SUPPORTING INFORMATION

Historical contaminants, flame retardants and halogenated phenolic compounds in peregrine falcon (*Falco peregrinus*) nestlings in the Canadian Great Lakes Basin

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Table S1. Concentrations (ng/g ww) of hydroxylated (OH-) polybrominated diphenyl ethers and polychlorinated biphenyls (OH-PCBs) detected in the plasma of peregrine nestlings across western Québec and Ontario throughout the Great Lakes Basin in Canada.[a]

	Overall concentrations (*N* = 34 nests)					North Shore of Lake Superior (*N* = 9 nests)					Thunder Bay Region (*N* = 13 nests)					Urban Region (*N* = 12 nests)				
	GM	AM	SEM	Max.	Min.	GM	AM	SEM	Max.	Min.	GM	AM	SEM	Max.	Min.	GM	AM	SEM	Max.	Min.
ΣOH-PBDEs	1.07	2.09	0.43	12.06	0.00	1.87	3.20	1.24	12.06	0.37	0.65	1.71	0.59	7.58	0.01	1.26	1.66	0.46	4.39	0.00
6OH-BDE47	1.11	1.15	0.33	7.58	0.00	3.21	1.22	0.69	5.06	0.00	0.49	1.19	0.63	7.58	0.00	2.18	1.06	0.44	4.39	0.00
4’OH-BDE49	0.47	0.41	0.14	3.86	0.00	0.90	0.60	0.26	2.31	0.00	0.44	0.30	0.13	1.57	0.00	0.26	0.37	0.32	3.86	0.00
4OH-BDE42	2.14	0.28	0.27	9.12	0.00	2.14	1.07	1.01	9.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6OH-BDE85	0.63	0.08	0.04	0.96	0.00	0.44	0.10	0.07	0.50	0.00	0.96	0.07	0.07	0.96	0.00	0.84	0.07	0.07	0.84	0.00
3OH-BDE47	0.21	0.07	0.03	0.69	0.00	0.58	0.06	0.06	0.58	0.00	0.27	0.11	0.06	0.69	0.00	0.11	0.03	0.02	0.14	0.00
4OH-BDE17	1.30	0.04	0.04	1.30	0.00	1.30	0.14	0.14	1.30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5OH-BDE47	0.34	0.01	0.01	0.34	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.07	0.00	0.34	0.03	0.03	0.34	0.00
6OH-BDE99	0.10	0.01	0.01	0.18	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.02	0.01	0.18	0.00	0.00	0.00	0.00	0.00	0.00
6’OH-BDE49	0.03	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.01	0.00	0.04	0.00	0.04	0.01	0.00	0.04	0.00
%4OH-CB187: sum OH-PCBs	12.18	16.66	4.02	100.00	2.94	8.75	9.38	1.25	14.92	0.95	17.51	20.01	4.74	46.71	10.51	12.32	20.52	10.03	100.00	2.94
4OH-CB187	1.38	2.67	0.58	15.51	0.11	1.84	2.89	1.17	11.80	0.32	1.89	3.86	1.19	15.51	0.11	0.80	1.21	0.36	4.08	0.20
4'OH-CB130	1.57	2.27	0.33	8.15	0.00	2.88	3.68	0.85	8.15	0.53	1.47	2.34	0.46	4.96	0.13	1.02	1.12	0.23	2.75	0.00
4OH-CB162	1.53	2.21	0.33	8.01	0.00	2.65	3.47	0.87	8.01	0.53	1.47	2.34	0.45	4.99	0.13	1.02	1.12	0.23	2.73	0.00
4OH-CB146	1.49	1.34	0.25	4.79	0.00	2.03	2.21	0.53	4.79	0.00	2.20	1.56	0.44	3.98	0.00	0.67	0.44	0.14	1.58	0.00
3OH-CB118	3.89	1.18	0.44	9.31	0.00	4.30	2.06	0.91	6.75	0.00	0.00	0.00	0.00	0.00	0.00	3.52	1.79	0.99	9.31	0.00
4OH-CB134	2.28	0.78	0.73	24.94	0.00	24.94	2.77	2.77	24.94	0.00	0.00	0.00	0.00	0.00	0.00	0.69	0.12	0.08	0.89	0.00
4'OH-CB177	0.64	0.75	0.13	2.48	0.00	0.78	1.05	0.26	2.48	0.13	1.07	0.89	0.24	2.38	0.00	0.33	0.37	0.10	1.28	0.00
4'OH-CB202	0.48	0.73	0.15	4.27	0.00	0.68	0.94	0.26	2.65	0.12	0.77	0.98	0.32	4.27	0.00	0.22	0.29	0.08	1.05	0.00
4'OH-CB199	0.53	0.62	0.10	2.60	0.00	0.67	0.83	0.18	1.74	0.15	0.58	0.69	0.19	2.60	0.00	0.39	0.38	0.09	0.99	0.00
4'OH-CB172	0.32	0.36	0.07	1.50	0.00	0.49	0.57	0.17	1.50	0.00	0.42	0.43	0.12	1.26	0.00	0.16	0.14	0.04	0.37	0.00
4OH-CB163	0.92	0.35	0.19	5.41	0.00	0.52	0.06	0.06	0.52	0.00	0.48	0.15	0.07	0.67	0.00	4.56	0.77	0.53	5.41	0.00
4'OH-CB201	0.26	0.22	0.07	2.06	0.00	0.25	0.32	0.10	1.02	0.00	0.37	0.33	0.16	2.06	0.00	0.09	0.02	0.01	0.17	0.00
4OH-CB178	0.26	0.16	0.05	0.94	0.00	0.20	0.11	0.10	0.94	0.00	0.40	0.30	0.09	0.90	0.00	0.10	0.03	0.02	0.20	0.00
4OH-CB107/ 4'MeO-CB108	0.28	0.13	0.05	1.68	0.00	0.51	0.31	0.18	1.68	0.00	0.25	0.10	0.04	0.35	0.00	0.14	0.04	0.02	0.19	0.00

4-OH-HpCS	0.09	0.09	0.03	0.71	0.00	0.12	0.16	0.05	0.51	0.00	0.07	0.04	0.01	0.12	0.00	0.09	0.10	0.06	0.71	0.00
3'-OH-CB203	0.14	0.09	0.02	0.48	0.00	0.14	0.13	0.05	0.48	0.00	0.18	0.10	0.04	0.46	0.00	0.09	0.03	0.01	0.12	0.00
4OH-CB193	0.13	0.07	0.06	1.97	0.00	1.97	0.22	0.22	1.97	0.00	0.10	0.03	0.02	0.26	0.00	0.05	0.01	0.01	0.10	0.00
4'OH-CB198	0.13	0.06	0.02	0.54	0.00	0.20	0.13	0.06	0.54	0.00	0.17	0.03	0.02	0.28	0.00	0.06	0.02	0.01	0.13	0.00
3'OH-CB180	0.21	0.03	0.02	0.36	0.00	0.20	0.09	0.04	0.36	0.00	0.00	0.00	0.00	0.00	0.00	0.28	0.02	0.02	0.28	0.00
4'OH-CB101	0.44	0.03	0.02	0.55	0.00	0.00	0.00	0.00	0.00	0.00	0.35	0.03	0.03	0.35	0.00	0.55	0.05	0.05	0.55	0.00
3'OH-CB138	0.08	0.01	0.01	0.12	0.00	0.11	0.04	0.02	0.12	0.00	0.06	0.01	0.01	0.08	0.00	0.00	0.00	0.00	0.00	0.00
4'OH-CB120	0.10	0.01	0.01	0.15	0.00	0.15	0.02	0.02	0.15	0.00	0.15	0.01	0.01	0.15	0.00	0.04	0.00	0.00	0.04	0.00
4'OH-CB159	0.03	0.01	0.01	0.24	0.00	0.24	0.03	0.03	0.24	0.00	0.02	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00
3'OH-CB182	0.13	0.00	0.00	0.13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.13	0.01	0.01	0.13	0.00
2'OH-CB114	0.09	0.00	0.00	0.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.01	0.01	0.09	0.00
3'OH-CB183	0.04	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00

[a] There were no significant differences among the regions in these concentrations of OH-PBDEs (measured as MeO-PBDE derivatives) or OH-PCBs (measured as MeO-PCB derivatives). GM, geometric mean; AM, arithmetic mean. The following OH-BDEs (6-OH-BDE-90, -137; 6’-OH-BDE17; 2’-OH-BDE68; 2-OH-BDE123), OH-PCBs (4’OH-CB79, -127, -200,4OH-CB97, 3’OH-CB184), and the 14 MeO-PBDEs, were undetected in the plasma of the nestlings. The 14 MeO-PBDE congeners monitored were the same structures as the OH-PBDE congeners monitored.

Figure S1. The mean BDE-99 to BDE-153 concentration ratios in the plasma of peregrine falcon nestlings across the Canadian Great Lakes Basin.

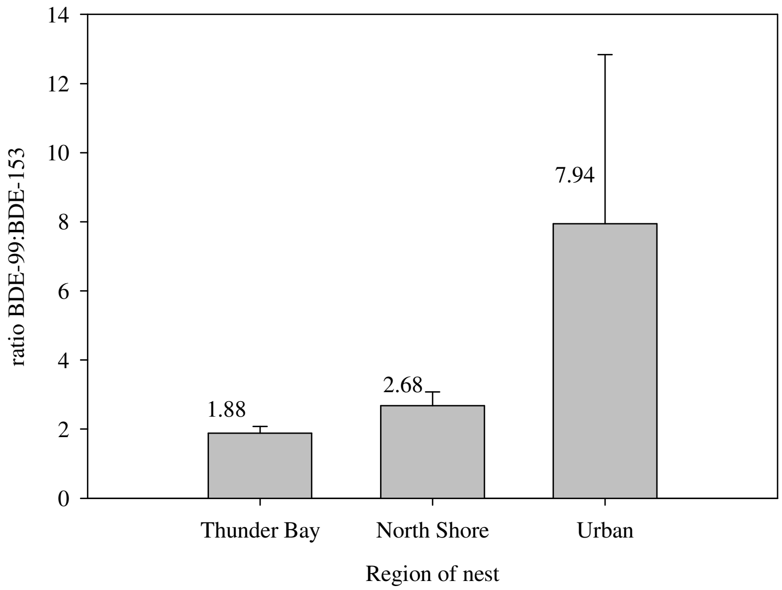
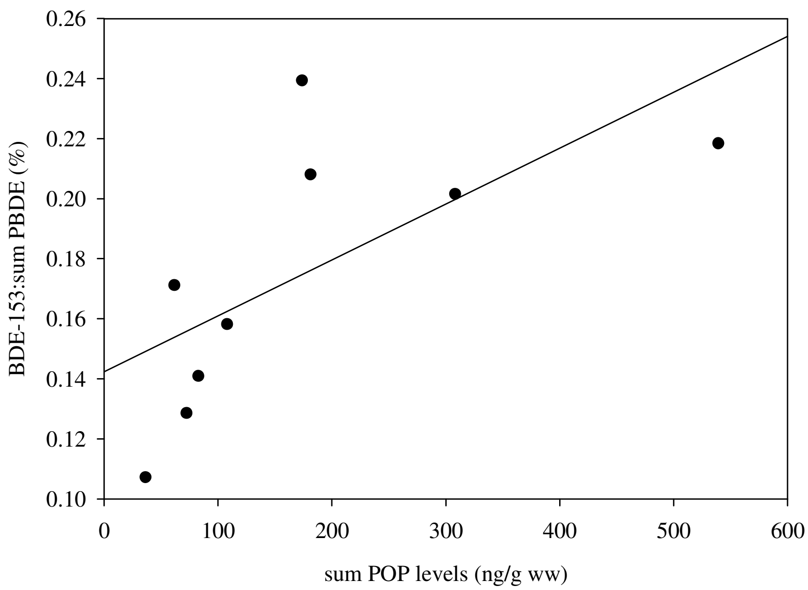
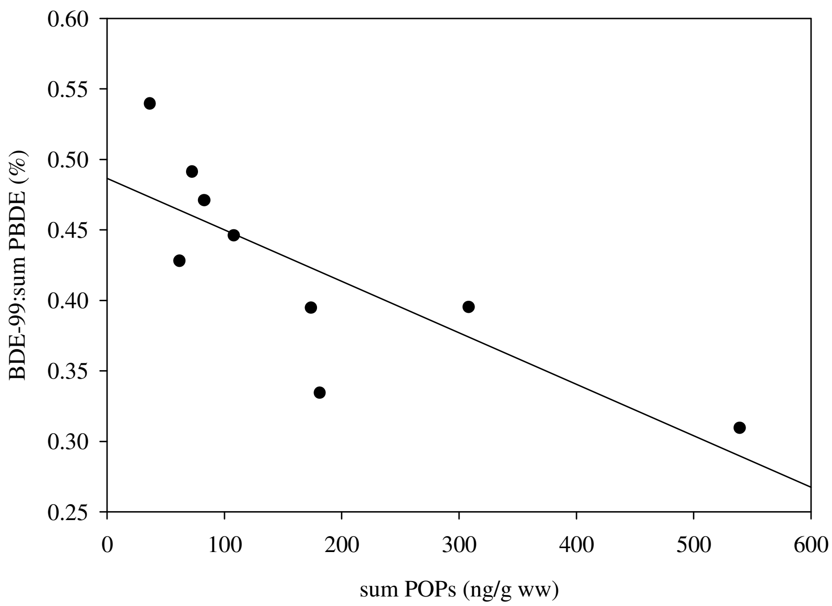


Figure S2. Correlations for (A) The BDE-153:Σ_{14}PBDE to ΣPOP concentrations ratio (N = 9 Spearman's r = 0.66724 p = 0.0496) and (B) the BDE-99:Σ_{14}PBDE concentrations ratio (N = 9 Spearman's r = -0.79573 p = 0.0103) in relation to ΣPOP concentrations in the plasma of North Shore Lake Superior peregrine falcon nestlings.

(A)



(B)


0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
BDE-99:sum PBDE (%)
0
100
200
300
400
500
600
sum POPs (ng/g ww)

Experimental Section

After spiking, the plasma samples were acidified with 1 mL HCl (6 M) and 3 mL of 2-propanol was added. The denatured plasma was extracted three times with 6 mL methyl-*tert*-butyl-ether (MtBE)/*n*-hexane (50:50 volume ratio (VR)). The solution was partitioned with 6 mL KOH (1 M in 50% ethanol), and two phases were obtained: an aqueous phase containing the deprotinated HPCs and an organic phase containing the neutral PCBs, other chlorinated hydrocarbons, and BFRs and other brominated compounds. The organic phase from the KOH partitioning step was concentrated and fractionated with a Florisil® column (8.0 g, 1.2% H_2O deactivated) (Magnesium silicate, F100 – 500, 60 – 100 mesh) (Fisher Scientific, Ottawa, ON, Canada), and concentrated to 1 mL for GC-MS(ECNI) analysis.

The determination of the brominated compounds was performed with GC-MS(ECNI). An Agilent gas chromatograph (GC) 6890 equipped with a 5973 quadruple mass spectrometer (MS) detector was used. The GC column was a 30 m × 0.25 mm i.d. HP-5MS capillary column with a film thickness of 0.25µm. Helium was used as carrier gas at a constant flow of 1 ml/min. A 2 µL of sample solution was injected with splitless mode. The injector temperature was 280°C, the purge time was 1 min after injection, and the vent flow was 50 ml/ min. The programmed oven temperature was 80°C, held for 2 min, then at 10°C/min to 290°C and held for 15 min. Ionization was performed in electron capture negative ionization (ECNI) mode, using methane as the reagent gas. The transfer line, source and quadruple temperatures were 280°, 250° and 150°C, respectively. BDE-209 was separated on a 15 m capillary column using the same GC conditions as for the standard GC-MS (ECNI) program.

Brominated compounds were identified on the basis of their retention times on the DB-5 columns relative to authentic standards, i.e., total-HBCD, PBBs (BB101), PBDEs (12 congeners). As any β- and γ-HBCD residues in the samples were thermally isomerized to α-HBCD in the GC injection port, the α-HBCD concentrations represented total-HBCD. Further assessment of MeO-tetrabromoDEs in the derivatized HPC fraction was via re-analysis of the fractions by monitoring the nominal mass of isotopic [M]- (*m/z* 512) and [M+2]- (*m/z* 514) of the molecular ion cluster, and [M]- (*m/z* 434) and [M+2]- (*m/z* 436) of the [M-Br]- fragment anion. Quantification of the brominated compounds was performed using an internal standard method based on the relative ECNI response factor (RRF) of the $^{79}Br+^{81}Br$ anions of BDE30 and 2'-OH-BDE28 and to that of authentic congener standards in the neutral and derivatized HPC fractions, respectively.

The 44 PCB congeners determined were CB 28/31, 52, 49, 44, 42, 64, 74, 70, 66/95, 60, 101, 99, 97, 87, 110, 151, 149, 118, 146, 153, 105, 141, 138, 158, 129, 182/187, 183, 185, 174, 171, 200, 172, 180, 170/190, 201, 203, 195, 194 and 206). The chlorinated hydrocarbons analyzed were hexachlorobenzene (HCB), octachlorostyrene (OCS), chlordanes (CHLs; *trans*-nonachlor, oxychlordane, *trans*-chlordane, *cis*-chlordane and heptachlor epoxide), Dieldrin, Mirex, Photo-mirex, *p,p'*-DDE and *p,p'*-DDT. The 20 $MeSO_2$-PCB congeners determined were 3-$MeSO_2$-CB52, 4-$MeSO_2$-CB52, 3'-$MeSO_2$-CB49, 4'-$MeSO_2$-CB49, 3-$MeSO_2$-CB64, 4-$MeSO_2$-CB64, 3-$MeSO_2$-CB91, 4-$MeSO_2$-CB91, 3-$MeSO_2$-CB70, 3'-$MeSO_2$-CB101, 4'-$MeSO_2$-CB101, 3-$MeSO_2$-CB87, 4-$MeSO_2$-CB87, 3-$MeSO_2$-CB110, 4-$MeSO_2$-CB110, 3-$MeSO_2$-CB149, 4-$MeSO_2$-CB149, 3'-$MeSO_2$-CB132, 4'-$MeSO_2$-CB132 and 4-$MeSO_2$-CB174. The 35 OH-PCB congeners analyzed were 4'-OH-CB61, 4'-OH-CB79, 4-OH-CB97, 4'-OH-CB101, 2'-OH-CB114, 4-OH-CB107, 4'-OH-CB108, 3-OH-CB118, 4'-OH-CB120, 4'-OH-CB127, 3'-OH-

CB130, 4-OH-CB134, 3'-OH-CB138, 4'-OH-CB159, 4-OH-CB162, 4-OH-CB163, 4'-OH-CB177, 3'-OH-CB180, 3'-OH-CB182, 4-OH-CB187, 4-OH-CB193, 4-OH-CB146, 4'-OH-CB199, 4'-OH-CB172, 4-OH-CB178, 3'-OH-CB183, 3'-OH-CB184, 4'-OH-CB198, 4'-OH-CB201, 4'-OH-CB202, 3'-OH-CB203, 4'-OH-CB200, 4'-OH-CB208, 4,4'-diOH-CB202 and 3,3'-diOH-CB155. Three other chlorinated phenolic compounds were analyzed for, pentchlorophenol (PCP), 4-OH-hepachlorostyrene (4-OH-HpCS) and tris(4-chlorophenyl)methanol (TCPM). The 14 PBDE congeners that were determined were BDE-17, -28, -47, -49, -66, -85, -99, -100, -138, -153, -154 (co-elutes with BB-153), -183, -190 and-209. Total (α) HBCD was also determined. The 14 OH-PBDE congeners that were analyzed for were 6'-OH-BDE17, 4'-OH-BDE17, 6'-OH-BDE49, 2'-OH-BDE68, 6-OH-BDE47, 3-OH-BDE47, 5-OH-BDE47, 4'-OH-BDE49, 4-OH-BDE42, 6-OH-BDE90, 6-OH-BDE99, 2-OH-BDE123, 6-OH-BDE85 and 6-OH-BDE137. The 14 MeO-PBDE congeners that were analyzed for were 6'-MeO-BDE17, 4'-MeO-BDE17, 6'-MeO-BDE49, 2'-MeO-BDE68, 6-MeO-BDE47, 3-MeO-BDE47, 5-MeO-BDE47, 4'-MeO-BDE49, 4-MeO-BDE42, 6-MeO-BDE90, 6-MeO-BDE99, 2-MeO-BDE123, 6-MeO-BDE85 and 6-MeO-BDE137.

Quality Control and Assurance

Mean recovery (±1 standard error) of the internal standards was 91 ± 12% for BDE30, 95±8% for $^{13}C_{12}$-labeled PCBs, 65±9% for $^{13}C_{12}$-labeled OH-PCBs, 75±12% for 3-$MeSO_2$-2-CH_3-2',3',4',5,5'-pentachlorobiphenyl and 60±9% for 2'-OH-BDE28. Concentrations were recovery-corrected as an internal standard method of quantification was used to reduce heterogeneity within and between analyte classes. Method blank samples were inserted with each batch of 5 samples to monitor interferences and co-eluting contamination. No substantial background contamination was encountered for any of the brominated compounds. The method limit of quantification (MLOQ) for individual analytes was based on a minimum of 10 times the noise level (S/N). MLOQs for the analytes under study in peregrine plasma ranged between 0.001 and 0.01 ng/g wet weight (ww). The extractable lipid content in plasma samples was determined by the sulfo-phospho-vanillin reaction using pure olive oil as the calibrator.

The analytical precision of quantitative determinations was tested by repeated injections of standard compounds, and where sample amount permitted, duplicate analyses of selected samples were performed. Duplicate samples demonstrated on average 10% variation of analyte concentrations. Furthermore, PCBs, other chlorinated hydrocarbon, and PBDE concentrations in repeated analyses of the NIST pilot whale blubber SRM1945 showed %RSD to be 12 ± 4% of the NIST certified values. This lab also achieved similarly high accuracy and precision for chlorinated hydrocarbons and PBDEs in analysis of SRM 1945 as part of the 2007 NIST/NOAA Inter-laboratory Comparison Exercise Program.