Anexos

Anexo I. Listado de publicaciones

Revistas

1. C.E. Rodríguez-Rodríguez, D. Lucas, E. Barón, P. Gago-Ferrero, **D. Molins-Delgado**, S. Rodríguez-Mozaz, E. Eljarrat, M.S. Díaz-Cruz, D. Barceló, G. Caminal, T. Vicent, "Re-inoculation strategies enhance the degradation of emerging pollutants in fungal bioaugmentation of sewage sludge," *Bioresource Technology*, vol. 168, pp.180-189, 2014.
2. **D. Molins-Delgado**, M.S. Díaz-Cruz, D. Barceló, "Removal of polar UV Stabilizers in biological wastewater treatments and ecotoxicological implications," *Chemosphere*, vol. 119, pp. S51-S57, 2015.
3. **D. Molins-Delgado**, M.S. Díaz-Cruz, D. Barceló, "Ecological risk assessment associated to the removal of endocrine-disrupting parabens and benzophenone-4 in wastewater treatment," *Journal of Hazardous Materials*, vol. 310, pp. 143-151, 2016.
4. **D. Molins-Delgado**, P. Gago-Ferrero, M.S. Díaz-Cruz, D. Barceló, "Single and joint ecotoxicity data estimation of organic UV filters and nanomaterials toward selected aquatic organisms. Urban groundwater risk assessment," *Environmental Research*, vol.145, pp.126-134, 2016.
5. J. Valle-Sistac, **D. Molins-Delgado**, M. Díaz, L. Ibáñez, D. Barceló, M.S. Díaz-Cruz, "Determination of parabens and benzophenone-type UV filters in human placenta. First determination of the existence of benzyl paraben and benzophenone-4," *Environment International*, vol. 88, pp. 243-249, 2016.
6. L. Mandaric, E. Diamantini, E. Stella, S. Malluci, J. Valle-Sistac, **D. Molins-Delgado**, A. Bellin, G. Chiogna, B. Majone, M.S. Diaz-Cruz, S. Sabater, D. Barceló, M, Petrovic," Contamination sources and distribution patterns of pharmaceuticals and personal care products in the Alpine rivers strongly affected by tourism," *Science of the Total Environment,* vol. 590-591, pp. 484-494, 2017.
7. **D. Molins-Delgado**, J. Távora, M.S. Díaz-Cruz, D. Barceló, "UV filters and benzotriazoles in urban aquatic ecosystems: the footprint of daily use products," *Science of the Total Environment*, vol. 601-602, pp. 975 – 986, 2017.
8. A. Mizukawa, **D. Molins-Delgado**; J.C. Rodrigues Azevedo; C.V. Scapulatempo Fernandes; M.S. Díaz-Cruz; D. Barceló, "Sediments as a sink for UV filters: The case study of Upper Iguaçu watershed, Curitiba (Brazil)," *Environmental Science and Pollution Research,* vol. 24, pp. 18284-18294, 2017.

9. **D. Molins-Delgado**, M. Máñez, A. Andreu, F. Hiraldo, E. Eljarrat, M. S. Díaz-Cruz, D. Barceló, "New threat to wild life: UV filters in bird eggs from a preserved área," *Environmental Science and Technology (en prensa)* DOI: 10.1021/acs.est.7b03300.
10. **D. Molins-Delgado**, D. García-Sillero, M.S. Díaz-Cruz, D. Barceló, "Development of a new on-line SPE-HPLC-(APPI)-MS/MS method for the determination of insect repellents in European rivers," *Journal of Chromatography A* (enviado).
11. **D. Molins-Delgado**, R. Muñoz, S. Nogueira, M.B. Alonso, J.P. Torres, O. Malm, R.L. Ziolli, R.A. Hauser-Davis, E. Eljarrat, D. Barceló, M.S. Díaz-Cruz, "Occurrence of organic UV filters and metabolites in lebranche mullet (Mugil liza) from Brazil, "*Science of the Total Environment* (enviado).
12. **D. Molins-Delgado**, M.M. Olmo-Campos, G. Valeta-Juan, V. Pleguezuelos-Hernández, D. Barceló, M.S. Díaz-Cruz, "Determination of UV filters in human breast milk using turbulent flow chromatography and babies' daily intake estimation," *Environmental Research* (enviado).
13. A.C. Soler de la Vega, **D. Molins-Delgado**, D. Barceló, M.S. Díaz Cruz, "Single and mixture toxicity of organic and inorganic UV-Filters and parabens on Daphnia magna and Phaeodactylum tricornutum," (en preparación).
14. Y. Valcárcel, M. López de Alda, S. González-Alonso, A. Silva, J.J. Durán, J. López, **D. Molins-Delgado**, M.S. Díaz-Cruz, J. Sanchís, M. Farré, Ò. Aznar-Alemany, E. Eljarrat, D. Barceló, L. Moreno, "Occurrence of anthropogenic organic contaminants (sunscreens filters, perfluorinated compounds and pirethroids) in inland surface waters from the Northern Antarctic peninsular region," (en preparación).

Capítulos de Libro

1. **D. Molins-Delgado**, M.S. Díaz-Cruz, D. Barceló, "Introduction: personal care products in the aquatic environment," In Personal Care Products in the Aquatic Environment, M.S. Díaz-Cruz, D. Barceló (Eds.), *The Handbook of Environmental Chemistry*, Springer International Publishing, pp. 1-34, 2015.
2. M.S. Díaz-Cruz, **D. Molins-Delgado**, "Toxicity and Risk Assessment of Organic UV Filters in Aquatic Ecosystems," In Insights in Ecotoxicology, R.A. Hauser-Davis, T. Parente (Eds.), Science Publishers (CRC Press), (aceptado).

Anexo II. Listado de participación en congresos

Presentaciones orales

(El ponente aparece subrayado)

1. **D. Molins-Delgado**, M.S. Díaz-Cruz, D. Barceló, "HPLC-MS/MS Trace determination of multiclass UV filters and UV blockers in milk," *XII Reunión Científica de la Sociedad Española de Cromatografía y Técnicas Afines (SECyTA)*, Tarragona, España, 2012.
2. **D. Molins-Delgado**, P. Gago-Ferrero, M.S. Díaz-Cruz, D. Barceló, "Determination of toxicity data of ultraviolet filters towards selected aquatic organisms for a preliminary environmental risk assessment," *SETAC Europe 24th Annual Meeting*, Basilea, Suiza, 2014.
3. M.S. Díaz-Cruz, **D. Molins-Delgado**, E. Pastoret, D. Barceló, "Removal of Parabens and Benzophenone-4 from wastewater and environmental impact assessment," *SETAC Europe 24th Annual Meeting*, Basilea, Suiza, 2014.
4. **D. Molins-Delgado**, M.S. Díaz-Cruz, D. Barceló, "Analytical strategies based on off-line and on-line (Turboflow®) extraction of chromatography-tandem mass spectrometry for the trace determination of UV blockers in milk," *10th Annual LC/MS/MS Workshop on Environmental Applications and Food Safety*, Barcelona, España, 2014.
5. D. Barceló, P. Verlicchi, M. Petrovic, P. Gago-Ferrero, **D. Molins-Delgado**, M.S. Díaz-Cruz, N. Mastroianni, M. Köck-Schulmeyer, C. Postigo, M. López de Alda, S. Pérez, A. Ginebreda, "Fate and risk of pesticides, pharmaceuticals, illicit drugs and personal care products in the Iberian river basins of Ebro and Llobregat: challenges and solutions using advanced treatment technologies," *248th ACS National Meeting*, San Francisco, California, Estados Unidos de América, 2014.
6. **D. Molins-Delgado**, M.S. Díaz-Cruz, D. Barceló, "Occurrence and fate of personal care products in the environment," *1st Meeting of Young Researchers from the IDAEA-CSIC*, Barcelona, España, 2015.
7. **D. Molins-Delgado**, F.M. Flores, M.S. Díaz-Cruz, D. Barceló, "UV filters bioaccumulation. The need for metabolites inclusion when carrying out ERA," *SETAC Europe 26th Annual Meeting,* Nantes, Francia, 2016.

Presentaciones en formato póster

1. **D. Molins-Delgado**, M.S. Díaz-Cruz, D. Barceló, "Removal of polar UV stabilizers in biological wastewater treatments," *SETAC Europe 23th Annual Meeting*, Glasgow, Reino Unido, 2013.
2. **D. Molins-Delgado**, M.S. Díaz-Cruz, D. Barceló, "Removal of personal care products in biological wastewater treatments," *VI Reunión de la Sociedad Española de Espectrometría de Masas (SEEM)*, Úbeda, España, 2013.
3. J. Valle-Sistac, **D. Molins-Delgado**, M.S. Díaz-Cruz, D. Barceló, "Analysis of personal care products in human placental tissue," *SETAC Europe 24th Annual Meeting*, Basilea, Suiza, 2014.
4. **D. Molins-Delgado**, M.S. Díaz-Cruz, D. Barceló, "Ecotoxicity and mixture of ultraviolet filters towards selected aquatic organisms," *SETAC Europe 25th Annual Meeting*, Barcelona, España, 2015.
5. **D. Molins-Delgado**, J. Távora, M.S. Díaz-Cruz, D. Barceló, "Occurrence and environmental impact of organic UV filters in urban aquatic ecosystems," *SETAC Europe 25th Annual Meeting*, Barcelona, España, 2015.
6. **D. Molins-Delgado**, M.S. Díaz-Cruz, D. Barceló, "Analysing personal care products in biota by liquid chromatography-atmospheric pressure photoionisation-mass spectrometry," *SETAC Europe 25th Annual Meeting*, Barcelona, España, 2015.
7. **D. Molins-Delgado**, J. Bazzan Arsand, M.S. Díaz-Cruz, L. Jank, M. Martins, R. Hoff, F. Barreto, C. Sirtori, T. Pizzolato, D. Barceló, "UV Aminoglycosides antibiotics residues analysis in bovine milk and bovine, swine and poultry muscle by LC-MS/MS and LC-QTOF-MS: a simple and fast non SPE method," *SETAC Europe 26th Annual Meeting*, Nantes, Francia, 2016.
8. M.P. Serra-Roig, **D. Molins-Delgado**, M.S. Díaz-Cruz, D. Barceló, "Automated LC-MS^2 analysis of sunscreen residues in salty waters," *12th Annual LC/MS/MS Workshop on Environmental Applications and Food Safety*, Barcelona, España, 2016.

Anexo III. Otras publicaciones (no incluidas en el cuerpo de la Memoria de Tesis)

Publicación Nº A1

Introduction: Personal Care Products in the Aquatic Environment

Por

D. Molins-Delgado, M.S. Díaz-Cruz, D. Barceló

en

Personal Care Products in the Aquatic Environment

M.S. Díaz-Cruz and D. Barceló (Eds.)

The Handbook of Environmental Chemistry

Springer International Publishing

pp. 1-34, 2015

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Publicación Nº A2

Contamination sources and distribution patterns of pharmaceuticals and personal care products in Alpine rivers strongly affected by tourism

Por

L. Mandaric, E. Diamantini, E. Stella, S. Malluci, J. Valle-Sistac, D. Molins-Delgado, A. Bellin, G. Chiogna, B. Majone, M.S. Diaz-Cruz, S. Sabater, D. Barceló, M, Petrovic

en

Science of the Total Environment, vol. 590-591, pp. 484-494, 2017.

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Anexo IV. Información adicional de las publicaciones

Información adicional - publicación Nº 1

UV filters and benzotriazoles in urban aquatic ecosystems: the footprint of daily use products

por

D. Molins-Delgado, J. Távora, M.S. Díaz-Cruz, D. Barceló

en

Science of the Total Environment, vol. 601-602, pp. 975-986, 2017

Supporting Information

For

UV FILTERS AND BENZOTRIAZOLES IN URBAN AQUATIC ECOSYSTEMS:

THE FOOTPRINT OF DAILY USE PRODUCTS

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Content

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Table A1. Name of the selected compounds, abbreviation, CAS number, and the log of the partition coefficient octanol water (Log K_{ow}).

Compound	**Abbreviation**	**CAS no.**	**Log K_{ow}**
Benzophenone-1	BP1	131-56-6	3.17
Benzophenone-3	BP3	131-57-7	3.79
4-hydroxybenzophenone	4HB	1137-42-4	3.02
4,4 -dihydroxybenzophenone	4DHB	611-99-4	2.55
4-methylbenzylidene camphor	4MBC	36861-47-9	4.95
Ethylhexyl methoxycinnamate	EHMC	5466-77-3	5.80
Ethylhexyldimethyl PABA	ODPABA	21245-02-3	6.15
Octocrylene	OC	6197-30-4	7.53
Ethyl 4-aminobenzoate	EtPABA	94-09-7	1.86
1H-benzotriazole	BZT	95-14-7	1.23
5-methyl-1-H-benzotriazole	MeBZT	136-85-6	1.89

Table A2. Operational parameters of the studied WWTPs. HRT: hydraulic retention time; -: not available, d: days.

WWTP	Location	Treatment	HRT (d)	Designed Treatment Capacity ($m^3 d^{-1}$)	Average Flow ($m^3 d^{-1}$) (operated)	Population served	Equivalent inhabitants (design)	Equivalent inhabitants (operated)
S3	Montcada i Reixac	Biologic	0.3	72600	50000	253364	423500	229000
S6	Sabadell	Biologic with P + N removal	-	35000	25500	118675	296333	-
S8	Terrassa	Biologic	29.9	60000	38000	195160	500000	165000
S11	St. Feliu de Llobregat	Biologic with P + N removal	0.36	64000	43000	279959	373333	198000
S14	Rubí	Biologic with N removal	0.3	27000	23000	77994	135000	142000
S17	Manresa	Biologic with P + N removal	-	53500	28000	85224	196.167	-

Table A3. Description of the sampling sites.

Sample name	Type of water sample	Sediment	Location	River	Coordinates
S2	river	Yes	Santa Coloma de Gramanet	Besòs	41.455497 N, 2.194237 E
S3I	influent WWTP	No	Montcada i Reixac WWTP	Besòs	41.472330 N, 2.190766 E
S3E	effluent WWTP	No			
S4	river	Yes	Montcada i Reixac	Ripoll	41.488159 N, 2.187565 E
S5	river	Yes	Montcada i Reixac	Besòs	41.489726 N, 2.192799 E
S6I	influent WWTP	No	Sabadell WWTP	Riu-Sec	41.517075 N, 2.101912 E
S6E	effluent WWTP	No			
S7	river	Yes	Sabadell	Riu-Sec	41.51441 N, 2.108685 E
S8I	influent WWTP	No	Terrassa WWTP	Riera de Rubí	41.517907 N, 2.034551 E
S8E	effluent WWTP	No			
S9	river	Yes	Les Fonts	Riera de Rubí	41.52172 N, 2.037274 E
S10	river	Yes	Les Fonts	Riera de Rubí	41.51161 N, 2.033814 E
S11I	influent WWTP	No	St. Feliu de Llobregat WWTP	Llobregat	41.381574 N, 2.033401 E
S11E	effluent WWTP	No			
S12	river	Yes	St. Feliu de Llobregat	Llobregat	41.381574 N, 2.033401 E
S13	river	Yes	St. Feliu de Llobregat	Llobregat	41.384444 N, 2.025893 E
S14I	influent WWTP	No	Rubí WWTP	Riera de Rubí	~41.461447 N, ~2.003419 E
S14E	effluent WWTP	No			
S15	river	Yes	Rubí	Riera de Rubí	41.456371 N, 2.001271 E
S16	river	Yes	Rubí	Riera de Rubí	41.460988 N, 2.000863 E
S17I	influent WWTP	No	Manresa WWTP	Cardener	41.703772 N, 1.843232 E
S17E	effluent WWTP	No			
S18	river	Yes	Manresa	Cardener	41.720803 N, 1.827565 E
S19	river	Yes	Castellgalí	Cardener	41.681077 N, 1.848878 E

Table A4. Instrumental performance for the water (a) and sediment and suspended particulate matter (b) analytical methods.

a)

HPLC-ESI-MS/MS analysis of water samples						
Compound	Linearity range (ng l^{-1})	r^2	ILOD (pg)	ILOQ (pg)	Precision (RSD%), n=7	
					Intra-day	Inter-day
BP1	0.5-500	0.9998	10	33	3	6
BP3	0.5-500	0.9998	4	13	3	5
4HB	0.5-500	0.9999	6	20	4	5
4DHB	0.5-500	0.9997	14	47	3	5
DHMB	0.5-500	0.9995	8	27	4	6
4MBC	1-500	0.9995	6	20	3	6
EtPABA	0.1-200	0.9991	0.2	0.7	5	7
BZT	1-10000	0.9995	1.3	4.2	5	6
MeBZT	1-10000	0.9995	0.7	2.3	3	5

ILOD - instrumental limit of detection; ILOQ - instrumental limit of quantification; RSD - relative standard deviation

b)

HPLC-ESI-MS/MS analysis of sediment and suspended particulate matter samples

Instrumental

Compound	Linearity range (ng l^{-1})	r^2	ILOD (pg)	ILOQ (pg)	Precision (RSD%), n=7	
					Intra-day	Inter-day
BP1	0.5-500	0.9998	10.0	33.0	3	6
BP3	0.5-500	0.9998	4.0	13.0	3	5
4HB	0.5-500	0.9999	6.0	20.0	4	5
4DHB	0.5-500	0.9997	14.0	47.0	3	5
4MBC	1-500	0.9995	6.0	20.0	3	6
OC	1-300	0.998	1.1	3.7	5	7
EHMC	1-500	0.993	1.5	4.9	5	7
OD-PABA	1-100	0.995	4.1	13.5	4	10
EtPABA	0.1-200	0.9991	0.2	0.7	5	7
BZT	1-10000	0.9995	1.3	4.2	5	6
MeBZT	1-10000	0.9995	0.7	2.3	3	5

ILOD - instrumental limit of detection; ILOQ - instrumental limit of quantification; RSD - relative standard deviation

Table A5. Concentrations of UV-Fs and benzotriazole in water samples. <LOQ: below the limit of quantification; n.d.: not detected.

Sample Name			Compound							
			BP1	BP3	4HB	4DHB	4MBC	EtPABA	BZT	MeBZT
River										
S2	Besòs		48,2	52,2	12,1	< LOQ	13,1	27,2	2498	4209
S4	Ripoll		14,5	15,9	< LOQ	< LOQ	13,9	7,7	4270,8	4315,9
S5	Besòs		31,2	20,9	10,1	< LOQ	< LOQ	38,6	2855,6	5004
S7	Riu-Sec		51,8	43,7	< LOQ	< LOQ	18,2	51,7	4852,8	3844,5
S9	Riera de Rubí		15,6	15,9	10,5	< LOQ	25,8	6,3	244,6	797,9
S10	Riera de Rubí		< LOQ	< LOQ	< LOQ	< LOQ	18,8	< LOQ	23,7	199,3
S12	Llobregat		5,3	< LOQ	< LOQ	< LOQ	< LOQ	n.d.	267,5	721,3
S13	Llobregat		< LOQ	< LOQ	< LOQ	< LOQ	34,3	< LOQ	198,7	538,8
S15	Riera de Rubí		24,8	30,1	< LOQ	9,2	13,9	111,9	8529,8	7181,4
S16	Riera de Rubí		28,3	38,5	< LOQ	< LOQ	< LOQ	44,2	1192,5	1934,8
S18	Cardaner		< LOQ	4,4	< LOQ	< LOQ	< LOQ	5,5	25	66,9
S19	Cardaner		< LOQ	5	< LOQ	< LOQ	n.d.	n.d.	262	284
WWTP										
S3	Montcada i Reixac	inf.	409,7	515,7	n.d.	n.d.	n.d.	184,2	2493,4	4593,2
		eff.	211,2	217,8	< LOQ	< LOQ	22	35,8	1469,2	4411,7
S6	Sabadell	inf.	687,9	326,9	10,7	< LOQ	n.d.	149,1	9481,6	6366,2
		eff.	23,6	29,7	< LOQ	< LOQ	< LOQ	32,1	2891,5	2376,9
S8	Terrassa	inf.	332	387,1	< LOQ	n.d.	30,1	224,5	2953,7	4342,4
		eff.	28	46,1	< LOQ	< LOQ	58,1	66	1172,1	2173,6
S11	St. Feliu de Llobregat	inf.	261,1	201	n.d.	n.d.	n.d.	12,3	1495,2	3715,1
		eff.	10,2	33,6	< LOQ	< LOQ	< LOQ	23,4	1084,1	4832,8
S14	Rubí	inf.	94,6	75,5	n.d.	7,7	n.d.	53,3	8281,9	5143,7
		eff.	5,2	9,4	< LOQ	10,9	34,6	129,1	16933,1	8913,3
S17	Manresa	inf.	379,7	297,1	24,8	n.d.	29,3	114,8	3272,6	3728,5
		eff.	4,3	27,1	< LOQ	< LOQ	n.d.	22,4	5100,4	2385,9

Table A6. Estimated daily mass loads (mg d^{-1} inh^{-1}) for each compound and the cumulative loads (∑UV-Fs), WWTP, and population served. n.a.: not applicable.

			Mass Loads (mg d^{-1} inh^{-1})								
	WWTP		BP1	BP3	4HB	4DHB	4MBC	EtPABA	BZT	MeBZT	∑UV-Fs
S3	Montcada i Reixac	inf.	0.008	0.010	n.a.	n.a.	n.a.	0.004	0.05	0.09	0.16
		eff.	0.004	0.004	n.a.	n.a.	0.0004	0.0007	0.03	0.09	0.13
S6	Sabadell	inf.	0.010	0.007	0.0002	n.a.	n.a.	0.003	0.20	0.13	0.36
		eff.	0.0005	0.0006	n.a.	n.a.	n.a.	0.0007	0.06	0.05	0.11
S8	Terrassa	inf.	0.006	0.008	n.a.	n.a.	0.0006	0.004	0.06	0.08	0.16
		eff.	0.0005	0.0009	n.a.	n.a.	0.001	0.001	0.02	0.04	0.07
S11	St. Feliu de Llobregat	inf.	0.004	0.003	n.a.	n.a.	n.a.	0.0002	0.02	0.06	0.09
		eff.	0.0002	0.0005	n.a.	n.a.	n.a.	0.0004	0.02	0.07	0.09
S14	Rubí	inf.	0.0030	0.002	n.a.	0.0002	n.a.	0.002	0.24	0.15	0.40
		eff.	0.0002	0.0003	n.a.	0.0003	0.001	0.004	0.50	0.26	0.77
S17	Manresa	inf.	0.010	0.010	0.0008	n.a.	0.001	0.004	0.11	0.12	0.26
		eff.	0.0001	0.0009	n.a.	n.a.	n.a.	0.0007	0.17	0.08	0.25

Table A7. Acute (a) and chronic (b) hazard quotients (HQs) for river waters. -: not available. BP3 (1) and (2) indicate HQs for two different LOEC values.

a)

		Daphnia magna				*Daphnia galeata*		*Vibrio fischeri*
		BP3	4MBC	BZT	MeBZT	BZT	MeBZT	MeBZT
LC_{50} (mg l^{-1})		1.9	0.56	107	51.6	15.8	8.58	8.7
Sample								
S2	Besòs	0.03	0.02	0.02	0.08	0.16	0.49	0.48
S4	Ripoll	0.01	0.02	0.04	0.08	0.27	**0.50**	**0.50**
S5	Besòs	0.01	-	0.03	0.10	0.18	**0.58**	**0.58**
S7	Riu-Sec	0.02	0.03	0.05	0.07	0.31	0.45	0.44
S9	Riera de Rubí	0.01	0.05	2E-03	0.02	0.02	0.09	0.09
S10	Riera de Rubí	-	0.03	2E-04	4E-03	2E-03	0.02	0.02
S12	Llobregat	-	-	3E-03	0.01	0.02	0.08	0.08
S13	Llobregat	-	0.06	2E-03	0.01	0.01	0.06	0.06
S15	Riera de Rubí	0.02	0.02	0.08	0.14	**0.54**	**0.84**	**0.83**
S16	Riera de Rubí	0.02	-	0.01	0.04	0.08	0.23	0.22
S18	Cardaner	2E-03	-	2E-04	1E-03	2E-03	0.01	0.01
S19	Cardaner	3E-03	-	2E-03	0.01	0.02	0.03	0.03

b)

		Pimephales promelas		*Oncorhynchus mykiss*			
		BP1	EtPABA	BP1	BP3 (1)	BP3 (2)	4MBC
	LOEC (µg l^{-1})	4919.9	4394	4919	3900	749	415
Sample							
S2	Besòs	0.01	0.01	0.01	0.01	0.07	0.03
S4	Ripoll	3E-03	2E-03	3E-03	4E-03	0.02	0.03
S5	Besòs	0.01	0.01	0.01	0.01	0.03	-
S7	Riu-Sec	0.01	0.01	0.01	0.01	0.06	0.04
S9	Riera de Rubí	3E-03	-	3E-03	4E-03	0.02	0.06
S10	Riera de Rubí	-	-	-	-	-	0.05
S12	Llobregat	1E-03	-	1E-03	-	-	-
S13	Llobregat	-	3E-02	-	-	-	0.08
S15	Riera de Rubí	0.01	0.03	0.01	0.01	0.04	0.03
S16	Riera de Rubí	0.01	0.01	0.01	0.01	0.05	-
S18	Cardaner	-	1E-03	-	-	0.01	-
S19	Cardaner	-	-	-	-	0.01	-

Table A8. Acute (a) and chronic (b) toxicity hazard quotients for influent (Inf) and effluent (Eff) wastewaters. -: not available. BP3 (1) and (2) indicate HQs for two different LOEC values.

a)

		Daphnia magna								*Daphnia galeata*				*Vibrio fischeri*	
		BP3		4MBC		BZT		MeBZT		BZT		MeBZT		MeBZT	
	LC_{50} (mg l^{-1})	1.9		0.56		107		51.6		15.8		8.58		8.7	
Sample		Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff
S3	Montcada i Reixac	0.27	0.11	-	0.04	0.02	0.01	0.09	0.09	0.16	0.09	**0.54**	**0.51**	**0.53**	**0.51**
S6	Sabadell	0.17	0.02	-	-	0.09	0.03	0.12	0.05	**0.60**	0.18	**0.74**	0.28	**0.73**	0.27
S8	Terrassa	0.20	0.02	0.05	0.10	0.03	0.01	0.08	0.04	0.19	0.07	**0.51**	0.25	**0.50**	0.25
S11	St. Feliu de Llobregat	0.11	0.02	-	-	0.01	0.01	0.07	0.09	0.09	0.07	0.43	**0.56**	0.43	**0.56**
S14	Rubí	0.04	5E-03	-	0.06	0.08	0.16	0.10	0.17	**0.52**	**1.07**	**0.60**	**1.04**	**0.59**	**1.02**
S17	Manresa	0.16	0.01	0.05	-	0.03	0.05	0.07	0.05	0.21	0.32	0.43	0.28	0.43	0.27

b)

		Pimephales promelas				*Oncorhynchus mykiss*							
		BP1		EtPABA		BP1		BP3 (1)		BP3 (2)		4MBC	
	LOEC (μg l^{-1})	4919.4		4394		4919		3900		749		415	
Sample		Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff
S3	Montcada i Reixac	0.08	0.04	0.04	0.01	0.08	0.04	0.13	0.06	**0.69**	0.29	-	0.05
S6	Sabadell	0.14	5E-03	0.03	0.01	0.14	5E-03	0.08	0.01	0.44	0.04	-	-
S8	Terrassa	0.07	0.01	0.05	0.02	0.07	0.01	0.10	0.01	**0.52**	0.06	0.07	0.14
S11	St. Feliu de Llobregat	0.05	2E-03	3E-03	0.01	0.05	2E-03	0.05	0.01	0.27	0.04	-	-
S14	Rubí	0.02	1E-03	0.01	0.03	0.02	1E-03	0.02	2E-03	0.10	0.01	-	0.08
S17	Manresa	0.08	9E-04	0.03	0.01	0.08	9E-04	0.08	0.01	0.40	0.04	0.07	-

Información adicional - publicación Nº 2

Development of a new on-line SPE-HPLC-(APPI)-MS/MS method for the determination of insect repellents in European rivers

Por

D. Molins-Delgado, D. García-Sillero, M.S. Díaz-Cruz, D. Barceló

en

Journal of Chromatgraphy A (enviado)

Supporting Information

A SPE-HPLC-(APPI)-MS/MS method for the analysis of selected anthropogenic infochemicals in water

Daniel Molins-Delgado[1], Daniel García-Sillero[1], M. Silvia Díaz-Cruz[1*], Damià Barceló[1,2]

Content

Table A1. Sample name, sampling description. n.a.: not available.

River Basin	Sample	Coordinates		Description
		Latitude	Longitude	
Sava	RAD2	46.29298	14.260754	Background location
	LIT1	46.08456	15.582632	Land use
	CAT1	45.89636	15.627037	Land use
	CAT2	45.86036	15.692068	
	ZAG1	45.78301	16.003184	Urban centre
	CRN1	n.a.	n.a.	Navigation; oil refinery; land use
	SLB1	45.15270	18.013906	Navigation
	SLB2	45.12622	18.084751	
	ZUP1	45.07481	18.687667	Urban centre; navigation; oil refinery
	ZUP2	45.01488	18.740313	
	SRM2	44.91358	19.752412	Navigation
	BEO1	44.76913	20.355572	Urban centre; navigation
	BEO2	44.80632	20.443683	
Evrotas	USkollini7	n.a.	n.a.	Reference drought location; woodlands
	USkollino22	n.a.	n.a.	
	DSkollini9	n.a.	n.a.	Land use
	DSkallio29	n.a.	n.a.	
	Vivariie10	n.a.	n.a.	Reference pollution location; land use
	Vivarioe15	n.a.	n.a.	
	WWTPi19	n.a.	n.a.	Urban centre; land use WWTP
	WWTPo5	n.a.	n.a.	
Adige	wb2a	46.25872	10.604122	High course of the river; holidays resorts
	wb2b/w1	46.25971	10.608057	
	wb3a	46.31971	10.818326	
	wb3b-1	46.32844	10.870947	
	wb1	46.42556	10.928332	Land use; holidays resorts
	wb4b	46.21917	11.101943	
	wb5b	46.15722	11.076386	
	wb6b	46.19250	11.128336	
	wb7a	46.00960	11.122896	Urban centre
	wb7a-1	45.94550	11.101080	
	wb7a-x	45.91262	11.038397	
	wb7b-1	45.88857	11.015244	

Table A2. IRs concentrations (ng l^{-1}) in the water samples.

River Basin	Sample	Concentrations (ng l^{-1})				
		DEET	m-toluamide	Bayrepel	MGK-264	PBO
Sava	RAD2	70.80	n.d.	103.80	n.d.	n.d.
	LIT1	39.23	n.d.	72.23	n.d.	n.d.
	CAT1	12.25	n.d.	31.77	n.d.	n.d.
	CAT2	8.92	n.d.	18.22	n.d.	n.d.
	ZAG1	57.37	n.d.	57.28	n.d.	n.d.
	CRN1	61.49	n.d.	105,336.01	n.d.	n.d.
	SLB1	12.34	n.d.	9.26	n.d.	n.d.
	SLB2	1.18	n.d.	2.23	n.d.	n.d.
	ZUP1	26.65	n.d.	266.31	n.d.	n.d.
	ZUP2	3.44	n.d.	148.48	n.d.	n.d.
	SRM2	7.69	n.d.	28.75	n.d.	n.d.
	BEO1	53.72	n.d.	314.69	n.d.	n.d.
	BEO2	8.33	n.d.	18.86	n.d.	n.d.
Evrotas	USkollini7	2,005.45	n.d.	17.36	n.d.	n.d.
	USkollino22	59.22	n.d.	31.93	n.d.	n.d.
	DSkollini9	398.98	n.d.	179.62	n.d.	n.d.
	DSkallio29	4,348.82	n.d.	44.35	n.d.	n.d.
	Vivariie10	636.37	n.d.	15.70	n.d.	n.d.
	Vivarioe15	510.10	n.d.	21.40	n.d.	19.33
	WWTPi19	414.09	n.d.	13.23	n.d.	n.d.
	WWTPo5	4,948.85	n.d.	6.48	n.d.	n.d.
Adige	wb2a	n.d.	n.d.	n.d.	n.d.	n.d.
	wb2b/w1	6.80	n.d.	2.92	n.d.	n.d.
	wb3a	n.d.	n.d.	n.d.	n.d.	n.d.
	wb3b-1	n.d.	n.d.	n.d.	n.d.	n.d.
	wb1	n.d.	n.d.	n.d.	n.d.	n.d.
	wb4b	n.d.	n.d.	n.d.	n.d.	n.d.
	wb5b	n.d.	n.d.	37.38	n.d.	n.d.
	wb6b	n.d.	n.d.	n.d.	n.d.	n.d.
	wb7a	n.d.	n.d.	n.d.	n.d.	n.d.
	wb7a-1	n.d.	n.d.	n.d.	n.d.	n.d.
	wb7a-x	6.01	n.d.	n.d.	n.d.	n.d.
	wb7b-1	n.d.	n.d.	n.d.	n.d.	n.d.

Table A3. Estimated hazard quotients (acute and chronic toxicity). EC_{50}: half maximal effective concentration; LC_{50}: half maximal lethal concentration; NOEC: No-observed-adverse-effects; n.a.: not applicable; n.s.: not specified.

		HQ				
Acute Toxicity Data	**Species**	Daphnia magna	Daphnia magna	Daphnia magna	Pseudokirchneriella subcapitata	Vibrio fischeri
	EC_{50}/LC_{50} (mg l^{-1})	75	34.4	108	4.1	21.2
	Criteria	Intoxication	Intoxication	48 h mortality	Growth Inhibition	Disminution of luminiscence
	Reference	[1]	[2]	[3]	[4]	[4]
Basin	**Sample**	**DEET**	**DEET**	**DEET**	**DEET**	**DEET**
Sava	RAD2	9.4E-04	2.1E-03	6.6E-04	1.7E-02	3.3E-03
	LIT1	5.2E-04	1.1E-03	3.6E-04	9.6E-03	1.9E-03
	CAT1	1.6E-04	3.6E-04	1.1E-04	3.0E-03	5.8E-04
	CAT2	1.2E-04	2.6E-04	8.3E-05	2.2E-03	4.2E-04
	ZAG1	7.6E-04	1.7E-03	5.3E-04	1.4E-02	2.7E-03
	CRN1	8.2E-04	1.8E-03	5.7E-04	1.5E-02	2.9E-03
	SLB1	1.6E-04	3.6E-04	1.1E-04	3.0E-03	5.8E-04
	SLB2	1.6E-05	3.4E-05	1.1E-05	2.9E-04	5.6E-05
	ZUP1	3.6E-04	7.7E-04	2.5E-04	6.5E-03	1.3E-03
	ZUP2	4.6E-05	1.0E-04	3.2E-05	8.4E-04	1.6E-04
	SRM2	1.0E-04	2.2E-04	7.1E-05	1.9E-03	3.6E-04
	BEO1	7.2E-04	1.6E-03	5.0E-04	1.3E-02	2.5E-03
	BEO2	1.1E-04	2.4E-04	7.7E-05	2.0E-03	3.9E-04
Evrotas	USkollini7	2.7E-02	5.8E-02	1.9E-02	0.49	9.5E-02
	USkollino22	7.9E-04	1.7E-03	5.5E-04	1.4E-02	2.8E-03
	DSkollini9	5.3E-03	1.2E-02	3.7E-03	9.7E-02	1.9E-02
	DSkallio29	5.8E-02	0.13	4.0E-02	**1.1**	0.21
	Vivariie10	8.5E-03	1.8E-02	5.9E-03	0.16	3.0E-02
	Vivarioe15	6.8E-03	1.5E-02	4.7E-03	0.12	2.4E-02
	WWTPi19	5.5E-03	1.2E-02	3.8E-03	0.1	2.0E-02
	WWTPo5	6.6E-02	0.14	4.6E-02	**1.2**	0.23
Adige	wb2a	n.a.	n.a.	n.a.	n.a.	n.a.
	wb2b/w1	9.1E-05	2.0E-04	6.3E-05	1.7E-03	3.2E-04
	wb3a	n.a.	n.a.	n.a.	n.a.	n.a.
	wb3b-1	n.a.	n.a.	n.a.	n.a.	n.a.
	wb1	n.a.	n.a.	n.a.	n.a.	n.a.
	wb4b	n.a.	n.a.	n.a.	n.a.	n.a.
	wb5b	n.a.	n.a.	n.a.	n.a.	n.a.
	wb6b	n.a.	n.a.	n.a.	n.a.	n.a.
	wb7a	n.a.	n.a.	n.a.	n.a.	n.a.
	wb7a-1	n.a.	n.a.	n.a.	n.a.	n.a.
	wb7a-x	8.0E-05	1.7E-04	5.6E-05	1.5E-03	2.8E-04
	wb7b-1	n.a.	n.a.	n.a.	n.a.	n.a.

Table A3. (Continued).

		HQ				
Acute Toxicity Data	**Species**	Photobacterium phosphoreum	Onchorhynchus mykiss	Pimephales promelas	Gambusa affinis	Oreochromis mossambicus
	EC_{50}/LC_{50} (mg l^{-1})	67.9	71.25	75.7	235	120
	Criteria	Disminution of luminiscence	96 h mortality	96 h mortality	48 h mortality	96 h static renewal
	Reference	[5]	[1]	[6]	[7]	[8]
Basin	**Sample**	**DEET**	**DEET**	**DEET**	**DEET**	**DEET**
Sava	RAD2	1.0E-03	9.9E-04	9.4E-04	3.0E-04	5.9E-04
	LIT1	5.8E-04	5.5E-04	5.2E-04	1.7E-04	3.3E-04
	CAT1	1.8E-04	1.7E-04	1.6E-04	5.2E-05	1.0E-04
	CAT2	1.3E-04	1.3E-04	1.2E-04	3.8E-05	7.4E-05
	ZAG1	8.4E-04	8.1E-04	7.6E-04	2.4E-04	4.8E-04
	CRN1	9.1E-04	8.6E-04	8.1E-04	2.6E-04	5.1E-04
	SLB1	1.8E-04	1.7E-04	1.6E-04	5.3E-05	1.0E-04
	SLB2	1.7E-05	1.7E-05	1.6E-05	5.0E-06	9.8E-06
	ZUP1	3.9E-04	3.7E-04	3.5E-04	1.1E-04	2.2E-04
	ZUP2	5.1E-05	4.8E-05	4.5E-05	1.5E-05	2.9E-05
	SRM2	1.1E-04	1.1E-04	1.0E-04	3.3E-05	6.4E-05
	BEO1	7.9E-04	7.5E-04	7.1E-04	2.3E-04	4.5E-04
	BEO2	1.2E-04	1.2E-04	1.1E-04	3.5E-05	6.9E-05
Evrotas	USkollini7	3.0E-02	2.8E-02	2.6E-02	8.5E-03	1.7E-02
	USkollino22	8.7E-04	8.3E-04	7.8E-04	2.5E-04	4.9E-04
	DSkollini9	5.9E-03	5.6E-03	5.3E-03	1.7E-03	3.3E-03
	DSkallio29	6.4E-02	6.1E-02	5.7E-02	1.9E-02	3.6E-02
	Vivariie10	9.4E-03	8.9E-03	8.4E-03	2.7E-03	5.3E-03
	Vivarioe15	7.5E-03	7.2E-03	6.7E-03	2.2E-03	4.3E-03
	WWTPi19	6.1E-03	5.8E-03	5.5E-03	1.8E-03	3.5E-03
	WWTPo5	7.3E-02	6.9E-02	6.5E-02	2.1E-02	4.1E-02
Adige	wb2a	n.a.	n.a.	n.a.	n.a.	n.a.
	wb2b/w1	1.0E-04	9.5E-05	9.0E-05	2.9E-05	5.7E-05
	wb3a	n.a.	n.a.	n.a.	n.a.	n.a.
	wb3b-1	n.a.	n.a.	n.a.	n.a.	n.a.
	wb1	n.a.	n.a.	n.a.	n.a.	n.a.
	wb4b	n.a.	n.a.	n.a.	n.a.	n.a.
	wb5b	n.a.	n.a.	n.a.	n.a.	n.a.
	wb6b	n.a.	n.a.	n.a.	n.a.	n.a.
	wb7a	n.a.	n.a.	n.a.	n.a.	n.a.
	wb7a-1	n.a.	n.a.	n.a.	n.a.	n.a.
	wb7a-x	8.9E-05	8.4E-05	7.9E-05	2.6E-05	5.0E-05
	wb7b-1	n.a.	n.a.	n.a.	n.a.	n.a.

Table A3. (Continued).

		HQ			
Acute Toxicity Data	**Species**	Chironomus riparius	Daphnid	Algae	Fish
	EC_{50}/LC_{50} (mg l^{-1})	70	34.7	32.13	87.97
	Criteria	96 h	Estimated	Estimated	Estimated
	Reference	[9]	ECOSAR v1.11	ECOSAR v1.11	ECOSAR v1.11
Basin	**Sample**	**DEET**	**Bayrepel**	**Bayrepel**	**Bayrepel**
Sava	RAD2	1.0E-03	3.0E-03	3.2E-03	1.2E-03
	LIT1	5.6E-04	2.1E-03	2.2E-03	8.2E-04
	CAT1	1.8E-04	9.2E-04	9.9E-04	3.6E-04
	CAT2	1.3E-04	5.3E-04	5.7E-04	2.1E-04
	ZAG1	8.2E-04	1.7E-03	1.8E-03	6.5E-04
	CRN1	8.8E-04	**3.0**	**3.3**	**1.2**
	SLB1	1.8E-04	2.7E-04	2.9E-04	1.1E-04
	SLB2	1.7E-05	6.4E-05	6.9E-05	2.5E-05
	ZUP1	3.8E-04	7.7E-03	8.3E-03	3.0E-03
	ZUP2	4.9E-05	4.3E-03	4.6E-03	1.7E-03
	SRM2	1.1E-04	8.3E-04	8.9E-04	3.3E-04
	BEO1	7.7E-04	9.1E-03	9.8E-03	3.6E-03
	BEO2	1.2E-04	5.4E-04	5.9E-04	2.1E-04
Evrotas	USkollini7	2.9E-02	5.0E-04	5.4E-04	2.0E-04
	USkollino22	8.5E-04	9.2E-04	9.9E-04	3.6E-04
	DSkollini9	5.7E-03	5.2E-03	5.6E-03	2.0E-03
	DSkallio29	6.2E-02	1.3E-03	1.4E-03	5.0E-04
	Vivariie10	9.1E-03	4.5E-04	4.9E-04	1.8E-04
	Vivarioe15	7.3E-03	6.2E-04	6.7E-04	2.4E-04
	WWTPi19	5.9E-03	3.8E-04	4.1E-04	1.5E-04
	WWTPo5	7.1E-02	1.9E-04	2.0E-04	7.4E-05
Adige	wb2a	n.a.	n.a.	n.a.	n.a.
	wb2b/w1	9.7E-05	8.4E-05	9.1E-05	3.3E-05
	wb3a	n.a.	n.a.	n.a.	n.a.
	wb3b-1	n.a.	n.a.	n.a.	n.a.
	wb1	n.a.	n.a.	n.a.	n.a.
	wb4b	n.a.	n.a.	n.a.	n.a.
	wb5b	n.a.	1.1E-03	1.2E-03	4.2E-04
	wb6b	n.a.	n.a.	n.a.	n.a.
	wb7a	n.a.	n.a.	n.a.	n.a.
	wb7a-1	n.a.	n.a.	n.a.	n.a.
	wb7a-x	8.6E-05	n.a.	n.a.	n.a.
	wb7b-1	n.a.	n.a.	n.a.	n.a.

Table A3. (Continued).

		HQ			
Acute Toxicity Data	**Species**	Pseudokirchneriella subcapitata	Pseudokirchneriella subcapitata	Pseudokirchneriella subcapitata	Pseudokirchneriella subcapitata
	NOEC (mg l-1)	7.6	3.8	15	0.521
	Criteria	Cell density	Biomass	Growth Inhibition	Growth Inhibition
	Reference	[10]	[10]	[10]	[4]
Basin	**Sample**	**DEET**	**DEET**	**DEET**	**DEET**
Sava	RAD2	9.3E-07	1.9E-05	4.7E-06	1.4E-04
	LIT1	5.2E-07	1.0E-05	2.6E-06	7.5E-05
	CAT1	1.6E-07	3.2E-06	8.2E-07	2.4E-05
	CAT2	1.2E-07	2.3E-06	5.9E-07	1.7E-05
	ZAG1	7.5E-07	1.5E-05	3.8E-06	1.1E-04
	CRN1	8.1E-07	1.6E-05	4.1E-06	1.2E-04
	SLB1	1.6E-07	3.2E-06	8.2E-07	2.4E-05
	SLB2	1.6E-08	3.1E-07	7.9E-08	2.3E-06
	ZUP1	3.5E-07	7.0E-06	1.8E-06	5.1E-05
	ZUP2	4.5E-08	9.1E-07	2.3E-07	6.6E-06
	SRM2	1.0E-07	2.0E-06	5.1E-07	1.5E-05
	BEO1	7.1E-07	1.4E-05	3.6E-06	1.0E-04
	BEO2	1.1E-07	2.2E-06	5.6E-07	1.6E-05
Evrotas	USkollini7	2.6E-05	5.3E-04	1.3E-04	3.8E-03
	USkollino22	7.8E-07	1.6E-05	3.9E-06	1.1E-04
	DSkollini9	5.2E-06	1.0E-04	2.7E-05	7.7E-04
	DSkallio29	5.7E-05	1.1E-03	2.9E-04	8.3E-03
	Vivariie10	8.4E-06	1.7E-04	4.2E-05	1.2E-03
	Vivarioe15	6.7E-06	1.3E-04	3.4E-05	9.8E-04
	WWTPi19	5.4E-06	1.1E-04	2.8E-05	7.9E-04
	WWTPo5	6.5E-05	1.3E-03	3.3E-04	9.5E-03
Adige	wb2a	n.a.	n.a.	n.a.	n.a.
	wb2b/w1	8.9E-08	1.8E-06	4.5E-07	1.3E-05
	wb3a	n.a.	n.a.	n.a.	n.a.
	wb3b-1	n.a.	n.a.	n.a.	n.a.
	wb1	n.a.	n.a.	n.a.	n.a.
	wb4b	n.a.	n.a.	n.a.	n.a.
	wb5b	n.a.	n.a.	n.a.	n.a.
	wb6b	n.a.	n.a.	n.a.	n.a.
	wb7a	n.a.	n.a.	n.a.	n.a.
	wb7a-1	n.a.	n.a.	n.a.	n.a.
	wb7a-x	7.9E-08	1.6E-06	4.0E-07	1.2E-05
	wb7b-1	n.a.	n.a.	n.a.	n.a.

Table A3. (Continued).

		HQ			
Chronic Toxicity Data	**Species**	Daphnia magna	Daphnia magna	Algae	Fish
	EC_{50}/LC_{50} (mg l^{-1})	26	3.7	9.65	8.42
	Criteria	21 d reproduction	n.s.	Estimated	Estimated
	Reference	[11]	[12]	[12]	[12]
Basin	**Sample**	**DEET**	**DEET**	**DEET**	**DEET**
Sava	RAD2	2.7E-03	1.9E-02	7.3E-03	8.4E-03
	LIT1	1.5E-03	1.1E-02	4.1E-03	4.7E-03
	CAT1	4.7E-04	3.3E-03	1.3E-03	1.5E-03
	CAT2	3.4E-04	2.4E-03	9.2E-04	1.1E-03
	ZAG1	2.2E-03	1.6E-02	5.9E-03	6.8E-03
	CRN1	2.4E-03	1.7E-02	6.4E-03	7.3E-03
	SLB1	4.7E-04	3.3E-03	1.3E-03	1.5E-03
	SLB2	4.5E-05	3.2E-04	1.2E-04	1.4E-04
	ZUP1	1.0E-03	7.2E-03	2.8E-03	3.2E-03
	ZUP2	1.3E-04	9.3E-04	3.6E-04	4.1E-04
	SRM2	3.0E-04	2.1E-03	8.0E-04	9.1E-04
	BEO1	2.1E-03	1.5E-02	5.6E-03	6.4E-03
	BEO2	3.2E-04	2.3E-03	8.6E-04	9.9E-04
Evrotas	USkollini7	7.7E-02	0.54	0.21	0.24
	USkollino22	2.3E-03	1.6E-02	6.1E-03	7.0E-03
	DSkollini9	1.5E-02	0.11	4.1E-02	4.7E-02
	DSkallio29	0.17	**1.20**	0.45	0.52
	Vivariie10	2.4E-02	0.17	6.6E-02	7.6E-02
	Vivarioe15	2.0E-02	0.14	5.3E-02	6.1E-02
	WWTPi19	1.6E-02	0.11	4.3E-02	4.9E-02
	WWTPo5	0.19	**1.30**	0.51	0.59
Adige	wb2a	n.a.	n.a.	n.a.	n.a.
	wb2b/w1	2.6E-04	1.8E-03	7.0E-04	8.1E-04
	wb3a	n.a.	n.a.	n.a.	n.a.
	wb3b-1	n.a.	n.a.	n.a.	n.a.
	wb1	n.a.	n.a.	n.a.	n.a.
	wb4b	n.a.	n.a.	n.a.	n.a.
	wb5b	n.a.	n.a.	n.a.	n.a.
	wb6b	n.a.	n.a.	n.a.	n.a.
	wb7a	n.a.	n.a.	n.a.	n.a.
	wb7a-1	n.a.	n.a.	n.a.	n.a.
	wb7a-x	2.3E-04	1.6E-03	6.2E-04	7.1E-04
	wb7b-1	n.a.	n.a.	n.a.	n.a.

Table A3. (Continued).

		HQ		
Chronic Toxicity Data	**Species**	Daphnid	Algae	Fish
	EC_{50}/LC_{50} (mg l^{-1})	3.92	9.46	6.03
	Criteria	Estimated	Estimated	Estimated
	Reference	ECOSAR v1.11	ECOSAR v1.11	ECOSAR v1.11
Basin	**Sample**	**Bayrepel**	**Bayrepel**	**Bayrepel**
Sava	RAD2	2.6E-02	1.1E-02	1.7E-02
	LIT1	1.8E-02	7.6E-03	1.2E-02
	CAT1	8.1E-03	3.4E-03	5.3E-03
	CAT2	4.6E-03	1.9E-03	3.0E-03
	ZAG1	1.5E-02	6.1E-03	9.5E-03
	CRN1	0.27	0.11	0.17
	SLB1	2.4E-03	9.8E-04	1.5E-03
	SLB2	5.7E-04	2.4E-04	3.7E-04
	ZUP1	6.8E-02	2.8E-02	4.4E-02
	ZUP2	3.8E-02	1.6E-02	2.5E-02
	SRM2	7.3E-03	3.0E-03	4.8E-03
	BEO1	8.0E-02	3.3E-02	5.2E-02
	BEO2	4.8E-03	2.0E-03	3.1E-03
Evrotas	USkollini7	4.4E-03	1.8E-03	2.9E-03
	USkollino22	8.1E-03	3.4E-03	5.3E-03
	DSkollini9	4.6E-02	1.9E-02	3.0E-02
	DSkallio29	1.1E-02	4.7E-03	7.4E-03
	Vivariie10	4.0E-03	1.7E-03	2.6E-03
	Vivarioe15	5.5E-03	2.3E-03	3.5E-03
	WWTPi19	3.4E-03	1.4E-03	2.2E-03
	WWTPo5	1.7E-03	6.8E-04	1.1E-03
Adige	wb2a	n.a.	n.a.	n.a.
	wb2b/w1	7.4E-04	3.1E-04	4.8E-04
	wb3a	n.a.	n.a.	n.a.
	wb3b-1	n.a.	n.a.	n.a.
	wb1	n.a.	n.a.	n.a.
	wb4b	n.a.	n.a.	n.a.
	wb5b	9.5E-03	4.0E-03	6.2E-03
	wb6b	n.a.	n.a.	n.a.
	wb7a	n.a.	n.a.	n.a.
	wb7a-1	n.a.	n.a.	n.a.
	wb7a-x	n.a.	n.a.	n.a.
	wb7b-1	n.a.	n.a.	n.a.

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Información adicional - publicación Nº 3

Sediments as a sink for UV filters and benzotriazoles: The case study of Upper Iguaçu watershed, Curitiba (Brazil)

Por

A. Mizukawa, D. Molins-Delgado; J.C. Rodrigues Azevedo; C.V. Scapulatempo Fernandes;

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en

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SUPPORTING INFORMATION

Sediments as a sink for UV filters and benzotriazoles: The case study of Upper Iguaçu watershed, Curitiba (Brazil)

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Table S1: SRM tansitions and operational MS/MS parameters for the detection of target UV filters and benzotriazoles. DP (V): Declustering Potential; CE (V): Collision Energy; CXP (V): Transfer potential. In bold, transitions employed for quantitative analysis. Grey cells denote the internal standard compounds used.

Compound	Precursors m/z	Product m/z	DP (V)	CE (V)	CXP (V)
BP1	**215**	**137**	40	27	10
	215	105	40	29	6
BP3	**229**	**151**	40	25	12
	229	105	40	27	16
4HB	**199**	**121**	40	25	8
	199	105	40	27	8
DHMB	**245**	**151**	43	27	12
	245	121	43	29	8
4MBC	**255**	**105**	61	41	6
	255	212	61	29	14
EHMC	**291**	**179**	51	13	4
	291	161	51	25	10
OC	**362**	**250**	71	15	20
	362	232	71	57	12
OD-PABA	**278**	**151**	86	43	42
	278	136	86	27	40
EtPABA	**166**	**138**	41	20	10
	166	120	41	25	28
BZT	**120**	**92**	56	25	16
	120	65	56	31	4
MeBZT	**134**	**95**	46	39	16
	134	79	46	29	10
TBHPBT	**268**	**212**	46	49	4
	268	57	46	49	4
BP3-d$_5$	**234**	**151**	36	27	12
	234	110	36	27	8
4MBC-d$_4$	**259**	**216**	76	27	14
	259	109	76	45	4
AllylBzt	**266**	**119**	51	31	8
	266	91	51	41	16

Información adicional - publicación Nº4

Removal of polar UV stabilizers in biological wastewater treatments and ecotoxicological implications

Por

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SUPPORTING INFORMATION

for

REMOVAL OF POLAR UV STABILIZERS IN BIOLOGICAL WASTEWATER TREATMENTS AND ECOTOXICOLOGICAL IMPLICATIONS

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TABLE S1

Table S1a. Instrumental performance of the HPLC-QqLIT-MS/MS analytical method developed. Instrumental limit of detection (ILOD); instrumental limit of quantification (ILOQ); relative standard deviation (RSD).

	lineality (ngL^{-1})	r2	ILOD (pg)	ILOQ (pg)	Precision (%RSD) n=5 Intraday	Precision (%RSD) n=5 Interday
BZT	1-10000	0.999	1.3	4.3	5	6
MeBZT	1-10000	0.999	0.7	2.3	3	5

Table S1b. Recovery rates, method limits of detection (MLOD) and quantification (MLOQ) and matrix effects (ME%) in influent and effluent wastewater samples for BZT and MeBZT, as well as for the IS (AllylBZT).

		BZT				MeBZT				IS
	Concentration (ngL^{-1})	RE% ±RSD	MLOD (ngL^{-1})	MLOQ (ngL^{-1})	ME %	RE%±RSD	MLOD (ngL^{-1})	MLOQ (ngL^{-1})	ME %	ME%
Influent	5	102±1	1.1	3.7	29	85±7	1.1	3.7	26	21
	50	101±4				89±3				
	100	100±6				91±9				
Effluent	5	106±6	0.3	1.1	33	84±7	0.3	0.8	37	30
	50	92±4				89±3				
	100	109±7				85±13				

TABLE S2 Concentrations (ngL^{-1}) of BZT and MeBZT in influent and effluent wastewater determined in each studied WWTP.

TABLE S2 Concentrations (ngL^{-1}) of BZT and MeBZT in influent and effluent wastewater determined in each studied WWTP.

	Concentrations (ngL^{-1})			
	BZT		MeBZT	
WWTPs	Influent	Effluent	Influent	Effluent
LLE	177.6	114.1	1289.0	1136.5
REU	3300.0	419.3	5406.6	2023.5
TAR	215.7	240.2	1341.8	1400.0
VDP	2097.0	504.6	3626.4	1329.4
VSS	76.5	26.7	778.7	676.5
LLA	855.0	214.1	8307.7	3576.5
SRS	2466.0	1513.8	6857.1	4682.4
GIR	768.0	258.7	2195.6	1400.0
MAT	474.0	122.9	2587.9	1729.4
MDV	1335.0	311.9	1681.3	1882.4
VIC	126.9	204.3	3560.4	2247.1
GAV	861.0	45.8	2096.7	587.1
MON	1092.0	383.5	3059.3	1482.4
PRA	1356.0	364.2	12857.1	3035.3
RUB	4380.0	583.5	47142.9	10541.2
SFL	672.0	324.8	3659.3	1435.3
BES	1029.0	362.4	3428.6	2117.6
GRA	1092.0	423.9	2254.9	1976.5
MAN	1476.0	250.0	3293.4	687.1
TEI	519.0	182.6	2465.9	1858.8

TABLE S3 Occurrence and removal rates of both BZTs in wastewater of this study and the literature.

BZT					MeBZT						
Concentrations ngL-1					Concentrations ngL-1						
Influent		Effluent			Influent		Effluent				
Max	Min	Max	Min		Max	Min	Max	Min		Location	Reference
4380	76.5	1513.8	26.7	-61 - 95	42900	778.7	10541.2	587.1	-12 - 79	Catalonia	This study
44000	17000	18000	7000	29 - 58	4900	1100	1700	1000	19 - 69	Berlin	Reemtma et al. 2010
73000	15000	100000	11000	-28 - 76	5600	1100	200	100	18 - 70	Switzerland	Voutsa et al. 2006
587	580	385	325	25 - 37	5737	5156	15841	7735	26 - 68	Athens	Asimakopoulos et al. 2013

Información adicional - publicación Nº 5

Ecological risk assessment associated to the removal of endocrine-disrupting parabens and benzophenone-4 in wastewater treatment

Por

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en

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SUPPORTING INFORMATION

for

ECOLOGICAL RISK ASSESSMENT ASSOCIATED TO THE REMOVAL OF ENDOCRINE-DISRUPTING PARABENS AND BENZOPHENONE 4 IN WASTEWATER TREATMENT

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Table A.1: Instrumental performance of the HPLC-MS/MS analytical method developed. Instrumental limit of detection (ILOD); instrumental limit of quantification (ILOQ); relative standard deviation (RSD).

	Retention time (min)	Linearity (ngL^{-1})	Correlation coefficient (r^2)	ILOD (pg)	ILOQ (pg)	Precision (RSD%) (n=5)	
						Intraday	Interday
Methylparaben	7.45	3 – 100	0.998	0.01	0.02	5	15
Propylparaben	8.21	0.1 – 500	0.997	0.03	0.10	3	7
Butylparaben	8.52	0.1 – 500	0.999	0.08	0.26	4	13
Benzylparaben	8.50	0.1 – 500	0.999	0.01	0.03	3	15
BP4	6.25	5 – 500	0.991	0.44	1.47	7	16

Table A.2: Recovery rates (REC), method limits of detection (LOD) and quantification (LOQ) and matrix effects (ME%) in influent (a) and effluent (b) wastewater samples for the parabens and benzophenone 4.

a)

	REC ± SD			LOD (ngL^{-1})	LOQ (ngL^{-1})	ME%
	30 ngL^{-1}	50 ngL^{-1}	100 ngL^{-1}			
Methylparaben	94 ± 2	93 ± 7	95 ± 14	2.1	7.1	11
Propylparaben	106 ± 15	111 ± 10	112 ± 13	2.1	7.1	8
Butylparaben	102 ± 11	101 ± 5	107 ± 7	2.1	7.1	6
Benzylparaben	105 ± 3	108 ± 7	103 ± 6	2.1	7.1	6
BP4	101 ± 5	99 ± 5	102 ± 5	4.8	15.9	22

b)

	REC ± SD			LOD (ngL^{-1})	LOQ (ngL^{-1})	ME%
	30 ngL^{-1}	50 ngL^{-1}	100 ngL^{-1}			
Methylparaben	92 ± 6	95 ± 15	96 ± 11	0.58	1.9	1
Propylparaben	112 ± 10	112 ± 14	107 ± 12	1.1	3.6	1
Butylparaben	108 ± 6	109 ± 5	109 ± 5	0.11	0.37	1
Benzylparaben	112 ± 5	104 ± 10	103 ± 2	0.05	0.27	1
BP-4	106 ± 5	103 ± 5	108 ± 5	2.3	7.7	10

Table A.3 Concentrations (ngL^{-1}) of parabens and BP4 in influent and effluent wastewater streams determined in each studied WWTP. <LOQ: below limit of quantification; n.d.: not detected.

WWTPs	Benzylparaben (ngL^{-1})		Butylparaben (ngL^{-1})		Propylparaben (ngL^{-1})		Methylparaben (ngL^{-1})		BP-4 (ngL^{-1})	
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
LLE	< LOQ	< LOQ	96	< LOQ	5010	< LOQ	2466	< LOQ	690	1080
REU	< LOQ	< LOQ	7.05	< LOQ	1371	< LOQ	< LOQ	< LOQ	1470	663
TAR	< LOQ	< LOQ	< LOQ	< LOQ	459	5.56	< LOQ	< LOQ	372	296
VDP	< LOQ	< LOQ	< LOQ	< LOQ	76.8	< LOQ	< LOQ	< LOQ	1062	277
VSS	< LOQ	< LOQ	39.3	< LOQ	858	83.6	714	137	1008	412
LLA	< LOQ	< LOQ	< LOQ	< LOQ	414	< LOQ	75.6	< LOQ	196.2	634
SRS	< LOQ	< LOQ	65.7	< LOQ	1695	2.58	< LOQ	< LOQ	1806	1060
GIR	< LOQ	< LOQ	16.35	< LOQ	1005	< LOQ	41.1	< LOQ	1332	585
MAT	< LOQ	< LOQ	< LOQ	< LOQ	696	< LOQ	801	< LOQ	1320	417
MDV	< LOQ	< LOQ	< LOQ	< LOQ	47.4	< LOQ	< LOQ	< LOQ	387	196
VIC	< LOQ	< LOQ	< LOQ	< LOQ	225.3	< LOQ	< LOQ	< LOQ	438	400
GAV	< LOQ	< LOQ	1.6	< LOQ	855	< LOQ	< LOQ	< LOQ	1317	487
MON	< LOQ	< LOQ	105	< LOQ	1494	< LOQ	< LOQ	< LOQ	1047	648
PRA	< LOQ	< LOQ	360	< LOQ	5700	< LOQ	2211	< LOQ	1074	720
RUB	< LOQ	< LOQ	< LOQ	< LOQ	156.6	< LOQ	< LOQ	< LOQ	516	321
SFL	< LOQ	< LOQ	< LOQ	< LOQ	363	< LOQ	< LOQ	< LOQ	969	376
BES	< LOQ	< LOQ	11.46	< LOQ	648	< LOQ	< LOQ	< LOQ	675	862
GRA	< LOQ	< LOQ	< LOQ	< LOQ	204.9	< LOQ	< LOQ	< LOQ	603	736
MAN	n.d.	< LOQ	71.1	< LOQ	2475	< LOQ	2220	< LOQ	984	86.1

Información adicional - publicación Nº 8

Occurrence of organic UV filters and metabolites in lebranche mullet (Mugil liza) from Brazil

Por

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Science of the Total Environment (enviado)

Supporting Information for

OCCURRENCE OF ORGANIC UV FILTERS AND METABOLITES IN LEBRANCHE MULLET (Mugil liza) FROM BRAZIL

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Table S1. Chemical name, abbreviation, CAS number, Log K_{ow}, and chemical structure for the target UV-Fs.

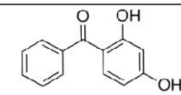
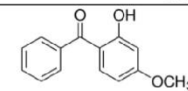
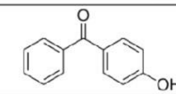
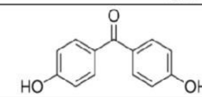
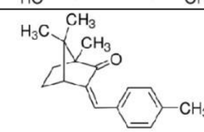
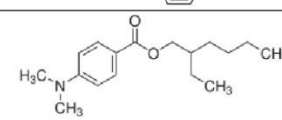
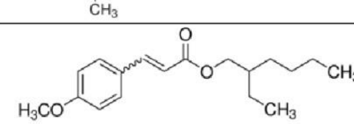
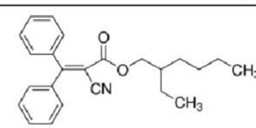
Name	Abbreviation	CAS number	Log K_{ow}	Structure
4-dihidroxybenzophenone	BP1	131-56-6	3.17	
2-hydroxy-4-methoxybenzophenone	BP3	131-57-7	3.79	
4-hydroxybenzophenone	4HB	1137-42-4	3.02	
4,4'-dihydroxybenzophenone	4DHB	611-99-4	2.55	
4-methylbenzyldiene camphor	4MBC	36861-47-9	4.95	
Ethylhexyl dimethyl p-aminobenzoic	ODPABA	21245-02-3	6.15	
Ethylhexyl methoxycinnamate	EHMC	5466-77-3	5.80	
Octocrylene	OC	6197-30-4	7.53	

Table S2. Fresh and sample tissue weight, length and sampling site for each Mugil liza individual.

Individual CODE	Individual data			Sample weight Gills (g dw)	Muscle (g dw)	Liver (g dw)
	Weight (g)	Length (cm)	Sampling site			
380	593.55	42.5	Ipiranga	0.52	0.53	0.5
389	721.79	45.0		0.51	0.55	0.56
392	662.33	43.0		0.53	0.57	0.57
399	932.45	47.0		0.51	0.54	0.54
404	678.00	47.0	Itaipu	0.51	0.53	0.53
406	811.47	46.5		0.45	0.54	0.53
407	900.00	46.9		0.46	0.51	0.57
408	543.05	39.5		0.51	0.55	0.5
409	803.31	47.6		0.52	0.55	0.58
413	935.47	46.5		0.54	0.53	0.59
415	625.84	43.0		0.53	0.53	0.54

Table S3. SRM transitions of the target compounds. E_{con}: cone energy; E_{col}: collision energy.

Compound	SRM Transition			E_{con}(V)	E_{col}(V)
BP1	215	→	137	40	27
		→	105		29
BP3	229	→	151	40	25
		→	105		27
4HB	199	→	121	40	25
		→	105		27
4DHB	215	→	121	45	27
		→	93		45
4MBC	255	→	212	61	29
		→	105		41
OC	362	→	250	71	15
		→	232		27
EHMC	291	→	179	51	25
		→	161		13
ODPABA	279	→	166	86	27
		→	151		43

Table S4. Linearity, instrumental limits of detection (ILOD) and quantification (ILOQ), precission, recovery rates and methods limits of detection (LOD) and quantification (LOQ) for each compound.

Compound	Linearity	r^2	ILOD (pg)	ILOQ (pg)	Precision (RSD%; n=7)		Recovery (%)	LOD (ngg^{-1} dw)	LOQ (ngg^{-1} dw)
					Intraday	Interday			
BP1	0.5-500	0.999	10	33	3	6	92	0.93	3.10
BP3	0.5-500	0.999	4	13	3	5	107	0.93	3.20
4HB	0.5-500	0.999	14	47	3	5	110	0.87	2.90
4DHB	0.5-500	0.999	14	47	3	5	96	0.93	3.10
4MBC	0.5-500	0.999	6	20	3	6	95	0.39	1.30
OC	0.5-500	0.999	10	33	5	8	75	0.39	1.30
EHMC	2.5-500	0.999	10	33	5	7	66	0.33	1.10
ODPABA	0.1-500	0.999	0.2	0.7	4	7	42	1.77	5.90

Table S5. Concentration of each compound in dry weight (dw) and the total amount of UV-Fs (ΣUV-Fs) in each individual in tissue of a) liver, b) muscle, and c) gills. <LOQ: below the limits of quantification; n.d.: not detected.

a)

Individual CODE	Concentrations of UV-Fs in liver (ngg^{-1} dw)								
	BP1	BP3	4HB	4DHB	EHMC	4MBC	ODPABA	OC	ΣUV-Fs
380	9.51	26.1	139	101	<LOQ	13.7	<LOQ	<LOQ	289
389	4.41	13.7	49.9	92.2	9.53	6.84	<LOQ	5.03	182
392	17.1	74.4	131	14.8	9.12	7.89	<LOQ	25.9	280
399	<LOQ	11.8	83.7	61.7	7.14	7.16	<LOQ	<LOQ	172
404	14.1	50.6	77.6	154	<LOQ	<LOQ	<LOQ	<LOQ	296
406	10.1	8.30	78.0	57.5	6.92	4.63	n.d	<LOQ	165
407	4.95	10.8	118	67.1	98.8	6.84	n.d	7.53	314
408	<LOQ	20.9	113	5.77	<LOQ	11.7	<LOQ	5.03	156
409	<LOQ	7.55	5.47	64.2	<LOQ	7.16	<LOQ	<LOQ	84.4
413	<LOQ	8.77	36.6	34.9	<LOQ	6.74	<LOQ	<LOQ	87.0
415	3.71	32.6	66.9	451	14.0	7.26	<LOQ	11.6	587

b)

Individual CODE	Concentrations of UV-Fs in muscle (ngg^{-1} dw)								
	BP1	BP3	4HB	4DHB	EHMC	4MBC	ODPABA	OC	ΣUV-Fs
380	< LOQ	12.1	3.25	6.40	49.4	9.26	<LOQ	57.8	138
389	< LOQ	3.5	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	5.24	8.74
392	< LOQ	3.91	< LOQ	17.4	< LOQ	5.16	< LOQ	< LOQ	26.5
399	< LOQ	15.4	3.15	16.6	17.1	23.4	< LOQ	24.9	101
404	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	n.a
406	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	n.a
407	n.d.	< LOQ	< LOQ	< LOQ	< LOQ	6.00	< LOQ	13.3	20.2
408	< LOQ	< LOQ	5.70	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	5.70
409	< LOQ	4.84	3.02	4.29	< LOQ	9.89	< LOQ	< LOQ	22.0
413	< LOQ	4.47	22.6	< LOQ	< LOQ	16.4	< LOQ	22.3	65.8
415	< LOQ	< LOQ	3.07	< LOQ	< LOQ	n.d.	< LOQ	n.d.	3.07

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c)

Individual CODE	Concentrations of UV-Fs in gills (ng g^{-1} dw)								
	BP1	BP3	4HB	4DHB	EHMC	4MBC	ODPABA	OC	ΣUV-Fs
380	<LOQ	6.62	9.45	23.5	<LOQ	6.21	<LOQ	9.96	55.7
389	<LOQ	3.33	12.1	19.4	<LOQ	5.79	<LOQ	9.85	50.5
392	<LOQ	3.07	6.45	17.1	<LOQ	7.47	<LOQ	2.40	36.5
399	<LOQ	<LOQ	18.2	6.59	<LOQ	<LOQ	<LOQ	<LOQ	24.8
404	<LOQ	24.0	8.64	11.3	<LOQ	4.42	<LOQ	9.85	58.2
406	<LOQ	9.42	9.45	15.3	7.27	13.3	<LOQ	10.7	65.4
407	<LOQ	<LOQ	7.27	3.86	<LOQ	7.16	<LOQ	6.20	24.5
408	<LOQ	<LOQ	5.28	3.29	<LOQ	4.95	<LOQ	<LOQ	13.5
409	<LOQ	6.80	31.64	13.7	<LOQ	14.5	<LOQ	16.4	83.0
413	<LOQ	3.74	16.36	8.76	<LOQ	4.63	<LOQ	16.8	50.3
415	<LOQ	3.26	10.45	11.4	<LOQ	6.21	<LOQ	9.59	41.0

Table S6. Concentrations of each compound in wet weight (ww) and the total load of UV-Fs (ΣUV-Fs) in each individual in a) liver, b) muscle, and c) gill. <LOQ: below the limits of quantification; n.d.: not detected.

a)

Individual	Concentrations of UV-Fs in liver (ngg^{-1} ww)								
CODE	BP1	BP3	4HB	4DHB	EHMC	4MBC	ODPABA	OC	ΣUV-Fs
380	2.9	7.8	41.7	30.3	<LOQ	4.1	<LOQ	<LOQ	86.8
389	1.3	4.1	15.0	27.7	2.9	2.1	<LOQ	1.5	54.5
392	5.1	22.3	39.4	4.4	2.7	2.4	<LOQ	7.8	84.1
399	<LOQ	3.5	25.1	18.5	2.1	2.1	<LOQ	<LOQ	51.5
404	4.2	15.2	23.3	46.2	<LOQ	<LOQ	<LOQ	<LOQ	88.9
406	3.00	2.5	23.4	17.3	2.1	1.4	n.d	<LOQ	49.6
407	1.5	3.2	35.4	20.1	29.6	2.1	n.d	2.3	94.2
408	<LOQ	6.3	33.9	1.7	<LOQ	3.5	<LOQ	1.5	46.9
409	<LOQ	2.3	1.6	19.3	<LOQ	2.1	<LOQ	<LOQ	25.3
413	<LOQ	2.6	11.0	10.5	<LOQ	2.0	<LOQ	<LOQ	26.1
415	1.1	9.8	20.1	135.3	4.2	2.2	<LOQ	3.5	176.1

b)

Individual	Concentrations of UV-Fs in muscle (ngg^{-1} ww)								
CODE	BP1	BP3	4HB	4DHB	EHMC	4MBC	ODPABA	OC	ΣUV-Fs
380	<LOQ	3.6	1.0	1.9	14.8	2.8	<LOQ	17.3	41.5
389	<LOQ	1.1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1.6	2.6
392	<LOQ	1.2	<LOQ	5.2	<LOQ	1.5	<LOQ	<LOQ	7.9
399	<LOQ	4.6	0.9	5.0	5.1	7.0	<LOQ	7.5	30.2
404	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.0
406	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.0
407	n.d.	<LOQ	<LOQ	<LOQ	<LOQ	1.8	<LOQ	4.0	6.0
408	< LOQ	<LOQ	1.7	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1.7
409	< LOQ	1.5	0.9	1.3	<LOQ	3.0	<LOQ	<LOQ	6.6
413	< LOQ	1.3	6.8	<LOQ	<LOQ	4.9	<LOQ	6.7	19.7
415	< LOQ	<LOQ	0.9	<LOQ	<LOQ	n.d.	<LOQ	n.d.	0.9

c)

Individual CODE	Concentrations of UV-Fs in gills (ngg^{-1} ww)								
	BP1	BP3	4HB	4DHB	EHMC	4MBC	ODPABA	OC	ΣUV-Fs
380	<LOQ	2.0	2.8	7.1	<LOQ	1.9	<LOQ	3.0	16.7
389	<LOQ	1.0	3.6	5.8	<LOQ	1.7	<LOQ	3.0	15.1
392	<LOQ	0.9	1.9	5.1	<LOQ	2.2	<LOQ	0.7	10.9
399	<LOQ	<LOQ	5.5	2.0	<LOQ	<LOQ	<LOQ	<LOQ	7.4
404	<LOQ	7.2	2.6	3.4	<LOQ	1.3	<LOQ	3.0	17.5
406	<LOQ	2.8	2.8	4.6	2.2	4.0	<LOQ	3.2	19.6
407	<LOQ	<LOQ	2.2	1.2	<LOQ	2.1	<LOQ	1.9	7.3
408	<LOQ	<LOQ	1.6	1.0	<LOQ	1.5	<LOQ	<LOQ	4.1
409	<LOQ	2.0	9.5	4.1	<LOQ	4.4	<LOQ	4.9	24.9
413	<LOQ	1.1	4.9	2.6	<LOQ	1.4	<LOQ	5.0	15.1
415	<LOQ	1.0	3.1	3.4	<LOQ	1.9	<LOQ	2.9	12.3

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Table S7. Concentrations of each compound in lipid weight (lw) and the total load of UV-Fs (ΣUV-Fs) in each individual in a) liver, b) muscle, and c) gill. <LOQ: below the limits of quantification; n.d.: not detected.

a)

Individual CODE	Concentrations of UV-Fs in liver (ngg^{-1} lw)								
	BP1	BP3	4HB	4DHB	EHMC	4MBC	ODPABA	OC	ΣUV-Fs
380	77	212	1130	821	<LOQ	111	<LOQ	<LOQ	2352
389	36	111	406	750	77	56	<LOQ	41	1477
392	139	605	1067	120	74	64	<LOQ	211	2280
399	<LOQ	96	680	502	58	58	<LOQ	<LOQ	1394
404	115	411	631	1252	<LOQ	<LOQ	<LOQ	<LOQ	2409
406	82	67	634	467	56	38	n.d	<LOQ	1345
407	40	88	959	546	803	56	n.d	61	2553
408	<LOQ	170	919	47	<LOQ	95	<LOQ	41	1272
409	<LOQ	61	44	522	<LOQ	58	<LOQ	<LOQ	686
413	<LOQ	71	298	284	<LOQ	55	<LOQ	<LOQ	707
415	30	265	544	3667	114	59	<LOQ	94	4773

b)

Individual CODE	Concentrations of UV-Fs in muscle (ngg^{-1} lw)								
	BP1	BP3	4HB	4DHB	EHMC	4MBC	ODPABA	OC	ΣUV-Fs
380	<LOQ	399	107	211	1630	306	<LOQ	1908	4561.4
389	<LOQ	116	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	173	288.4
392	<LOQ	129	<LOQ	574	<LOQ	170	<LOQ	<LOQ	873.6
399	<LOQ	508	104	548	564	772	<LOQ	822	3318.5
404	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	n.a
406	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	n.a.
407	n.d.	<LOQ	<LOQ	<LOQ	<LOQ	198	<LOQ	439	665.0
408	< LOQ	< LOQ	188	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	188.1
409	< LOQ	160	100	142	<LOQ	326	<LOQ	<LOQ	727.4
413	< LOQ	148	746	<LOQ	<LOQ	541	<LOQ	736	2170.6
415	< LOQ	< LOQ	101	<LOQ	<LOQ	n.d.	<LOQ	n.d.	101.3

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c)

Individual CODE	Concentrations of UV-Fs in gills (ngg^{-1} lw)							
	BP1	BP3	4HB	4DHB	EHMC	4MBC	ODPABA	OC	ΣUV-Fs
380	<LOQ	218	312	776	<LOQ	205	<LOQ	329	1840
389	<LOQ	110	399	640	<LOQ	191	<LOQ	325	1666
392	<LOQ	101	213	564	<LOQ	247	<LOQ	79	1204
399	<LOQ	<LOQ	601	217	<LOQ	<LOQ	<LOQ	<LOQ	818
404	<LOQ	792	285	373	<LOQ	146	<LOQ	325	1921
406	<LOQ	311	312	505	240	439	<LOQ	353	2160
407	<LOQ	<LOQ	240	127	<LOQ	236	<LOQ	205	808
408	<LOQ	<LOQ	174	109	<LOQ	163	<LOQ	<LOQ	446
409	<LOQ	224	1044	452	<LOQ	479	<LOQ	541	2741
413	<LOQ	123	540	289	<LOQ	153	<LOQ	554	1660
415	<LOQ	108	345	376	<LOQ	205	<LOQ	317	1350

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Información adicional - publicación Nº 9

A potential new threat to wild life:

presence of UV filters in bird eggs from a preserved area

Por

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Supporting Information for

A POTENTIAL NEW THREAT TO WILD LIFE: PRESENCE OF UV FILTERS IN BIRD EGGS FROM A PRESERVED AREA

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Content:

A.1. Sample pre-treatment and analysis

The method was optimised using hen eggs purchased from a local market. 0.1 g of the homogenized whole egg (without eggshell) were placed in beakers, completely covered with acetone and spiked with 50 ng of the surrogate standard solution of BP-^{13}C. The acetone was left to evaporate at room temperature overnight, thus the eggs samples were dry prior analysis.

UV-Fs extraction was carried out by pressurised liquid extraction (PLE) using an ASE 350 Accelerated Solvent Extractor (Dionex Corporation, Sunnyvale, CA, USA). The experiments were conducted as follows: a cellulose filter followed by 1 g of Florisil (previously heated at 130 ◦C for 24 h) was placed at the bottom of the PLE cells. The freeze-dried eggs spiked with 50 ng of the surrogate standards were mixed in the PLE extraction cells with Florisil in order to perform first in-cell purification. Extraction was achieved in 2 static cycles of 5 min each at 100 ºC and 1500 psi using the mixture AcEt/DCM (1:1, v/v) as extracting solvent.

The PLE extracts were diluted to 200 mL with water (to keep MeOH < 5%), and further purified by solid phase extraction (SPE) using Isolute C18 cartridges, from Biotage. The cartridges were conditioned with 5 mL of the mixture AcEt/DCM (1:1, v/v) followed by 5 ml of MeOH and 5 mL of water. Then the PLE diluted extracts were loaded onto the SPE cartridges using a Baker vacuum system (J.T. Baker, The Netherlands). Further, the cartridges were washed with 5 ml of water and dried. Then, the compounds retained in the SPE cartridges were eluted with 7 mL of the mixture AcEt/DCM (1:1, v/v) and 2 mL of DCM. Finally, the joint extracts were evaporated with nitrogen and reconstituted with 1 mL of the internal standards solution containing BP3-d_5, 4MBC-d_4, and AllylBZT at 20 ngmL^{-1} in ACN. Analyses were carried out in triplicate. The lipid content was determined gravimetrically.

UV-Fs' separation and detection were performed by liquid chromatography-tandem mass spectrometry using a Symbiosis Pico chromatograph from Spark Holland (Emmen, The Netherlands) attached to a 4000 Q TRAP™ MS/MS analyser from Applied Biosystems-Sciex (Foster City, California, USA) (HPLC-QqLIT-MS/MS). The chromatographic separation was achieved on a Hibar Purospher® STAR® HR R-18 ec. (50 mm × 2.0 mm, 5 μm) from Merck, preceded by a guard column of the same packaging material. The mobile phase consisted of HPLC-grade water and ACN, both 0.1% formic acid. The total run time was 20 min. The mobile phase flow rate and the injection volume were set to 0.3 mL min^{-1} and 20 μL, respectively. The chromatographic gradient started at 5% organic phase and reached 25% during the next 6 min., 4 min. later the gradient reached 100%, keeping it constant for 8 min. At minute 18 the gradient went back to the initial conditions.

MS/MS detection was performed in positive electrospray ionization (ESI+) under selected reaction monitoring (SRM) mode for enhanced selectivity and sensitivity. The two most intense transitions from the precursor molecular ion ($(M+H)^+$) were monitored per compound. The most abundant transition was used for quantification, whereas the other one was used for confirmation. Instrument control, data acquisition and processing were performed with Analyst 1.4.2 software from Applied Biosystems/MDS Sciex.

Table S1. Name, abbreviation, CAS number and Log K_{ow} of the studied UV filters. In italic, metabolites of BP3.

Name	**Abbreviation**	**CAS number**	**Log K_{ow}**
Benzophenones			
2,4-Dihydroxybenzophenone	BP1	131-56-6	3.17
2-Hydroxy-4-methoxybenzophenone (oxybenzone)	BP3	131-57-7	3.79
4-Hydroxybenzophenone	4HB	1137-42-4	3.02
4,4'-Dihydroxybenzophenone	4DHB	611-99-4	2.55
Crylenes			
2-Ethylhexyl-2-cyano-3,3-diphenylacrylate	OC	6197-30-4	7.53
p-aminobenzoic acid derivatives			
2-Ethylhexyl-4-(dimethyl-amino) benzoate	ODPABA	21245-02-3	6.15
Benzotriazole derivatives			
2-(2-Benzotriazolyl)-p-cresol	UVP	2440-22-4	4.3

Table S2. Sample name, species, $\delta^{13}C$, $\delta^{15}N$, water content (%H_2O) and total lipids content (%lipid) per sample.

Sample Name	Order	Common name	Scientific name	$\delta^{13}C$	$\delta^{15}N$	%H_2O	%lipid*
27e		Western marsh harrier	Circus aeruginosus	-23.86	14.98	75.6	24.4
28e				-23.99	8.64	81.7	---
29e				-23.75	8.91	82.1	32.8
30e				-23.60	8.77	81.0	27.2
34e				-22.38	7.96	81.9	30.5
42e				-23.99	9.53	79.1	21.4
43e				-24.09	8.92	79.4	23.8
44e				-24.29	8.58	76.7	10.6
45e				-23.73	11.44	71.3	29.6
46e				-23.41	11.45	78.8	25.6
47e				-22.88	11.29	79.7	29.5
1e				-21.80	9.38	77.6	33.3
2e				-22.09	8.84	76.5	31.5
3e				-21.55	9.04	76.7	18.3
4e				-22.18	8.81	76.8	21.6
5e				-23.90	11.78	76.3	32.0
6e				-23.34	10.48	76.3	33.8
7e				-23.34	10.94	80.8	26.9
8e				-22.90	9.62	76.8	31.0
14e		Slender-billed gull	Chrococephalus genei	-18.87	12.37	73.4	36.9
19e				-19.05	9.47	72.2	36.8
21e				-17.51	11.42	72.7	36.2
23e				-17.62	10.22	70.8	42.5
24e				-18.02	11.39	74.2	33.8
52e				-22.96	14.20	67.1	37.7
54e				-23.68	13.17	72.3	18.6
57e				-22.11	12.34	73.6	47.1
59e				-23.92	15.07	69.3	41.9
61e				-18.42	15.85	29.5	42.6
64e				-20.46	13.04	31.0	45.2
65e				-20.20	14.51	32.1	41.0
66e				-16.05	14.54	31.9	39.2
67e				-20.15	14.59	33.4	35.3
68e				-16.72	15.70	30.3	46.9
69e				-19.20	14.04	32.2	44.2
70e				-20.07	13.00	32.5	40.5
71e				-20.92	13.32	32.8	46.3
72e				-16.55	15.68	32.7	45.2
73e				-19.14	14.81	34.2	46.1

*lipids determined in dry-frozen samples.

Table S3. HPLC-MS/MS instrumental performance, recovery rates and method limit of detection (MLOD) and quantification (MLOQ). ILOD: instrumental limits of detection; ILOQ: instrumental limit of quantification. RSD: relative standard deviation.

Compound	Calibration range ($ng\ g^{-1}$ dw)	r^2	ILOD (pg)	ILOQ (pg)	Precision (RSD)		Recovery rate (%)		MLOD ($ng\ g^{-1}$dw)	MLOQ ($ng\ g^{-1}$dw)
					Intraday	Inteday	25 $ng\ g^{-1}$dw	50 $ng\ g^{-1}$ dw		
BP3	0.1-500	0.999	0.66	2.21	3	11	74 ± 5	77 ± 2	0.29	0.97
BP1	0.1-500	0.999	5.66	18.97	5	7	46 ± 3	39 ± 2	0.25	0.85
4HB	0.1-500	0.999	3.18	10.60	5	10	45 ± 4	57 ± 3	0.53	1.77
4DHB	0.1-500	0.999	0.54	1.80	1	5	54 ± 3	55 ± 2	0.15	0.51
ODPABA	0.1-500	0.999	0.14	0.49	7	9	54 ± 11	39 ± 5	0.04	0.13
OC	0.1-500	0.999	0.63	2.12	9	15	107 ± 17	90 ± 7	0.26	0.86
UVP	0.1-500	0.999	0.14	0.49	10	18	125 ± 8	124 ± 10	0.13	0.43

Table S4. Concentrations of UV-Fs expressed in ngg^{-1} dw of freeze-dried egg each sample. <MLOQ: below the limit of quantification. n.d.: not detected.

				Concentration (ng g^{-1} dw)						
Sample Name	Order	Common name	Scientific name	BP1	BP3	4HB	4DHB	ODPABA	OC	UVP
27e		Western marsh harrier	Circus aeruginosus	40.6	46.7	895	<MLOQ	<MLOQ	<MLOQ	2.7
28e				40.4	27.2	267	<MLOQ	<MLOQ	<MLOQ	3.0
29e				53.5	18.3	70.6	<MLOQ	<MLOQ	<MLOQ	0.4
30e				28.0	24.9	20.0	<MLOQ	<MLOQ	<MLOQ	1.0
34e				36.4	25.5	48.1	<MLOQ	<MLOQ	<MLOQ	<MLOQ
42e				27.9	35.2	82.9	<MLOQ	<MLOQ	<MLOQ	<MLOQ
43e				38.1	21.3	26.2	132	<MLOQ	<MLOQ	<MLOQ
44e				42.7	23.7	1,200	<MLOQ	<MLOQ	<MLOQ	<MLOQ
45e				42.3	27.0	n.d.	<MLOQ	<MLOQ	<MLOQ	<MLOQ
46e				47.4	18.5	153	<MLOQ	<MLOQ	<MLOQ	<MLOQ
47e				36.2	26.0	27.3	<MLOQ	<MLOQ	<MLOQ	<MLOQ
1e				<MLOQ	20.6	104	<MLOQ	<MLOQ	26.7	<MLOQ
2e				<MLOQ	19.5	224	<MLOQ	<MLOQ	15.2	<MLOQ
3e				<MLOQ	29.2	1,059	<MLOQ	<MLOQ	<MLOQ	<MLOQ
4e				<MLOQ	25.6	360	<MLOQ	<MLOQ	<MLOQ	n.d.
5e				<MLOQ	19.8	408	<MLOQ	<MLOQ	<MLOQ	<MLOQ
6e				<MLOQ	20.9	3,348	<MLOQ	<MLOQ	<MLOQ	<MLOQ
7e				<MLOQ	22.0	210	<MLOQ	n.d.	<MLOQ	<MLOQ
8e				<MLOQ	20.7	378	29.04	<MLOQ	<MLOQ	<MLOQ
14e		Slender-billed gull	Chrococephalus genei	<MLOQ	22.5	266	<MLOQ	<MLOQ	<MLOQ	<MLOQ
19e				<MLOQ	24.7	86.0	<MLOQ	<MLOQ	<MLOQ	n.d.
21e				594	44.4	72.8	<MLOQ	<MLOQ	23.8	<MLOQ
23e				677	38.5	111	<MLOQ	<MLOQ	65.2	8.4
24e				27.8	31.4	83.8	<MLOQ	<MLOQ	11.4	1.4
52e				66.1	49.3	472	<MLOQ	<MLOQ	<MLOQ	<MLOQ
54e				34.9	18.2	35.8	<MLOQ	<MLOQ	<MLOQ	<MLOQ
57e				29.0	21.2	12.0	<MLOQ	<MLOQ	<MLOQ	1.8
59e				39.9	24.3	37.0	<MLOQ	<MLOQ	<MLOQ	2.0

Table S4. Continued.

				Concentration (ng g^{-1} dw)						
Sample Name	Order	Common name	Scientific name	BP1	BP3	4HB	4DHB	ODPABA	OC	UVP
61e				41.0	17.1	560	<MLOQ	<MLOQ	<MLOQ	<MLOQ
64e				87.3	16.9	332	<MLOQ	<MLOQ	<MLOQ	<MLOQ
65e				24.9	17.3	66.2	<MLOQ	<MLOQ	<MLOQ	<MLOQ
66e				23.3	23.7	18.0	<MLOQ	<MLOQ	<MLOQ	<MLOQ
67e				37.1	22.6	13.5	<MLOQ	<MLOQ	<MLOQ	<MLOQ
68e				27.2	18.5	24.5	<MLOQ	<MLOQ	<MLOQ	<MLOQ
69e				30.7	22.4	41.9	<MLOQ	<MLOQ	<MLOQ	0.2
70e				33.4	31.2	107	<MLOQ	<MLOQ	<MLOQ	<MLOQ
71e				33.9	25.7	38.7	<MLOQ	<MLOQ	<MLOQ	<MLOQ
72e				50.3	21.9	120	<MLOQ	<MLOQ	<MLOQ	<MLOQ
73e				29.4	25.3	20.7	<MLOQ	<MLOQ	<MLOQ	<MLOQ

Table S5. Concentrations of UV-Fs expressed in ngg^{-1} lw of each freeze-dried egg sample. <MLOQ: below the limits of quantification. n.d.: not detected; n.a.: not applicable.

				Concentration (ng g^{-1} lw)						
Sample Name	Order	Common name	Scientific name	BP1	BP3	4HB	4DHB	ODPABA	OC	UVP
27e		Western marsh harrier	Circus aeruginosus	167	191	3,670	<MLOQ	<MLOQ	<MLOQ	11.2
28e				n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
29e				163	55.8	215	<MLOQ	<MLOQ	<MLOQ	1.25
30e				103	91.7	73.5	<MLOQ	<MLOQ	<MLOQ	3.7
34e				119	83.4	158	<MLOQ	<MLOQ	<MLOQ	<MLOQ
42e				130	165	387	<MLOQ	<MLOQ	<MLOQ	<MLOQ
43e				160	89.7	110	553	<MLOQ	<MLOQ	<MLOQ
44e				403	223	11,318	<MLOQ	<MLOQ	<MLOQ	<MLOQ
45e				143	91.1	n.d.	<MLOQ	<MLOQ	<MLOQ	<MLOQ
46e				185	72.3	596	<MLOQ	<MLOQ	<MLOQ	<MLOQ
47e				123	88.3	92.5	<MLOQ	<MLOQ	<MLOQ	<MLOQ
1e				<MLOQ	61.7	311	<MLOQ	<MLOQ	26.6	<MLOQ
2e				<MLOQ	61.9	711	<MLOQ	<MLOQ	15.2	<MLOQ
3e				<MLOQ	160	5,785	<MLOQ	<MLOQ	<MLOQ	<MLOQ
4e				<MLOQ	119	1,668	<MLOQ	<MLOQ	<MLOQ	n.d.
5e				<MLOQ	62.0	1,274	<MLOQ	<MLOQ	<MLOQ	<MLOQ
6e				<MLOQ	61.7	9,905	<MLOQ	<MLOQ	<MLOQ	<MLOQ
7e				<MLOQ	81.8	780	<MLOQ	n.d.	<MLOQ	<MLOQ
8e				<MLOQ	66.8	1,221	93.7	<MLOQ	<MLOQ	<MLOQ
14e		Slender-billed gull	Chrococephalus genei	<MLOQ	61.0	722	<MLOQ	<MLOQ	<MLOQ	<MLOQ
19e				<MLOQ	67.1	231	<MLOQ	<MLOQ	<MLOQ	n.d.
21e				1,642	123	201	<MLOQ	<MLOQ	65.8	<MLOQ
23e				1,594	90.6	262	<MLOQ	<MLOQ	153	19.7
24e				82.2	93.0	248	<MLOQ	<MLOQ	11.4	1.4
52e				175	131	1,252	<MLOQ	<MLOQ	<MLOQ	<MLOQ
54e				187	98.1	193	<MLOQ	<MLOQ	<MLOQ	<MLOQ
57e				61.5	45.0	25.5	<MLOQ	<MLOQ	<MLOQ	2.5
59e				95.2	58.0	88.2	<MLOQ	<MLOQ	<MLOQ	4.7

Table S5. Continued.

				Concentration (ng g^{-1} lw)						
Sample Name	**Order**	**Common name**	**Scientific name**	**BP1**	**BP3**	**4HB**	**4DHB**	**ODPABA**	**OC**	**UVP**
61e				96.4	40.8	1,315	<MLOQ	<MLOQ	<MLOQ	<MLOQ
64e				193	37.3	735	<MLOQ	<MLOQ	<MLOQ	<MLOQ
65e				60.8	42.1	161	<MLOQ	<MLOQ	<MLOQ	<MLOQ
66e				59.3	60.5	46.0	<MLOQ	<MLOQ	<MLOQ	<MLOQ
67e				105	64.1	38.2	<MLOQ	<MLOQ	<MLOQ	<MLOQ
68e				58.1	39.5	52.4	<MLOQ	<MLOQ	<MLOQ	<MLOQ
69e				69.4	50.6	94.7	<MLOQ	<MLOQ	<MLOQ	0.4
70e				82.4	77.7	265	<MLOQ	<MLOQ	<MLOQ	<MLOQ
71e				73.3	55.5	83.7	<MLOQ	<MLOQ	<MLOQ	<MLOQ
72e				111	48.5	266	<MLOQ	<MLOQ	<MLOQ	<MLOQ
73e				63.8	54.8	44.9	<MLOQ	<MLOQ	<MLOQ	<MLOQ

Table S6. Concentrations of UV-Fs expressed in ngg^{-1} ww of each freeze-dried egg sample. <MLOQ: below the limit of quantification. n.d.: not detected.

				Concentration (ng g^{-1} ww)						
Sample Name	**Order**	**Common name**	**Scientific name**	**BP1**	**BP3**	**4HB**	**4DHB**	**ODPABA**	**OC**	**UVP**
27e		Western marsh harrier	Circus aeruginosus	9.9	11.4	219	<MLOQ	<MLOQ	n.d.	0.7
28e				7.4	5.0	48.8	<MLOQ	<MLOQ	<MLOQ	0.5
29e				9.6	3.3	12.7	<MLOQ	<MLOQ	<MLOQ	0.1
30e				5.3	4.7	3.8	<MLOQ	<MLOQ	<MLOQ	0.2
34e				6.6	4.6	8.7	<MLOQ	<MLOQ	<MLOQ	<MLOQ
42e				5.8	7.4	17.3	<MLOQ	<MLOQ	<MLOQ	<MLOQ
43e				7.9	4.4	5.4	27.2	<MLOQ	<MLOQ	<MLOQ
44e				10.0	5.5	280	<MLOQ	<MLOQ	<MLOQ	<MLOQ
45e				12.2	7.7	<MLOQ	<MLOQ	<MLOQ	<MLOQ	<MLOQ
46e				10.1	3.9	32.4	<MLOQ	<MLOQ	<MLOQ	<MLOQ
47e				7.3	5.3	5.5	<MLOQ	<MLOQ	<MLOQ	<MLOQ
1e				<MLOQ	4.6	23.3	<MLOQ	<MLOQ	6.0	<MLOQ
2e				<MLOQ	4.6	52.6	<MLOQ	<MLOQ	3.6	<MLOQ
3e				<MLOQ	6.8	247	<MLOQ	<MLOQ	<MLOQ	<MLOQ
4e				<MLOQ	5.9	83.5	<MLOQ	<MLOQ	<MLOQ	n.d.
5e				<MLOQ	4.7	96.8	<MLOQ	<MLOQ	<MLOQ	<MLOQ
6e				<MLOQ	5.0	795	<MLOQ	<MLOQ	<MLOQ	<MLOQ
7e				<MLOQ	4.2	40.4	<MLOQ	n.d.	<MLOQ	<MLOQ
8e				<MLOQ	4.8	87.9	6.7	<MLOQ	<MLOQ	<MLOQ
14e		Slender-billed gull	Chrococephalus genei	<MLOQ	6.0	71.0	<MLOQ	<MLOQ	<MLOQ	<MLOQ
19e				<MLOQ	6.9	23.9	<MLOQ	<MLOQ	<MLOQ	n.d.
21e				162	12.1	19.9	<MLOQ	<MLOQ	6.5	<MLOQ
23e				198	11.2	32.4	<MLOQ	<MLOQ	19.0	2.4
24e				7.2	8.1	21.7	<MLOQ	<MLOQ	3.0	0.4
52e				21.8	16.2	155	<MLOQ	<MLOQ	<MLOQ	<MLOQ
54e				9.7	5.1	9.9	<MLOQ	<MLOQ	<MLOQ	<MLOQ
57e				7.6	5.6	3.2	<MLOQ	<MLOQ	<MLOQ	0.3
59e				12.2	7.4	11.3	<MLOQ	<MLOQ	<MLOQ	0.6

Table S6. Continued.

				Concentration (ng g^{-1} ww)						
Sample Name	**Order**	**Common name**	**Scientific name**	**BP1**	**BP3**	**4HB**	**4DHB**	**ODPABA**	**OC**	**UVP**
61e				28.9	12.3	395	<MLOQ	<MLOQ	<MLOQ	<MLOQ
64e				60.2	11.6	229	<MLOQ	<MLOQ	<MLOQ	<MLOQ
65e				16.9	11.7	44.9	<MLOQ	<MLOQ	<MLOQ	<MLOQ
66e				15.8	16.2	12.2	<MLOQ	<MLOQ	<MLOQ	<MLOQ
67e				24.7	15.1	9.0	<MLOQ	<MLOQ	<MLOQ	<MLOQ
68e				19.0	12.9	17.1	<MLOQ	<MLOQ	<MLOQ	<MLOQ
69e				20.8	15.2	28.4	<MLOQ	<MLOQ	<MLOQ	0.1
70e				22.6	21.3	72.4	<MLOQ	<MLOQ	<MLOQ	<MLOQ
71e				22.8	17.3	26.0	<MLOQ	<MLOQ	<MLOQ	<MLOQ
72e				33.8	14.8	81.0	<MLOQ	<MLOQ	<MLOQ	<MLOQ
73e				19.4	16.6	13.6	<MLOQ	<MLOQ	<MLOQ	<MLOQ

Table S7. Total mean concentrations (expressed in ng g^{-1} lw) of PBDEs, dechloranes, pyrethroids, and UV-Fs in the studied species from Doñana. n.a.: not applicable. SD, standard deviation.

Order	Common Name	Species	∑PBDE[1]	SD	∑Dechloranes[1]	SD	∑Pyrethroid[2]	SD	∑UV-Fs	SD
	Western marsh harrier	Circus aeruginosus	23.4	n.a.	161	n.a.	4.88	n.a.	4,046.80	n.a.
	Common kestrel	Falco tinnunculus	12.7	9.37	8.88	7.18	6.17	9.7	397.91	3,639.06
Ciconiiformes	White stork	Ciconia ciconia	80	16	66.1	57.6	31.4	39	1,357.80	3,371.27
	Slender-billed gull	Chrococephalus genei	5.03	1	39.4	11.6	3.35	2	782.80	n.a.
	Black-headed gull	Chrococephalus ridibundus	5.98	1.99	63.4	30.5	162	128	1,247.35	981.46
	Gull-billed tern	Gelochelidon nilotica	6.62	3.19	23.6	16.6	61.5	80	361.72	651.16
Anseriformes	Gadwall	Anas strepera	5.66	1.2	5.93	1.33	5.79	3.4	215.20	415.15

[1] Barón, E.; Máñez, M.; Andreu, A. C.; Sergio, F.; Hiraldo, F.; Eljarrat, E.; Barceló, D. Bioaccumulation and biomagnification of emerging and classical flame retardands in birds of 14 species from Doñana Natural Space and surrounding areas (South-western Spain). Environ. Int. 2014, 68, 118-126.

[2] Corcellas, C.; Andreu, A.; Máñez, M.; Sergio, F.; Hiraldo, F.; Eljarrat, E.; Barceló, D. Pyrethroid insecticides in wild bird eggs from a World Heritage Listed Park: A case study in Doñana National Park (Spain). Environ. Pollut. 2017, 228, 321-330.

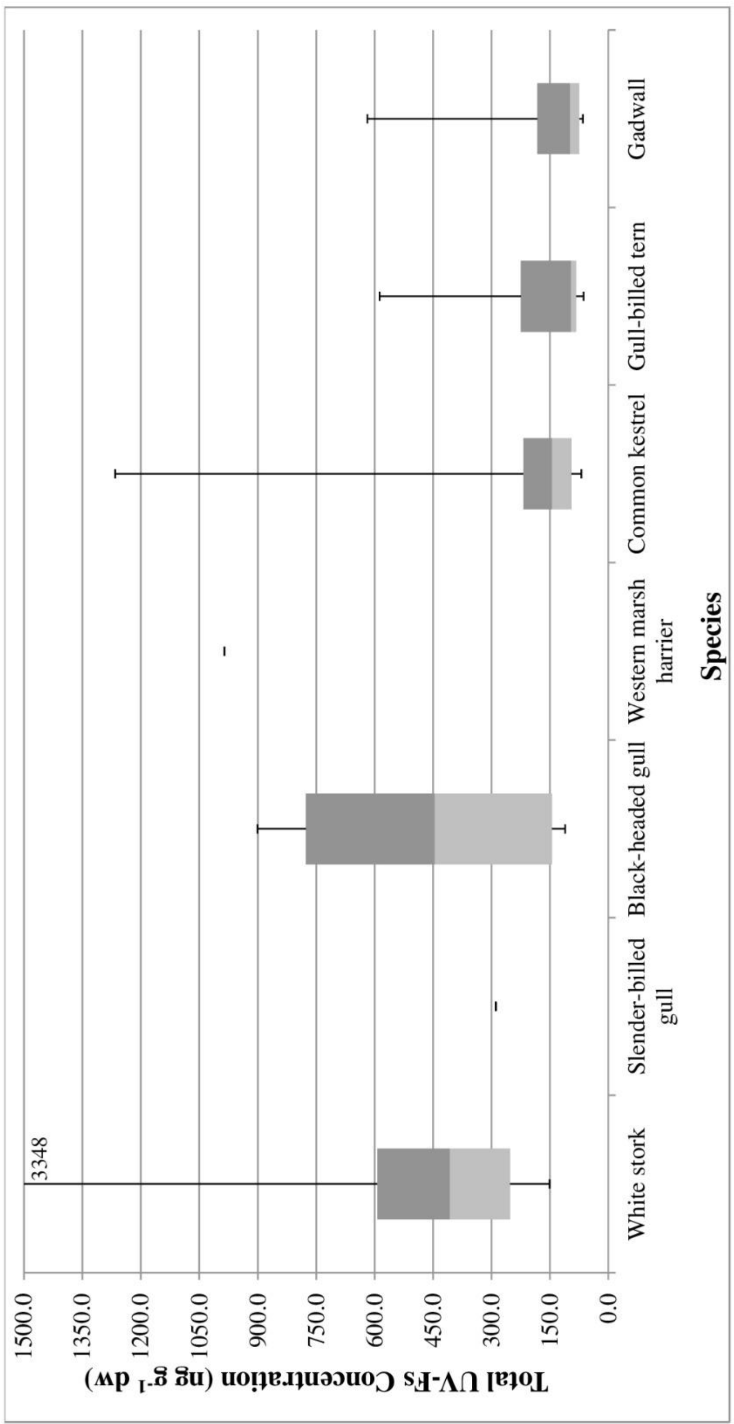

Figure S1. Total concentrations of UV-Fs in the studied eggs from wild bird species.

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a) b)

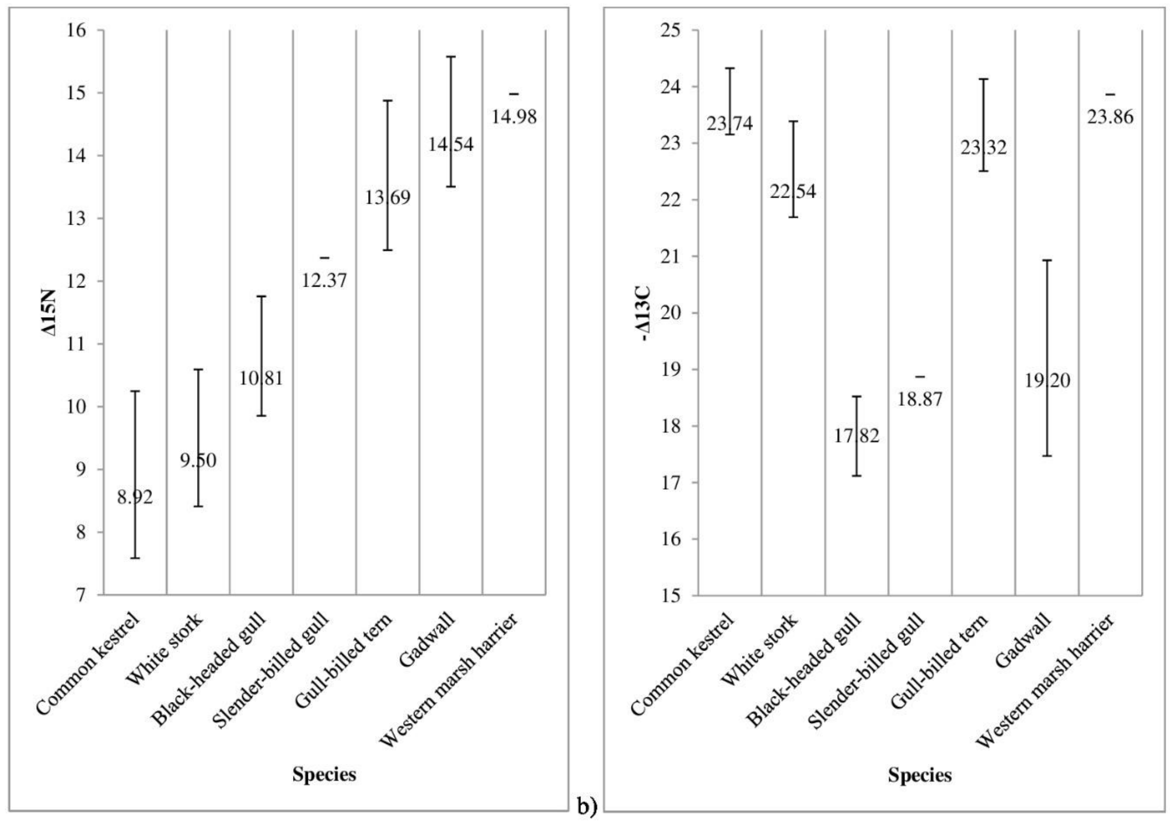

Figure S2. $\delta^{15}N$ (a) and $\delta^{13}C$ (b) ranges for the eggs from wild bird species. Mean value is indicated in each range.

Información adicional - publicación Nº 10

Determination of UV filters in human breast milk using turbulent flow chromatography and babies' daily intake estimation

Por

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en

Environmental Research (enviado)

Supporting information

for

Determination of UV filters in human breast milk using turbulent flow chromatography and babies' daily intake estimation

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Content:

Table A1. Target compounds name, abbreviation, CAS number, and Log Kow.

Compound name	Abbreviation	CAS N.	Log K_{ow}
Benzophenone derivatives			
2-Hydroxy-4-methoxybenzophenone	BP3	131-57-7	3.79
2,4-Dihydroxybenzophenone	BP1	131-56-6	3.14
4-Hydroxybenzophenone	4HB	1137-42-4	3.02
4,4'-Dihydroxybenzophenone	4DHB	611-99-4	2.55
Camphor derivatives			
4-Methylbenzyldiene camphor	4MBC	36861-47-9	4.95
p-aminobenzoic acid derivatives			
Ethylhexyl dimethyl-p-aminobenzoic acid	ODPABA	21245-02-3	6.15
Ethyl p-aminobenzoic acid	EtPABA	94-09-7	1.86
Cinamates			
Ethylhexyl methoxycinamate	EHMC	5466-77-3	5.8
Crylenes			
Octocrylene	OC	6197-30-4	7.53
Benzotriazole derivatives			
2-(5-tert-Butyl-2-hydroxyphenyl)benzotriazole	TBHPBT	3147-76-0	3.24
2-(2-Hydroxy-5-methylphenyl)benzotriazole	UVP	2440-22-4	4.3
2-(2-H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol	UV234	70321-86-7	7.67
2-(2'-Hydroxy-3',5'-di-tert-butylphenyl)benzotriazole	UV320	3846-71-7	5.3
2-tert-butyl-6-(5-chloro-2-H-benzotriazol-2-yl)-4-methylphenol	UV326	3896-11-5	7.2
2,4-di-tert-butyl-6-(5-chloro--2-H-benzotriazol-2-yl)phenol	UV327	3864-99-1	6.6
2-(2-H-benzotriazol-2-yl)-4,6-di-tert-penthylphenol	UV328	25973-55-1	7.8
2-(2-H-Benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol	UV329	3147-75-9	6.21
Benzotriazole	BZT	95-14-7	1.23
Methyl benzotriazole	MeBZT	136-85-6	1.89

Table A2. Summary of the information present in the questionnaires handed out to the mothers.

Participating mothers		79
Sampling campaign		April-October 2015
Mother ‘s age		34.4±4.0
Mothers with allergies		29%
Mothers who drink coffee		33%
Coffee consumption (per day)		1.2±0.4
Mothers who drink infusions		3%
Vegetarian diet (partially)		1%
Pregnancies		
	Primiparous	90%
	Multiparous	10%
Birth procedure		
	Natural	77%
	Cesarean	23%
Baby sex		
	Male	51%
	Female	49%
Weight at birth (g)		3170±734
Gestation (weeks)		38±4
Lactation (months)		7±6

Table A3. Summary of the macronutrient analysis of the milk samples and related parameters. SNF: non-lipid solids.

Fat content (%)	3.7 ± 1.0
SNF (%)	8.1 ± 0.3
Lactose (%)	6.6 ± 0.3
Proteins (%)	1.2 ± 0.1
Density (kg m^{-3})	27.5 ± 1.4
pH	6.6 ± 0.2

Table A4. Turbulent Flow and Liquid Chromatographic experimental conditions. f.a.: formic acid.

	Turbulent Flow Chromatography				Liquid Chromatography		
Time (min)	**Flow ($ml\ min^{-1}$)**	**%Water (0.1% f.a.)**	**%MeOH (0.1% f.a.)**	**Status**	**Flow ($ml\ min^{-1}$)**	**%Water (0.1% f.a.)**	**%MeOH (0.1% f.a.)**
00:40	1	75	25	Loading Sample	0.3	75	25
02:40	0.2	0	100	**Transfer to the chromatograph**	0.2	50	50
04:10	1	50	50	Washing	0.3	10	90
04:25	1	0	100	Washing	0.3	0	100
14:00	1	0	100	Washing / Loading Loop	0.3	0	100
16:00	1	75	25	Conditioning	0.3	75	25
18:00	1	75	25	Conditioning	0.3	75	25

Table A5. Transitions, ion guide stacked ring energy (S-Lens), and collision energy (CE) for each compound.

Compound	Precursor ion m/z	Product ion m/z	S-Lens (V)	CE (V)
	215	137	61	18
	215	81	61	33
	229	151	76	24
	229	77	76	35
	199	121	54	17
	199	77	54	31
	215	121	62	18
	215	93	62	29
	255	165	67	38
	255	141	67	37
	291	161	30	63
	291	133	30	63
	362	232	71	21
	362	204	34	34
	278	151	119	30
	278	166	119	20
	166	120	60	18
	166	94	60	17
	120	92	76	21
	120	65	76	15
	134	79	78	24
	134	77	78	17
	268	212	73	19
	268	57	73	23
	226	120	54	30
	226	107	54	15
	448	370	117	22
	448	91	117	19
	324	212	113	18
	324	57	113	28
	316	260	74	18
	316	107	74	24
	358	302	69	17
	358	246	69	34
	352	282	88	13
	352	43	88	23
	324	167	60	47
	324	92	60	41

Table A6. Recovery rates at three spike levels for the different columns tested: a) Cyclone; b) Cyclone P; c) Cyclone MAX; d) C18 XL. n.a. not applicable-not results.

a)

Recovery rates (%) (n=7)						
Compound	**Spike level 100 ngg^{-1}**	**RSD (%)**	**Spike level 50 ngg^{-1}**	**RSD (%)**	**Spike level 25 ngg^{-1}**	**RSD (%)**
Cyclone						
BP1	82	5	71	1	67	1
BP3	79	4	69	1	54	6
4HB	79	2	71	2	62	2
4DHB	67	3	70	6	57	2
4MBC	66	3	61	8	61	3
ODPABA	77	6	64	6	63	4
EtPABA	54	7	53	8	47	7
OC	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
EHMC	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
BZT	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
MeBZT	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
TBPHBT	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
UVP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
UV234	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
UV320	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
UV326	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
UV327	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
UV328	18	4	39	13	57	4
UV329	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

b)

Recovery rates (%) (n=7)						
Compound	**Spike level 100 ngg^{-1}**	**RSD (%)**	**Spike level 50 ngg^{-1}**	**RSD (%)**	**Spike level 25 ngg^{-1}**	**RSD (%)**
			Cyclone P			
BP1	77	1	64	7	63	6
BP3	73	7	69	6	65	13
4HB	73	1	64	5	65	8
4DHB	69	3	61	4	69	7
4MBC	70	8	69	6	65	3
ODPABA	47	2	41	6	39	10
EtPABA	61	3	65	9	80	15
OC	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
EHMC	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
BZT	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
MeBZT	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
TBPHBT	51	6	34	4	35	15
UVP	62	2	58	9	27	14
UV234	45	2	51	4	67	5
UV320	37	5	39	8	45	11
UV326	11	5	13	9	13	3
UV327	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
UV328	2	18	3	12	3	18
UV329	44	2	42	7	35	1

c)

Recovery rates (%) (n =7)						
Compound	Spike level 100 ngg^{-1}	RSD (%)	Spike level 50 ngg^{-1}	RSD (%)	Spike level 25 ngg^{-1}	RSD (%)
Cyclone MAX						
BP1	91	5	77	1	74	1
BP3	76	4	75	1	73	6
4HB	87	2	73	2	66	2
4DHB	177	3	66	6	10	2
4MBC	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
ODPABA	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
EtPABA	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
OC	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
EHMC	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
BZT	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
MeBZT	67	13	63	10	80	12
TBPHBT	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
UVP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
UV234	37	5	49	14	59	15
UV320	37	17	54	10	60	6
UV326	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
UV327	53	6	86	8	180	3
UV328	33	6	68	6	125	5
UV329	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

d)

Recovery rates (%) (n =7)						
Compound	Spike level 100 ngg^{-1}	RSD (%)	Spike level 50 ngg^{-1}	RSD (%)	Spike level 25 ngg^{-1}	RSD (%)
C18 XL						
BP1	62	1	41	7	22	6
BP3	65	7	48	6	35	14
4HB	66	1	39	5	6	3
4DHB	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
4MBC	85	8	58	6	46	11
ODPABA	84	2	60	6	40	9
EtPABA	80	3	23	9	31	12
OC	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
EHMC	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
BZT	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
MeBZT	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
TBPHBT	75	5	75	7	83	12
UVP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
UV234	46	6	53	6	74	1
UV320	34	1	27	8	37	7
UV326	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
UV327	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
UV328	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
UV329	55	7	54	6	56	14

Table A7. Concentrations of UV-Fs (ng g^{-1} milk) in the samples where UV-Fs where detected. <LOQ: below the limits of quantification; n.d.; not detected. In parenthesis, the value of the corresponding LOQ expressed in (ng g^{-1} milk).

	UV-Fs concentrations (ng g^{-1} milk)							
Sample	**BP3**	**4HB**	**4DHB**	**4MBC**	**TBHPBT**	**UV320**	**UV329**	**∑UV-Fs***
14.10-07	n.d.	n.d.	<LOQ (2.0)	n.d.	n.d.	n.d.	n.d.	0.2
21.10-02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOQ (3.3)	2.1
21.10-05	<LOQ (0.30)	n.d.	n.d.	2.6	35.2	n.d.	n.d.	38.0
22.10-02	n.d.	n.d.	n.d.	n.d.	84.7	n.d.	n.d.	84.7
22.10-04	2.8	n.d.	n.d.	<LOQ (1.6)	n.d.	n.d.	n.d.	3.9
22.10-06	n.d.	n.d.	n.d.	<LOQ (1.6)	<LOQ (5.1)	n.d.	n.d.	4.4
23.10-06	<LOQ (0.3)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.2
23.10-07	<LOQ (0.3)	n.d.	n.d.	n.d.	<LOQ (5.1)	n.d.	n.d.	3.5
23.10-10	<LOQ (0.3)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.2
23.10-13	<LOQ (0.3)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.2
28.10-03	<LOQ (0.3)	n.d.	n.d.	n.d.	n.d.	n.d.	98.9	99.1
28.10-04	<LOQ (0.3)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.2
28.10-06	n.d.	n.d.	n.d.	n.d.	<LOQ (5.1)	n.d.	n.d.	3.3
28.10-08	n.d.	n.d.	n.d.	n.d.	<LOQ (5.1)	n.d.	n.d.	3.3
29.10-01	n.d.	n.d.	n.d.	n.d.	<LOQ (5.1)	n.d.	n.d.	3.3
29.10-06	n.d.	n.d.	n.d.	n.d.	<LOQ (5.1)	n.d.	n.d.	3.3
29.10-09	39.8	n.d.	19.9	n.d.	n.d.	n.d.	n.d.	59.7
29.10-10	52.1	3.9	23.3	n.d.	n.d.	n.d.	<LOQ (3.3)	81.4
29.10-11	40.2	n.d.	27.9	n.d.	n.d.	n.d.	116.9	185.0
29.10-12	226.5	n.d.	30.3	n.d.	n.d.	n.d.	n.d.	256.8
29.10-13	147.7	n.d.	43.3	n.d.	n.d.	346.0	434.1	971.1
30.10-01	76.1	n.d.	n.d.	n.d.	n.d.	523.6	186.5	786.1
30.10-02	68.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	68.6
30.10-03	799.9	n.d.	30.6	n.d.	n.d.	n.d.	n.d.	830.5
30.10-04	47.1	n.d.	n.d.	n.d.	<LOQ (5.1)	n.d.	n.d.	50.3
30.10-05	108.0	n.d.	n.d.	10.8	<LOQ (5.1)	n.d.	<LOQ (3.3)	124.2
30.10-06	371.0	4.7	24.0	n.d.	n.d.	n.d.	n.d.	399.6

*For the calculation of the total loads, ∑UV-Fs, (LOD+LOQ)/2 was taken as the concentration value for those <LOQs.

Table A8. Concentrations of UV-Fs (ng g^{-1} lw milk) in the sample where UV-Fs where detected. <LOQ: below the limits of quantification; n.d.; not detected. In parenthesis, the value of the corresponding LOQ expressed in (ng g^{-1} lw milk).

	Concentrations ng g^{-1} lw							
Sample	**BP3**	**4HB**	**4DHB**	**4MBC**	**TBHPBT**	**UV320**	**UV329**	**∑UV-Fs***
14.10-07	n.d.	n.d.	<LOQ	n.d.	n.d.	n.d.	n.d.	7.6
21.10-02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOQ	52.2
21.10-05	<LOQ	n.d.	n.d.	46.6	643.5	n.d.	n.d.	693.8
22.10-02	n.d	n.d.	n.d.	n.d.	2,258.7	n.d.	n.d.	2,258.7
22.10-04	70.4	n.d.	n.d.	<LOQ	n.d.	n.d.	n.d.	96.7
22.10-06	n.d.	n.d.	n.d.	<LOQ	<LOQ	n.d.	n.d.	131.8
23.10-06	<LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3.6
23.10-07	<LOQ	n.d.	n.d.	n.d.	<LOQ	n.d.	n.d.	92.1
23.10-10	<LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4.5
23.10-13	<LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	5.1
28.10-03	<LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	2,050.8	2,055.0
28.10-04	<LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4.6
28.10-06	n.d.	n.d.	n.d.	n.d.	<LOQ	n.d.	n.d.	102.5
28.10-08	n.d.	n.d.	n.d.	n.d.	<LOQ	n.d.	n.d.	90.7
29.10-01	n.d.	n.d.	n.d.	n.d.	<LOQ	n.d.	n.d.	57.2
29.10-06	n.d.	n.d.	n.d.	n.d.	<LOQ	n.d.	n.d.	94.3
29.10-09	975.5	n.d.	486.5	n.d.	n.d.	n.d.	n.d.	1,462.0
29.10-10	1,160.4	85.7	518.9	n.d.	n.d.	n.d.	<LOQ	1,812.9
29.10-11	1,145.3	n.d.	793.4	n.d.	n.d.	n.d.	6,661.0	5,269.2
29.10-12	6,056.2	n.d.	810.2	n.d.	n.d.	n.d.	n.d.	6,866.3
29.10-13	3,274.9	n.d.	960.1	n.d.	n.d.	7,670.7	4,812.6	21,531.0
30.10-01	1,217.6	n.d.	n.d.	n.d.	n.d.	8,376.8	2,983.2	12,577.6
30.10-02	1,348.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1,348.7
30.10-03	34,183.8	n.d.	1,307.7	n.d.	n.d.	n.d.	n.d.	35,491.5
30.10-04	1,336.7	n.d.	n.d.	n.d.	<LOQ	n.d.	n.d.	1,430.4
30.10-05	2,306.6	n.d.	n.d.	230.8	<LOQ	n.d.	<LOQ	2,653.8
30.10-06	10,449.3	131.0	676.1	n.d.	n.d.	n.d.	n.d.	11,256.3

*For the estimation of the total loads, ∑UV-Fs, (LOD+LOQ)/2 was taken as the concentration value for those <LOQs Fat values applied for each individual sample in Table A7. <LOQ not specified for each sample.

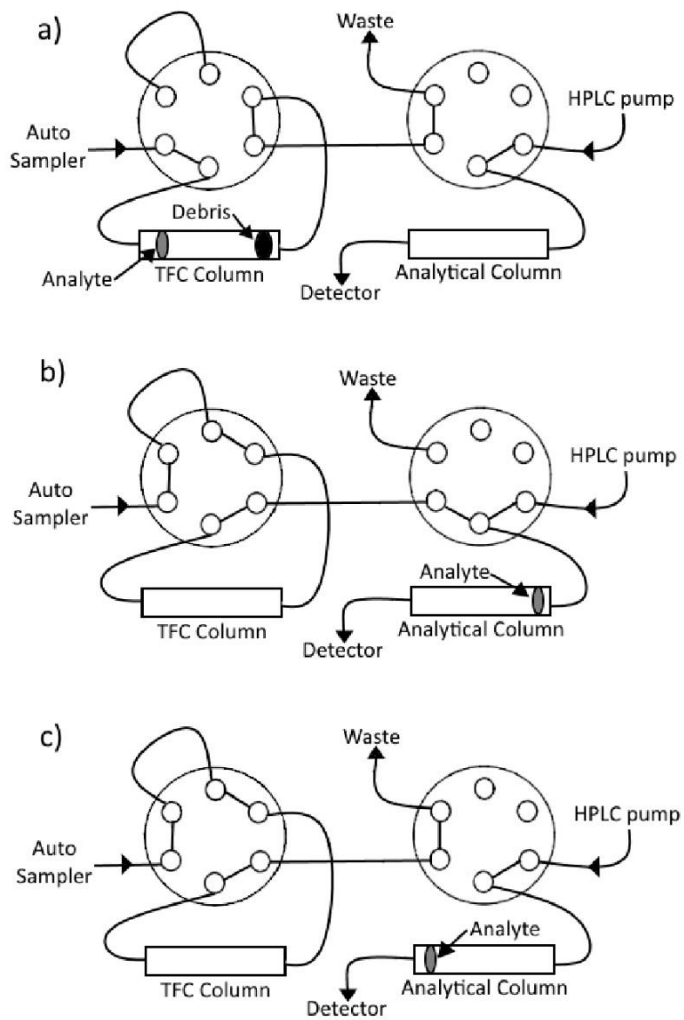

Figure A1.

1a. Focus-Mode: Loading step. The sample is injected onto the TFC column, where the analyte is retained whereas the debris from the matrix is led to waste.

1b. Focusing: Transfer step. The flow of both columns is combined and led into the analytical column.

1c. Focus-Mode: Eluting Step. The analytes eluted from the TFC column into the analytical column. The TFC column is washed and conditioned for the next injection.