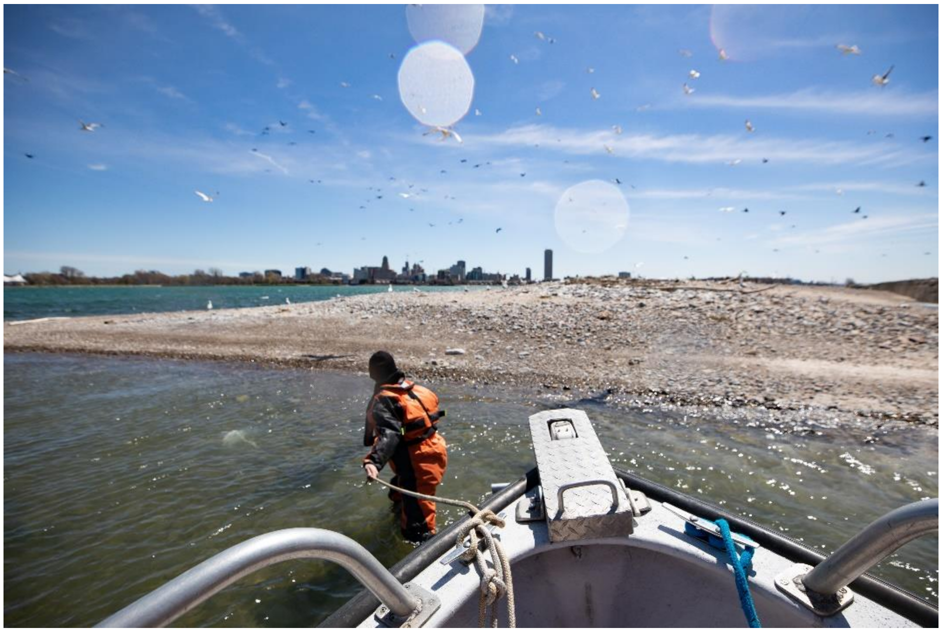
 

Degradation of Fish and Wildlife Populations in the Niagara River (Ontario) AOC - Colonial Waterbird Populations and Current Trends



Environment and Climate Change Canada – Ecotoxicology & Wildlife Health Division
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Photo credit (boat): Scott Gable

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PURPOSE

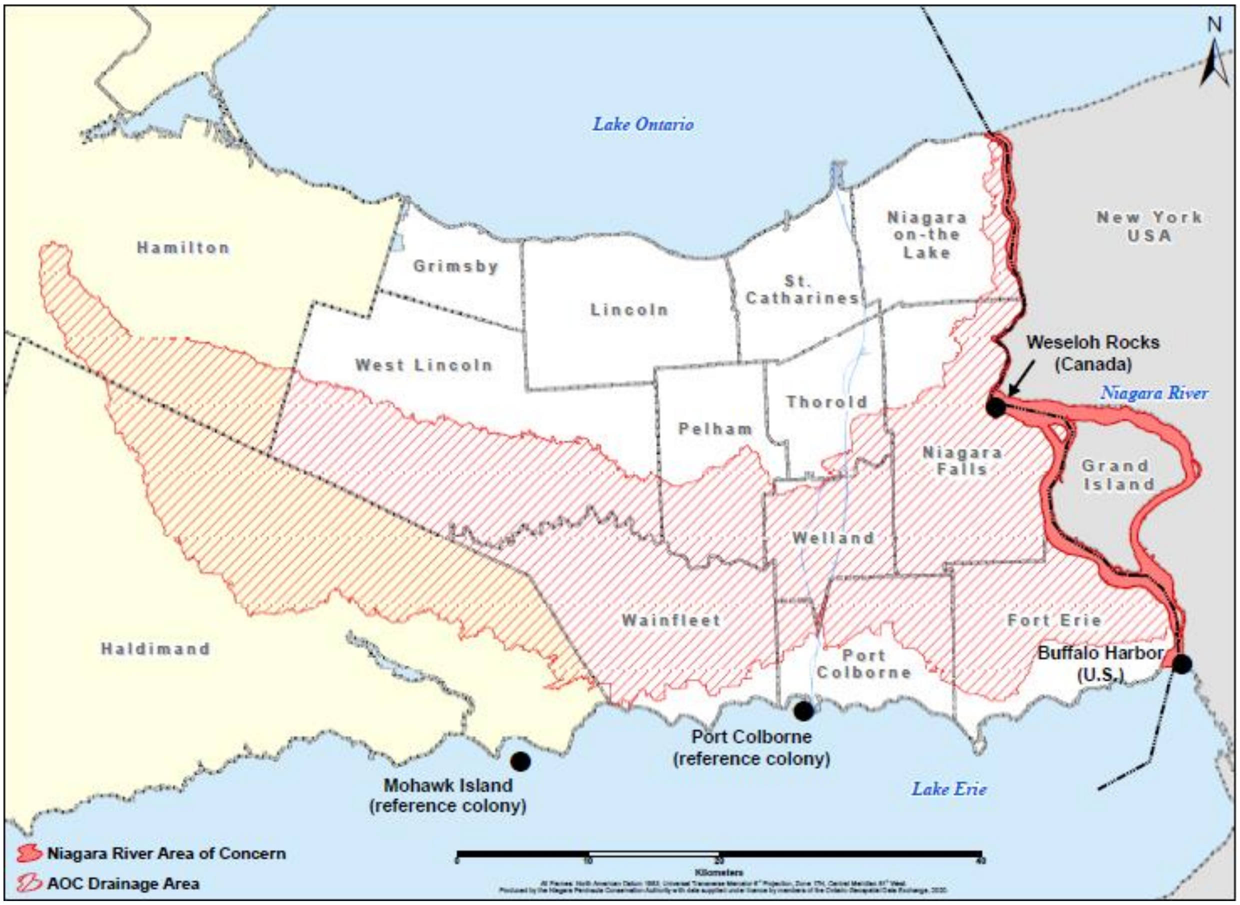
This summary provides updated trends for the assessment of colonial waterbird populations in the Niagara River (Ontario) Area of Concern (AOC). Two colonial waterbird species that breed and forage within the Niagara River AOC were selected for assessment purposes. The Herring Gull (*Larus argentatus*) is a long-lived, primarily fish-eating colonial waterbird that, from the time it reaches breeding age, is a year-round resident in the Great Lakes basin. The Herring Gull has been used as an avian sentinel species in the Great Lakes for decades. A second aquatic-feeding colonial waterbird species, the Double-crested Cormorant (*Phalacrocorax auritus*), was also selected for assessment. This species feeds almost exclusively on fish compared to Herring Gulls that are opportunistic feeders and will consume terrestrial prey if fish are not readily available. This close connection to the aquatic environment is vital for assessment of local conditions in the AOC.

Delisting criteria for the *Degradation of Fish and Wildlife Populations* Beneficial Use Impairment (BUI 3) were updated by the Niagara River Remedial Action Plan (RAP) team in 2020 as part of their Delisting Strategy (Green et al., in prep). For the Niagara River (Ontario) AOC, the wildlife portion of this BUI will no longer be considered impaired when:

> **Criterion 1.** a monitoring plan is developed and there is a commitment confirmed by local partners for long-term implementation at suitable wetland sites along the upper Niagara River;
>
> **Criterion 2.** breeding colonial waterbird populations within the Niagara River AOC are the same as (or better than) suitable reference sites;
>
> **Criterion 3a.** temporal trends in contaminant concentrations in eggs, tissues, or whole-body burden of sentinel species in the Niagara River AOC are stable or declining; <u>AND</u>
>
> **Criterion 3b.** spatial comparisons show that contaminant concentrations in eggs, tissues, or whole-body burden of sentinel species in the Niagara River AOC are the same as (or better than) other suitable reference sites; <u>OR</u>
>
> **Criterion 3c.** if the contaminant concentrations in 3a or 3b are not met, then they must not exceed established thresholds associated with potential population-level effects (i.e., reproductive impacts).

This colonial waterbird study was conducted to assess delisting criteria #2 and 3 and not criterion 1 which will be assessed separately by the RAP team. With respect to criterion #2, one approach for assessing the health of breeding colonial waterbird populations is through artificial incubation of eggs under controlled conditions in the laboratory. This method is valuable for assessing the importance of intrinsic factors such as contaminants that may induce embryonic mortality at this critical developmental stage and thereby impact bird populations. This was examined in the current study using cormorant eggs. Population trends of nesting colonial waterbirds in the AOC were also assessed previously based on nest count surveys conducted until 2017 on the Canadian side of the Niagara River (Hughes *et al.* 2014, 2017). Since then, no surveys have been conducted and therefore no additional nest count data are available to supplement those trends.

Figure 1. Map of the Niagara River Area of Concern and its watershed. Nesting locations of colonial waterbirds are shown at Weseloh Rocks where annual collections of Herring Gull eggs were conducted from 1979 to 2015 and Buffalo Harbor where collections of colonial waterbird eggs were conducted in 2018 and 2019 for the current study. Nesting locations at Mohawk Island and Port Colborne in the eastern basin of Lake Erie used as reference sites in this study are also shown (map credit: T. Gaade, Niagara Peninsula Conservation Authority).



For delisting criteria #3a and 3b, annual assessments of contaminants in eggs of Herring Gulls nesting on the Canadian side of the Niagara River have been conducted at Weseloh Rocks since 1979 (Figure 1; note criterion #3c only applies should criteria #3a and 3b fail). This site comprises several small islands and rocks and is one of a few Canadian nesting sites situated at the top of Niagara Falls. However due to high water levels on the Niagara River and elsewhere on the Great Lakes, it has not been possible to access this site and collect gull eggs for contaminant analysis since 2015. High water levels at this site have also reduced nesting habitat available for Herring Gulls (as ground-nesters) compared to earlier years. In order to assess the current status of wildlife populations BUI 3 for colonial waterbirds, an alternate site was selected on the Niagara River. This site is situated approximately 25 kilometres upstream at the North Breakwall outside of Buffalo Harbor (Figure 1). Nesting colonies of both Herring Gulls and Double-crested Cormorants are established at this site and cormorant eggs are laid in ground nests (vs trees) making them easily accessible for collection. While this site is within the Niagara River AOC boundary in the state of New York in the United States, these results will be used to assess the status of BUI 3 in the Niagara River AOC in Ontario. The North Breakwall site is approximately 1.2 kilometres from the entrance lighthouse that marks the boundary of another Great Lakes AOC (Buffalo River). The daily foraging ranges of nesting gulls and cormorants at the North Breakwall site would include areas where prey (fish) is abundant particularly in the Upper Niagara River and downstream; hence contaminant burdens acquired are likely reflective of environmental conditions within this binational AOC. It is possible that these birds may spend some time foraging beyond the Niagara River and outside of the AOC including at Buffalo Harbor and Lake Erie.

Gull and cormorant eggs were collected from the Buffalo Harbor site in the Niagara River AOC and appropriate reference sites in eastern Lake Erie in 2018 and 2019. There were two components to this BUI 3 colonial waterbird populations assessment: 1) artificial incubation of cormorant eggs to assess embryonic viability and deformity frequencies in the laboratory and 2) contaminant analysis of gull and cormorant eggs to examine spatial trends in the AOC, assess burdens against thresholds associated with population-level effects, and update temporal trends last measured in eggs from the AOC at Weseloh Rocks in 2015. The results of this study will be examined against delisting criteria #2 and 3 to assess the current status of this BUI using these sentinel species.

METHODS

For the artificial incubation component of this study, Double-crested Cormorant eggs were collected from the North Breakwall site (42.8843°, -78.9009°) - hereafter referred to as “Buffalo Harbor” - in 2018 and 2019 (Figure 1). Mohawk Island (42.8338°, -79.5228°), situated in the eastern basin of Lake Erie, was selected as the reference site for this component of the study (Figure 1). For analysis of contaminants, eggs of both cormorants and gulls were collected from Buffalo Harbor in the two years. Port Colborne (42.8683°, -79.2568°) is also in the eastern basin of Lake Erie and this nesting site has been monitored annually for contaminants in Herring Gulls since 1974 (Figure 1). Thus, Port Colborne was selected as the reference site for the contaminant burden component of this study and is where Herring Gull and cormorant eggs were collected in the two study years. Herring Gull eggs were also collected from Mohawk Island in 2018 for contaminant analysis and these data are provided for comparison.

Artificial Incubation of Double-crested Cormorant Eggs:

In early May of 2018 and 2019, unincubated cormorant eggs were collected in the field from nests containing a single egg, transported to the National Wildlife Research Centre (NWRC) in Ottawa in insulated coolers with foam inserts, and set in a Petersime incubator (model# MX-1) at 37°C, 58% humidity and turned every two hours. Numbers of eggs collected for artificial incubation from each site ranged from 13–30 in the two study years. Just prior to the pipping stage of development (i.e., embryonic day 26–27), embryos were removed from their shells and euthanized by decapitation. Each embryo was examined for physical deformities. Embryonic viability was determined as the number of viable embryos that survived to the designated embryonic day (i.e., just prior to pipping) divided by the total number of fertile eggs. Eggs that were nonviable were staged if possible (e.g., infertile; early, mid or late embryo death). Individual embryos were weighed and head-bill length, tarsus length, and liver mass were determined. As an index of contaminant exposure, a liver somatic index was calculated as liver mass divided by embryo mass. Body condition was estimated using residuals calculated from a linear regression of embryo mass on tarsus length in each of the two study years.

Contaminant Analyses:

For contaminant analysis, single Herring Gull and cormorant eggs were collected from 13 nests containing $\geq$ 3 eggs at each colony in the two years. After collection, the eggs were sent to NWRC where contents were placed in chemically-cleaned glass jars, homogenized, and frozen until chemical analysis. Eggs from each colony were pooled together as a single sample for chemical analysis in each study year.

Chemical analyses of eggs for organochlorine compounds and polybrominated diphenyl ethers (PBDEs) were conducted at NWRC. Prior to chemical analysis, thawed eggs were homogenized, lipids were removed, and chemicals of interest in the extracts were separated from remaining lipids and biogenic compounds by gel permeation chromatography. Purified sample extracts were then analyzed for organochlorine compounds and flame retardants (including PBDEs) using the capillary gas chromatograph coupled with a mass selective detector (GC-MSD). Organochlorine compounds measured included *p,p'*-DDE (dichlorodiphenyldichloroethylene), oxychlordane, *cis*-chlordane, *trans*-chlordane, *cis*-nonachlor, *trans*-nonachlor, hexachlorobenzene (HCB), dieldrin, heptachlor epoxide (HE), mirex, octachlorostyrene (OCS), and polychlorinated biphenyls (PCBs). Sum chlordane is based on the sum concentration of oxychlordane, *cis*-chlordane, *trans*-chlordane, *cis*-nonachlor, and *trans*-nonachlor. Sum PCBs are based on the sum concentration of 35 individual or co-eluting PCB congeners found above the limit of detection. Similarly, sum PBDEs are based on the sum concentration of 15 individual or co-eluting PBDE congeners found above the limit of detection. Certified internal standards were used for quantification and certified reference materials, blanks and duplicate samples were analyzed for quality assurance purposes. Concentrations of organochlorines and PBDEs are reported in µg/g on a wet weight basis. Method detection limits for organochlorine compounds and individual PBDE congeners ranged from 0.00001–0.004 µg/g.

Herring Gull eggs were analyzed in 2018 for non-*ortho s*ubstituted PCBs, polychlorinated dibenzo-*p*-dioxins, including 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), and polychlorinated dibenzofurans using gas chromatography high resolution mass spectrometry (GC/HRMS) at ALS Life Sciences in Burlington, Ontario. Reference materials, blanks, and duplicates were analyzed for quality assurance purposes.

Total mercury was quantified on a DMA-80 (Direct Mercury Analyzer) at NWRC on a dry weight basis and is reported in µg/g. Method detection limits ranged from 0.001–0.003 µg/g. Certified reference materials and duplicate samples were also analyzed to ensure correct calibration, accuracy, and reproducibility of test methods. Mercury concentrations are also reported on a wet weight basis using percent moisture content.

Stable Isotopes:

Stable isotope analyses of samples were conducted at the Ján Veizer Stable Isotope Laboratory at the University of Ottawa in Ontario. Following lipid-extraction, samples were weighed into tin capsules and loaded into an elemental analyser. The sample was flash combusted at ~1800^{o}C (Dumas combustion) and the resultant gas products were carried by helium through columns of oxidizing/reducing chemicals optimised for CO_2 and N_2. The gases were separated by a purge and trap adsorption column and sent to the Delta Advantage isotope ratio mass spectrometer coupled with Conflo IV. Samples were normalized to internal standards and calibrated to international standards. Stable isotope ratios are expressed in δ notation as the deviation from standards in parts per thousand (‰) according to the following relationship:

$$\delta X = (R_{sample}-R_{standard})/R_{standard} \times 1000$$

where X is ^{15}N or ^{13}C and R is the corresponding ratio $^{15}N/^{14}N$ or $^{13}C/^{12}C$. In this study, $\delta^{15}N$ signatures were compared to infer relative (and not absolute) trophic position at colonies.

Statistical Analysis:

Contaminants and biological endpoints were statistically analyzed using a Student's *t*-test for between colony comparisons. Data were log-transformed (log_{10}) to meet conditions of equal variance and normality for parametric analysis. If data failed these assumptions, comparisons were made using a Mann-Whitney U non-parametric test. Mercury concentrations in samples were statistically analyzed on a dry weight basis; however, concentrations are reported on a wet weight basis for comparison to a published protective level threshold. A Fisher exact test was used to test for a significant difference in embryonic viability and deformity frequencies between colonies combined for the two study years. All results were considered significant at $p<0.05$. Concentrations of 2,3,7,8-TCDD toxic equivalents (TEQs) were calculated for dioxin-like PCBs, furans, and dioxins and are based upon toxic equivalency factors developed by van den Berg *et al.* (1998) for birds. Dioxin-like PCBs include four non-*ortho* PCB congeners (77, 81, 126, and 169) and seven individual or co-eluting mono-*ortho* PCB congeners (105, 114, 118, 123, 156/157, 167, and 189). Total TEQ concentration is based on the sum concentration of TEQs calculated for the 4 non-*ortho* PCBs, 7 mono-*ortho* PCBs, and 17 dioxin and furan congeners.

RESULTS

A) Artificial Egg Incubation Study

Embryonic Viability and Deformities:

Embryonic viability was equal to 81% and 90% in Double-crested Cormorants from the Niagara River AOC colony at Buffalo Harbor in 2018 and 2019, respectively (Table 1). Embryonic viability was slightly lower overall in cormorants from the Lake Erie reference colony at Mohawk Island and equal to 85% in 2018 and 76% in 2019. Of 55 fertile eggs examined at Buffalo Harbor, five died in 2018 (embryonic day 23–27; i.e., late-stage deaths) and three died in 2019 (embryonic day 10 [1 embryo] and embryonic day 25 [2 embryos]). Of 30 fertile eggs examined at Mohawk Island, two died in 2018 (developmental stage not determined) and four died in 2019 (embryonic day 4–6 [2 embryos] and embryonic day 8–10 [2 embryos]. Deformed embryos were found in a single egg in each year at Buffalo Harbor (one with an exposed abdomen and one with gastroschisis) resulting in an overall incidence of embryonic deformities of 4% at the AOC colony (2 deformed embryos/55 fertile embryos). Embryonic deformities were not observed in incubated eggs from the reference colony (0 deformed embryos/30 fertile embryos). For both years combined, there was no significant difference in embryonic viability between the AOC colony

Table 1. Embryonic viability and incidence of embryonic deformities in artificially incubated Double-crested Cormorant eggs collected from the Niagara River AOC colony (Buffalo Harbor) and the reference colony in eastern Lake Erie (Mohawk Island) in 2018 and 2019.

Colony	AOC/ Ref	Year	Total No. Eggs	No. Infertile Eggs	No. Fertile Eggs	No. Viable Eggs	No. Dead Eggs	Embryonic Viability (%)	No. Deformities	Deformities (%)
Buffalo Harbor	AOC	2018	27	1	26	21	5	81%	1	4%
	AOC	2019	30	1	29	26	3	90%	1	3%
Overall	**AOC**		**57**	**2**	**55**	**47**	**8**	**85%**	**2**	**4%**
Mohawk I.	REF	2018	13	0	13	11	2	85%	0	0%
	REF	2019	21	4	17	13	4	76%	0	0%
Overall	**REF**		**34**	**4**	**30**	**24**	**6**	**80%**	**0**	**0%**

and the reference colony. Similarly, there was no significant difference in deformity frequencies of embryos between the two study colonies.

Liver Somatic Index and Body Condition of Embryos:

The liver somatic index was significantly higher in cormorant embryos from the reference colony at Mohawk Island compared to the Buffalo Harbor AOC colony in 2018 (Mann Whitney U=21.0, $p=0.02$; Figure 2a). There was no significant difference for this metric between the two study colonies in 2019. Body condition of embryos, estimated using body mass and tarsus length, was not significantly different between embryos from the two colonies in both study years (Figure 2b).

B) Contaminants in Eggs

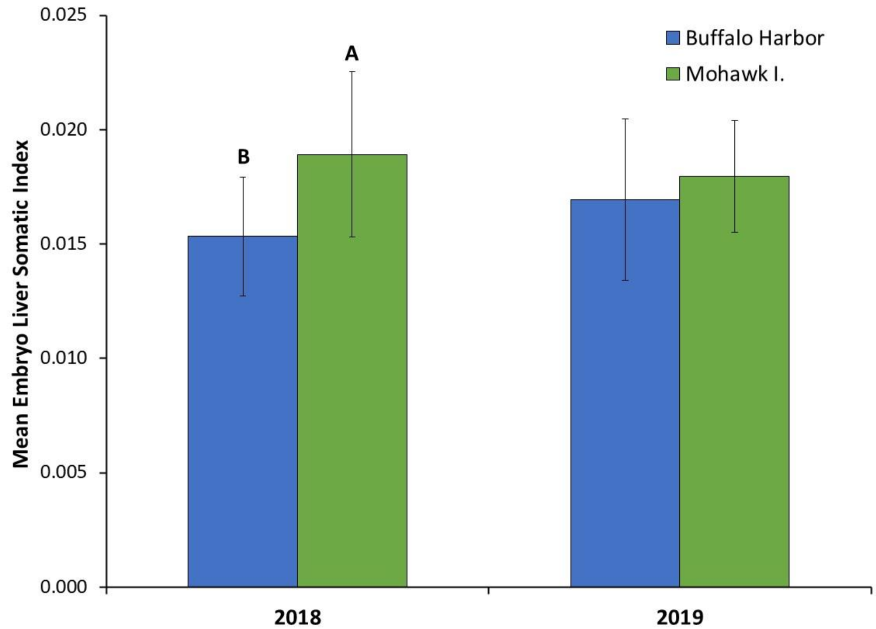
Spatial Trends:

Overall, there were no significant differences in mean concentrations of sum PCBs, other organochlorines, and sum PBDEs in Herring Gull eggs collected from the AOC colony in Buffalo Harbor and the upstream reference colony at Port Colborne in 2018 and 2019 (Table 2; based on analysis of single pooled samples in each year). Herring Gull eggs from Mohawk Island were not included in this comparison since data for 2018 only are available; however, concentrations at this colony were very similar to those at the other two gull colonies. Contaminant burdens were also largely comparable between cormorant eggs from Buffalo Harbor in the two study years and those from Port Colborne in 2019 (for which no statistical comparisons were conducted). Of all organochlorine compounds, sum PCBs were found at the highest concentrations in eggs with concentrations ranging from 1.35 µg/g in cormorant eggs from Buffalo Harbor in 2019 to 3.38 µg/g in gull eggs from Port Colborne in 2018. Concentrations of *p,p'*-DDE in all eggs were below 1 µg/g followed by sum PBDEs that were below 0.4 µg/g. Concentrations of remaining organochlorines were below 0.05 µg/g in all eggs. Percent lipid content was not significantly different between the two colonies in 2018 and 2019 with means in Herring Gull eggs of 7.6% and 6.8% at Buffalo Harbor and Port Colborne, respectively; percent lipid content was equal to 8.2% in gull eggs from Mohawk Island (2018). In cormorants, percent lipid content was relatively lower and equal to 4.1% in eggs from Buffalo Harbor (mean, 2018 and 2019) and 4.4% in eggs from Port Colborne. While contaminant burdens appeared to be higher in gulls compared to cormorants, this is related to differences in lipid content in eggs between the two species. Concentrations of these lipophilic compounds were much more similar between the two species when expressed on a lipid weight basis (data not shown).

In 2018, concentrations of non-*ortho* PCBs and 2,3,7,8-TCDD were not notably elevated in Herring Gull eggs from Buffalo Harbor compared to Port Colborne and Mohawk Island and frequently were within the range of burdens found at the two reference colonies (Table 3). Similarly, TEQs calculated for non-*ortho* PCBs and mono-*ortho* PCBs in eggs from Buffalo Harbor were within the range of concentrations at the two reference colonies or, in the case of TEQs for dioxins and furans, were lower compared to the reference colonies. Toxicity associated with non-*ortho* PCBs contributed approximately 82% to total TEQ concentrations while toxicity associated with dioxins and furans and mono-*ortho* PCBs were more similar (7–10% range). Cormorant eggs from Buffalo Harbor had the highest concentrations of PCB-77, PCB-81, and TEQs for dioxins and furans reported in 2018. In general, TEQ concentrations for dioxin-like

Figure 2. Liver somatic index (a) and body condition (b) in Double-crested Cormorant embryos in artificially incubated eggs collected from the Niagara River AOC colony (Buffalo Harbor) and the reference colony in eastern Lake Erie (Mohawk Island) in 2018 and 2019. Mean values (SD) are based on 6–23 individual embryos at each colony. Different uppercase letters indicate a significant difference in the mean estimate within a study year.

a) Liver somatic index



b) Body condition

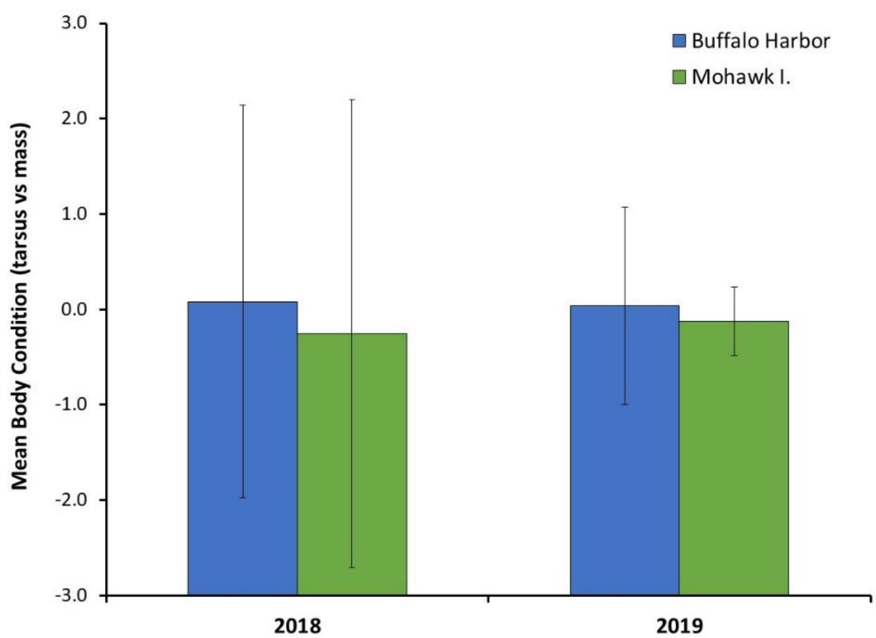


Table 2. Mean concentrations (SD) of organochlorines and sum PBDEs (µg/g, wet weight) in eggs of Herring Gulls (HERG) and Double-crested Cormorants (DCCO) collected from the Niagara River AOC colony (Buffalo Harbor) and two upstream reference colonies in eastern Lake Erie at Port Colborne and Mohawk Island in 2018 and/or 2019 where data are available. Sum PCBs are based on the sum concentration of 35 congeners and sum PBDEs are based on the sum concentration of 15 congeners. Each year comprises a single pooled sample consisting of 13 eggs.

Colony	AOC/ REF	HERG/ DCCO	Sum PCBs	*p,p'*-DDE	Sum Chlordane	OCS	HCB	Mirex	HE	Dieldrin	Sum PBDEs
Buffalo Harbor 2018 & 2019	AOC	HERG	3.06 (0.04)	0.45 (0.005)	0.032 (0.004)	0.002 (0.001)	0.010 (0.002)	0.021 (0.004)	0.007 (0.001)	0.016 (0.004)	0.32 (0.02)
Port Colborne 2018 & 2019	REF	HERG	2.72 (0.93)	0.58 (0.17)	0.042 (0.010)	0.003 (0)	0.012 (0.001)	0.028 (0.006)	0.011 (0.001)	0.028 (0.003)	0.32 (0.09)
Mohawk I. 2018	REF	HERG	2.78	0.66	0.040	0.002	0.011	0.013	0.008	0.023	0.21
Buffalo Harbor 2018 & 2019	AOC	DCCO	1.64 (0.41)	0.71 (0.13)	0.015 (0.009)	0.001 (0.0001)	0.007 (0.003)	0.015 (0.003)	0.010 (0.006)	0.021 (0.009)	0.04 (0.02)
Port Colborne 2019	REF	DCCO	1.80	0.99	0.011	0.003	0.007	0.006	0.008	0.024	0.03

Table 3. Concentrations of non-*ortho* PCBs, 2,3,7,8-TCDD, and 2,3,7,8-TCDD toxic equivalents as TEQs (pg/g, wet weight) in eggs of Herring Gulls (HERG) and Double-crested Cormorants (DCCO) collected from the Niagara River AOC colony (Buffalo Harbor) and two upstream reference colonies in eastern Lake Erie at Port Colborne and Mohawk Island in 2018. TEQs associated with 4 non-*ortho* PCBs, 17 dioxins and furans (PCDD/Fs), and 7 mono-*ortho* PCBs (105, 114, 118, 123, 156/157, 167, and 189) and which together comprise total TEQs are also provided. Each sample represents a single pooled sample consisting of 13 eggs.

Colony	AOC/ REF	HERG/ DCCO	PCB-77	PCB-81	PCB-126	PCB-169	2,3,7,8 – TCDD	TEQ – non-*ortho* PCBs	TEQ – PCDD/Fs	TEQ – mono-*ortho* PCBs	Total TEQs
Buffalo Harbor	AOC	HERG	214	63.5	721	82.0	2.78	89.2	8.44	9.97	107.6
Port Colborne	REF	HERG	173	78.4	997	34.5	4.80	116.2	13.01	12.16	141.4
Mohawk I	REF	HERG	135	17.5	681	99.0	2.01	76.7	8.81	9.84	95.4
Buffalo Harbor	AOC	DCCO	259	115	772	76.8	3.51	101.7	13.93	8.73	124.4

PCBs and dioxins and furans in cormorant eggs were very similar to those in Herring Gull eggs with a total TEQ concentration in cormorant eggs that was within the range of those in gull eggs.

Spatial differences were found for mercury for which mean concentrations, on a dry weight basis, were significantly higher in Herring Gull eggs from Buffalo Harbor compared to the Port Colborne reference colony in 2018 and 2019 (t_2=8.58, p=0.01; Table 4). This was also found when concentrations were compared on a wet weight basis (t_2=6.48, p=0.02). Although no statistical analysis was conducted for cormorant eggs, mercury concentrations were similar between the two colonies since the concentration in eggs from Port Colborne in 2019 was within the range of that found in the two pooled samples from Buffalo Harbor in 2018 and 2019. Maximum mercury concentrations were 1.01 µg/g in cormorant eggs from Buffalo Harbor in 2018 on a dry weight basis and 0.18 µg/g in gull eggs from Buffalo Harbor in 2019 on a wet weight basis.

Table 4. Mean concentrations (SD) of total mercury and mean values (SD) for $\delta^{15}N$ and $\delta^{13}C$ in eggs of Herring Gulls (HERG) and Double-crested Cormorants (DCCO) collected from the Niagara River AOC colony (Buffalo Harbor) and two upstream reference colonies in eastern Lake Erie at Port Colborne and Mohawk Island in 2018 and/or 2019 where data are available. Mercury concentrations are in µg/g and reported as dry weight (dw) and wet weight (ww). Each year comprises a single pooled sample consisting of 13 eggs. Different uppercase letters indicate significant differences in mean concentrations between gull colonies at Buffalo Harbor and Port Colborne.

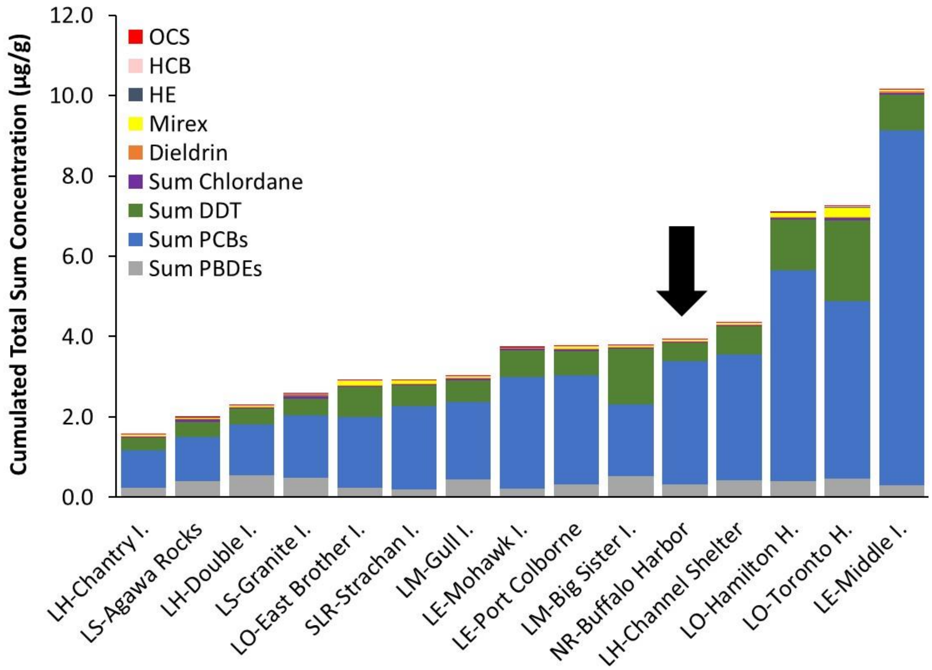
Colony	AOC/ REF	HERG/ DCCO	Mercury dw	Mercury ww	$\delta^{15}N$	$\delta^{13}C$
Buffalo Harbor 2018 & 2019	AOC	HERG	0.74 (0.02) **A**	0.17 (0.01) **A**	15.0 (0.2)	-22.1 (0.2)
Port Colborne 2018 & 2019	REF	HERG	0.62 (0.01) **B**	0.14 (0.002) **B**	14.5 (0.9)	-22.1 (0.1)
Mohawk I 2018	REF	HERG	0.51	0.12	13.8	-22.4
Buffalo Harbor 2018 & 2019	AOC	DCCO	0.85 (0.22)	0.14 (0.04)	16.9 (0.2)	-22.6 (0.1)
Port Colborne 2019	REF	DCCO	0.71	0.11	15.8	-23.4

Stable isotopes of nitrogen and carbon are used to provide information on trophic position and carbon source in the food web, respectively. No significant differences in mean $\delta^{15}N$ values and $\delta^{13}C$ values were found between Herring Gull eggs from Buffalo Harbor and Port Colborne (Table 4). This suggests that gulls were feeding at similar trophic levels with similar carbon sources at the two colonies. Comparing isotopic signatures between the two colonial waterbird species at study colonies, $\delta^{15}N$ values were relatively higher and $\delta^{13}C$ values were relatively lower in eggs of cormorants relative to gulls which is consistent with the more fish-based diet of cormorants compared to gulls which may feed on terrestrial food sources if available.

Spatial trends in contaminant burdens for gull and cormorant eggs from the Niagara River AOC colony in relation to other Great Lakes colonies are valuable for providing a broad perspective of spatial trends including those at other AOCs (Figures 3–6). Concentrations of cumulative total sum concentrations of

Figure 3. Cumulated total sum concentration (µg/g, wet weight) of mean sum PCBs, seven organochlorines, and sum PBDEs in eggs of Herring Gulls (a) and Double-crested Cormorants (b) from the Niagara River AOC colony (Buffalo Harbor) and other Great Lakes colonies in 2018 and 2019. Means are arranged in increasing order from lowest to highest concentrations. Colony locations are associated with the following lakes/rivers: LH=Lake Huron, LO=Lake Ontario, LE=Lake Erie, SLR=St. Lawrence River, NR=Niagara River, DR=Detroit River, LS=Lake Superior, and LM=Lake Michigan.

a) Herring Gull eggs



b) Double-crested Cormorant eggs

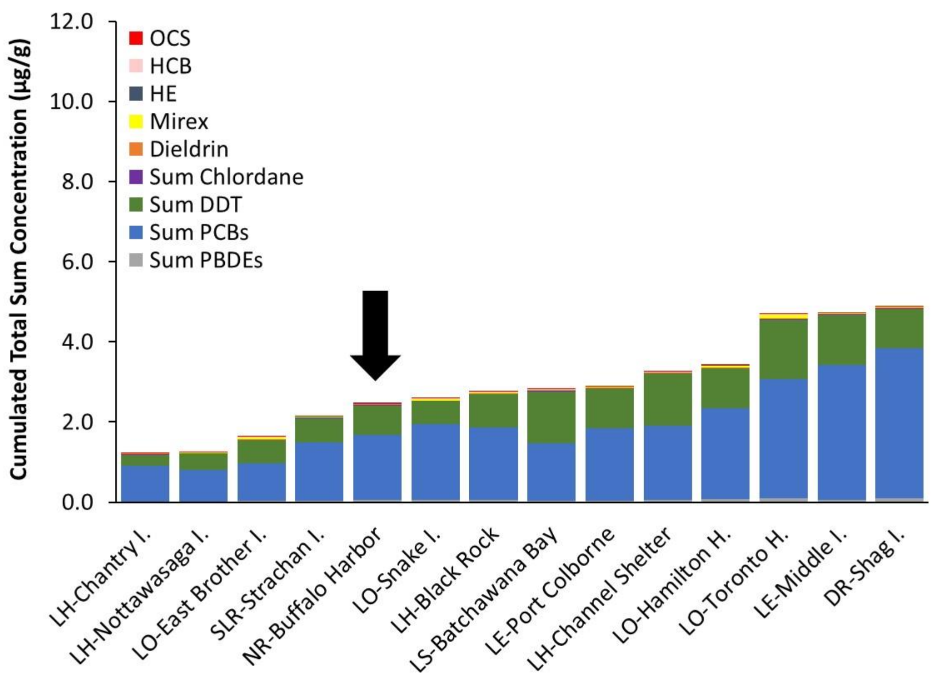
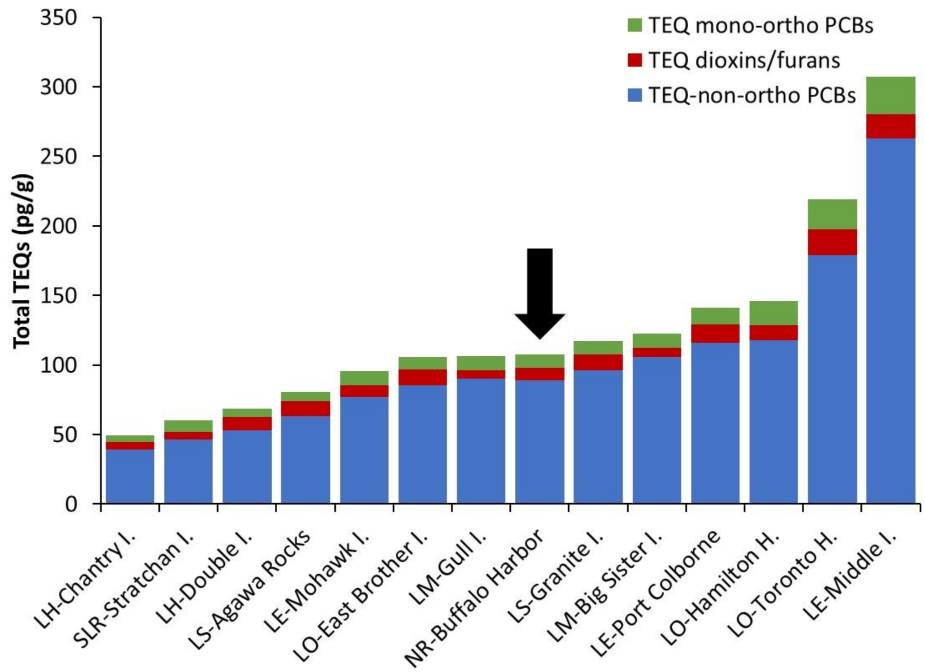


Figure 4. Total TEQ concentrations (pg/g, wet weight) in eggs of Herring Gulls (a) and Double-crested Cormorants (b) from the Niagara River AOC colony (Buffalo Harbor) and other Great Lakes colonies in 2018. The contributions of TEQ concentrations associated with mono-*ortho* PCBs, dioxins and furans, and non-*ortho* PCBs to the total TEQ concentration are shown. Concentrations are arranged in increasing order from lowest to highest. Colony locations are associated with the following lakes/rivers: LH=Lake Huron, LO=Lake Ontario, LE=Lake Erie, SLR=St. Lawrence River, NR=Niagara River, DR=Detroit River, LS=Lake Superior, and LM=Lake Michigan.

a) Herring Gull eggs



b) Double-crested Cormorant eggs

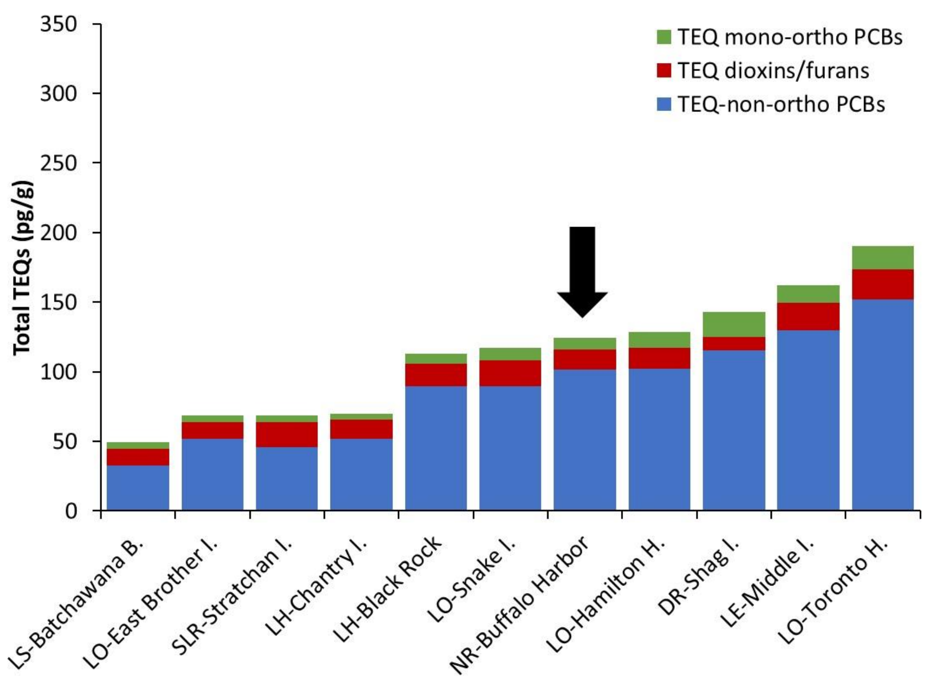
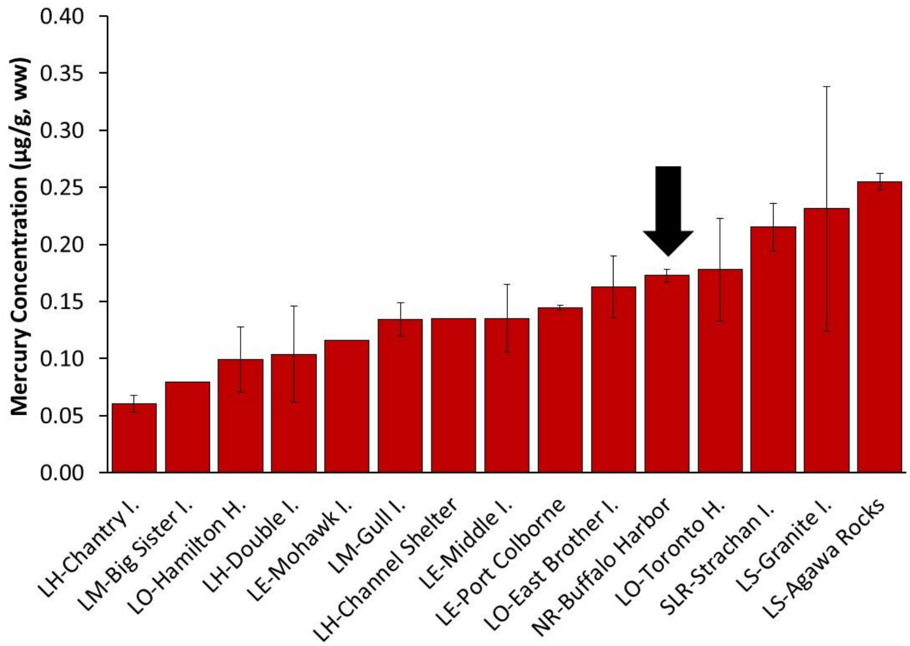


Figure 5. Mean total mercury concentrations (µg/g, wet weight) in eggs of Herring Gulls (a) and Double-crested Cormorants (b) from the Niagara River AOC colony (Buffalo Harbor) and other Great Lakes colonies in 2018 and 2019. Means (SD) are arranged in increasing order from lowest to highest concentrations. Colony locations are associated with the following lakes/rivers: LH=Lake Huron, LO=Lake Ontario, LE=Lake Erie, SLR=St. Lawrence River, NR=Niagara River, DR=Detroit River, LS=Lake Superior, and LM=Lake Michigan.

a) Herring Gull eggs



b) Double-crested Cormorant eggs

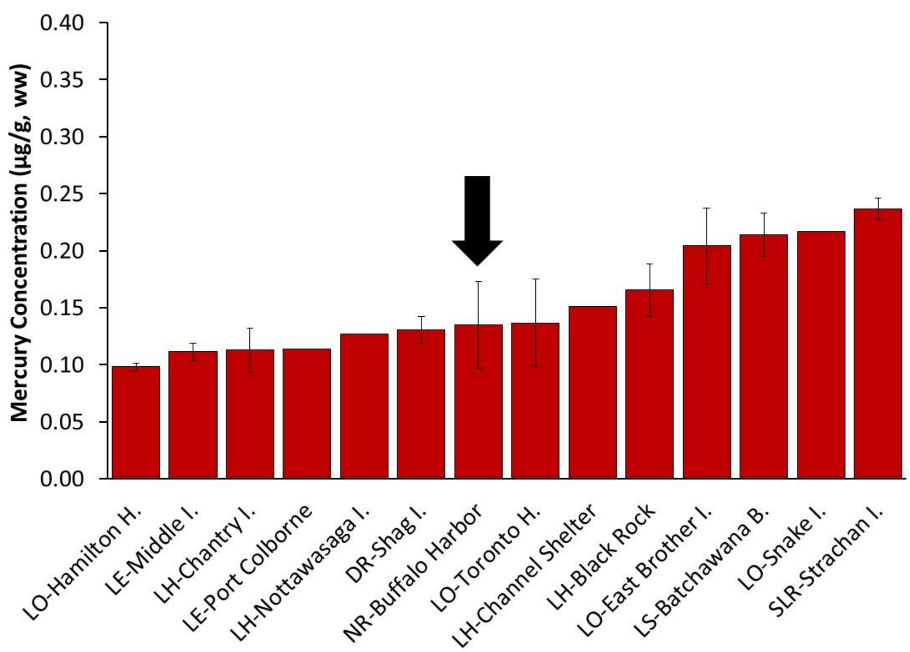
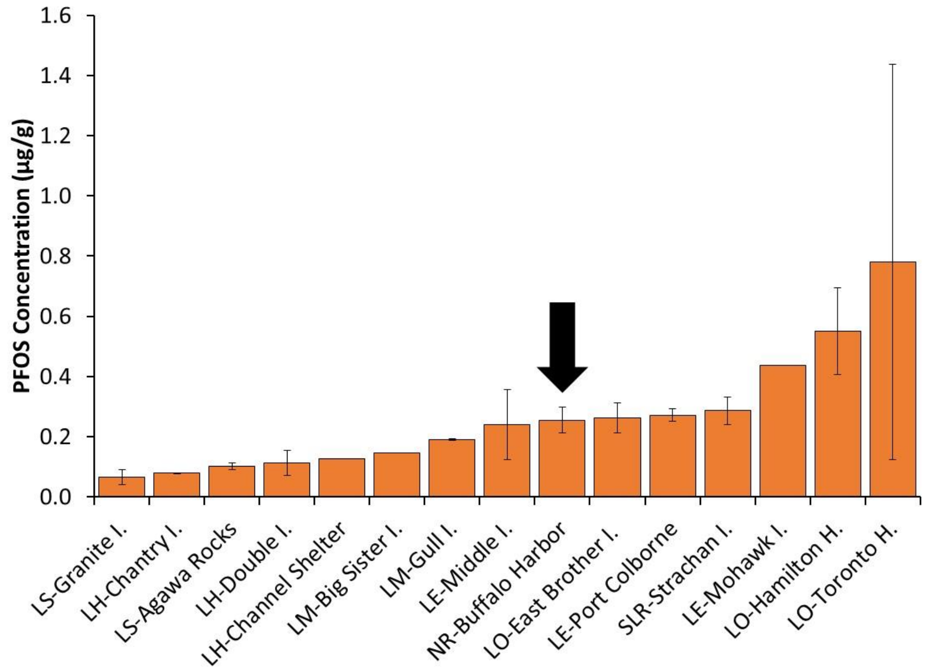
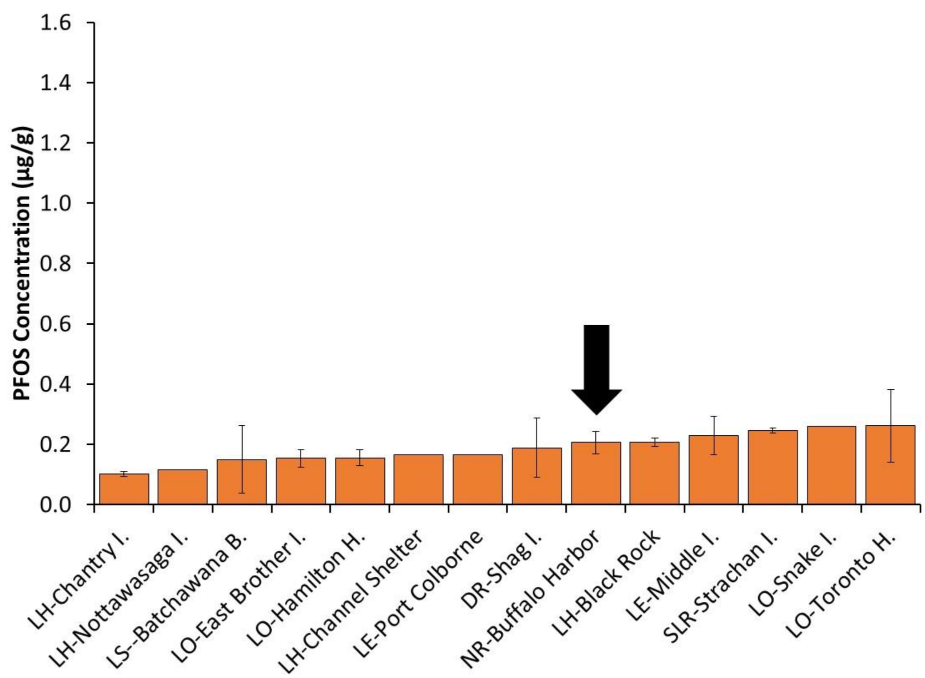


Figure 6. Mean PFOS concentrations (µg/g, wet weight) in eggs of Herring Gulls (a) and Double-crested Cormorants (b) from the Niagara River AOC colony (Buffalo Harbor) and and other Great Lakes colonies in 2018 and 2019. Means (SD) are arranged in increasing order from lowest to highest concentrations. Colony locations are associated with the following lakes/rivers: LH=Lake Huron, LO=Lake Ontario, LE=Lake Erie, SLR=St. Lawrence River, NR=Niagara River, DR=Detroit River, LS=Lake Superior, and LM=Lake Michigan.

a) Herring Gull eggs



b) Double-crested Cormorant eggs



organochlorines, total TEQs, and mercury in gull and cormorant eggs from the AOC colony at Buffalo Harbor were within the range of concentrations found at other Great Lakes colonies in 2018 and 2019 (where data are available). As a compound of concern globally, PFOS (perfluorooctane sulfonate) was also found in gull and cormorant eggs from Buffalo Harbor at mean concentrations that were within those found at other colonies on the Great Lakes.

Temporal Trends:

Long term collections and contaminant analysis of Herring Gull eggs from the Niagara River AOC allow for an assessment of temporal trends in exposure in gulls foraging within the AOC. As part of the Great Lakes Herring Gull Egg Monitoring Program, eggs have been collected annually from Weseloh Rocks on the Niagara River since 1979 and analyzed for a suite of contaminants (generally as a single pooled sample). Large declines in concentrations of several contaminants have been reported in eggs collected from this site until 2015 after which egg collections were no longer possible. Herring Gull eggs collected from Buffalo Harbor within the boundary of the Niagara River AOC in 2018 and 2019 can serve to supplement existing contaminant data for gulls foraging in this area.

Generally, contaminant burdens from the AOC colony in the two study years aligned well with concentrations found in Herring Gull eggs from Weseloh Rocks in the 2000s when declines had begun to plateau (Figure 7). Temporal trends indicate that concentrations of sum PCBs (based on the sum concentration of 26 PCB congeners common to all analyses), several organochlorines, and 2,3,7,8-TCDD declined significantly in Herring Gull eggs collected from Weseloh Rocks and Buffalo Harbor from the late 1970s/1980s to 2019 (range in r^2=0.13–0.89; p<0.04). These results are consistent with significant declines reported for these compounds in eggs from Weseloh Rocks only to 2015 (Hughes *et al.* 2017). Also consistent is the temporal pattern of no significant change in sum PBDE concentrations in eggs including Buffalo Harbor and those at Weseloh Rocks to 2015 only. However, there were temporal differences for two compounds between the two sets of analyses. No significant decline was found for OCS in eggs from Weseloh Rocks from 1987 to 2015; however, this relationship was significant when Buffalo Harbor eggs were included in the trend analysis. The opposite was true for mercury; while a significant decline in mercury concentrations was found at Weseloh Rocks from 1981 to 2015, this was no longer significant when Buffalo Harbor eggs were included in the analysis. Relatively higher mercury concentrations found in Buffalo Harbor eggs in 2018 and 2019 compared to three previous years and general variability from year-to-year in concentrations in eggs from Weseloh Rocks contributed to this change (Figure 7). Overall, these results indicate that exposure to these compounds has decreased or, in the case of mercury, remained stable in Herring Gulls foraging in the AOC.

DISCUSSION

Since 2016, logistical constraints associated with high water levels have precluded the ability to continue Herring Gull egg collections and perform annual contaminants monitoring at Weseloh Rocks in the Niagara River AOC. However, another colonial waterbird nesting site at Buffalo Harbor has proved valuable for continued contaminants monitoring thereby facilitating a current assessment of exposure in colonial waterbird populations foraging in the AOC. Concentrations of several contaminants in egg collections from Buffalo Harbor in 2018 and 2019 aligned well with trends reported in earlier years for

Figure 7. Temporal trends in concentrations of 12 contaminants in Herring Gull eggs collected annually from Weseloh Rocks in the Niagara River from the late 1970s/1980s (or 2000 for sum PBDEs) to 2015. Contaminant concentrations are also provided in Herring Gull eggs collected from the Buffalo Harbor colony in 2018 and 2019 (shown as patterned circles). Sum PCBs are based on 26 common PCB congeners quantified over time and white open circles represent estimated concentrations based on measured Aroclor 1254:1260 concentrations. Note that no data are available for Aroclor 1254:1260 in 2018 and 2019. Concentrations are based on analysis of a single pooled sample of eggs with the exception of 1979, 1981, and 1983–1986 when a mean concentration based on 10 or 11 eggs is shown. Concentrations, as wet weights, are in µg/g for all contaminants except 2,3,7,8-TCDD which is in pg/g. Exponential curves are provided where declines from late 1970s/1980s to 2019 were significant.

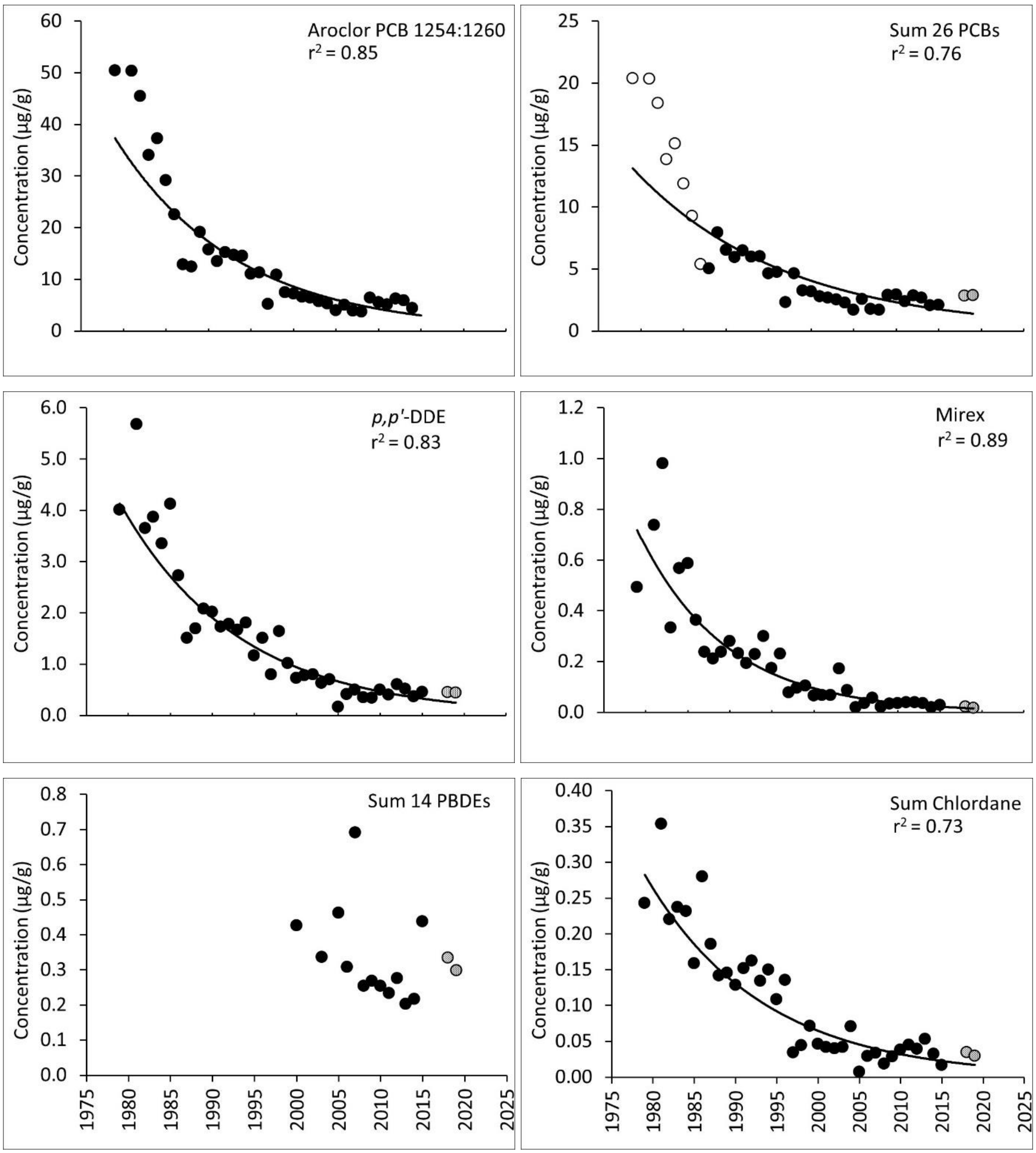
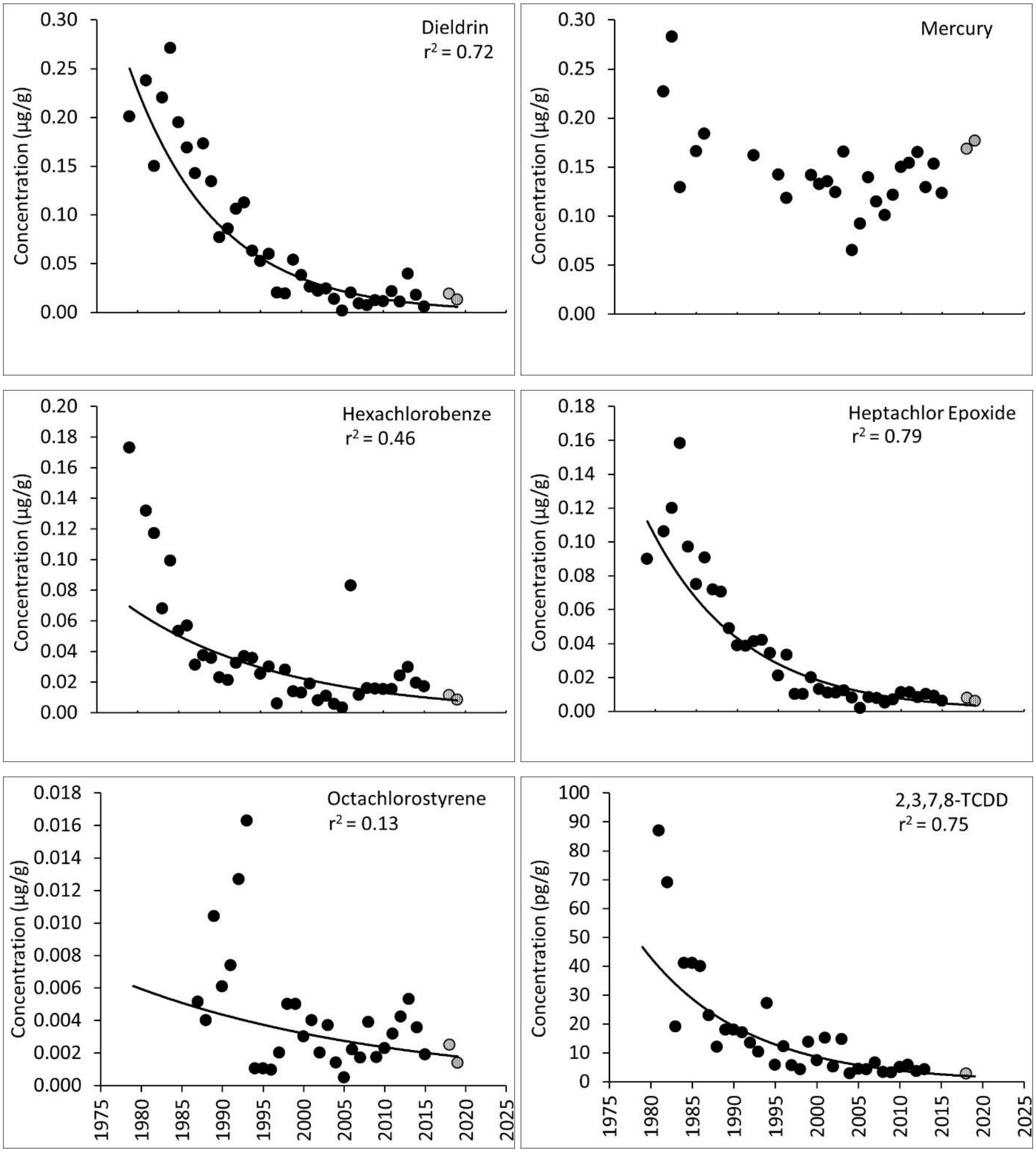


Figure 7 (continued).



egg collections from Weseloh Rocks. Significant declines were reported for most contaminants in gull eggs since 1979 or, in the case of sum PBDEs, no significant change was found in eggs since 2000.

Overall, concentrations of PCBs, *p*,*p*′-DDE, and PBDEs in gull and cormorant eggs from Buffalo Harbor were not sufficiently elevated to adversely impact hatching success of these species foraging in the Niagara River (Ontario) AOC based on the results of several studies examining concentrations associated with impacts on reproduction in colonial waterbirds (Pearce *et al.* 1979; Henny *et al.* 1984; Kubiak *et al.* 1989; Hoffman *et al.* 1996; Powell *et al.* 1998; McKernan *et al.* 2009). The total TEQ concentration in gull and cormorant eggs were also well below 1200–1300 pg TEQ/g at which high frequencies (6–10%) of embryonic deformities were found in cormorants at two Lake Michigan colonies in 1988 (Yamashita *et al.* 1993).

Mercury concentrations in gull eggs were considered stable, i.e., no significant change, when eggs from Buffalo Harbor in 2018 and 2019 were included in the temporal analysis. Higher mercury concentrations in gull eggs from Buffalo Harbor in these two years compared to earlier years in eggs from Weseloh Rocks may be associated with birds from this site foraging in areas where mercury exposure is relatively higher. Significantly higher mercury concentration in gull eggs from Buffalo Harbor compared to the upstream colony at Port Colborne also support this finding. Mercury levels also started increasing at some locations in both fish and gulls in Lake Erie, including Weseloh Rocks and nearby Port Colborne, starting in the mid 2000s to 2015 (the last year of the study; Blukacz-Richards *et al*. 2017). Hence, higher levels of mercury in Buffalo Harbor eggs collected in recent years relative to Weseloh Rocks eggs may, at least partially, reflect a general upward trend in mercury. This increase in exposure may be in part due to resuspension of contaminated sediment following dredging activities in the Detroit River that impacted downstream sites in Lake Erie and Lake Ontario (as reported for another set of legacy compounds in McGoldrick *et al.* 2018). Regardless of the cause of higher mercury in Buffalo Harbor, mercury concentrations in all eggs in this study were below the predicted threshold of 0.6 µg/g (wet weight) in eggs set to be protective against adverse reproductive effects for 95% of non-marine avian species (Shore *et al.* 2011). The maximum mercury concentration found in gull eggs from Buffalo Harbor in 2019 (0.18 µg/g) was one-third of the no-effect level threshold concentration. Mercury concentrations at the AOC colony were also within the range of those found at other Great Lakes colonies for both species. These data suggest that it is unlikely mercury concentrations would reduce reproduction and survival of breeding colonial waterbirds in the Niagara River AOC.

The results of the artificial incubation study suggest that egg viability is not impaired to an extent that would elicit population-level effects in the AOC. Egg viability was similar in cormorant eggs collected from Buffalo Harbor (85%) and the reference colony (80%) following artificial incubation in the two study years. Deformity frequencies of embryos did not differ significantly between the two study colonies. Body condition was similar in embryos between study colonies in both study years, while a significant difference was found for the liver somatic index in embryos in one of two years. Contaminant burdens in eggs, reported at concentrations below threshold levels associated with population level effects, also support these results.

CONCLUSIONS

The results of this study indicate that the *Wildlife Populations* BUI criteria #2 and #3 (see below) have been met and that there is no impairment of colonial waterbirds in the Niagara River (Ontario) AOC.

Criterion 2. Breeding colonial waterbird populations within the Niagara River AOC are the same as (or better than) suitable reference sites.

Egg viability was similar in cormorant eggs collected from Buffalo Harbor (85%) and the reference colony (80%) following artificial incubation in the two study years. Egg viability in cormorants was considered to be not impaired.

Criteria 3a and 3b. Temporal trends in contaminant concentrations in eggs, tissues, or whole-body burden of sentinel species in the Niagara River AOC are stable or declining; AND spatial comparisons show that contaminant concentrations in eggs, tissues, or whole-body burden of sentinel species in the Niagara River AOC are the same (or better than) other suitable reference sites.

Based on long-term collections of Herring Gull eggs from Weseloh Rocks, a colony within the Niagara River (Ontario) AOC, and recent egg collections from another colony within the AOC at Buffalo Harbor, temporal trends in contaminant levels indicate that concentrations have declined (e.g., PCBs) or are stable (i.e., mercury) between the late 1970s/early 1980s to 2019.

Spatial comparisons indicate that, for the majority of contaminants, concentrations in eggs under the influence of the AOC are the same as those at the upstream reference site and outside of the influence of the AOC.

Criterion 3c. If the contaminant concentrations in 3a or 3b are not met, then they must not exceed established thresholds associated with potential population-level effects (i.e., reproductive impacts).

For mercury, significantly higher concentrations were found in gull eggs from the AOC colony compared to the reference colony; however, mercury burdens were well below those associated with population-level effects in colonial waterbirds.

Provided that delisting criterion 1 is also met (as assessed through a separate study), then it is recommended that the RAP Team proceed with changing the status of this BUI from ‘Impaired’ to ‘Not Impaired’.

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