Supporting Information for

"Degradation of Organic UV filters in Chlorinated Seawater Swimming Pools: Transformation Pathways and Bromoform Formation"

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Tarek Manasfi^a, Bruno Coulomb^a, Sylvain Ravier^a, Jean-Luc Boudenne^{a,*}

^aAix Marseille Univ, CNRS, LCE, Marseille, France.

* Corresponding author. Phone +33-(0)413-551-031; Fax +33-(0)413-551-060; e-mail: jean-luc.boudenne@univ-amu.fr

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Analyte	RT (min)	Parent Ion [M+H] ⁺	Cone Voltage (V)	Fixed CE* Value (V)	Fragments
DIOXY	3.65	245.1	25	6	151.0397, 121.0293
OXY	3.83	229.1	30	7	105.0341, 151.0394
OC	4.08	362.2	30	1	232.0764, 250.0872
AVO	4.26	311.2	25	8	135.0443, 161.0965
OMC	4.29	291.2	15	1	161.0601, 179.0708
BD-10 (surrogate)	3.85	193.1	20	8	82.0703, 110.0650

Table S1. UV Filter Retention time (RT) and MS/MS operating conditions

*CE: Collision Energy

Fable S2. LLE-LC-MSMS method performance characteristics for the analysis of	UV
ïlters	

Analyte	Recovery (%) (n=3)	Precision (%) (repeatability) (n=3)	Linearity (r ²)	Range (ng/L)	LOD (ng/L)	LOQ (ng/L)
BP-3	93	13	0.997	5-1000	1	5
BP-8	89	16	0.992	10-1000	8	20
Avobenzone	97	8	0.998	15-1000	5	15
OMC	102	11	0.998	25-1000	5	15
OC	117	14	0.995	20-1000	5	15
BP-d10	94	10	0.991	10-1000	10	30

Table S3. Physicochemical parameters, bromide concentration, free and combined chlorine

Pool	Temperature (°C)	рН	[Br-] (mg L ⁻¹)	Conductivity (mS cm ⁻¹)	Free Chlorine (mg L ⁻¹)	Combined chlorine (mg L ⁻¹)
Adults' Pool	26.8	8.08	73.2	56.2	1.7	0.6
Children's Pool	29.6	8.04	68.1	55.7	3.1	1.8



Figure S1. Disappearance of UV filters in chlorination reactions with solar irradiation (red points) and without solar irradiation (blue points). Chlorination reactions were conducted according to the protocol described in the manuscript at a ratio of UV filter:chlorine concentration of 1:25.

Separation of analytes were achieved using a CORTECS UPLC column (Waters Acquity C18 2.1×100 mm, 1.6 µM) at 40 °C. The mobile phase consisted of A: water and B: methanol (ULC/MS grade, Bisolve). Both solvents A and B contained 5 mM ammonium formate. Elution was performed at a flow rate of 0.4 ml min⁻¹ with a gradient starting at 15% of B and increasing to reach 100% within 6 min and held for 1 min. The sample injection volume was 5 µL. The ESI source contained two individual orthogonal sprays. One spray was for the column eluent while the other was for the internal standard (lockmass). During each chromatographic run, leucine enkephalin (2 mg L⁻¹, C₂₈H₃₇N₅O₇, MW 555.27, Waters Q-ToF product) was used for lock-mass correction to obtain accurate masses for each organic component eluting from the column. A solution of sodium formate (HCOONa, Waters Q-ToF product) was infused daily in the ESI source to calibrate the instrument. Optimum ESI conditions were found using a 2.5 kV capillary voltage, 450 °C desolvation temperature, 120 °C source temperature, 20 L h⁻¹ cone gas flow rate and 800 L h⁻¹ desolvation gas flow rate. The optimum sample cone voltage for each analyte is described in Table S1. The ESI source has been optimized directly with the samples. These parameters allowed increasing the signal to noise ratio maintaining soft ionization technique. Data were collected from 50 to 600 Da in the positive and negative ionization modes. The mass spectrometer was used in its resolution mode. Compounds responding in positive mode were detected as their protonated molecules $([M + H]^{+})$ or sodium adducts $([M + Na]^{+})$ or potassium adducts $([M + K]^{+})$ while compounds responding in the negative mode were detected as deprotonated molecules ($[M - H]^{-}$).

Target analytes were separated on a capillary column DB5-ms (30 m × 0.25 mm × 1 μ m). Helium 5.0 was used as a carrier gas at a programmed flow of 1 ml min⁻¹ and nitrogen as makeup gas at a flow of 30 ml min⁻¹. Injection volume was 1 μ L and injector temperature was 200 °C. Detector temperature was adjusted to 290 °C. The GC oven temperature started at 35 °C, held for 22 min, increased to 145 °C at 20°C min⁻¹ and held for 2 min, then increased to 225 °C at 20 °C min⁻¹ and held for 15 min, finally temperature increased to 260 °C at 10 °C min⁻¹ and held for 2 min.

SI-3. Operating Conditions for GC-MS Analysis

The chromatographic separation was accomplished on a TR-5MS capillary column (Thermo Electron, 30 m \times 0.25 mm \times 0.25 µm). Samples (2 µL) were injected at 280 °C in splitless mode. Helium was used as a carrier gas at a flow of 1 mL min⁻¹. Oven program was adjusted according to U.S.EPA Method 551.1 (1995). Data was recorded in the full scan mode in the mass range m/z 50–600.

SI-4. Mass Spectra of DIOXY Transformation Products









MSMS Spectrum of dibrominated DIOXY



MSMS Spectrum of tribrominated DIOXY





S8



MSMS Spectrum of tetrabrominated DIOXY

160617_DIOXY-Br4_MSMS_neg 52 (6.486) Cm (52) 5: TOF M	SMS 562.70ES-
100 3562	.6956 119
59.0945 125.4706 151.0335 228.0284 268.7022 342 1169 390.4886 421.2296 461.0909 508.9914	582 3660
50 75 100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550	575 600
160617_DIOXY-Br4_MSMS_neg 52 (6.482) Cm (52:53) 4: TOF M	SMS 560.70ES-
100- 	
⁶ 79.4701 129.0361 171.2894 198.3310 282.8677 309.1918 388.4617 422.6567 456.0241 529.6846	560.7598
0 - <u>hollowing and the second state of the second s</u>	575 600
160617 DIOXY-Br4 MSMS neg 53 (6.497) Cm (52:53) 3:00 3:23 3:00 3:23 3:00 3:23 3:00 3:00	SMS 558.70ES-
100 ₇ 558.	045 1.16e3
_	
59.8355 111.8668 202.3785 250.8530 280.8668 339.1905 384.3942 426.5471 462.7629 519.3786	574.7980
50 75 100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550	575 600
160617_DIOXY-Br4_MSMS_neg 52 (6.475) Cm (52:54) 2: TOF M	SMS 556.71ES-
100 ₇ 556.7	025 541
72.3829 122.6054 163.6661 220.4215 240.5118.256 3105 324.7283 394.4805.430.9604 472.9430 516.6662	575 9131
	m/z
50 75 100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 160617 DIOXX-Brd MSMS peg 52 (6 471) Cm (52:54) 1: TOE M	575 600 SMS 554 71FS-
100- 554.7	036 231
51.5928	
98.4257 124.6655 208.2046 241.1844 313.8752 374.8652 413.1840 474.4294 509.2438 5	55.2838
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	m(7









SI-5. Mass Spectra of OMC Transformation Products

MSMS Spectrum of Monobrominated OMC



MS Spectrum of Dibrominated OMC



SI-5. Mass Spectra of AVO Transformation Products

MSMS Spectrum of Monobrominated AVO MSMS 160617_AVO-Br_MSMS_pos 135 (6.030) Cm (131:140) 2: TOF MSMS 391.07ES+ 9.26e5 135.0410 100-161.0931 % 391.0726 416.1612 498.1507 162.0958 215.9599 534.1425 559.3821 107.0452 316.9960 n. ---- m/z 100 550 150 250 500 200 300 350 400 450 600 50 160617_AVO-Br_MSMS_pos 134 (6.019) Cm (134:139) 1: TOF MSMS 389.08ES+ 135.0410 6.78e5 100-CH₃ H₃(CH3 Вr H₃C Βí CH3 Ω H₃Ć °CH₃ 161.0931 389.074676 Da [M+H]+: H₃C $C_8H_7O_2$ % 135.0446 Da 2 $C_{11}H_{13}O$ 161.0966 Da 389.0745 218.0941 571.3985 162.0965 107.0453 503.2596 545.3477 314.9959 449.1728 0 ----- m/z 600 500 550 100 150 200 250 300 350 400 450 50

MS Spectrum of Dibrominated AVO

