Supplementary Material

Pollutant Source or Sink? Adsorption and Mobilization of PFOS and PFOA in a Large Shallow Lake with Extended Reed Belt

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S1) Overview of sampling points and further procedure

Table S1 gives an overview of the origin and further procedure of the sediment and water samples used to assess the occurrence of PFAS in different Lake compartments and the lab experiments.

Table S1. The concentration of primary pollutants in the river Wulka and targeted concentrations applied in the adsorption experiments.

	Sampling area	Sampling point	Characterization of occurrence	Adsorption batch-tests		Reactor tests
				Test A	Test B	
2018	Illmitz	IL5		x		
2018	Moerbisch	MO3		x		
2018	Wulka	WU6		x		
2019	Illmitz	IL2	x			
2019	Illmitz	IL5	x		x	x
2019	Illmitz	IL8	x			
2019	Moerbisch	MO1	x		x	x
2019	Moerbisch	MO3	x		x	x
2019	Moerbisch	MO5	x		x	x
2019	Wulka	WU1	x			
2019	Wulka	WU2	x		x	x
2019	Illmitz	WU3	x			
2019	Lake	IL1	x			

S2) Kinetic experiments

First, PFOS and PFOA adsorption kinetics on natural sediments were investigated in batch tests conducted with sample A from Illmitz under conditions A (25°C and aerobic). The normalized concentrations are given in Figure S1.

The initial concentrations of PFOS and PFOA in the water were 7,951 ng L^{-1} and 1,788 ng L^{-1}, respectively. Equilibrium between the PFAS and the sediments was obtained after approximately 4 hours. PFOS and PFOA were detected in concentrations of 4,272±54 ng L^{-1} and 1,125±69 ng L^{-1}, respectively, after the experimental time of 48h.
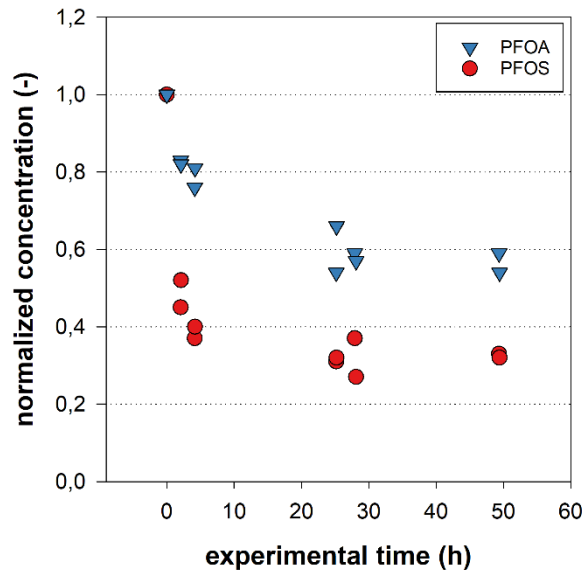
Figure S1: Decrease of the normalized concentrations of PFOS and PFOA during 48 h- kinetic experiments.

S3) Concentrations of substances in the stock-solution

The primary pollutants in the Lake were identified and added to the stock solution to simulate increased pollutant concentration due to evaporation and to consider competing effects during adsorption. The concentration range of the primary pollutants is given inTable S2.

Table S2. The concentration of primary pollutants in the river Wulka and targeted concentrations applied in the adsorption experiments.

substance	concentration in Lake water	targeted concentration in tests solution
	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$
mercury	0.001–0.0038	0.01
cadmium	0.0024–0.01	0.05
copper	0.97–4.3	10
lead	0.017–0.18	1
nickel	0.85–1.8	10
zinc	3.8–8.3	50
PFOS	0.004–0.011	0.05
PFOA	0.001–0.0058	0.05

S4) Chemical analysis of sediment and water samples

Table S3 contains a description of the chemical analysis performed for the characterization of sediment and water samples.

Table S3: Description of analytical methods.

parameter	method	description
Chemical oxygen demand	COD	DIN ISO 15705	The samples' chemical oxygen demand was determined in accordance with DIN EN ISO 15705, by silver-catalyzed oxidation with potassium dichromate solution in sulfuric acid at 148 °C over a period of two hours. The reaction took place in small-scale sealed tubes and the chromate concentration decrease was measured photometrically (UV-VIS spectrometer, Hach).
Total kjedahl nitrogen	TKN	DIN EN ISO 25663	The modified DIN EN ISO 25663 method was used to determine Kjeldahl nitrogen in water and solid samples. The sample is mixed with sulfuric acid and catalyst ($CuSO_4$ x 5 H_2O, TiO_2) and heated at 360-410°C (Kjeldatherm, Gerhard). The particles are decomposed and the nitrogen is converted to ammonia. The ammonia concentration is then measured according to DIN EN ISO 11732.
Total phosphorus	TP	DIN EN ISO 6878	After oxidation of the sample with alkaline potassium peroxodisulfate (Oxisolv, Merck) during pressure microwave digestion (Speedwave, Berghof), total phosphorus was determined according to DIN EN ISO 6878. The LOQ for the total phosphorus determination is 0.5 mg L^{-1}.
Suspended solids	SS	DIN 384089-2	In accordance with DIN 38409-2, the suspended solids content of the water sample was determined. The sample was filtered with a dried and weighed membrane filter (CA, 42 mm, 0.45 µm). After a second drying at 104°C, the membrane filter was weighed and the suspended solids were determined gravimetrically. The LOQ of the suspended solids determination method is 0.5 mg L^{-1}.
Total organic carbon	TOC	DIN EN1484	Total organic carbon (TOC) was analyzed by the combustion method (thermocatalytic oxidation) according to DIN EN 1484. After acidification to remove the inorganic carbon (IC) and combustion of the carbon, the sample's non-volatile DOC (NPOC) was determined. An infrared detector was used to measure the CO_2 produced and a LOQ of 0.27 mg L^{-1} was determined for TOC.
Dissolved organic carbon	DOC	DIN EN1484	Dissolved organic carbon (DOC) was analyzed by the combustion method (thermocatalytic oxidation) according to DIN EN 1484. After filtration of the sample through a 0.45-um filter, acidification to remove inorganic carbon (IC) and combustion of the carbon, the non-volatile DOC (NPOC) in the water sample was analyzed. An infrared detector was used to measure the CO_2 produced and a LOQ of 0.27 mg L^{-1} was determined for DOC.
Ammonia	NH_4-N	DIN EN ISO 11732	Following DIN EN ISO 11732, ammonia was determined in water samples using continuous flow analysis (CFA) and photometric detection by SKALAR. The sample was injected into a continuously flowing air-filled reagent stream. Ammonium from the sample reacts with hypochlorite and salicylate in a basic solution to form a blue-green indophenol complex. The color is measured with a photometer and a LOQ of 0.9 mg L^{-1} was determined.
Nitrate / nitrite	NO_3-N NO_2-N	DIN EN ISO 13395	Following DIN EN ISO 13395, nitrate and nitrite were determined in water samples using continuous flow analysis (CFA) and photometric detection of SKALAR. The sample was injected into a continuously flowing air-filled reagent stream, and first nitrate is reduced with cadmium to nitrite. Nitrite reacted with sulfonamide and N-(1-phthyl)- ethylenediamine in an acidic solution, and the resulting purple color complex was measured with a photometer, determining a LOQ of 0.01 mg L^{-1} for nitite and 0.9 mg L^{-1} for nitrate.

Ortho-phosphate	$PO_4\text{-}P$	DIN EN ISO 6878	Following DIN EN ISO 6878, orthophosphate was determined in water samples using continuous flow analysis (CFA) and photometric detection by SKALAR. The sample was injected into a continuously flowing, air-filled reagent stream. Orthophosphate from the water sample reacted with molybdate and antimony ions in an acidic solution. The resulting yellow color complex is reduced with ascorbic acid to a blue color complex and measured with a photometer. A LOQ of 0.28 mg L^{-1} was determined.
Anions (chloride / sulfate)	Cl^-, SO_4^-	DIN EN ISO 10304-1	In this study, anions (chloride and sulfate) in water samples were analyzed by high-performance ion chromatography (HPIC) according to DIN EN ISO 10304-1. The HPIC system consisted of a binary pump, suppressor and ion conductivity detector from Metrohm (Eco IC) and an autosampler from Hitachi. A Dionex AS9-HC (4x250 mm) analytical HPIC column and eluent 1mM $NaHCO_3$ /3.2 mM Na_2CO_3 with flow 0.7 mL/min in isocratic mode were used for HPLC separation. Injection volumes of 40 µL of sample and a solution of 100 mM H_2SO_4 as suppressor were applied. Based on the chromatogram of HPIC anion analysis, the limits of quantification (LOQ) and detection (LOD) were determined. Using chloride and sulfate standard solutions (5-100 mg L^{-1}), a LOQ of 0.5 mg L^{-1} and a LOD of 0.2 mg L-1 were obtained.
Cations (potassium, sodium, magnesiu, calcium)	K^+, Na^+, Mg^{2+}, Ca^{2+}	DIN EN ISO 14911	In accordance with DIN EN 14911, cations (sodium, potassium, calcium, magnesium) were determined in water samples using high-performance ion chromatography (HPIC). The HPIC system consisted of a binary pump with an autosampler from Hitachi and a conductivity detector from Metrohm. For HPIC separation, a ReproSil 100 CAT 0.5, µm (125x4.6 mm) analytical column, eluent 1 mM pyridine dicarboxylic acid /4 mM tartaric acid with a flow of 1.3 mL/min in isocratic mode and injection volumes of 15 µL of sample were used. Using a standard cation solution (5-100 mg L^{-1}), an LOQ of 0.8 mg L^{-1} and an LOD of 0.4 mg L^{-1} were determined.

The results of the characterization of the sediment samples are given in Table S4. The samples' dry matter and organic dry matter content were 222.0 - 590.8 g kg^{-1} and 18.9 – 49.1 g kg^{-1}, respectively. The highest COD and f_{OC} were found for samples from Wulka. The median diameter obtained from the particle size analysis for the sediments used in the first experiments were 58.77 µm, 27.05 µm, and 25.73 µm for Illmitz, Moerbisch, and Wulka, respectively. The median of the sediments from the second samplings were 49.88 µm, 40.25 µm, and 13.48 µm for Illmitz, Moerbisch, and Wulka. The specific surface areas per gram of sediment were between 0.57 m^2 g^{-1} (Illmitz-1) and 1.76 m^2 g^{-1} (Wulka-2).

Table S4. Characteristics of the sediment samples used in the lab experiments.

	Sampling site	tests	Dry matter	Organic dry matter	COD	f_{OC}	d_{10}	d_{50}	d_{90}	specific surface
			g kg^{-1}	g kg^{-1}	mg kg^{-1}	%	µm	µm	µm	m^{2}g^{-1}
Illmitz - 2018	IL5	A	517.2	26.5	21,025	0.50	10.39	58.77	360.03	0.57
Illmitz - 2019	IL5	B, C	590.8	18.9	17,618	0.26	9.73	49.88	251.17	0.66
Moerbisch - 2018	MO3	A	245.4	49.1	25,669	0.53	4.05	27.03	295.19	1.02
Moerbisch - 2019	MO3	B, C	222.0	34.6	28,529	0.80	5.54	40.25	278.35	0.90
Wulka - 2018	WU6	A	564.1	28.8	31,842	1.45	4.83	25.73	327.06	0.73
Wulka - 2019	WU2	B, C	444.6	49.8	39,953	2.20	0.92	13.48	137.84	1.76

Moreover, the oxide content of the sediments used in the first round of experiments (stocked-up adsorption tests A) was analyzed and is illustrated in Figure S2. The highest fractions of the Illmitz sediment were 59% silicon dioxide (SiO_2), 14% calcium oxide (CaO), and 14% carbonates. The major oxide components of the Moerbisch sediments were: 34% CaO, 24% carbonates, and 20% SiO_2. In the Wulka sediments, the highest proportion was observed for CaO (32%), followed by SiO_2 (27%) and carbonates (26%).
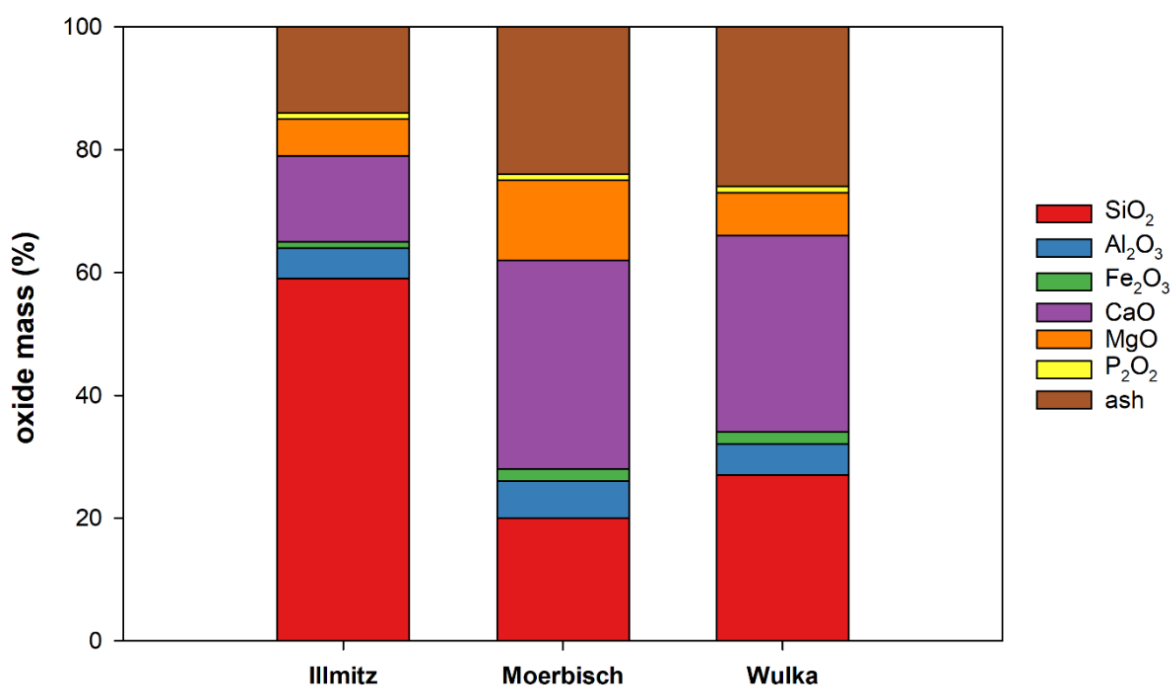

Figure S2: Relative oxide content of the sediment samples used in the first batch experiments with stocked-up concentrations (tests A).

We analyzed organic carbon parameters (TOC, DOC), nutrients (ortho-phosphate, total and dissolved phosphorus, ammonia, nitrate, nitrite, total and dissolved nitrogen), and suspended solids within the water samples. The obtained results are given in Table S5.

Table S5. Total and dissolved organic carbon, nutrient, and suspended solid concentrations in the water samples used in the experiments. All numbers are given in mg L^{-1}.

analytical method		DIN EN 1484	DIN EN 1484	DIN EN ISO 6878	DIN EN ISO 11732	DIN EN ISO 13395	DIN EN ISO 13395	DIN EN ISO 6878	DIN EN ISO 6878	DIN EN ISO 11905-1	DIN EN ISO 11905-1	DIN 38409-2
parameter		TOC	DOC	PO_4-P	NH_4-N	NO_3-N	NO_2-N	TP_{mf}	TP	TN_{mf}	TN	SS
Illmitz	Reed belt - 1	39.3	37.3	0.013	0.051	0.08	0.01	0.031	0.047	2.88	3.44	9.5
	Reed belt - 2	41.2	39.3	0.022	0.049	0.06	0.01	0.056	0.093	3.14	3.72	25.8
	Lake	28.6	16.4	0.024	0.036	0.03	0.00	0.049	0.296	1.33	2.94	430.0
	Dil. Lake	16.2	9.6	0.011	0.021	0.11	0.00	0.037	0.179	0.85	1.57	244.0
Moerbisch	Reed belt - 1	26.7	25.0	0.010	0.117	0.04	0.00	0.028	0.048	1.96	2.25	17.4
	Reed belt - 2	23.5	20.8	0.013	0.028	0.15	0.01	0.024	0.052	1.73	2.10	34.7
	Lake	23.8	15.1	0.014	0.036	0.19	0.01	0.093	0.203	1.40	2.49	332.0
	Dil. Lake	21.0	10.2	0.013	0.025	0.11	0.01	0.075	0.189	0.98	2.13	301.5
Wulka	Reed belt - 1	5.1	4.2	0.079	0.041	2.62	0.02	0.116	0.144	3.04	3.26	2.7
	Reed belt - 2	6.8	4.8	0.107	0.064	2.61	0.04	0.184	0.266	3.25	3.62	64.0
	Lake	15.5	14.5	0.013	0.026	0.19	0.01	0.035	0.057	1.36	1.61	42.0
	Wulka river	8.6	7.4	0.134	0.036	1.00	0.03	0.222	0.234	1.74	2.03	30.0

Moreover, the anions (chloride, sulfate) and cations (potassium, sodium, calcium, magnesium) were determined and given in Table S6.

Table S6. Ionic compositions of the water samples used in the experiments. All numbers are given in mg L-1.

analytical method		DIN EN ISO 10304-1	DIN EN ISO 10304-1	DIN EN ISO 14911	DIN EN ISO 14911	DIN EN ISO 14911	DIN EN ISO 14911	DIN 38409-7:2005-12
parameter		chloride	sulfate	sodium	potassium	calcium	magnesium	carbonate
Illmitz	Reed belt - 1	386.0	595.0	488.9	46.1	12.7	131.4	40.5
	Reed belt - 2	449.5	575.3	522.1	56.4	17.6	180.1	51.5
	Lake	301.1	417.6	343.4	35.9	37.9	123.8	34.2
	Dil. Lake	164.5	222.3	183.0	15.1	17.2	77.1	19.2
Moerbisch	Reed belt - 1	368.0	556.0	426.2	54.0	25.1	149.8	40.3
	Reed belt - 2	280.5	467.2	364.9	40.0	23.0	133.0	35.8
	Lake	255.2	435.6	359.4	46.3	35.9	78.7	31.4
	Dil. Lake	151.7	265.7	215.7	26.7	46.1	83.3	19.5
Wulka	Reed belt - 1	94.3	130.4	62.3	17.1	104.1	41.5	17.6
	Reed belt - 2	122.8	95.2	31.1	6.7	79.1	43.2	12.3
	Lake	319.6	416.9	326.2	40.6	10.1	122.8	30.7
	Wulka river	117.1	81.2	46.4	20.1	78.9	33.7	11.5

S5) PFOS and PFOA concentrations in sediment, pore water, and water samples

The specific values of the three sediments used in the adsorption/ desorption batch tests and the reactor tests are illustrated in Figure S3. The PFOS loading of the sediment from the Wulka area was approximately ten times higher than the loadings of sediments from Moerbisch and Illmitz. However, the PFOA loadings of Moerbsich were double of the Illmitz one. However, both compounds' pore and bulk water concentrations were lower for Wulka than for Moerbisch.
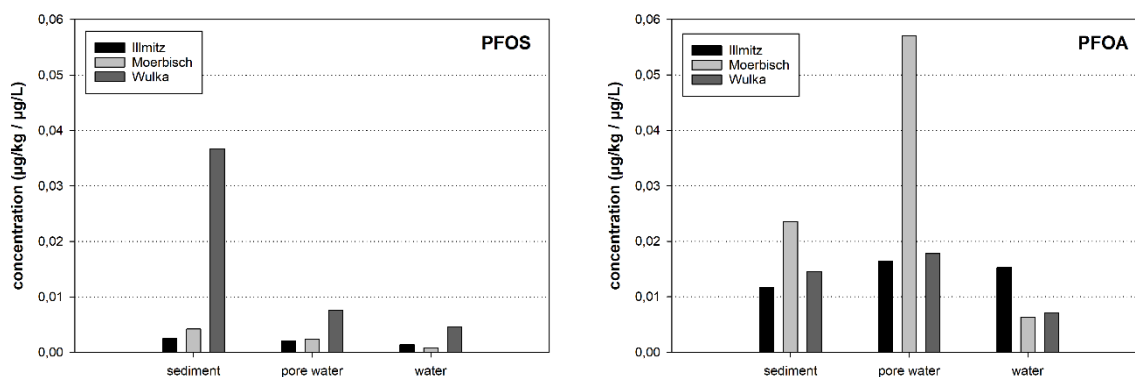

Figure S3: PFAS concentrations in sediment, pore water, and water samples used in the adsorption/ desorption batch tests and the reactor tests.

S6) Experimental conditions in tests A and B

The initial concentration, the minimum and maximum dry sediment concentrations, and initial, minimum, and maximum temperature, pH, and dissolved oxygen during tests A and B are given in Table S7 and Table S8, respectively. Dissolved oxygen (DO) was measured after 15 minutes of settling time in the bulk phase and depending on the sediment concentration during oxic tests.

Table S7. Experimental conditions during tests A.

	c_0 PFOS	c_0 PFOA	$c_{sed,min}$	$c_{sed,max}$	pH_0	$pH_{eq,min}$	$pH_{eq,max}$	T
	µg/L	µg/L	g/L	g/L	-	-	-	°C
Illmitz	0.027	0.038	49.13	374.45	8.71	8.71	8.75	24.8
Moerbisch	0.071	0.029	4.18	491.78	7.65	7.645	8.45	24.5
Wulka	0.043	0.043	9.59	1119.17	8.12	8.12	7.89	22.8

Table S8. Experimental conditions during tests B.

	Experimental conditions		PFOS $c_{0,min}$	PFOS $c_{0,max}$	PFOA $c_{0,min}$	PFOA $c_{0,max}$	$c_{sed,min}$	$c_{sed,max}$	pH_0	$pH_{eq,min}$	$pH_{eq,max}$	T	$DO_{eq,min}$	$DO_{eq,max}$
			µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	g L^{-1}	g L^{-1}	-	-	-	°C	mg L^{-1}	mg L^{-1}
Illmitz	reed belt water	A	0.00145	0.00151	0.01529	0.01614	111.12	245.72	8.57	8.74	8.87	23.59	8.00	7.27
	reed belt water	C	0.00142	0.00149	0.01498	0.01578	61.16	188.54	8.69	8.66	8.66	23.59	0.22	0.13
	Lake water	A	0.00145	0.00151	0.00839	0.00993	111.06	245.06	8.55	8.22	8.10	20.31	7.95	6.96
	Lake water	C	0.00142	0.00149	0.00782	0.00931	61.53	191.59	8.58	8.27	8.05	20.31	0.35	0.13
Moerbisch	reed belt water	A	0.00100	0.00124	0.16141	0.14400	39.04	80.02	8.66	8.03	7.32	24.28	1.55	8.18
	reed belt water	C	0.00091	0.00114	0.16859	0.15107	39.02	79.84	8.68	7.84	7.71	23.68	0.00	0.15
	Lake water	A	0.00100	0.00123	0.02043	0.02652	22.14	63.37	8.77	8.63	8.44	24.28	1.13	7.55
	Lake water	C	0.00091	0.00115	0.01793	0.0242	22.27	64.29	8.80	7.88	7.71	23.68	0.00	0.09
Wulka	reed belt water	A	0.00322	0.00379	0.00493	0.0051	81.98	174.29	7.96	8.45	8.08	25.46	7.71	7.66
	reed belt water	C	0.00300	0.00356	0.00486	0.00503	45.34	135.55	7.86	7.76	7.64	26.85	0.15	0.07
	Lake water	A	0.00300	0.00379	0.01105	0.01043	81.34	173.85	8.92	8.76	8.30	25.46	7.74	7.72
	Lake water	C	0.00300	0.00357	0.01129	0.01068	45.61	137.65	8.94	8.05	7.76	26.85	0.10	0.17

S7) K_d- values obtained in experiments

The K_d values obtained during tests A without considering the initial loading were: 8.98 L/kg for Illmitz, 51.18 L/kg for Moerbisch and 11.97 L/kg for Wulka. Furthermore, the Kd- values obtained in test B are given in Table S9.

Table S9. Obtained K_d sediment-water distribution coefficients given in L/kg.

	reed belt water				lake water			
	A		C		A		C	
	K_d	R^2	K_d	R^2	K_d	R^2	K_d	R^2
PFOS								
Illmitz	2.38	0.79	3.22	0.63	4.78	0.85	5.59	0.63
Moerbisch	11.78	0.96	-0.42	0.03	9.29	0.97	-3.05	0.73
Wulka	4.81	0.87	2.62	0.60	4.43	0.92	4.29	0.88
PFOA								
Illmitz	1.85	0.37	4.92	0.79	4.92	0.02	4.53	0.69
Moerbisch	321.59	0.96	137.78	0.65	34.41	0.94	-4.40	0.76
Wulka	0.40	0.63	1.43	0.46	-0.09	0.30	1.59	0.90

S8) Comparison of different log K_OC values

The log K_{OC} values obtained in experiments with stocked-up concentrations, in tests with original reed belt samples and the ones which were derived from environmental pore and bulk water samples are given in Figure S4.
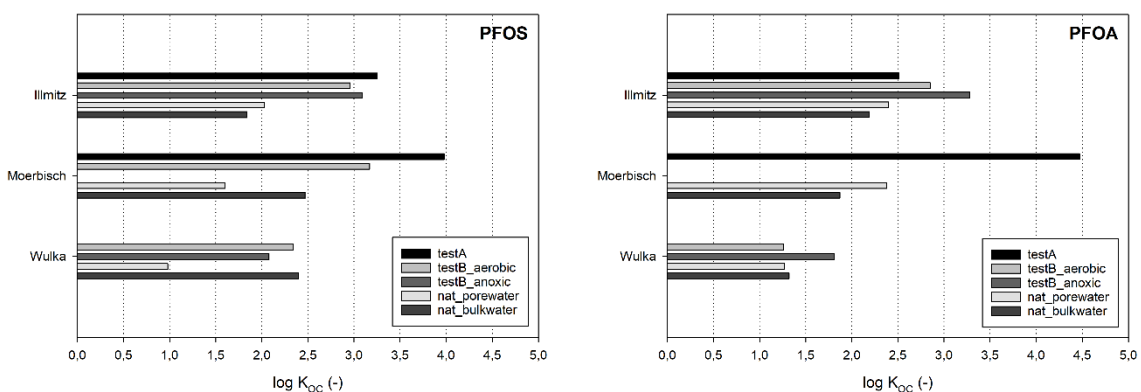

Figure S4: Obtained log K_{OC} with stocked up concentration (tests A), original samples (tests B) and naturally derived ones for PFOS and PFOA.