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Distribution, removal efficiencies and environmental risk assessment of benzophenone and salicylate UV filters in WWTPs and surface waters from Romania

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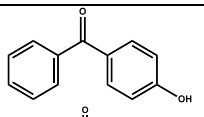
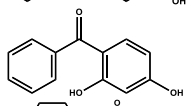
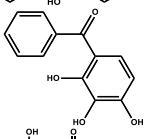
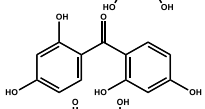
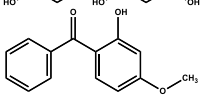
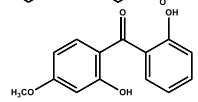
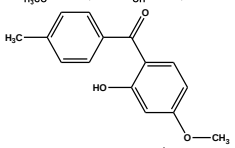
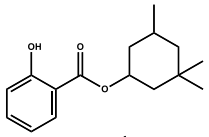
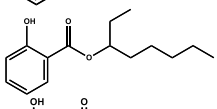
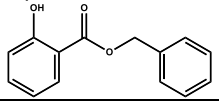
Table S1. Phisico-chemical properties

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	EHS	$C_{15}H_{22}O_3$	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 Sampling points

Locality	Dates	Sample Cod	WWTPs				Receiving Rivers		
			Served population	Average daily flow (m^3/zi)	Types of sample	Sample Cod	Name	Types of sample	Sample Cod
Iasi	14.10.2019 15.10.2019 16.10.2019	WWTP1	793500	777600	Influent Effluent Sludge	I1 E1 S1	Bahlui	Upstream Downstream	U1 D1
Galati	14.10.2019 15.10.2019 16.10.2019	WWTP2	504000	224640	Influent Effluent Sludge	I2 E2 S2	Siret	Upstream Downstream	U2 D2
Targoviste	21.10.2019 22.10.2019 23.10.2019	WWTP3	79600	47606	Influent Effluent Sludge	I3 E3 S3	Ialomita	Upstream Downstream	U3 D3
Glina	21.10.2019 22.10.2019 23.10.2019	WWTP4	1830000	1028160	Influent Effluent Sludge	I4 E4 S4	Somes	Upstream Downstream	U4 D4
Cluj	28.10.2019 29.10.2019 30.10.2019	WWTP5	706900	110000	Influent Effluent Sludge	I5 E5 S5	Dambovita	Upstream Downstream	U5 D5

1. LC-MS/MS method development

To determine the 10 UV filters from environmental matrices, a LC-MS/MSl method previously reported by us was modified and extended.[1] All operational parameters of the new LC-MS / MS method required optimization.

1.1. Optimization of liquid chromatographic parameters

The separation of the ten organic pollutants was performed using a C18 hydrophobic column. The mobile phase composition consisted of Aq:ACN 45/55 (v/v). Liquid chromatographic separation optimization was achieved by varying the formic acid percentage in the aqueous phase, gradient program modification, chromatographic column temperature variation, different samples diluent and injection volumes. Three concentrations of formic acid were tested: Aq 0.1AF: ACN, Aq 0.15AF: ACN and Aq 0.2 AA: ACN, in a ratio of 45:55 v/v. The most intense analytical signal was obtained using the aqueous phase modified with 0.15% formic acid (Table S4).

Table S4 Peak areas generated using different organic modifier concentration

Compounds	**0.1% FA**	**0.15% FA**	**0.2% FA**
BP-2	27926	29120	28856
2,3,4HBP	14206	15715	15225
4HBP	56964	58975	58212
BP-1	101032	105712	104354
BP-8	502109	512485	502553
BP-^{13}C	62097	62728	61928
BP-3	1507659	1519954	1519128
BP-10	2842018	2849891	2881315
BS	2656	2851	2857
HS	160452	159065	156507

EHS	228668	230993	223640

The gradient used to separate the 10 compounds was according to Table S5. This gradient generated a good peak shape with a narrow peak width.

Table S5 The gradient program used for analytes elution

Time (min)	ACN (%)	Flow (mL/min)	Gradient programe
0.00	55	0.200	Analytical separation
3.00	95	0.200	
12.00	95	0.200	
12.10	55	0.200	Chromatographic column reechilibration

Analytes ionization in the electrospray source was favored by the low flow rate of only 0.2 mL/min. The chromatographic column temperature was varied between 20-30°C. (25 °C, 30 °C and 35°C) (**Fig. S1 and Fig. S2**).

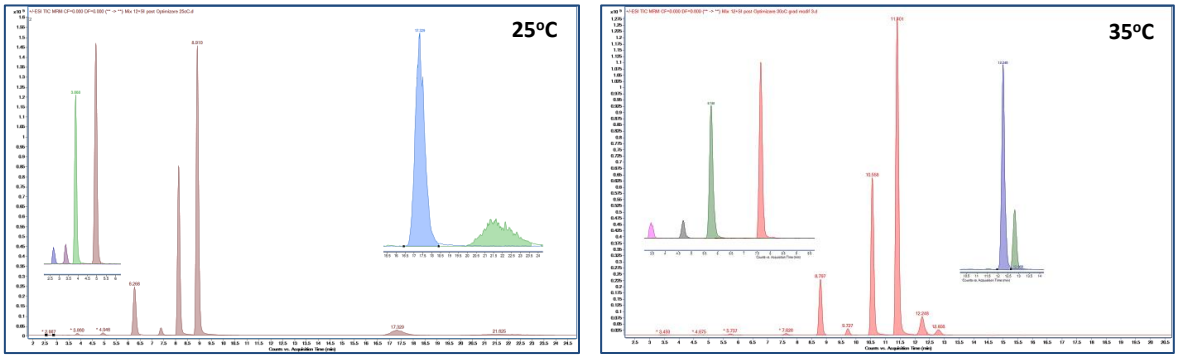


Fig. S1 MRM chromatograms obtained at 25°C and 35°C

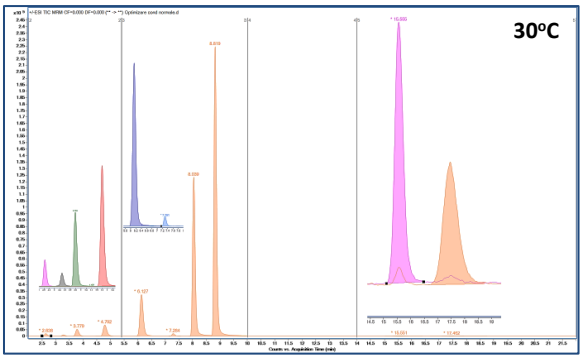


Fig. S2 MRM chromatogram obtained at 30°C

Following these studies, it has been shown that, although a low column temperature (25°C) favors a better analytes separation, it also leads to a widening of the chromatographic peaks of the last two compounds. Studying the chromatogram obtained at 35°C, it was observed that, although for the last 2 compounds the retention time are decreasing, the separation of the 10 compounds was affected. In this context, it was proved that the temperature of 30°C favors both a better separation and narrow peak shape for all ten analytes (Fig. S2). Setting the MRM transitions for quantification of the analytes on individual time segments, except for compounds BP-10 and BS for which only one time segment was allocated, allowed a significant increase of method sensitivity (Table S6 and Fig. S5).

Table S6 Acquisition time segment set for sensitive detection enhensment of the investigated analytes

Time segment	Start time (min)	Scan type	Ionization mod	Div Valve	Store
1	0	MRM	ESI	To Waste	No
2	2.3	MRM	ESI	To MS	Yes
3	2.95	MRM	ESI	To MS	Yes
4	3.53	MRM	ESI	To MS	Yes
5	4.2	MRM	ESI	To MS	Yes
6	5.4	MRM	ESI	To MS	Yes
7	6.6	MRM	ESI	To MS	Yes
8	7.8	MRM	ESI	To MS	Yes
9	8.5	MRM	ESI	To MS	Yes
10	10	MRM	ESI	To Waste	No
11	12	MRM	ESI	To MS	Yes
12	14	MRM	ESI	To Waste	No

The Dwell time parameter was set to two values of 250 and 300 msec, respectively, generating a lower noise and implicitly a higher signal/noise ratio. To optimize the sample diluent, two diluent mixtures were tested: Aq 0.15AF:MeOH 1:1 v/v and Aq 0.15AF: ACN 60:40 v/v. The use of Aq 0.15AF:MeOH 1:1 v/v generated a solvent focus of all compounds and a slightly peak shape due to the presence of methanol (Fig. S3). In this context, it was chosen as diluent samples: Aq0.15AF:ACN 60/40.

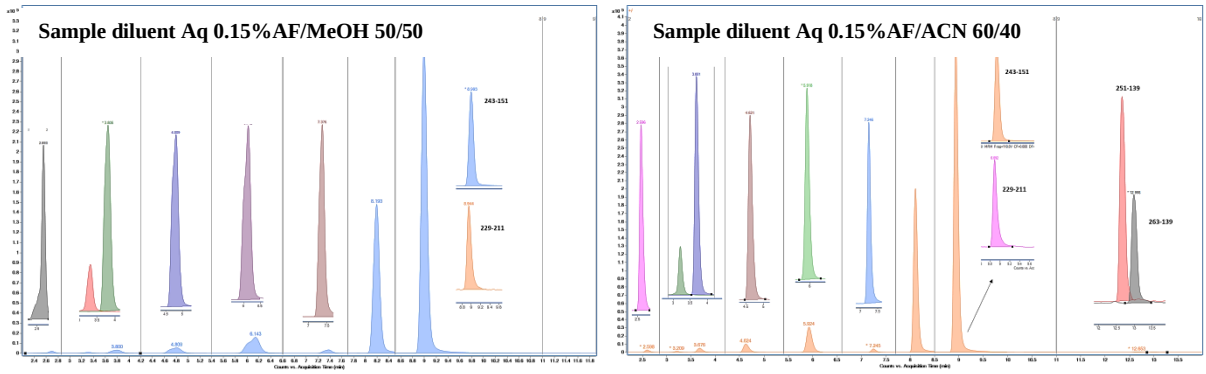


Fig. S3 The peak shapes obtained after testing both sample diluent mixtures

The injection volume was tested using 10 and 20 µL, respectively, the latter being chosen as the final injection volume for a better method sensitivity (Fig. S4).

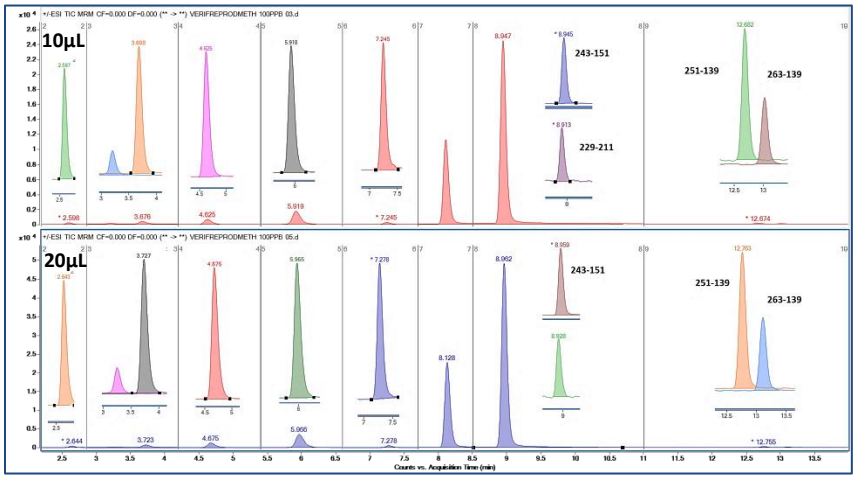


Fig. S4 Injection volume modification

The optimized conditions of the chromatographic parameters allowed the separation of the 10 analytes in less than 24 minutes. The optimal liquid-chromatographic separation (LC) parameters were:

- Chromatographic column: Luna, C18, 100Å 150 mm x 2.0 mm x 3.0 µm;
- Column temperature: 30°C
- Injection volume: 20 µl
- Mobile phase: Aq 0.15% AF/ACN
- Flow rate: 0.2 ml/min
- Sample diluent: Aq 0.15% AF/ACN = 60/40 (v/v)
- Elution mode: gradient
- Run-time: 24 minutes

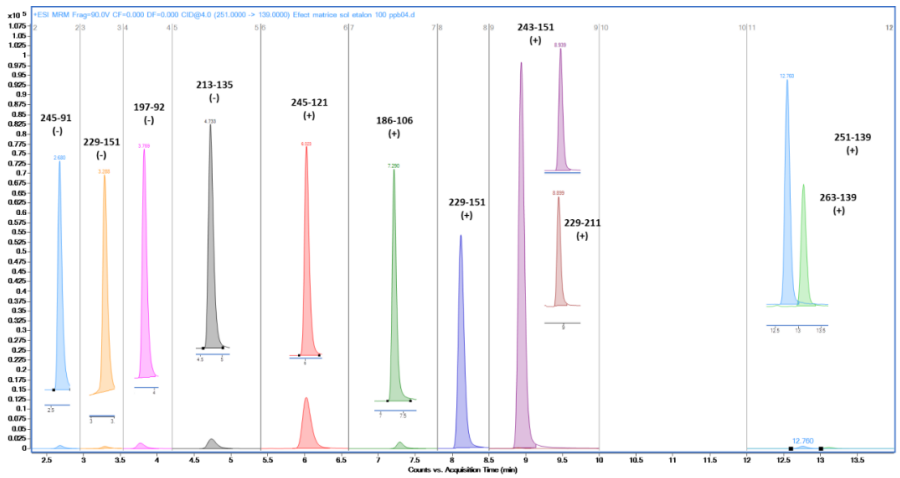


Fig. S5 Acquisition segments used to optimize the separation of the 10 analytes and the IS (100ng/mL)

1.2. Optimization of mass-spectrometric detection parameters (MS)

Analytes were determined by ESI-LC-MS/MS either in positive or negative mode by multiple reaction monitoring (MRM). All parameters of the quadrupole triple MS detector (QQQ) have been optimized: fragmentor voltage, collision energy (CE), cell accelerator voltage, quadrupoles resolution (MS1, MS2 Res), acquisition time per MRM transition (dwell time) and capillary voltage. For the optimization process, an analyte mixture solution with a concentration of 10 mg/L and an injection volume of 2µL was used. It was chosen the mass spectrometric parameters which generated the highest sensitivity (peak area and signal-to-noise ratio) for the studied compounds. The fragmentor voltage values were varied between 90 and 160 volts (**Fig. S6**).

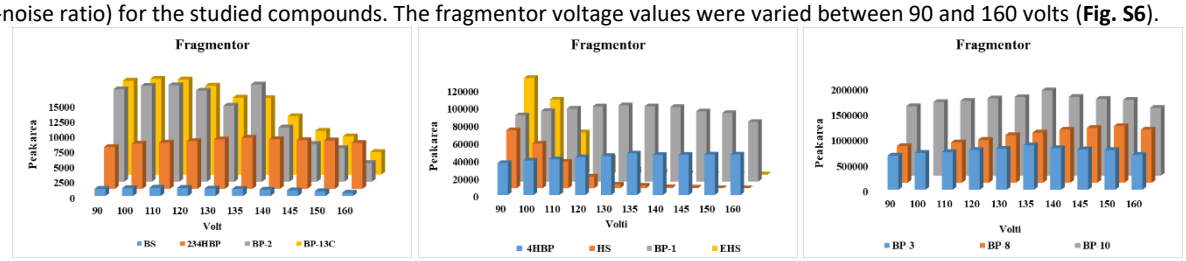


Fig. S6 Peak area values during the fragmentor voltage optimization

For the collision energy, different values were tested around the one at which the MRM transitions were determined (**Table S7**).

Table S7 Peak area variation during the Collision energy

Compounds	Collision energy values				
234HBP	**20** 1683	**25** 14771	**30** 8237	**35** 3467	**40** 1199
BP-1	**5** 9812	**10** 3358	**15** 79629	**20** 113361	**25** 90596
4HBP	**25** 16568	**30** 34660	**35** 44153	**40** 48547	**45** 43762
BP-2	**15** 3931	**20** 9414	**25** 14269	**30** 19626	**35** 19296
BP-10	**20** 2161298	**25** 2025529	**30** 1487092	**35** 1067071	**40** 614398
BS	**10** 1337	**15** 1574	**20** 953	**25** 682	**30** 244
BP-3	**20** 1137988	**25** 1083214	**30** 832501	**35** 541978	**40** 304764
BP -^{13}C	**5** 2993	**7** 5688	**10** 12855	**13** 16193	**15** 18917
BP-8	**20** 509189	**25** 484825	**30** 261190	**35** 317111	**40** 208193
EHS	**3** 4031	**4** 4091	**5** 3699	**6** 3853	**7** 3865
HS	**3** 2821	**4** 2845	**5** 2934	**6** 2694	**7** 2778

The capillary voltage was varied between 3000 and 5500V (Fig. S7), the acceleration voltage in the collision cell between 0 and 6V (Fig. S8) and the nebulizer pressure between 40-50 psi (Fig. S9).

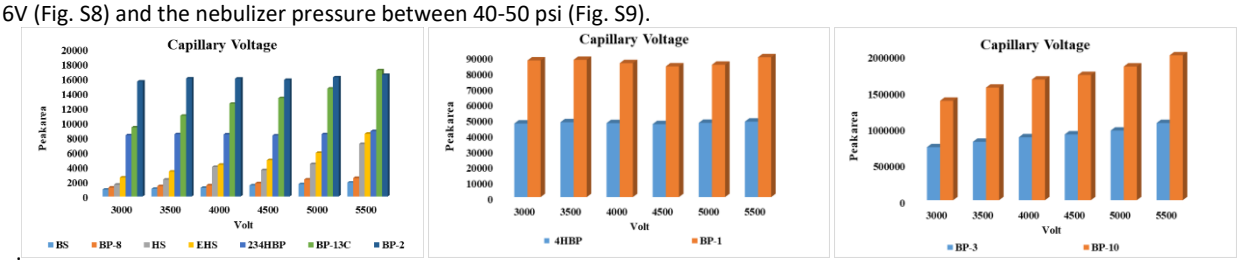


Fig. S7 Peak area values during the capillary voltage optimization

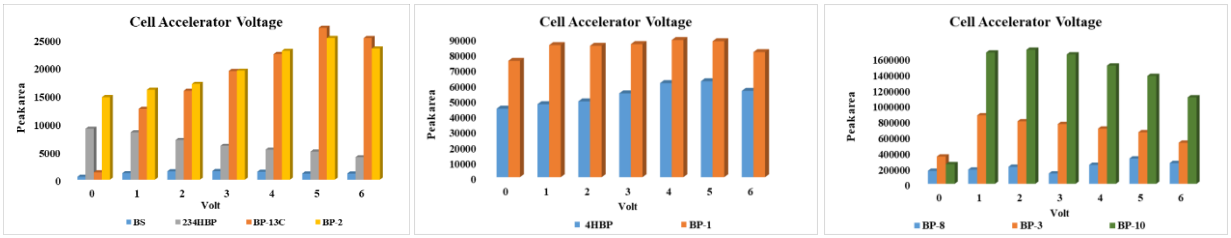


Fig. S8 Peak area values during the cell accelerator voltage optimization

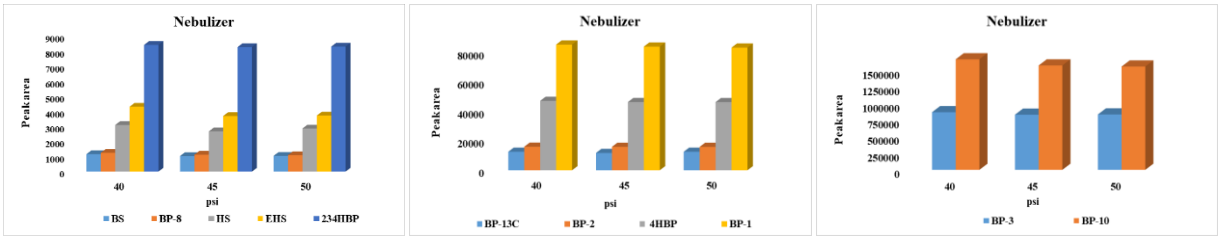


Fig. S9 Peak area values during the nebulizer presure optimization

Following the MS detection optimization procedure, the parameters that generated maximum sensitivity for all analyzed compounds were chosen. The optimized values are given in Table S8:

- Ionization mode: Electrospray negativ ESI(-) and positive ESI (+)
- Drying gas temperature: 300°C
- Drying gas flow: 9 L/min
- Nebulizer presure: 40 psi
- MSmode: Multiple Reaction Monitoring (MRM)

Table S8 LC-MS/MS mass transitions, retention times and operational MS parameters for target analytes and mass-labeled standard

Analyte	Retention time (min)	MRM Tranzition	Fragmentor Voltage (V)	Collision Energy (V)	Cell Accelerator Voltage (V)	Dwell time (msec)	ESI mode
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
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
EHS	12.75	251→139	90	4	5	300	Pozitive
HS	13.10	263→139	90	5	5	300	Pozitive

2. Solid phase extraction optimization

Aqueous samples were concentrated and cleaned up by a solid phase extraction (SPE) system, SPE AutoTrace 280 Thermo Scientific Dionex. The recovery efficiency of the 10 UV filters and the internal standard was evaluated using two types of cartridges: Strata X 30 µm cartridges with polymeric stationary phase and Strata C18 with hydrophobic stationary phase.

The cartridges were preconditioned with 10 mL methanol and 10 mL Milli-Q water. The samples were loaded into cartridges at a flow rate of 5 mL/min. The cartridges were washed with 10 mL Milli-Q water at a flow rate of 20 mL/min. The adsorbent phase was dried under a stream of nitrogen for 30 minutes. The analytes were eluted with 2 x 5 mL methanol at a flow rate of 5 mL/min. The extracts were concentrated to dryness under a gentle nitrogen stream, at 60°C, taken up in a volume of 1.0 mL with Aq 0.15% AF/ACN in a ratio of 60/40 (v/v) binary mixture and analyzed by LC-MS/MS. Recovery yields were higher than 87.7% for hydrophobic C18 cartridges (Table S9).

Table S9 Recovery yields determined following the use of Strata X and Strata C18 SPE cartridges

Analytes	Recovery yields %	
	Strata X	Strata C18
BP-2	66.0	88.9
234HBP	61.0	84.9
4HBP	77.8	93.3
BP-1	66.9	99.3
BP-8	64.8	96.9
BP-^{13}C	69.9	91.1
BP-3	67.1	102.1
BP-10	70.9	95.2
BS	48.4	97.7
EHS	67.7	101.3
HS	68.2	87.7

3. Method Validation

3.1. Liniarity

The linear regressions obtained for the 10 analytes were plotted between 1 ÷ 100 ug/L and exhibit correlation coefficients higher than 0.998.

3.2. Selectivity / Specificity of the method

To test the selectivity of the method, the sample preparation procedure was applied to a water sample that did not contain selected analytes. The sample was subjected to the SPE extraction procedure in triplicate. It was proved that none of the analytes have been observed at the characteristic retention times and that there are no interferences on their MRM transitions. Thus, the developed method could be considered specific/selective**. (Fig. S10).**

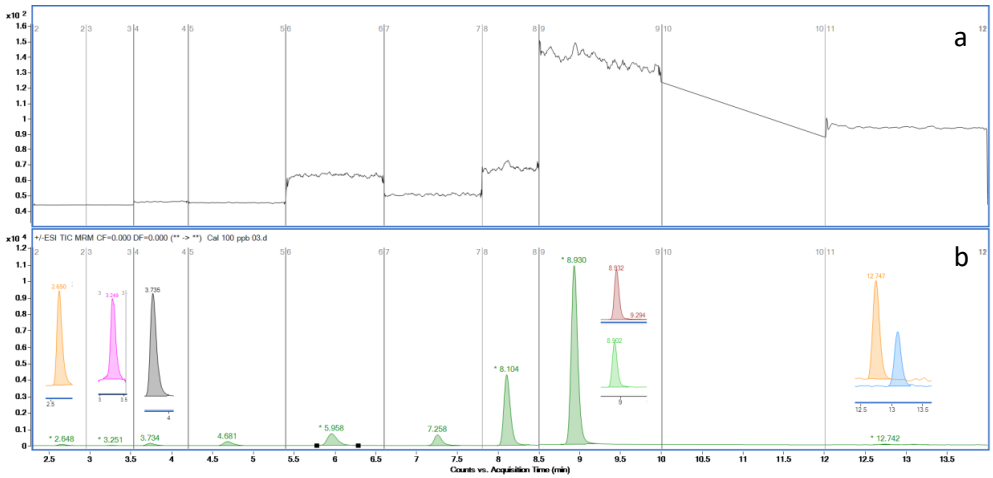


Fig. S10 Chromatogram of a water sample that does not contain interferences on the MRM transitions of the compounds of interest (a) versus the chromatogram of a standard solution of 100 ng/mL (b)

3.3. Precision

The accuracy of the method was determined by evaluating the repeatability (instrument repeatability, analysis repeatability) and intermediate precision, both for surface water, wastewater and sludge matrices. The results are summarized in Fig. S11 and Table S10.

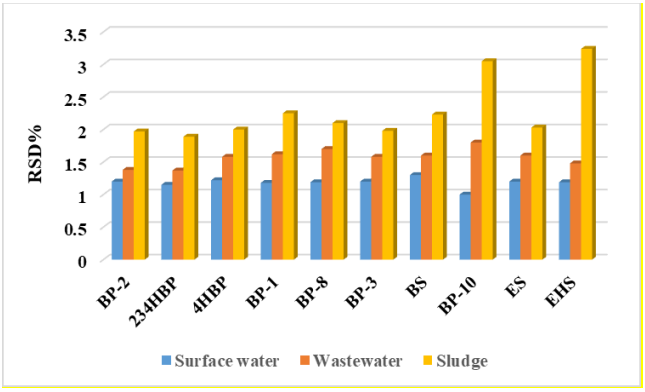


Fig. S11 The results obtained for the instrument repeatability for the ten analytes at a concentration of 10 ng/mL

Regarding the analysis repeatability and the intermediate precision, the RSD% values obtained were higher, but were within the acceptability limit for an LC-MS method of 15%. The analysis repeatability was determined at two concentration levels, 10 and 50 ng/L, respectively, for all three types of matrices (surface water, wastewater and sewage sludge samples), concentration found after extraction of controlled contaminated samples and taken up in 1 mL of sample solvent. The values obtained for the relative standard deviation (RSD%) are presented in Table S10. The method accuracy was evaluated for all three matrices, in triplicate, after they were contaminated with 1 mL of standard solution of concentration of 10 ng/mL and 50ng/mL, respectively. The values obtained were below ± 10% of the theoretical value (Table S10).

Table S10 The RSD values obtained for the method repeatability, intermediate precision and accuracy

Compounds	Surface water						Wastewater					
	10ng/mL			50ng/L			10ng/mL			50ng/L		
	RSD_r	RSD_R	Accuracy	RSD_r	RSD_R	Accuracy	RSD_r	RSD_R	Accuracy	RSD_r	RSD_R	Accuracy
BP-2	1.88	9.23	-3.90	1.65	8.76	-2.95	3.09	12.25	-1.42	2.66	11.95	3.90
234HBP	1.65	8.95	4.72	1.37	8.15	5.66	2.58	12.63	5.19	2.12	11.73	4.72
4HBP	1.44	8.66	3.27	1.39	7.95	4.86	2.31	11.96	3.40	1.97	10.41	2.13
BP-1	1.65	9.18	2.41	1.48	8.78	3.25	2.44	12.58	3.73	2.02	10.95	4.80
BP-8	1.76	9.23	0.03	1.53	8.93	1.39	3.02	10.83	3.34	2.45	9.97	5.56
BP-3	1.83	9.45	1.38	1.69	9.02	2.68	3.18	10.95	4.22	2.58	10.02	3.01
BS	1.81	10.12	0.85	1.56	9.44	3.76	2.96	12.49	5.19	2.31	11.75	4.72
BP-10	1.73	9.67	-0.06	1.49	9.05	5.57	2.45	11.66	6.53	1.83	10.75	6.23
ES	1.98	10.53	5.10	1.71	9.76	7.84	3.21	12.88	10.20	2.64	11.23	10.36
HS	1.92	10.61	-2.40	1.73	9.83	-1.29	3.01	12.73	7.56	2.41	11.49	8.12

Compounds	Sludge					
	10ng/g			50ng/g		
	RSD_r	RSD_R	Accuracy	RSD_r	RSD_R	Accuracy
BP-2	7.15	14.25	8.72	5.88	12.71	9.44
234HBP	5.96	12.27	7.25	5.21	11.16	10.14
4HBP	5.89	12.83	4.82	4.96	11.85	8.51
BP-1	6.38	14.17	5.49	4.17	13.05	10.13
BP-8	7.44	13.83	6.17	6.11	12.41	7.25
BP-3	7.75	14.59	8.23	5.87	12.07	8.77
BS	5.83	14.22	7.41	5.01	13.15	6.48
BP-10	5.91	13.68	9.22	5.23	11.18	6.12
ES	7.92	14.89	8.94	6.82	12.23	7.95
HS	6.78	14.23	10.21	4.93	13.49	8.11

3.4. Recovery

The recovery was calculated following the application of the extraction procedure on a number of 3 surface water, wastewater and sludge samples. Samples were spiked with a known concentration of each native compound and internal standard (50 ng/mL). The data obtained for the absolute recovery efficiency are presented in Table S11.

Table S11. Recovery values obtained after solid phase extraction for all three matrices

Compounds	Recovery, %				
	Upstream	Downstream	Effluent	Influent	Sludge
BP-2	82.7	80.7	74.2	63.1	63.9
234HBP	81.4	79.4	73.6	66.5	76.1
4HBP	90.0	75.8	81.8	68.4	64.3
BP-1	101.2	86.7	105.4	104	79.8
BP-8	89.5	83.3	101.9	70.2	69.1
BP-3	108.7	93.3	90.7	78.3	85.2
BS	99.8	94.1	90.1	64.5	68.9
BP-10	90.2	82.5	91.4	65.7	74.1
ES	92.7	91.4	93.8	78.2	65.0
HS	103.4	93.7	98.5	81.8	72.6
EHS	86.8	83.1	76.2	72.5	70.0

3.5. Sensitivity. Detection and quantification limit

Detection (LOD) and quantification (LOQ) limits were determined by injecting lower solutions until the experimentally determined signal-to-noise ratio was 3 (LOD) and 10 (LOQ), respectively. The values are given in Table S12.

Table S12 LOD and LOQ values

Compounds	IQL, µg/L	Surface water, ng/L				Wastewater, ng/L				Sludge ng/g dw	
		Upstream		Downstream		Effluent		Influent			
		LOD	LOQ	LOD	LOQ	LOD	LOQ	LOD	LOQ	LOD	LOQ
BP-2	0.19	0.35	1.15	0.35	1.18	0.77	2.56	0.91	3.02	3.22	10.72
234THBP	0.15	0.28	0.92	0.28	0.94	0.61	2.03	0.68	2.26	3.07	9.21
4HBP	0.12	0.20	0.68	0.24	0.81	0.45	1.50	0.54	1.80	2.61	7.84
BP-1	0.16	0.24	0.81	0.28	0.95	0.47	1.56	0.47	1.58	2.30	6.89
BP-8	0.04	0.06	0.20	0.06	0.21	0.10	0.35	0.15	0.51	2.34	7.01
BP-3	0.35	0.37	1.22	0.41	1.38	8.86	2.87	1.05	3.50	3.57	11.89
BP-10	0.10	0.15	0.51	0.16	0.54	0.34	1.13	0.48	1.59	2.66	7.98
BS	0.19	0.31	1.05	0.34	1.15	0.62	2.07	0.87	2.91	3.47	11.55
HS	0.49	0.49	1.64	0.51	1.68	0.97	3.23	1.28	4.28	5.95	19.81
EHS	0.52	0.45	1.51	0.53	1.77	0.98	3.28	1.33	4.42	6.53	21.74

3.6. Matrix effects

Matrix effect was evaluated by the post-extraction addition method for both liquid and solid matrices. The extracts obtained were contaminated with a known concentration of analyte mixture (50 ng/mL) and internal standard. Matrix effects were evaluated by comparing the differences between responses obtained for non-spiked and spiked extracts with those measured for a standard solution of the same concentration. The matrix effects were calculated as the ratio between the analytical signal generated by the analyte in the sample and the signal generated by the analyte in the standard solution, expressed in %ME (Ecuation S1):

$$ME = \frac{A_S - A_N}{A_0} x100 \quad , \qquad \text{Ecuation S1}$$

where A_S is the peak area of analyte compounds in the sample extracts spiked with standard solution, A_N is the peak area of analyte compounds in the corresponding sample extracts spiked with standard solution, A_0 is the peak area of analyte compounds in the standard spiking solution.

%ME = 100% - no matrix effects
%ME < 100% - ionization suppression
%ME > 100% - ionization enhancement

The data obtained for the matrix effect for each analyte are presented in Table S13.

Table S13 Matrix effect values obtained for the target analytes in all three matrices

Compounds	Matrix effect, %				
	Upstream	Downstream	Effluent	Influent	Sludge
BP-2	86	81	75	71	67
234HBP	91	82	77	70	66
4HBP	93	78	72	71	66
BP-1	103	90	109	105	83
BP-8	97	95	112	77	72
BP-^{13}C	115	106	101	82	103
BP-3	105	97	94	72	64
BP-10	92	84	86	72	64
BS	97	93	100	86	77
EHS	107	103	105	88	75
HS	93	98	91	79	70

The values determined for the three types of matrices generated either a suppression of the signal or an erroneous eenhancement of it, depending on both the nature of the analyte and the complexity of the respective matrix. (Fig. S12).

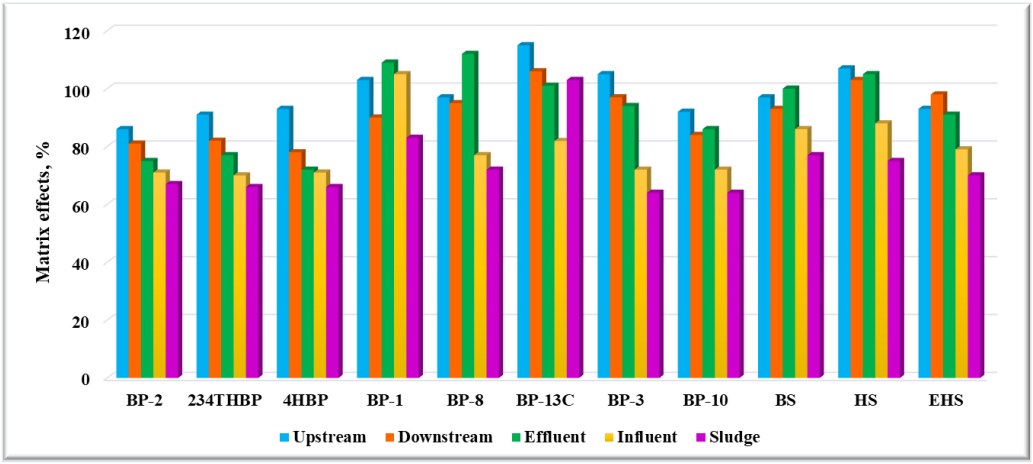


Fig. S12 Assesment for matrix effects for surface water, wastewater and sludge matrices

Table S14 Concentration values obtained for all environmental water samples (ng/L) and sewage sludge samples (ng/g, su)

Samples	BP-2	234THBP	4HBP	BP-1	BP-8	BP-3	BP-10	BS	HS	EHS
U1	10.7	39.9	42.0	64.9	60.3	13.2	9.71	ND	ND	125
U2	ND	ND	ND	9.27	ND	6.81	0.75	ND	ND	10.4
U3	10.7	ND	44.6	78.8	53.0	52.4	8.23	ND	ND	ND
U4	2.13	ND	7.35	17.4	10.6	3.03	1.75	2.25	ND	ND
U5	ND	ND	1.58	9.51	4.38	4.04	0.62	2.13	ND	31.8
D1	3.00	16.0	4.00	11.0	14.0	2.63	0.56	ND	14.0	139
D2	14.1	ND	11.22	94.2	16.5	17.7	1.10	ND	ND	12.0
D3	28.1	19.2	159	206	108	18.7	17.1	ND	ND	ND
D4	2.81	15.4	10.4	66.9	12.0	5.69	2.03	ND	ND	47.0
D5	ND	7.68	3.48	7.31	ND	2.67	<LOQ	3.45	ND	43.5
I1	40.9	88.7	104	2784	53.8	37.6	122	62.1	70.8	370
I2	16.4	88.7	42.7	1874	29.5	35.6	3.53	23.8	212	375
I3	32.7	88.7	97.6	2712	131	101	51.2	8.06	ND	ND
I4	8.18	1108	19.5	695	38.8	29.9	4.36	22.5	51.9	59.9
I5	13.1	142	14.6	637	32.9	32.8	4.45	56.1	75.5	257
E1	11.8	42.5	25.9	60.6	37.4	12.5	7.02	9.75	42.3	217
E2	7.84	ND	14.4	39.4	8.35	6.62	<LOQ	ND	ND	44.0
E3	23.5	ND	77.8	105	12.7	10.3	15.7	6.10	ND	ND
E4	4.70	25.5	16.1	181	18.3	7.88	1.15	19.3	21.2	ND
E5	4.70	ND	12.7	23.0	21.3	23.0	<LOQ	11.7	50.8	219
S1	<LOQ	<LOQ	13.7	6.49	ND	38.8	<LOQ	1381	308	444
S2	<LOQ	<LOQ	13.7	14.9	<LOQ	302	15.4	643	1035	688
S3	<LOQ	<LOQ	14.2	18.4	<LOQ	59.4	11.4	710	645	377
S4	<LOQ	<LOQ	19.8	39.8	<LOQ	75.9	<LOQ	1395	319	203
S5	<LOQ	<LOQ	173	15.9	<LOQ	359	15.8	766	719	347

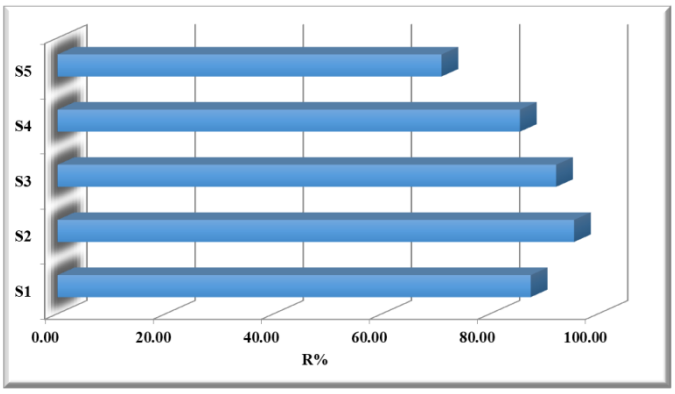


Fig. S13 Removal efficiencies of the analyzed WWTPs

Table S15 Daily consumption levels of UV-Flilters (mg/day/1000 people)

	maximum daily consumption levels (mg/day/1000 people)									
	BP-2	234THBP	4HBP	BP-1	BP-8	BP-3	BP-10	BS	HS	EHS
I1	40	87	102	2728	53	37	119	61	69	362
I2	7	40	19	835	13	16	2	11	95	167
I3	20	53	58	1622	78	60	31	5	0	0
I4	5	623	11	390	22	17	2	13	29	34
I5	2	22	2	99	5	5	1	9	12	40

Table S16 Total environmental emission of UV-Flilters (mg/day/1000 people)

	BP-2	234THBP	4HBP	BP-1	BP-8	BP-3	BP-10	BS	HS	EHS
E1	12	42	25	59	37	12	7	10	41	213
E2	3	0	6	18	4	3	0	0	0	20
E3	14	0	47	63	8	6	9	4	0	0
E4	3	14	9	102	10	4	1	11	12	0
E5	1	0	2	4	3	4	0	2	8	34

Table S17 Spearman correlation between Upstream-Downstream and Effluent-Downstream resulted values

	D1	**D2**	**D3**	**D4**	**D5**
U1	0.615(p=0.058)				
E1	0.900(p=0.0004)				
U2		0.585(p=0.076)			
E2		0.733(p=0.016)			
U3			0.824(p=0.003)		
E3			0.824(p=0.006)		
U4				0.321(p=0.365)	
E4				0.273(p=0.446)	
U5					0.430(p=0.209)
E5					0.297(p=0.405)

Table S18 Spearman correlation coefficients of organic UV filters in Upstream samples

		S1 (n=5)								
		BP-2	234THBP	4HBP	BP-1	BP-8	BP-3	BP-10	BS	HS
234THBP	Spearman Corr.	0.895								
	p value	0.0404								
4HBP	Spearman Corr.	0.895	0.838							
	p value	0.0404	0.0765							
BP-1	Spearman Corr.	0.984	0.838	1.000						
	p value	0.0025	0.0765	0.0000						
BP-8	Spearman Corr.	0.984	0.919	0.968	0.968					
	p value	0.0025	0.0274	0.0070	0.0070					
BP-3	Spearman Corr.	0.886	0.886	0.870	0.870	0.838				
	p value	0.0451	0.6325	0.0550	0.0550	0.0765				
BP-10	Spearman Corr.	0.984	0.984	0.935	0.935	0.968	0.870			
	p value	0.0025	0.0025	0.0196	0.0196	0.0070	0.0550			
BS	Spearman Corr.	0.627	0.627	0.643	0.643	0.643	0.449	0.578		
	p value	0.2576	0.2576	0.2416	0.2416	0.2416	0.4486	0.3070		
HS	Spearman Corr.	0.854	0.919	0.838	0.838	0.838	0.838	0.838	0.870	
	p value	0.0654	0.0274	0.0765	0.0765	0.0765	0.0765	0.0765	0.0550	
EHS	Spearman Corr.	0.676	0.927	0.676	0.586	0.700	0.749	0.732	0.570	0.846
	p value	0.2106	0.0274	0.2106	0.2986	0.1881	0.1454	0.1593	0.3155	0.0709

Table S19 Spearman correlation coefficients of organic UV filters in Downstream samples

		S1 (n=5)								
		BP-2	234THBP	4HBP	BP-1	BP-8	BP-3	BP-10	BS	HS
234THBP	Spearman Corr.	0.805								
	p value	0.1000								
4HBP	Spearman Corr.	0.805	0.773							
	p value	0.1000	0.1253							
BP-1	Spearman Corr.	0.968	0.773	1.000						
	p value	0.0070	0.1253	0.0000						
BP-8	Spearman Corr.	1.000	0.805	0.968	0.968					
	p value	0.0000	0.1000	0.0070	0.0070					
BP-3	Spearman Corr.	0.903	0.903	0.968	0.968	0.903				
	p value	0.0359	0.7000	0.0070	0.0070	0.0359				
BP-10	Spearman Corr.	0.903	0.903	0.968	0.968	0.903	0.935			
	p value	0.0359	0.0359	0.0070	0.0070	0.0359	0.0196			
BS	Spearman Corr.	0.481	0.481	0.578	0.578	0.481	0.643	0.676		
	p value	0.4120	0.4120	0.3070	0.3070	0.4120	0.2416	0.2106		
HS	Spearman Corr.	0.757	0.838	0.676	0.676	0.757	0.595	0.676	0.708	
	p value	0.1386	0.0765	0.2106	0.2106	0.1386	0.2903	0.2106	0.1808	
EHS	Spearman Corr.	0.481	0.676	0.481	0.449	0.481	0.384	0.514	0.805	0.919
	p value	0.4120	0.0765	0.4120	0.4486	0.4120	0.5236	0.3762	0.1000	0.0274

Table S20 The environmental risk assessment of UV filters in effluent from WWTPs

	Effluents							
	Toxicity	Species	NOEC (ng/L)	MEC ng/L	AF	PNEC	RQ	ER
BP-2	Chronic	*Fish (P. promelas)*	8783	24	100	87.83	0.27	MEDIUM
234THBP	Chronic	*Daphia magna*	29.4×10^6	42	100	294000	0.00	LOW
4HBP	Chronic			78	100	0		
BP-1	Chronic	*Fish (P. promelas)*	4919	181	100	49.19	3.68	HIGH
BP-8	Chronic	*Freshwater algae*	471×10^3	37	100	4710	0.01	LOW
BP-3	Chronic	*Daphia magna*	180×10^3	23	100	1800	0.01	LOW
BP-10	Chronic			16	100			
BS	Chronic	*Daphia magna*	894×10^3	19	100	8940	0.00	LOW
HS	Chronic	*Daphia magna*	8.9×10^3	51	100	89	0.57	MEDIUM
EHS	Chronic	*Freshwater algae*	11×10^3	219	100	110	1.99	HIGH

Table S21 The environmental risk assessment of UV filters in samples collected upstream the WWTPs

	Upstream							
	Toxicity	Species	NOEC (ng/L)	MEC ng/L	AF	PNEC	RQ	ER
BP-2	Chronic	*Fish (P. promelas)*	8783	11	100	87.83	0.12	LOW
234THBP	Chronic	*Fish (P. promelas)*	29.4×10^6	40	100	294000	0.00	LOW
4HBP	Chronic	*Daphia magna*		45	100	0		
BP-1	Chronic		4919	79	100	49.19	1.60	HIGH
BP-8	Chronic	*Fish (P. promelas)*	471×10^3	60	100	4710	0.01	LOW
BP-3	Chronic	*Daphia magna*	180×10^3	52	100	1800	0.03	LOW
BP-10	Chronic			10	100	0		
BS	Chronic	*Daphia magna*	894×10^3	2	100	8940	0.00	LOW
HS	Chronic	*Daphia magna*	8.9×10^3	0	100	89	0.00	LOW
EHS	Chronic	*Daphia magna*	11×10^3	175	100	110	1.60	HIGH

Table S22 The environmental risk assessment of UV filters in samples collected downstream the WWTPs

	Downstream							
	Toxicity	Species	NOEC (ng/L)	MEC ng/L	AF	PNEC	RQ	ER
BP-2	Chronic	*Fish (P. promelas)*	8783	28	100	87.83	0.32	MEDIUM
234THBP	Chronic	*Daphia magna*	29.4×10^6	19	100	294000	0.00	LOW
4HBP	Chronic			159	100	0		
BP-1	Chronic	*Fish (P. promelas)*	4919	206	100	49.19	4.19	HIGH
BP-8	Chronic	*Freshwater algae*	471×10^3	108	100	4710	0.02	LOW
BP-3	Chronic	*Daphia magna*	180×10^3	19	100	1800	0.01	LOW
BP-10	Chronic			17	100	0		
BS	Chronic	*Daphia magna*	894×10^3	9	100	8940	0.00	LOW
HS	Chronic	*Daphia magna*	8.9×10^3	14	100	89	0.16	MEDIUM
EHS	Chronic	*Freshwater algae*	11×10^3	139	100	110	1.27	HIGH

References

1. F. L. Chiriac, I. Paun, F. Pirvu, L. F. Pascu, T. Galaon, Rev. Chim. (Bucharest), 2020, **71**, 92.