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Contaminants in Bald Eagle Nestlings at Apostle Islands National Lakeshore, Mississippi National River and Recreation Area, and the St. Croix National Scenic Riverway

Data Summary: 2006—2008

Natural Resource Data Series NPS/GLKN/NRDS—2009/001

ON THE COVER
From left to right: Jim Spickler bringing two bald eagle nestlings to Mark Martell, Dan McGuiness weighing a nestling, Bill Route measuring a nestling's 8^{th} primary. Photographs from NPS files.

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Bill Route

National Park Service
Great Lakes Inventory & Monitoring Network
2800 Lake Shore Dr. East
Ashland, WI 54806

Rebecca Key

National Park Service
Great Lakes Inventory & Monitoring Network
2800 Lake Shore Dr. East
Ashland, WI 54806

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The National Park Service, Natural Resource Program Center publishes a range of reports that address natural resource topics of interest and applicability to a broad audience in the National Park Service and others in natural resource management, including scientists, conservation and environmental constituencies, and the public.

The Natural Resource Data Series is intended for timely release of basic data sets and data summaries. Care has been taken to assure accuracy of raw data values, but a thorough analysis and interpretation of the data has not been completed. Consequently, the initial analyses of data in this report are provisional and subject to change.

All manuscripts in the series receive the appropriate level of peer review to ensure that the information is scientifically credible, technically accurate, appropriately written for the intended audience, and designed and published in a professional manner. This report received informal peer review by subject-matter experts who were not directly involved in the collection, analysis, or reporting of the data. Data in this report were collected and analyzed using methods based on an established, peer-reviewed protocol and were analyzed and interpreted within the guidelines of that protocol.

Views, statements, findings, conclusions, recommendations, and data in this report are those of the author(s) and do not necessarily reflect views and policies of the National Park Service, U.S. Department of the Interior. Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the National Park Service.

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Corresponding Author: Bill Route bill_route@nps.gov

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Contents

Figures

Page

Tables

Executive Summary

From 2006 through 2008 the National Park Service Great Lakes Inventory and Monitoring Network assessed levels of targeted environmental contaminants in bald eagle (*Haliaeetus leucocephalus*) nestlings in and near Apostle Islands National Lakeshore, Mississippi National River and Recreation Area, and St. Croix National Scenic Riverway. Two hundred bald eagle nestlings were handled and 194 of them sampled. Of the 194 nestlings sampled, 111 plasma and 108 breast-feather samples were analyzed for six contaminants: total mercury, lead, DDT (and metabolites DDE and DDD), total PCBs (75 congeners), total PBDEs (9 congeners), and total PFCs (16 telomers). The remaining samples (n= 76 plasma and 78 feather samples) were siblings to the nestlings analyzed and these tissues were archived for future analysis. Herein we provide a summary of samples analyzed.

All study areas had $\geq$ 1.0 young per occupied territory, considered the threshold for a healthy bald eagle population. The Apostle Islands had the lowest productivity (1.0 in 2008) and the Mississippi National River and Recreation Area had the highest (2.2 in 2006). The percent of territories that were successful ranged from 62.5% in 2008 at Apostle Islands to 100% in 2007 on the lower St. Croix River.

Contaminant levels varied between study areas and years. The geometric mean ($\bar{x}_{geo}$) mercury levels in feathers ranged from 2.67 ug/g in nestlings on pools 3&4 of the Mississippi River in 2008 to 7.88 ug/g on the upper St. Croix Riverway in 2006. Mean ($\bar{x}_{geo}$) lead levels in feathers were lowest on the Apostle Islands in 2006 (0.07 ug/g) and highest in the lower St. Croix River in 2006 (0.99 ug/g). Generally, lead was highest in the lower St. Croix River and along the Mississippi River and lowest on the Apostle Islands and the upper St. Croix Riverway. We found DDT, which was banned in North America 37 years ago, in seven Lake Superior nestlings and in one nestling from the Mississippi National River and Recreation Area. We found DDE in all nestlings sampled and at high levels in the Apostle Islands in 2006 ($\bar{x}_{geo}$ = 28.9 ug/L). Nestlings on islands furthest out in to Lake Superior had among the highest DDE levels all three years. Levels of DDE were lowest on the upper St. Croix River in 2006 ($\bar{x}_{geo}$ = 2.53 ug/L). Levels of PCBs were lowest on the upper St. Croix River in 2006 ($\bar{x}_{geo}$ = 10.01 ug/L) and highest on the lower St. Croix in 2006 ($\bar{x}_{geo}$ = 136.06 ug/L). Polybrominated diphenyl ethers (PBDEs), a group of chemicals of increasing concern, ranged from $\bar{x}_{geo}$ of 1.39 ug/L in the lower St. Croix River in 2006 to $\bar{x}_{geo}$ of 14.56 ug/L along the south shore of Lake Superior in 2008. Generally, spatial patterns of PBDEs were similar to PCBs across the study areas. Perfluorinated compounds (PFCs), another group of chemicals of increasing concern, were found in all samples and the primary telomer was PFOS (64% of all samples by volume). In 2006 we found PFOS at very high levels in nestlings on the lower St Croix River ($\bar{x}_{geo}$ = 1550.27 ug/L) and in the Mississippi National River and Recreation Area ($\bar{x}_{geo}$ = 1234.17 ug/L). Levels in these study areas declined by 2008 but were high in pools 3&4 ($\bar{x}_{geo}$ 2008 = 1480.56 ug/L). PFOS was generally low on the upper St. Croix Riverway ($\bar{x}_{geo}$ = 13.94 ug/L in 2007) and at moderate levels on the Apostle Islands. A second PFC telomere, PFDS, comprised 30% of all samples by volume and its distribution was similar to PFOS in 2008 - the only year data are available. Interestingly, PFOA, a PFC telomer of high interest due to its toxicity and global distribution, was found at very low

levels in nestling plasma in our study areas (< 1% of the 16 PFCs by volume); yet this telomer was highest in two of the three years from nestlings on outer islands of the Apostle Islands.

Acknowledgements

This study was funded in 2006 and 2007 by the National Park Service, Great Lakes Inventory and Monitoring Network. In 2008, substantial funding was provided by the Minnesota Pollution Control Agency and the Donald Weesner Foundation. The Wisconsin Department of Natural Resources conducted occupancy and productivity surveys for APIS and SACN and the Ramsey County Parks Department conducted occupancy surveys at MISS. Nest-tree climbing expertise was provided by the Institute for Wildlife Studies and Eco-Ascension Research and Consulting. We had logistical support from Audubon Minnesota and the US Fish and Wildlife Service's Ashland Fisheries Resource Office. We received assistance with data analysis from Raptor Environmental and the Wisconsin Department of Natural Resources. All laboratory analyses were preformed by the Wisconsin State Laboratory of Hygiene. Earlier drafts of this report were reviewed by staff from the three national parks that were sampled, the Wisconsin Department of Natural Resources and the Minnesota Pollution Control Agency.

Introduction

In the upper Midwestern states of Minnesota, Wisconsin, and Michigan over 120 million pounds of toxic waste was reported released in to the air, discharged in to the water, or disposed on land in 2006 (EPA 2008). Some of this toxic waste ultimately ends up in aquatic systems through direct discharge, air deposition, or through ground water. Many of these chemicals, and the metabolites that result from their decomposition, are highly persistent and remain available for up-take by aquatic organisms. Chemicals that are persistent tend to accumulate - or bio-magnify - as they are ingested by progressively larger individuals or species higher on the trophic-scale. Some of these persistent and bioaccumulative chemicals are also highly toxic to fish, wildlife, and humans (Hudson et al. 1984).

The National Park Service (NPS) has a responsibility to understand the levels and potential effects of human-made chemicals on the natural resources they manage and to inform the visiting public about the potential human health hazards. The NPS Great Lakes Inventory and Monitoring Network (GLKN) began monitoring levels of human-made contaminants in 2006. The monitoring involves sampling nestling bald eagles (*Haliaeetus leucocephalus*) to track the bio-availability of targeted contaminants. Bald eagles are high on the aquatic food web and are known to accumulate persistent chemicals, thus acting as effective indicators of contamination.

From hundreds of potential chemicals, we narrowed our scope to those that are persistent, bioaccumulative, and toxic to fish, wildlife, and humans. We further reduced this list by considering only those chemicals that are either: the cause of waters within a park being listed in section 303(d) of the Water Quality Act (including fish consumption advisories); listed as a Level I Substance under the Great Lakes Binational Toxics Strategy; or recently identified by state and federal authorities as a new and emerging chemical of concern. We then excluded chemicals that are being adequately monitored by other agencies or that were prohibitively expensive to monitor. Our current list of target chemicals is:

- Lead (Pb)
- Total Mercury (THg)
- DDT (including DDE & DDD)
- PCBs (including 75 congeners)
- PBDE (polybrominated diphenyl ether; including 9 congeners)
- PFCs (perfluorinated compounds; including 16 telomers)

For our study areas, the monitoring program is designed to answer the following questions:

1) What is the direction and magnitude of change in concentrations of DDT (including metabolites DDE and DDD), total PCBs, total PFCs, and total PBDEs in blood plasma, and of total mercury and lead in feathers, from nestling bald eagles?
2) What is the incidence of addled eggs, dead nestlings, and developmental deformities in nestling bald eagles?
3) What is the direction and magnitude of change in the percent successful bald eagle territories and the number of young produced per occupied bald eagle territory?

Study Areas and Methods

This monitoring program is conducted at the Apostle Islands National Lakeshore (APIS) located on Lake Superior in extreme northern Wisconsin; the Mississippi National River and Recreation Area (MISS), a section of the Mississippi River in west central Minnesota; and the St. Croix National Scenic Riverway (SACN), encompassing the St Croix and Namekagon Rivers in northwest Wisconsin (Fig. 1). Additionally, we occasionally conduct supplemental sampling in areas adjacent to these national parks when considered necessary for regional context or when funding was provided by collaborating agencies. In 2007 we sampled west of APIS along the Wisconsin shoreline of Lake Superior to the St Louis River. This effort was supported in-part by the Wisconsin Department of Natural Resources (WDNR) to replicate their efforts five years earlier on PBDEs. In 2008 we sampled south of the MISS boundary along the Mississippi River to southern Lake Pepin to evaluate the downstream extent of contamination from the Twin Cities metropolitan area, a study fully funded by the Minnesota Pollution Control Agency (MPCA).

Occupancy and Productivity Estimates

Bald eagle nest occupancy was determined during April and May each year by observers in a fixed-wing aircraft, helicopter, or from a boat. The WDNR conducted all fixed-wing occupancy surveys for APIS and SACN each year. The WDNR has conducted these occupancy surveys since the early 1980’s. The Minnesota Department of Natural Resources (MDNR) discontinued annual occupancy surveys after 1995. Therefore, we conducted the occupancy survey at MISS by boat in 2006, and in 2007 and 2008 we partnered with the Ramsey County Parks Department to conduct occupancy surveys from a helicopter.

A nest was considered occupied, and hence the eagle territory occupied, if any of the following were observed: an adult on a nest in incubating posture; eggs or young in a nest; two breeding-aged adults near an empty nest; or a recently repaired or new nest (e.g., egg cup, fresh nesting material) even if the adult(s) were not observed (Postupalsky 1983).

Occupancy surveys resulted in GPS locations of most active bald eagle nests within and directly adjacent to the parks. (Note: observers make every attempt to document all active nests in each study area, but occasionally nests are missed.) Occupied nests were subsequently visited on the ground to collect samples for contaminants.

The combined occupancy and productivity data provided three measures of bald eagle reproductive success for each study area: 1) total number of occupied territories each year; 2) the number of young per occupied territory (# live young / # occupied territories); and 3) the percent of occupied territories that were successful (# occupied territories / # territories that produced at least one young). Measures of reproductive success can be plotted by year, correlated with contaminant levels, and compared with historical information for these and similar bald eagle populations.

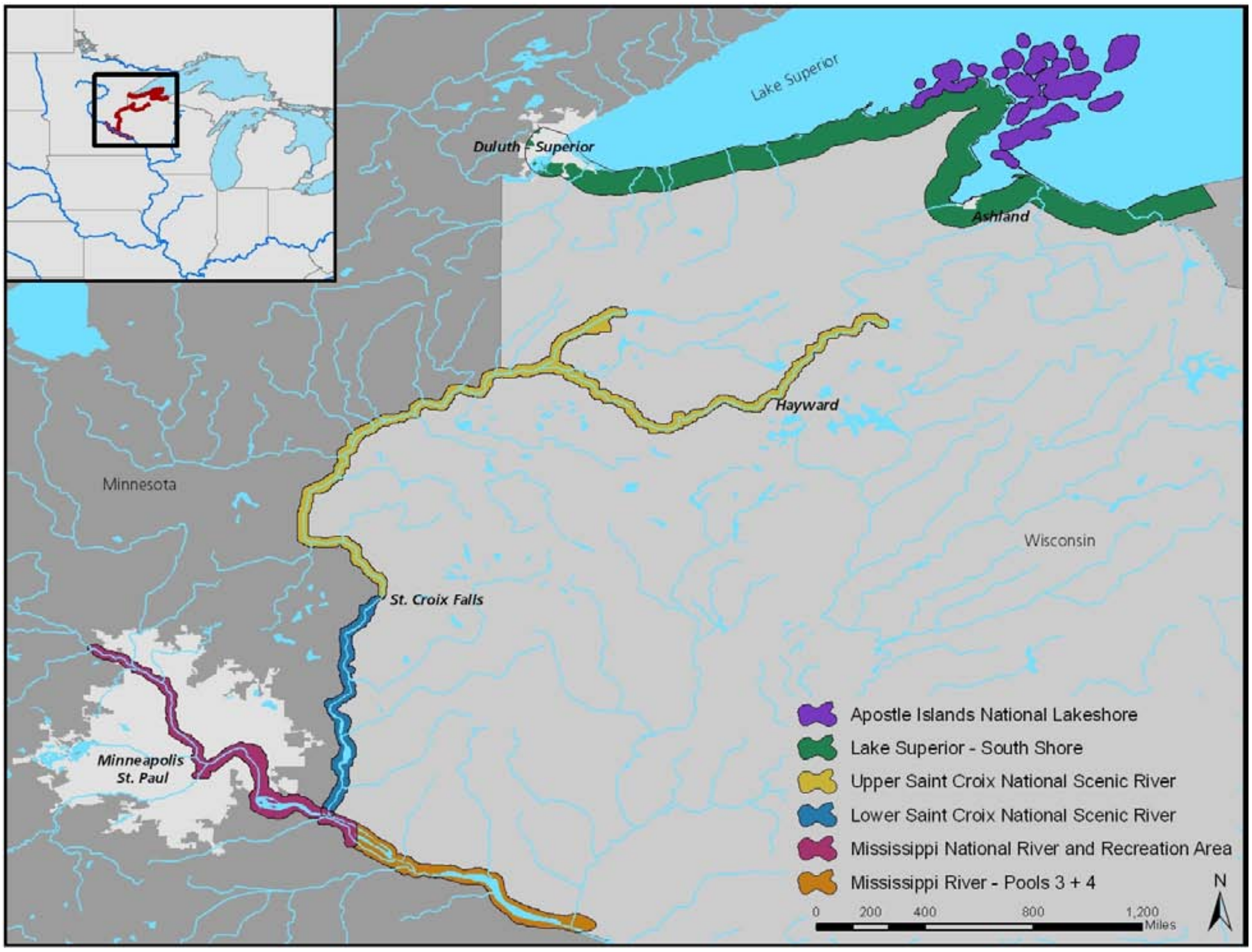

Figure 1. Study areas for sampling bald eagle nestlings for environmental contaminants in and adjacent to three national parks in the western Great Lakes region.

Sample Collections

We used GPS coordinates from occupancy surveys to map all occupied bald eagle nests in each study area. In late May and early June each year, when eaglets were between five and nine weeks old, we attempted to climb to each nest and bring eaglets to the ground for sampling. Nests were excluded if they could not be reasonably accessed (e.g., a nest in the middle of an extensive swamp), unsafe to climb (dead tree or unstable nest structure), or if the landowner denied access. In addition, some nests were not sampled when young were too old to safely handle or when high winds made climbing unsafe.

All safe, accessible nests were climbed using either climbing spurs (~80% of 2006 nests) or using soft-climbing techniques (~20% of 2006 and all 2007-2008 nests). Soft-climbing involved using a crossbow to shoot a line over a branch near the nest. Successively larger lines were then pulled over the branch until a climbing rope could be anchored. The climbing rope was climbed using mechanical ascenders. Soft-climbing reduces injury to tree bark caused by traditional climbing spurs.

Climbers hand-captured young eaglets in the nest and brought them to the ground in individual handling bags. Once on the ground nestlings were examined for general health and presence of abnormalities. The following measurements were taken as described by Bortolotti (1984).

- Weight to the nearest 0.5 kg using a spring scale;
- Footpad length to the nearest mm (distance between points of insertion of the hallux and the front middle toe);
- Length of 6^{th} and/or 8^{th} primary to the nearest mm (in 2006 the 6^{th} was measured, in 2007 both 6^{th} and 8^{th} were measured, and in 2008 only the 8^{th} was measured);
- Length and depth of the beak to the nearest mm using a caliper.

We took up to 11 ml of blood to determine concentrations of DDT, DDE, DDD, PCBs, PBDEs, and PFCs. Blood was drawn from the brachial vein using a sterile, 10 cc polypropylene syringe, and 20 gauge needle. The blood sample was immediately transferred to a 10 cc, green-top vacutainer containing sodium heparin to prevent clotting. The small amount of blood remaining in the syringe was forced on to a small square (two to four inch) of cotton gauze. This blot was sent to a genetics laboratory to verify the nestling's sex. Three to four breast feathers were plucked from each nestling to determine concentrations of total mercury (THg), lead (Pb), and selenium (Se; 2007 only). All samples were individually marked, dated, and placed in a cooler on blue ice until they were processed at the end of each field day.

Within 12 hours of collection blood samples were spun for 10-12 minutes at 1200 rpm in a centrifuge to separate plasma from the red blood cells. A sterile glass pipette is used to draw-off the plasma into separate vials provided by the lab. All plasma samples and the remaining red blood cells were immediately frozen and kept frozen until delivery to the laboratory. At the end of the season we randomly selected one nestling per nest and sent those samples to the Wisconsin State Laboratory of Hygiene (WSLH) to determine levels of target contaminants. Samples that were not sent for lab analysis were archived (plasma @ -20 C; feathers dried in envelopes) for future assessments of new and emerging contaminants.

Laboratory Analysis

Analyses of plasma and feathers for target contaminants were done using published methods as follows (specific methods available from WSLH on request):

- DDT/DDE/DDD - Gas chromatograph equipped with an electron-capture detector (ESS ORG Method 1810).
- PCBs and PBDEs - Gas chromatograph-mass spectrometer operating in the negative ion mode (ESS ORG Method 1810).
- PFCs - Turbo ion spray, triple quadruple mass spectrometer in the negative ionization mode (WSLH Method 1470).
- Total mercury – Cold vapor atomic absorption (ESS INO Method 540.4).
- Lead – Inductively coupled plasma spectroscopy (ESS INO Method 620.2).

In addition, we sent 0.5 ml of plasma from all nestlings to the Environmental Protection Agency's (EPA) contaminants laboratory, Research Triangle Park, NC. The EPA is developing standardized methods for determining levels of PFCs in plasma. This effort was at no cost to the project and will have the added benefits of providing a double blind on our original PFC analysis and data on siblings to assess variability in contaminants between nest-mates.

Data from WSLH are completed and summarized below; EPA analyses were not completed in time for this summary.

Data Handling and Analysis

All field data were entered on hardcopy data sheets and later entered into a relational database (Microsoft Access™). All (100%) computer data records were checked against original data sheets for accuracy. Lab QA/QC included matrix spikes to assess percent recovery (Appendix A). For this summary, contaminant values that fell below the labs limits of detection (LOD) were assigned one-half the detection limit for calculating means and confidence intervals; however, samples below LOD were removed for showing spatial patterns (Figures 2 – 8). To correct for skewed data we $\log_{10}$ transformed raw data, generated means and confidence intervals, and then back-transformed the results for tables and charts. All data values are provided as wet weight (ww) for organics analyzed in plasma and dry weight (dw) for heavy metals analyzed in feathers.

Results

The following data are provisional and subject to change. A more in-depth analysis and interpretation of the data could result in the removal or re-coding of data for some contaminants. For example, outliers may be removed if there are valid reasons. There are also a variety of methods for summarizing samples that are below the laboratories limits of detection. In future analyses we may choose other methods, which may alter some results, though the differences should be minor.

Reproductive Success and Sampling Effort

All study areas had $\geq$ 1.0 young per occupied territory, which is considered the threshold for a healthy bald eagle population (Wiemeyer et al., 1984; Table 1). Considering park areas only, the average number of young / occupied territory was highest at MISS (1.9), followed by lower SACN (1.6), upper SACN (1.5), and APIS (1.2). On average there were 1.5 young / occupied territory across all years and study areas. The percent of territories that were successful each year was highly variable ranging from 62.5% in 2008 at APIS to 100% in 2007 on the lower SACN.

In total, we observed 265 live nestlings; 254 of those were also observed during occupancy surveys. Of those nestlings, we banded 200 and took samples for contaminants from 194 over the three years. Some siblings were not banded or sampled to minimize stress when deemed necessary. We found seven dead nestlings, of which three were in good enough condition to determine cause of death. Two drowned when their nest fell into a lake (MISS in 2006) and one died of *Pasteurella multocida* septicemia (MISS in 2007).

Sample distribution included 108 feathers to WSLH for heavy metal analysis, 111 to WSLH for the full suite of organic chemicals, and 128 to EPA for PFCs only. In addition, 78 feather samples and 76 plasma samples have been archived for future analysis.

Table 1. Bald eagle territory occupancy and measures of success; number of young handled and banded; and number of samples collected, analyzed, and archived for monitoring persistent contaminants at Apostle Islands National Lakeshore (APIS), Mississippi National River and Recreation Area (MISS), the lower and upper sections of the St. Croix National Scenic Riverway (SACN), Wisconsin (WI) South Shore of Lake Superior, and pools 3&4 on the Mississippi River from 2006 through 2008.

Measures of success / Young handled / Samples taken	Study Area / Year[a]													Totals
	APIS			MISS			SACN Upper		SACN Lower			WI South Shore	Miss Pools 3+4	
	2006	2007	2008	2006	2007	2008	2006	2007	2006	2007	2008	2007	2008	
# Occupied Territories	11	9	8	11	15	14	20	19	5	4	10	14	24	**164**
# Failed Territories	1	3	3	1	3	0	2	4	1	0	3	3	3	**27**
# Successful Territories	10	6	5	10	12	14	18	15	4	4	7	11	21	**137**
% Success of Occupied Territories	90.9%	66.7%	62.5%	90.9%	80.0%	100.0%	90.0%	78.9%	80.0%	100.0%	70.0%	78.6%	87.5%	**83.5%**
# Young / Occupied Territory[b]	1.5	1.1	1.0	2.2	1.5	2.1	1.6	1.5	1.8	1.5	1.6	1.3	1.5	**1.5**
# Live Young[c]	16	12 (10)	8	24	22	35 (30)	31	30 (28)	9	6	16	20 (18)	36	**265 (254)**
# Dead Young[d]	0	0	0	3	2	0	1	0	0	1	0	0	0	**7**
# of Young Banded[e]	10	10	8	24	18	33	17	14	5	6	16	10	29	**200**
# Feather Samples Analyzed	9	6	4	11	11	14	11	8	3	4	7	6	14	**108**
# Plasma Samples Analyzed	8	6	5	11	12	15	11	8	3	4	7	6	15	**111**
# Plasma Samples sent to EPA[f]	8	6	8	11	11	20	11	8	3	4	16	6	16	**128**
# Feather Samples Archived[g]	2	3	3	9	6	14	6	5	2	3	9	4	12	**78**
# Plasma Samples Archived[g]	2	3	3	7	5	15	6	5	2	2	9	4	13	**76**

a = Does not include samples collected adjacent to APIS in 2008 (n=3); samples trimmed to reflect park only.
b = Young per occupied territory = (# live young) / # occupied territories; only data for territories detected during occupancy surveys were used (see c).
c = Total live-young observed; numbers in perentheses are from nests detected during occupancy surveys and are used in calculating young / occupied territory.
d = Three specimens were found in good condition; two provided to the Bell Museum, one to the University of MN Raptor Center; others too decomposed for necropsy.
e = Number banded may not equal number observed or sampled since some were left in the nest unbanded and others banded and not sampled depending on available time and eaglet stress.
f = Samples sent to US Environmental Protection Agency lab for PFC analysis only; analysis not yet completed.
g = Feathers archived at the Great Lakes Network office; plasma archived at WSLH at -20^{o} C.

Summary of Contaminant Levels

Mercury concentrations were lowest in nestlings from Miss pools 3&4, APIS, and MISS; highest along the upper portions of SACN where extensive wetlands likely contribute to methyl mercury production and availability (Table 2; Fig. 2). Levels varied along the Lake Superior shoreline in 2007; elevated in nestlings near rivers that drained areas with a high percent of wetland and low in areas with few wetlands (Fig. 2).

Lead concentrations were highest in nestlings from the lower SACN, MISS, and Miss pools 3&4; and low in nestlings from the upper SACN, APIS, and WI south shore (Table 3; Fig. 3). Lead levels were highly variable between years. In 2007 interference with another chemical resulted in no detections in the Apostles and in several nests along the upper St Croix and Namekagon Rivers (Fig. 3).

Table 2. Sample size, measures of central tendency, and variability of total mercury (ug/g dw) in breast feathers of bald eagle nestlings, 2006-2008. See text for study area names.

Study Area	Year	N	Arithmetic Mean	Median	SD	SE	Geometric Mean	Upper 95% CI	Lower 95% CI
APIS	2006	9	3.26	3.70	1.04	0.35	2.94	3.82	2.22
APIS	2007	6	3.78	3.20	2.14	0.87	3.31	4.85	2.18
APIS	2008	4	3.40	3.15	0.88	0.44	3.30	4.18	2.57
WI - South Shore	2007	6	7.48	5.85	4.45	1.82	6.47	9.64	4.25
WI - South Shore	2008	4	4.38	4.40	0.70	0.35	4.32	5.06	3.67
SACN Upper	2006	11	8.25	8.30	2.44	0.74	7.88	9.28	6.67
SACN Upper	2007	8	5.89	6.35	1.63	0.58	5.58	6.91	4.47
SACN Lower	2006	3	6.20	5.70	1.51	0.87	6.05	7.88	4.60
SACN Lower	2007	4	4.05	4.25	0.76	0.38	3.97	4.81	3.25
SACN Lower	2008	7	4.40	3.80	1.17	0.44	4.25	5.09	3.53
MISS	2006	11	3.76	3.70	0.73	0.22	3.68	4.13	3.26
MISS	2007	11	3.31	2.80	1.34	0.40	3.08	3.77	2.48
MISS	2008	14	3.46	3.55	0.97	0.26	3.29	3.82	2.82
Miss - Pools 3&4	2008	14	2.76	2.65	0.67	0.18	2.67	3.02	2.35

Table 3. Sample size, measures of central tendency, and variability of lead (ug/g dw) in breast feathers of bald eagle nestlings, 2006-2008. See text for study area names.

Study Area	Year	N	Arithmetic Mean	Median	SD	SE	Geometric Mean	Upper 95% CI	Lower 95% CI
APIS	2006	9	0.39	0.33	0.21	0.07	0.35	0.48	0.23
APIS	2007	6	0.07	0.07	0.00	0.00	0.07	0.07	0.07
APIS	2008	4	0.15	0.11	0.11	0.06	0.12	0.23	0.02
WI - South Shore	2007	6	0.15	0.13	0.10	0.04	0.13	0.20	0.06
WI - South Shore	2008	4	0.22	0.16	0.20	0.10	0.15	0.35	-0.02
SACN Upper	2006	11	0.30	0.34	0.10	0.03	0.27	0.34	0.21
SACN Upper	2007	8	0.16	0.07	0.14	0.05	0.12	0.21	0.03
SACN Lower	2006	3	1.28	0.87	1.03	0.59	0.99	2.22	0.23
SACN Lower	2007	4	0.23	0.16	0.21	0.10	0.17	0.37	0.00
SACN Lower	2008	7	0.37	0.28	0.28	0.11	0.27	0.47	0.10
MISS	2006	11	1.06	0.75	1.01	0.30	0.71	1.17	0.34
MISS	2007	11	0.74	0.40	0.62	0.19	0.54	0.86	0.28
MISS	2008	14	0.34	0.33	0.25	0.07	0.24	0.36	0.12
Miss - Pools 3&4	2008	14	0.20	0.19	0.12	0.03	0.16	0.23	0.11

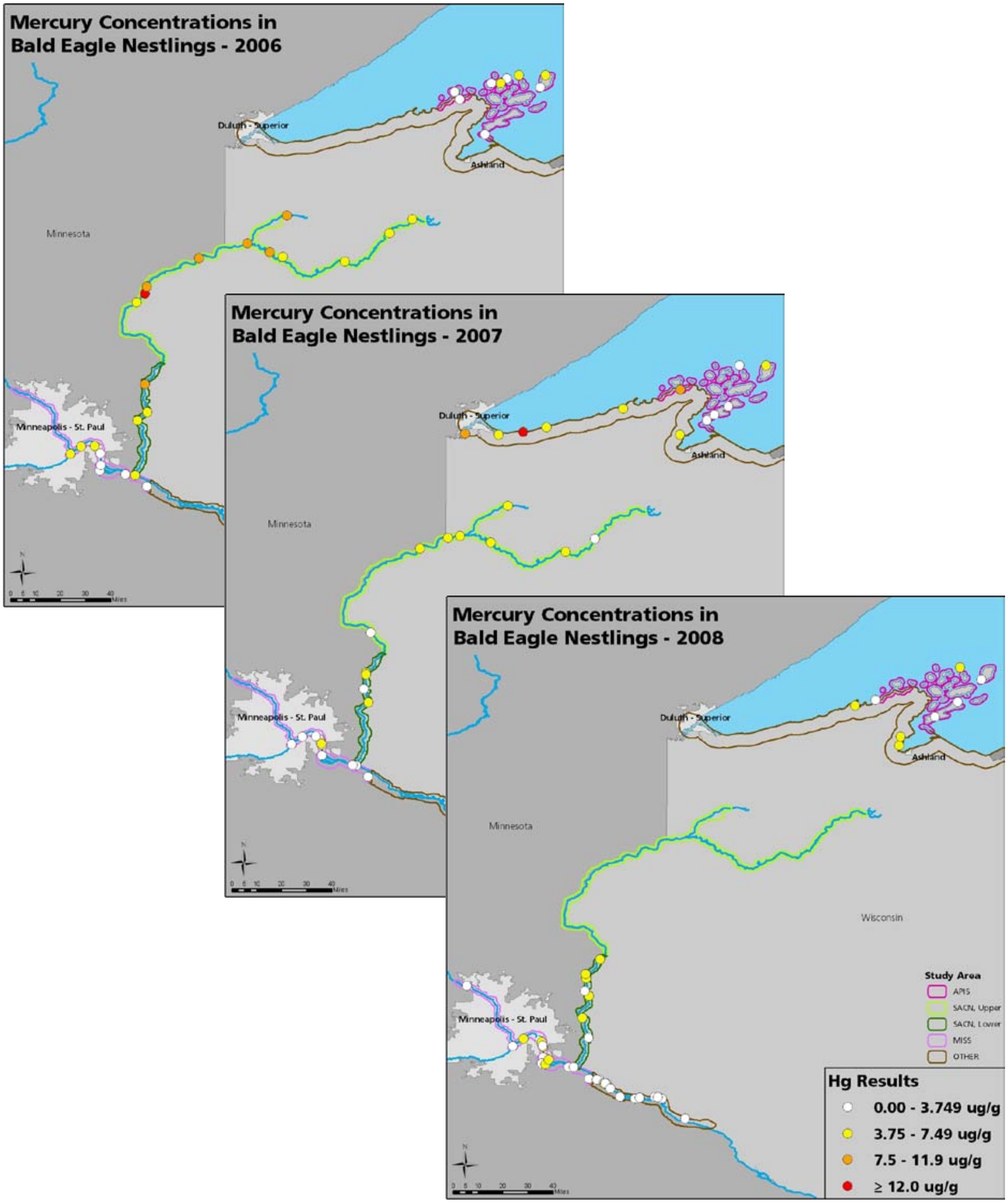

Figure 2. Spatial patterns of mercury in feathers of bald eagle nestlings from 2006 to 2008 in and adjacent to three national parks in the western Great Lakes region. Study areas: APIS = Apostle Islands National Lakeshore; U SACN & L SACN = upper and lower sections of the St. Croix National Scenic Riverway respectively; MISS = Mississippi National River and Recreation Area; P 3&4 = pools 3 and 4 of the Mississippi River below MISS. *Upper SACN was not sampled in 2008 and pools 3 & 4 were not sampled in 2006 or 2007. Samples below the limits of detection were removed.

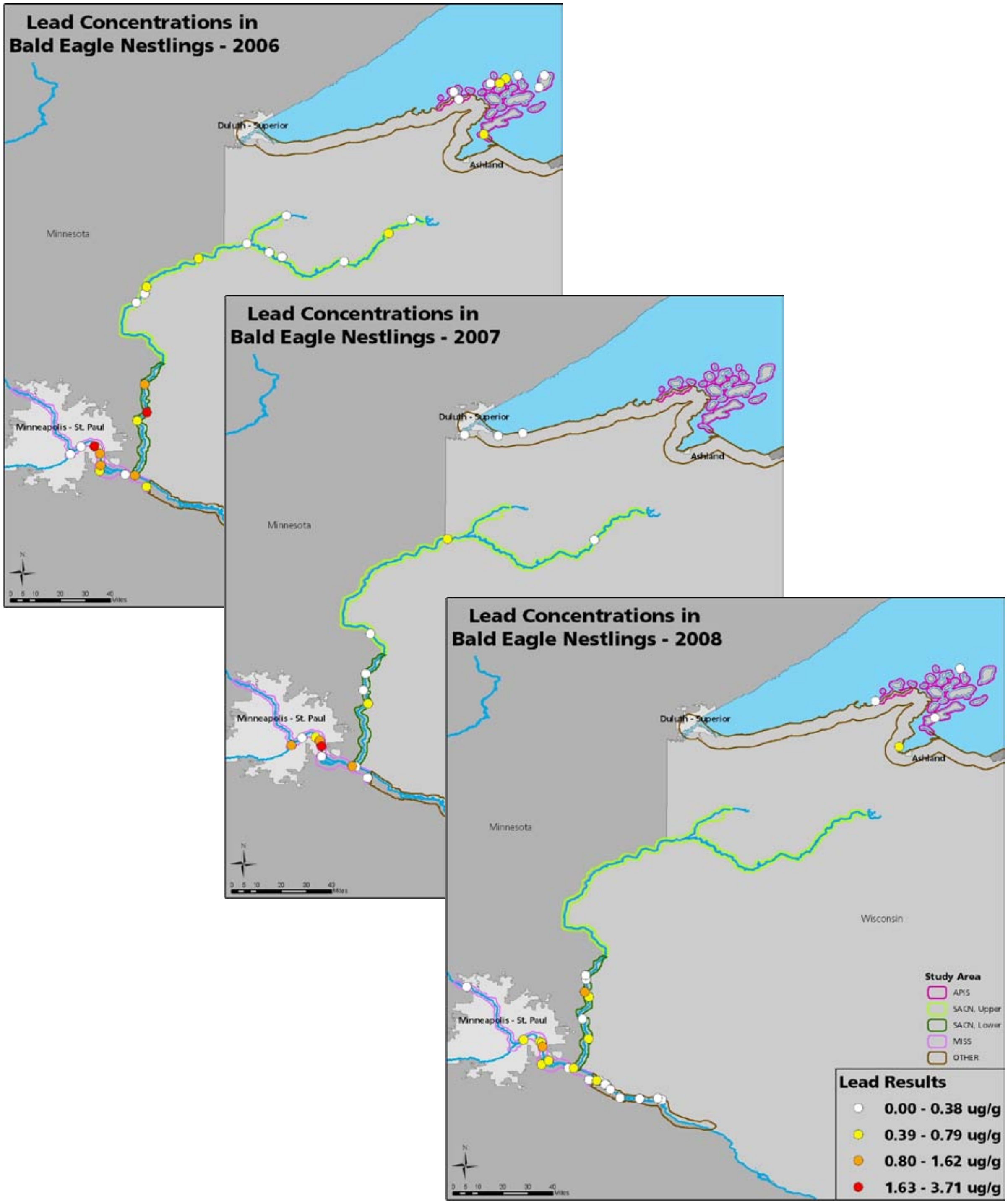

Figure 3. Spatial patterns of lead in feathers of bald eagle nestlings from 2006 to 2008 in and adjacent to three national parks in the western Great Lakes region. Study areas: APIS = Apostle Islands National Lakeshore; U SACN & L SACN = upper and lower sections of the St. Croix National Scenic Riverway respectively; MISS = Mississippi National River and Recreation Area; P 3&4 = pools 3 and 4 of the Mississippi River below MISS. *Upper SACN was not sampled in 2008 and pools 3 & 4 were not sampled in 2006 or 2007. Samples below the limits of detection were removed.

DDT/DDE - In 2006, DDT was detected at low levels in four nestlings - three from APIS and one from MISS (Fig. 4). In 2007, one nestling from APIS and three along WI south shore had detectable levels of DDT.

Levels of DDE, the breakdown product of DDT, varied across the study areas but were often higher in nestlings at APIS, particularly at nests on Outer and North Twin islands in APIS (Table 4; Fig. 4). Three of five nestlings sampled west of APIS in 2007 also had elevated levels of DDE. By contrast, nestlings at MISS and SACN generally had low levels of DDE and only one nestling had detectable levels of DDT.

PCBs were detected in all nestlings sampled and were generally higher along the lower SACN, MISS, Miss pools 3&4, and on the outer islands of APIS (Table 5; Fig. 5). Nestlings on the upper SACN had the lowest levels.

Table 4. Sample size, measures of central tendency, and variability of DDE (ug/L ww) in plasma of bald eagle nestlings, 2006-2008. See text for study area names.

Study Area	Year	N	Arithmetic Mean	Median	SD	SE	Geometric Mean	Upper 95% CI	Lower 95% CI
APIS	2006	8	33.88	28.00	21.60	7.64	28.90	41.26	20.16
APIS	2007	6	29.23	21.00	29.61	12.09	15.33	37.59	5.91
APIS	2008	5	29.34	13.00	29.26	13.09	15.09	41.82	5.05
WI - South Shore	2007	6	17.78	16.50	12.21	4.98	13.95	23.82	8.01
WI - South Shore	2008	4	7.70	7.70	3.52	1.76	6.79	11.12	4.01
SACN Upper	2006	11	3.78	2.10	4.53	1.37	2.53	4.01	1.49
SACN Upper	2007	8	2.80	2.75	1.12	0.40	2.57	3.35	1.93
SACN Lower	2006	3	14.67	11.00	6.35	3.67	13.66	21.43	8.58
SACN Lower	2007	4	7.10	6.00	3.49	1.75	6.39	9.95	3.98
SACN Lower	2008	7	5.81	6.10	2.46	0.93	5.13	7.25	3.56
MISS	2006	10	12.65	11.50	6.41	2.03	11.15	14.80	8.35
MISS	2007	11	10.89	10.00	3.06	0.92	10.39	12.28	8.77
MISS	2008	15	13.31	11.00	8.86	2.29	11.48	14.51	9.04
Miss - Pools 3&4	2008	15	7.45	6.90	2.71	0.70	6.86	8.27	5.67

Table 5. Sample size, measures of central tendency, and variability of total PCBs (ug/L ww) in plasma of bald eagle nestlings, 2006-2008. See text for study area names.

Study Area	Year	N	Arithmetic Mean	Median	SD	SE	Geometric Mean	Upper 95% CI	Lower 95% CI
APIS	2006	8	125.18	112.44	94.74	33.49	94.00	156.92	56.15
APIS	2007	6	52.80	49.96	28.53	11.65	44.63	70.88	27.97
APIS	2008	5	57.95	65.45	29.32	13.11	49.84	81.90	30.18
WI - South Shore	2007	6	88.87	89.38	34.74	14.18	80.21	117.07	54.86
WI - South Shore	2008	4	36.56	40.14	11.28	5.64	34.57	48.98	24.31
SACN Upper	2006	11	10.19	9.55	1.99	0.60	10.01	11.06	9.05
SACN Upper	2007	8	10.81	9.79	2.95	1.04	10.47	12.30	8.89
SACN Lower	2006	3	156.12	118.09	95.03	54.87	136.06	261.70	70.51
SACN Lower	2007	4	68.76	67.00	25.11	12.55	64.45	93.46	44.35
SACN Lower	2008	7	84.95	92.89	30.42	11.50	78.11	106.31	57.32
MISS	2006	10	100.40	85.36	76.99	24.35	82.04	116.84	57.52
MISS	2007	11	92.19	99.50	42.31	12.76	82.36	107.60	62.98
MISS	2008	15	91.74	94.24	32.32	8.34	85.27	102.66	70.80
Miss - Pools 3&4	2008	15	112.44	109.36	26.66	6.88	108.69	123.30	95.80

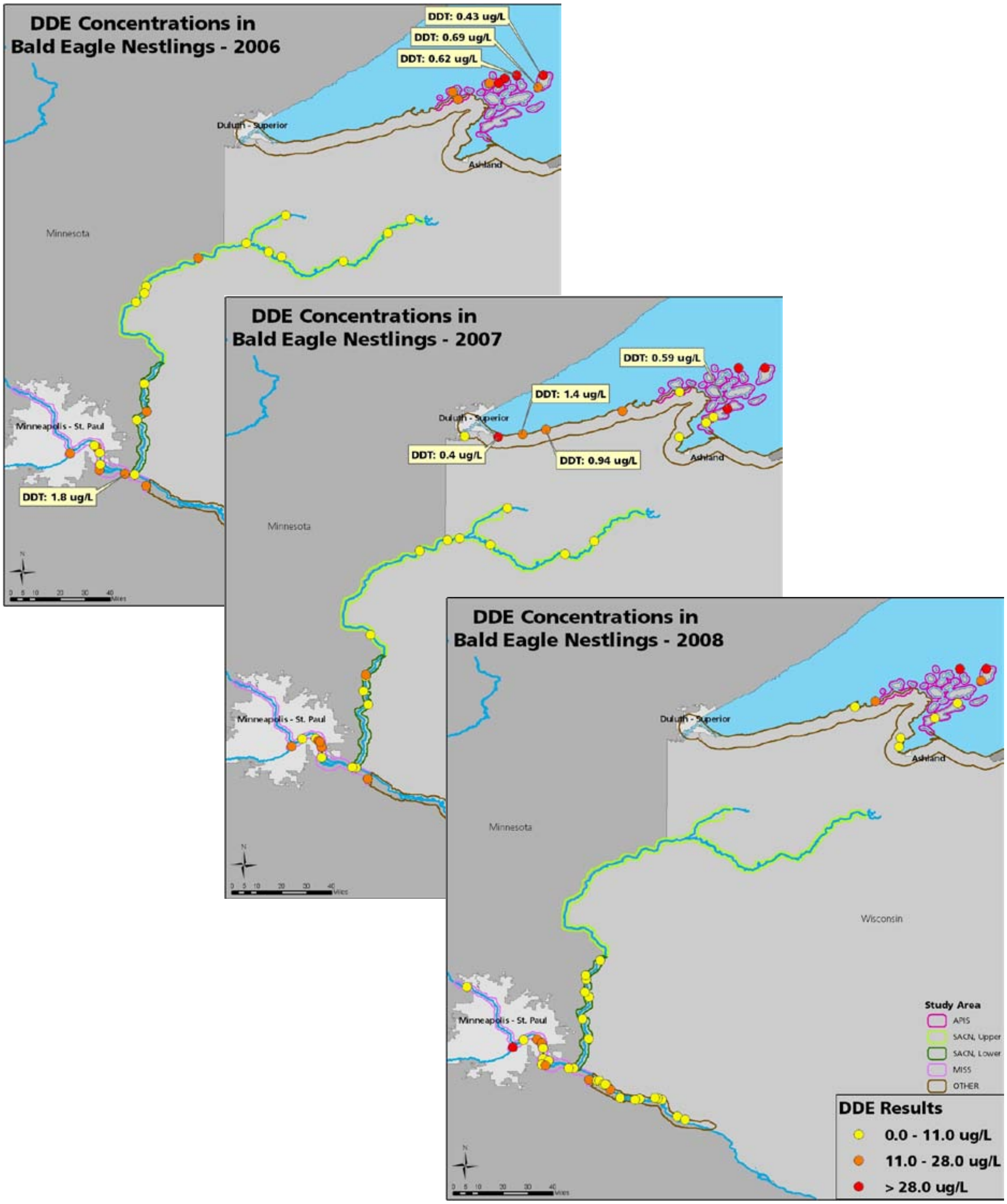

Figure 4. Spatial patterns of DDE and DDT in plasma of bald eagle nestlings from 2006 to 2008 in and adjacent to three national parks in the western Great Lakes region. Study areas: APIS = Apostle Islands National Lakeshore; U SACN & L SACN = upper and lower sections of the St. Croix National Scenic Riverway respectively; MISS = Mississippi National River and Recreation Area; P 3&4 = pools 3 and 4 of the Mississippi River below MISS. *Upper SACN was not sampled in 2008 and pools 3 & 4 were not sampled in 2006 or 2007. Samples below the limits of detection were removed.

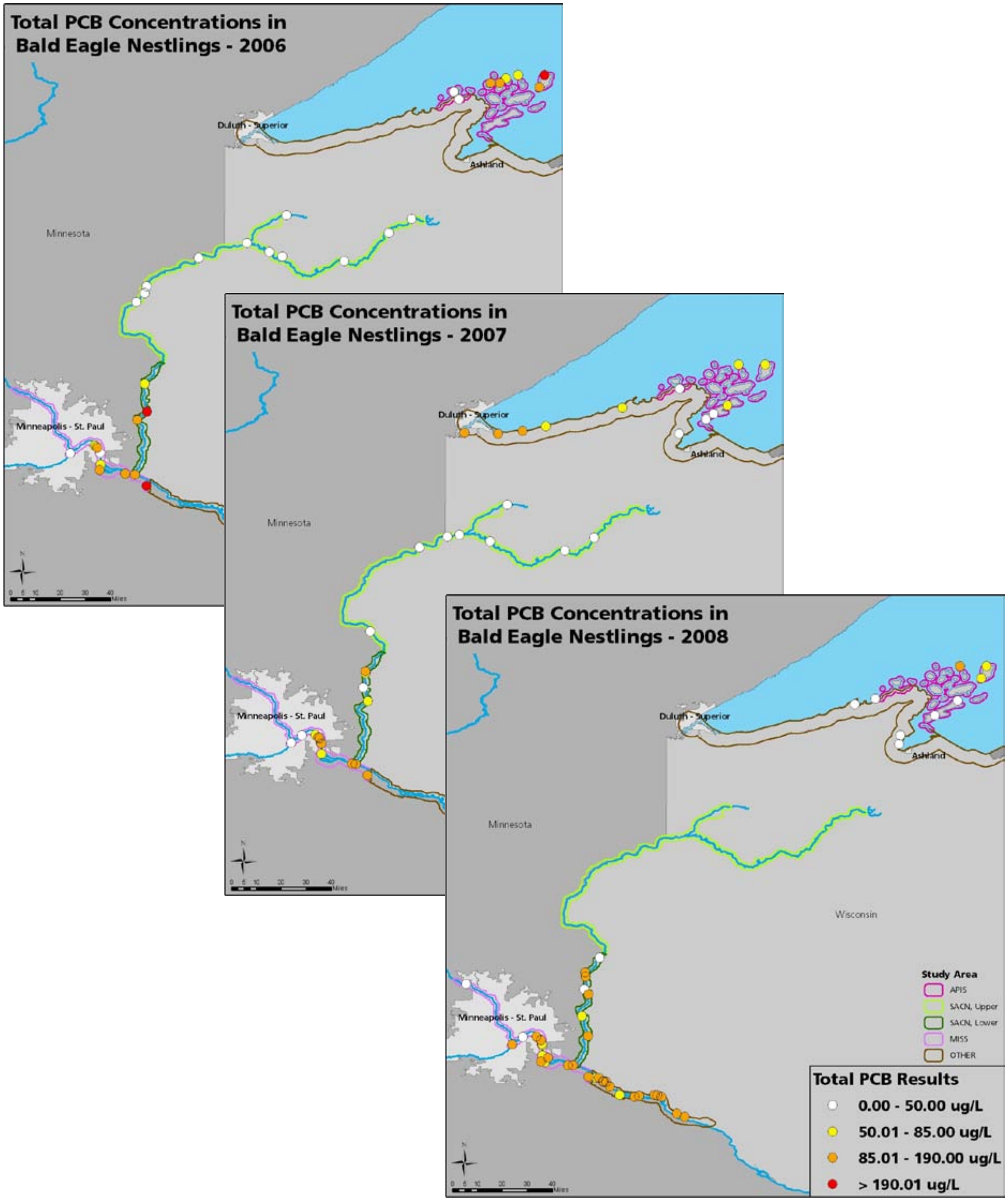

Figure 5. Spatial patterns of PCBs in plasma of bald eagle nestlings from 2006 to 2008 in and adjacent to three national parks in the western Great Lakes region. Study areas: APIS = Apostle Islands National Lakeshore; U SACN & L SACN = upper and lower sections of the St. Croix National Scenic Riverway respectively; MISS = Mississippi National River and Recreation Area; P 3&4 = pools 3 and 4 of the Mississippi River below MISS. *Upper SACN was not sampled in 2008 and pools 3 & 4 were not sampled in 2006 or 2007. Samples below the limits of detection were removed.

PBDE levels generally mirrored those of PCBs, highlighting the similarity in transfer pathways and the persistency of the two chemical groups (Table 6; Fig. 6). We found PBDEs in all nestlings sampled and when compared to published literature, our data suggest a near doubling of the concentrations in nestlings along the south shore of Lake Superior over the last five years.

PFCs - In 2006-07 WSLH was able to analyze for two PFC telomers, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). Beginning in 2008 WSLH provided data on 16 telomers. Total PFC levels were highest at MISS, Miss pools 3&4, and lower SACN; mid-level at APIS; and lowest on the upper SACN (Table 7). Figures 7 and 8 show spatial patterns for three telomers; PFOS was consistently highest at MISS in all years, and at Miss pools 3&4 in 2008. Nonetheless, in 2006 two nestlings on the lower SACN had among the highest levels found. PFOA was found in low levels at all study areas, but consistently elevated at APIS, whereas PFDS was highest along the Mississippi River (Fig. 8). The remaining PFC telomers were at low levels and patterns have not yet been mapped.

Table 6. Sample size, measures of central tendency, and variability of total PBDEs (ug/L ww) in plasma of bald eagle nestlings, 2006-2008. See text for study area names.

Study Area	Year	N	Arithmetic Mean	Median	SD	SE	Geometric Mean	Upper 95% CI	Lower 95% CI
APIS	2006	8	16.52	12.55	9.21	3.26	13.33	20.58	8.52
APIS	2007	6	8.94	8.44	3.52	1.44	8.24	11.21	5.99
APIS	2008	5	6.91	7.54	1.45	0.65	6.74	8.16	5.54
WI - South Shore	2007	6	18.01	14.24	13.64	5.57	14.56	23.51	8.88
WI - South Shore	2008	4	6.47	6.18	2.32	1.16	6.08	8.59	4.23
SACN Upper	2006	11	1.42	1.29	0.29	0.09	1.39	1.56	1.22
SACN Upper	2007	8	1.69	1.22	1.09	0.39	1.46	2.07	0.97
SACN Lower	2006	3	14.06	12.81	7.67	4.43	12.27	23.12	6.30
SACN Lower	2007	4	6.53	6.29	2.76	1.38	5.95	9.06	3.81
SACN Lower	2008	7	6.13	6.81	2.16	0.82	5.64	7.49	4.20
MISS	2006	10	15.99	13.49	7.17	2.27	14.30	18.76	10.85
MISS	2007	11	18.74	13.32	10.11	3.05	16.34	21.59	12.32
MISS	2008	15	14.45	14.73	4.11	1.06	13.64	16.00	11.60
Miss - Pools 3&4	2008	15	9.74	9.57	3.24	0.84	9.14	10.75	7.74

Table 7. Sample size, measures of central tendency, and variability of total PFCs (ug/L ww) in plasma of bald eagle nestlings, 2006-2008. See text for study area names.

Study Area	Year	N	Arithmetic Mean	Median	SD	SE	Geometric Mean	Upper 95% CI	Lower 95% CI
APIS	2006	8	189.78	199.45	73.94	26.14	175.32	230.20	133.46
APIS	2007	6	169.63	138.00	101.76	41.54	149.17	218.95	101.53
APIS	2008	5	347.96	322.52	83.36	37.28	338.91	417.06	275.37
WI - South Shore	2007	6	192.32	176.61	77.14	31.49	175.61	249.81	123.37
WI - South Shore	2008	4	263.09	266.92	66.39	33.20	255.15	331.81	196.14
SACN Upper	2006	11	30.83	29.06	19.47	5.87	25.59	35.65	18.30
SACN Upper	2007	8	15.18	14.23	6.14	2.17	13.94	18.20	10.62
SACN Lower	2006	3	1807.10	2300.33	942.58	544.20	1550.27	3357.34	715.56
SACN Lower	2007	4	348.10	350.77	266.23	133.11	164.37	752.67	35.28
SACN Lower	2008	7	901.39	758.90	513.06	193.92	789.45	1145.28	544.08
MISS	2006	10	1363.13	1250.50	639.78	202.32	1234.17	1612.83	944.35
MISS	2007	11	829.45	830.97	250.41	75.50	787.00	952.68	650.10
MISS	2008	15	1145.79	1074.95	571.72	147.62	956.02	1331.38	686.41
Miss - Pools 3&4	2008	15	1609.49	1455.60	632.88	163.41	1480.56	1813.29	1208.84

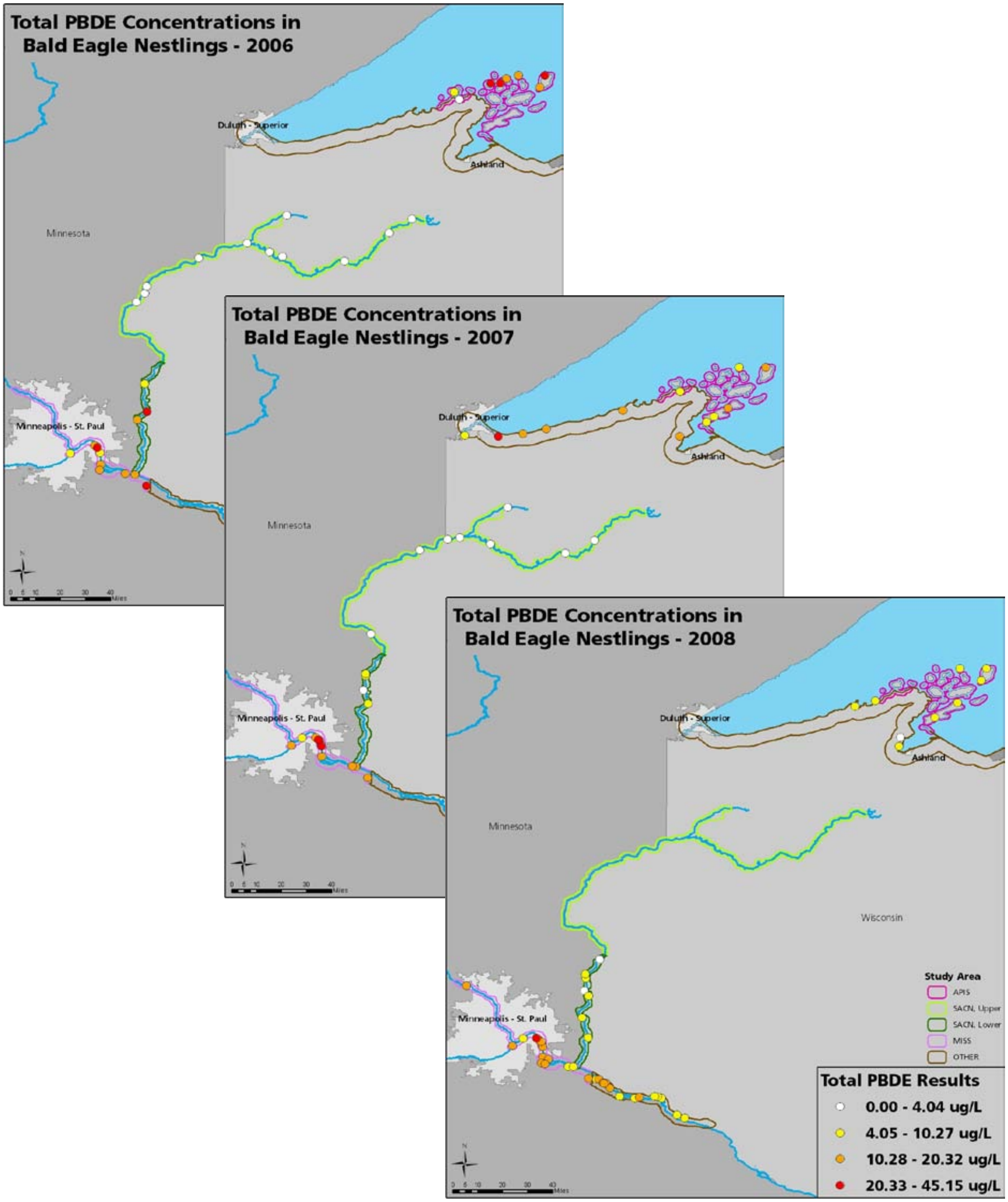

Figure 6. Spatial patterns of PBDEs in plasma of bald eagle nestlings from 2006 to 2008 in and adjacent to three national parks in the western Great Lakes region. Study areas: APIS = Apostle Islands National Lakeshore; U SACN & L SACN = upper and lower sections of the St. Croix National Scenic Riverway respectively; MISS = Mississippi National River and Recreation Area; P 3&4 = pools 3 and 4 of the Mississippi River below MISS. *Upper SACN was not sampled in 2008 and pools 3 & 4 were not sampled in 2006 or 2007. Samples below the limits of detection were removed.

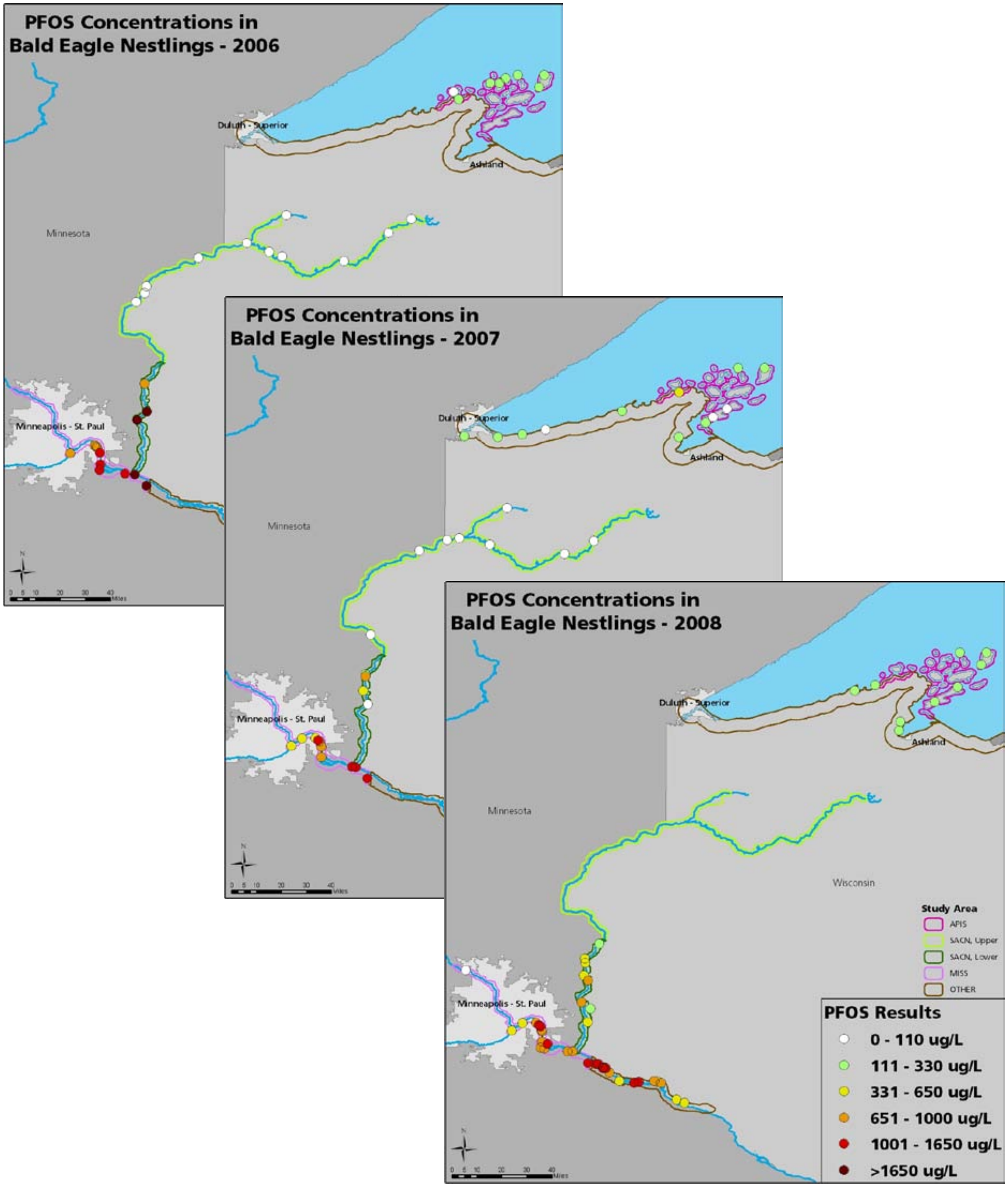

Figure 7. Spatial patterns of PFOS in plasma of bald eagle nestlings from 2006 to 2008 in and adjacent to three national parks in the western Great Lakes region. Study areas: APIS = Apostle Islands National Lakeshore; U SACN & L SACN = upper and lower sections of the St. Croix National Scenic Riverway respectively; MISS = Mississippi National River and Recreation Area; P 3&4 = pools 3 and 4 of the Mississippi River below MISS. *Upper SACN was not sampled in 2008 and pools 3 & 4 were not sampled in 2006 or 2007. Samples below the limits of detection were removed.

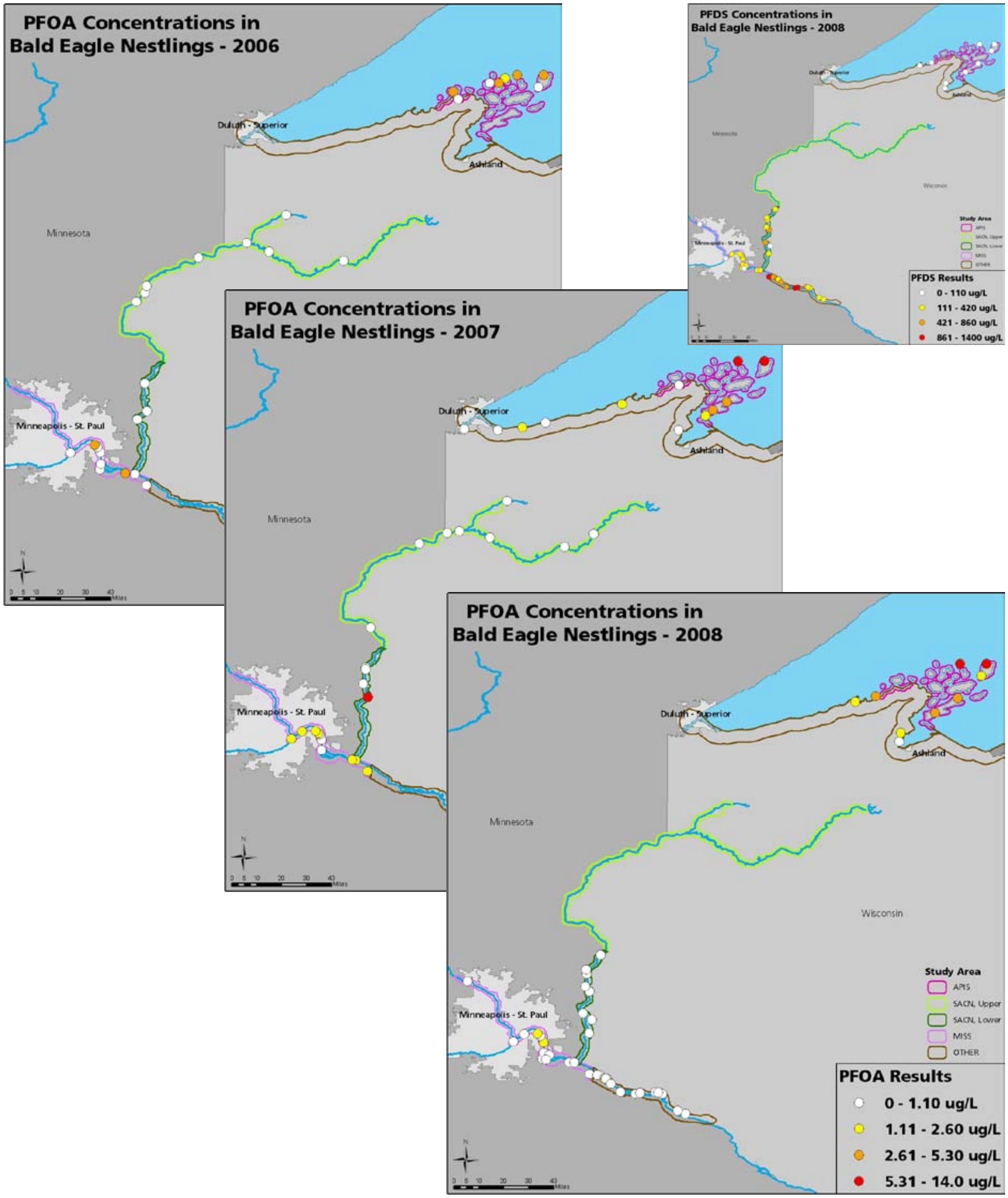

Figure 8. Spatial patterns of PFOA and PFDS in plasma of bald eagle nestlings from 2006 to 2008 in and adjacent to three national parks in the western Great Lakes region. Study areas: APIS = Apostle Islands National Lakeshore; U SACN & L SACN = upper and lower sections of the St. Croix National Scenic Riverway respectively; MISS = Mississippi National River and Recreation Area; P 3&4 = pools 3 and 4 of the Mississippi River below MISS. *Upper SACN was not sampled in 2008 and pools 3 & 4 were not sampled in 2006 or 2007. Samples below the limits of detection were removed.

In 2008, when results were available for all 16 telomers, we found that PFOS made up 64% by volume of the total PFCs in nestling blood (Fig. 9). PFOA, on the other hand, made up < 1% of total PFC volume. The second most abundant telomer was PFDS at 30%. The high concentrations of PFDS were unexpected. Other studies in the region have not looked for PFDS; its origin and toxicity are currently under investigation.

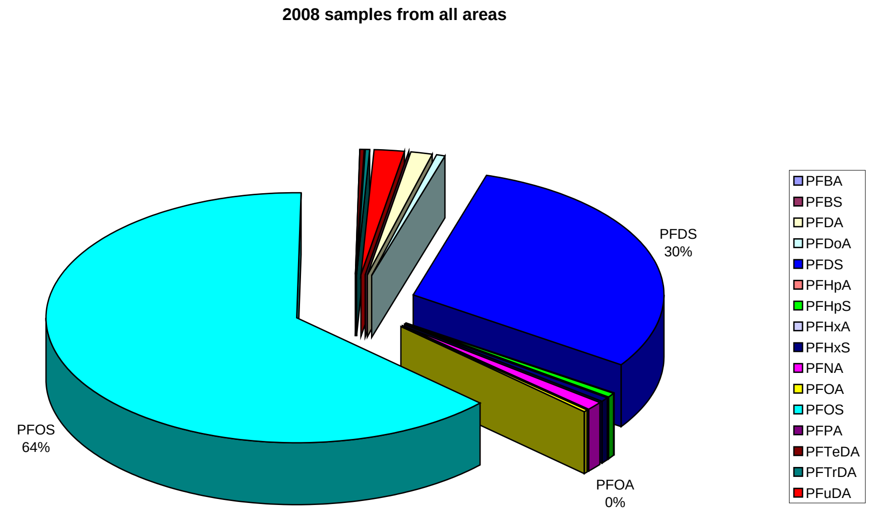

Figure 9. Percent of the total ug/L by volume for 16 perfluorinated telomers found in bald eagle nestling blood samples (n= 111) from three national parks and adjacent study areas in the Great Lakes Inventory and Monitoring Network in 2008. See Table 1 for sample distribution across study areas.

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Appendix A

Number of matrix spikes preformed with average percent recovery and standard deviations as part of a quality assurance program conducted on nestling bald eagle plasma for 16 PFC-telomers and 9 PBDE congeners. Analysis by the Wisconsin State Laboratory of Hygiene, Madison, WI. Plasma collected by the National Park Service, Great Lakes Inventory and Monitoring Network, 2008.

Analyte	**# of spikes**	**Average % recovery**	**Standard deviation**
Perfluorinated compounds (PFCs):			
PFOS	32	103.8	7.7
PFOA	13	105.5	10.2
PFBS	13	105.9	8.0
PFHxS	13	96.6	23.2
PFHpS	13	96.0	11.8
PFDS	13	97.4	25.1
PFBA	13	91.9	18.3
PFPA	13	93.1	29.6
PFHxA	13	95.7	15.6
PFHpA	13	100.0	15.0
PFNA	13	107.1	13.9
PFDA	13	83.6	18.6
PFuDA	13	98.2	18.0
PFDoA	13	126.5	32.7
PFTrDA	13	86.6	18.5
PFTeDA	13	88.9	17.5
Polybrominated diphenyl ethers (PBDEs):			
PBDE#28	5	101.6	10.5
PBDE#47	5	87.8	6.6
PBDE#66	5	94.0	8.3
PBDE#100	5	97.8	4.3
PBDE#99	5	90.0	7.3
PBDE#85	5	87.8	19.5
PBDE#154	5	91.8	8.5
PBDE#153	5	95.2	4.4
PBDE#138	5	95.4	16.8