005
BDE-85	N.D.	0.01	N.D.	N.D.	0.02	N.D.	N.D.	N.D.	N.D.	0.01
BDE-99	0.18	0.18	0.18	0.23	0.49	0.18	0.14	0.17	0.20	0.20
BDE-100	0.05	0.04	0.04	0.01	0.14	0.04	0.03	0.04	0.04	0.05
BDE-138	N.D.	0.01	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
BDE-153	0.06	0.06	0.07	0.07	0.06	0.06	0.05	0.06	0.07	0.07
BDE-154	0.06	0.05	0.06	N.D.	0.06	0.06	0.07	0.06	0.07	0.06
BDE-183	0.13	0.12	0.13	0.14	0.08	0.11	0.19	0.12	0.14	0.13
BDE-191	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
BDE-196	0.05	0.11	0.13	N.D.	0.05	0.10	0.08	0.23	0.12	0.12
BDE-197	0.05	0.10	0.07	N.D.	0.04	0.07	0.07	0.18	0.08	0.08
BDE-206	N.D.	0.91	2.55	3.39	N.D.	1.59	N.D.	1.93	N.D.	7.05
BDE-207	N.D.	0.57	N.D.	1.68	N.D.	0.58	N.D.	0.65	N.D.	1.59
BDE-209	N.D.	0.09	3.39	7.32	N.D.	9.54	3.82	17.41	N.D.	2.85
Σ PBDEs	0.89	2.40	6.86	12.99	1.96	12.43	4.62	20.96	0.97	12.38
DBDPE	N.D.	N.D.	N.D.	N.D.	N.D.	0.22	N.D.	N.D.	N.D.	1.30
anti-DP	N.D.	N.D.	1.86	3.29	1.54	6.49	0.79	2.05	4.90	6.83
syn-DP	N.D.	N.D.	0.49	3.32	0.58	2.62	0.47	0.71	1.95	2.95
Σ DP	N.D.	N.D.	2.35	6.61	2.12	9.11	1.26	2.76	6.85	9.78

f_{syn}	-	-	0.21	0.50	0.27	0.29	0.37	0.26	0.28	0.30
Dec 602	0.002	0.001	0.001	0.002	0.002	0.002	0.002	0.003	0.002	0.002
2nd event										
BDE-28	N.D.	N.D.	N.D.	N.D.	0.23	N.D.	N.D.	N.D.	N.D.	N.D.
BDE-47	N.D.	N.D.	N.D.	2.25	N.D.	N.D.	0.05	N.D.	N.D.	N.D.
BDE-99	N.D.	N.D.	N.D.	0.32	N.D.	0.01	N.D.	0.02	N.D.	0.02
BDE-100	N.D.	N.D.	N.D.	0.11	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
BDE-153	N.D.	0.02	0.04	N.D.	0.05	0.03	0.08	0.04	0.03	0.04
BDE-154	N.D.	0.03	0.05	N.D.	0.10	0.03	0.08	0.04	0.04	0.03
BDE-183	N.D.	0.05	N.D.	N.D.	N.D.	0.08	N.D.	0.09	N.D.	0.10
BDE-196	N.D.	0.04	N.D.	N.D.	N.D.	0.07	N.D.	0.07	N.D.	0.11
BDE-197	N.D.	0.07	N.D.	N.D.	N.D.	0.08	N.D.	0.08	1.53	0.11
BDE-206	1.77	0.27	3.08	0.61	1.64	1.07	2.09	0.96	2.05	5.31
BDE-207	1.25	0.73	2.22	1.33	6.92	1.31	3.77	1.48	3.42	3.47
BDE-209	N.D.	N.D.	57.40	41.03	24.95	27.42	35.95	26.86	68.29	147.08
Σ PBDEs	3.01	1.21	62.78	45.65	33.87	30.10	42.01	29.63	75.35	156.27
DBDPE	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1.80
anti-DP	N.D.	N.D.	1.57	4.95	1.27	4.29	0.95	4.59	N.D.	5.78
syn-DP	N.D.	N.D.	0.66	0.19	0.38	0.59	0.59	2.56	N.D.	1.67
Σ DP	N.D.	N.D.	2.23	5.13	1.65	4.88	1.54	7.15	N.D.	7.45
f_{syn}	-	-	0.30	0.04	0.23	0.12	0.38	0.36	-	0.22
Dec 602	N.D.	0.001	N.D.	0.01	0.003	0.003	0.002	0.001	N.D.	0.001
3rd event										
BDE-17	N.D.	N.D.	N.D.	N.D.	N.D.	0.004	N.D.	N.D.	N.D.	0.01

BDE-28	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
BDE-66	N.D.	N.D.	N.D.	N.D.	N.D.	0.01	N.D.	N.D.	N.D.	0.03
BDE-85	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.04
BDE-99	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.05	N.D.	N.D.
BDE-100	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.02
BDE-153	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.02	N.D.	N.D.
BDE-154	N.D.	0.04	N.D.	0.06	N.D.	0.04	N.D.	0.02	N.D.	0.03
BDE-183	N.D.	0.01	N.D.	0.04	N.D.	0.05	0.42	0.12	0.49	0.06
BDE-184	0.01	0.02	N.D.	0.02	0.02	0.02	N.D.	N.D.	N.D.	0.13
BDE-191	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.05
BDE-196	0.17	0.22	0.14	0.31	0.12	0.29	0.56	0.10	0.41	0.12
BDE-197	0.16	0.14	0.09	0.15	0.12	0.16	0.44	0.01	0.43	0.12
BDE-206	1.00	0.69	1.23	17.32	1.34	6.21	2.03	2.66	1.05	13.35
BDE-207	1.00	0.59	0.93	5.63	1.01	2.91	1.79	1.08	1.07	3.36
BDE-209	0.03	0.73	59.59	805.29	65.21	299.66	69.86	154.39	49.91	447.39
Σ PBDEs	2.36	2.43	61.97	828.80	67.82	309.36	75.11	158.46	53.36	464.70
DBDPE	N.D.	N.D.	N.D.	0.26	N.D.	0.32	0.24	1.63	2.10	4.80
anti-DP	N.D.	N.D.	0.95	11.06	N.D.	2.55	N.D.	3.27	0.43	15.86
syn-DP	N.D.	N.D.	N.D.	4.51	N.D.	1.84	N.D.	0.99	0.02	5.43
Σ DP	N.D.	N.D.	0.95	15.57	N.D.	4.39	N.D.	4.26	0.45	21.29
<i>f_{syn}</i>	-	-	-	0.29	-	0.42	-	0.23	0.04	0.26
Dec 602	N.D.	0.003	N.D.	0.01	N.D.	0.004	N.D.	N.D.	N.D.	N.D.

N.D.: not detected.

BDE-77, -119, -156, Dec 603, Dec 604, CP and Mirex were not detected in any sample.

Table S7. Calculation of the amount (%) of PFOS, BDE-209 and DP removed from soil through leachate and runoff in the different rainfall events.

	PFOS					BDE-209					DP				
	[PFOS] (ng/L)	Water volume (L)	Amount eluted (ng)	Amount in soil (mg)	Amount removed from soil (%)	[BDE-209] (ng/L)	Water volume (L)	Amount eluted (ng)	Amount in soil (mg)	Amount removed from soil (%)	[DP] (ng/L)	Water volume (L)	Amount eluted (ng)	Amount in soil (mg)	Amount removed from soil (%)
Leachate															
1st event															
T-1	23.9	167	19956.5	10.1	0.198 ^{*A}	N.D.	167	N.D.	192.4	---	N.D.	167	N.D.	3.9	---
T-2	11.7	169	9886.5	10.4	0.095	N.D.	169	N.D.	69.5	---	0.4	169	338.0	3.0	0.011
T-3	6.1	162	4941.0	8.7	0.057	0.4	162	324.0	49.4	0.001	0.1	162	81.0	2.8	0.003
T-4	22.9	163	18663.5	22.9	0.082	N.D.	163	N.D.	197.7	---	0.8	163	652.0	5.8	0.011
2nd event															
T-1	23.4	169	19773.0	10.1	0.196 ^{*A}	2.1	169	1774.5	192.4	0.001	0.1	169	84.5	3.9	0.002
T-2	5.5	169	4647.5	10.4	0.045	1.0	169	845.0	69.5	0.001	0.1	169	84.5	3.0	0.003
T-3	3.1	169	2619.5	8.7	0.030	1.6	169	1352.0	49.4	0.003	0.1	169	84.5	2.8	0.003
T-4	14.7	169	12421.5	22.9	0.054	3.3	169	2788.5	197.7	0.001	N.D.	169	N.D.	5.8	---
3rd event															
T-1	6.8	413	14042.0	10.1	0.139 ^{*A}	6.5	413	13422.5	192.4	0.007 ^{*B}	0.1	413	206.5	3.9	0.005
T-2	5.7	448	12768.0	10.4	0.123	11.5	448	25760.0	69.5	0.037 ^{*B}	N.D.	448	N.D.	3.0	---
T-3	4.0	429	8580.0	8.7	0.099	7.2	429	15444.0	49.4	0.031 ^{*B}	N.D.	429	N.D.	2.8	---
T-4	11.8	409	24131.0	22.9	0.105	7.0	409	14315.0	197.7	0.007 ^{*B}	0.1	409	204.5	5.8	0.004
Total															
T-1	54.1	749	53771.5	10.1	0.532	8.6	749	15197.0	192.4	0.008	0.2	749	291.0	3.9	0.007

T-2	22.9	786	27302.0	10.4	0.263	12.5	786	26605.0	69.5	0.038	0.5	786	422.5	3.0	0.014
T-3	13.2	760	16140.5	8.7	0.186	9.2	760	17120.0	49.4	0.035	0.2	760	165.5	2.8	0.006
T-4	49.4	741	55216.0	22.9	0.241	10.3	741	17103.5	197.7	0.009	0.9	741	856.5	5.8	0.015

Runoff

1st event															
T-1	219.3	30	32895.0	10.1	0.326	10.7	30	1605.0	192.4	0.001	9.7	30	1455.0	3.9	0.037
T-2	59.2	28	8288.0	10.4	0.080	15.1	28	2114.0	69.5	0.003	14.4	28	2016.0	3.0	0.067
T-3	115.3	41	23636.5	8.7	0.272	29.7	41	6088.5	49.4	0.012	4.7	41	963.5	2.8	0.034
T-4	415.1	35	72642.5	22.9	0.317	3.7	35	647.5	197.7	0.0003	12.6	35	2205.0	5.8	0.038
2nd event															
T-1	72.8	7	2548.0	10.1	0.025	10.0	7	350.0	192.4	0.0002	1.3	7	45.5	3.9	0.001 ^{*B}
T-2	92.0	16	7360.0	10.4	0.071	6.2	16	496.0	69.5	0.0007	1.1	16	88.0	3.0	0.003 ^{*B}
T-3	79.0	35	13825.0	8.7	0.159	9.0	35	1575.0	49.4	0.003	2.4	35	420.0	2.8	0.015 ^{*B}
T-4	310.2	34	52734.0	22.9	0.230	31.4	34	5338.0	197.7	0.003	1.6	34	272.0	5.8	0.005 ^{*B}
3rd event															
T-1	33.8	60	10140.0	10.1	0.100	179.2	60	53760.0	192.4	0.028 ^{*B}	3.5	60	1050.0	3.9	0.027
T-2	67.6	54	18252.0	10.4	0.176	71.1	54	19197.0	69.5	0.028 ^{*B}	1.0	54	270.0	3.0	0.009
T-3	73.6	67	24656.0	8.7	0.283	235.3	67	78825.5	49.4	0.160 ^{*B}	6.5	67	2177.5	2.8	0.078
T-4	93.2	66	30756.0	22.9	0.134	328.6	66	108438.0	197.7	0.055 ^{*B}	15.6	66	5148.0	5.8	0.089
Total															
T-1	325.9	97	45583.0	10.1	0.451	199.9	97	55715.0	192.4	0.029	14.5	97.0	2550.5	3.9	0.065
T-2	218.8	98	33900.0	10.4	0.326	92.4	98	21807.0	69.5	0.031	16.5	98.0	2374.0	3.0	0.079
T-3	267.9	143	62117.5	8.7	0.714	274.0	143	86489.0	49.4	0.175	13.6	143.0	3561.0	2.8	0.127
T-4	818.5	135	156132.5	22.9	0.682	363.7	135	114423.5	197.7	0.058	29.8	135.0	7625.0	5.8	0.131

N.D.: not detected. Concentrations of BDE-209 and DP in leachate and runoff (ng/g d.w.) have been normalized to ng/L.

Water volume (L): absolute volume of leachate or runoff water collected. Amount eluted: amount of pollutants (ng) in leachate or runoff water (corresponding at <0.5 m area). Amount in

soil: amount of pollutants (mg) in soil (< 0.5 m) at the beginning of the experiment. ^{*A} Data showed statistically significant differences ($p < 0.05$; Mann-Whitney U-test) between treatments.
^{*B} Data showed statistically significant differences ($p < 0.05$; Mann-Whitney U-test) between events.

Table S8. Main physicochemical properties of PFOS, BDE-209 and DP for the calculation of leaching potential (L_p) and the Groundwater Ubiquity Score (GUS).

Compound	Molecular weight (g/mol)	Water solubility (S) (mg/L)	Vapour pressure (V_p) (Pa)	Organic carbon-water partition coefficient (K_{oc}) (cm^3/g)	$T_{1/2}$ (soil) (d)	Leaching potential (L_p) ^A	GUS index ^B
PFOS	500.13	0.1039	0.853	2.56×10^3	2430	4.75×10^{-5}	2 (Transitional)
BDE-209	959.17	2.84×10^{-11}	6.23×10^{-10}	4.78×10^7	3650	9.54×10^{-10}	-13.11 (Non-leacher)
DP	653.73	1.68×10^{-8}	9.41×10^{-8}	6.04×10^9	30000	2.97×10^{-11}	-25.88 (Non-leacher)

S, V_p , K_{oc} and $T_{1/2}$ values were calculated using EPISuite 4.1 software.

^A $L_p = S/(V_p \times K_{oc})$. Compounds with higher leachability in the environment are indicated by the higher L_p values (Laskowski et al. 1982; Wilson et al. 1996).

^B GUS = $\log_{10}(T_{1/2} \text{ soil}) \times (4 - \log_{10}K_{oc})$. GUS value > 2.8 (Leacher); GUS value = 1.8 - 2.8 (Transition zone); GUS value < 1.8 (Non-leacher) (Gustafson 1989).

Table S9. Calculation of the field-based K_d and K_{oc} distribution coefficients of PFOS between water and soil samples analyzed.

	Log K_d	Log K_{oc}
Leachate		
T-1	3.36	4.73
T-2	3.77	5.21
T-3	3.94	5.40
T-4	3.76	5.14
Total	3.71 ± 0.24	5.12 ± 0.28
Runoff		
T-1	2.59	3.95
T-2	2.79	4.23
T-3	2.63	4.09
T-4	2.54	3.92
Total	2.64 ± 0.11	4.05 ± 0.14

Leachate: concentration (ng/kg) in soils in relation to concentration in leachate (ng/L).

Runoff: concentration (ng/kg) in soils in relation to concentration in runoff (ng/L).

F_{oc} : 4.30 % (T-1), 3.66 % (T-2), 3.42% (T-3) and 4.13 % (T-4).