

Supporting Information

Identification and Occurrence of Analogues of Dechlorane 604 in Lake Ontario Sediment and their Accumulation in Fish

Li Shen^{†‡}, Karl J. Jobst^{§‡}, Eric J. Reiner[‡], Paul A. Helm[‡], Robert McCrindle[†], Vince Y. Taguchi[‡], Chris H. Marvin[§], Sean Backus[§], Karen A. MacPherson[‡], Ian D. Brindle[†]

[†]Department of Chemistry, Brock University, 500 Glenridge Avenue, St. Catharines, Ontario, Canada L2S 3A1

[‡]Ontario Ministry of the Environment, 125 Resources Road, Toronto, Ontario, Canada M9P 3V6

[§] Environment Canada, 867 Lakeshore Road, Burlington, Ontario, Canada L7R 4A6

[†] Wellington Laboratories Inc., Guelph, Ontario, Canada N1G 3M5

Table S1. Monitored ions and their mass to charge ratios of Br_xDec604, Cl_yDec604 and HCPN analogues

Table S2. Monitored ions and their mass to charge ratios of Br_xCl_yDec604 analogues

Table S3. Summary of Br_xDec604 analogues and HCPN detected (Y) in the study.

Table S4. Concentrations of Br_xCl_yDec604 analogues in Lake Ontario surface sediment (pg/g dry wt) and fish (pg/g lipid wt)

Table S5. Concentrations (pg/g dry wt) of Dec604, Dec604 CB, total Br₂Dec604, BrDec604-III and HCPN in the Lake Ontario sediment core from site O-04.

Figure S1. Sediment sample locations in Lake Ontario

Figure S2. Illustrative chromatograms of BrDec604 analogues in standards, lake trout and sediment samples, and extracts of UV exposures of Dec604 and Dec604 CB

Figure S3. Illustrative chromatograms of tetrahalogenated Br_xCl_yDec604 analogues in sediment and lake trout

Figure S4. Illustrative chromatograms of trihalogenated Br_xCl_yDec604 analogues in sediment and lake trout

Table S1. Monitored ions and their mass to charge ratios of Br_xDec604, Cl_yDec604 and HCPN analogues.

Target Analytes	Ion Formula	<i>m/z</i>		Theoretical Ratios Ion 1 / Ion 2
		Isotopic Ion 1	Isotopic Ion 2	
1 ≤ x ≤ 5				
Br ₅ Dec604	^a C ₁₃ H ₃ Br ₅ Cl ₆	769.4212	771.4192	^d 0.88
	^b C ₈ H ₃ Br ₅	497.6111	499.6090	1.03
	^c C ₇ HBr ₅ Cl	518.5643	520.5622	0.90
Br ₄ Dec604	C ₁₃ H ₄ Br ₄ Cl ₆	691.5107	693.5078	1.08
	C ₈ H ₄ Br ₄	417.7026	419.7006	0.68
	C ₇ H ₂ Br ₄ Cl	440.6538	442.6517	1.25
Br ₃ Dec604	C ₁₃ H ₅ Br ₃ Cl ₆	611.6023	613.6002	0.86
	C ₈ H ₅ Br ₃	339.7921	341.7901	1.03
	C ₇ H ₃ Br ₃ Cl	360.7453	362.7433	0.86
Br ₂ Dec604	C ₁₃ H ₆ Br ₂ Cl ₆	533.6918	535.6888	1.12
	C ₈ H ₆ Br ₂	259.8836	261.8816	0.51
	C ₇ H ₄ Br ₂ Cl	282.8348	284.8327	1.43
BrDec604	C ₁₃ H ₇ BrCl ₆	453.7833	455.7812	0.84
	C ₈ H ₇ Br	181.9731	183.9711	1.03
	C ₇ H ₅ BrCl	202.9263	204.9243	0.77
1 ≤ y ≤ 5				
Cl ₅ Dec604	C ₁₃ H ₃ Cl ₁₁	547.675	549.672	1.03
	C ₈ H ₃ Cl ₅	275.8648	277.8619	1.54
	C ₇ HCl ₆	296.8180	298.815	1.23
Cl ₄ Dec604	C ₁₃ H ₄ Cl ₁₀	513.7139	515.7110	1.16
	C ₈ H ₄ Cl ₄	239.9067	241.9038	0.77
	C ₇ H ₂ Cl ₅	262.8570	264.8540	1.54
Cl ₃ Dec604	C ₁₃ H ₅ Cl ₉	477.7559	479.7529	0.77
	C ₈ H ₅ Cl ₃	205.9457	207.9427	1.03
	C ₇ H ₃ Cl ₄	226.8989	228.8959	0.77
Cl ₂ Dec604	C ₁₃ H ₆ Cl ₈	443.7948	445.7919	0.88
	C ₈ H ₆ Cl ₂	171.9847	173.9817	1.54
	C ₇ H ₄ Cl ₃	192.9379	194.9349	1.03
ClDec604	C ₁₃ H ₇ Cl ₇	409.8338	411.8308	1.03
	C ₈ H ₇ Cl	138.0236	140.0207	3.09
	C ₇ H ₅ Cl ₂	158.9768	160.9739	1.54
HCPN	C ₁₃ H ₈ Cl ₆	375.8728	377.8698	1.23
	C ₈ H ₈	104.0626		
	C ₇ H ₆ Cl	125.0158	127.0128	3.09

^a C₁₃: molecular ions; ^b C₈: styrene ion fragments; ^c C₇: tropylium ion fragments; ^d acceptable limits of measurement: ±15 % of the corresponding theoretical ratios.

Table S2. Monitored ions and their mass to charge ratios of Br_xCl_yDec604 analogues.

Target Analytes	Ion Formula	<i>m/z</i>		Theoretical Ratios Ion 1 / Ion 2
		Isotopic Ion 1	Isotopic Ion 2	
<i>x+y = 5</i>				
Br ₄ ClDec604	^a C ₁₃ H ₃ Br ₄ Cl ₇	725.4718	727.4688	^d 0.98
	^b C ₈ H ₃ Br ₄ Cl	453.6616	455.6595	1.25
	^c C ₇ HBr ₄ Cl ₂	474.6148	476.6118	1.06
Br ₃ Cl ₂ Dec604	C ₁₃ H ₃ Br ₃ Cl ₈	681.5214	683.5193	1.09
	C ₈ H ₃ Br ₃ Cl ₂	407.7142	409.7121	0.74
	C ₇ HBr ₃ Cl ₃	430.6644	432.6624	1.29
Br ₂ Cl ₃ Dec604	C ₁₃ H ₃ Br ₂ Cl ₉	637.5719	639.5689	1.23
	C ₈ H ₃ Br ₂ Cl ₃	363.7647	365.7617	0.92
	C ₇ HBr ₂ Cl ₄	384.7179	386.7149	0.79
BrCl ₄ Dec604	C ₁₃ H ₃ BrCl ₁₀	591.6244	593.6224	0.91
	C ₈ H ₃ BrCl ₄	319.8143	321.8122	1.20
	C ₇ HBrCl ₅	340.7675	342.7654	0.98
<i>x+y = 4</i>				
Br ₃ ClDec604	C ₁₃ H ₄ Br ₃ Cl ₇	647.5612	649.5583	1.22
	C ₈ H ₄ Br ₃ Cl ₁	373.7531	375.7511	0.85
	C ₇ H ₂ Br ₃ Cl ₂	394.7063	396.7043	0.74
Br ₂ Cl ₂ Dec604	C ₁₃ H ₄ Br ₂ Cl ₈	601.6138	603.6109	0.88
	C ₈ H ₄ Br ₂ Cl ₂	329.8036	331.8007	1.12
	C ₇ H ₂ Br ₂ Cl ₃	350.7569	352.7539	0.92
BrCl ₃ Dec604	C ₁₃ H ₄ BrCl ₉	557.6634	559.6614	1.01
	C ₈ H ₄ BrCl ₃	285.8542	287.8512	1.54
	C ₇ H ₂ BrCl ₄	306.8064	308.8044	1.20
<i>x+y = 3</i>				
Br ₂ ClDec604	C ₁₃ H ₅ Br ₂ Cl ₇	567.6528	569.6498	0.99
	C ₈ H ₅ Br ₂ Cl	295.8426	297.8406	1.43
	C ₇ H ₃ Br ₂ Cl ₂	316.7958	318.7929	1.12
BrCl ₂ Dec604	C ₁₃ H ₅ BrCl ₈	523.7024	525.7003	1.14
	C ₈ H ₅ BrCl ₂	249.8952	251.8931	0.62
	C ₇ H ₃ BrCl ₃	272.8463	274.8434	1.54
<i>x+y = 2</i>				
BrClDec604	C ₁₃ H ₆ BrCl ₇	489.7423	491.7393	1.31
	C ₈ H ₆ BrCl	215.9341	217.9321	0.77
	C ₇ H ₄ BrCl ₂	236.8874	238.8853	0.62

^a C₁₃: molecular ions; ^b C₈: styrene ion fragments; ^c C₇: tropylium ion fragments; ^d acceptable limits of measurement: ±15 % of the corresponding theoretical ratios.

Table S3. Summary of Br_xDec604 analogues detected (Y) in the study.

Br _x Dec604	Lake Ontario		Standard		Tech604		UV Exposure	
	Sediment	Fish	Wellington	TRC	Mix-A	Mix-B	Dec604	Dec604 CB ^a
Dec604	Y	Y	Y		Y			
Br ₃ Dec604								
-I (2,4,5-)	Y	Y	Y		Y		Y	Y
-II	Y	Y			Y		Y	
-III	Y	Y					Y	
2,4,6-				Y				
Br ₂ Dec604								
-I	Y	Y				Y	Y	Y
-II (3,5-)	Y	Y		Y			Y	
-III	Y	Y				Y	Y	Y
-IV	Y	Y				Y	Y	Y
BrDec604								
-I	Y	Y		Y		Y	Y	Y
-II				Y			Y	Y
-III				Y		Y	Y	Y
HCPN	Y	Y	Y			Y	Y	Y

^a Dec604 CB: 2,4,5-Br₃Dec604.

Table S4. Concentrations of Br_xCl_yDec604 analogues in Lake Ontario surface sediment (pg/g dry wt) and fish (pg/g lipid)

Sample ID	Dec604	Br ₃ Cl (total)	Br ₂ Cl ₂ (total)	Dec604CB	Br ₂ Cl (total)	BrCl ₂ (total)	Br ₂ (total)	Br-III	HCPN
<i>Sediment</i>									
O-04 ^a	7000	1700	73	1400	300	14	81	15	39
O-34 ^b	26	640	72	1100	480	18	100	23	5.0
O-46	8000	1300	110	1900	550	20	120	34	41
<i>Lake Trout</i> ^b									
O1M	63	74	37	15000	5200	360	3100	860	110
O2M	370	230	60	21000	8100	650	6500	2200	320
O3M	400	280	93	35000	14000	1100	12000	3900	180
O4F	100	99	48	20000	7300	520	4700	1400	150
O5F	110	76	28	10000	3900	280	3200	870	38
<i>Whitefish</i> ^b									
O6M	230	230	65	16000	5700	420	4000	960	75
O7M	650	600	150	25000	6900	390	2300	430	21
O8M	390	440	130	34000	11000	730	5300	1500	49
O9F	1300	890	150	21000	7100	500	5800	1800	320
O10F	340	390	190	60000	21000	1300	7200	2300	45

^a Dec604 data were taken from Shen et al.(18); ^b Dec604 data were taken from Shen et al.(16).

Table S5. Concentrations (pg/g dry wt) of Dec604, Dec604 CB, total Br₂Dec604, BrDec604-III and HCPN in Lake Ontario sediment core

Depth (cm)	Dating Year	Dec604 ^a	Dec604 CB	Br ₂ Dec604	BrDec604-III	HCPN
1	2004	7200	1100	61	10	13
2	2001	5100	1200	69	13	29
3	1995	8700	1800	110	20	75
4	1988	10000	1400	100	21	60
5	1980	6900	1600	150	21	15
6	1972	1300	400	47	6	25
7	1963	120	53	9		
8	1953	56	10			

^a Shen et al.(18).

Figure S1. Sediment sample locations in Lake Ontario.

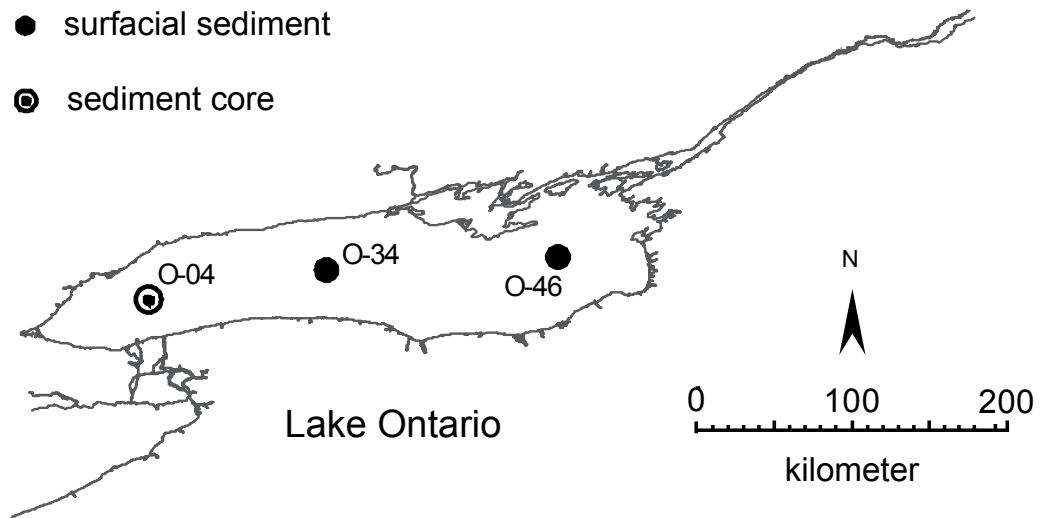


Figure S2. Illustrative fragment ion chromatograms of BrDec604 analogues in standards, lake trout and sediment samples, and extracts of UV exposures of Dec604 and Dec604 CB.

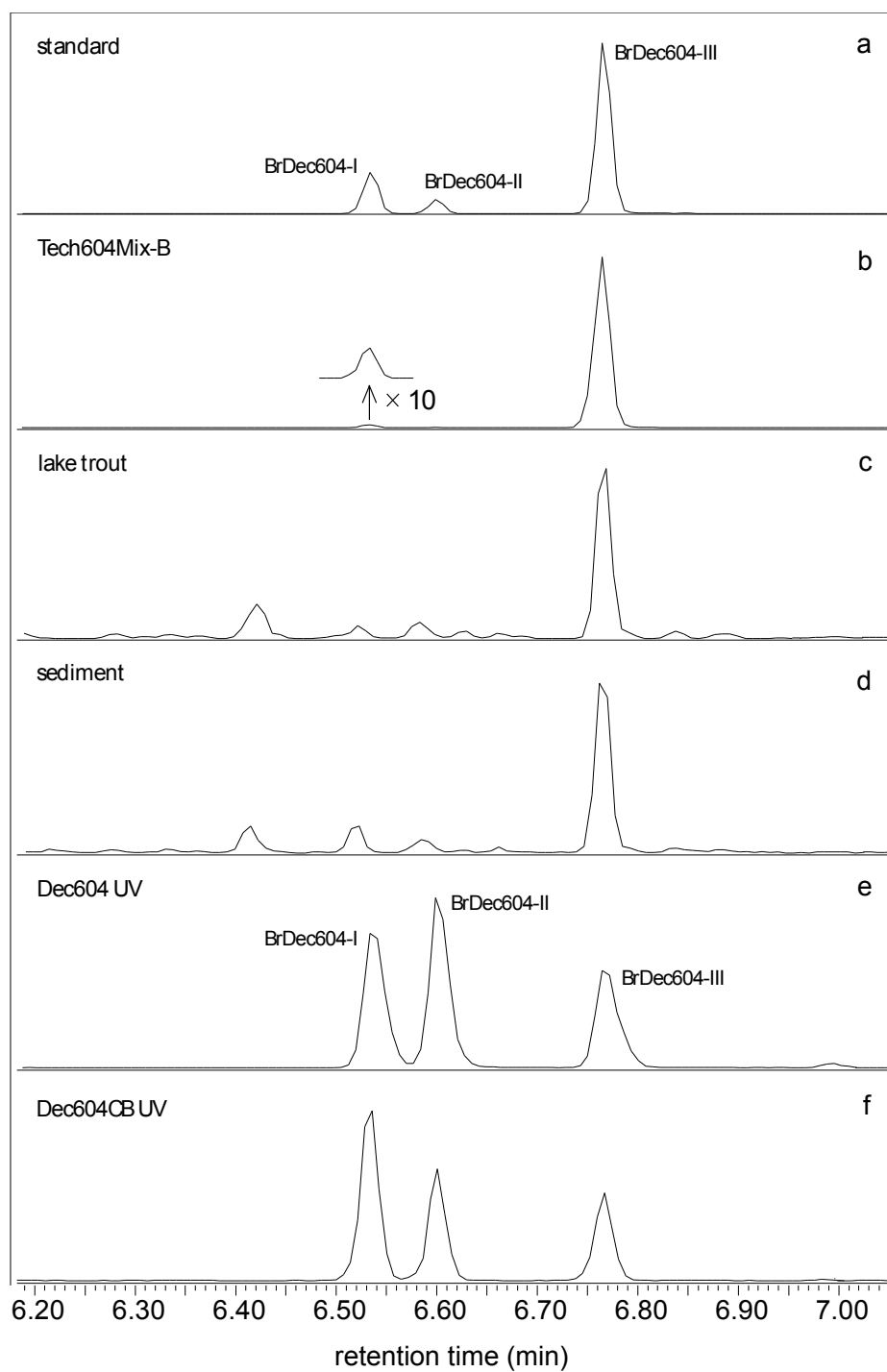


Figure S3. Illustrative chromatograms of tetrahalogenated $\text{Br}_x\text{Cl}_y\text{Dec604}$ analogues sediment (a,e-molecular ions; b,f-fragment ions) and lake trout (c,g-molecular ions; d,h-fragment ions).

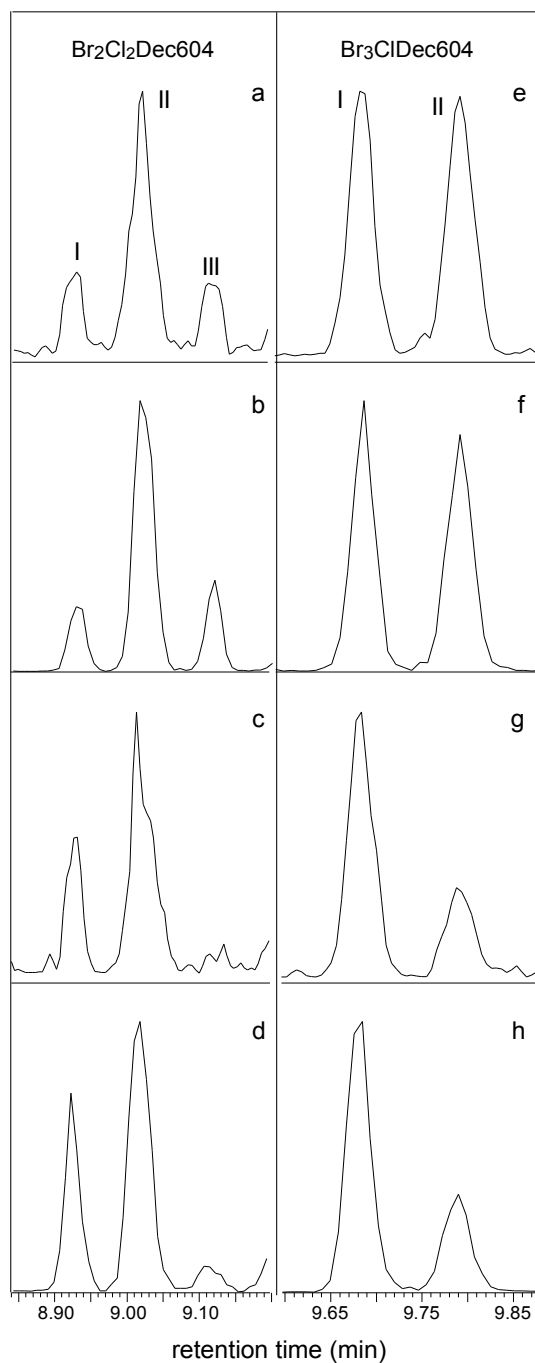


Figure S4. Illustrative chromatograms of trihalogenated $\text{Br}_x\text{Cl}_y\text{Dec604}$ analogues in sediment (a,e-molecular ions; b,f-fragment ions) and lake trout (c,g-molecular ions; d,h-fragment ions).

