



Contaminants Affect All Levels of the Aquatic Food Chain

Fishing is a popular activity in the Great Lakes national parks, and many people like to eat what they catch. For those who do, it is important to know about contaminants that are showing up in fish across the Great Lakes parks. Concentrations of some of these contaminants exceed state and federal guidelines for human health as well as thresholds for affecting behavior and reproduction of the fish themselves and fish-eating wildlife.

Concentrations of mercury were measured at all levels of the aquatic food chain: soil and lake-bottom sediments, water, seston (particulate matter, mostly algae, suspended in the water column), zooplankton, *larval dragonflies*, *prey fish* (such as central mudminnows, darters, and small yellow perch), and *predator fish* (such as adult northern pike or bass). Concentrations of the other contaminants (*see sidebar*) were only measured in adult fish.

Samples were collected from 2008 through 2012 at Grand Portage National Monument (three streams), Indiana Dunes National Lakeshore (three sites), Isle Royale National Park (four lakes), Pictured Rocks National Lakeshore (five lakes), Sleeping Bear Dunes National Lakeshore (four lakes), and Voyageurs National Park (four lakes) (*see map*).

Where Do These Contaminants Come From?

Mercury — About half of the human-caused emissions of mercury in the United States are from coal-burning power plants. It is carried on the wind and in snow and rain, eventually settling out of the atmosphere and into park lakes. Most of the mercury accumulated in the aquatic food chain is *methylmercury*. This toxic organic compound is created through a process in which certain bacteria acting on the inorganic mercury from the atmosphere convert it to methylmercury. These bacteria are especially prevalent in wetlands and non-oxygenated bottom waters.

Legacy contaminants have a long history of environmental contamination. They include lead, DDT and its metabolites, and PCBs.

Lead — Lead used to come from paint and from the combustion and emission of leaded gasoline in vehicles. But lead in paint was banned in the 1980s, and leaded gasoline was banned in 1996. Today, atmospheric lead is a by-product of coal combustion and industrial processing of lead ore. Some also comes from fishing sinkers and shotgun ammunition used to hunt waterfowl.

DDT — The insecticidal properties of DDT were discovered in 1939. After that, it was used liberally to control mosquitoes and agricultural pests until it was banned in the United States in 1972.

PCBs — Polychlorinated biphenyls were used in hydraulic fluids, electrical transformers, and capacitors, beginning in

Contaminants Studied

Mercury / Methylmercury (toxic form of mercury)

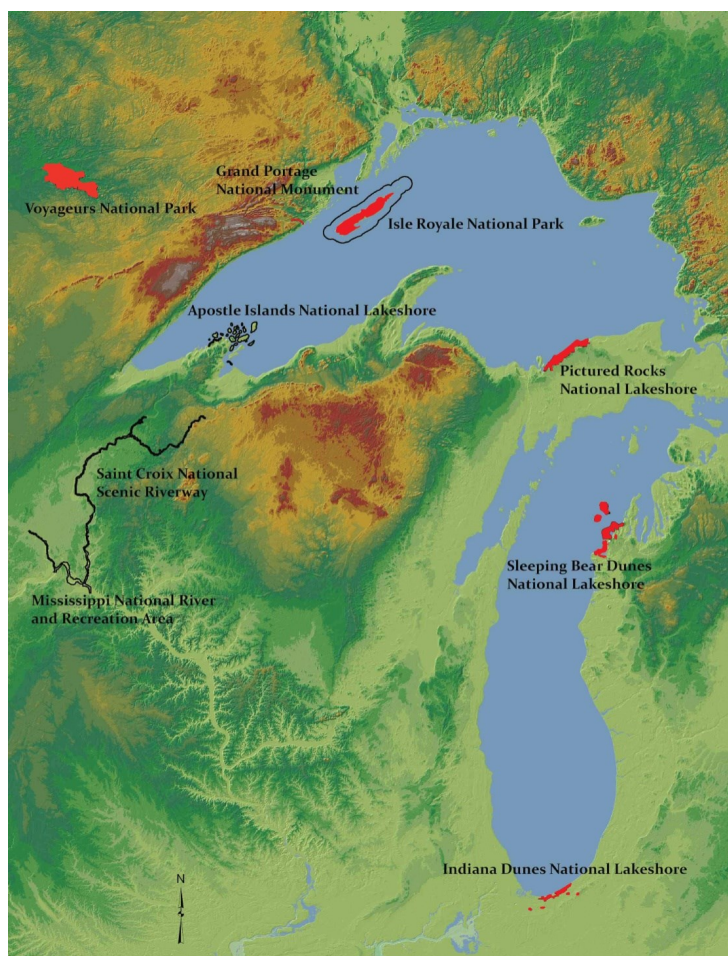
Total lead

DDT and its metabolites DDE and DDD

Polychlorinated biphenyls (PCBs)

Perfluorochemicals (PFCs)

Polybrominated diphenyl ethers (PBDEs)



Great Lakes Network parks. Parks in red were part of the fish and dragonfly contaminants analysis.

the late 1920s. Environmental contamination by PCBs was detected in the mid 1930s, and they were banned in the United States in 1977.

Emerging contaminants are relatively newer chemical compounds that include PFCs and PBDEs.

PFCs — Perfluorochemicals have been manufactured since 1949 for use in a variety of industrial applications and consumer products, including polyurethane production, water and stain repellants, fire-fighting foams, lubricants, and surfactants. Sources of PFCs to the environment include manufacturing plants, sewage treatment plants, landfills, and households. PFOS (perfluorooctane sulfonate) is the dominant form found in fish and wildlife, generally accounting for 60% to 90% or more of total PFCs in the tissues analyzed.

PBDEs — Polybrominated diphenyl ethers are a class of persistent, halogenated flame retardants first used in the 1970s in plastics, polyurethane foams, furniture, textiles, and automobiles. PBDEs are released to the environment during the use and disposal of such products, entering the aquatic environment in effluents from wastewater treatment plants, runoff and stream flow from nonpoint sources, and atmospheric deposition.

Legacy and Emerging Contaminants Are Low-Level Players

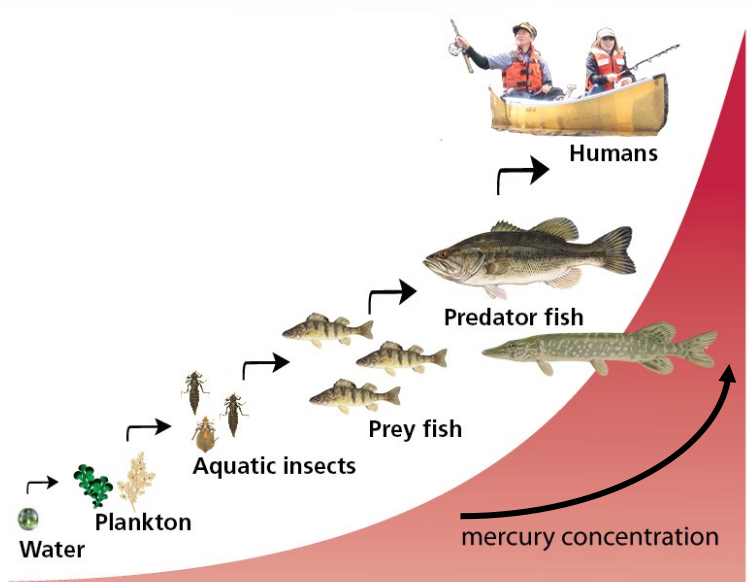
Concentrations of legacy and emerging contaminants in both predator and prey fish **were low or below the limits of detection** at all six parks. However, concentrations in prey fish from one of the three study sites **at Indiana Dunes (Middle Lagoon), had elevated concentrations of DDT and its metabolites, PCBs, and total lead**. In particular, gizzard shad from the lagoon had maximum concentrations of 570 nanograms/gram (ng/g) of DDE, 446 ng/g total PCBs, and 304 ng/g total lead. Concentrations of total DDT (combined DDT + DDE + DDD) exceeded screening-level benchmark concentrations associated with altered health and reproduction in fish, belted kingfisher, and American mink.

Mercury Is Of Greatest Concern

Fish in some parks have accumulated mercury to significant levels. Mercury concentrations in adult predator fish from several water bodies substantially exceeded 300 ng/g (*see sidebar*)—these included one or more *individual fish* from four of five study lakes at Pictured Rocks and all four study lakes at Isle Royale, Sleeping Bear Dunes, and Voyageurs. None of the individual fish from streams at Grand Portage and only one fish from Indiana Dunes exceeded 300 ng/g. **Average** mercury concentrations in predatory fish exceeded 300 ng/g in four lakes at Voyageurs, three lakes at Pictured Rocks, two lakes at Isle Royale, and two lakes at Sleeping Bear Dunes.

Mercury concentrations in some predator fish exceeded 500 ng/g wet weight (*see sidebar*).

Concentrations in one or more *individual* predatory fish from a total of 16 water bodies at Isle Royale, Pictured Rocks, Sleeping Bear Dunes, and Voyageurs exceeded this benchmark. **Average** concentrations exceeded this benchmark level in predatory fish from eight water bodies—all four study lakes at Voyageurs, two lakes at Pictured Rocks, one lake at Isle Royale, and one lake at Sleeping Bear Dunes. Mercury levels in both prey and predator fish from three water bodies at Indiana Dunes were generally lower than those in fish from the other park units.



Mercury becomes more concentrated and more toxic as it moves up the food chain. Diagram adapted from NPS Air Resources Division.

Important Mercury Numbers

500 nanograms/gram (ng/g, or parts per billion)

A benchmark concentration associated with altered biochemical processes, damage to cells and tissues, and diminished reproduction in *fish*.

300 ng/g

The U.S. Environmental Protection Agency's tissue residue criterion for methylmercury, established to protect the health of *humans* who eat fish that they catch.

70 ng/g

Mercury concentration in prey fish, above which the health and reproduction of *American mink* are at risk.

30 ng/g

Mercury concentration in prey fish, above which the health and reproduction of *belted kingfishers* are at risk.

Mercury concentrations in prey fish from some water bodies were high enough to adversely affect predator fish or fish-eating wildlife such as the common loon, which is moderately sensitive to methylmercury, and mink, which is highly sensitive to methylmercury.

Methylmercury concentrations in zooplankton were strongly related to concentrations in water. Factors that increase bacterial production of methylmercury and its transport in water and sediment will strongly influence mercury levels in fish and fish-eating wildlife. One such factor is the abundance of wetland and forest cover in the watershed. **There was a general increase in methylmercury in water and zooplankton from southeast (Indiana Dunes and Sleeping Bear Dunes) to northwest (Voyageurs), corresponding to increased wetland and forest cover**, as well as other factors.

Grand Portage's Unique Mercury Source

Grand Portage is a mercury-sensitive landscape with high rates of methylmercury production—streams there had the **highest methylmercury concentrations of any of the park sites**. What was most interesting (and unexpected) was that mercury concentrations in soil and sediment from Grand Portage streams were *three- to four-fold higher* per unit of organic matter than those in sampled water bodies at any of the other parks. Where does this excess contamination come from? While atmospheric deposition is the primary pathway for entry of mercury into other Great Lakes Network parks, it is **very likely that a significant fraction of the mercury in Grand Portage streams is from vermilion used in the fur trade**.

Dragonflies Are the Future

Most of the mercury in larval dragonflies was methylmercury. Average proportions of methylmercury in dragonfly larvae from individual park units ranged from 69% to 93% of total mercury levels. Average concentrations of methylmercury in three regionally widespread families of dragonfly were highest at Grand Portage, Pictured Rocks, and Voyageurs. **Average methylmercury concentrations in dragonfly larvae generally reflected mercury levels in fish from the same lakes**. In other words, the methylmercury concentrations in dragonflies could be used to predict the concentrations in fish. Thus, larval dragonflies can be useful biosentinels of methylmercury in aquatic food chains.



Powdered vermilion is composed of mercury and sulfides. It was a popular bartering item during the fur trade era and was used by the Ojibwe for facial decoration and painting. It is thought that remnants of it in the soil and the stream-bottom sediments contribute to the unusually high mercury concentrations found at Grand Portage today. Photo from Wikimedia Commons.



The dusky clubtail (*Gomphus spicatus*) is a widespread species of burrowing dragonfly found in 13 of the 17 lakes sampled in four national parks and lakeshores. Photo by Roger Haro.



Sean Bailey/UWL

Photos by Kris Rolfhus/UWL

Recommendations to Park Managers

Use larval dragonflies as biosentinels of methylmercury. The correlation between methylmercury levels in dragonfly larvae and fish from the same lake shows the usefulness of larval dragonflies as an indicator species in the aquatic food chain. The benefits over using fish or any larger predators include more affordable field sampling, the ability to monitor contaminants in lakes that naturally lack a fish population, and an excellent opportunity for citizen involvement in park science.

Discontinue any further monitoring of PBDEs and PFCs in fish. Concentrations of these contaminants were low or non-detectable in fish. However, park managers should be alert for new information about other emerging, bioaccumulative compounds that could be included in future analyses.

Periodically reassess the status of mercury contamination in fish. Both predator and prey fish should be sampled and analyzed at 5- to 10-year intervals to reassess ecological risks to fish-eating wildlife and potential health risks to persons who eat fish they catch in the parks.

Assess exposure and reproductive effects of methylmercury on fish-eating wildlife. Mercury concentrations in prey fish from several water bodies in the six parks exceeded screening-level dietary benchmarks for fish-eaters that are highly sensitive (mink, belted kingfisher) or moderately sensitive (common loon) to methylmercury exposure.

Provide fish consumption advice to persons who eat fish caught in the parks. Such information should focus on mercury and make special mention of the large variation in mercury levels among park units and water bodies. Park managers are encouraged to quantify mercury levels in sport fish from any intensively fished lakes that have not yet been surveyed.

Assess contaminants in sport fish from Middle Lagoon at Indiana Dunes. Some prey fish in Middle Lagoon contained high concentrations of DDD, DDE, PCBs, and PFOS (a type of PFC). Candidate species for sampling and analyses include largemouth bass, grass pickerel, bluegill, and channel catfish.

Continue trend monitoring of mercury in lakes at Voyageurs National Park. Continued monitoring of mercury in small yellow perch (i.e., prey fish) and lake water provides a cost-effective and scientifically defensible approach for assessing responses of lakes to changes in atmospheric mercury deposition over time. ●



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Read the Complete Report—

Wiener, J.G., R.J. Haro, K.R. Rolhus, M.B. Sandheinrich, S.W. Bailey, R.M. Northwick, and T.J. Gostomski. 2016. [Bioaccumulative contaminants in aquatic food webs in six national park units of the western Great Lakes region: 2008–2012](#). Natural Resource Report NPS/GLKN/NRR—2016/1302. National Park Service, Fort Collins, Colorado.
