SUPPLEMENTAL INFORMATION

Volatile Methylsiloxanes and Organophosphate Esters in the Eggs of European Starlings (*Sturnus vulgaris*) and Congeneric Gull Species from Locations across Canada

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Table S1. Predicted physicochemical properties (log K_{aw}, log K_{ow}, log K_{oa}, log K_{oc}, half-lives ($t_{1/2}$)), fugacity III model predictions and overall persistence and long-range transport potential parameters of target VMSs and OPEs. [a] Predicted by EPI suite V4.1; [b]Predicted by OECD Pov-LRTP Tool; [c]Pov: overall persistence; [d]CTD: characteristic travel distance; [e] Data is provided by the experiment database in EPI suite.

Compounds	Molecular Weight ($g\ mol^{-1}$)	Physicochemical properties[a]									Fugacity III model predictions[a]				Predicted total persistent and transport potential[b]	
		Log K_{aw}	Log K_{ow}	Log K_{oa}	Log K_{oc}	$t_{1/2}$ air (days)	$t_{1/2}$ water (days)	$t_{1/2}$ soil (days)	$t_{1/2}$ sediment (days)	$t_{1/2}$ fish (days)	Air (%)	Water (%)	Soil (%)	Sediment(%)	Pov[c] (days)	CTD[d] (km)
D3	222.47	0.41	5.64	5.23	4.89	20.6	37.5	75	338	12.5	34.0	36.7	25.5	3.8	75	10170
D4	296.62	0.68	6.74[e]	6.06	5.85	10.6	37.5	75	338	54.3	15.1	22.3	47.9	14.7	98	5251
D5	370.78	1.1	8.03[e]	6.93	6.97	6.9	37.5	75	338	267	5.5	20.1	53.7	20.6	105	3436
D6	444.93	0.63	9.06[e]	8.43	7.86	6	60	120	542	1116	1.4	11.8	72.9	13.8	171	2944
M4Q	384.85	1.51	9.61	8.10	8.34	6	37.5	75	338	2355	7.5	36.9	53.9	1.7	107	2950
L2	162.38	0.27	5.25	4.98	4.56	7.8	15	30	135	13.5	42.9	45.3	11.2	0.6	33	3850
L3	236.54	2.13	6.60[e]	4.47	5.73	8.9	37.5	75	338	70.1	39.1	52.9	1.4	6.6	44	4431
L4	310.69	2.84	8.21[e]	5.37	7.13	7.2	37.5	75	338	437	21.3	68.3	1.3	9.1	74	3563
L5	384.85	1.51	9.61	8.10	8.34	6	37.5	75	338	2355	7.5	36.9	53.9	1.7	107	2950
TEP	182.16	-5.83	0.8[e]	6.63	1.47	0.2	15	30	135	0.03	0.3	25.9	73.7	0.1	31	88
TCEP	285.49	-3.87	1.44[e]	5.31	1.83	0.5	60	120	542	0.06	0.3	16.3	83	0.4	83	231
TPP	224.24	-4.56	1.87[e]	6.43	2.06	0.1	15	30	135	0.05	0.3	25.4	73.9	0.4	34	70
TClPP	327.57	-5.61	2.59[e]	8.20	2.46	0.2	60	120	542	0.14	0.1	12.4	86.2	1.3	144	149
TPHP	326.29	-3.87	4.59[e]	8.46	3.24	1	37.5	75	338	0.22	0.5	13.8	77.1	8.6	107	445
TDClPP	430.91	-6.97	3.65[e]	10.6	3.05	0.6	180	360	1621	0.41	0.01	3.8	91.3	4.9	489	445
TDBPP	697.62	-3.05	4.29[e]	7.34	3.40	0.4	60	120	542	0.04	0.2	9.9	82.7	7.2	165	189
TNBP	266.32	-4.24	4.00[e]	8.24	3.24	0.13	8.7	17.3	78	0.29	0.5	27.1	71	1.4	25	67
TMPP	368.37	-4.48	5.11[e]	9.59	3.53	0.78	37.5	75	338	4.70	0.4	10.9	60.4	28.3	108	361
TBOEP	398.48	-9.31	3.75[e]	13.1	2.83	0.08	8.7	17.3	78	0.14	4×10^{-4}	18.3	81.2	0.5	25	41
EHDPP	362.41	-2.65	5.73[e]	8.38	3.87	0.27	15	30	30	0.56	0.6	17.8	65.7	15.9	43	133
T2B4MP	605.06	-6.86	9.01	15.9	5.68	1.4	180	360	1621	45.1	0.04	4.1	94	1.9	519	2860
T3B4MP	605.06	-6.86	9.01	15.9	5.68	1.2	180	360	1621	45.1	0.04	4.1	94	1.9	519	2860
T4B3MP	605.06	-6.86	9.01	15.9	5.68	1.3	180	360	1621	45.1	0.04	4.1	94	1.9	519	2860
TTBNPP	1018.47	-11.96	9.83	21.8	6.47	5.4	180	360	1621	3.04	4.8×10^{-7}	3.8	95.5	0.7	519	2861
TEHP	434.65	-5.49	9.49	14.9	6.28	0.1	8.7	17.3	78	10.6	0.3	23.9	69	6.8	25	2842
BCMP-BCEP	583	-12.2	3.31	15.5	2.86	0.1	180	360	1621	0.09	1.6×10^{-7}	0.7	54.1	45.2	462	445

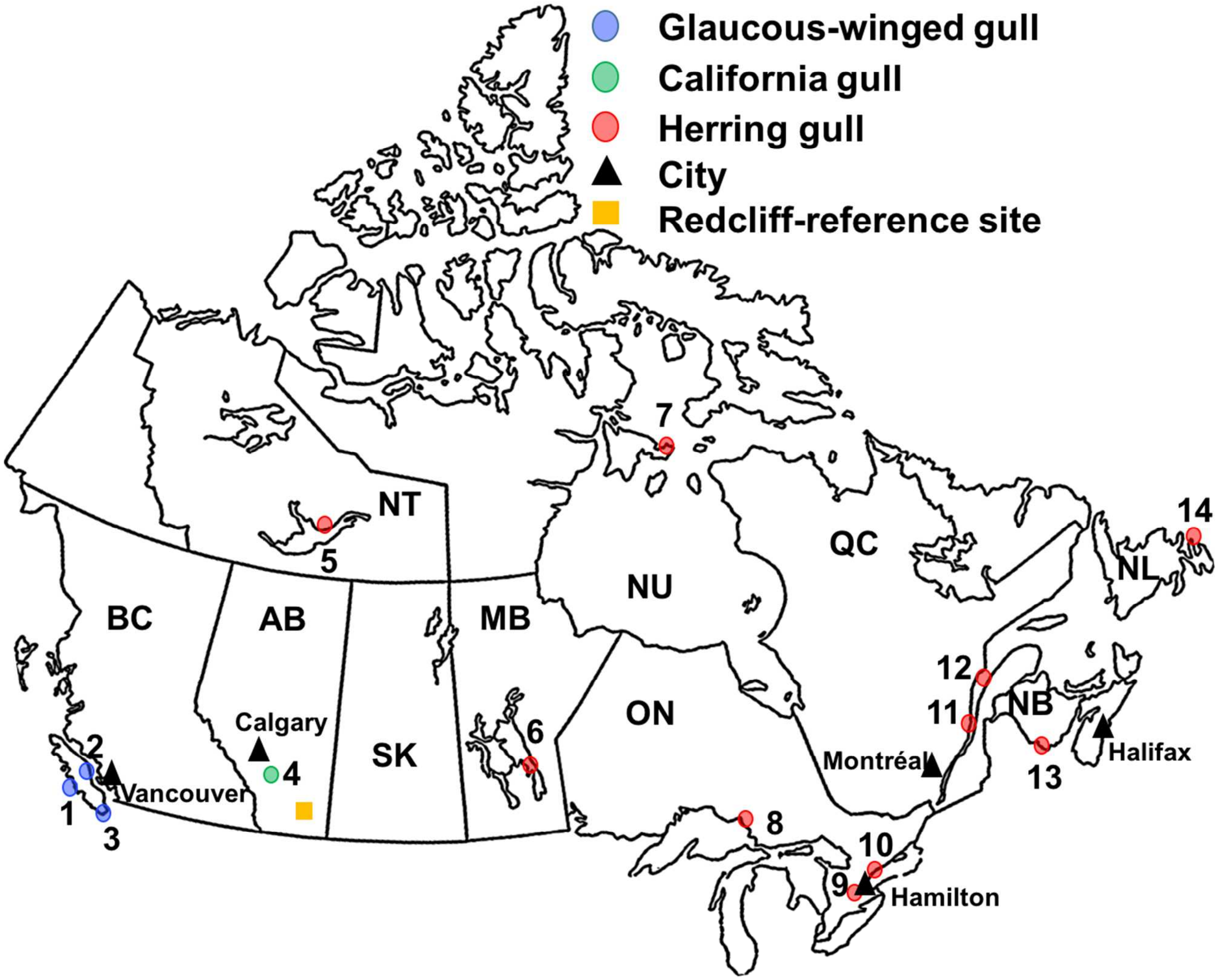

Figure S1. Sampling locations for European starling and gull eggs across Canada.

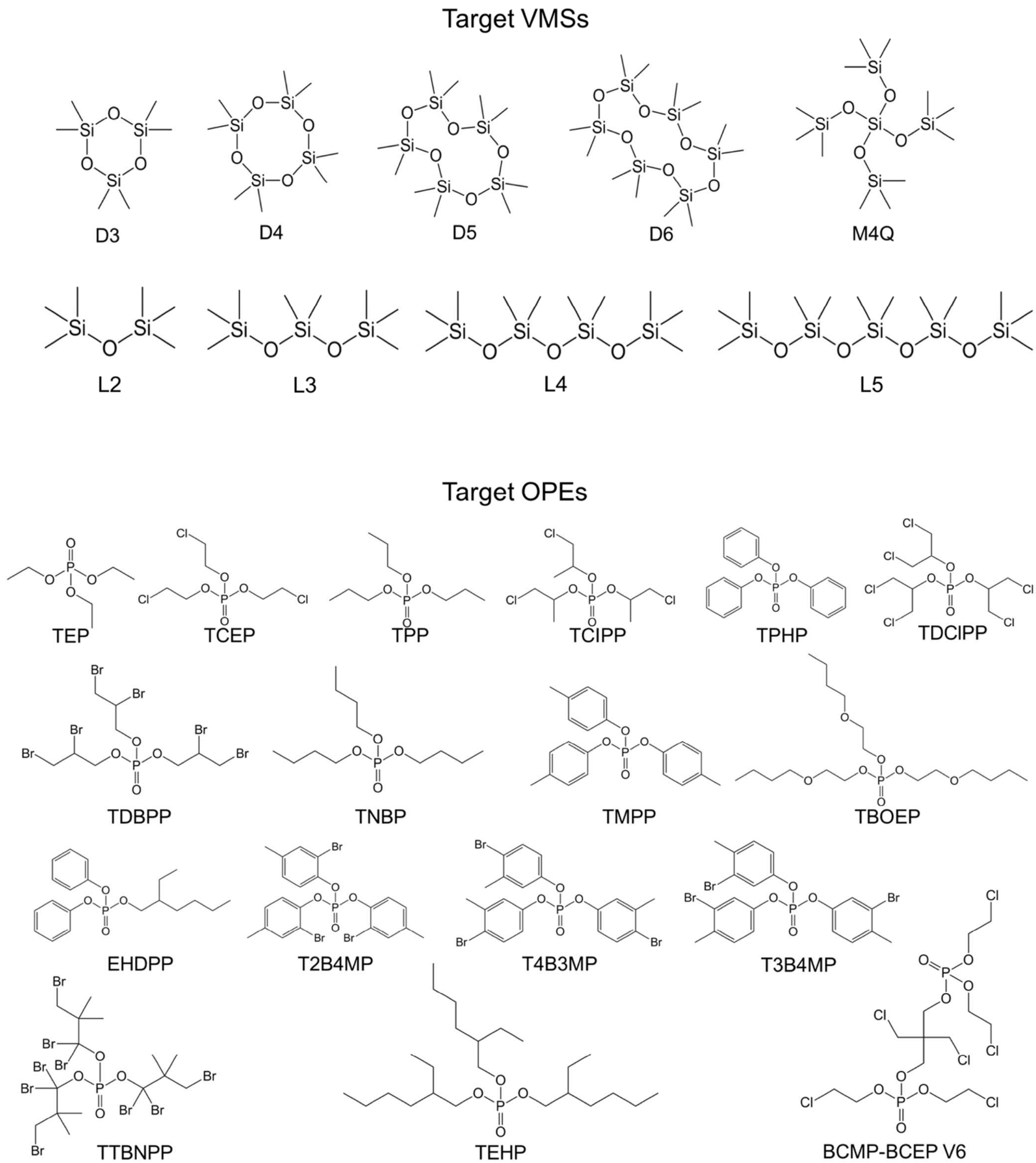

Figure S2. Structures of target VMSs and OPEs.

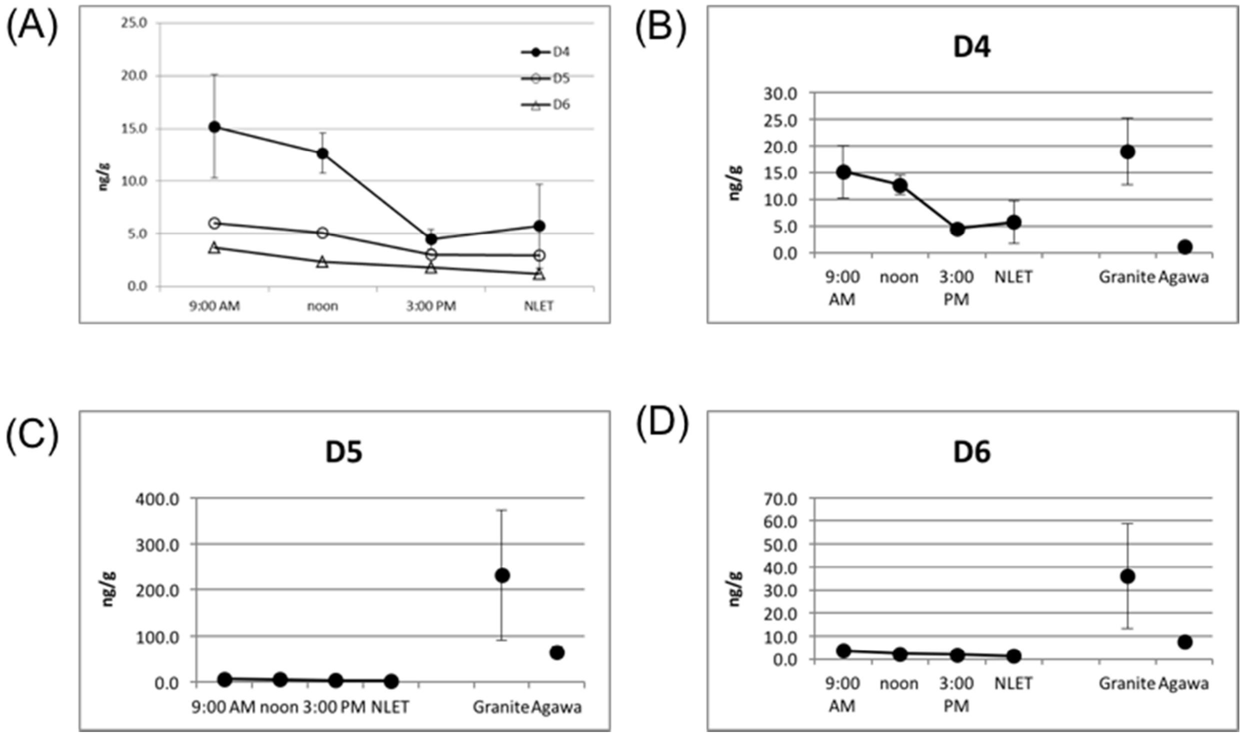

Figure S3. Background contamination of VMSs during storage and transportation (arithmetic mean ± standard deviation). (A) Concentrations of D4, D5 and D6 in chicken eggs (method blank) processed at NWRC at three times (i.e, 9am, noon and 3pm) of the day and at NLET (*n* = 3 replicates for each group); Concentrations of (B) D4, (C) D5 and (D) D6 in chicken eggs (method blank) processed at NWRC at three times (i.e, 9am, noon and 3pm) of the day, at NLET and in herring gull eggs collected from remote colonies on Lake Superior (Granite and Agawa) (*n* = 3 replicates for each group).

The results (Figure S3A) demonstrated that there were no significant differences among the times of chicken egg processing, or between eggs processed at NWRC versus the eggs processed in the ultraclean lab at NLET, in any of the VMS. However, the background concentration of D4 in blank chicken eggs processed at NWRC (9am and noon) were apparently higher than the measured values in NLET (Figure S3A).

In addition, concentrations of D4 (Figure S3B), D5 (Figure S3C) and D6 (Figure S3D) in Lake Superior herring gull eggs were higher than the chicken eggs (method blank) processed at NLET, suggesting that even at these remote sites in the environment, concentrations in free-living bird eggs were discernibly higher than those of the method blanks, indicating that measured concentrations were not simply a result of laboratory contamination.

Overall, the results indicate that storage and transportation of eggs did not contaminate the egg samples with VMS. The egg samples processed at NLET ultraclean lab showed acceptable method blanks of VMS. Thus, NLET was selected to further process all egg samples for VMS analysis.

METHODS

Sample preparation and chemical analysis

VMSs. Ten mL of methanol was added in 1g of egg sample and then surrogate standards ($^{13}C_4$-D4, $^{13}C_5$-D5 and $^{13}C_6$-D6) were added in the mixture. The sample was treated by 15 min of vortex and 10 min of centrifugation. The solvent was collected in another vial for further processing. The methanol extraction was repeated twice. The combined methanol extract was mixed with 5 mL of Millipore water and 5 mL of pentane and followed by 5 min of vortex. The top layer was collected in a glass centrifuge tube and the pentane extraction was repeated for 3 times. The combined extracts were concentrated to 1mL using a TurboVap® and d_8-Napthalene was added as internal standard before instrument analysis. VMSs were quantified using an Agilent 6890 N gas chromatograph coupled with a 5975B inert XL EI/CI mass detector (Agilent Technologies, CA, USA) (GC-MS) and a HP-5MS capillary column (30 m × 0.25 mm ID × 0.25 μm film thickness). Five μL (0.75μL/s) samples were injected by cryo-focused mode using a Programmable Temperature Vaporization (PTV) injector. Initial injector temperature was set at -40 ºC, held for 0.75 min and ramped to 250 ºC at a rate of 600 ºC /min in 29 s and held for 12min. Initial oven temperature was set at 35 ºC for 1 min, ramped to 195 ºC at 20 ºC /min and then ramped to 290 ºC at 100 ºC /min and held for 2.5 min. GC-MS parameters for VMSs analyses are presented in Table S2.

OPEs. Five deuterium-labeled surrogate standards (d_{27}-TNBP, d_{15}-TPHP, d_{12}-TCEP, d_{15}-TDCIPP, and d_{15}-TEP) were added in 1 g of egg homogenate and then ground with diatomaceous earth. The samples were then extracted with 50:50 dichloromethane:n-hexane (DCM:HEX) using an accelerated solvent extractor (ASE) (Dionex ASE 200, Sunnyvale, CA, USA) at 100 °C and 1500 psi. Approximately 1 g of Na_2SO_4 was added to the ASE collection eluent to remove moisture. The solvent was then evaporated under N_2 to 0.5 mL, and cleaned up using 1 g of ISOLUTE aminopropyl silica gel packed into a 6 mL Supelclean glass cartridge (Sigma-Aldrich). The SPE column was pre-washed with 15 mL of 50:50 DCM:methanol, 15 mL of DCM and 20 mL of HEX to clean and condition the silica gel sorbent. After loading the sample, the first fraction, eluted with 3 mL of 20:80 DCM:HEX, was discarded. The second fraction, eluted with 3 mL of 20:80 DCM:HEX followed by 6 mL of DCM and 4 mL of 10:90 methanol:DCM, contained the target OPEs. After SPE cleanup, the sample fraction was reduced to dryness under N_2 and was subsequently reconstituted in 500 μL of methanol. The sample was transferred to a 1 mL GC micro-centrifuge tube with 0.2 μm filter membrane, and spun at 10000 revolutions/min for five minutes. Finally, the upper 250 μL extract was used for LC-MS/MS analysis.

A Waters Alliance 2695 HPLC system coupled to a Micromass QuattroUltima triple quadrupole mass spectrometer was used for the determination of OPEs in European starling eggs. The mass spectrometer was operated in positive electrospray ionization (ESI) mode. A Waters Symmetry C_{18} column (2.1 × 100 mm, 3.5 μm particle size) was used for chromatographic separation. Water and methanol, both containing 0.1% of formic acid, were used as mobile phases. The instrument parameters including selected reaction monitoring transitions (SRM) and LC gradient are shown in Table S3 and

S4, respectively. Column temperature was set at 40°C. Injection volume was 10 µL. A Waters (Mississauga, ON, Canada) Acquity I-Class ultra-performance liquid chromatograph coupled with a Xevo TQ-S mass spectrometer system (UPLC-MS/MS) was used for the determination of OPEs in gull eggs. The mass spectrometer was operated in positive atmospheric pressure chemical ionization (APCI) mode. A 50 mm × 2.1 mm CortecsTM UPLC C_{18} analytical column (1.6 µm particle size) (Phenomenex, CA, USA) with a stainless steel frit (Porosity: 0.2µm; Diameter Inside: 2.1 mm) was used for chromatographic separation. Water and methanol were used as mobile phases. The instrument parameters including multiple reaction monitoring transitions (MRM) (Table S5) and LC gradient (Table S4) are shown below. Column temperature was set at 60°C. Injection volume was 10 µL.

Table S2. Optimized GC-MS (EI) parameters for VMS analyses. NA-not applicable.

VMS	Quantification Ions (*m/z*)	Qualification Ions (*m/z*)	MLOQ (ng/g)	MLOD (ng/g)
D3	207	133/147	0.88	0.27
D4	281	282	0.94	0.24
D5	267	355	15.3	0.20
D6	341	429	0.77	0.15
L2	147	148	0.30	0.12
L3	221	222/133	0.45	0.17
L4	207	295	0.30	0.12
L5	281	147/369	0.30	0.11
M4Q	281	147/369	0.30	0.10
$^{13}C_4$-D4	285	284	NA	NA
$^{13}C_5$-D5	360	270	NA	NA
$^{13}C_6$-D6	435	346	NA	NA
d_8-Napthalene	136	137	NA	NA

Table S3. UPLC-ESI(+)-MS/MS experimental parameters of OPEs in European starling eggs. NA-not applicable.

OPEs	SRM transitions (m/z)	Cone voltage (V)	Collision energy (eV)	MLOQ (ng g^{-1},ww)	MLOD (ng g^{-1},ww)
TEP	183.1 > 98.7	35	17	0.2	0.10
TPP	225.1 > 99.0	40	5	0.1	0.04
TNBP	267.2 > 99.0	35	20	5.0	0.03
TBOEP	399.0 > 199.0	35	15	4.4	0.04
TEHP	435.3 > 99.0	50	20	0.2	0.06
TCEP	284.9 > 63.0	35	25	2.0	0.04
TCIPP	327.1 > 99.0	35	20	5.0	0.12
TDCIPP	430.9 > 99.0	60	25	0.7	0.12
BCMP-BCEP	582.9 > 360.8	35	16	0.6	0.20
T2B4MP	604.9 > 90.0	110	70	0.2	0.05
T3B4MP	604.9 > 90.0	110	70	0.3	0.10
T4B3MP	604.9 > 90.0	110	70	0.2	0.06
TDBPP	698.6 > 99.0	55	30	0.2	0.06
TTBNPP	1018.4 > 144.9	90	50	0.8	0.26
TPHP	327.1 > 77.1	100	40	7.0	0.05
EHDPP	363.2 > 250.8	35	10	3.7	0.05
TMPP	369.1 > 91.0	90	40	0.1	0.03
d_{15}-TEP	198.2 > 101.7	35	17	NA	NA
d_{12}-TCEP	297.0 > 67.0	35	25	NA	NA
d_{15}-TPHP	342.2 > 82.0	100	40	NA	NA
d_{15}-TDCIPP	446.0 > 101.8	60	25	NA	NA
d_{27}-TNBP	294.3 > 102.0	35	20	NA	NA

Table S4. LC gradient parameters for OPEs analyses.

European starling eggs-ESI				Gull eggs-APCI			
Time (min)	Flow Rate (mL/min)	% A[a]	% B[b]	Time (min)	Flow Rate (mL/min)	% A[c]	% B[d]
0	0.2	95	5	0	0.5	95	5
3	0.2	30	70	3.0	0.5	0	100
12	0.2	20	80	8.0	0.5	0	100
15	0.2	5	95	8.1	0.5	95	5
16	0.2	95	5	12.0	0.5	95	5

[a] MilliQ Water with 0.1% of formic acid; [b] CHROMASOLV® Plus grade methanol with 0.1% of formic acid.

[c] MilliQ Water; [d] CHROMASOLV® Plus grade methanol

Table S5. UPLC-APCI(+)-MS/MS experimental parameters of OPEs in gull eggs. [a] The transition used for analyte quantification; [b] The transition used for analyte qualification. NA-not applicable.

OPEs	MRM transitions (m/z)	Cone voltage (V)	Collision energy (eV)	MLOQ (ng g^{-1},ww)	MLOD (ng g^{-1},ww)
TEP	183.08 > 98.98 [a]	14	16	0.1	0.04
	183.08 > 127.02 [b]	14	10		
TPP	225.13 > 98.98 [a]	24	16	0.2	0.05
	225.13 > 141.03 [b]	24	10		
TNBP	267.17 > 98.98 [a]	32	18	0.5	0.03
	267.17 > 211.11 [b]	32	8		
TBOEP	399.25 > 299.16 [a]	26	12	0.6	0.02
	399.25 > 199.07 [b]	26	16		
TEHP	435.36 > 98.98 [a]	16	12	0.8	0.06
	435.36 > 71.09 [b]	16	12		
TCEP	284.96 > 98.98 [a]	30	20	0.1	0.05
	284.96 > 222.97 [b]	30	12		
TCIPP	327 > 98.98 [a]	32	18	0.2	0.05
	327 > 174.99 [b]	32	12		
TDCIPP	430.89 > 98.98 [a]	34	26	0.1	0.04
	430.89 > 208.95 [b]	34	16		
BCMP-BCEP	582.91 > 360.00 [a]	28	18	0.1	0.03
	582.91 > 234.97 [b]	28	34		
T2B4MP	604.85 > 418.89 [a]	58	28	0.1	0.03
	604.85 > 184.96 [b]	58	42		
T3B4MP	604.85 > 90.05 [a]	100	60	0.1	0.06
	604.85 > 178.08 [b]	100	62		
T4B3MP	604.85 > 90.05 [a]	100	60	0.2	0.08
	604.85 > 178.08 [b]	100	62		
TDBPP	698.58 > 98.98 [a]	34	28	0.1	0.04
	698.58 > 298.85 [b]	43	17		
TTBNPP	1018.41 > 144.96 [a]	50	41	0.1	0.02
	1018.41 > 226.89 [b]	45	31		
TPHP	327.08 > 152.06 [a]	48	32	0.1	0.03
	327.08 > 77.04 [b]	48	36		
EHDPP	363.17 > 251.05 [a]	24	12	0.3	0.13
	363.17 > 77.04 [b]	24	38		
TMPP	369.13 > 91.05 [a]	72	40	0.1	0.06
	369.13 > 165.07 [b]	72	38		
d_{15}-TEP	198.17 > 102	14	16	NA	NA
d_{12}-TCEP	297.04 > 102	30	20	NA	NA
d_{15}-TPHP	342.17 > 160.11	48	36	NA	NA
d_{15}-TDCIPP	445.98 > 102	34	26	NA	NA
d_{27}-TNBP	294.34 > 102	32	18	NA	NA

Table S6. Concentrations of VMSs in blanks (ng g^{-1}, ww). The concentrations of other target VMSs were all < MLOD and not shown in this table.

Compound	D3	D4	D5	D6
Batch 1	0.25	0.97	12.8	0.65
Batch 2	0.32	1.14	16.6	0.66
Batch 3	1.40	1.27	5.68	0.60
Batch 4	0.18	1.29	14.4	0.81
Batch 5	0.21	0.79	5.02	0.43
Batch 6	0.24	0.64	3.48	0.39
Batch 7	0.25	0.74	3.36	0.43
Batch 8	0.11	0.86	3.71	0.42
Batch 9	0.17	0.79	4.14	0.36
Batch 10	0.27	0.92	5.00	1.21
Batch 11	0.30	0.51	0.75	0.21
Batch 12	0.30	0.57	0.72	0.29
Batch 13	0.17	0.38	0.70	0.32
Batch 14	0.18	0.32	0.52	0.22
Batch 15	0.17	0.34	0.62	0.20
Batch 16	0.21	0.46	0.76	0.45
Batch 17	0.16	0.46	1.13	0.37

Table S7. Concentrations of OPEs in blanks (ng g^{-1}, ww). The concentrations of other target OPEs were all < MLOD and not shown in this table.

Compound	TEP	TCEP	TPP	TCIPP	TPHP	TDCPP	TDBPP	TNBP	TBOEP	TMPP	EHDPP
Experiment batches for European starling eggs (3 blanks for each batch) mean ± SD											
Batch 1	0.37 ± 0.06	2.32 ± 0.94	< MLOD	6.81 ± 2.50	0.87 ± 0.40	0.68 ± 0.13	< MLOD	5.91 ± 2.18	4.87 ± 1.49	0.07 ± 0.03	0.74 + 0.20
Batch 2	0.34 ± 0.07	5.51 ± 2.94	< MLOD	13.9 ± 6.80	1.79 ± 0.86	0.93 ± 0.09	< MLOD	13.2 ± 6.60	4.68 ± 1.70	0.07 ± 0.01	1.68 + 1.55
Batch 3	0.28 ± 0.25	1.63 ± 0.10	< MLOD	4.73 ± 0.96	6.91 ± 0.32	0.63 ± 0.10	< MLOD	6.79 ± 1.38	4.02 ± 0.90	0.11 ± 0.09	0.63 + 0.24
Batch 4	0.17 ± 0.03	3.11 ± 0.72	< MLOD	8.28 ± 1.55	5.07 ± 6.03	1.37 ± 0.71	< MLOD	7.07 ± 0.96	4.33 ± 3.10	< MLOD	4.21 + 4.93
Batch 5	0.22 ± 0.02	1.57 ± 0.35	< MLOD	3.72 ± 0.70	5.48 ± 6.87	0.64 ± 0.03	< MLOD	3.04 ± 0.41	2.68 ± 0.88	< MLOD	0.90 + 0.10
Batch 6	0.18 ± 0.05	1.02 ± 0.43	< MLOD	3.74 ± 1.77	3.76 ± 5.20	0.49 ± 0.09	< MLOD	3.70 ± 0.88	3.08 ± 0.76	0.11 ± 0.10	0.38 + 0.12
Batch 7	0.24 ± 0.05	1.71 ± 0.29	< MLOD	5.57 ± 0.77	7.91 ± 2.13	0.58 ± 0.12	< MLOD	5.35 ± 1.30	3.71 ± 0.60	< MLOD	0.95 + 0.61
Batch 8	0.23 ± 0.08	4.22 ± 0.71	< MLOD	8.57 ± 0.63	2.63 ± 0.61	1.74 ± 0.92	< MLOD	5.44 ± 0.78	< MLOD	0.05 ± 0.01	1.51 + 0.32
Batch 9	0.25 ± 0.04	1.65 ± 0.19	< MLOD	2.94 ± 0.74	0.61 ± 0.15	0.28 ± 0.08	< MLOD	3.99 ± 1.56	4.98 ± 2.34	< MLOD	0.78 + 0.32
Batch 10	0.40 ± 0.01	1.69 ± 0.03	< MLOD	5.36 ± 0.24	1.67 ± 0.55	0.79 ±0.04	< MLOD	6.26 ± 0.52	4.88 ± 2.83	0.05 ± 0.07	3.94 + 4.06
Experiment batches for gull eggs (1 blank for each batch)											
Batch 11	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	0.10	0.06	< MLOD	< MLOD
Batch 12	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	0.09	0.14	< MLOD	< MLOD
Batch 13	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	0.11	0.23	< MLOD	< MLOD
Batch 14	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	0.37	0.31	< MLOD	< MLOD
Batch 15	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	0.40	0.48	< MLOD	< MLOD
Batch 16	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	0.48	0.30	< MLOD	< MLOD
Batch 17	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	0.38	0.57	< MLOD	< MLOD
Batch 18	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	0.11	0.55	< MLOD	< MLOD

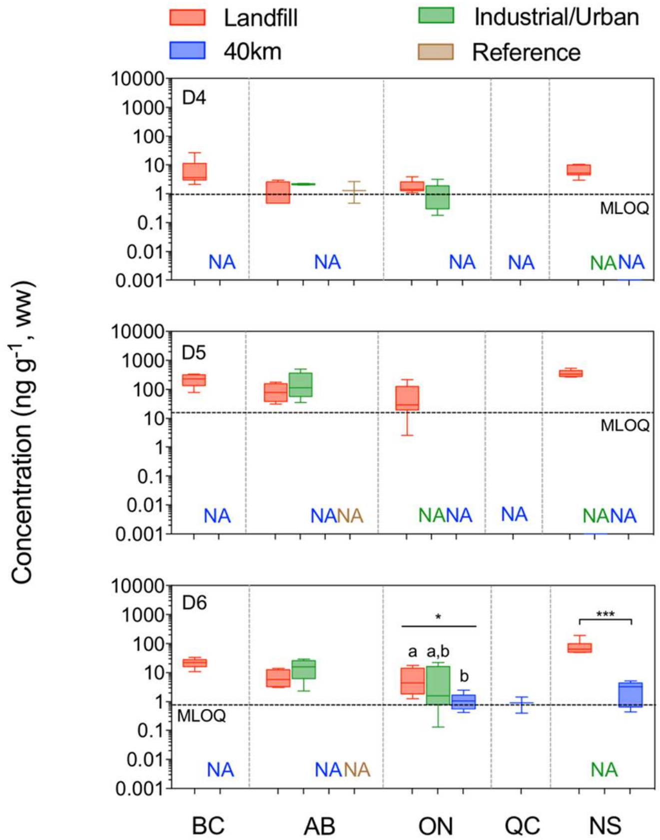

Figure S4. Boxplots of VMSs concentrations (ng g^{-1}, wet weight (ww)) in European starling eggs collected in 2013 and 2014 from landfill, urban industrial sites and rural sites from different provinces of Canada. The rural sites are 40 km distant from the Vancouver, British Columbia (BC); Calgary, Alberta (AB); Hamilton, Ontario(ON); and Halifax, Nova Scotia (NS). For Québec (QC), data is only available for the rural sites 40 km away from Montréal. The reference site for the overall study is located about 300 km southeast of Calgary (Redcliff, AB). Boxplots are defined as follows: center line, median; boxplot edges, 25th and 75th percentile; whiskers, 5th and 95th percentile of distribution. Black dashed lines represent the MLOQs of target compounds. Unpaired two-tailed *t* test with Welch's correction was performed to evaluate the D6 differences between different sampling sites in NS. For ON, differences were tested by one-way ANOVA analysis followed by Tukey's multiple comparison test (* $p<0.05$, *** $p< 0.001$). Different letters indicate significant differences. NA: statistics was not performed due to low detection frequency.

Table S8. Concentrations (ng g^{-1}, wet weight) of VMSs (D4, D5 and D6) in freshwater organisms from peer-reviewed literature.

Organisms	Species	Location	Year	Tissue	D4	D5	D6	Reference
Fish	Brown trout (*Salmo trutta*)	Norway (Lake Mjøsa)	2010	Filets	< MLOQ-4.5	6.4-230	< MLOQ-5.7	1
Fish	Smelt (*Osmerus eperlanus*)	Norway (Lake Mjøsa)	2010	Filets	< MLOQ-2.3	123-199	2.8-7.2	1
Fish	Vendace (*Coregonus albula*)	Norway (Lake Mjøsa)	2010	Filets	< MLOQ-4.0	32-214	1.1-6.7	1
Fish[a]	Vendace (*Coregonus albula*)	Norway (Lake Mjøsa)	2012	Filets	1.0	170	9.5	2
Fish[a]	Small Smelt (*Osmerus eperlanus*)	Norway (Lake Mjøsa)	2012	Filets	0.2	35.3	1.8	2
Fish[a]	Large Smelt (*Osmerus eperlanus*)	Norway (Lake Mjøsa)	2012	Filets	0.2	68.4	4.3	2
Fish[a]	Brown trout (*Salma trutta*)	Norway (Lake Mjøsa)	2012	Filets	0.8	163	8.4	2
Fish[a]	Whitefish (*Coregonus lavaretus*)	Norway (Lake Randsfjorden)	2012	Filets	< MLOQ	1.3	< MLOQ	2
Fish[a]	Smelt (*Osmerus eperlanus*)	Norway (Lake Randsfjorden)	2012	Filets	< MLOQ	19.4	1.2	2
Fish[a]	Brown trout (*Salma trutta*)	Norway (Lake Randsfjorden)	2012	Filets	< MLOQ	56.7	2.9	2
Fish[a]	Arctic char (*Salvelinus alpinus*)	Norway (Lake Femunden)	2012	Filets	< MLOQ	< MLOQ	< MLOQ	2
Fish[a]	Brown trout (*Salma trutta*)	Norway (Lake Femunden)	2012	Filets	< MLOQ	0.3	< MLOQ	2
Fish	Perch[b]	Sweden (Lake Stora Envättern)	2007	Muscle	NA	< MLOQ	NA	3
Fish	Perch[b]	Sweden (Lake Fysingen)	2007	Muscle	NA	< MLOQ	NA	3
Fish	Perch[b]	Sweden (Lake Tärnan)	2007	Muscle	NA	< MLOQ	NA	3
Fish	Perch[b]	Sweden (Lake Gipsjön)	2007	Muscle	NA	< MLOQ	NA	3
Fish	Perch[b]	Sweden (Lake Spjutsjön)	2007	Muscle	NA	< MLOQ	NA	3
Fish	Perch[b]	Sweden (Lake Bysjön)	2007	Muscle	NA	< MLOQ	NA	3
Fish	Perch[b]	Sweden (Lake Östersjön)	2009	Muscle	NA	< MLOQ-1.0	NA	3
Fish	Perch[b]	Sweden (Lake Mälaren)	2009	Muscle	NA	< MLOQ-3.6	NA	3
Fish	Perch[b]	Sweden (Lake Hemfjärden)	2009	Muscle	NA	< MLOQ-3.8	NA	3
Fish	Perch[b]	Sweden (Lake Kyrkviken)	2009	Muscle	NA	2.8-9.6	NA	3
Fish	Perch[b]	Sweden (Lake Ekoln)	2009	Muscle	NA	2.3-19.6	NA	3
Fish	Perch[b]	Sweden (Lake Runn)	2009	Muscle	NA	6.6-30	NA	3
Fish	Various	Lake Erie	2009	Whole	7.9-13	14-36	6.9-14	4
Fish[c]	Lake trout (*Salvelinus namaycush*) or walleye (*Sander vitreus*)	Canada	2009-2010	Whole	0.8-13	5.6-353	0.8-7.5	5
Invertebrate	*Mysis relicta*	Norway (Lake Mjøsa)	2010	Whole	< MLOQ	11-15	< MLOQ-5.7	1
Invertebrate[a]	*Mysis relicta*	Norway (Lake Mjøsa)	2012	Whole	1.3	23.3	1.5	2
Zooplankton epilimnion		Norway (Lake Mjøsa)	2010	Whole	< MLOQ	< MLOQ	< MLOQ-4.4	1
Zooplankton hypolimnion		Norway (Lake Mjøsa)	2010	Whole	< MLOQ	31-50	< MLOQ	1
Zooplankton epilimnion[a]		Norway (Lake Mjøsa)	2012	Whole	< MLOQ	2.4	< MLOQ	2
Zooplankton hypolimnion[a]		Norway (Lake Randsfjorden)	2012	Whole	1.3	58.1	1.7	2
Zooplankton epilimnion[a]		Norway (Lake Mjøsa)	2012	Whole	< MLOQ	1.8	< MLOQ	2
Zooplankton hypolimnion[a]		Norway (Lake Randsfjorden)	2012	Whole	0.9	38.3	0.8	2

a

The wet weight based mean concentrations were estimated from the lipid weight based concentrations and lipid content. [b] The specific species is unknown; [c]Reported as the median concentration range; NA: not measured.

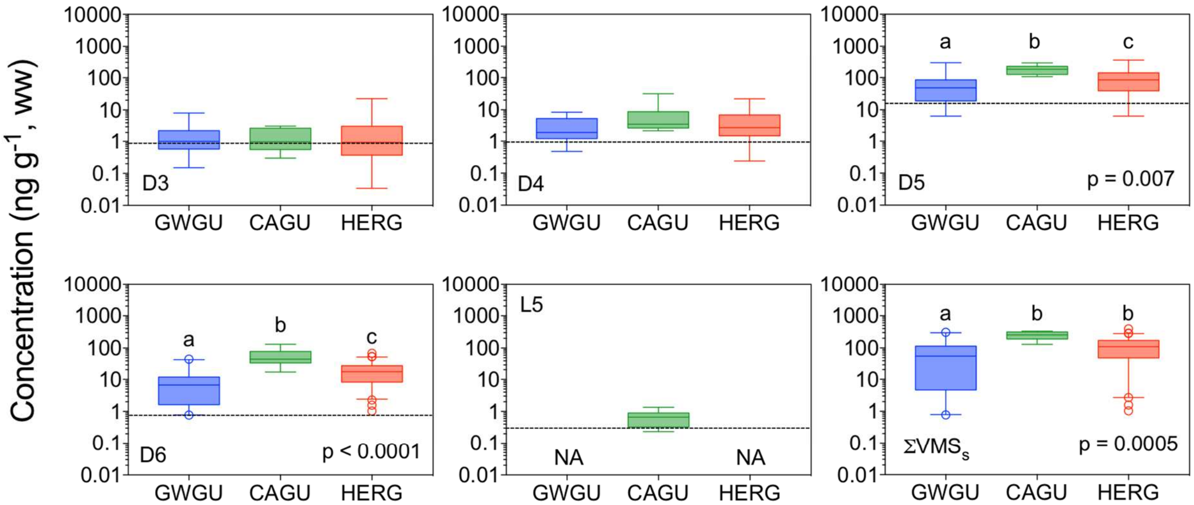

Figure S5. VMSs concentrations (ng g^{-1}, wet weight (ww)) in glaucous-winged gull (GWGU; *n*=21; blue), California gull (CAGU; *n*=8; green) and herring gull (HERG; *n*=70; red) collected in 2011 and 2013 from locations across Canada. Boxplots are defined as follows: center line, median; boxplot edges, 25^{th} and 75^{th} percentile; whiskers, 5^{th} and 95^{th} percentile of distribution. Black dashed lines represent the MLOQs of target compounds. Differences were tested by one-way ANOVA analysis followed by Tukey's multiple comparison test. Different letters indicate significant differences. NA: statistics was not performed due to low detection frequency.

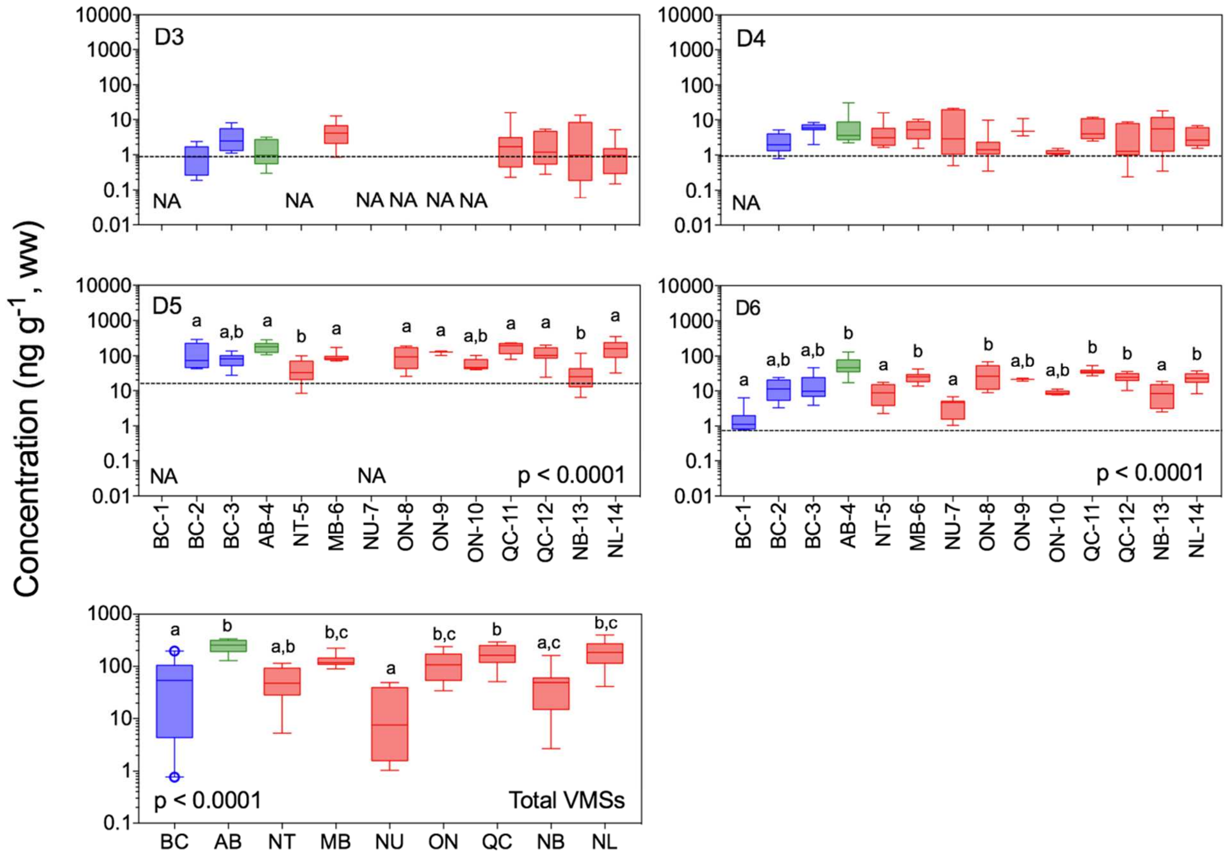

Figure S6. Boxplots of VMSs concentrations (ng g^{-1}, wet weight (ww)) in the eggs of glaucous-winged gull (blue), California gull (green) and herring gull (red) collected in 2011 and 2013 from different locations across Canada. Boxplots are defined as follows: center line, median; boxplot edges, 25th and 75th percentile; whiskers, 5th and 95th percentile of distribution. Black dash lines represent the MLOQs of target compounds. Differences were tested by one-way ANOVA analysis followed by Tukey's multiple comparison test. Different letters indicate significant differences. NA: statistics was not performed due to low detection frequency.

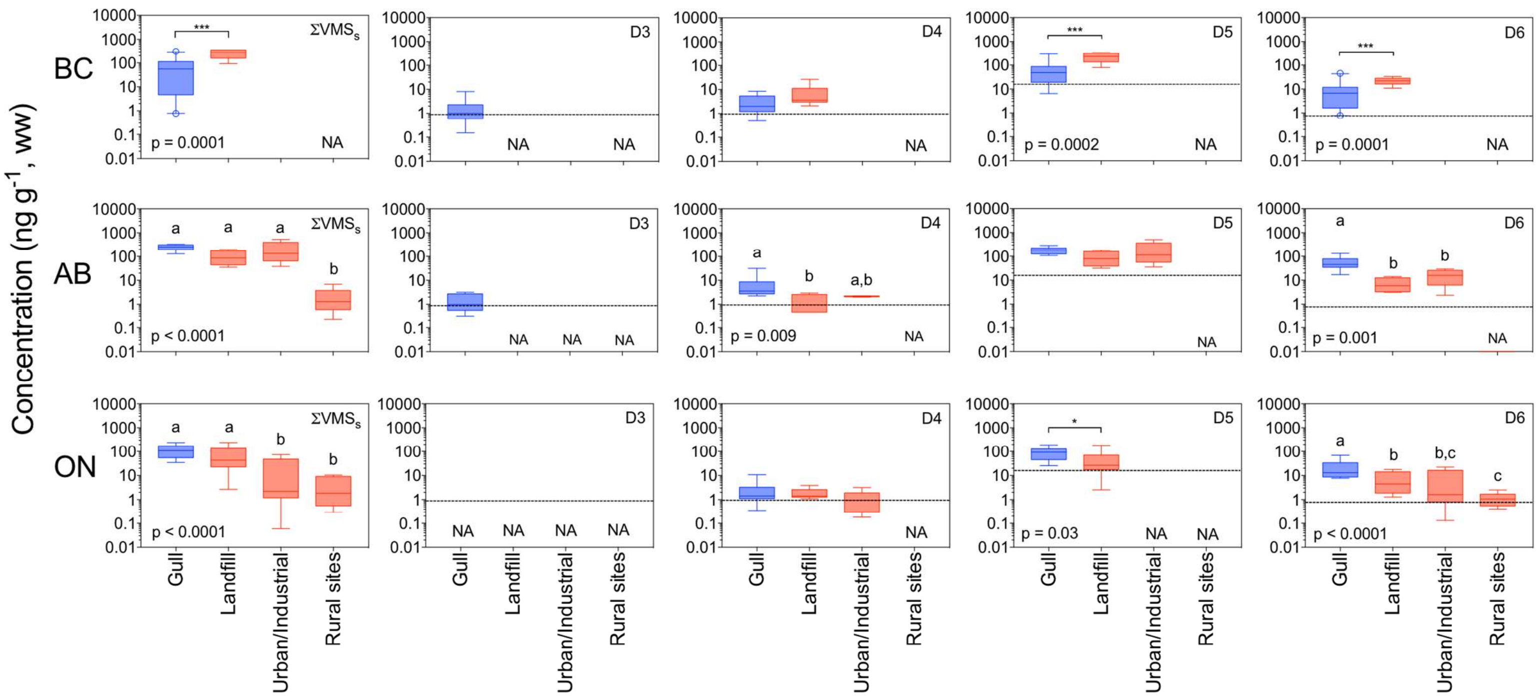

Figure S7. Comparisons of VMSs (ng g^{-1}, wet weight (ww)) in the gulls (blue) and European starling (red) eggs from BC, AB and ON in Canada. Boxplots are defined as follows: center line, median; boxplot edges, 25th and 75th percentile; whiskers, 5th and 95th percentile of distribution. The circles represent outliers. Black dash lines represent the MLOQs of target compounds. The differences were tested by one-way ANOVA analysis followed by Tukey's multiple comparison test or unpaired two-tailed *t* test with Welch's correction. The "Urban/Industrial" data is not available for BC because no sample was collected from this type of site. NA: statistics was not performed due to low detection frequency.

Table S9. Target OPEs concentration ranges (ng g^{-1}; wet weight) in European starling egg homogenates from locations across Canada. Land use type includes landfill, urban industrial, 10 km and 40 km distant from the major urban center, and a reference site. BC = British Columbia; AB = Alberta; ON = Ontario; QC = Québec; NS = Nova Scotia. MLOD = method limit of detection; MLOQ = method limit of quantification. The concentrations of TPHP, T2B4MP, T4B3MP, T3B4MP, TTBNPP, BCMP-BCEP, TEP, TPP, TDBPP were lower than MLOQs for all samples. The concentrations of TEHP were only detected in one sample from the NS-landfill site with 0.46 ng g^{-1} (ww). TEP was not measured in 2011 egg samples.

Sites	Collection year	n	TCEP	TCIPP	TDCIPP	TNBP	TMPP	TBOEP	EHDPP
BC-Landfill-Delta	2011/2013	8	< MLOQ	< MLOQ	< MLOQ	< MLOQ	< MLOD-0.32	< MLOD-4.70	< MLOQ
BC-Industrial/Urban-Abbotsford	2013	2	< MLOD	< MLOD	< MLOQ	< MLOD	< MLOQ-0.11	< MLOQ	< MLOD
BC-40km-Langley	2013	5	< MLOQ	< MLOQ	< MLOQ	< MLOQ	< MLOD	< MLOD-7.17	< MLOQ
AB-Landfill-Calgary	2013	2	< MLOD	< MLOD	< MLOQ	< MLOD	< MLOD	< MLOQ	< MLOD
AB-Industrial/Urban-Calgary	2011/2013	8	< MLOQ-3.89	< MLOQ-7.90	< MLOD-0.94	< MLOQ-7.37	< MLOD-0.11	< MLOQ	< MLOQ-5.35
AB-40km-Strathmore	2013	6	< MLOQ	< MLOQ	< MLOQ	< MLOD-5.79	< MLOQ	< MLOQ-10.3	< MLOQ
AB-reference site-Redcliff	2011/2013	8	< MLOQ-2.08	< MLOQ	< MLOQ	< MLOQ	< MLOD-0.31	< MLOQ	< MLOQ
ON-Landfill-Halton	2013	5	< MLOD-2.86	< MLOQ	< MLOD-1.16	< MLOQ	< MLOD-0.13	< MLOD-5.38	< MLOD
ON-Landfill-Brantford	2011/2013	5	< MLOD-2.96	< MLOQ	< MLOD-3.66	< MLOD	< MLOD	< MLOQ	< MLOQ
ON-Industrial/Urban-Hamilton	2013	5	< MLOD	< MLOD	< MLOQ	< MLOQ	< MLOD-0.20	< MLOQ	< MLOD
ON-10km-Saint George	2011	3	< MLOQ	< MLOQ	< MLOD	< MLOD	< MLOD	< MLOQ	< MLOQ
ON-40km-Delhi	2013	5	< MLOQ-2.24	< MLOQ	< MLOD	< MLOD-12.7	< MLOD	< MLOQ	< MLOQ
QC-Landfill-Lachenaie	2011/2013	6	< MLOD-2.03	< MLOD-5.77	< MLOQ	< MLOQ	< MLOD	< MLOQ	< MLOD
QC-Industrial/Urban-Pointe aux prairies	2013	2	< MLOD	< MLOD	< MLOQ	< MLOD	< MLOD	< MLOD	< MLOD
QC-40km-Lanoraie	2011/2013	8	< MLOQ	< MLOD-5.77	< MLOD-14.0	< MLOD-15.0	< MLOD-0.12	< MLOD	< MLOQ
NS-Landfill-Otter Lake Waste Facility	2011/2013	8	< MLOQ	< MLOQ	< MLOD-20.6	< MLOD	< MLOD-0.14	< MLOQ	< MLOQ
NS-Industrial/Urban-NS Hospital	2013	5	< MLOD	< MLOD	< MLOQ	< MLOD-20.8	< MLOD	< MLOQ	< MLOD
NS-10km-Oakfield Provincial Park	2013	5	< MLOQ	< MLOQ	< MLOD	< MLOD	< MLOD-0.26	< MLOD	< MLOQ
NS-40km-Graves Island Provincial Park	2013	5	< MLOQ	< MLOQ	< MLOD-1.21	< MLOQ-7.49	< MLOD-0.24	< MLOQ	< MLOQ-4.00

Table S10. Target OPEs concentration ranges (ng g^{-1}; wet weight) in gull egg pool homogenates from locations across Canada. BC = British Columbia; AB = Alberta; NT = Northwest Territories; MB = Manitoba; NU = Nunavut; ON = Ontario; QC = Québec; NB = New Brunswick; NL = Newfoundland and Labrador. MLOD = method limit of detection; MLOQ = method limit of quantification. The concentrations of T2B4MP, T3B4MP, T4B3MP, TTBNPP, TEHP, BCMP-BCEP, TPP, TMPP, TDBPP were lower than MLOQ for all samples. TEP was not measured in 2011 egg samples.

	Collection year	n	TEP	TCEP	TCIPP	TPHP	TDCIPP	TNBP	TBOEP	EHDPP
BC-1-Cleland Island	2011/2013	10	< MLOD	< MLOD-0.11	< MLOD-1.19	< MLOD-1.19	< MLOD-0.27	< MLOQ-0.71	< MLOD-2.68	< MLOD-8.74
BC-2-Mitlenatch Island	2011/2013	10	< MLOQ	< MLOD-1.15	< MLOQ	< MLOD-0.90	< MLOQ	< MLOQ	< MLOD-3.35	< MLOQ
BC-3-Mandarte Island	2011/2013	10	< MLOD	< MLOQ	< MLOQ	< MLOQ	< MLOQ	< MLOQ	< MLOQ	< MLOQ
AB-4-Dalmead	2011/2013	10	0.11-0.40	< MLOQ	< MLOD-0.95	< MLOD-0.29	< MLOQ	< MLOQ	< MLOQ	< MLOD-2.99
NT-5-Great Slave Lake	2011	5	not measured	< MLOQ	< MLOQ	< MLOQ	< MLOQ-0.19	< MLOQ-8.80	< MLOQ-9.20	< MLOQ
MB-6-Pipestone Rocks	2011/2013	10	< MLOD	< MLOD	< MLOQ	< MLOQ	< MLOQ	< MLOQ	< MLOQ	< MLOQ
NU-7- Southampton Island-East Bay	2011/2013	10	< MLOD	< MLOD-0.43	< MLOQ	< MLOQ	< MLOQ	< MLOQ	< MLOD-1.20	< MLOQ
ON-8-Agawa Rocks	2013	5	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD	< MLOD
ON-10-Tommy Thompson Park	2013	5	< MLOD	< MLOD	< MLOQ	< MLOD-0.10	< MLOD	< MLOD-0.10	< MLOD-0.69	< MLOD
QC-11-Ile Deslauriers	2011/2013	9	< MLOQ	< MLOD-2.60	< MLOD-5.50	< MLOD-1.40	< MLOD-0.17	< MLOQ	< MLOD-1.10	< MLOD-1.47
QC-12-Ile Bellechasse	2011/2013	10	< MLOD-0.12	< MLOD-2.35	< MLOQ	< MLOD-2.65	< MLOD-0.32	< MLOD-2.30	< MLOD-4.95	< MLOQ
NB-13-Kent Island	2011/2013	10	< MLOD	< MLOD-0.16	< MLOD-2.4	< MLOD-0.42	< MLOQ	< MLOD-8.70	< MLOD-9.10	< MLOQ
NL-14-Gull Island	2011/2013	10	< MLOQ	< MLOQ	< MLOD-2.32	< MLOQ	< MLOD-0.16	< MLOQ	< MLOQ	< MLOQ

Table S11. Concentrations (ng g^{-1}, wet weight) of OPEs in different tissues of birds in peer-reviewed literature.

Species	Location	Year	Tissue	TEP	TCEP	TCIPP	TPHP	TDCIPP	TNBP	TBOEP	EHDPP	TEHP	Reference
Herring gull (*Larus argentatus*)	Lake Ontario	2010	Egg	NA	NA	0.45	ND	ND	ND	0.55	NA	NA	6
Herring gull (*Larus argentatus*)	Lake Erie	2010	Egg	NA	NA	0.83	ND	ND	ND	0.83	NA	NA	6
Herring gull (*Larus argentatus*)	Lake Huron	2010	Yolk	ND-0.81	1.38	6.05	0.89	0.93	3.63	1.89	ND-2.49	< MLOQ	7
Herring gull (*Larus argentatus*)	Lake Huron	2010	Albumen	< MLOQ-23	1.46	2.31	< MLOQ-4.18	0.47	< MLOQ-28	8.09	< MLOQ-10.9	< MLOQ-1.94	7
Herring gull (*Larus argentatus*)	Lake Huron	2010	Fat	< MLOQ-5.89	0.65	2.14	2.11	4.43	2.02	13.4	< MLOQ-2.11	7.49	7
Herring gull (*Larus argentatus*)	Lake Huron	2010	Muscle	0.68	< MLOQ-1.51	1.42	< MLOQ-1.03	5.04	1.79	1.37	0.41	< MLOQ-0.22	7
Chicken (*Gallus gallus domesticus*)	China	2010	Egg	NA	0.32-2.38	< MLOQ-3.49	< MLOQ-0.69	< MLOQ-13.1	< MLOQ	< MLOQ	< MLOQ-0.83	< MLOQ	8

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