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Electronic Supplementary Material

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Title: ANTHROPOGENIC CONTAMINANTS IN FRESHWATER FROM THE NORTHERN ANTARCTIC PENINSULA REGION

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Table S1. UV Filters analyzed and their properties.

Acronym	Name	CAS number	Log K_{ow}*
BP1	Benzophenone 1	131-56-6	3.17
BP3	Oxybenzone, Benzophenone 3	131-57-7	3.79
4HB	4-Hydroxybenzophenone	1137-42-4	3.02
4DHB	4,4'-Dihydroxybenzophenone	611-99-4	2.55
DHMB	2,2'-dihydroxy-4-methoxybenzophenone, Benzophenone 8	131-53-3	3.82
EHMC	Ethylhexyl methoxycinamate	5466-77-3	5.80
4MBC	4-methylbenzilydene camphor	36861-47-9	4.95
OC	Octrocrylene	6197-30-4	7.53
ODPABA	Ethylhexyl dimethyl PABA	21245-02-3	6.15
Et-PABA	Ethyl PABA	94-09-7	1.86
BZT	1-H-benzotriazole	95-14-7	1.23
MeBZT	Methyl-benzotriazole	136-85-6	1.89

BP1, BP3, 4HB, 4DHB, DHMB, OC, EHMC, OD-PABA, EtPABA, and (BZT were obtained from Sigma-Aldrich (Steinheim, Germany) with a purity above 99%; 4MBC (99% of purity) was supplied by Dr. Ehrenstorfer (Augsburg, Germany) and MeBZT, purity >99% by TCI (Zwijndrecht, Belgium). Isotopically labelled compounds 2-hydroxy-4-methoxy-2',3',4',5',6'-d5 (BP3-d5) and 3-(4-methylbenzylidene-d4) camphor used as internal standards (99% purity) were supplied by CND isotopes (Quebec, Canada).

*Data on Kow from Gago-Ferrero et al. (2012). An overview of UV-absorbing compounds (organic UV filters) in aquatic biota. *Analytical and Bioanalytical Chemistry*, 404: 2597-2610.

Table S2. Pyrethroids analyzed and their properties.

Pyrethroids	**Molecular formula**	**Molecular mass (g mol^{-1})**	**Log K_{ow}**	**Solubility in water at 20 °C (µg L^{-1})**	**DT$_{50}$* in soil (days)**	**DT$_{50}$* in water (days)**
Bifenthrin	$C_{23}H_{22}O_2ClF_3$	422.9	6.6	1	26	8
Permethrin	$C_{21}H_{20}O_3Cl_2$	391.3	6.1	200	13	23
Resmethrin	$C_{22}H_{26}O_3$	338.5	5.43	10	30	-
Tetramethrin	$C_{19}H_{25}NO_4$	331.4	4.6	1.830	3	-
Cyfluthrin	$C_{22}H_{18}NO_3Cl_2F$	434.3	6	6.6	33	1
Cyhalothrin	$C_{23}H_{19}NO_3ClF_3$	449.9	6.9	4	57	-
Cypermethrin	$C_{22}H_{19}NO_3Cl_2$	416.3	5.3	9	22	3
Deltamethrin	$C_{22}H_{19}NO_3Br_2$	505.2	4.6	0.2	58	17
Fenvalerate	$C_{25}H_{22}NO_3Cl$	419.9	5.01	1	67	30
Fluvalinate	$C_{26}H_{22}N_2O_3ClF_3$	502.9	3.85	2	7	-

*degradation time for 50% of the substance.

Table S3.Per- and polyfluoroalkyl substances (PFASs) analyzed.

Compound	Acronym	CAS No.
Perfluorocarboxilic acids		
Perfluorobutanoic acid	PFBA	375-22-4
Perfluoropentanoic acid	PFPA	2706-90-3
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluoroheptanoic acid	PFHpA	375-85-9
Perfluorooctanoic acid	PFOA	335-67-1
Perfluorononanoic acid	PFNA	375-95-1
Perfluorodecanoic acid	PFDA	335-76-2
Perfluoroundecanoic acid	PFUdA	2058-94-8
Perfluorododecanoic acid	PFDoDA	307-55-1
Perfluorotridecanoic acid	PFTrA	72629-94-8
Perfluorotetradecanoic acid	PFTeA	376-06-7
Perfluorohexadecanoic acid	PFHxDA	67905-19-5
Perfluorooctadecanoic acid	PFODA	16517-11-6
Perfluorosulfonic acids		
Perfluorobutanesulfonate acid	PFBS	374-73-5
Perfluorohexasulfonate acid	PFHxS	29420-49-3
Perfluorooctanesulfonate acid	PFOS	1763-23-1
Perfluorodecanesulfonate acid	PFDS	335-77-3
Perfluorosulfonamides		
Perfluorooctanesulfonamide acid	PFOSA	4151-50-2
Fluoro Telomer acids		
2-perfluorohexyl ethanoic acid	FHEA	53826-12-3
2-Perfluorooctyl ethanoic acid (8:2)	FOEA	27854-31-5
2-perfluorodecyl ethanoic acid	FDEA	53826-13-4

Chemical Analysis

UV-Fs and benzotriazoles

Detailed Description of the analytical methods applied:

On-line trace enrichment and purification for water samples

Preconcentration of the samples and its chromatographic separation was performed using an automated on-line SPE–LC device SymbiosisTM Pico from Spark Holland (Emmen, The Netherlands). The base of the SymbiosisTM Pico system is a high-end HPLC system with a high performance injector that handles sample volumes from 10 µL up to 5 mL fully automated. This equipment also counts with the AliasTM autosampler that includes positive headspace pressure, extensive wash routines for minimal carry over and 2 injection modes, off-line and on-line SPE.

On-line SPE preconcentration of all samples (previously filtered), aqueous standard solutions and blanks was performed by loading 5 mL of the corresponding solutions at 1 mL/min through a PLRP-s cartridge previously conditioned with 1 mL of MeOH, 1 mL of ACN and 1 mL of HPLC water (flow rate 5 mL/min). After sample loading and prior to elution, the cartridges are washed with 0.5 mL of HPLC water at a flow rate of 5 mL/min to complete transfer of the sample and remove interferences such as inorganic salts.

After completion of each SPE sampling load, the trapped analytes are eluted to the LC column with the chromatographic mobile phase.

Trace enrichment and purification for suspended particulate matter

The solid samples were automatically extracted and purified by pressurized liquid extraction (PLE) with an ASE-350 Accelerated Solvent Extractor from Dionex Corporation (Thermo Fisher Scientific, Sunnyvale, CA, USA). The sample (1 g of the previously weighted filter containing the suspended particulate matter) was added to 1 g of activated neutral alumina,

which had been put over a cellulose filter placed at the bottom of the PLE cell. Finally, the cell was filled until the top with alumina to avoid any empty volume. The PLE extraction was achieved by using MeOH and the mixture MeOH:HPLC-water (1:1 v/v) as extracting solvents. The obtained extracts were diluted to 25 ml with MeOH. A 2 ml aliquot of the diluted extract was then passed twice through 0.45 µm syringe filters to a LC-vial and evaporated to dryness under nitrogen in a TurboVap LV evaporator (Zymark, Hopkin, MA, USA). Finally, the residues were reconstituted with the internal standards solution to a final volume of 1 mL for further LC-ESI-(QqLIT) MS/MS analysis.

LC-ESI-(QqLIT) MS/MS analysis

Analyses were performed by liquid chromatography-tandem mass spectrometry using a 4000 Q TRAP™ MS/MS system from Applied Biosystems-Sciex (Foster City, California, USA). 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. In the optimized method for the positive ionization (PI) mode, elution of the trapped analytes to the LC system were performed with the chromatographic gradient. The mobile phase consisted of a mixture of HPLC grade water and ACN, both 0.1% formic acid. In the negative ionization (NI) mode, the mobile phase consisted of HPLC grade water containing 5 mM of ammonium acetate (pH 6.8). The adopted elution gradient started with 5 % of ACN, increasing to 75 % in 7 min, and then to 100 % in the following 3 min. Pure organic conditions were kept constant for 5 min and finally initial conditions were reached in the next 2 min. The total run time for each injection was 23 min. The mobile phase flow rate was set to 0.3 mL/min.

MS/MS detection was performed in PI and NI electrospray (ESI) ionization mode under selected reaction monitoring (SRM) mode. Two major characteristic fragments of the precursor molecular ion ($[M+H]^+$ or $[M-H]^-$) were monitored per analyte to enhance method sensitivity and selectivity. The most abundant transition was used for quantification, whereas the second most abundant was used for confirmation. Fragmentation voltage and collision energy were optimized for each transition. For the PI mode, ESI conditions were obtained as a compromise

using the optimum values for most compounds. Optimum conditions were: capillary voltage, 5000 V; source temperature, 700 ºC; curtain gas, 30 psi; ion source gas 1, 50 psi, ion source gas 2, 60 psi; entrance potential 10 V. For the NI mode, ESI conditions were as follows: capillary voltage, -4000 V; source temperature, 500 ºC, curtain gas 20 psi, ion source gas 1, 50 psi, ion source gas 2, 60 psi; entrance potential -10 V.

This procedure was in compliance with the European Council Directive 2002/657/EC, that although it was initially conceived for food residue analysis, it has been accepted by the scientific community for environmental analysis. Chromatographic retention times (t_R), SRM transitions, cone voltages, collision energies and the proposed ions for the transitions can be found in Gago-Ferrero et al., 2013. Instrument control and data acquisition and evaluation were performed with Analyst 1.4.2 software from Applied Biosystems/MDS Sciex and the Symbiosis from the Symbiosis Pico for Analyst software.

Table S4. Particulate matter-water distribution coefficient. For calculations, the values <LOQ were assigned the respective LOD, and for <LOD zero was used.

Kd	**BP3**	**BP1**	**4HB**	**4DHB**	**4MBC**	**EtPABA**	**BZT**	**MeBZT**
Stream 1	0.76	0.00	0.31	0.27	0.48	0.00	0.00	0.00
Stream 2	0.12	0.33	0.07	0.27	0.04	0.00	0.22	0.10
Stream 3	0.28	0.13	0.65	0.27	0.05	0.00	0.16	0.01
Stream 4	3.17	0.00	14.3	0.27	0.48	0.00	4.67	0.00
Stream 5	0.08	0.04	1.58	0.27	0.48	0.00	0.00	0.00
Stream 6	0.03	2.11	7.42	0.27	0.48	0.00	0.00	
Pond 1	0.49	0.00	1.10	0.27	0.11	0.00	0.04	0.00
Pond 2	0.09	0.00	87.0	0.37	0.48	0.00	0.00	0.00
Glaciar Drain	0.73	0.14	0.84	0.27	0.48	0.00	0.29	14.0
WWD	0.13	0.00	0.71	0.27	0.48	0.00	0.02	0.00

Pyrethroids

Table S5. Recoveries, relative standard deviations (RSD), limits of detection (mLOD) and limits of quantification (mLOQ) for each analysed pyrethroid.

Compound	Recovery (%)	RSD (%)	mLOD (ng/L)	mLOQ (ng/L)
Resmethrin	68	5	2.19	7.30
Bifenthrin	100	4	0.04	0.12
Tetramethrin	94	13	2.03	6.77
Cyhalothrin	100	5	0.03	0.11
Permethrin	98	3	0.48	1.60
Cyfluthrin	97	2	0.10	0.33
Cypermethrin	95	1	0.14	0.45
Esfenvalerate	100	3	0.14	0.48
Fluvalinate	99	4	0.03	0.09
Deltamethrin	96	15	0.38	1.25

References

Gago-Ferrero, P., Mastroianni, N., Díaz-Cruz, M.S., Barceló, D., 2013. Fully automated determination of nine ultraviolet filters and transformation products in natural waters and wastewaters by on-line solid phase extraction-liquid chromatography-tandem mass spectrometry. *Journal of Chromatography A* 1294: 106.