Supporting Information

C12-30 α-Bromo-Chloro "Alkenes": Characterization of a Poorly Identified Flame Retardant and Potential Environmental Implications

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The Supporting Information contains 4 Figures and 3 Tables

Supporting Information

Methods – Octanol-water retention capacity, k**, determination**

Tables:

Methods

Octanol-water coefficients were determined using the OECD guidelines for the testing of chemicals.[1]

The retention capacity, k, was calculated using the equation:

$k = (t_r - t_0)/t0$,

where tr = retention time of the compound and t0 = was the retention time of methanol.

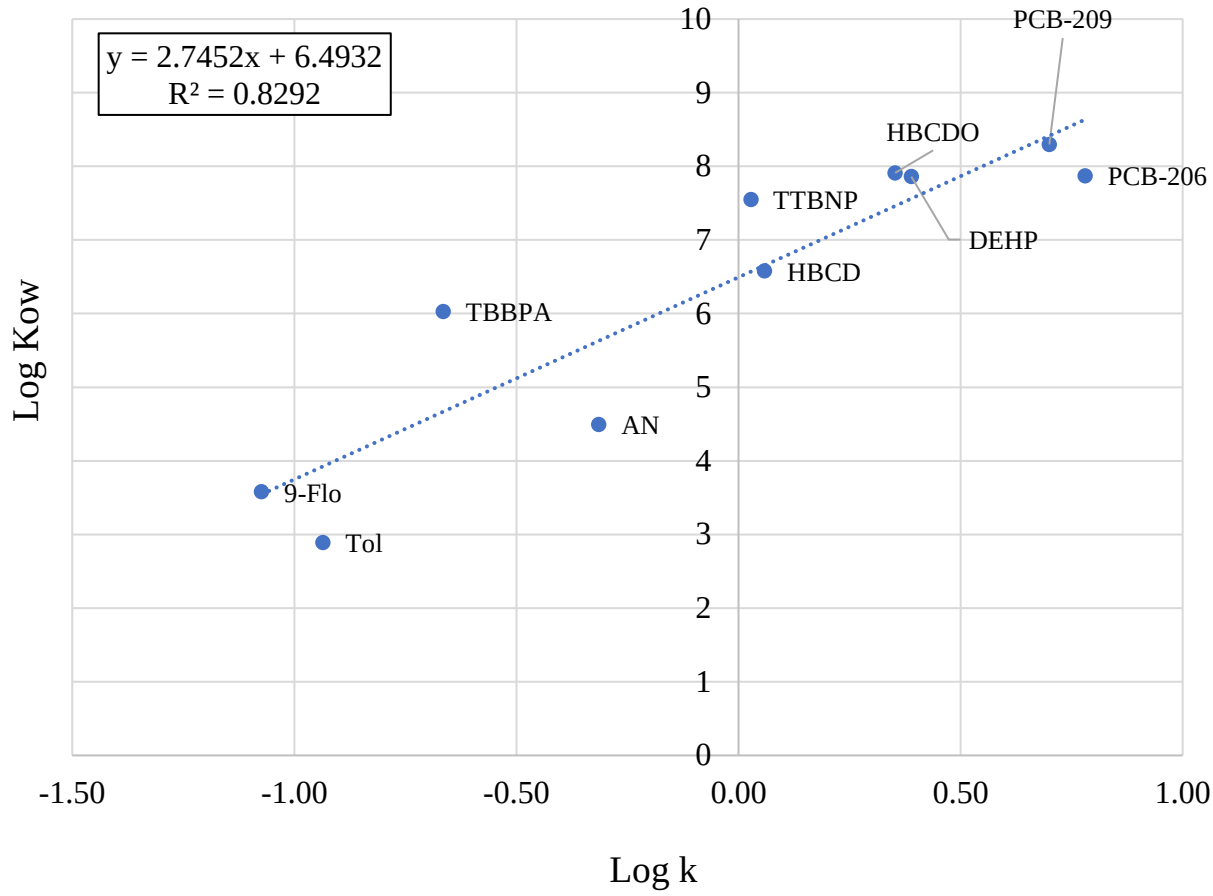

Figure S1. Regression curve of Log k vs Log K_{OW} of chemical standards.

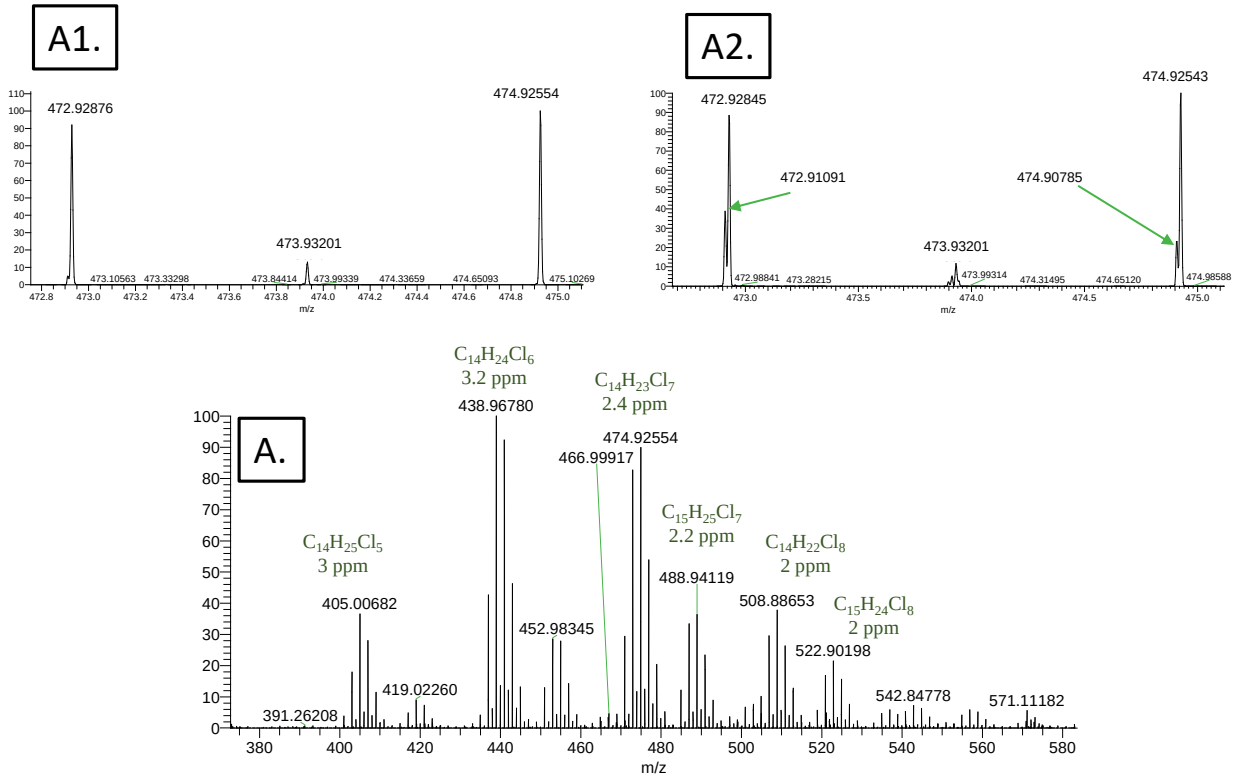

Figure S2. Averaged mass spectra of (A) CP C14-C17, 52%C, with (A1) and without (A2) Cl-enhanced APCI, shows the dominant formation of $[M+Cl]^-$ adducts.

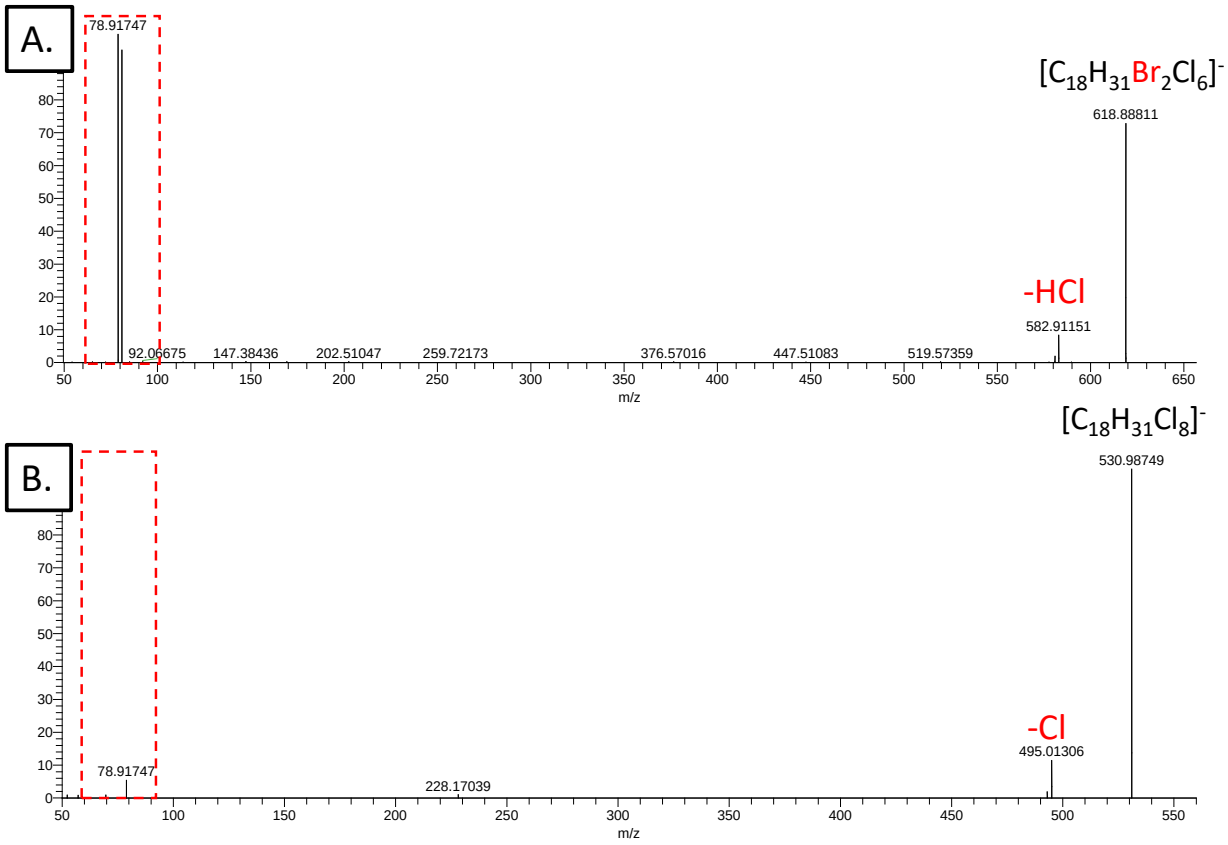

Figure S3. Full MS-ddms2 of (A) Bromine-containing C18H31Br2Cl6- and (B) Non-Bromine containing C18H31Cl8- ion in Doverguard 8207A using LC-APCI(-)-HRMS.

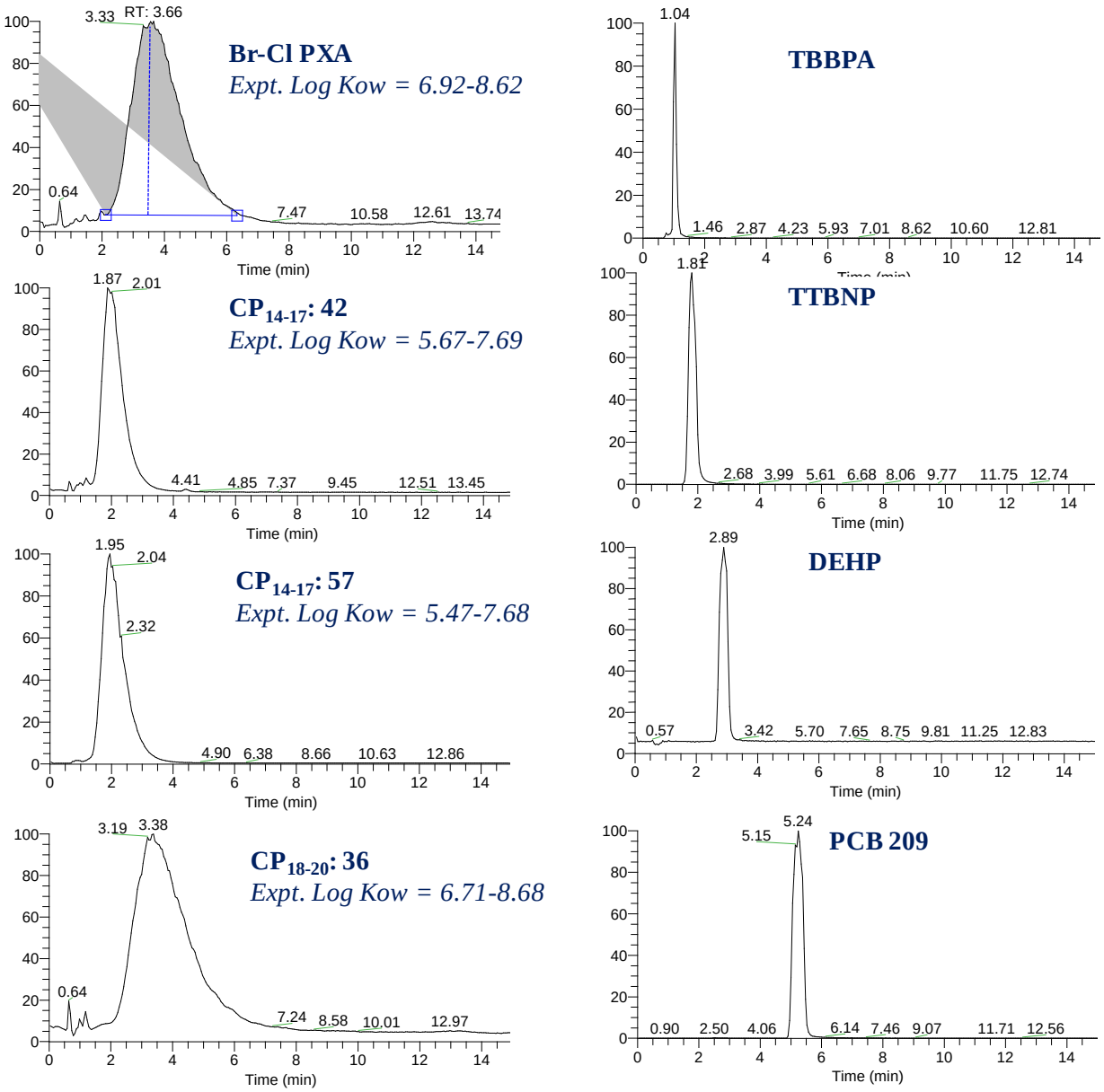

Figure S4. Chromatograms of chemical standards used in Log Kow experiments with LC-APCI(-)-HRMS.

Table S1. Chemical Standards used for regression function of Log k vs. Log K_{OW}.

Compound	Abbrv.	Log Kow	Range	Reference
9-Fluorenone	9-Flo	3.58	3.58	2, 3
Toluene	Tol	2.89	2.70-3.08	2-4
Anthrancene	AN	4.50	4.45-4.54	2, 3, 5
1,2,5,6,9,10-Hexabromocyclododecane	HBCD	6.58	5.62-7.92	6-11
Tris(tribromoneopentyl)phosphate	TTBNP	7.55		7, 8
Diethylhexylphthalate	DEHP	7.86		4
Hexachlorocyclopentadienyl-dibromocyclooctane	HBCDO	7.91		11-13
Nonachlorobiphenyl	PCB-206	7.87	7.69-8.09	14-16
Perchlorobiphenyl	PCB-209	8.30	8.16-8.28	14-17
Tetrabromobisphenol A	TBBPA	6.03	4.9-6.78	7, 8, 18, 19

Table S2. Summary of five analytical approaches used to characterize prominent PXA ions present in Doverguard 8207A.

Method	Observed/(proposed) of prominent ions	Elemental composition	Comments
GC×GC-EI-HRMS			Significant fragmentation containing Br, Cl ions; parent PXAs containing C18
GC-APCI(-)-HRMS, FTICR-MS	$C_{18}H_{29}Br_2Cl_6^-$	*Parent PXAs [M-H]$^-$ [M-X]$^-$*	Parent PXAs [M-H]$^-$ [M-Cl]$^-$ or [M-Br]$^-$
	$C_{18}H_{30}BrCl_6^-$		Lesser intensity oxygen adducts [M-Cl+O]-
	$C_{18}H_{30}Br_2Cl_5^-$		Average mass accuracy: 1.2 ppm (FTICR-MS)
	$C_{18}H_{31}BrCl_5^-$		
	$C_{18}H_{31}Br_2Cl_4^-$		
LC-APCI(-)-Orbitrap MS	$C_{18}H_{30}BrCl_8^-$	$C_{18}H_{30}BrCl_7$	[M+Cl]$^-$ adducts enhanced formation with DCM
	$C_{18}H_{30}Br_2Cl_7^-$	$C_{18}H_{30}Br_2Cl_6$	Presence $C_xH_{(2\,x-y+3)}Cl_y$ LCCPs with lesser intensities
	$C_{18}H_{30}Br_3Cl_6^-$	$C_{18}H_{30}Br_3Cl_5$	Average mass accuracy: 2.8 ppm
	$C_{18}H_{31}BrCl_7^-$	$C_{18}H_{31}BrCl_6$	
	$C_{18}H_{31}Br_2Cl_6^-$	$C_{18}H_{31}Br_2Cl_5$	
	$C_{18}H_{31}Br_3Cl_5^-$	$C_{18}H_{31}Br_3Cl_4$	
	$C_{18}H_{32}BrCl_6^-$	$C_{18}H_{32}BrCl_5$	
	$C_{18}H_{32}Br_2Cl_5^-$	$C_{18}H_{32}Br_2Cl_4$	
	$C_{18}H_{32}Br_3Cl_4^-$	$C_{18}H_{32}Br_3Cl_3$	
	$C_{18}H_{33}BrCl_5^-$	$C_{18}H_{33}BrCl_4$	
	$C_{18}H_{33}Br_2Cl_4^-$	$C_{18}H_{33}Br_2Cl_3$	
Br-enhanced APCI(-)-QTOF MS	$C_{18}H_{32}Br_4Cl_3^-$	$C_{18}H_{32}Br_3Cl_3$	[M+Br]$^-$ adducts
	$C_{18}H_{31}Br_4Cl_4^-$	$C_{18}H_{31}Br_3Cl_4$	Presence $C_{18}H_{38-y}BrCl_y$ LCCPs
	$C_{18}H_{30}Br_4Cl_5^-$	$C_{18}H_{30}Br_3Cl_5$	Average mass accuracy: 4.8 ppm
	$C_{18}H_{33}Br_3Cl_3^-$	$C_{18}H_{33}Br_2Cl_3$	
	$C_{18}H_{32}Br_3Cl_4^-$	$C_{18}H_{32}Br_2Cl_4$	
	$C_{18}H_{31}Br_3Cl_5^-$	$C_{18}H_{31}Br_2Cl_5$	
	$C_{18}H_{30}Br_3Cl_6^-$	$C_{18}H_{30}Br_2Cl_6$	
	$C_{18}H_{33}Br_2Cl_4^-$	$C_{18}H_{33}BrCl_4$	
	$C_{18}H_{32}Br_2Cl_5^-$	$C_{18}H_{32}BrCl_5$	
	$C_{18}H_{31}Br_2Cl_6^-$	$C_{18}H_{31}BrCl_6$	
	$C_{18}H_{30}Br_2Cl_7^-$	$C_{18}H_{30}BrCl_7$	

Table S3. Comparison of experimental and estimated octanol-water partition coefficients for chrlorinated parrafins. Values from the current study are shown in bold.

	Experimental		**Estimation**	
Substance	Average	range	Substance	Range
		MCCPs		
CP_{14-17}: 42.0	***6.70 ± 0.02[e]***	***5.67 - 7.69[f]***	$MCCP_{14}$[b]	6.21 - 8.09
CP_{14-17}: 57.0	***6.69 ± 0.02[e]***	***5.47 - 7.68[f]***	$MCCP_{15}$[b]	6.88 - 8.62
CP_{14}: 47.0[a]	6.30 ± 0.01	5.56 - 7.71	$MCCP_{16}$[b]	7.20 - 9.12
$C_{14}H_{23}Cl_7$[c]	5.47		$MCCP_{17}$[b]	7.35 - 9.85
CP_{15}: 50.4[a]	6.65 ± 0.02	5.84 - 7.81		
CP_{16}: 61.0[a]	6.81 ± 0.02	5.78 - 8.38		
$C_{16}H_{31}Cl_3$[d]	7.2			
$C_{16}H_{21}Cl1_3$[d]	7.36			
$C_{17}H_{31}Cl_5$[c]	8.21			
$C_{17}H_{31}Cl_7$[c]	8.01			
CP_{14-17}: 46.7[a]	6.67 ± 0.03	5.57 - 7.90		
		LCCPs		
CP_{18-20}: 36.0	***7.71 ± 0.03***	***6.71 – 8.68***		
CP_{18}: 57.7[a]	7.33 ± 0.05	6.58 - 8.60		
CP_{22}: 52.2[a]	8.57 ± 0.04	7.55 - 9.52		
CP_{24}: 56.2[a]	8.9 ± 0.04	7.26 - 10.42		
CP_{28}: 54.8[a]	10.1 ± 0.09	9.08 - 11.34		

[a] Hilger, B. et al. (2011) - Determined from reversed-phase high performance liquid chromatography
[b] Glüge, J. et al (2013) - Estimated from COSMO*therm*, SPARC, and EPI Suite™
[c] Renberg, L. et al. (1980) - Determined from reversed phase high performance thin layer chromatography
[d] Fisk, A. T., et al (1998) Determined from reversed-phase high performance liquid chromatography
[e] average log K_{OW} based on retention time corresponding to maximum intensity of peak
[f] range log K_{OW} based on minimum and maximum retention times for the chromatographic peak

1. OECD, *Test No. 117: Partition Coefficient (n-octanol/water), HPLC Method*. 2004.
2. Leo, A.; Hansch, C.; Elkins, D., Partition coefficients and their uses. *Chemical reviews* **1971,** *71*, (6), 525-616.
3. Hoekman, D., Exploring QSAR Fundamentals and Applications in Chemistry and Biology, Volume 1. Hydrophobic, Electronic and Steric Constants, Volume 2 J. Am. Chem. Soc. 1995, 117, 9782. *Journal of the American Chemical Society* **1996,** *118*, (43), 10678-10678.
4. Klein, W.; Kördel, W.; Weiss, M.; Poremski, H., Updating of the OECD test guideline 107 "partition coefficient n-octanol/water": OECD laboratory intercomparison test on the HPLC method. *Chemosphere* **1988,** *17*, (2), 361-386.
5. Mackay, D.; Shiu, W. Y.; Ma, K.-C., *Illustrated handbook of physical-chemical properties of environmental fate for organic chemicals*. CRC press: 1997; Vol. 5.
6. Veith, G. D.; DeFoe, D. L.; Bergstedt, B. V., Measuring and estimating the bioconcentration factor of chemicals in fish. *Journal of the Fisheries Board of Canada* **1979,** *36*, (9), 1040-1048.
7. Bergman, Å.; Rydén, A.; Law, R. J.; de Boer, J.; Covaci, A.; Alaee, M.; Birnbaum, L.; Petreas, M.; Rose, M.; Sakai, S., A novel abbreviation standard for organobromine, organochlorine and organophosphorus flame retardants and some characteristics of the chemicals. *Environment international* **2012,** *49*, 57-82.
8. Gustavsson, J.; Ribéli, E.; Wiberg, K.; Josefsson, S.; Minh Nguyen, A.; Ahrens, L. *Re-analysis of organic flame retardants in Swedish rivers*; 2016.
9. Eljarrat, E., & Barceló, *Brominated flame retardants*. Springer Science & Business Media: 2011; Vol. 16.
10. Veith, G. D., DeFoe, D. L., & Bergstedt, B. V., Measuring and estimating the bioconcentration factor of chemicals in fish,. *Journal of the Fisheries Board of Canada* **1979,** *36*, (9), 1040-1048.
11. Office of Environmental Health Hazard Assessment (OEHHA). Brominated and Chlorinated Organic Chemical Compounds Used As Flame Retardants. 2008. https://biomonitoring.ca.gov/downloads/brominated-and-chlorinated-organic-chemical-compounds-used-flame-retardants-0
12. Sjödin, A.; Patterson Jr, D. G.; Bergman, Å., A review on human exposure to brominated flame retardants—particularly polybrominated diphenyl ethers. *Environment international* **2003,** *29*, (6), 829-839.
13. Ruan, T.; Wang, Y.; Wang, C.; Wang, P.; Fu, J.; Yin, Y.; Qu, G.; Wang, T.; Jiang, G., Identification and evaluation of a novel heterocyclic brominated flame retardant tris (2, 3-dibromopropyl) isocyanurate in environmental matrices near a manufacturing plant in southern China. *Environmental science & technology* **2009,** *43*, (9), 3080-3086.
14. Ballschmiter, K., Klingler, D., Ellinger, S., & Hackenberg, R. , High-resolution gas chromatography retention data as a basis for estimation of the octanol–water distribution coefficients (Kow) of PCB: the effect of experimental conditions. *Analytical and bioanalytical chemistry* **2005,** *382*, (8), 1859-1870.
15. Brodsky, J., & Ballschmiter, K., Reversed phase liquid chromatography of PCBs as a basis for the calculation of water solubility and log K ow for polychlorobiphenyls. *Fresenius' Zeitschrift für analytische Chemie* **1988,** *331*, (3-4), 295-301.
16. Hansen, B. G., Paya-Perez, A. B., Rahman, M., & Larsen, B. R., QSARs for KOW and KOC of PCB congeners: a critical examination of data, assumptions and statistical approaches. *Chemosphere* **1999,** *39*, (13), 2209-2228.
17. De Bruijn, J., Busser, F., Seinen, W., & Hermens, J. , Determination of octanol/water partition coefficients for hydrophobic organic chemicals with the "slow‐stirring" method. *Environmental Toxicology and Chemistry* **1989,** *8*, (9), 499-512.

18. Kuramochi, H.; Maeda, K.; Kawamoto, K., Physicochemical properties of selected polybrominated diphenyl ethers and extension of the UNIFAC model to brominated aromatic compounds. *Chemosphere* **2007,** *67*, (9), 1858-1865.
19. Li, X. W., Shibata, E., Kasai, E., & Nakamura, T., Vapor pressures and enthalpies of sublimation of 17 polychlorinated dibenzo‐p‐dioxins and five polychlorinated dibenzofurans. *Environmental Toxicology and Chemistry: An International Journal* **2004,** *23*, (2), 348-354.