Occurrence and Distribution of sun-blocking agents in the Danube River: Implications for Aquatic Ecosystem Health

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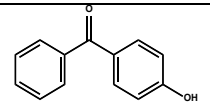
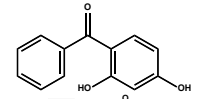
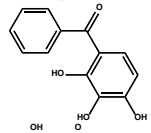
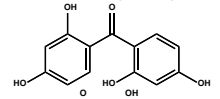
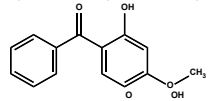
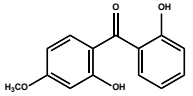
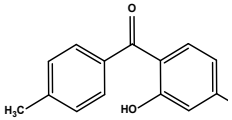
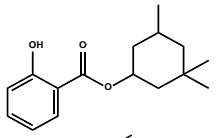
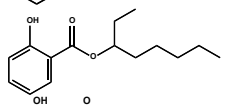
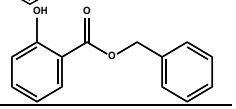
Table S1. Phisico-chemical properties

Compound	Abrev.	Molecular Formula	Molecular weight	Solub.[a,b]	Log Kow[b]	Log Koc[b]	BCF[b,c]	Chemical structure
4-hydroxybenzophenone	4HBP	$C_{13}H_{10}O_2$	198.2	405.8	3.07	3.24	6.67	
2,4-dihydroxybenzophenone	BP-1	$C_{13}H_{10}O_3$	214.2	413.4	2.96	3.46	5.52	
2,3,4-trihydroxybenzophenone	2,3,4HBP	$C_{13}H_{10}O_4$	230.2	381.1	2.91	3.68	4.98	
2,2',4,4'-tetrahydroxybenzophenone	BP-2	$C_{13}H_{10}O_5$	246.2	398.5	3.16	3.88	3.99	
2-hydroxy-4-methoxy-benzophenone	BP-3	$C_{14}H_{12}O_3$	228.2	68.56	3.52	3.10	23.9	
2,2'-dihydroxy-4-methoxy-benzophenone	BP-8	$C_{14}H_{12}O_4$	244.2	52.37	4.31	3.32	25.3	
2-hydroxy-4-methoxy-4'-methyl-benzophenone	BP-10	$C_{15}H_{14}O_3$	242.2	33.3	4.07	3.31	39.4	
Homosalate	HS	$C_{16}H_{22}O_3$	262.3	0.42	6.16	4.03	11080	
Ethylhexyl salicylate	ES	$C_{15}H_{22}O_3$	250.3	24.6	5.97	3.71	416.7	
Benzyl salicylate	BS	$C_{14}H_{12}O_3$	228.2	0.72	4.31	3.93	7856	

[a]Solub.: solubility (mg/L) in water at 25°C. [b]log Kow (octanol–water partition coefficient) and log Koc (soil organic carbon–water partitioning coefficient) was obtained by the Estimation Programs Interface (EPI) Suite developed by the US EPA and Syracuse Research Corp. [c]BCF: bioconcentration factor (L/kg wet weight).

Table S2. Adsorption Classifications (Estimating Physical/Chemical and Environmental Fate Properties with EPI Suite™. Sustainable Futures/Pollution Prevention (P2) Framework Manual. EPA-748-B12-001. U.S. Environmental Protection Agency, OCSPP)

Log K_{oc}	Adsorption Classifications
> 4.5	Very strong sorption to soil / sediment, negligible migration to ground water
3.5 - 4.4	Strong sorption to soil / sediment, negligible to slow migration to ground water
2.5 - 3.4	Moderate sorption to soil / sediment, slow migration to ground water
1.5 - 2.4	Low sorption to soil / sediment, moderate migration to ground water
< 1.5	Negligible sorption to soil / sediment, rapid migration to ground water

Table S3. The LC-MS/MS parameters for the 10 UV filters and mass-labelled standard detection and quantification.

Analyte	Retention time (min)	Precursor Ion	Product Ion	Fragmentor Voltage (V)	Collision Energy (V)	Cell Accelerator Voltage (V)	Dwell time (msec)	ESI mode	Drying gas flow (L/min)	Drying gas temperature (°C)	Nebulizer pressure (psi)	Capillary voltage (V)
BP-2	2.65	245	91.0	110	30	5	250	Negative				
234HBP	3.26	229	151	135	25	0	250	Negative				
4HBP	3.72	197	92.0	150	45	5	250	Negative				
BP-1	4.68	213	135	130	20	4	250	Negative				
BP-8	5.97	245	121	150	20	5	250	Pozitive				
BP-^{13}C	7.27	184	106	100	15	5	250	Pozitive	8	300	40	5000
BP-3	8.12	229	151	135	20	1	250	Pozitive				
BP-10	8.91	243	151	130	20	2	100	Pozitive				
BS	8.94	229	211	115	15	3	300	Pozitive				
ES	12.75	251	139	90	4	5	300	Pozitive				
HS	13.10	263	139	90	5	5	300	Pozitive				

Table S4. Quantitation and confirmation information of analytes in surface water

Compound	R^2	Accuracy (%)	Recovery in sample (%)	LOD (ng/L)	LOQ (ng/L)	Matrix effect
BP-2	0.998	97.3	89.1	0.14	0.40	93.1
234THBP	0.999	98.4	86.4	0.10	0.28	90.4
4HBP	0.998	101.6	94.1	0.15	0.43	95.6
BP-1	0.998	99.5	103.2	0.13	0.36	100.9
BP-8	0.999	104.5	91.6	0.04	0.10	95.1
BP-3	1.002	106.1	110.4	0.13	0.37	106.5
BP-10	0.999	101.4	92.2	0.13	0.35	95.2
BS	0.998	99.2	93.9	0.22	0.61	94.3
HS	0.998	98.5	105.4	0.25	0.69	100.1
ES	1.000	97. 8	89.3	0.19	0.54	96.6

Table S5. Quantitation and confirmation information of analytes in sediment

Compound	R^2	Accuracy (%)	Recovery in sample (%)	LOD (ng/g d.w.)	LOQ (ng/g d.w.)	Matrix effect
BP-2	0.993	96.8	86.1	0.18	0.50	87.2
234THBP	0.997	94.6	83.7	0.13	0.36	87.7
4HBP	0.998	102.3	90.6	0.19	0.53	92.1
BP-1	0.997	98.2	105.2	0.18	0.49	102.4
BP-8	0.999	97.7	87.4	0.08	0.21	90.7
BP-3	1.002	93.9	112.5	0.16	0.45	108.2
BP-10	0.996	94.6	88.6	0.19	0.54	91.6
BS	0.998	97.9	90.4	0.28	0.79	92.8
HS	0.994	102.4	107.3	1.21	3.39	103.2
ES	1.000	98.9	86.5	0.75	2.10	93.1

Table S6. Concentration levels (ng/L) of the 10 UV filters in surface water samples

Analyte	SW S1	SW S2	SW S3	SW S4	SW S5
	Conc (n=3)				
BP-2	ND	ND	ND	ND	ND
234HBP	16.2	80.0	41.0	22.4	5.0
4HBP	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
BP-1	2.4	39.3	88.6	10.9	0.3
BP-8	0.3	ND	0.3	ND	ND
BP-3	558	1009	1919	2136	2224
BP-10	0.7	<LOQ	0.6	<LOQ	<LOQ
BS	ND	31.6	ND	ND	43.5
HS	ND	ND	ND	ND	ND
ES	ND	ND	ND	ND	ND

Table S7. Concentration levels (ng/g s.u.) of the 10 UV filters in sediment samples

Analyte	Sed S1	Sed S2	Sed S3	Sed S4	Sed S5
	Conc (n=3)				
BP-2	4.5	ND	ND	ND	ND
234HBP	16.7	41.7	ND	ND	ND
4HBP	2.2	2.5	3.4	3.0	3.9
BP-1	6.2	2.4	2.5	2.0	3.3
BP-8	ND	ND	ND	ND	ND
BP-3	51.5	66.2	86.4	100.1	128.6
BP-10	0.8	<LOQ	1.2	2.2	<LOQ
BS	79.4	102.1	136.1	200.4	244.0
HS	ND	ND	ND	ND	ND
ES	ND	ND	ND	ND	ND

Table S8. The total amount of UVFs and TOC concentration levels

Sampling points	SW		SED	
	Σ_{UVFs} (ng/L)	TOC (mg/L)	Σ_{UVF} (ng/g)	TOC (mg/Kg)
S1	578	2.8	161	157
S2	1161	2.4	215	79
S3	2050	2.7	230	212
S4	2170	3.6	308	36
S5	2273	3.8	380	118

Table S9. Pearson correlation calculated between UVFs and TOC amount

Analytes		SW (n=5)	SED (n=5)
234THBP	Pearson Corr.	-0.700	-0.112
	p value	0.188	0.858
4HBP	Pearson Corr.	0.154	0.100
	p value	0.805	0.873
BP-1	Pearson Corr.	-0.600	0.700
	p value	0.285	0.188
BP-8	Pearson Corr.	-0.224	-
	p value	0.718	-
BP-3	Pearson Corr.	0.600	-0.300
	p value	0.285	0.624
BP-10	Pearson Corr.	-0.600	-0.100
	p value	0.116	0.873
BS	Pearson Corr.	-0.112	-0.300
	p value	0.858	0.624