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Twenty Years of Temporal Changes in Perfluoroalkyl Sulfonate and Carboxylate Contaminants in Herring Gull Eggs from the Laurentian Great Lakes

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SUPPLEMENTARY INFORMATION

Table S1. Chemical structures of the target compounds and the internal standards used.

Target Compound	Chemical Structure	Internal Standard
PFBS	$CF_3(CF_2)_3SO_3^-$	PFHxA-$^{13}C_2$
PFHxS	$CF_3(CF_2)_5SO_3^-$	PFHxS-$^{18}O_2$
PFOS	$CF_3(CF_2)_7SO_3^-$	PFOS-$^{13}C_4$
PFDS	$CF_3(CF_2)_9SO_3^-$	PFUnA-$^{13}C_2$
PFOSA	$CF_3(CF_2)_7SO_2NH_2$	PFOSA-$^{13}C_8$
N-Me-FOSA	$CF_3(CF_2)_7SO_2NCH_3H$	d-N-Me-FOSA
PFHxA	$CF_3(CF_2)_4COOH$	PFHxA-$^{13}C_2$
PFHpA	$CF_3(CF_2)_5COOH$	PFHxS-$^{18}O_2$
PFOA	$CF_3(CF_2)_6COOH$	PFOA-$^{13}C_4$
PFNA	$CF_3(CF_2)_7COOH$	PFNA-$^{13}C_5$
PFDA	$CF_3(CF_2)_8COOH$	PFDA-$^{13}C_2$
PFUnA	$CF_3(CF_2)_9COOH$	PFUnA-$^{13}C_2$
PFDoA	$CF_3(CF_2)_{10}COOH$	PFDoA-$^{13}C_2$
PFTriA	$CF_3(CF_2)_{11}COOH$	PFDoA-$^{13}C_2$
PFTeA	$CF_3(CF_2)_{12}COOH$	PFDoA-$^{13}C_2$
PFPA	$CF_3(CF_2)_{13}COOH$	PFDoA-$^{13}C_2$
6:2 FTUCA	$CF_3(CF_2)_4CFCH_2COOH$	6:2 FTUCA-$^{13}C_2$
8:2 FTUCA	$CF_3(CF_2)_6CFCH_2COOH$	8:2 FTUCA-$^{13}C_2$
10:2 FTUCA	$CF_3(CF_2)_8CFCH_2COOH$	10:2 FTUCA-$^{13}C_2$
6:2 FTOH	$CF_3(CF_2)_4CF(CH_2)_2OH$	6:2 FTOH-$^{13}C_2$
8:2 FTOH	$CF_3(CF_2)_6CF(CH_2)_2OH$	8:2 FTOH-$^{13}C_2$
10:2 FTOH	$CF_3(CF_2)_8CF(CH_2)_2OH$	10:2 FTOH-$^{13}C_2$

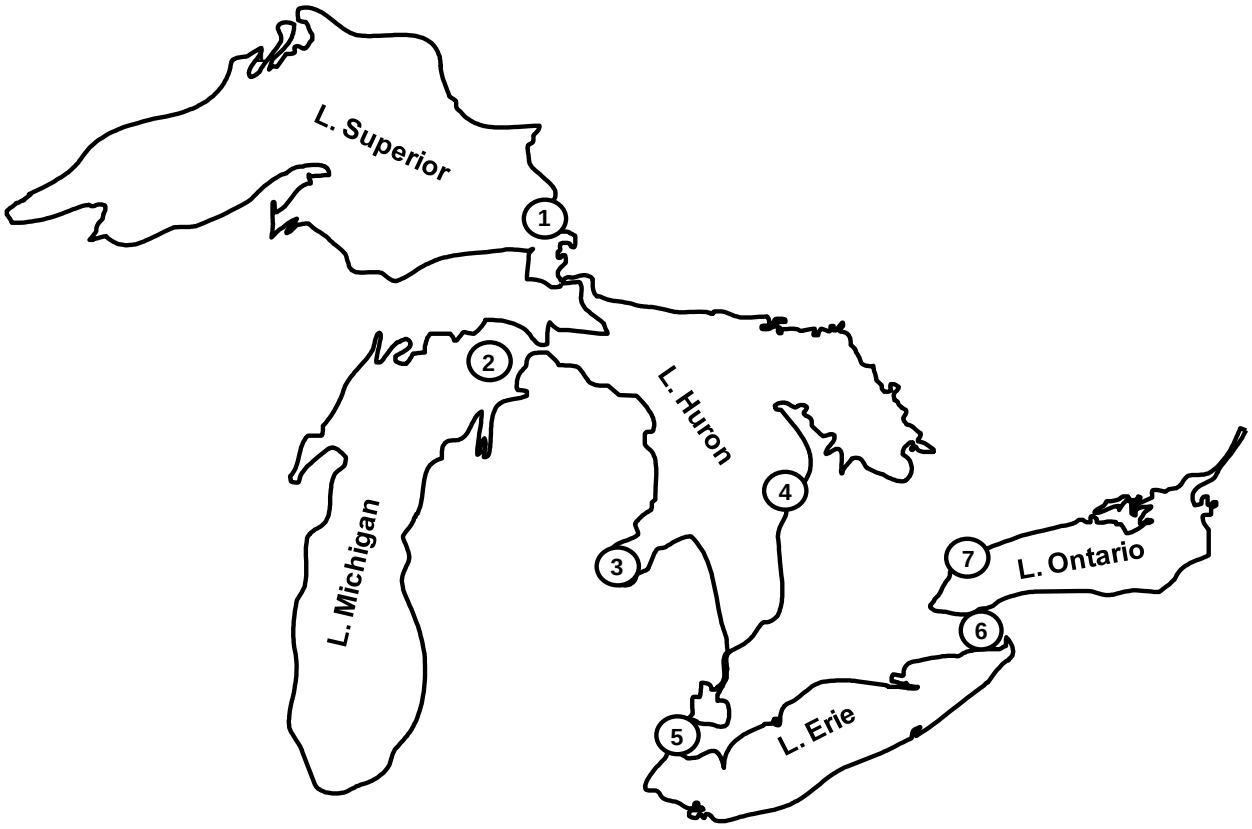

Figure S1. Location of the herring gull colonies throughout the Laurentian Great Lakes of North America: 1 Agawa Rocks, 2 Gull Island, 3 Channel-Shelter Island, 4 Chantry Island, 5 Fighting Island, 6 Niagara River, 7 Toronto Harbour.

Table S2. Average percent (range) of individual perfluorinated sulfonate (PFSA) to ∑PFSA concentrations and individual perfluorinated carboxylate (PFCA) to ∑PFCA concentrations in herring gull eggs, and temporal changes of percent PFSA and PFCA between 1990 and 2010[a]. The bold the line separates the PFSA and PFCA compounds.

PFC		Colony						
		Agawa Rocks	Gull Is	Channel-Shelter Is	Chantry Is	Fighting Is	Niagara R	Toronto Hbr
PFHxS	Average	0.23 (0–1.6)	0.22 (0.01–0.73)	0 – 0.25[b]	0.15 (0–0.39)	0.17 (0–0.56)	0.11 (0–0.32)	0.34 (0.15–0.79)
	r	0.070	0.094		-0.136	-0.172	-0.321	-0.086
	p	0.80	0.74		0.63	0.56	0.24	0.76
PFOS	Average	98.1 (94.3–99.1)	98.4 (96.8- 99.2)	94.0 (88.3–97.2)	97.2 (92.5–98.6)	90.1 (79.8–97.1)	98.2 (95.9–99.4)	96.2 (88.2–99.2)
	r	0.279	0.220	**0.643**	0.407	**0.600**	0.466	**0.928**
	p	0.31	0.43	**0.001**	0.13	**0.02**	0.08	**0.0001**
PFDS	Average	1.7 (0.77–4.1)	1.4 (0.65–2.5)	6.0 (2.8–11.6)	2.7 (1.2–7.1)	9.7 (2.9–20.2)	1.7 (0.53–4.0)	3.4 (0.68–11.7)
	r	-0.382	-0.275	**-0.634**	-0.410	**-0.597**	-0.445	**-0.921**
	p	0.16	0.32	**0.01**	0.13	**0.02**	0.10	**0.0001**
PFOA	Average	0.62 (0–1.6)	1.3 (0–3.7)	0 – 0.53	1.3 (0.07–3.2)	0 – 1.8	0 – 0.72	1.2 (0.27–2.2)
	r	-0.269	-0.464		-0.483			**-0.632**
	p	0.33	0.08		0.07			**0.01**
PFNA	Average	14.2 (9.7–18.7)	9.0 (2.5–14.8)	5.4 (2.1–11.0)	10.8 (5.7–20.3)	1.7 (0.47–4.6)	7.2 (3.7–11.6)	7.7 (4.4–11.6)
	r	0.320	0.110	0.106	**-0.715**	0.002	0.015	-0.446
	p	0.24	0.70	0.71	**0.003**	0.99	0.96	0.10
PFDA	Average	12.9 (10.3–17.3)	15.5 (7.2–25.5)	15.6 (8.6–19.4)	12.2 (9.2–15.7)	13.3 (9.9–17.0)	20.9 (16.1–29.3)	17.1 (14.2–21.6)
	r	-0.350	-0.443	**0.568**	0.137	**0.739**	0.419	**-0.557**
	p	0.20	0.10	**0.03**	0.63	**0.003**	0.12	**0.03**
PFUnA	Average	28.0 (22.0–33.0)	22.8 (17.0–27.9)	37.0 (27.5–52.2)	20.9 (17.8-29.4)	22.0 (17.4–29.1)	27.6 (22.8–34.5)	22.0 (18.3–30.0)
	r	0.282	0.163	-0.456	**-0.644**	-0.372	-0.504	-0.152
	p	0.31	0.56	0.09	**0.001**	0.19	0.06	0.59
PFDoA	Average	10.4 (8.1–12.2)	11.5 (7.5–15.3)	11.1 (8.1–14.4)	11.3 (8.4–19.0)	19.7 (13.7–26.8)	11.6 (9.2–13.4)	18.8 (14.7–27.0)
	r	-0.001	0.118	**0.544**	**0.680**	**0.542**	-0.005	-0.291
	p	0.99	0.67	**0.04**	**0.005**	**0.05**	0.99	0.29
PFTrA	Average	26.4 (13.4–32.9)	28.9 (19.5–45.1)	22.7 (14.5–29.3)	30.8 (18-9–39.9)	27.3 (16.9–37.6)	25.0 (20.1–30.8)	20.2 (14.7–26.4)
	r	-0.169	0.315	-0.186	0.141	**-0.79**	-0.153	0.331
	p	0.55	0.25	0.51	0.62	**0.0009**	0.59	0.23
PFTeA	Average	4.9 (3.3–8.1)	7.2 (3.2–10.5)	5.4 (0–8.4)	8.6 (3.1–14.2)	11.3 (3.8–16.2)	5.1 (2.7–8.0)	10.7 (6.2–19.2)
	r	-0.188	-0.081	**0.445**	**0.574**	0.361	0.011	0.452
	p	0.50	0.78	**0.01**	**0.03**	0.20	0.97	0.09
PFPA	Average	2.6 (0–5.4)	3.5 (0–8.9)	2.8 (0.40–5.0)	4.2 (0–8.1)	4.4 (0–8.3)	2.5 (0.13–6.7)	2.5 (0–5.7)
	r	0.008	-0.055	-0.007	0.229	0.262	0.247	**0.754**
	p	0.98	0.85	0.98	0.41	0.36	0.37	**0.001**

[a] Pearson's coefficient and significance are given for each percent of PFSA/CA to ∑PFSA/CA as a function of year.
[b] Detection of individual PFSA or PFCA was in <60% of the analyzed years, range of percent to the sum concentrations are given.
Note. The bold values indicate that the linear correlations were statistically significant ($p<0.05$).