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Trends and patterns of PCB, DDE, and mercury contamination in bald eagle nestlings in the upper Midwest

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ABSTRACT

We analyzed concentrations and trends of DDE, total PCBs, and mercury in bald eagle (*Haliaeetus leucocephalus*) nestlings at six study areas in the upper Midwest, 2006–2015, and long-term trends at two Lake Superior sites, 1989–2015. Eaglet plasma from the Apostle Islands in Lake Superior had the highest concentrations of DDE (geometric mean [GM] = 10.6 µg/L), and DDE concentrations decreased at 5.8% per year across the region from 2006 to 2015, and at 5.5% per year at Lake Superior sites from 1989 to 2015. Concentrations of the sum of 75 PCB congeners (ΣPCB₇₅) were highest at Pools 3 and 4 of the Mississippi River (GM = 114.8 µg/L) and did not decline significantly region-wide (all study areas together) between the years of 2006 and 2011. However, at Lake Superior, ΣPCB₇₅ declined from 1995 to 2011 along the south shore at 3.6% per year, with a non-significant decline at the Apostle Islands. Concentrations of mercury in nestling breast feathers were highest at the upper St. Croix River (GM = 6.66 µg/g wet weight). At Lake Superior study areas, mercury declined at 1.6% per year from 1991 to 2015; however, from 2006 to 2015 we found no significant trend at one of these same study areas and mercury concentrations apparently increased at two study areas. Mean concentrations of contaminants were below levels associated with significant impairment of reproduction at all sites and mean reproductive rates were > 1.4 young per nest. However, increasing concentrations of mercury in some areas, combined with relatively high concentrations at some nests, suggest that continued monitoring of mercury should be a management priority.

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Introduction

Bald eagles (*Haliaeetus leucocephalus*) have served as biosentinels for chemical contamination in the Great Lakes and elsewhere in North America since as early as the 1970s (Wiemeyer et al., 1972, 1984; Colborn, 1991; Bowerman IV, 1993; Anthony et al., 1999; Dykstra et al., 2001; Buck et al., 2005; Cesh et al., 2010). As a top predator of aquatic systems, bald eagles bioaccumulate environmental contaminants and are susceptible to the toxic effects of some contaminants such as DDE (Ludwig et al., 1993; Elliott and Harris, 2001/2002; Elliott et al., 2009). Moreover, their young are fed prey from an area relatively localized to the nest, making them good indicators of local contamination (Elliott et al., 2009; Route et al., 2009).

Great Lakes bald eagles continued to experience depressed reproductive rates long after many eagle populations in North America had recovered following the bans on DDT and PCBs in the 1970s. As numbers of breeding pairs grew (Bowerman et al., 1998), mean reproductive rate

remained below the level associated with healthy populations of 1.0 young per occupied territory (Best et al., 1994). By the early 1990s, productivity of Great Lakes eagles averaged 0.79 young per occupied territory, compared to 1.0 young per occupied territory in healthy populations in inland Michigan and Minnesota (Bowerman IV, 1993). Reproductive rates were inversely correlated with the concentrations of the legacy organochlorine contaminants DDE and PCBs on a region-wide basis (Bowerman et al., 2003) and also associated with low productivity at individual contaminant hotspots such as Green Bay (Dykstra et al., 2001). At Lake Superior, however, depressed eagle productivity was attributed to the naturally low food supply of this oligotrophic lake, rather than to lingering contaminants in the prey base (Dykstra et al., 1998).

Concentrations of DDE and PCBs in Great Lakes air (Shunthirasingham et al., 2016), sediment (Painter et al., 2001; Schneider et al., 2001; Marvin et al., 2003), and biota (DeVault et al., 1986; Weseloh et al., 1994; Fox et al., 2002; Heinz and Stromborg, 2009; Best et al., 2010; Dellinger et al., 2014; Rasmussen et al., 2014; Visha et al., 2016) have decreased dramatically since the mid-1970s. More recently, although organochlorine concentrations have generally continued to decline, trends have changed in

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some species in some Great Lakes locations. Concentrations of total PCBs in Great Lakes herring gull (*Larus argentatus*) eggs had stopped declining by the mid-1980s to 1990s in many locations (Hebert et al., 1994; Stow, 1995; Pekarik and Weseloh, 1998), and PCBs in Lake Michigan fish had reached plateau concentrations by the late 1980s (Stow et al., 1995). In Lake Ontario, lake trout DDE concentrations had stabilized in the 1980s (Borgmann and Whittle, 1991). PCB concentrations in four species of Lake Erie fish had stopped decreasing by the early 2000s (Sadraddini et al., 2011) but continued to decline in two other species. Total PCBs in Lake Erie mink (*Mustela vison*) had stabilized or increased by the late 1990s, although DDE continued to decline relative to 1970s levels (Martin et al., 2006). In some cases, trends in contaminant concentrations were associated with changes in the food web (Hebert et al., 2000) rather than changes in contaminant availability.

Similarly, concentrations of mercury in Great Lakes fish (Weis, 2004; Visha et al., 2016) and birds (Dykstra et al., 2010; Weseloh et al., 2011) have mostly been in decline. These declines are not universal, however, and recent data suggest decreases have slowed or in some cases have reversed. Zhou et al. (2017) showed that mercury levels continue to fall in Lake Superior and Lake Huron fish, but have stopped decreasing in other Great Lakes and have actually increased in some cases. Mercury levels stopped decreasing in some locations in Great Lakes herring gull eggs (Weseloh et al., 2011) and three species of fish in the 2000s (Dellinger et al., 2014; Visha et al., 2016), and have increased in Lake Superior lake trout (Blukacz-Richards et al., 2017), and several fish species in Lake Erie (Sadraddini et al., 2011). Mercury concentrations continue to increase in Ontario fish, which has been attributed to re-circulation of “legacy” mercury, possibly as an effect of climate change (Chen et al., 2018). Increasing levels of mercury in bald eagle nestlings in Voyageurs National Park, MN, since 2000, likely reflect continued atmospheric input (Pittman et al., 2011).

The US Environmental Protection Agency (USEPA) and Environment Canada (EC) continue to monitor chemical contamination in the Great Lakes under the Great Lakes Water Quality Agreement, an international environmental agreement first signed in 1972, and amended in 1978, 1987, and 2012 (Johns et al., 2018). Bald eagle nestlings have played an important role in that effort and were selected as one of several indicators of Great Lakes water quality in the late 1990s (State of the Lakes Ecosystem Conference [SOLEC], 1998). Inland populations of bald eagles have long been compared to Great Lakes bald eagles to better understand not only contaminant concentrations and population growth (Best et al., 1994; Bowerman et al., 2003), but also how habitat, different hydrological regimes, and prey bases have influenced the accumulation of contaminants and population dynamics (Dykstra et al., 1998, 2001, 2005a; Route et al., 2014a, 2014b). Such comparisons enhance our understanding of the factors influencing both Great Lakes and inland populations' health and trends.

Within the upper Midwest, the National Park Service (NPS), in conjunction with Wisconsin Department of Natural Resources (WDNR), has monitored the contaminant burdens and productivity of bald eagles to provide an index of aquatic contamination in three parks in the western Great Lakes region (Route and Elias, 2007; Route et al., 2009). These parks, the Apostle Islands National Lakeshore (APIS) in Lake Superior, the St. Croix National Scenic Riverway (SACN), and the Mississippi National River and Recreation Area (MISS), encompass three different regimes of habitat, hydrology, prey availability, and anthropogenic disturbance, which represent a large portion of the upper Midwest. Lake Superior is deep, cold, and oligotrophic, with a long water-retention time and minimal human disturbance along its shores. In its upper reaches, the St. Croix River is narrow and runs through areas of limited anthropogenic impact, but it progressively slows, widens, and accumulates silt and contaminants from many communities. Our study area on the Mississippi River runs through areas of significant agricultural, suburban, and urban development, particularly as it runs through the Twin Cities of Minneapolis and St. Paul, MN.

Because of the changing trends in these contaminants, as well as increasing questions about ecological instabilities caused by global climate change and other anthropogenic pressures, continued monitoring of bald eagle populations is recommended (SOLEC, 1998; Evers et al., 2011a). The continued surveillance of the contaminant burdens and reproductive success of bald eagles is a high priority in monitoring due to the abundance of historical data and the high potential of these top predators for accumulating contaminants (Bowerman et al., 1998; Route et al., 2009; International Joint Commission [IJC], 1994).

We here compare and contrast spatial patterns and temporal trends in concentrations of DDE, PCBs, and mercury in bald eagle nestlings from 1989 to 2015 at six study areas in the upper Midwest. This report extends our previous contribution (Dykstra et al., 2010) on the trends of these legacy contaminants and provides novel information on the distribution and temporal trends of dioxin-like PCB congeners. We also present mean bald eagle reproductive rates and examine differences between inland and Great Lakes populations.

Methods

Study areas

We studied contaminant concentrations in bald eagle nestlings in six study areas of the upper Midwestern United States (Fig. 1). Apostle Islands (APIS) nests were located on Lake Superior within 0.5 km of the Apostle Islands National Lakeshore. Lake Superior southern shore (LSSS) nests included nests within 8 km of the Lake Superior shoreline in northern Wisconsin and adjacent areas of Minnesota. Eagles in these two areas have historically diverged in terms of diet, contaminant exposure, and reproductive success, with the eagles on the Apostle Islands consuming more birds, and exhibiting higher loads of the legacy contaminants and lower reproductive rates (Warnke et al., 2002; Dykstra, 1995; Dykstra et al., 2010).

Nests within the St. Croix National Scenic Riverway were divided into two study areas, based on ecological, hydrological, and land-use differences previously documented (Dykstra et al., 2010). Nests downstream of the St. Croix Falls dam were classified as lower St. Croix River (L-SACN), and those upstream of St. Croix Falls along both the St. Croix River and the Namekagon River, were termed upper St. Croix River (U-SACN).

Nests along the Mississippi River from Anoka County to just below the confluence with the St. Croix River were classified as Mississippi River (MISS). The nests in this study area were located within the Mississippi National River and Recreation Area, a linear park running through the urban area of Minneapolis/St. Paul. Nests located along portions of Pools 3 and 4 of the Mississippi River were considered a separate study area (Pools 3 + 4). Pool 4 (Lake Pepin) is wide and lake-like, with lower levels of suspended sediments and longer water residence time (Heiskary and Wasley, 2012) than any of the other pools on the upper river.

Samples for contaminant analysis

From 2006 to 2015, we collected blood and breast feather samples from nestlings across the six study areas. In addition, we analyzed archived blood samples collected by the Wisconsin Department of Natural Resources at APIS and LSSS from 1995 to 2002 and feather samples collected at APIS and LSSS from 1991 to 2002. Annual sample size varied for each contaminant and study area due to funding and objectives of collaborating agencies (Table 1).

Nestlings were approximately age 5–10 weeks at the time of sampling based on the 8th primary length (Bortolotti, 1984). Two to four breast feathers were collected from each nestling, stored dry, and one was used for mercury analysis. Blood samples of approximately 10 mL were collected from the brachial vein, transferred to heparinized vacutainers, stored on wet ice, and then centrifuged within 48 h for

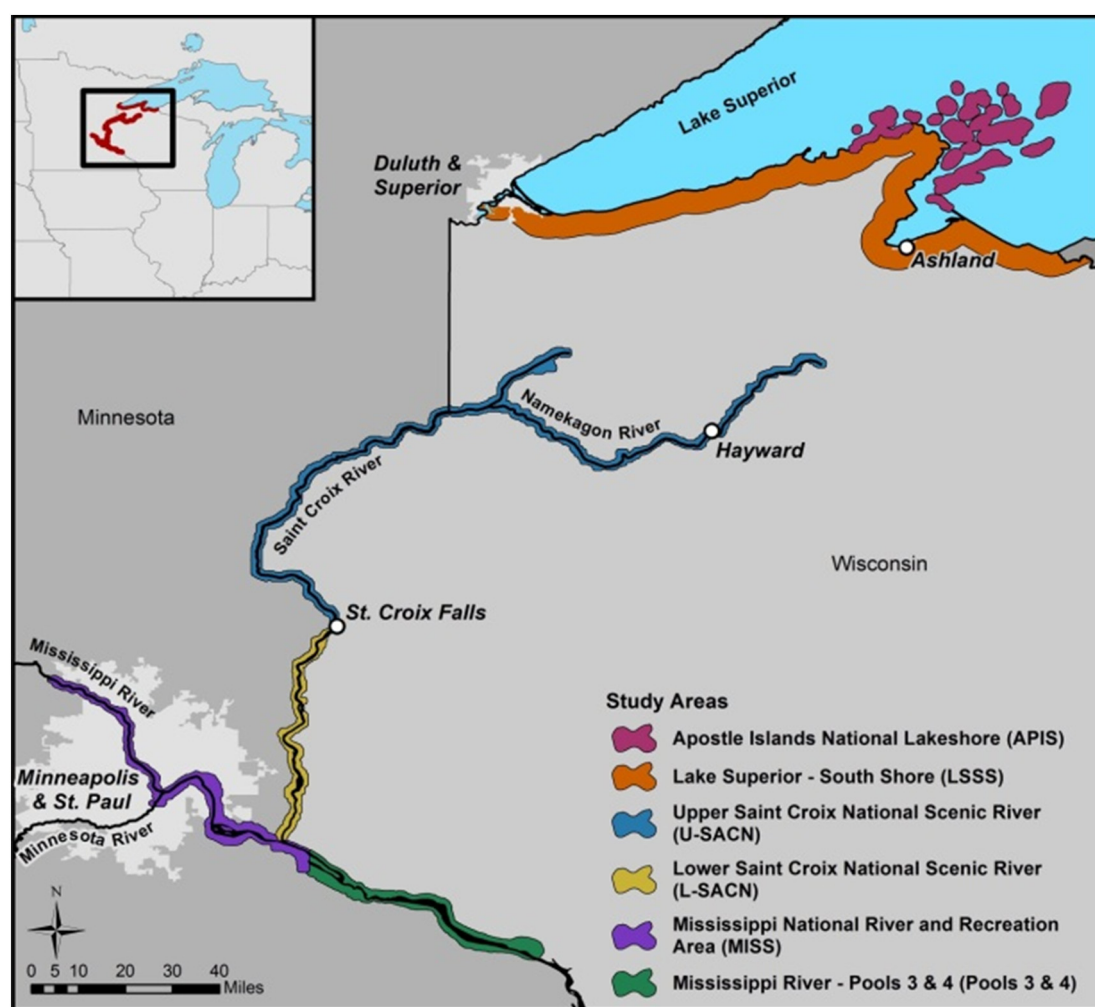


Fig. 1. Locations of the six study areas in the upper Midwestern United States where bald eagle nestlings were sampled for DDE, PCBs, and mercury (map previously published in [Route et al., 2014a](#)).

organic chemical analysis. The resulting plasma was frozen at -20°C until analysis.

Total mercury concentrations in breast feathers were determined by subjecting one unwashed breast feather for each nestling to cold-vapor atomic absorption (CVAA) spectrophotometry at the Wisconsin State Laboratory of Hygiene (WSLH), Madison, WI, as previously described

Table 1

Bald eagle nestling sample size used in analyses of PCBs, mercury, and DDE at six study areas during three time periods. Total number of samples = 414 for DDE, 307 for PCBs, and 739 for mercury. APIS = Apostle Islands, LSSS = the south shore of Lake Superior in Wisconsin, U-SACN = upper Saint Croix National Scenic River, L-SACN = lower Saint Croix National Scenic River, MISS = Mississippi National River and Recreation Area, and Pools 3 + 4 = pools 3 and 4 of the Mississippi River.

Contaminant	Years	Study area					
		APIS	LSSS	U-SACN	L-SACN	MISS	Pools 3 + 4
DDE ^a	1995–2002	11	29	0	0	0	0
DDE	2006–2015	58	16	65	64	138	33
PCB ₇₅ ^a	1995–2002	11	29	0	0	0	0
PCB ₇₅	2006–2015	37	11	42	48	96	33
Mercury	1991–1993	8	13	0	0	0	0
Mercury	1995–2002	18	51	0	0	0	0
Mercury	2006–2015	93	16	88	120	267	61

^a Earlier samples from 1989 to 1993 ($n = 36$ samples for PCB_{Total} and $n = 33$ samples for DDE; [Dykstra et al., 2005b](#)) were also used for analysis of long-term trends along the Lake Superior shore (APIS and LSSS study areas), but were not used in the primary analyses of patterns and trends at the six study areas.

([Dykstra et al., 2010](#)). The laboratory's limit of detection for mercury in feathers was $0.004\text{ }\mu\text{g/g}$ from 1991 through 2011 and varied from 0.0270 to $0.518\text{ }\mu\text{g/g}$ in 2014 and 2015. The laboratory used standard reference materials, ran quality assurance blanks, spiked samples, and duplicates for each batch to calibrate equipment and measure precision. The laboratory reported no flagged results, had no exceedances, and the percent recovery ranged from 87% to 109%.

Concentrations of DDE and PCBs in plasma samples were determined by gas chromatography with electron capture detection and were confirmed by mass spectrometry at the WSLH (1995–2015) or Michigan State University Veterinary Diagnostic Laboratory (MSU-VDL; 1989–1993) as described earlier ([Bowerman IV, 1993](#); [Mora et al., 1993](#); [Dykstra et al., 2010](#)). Detection limits for WSLH were $0.2\text{ }\mu\text{g/L}$ for DDE and ranged from 0.1 to $6.0\text{ }\mu\text{g/L}$ for the PCB congeners. Detection limits for MSU-VDL were $0.2\text{ }\mu\text{g/L}$ for DDE and $5.0\text{ }\mu\text{g/L}$ for total PCB concentrations (no congener-specific measurements). For the 2006–2011 period, percent recovery for PCBs varied by congener (range 31%–124%) and ranged from 86% to 96% for the sum of all PCBs; as stated below, congeners with low recovery rates were censored from analyses. For DDE, percent recovery ranged from 77% to 115% from 2006 to 2011 and 71% to 120% in 2014 and 2015. Percent recovery data were not available for PCB and DDE analyses from 1989 to 2003.

All bald eagle measurement and chemical concentration results were collected, handled, and archived by GLKN under a quality assurance plan (QAP; [Route and VanderMeulen, 2018](#)) and certified as meeting accepted standards for quality.

For analysis of long-term trends of DDE and PCB concentrations in eaglets along the Lake Superior shore (APIS and LSSS study areas) we included previously published samples ($n = 36$ for PCBs and $n = 33$ for DDE) from 1989 to 1993 (Dykstra et al., 2005b). All samples were collected and analyzed using similar methods (see Bowerman IV, 1993; Mora et al., 1993; Dykstra et al., 2005b; Dykstra et al., 2010).

Reproductive rate

We defined reproductive rate as the number of young present in the nest at the latest date of counting. In most cases, this was the day when sampling occurred. In a few cases, nests were observed post-sampling and were determined to have fewer young than were present at sampling; in these instances, the later count was used.

This measure of reproduction is not equivalent to the number of young per occupied nest, which is often reported because it includes nest failures. Rather, we only included nests that had live young available for sampling for a direct comparison to levels of contamination at that nest. Our measure of reproduction is most similar to the number of young per successful nest (Steenhof and Newton, 2007), as reported in other studies; however, we note that in one instance a nest was found to have failed after sampling and that nest was included in our analysis with a productivity of 0. We counted all young in the nest and sampled those that were old enough to sample safely (range 19–71 d, mean = 43.6 ± 0.2 , as determined by 8th primary length (Bortolotti, 1984)).

Statistical analysis

We used mixed-effects models to compare samples collected at the six study areas between 2006 and 2015, and to evaluate long-term trends (1989–2015) at LSSS and APIS. We included study area and year as fixed effects, and eagle territory as a random effect (because the same adults use the same territory in multiple years and thus samples within a territory are not independent). We $\log_{10}$ -transformed contaminant concentrations prior to analyses and checked appropriate plots of residuals to ensure model assumptions were met.

All models were fit using generalized least squares and mixed effects models with maximum likelihood using package nlme (Pinheiro, J., Bates, D., DebRoy, S., Sarkar, D., 2017. <https://cran.r-project.org/web/packages/nlme/nlme.pdf>, accessed 11 October 2018). We then compared the models using AIC_c (Burnham and Anderson, 2002) using the function model.sel in package MuMIn (Barton, K., 2016. MuMIn: Multi-model inference. R package version 1.15.6., <https://CRAN.R-project.org/package=MuMIn>, accessed 11 October 2018) to determine the fixed and random structure of each model. The AIC_c selected model was refit using restricted maximum likelihood (REML) to avoid biased estimates (Zuur et al., 2009) and inferences were made from this model. We used Tukey's post hoc tests in the package lsmeans (Lenth, 2016) to determine differences among study areas for contaminants and reproduction. All analyses were conducted in R version 3.4.3 (R Development Core Team, 2017. R Foundation for Statistical Computing, Vienna, Austria. <http://www.R-project.org>, accessed 11 October 2018). Because the structure of data varied among contaminants, some specific analyses differed and are described below.

DDE

We compared samples collected between 2006 and 2015 at the six study areas (APIS, L-SACN, LSSS, MISS, Pools 3 + 4, and U-SACN). We included study area, year, and the interaction between study area and year as fixed effects and territory as a random effect. To compare long-term trends (1989–2015) of DDE concentrations in eaglets at APIS and

LSSS, we used a mixed effects model with year and study area as fixed effects and territory as a random effect.

PCBs

We calculated the sum of PCB (Σ PCB) congeners using the Kaplan-Meier (KM) technique (Helsel, 2012), with the function cenfit in the package NADA (Lee, 2017. NADA: Nondetects and data analysis for environmental data. R package version 1.6–1. <https://CRAN.R-project.org/package=NADA>; accessed 11 October 2018). We calculated the KM sums for each sample by multiplying the KM mean by the number of congeners (Helsel, 2012).

To compare samples collected at the six study areas, we used $\log_{10}(\Sigma$ PCB congener concentrations + 1) as the response variable, to meet assumptions of normality. The full model included study area, sample year, and the interaction between study area and year as fixed effects, and territory as a random effect. We calculated geometric means by back-transforming the least square means, then subtracting 1.

To examine temporal trends for samples collected at LSSS and APIS between 1989 and 2011, we used two separate mixed effects models in package nlme (Pinheiro, J., Bates, D., DebRoy, S., Sarkar, D., 2017. <https://cran.r-project.org/web/packages/nlme/nlme.pdf>, accessed 11 October 2018). We used Σ PCB_{Total} as the response variable for samples collected from 1989 to 1993 because those samples were analyzed by MSU-VDL and individual PCB congeners (209 possible) were not quantified in those early years. We used Σ PCB₇₅ as the response variable for the 1995–2011 samples, which is the Kaplan-Meier sum of 75 PCB congeners that WSLH quantifies based on the Mullin Standard Mix (Frame, 2001). These 75 congeners likely include 95–99% of the PCBs that can be measured in the environment (National Research Council, 2001). These response variables should be very similar; nonetheless, we did separate analyses because total and sum of 75 congeners may not be completely comparable. The PCB concentration (total or sum) was $\log_{10}$ -transformed and used as the response variable with year as a fixed effect and territory as a random effect.

For the time period 1995–2011, we also examined six PCB congeners or colluded groups of congeners that are classified as dioxin-like in terms of their toxicity: PCBs 77/110, 132/153/105, 118, 123/149, 156, and 167. For temporal trends we combined samples from APIS and LSSS because there was no significant difference in the KM sum of the dioxin-like PCBs between these study areas ($t = -0.09$, $P = 0.93$).

Mercury

To compare mercury concentrations among study areas (2006–2015), we dropped nestling age from the model because age had a small ($\beta = 0.0009$) and nonsignificant effect ($t = 1.74$, $p = 0.08$) on mercury concentrations. Because of low sampling intensity at LSSS and Pools 3 + 4, we omitted these two study areas from our mercury analysis.

To evaluate long-term trends for samples collected from Lake Superior nestlings (APIS and LSSS), our full model included $\log_{10}$ mercury concentration as the response variable, year, study area, and the interaction between study area and year as fixed effects, and territory as a random effect.

Reproductive rate

We used a generalized linear mixed effects model with a Poisson distribution of the number of nestlings present as the response variable, study area and year as fixed effects, and territory as a random effect. We used lsmeans with the Tukey method for post hoc comparisons among study areas.

Results

Contaminant concentrations in nestling bald eagles

DDE

We compared DDE concentrations in eaglet plasma ($n = 374$ nestlings on 162 territories) among the six study areas for 2006–2015. The best-fitting model included study area and year and indicates that DDE concentrations decreased at a rate of 5.8% per year across the region for this time period (-0.026 on the $\log_{10}$ scale; $t = -6.23$, $P < 0.001$; Fig. 2). Eaglets at APIS had the highest concentrations ($GM = 10.6 \mu\text{g/L}$) and those at U-SACN had the lowest ($GM = 2.9 \mu\text{g/L}$; Table 2), and Tukey post-hoc tests indicated differences among pairs of study areas (APIS and L-SACN, $p = 0.04$; APIS and U-SACN, $p < 0.001$; L-SACN and U-SACN, $p < 0.001$; LSSS and U-SACN, $p < 0.001$; MISS and U-SACN, $p < 0.001$; Pools 3 + 4 and U-SACN, $p < 0.001$; Table 2).

Long-term trend analysis for the two Lake Superior study areas (APIS and LSSS) from 1989 to 2015 indicated that concentrations of DDE in nestling plasma decreased in Lake Superior over the 26 years of this monitoring. The best-fitting model included only year and estimated that DDE concentrations in nestling plasma decreased 5.5% per year (-0.0232 on the $\log_{10}$ scale; intercept on the $\log_{10}$ scale = 1.4950 for the mean of both study areas together; $t = -7.25$, $P < 0.001$; Fig. 3).

PCBs

We compared the ΣPCB_{75} concentrations in eaglet plasma ($n = 267$ nestlings on 127 territories) among the six study areas for 2006–2011. The best-fitting model included study area as a fixed effect and territory as a random effect. ΣPCB_{75} concentrations in eaglet plasma were higher at APIS, L-SACN, LSSS, MISS, and Pools 3 + 4 than at U-SACN ($P < 0.001$), but there were no other significant differences among study areas (Table 2).

Long-term trend analyses for Lake Superior nestlings indicated that ΣPCB_{75} concentrations declined from 1995 to 2011 at LSSS, but not at APIS. For LSSS, the best-fitting model, which included year as a fixed effect and territory as a random effect, indicated that ΣPCB_{75} concentrations decreased by 3.6% per year (-0.0156 on the $\log_{10}$ scale; $t = -2.41$, $P = 0.025$; AIC weight = 0.94; Fig. 4). For APIS, the best model included year as a fixed effect and territory as a random effect, but we found no statistically significant trend in ΣPCB_{75} concentrations ($t = -0.47$, $P = 0.64$; AIC weight =

0.94; Fig. 5). For samples in which $\Sigma\text{PCB}_{\text{Total}}$ was measured (1989–1993 only), no temporal trends were detected for the 5-year period at either LSSS or APIS ($t = -1.74$, $P = 0.12$, Fig. 4 for LSSS; $t = -1.74$, $P = 0.12$, Fig. 5 for APIS); however, sample sizes for each year were low.

For the dioxin-like PCB congeners, the sum of these congener concentrations were highest at Pools 3 + 4 and lowest at U-SACN, but the differences were not statistically significant. For temporal trends at Lake Superior study areas, the best model included only year and indicated a 2.7% per year decline in the KM sum of dioxin-like PCBs (-0.0117 on the $\log_{10}$ scale; $t = -2.02$, $P = 0.05$; Fig. 6).

Mercury

Concentrations of mercury in breast feathers of nestlings differed significantly among the four study areas from 2006 to 2015 and were highest at U-SACN and lowest at APIS (Table 2). The best-fitting model included a random slope and random intercept, and study area and year as fixed effects. There was a small but significant increase by year ($\beta = 0.0079$, $t = 3.14$, $P = 0.002$), but slope varied by study area (Fig. 7) and the model suggested significant differences among all study areas (pairwise Tukey independent contrasts, $P < 0.001$). Individual study area slopes (Fig. 7) indicate that after 2006, there was no observable trend in mercury concentrations at the APIS and U-SACN study areas, and weak evidence of increase at the MISS and L-SACN study areas.

Long-term trend analysis indicated that concentrations of mercury in breast feathers of Lake Superior nestlings declined from 1991 to 2015, an average of 1.6% per year (-0.00688 on the $\log_{10}$ scale; $t = -4.16$, $P < 0.001$; Fig. 8). The best-fitting model included study area and year as fixed effects (AIC weight = 0.62). Nestlings at LSSS had higher loads of mercury ($GM = 6.83 \mu\text{g/g}$) than those at APIS ($GM = 3.92$; $t = 5.70$, $P < 0.001$).

Reproductive rate

The mean reproductive rate in the six study areas varied from 1.4 to 2.1 young per sampled nest (Table 3) from 2006 through 2015. The highest numbers of young produced were found at MISS and Pools 3 + 4, and the lowest at U-SACN and LSSS. The best model of reproductive rate included only study area, suggesting differences among some study areas (i.e., MISS > APIS; $z = 1.96$, $P = 0.05$). However, post-hoc comparisons showed only one significant difference in reproductive rate among sites (MISS > U-SACN; $z = 3.32$, $P = 0.01$).

Discussion

DDE

Geometric mean DDE concentrations in eaglet plasma for the six study areas were below the estimated threshold for adverse reproductive effects on bald eagle populations ($28 \mu\text{g/L}$; Elliott and Harris, 2001/2002). DDE concentrations were highest in nestlings on the Apostle Islands in Lake Superior, which was consistent with our earlier findings (Dykstra et al., 2010) and likely due, in part, to the slow degradation of contaminants in this deep, cold lake that retains water for many years. However, even on the Apostle Islands, all nestling plasma concentrations were below the estimated threshold for reproductive impairment (equivalent to $1.4 \mu\text{g/L}$ on the log scale) by 2014 (Fig. 3; Electronic Supplementary Material (ESM) Fig. S1). Measured reproductive rates (Table 3, Dykstra et al., 2010) also corroborate the conclusion that neither DDE nor PCBs are depressing current reproduction at any of the study sites.

DDE concentrations in nestlings decreased over the entire region at 5.8% annually from 2006 to 2015. Similarly, long-term trends at Lake Superior continue to indicate decreasing levels, at a rate of 5.5% per year, slightly faster than what we reported from 1989 to 2008 (3% per year; Dykstra et al., 2010). Declines in plasma DDE concentrations were also

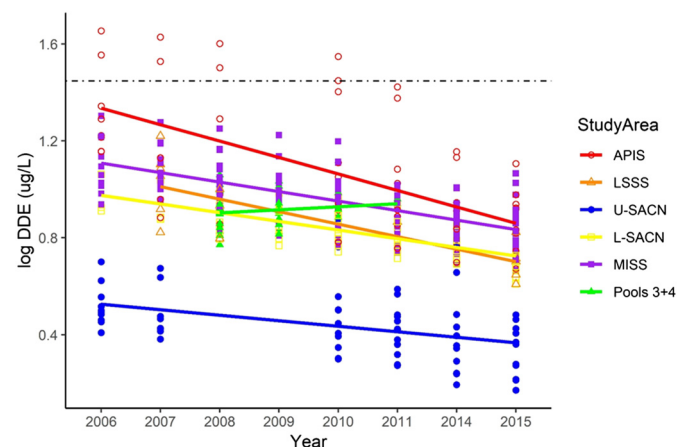


Fig. 2. DDE concentrations ($\mu\text{g/L}$ wet weight) in plasma of nestling bald eagles from six study areas in Wisconsin/Minnesota, 2006–2015. APIS = Apostle Islands, LSSS = the south shore of Lake Superior in Wisconsin, U-SACN = upper Saint Croix National Scenic River, L-SACN = lower Saint Croix National Scenic River, MISS = Mississippi National River and Recreation Area, and Pools 3 + 4 = pools 3 and 4 of the Mississippi River. Lines indicate the estimated trends from the mixed effects model, which included study area and year as fixed effects and territory as a random effect. Broken line is estimated threshold for reproductive impairment.

Table 2

Estimated geometric mean concentrations of DDE ($\mu\text{g/L}$) and PCB₇₅ ($\mu\text{g/L}$) in plasma, and mercury ($\mu\text{g/g}$) in feathers of nestling bald eagles in northern Wisconsin, 2006–2015. Contaminant concentrations were $\log_{10}$ -transformed for analyses. PCB₇₅ were calculated as the sum of 75 congeners. Geometric means were estimated from analysis using mixed effects models, which accounted for multiple years of data from individual nests. Mean is the estimated geometric mean. Estimated means followed by the same letter do not differ statistically. APIS = Apostle Islands, LSSS = the south shore of Lake Superior in Wisconsin, U-SACN = upper Saint Croix National Scenic River, L-SACN = lower Saint Croix National Scenic River, MISS = Mississippi National River and Recreation Area, and Pools 3 + 4 = pools 3 and 4 of the Mississippi River.

Study area	DDE			PCB ₇₅			Mercury		
	n	Mean ($\mu\text{g/L}$)	Range	n	Mean ($\mu\text{g/L}$)	Range	n	Mean ($\mu\text{g/g}$)	Range
APIS	58	10.64 a	2.6–88	37	70.37 a	28.79–397.71	93	2.69 a	1–7.9
LSSS	16	7.69 ab	2.3–40	11	67.20 a	25.14–291.12	16	5.25 ¹	2.3–19.2
U-SACN	65	2.86	1–26	42	5.42 b	0–109.3	88	6.66 d	3.4–16
L-SACN	64	6.90 b	2.1–22	48	97.37 a	42.85–273.88	120	4.63 b	3–9.72
MISS	138	8.82 ab	2.2–61	96	90.19 a	24.7–315.0	267	3.46 c	1.54–6.84
Pools 3 + 4	33	7.08 ab	3.5–21	33	114.83 a	70.89–232.61	61	3.22 ^a	1.8–5.8

^a Samples from LSSS and Pools 3 + 4 were not used in mercury analysis, due to low sampling intensity at those sites (3 years at LSSS and 4 years at Pools 3 + 4; see text).

reported for eaglets along the Great Lakes in Michigan (Wierda et al., 2016) and at Voyageurs National Park, Minnesota (Pittman et al., 2015). Nonetheless, we found DDE in all (100%) samples analyzed, likely a result of atmospheric deposition as well as sources remaining within the sediment and biota (e.g., Anthony et al., 2007).

Our data on DDT, the parent material of DDE that was banned in 1972, shows that this pesticide continues to occasionally enter our study areas (6.7% of samples had DDT concentrations above detection limits; see ESM Fig. S1). These rare occurrences contribute to the prevalence of DDE in midwestern bald eagle populations and may be derived from prey such as migratory birds that are exposed to DDT in wintering areas where it is still used (e.g. South America; USEPA, 2017. <https://www.epa.gov/ingredients-used-pesticide-products/ddt-brief-history-and-status>, accessed 24 August 2018). Alternatively, it could come from inadvertent or intentional releases locally. For example, a local release was likely the cause of the high concentration of DDT (7.3 $\mu\text{g/L}$; ESM Fig. S1) we found in one nestling on the Mississippi River in 2009. Similarly, a telemetry study of Ospreys (*Pandion haliaetus*) in the Pacific Northwest found that sources of DDE were primarily on the breeding sites rather than on southern wintering grounds (Elliott et al., 2007).

PCBs

Geometric mean ΣPCB_{75} and total concentrations for all six study areas were below 190 $\mu\text{g/L}$, the estimated threshold for adverse reproductive

effects on bald eagle populations (Elliott and Harris, 2001/2002), and have been below that threshold since our monitoring began. As in our previous report (Dykstra et al., 2010), ΣPCB concentrations were higher along the Mississippi River, lower St. Croix River, and Pools 3 + 4, where past and current industries likely contribute to accumulation (ESM Fig. S2). Though they were banned in 1979, PCBs continue to enter the aquatic food web from degradation or burning of old products containing PCBs, contaminated sediments, and low-temperature burning of industrial and residential waste (USEPA, 2018. <https://www.epa.gov/pcbs/learn-about-polychlorinated-biphenyls-pcbs#release>, accessed 19 September 2018).

PCB concentrations in Lake Superior eaglets continue to decline. We found a statistically significant decline of 3.6% per year at LSSS for ΣPCB_{75} and a significant decline of 2.7% per year for the dioxin-like PCBs at both LSSS and APIS. The decline of ΣPCB_{75} for LSSS was slightly lower than the 4.3% we reported for both APIS and LSSS from 1989 to 2008 (Dykstra et al., 2010). However, our current analysis includes additional contemporary and historical samples and a re-evaluation of the congeners used in long-term trends. For our 2010 report, we assumed the 75 congeners we measured were a reasonable approximation of the sum of all PCBs, but after reviewing the pre-1995 data, we concluded that the historical $\text{PCB}_{\text{total}}$ could not be assumed equivalent to the PCB_{75} data for long-term trend analysis. Hence our current analysis is more conservative, because we separated the 1989–1993 data from the long-term trend analysis.

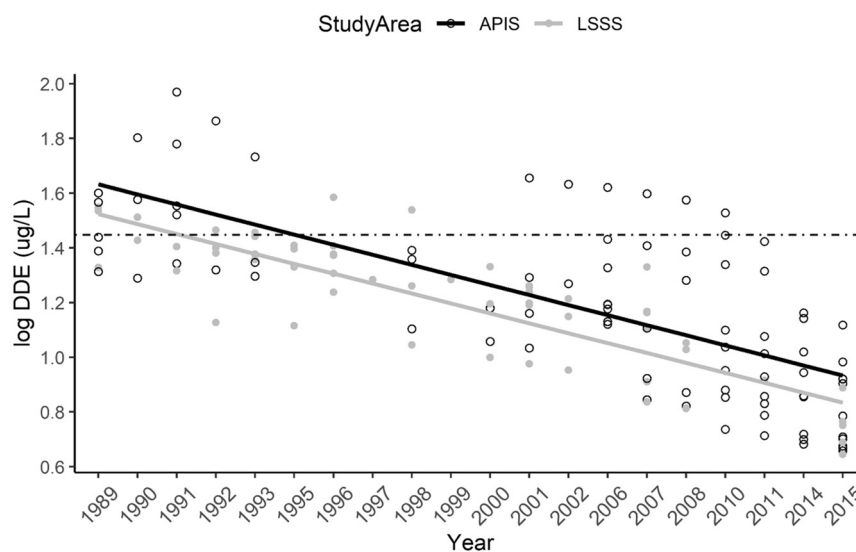


Fig. 3. DDE concentrations ($\mu\text{g/L}$ wet weight) in plasma of nestling bald eagles from two subregions of Lake Superior in Wisconsin, 1989–2015. APIS = Apostle Islands, LSSS = the south shore of Lake Superior <8 km from the shoreline. Lines indicate the estimated rate of decline at 5.5% per year from the mixed effects model, which included year as a fixed effect and territory as a random effect. There was no significant difference between the two study areas. Broken line is estimated threshold for reproductive impairment.

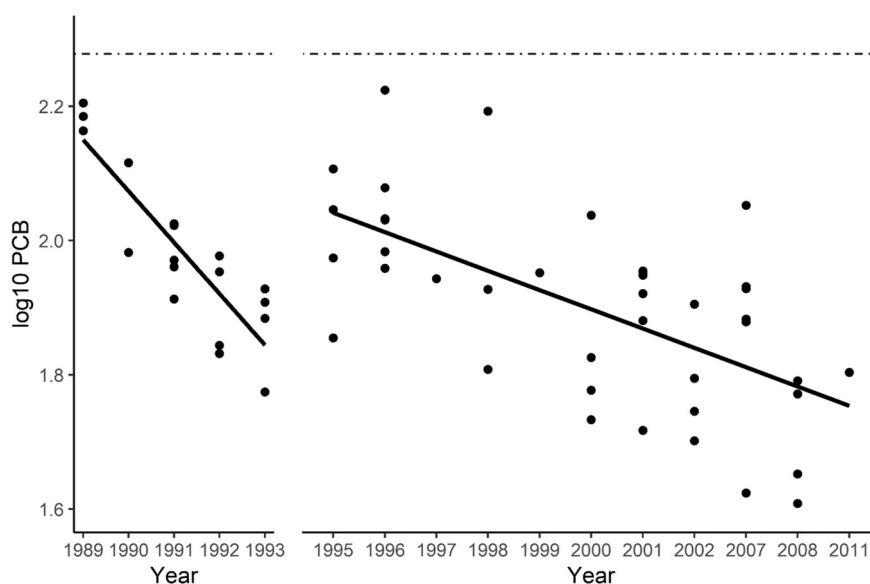


Fig. 4. PCB_{Total} (left) and PCB₇₅ (right) concentrations ($\mu\text{g/L}$ wet weight) in plasma of nestling bald eagles from the south shore of Lake Superior in Wisconsin (LSSS), 1989–2011. Lines indicate the estimated trends from the mixed effects models, which included year as a fixed effect and territory as a random effect. From 1989 to 1993, the trend for PCB_{Total} concentrations was not statistically significant; however, sample sizes in each year were small. From 1995 to 2011, PCB₇₅ concentrations decreased 3.6% per year. Broken line is estimated threshold for reproductive impairment.

Mercury

In contrast with DDE and PCBs, mercury concentrations were highest on the upper St Croix River (Fig. S2). The higher levels of mercury in this otherwise minimally contaminated area were likely due to the high proportion of wetlands in the upper St. Croix River and Namekagon River basins where elemental mercury is methylated by anaerobic bacteria found in wetlands (Wiener et al., 2012). This contribution of wetlands to mercury accumulation is also likely responsible for the higher concentrations along the south shore of Lake Superior relative to the Apostle Islands (Fig. 8). In LSSS, eagles nest at the mouths of creeks or rivers, which often have high proportions of wetlands in their drainage areas. By contrast, the Apostle Islands, constrained by

the relatively small size of most islands, have short tributaries with less wetland area.

When analyzing long-term trends at the Lake Superior study areas alone, we found a significant decline in mercury concentrations since the early 1990s. However, when examining regional trends over the past 10 years (2006–2015), we detected no evidence of such decline for one of those Great Lakes study areas (the Apostle Islands) or for the upper St. Croix and Namekagon Rivers. Moreover, we found evidence for an increase at the lower St. Croix and Mississippi River study areas (Fig. 7). Similarly, mercury concentrations in nestling eagles in Voyageurs National Park may have increased between 2000 and 2010 (Pittman et al., 2011), and concentrations in common loons (*Gavia immer*) at Wisconsin lakes increased from 2002 to 2010 (Meyer et al.,

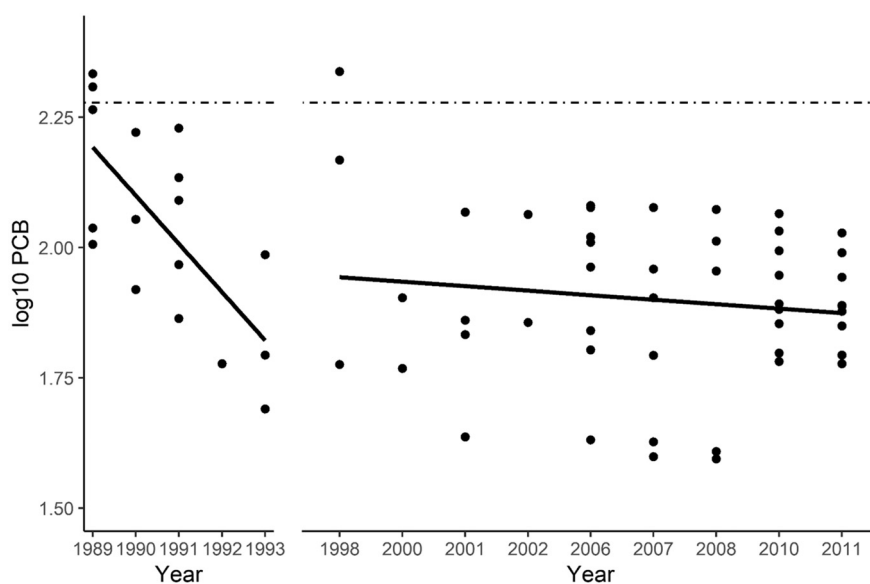


Fig. 5. PCB_{Total} and PCB₇₅ concentrations ($\mu\text{g/L}$ wet weight) in plasma of nestling bald eagles from the Apostle Islands study area (APIS), 1989–2011. Lines indicate the estimated trends from the mixed effects models, which included year as a fixed effect and territory as a random effect. Trends for both PCB_{Total} and PCB₇₅ concentrations were not significant in either time period; however, sample sizes in 1989–1993 were small. Broken line is estimated threshold for reproductive impairment.

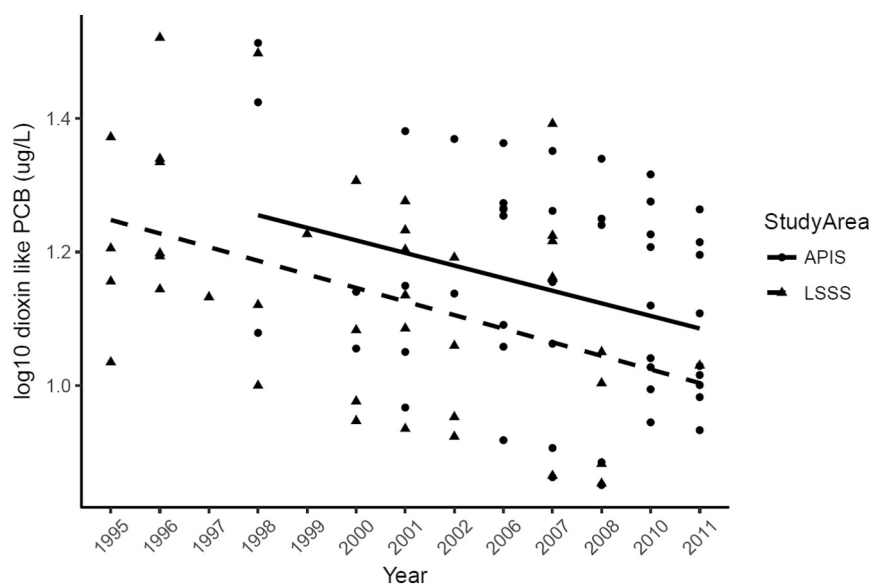


Fig. 6. Trends in the sum of six dioxin-like PCB congeners in bald eagle nesting plasma from LSSS and APIS. There was no significant difference between the study areas and the overall trend was a significant decline of 2.7% annually.

2011). Measurements in other species in the upper Midwest also suggest mercury has either ceased to decline or has started to increase in recent years (Monson, 2009; Rasmussen et al., 2007; Wiener and Sandheinrich, 2010; Evers et al., 2011a; Weseloh et al., 2011). Although anthropogenic emissions of mercury associated with coal-fired power plants in the United States and Canada have declined in recent years, the wet deposition of mercury has increased in many locations, particularly in central United States including the upper Midwest (2007–2013; Weiss-Penzias et al., 2016), and atmospheric deposition rates are positively correlated with mercury levels in the feathers of nestling raptors (Guigueno et al., 2012). Increasing atmospheric deposition may be attributable to emissions from developing nations and changes in environmental availability linked to global climate change (Weiss-Penzias et al., 2016). After deposition, the bioavailability of mercury is influenced by a variety of landscape, habitat, and biogeophysical factors (DeSorbo et al., 2018). Due to the abundance of wetlands and low-pH lakes, among other factors, northern Wisconsin and northern

Minnesota are considered mercury-sensitive landscapes (Evers et al., 2011b), so wildlife there may be at higher risk of exposure and potential negative impacts of mercury.

The threshold levels of mercury that impair eagle reproduction or survival are difficult to establish, making interpretation of current or historical contamination difficult. Mercury at levels exceeding 3.0 µg/g in blood of adult common loons is associated with decreased reproduction and aberrant behavior (Evers et al., 2011b), and mercury exposure has been linked to reduced productivity in Wisconsin loons (Burgess and Meyer, 2008). However, bald eagles are less sensitive than loons due to their greater ability to demethylate mercury (Scheuhammer et al., 2008), and some authors have suggested a threshold level of 20 µg/g in adult eagle feathers for population-level toxic effects (Evers et al., 2004; DeSorbo and Evers, 2005). Rutkiewicz et al. (2011) found that mercury levels in feathers were positively associated with mercury levels in brain tissue and were correlated with changes in adult bald eagle brain chemistry. These authors calculated that 14–27% of eagles

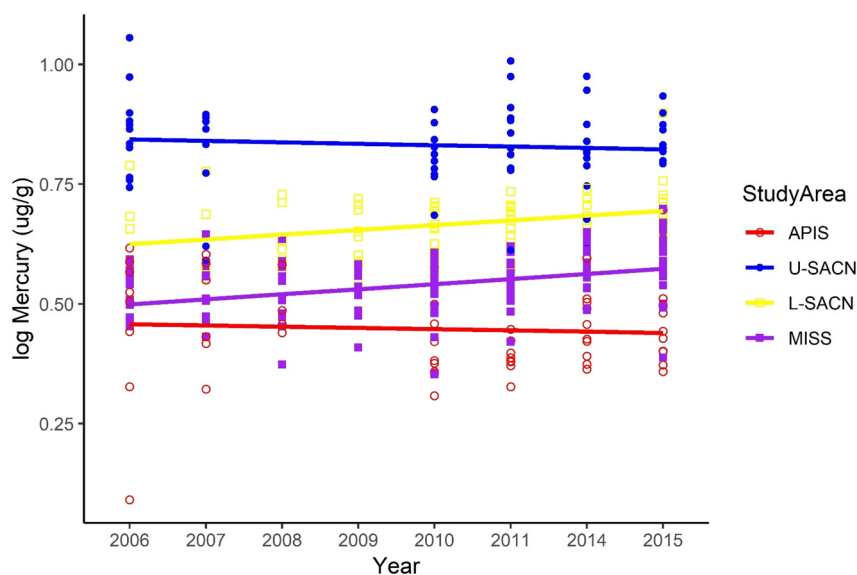


Fig. 7. Mercury concentrations (µg/g) in feathers of bald eagle nestlings in four study areas of Wisconsin/Minnesota. APIS = Apostle Islands, U-SACN = upper Saint Croix National Scenic River, L-SACN = lower Saint Croix National Scenic River, and MISS = Mississippi National River and Recreation Area. Lines indicate the estimated trends from the mixed effects model, which included study area and year as fixed effects and territory as a random effect.

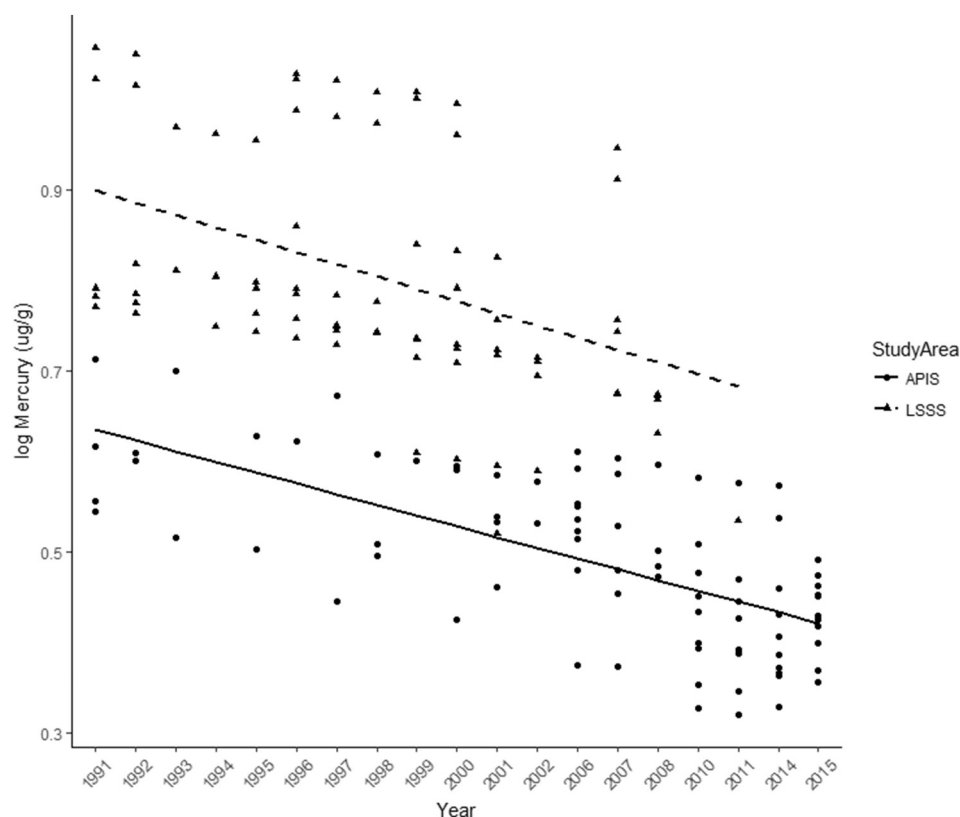


Fig. 8. Mercury concentrations ($\mu\text{g/g}$) in the feathers of bald eagle nestlings on Lake Superior in Wisconsin, 1991–2015. APIS = Apostle Islands; LSSS = south shore of Lake Superior. LSSS had higher concentrations, and estimated trends from the mixed effect model with study area and year as fixed effects and territory as a random effect indicate a 1.6% decline per year in both study areas.

in the Great Lakes region during 2002–2010 may have been exposed to levels of mercury capable of causing subclinical neurological change. In British Columbia, one eagle died as a result of mercury poisoning, and 20% of eagles found dead or dying had moderate or greater liver mercury levels (Weech et al., 2003). Few other studies have shown an association between mercury exposure and negative effects in bald eagles, although this may be confounded by the effects of the organochlorine legacy contaminants nearly always present in areas with high levels of mercury (DeSorbo et al., 2018).

Decreasing reproductive rate was associated with increasing levels of mercury among eagles nesting on Maine's inland lakes (DeSorbo and Evers, 2007; DeSorbo et al., 2009). In contrast, eagles with elevated mercury levels similar to those in Maine had good body condition and reproduced well in British Columbia (Weech et al., 2006). However, mercury concentrations in nestling feathers at both these locations were three times higher than those in the upper St. Croix River basin (our study area with highest mercury levels) and were among the highest in North America (Weech et al., 2006; DeSorbo et al., 2018).

Table 3

Reproductive rates of bald eagles in the six study areas in Wisconsin/Minnesota, 2006–2015. Reproductive rate was defined as the number of young present in the nest at the latest date of counting. In most cases, this was the day when sampling and banding were done.

Study area	n	Mean reproductive rate	SE
APIS	58	1.69	0.06
LSSS	16	1.5	0.13
U-SACN	65	1.43	0.07
L-SACN	64	1.91	0.08
MISS	138	2.12	0.06
Pools 3 + 4	33	2.03	0.12

Management implications

The bald eagle has been established as a bioindicator species by multiple agencies and monitoring programs throughout the Great Lakes region. The position of the bald eagle at the top of the trophic food web, the wealth of historical data, and the regulatory imperatives all support continued monitoring of this iconic species. Moreover, the apparently increasing levels of mercury in some of our study areas, combined with the mercury-sensitive landscape and the potential for population-level impacts, suggest that particular concern and focused monitoring of regional hotspots for mercury are warranted.

We expect DDE concentrations to continue declining slowly or reach a plateau at low levels without further management efforts. However, periodic monitoring is recommended to better understand the complete trajectory (from height of use through banning and the eventual low point) of this toxic chemical. The cost of measuring DDE is relatively low and includes the parent material DDT. Continued monitoring of DDT will be important because of the potential for expanded use of this compound in the tropics and subtropics to control mosquito populations in the face of global warming.

We expect PCB concentrations to also continue their slow decline and to reach a plateau at low levels. Managers can enhance this decline by continuing to collect PCB-containing equipment and products and by banning and/or enforcing unnecessary burning of petroleum-based products such as plastics and Styrofoam that emit PCBs when burned at low temperatures (Shibamoto et al., 2007). According to the USEPA, the continued use of burn barrels constitutes a significant source of PCBs and dioxins (Lemieux et al., 2000). Currently several Great Lakes states and provinces have banned the use of residential burn-barrels for burning trash, but PCB levels in biota should continue to be measured periodically to monitor the effectiveness of education and enforcement.

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Ethics statement

This study was conducted under Minnesota and Wisconsin state scientific collecting permits and a U.S. Fish and Wildlife Service Bald Eagle Scientific Collecting permit, and was carried out under guidelines and review of the National Park Service Institutional Animal Care and Use Committee.

Author contributions

WTR conceived the idea and study design. WTR, CRD, MWM, and RLK collected the samples. KAW and RLK analyzed the data. CRD and WTR wrote the paper, with input from KAW and MWM. All authors approved the final version of the paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jglr.2019.01.010>.

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