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Using nestling plasma to assess long-term spatial and temporal concentrations of organochlorine compounds in bald eagles within Voyageurs National Park, Minnesota, USA

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HIGHLIGHTS

- Polychlorinated biphenyls (PCBs) are decreasing in Voyageurs National Park (VNP), MN.
- Most organochlorine pesticides are decreasing in Voyageurs National Park (VNP), MN.
- Dieldrin concentrations in bald eagle nestling blood plasma are increasing.
- Dieldrin concentrations may be tied to a new source or environmental processes.

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ABSTRACT

The bald eagle (*Haliaeetus leucocephalus*) population at Voyageurs National Park (VNP) provides an opportunity to assess long-term temporal and spatial trends of persistent environmental contaminants. Nestling bald eagle plasma samples collected from 1997 to 2010 were analyzed for polychlorinated biphenyls (PCBs) and organochlorine pesticides. Trends of total PCBs, total DDTs, 4,4′-DDE, and Dieldrin were analyzed since >50% of nestling plasma samples had detectable concentrations. Total PCBs, total DDTs, and 4,4′-DDE concentrations have all decreased over time (26.09%, 24.09%, and 40.92% respectively). Concentrations of Dieldrin have increased by 50.25%. In this study, 61.1% of all nestlings sampled had detectable concentrations of Dieldrin from all time periods and all areas of VNP. Since Dieldrin is a banned pesticide in North America, the source of this increase is unknown. However, increases and fluctuations in Dieldrin concentration suggest contaminant levels in VNP may be linked to a new source or environmental process.

1. Introduction

In the period following World War II, industry and agriculture heavily used organochlorine compounds, specifically polychlorinated biphenyls (PCBs) and organochlorine (OC) pesticides until their ban in the 1970s (Bowerman et al., 1995). PCBs and OC pesticides are highly persistent, bioavailable organochlorine compounds that have harmful effects on avian species (Dykstra et al., 2010). Dichlorodiphenyltrichloroethane (DDT) and its degradation product 4,4′-Dichlorodiphenyltrichloroethylene (4,4′-DDE) were the main factors contributing to the great decline in bald eagle (*Haliaeetus leucocephalus*) populations in North America during the mid-1900s due to its wide spread use as an agricultural insecticide and subsequent environmental degradation (Wiemeyer et al., 1984, 1993; Gilliom and Clifton, 1990). After the ban of DDT and many other OC pesticides in the 1970s, the populations began to recover, but reproductive rates of populations associated with the

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Great Lakes region of the United States were still low (Bowerman et al., 1995, 1998; Donaldson et al., 1999). Later researchers discovered that other organochlorine compounds, like PCBs, were also contributing factors in the decline and slow recovery of populations in the Great Lakes region (Bowerman et al., 1995, 1998). PCB compounds are very persistent environmental pollutants that can bioaccumulate and biomagnify similar to other organochlorine compounds (Donaldson et al., 1999; Dykstra et al., 2010). PCB contaminations have resulted from their intentional or accidental release in effluent from factories or from poorly constructed waste dumps, waste incineration facilities, and landfills (Breivik et al., 2002). PCBs have contributed to low viability of eggs and teratogenic effects such as crossed beaks in bald eagles (Bowerman et al., 1994; Donaldson et al., 1999). Negative effects of organochlorine compounds persist in current populations and are testament to their long-term impacts in the environment (Cesh et al., 2008).

Historically PCBs and OC pesticides originated from their use and direct release into the environment, but new sources have emerged recently. Organochlorine compound atmospheric deposition is a major contributor to the transport and distribution of PCBs and OC pesticides throughout the environment (Atlas et al., 1986; Gregor and Gummer, 1989; Odabasi et al., 2008; Kim et al., 2009; Lohmann et al., 2009; Pacyna et al., 2009). Research suspects that sources of PCBs and OC pesticides are a result of their continued use, especially in developing nations in Europe, Asia, and the Caribbean (Anthony et al., 2007; Zhang et al., 2008; Wang et al., 2010). Less chlorinated PCBs and OC pesticides can volatilize in southerly latitudes and eventually be deposited in more northerly latitudes including regions of North America (Hoff et al., 1992; Anthony et al., 2007). Deposition of volatilized organochlorine compounds most commonly occurs through gas exchange with surface water (Bruhn et al., 2003). Cooler climates and longer winters lead to deposition rates, which are greater than the rate of volatilization, causing an accumulation of residues in bodies of water. Gregor and Gummer (1989) first found evidence to support this concept then they found trace levels of OC pesticides and PCBs in Canadian arctic snowpack and reason the only possible source was long range atmospheric transport. The characteristic climate of the Upper Midwest and global climate patterns potentially create a sink for historical depositions of PCBs and OC pesticides from current application and volatilization in distant areas.

PCBs and OC pesticides are extremely persistent in the environment, so much so that they are still present in Great Lakes sediments 30 years after production in North America stopped. Saginaw Bay, one of the most well-known contamination sites in the Great Lakes had extremely high concentrations of organochlorine compounds that, although decreased over time, were still present at elevated levels in 2007 (Froese et al., 1998; Jude et al., 2010). Sediments are a very important factor in the retention and persistence of these compounds since they retain less volatile species, especially in more northerly latitudes (Iwata et al., 1995). This retention occurs because cooler air and water temperatures in the Great Lakes increase the persistence of organochlorine compounds in sediments, especially aquatic sediments (Grimalt et al., 2004). The combination of remnant organochlorine compound contaminations, their retention and persistence in the environment, climatic conditions and the potential threat of new sources from atmospheric deposition make environmental monitoring critical to continued maintenance or improvement of ecosystem health.

Bald eagles are bioindicators for environmental concentrations of organochlorine compounds (Wiemeyer et al., 1989, 1993; Bowerman et al., 2002; Hollamby et al., 2006). Their well-documented life histories, accurate population measures, long-term productivity monitoring, and position in the food web makes them ideal as a bioindicator species (Bowerman et al., 2002). Bald eagles are a tertiary piscivorous predator, optimally positioned for examination of bioaccumulation and biomagnifications in aquatic ecosystems (Kozie and Anderson, 1991; Anthony et al., 1993). Research has documented the effects of many organochlorine compounds on bald eagles and these effects are a reference for assessing the potential hazards of concentrations in the environment (Strause et al., 2007). We are also able to calculate accurate population and productivity measures and correlate these with environmental contaminant concentration to indicate any potential negative population level effects (Bowerman et al., 2003). Nestling bald eagle plasma concentrations, the focus of this study, reflect contaminant levels of the selected available prey in the territory its parents defended during the nesting season (Bowerman et al., 2002; Hollamby et al., 2006; Strause et al., 2007). The bald eagles ability to bioaccumulate contaminants combined with contaminants sampling and population-monitoring techniques allow us to assess temporal and spatial trends of those contaminant concentrations.

In this study we determined concentrations of 30 organochlorine compounds (Table 1), including 20 PCB congeners, DDT, 4,4′-DDE, other DDT degradation products, and Dieldrin, in blood plasma of nestling bald eagles within Voyageurs National Park (VNP), Minnesota, USA from 1997 to 2010. We examined concentrations for temporal variation in all 30 organochlorine compounds. We also determined if concentrations varied across the parks three main impoundments. We also examined the data for hot spots of contamination across spatial and temporal gradients within VNP. This study functioned as the control study for a larger Great Lakes bald eagle biosentinel project.

2. Methods

2.1. Study area

Voyageurs National Park was established in 1975 to protect 88 628 ha, of which most is waterways or southern boreal forest on the United States border with Canada in northern Minnesota

Table 1
Organochlorine contaminant analytes measured in nestling bald eagle plasma samples from 1997 to 2010, with parameter-specific method detection limits (MDLs) in $\mu g\ kg^{-1}$ and quantification limits (QLs) in $\mu g\ kg^{-1}$.

Organochlorine contaminant	MDL	MDL/2	QL
Dieldrin	0.97	0.485	2.01
2,4′-Dichlorodiphenyldichloroethylene (2,4′-DDE)	0.86	0.43	2.01
4,4′-DDE	0.61	0.305	2.01
2,4′-Dichlorodiphenyldichloroethane (2,4′-DDD)	1.55	0.775	2.01
4,4′-DDD	1.18	0.59	2.00
2,4′-Dichlorodiphenyltrichloroethane (2,4′-DDT)	1.57	0.785	2.01
4,4′-DDT	1.95	0.975	2.01
PCB congener 8	1.94	0.97	1.98
PCB congener 18	1.21	0.605	1.98
PCB congener 28	1.23	0.615	1.99
PCB congener 44	1.52	0.76	1.98
PCB congener 52	0.64	0.32	1.98
PCB congener 66	0.87	0.435	2.00
PCB congener 101	0.38	0.19	2.00
PCB congener 105	1.44	0.72	1.98
PCB congener 110	1.91	0.955	2.01
PCB congener 118	0.58	0.29	1.99
PCB congener 128	0.75	0.375	1.99
PCB congener 138	0.65	0.325	2.00
PCB congener 153	0.57	0.285	1.99
PCB congener 156	1.84	0.92	2.01
PCB congener 170	1.28	0.64	1.98
PCB congener 180	1.62	0.81	2.00
PCB congener 187	1.12	0.56	1.98
PCB congener 195	1.03	0.515	2.00
PCB congener 206	1.19	0.595	1.98
PCB congener 209	1.03	0.515	1.99

(Fig. 1). The park consists of three large human regulated impoundments, hereafter referred to as Rainy, Namakan, and Kabetogama lakes. These large lakes make up 39% of the total park area and are interconnected and regulated by dams used for power generation (Grim and Kallemeyn, 1995). Namakan Lake in this study was a grouping of Namakan, Crane, and Sand Pointe lakes. The lakes of VNP make ideal habitat for bald eagles, but have not been completely isolated from the effects of global industrialization due to atmospheric deposition (Evers et al., 2005). Bald eagle populations at VNP have been monitored since 1973, with nestling blood samples collected in 1989 and annually from 1997 to 2010 (Grim and Kallemeyn, 1995).

2.2. Field methods

We used aerial surveys flown during March each year to determine occupied nests. Occupied nests are any nests with the presence of adults (Postupalsky, 1974). After we identified occupied nests, we removed nestlings from the nest and collected morphometric measurements for age and sex determination, and blood samples at the nest site before the nestlings were banded and returned to the nest (similar to Bortolotti, 1984; Bowerman et al., 1995). We collected no more than 10 mL of whole blood from each nestling in accordance with Clemson University Animal Use Protocol (30067 & AUP2009-005), United States Geological Survey Bird Banding permit, and the United States Fish and Wildlife Service. We stored blood samples on ice for no more than 48 h until we centrifuged the whole blood to separate the plasma from the red blood cells. We then transferred plasma into separate vacuum tubes, and froze plasma samples at approximately −20 °C until laboratory analysis.

2.3. Laboratory methods

We prepared Bald eagle nestling plasma samples for analysis through extraction and cleanup methods described in U.S. Environmental Protection Agency (EPA) Methods 8081 and 8082. We then analyzed nestling plasma for concentration of 30 organochlorine compounds, 20 congeners of PCBs and 10 OC pesticides, using techniques described in Clemson Institute of Environmental Toxicology protocol CIET/SOP 401-78-01 and Environmental Protection Agency methods 8081 and 8082, available from authors upon request. We report the total PCBs, the sum of 18 non-planar congeners and 2 coplanar congeners, as a surrogate for Polychlorinated dibenzodioxin-like PCBs, which are often difficult to quantify (Bergen et al., 1996). Briefly, we denatured 1 mL of nestling plasma using methanol, extracted with dichloromethane, and purified using alumina and silica solid phase extraction. We then analyzed the samples using dual column gas chromatography (GC) with electron-capture detection (Agilent Technologies 7890A GC). We used method detection limits of approximately 2 $\mu g\ kg^{-1}$ for all compounds (Table 1). We extracted Chicken (*Gallus domesticus*) plasma blanks and spikes containing known amounts of all organochlorine compounds alongside nestling plasma for quality assurance. Spiking solutions were produced from pre-manufactured stock solutions with certified quantities of all analytes of interest. We calculated mean percent recovery for all standards and spikes, and required recovery to range from 70% to 130% before samples could be used in subsequent analyses. We only report

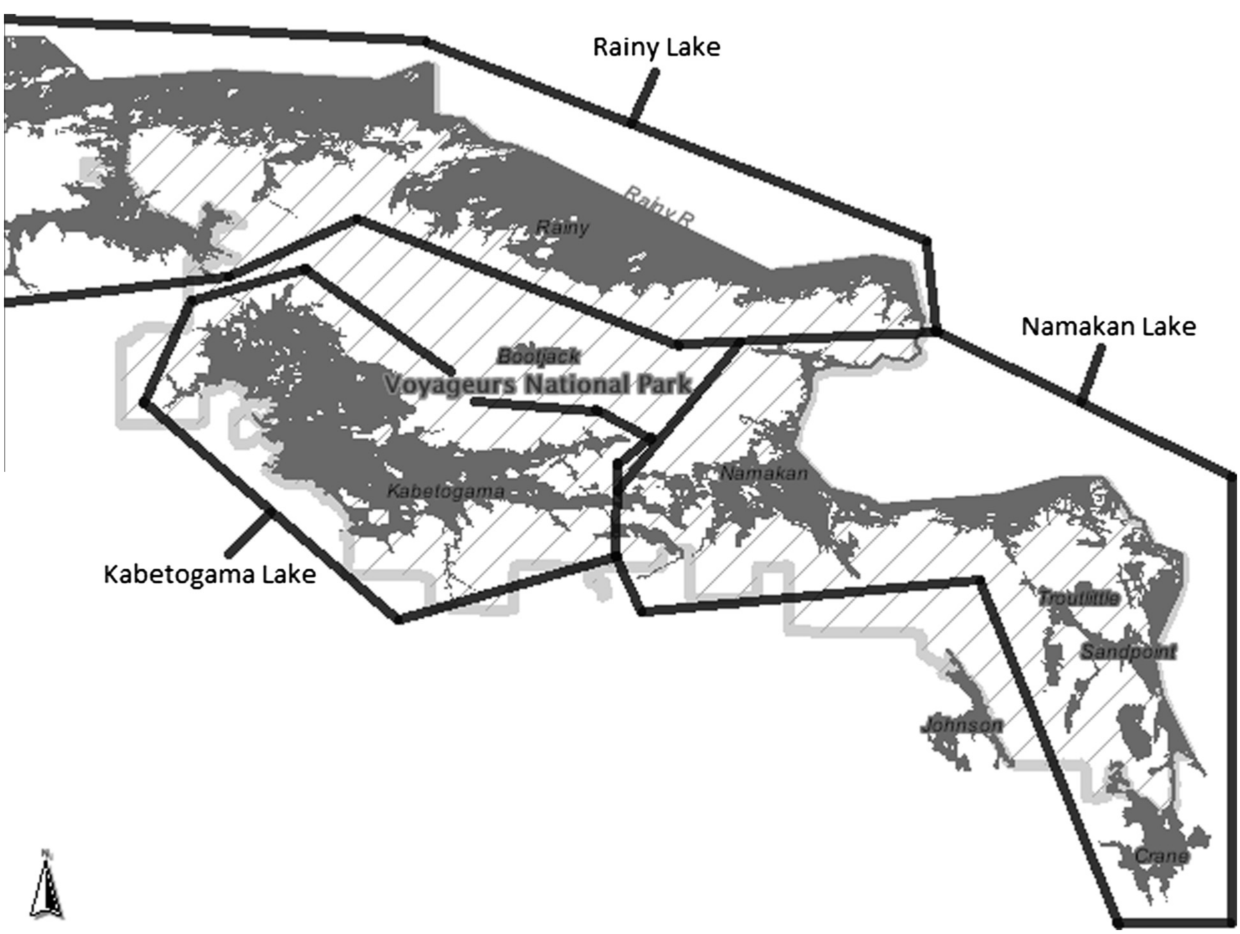

Fig. 1. Designation of major lake units for this study within Voyageurs National Park, Minnesota.

concentration for organochlorine compounds that were present above the method detection limit in greater than 30% of nestling plasma samples. We also report total DDTs as the sum concentration of all DDT degradation products, including 4,4′-DDE, as a measure of DDT in the environment. We reported the degradation product 4,4′-DDE separately as it was the most common DDT degradation product typically representing 50–90% of the total DDTs (Jarvinen et al., 1977). We also report total PCBs rather than individual congeners as effects of individual congeners are often difficult to differentiate. We replaced concentrations below the detection limit of the GC with half of the detection limit of each specific compound for total PCB and DDT calculations. In the case of nests containing multiple samples in a single year, we randomly selected one individual sample before extraction.

2.4. Data analysis

We analyzed concentrations of total PCBs, total DDTs, 4,4′-DDE, and Dieldrin in plasma of nestling eagles at the impoundment level and across years. We also identified individual nest sites where nestling plasma concentrations were high. Individual nests are a single nest location where we sampled nestlings. On occasions where we sampled multiple nestlings from the same nest site in the same year, we randomly selected one nestling to represent that nest site. Since we did not sample every nest-sites in every year, we only report annual and lake means, and relate high concentrations to general portions of the park. Because our data are right skewed and bound on the left by zero, we performed a log-transformation and calculated geometric means from the transformed data (Dykstra et al., 2010). We tested normality of the transformed data using a Shapiro–Wilk test (alpha = 0.05). We examined concentrations from the separate impoundments using a Kruskal–Wallis test (alpha = 0.05) to determine if the impoundment samples belonged to the same distribution. We plotted geometric means to evaluate trends and/or patterns in total DDTs, total PCBs, 4,4′-DDE, and Dieldrin concentrations across years for each impoundment. We used linear regression trend lines (alpha = 0.05) to determine if any statistically significant relationships existed. Since individual samples on the same water body are not spatially independent, we only quantitatively analyze impoundment geometric means. We only analyzed individuals nest from a qualitative perspective because independence would be difficult to assume in these cases. We also compared five year means to determine percent change from 1997 to 2010. We used No Observable Adverse Effects Concentrations (NOAECs) as a benchmark to determine if individual nest samples or lakes were at high risk of possible effects. We considered an area at high risk, compared to other VNP areas, when any individual sample concentration was greater than the NOAECs. We preformed all statistical and summary analyses using the SAS based statistical program JMP 8 (JMP, 2009) and R-statistical program (R Development Core Team, 2010).

3. Results

3.1. Total PCBs

We collected and analyzed plasma samples from 203 nestling bald eagles at VNP from 1997 to 2010 (Table 2). Of all nestlings sampled, we found 48.7% had concentrations of total PCBs below the reportable detection limit for the method and equipment. In every sampling year, we detected concentrations of PCBs in at least one nestling. Levels of total PCBs ranged from non-detects (ND) to 280.1 μg kg^{-1}. We found detectable concentrations of total PCBs have changed from 1997 to 2010, at VNP (Fig. 2). We compared 5-year geometric means from 1997 to 2001 and 2006 to 2010, and found total PCBs have decreased by 26.09%. However, we did not observe a statistically significant decreasing trend in total PCBs. We were able to document that total PCB geometric means concentration have been consistently below the productivity NOAEC of 36.4 μg kg^{-1} established for bald eagles (Bowerman et al., 2003).

Table 2
Number of bald eagle nestling plasma samples collected from 1997 to 2010 at Voyageurs National Park, Minnesota, USA.

Year	*n*
1997	12
1998	11
1999	13
2000	7
2001	15
2002	15
2003	14
2004	9
2005	16
2006	15
2007	11
2008	20
2009	27
2010	18
Total	203

3.2. Total DDTs

In every year of sampling, there were detectable concentrations of total DDTs in 97% of nestlings sampled. Levels of total DDTs ranged from non-detects (ND) to 71.9 μg kg^{-1} (Fig. 2). Detectable concentrations of total DDTs changed from 1997 to 2010, decreasing by 24.09% when we compare the 1997–2001 5-year geometric with the 5-year geometric means of 2006–2010. We observed one significantly decreasing trend on Rainy Lake, one of the three impoundments at VNP ($P = 0.0453$, Fig. 3).

3.3. 4,4′-DDE

In every year of sampling there were detectable concentrations of 4,4′-DDE, and 4,4′-DDE was detected in 95.1% of all nestlings sampled ($n = 203$). Levels of 4,4′-DDE ranged from non-detects (ND) to 68.3 μg kg^{-1}. Detectable concentrations of 4,4′-DDE changed from 1997 to 2010, decreasing by 40.92% when we compared five year geometric means from 1997 to 2001 and 2006 to 2010 (Fig. 2). However, we did not observe any significantly decreasing trends in 4,4′-DDE. This being the case geometric mean concentrations of 4,4′-DDE were consistently below the productivity NOAEC of 11.4 μg kg^{-1} (Bowerman et al., 2003).

3.4. Dieldrin

In every year of sampling, we found detectable concentrations of Dieldrin in at least one sample, and detectable Dieldrin in 61.1% of all samples. Every sample from 2009 and 2010 had measurable concentrations of Dieldrin (2009, $n = 27$ & 2010, $n = 18$). We also observed a 50.25% increase in the 5 year geometric mean concentration when we compared the 1997–2006 geometric mean to the 2006–2010 geometric mean. In 2009 and 2010, we found the greatest geometric mean concentrations, 16.1 μg kg^{-1} and 9.94 μg kg^{-1}, respectively. In every year sampled except 1999 and 2004, we documented an annual geometric mean above the detectable limits (Fig. 2).

3.5. Spatial trends

Overall, we found general trends in total PCB, total DDTs and 4,4′-DDE throughout the park seemed to decrease over the course

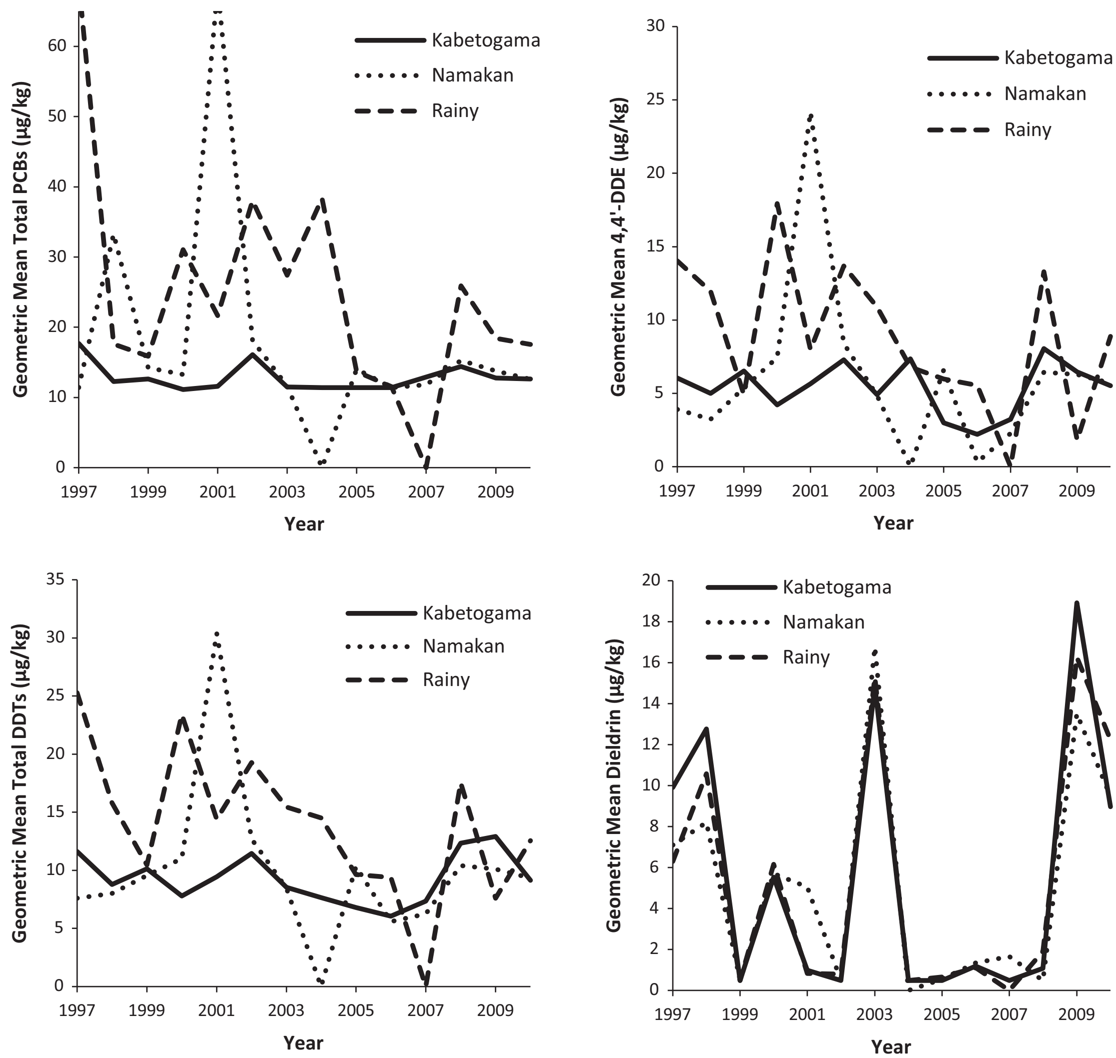

Fig. 2. Annual geometric means for total PCBs, total DDTs, 4,4′-DDE, and Dieldrin for each lake unit from 1997 to 2012.

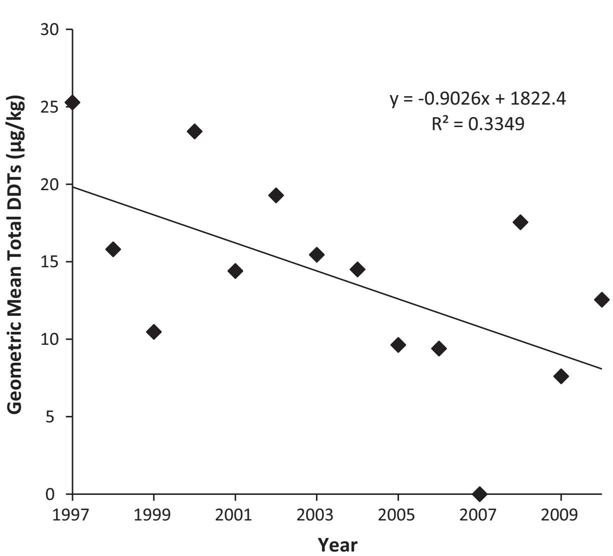

Fig. 3. Annual geometric means of total DDT's on Rainy Lake.

of the study, but only on Rainy Lake was this decrease significant (Fig. 2; $P = 0.0453$, Fig. 3). Namakan (2001) and Rainy (2002, 2004) lakes had annual geometric means greater than the NOAEC of 36.4 $\mu g\ kg^{-1}$ for total PCBs. Annual geometric means of 4,4′-DDE were below the NOAEC (11.4 $\mu g\ kg^{-1}$) on Kabetogama and Namakan lakes but not on Rainy Lake. We documented four annual geometric means of 4,4′-DDE on Rainy Lake, 1997, 2000, 2003, 2008, greater than the NOAEC, ranging from 11.95 to 17.93 $\mu g\ kg^{-1}$. We found Dieldrin concentrations were greater than the method detection limit in 1997, 2000, 2003, 2009 and 2010 across all lakes within VNP.

We examined contaminant concentrations at individual nests to determine possible point sources and relationships between locations on each lake. Of the 203 individual nestling samples collected, 9.4% had total PCB concentrations greater than the PCB NOAEC. Of the 9.4% of nest with concentration greater than the NOAEC, a majority (7.4%) were concentrated on Rainy Lake, while 1.5% were on Namakan Lake and 0.5% were on Kabetogama Lake. We documented 18.2% of all individual nests with 4,4′-DDE concentrations greater than the 4,4′-DDE NOAEC. Of those 18.2% of all nests, 10.8% were located on Rainy Lake, 2.5% on Namakan Lake, and 4.5% on Kabetogama Lake. Our results indicate that Rainy Lake was carrying a majority of the contaminant load within VNP, while Namakan and Kabetogama lakes carried considerably less. We also found concentrations of Dieldrin in nestling plasma samples from all areas of the park rather than concentrated on a single lake or region.

4. Discussion

Researchers have monitored concentrations of PCBs, DDTs, 4,4′-DDE, and Dieldrin in bald eagle nestlings throughout the entire Great Lakes region and found concentrations that are considerably higher than those we found at VNP. Overall concentrations in the Great Lakes have been significantly decreasing since the early 1980s (Roe, 2001; Bowerman et al., 2002). In VNP, geometric means of total PCBs and 4,4′-DDE were considerably higher in nestling plasma from 1989 to 1992 than those from 1997 to 2010 (Bowerman et al., 1993). The levels have dropped from 47.36 μg kg^{-1} to 0.05 μg kg^{-1}, which is a 70.78% decrease in total PCBs from 1989–92 to 2010. Concentrations of 4,4′-DDE at VNP from 1989 to 1992 were 20.28 μg kg^{-1}, and have decrease to 6.36 μg kg^{-1} in 2010, accounting for a 68.6% decrease in concentrations of 4,4′-DDE. Comparison to the Great Lakes of Michigan also shows that VNP has considerably lower concentrations of total PCBs and 4,4′-DDE. The closest comparable levels to any found at VNP over the past 14 years are in inland sections of the Upper and Lower Peninsulas of Michigan (Wierda, 2009). The closest comparable 4,4′-DDE concentrations were in the Lower Peninsula Michigan (Wierda, 2009). Overall VNP has had considerable decreases in total PCB and 4,4′-DDE concentrations since the early 1990s as would be expected, and similar to trends observed in the Great Lakes (Bowerman et al., 2002). Concentrations at VNP are also lower than ones observed on the Wisconsin Shoreline of Lake Superior and the upper Mississippi River from 2006 to 2008 (Dykstra et al., 2010). However, concentrations on the St. Croix River, a partial border between Wisconsin and Minnesota, of total PCBs and 4,4′-DDE were comparable or lower than those at VNP. Overall, concentrations of total PCBs and most OC pesticides at VNP are among some of the lowest in the Great Lakes and Upper Midwest Regions of North America and are decreasing in concentrations similar to other in the region.

PCBs and OC pesticides demonstrate similar effects in aquatic systems that are difficult if not impossible to contribute to one or the other (Bowerman et al., 1995). In many cases, both PCBs and OCs are associated with diminished productivity and health in bald eagles (Kozie and Anderson, 1991; Bowerman et al., 2003). However, 4,4′-DDE was found to be the causative agent in the historic decline of bald eagles because high eggshell concentrations resulted in thinner eggshells that significantly reduced the reproductive performance of bald eagles (Wiemeyer et al., 1984, 1993). 4,4′-DDE has also been associated with low productivity in Maine, the Great Lakes, and the west coast of North America (Krantz et al., 1970; Bowerman et al., 1995; Weseloh et al., 2002; Cesh et al., 2008). Further, 4,4′-DDE has also been associated with low reproduction in Osprey (*Pandion haliaetus*) along the Delaware River (Anthony et al., 1993). That being the case, it is difficult to determine what effects PCBs and other OC pesticides may have on bald eagles since they are usually positively correlated with 4,4′-DDE (Anthony et al., 1993). Until 4,4′-DDE concentration are at or near zero in the environmental or controlled laboratory experiments can be conducted we cannot easily determine the direct effects of PCBs and other OCs (Bowerman et al., 1995; and others).

The relationship between productivity, the number of nestlings per nest, and total PCBs and 4,4′-DDE concentrations has been established for bald eagles of the Great Lakes prior to the recovery of this population (Bowerman et al., 1995). 4,4′-DDE and total PCBs are often in these areas a limiting factor to population growth. Based on established equations to calculate productivity in bald eagles of the Great Lakes, estimates of productivity can be found for VNP (Bowerman et al., 2003). At the concentrations observed in 2010, productivity based on PCB concentrations would be 1.16 nestlings per active nest, and based on 4,4′-DDE it would be 1.09 nestlings per active nest. Researchers suggest that productivity rates of 1.0 nestling per active nest are adequate for population growth and that productivity as low as 0.7 nestling per active nest is enough to maintain populations (Sprunt et al., 1973; Elliott and Harris, 2001; Bowerman et al., 2002, 2003). The long-term estimated productivity rates at VNP are indicative of a growing and healthy population of bald eagles based on previously established relationships between productivity and environmental contaminants (Wiemeyer et al., 1993). According to concentrations observed at VNP and estimated productivity based on Great Lakes bald eagles the population at VNP during 1997–2010 has been in good health and growing.

In the 1970s new environmental regulations almost eliminated direct sources of PCBs and OCs (Anthony et al., 2007). However, in recent decades atmospheric deposition been considered a means of transport and distribution of PCBs and OCs throughout the environment (Anthony et al., 2007). Many countries in Asia and Africa still have minimal regulations on the use of OCs and PCBs, resulting in higher levels and continued deposition of these compounds (Hoff et al., 1992; Anthony et al., 2007; Odabasi et al., 2008; Kim et al., 2009) and these countries could be a source for atmospheric concentrations (Jaward et al., 2004; Pozo et al., 2006, 2009; Lee et al., 2007). Volatilization of PCBs and OCs is a potential source of concentrations in VNP, as well those sources still present in sediments (Froese et al., 1998; Schneider et al., 2001). Unusual spikes and fluctuations in concentrations could be attributed to atmospheric or sediment loadings of PCBs and OCs (Froese et al., 1998; Agrell et al., 2002). Seasonal fluctuations from atmospheric deposition are dependent on precipitation, temperature, and atmospheric concentrations of PCBs and OCs (Agrell et al., 2002). We found several fluctuations in nestling concentrations at VNP of 4,4′-DDE. These fluctuations come after water level stabilization by the International Joint Commission in 2000 and could possibly be due to atmospheric deposits of PCBs and OCs on the surface waters of VNP (International Rainy Lake Board of Control, 2004). These fluctuations would be cause for concern if concentrations were above NOAECs, but no fluctuations have been above these concentrations.

Dieldrin is an OC pesticide very similar in production, use, and environmental fate to DDT. It was the second most utilized OC only to DDT in the 1960s (Jorgenson, 2001). Dieldrin was still being produced in the US, and global stockpiles of the chemical still exist as of 1999 (Jorgenson, 2001). Dieldrin is very persistent in the environment and its presence in the Canadian arctic snowpack suggests its possible transportation via atmospheric pathways (Gregor and Gummer, 1989). Dieldrin has the potential to be a serious environmental contaminant and is a persistent organic pollutant of global concern (Jorgenson, 2001). It can cause egg lethality in golden eagles (1000.0 μg kg^{-1} Wiemeyer et al., 1984), and has been implicated in lethal and sub-lethal effects in adult bald eagles (Coon et al., 1970).

Dieldrin was the only monitored compound at VNP that has been increasing over the past 14 years. The rate of increase raises concerns about effects in the environment, and the source of this compound. While there are no significant trends in geometric means concentrations over time, we did observe a 52.25% increase when we compare the 5-year geometric mean from 1997 to 2001 to the mean from 2006 to 2010. The geometric means from samples collected in 2009 and 2010 (16.1, 9.94 μg kg^{-1} respectively) were also much higher than those observed elsewhere in the Great Lakes region (Donaldson et al., 1999). Concentrations in nestling plasma from the early 1990s from lakes Erie, Nipigon, Superior, and Lake of the Woods (geometric means 3.1, 3.0, 5.1, and 3.1 μg kg^{-1}, respectively) were much lower (Donaldson et al., 1999). Further research of the effects and accumulation rates of Dieldrin is necessary to determine if current nestling concentrations might affect bald eagles in the future. In addition, a 52.25% increase in concentrations over the past 14 years causes reason to believe a source or sources of Dieldrin may be present in the VNP area, legacy contaminations still persist in the VNP area, or an atmospheric source maybe present similar to other legacy OC pesticides (Weber et al., 2010; Bergknut et al., 2011) and needs further examination.

In summary, VNP has a growing and healthy bald eagle population, and to maintain that population, continued environmental monitoring will be necessary. The persistence of PCBs and OCs in the environment warrants continued monitoring since new and past sources could arise. Although only one trend was significant, Rainy Lake total DDTs, most concentrations have been decreasing over the 14 year study period. Concentrations of total PCBs and 4,4′-DDE are among the lowest in North America, but trends in annual concentrations are not consistent enough due to annual fluctuations to discontinue monitoring programs. Concentrations of Dieldrin are among the highest observed in nestling plasma samples in recent years and annual fluctuations suggest the presence of some type of environmental process or deposition source. Overall VNP's bald eagle population and ecosystem health are not in jeopardy from environmental contaminants at the present time, but future monitoring will be necessary and could provide useful insight to the environmental process that effect the concentrations of persistent OC contaminants.

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