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CONCENTRATIONS OF ENVIRONMENTAL CONTAMINANTS IN HERRING GULL EGGS FROM GREAT LAKES COLONIES IN MICHIGAN 2002-2006 AND 2008-2012

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EXECUTIVE SUMMARY

The following are some of the important findings of this report:

- The 2008 to 2012 five-year medians for total PCBs, TEQs, *beta*-Hexachlorocyclohexane, Octachlorostyrene, Dieldrin, Oxychlordane, *alpha*-Chlordane, *cis*-Nonachlor, *p,p'*-DDT, *p,p'*-DDE, and *p,p'*-DDD varied significantly among the ten Michigan colonies. The following are noteworthy findings:

    - The Detroit Edison colony (Lake Erie) had the highest concentrations of total PCBs, Octachlorostyrene, Dieldrin, *alpha*-Chlordane, and the second highest concentrations of TEQ, *p,p'*-DDT, and *p,p'*-DDD.
    - The West Twin Pipe colony (St. Marys River) had the highest concentrations of *p,p'*-DDT, *p,p'*-DDE, and *p,p'*-DDD.
    - The Scarecrow Island colony (Lake Huron) had the highest TEQ concentration.
    - The Net Island colony (Lake Superior) had the highest concentrations of *beta*-Hexachlorocyclohexane and Oxychlordane.
    - The Tahquamenon colony (Lake Superior) had the highest concentrations of *cis*-Nonachlor, and second highest concentration of *beta*-Hexachlorocyclohexane, Dieldrin, Oxychlordane, and *p,p'*-DDE.

- The concentration of total PCBs in two of the ten Michigan colonies, Detroit Edison (Lake Erie) and Little Charity Island (Lake Huron), exceeded the no-observed-adverse-effect-level established for double-crested cormorants.

- The 2008 to 2012 five-year medians for total PCBs, TEQ, *beta*-Hexachlorocyclohexane, Octachlorostyrene, Dieldrin, Oxychlordane, *alpha*-Chlordane, *trans*-Nonachlor, *cis*-Nonachlor, *p,p'*-DDT, *p,p'*-DDD, and Mirex varied significantly among lakes. The following are noteworthy findings:

    - Lake Erie had the highest concentration of total PCBs, TEQ, Octachlorostyrene, Dieldrin, *alpha*-Chlordane, *trans*-Nonachlor, *p,p'*-DDT, and *p,p'*-DDD.
    - Lake Superior had the highest concentration of *beta*-Hexachlorocyclohexane, and Oxychlordane, and *cis*-Nonachlor.
    - St. Marys River had the highest concentration of Mirex.
    - Lake Huron had the second highest concentrations of PCBs, TEQ, *beta*-Hexachlorocyclohexane, Octachlorostyrene, and *p,p'*-DDT.

- Five-year medians for total PCBs, Hexachlorobenzene, Heptachlor epoxide, Dieldrin, Oxychlordane, *trans*-Nonachlor, *cis*-Nonachlor, *p,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD, Mirex, and Mercury varied significantly between time periods 2002-2006 and 2008-2012.

    - Post-hoc analyses showed that concentrations of total PCBs, *beta*-Hexachlorocyclohexane, Heptachlor epoxide, Dieldrin, Oxychlordane, *alpha*-Chlordane, *trans*-Nonachlor, *cis*-Nonachlor, *p,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD, Mirex, and Mercury decreased significantly by colony between the two time periods.
    - There were observable increases in *alpha*-Chlordane concentration at the Huron Island colony (Lake Superior), and in Hexachlorobenzene and Mirex concentrations at West Twin Pipe (St. Marys River).
    - There were significant decreases in total PCBs, Hexachlorobenzene, Heptachlor epoxide, Dieldrin, Oxychlordane, *trans*-Nonachlor, *cis*-Nonachlor, *p,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD, Mirex, and Mercury by lakes between the two time periods.

INTRODUCTION

The ability to determine spatial and temporal differences in bioaccumulative chemicals of concern (BCCs) is important for understanding risks to human and wildlife populations in affected areas. Most BCCs are biomagnified in the aquatic system through ingestion of prey and increase in concentrations at higher trophic levels. Biosentinel wildlife species are typically tertiary predators that integrate these compounds in their tissues. These tissues can be analyzed to determine concentrations of BCCs and to assess spatial and temporal trends.

Herring gull (*Larus argentatus*) eggs can be easily collected from known sites annually to determine trends in adult exposure. Herring gulls are an intermediary fish-eating predator that nests along the Great Lakes coast of Michigan each year. Herring gulls breed every year and are less sensitive to the effects of BCCs than eagles; therefore, availability of eggs each year is virtually guaranteed. The population in the Great Lakes basin is robust enough to withstand annual collections of eggs from colonies without any effect on the gull population. Herring gulls display a great fidelity to their breeding colonies and are year-round residents of the Great Lakes. Only those nesting along Lake Superior are known to migrate among lakes during the winter.

The longest continuous wildlife monitoring program of water-borne environmental pollutants in the Great Lakes is the Canadian Wildlife Service's (CWS) Great Lakes Herring Gull Monitoring Program, which began in 1974 (Hebert et al., 1999). Herring gull eggs are collected annually in 15 colonies across the Great Lakes and are analyzed for organochlorine (OC) pesticides, polychlorinated biphenyls (PCBs), polychlorinated dibenzofurans (PCDFs), polychlorinated dibenzodioxins (PCDDs), and metals. Eggs are archived for use in monitoring new and emerging chemicals such as dioxin-like compounds, brominated fire-retardants, and perfluorinated compounds.

In April of 1999, the Michigan Department of Environmental Quality (MDEQ), Water Bureau, began monitoring environmentally persistent and toxic contaminants in bald eagles. This study is part of the wildlife contaminant monitoring component of the MDEQ's monitoring strategy (MDEQ, 1997). The November 1998 passage of the Clean Michigan Initiative-Clean Water Fund (CMI-CWF) bond proposal resulted in a substantial increase in annual funding for statewide surface water quality monitoring beginning in 2000. The CMI-CWF offers reliable funding for the monitoring of surface water quality over an extended period of time. This is important since one of the goals of the monitoring strategy is to measure temporal and spatial trends in contaminant levels in Michigan's surface waters.

The CMI funds were used to continue the bald eagle (*Haliaeetus leucocephalus*) contaminant monitoring project. In 2002, a second biosentinel species, herring gulls, was added to better monitor BCCs along the coastal regions of Michigan's Great Lakes. The herring gull monitoring study was designed in consultation with the CWS program managers to ensure that it would complement and not duplicate the ongoing CWS program. In addition, all gull egg analytical work is completed either by the CWS or an approved contract laboratory. The results of herring gull egg samples collected from 2002-2006 have been reported previously (Bowerman et al., 2012). This report assesses the results of the herring gull egg samples collected from 2008 to 2012 and compares this period to data collected in previous years.

METHODS

GULL COLONY SELECTION

In 2002, ten colonies across the Michigan waters of the Great Lakes were selected to complement the current 15 colonies used for the CWS program (Figure 1). Three colonies were

selected on Lake Superior, two on the St. Marys River, two on Lake Michigan, two on Lake Huron, and one on Lake Erie. The Lake Superior colonies were located on Net Island near Isle Royale, Huron Islands National Wildlife Refuge, and Tahquamenon Island. The St. Marys River colonies were originally the Sault Locks and West Twin Pipe Island so that both the upper and lower river segments could be studied. However, since the colony at the locks was not active in 2002, a new colony was found downstream at Five Mile Island. The Lake Michigan colonies were located at Green Island near the Straits of Mackinac, and Bellow Island, in the West Bay of Grand Traverse Bay. These locations complemented the CWS colony within the Beaver Island chain. The Lake Huron colonies were located at Scarecrow Island National Wildlife Refuge, and Little Charity Island in Saginaw Bay. The Lake Erie colony was located near the River Raisin on the Detroit Edison property. Table 1 provides the lake, colony name, and abbreviations for the colonies.

In 2009, the first five years of data (2002-2006) were assessed to determine whether the design of the monitoring project could be streamlined to reduce cost and still get the necessary information. Based on this assessment, it was determined that the number of colonies monitored could be reduced from ten to five starting with the 2010 season. One colony was selected from the St. Marys River and from each of the four Great Lakes adjacent to Michigan. The specific colonies were chosen because they were either in Areas of Concern (Little Charity Island, Detroit Edison, and Five Mile Island) or they had high contaminant levels (Bellow Island and Net Island). To save additional funds, it was also decided at this time that the eggs could be analyzed as pooled samples rather than individual samples. The use of pooled samples has been shown to be an acceptable method for monitoring contaminants in wildlife (Turle and Collins, 1992). Due to the colony moving, the monitored colony in Lake Superior was changed from Net Island to Huron Island in 2010.

GULL EGG COLLECTIONS

Thirteen eggs were collected from each colony using protocols identical to the ones used by the CWS (Hebert et al., 1999). One egg was collected from three-egg clutches at random nests across a colony. Eggs were measured, floated in a container to ensure they were freshly laid, and then placed into a container filled with a foam insert to ensure they were protected during handling and shipping.

Eggs were processed using the CWS protocol (Hebert et al., 1999). Each egg was measured, weighed, volume was determined using the water displacement method, scored equatorially, contents were poured into a chemically clean jar, the jar was sealed, and then placed in a freezer. Eggs were transferred to the Great Lakes Institute for Environmental Research at the University of Windsor, Ontario, Canada, for analyses.

CHEMICAL ANALYSIS

From 2002-2009, eggs were analyzed individually. Starting in 2010, eggs from each colony were analyzed as composites to save on analytical costs. Since a single analysis per site per year limits the extent of statistical analysis that can be done on the data, spatial and temporal trends were assessed using five-year medians.

EXTRACTION AND CLEANUP (PCBS, NON-*ORTHO* PCBS (NO-PCBS), OC-PESTICIDES AND PCDD/PCDFS)

Analytical methods for congener-specific PCB and OC-pesticide analysis were performed using a gas chromatography-mass selective detector (GC-MSD) as described fully in the Great Lakes Institute for Environmental Research SOP-02-004, which is accredited under the Canadian Association for Environmental Analytical Laboratories (ISO17025). Additional literature on

sample extraction and cleanup for PCBs, NO-PCBs, and OC-pesticides are provided in Lazar et al (1992) and GC-MSD instrument conditions for PCBs in O'Rourke et al (2004). Coplanar PCBs and PCDD/PCDFs were analyzed by gas chromatography-high resolution (time-of-flight) mass selective detection (GC-HR (TOF) MSD) using the method described below. For each batch of six samples extracted, a method blank (sodium sulfate) and reference tissue (CWS double-crested cormorant egg homogenate for PCBs/OC-pesticides) were extracted and analyzed. For PCDD/PCDFs, an additional in-house reference tissue consisting of a chicken egg homogenate spiked with priority PCDD/PCDFs was extracted with every batch of six samples.

Twenty grams of egg homogenates were dried with 60-80 grams of anhydrous sodium sulfate using a glass mortar and pestle. The dried homogenate powder was wet packed into a 60 x 2.5 i.d.-cm glass chromatography column containing 15 grams sodium sulfate over a glass wool plug at the outlet and 100 mL of dichloromethane (DCM):hexane (1:1 v/v). Each column was then spiked with a series of internal recovery standards. For PCB/OCs, the column was spiked with 100 ng each of ^{13}C-PCB 52 and 153 (Cambridge Isotopes, MA). For NO-PCBs, the column was spiked with 20 ng each of ^{13}C-PCB 77, 126 and 169 (Wellington Scientific). For PCDD/PCDFs, the column was spiked with 4-20 ng each of ^{13}C-labelled PCDDs (2,3,7,8-TCDD, 1,2,3,7,8-PCDD, 1,2,3,6,7,8-HCDD, 1,2,3,4,6,7,8-HpCDD, and OCDD) and ^{13}C-labelled PCDFs (2,3,7,8-TCDF, 1,2,3,7,8-PCDF, 1,2,3,4,7,8-HCDF, and 1,2,3,4,6,7,8-HpCDF) obtained from Wellington Laboratories (8290SFS Solution). After 1 hour, the column was eluted into a 500 mL round bottom flask followed by additional elution with 250 mL DCM:Hexane (1:1 v/v). The extracts were reduced to approximately 5 mL by rotary evaporator and then made up to 10 mL in a volumetric flask. One mL was removed for neutral lipid determination (Drouillard et al., 2004) by gravimetric technique and the remaining 9 mL were concentrated to 2 mL by rotary evaporator.

Gel permeation chromatography (GPC) was performed to remove lipids and co-extracted high molecular weight biogenic molecules. The GPC columns consisted of 50 cm x 2.2 cm glass chromatography columns with a 2 cm glass wool plug wet packed with 50 grams of S-X3 BioBeeds (BioRad) in 50% DCM/Hexane (v/v). Each column was fitted with a 250 mL pressure equalizing separatory funnel. Due to the large sample size and high lipid content of egg homogenates, each sample extract was split into three equal aliquots and each aliquot run simultaneously on three separate GPC-columns. Each aliquot was loaded onto a GPC column and eluted with 300 mL DCM/hexane (50% v/v). The first 120 mL of eluant containing high molecular weight biogenic materials was discarded and the remaining 180 mL collected. The collected fraction from the three aliquots were combined and concentrated to 2 mL by rotary evaporator.

Florisil chromatography was performed using 25 cm x 1 i.d.-cm glass columns fixed with 250 mL reservoirs. The column was plugged with 2 cm glass wool and wet packed with 6 grams fully activated (activated by heating at 120^{o}C overnight) florisil in hexane with a 2 cm sodium sulfate cap. The sample was added to the florisil column and the column eluted in four fractions. The first fraction, containing PCBs and some OC-pesticides (e.g., DDTs), was collected by elution with 50 mL hexanes. The second fraction containing the remaining OC-pesticides and NO-PCBs (Lazar et al., 1992) was collected by elution with 50 mL of DCM/Hexane (15/85% v/v). The third fraction containing Dieldrin and Heptachlor Epoxide was eluted with 50 mL of DCM/Hexane (60/40% v/v). The final fraction, containing PCDDs and PCDFs was collected by elution with 100 mL toluene. Fractions 1-3 were concentrated to 5 mL by rotary evaporator and stored in GC-vials at 4^{o}C until instrument analysis. Following analysis for PCBs and OC-pesticides (described below), fraction 2 was recapped and submitted for analysis of NO-PCBs by GC-HR (TOF) MSD. Fraction 4 was concentrated to 2 mL and subjected to additional cleanup by acidic/basic silica gel and carbon column.

ACIDIC/BASIC SILICA GEL AND CARBON COLUMN CLEANUP (PCDD/PCDFS)

Fraction 4 was concentrated to 1 mL and added to an acid/basic silica gel column consisting of 25 cm x 1 i.d.-cm chromatography column wet packed with: 1 cm sodium sulfate; 1 gram basic silica gel (100-200 µm mesh silica prepared the previous night by adding 35 grams 1N KOH to 100 grams activated silica gel and shaking until free flowing), 1 cm sodium sulfate layer; 2 grams acid silica (prepared by addition of 27.2 mL concentrated H_2SO_4 to 100 grams activated silica gel and shaking overnight) and a 1 cm sodium sulfate cap. The extracts were eluted from the acid/basic silica gel column with 50 mL DCM and concentrated to 1 mL under reduced pressure.

The carbon column consisted of a 0.6 cm x 10 cm glass column with 7/25 ground joints at both ends. A 2 cm bed of 5% activated carbon (AX-21, Anderson Development Company)/silica gel (100-200 µM mesh, Supelco) was packed in the center of the column between 2 x 1 cm glass wool beds. Prior to adding the sample, the column was activated by rinsing with 5 mL toluene, 10 mL of DCM, followed by 5 mL hexane. The concentrated sample was then added to the top of the column and allowed to drip into the activated carbon bedding. The carbon column was eluted with 5 mL hexane followed by 5 mL DCM and the eluant discarded. The column was then inverted and eluted with 25 mL toluene. The toluene was concentrated to approximately 1 mL by rotary evaporation and further concentrated to 200 µL under a nitrogen gas stream.

GAS CHROMATOGRAPHY ANALYSIS (GC-LOW RESOLUTION MSD) FOR PCBS/OC-PESTICIDES

Analysis was conducted using a Hewlett-Packard 5890 gas chromatograph with a low resolution 5973 MSD, and 7673 auto sampler. The GC was equipped with a DB-5 column (60 m X 0.25 mm i.d. X 0.10 µm film thickness) and used helium as a carrier gas (1 mL/min). The injection volume was 2 µL splitless at an injection port temperature of 250^{o}C. Separate GC methods were run for PCBs and OC-pesticides in selective ion monitoring mode, necessitating injection of each sample two times in sequence. Both methods used the same temperature program. The temperature program was as follows: 90^{o}C for 3 min followed by a 7^{o}C/min temperature ramp until 150^{o}C, followed by another increase of 3^{o}C/min until a final temperature of 280^{o}C where it was held for 5.1 min. For PCBs, the following ion windows were used: 10-27 min (ions 256, 290), 27-33 min (ions 290, 326, 360, 337), 33-39.5 min (ions 326, 360, 360, 372), 39.5-43.5 min (ions 360, 394, 428), 43.5-60 min (ions 394, 428, 464, 494). For the OC-pesticide method the ion windows were: 15-20 min (ions 250, 284), 20-27 min (ions 284, 219, 308), 27-31.5 min (ions 308, 353, 387), 31.5-34 min (ion 409), 34-36 min (ions 409, 380), 36-38 min (ions 409-235), and 38-60 min (ions 235-272).

Instrument analysis was performed in the sequence of sample batch extractions. The analysis order of sample injections onto the GC-MSD was as follows: External PCB Standard (Accustandard C-QME-01 containing: PCB IUPAC # 18, 17, 28/31, 33, 52, 49, 44, 74, 70/76, 95, 101, 99, 87, 110, 118, 105, 82, 151, 149, 153/132, 138, 158, 128, 156, 187/182, 183, 177, 171, 180, 191, 170/190, 201, 195, 194, 205, 208, 206, 209); OC-Pesticide Standard #2 (Accustandard custom standard containing: 1,2,4,5-TCB; 1,2,3,4-TCB; QCB, HCB, *alpha*-HCH, *beta*-HCH, *gamma*-HCH, *delta*-HCH, OCS, Oxychlordane, *alpha*-Chlordane, *gamma*-Chlordane, *trans*-Nonachlor, *cis*-Nonachlor, *p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT, and Mirex); OC-Pesticide Standard #3 (Accustandard custom standard containing: Dieldrin and heptachlor epoxide); Recovery Standard (^{13}C-PCB-52 and 153); Sample Blank, Samples 1-6 and Sample Reference Tissue. The blank, samples, and reference tissues were injected in duplicate, the first injection corresponding to the PCB method and the second injection using the OC-pesticide method.

GAS CHROMATOGRAPHY ANALYSIS (GC-HR (TOF) MSD) FOR NO-PCBS, PCDDS, AND PCDFS

Analysis for NO-PCBs, PCDDs, and PCDFs was conducted using a Waters GCT-premier instrument that consisted of an Agilent 6890 GC, 7673B auto sampler with a DB-5 column (30 m x 0.25 mm. i.d. x 0.10 µm film thickness; helium as a carrier gas (1 mL/min)) coupled with a Waters Premier orthogonal acceleration time-of-flight (oa-TOF) mass spectrometer. The injector temperature was maintained at 275^{o}C in splitless mode. The oven program was: 90^{o}C held for 1 min, ramped at 30^{o}C/min to 200^{o}C held for 2 min and ramped at 3^{o}C/min to 280^{o}C and held for 10 min. The oa-TOF was run in EI-mode following daily tuning and mass resolution calibration using Metri (68.9952, 121.0014, 189.9966, 265.9965, and 284.9949) calibration solution. The 284.9949 ion was used as the lock mass during sample runs.

Fraction 2 from the florisil cleanup was analyzed for NO-PCBs, while fraction 4 from florisil/acid-basic silica gel/carbon column cleanup was examined for PCDD/PCDFs. For each batch of samples extracted, the sample injection sequences were set in the following manner: 5 external standard calibration curve for NO-PCBs (Wellington Laboratories certified PCB 77, 126, 169 standard series) or for PCDD/PCDF (Wellington Laboratories EPA-8290HRCC1-5); Dioxin Performance Standard Solution (dioxin analysis only; Wellington Laboratories 8290RSS); sample Blank, sample reference homogenate and 6 egg homogenate samples. An additional 5 calibration external standard curves for NO-PCBs or PCDD/PCDF were run at the conclusion of each sample batch injection series to check for instrument response.

Post processing of HR-MSD output was performed using QuanLynx software. The three dominant ions (e.g., for 2,3,7,8 -TCDD ions: 319.87, 321.893, 323.891) were extracted from the total ion chromatogram over a window of ± 10 seconds from the expected analyte retention time. For PCDD/PCDF samples, peak areas were adjusted based on the dioxin performance standard response spiked into the GC vial just prior to capping. Raw areas (NO-PCBs) or performance compound adjusted areas (PCDD/PCDFs) were then quantified using the analyte response relative to the external standard calibration curve.

Mercury Analysis

The sample is prepared by first weighing 2.00 grams of tissue in a 125 mL Erlenmeyer flask. The tissue is then digested in 15 mL of a 2:1 solution of sulfuric acid:nitric acid at a constant temperature of 60^{o}C in a water bath. Once the tissue is completely dissolved, the heat is turned off and the temperature is allowed to drop to 20^{o}C before continuing. Twenty mL of a 5% potassium permanganate solution is added in 5 mL increments and the container is swirled to mix. The foam is allowed to subside and cool between additions (during permanganate additions, the container is cooled in an ice bath before and during additions to control exothermic reactions). After 30 minutes, 10 mL of the 5% potassium persulfate solution is added and the container is swirled to mix. The samples are allowed to stand overnight at room temperature. If the color has not persisted into the next day, additional potassium permanganate is added until the color persists for 15 minutes. Finally, 5 mL of a 10% hydroxylamine hydrochloride-sodium chloride ACS grade solution is added and the container is allowed to stand 30 minutes with the container being shaken thoroughly every 10 minutes. The solution is transferred into dry pre-weighed 125 mL Nalgene bottles using a funnel. The Erlenmeyer flasks are rinsed five times with purified water during transfer. The funnel is rinsed twice between individual samples with 1% nitric acid, then three times with purified water. The solution is made to 100 grams +/- 0.01 grams.

Atomic Absorption Spectrometry is used to measure total recoverable mercury. The cold vapor technique can be used because mercury exists as free atoms at room temperature. Mercury in its ionic form is reduced using the appropriate reducing agent (stannous chloride) producing volatile free mercury that is carried to the spectrophotometer via purged argon gas.

TEQ Calculation

Toxic equivalents (TEQs) were calculated by multiplying the concentration of the individual PCB and PCDD/PDCF congeners in the eggs by the congener-specific Toxic Equivalency Factor for birds (Van den Berg et al., 1998) and then summing the values. The analytical method does not analyze for five congeners (PCB congener 114, 123, 157, 167, or 189) and one chlorinated dioxin (1,2,3,4,5,7-Hexa CDD) that have Toxic Equivalency Factors. However, analytical data for total TEQs for 112 carp fillets from 9 different sites in Michigan suggest that these congeners are not a significant part of the total TEQs (Joseph Bohr, personal communication).

STATISTICAL ANALYSIS

Statistical analyses were performed using the SAS 9.2 statistical package (SAS Institute Inc. 2007). The fit of the data to first normal then lognormal distribution was assessed using the Kolmogorov-Smirnof test. Due to the nonparametric nature of the distributions, medians and interquartile ranges are reported as the measures of central tendency and dispersion, respectively. Differences for all BCC concentrations were analyzed among colonies and Great Lakes using rank converted analysis of variance and general linear models. A conservative post-hoc pairwise comparison was used because there were multiple comparisons (Tukeys, experiment-wise *alpha* = 0.05). In cases where rank conversion was not sufficient to homogenize variance, the Satterthwaite statistic was used and effective degrees of freedom were rounded to the nearest integer.

RESULTS

The results for the following BCCs are reported here: Total PCBs, TEQs, HCB, *beta*-HCH, OCS, Heptachlor Epoxide, Oxychlordane, *alpha*-Chlordane, *trans*-Nonachlor, *p,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD, Dieldrin, *cis*-Nonachlor, Mirex, and Mercury. Three analytes, *alpha*-Hexachlorocyclohexane, *gamma*-Hexachlorocyclohexane, and *gamma*-Chlordane are not included in these analyses since >50% of all samples analyzed were below detection limits (94%, 97%, and 82%, respectively). Table 2 lists the 19 BCCs and their abbreviations used in this report. The following appendices provide the data used for the various analyses:

- Appendix A provides the five-year median BCC concentrations in herring gull eggs for ten breeding colonies in Michigan from 2002 to 2006.
- Appendix B provides the five-year median BCC concentrations by year for each of the Great Lakes for ten breeding colonies in Michigan from 2002 to 2006.
- Appendix C provides the five-year median BCC concentrations in herring gull eggs for ten breeding colonies in Michigan from 2008 to 2012.
- Appendix D provides the five-year median BCC concentrations by year for each of the Great Lakes for ten breeding colonies in Michigan from 2008 to 2012.

SPATIAL ANALYSIS

AMONG COLONIES – FIVE-YEAR MEDIANS

The five-year median concentration of each BCC was calculated for each colony for the period 2008 to 2012. Concentrations of total PCBs, TEQs, *beta*-HCH, OCS, DIEL, *oxy*-CHL, *alpha*-CHL, *cis*-NON, DDT, DDE, and DDD varied significantly among colonies. The following is a summary of the results for each of these contaminants:

- Median total PCBs ranged from 1221.96 to 7815.36 ppb for the 10 colonies sampled. Total PCBs were significantly different among colonies ($F = 13.14$, $df = 9$, $p < 0.0001$). Detroit Edison was significantly higher in total PCBs than Bellow Island, Scarecrow Island, Huron Island, Green Island, and Five Mile Island (Table 3, Figure 2).

- Median total TEQs ranged from 187.66 to 511.43 ppt for the 10 colonies sampled. Total TEQs were significantly different among colonies ($F = 3.11$, $df = 9$, $p = 0.0143$). Due to conservativeness of the pairwise comparison, no post-hoc significant differences were found (Table 4, Figure 3).

- Median *beta*-HCH concentrations ranged from 0.39 to 1.03 ppb for the 10 colonies sampled. The concentrations of *beta*-HCH were significantly different among colonies ($F = 2.47$, $df = 9$, $p = 0.0407$). Due to conservativeness of the pairwise comparison, no post-hoc significant differences were found (Table 5, Figure 4).

- Median concentrations of OCS ranged from 1.07 to 7.20 ppb for the 10 colonies sampled. Concentrations of OCS were significantly different among colonies ($F = 5.27$, $df = 9$, $p = 0.0007$). Due to conservativeness of the pairwise comparison, no post-hoc significant differences were found (Table 6, Figure 5).

- Median concentrations of DIEL ranged from 7.97 to 41.41 ppb for the 10 colonies sampled. Concentrations of DIEL were significantly different among colonies ($F = 3.67$, $df = 9$, $p = 0.0062$). Detroit Edison and Tahquamenon Island colonies had significantly higher DIEL concentrations than Scarecrow Island (Table 7, Figure 6).

- Median concentrations of *oxy*-CHL ranged from 14.11 to 39.15 ppb for the 10 colonies sampled. Concentrations of *oxy*-CHL were significantly different among colonies ($F = 4.36$, $df = 9$, $p = 0.0023$) with Net Island being significantly higher in *oxy*-CHL concentration than Five Mile Island and Scarecrow Island (Table 8, Figure 7).

- Median concentrations of *alpha*-CHL ranged from 0.21 to 2.23 ppb for the 10 colonies sampled. Concentrations of *alpha*-CHL were significantly different among colonies ($F = 7.43$, $df = 9$, $p < 0.0001$). Detroit Edison was significantly higher in *alpha*-CHL concentration than West Twin Pipe, Scarecrow Island, Net Island, and Five Mile Island (Table 9, Figure 8).

- Median concentrations of *cis*-NON ranged from 7.56 to 17.77 ppb for the 10 colonies sampled. Concentrations of *cis*-NON were significantly different among colonies ($F = 2.79$, $df = 9$, $p = 0.0240$). Net Island and Tahquamenon Island had significantly higher *cis*-NON concentrations than Scarecrow Island (Table 10, Figure 9).

- Median concentrations of DDT ranged from 3.66 to 19.81 ppb for the 10 colonies sampled. Concentrations of DDT were significantly different among colonies ($F = 3.38$, $df = 9$, $p = 0.0096$). Due to conservativeness of the pairwise comparison, no post-hoc significant differences were found (Table 11, Figure 10).

- Median concentrations of DDE ranged from 430.85 to 909.52 ppb for the 10 colonies sampled. Concentrations of DDE were significantly different among colonies ($F = 7.07$, $df = 9$, $p < 0.0001$). West Twin Pipe was significantly higher in DDE concentration than Huron Island, Scarecrow Island, and Five Mile Island (Table 12, Figure 11).

- Median concentrations of DDD ranged from 0.30 to 4.48 ppb for the 10 colonies sampled. Concentrations of DDD were significantly different among colonies ($F = 3.35$, $df = 9$, $p = 0.0099$). Due to conservativeness of the pairwise comparison, no post-hoc significant differences were found (Table 13, Figure 12).

Colonies were ranked from 1 to 10 for most contaminated to least contaminated for each contaminant that was found to differ significantly (Table 14). Detroit Edison was ranked first (most contaminated) for total PCBs, OCS, DIEL, and *alpha*-CHL and second for TEQ, DDT, and DDD. West Twin Pipe was ranked first for DDT, DDE, and DDD, and second for *beta*-HCH. Tahquamenon was ranked first for *cis*-NON, and second for *beta*-HCH, DIEL, *oxy*-CHL, and DDE. When comparing ranks of colonies with the same lake or river association, Tahquamenon was the most contaminated colony of Lake Superior. Little Charity Island was the most contaminated site in Lake Huron. Bellow Island was more contaminated than Green Island in Lake Michigan. For the two colonies in the St. Marys River, West Twin Pipe was more contaminated than Five Mile Island. The Detroit Edison colony was the only one located on Lake Erie.

The percentage of total TEQs contributed by dioxin/furans versus dioxin-like PCB congeners was assessed for the five colonies with the most data for the period 2008 to 2012 (Figure 13). This analysis showed that PCBs are the predominant source of TEQs for all five colonies. Total PCBs comprised 62%, 83%, 89%, 92%, and 95% of the total TEQs for Five Mile Island, Huron Island, Little Charity Island, Detroit Edison, and Bellow Island, respectively.

AMONG LAKES – FIVE-YEAR MEDIANS

The five-year median of each BCC was calculated for each lake. Concentrations of total PCBs, TEQ, *beta*-HCH, OCS, DIEL, *oxy*-CHL, *alpha*-CHL, *trans*-NON, *cis*-NON, DDT, DDD, and MIR varied significantly among lakes. The following is a summary of the results for each of these contaminants:

- Total PCBs were significantly different among lakes ($F = 8.80$, $df = 4$, $p < 0.0001$) with Lake Erie being significantly higher in total PCB concentration than Lake Superior, Lake Michigan, and St. Marys River (Table 15, Figure 14).

- TEQ concentrations were significantly different among lakes ($F = 6.14$, $df = 4$, $p = 0.0012$). Lake Erie was significantly higher in TEQ concentration than St. Marys River, Lake Superior, and Lake Michigan (Table 16, Figure 15).

- The concentrations of *beta*-HCH were significantly different among lakes ($F = 4.55$, $df = 4$, $p = 0.0061$). Lake Superior was significantly higher in *beta*-HCH concentration than Lake Michigan and Lake Erie (Table 17, Figure 16).

- Concentrations of OCS were significantly different among lakes ($F = 7.83$, $df = 4$, $p = 0.003$) with Lake Erie being significantly higher in concentrations of OCS than Lake Superior, St. Marys River, and Lake Michigan (Table 18, Figure 17).

- Concentrations of DIEL were significantly different among lakes ($F = 5.54$, $df = 4$, $p = 0.0022$) with Lake Erie being significantly higher in DIEL concentration than St. Marys River and Lake Huron (Table 19, Figure 18).

- Concentrations of *oxy*-CHL were significantly different among lakes ($F = 7.27$, $df = 4$, $p = 0.0004$) with Lake Superior being significantly higher in concentrations of *oxy*-CHL than St. Marys River and Lake Huron (Table 20, Figure 19).

- Concentrations of *alpha*-CHL were significantly different among lakes ($F = 11.73$, $df = 4$, $p < 0.0001$). Lake Erie was significantly higher in *alpha*-CHL concentrations than Lake Huron and St. Marys River (Table 21, Figure 20).

- Concentrations of *trans*-NON were significantly different among lakes ($F = 4.21$, $df = 4$, $p = 0.0089$) with Lake Erie and Lake Superior being significantly higher in *trans*-NON concentrations than St. Marys River (Table 22, Figure 21).

- Concentrations of *cis*-NON were significantly different among lakes ($F = 3.83$, $df = 4$, $p = 0.0137$) with Lake Superior being significantly higher in *cis*-NON concentrations than Lake Huron (Table 23, Figure 22).

- Concentrations of *p,p'*-DDT were significantly different among lakes ($F = 2.84$, $df = 4$, $p = 0.0439$). Lake Erie was significantly higher in *p,p'*-DDT concentration than Lake Superior (Table 24, Figure 23).

- Concentrations of *p,p'*-DDD were significantly different among lakes ($F = 4.99$, $df = 4$, $p = 0.0038$). Lake Erie was significantly higher in *p,p'*-DDD concentration than Lake Superior and St. Marys River (Table 25, Figure 24).

- Concentrations of MIR were significantly different among lakes ($F = 3.10$, $df = 4$, $p = 0.0318$) with St. Marys River and Lake Superior being significantly higher in MIR concentration than Lake Erie (Table 26, Figure 25).

For each of the compounds that were found to differ significantly among lakes, lakes were ranked from 1 to 5 for most contaminated to least contaminated (Table 27). Lake Erie was ranked first for 8 of the 12 BCCs, specifically total PCBs, TEQs, OCS, DIEL, *alpha*-CHL, *trans*-NON, DDT, and DDD. Lake Superior was ranked first for 3 of the 12 BCCs, *beta*-HCH, *oxy*-CHL, and *cis*-NON. Lake Huron was ranked second for 5 of 12 of the BCCs including total PCBs, TEQ, *beta*-HCH, OCS, and DDT.

TEMPORAL ANALYSIS

Compound concentrations were compared between two time periods, 2002-2006 and 2008-2012. Observable differences in BCCs between time periods can be seen in Figures 26-27. Concentrations of total PCBs, HCB, HEP, DIEL, *oxy*-CHL, *trans*-NON, *cis*-NON, DDT, DDE, DDD, MIR, and Hg varied significantly between time periods. The following is a summary of the results for each of these contaminants:

- Concentrations of total PCBs were significantly different between time periods ($F = 17.97$, $df = 1$, $p < 0.0001$).

- Concentrations of HCB were significantly different between time periods ($F = 9.39$, $df = 1$, $p = 0.0031$).

- Concentrations of HEP were significantly different between time periods ($F = 84.88$, $df = 1$, $p < 0.0001$).

- Concentrations of DIEL were significantly different between time periods ($F = 13.90$, $df = 1$, $p = 0.0004$).

- Concentrations of *oxy*-CHL were significantly different between time periods ($F = 47.92$, $df = 1$, $p < 0.0001$).

- Concentrations of *trans*-NON were significantly different between time periods ($F = 63.03$, $df = 1$, $p < 0.0001$).

- Concentrations of *cis*-NON were significantly different between time periods ($F = 69.10$, $df = 1$, $p < 0.0001$).

- Concentrations of DDT were significantly different between time periods ($F = 11.91$, $df = 1$, $p = 0.0009$).

- Concentrations of DDE were significantly different between time periods ($F = 100.74$, $df = 1$, $p < 0.0001$).

- Concentrations of DDD were significantly different between time periods ($F = 35.50$, $df = 1$, $p < 0.0001$).

- Concentrations of MIR were significantly different between time periods ($F = 26.47$, $df = 1$, $p < 0.0001$).

- Concentrations of Hg were significantly different between time periods ($F = 29.08$, $df = 1$, $p < 0.0001$).

Post-hoc analyses showed that concentrations of PCB, HCB, HEP, DIEL, *oxyo*-CHL, *alpha*-CHL, *trans*-NON, *cis*-NON, DDT, DDE, DDD, MIR, and Hg decreased significantly by colony between the two time periods. There were observable increases in *alpha*-CHL concentration at Huron Island, and in HCB and MIR concentration at West Twin Pipe. There were significant decreases in total PCBs, HCB, HEP, DIEL, *xy*-CHL, *trans*-NON, *cis*-NON, DDT, DDE, DDD, MIR, and Hg between lakes for the two time periods. There were observable decreases in all lakes.

Table 28 shows the temporal changes for select contaminants (total PCBs, DDE, TEQ, and Hg) measured in herring gull eggs collected from ten colonies. Four colonies (Bellow Island, Little Charity Island, Five Mile Island, and Detroit Edison) had sufficient data to assess temporal trends. The data for the three colonies in Lake Superior (Net Island, Tahquamenon Island, and Huron Island) were combined for this analysis since there were limited data to analyze these colonies separately.

- Bellow Island (Grand Traverse Bay, Lake Michigan) had a significant decrease in PCBs, DDE, and Hg over time. The concentration of TEQs also decreased during this time period, but the decrease was only significant at $p < 0.10$.
- Little Charity Island (Saginaw Bay, Lake Huron) had a significant decrease in total PCBs and DDE over time. No significant changes occurred in TEQs or Hg.
- Five Mile Island in the St. Marys River had a significant decrease in total PCBs, DDE, and Hg over time. No significant changes occurred in TEQs.
- Detroit Edison had a significant decrease in DDE. The concentration of PCBs also decreased, but the decrease was only significant at $p<0.10$.
- The combined data for Net Island, Tahquamenon Island, and Huron Island showed a decrease in total PCBs, DDE, and Hg in Lake Superior over time.
- A significant increase in TEQ levels at $p < 0.10$ occurred in Tahquamenon Island and Scarecrow Island during the duration of this study.

DISCUSSION

COMPARISON TO TOXIC REFERENCE VALUES (TRVS)

A PCB TRV is currently not available for herring gulls. However, a NOAEC and LOAEC (based on the incidence of deformities) of 3.6 and 7.3 mg/kg were found for double-crested cormorants (*Phalacrocorax auritus*) and a LOAEC (based on the incidence of egg lethality and deformities) was found for Caspian terns (*Hydroprongne caspia*) (Yamashita et al., 1993). For the period 2008-2012, two colonies had a five-year median concentration that was at, or above, the NOAEC found for double-crested cormorants. The Detroit Edison colony had a five-year median concentration of 7.8 mg/kg, whereas, the Little Charity Island had a five-year median concentration of 3.6 mg/kg.

A TEQ TRV is currently not available for herring gulls. However, a NOAEC and LOAEC (hatching success) of 0.22 and 2.18 ug/kg, respectively, are available for Forster's terns (Kubiak et al., 1989), a NOAEC and LOAEC (6-7% deformities) of 0.35 and 1.20 ug/kg, respectively, are available for double-crested cormorants (Yamashita et al., 1993), and a NOAEC and LOAEC of 0.22 and 0.36 ug/kg, respectively, are available for great blue herons (Elliott et al., 2001). The Detroit Edison and Little Charity Island colonies had five-year median TEQ levels of 0.511 and 0.466 ug/kg, respectively, suggesting that they may be impacted by TEQs. TEQ concentrations in eggs from Scarecrow Island and Tahquamenon Island colonies were also elevated (0.555 and 0.404 ug/kg, respectively), but only two years of data were available for both colonies for the period 2008 to 2012.

A DDE TRV is currently not available for herring gulls. However, a LOAEC (based on a 20% decrease in egg shell thickness) of 10 mg/kg was found for double-crested cormorants (*Phalacrocorax auritus)* (Pearce et al., 1979) and a NOAEC of 3.5 mg/kg is used as a NOAEC has been determined for eggshell thinning in bald eagles (*Haliaeetus leucocephalus*) (Wiemeyer et al., 1984). For the period 2008-2012, no colonies exceeded these values.

Spatial Assessment

The more-contaminated sites in Michigan's Lower Peninsula were located south and north of Lake St. Clair in Lakes Erie (Detroit Edison) and Huron (Little Charity Island), which are within the River Raisin and Saginaw Bay/River Areas of Concern, respectively. These findings are not surprising since these two colonies are in Areas of Concern with beneficial use impairments due to elevated levels of PCBs and/or TEQs. Tahquamenon and West Twin Pipe Islands were the more contaminated sites located in Michigan's Upper Peninsula. It is noteworthy that West Twin Pipe Island in the lower St. Marys River had higher concentrations of *p,p'*-DDT (and its metabolites, *p,p'*-DDE and *p,p'*-DDD), total PCBs, and TEQs than the colony in the upper St. Marys River (Five Mile Island). The spike in contamination levels downstream could be attributed to remediation efforts in the St. Marys River Area of Concern.

Temporal Trends

Twelve of the 16 BCCs analyzed in this study were shown to be significantly changing over time. For all of these contaminants except TEQs, contaminant levels were decreasing in herring gull eggs over time. For some unknown reason, the TEQ concentrations for the period 2008-2012 were higher than the concentrations for the period 2002-2006 for six of the ten colonies. Changes in TEQ concentration were not significant at the $p < 0.05$ level. However, TEQ concentrations were shown to be increasing at the $p < 0.10$ level for Scarecrow Island and Tahquamenon Island and decreasing at the $p < 0.10$ level for Bellow Island. It is noteworthy that Scarecrow Island and Tahquamenon Islands only had two years of data for the period

2008-2012, whereas, Bellow Island had data for all five years. For the most part, the changes seen in contaminant levels in herring gull eggs over the duration of this study suggest environmental improvements.

FUTURE DIRECTION

A refinement for herring gull egg collection protocol would be the potential integration of both embryo toxicokinetic models for PCBs (Drouillard et al., 2003) and egg volume loss models to correct for non-fresh egg collections. Due to logistical problems and problems caused by global climate change, the loss of data for a single year can occur. Having a series of correction factors for egg concentrations that are defendable and allow for the conversion of concentrations to fresh egg volumes allows for non-fresh eggs to potentially be used. As budgets for monitoring programs shrink or become less dependable, and personnel reach retirement age, these types of correction factors may be more important, especially when new collectors are added to the program. Correction factors will also be useful in dealing with changes associated with global climate change. Unpredictable or catastrophic weather events could delay egg collection, change the timing of egg-laying, and affect sediment transfer of contaminants. Changing weather may also affect the feeding of adult herring gulls, changing the composition and abundance of prey species.

Further analysis of the herring gull data needs to occur to assess the relationship between the concentrations of OC substances and trophic level. It is important to understand how changes in diet may influence spatial and temporal patterns of concentrations of BCCs within herring gull eggs (Hebert et al., 1999 and 2006). Spatial trends reflecting great changes in trophic status have been observed in environmental pollutants monitored in gull eggs (Pekarik and Weseloh, 1998) and a number of these changes were observed after dreissenid mussel (*Dreissena polymorpha, D. bugensis*) invasions occurred.

This report represents the first opportunity for Michigan to evaluate consecutive five-year sampling efforts allowing analyses of spatial and temporal trends between time periods. The ten colonies provide data that can be used independently or concurrently with the CWS herring gull monitoring data.

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TABLES

Table 1. Herring gull colony abbreviations sorted by lake with map reference numbers.

Lake (Abbreviation)	Colony Name	Abbreviation	Map Reference*
Lake Superior (LS)	Net Island	NI	1
	Huron Island	HI	2
	Tahquamenon	T	3
St. Marys River (SMR)	Five Mile Island	FMI	4
	West Twin Pipe	WTP	5
Lake Huron (LH)	Scarecrow Island	SCI	6
	Little Charity Island	LCI	7
Lake Michigan (LM)	Green Island	GRI	8
	Bellow Island	BI	9
Lake Erie (LE)	Detroit Edison	DE	10

*See Figure 1.

Table 2. BCCs assessed in herring gull eggs.

BCC	Abbreviation
Polychlorinated biphenyls	PCB
Hexachlorobenzene	HCB
alpha-Hexachlorocyclohexane	*alpha*-HCH
beta-Hexachlorocyclohexane	*beta*-HCH
gamma-Hexachlorocyclohexane	*gamma*-HCH
Octachlorostyrene	OCS
Heptachlor epoxide	HEP
Oxychlordane	*oxy*-CHL
gamma-Chlordane	*gamma*-CHL
alpha-Chlordane	*alpha*-CHL
trans-Nonachlor	*trans*-NON
Dichlorodiphenyldichloroethylene	DDE
Dieldrin	DIEL
Dichlorodiphenyldichloroethane	DDD
cis-Nonachlor	*cis*-NON
Dichlorodiphenyltrichloroethane	DDT
Mirex	MIR
Mercury	Hg
Toxicity Equivalent	TEQ

AMONG COLONIES – FIVE-YEAR MEDIANS

Table 3. Significant differences among colonies for total PCB concentration (colonies with the same letter are not significantly different).

Colony	Median (ppb)				
DE	7815.36	A			
LCI	3621.15	A	B		
WTP	2527.64	A	B	C	
T	2334.28	A	B	C	
NI	2262.60	A	B	C	D
BI	1824.20		B	C	D
SCI	1763.62		B	C	D
HI	1531.27			C	D
GRI	1639.11			C	D
FMI	1221.96				D

Table 4. Significant differences among colonies for TEQ concentration (colonies with the same letter are not significantly different).

Colony	Median (ppt)	
DE	511.43	A
SCI	555.42	A
LCI	466.06	A
T	404.42	A
GRI	325.16	A
WTP	320.97	A
FMI	239.17	A
NI	288.60	A
BI	250.84	A
HI	187.66	A

Table 5. Significant differences among colonies for *beta*-HCH concentration (colonies with the same letter are not significantly different).

Colony	Median (ppb)	
NI	1.03	A
WTP	0.72	A
T	0.72	A
LCI	0.60	A
HI	0.61	A
SCI	0.67	A
FMI	0.51	A
GRI	0.43	A
BI	0.38	A
DE	0.39	A

Table 6. Significant differences among colonies for OCS concentration (colonies with the same letter are not significantly different).

Colony	**Median (ppb)**	
DE	7.20	A
LCI	4.27	A
WTP	3.63	A
SCI	2.75	A
T	1.87	A
NI	1.64	A
HI	1.27	A
GRI	1.72	A
FMI	1.12	A
BI	1.07	A

Table 7. Significant differences among colonies for DIEL concentration (colonies with the same letter are not significantly different).

Colony	**Median (ppb)**		
DE	41.41	A	
T	39.21	A	
BI	18.84	A	B
GRI	32.42	A	B
WTP	17.96	A	B
HI	17.48	A	B
LCI	15.57	A	B
FMI	14.86	A	B
NI	13.11	A	B
SCI	7.97		B

Table 8. Significant differences among colonies for *oxy*-CHL concentration (colonies with the same letter are not significantly different).

Colony	**Median (ppb)**			
NI	39.15	A		
T	38.09	A	B	
HI	29.15	A	B	
BI	27.88	A	B	C
WTP	23.71	A	B	C
DE	21.58	A	B	C
GRI	20.48	A	B	C
LCI	15.11	A	B	C
FMI	19.98		B	C
SCI	14.11			C

Table 9. Significant differences among colonies for *alpha*-CHL concentration (colonies with the same letter are not significantly different).

Colony	**Median (ppb)**			
DE	2.23	A		
BI	2.15	A	B	
HI	0.85	A	B	C
T	0.75	A	B	C
GRI	0.85	A	B	C
LCI	0.64	A	B	C
WTP	0.36		B	C
SCI	0.38		B	C
NI	0.25		B	C
FMI	0.21			C

Table 10. Significant differences among colonies for *cis*-NON concentration (colonies with the same letter are not significantly different).

Colony	**Median (ppb)**		
NI	17.77	A	
T	20.29	A	
WTP	14.61	A	B
HI	16.07	A	B
BI	13.06	A	B
FMI	13.27	A	B
DE	11.17	A	B
LCI	9.49	A	B
GRI	9.04	A	B
SCI	7.56		B

Table 11. Significant differences among colonies for *p,p'*-DDT concentration (colonies with the same letter are not significantly different).

Colony	**Median (ppb)**	
DE	19.81	A
WTP	53.84	A
LCI	15.59	A
BI	8.67	A
T	5.98	A
NI	4.99	A
SCI	5.41	A
FMI	4.12	A
HI	4.59	A
GRI	3.66	A

Table 12. Significant differences among colonies for *p,p'*-DDE concentration (colonies with the same letter are not significantly different).

Colony	**Median (ppb)**			
WTP	909.52	A		
T	852.37	A	B	
NI	855.39	A	B	
DE	785.69	A	B	
BI	795.88	A	B	C
LCI	667.01	A	B	C
GRI	570.93	A	B	C
HI	522.92		B	C
SCI	451.62			C
FMI	430.85			C

Table 13. Significant differences among colonies for *p,p'*-DDD concentration (colonies with the same letter are not significantly different).

Colony	**Median (ppb)**	
DE	4.48	A
BI	1.63	A
WTP	5.41	A
LCI	1.23	A
T	1.02	A
GRI	1.28	A
NI	0.91	A
SCI	0.63	A
FMI	0.32	A
HI	0.30	A

Table 14. Colony rankings (colonies are ranked from most contaminated to least contaminated [1-10]). Only BCCs with significant differences are shown.

		PCB		TEQ		*beta*-HCH		OCS		DIEL		*oxy*-CHL	
Colony	**Lake**	**Rank**	**ppb**	**Rank**	**ppt**	**Rank**	**ppb**	**Rank**	**ppb**	**Rank**	**ppb**	**Rank**	**ppb**
NI	LS	5	2262.6	7	288.6	1	1.0	7	1.6	9	13.1	1	39.2
HI	LS	9	1531.3	10	187.7	5	0.6	8	1.3	6	17.5	3	29.2
T	LS	4	2334.3	4	404.4	2	0.7	5	1.9	2	39.2	2	38.1
FMI	SMR	10	1222.0	9	239.2	7	0.5	9	1.1	8	14.9	8	20.0
WTP	SMR	3	2527.6	6	321.0	2	0.7	3	3.6	5	18.0	5	23.7
SCI	LH	7	1763.6	1	555.4	4	0.7	4	2.8	10	8.0	10	14.1
LCI	LH	2	3621.2	3	466.1	6	0.6	2	4.3	7	15.6	9	15.1
GRI	LM	8	1639.1	5	325.2	8	0.4	6	1.7	3	32.4	7	20.5
BI	LM	6	1824.2	8	250.8	10	0.4	10	1.1	4	18.8	4	27.9
DE	LE	1	7815.4	2	511.4	9	0.4	1	7.2	1	41.4	6	21.6

Table 14 (cont). Colony rankings (colonies are ranked from most contaminated to least contaminated [1-10]). Only BCCs with significant differences are shown.

		alpha-CHL		*cis*-NON		*p,p'*-DDT		*p,p'*-DDE		*p,p'*-DDD	
Colony	**Lake**	**Rank**	**ppb**	**Rank**	**ppb**	**Rank**	**ppb**	**Rank**	**ppb**	**Rank**	**ppb**
NI	LS	9	0.3	2	17.8	7	5.0	3	852.4	7	0.9
HI	LS	3	0.9	3	16.1	8	4.6	8	522.9	10	0.3
T	LS	5	0.8	1	20.3	5	6.0	2	855.4	6	1.0
FMI	SMR	10	0.2	5	13.3	9	4.1	10	430.9	9	0.3
WTP	SMR	8	0.4	4	14.6	1	53.8	1	909.5	1	5.4
SCI	LH	7	0.4	10	7.6	6	5.4	9	451.6	8	0.6
LCI	LH	6	0.6	8	9.5	3	15.6	8	667.0	5	1.2
GRI	LM	3	0.9	9	9.0	10	3.7	7	570.9	4	1.3
BI	LM	2	2.2	6	13.1	4	8.7	4	795.9	3	1.6
DE	LE	1	2.2	7	11.2	2	19.8	5	785.7	2	4.5

AMONG LAKES – FIVE-YEAR MEDIANS

Table 15. Significant differences among lakes for total PCB concentration (lakes with the same letter are not significantly different).

Lake	**Median (ppb)**		
Lake Erie	7815.36	A	
Lake Huron	2739.34	A	B
Lake Superior	2111.14		B
Lake Michigan	1824.20		B
St. Marys River	1466.82		B

Table 16. Significant differences among lakes for TEQ concentration (lakes with the same letter are not significantly different).

Lake	**Median (ppt)**			
Lake Erie	511.43	A		
Lake Huron	466.06	A	B	
St. Marys River	239.17		B	C
Lake Superior	305.34		B	C
Lake Michigan	250.84			C

Table 17. Significant differences among lakes for *beta*-HCH concentration (lakes with the same letter are not significantly different).

Lake	**Median (ppb)**			
Lake Superior	0.69	A		
Lake Huron	0.60	A	B	
St. Marys River	0.51	A	B	C
Lake Michigan	0.38		B	C
Lake Erie	0.39			C

Table 18. Significant differences among lakes for OCS concentration (lakes with the same letter are not significantly different).

Lake	**Median (ppb)**			
Lake Erie	7.20	A		
Lake Huron	3.95	A	B	
Lake Superior	1.67		B	C
St. Marys River	1.36			C
Lake Michigan	1.07			C

Table 19. Significant differences among lakes for DIEL concentration (lakes with the same letter are not significantly different).

Lake	**Median (ppm)**		
Lake Erie	41.41	A	
Lake Michigan	18.84	A	B
Lake Superior	22.84	A	B
St. Marys River	15.24		B
Lake Huron	10.58		B

Table 20. Significant differences among lakes for *oxy*-CHL concentration (lakes with the same letter are not significantly different).

Lake	**Median (ppb)**		
Lake Superior	34.83	A	
Lake Michigan	23.91	A	B
Lake Erie	21.58	A	B
St. Marys River	20.17		B
Lake Huron	15.09		B

Table 21. Significant differences among lakes for *alpha*-CHL concentration (lakes with the same letter are not significantly different).

Lake	**Median (ppb)**			
Lake Erie	2.23	A		
Lake Michigan	1.35	A	B	
Lake Superior	0.77	A	B	
Lake Huron	0.64		B	C
St. Marys River	0.29			C

Table 22. Significant differences among lakes for *trans*-NON concentration (lakes with the same letter are not significantly different).

Lake	**Median (ppb)**		
Lake Erie	9.17	A	
Lake Superior	8.70	A	
Lake Michigan	8.15	A	B
Lake Huron	6.31	A	B
St. Marys River	5.96		B

Table 23. Significant differences among lakes for *cis*-NON concentration (lakes with the same letter are not significantly different).

Lake	**Median (ppb)**		
Lake Superior	17.43	A	
St. Marys River	14.04	A	B
Lake Michigan	11.50	A	B
Lake Erie	11.17	A	B
Lake Huron	9.49		B

Table 24. Significant differences among lakes for DDT concentration (lakes with the same letter are not significantly different).

Lake	**Median (ppb)**		
Lake Erie	19.81	A	
Lake Huron	12.91	A	B
Lake Michigan	6.71	A	B
St. Marys River	6.05	A	B
Lake Superior	4.79		B

Table 25. Significant differences among lakes for DDD concentration (lakes with the same letter are not significantly different).

Lake	**Median (ppb)**		
Lake Erie	4.48	A	
Lake Michigan	1.63	A	B
Lake Huron	1.00	A	B
Lake Superior	0.52		B
St. Marys River	0.32		B

Table 26. Significant differences among lakes for MIR concentration (lakes with the same letter are not significantly different).

Lake	**Median (ppb)**		
St. Marys River	20.44	A	
Lake Superior	17.55	A	
Lake Huron	16.53	A	B
Lake Michigan	11.73	A	B
Lake Erie	9.63		B

Table 27. Lake rankings, with lakes ranked from most contaminated to least contaminated (1-5). Only BCCs with significant differences are reported.

	PCB		TEQ		*beta*-HCH		OCS		DIEL		*oxy*-CHL		*alpha*-CHL		*trans*-NON	
Lake	**Rank**	**ppb**	**Rank**	**Ppb**	**Rank**	**ppb**	**Rank**	**ppb**	**Rank**	**ppb**	**Rank**	**ppb**	**Rank**	**ppb**	**Rank**	**ppb**
Lake Erie	1	7815.36	1	511.43	4	0.39	1	7.20	1	41.41	3	21.58	1	2.23	1	9.17
Lake Huron	2	2739.34	2	466.06	2	0.60	2	3.95	5	10.58	5	15.09	4	0.64	4	6.31
Lake Michigan	4	1824.20	4	250.84	5	0.38	5	1.07	3	18.84	2	23.91	2	1.35	3	8.15
Lake Superior	3	2111.14	3	305.34	1	0.69	3	1.67	2	22.84	1	34.83	3	0.77	2	8.7
St. Marys River	5	1466.82	5	239.17	3	0.51	4	1.36	4	15.24	4	20.17	5	0.29	5	5.96

Table 27 (cont). Lake rankings, with lakes ranked from most contaminated to least contaminated (1-5). Only BCCs with significant differences are reported.

	cis-NON		DDT		DDD		MIR	
Lake	**Rank**	**ppb**	**Rank**	**ppb**	**Rank**	**ppb**	**Rank**	**ppb**
Lake Erie	4	11.17	1	19.81	1	4.48	5	9.63
Lake Huron	5	9.49	2	12.91	3	1.00	3	16.53
Lake Michigan	3	11.50	3	6.71	2	1.63	4	11.73
Lake Superior	1	17.43	4	4.79	4	0.52	2	17.55
St. Marys River	2	14.04	5	3.05	5	0.32	1	20.44

Table 28. Median concentrations of PCBs, p,p'-DDE, TEQ, and Hg in samples of herring gull eggs collecting from colonies in Michigan.

	N		Median Concentration							
			PCB (ppm)		p,p'- DDE (ppm)		TEQ (ppt)		Hg (ppm WW)	
	2002-2006	2008-2012	2002-2006	2008-2012	2002-2006	2008-2012	2002-2006	2008-2012	2002-2006	2008-2012
Lake Michigan	10	7	3.1	1.8*	1.8	0.7*	426	279	0.7	0.39*
BI	5	5	3.1	1.8*	2.2	0.8*	759	251†	0.69	0.41*
GRI	5	2	3	1.6†	1.6	0.6†	279	325	0.72	0.52
Lake Huron	8	7	4.6	2.7*	1.5	0.6**	199	466	0.73	0.33*
LCI (Saginaw Bay/River AOC)	3	5	6	3.6*	1.3	0.7*	768	466	0.47	0.4
SCI	5	2	4.1	1.8†	1.5	0.4†	178	555†	0.94	0.30†
St. Marys River AOC‡	9	7	3.1	1.5*	1	0.4*	226	239	0.65	0.40*
FMI	4	5	2.8	1.2*	0.9	0.4*	221	239	0.66	0.40*
WTP	5	2	3.1	2.5	1.5	0.9	438	321	0.65	0.41
Lake Superior	10	6	3.3	2.1**	1.5	0.7**	200	305	0.82	0.50*
NI	4	1	3.6	2.3	1.9	0.8	210	289	0.85	0.43
T	4	2	3.3	2.3†	1.5	0.8†	188	404†	0.95	0.67
HI (Huron NWR)	2	3	3	1.5†	1.5	0.5†	391	188	0.72	0.45
Lake Erie	.	.	.	.	.	.	.	.	.	.
DE (River Raisin AOC)	5	5	10.8	7.8†	1.1	0.8*	719	511	0.42	0.32
All non-AOC Sites Combined	25	15	3.4	1.9**	1.6	0.7**	219	311	0.75	0.42**

* - Mann-Whitney test: significant at $p < 0.05$

** - Mann-Whitney test: significant at $p<0.001$

† - Mann-Whitney test: significant at $p \leq 0.10$

‡ - AOC with Wildlife BUI

Note: no significant differences in lipid content (Groups were compared using Kruskal-Wallis nonparametric test)

FIGURES

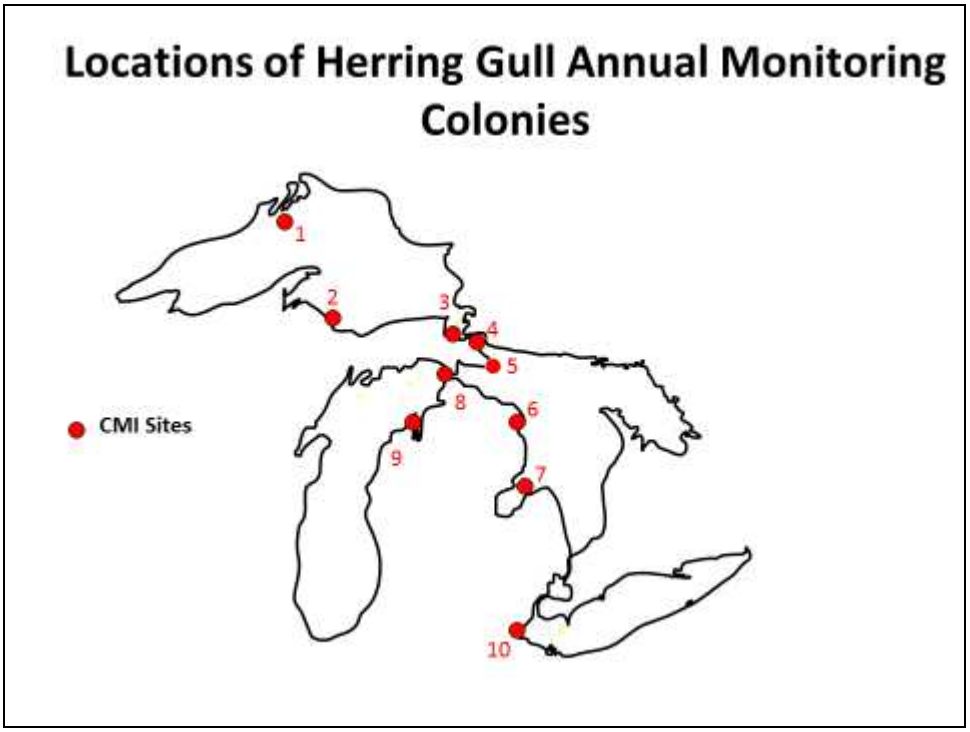

Figure 1. Location of herring gull annual monitoring colonies.

SPATIAL TRENDS

AMONG COLONIES – FIVE-YEAR MEDIANS

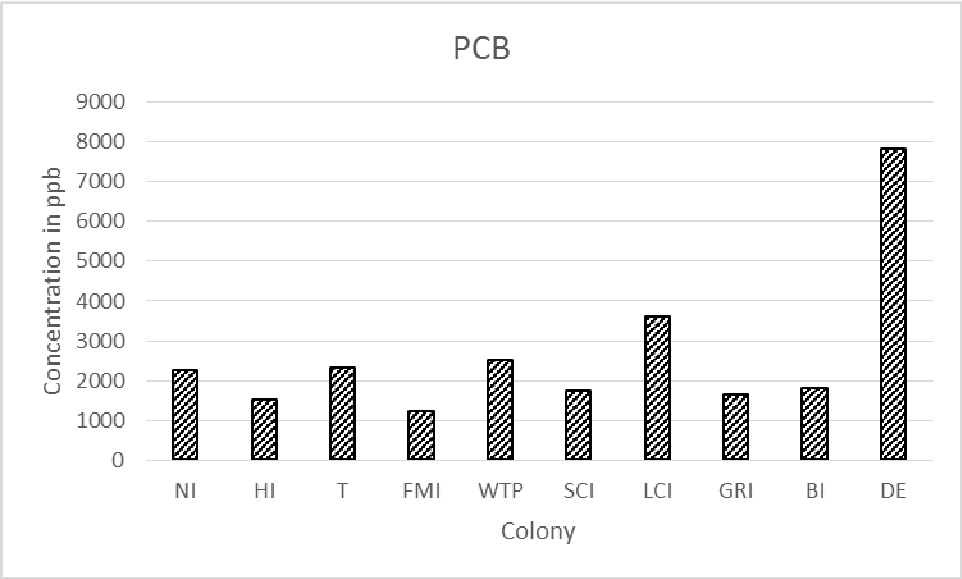

Figure 2. Five-year median concentrations of total PCBs in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2008-2012.

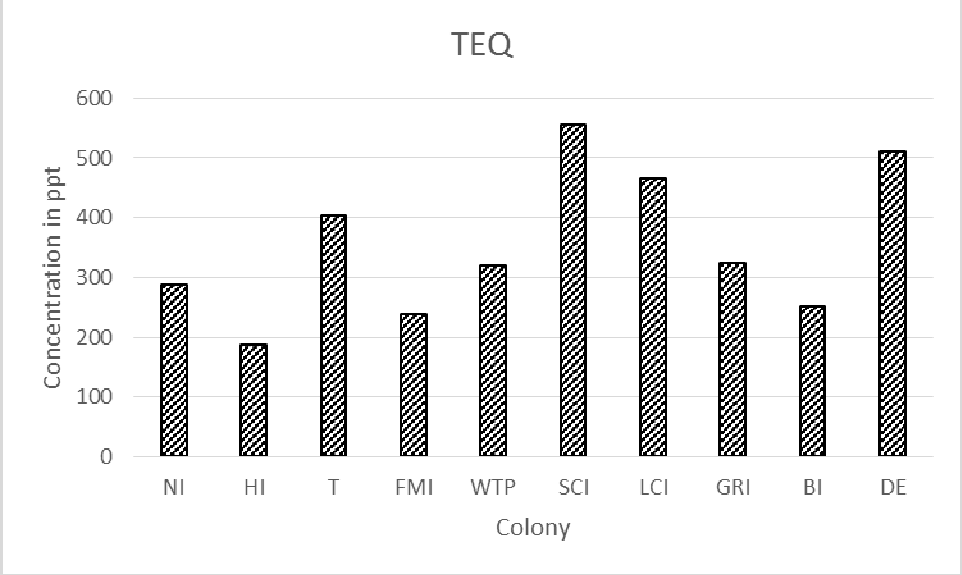

Figure 3. Five-year median concentrations of total TEQs in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2008-2012.

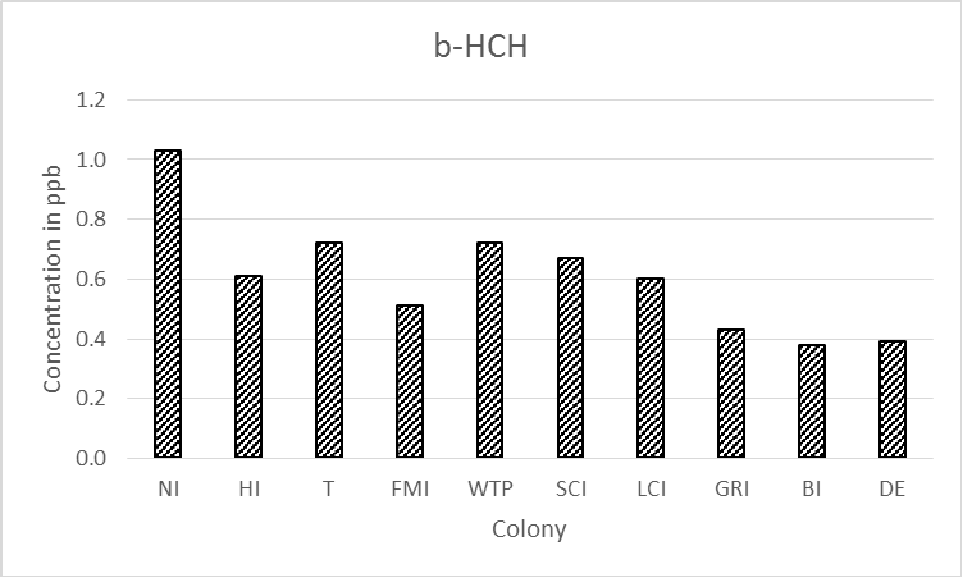

Figure 4. Five-year median concentrations of *beta*-HCH in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2008-2012.

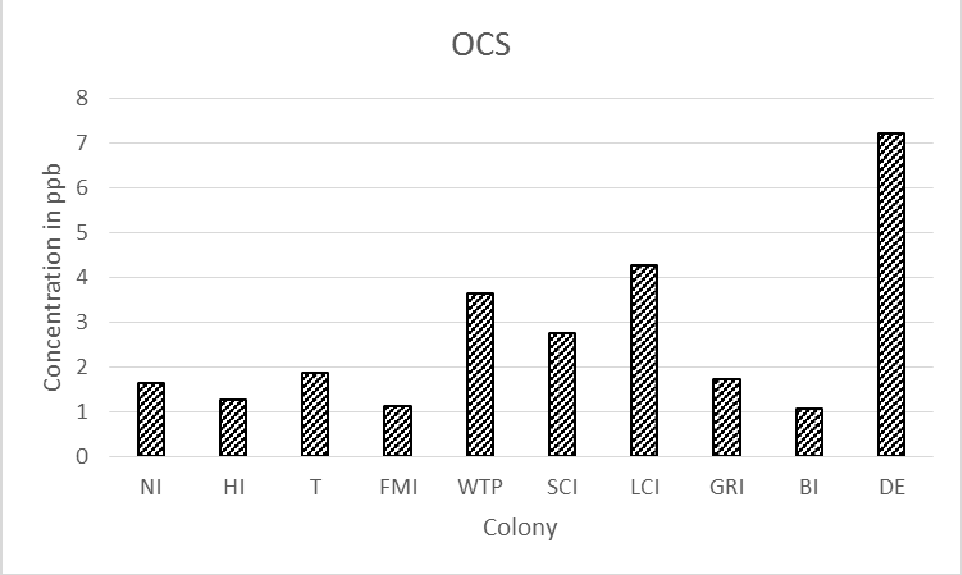

Figure 5. Five-year median concentrations of OCS in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2008-2012.

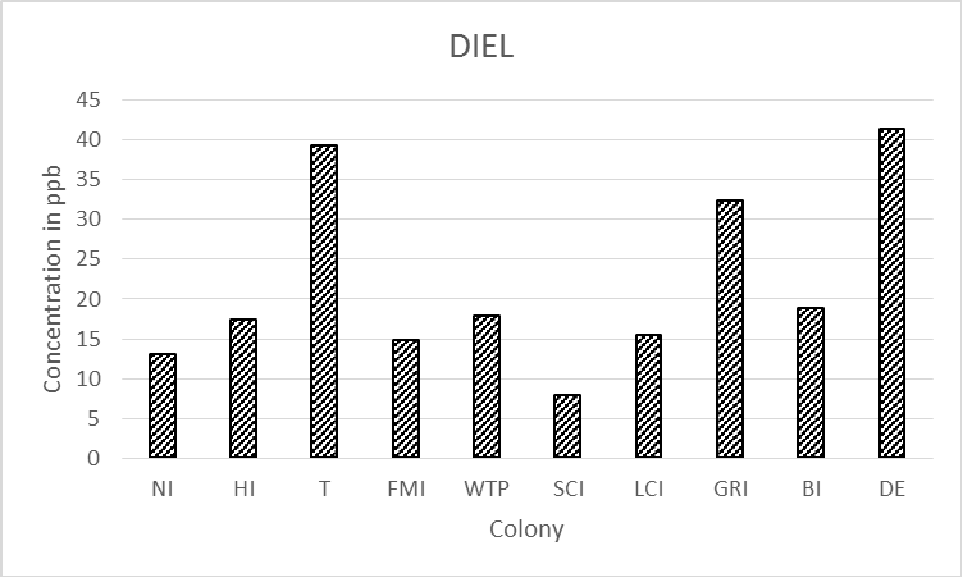

Figure 6. Five-year median concentrations of Dieldrin in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2008-2012.

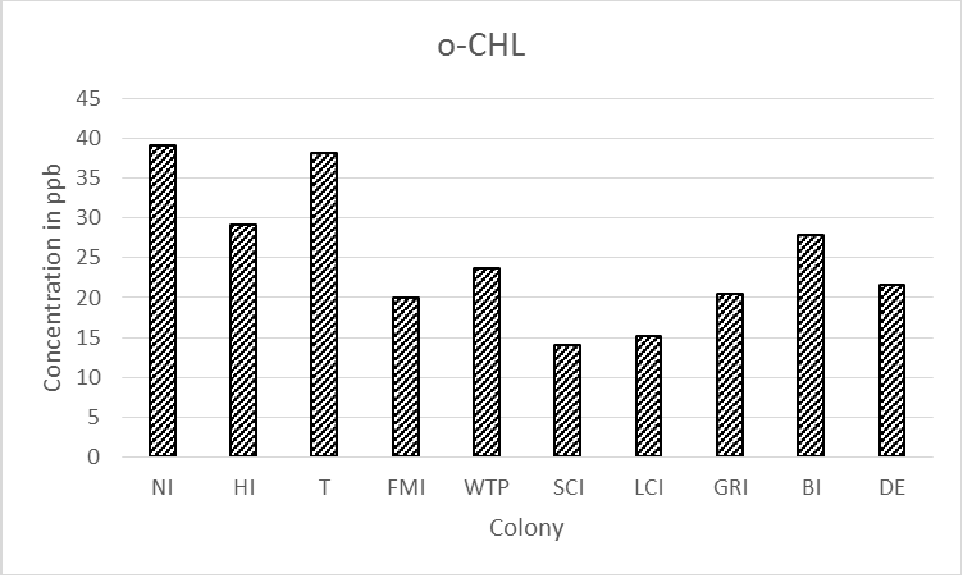

Figure 7. Five-year median concentrations of Oxychlordane in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2008-2012.

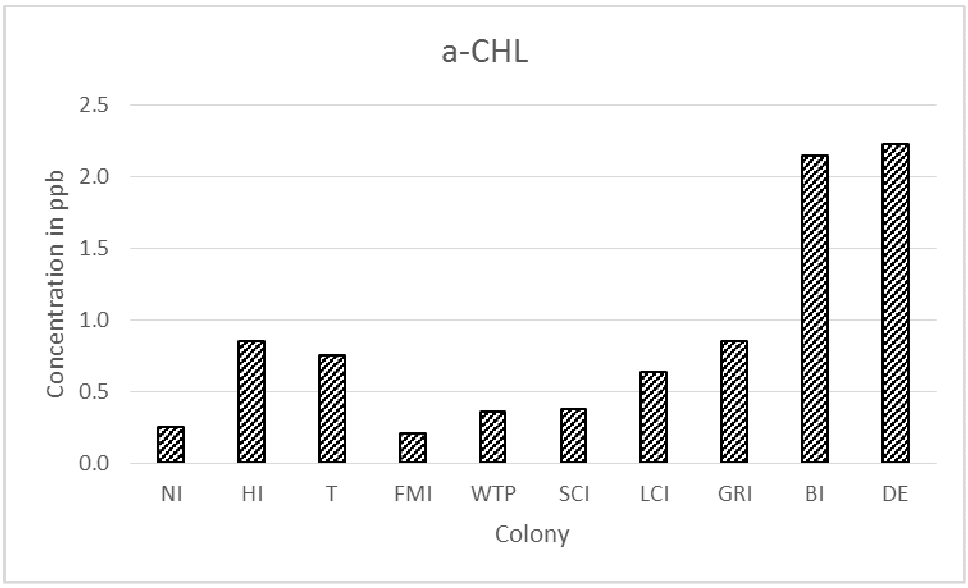

Figure 8. Five-year median concentrations of *alpha*-Chlordane in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2008-2012.

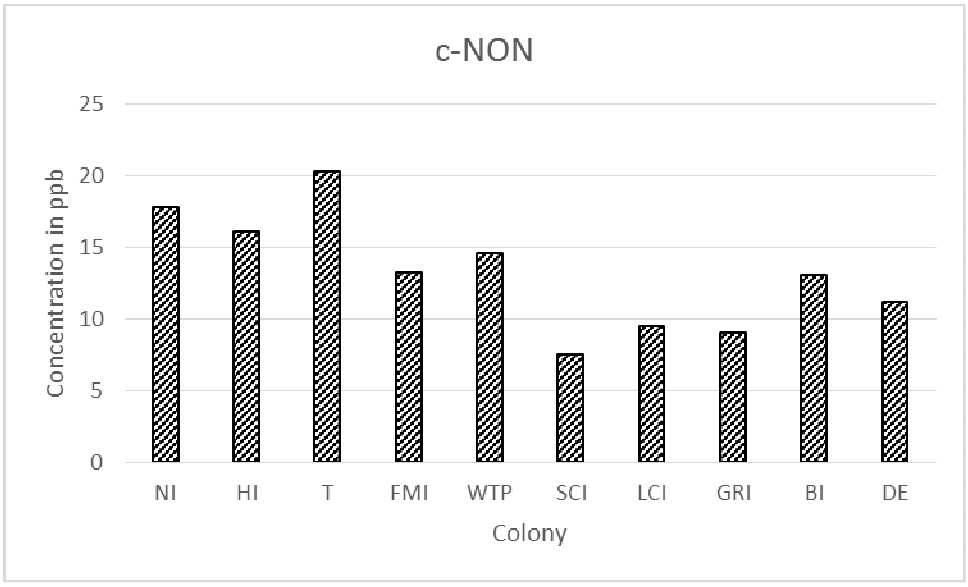

Figure 9. Five-year median concentrations of *cis*-Nonachlor in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2008-2012.

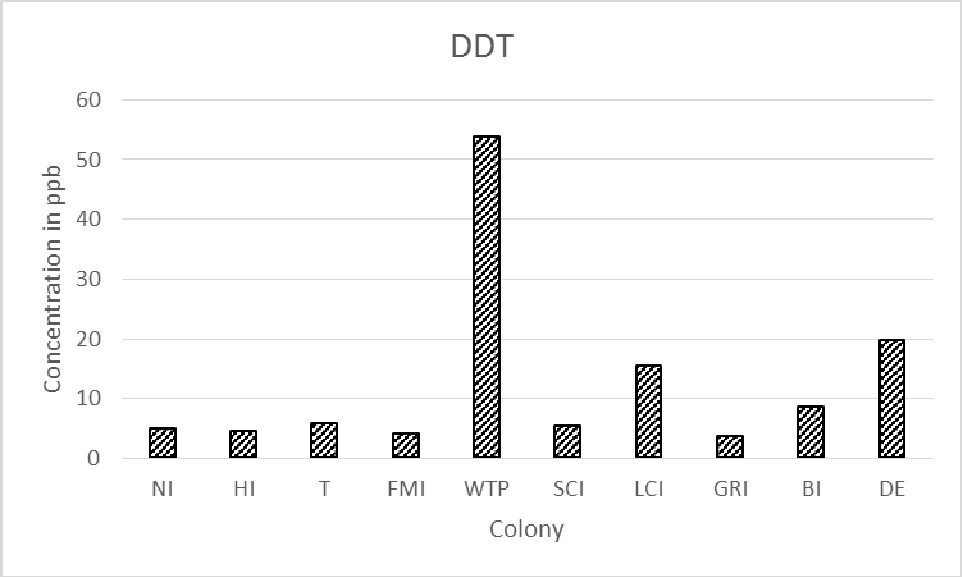

Figure 10. Five-year median concentrations of *p,p'*-DDT in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2008-2012.

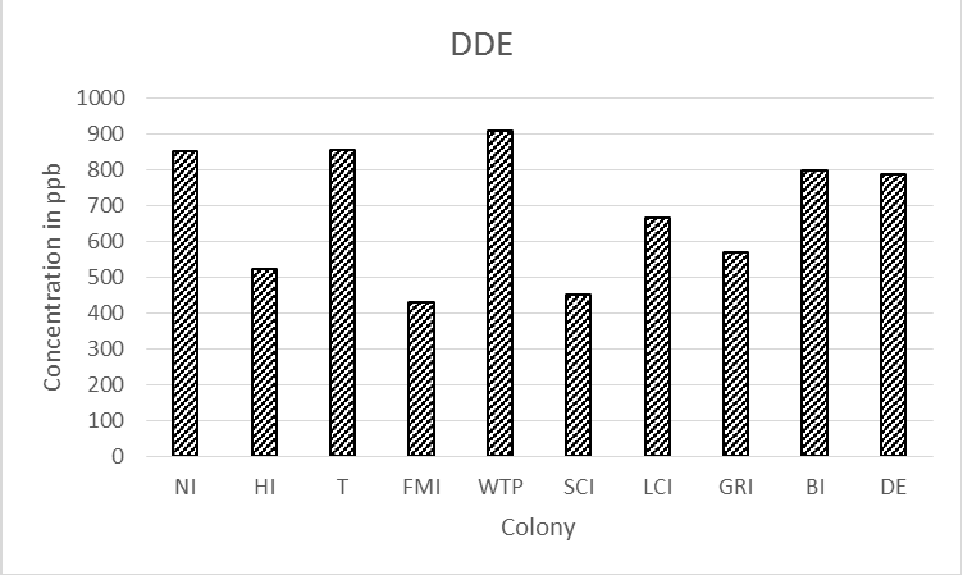

Figure 11. Five-year median concentrations of *p,p'*-DDE in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2008-2012.

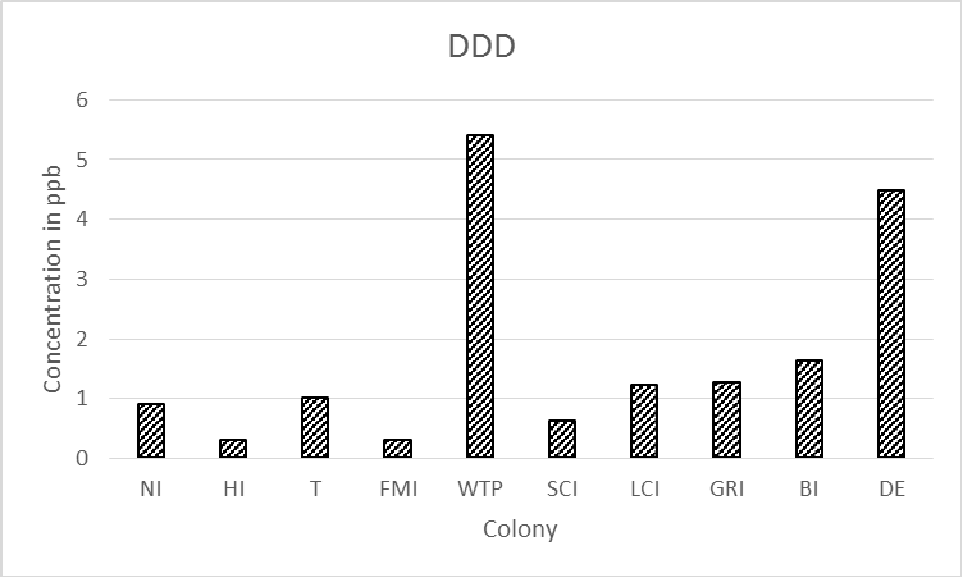

Figure 12. Five-year median concentrations of *p,p'*-DDD in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2008-2012.

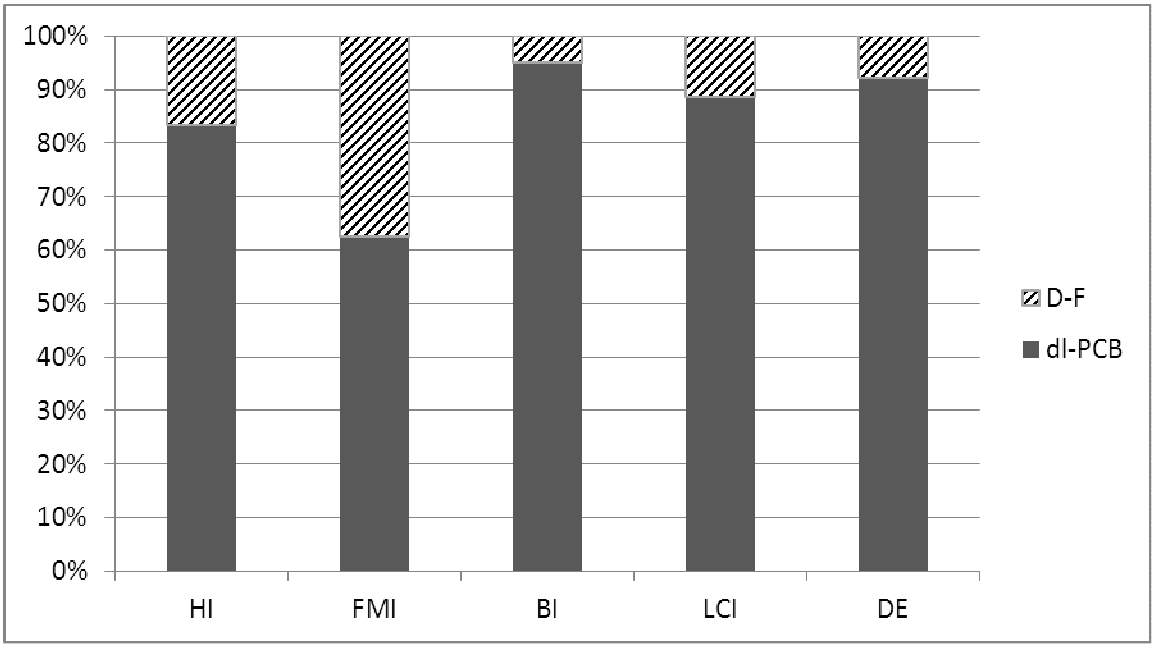

Figure 13. Dioxin/furan congener TEQ (D-F) and dioxin-like PCB congener (dl-PCB) TEQ as a proportion of the total TEQ in herring gull eggs collected from the five colonies monitored from 2008 through 2012.

AMONG LAKES – FIVE-YEAR MEDIANS

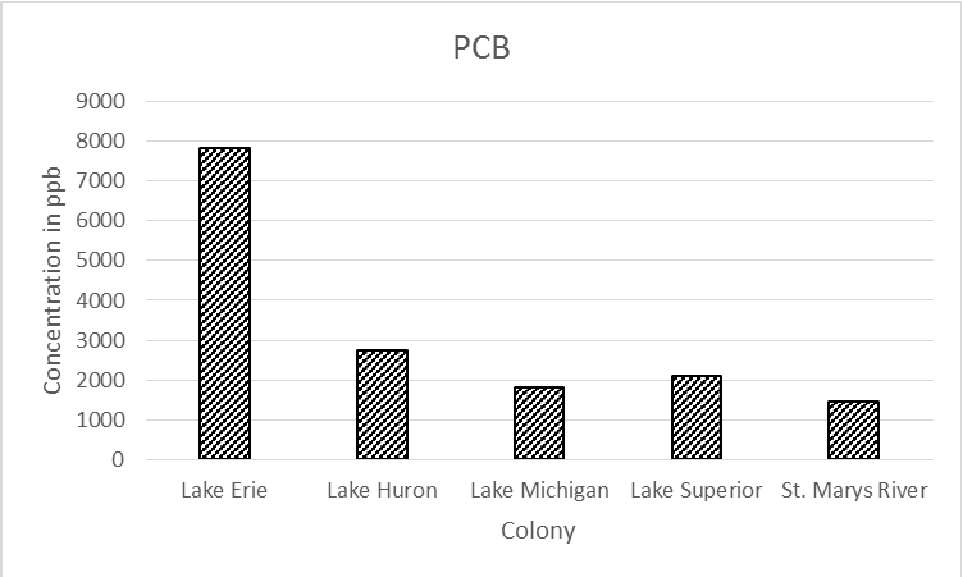

Figure 14. Five-year median concentrations of total PCBs in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2008-2012.

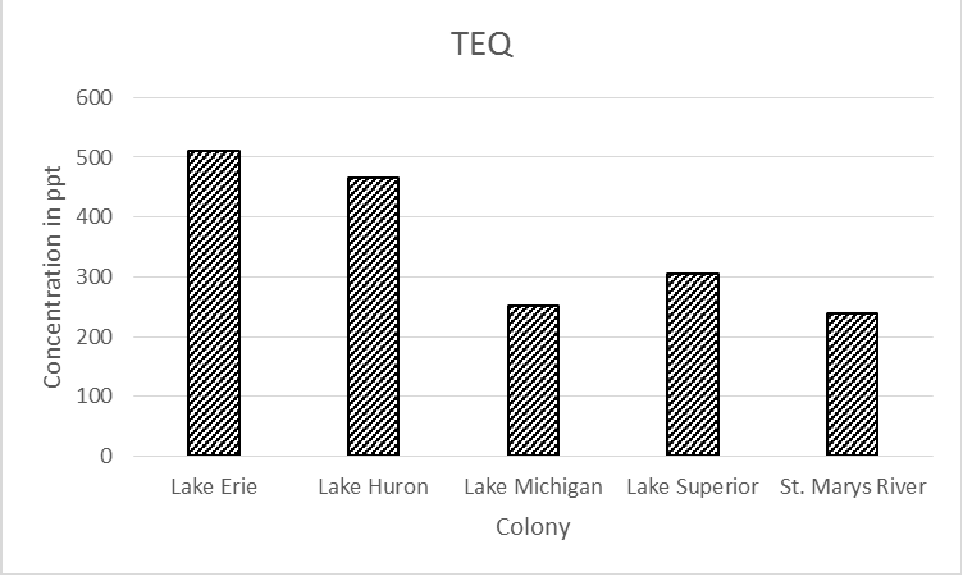

Figure 15. Median concentrations of TEQ in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2008-2012.

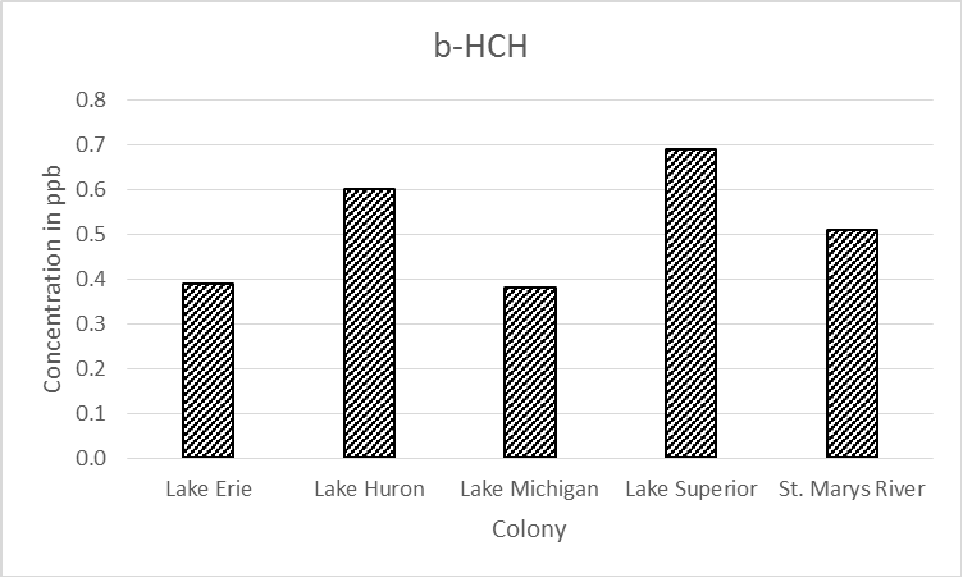

Figure 16. Median concentrations of *beta*-HCH in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2008-2012.

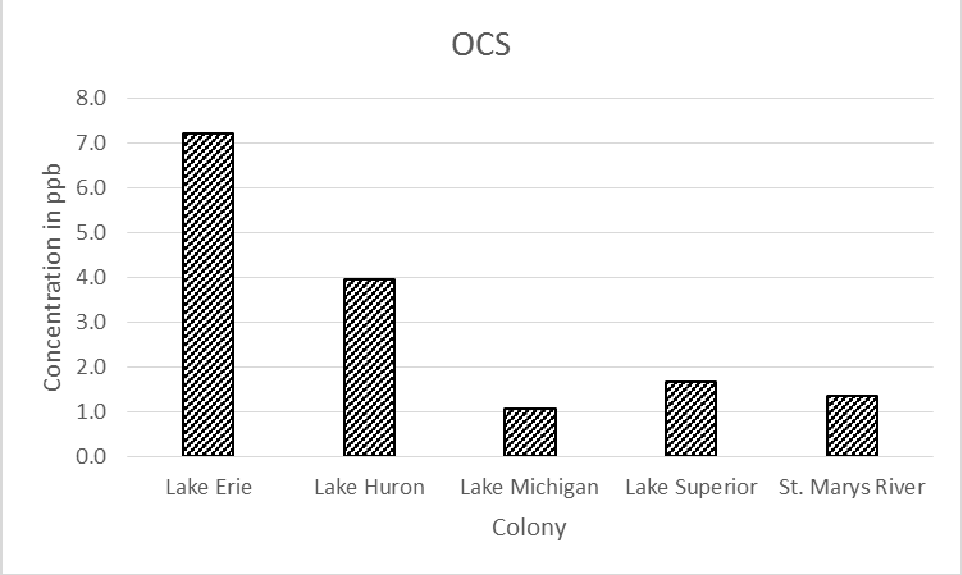

Figure 17. Five-year median concentrations of OCS in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2008-2012.

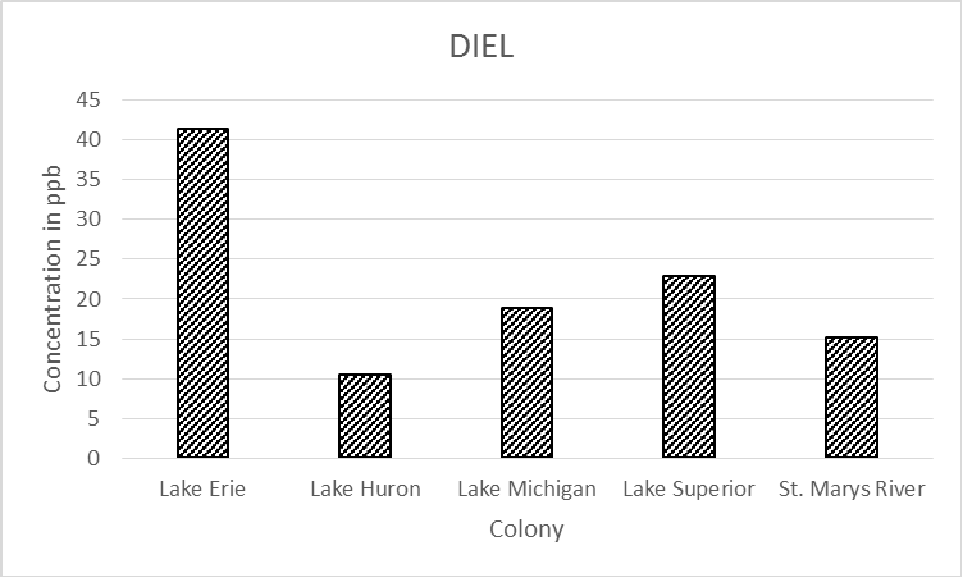

Figure 18. Five-year median concentrations of Dieldrin in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2008-2012.

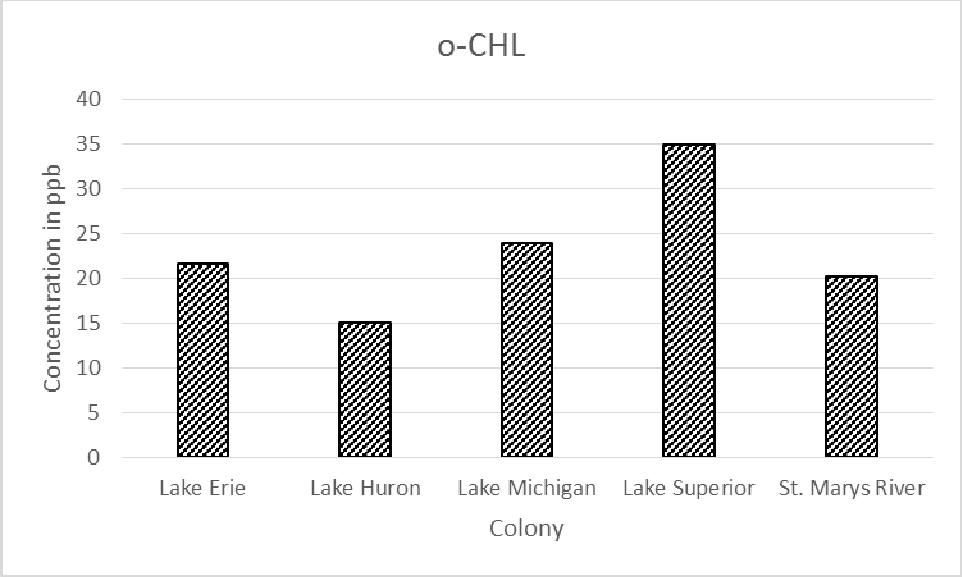

Figure 19. Five-year median concentrations of Oxychlordane in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2008-2012.

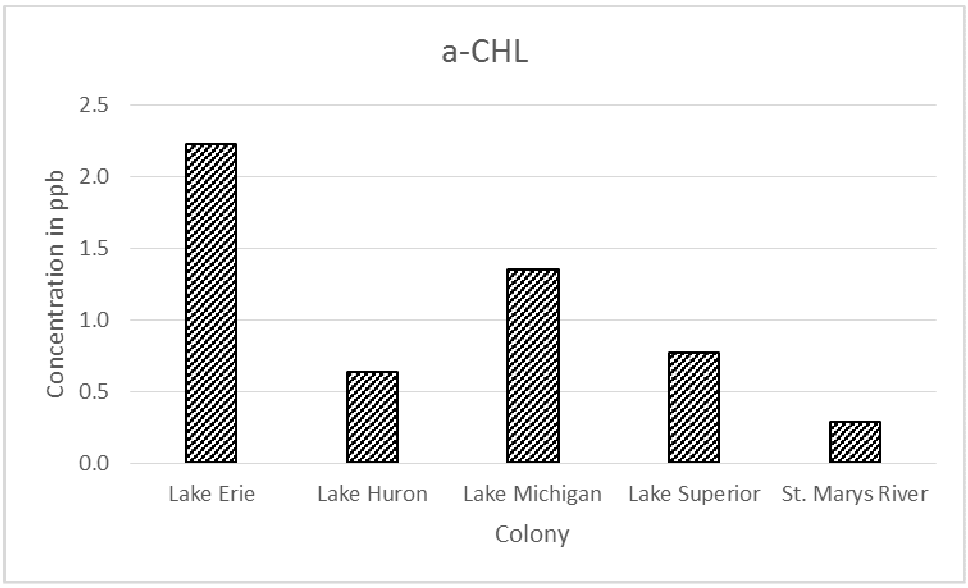

Figure 20. Five-year median concentrations of *alpha*-Chlordane in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2008-2012.

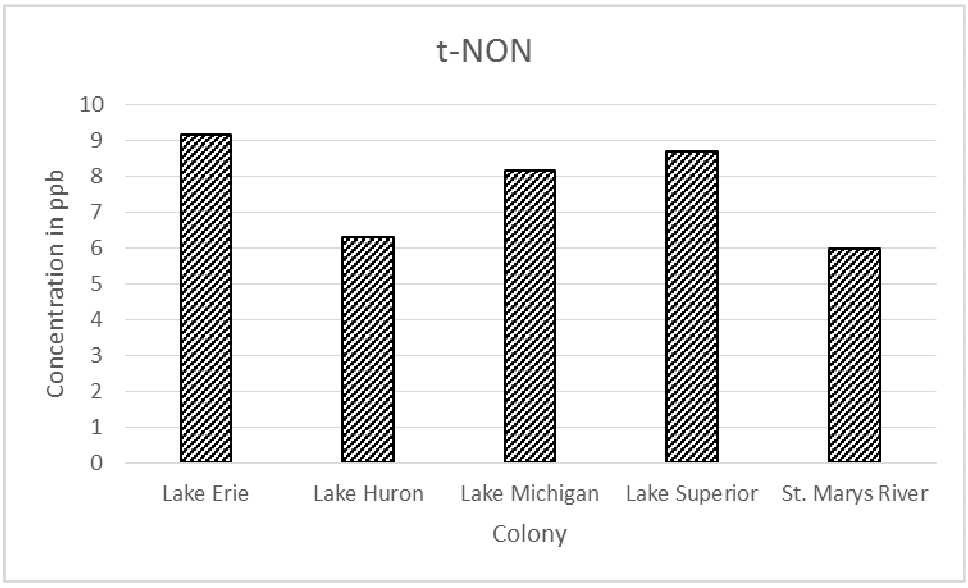

Figure 21. Five-year median concentrations of *trans*-Nonachlor in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2008-2012.

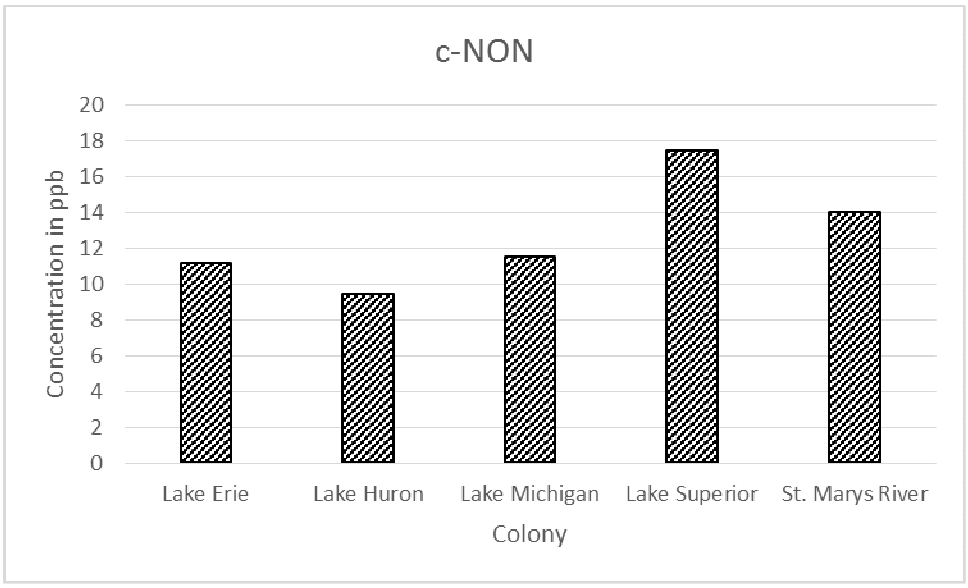

Figure 22. Five-year median concentrations of *cis*-Nonachlor in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2008-2012.

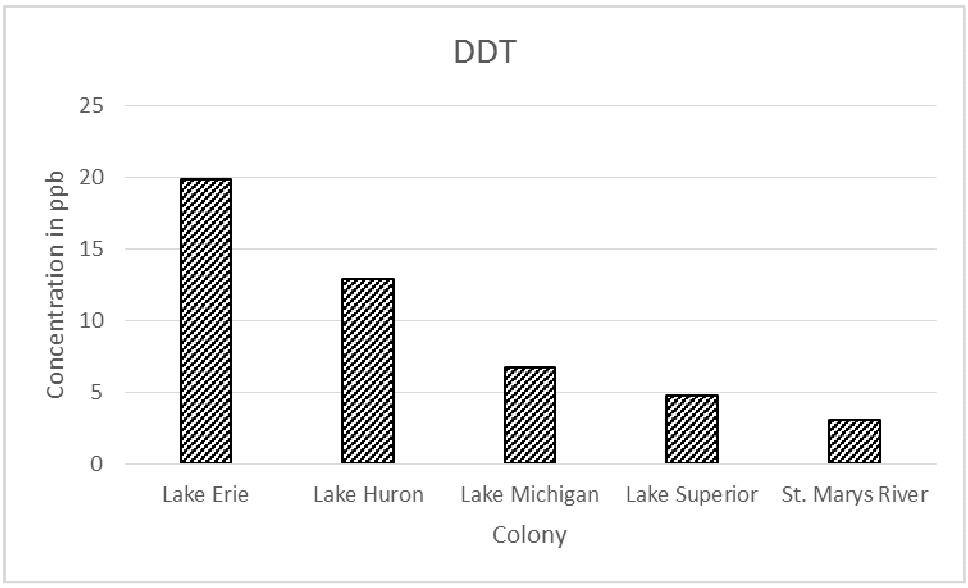

Figure 23. Five-year median concentrations of *p,p'*-DDT in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2008-2012.

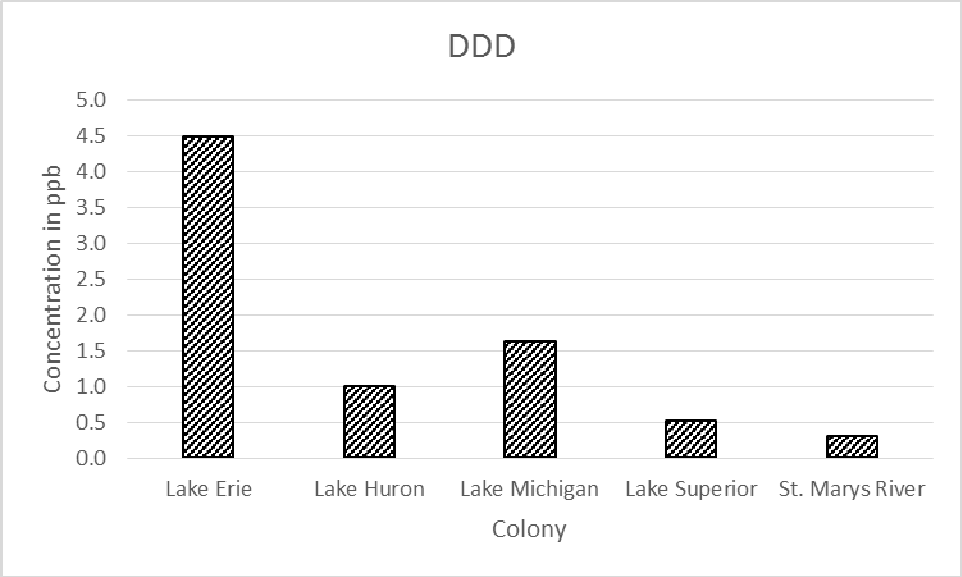

Figure 24. Five-year median concentrations of *p,p'*-DDD in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2008-2012.

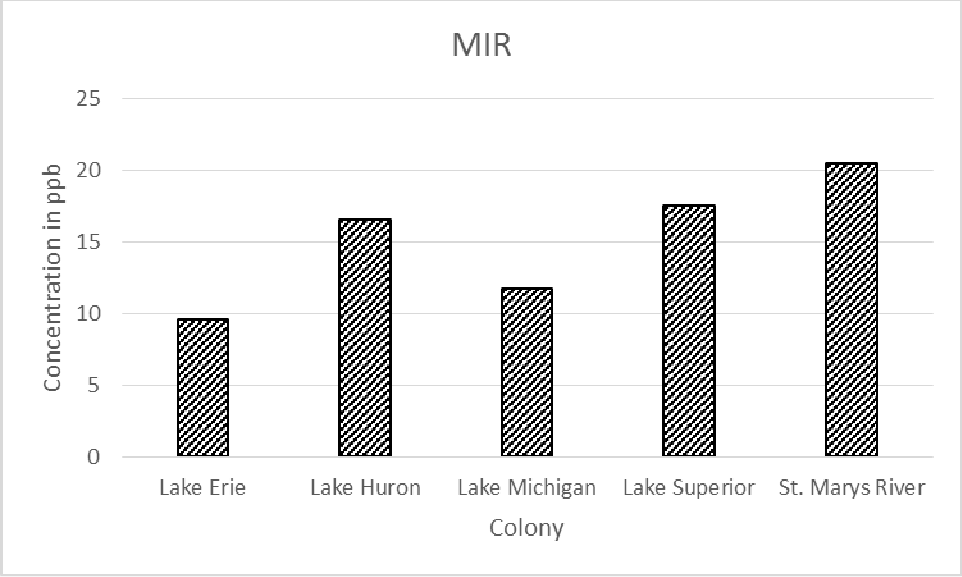

Figure 25. Five-year median concentrations of Mirex in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2008-2012.

TEMPORAL TRENDS
BETWEEN TIME PERIODS - FIVE-YEAR MEDIANS

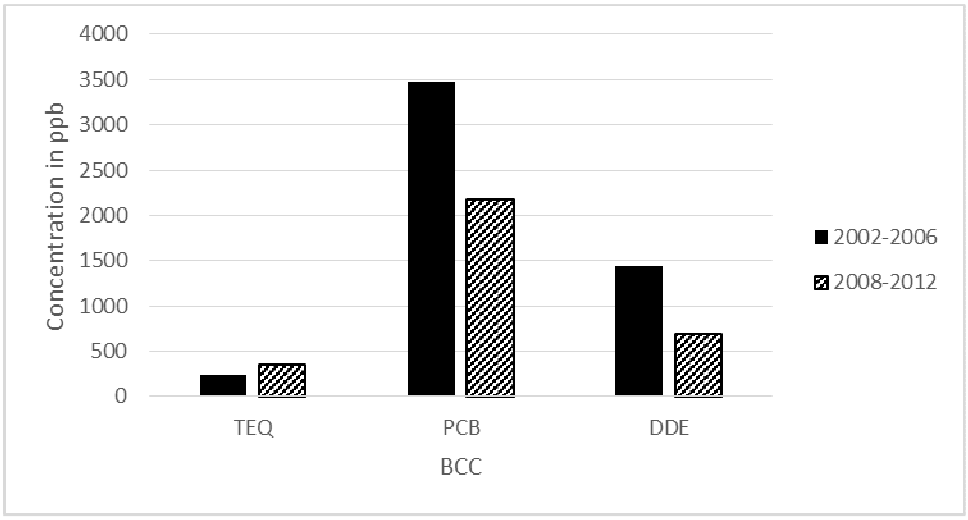

Figure 26. Comparison of five-year median concentrations of BCCs in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan between 2002-2006 and 2008-2012 (TEQ concentrations in ppt).

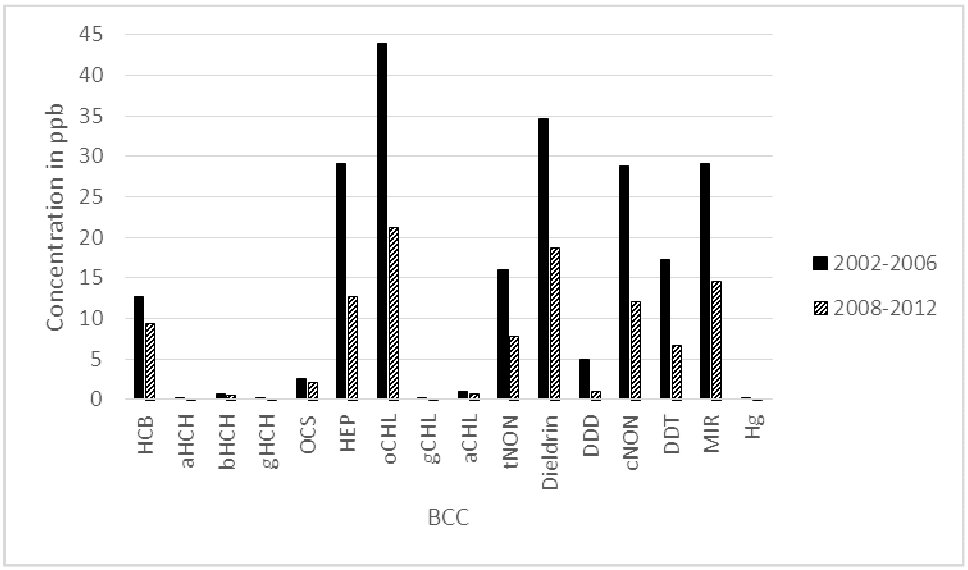

Figure 27. Comparison of five-year median concentrations of BCCs in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan between 2002-2006 and 2008-2012.

Appendix A. Five-year median concentrations by colony of BCCs in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2002-2006 (all concentrations in ppb except Hg (ppm) and TEQs (ppt)).

		BI		DE		FMI		GRI		HI		LCI	
	Units	**Median**	**IQR**	**Median**	**IQR**	**Median**	**IQR**	**Median**	**IQR**	**Median**	**IQR**	**Median**	**IQR**
PCB	ppb	3144.0	2468.2	10782.7	1586.0	2772.5	1264.5	3038.4	2185.3	3032.2	1182.2	5952.4	7012.1
HCB	ppb	15.2	9.3	15.5	6.1	7.7	3.7	15.7	15.0	9.1	3.0	14.4	4.4
***alpha*-HCH**	ppb	0.1	0.0	0.1	0.0	0.1	0.0	0.1	0.0	0.1	0.1	0.1	0.1
***beta*-HCH**	ppb	0.7	0.4	0.2	0.5	0.5	0.3	1.1	0.8	0.7	0.3	0.6	0.3
***gamma*-HCH**	ppb	0.4	0.3	0.2	0.6	0.9	1.2	0.2	0.0	0.7	1.0	0.2	0.7
OCS	ppb	1.7	2.7	11.2	4.4	1.4	1.6	2.7	0.4	1.4	1.6	6.8	10.4
Heptachlor epoxide	ppb	45.2	35.7	23.5	2.8	18.6	8.2	26.9	32.4	35.0	3.3	24.8	14.0
Oxychlordane	ppb	67.1	18.0	28.8	9.1	26.6	10.7	33.9	38.3	65.3	49.7	29.4	20.8
***gamma*-Chlordane**	ppb	0.1	0.0	0.1	0.0	0.1	0.0	0.1	0.0	0.1	0.0	0.1	0.0
***alpha*-Chlordane**	ppb	2.3	5.0	2.0	1.5	0.4	0.4	1.9	0.7	0.4	0.4	0.6	1.3
***trans*-Nonachlor**	ppb	23.2	20.2	13.9	5.4	10.3	3.7	20.9	15.2	14.3	5.2	15.4	9.9
***p,p'*-DDE**	ppb	2184.0	813.9	1119.7	138.6	883.3	405.3	1657.8	890.5	1519.1	1074.3	1260.6	1121.4
Dieldrin	ppb	124.4	98.5	65.5	25.6	23.1	16.8	31.0	31.5	28.2	11.2	41.8	45.5
***p,p'*-DDD**	ppb	5.3	3.6	7.9	2.9	2.6	3.4	6.6	6.1	2.5	0.8	5.5	10.8
***cis*-Nonachlor**	ppb	42.4	17.0	17.2	4.3	20.9	10.5	37.2	45.0	29.6	1.7	21.0	16.2
***p,p'*-DDT**	ppb	27.8	10.7	25.1	20.9	3.9	3.5	19.0	32.0	10.4	6.1	30.5	9.7
Mirex	ppb	29.2	23.3	11.2	3.1	17.5	8.6	34.6	38.8	19.2	7.2	37.6	29.5
Mercury [a]	ppm	0.2	0.1	0.1	0.0	0.2	0.1	0.2	0.1	0.2	0.1	0.2	0.1
TEQ	ppb	738.9	277.1	686.3	37.5	221.4	38.2	228.5	79.0	397.1	403.8	738.8	958.0

[a] values expressed as wet weight.

Appendix A (cont.). Five-year median concentrations by colony of BCCs in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2002-2006 (all concentrations in ppb except Hg (ppm) and TEQs (ppt)).

	NI		SCI		TI		WTP	
	Median	**IQR**	**Median**	**IQR**	**Median**	**IQR**	**Median**	**IQR**
PCB	3586.5	1059.5	4088.6	893.2	3321.6	940.4	3093.8	1150.2
HCB	12.7	6.7	11.1	8.5	16.9	8.1	11.0	4.3
***alpha*-HCH**	0.1	0.0	0.1	0.0	0.1	0.1	0.1	0.0
***beta*-HCH**	1.0	1.4	0.4	0.1	1.4	0.4	1.3	0.8
***gamma*-HCH**	1.0	4.6	0.2	0.0	0.9	1.3	0.2	0.0
OCS	2.4	2.2	3.4	1.5	2.1	6.7	2.3	1.2
Heptachlor epoxide	36.7	38.9	25.7	11.6	48.7	150.0	43.6	24.8
Oxychlordane	79.8	64.6	47.4	32.4	55.6	120.6	80.7	57.5
***gamma*-Chlordane**	0.1	0.0	0.1	0.0	0.1	0.8	0.1	0.0
***alpha*-Chlordane**	0.7	0.6	0.5	0.5	3.7	53.7	0.6	3.5
***trans*-Nonachlor**	21.3	13.6	16.0	11.7	30.4	193.0	10.9	15.6
***p,p'*-DDE**	1881.5	1168.5	1537.3	29.5	1481.7	468.2	1470.5	700.7
Dieldrin	49.0	37.9	26.8	14.5	44.3	68.9	24.6	33.4
p,p'-DDD	4.9	2.5	4.8	3.2	3.6	6.7	3.6	3.1
***cis*-Nonachlor**	37.6	32.4	29.8	19.5	39.4	55.1	37.8	20.2
***p,p'*-DDT**	15.7	13.8	12.7	10.1	9.5	19.6	18.6	11.3
Mirex	61.0	25.7	56.3	37.5	31.4	26.2	27.1	18.2
Mercury [a]	0.2	0.1	0.2	0.1	0.3	0.2	0.2	0.1
TEQ	217.5	350.8	182.7	60.2	185.0	65.4	412.3	321.1

[a] values expressed as wet weight.

Appendix B. Five-year median concentrations and interquartile ranges by colony of BCCs in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2008-2012 (all concentrations in ppb except Hg (ppm) and TEQs (ppt)).

		BI		DE		FMI		GRI		HI	
	Units	**Median**	**IQR**	**Median**	**IQR**	**Median**	**IQR**	**Median**	**IQR**	**Median**	**IQR**
PCB	ppb	1824.2	271.0	7815.4	2017.8	1222.0	266.4	1639.1	811.8	1531.3	496.3
HCB	ppb	7.8	6.1	9.4	2.9	8.3	1.9	9.0	3.1	7.8	9.0
***alpha*-HCH**	ppb	0.1	0.0	0.1	0.0	0.1	0.0	0.1	0.0	0.1	0.1
***beta*-HCH**	ppb	0.4	0.1	0.4	0.1	0.5	0.1	0.4	0.3	0.6	0.1
***gamma*-HCH**	ppb	0.2	0.0	0.2	0.0	0.2	0.0	0.2	0.0	0.2	0.0
OCS	ppb	1.1	0.5	7.2	6.0	1.1	0.3	1.7	1.7	1.3	3.9
Heptachlor epoxide	ppb	14.5	7.9	13.3	0.5	11.3	1.9	12.4	7.0	10.8	6.2
Oxychlordane	ppb	27.9	13.0	21.6	3.5	20.0	6.8	20.5	6.9	29.2	6.2
***gamma*-Chlordane**	ppb	0.1	0.0	0.1	0.0	0.1	0.0	0.1	0.0	0.1	0.0
***alpha*-Chlordane**	ppb	2.2	1.6	2.2	0.5	0.2	0.2	0.9	1.0	0.9	0.2
***trans*-Nonachlor**	ppb	8.8	3.5	9.2	1.4	5.3	2.1	6.6	3.2	8.6	3.5
***p,p'*-DDE**	ppb	795.9	217.7	785.7	180.5	430.9	95.7	570.9	226.3	522.9	119.1
Dieldrin	ppb	18.8	19.2	41.4	15.9	14.9	0.4	32.4	42.9	17.5	15.9
***p,p'*-DDD**	ppb	1.6	3.4	4.5	2.7	0.3	0.2	1.3	2.0	0.3	0.3
***cis*-Nonachlor**	ppb	13.1	3.3	11.2	1.2	13.3	2.9	9.0	3.4	16.1	7.8
***p,p'*-DDT**	ppb	8.7	7.3	19.8	5305.0	4.1	2.6	3.7	2.6	4.6	1.6
Mirex	ppb	11.7	6.2	9.6	3.7	14.7	9.0	13.3	3.5	15.4	16.9
Mercury [a]	ppm	0.1	0.1	0.1	0.0	0.1	0.0	0.1	0.1	0.1	0.1
TEQ	ppt	250.8	87.2	511.4	94.0	239.2	114.9	325.2	410.2	187.7	214.5

[a] values expressed as wet weight.

Appendix B (cont.). Five-year median concentrations and interquartile ranges by colony of BCCs in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2008-2012 (all concentrations in ppb except Hg (ppm) and TEQs (ppt)).

		LCI		NI		SCI		T		WTP	
	Units	**Median**	**IQR**	**Median**	**IQR**	**Median**	**IQR**	**Median**	**IQR**	**Median**	**IQR**
PCB	ppb	3621.2	956.7	2262.6	0.0	1763.6	799.2	2334.3	123.2	2527.6	665.2
HCB	ppb	9.3	3.3	9.7	0.0	9.6	5.1	11.1	1.8	15.1	11.0
***alpha*-HCH**	ppb	0.1	0.0	0.1	0.0	0.1	0.0	0.1	0.0	0.1	0.0
***beta*-HCH**	ppb	0.6	0.2	1.0	0.0	0.7	0.5	0.7	0.0	0.7	0.2
***gamma*-HCH**	ppb	0.2	0.0	0.2	0.0	0.2	0.0	0.2	0.0	0.2	0.0
OCS	ppb	4.3	1.5	1.6	0.0	2.8	2.4	1.9	0.3	3.6	2.7
Heptachlor epoxide	ppb	10.7	2.8	15.8	0.0	8.7	3.2	25.7	0.4	14.8	3.4
Oxychlordane	ppb	15.1	3.8	39.2	0.0	14.1	2.0	38.1	1.0	23.7	6.1
***gamma*-Chlordane**	ppb	0.1	0.0	0.1	0.0	0.1	0.0	0.1	0.0	0.1	0.0
***alpha*-Chlordane**	ppb	0.6	0.2	0.3	0.0	0.4	0.5	0.8	0.0	0.4	0.1
***trans*-Nonachlor**	ppb	6.3	3.0	8.9	0.0	5.0	4.7	9.0	2.2	6.2	0.5
***p,p'*-DDE**	ppb	667.0	200.4	852.4	0.0	451.6	78.7	855.4	44.8	909.5	109.6
Dieldrin	ppb	15.6	12.4	13.1	0.0	8.0	0.5	39.2	22.0	18.0	4.3
***p,p'*-DDD**	ppb	1.2	0.5	0.9	0.0	0.6	0.7	1.0	1.0	5.4	10.3
***cis*-Nonachlor**	ppb	9.5	4.5	17.8	0.0	7.6	4.1	20.3	6.2	14.6	0.0
***p,p'*-DDT**	ppb	15.6	14.5	5.0	0.0	5.4	6.0	6.0	5.2	53.8	94.3
Mirex	ppb	16.5	5.0	27.7	0.0	21.7	13.1	14.2	11.0	57.2	31.8
Mercury [a]	ppm	0.1	0.0	0.1	0.0	0.1	0.0	0.2	0.1	0.1	0.1
TEQ	ppt	466.1	70.0	288.6	0.0	555.4	385.7	404.4	133.1	321.0	418.9

[a] values expressed as wet weight.

Appendix C. Median concentrations by lake of BCCs in herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2002-2006 (all concentrations in ppb except Hg (ppm) and TEQs (ppt)).

Dataset	**CMI**											
Year	**2002**				**2003**				**2004**			
Lake	**LE**	**LH**	**LM**	**LS**	**LE**	**LH**	**LM**	**LS**	**LE**	**LH**	**LM**	**LS**
PCB	10914.20	4123.75	6069.90	3623.30	10782.70	6084.20	2392.05	3207.35	9328.20	4088.60	4056.90	3221.90
HCB	16.34	14.64	16.86	13.27	15.49	17.97	21.33	15.55	10.02	11.09	13.99	15.02
***alpha*-HCH**	0.10	0.17	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.08	0.08
***beta*-HCH**	0.10	0.50	0.90	0.70	0.20	0.45	0.90	1.15	0.90	0.20	0.95	2.10
***gamma*-HCH**	0.20	0.57	0.30	0.20	0.75	0.20	0.20	0.36	1.33	0.40	1.92	4.57
OCS	8.74	2.41	2.18	4.82	13.18	5.29	2.04	2.50	11.20	3.40	4.01	2.48
Heptachlor epoxide	24.49	26.10	48.09	41.38	20.92	37.45	55.54	42.77	23.74	25.73	51.23	63.12
Oxychlordane	36.02	51.08	106.63	108.10	28.82	60.89	65.00	55.93	24.83	47.39	70.78	81.29
***gamma*-Chlordane**	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
***alpha*-Chlordane**	4.25	0.90	1.43	0.43	1.89	0.69	7.61	3.38	2.02	0.10	1.77	0.83
***trans*-Nonachlor**	15.99	16.38	25.80	23.26	13.86	20.79	48.46	31.07	10.64	8.78	21.94	24.79
***p,p'*-DDE**	1231.87	1337.67	2844.33	2056.31	1119.72	1398.72	1792.49	1277.36	1093.32	1751.31	1714.25	1664.00
Dieldrin	80.49	30.09	43.89	45.42	54.90	38.57	164.45	93.80	65.51	20.82	75.44	64.70
***p,p'*-DDD**	16.41	4.61	8.50	4.46	9.44	11.44	9.05	5.12	7.86	6.87	6.31	4.16
***cis*-Nonachlor**	17.17	27.31	49.25	42.87	19.29	31.34	56.75	41.21	14.96	21.35	35.25	49.13
***p,p'*-DDT**	48.94	21.24	34.32	7.28	25.07	18.79	36.31	26.07	17.56	5.53	23.35	17.13
Mirex	11.19	33.27	71.88	52.22	10.45	90.60	44.45	38.71	10.03	31.58	26.14	41.63
Mercury[a]	0.09	0.18	0.19	0.21	0.14	0.25	0.26	0.29	0.10	0.09	0.24	0.17
TEQ	680.1	581.7	530.90	209.8	686.3	182.4	186.1	175.3	248.5	221.9	453.6	494.5

[a] values expressed as wet weight.

Appendix C (cont.). Median concentrations by lake of BCCs in fresh herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2002-2006 (all concentrations in ppb except Hg (ppm) and TEQs (ppt)).

Dataset	**CMI**								
Year	**2005**					**2006**			
Lake	**LE**	**LH**	**LM**	**LS**		**LE**	**LH**	**LM**	**LS**
PCB	8098.30	2548.20	2766.05	2509.55		19947.90	8076.40	3656.85	4029.30
HCB	6.38	9.81	8.42	7.82		16.14	11.53	18.24	14.85
***alpha*-HCH**	0.10	0.10	0.33	0.10		0.10	0.10	0.10	0.10
***beta*-HCH**	0.20	0.50	0.50	1.10		0.70	0.75	1.35	1.40
***gamma*-HCH**	0.20	0.20	0.33	1.53		0.20	0.20	0.20	0.20
OCS	5.87	2.11	1.32	1.02		17.98	8.82	4.35	1.44
Heptachlor epoxide	11.63	24.56	17.76	26.35		23.48	20.86	51.82	43.82
Oxychlordane	14.55	39.70	26.48	41.95		33.91	25.54	48.51	48.88
***gamma*-Chlordane**	0.10	0.10	0.10	0.10		0.10	0.10	0.10	0.10
***alpha*-Chlordane**	1.39	0.46	0.64	0.43		3.35	1.05	5.31	1.61
***trans*-Nonachlor**	5.72	15.96	10.47	9.26		22.68	15.51	47.33	17.98
***p,p'*-DDE**	838.88	1122.80	1142.06	1283.48		2857.80	1912.92	1920.90	1888.41
Dieldrin	20.34	26.75	15.79	27.33		84.46	39.57	79.64	29.00
***p,p'*-DDD**	5.18	4.79	2.91	1.93		6.59	1.75	5.96	1.00
***cis*-Nonachlor**	8.16	29.79	20.42	15.32		34.15	25.64	67.59	28.73
***p,p'*-DDT**	9.81	17.22	12.47	8.46		38.40	23.36	23.62	8.52
Mirex	13.58	56.31	28.07	33.99		32.19	62.16	44.81	19.59
Mercury[a]	0.08	0.23	0.16	0.15		0.19	0.40	0.33	0.73
TEQ	717.6	182.7	352.8	179.8		1095.5	410	761.7	196.3

[a] values expressed as wet weight.

Appendix D. Median concentrations by lake of BCCs in fresh herring gull (*Larus argentatus*) eggs collected from ten breeding colonies in Michigan, 2008-2012 all concentrations in ppb except Hg (ppm) and TEQs (ppt)).

Year	2008					2009					2010			
Lake	**LE**	**LH**	**LM**	**LS**		**LE**	**LH**	**LM**	**LS**		**LE**	**LH**	**LM**	**LS**
PCB	10761.4	2892.2	1763.0	2262.6		7815.4	2530.0	1528.7	2395.9		9679.3	4148.9	1891.4	1463.3
HCB	10.0	24.9	8.5	12.0		10.4	8.2	10.0	10.2		5.5	8.2	7.8	7.1
***alpha*-HCH**	0.1	0.1	0.1	0.1		0.1	0.1	0.1	0.1		0.1	0.1	0.1	0.1
***beta*-HCH**	0.3	1.1	0.4	0.7		0.4	0.5	0.4	0.7		0.4	0.6	0.3	0.6
***gamma*-HCH**	0.2	0.2	0.2	0.2		0.2	0.2	0.2	0.2		0.2	0.2	0.2	0.2
OCS	10.2	8.9	1.6	2.0		10.1	3.4	1.0	1.7		3.2	3.8	0.8	0.9
Heptachlor epoxide	15.0	10.5	13.4	16.9		13.3	8.2	13.8	25.4		13.2	17.6	14.5	10.7
Oxychlordane	24.2	16.8	20.7	37.6		21.6	14.1	22.5	38.6		25.0	26.6	34.1	29.2
***gamma*-Chlordane**	0.1	0.1	0.1	0.1		0.1	0.1	0.1	0.1		0.1	0.1	0.1	0.1
***alpha*-Chlordane**	2.1	0.6	1.8	0.7		1.4	0.3	1.3	0.8		2.2	0.7	0.7	1.0
***trans*-Nonachlor**	10.9	6.8	8.5	8.9		7.7	4.2	7.8	8.0		9.0	10.5	7.0	8.6
***p,p'*-DDE**	1026.7	579.0	659.9	833.0		785.7	589.8	626.8	877.8		954.7	840.8	905.4	575.4
Dieldrin	56.4	17.3	36.4	28.2		40.4	9.4	24.3	50.2		35.5	15.6	18.5	17.5
***p,p'*-DDD**	4.5	1.1	3.8	0.9		2.8	0.5	1.0	0.5		3.7	1.7	0.6	0.3
***cis*-Nonachlor**	11.2	9.5	10.4	17.8		10.9	6.6	11.1	17.2		12.1	12.1	13.1	16.1
***p,p'*-DDT**	16.2	10.7	6.8	5.0		6.7	4.3	4.5	3.4		30.6	27.5	3.4	5.1
Mirex	10.1	20.4	11.6	19.7		4.9	12.2	12.9	8.7		10.5	17.6	11.7	31.3
Mercury[a]	0.1	0.1	0.1	0.1		0.1	0.1	0.1	0.2		0.1	0.1	0.1	0.1
TEQ	644.0	630.3	378.8	322.1		418.0	457.0	185.5	337.9		511.4	442.4	170.2	187.7

[a] values expressed as wet weight.

Appendix D (cont.). Median concentrations by lake of BCCs in fresh herring gull (Larus argentatus) eggs collected from ten breeding colonies in Michigan, 2008-2012 all concentrations in ppb except Hg (ppm) and TEQs (ppt)).

Year	2011					2012			
Lake	**LE**	**LH**	**LM**	**LS**		**LE**	**LH**	**LM**	**LS**
PCB	6998.8	2739.3	2583.0	.		7661.5	2523.1	1620.4	1531.3
HCB	9.4	11.5	18.5	.		7.1	7.5	6.4	7.8
***alpha*-HCH**	0.1	0.1	0.1	.		0.1	0.1	0.1	0.1
***beta*-HCH**	0.6	0.8	0.7	.		0.2	0.5	0.4	0.6
***gamma*-HCH**	0.2	0.2	0.2	.		0.2	0.2	0.1	0.2
OCS	7.2	4.3	2.3	.		4.1	3.5	1.2	1.3
Heptachlor epoxide	11.8	12.1	27.7	.		13.7	8.0	10.1	10.8
Oxychlordane	18.0	14.6	48.2	.		20.8	14.7	21.1	25.8
***gamma*-Chlordane**	0.1	0.1	0.1	.		0.3	0.1	0.1	0.1
***alpha*-Chlordane**	2.5	0.8	4.0	.		3.4	0.1	0.5	0.9
***trans*-Nonachlor**	10.4	8.7	25.4	.		9.2	5.0	6.6	11.2
***p,p'*-DDE**	768.3	514.7	1310.3	.		774.2	566.9	687.8	456.2
Dieldrin	41.4	23.0	72.4	.		62.7	7.4	17.6	13.9
***p,p'*-DDD**	6.5	1.3	4.6	.		8.8	0.4	1.2	0.3
***cis*-Nonachlor**	13.1	13.5	46.3	.		9.4	6.1	11.5	17.7
***p,p'*-DDT**	19.8	15.6	16.6	.		21.2	28.1	14.0	3.5
Mirex	6.4	16.5	30.0	.		9.6	22.5	4.3	14.4
Mercury[a]	0.1	0.1	0.1	.		0.1	0.0	0.0	0.2
TEQ	496.4	417.5	314.5	.		590.3	466.1	318.7	107.6

[a] values expressed as wet weight.