Ecotoxicology (2011) 20:1626–1635
DOI 10.1007/s10646-011-0736-8

Using nestling feathers to assess spatial and temporal concentrations of mercury in bald eagles at Voyageurs National Park, Minnesota, USA

H. T. Pittman · W. W. Bowerman · L. H. Grim · T. G. Grubb · W. C. Bridges

Accepted: 2 July 2011 / Published online: 16 July 2011

Abstract Bald eagles (*Haliaeetus leucocephalus*) have been utilized as a biosentinel of aquatic ecosystem health in the Great Lakes Region since the early 1960s. Bald eagle populations have been monitored at Voyageurs National Park (VNP), Minnesota, since 1973. For the past 20 years, researchers have collected feathers from nestling bald eagles to assess their dietary exposure to mercury (Hg) on Rainy, Kabetogama, and Namakan lakes in VNP. Mercury is an environmental pollutant with both natural and anthropogenic sources, and negatively affects many species of wildlife. In a previous study, geometric mean concentrations of Hg in feathers of nestling bald eagles were greater at VNP (20 mg/kg Dry Weight (DW)) than in nestling feathers from other Great Lakes subpopulations ($\sim$7 mg/kg DW), for the period 1985–1989. Current geometric mean concentrations have declined by 77.4% since 1989 at VNP. While all samples from 1985 to 1989 had detectable concentrations of Hg, 10% of current samples had concentrations below the reportable detection limit (0.001 mg/kg DW, $n = 180$). The major lakes at VNP are impounded, and Hg concentrations also declined greatly after the lake level stabilization order by the International Joint Commission was implemented in 1999. Mercury concentrations in feathers of nestling bald eagles from 1989 to 2010 ranged from ND (<0.001) to 34.97 mg/kg DW. The highest single concentration in a nestling was from Namakan Lake in 2010. The five-year geometric means for Rainy, Kabetogama, and Namakan lakes for 2006–2010 were 6.08, 1.07, and 5.56 mg/kg DW ($n = 28$, $n = 32$, $n = 27$) respectively. Although Hg concentrations in feathers of nestlings greatly declined after the change in water level management in 1999 and are lower than 1989 concentrations, recent samples suggest a gradual increase. Continued monitoring of nestling feather concentrations will be essential to assess this increase, to determine the source of Hg, to determine if there are changes to methylation potential, and to evaluate and optimize water level management.

Keywords Mercury · Hg · Bald eagle · *Haliaeetus leucocephalus* · Nestlings · Voyageurs National Park

H. T. Pittman · W. W. Bowerman
Department of Forestry and Natural Resources, Clemson University, 261 Lehotsky Hall, Clemson, SC 29631, USA

Present Address:
H. T. Pittman
Arkansas Cooperative Fish and Wildlife Research Unit, Department of Biological Sciences, SCEN 632, 1 University of Arkansas, Fayetteville, AR 72701, USA

W. W. Bowerman (✉)
Department of Environmental Science and Technology, University of Maryland, 1109 H. J. Patterson Hall, College Park, MD 20742, USA
e-mail: wbowerma@umd.edu

L. H. Grim
Voyageurs National Park, 3131 Highway 53 South, International Falls, MN 56649, USA

T. G. Grubb
US Forest Service, Rocky Mountain Research Station, 2500 South Pine Knoll Drive, Flagstaff, AZ 86001, USA

W. C. Bridges
Department of Applied Economics and Statistics, Clemson University, 243 Barr Hall, Clemson, SC 29687, USA

Introduction

Mercury (Hg) and methylmercury (MeHg), its bioavailable form, are present naturally in the environment, but in recent years, concentrations have increased in the aquatic environment. These concentrations are at levels that may affect avian species. Mercury has three major sources in the environment: natural deposits in the soil; point and non-point source anthropogenic releases; and, wet and dry atmospheric deposition from both of these sources (Chan et al. 2003; Driscoll et al. 2007). Natural releases of Hg depend on the amount present in the bedrock and soils of an area. Mercury is released as the soils and bedrock weather by chemical processes over time. Anthropogenic point sources are typically associated with toxic waste dumps/spills, chlor-alkali plants (Firmreite 1974; Gardner et al. 1978; Barr 1986; Adair et al. 2003), mining and smelting operations (Chan et al. 2003; Evers et al. 2005; Driscoll et al. 2007), wastewater treatment plants (Glass et al. 1990), and medical waste incineration (Driscoll et al. 2007). Atmospheric deposition of Hg from both natural and anthropogenic sources can affect ecosystems on a global scale (Chan et al. 2003; Evers et al. 2005; Driscoll et al. 2007). While Hg is released into the atmosphere by geological events such as volcanic activity (Chan et al. 2003), anthropogenic sources currently contribute 33% to 36% of global Hg emissions through electric utilities, burning fossil fuels, and waste incinerators (Chan et al. 2003; Driscoll et al. 2007). Much of the anthropogenic deposition at Voyageurs National Park (VNP) potentially comes from an airshed shared with many rapidly developing and less regulated Asian countries (Strode et al. 2008). These factors have all contributed to the increase in Hg concentrations in VNP and its surrounding areas.

Annual water level fluctuations are a major factor in the availability and chemical form of Hg in the environment (Ramlal et al. 1987; Sorensen et al. 1990). Natural processes involving sulfate-reducing bacteria convert inorganic Hg to MeHg, Hg's most toxic form, in inundated soils (Westcott and Kalff 1996). MeHg, unlike inorganic Hg, is bioavailable. Similar to other environmental contaminants, MeHg causes adverse effects as it biomagnifies in food webs causing the greatest adverse effects on tertiary species (Evers et al. 2003). This characteristic of MeHg makes it a relevant contaminant for study and requires regular monitoring to ensure concentrations do not reach thresholds associated with serious harm at the individual, subpopulation, population, or ecosystem level.

Bald eagles (*Haliaeetus leucocephalus*) are tertiary predators of aquatic food webs that have been used as efficient and effective sentinels to monitor contaminants such as MeHg in North America since the 1960s (Bowerman et al. 1994; Jagoe et al. 2002; Evers et al. 2005; Bechard et al. 2009). Since the 1960s, the effects of MeHg on avian species have caused increased concern for scientists and policy makers. Bald eagles were first recommended for use as a biosentinel of water quality in the Great Lakes Water Quality Agreement and have been used by the International Joint Commission (IJC) as a monitor of ecosystem health and water quality (Bowerman et al. 2002). Numerous studies from Florida, South Carolina, Maine, and the Great Lakes region have used bald eagle adults and nestlings as an indicator of Hg concentrations and ecosystem health (Bowerman et al. 1994; Jagoe et al. 2002; Evers et al. 2005; Bechard et al. 2009; Dykstra et al. 2010).

Life history characteristics and sampling methods are well documented for bald eagles, making them an ideal bioindicator species of Hg concentrations (Hollamby et al. 2006). Because the bald eagle has been intensively studied, and nearly all of the active nests in a study area can be observed, it is one of a few species for which a population measure can be determined (Bowerman et al. 2002). Since bald eagles are long-lived, territorial nesters, and show high nest fidelity, they provide a representation of the Hg concentrations in a tertiary predator of the aquatic environment for both spatial and temporal trends (Bowerman et al. 1995; Hollamby et al. 2006). Their primarily piscivorous diet allows monitoring efforts to assess bioaccumulation of Hg in the environment and provides insight into the health of the ecosystem and water quality (Bowerman et al. 2002; Bowerman et al. 1995).

While eagles provide a good indication of Hg accumulation, they are not a sensitive indicator of the effects of Hg. To date, no study has found a significant relationship between feather Hg concentrations and bald eagle reproductive rates (Bowerman et al. 1994). Recent studies have shown that bald eagles can convert the more harmful MeHg to less harmful inorganic forms (Scheuhammer et al. 2007; Scheuhammer et al. 2008). However, Hg has been shown to cause adverse effects on behavior, reproduction, hormone production, and neurological function in other avian species (Chan et al. 2003; Scheuhammer et al. 2007; Burgess and Meyer 2008; Evers et al. 2007). Moreover, Scheuhammer et al. (2008) argued, and Rutkiewicz et al. (2011 in press) confirmed, that increased Hg levels are correlated with changes in certain neurobiochemicals in the eagle brain. Indeed, controlled studies on the sub lethal, neurological, and behavioral effects of Hg on bald eagles have not been conducted as they have on other species (Bowerman et al. 1994; Scheuhammer et al. 2008).

Study Area

VNP was established in 1975 to protect 88,628 ha, of which most is water ways or southern boreal forest on the United States border with Canada in northern Minnesota (Fig. 1). Bald eagle populations at VNP have been monitored since 1973, with feather samples collected from nestlings since 1989 (Grim and Kallemeyn 1995). The park consists of

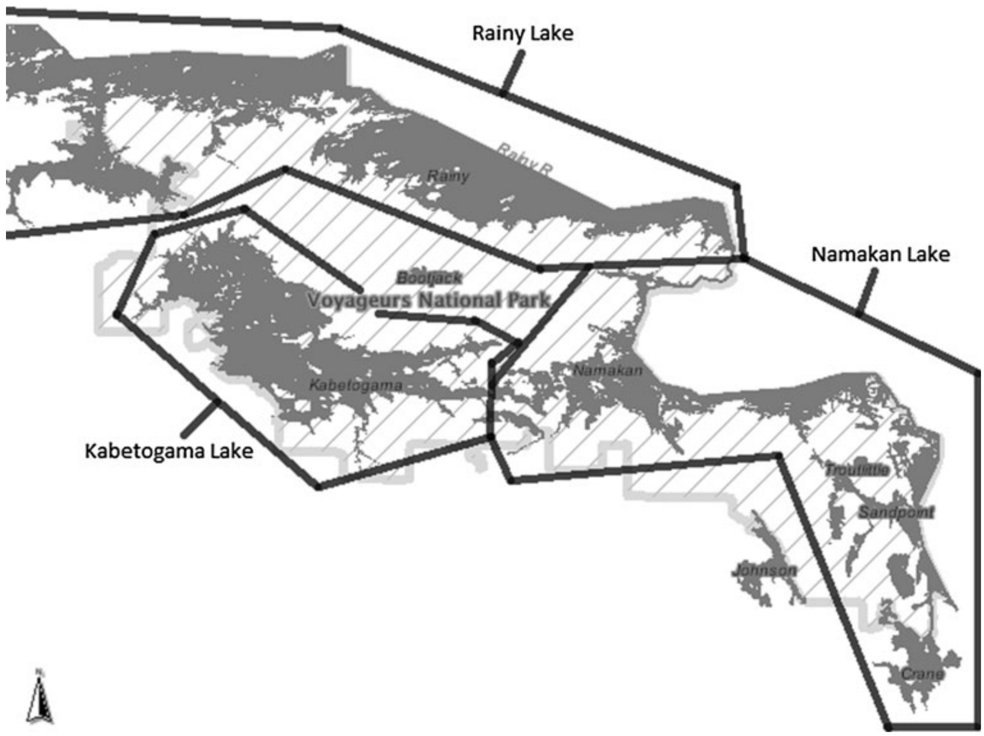

Fig. 1 Designation of major lake units for this study within Voyageurs National Park, Minnesota

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. These lakes 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). Lakes, especially impoundments, tend to have the highest Hg concentrations compared to riverine and coastal ecosystems (Scheuhammer et al. 2007). VNP has a high potential for methylating Hg due to an abundance of wetland habitat (Grim and Kallemeyn 1995). These factors combined make VNP a potential high risk area for high environmental Hg concentrations. The objective of this study was to determine if Hg concentrations in feathers of nestling bald eagles from nests in VNP varied spatially (i.e., differed among lakes) and/or temporally, for the period 1989–2010, with a focus on the period of 1999–2010.

Methods

Field methods

Aerial surveys are flown during the second week of April each year. The shorelines of all three large impoundments and inland lakes where eagle activity has been observed are surveyed and occupied nests are recorded. An occupied nest is any nest with the presence of adults, eggs, or nestlings. A second survey is conducted the first week of May to determine those nests that have become active due to late nesting birds. Active nests are surveyed in mid-June prior to banding to determine the productivity or number of young produced per active nest. Aerial surveys determine the number of nests with young present for the field crew to sample in late June. Nest trees are climbed and nestlings are lowered to the ground where morphometric measurements are taken, for age and sex determination, and 3–5 breast feathers are taken before the nestlings are banded and returned to the nest (Bortolotti 1984). In early July, a final flight is conducted to determine successful nests where at least one young fledged.

Lab methods

Sample preparation

Feather samples were washed using 50 ml of an approximate 5% commercial low acid detergent (Citranox®) and water solution in a plastic bag. The feathers were then placed in clean bags and rinsed three times with distilled water before storage in 2 ml screw top vials with Chemwipes® folded around the open top and secured with rubber bands. After all feather samples were washed and prepared, they were frozen at −20°C for at least 24 h before freeze drying. The nestling feathers were freeze dried for

72 h after which they were placed in a vacuum to keep out moisture until the samples are digested. Samples were then weighed to 0.05 g (±0.005 g), placed in 100 ml glass digestion tubes, and capped with a glass marble. Samples are digested in groups of 16. Once a group was weighed, 10 ml of a 70:30 concentrated trace metal grade nitric and sulfuric acid solution were added to the tubes to liquefy the feather samples. The samples were placed in a block heater at 80°C for 30 min then removed and allowed to cool for 30 min. The solutions were then poured into 250 ml glass jars and diluted to 1:20 (v/v) using deionized water. Parafilm® was placed over the jars and the caps were tightened.

Hg analysis

Samples were analyzed using the United States Environmental Protection Agency Method 245.7. This method for total Hg requires use of a cold vapor Atomic Florescence Spectrometer (AFS) (Aurora AI 3200). The instrument parameters for Hg are: detector wavelength 237.7 nm, gas flow rate = 400 ml/min, pump speed = 60 rpm, atomized temperature = 200°C, rinse time = at least 60 s, uptake time = 60 s, integration time = 20 s, 3 replicates, and reductant = 10% (w/v $SnCl_2$ in 10% (v/v) HCl). The detection limit for Hg on the AFS is 1.0 ng/l.

The sample Hg concentrations are estimated and checked for quality assurance using Hg Reference Standard Solution by Fisher Scientific and prediction curves. An initial standard solution of 1000 mg/kg dry weight (DW) (±1%) is used to make five different Hg solutions (1, 2, 5, 10, and 20 mg/kg DW). These standards are analyzed on the AFS with three replicates to calculate a standard curve for estimation of sample Hg concentrations. Quality checks are preformed every five samples. If the quality check differed from the standard curve, the concentrations were not accepted, a new standard curve was calculated, and the samples were rerun. Samples were adjusted to dry weight (DW) in mg/kg using initial feather weights.

Data analysis

Concentrations of Hg in feathers of nestling eagles were analyzed for both spatial and temporal variation. All Hg concentrations below the detection limit of the AFS were replaced with half of the detection limit (0.0005 mg/kg DW) and in the case of territories and nests containing multiple samples in a single year, only one individual sample was randomly selected prior to Hg analysis. The normality assumption was tested using a Shapiro–Wilk test (alpha = 0.05). Lake samples were examined using a Kruskal–Wallis test (alpha = 0.05) to determine if the lake samples belonged to the same distribution. Geometric means were calculated from the log transformed concentrations to adjust for the data being right skewed and bound by zero on the left as in Dykstra et al. (2010). The use of geometric means also reduces the effect of extreme values on the interpretability of means. These geometric means were then plotted to look for trends and/or patterns in Hg across years for the lakes using linear regression to find trend lines (alpha = 0.05). The assumption of sample independence was accounted for by only quantitatively analyzing lake means, other analysis of territories and individual nest were left to strictly qualitative analysis since independence would be difficult to assume in these cases. Five year means were also compared to examine percent change from 1999 to 2010. Since no threshold concentration has been established for nestling feather Hg, the upper fence or approximate 95th percentile was used, 10 mg/kg DW for territories and 20 mg/kg DW for individual nest sites. A territory is a defined area that may contain one or more individual nests over the study period but during any single year will only contain one individual nest. An individual nest is defined as a single nest location where nestlings were sampled. Any territories with means greater than 10 mg/kg DW and any individual nest with concentrations greater than 20 mg/kg DW were considered high with respect to other VNP samples. The general location of territories with geometric means that were considered high were determined, and were confirmed by the locations of nest with concentrations greater than 20 mg/kg DW. Calculations and plotting were performed using the SAS based statistical program JMP 8 (JMP 1989–2007) and R-statistical program (R Development Core Team 2008).

Results

The ability to report detectable concentrations of Hg in feathers of nestling eagles has changed over time. Our findings indicate that 90% of nestling feather samples contain detectable concentrations of Hg. The findings also indicate that between 1989 and the five year mean from 2006 to 2010, concentrations decreased 77.4%. The range of Hg concentrations in VNP since 1999 was ND to 34.97 mg/kg DW with the highest concentration from a nestling sampled on Namakan Lake in 2010. The geometric standard deviations (GSD) of concentrations and sample sizes for Kabetogama, Namakan, and Rainy lakes were respectively, GSD = 7.27, 6.97, and 5.77, and $n = 63$, 53, and 62. The greatest decrease in Hg concentrations from year to year occurred between 1999 and 2000 on Rainy and Kabetogama lakes with a less extreme decrease on Namakan Lake (Fig. 2). This is the period when lake levels on Rainy and Namakan lakes were stabilized by the IJC to

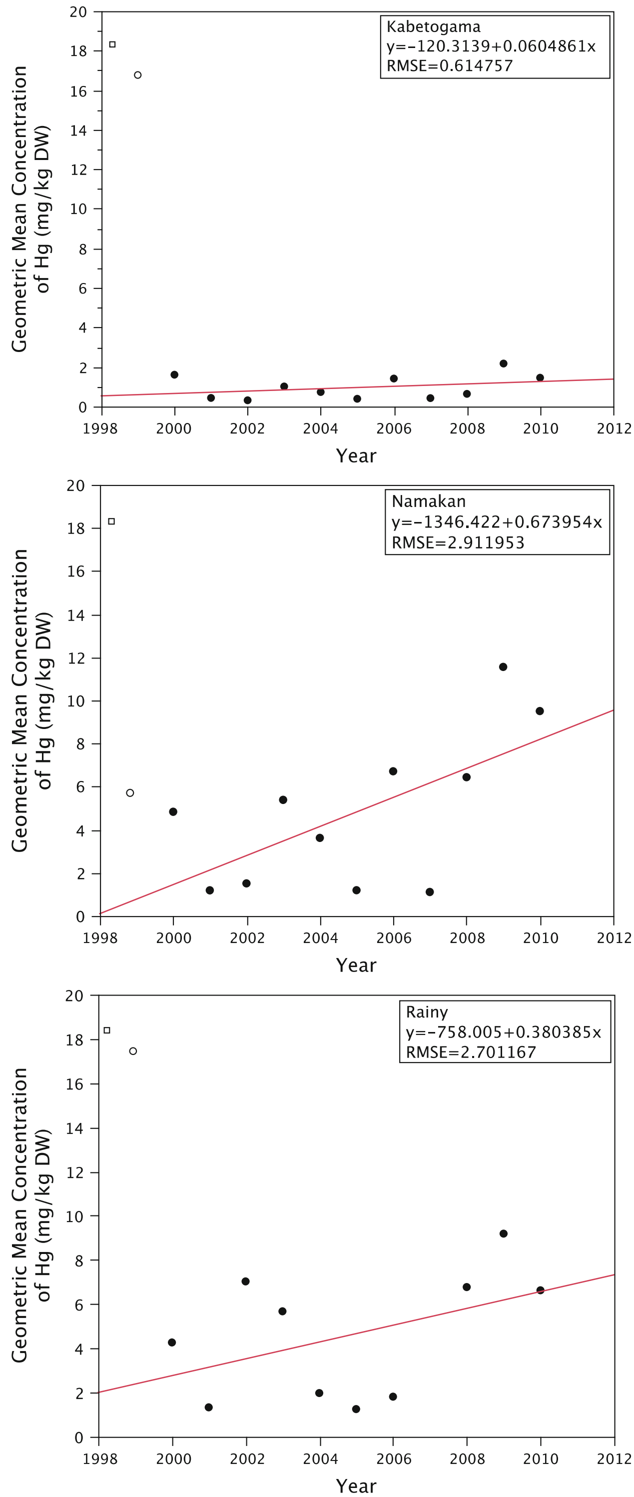

Fig. 2 Post stabilization (2000–2010) yearly geometric means of Hg in feathers of nestling eagles by lake. Solid lines represent trends. Only the trend on Namkan Lake was significant but still only represent a moderate proportion of the variation in yearly means ($r^2 = 0.241649$, 0.249757, 0.103616 respectively). Root Mean Squared Error (RMSE) is reported for all analysis. *Square symbol* indicates the 1989 geometric mean of Hg for VNP (18.3 mg/kg DW). The Hollow data points represent 1999 means but are not included in the trend lines

mimic more natural fluctuations (International Rainy Lake Board of Control 2004). Hg concentrations in feathers of nestlings from 2005 to 2010 for Rainy, Kabetogama, and Namakan lakes were 6.08, 1.07, and 5.56 mg/kg DW respectively, which represent major decreases since 1989 on all three lakes (68.9, 72.1, and 58.4% respectively; Fig. 2). In the same period 22% of the samples were below detectable limits and only two samples were greater than 20 mg/kg DW. No significant trends in the original data were found on Rainy and Kabetogama lakes ($P = 0.6421$, $P = 0.1531$, respectively), but a significant increase was observed on Namakan Lake ($P = 0.0118$, Fig. 2). Trends were also examined for the period after the lake stabilization order, 2000–2010. On all three lakes, trends were increasing, yet none were significant and regression only explained a moderate proportion of the variation in means (Fig. 2). Spatial analysis of the VNP data over the past 12 years shows that some nest locations, territories, and portions of the park suggest localized areas of high mercury concentrations. Four territories with means greater than 10 mg/kg DW and nine individual nests with concentrations greater than 20 mg/kg DW were concentrated in two areas of the park. One area was in the northwestern portion of the park on Rainy Lake, specifically near Black Bay. The other area was on Sand Point and Crane lakes in the southeastern portion of the park listed in the Namakan Lake study area.

Discussion

Mercury at high concentrations has been linked to hormonal, behavioral, and neurological effects, all of which have been implicated in diminished reproductive success in wildlife. Mercury's effects have been studied in multiple instances with amphibians, reptiles, mammals, and birds, but no adverse effects on productivity have been observed in bald eagles (Bowerman et al. 1994). Also no field studies have found a relationship between Hg concentrations and reproduction at observed levels, but this does not rule out the possibility of a relationship at levels greater than those previously observed (Bowerman et al. 1994; Scheuhammer et al. 2008). A concentration of 0.5 mg/kg wet weight (WW) of Hg in the eggs of bald eagles has been considered a lethal threshold for failure to hatch based on effects observed in mallard ducks (*Anas platyrhynchus*) (Heinz 1979; Wiemeyer et al. 1984). Concentrations in adults as low as 7.5 mg/kg DW in feathers have been linked to sublethal effects in other avian species (Eisler 1987). These threshold concentrations may be underestimated since no organochlorine and polychlorinated biphenyl analyses were conducted, which is critical since these compounds can have similar effects that can be mistaken for effects caused by high concentrations of Hg. Also other studies have shown bald eagles have an inherent ability to metabolically demethylate MeHg in the body reducing concentrations in the critical organs such as the brain and liver (Scheuhammer et al. 2008). Research has also determined that in bald eagles, like other birds, that feathers are a major excretory route, with 49–93% of the total Hg burden being sequestered in the feathers and eliminated from the body with each molt (Tejning 1967; Hakkinen and Hasanen 1980; Buhler and Norheim 1982; Braune and Gaskin 1987). This evidence supports the suggestion that Hg may not affect reproduction in bald eagles but until areas with higher than previously found concentrations are examined, without confounding concentrations of organochlorine pesticides or PCBs, or/and controlled laboratory studies are preformed, the link cannot be definitively ruled out.

Mercury has been monitored in bald eagles from the Great Lakes region since the mid 1980s and data exists for comparative purposes covering the same time periods as this study (Fig. 3). The geometric means for nestlings in Michigan from 1984 to 1989 were 8.0 mg/kg DW, while nestlings in VNP had a mean of 18.33 mg/kg DW (Bowerman et al. 1994). Nestling concentrations from the same time period at lakes within VNP were also greater than those observed on lakes Superior, Huron, and Michigan (Bowerman et al. 1994). Mercury concentrations in nestling feathers from around the Great Lakes ranged from 1.5 to 27 mg/kg DW, which is similar to the ND-34.97 mg/kg DW range observed at VNP in this study. Mercury concentrations on the Wisconsin shore line of Lake Superior from 2006 to 2008 (3.88 mg/kg WW) were greater than those during the same period at VNP (1.73, 0.14, and 1.45 mg/kg DW). Concentrations on the Mississippi and St. Croix rivers in Wisconsin were also greater than those at VNP from 2006 to 2008 (3.13, 4.54, and 6.81 mg/kg WW) (Dykstra et al. 2010). VNP is adjacent to the Great

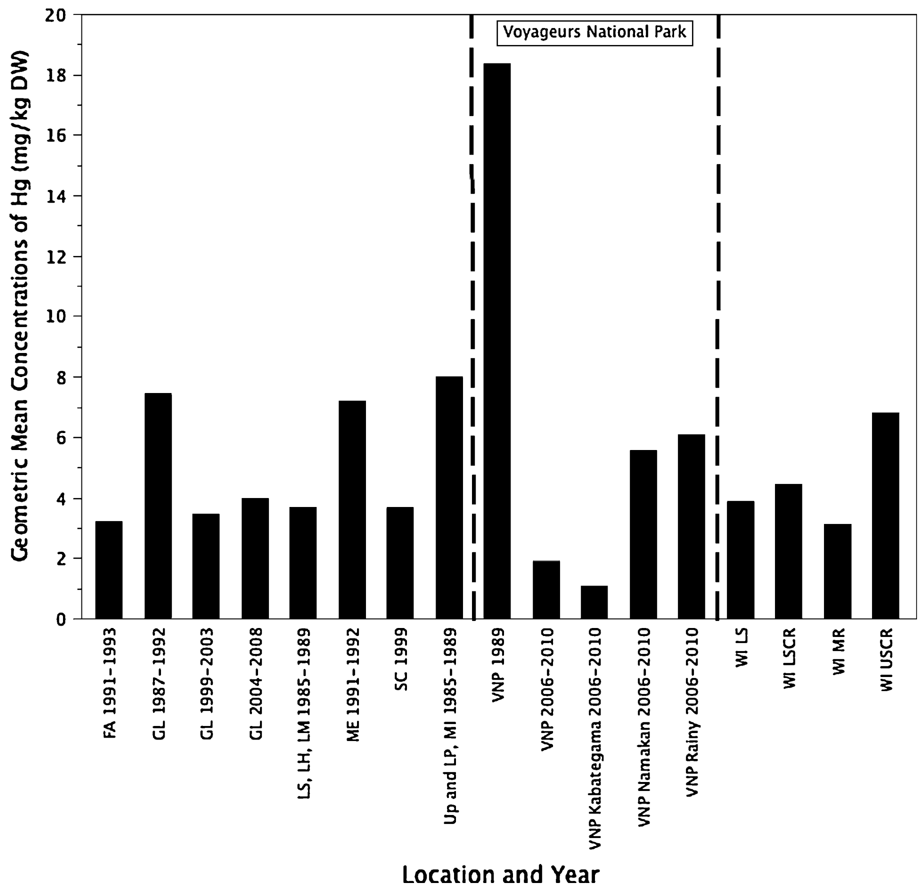

Fig. 3 Values are geometric means except for South Carolina 1999, which is an arithmetic mean. All values are calculated from Hg levels determined by analysis of nestling bald eagle feathers. VNP = Voyageurs National Park, Minnesota (*n* = 8, 32, 27, 28 GSD = 7.5, 7.94, 5.09, 6.12), USA; UP = Upper Peninsula, Michigan, USA (*N* = 64); LP = Lower Peninsula, Michigan, USA (*n* = 49) (Bowerman Unpublished); ME = Maine, USA (Welch 1994); FA = Florida, USA (*n* = 61 Range (0.76–14.30)) (Wood et al. 1996); SC = South Carolina (*n* = 10 SD = ±1.91), USA (Jagoe et al. 2002); GL = Great Lakes Region, USA; LS, LH, LM = lakes Superior, Huron, and Michigan (*n* = 92) (Bowerman et al. 2002);WS LS = Wisconsin Lake Superior (*n* = 29); WI MR = Wisconsin Mississippi River (*n* = 51); WI LSCR = Wisconsin Lower St. Croix River (*n* = 14); WI USCR = Wisconsin Upper St. Croix River (*n* = 19) (Dykstra et al. 2010)

Lakes region, but based on historical and current Hg concentrations, the difference in Hg concentrations is likely due to changes in water level management, affecting methylation, as opposed to changes of input levels to the Great Lakes. According to previous research, the major source of Hg in VNP is atmospheric deposition, which can be confounded by the great methylation potential at VNP (Wiener et al. 2006). This being the case, the gradual increase in mean concentrations since 2000 at VNP, is cause for concern, possibly suggesting emissions from developing Asian countries or domestic emissions as the cause (Strode et al. 2008). This can be inferred since the large changes in methylation rate and Hg release from organic material were considerably reduced when lake levels were controlled to resemble more natural conditions in 1999. This portion of North America is typically vulnerable to this source of Hg since atmospheric Hg from global sources does reach the upper Midwest and potential for methylation is great (Strode et al. 2008).

Mercury concentrations in nestling bald eagles have been studied in fresh water ecosystems in areas outside the Great Lakes, including Florida, South Carolina, and Maine over the past 20 years (Fig. 3). Mean concentrations in Florida lakes (3.23 mg/kg WW) were similar to Great Lakes concentrations in 1991–1993 but the closest years at VNP 1989 and 1999 were much higher, 18.33 mg/kg DW and 13.73 mg/kg DW respectively (Wood et al. 1996). In South Carolina, 1998–1999, Hg arithmetic mean concentrations from nestling feathers were 2.49 and 3.67 mg/kg DW respectively, while in 1999 at VNP nestling concentrations ranged from 5.57 to 25.55 mg/kg DW, considerably higher (Jagoe et al. 2002). Concentrations in feathers in nestlings from Florida did not differ from those in South Carolina, which is reasonable, considering that they share similar air sheds. Bald eagles in Maine show slightly higher concentrations than Florida and South Carolina, with a geometric mean of 7.2 mg/kg DW, but concentrations from Maine are likely less than would be expected if the airshed influenced was on a freshwater ecosystems due to the inherent differences of contaminant concentrations between marine and freshwater systems (Welch 1994). This could be because the air shed of Maine includes more heavily industrialized areas than those in Florida and South Carolina. These findings again support the observation that concentrations are higher at VNP than other North American study sites, due to influences on its air shed from trans-pacific sources. Other Great Lakes species also show these elevated trends in Hg especially those with piscivorous feeding habits (Giesy et al. 1994; Haines et al. 2004).

Fish, mammals, and birds all bioconcentrate Hg at VNP, and these species show similar concentrations to nestling bald eagles. Fish are of major concern at VNP because of human consumption of fish from the park's lakes (Wiener et al. 2006). Lake trout (*Salvelinus namaycush*), walleye (*Sander vitreus*), and northern pike (*Esox lucius*) have the highest Hg concentrations of fish at VNP (Sorensen et al. 1990; Bhavsar et al. 2010). Northern pike make up a significant portion of the bald eagle's diet (Giesy et al. 1994). Hg concentrations have been increasing in nestling feather samples from the Great Lakes since 2000, which has also been observed at VNP (Fig. 2). This may indicate increases in fish tissues. Previous studies also indicate Hg concentrations are increasing in other piscivorous wildlife species such as river otters (*Lutra* canadensis) and mink (*Mustela* vison) (Evans et al. 2000; Basu et al. 2007). River otters, like bald eagles, have an inherent ability to demethylate MeHg in the brain acting as an Hg buffering system (Haines et al. 2004). Mink, like common loons (*Gavia immer*), do not have this metabolic pathway and show effects of Hg concentrations on their reproduction, behavior, and neurological function (Evans et al. 2000; Scheuhammer et al. 2007). These species, like eagles, have shown recent increases in mean Hg concentrations, which could be a product of their microenvironments and prey sources.

This examination of VNP also suggests specific areas of the park have high Hg concentrations. All nesting locations and territories with elevated Hg concentrations were located on Rainy and Namakan lakes except those from 1989. The areas of the park with elevated concentrations are on the northwestern and southeastern boundaries of the park. The northwestern area of high concentrations in Black Bay is potentially due to the fact that Rainy Lake has more human influence and industry surrounding it. The southeastern areas are located on Sandpoint and Crane lakes, which are grouped in this study as Namakan Lake. These areas have had high Hg concentrations in fish, and an advisory was issued for fish consumption (Sorensen et al. 1990). Although samples in these areas are not at consistent nest sites from year to year, territories in the areas were. The presence of nesting territories with consistently high individual nest samples does strongly suggest the prey collected by nesting adults in these territories has higher concentrations of Hg, likely as a result of environmental conditions. This being said these results are only suggestions since there is a lack of independence between individual nest samples due to no physical barriers for prey species traveling between territories on any one impoundment. During the period from 2000 to 2006 nestling feather Hg concentrations in the park were considerably less than those in 1999. This drop is probably attributed to the stabilization of the water levels in the three main lakes of the park to mimic more natural occurrences since research has shown that great change in water levels increase MeHg concentrations in the ecosystem (Rudd 1995; St. Louis et al. 2004; Sorensen et al. 2005). This is because prior to stabilization, large fluctuations in water level exposed and submerged embayments causing vegetation growth and decay both of which promote the release and methylation of Hg (Rudd 1995; St. Louis et al. 2004). When vegetation death occurs in these embayments due to inundation, Hg is methylated and incorporated into lake sediments causing increases of Hg in the ecosystem (Rudd 1995; St. Louis et al. 2004). This control order was likely responsible for the annual geometric mean of Hg concentrations in nestling feathers decreasing 74.4% from 1989 to 2010. However, since 2000, Hg geometric mean concentrations in nestling feathers have been increasing (Fig. 2). This is likely due to another source of Hg in the VNP ecosystem rather than changes in methylation, since the observed increase is gradual.

Natural substrate, anthropogenic inputs, and atmospheric deposition are the three major sources of Hg in most environments. Bedrock high in Hg is typically not found east of the Rocky Mountains. This source of Hg at VNP in not the main contributing factor since VNP sits on gabbros and granite glacial deposits, which are inherently low in Hg (Sorensen et al. 1990). Anthropogenic point source inputs have a minor influence on Hg concentrations in VNP because it is a fairly remote area, yet not free of all human input (Sorensen et al. 1990). Of the Hg in the sediments of VNP, 40% originates from watershed inputs from the moderately populated surrounding areas while the other 60% is contributed to atmospheric sources (Sorensen et al. 1990; Wiener et al. 2006). Atmospheric deposition mostly occurs in the form of wet deposition through precipitation, but Hg can be directly incorporated into plant material from the atmosphere (Sorensen et al. 2005). This plant material is then decomposed where the Hg can enter the watershed. These atmospheric concentrations of Hg do fluctuate at VNP, but not to the same magnitude as concentrations of MeHg found in the ecosystem (Wiener et al. 2006). It is more likely that the process affecting the fluctuations in ecosystem concentrations at VNP is due to water level fluctuations while the gradual increase is due to increased atmospheric inputs.

Concentrations of MeHg are dependent on microbial production and environmental processes that are typically dictated by environmental factors. Water chemistry is a major factor affecting the concentration of MeHg and the degree of methylation. High sulfate content in sediments and water promotes growth of sulfate-reducing bacteria, which in turn increases methylation of inorganic Hg (Rudd 1995; St. Louis et al. 2004; Wiener et al. 2006). Also lower pH increases the efficiency of sulfate-reducing bacteria, thus increasing methylation (Wiener et al. 2006). Wetland connectivity is an important factor in methylation of Hg and concentrations of MeHg (Wiener et al. 2006). Wetlands are typically associated with methylation because they provide ideal habitats for sulfate-reducing bacteria. The large number of beaver ponds (Grim and Kallemeyn 1995) also contributes to the amount of MeHg in the VNP ecosystem. These ponds where soils are typically inundated year round, have been linked to elevated methylation rates before (Roy et al. 2009) and are likely a major component of the wetland contribution to methylation in the park. These wetland systems are also high in dissolved organic matter from decomposing plant material, which aids in methylation and transportation of MeHg in aquatic ecosystems (Wiener et al. 2006; Roy et al. 2009). These environmental characteristics and deviations from the more natural water level control cycles are likely the contributing factors to the fluctuations observed in MeHg concentrations at VNP but the gradual increase in nestling feather concentrations since 2000 is more likely contributed to increased atmospheric inputs.

Conclusions

This study suggests that Hg is not at sufficient concentrations to cause adverse effects on the bald eagle population at VNP. Continued monitoring will become increasingly more important with increasing industrialization and demand for energy. Since most of VNP's Hg contamination comes from atmospheric deposition it can be a useful location in monitoring atmospheric Hg concentrations. Further monitoring of the bald eagle population at VNP will be essential to evaluate possible point sources and assess how lake and park management are affecting the Hg in the ecosystem. It is an example of how water management can be used to reduce concentrations of harmful contaminates in aquatic ecosystems. The longer this monitoring effort is continued, the more knowledge can be gained concerning environmental pollution, bioavailability, biomagnification, species adaptation and tolerance to Hg, and management practices that can aid in contaminant mitigation and control.

Acknowledgments This project was supported by Voyageurs National Park, U.S. Forest Service, and the Michigan Department of Environmental Quality through the Clean Michigan Fund, and Friends of Voyageurs National Park. This material is based upon work supported by NIFA/USDA, under project number SC-1700281, Technical Contribution No. 5873 of the Clemson University Experiment Station.

References

Adair BM, Reynolds KD, McMurry ST, Cobb GP (2003) Mercury occurrence in prothonotary warblers (*Protonotaria citrea*) inhabiting a national priorities list site and reference areas in southern Alabama. Arch Environ Contam Toxicol 44:265–271

Barr JF (1986) Population dynamics of the common loon (*Gavia immer*) associated with mercury contaminated waters in Northwestern Ontario. Occas Pap 56:1–23

Basu N, Scheuhammer AM, Bursain SJ, Elliott J, Rouvinen-Watt K, Chan HM (2007) Mink as a sentinel species in environmental health. Environ Res 103:130–144

Bechard MJ, Perkins DN, Kaltenecker GS, Alsup S (2009) Mercury contamination in Idaho bald eagles, *Haliaeetus leucoephalus*. Bull Environ Contam Toxicol 83:698–702

Bhavsar SP, Gewurtz SB, Mcgoldrick DJ, Keir MJ, Backus SM (2010) Changes in mercury levels in Great Lakes fish between 1970s and 2007. Environ Sci Technol 44:3273–3279

Bortolotti G (1984) Criteria for determining age and sex of nestling bald eagles. J Field Ornithol 55:467–481

Bowerman WW, Evans ED, Giesy JP, Postupalsky S (1994) Using feathers to assess risk of mercury and selenium to bald eagle reproduction in the Great Lakes region. Arch Environ Contam Toxicol 27:294–298

Bowerman WW, Giesy JP, Best DA, Kramer VJ (1995) A review of factors affecting productivity of bald eagles in the Great Lakes region: implications for recovery. Environ Health Perspect 3:51–59

Bowerman WW, Roe AS, Gilbertson MJ, Best DA, Sikarskie JG, Mitchell RS et al (2002) Using bald eagles to indicate the health of the Great Lakes' environment. Lakes Reserv Res Manag 7:183–187

Braune BM, Gaskin DE (1987) Mercury levels in Bonaparte's bulls (*Larus philadephia*) during autumn molt in the Quoddy Region, New Brunswick, Canada. Arch Environ Contam Toxicol 16:539–549

Buhler U, Norheim G (1982) The mercury content in feathers of the sparrowhawk *Accipiter nisus* in Norway. Fuana Norv Ser C Cinclus 5:43–46

Burgess NM, Meyer MW (2008) Methylmercury exposure associated with reduced productivity in common loons. Ecotoxicology 17:83–91

Chan HM, Scheuhammer AM, Ferran A, Loupelle C, Holloway J, Weech S (2003) Impacts of mercury on freshwater fish-eating wildlife and humans. Hum Ecol Risk Assess 9(4):867–883

Driscoll CT, Han Y, Chen CY, Evers DC, Lambert KF, Holsen TM, Kamman NC, Munson RK (2007) Mercury contamination in forest and freshwater ecosystems in the Northeastern United States. Bioscience 57:17–28

Dykstra CR, Route WT, Meyer MW, Rasmussen PW (2010) Contaminant concentrations in bald eagles nesting on Lake Superior, the upper Mississippi River, and the St. Croix River. J Great Lakes Res 36:3561–3569

Eisler R (1987) Mercury hazards to fish, wildlife and invertebrates: a synoptic review. Contaminant Hazard Reviews. Biological Report 85(1.10). Fish and Wildlife Service. U.S. Department of the Interior, Washington, DC

Evans RD, Addison EM, Villeneuve JY, MacDonald KS, Joachim DG (2000) Distribution of inorganic and methylmercury among tissues in mink (*Mustela vison*) and otter (*Lutra canadensis*). Environ Res 84:133–139

Evers DC, Taylor KM, Major A, Taylor RJ, Poppenga RH, Scheuhammer AM (2003) Common loon eggs as indicators of methylmercury availability in North America. Ecotoxicology 12:69–81

Evers DC, Burgess NM, Champoux L, Hoskins B, Major A, Goodale WM et al (2005) Patterns and interpretation of mercury exposure in freshwater avian communities in Northeastern North America. Ecotoxicology 14:193–221

Evers DC, Han Y, Driscoll CT, Kamman NC, Goodale MW, Lambert KF, Holsen TM, Chen CY, Clair TA, Butle T (2007) Biological Mercury Hotspots in the Northeastern United States and Southeastern Canada. Bioscience 57(1):29–43

Firmreite N (1974) Mercury contamination of aquatic birds in northwestern Ontario. J Wildl Manag 38:120–131

Gardner WS, Kendall DR, Odom RR, Windom HL, Stephens JJ (1978) The distribution of methylmercury in a contaminated salt marsh ecosystem. Environ Pollut 15:243–251

Giesy JP, Ludwig JP, Tillitt DE (1994) Deformities of birds in the Great Lakes region: assigning causality. Environ Sci Technol 28:128A–135A

Glass GE, Sorensen JA, Schmidt KW, Rapp GR (1990) New source identification of mercury contamination in the Great Lakes. Environ Sci Technol 24:1059–1069

Grim LH, Kallemeyn LW (1995) Reproduction and distribution of bald eagles in Voyageurs National Park, Minnesota, 1973–1993. Biological Report 1. U.S. Department of the Interior, National Biological Service

Haines K, Evans R, O'Brien M (2004) Relationship between mercury and selenium in the brain of river otter (*Lutra canadensis*) and wild mink (*Mustela vison*) from Nova Scotia, Canada. RMZ Mater Geoenviron 51:1028–1030

Hakkinen I, Hasanen E (1980) Mercury in eggs and nestling of the osprey, *Pandion haliaetus*, in Finland and its bioaccumulation from fish. Annu Zoologia Fennici 17:131–139

Heinz GH (1979) Methylmercury: reproductive and behavioral effects on three generations of mallard ducks. J Widl Manag 43: 394–401

Hollamby S, Afema-Azikuru J, Waigo S, Cameron K, Gandolf AR, Norris A, Sikarskie JG (2006) Suggested guidelines for use of avian species as biomonitors. Environ Monit Assess 118:13–20

International Rainy Lake Board of Control (2004) Spring report. International Joint Commission

Jagoe CH, Bryan AL, Brant HA, Murphy TM, Brisbin IL (2002) Mercury in bald eagle nestlings from South Carolina, USA. J Wildl Dis 38(4):706–712

JMP (1989–2007) Version 8. SAS Institute Inc., Cary

Ramlal PS, Anema C, Furutani A, Hecky RE, Rudd JWM (1987) Mercury methylation and demethylation studies in Southern Indian Lake, Manitoba. Can Tech Rep Fish Aquat Sci 1490:1–35

R Development Core Team (2008) R: A language and environment for statistical computing. R Foundation for Statistical Computing. Vienna. ISBN 3-900051-07-0, http://www.R-project.org

Roy V, Amyot M, Carignan R (2009) Beaver ponds increase methylmercury concentrations in Canadian shield streams along vegetation and pond-age gradients. Environ Sci Technol 43: 5601–5611

Rudd JWM (1995) Sources of methyl mercury to freshwater ecosystems: A review. Water Air Soil Pollut 80(1-4):697–713

Scheuhammer AM, Meyer MW, Sandheinrich MB, Murray MW (2007) Effects of environmental methylmercury on the health of wild birds, mammals, and fish. Ambio 36(1):12–18

Scheuhammer AM, Basu N, Burgess NM, Elliott JE, Campbell GD, Wayland M, Champoux L, Rodrigue J (2008) Relationships among mercury, selenium, and neurochemical parameters in common loons (*Gavia immer*) and bald eagles (*Haliaeetus leucocephalus*). Ecotoxicology 17:93–101

Sorensen JA, Glass GE, Schmidt KW, Huber JK, Rapp GR (1990) Airborne mercury deposition and watershed characteristics in relation to mercury concentrations in water, sediments, plankton, and fish of eighty Northern Minnesota lakes. Environ Sci Technol 24:1716–1727

Sorensen J, Kallemeyn L, Sydor M (2005) Relationship between mercury accumulation in young-of-the-year yellow perch and water level fluctuations. Environ Sci Technol 39:9237–9243

St. Louis VL, Rudd JWM, Kelly CA, Bodaly RA, Paterson JM, Beaty KG, Hesslein RH, Heyes A, Majewski AR (2004) The rise and fall of mercury methylation in an experimental reservoir. Environ Sci Technol 38:1348–1358

Strode SA, Jaegle L, Jaffe DA, Swartzendruber PC, Selin NE, Holmes C, Yantoxca RM (2008) Trans-Pacific transport of mercury. J Geophys Res 113:(D15305) doi:10.1029/2007JD009428

Tejning S (1967) Biological effects of methyl mercury diacyaniamide-treated grain in the domestic fowl *Gallus gallus*. L. Oikos Suppl 8:1–116

Welch L (1994) Contaminant burdens and reproductive rates of bald eagles breeding in Maine. M.S. thesis, University of Maine

Westcott K, Kalff J (1996) Environmental factors affecting methylmercury accumulation in zooplankton. Can J Fish Aquat Sci 53:2221–2228

Wiemeyer SN, Lamont TG, Bunck CM, Sindelar CR, Gramlich FJ, Fraser JD et al (1984) Organochlorine pesticides, polychlorobiphenyl, and mercury residues in bald eagle eggs-1969–1979-and their relationships to shell thinning and reproduction. Arch Environ Contam Toxicol 13:529–549

Wiener JG, Knights BC, Sandheinrich MB, Jeremiason JD, Brigham ME, Engstrom DR, Woodruff LG, Cannon WF, Balogh SJ (2006) Mercury in soils, lakes, and fish in Voyageurs National Park (Minnesota): Importance of atmospheric deposition and ecosystem factors. Environ Sci Technol 40:6261–6268

Wood PB, White JH, Steffer A, Wood JM, Facemire CF, Percival HF (1996) Mercury concentrations in tissues of Florida bald eagles. J Wildl Manag 60:178–185