GREAT LAKES FISH MONITORING AND SURVEILLANCE PROGRA M TECHNICAL REPOR T

Status and Trends of Contaminants in Whole Fish through 2019 with Special Studies in Lakes Ontario and Erie

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1 EXECUTIVE SUMMARY

The U.S. Environmental Protection Agency (EPA) Great Lakes National Program Office (GLNPO) Great Lakes Fish Monitoring and Surveillance Program (GLFMSP) is a long-term monitoring program designed to: 1) collect, analyze, and report contaminant concentrations in Great Lakes top-predator fish (Lake Trout [*Salvelinus namaycush*] and Walleye [*Sander vitreus*]), 2) improve understanding of contaminant cycling throughout food webs in the Great Lakes, and 3) screen for emerging chemicals in fish tissue to identify priority chemicals warranting future trend analysis and study. Samples collected for the GLFMSP are screened for emerging chemicals and analyzed for several different classes of contaminants including polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), mercury, hexabromocyclododecane (HBCDD), per- and polyfluoroalkyl substances (PFAS), toxaphene, chlordanes, polychlorinated naphthalene (PCN) congeners, dioxins/furans, and other organochlorine pesticides (OCPs).

This report presents summarized data and trends for PCBs, PBDEs, mercury, HBCDD, and PFAS in Lake Trout and Walleye and contaminants of emerging concern (CEC) screening analyses in Lake Trout and Walleye for the five GLFMSP sites sampled in odd years and the five GLFMSP sites sampled in even years. The analytical results from 2018 and 2019 are placed into the context of long-term trends beginning when each contaminant was first subjected to routine monitoring, with the exception of the Dunkirk, Lake Erie eastern basin site. Collection of Lake Trout in the eastern basin of Lake Erie began in 2008; therefore, trends from 2008-2018 and 2009-2019 are reported for Lake Erie. Trends in this report may be different for evenyear sites and odd-year sites within each lake due to local factors at the sampling sites.

An assessment of data through 2018 at even-year sampling sites and 2019 at odd-year sampling sites shows that various legacy contaminant concentrations are decreasing in Great Lakes top predator fish. Key highlights of concentration trends include:

- Mean total PCB concentrations in Lake Trout at all even-year and odd-year sampling sites have declined significantly since 1991/1992 in Lakes Huron (Port Austin: 81%; Rockport: 84%), Michigan (Sturgeon Bay: 78%; Saugatuck 83%), Superior (Keweenaw Point: 92%; Apostle Islands 82%), and Ontario (North Hamlin: 86%; Oswego 83%). Mean total PCB concentrations in Walleye at the Middle Bass Island sampling site in Lake Erie have also declined significantly since 1991/1992 (71%). Concentrations have significantly declined at the Dunkirk sampling site in the eastern basin of Lake Erie over the past ten years (37%, ten-year trend estimated using 2008-2019 data).
- Mean total PBDE concentrations in Lake Trout at even-year sampling sites declined significantly since 2002 in Lakes Huron (59%), Michigan (74%), Superior (47%), and Ontario (61%). Mean total PBDE concentrations in Walleye at the Middle Bass Island site in Lake Erie also have declined significantly since 2002 (40%). Mean total PBDE concentrations in Lake Trout have declined significantly at odd-year sampling sites since 2001 in Lakes Michigan (75%), Ontario (56%), and Superior (40%). No statistically significant changes in concentrations were found at the Port Austin sampling site in Lake Huron since 2001, or at the Dunkirk sampling site in Lake Erie since monitoring of Lake Trout began in 2008.
- Mercury concentrations in Lake Trout have exhibited a statistically significant decline since 2000 at the Apostle Islands sampling site in Lake Superior (50%). Mercury concentrations in Walleye at the Middle Bass Island sampling site in Lake Erie also have exhibited a statistically significant decline since 2000 (23%). No statistically significant changes have occurred at any other sampling sites since 1999/2000. Mercury concentrations in Lake Trout at the Sturgeon Bay sampling site in Lake Michigan have increased since 2009 (19%). The mercury concentrations in fish do not show a statistically significant change in the 1999-2019 period at this site.

The most abundant CEC compound class detected in Lake Trout and Walleye in 2018 at even-year sampling sites, and in Lake Trout in 2019 at odd-year sampling sites in all Lakes was

halomethoxyphenols. Only 2018 and 2019 CEC screening results are presented, as there are currently not enough years of data to evaluate temporal trends for CECs. In 2018, mean total HBCDD was highest in Lake Trout at the Apostle Islands sampling site in Lake Superior and lowest in Walleye at the Middle Bass Island sampling site in Lake Erie. In 2019, mean total HBCDD in Lake Trout was highest at the Port Austin sampling site in Lake Huron and lowest at the Dunkirk sampling site in Lake Erie. In 2018, mean concentrations of perfluorooctanesulfonic acid (PFOS) were highest at the Oswego sampling site in Lake Ontario and lowest at the Apostle Islands sampling site in Lake Superior. In 2019, mean concentrations of PFOS were highest at the Dunkirk sampling site in the eastern basin of Lake Erie and lowest at the Keweenaw Point sampling site in Lake Superior.

Field and biological data collection results for these Lake Trout and Walleye are presented in this report as well, along with field and biological data collection results for Lake Trout, Walleye, forage fish, and invertebrates that were collected by the GLFMSP in support of the 2018 Lake Ontario and 2019 Lake Erie Cooperative Science and Monitoring Initiative (CSMI) studies of contaminant cycling in the Lake Ontario and Lake Erie food webs. Analytical results of the CSMI studies will be presented in future reports.

2 INTRODUCTION

The U.S. Environmental Protection Agency (EPA) Great Lakes National Program Office (GLNPO) Great Lakes Fish Monitoring and Surveillance Program (GLFMSP) is a long-term monitoring program that was initiated in 1977 and designed to: 1) collect, analyze, and report contaminant concentrations in Great Lakes top-predator fish (Lake Trout [*Salvelinus namaycush*] and Walleye [*Sander vitreus*]), 2) improve understanding of contaminant cycling throughout food webs in the Great Lakes, and 3) screen for emerging chemicals in fish tissue to identify priority chemicals warranting future trend analysis and study. Lake Trout and Walleye are targeted by the GLFMSP for biomonitoring because these top predator fish occupy the highest trophic levels in the Great Lakes aquatic food web and as such, tend to accumulate higher levels of persistent and bioaccumulative contaminants [\(McGoldrick and Murphy 2016\)](#page-31-1).

The present design of the GLFMSP includes two components: 1) Base Monitoring Program and 2) Cooperative Science and Monitoring Initiative (CSMI)/Special Studies.

The GLFMSP helps EPA satisfy its statutory requirements under Section 118 of the Clean Water Act to establish a Great Lakes system-wide surveillance network to monitor the water quality of the Great Lakes [\(33 U.S.C. § 1268\)](#page-31-2) with a specific emphasis on the monitoring of toxic pollutants. It also helps satisfy the Agency's obligations under the Great Lakes Water Quality Agreement (GLWQA) to "monitor environmental conditions so that the Parties may determine the extent to which General Objectives, Lake Ecosystem Objectives, and Substance Objectives are being achieved," and "undertake monitoring and surveillance to anticipate the need for further science activities and to address emerging environmental concerns" [\(GLWQA 2012\)](#page-31-3). Further, this program allows EPA to meet commitments in the Great Lakes Restoration Initiative (GLRI) Action Plan III to "assess the overall health of the Great Lakes ecosystem and identify the most significant remaining problems" [\(GLRI 2019\)](#page-31-2).

This report summarizes chemical and biological data collection results for the 2018 and 2019 Base Monitoring Program and CSMI/Special Studies collection efforts. Long-term trends (ranging from 10 years to 28 years) for Base Monitoring Program analytical results are presented.

3 DESCRIPTION OF METHODS

This section summarizes methods for sample collection, biological data collection, homogenization, and analysis.

3.1 SAMPLE COLLECTION

Field sampling teams perform sample collections every year in the late summer to fall according to sample collection standard operating procedures (SOPs) [\(EPA 2012a\)](#page-32-0) and deliver fish to a homogenization laboratory after collection. A total of eight sampling teams collected fish for the Base Monitoring Program and CSMI/Special Studies components in 2018 and 2019:

- Great Lakes Indian Fish and Wildlife Commission
- Michigan Department of Natural Resources Alpena Fisheries Research Station
- Michigan Department of Natural Resources Charlevoix Fisheries Research Station
- New York State Department of Environmental Conservation Lake Erie Fisheries Research Unit
- Ohio Department of Natural Resources Sandusky Fisheries Research Unit
- U.S. Fish and Wildlife Service (USFWS) Green Bay Fish and Wildlife Conservation Office
- U.S. Geological Survey (USGS) Lake Ontario Biological Station
- Wisconsin Department of Natural Resources

Detailed information on collection methods can be found in the subsections below.

3.1.1 Base Monitoring Program

Top predator fish are collected at two sites in each of the Great Lakes with sites alternating within each lake annually [\(Figure 1\)](#page-7-0) for the Base Monitoring Program. Collection sites are intended to be representative of offshore conditions in each lake. Lake Trout are collected in all lakes and Walleye are collected at one site located in the western basin of Lake Erie, which is too shallow to support Lake Trout. In 2011, after two years (2008 and 2010) of comparison of contaminant body burden in Lake Trout and Walleye, Lake Trout replaced Walleye as the GLFMSP target species in the eastern basin of Lake Erie. Lake Trout were found to be more readily available for collection at the eastern basin site (Dunkirk) and had comparable contaminant burdens to Walleye. Additionally, this change allowed the GLFMSP to compare contaminants in Lake Trout across all five Great Lakes. Lake Trout data collected in 2008 and 2010 at Dunkirk for the comparison study are included in this report. Lake Trout in the size range of 600- 700 mm and Walleye in the size range of 400-500 mm are targeted for collection (target number of fish per site = 50). Fish size ranges were determined with the assumption that they represent specific age ranges, 6-8 years for Lake Trout and 4-5 years for Walleye. Detailed collection and site information for the GLFMSP Base Monitoring Program is located in the GLFMSP Quality Assurance Project Plan (QAPP) [\(EPA 2012a\)](#page-32-0).

3.1.2 CSMI / Special Studies

The Cooperative Science and Monitoring Initiative (CSMI) is a binational effort instituted under the 2012 GLWQA to coordinate science and monitoring activities in one of the five Great Lakes each year to generate data and information for environmental management agencies. The GLFMSP supports the CSMI via additional sample collection efforts and analyses to gather information regarding contaminant cycling throughout food webs in the Great Lakes. During the CSMI field year, fish are collected at both GLFMSP sites within the CSMI lake; in 2018 and 2019, the CSMI lakes were Lake Ontario and Lake Erie, respectively. Lake Trout in the size and age range collected as part of the Base Monitoring Program are targeted (target number of fish per site $= 10$). The top five most abundant species of forage fish in the CSMI lake are also collected at both sites when available (total target number of fish per site $= 110$). The GLFMSP cooperators collect sediment, benthic invertebrates, *Mysis*, phytoplankton, zooplankton/seston and water samples in the CSMI lake aboard the Research Vessel (R/V) *Lake Guardian*. Detailed collection and site information for the GLFMSP CSMI/Special Studies component is provided in the GLFMSP QAPP [\(EPA 2012a\)](#page-32-0).

Figure 1. GLFMSP collection sites.

3.2 BIOLOGICAL DATA COLLECTION AND HOMOGENIZATION

The homogenization laboratory receives fish from the field sampling teams and processes these fish in the winter to spring time period. In 2018 and 2019, the homogenization laboratory was Aquatec Environmental, Inc. (Aquatec). Aquatec follows approved GLFMSP-specific SOPs [\(Aquatec 2016\)](#page-31-4) when processing samples.

The homogenization laboratory recorded biological data (e.g., length, width, weight) and any abnormalities (e.g., tumors, fins missing, wounds), collected samples for aging purposes (e.g., scales, maxillae, coded wire tags [CWTs]), and aged the fish. In 2018 and 2019, Lake Trout age was determined based on CWTs where available and based on annuli enumeration of maxillae if no CWT was present. For Walleye, final age was determined based on dorsal spine, or if not available, enumeration of maxillae. Fish age is an important variable when assessing contaminant trends and as such, the GLFMSP compositing scheme was amended in 2013 to group fish according to age (rather than by length) prior to homogenization and chemical analysis. More information on this change can be found in the *Journal of Great Lakes Research* publication "Revised fish aging techniques improve fish contaminant trend analyses in the face of changing Great Lakes food webs" [\(Murphy et al. 2018\)](#page-31-5) and in the Great Lakes Fish Monitoring and Surveillance Program Technical Report: Status and Trends of Contaminants in Whole Fish through 2016 [\(EPA 2021a\).](#page-32-1) EPA reviewed the ages for 2018 and 2019 Lake Trout and Walleye and assigned fish into five fish per composites (target number of composites per site $= 10$) based on age for sites where the target 50 fish were collected. At the Keweenaw Point site in 2019, a total of 43 Lake Trout were collected, so seven composites of five fish and two composites of four fish were created.

After grouping fish into composites based on the EPA criteria noted above, the homogenization laboratory processed the whole fish and prepared composites of these samples. In addition, a megacomposite was prepared (i.e., tissue from all composites from a single site) where applicable for screening of contaminants of emerging concern (CECs). Other additional compound classes are also measured in the mega-composite samples. This list is noted in [Table 1](#page-9-1) below. The homogenization laboratory created tissue aliquots and delivered them to the analytical laboratory cooperator and to EPA's archival facility.

3.3 ANALYSIS

The analytical laboratory cooperator receives fish tissue aliquots from the homogenization laboratory in the spring of the year following the collection year. The analytical laboratory cooperators that analyzed the 2018 and 2019 collected fish tissue were Clarkson University, State University of New York (SUNY) Oswego, SUNY Fredonia, and AEACS, LLC. The 2018 and 2019 Base Monitoring Program analytical data sets are presented in [Table 1.](#page-9-1) All analytical data generated to support the GLFMSP are prepared in accordance with an approved QAPP and SOPs [\(Clarkson University 2016\)](#page-31-6).

Upon sample receipt, the analytical laboratory cooperator analyzed the homogenized tissue for different classes of contaminants including polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), mercury, hexabromocyclododecane (HBCDD), per- and polyfluoroalkyl substances (PFAS), toxaphene, chlordanes, polychlorinated naphthalene (PCN) congeners, dioxins/furans, and other organochlorine pesticides (OCPs). The analytical laboratory cooperator also utilized mega-composite samples collected for the Base Monitoring Program to determine the presence of CECs. Following data review by EPA, the data are used for reporting and made available to the public in the Great Lakes Environmental Database (GLENDA) and can also be requested from EPA (contact information is provided on [page ii](#page-1-1) of this report).

Collection Effort	Analytes				
Composites and mega-composites	Percent Moisture Mercury PCBs/OCPs/PBDEs/Lipids/Mirex Toxaphene				
Composites only	PFAS \bullet				
Mega-composites only	Dioxins / Furans & Co planar PCB congeners PCN Congeners HBCDD CECs				

Table 1: 2018 and 2019 Base Monitoring Program Analytical Data Sets

Results generated by all analytical methods were reported on a wet weight basis in accordance with SOPs [\(Clarkson University 2016\)](#page-31-6). No mathematical adjustments based on lipid content or fish age were performed on the 2018 and 2019 results or as part of the trend analyses presented in this report. Longterm analytical data in the GLFMSP presented in this report have not been corrected to adjust for fish age. The reason being is that fish have only been aged since 2003 as part of the sampling process and historically were grouped into estimated age composites according to length measurements. To ensure consistency in how data are reported, publicly available data for the GLFMSP are reported as contaminant concentrations for each composite for a given sampling year at each collection site. Age-corrected data from the 2018 and 2019 GLFMSP collected fish are presented in [Pagano et al.](#page-31-7) (2020).

4 QUALITY ASSURANCE AND CONTROL

The GLFMSP operates under a quality management plan (QMP), a QAPP, and numerous SOPs. The GLFMSP quality management system is defined in the GLFMSP QMP [\(EPA 2012b\)](#page-32-2). Quality assurance/quality control (QA/QC) activities and procedures associated with the sample collection, biological data collection, homogenization, and analysis of fish samples are described in the QAPPs and SOPs identified in [Section 3.](#page-5-1)

Several types of laboratory QC measures including equipment blanks, standard reference materials, blind duplicates, method blanks, replicate samples and surrogate spikes, are implemented at both the homogenization laboratory and the analytical laboratory to monitor data quality. These measures assist in identifying and correcting problems as they occur. They also define the quality of data generated by the program. QC metrics are tailored to specific sample and analytical processes. The analytical laboratory cooperator's QAPP provides specific QC requirements to identify background contamination and extraction efficiency and ensure accurate identification and quantification of targeted analytes. If any QC criteria are not met, the data are reviewed carefully to identify the cause of the problem and determine the appropriate corrective action. If reanalysis is not warranted, the data are submitted with QC flags to indicate the nature of the failure.

No major QA/QC issues have been identified through 2019.

5 RESULTS

This section summarizes results from 2018 and 2019 sample collection, biological data collection, and analysis, and presents the 2018 and 2019 Base Monitoring Program analytical results in context with long-term (10-year to 28-year) trends. Lake Ontario (2018) and Lake Erie (2019) CSMI analytical results could not be evaluated for long-term trends given the limited temporal data for these studies.

5.1 SAMPLE COLLECTION

5.1.1 Base Monitoring Program

In 2018, a total of 200 Lake Trout were collected in Lakes Huron, Michigan, Ontario, and Superior and 50 Walleye were collected in Lake Erie. In 2019, a total of 243 Lake Trout were collected in Lakes Erie, Huron, Michigan, Ontario, and Superior [\(Table 2\)](#page-10-4). In 2019, due to low availability of Lake Trout in the target size range at the Keweenaw Point collection site, a total of 43 Lake Trout were collected instead of the target 50.

Table 2: 2018 and 2019 Base Monitoring Program Field Data

^a Sampling depth was not recorded for Lake Trout collected from Dunkirk in 2019.

5.1.2 CSMI / Special Studies

In 2018, 27 additional Lake Trout were collected in Lake Ontario, from North Hamlin and Oswego (Table [3\)](#page-11-1). In 2019, 15 additional Lake Trout were collected in Lake Erie from Dunkirk and 10 additional Walleye were collected in Lake Erie from Middle Bass Island. A total of 211 forage fish were collected from both Lake Ontario sites in 2018 and a total of 1,089 forage fish were collected from both Lake Erie sites in 2019 [\(Table 4\)](#page-11-3). Sediment, benthic invertebrates, zooplankton, and *Mysis* samples were collected from both Lake Ontario sites in 2018 and both Lake Erie Sites in 2019 during dedicated R/V *Lake Guardian* CSMI surveys [\(Table 5\)](#page-12-0). Water samples were also collected during these surveys from North Hamlin in 2018 and from both Lake Erie sites in 2019.

^a Sampling depth was not recorded for Lake Trout collected from Dunkirk in 2019.

Table 4: 2018 and 2019 CSMI Forage Fish Field Data

^a Sampling depth was not recorded for forage fish collected from Dunkirk in 2019.

Table 5: 2018 and 2019 CSMI R/V Lake Guardian Collected Field Data

^a Water samples were not collected from Oswego in 2018.

5.2 BIOLOGICAL DATA COLLECTION AND HOMOGENIZATION

[Tables 6](#page-13-1) and [7](#page-14-1) provide a summary of biological data measurements (excluding age results which are included in [Table 8\)](#page-15-2) as recorded by the homogenization laboratory for the 2018 and 2019 Base Monitoring Program and CSMI/Special Studies samples.

Table 6: 2018 and 2019 Base Monitoring Program Biological Data

^a Mature = maturity stage in which fish is sexually mature (egg deposition status is either unknown, unimportant, or nonapplicable); Gravid = maturity stage in which ovary is full of eggs that are not yet ready for deposition or fertilization (eggs still contained within ovary wall structure).

^b % = percentage out of total number of fish collected at each site.

Table 7: 2018 and 2019 CSMI/Special Studies Lake Trout/Walleye Biological Data

^a Mature = maturity stage in which fish is sexually mature (egg deposition status is either unknown, unimportant, or nonapplicable); Gravid = maturity stage in which ovary is full of eggs that are not yet ready for deposition or fertilization (eggs still contained within ovary wall structure). b % = percentage out of total number of fish collected at each site.

[Table 8](#page-15-2) provides a summary of age data for 2018 and 2019 Base Monitoring Program and CSMI/Special Studies Lake Trout and Walleye samples. Age results included in the table were determined based on annuli enumeration of maxillae, dorsal spines, and CWTs. The dominant aging method used to obtain the final age for each fish is listed. For Lake Trout, final age was determined based on CWT where available

and based on annuli enumeration of maxilla if no CWT was present. For Walleye, final age was determined based on dorsal spines, or if not available, enumeration of maxilla. In 2018, the majority of Lake Trout exceeded the target age range of 6-8 years at Rockport (66%) and Apostle Islands (66%), while Saugatuck, North Hamlin (CSMI Lake Trout only), and Oswego exceeded the age range by 12%, 10%, and 6%, respectively. In 2019, the majority of Lake Trout exceeded the target age range of 6-8 years at Keweenaw Point (67%) and Port Austin (64%), while Dunkirk and Sturgeon Bay exceeded the age range by 31%, and 8%, respectively, and no Lake Trout exceeded the target age range at North Hamlin. No Walleye exceeded the target age range at Middle Bass Island in 2018 or 2019. It would be expected that fish exceeding the age range may have higher contaminant concentrations due to longer exposure times (i.e., bioaccumulation) of the environmental contaminants.

^a Lake Erie was the 2019 CSMI lake. 10 Walleye were collected from Middle Bass Island and 15 Lake Trout were collected from Dunkirk for CSMI/Special Studies.

^b Lake Ontario was the 2018 CSMI lake. 17 Lake Trout were collected from Oswego and 10 Lake Trout were collected from North Hamlin for CSMI/Special Studies.

5.3 ANALYSIS

The sections below summarize results for five contaminants (PCBs, PBDEs, mercury, HBCDD, and PFAS) in fish collected for the Base Monitoring Program in 2018 and 2019, place these results in context with long-term trends where feasible, and present results from the CEC screening analyses performed on these samples. Sample collection site locations for 2018 (even-year sites) and 2019 (odd-year sites) can be viewed in [Figure 1](#page-7-0) in [Section 3.1.](#page-6-3) The 2018 and 2019 CSMI/Special Studies Program analytical results will be presented in future GLFMSP reports.

For PCBs, PBDEs, and mercury, trends over time were evaluated using linear regression models between the sampling year and natural log-transformed composite sample results. The fitted models were used to estimate the change over two distinct time periods: 1) the last ten years (i.e., 2008-2018 for even-year sites and 2009-2019 for odd-year sites) and 2) a longer-term period starting when routine monitoring first began for each contaminant. Additionally, 95% confidence bounds for the estimated decline were calculated for each time period, site, and contaminant. The width of each confidence bound is a function of the overall model variability, amount of data in the model, and the estimated decline of the given period. Because the evaluations in this report focus on estimated changes over specified time periods rather than year-to-year changes, statistical significance was determined based on confidence intervals instead of a hypothesis test for statistically significant slope. These particular confidence intervals provide inference regarding the mean change over the time period at the 95% probability, and whether or not those bounds include a value of 0 can be used to evaluate whether the change is statistically significant or not. For example, if an estimated decline over ten years is 81%, with 95% confidence bounds of 73% and 86%, the fact that those bounds do not contain 0 allows one to conclude that the probability of observing a decline this large over ten years due to chance (i.e., if the contaminant was not in fact changing) is minimal enough to be rejected. Temporal trends for HBCDD and PFAS are not presented because comparable data currently available for these contaminants does not cover the ten-year time period used for trend evaluations in this report. Trends for HBCDD and PFAS will be evaluated in future GLFMSP technical reports once 10 years of comparable data are available.

Ten-year trends as well as longer term trends for contaminants at each collection site are presented in the sections below, with the exception of the Dunkirk collection site in Lake Erie. When the GLFMSP was designed, Walleye were selected to be collected in Lake Erie due to limited availability of Lake Trout at both collection sites [\(EPA 2012a\)](#page-32-0). Walleye were collected exclusively at both collection sites through 2007. The abundance of Lake Trout in the eastern basin of Lake Erie (where the Dunkirk site is located) slowly began to increase starting in 2000 [\(NYSDEC 2009\)](#page-31-8) and increased dramatically in 2011 [\(NYSDEC](#page-31-9) [2012\)](#page-31-9). The GLFMSP had Lake Trout collected at Dunkirk in 2008 and 2010, and then switched to collecting Lake Trout at Dunkirk in odd years starting in 2011 [\(EPA 2012a\)](#page-32-0). The GLFMSP has Dunkirk Lake Trout data from 2008, 2010, and odd years 2011-present; therefore, the sections below only present a ten-year trend estimated using the 2008-2019 Lake Trout data from Dunkirk. Even though there were no Lake Trout data from 2009 from Dunkirk, a ten-year trend was estimated from this site so that the trend evaluation would be consistent with those from the other sites. A separate full time series 2008-2019 trend was not evaluated because it would provide similar information to the ten-year trend and would not be comparable to long-term trends from the other sites.

5.3.1 PCBs

The GLFMSP provides long-term data trends for PCBs in Lake Trout and Walleye from the 1970s present. Prior to 1991, methods and target congeners varied. In this report, PCB trends for odd-year sites from 1991– 2019 (at all sites except Dunkirk, for which trends are presented from 2008-2019, as explained in [Section 5.3\)](#page-15-3) and even-year sites from 1992-2018 are presented as these are the date ranges for which the current sampling design (i.e., 10 composites of five fish with sites alternating within each lake annually) has been implemented.

Site mean total PCB concentrations ranged from 182 to 464 ng/g across the five sites in 2018 and ranged from 98.8 to 414 ng/g across the five sites in 2019 [\(Table 9\)](#page-17-0). Mean total PCB concentrations were calculated based on 142 out of 209 individual PCB congeners. Measured results were not censored based on reporting or detection limits and all reported results were included in the totals. Mean total PCB concentrations have exhibited a statistically significant decreasing trend at all sites over the ten-year (2008-2018 or 2009-2019) time series (2008-2019 time series for Dunkirk) [\(Table 9\)](#page-17-0). The 2008-2018 declines ranged from 42% at Oswego to 75% from Apostle Islands. The 2009-2019

declines ranged from 37% at Dunkirk (ten-year trend calculated using 2008-2019 data as noted in section 5.3) to 73% at Port Austin. Mean total PCB concentrations have also exhibited a statistically significant decreasing trend at all sites over the larger 1991-2019 or 1992-2018 [\(Table 9](#page-17-0) and [Figure 2\)](#page-18-1) time series, excluding Dunkirk for which we do not have Lake Trout data prior to 2008. Estimated PCB declines since 1991 at all non-Dunkirk sites range from 71% at Middle Bass Island to 92% at Keweenaw Point.

Table 9: Summary of 2018 and 2019 Total PCB Site Means and Temporal Trends

Lake	Year	Site	# Composites	Species	2018/2019 Total PCB Site Mean Concentration (standard error) (ng/g)	Estimated % Decline 1992-2018 or 1991- 2019 (95%) CI LL-UL)	Estimated % Decline Over Ten Years (95% CI LL- UL
Superior	2018	Apostle Islands	10	Lake Trout	182 (28.06)	81 (73 to 86)	75 (65 to 83)
	2019	Keweenaw Point	10		98.8 (22.27)	92 (89 to 94)	54 (30 to 69)
Michigan	2018	Saugatuck	10		464 (53.51)	83 (80 to 86)	52 (35 to 65)
	2019	Sturgeon Bay	10	Lake Trout	402(21.11)	78 (73 to 81)	51 (37 to 62)
Huron	2018	Rockport	10	Lake Trout	296 (66.90)	84 (80 to 87)	49 (24 to 66)
	2019	Port Austin	10		336 (105.6)	81 (77 to 85)	73 (61 to 81)
Erie	2018	Middle Bass Island	10	Walleye	344 (32.06)	71 (64 to 76)	57 (48 to 64)
	2019	Dunkirk	10	Lake Trout	379 (50.21)	N/A ^b	37 (27 to 46) \degree
Ontario	2018	Oswego	10	Lake Trout	432 (50.44)	83 (80 to 85)	42 $(26 \text{ to } 55)$
	2019	North Hamlin	9		414 (26.91)	86 (84 to 88)	44 (31 to 55)

a CI LL-UL indicates confidence interval lower level-upper level. b Lake Trout were not collected at Dunkirk until 2008.

c Dunkirk estimated % decline is for the 2008-2019 period.

LAKE SUPERIOR LAKE MICHIGAN 4000 4000 ● Keweenaw Point (Lake Trout) Sturgeon Bay (Lake Trout) O Apostle Islands (Lake Trout) O Saugatuck (Lake Trout) ϕ Total PCBs (ppb) 3000 Total PCBs (ppb) 3000 Total PCBs (ppb) $\overline{\mathbf{e}}$ 2000 2000 $\overline{\bullet}$ $\overline{\bullet}$ $\overline{\Phi}$ 1000 1000 $\overline{\bigcap}$ $\mathsf 0$ $\mathbf 0$ 1 019 1.019 ୄ୰ `ිද ′⊗ ୡ ୡ ୡ K). **LAKE ERIE LAKE ONTARIO** 4000 4000 ● North Hamlin (Lake Trout) • Dunkirk (Lake Trout) ø O Oswego (Lake Trout) O Middle Bass Island (Walleye) ¢ Total PCBs (ppb) 3000 Total PCBs (ppb) 3000 $\overline{\Phi}$ Φ $\overline{\Phi}$ 2000 2000 1000 1000

0

1991

1019

LAKE HURON

Figure 2. Mean total PCB concentration (ppb) in Lake Trout/Walleye 1991-2019 (even and odd-year sites).

Notes: 1) Stations are not representative of entire lake; 2) Missing dot = samples not collected for that site/year; 3) Asterisk () indicates less than 5 composites are included in the sampling period. 4) Error bars represent standard error.*

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5.3.2 PBDEs

The GLFMSP began monitoring for PBDEs using congener-specific analyses in 2000, with a complete set of analyses for most lakes available beginning in 2001. [Figure 3](#page-21-1) shows changes in mean total PBDE concentrations over time at collection sites for all years where PBDEs were analyzed. This includes data from 2001-2019 for odd-year sites except Dunkirk, for which data are presented from 2008-2019 as explained in [Section 5.3,](#page-15-0) and data from 2002-2018 for even-year sites.

Site mean total PBDE concentrations ranged from 6.33 to 51.6 ng/g across the five sites [\(Table 10\)](#page-20-0) in 2018 and ranged from 16.7 to 44.0 ng/g across the five sites in 2019. Mean total PBDE concentrations were calculated based on five congeners (47, 99, 100, 153, and 154) that have been analyzed consistently across all years. These are the only PBDE congeners that have been consistently measured by GLFMSP and are the PBDE congeners found in the highest concentrations in Great Lakes fish [\(Zhou et al. 2018\)](#page-32-3). Measured results were not censored based on reporting or detection limits and all reported results were included in the totals. Mean total PBDE concentrations showed a statistically significant decline at all even-year sites other than Rockport over the 2008-2018 time series [\(Table 10\)](#page-20-0), with ten-year declines ranging from 0% at Rockport to 54% at Apostle Islands. Two of the five odd-year sites exhibited a statistically significant decline over the 2009-2019 time series [\(Table 10\)](#page-20-0), with a ten-year decline of 52% at North Hamlin and a ten-year decline of 47% at Port Austin.

Estimated total PBDE concentration declines over the 2002-2018 time series for even-year sites [\(Table 10](#page-20-0) and [Figure 3\)](#page-21-1) are statistically significant at all five sites, and range between 40% at Middle Bass Island and 74% at Saugatuck. Estimated total PBDE concentration declines over the 2001-2019 time series for odd-year sites [\(Table 10](#page-20-0) and [Figure 3\)](#page-21-1) are statistically significant at the Sturgeon Bay, North Hamlin and Keweenaw Point sites, with estimated declines ranging between 40% and 75%.

Table 10: Summary of 2018 and 2019 Total PBDE (5 congeners) Site Means and Temporal Trends

a CI LL-UL indicates confidence interval lower level-upper level. b Lake Trout were not collected at Dunkirk until 2008.

c Dunkirk estimated % decline is for the 2008-2019 period.

LAKE SUPERIOR

LAKE ERIE

LAKE MICHIGAN

LAKE ONTARIO

2019

2011

 \cdot $v_{\alpha,2}$ **2015**

Figure 3. Mean total PBDE (5 congeners) concentration (ppb) in Lake Trout/Walleye 2001-2019 (even and odd-year sites).

Notes: 1) Stations are not representative of entire lake; 2) Missing dot = samples not collected for that site/year; 3) Asterisk () indicates less than 5 composites are included in the sampling period; 4) Total PBDE = sum of congeners 47, 99, 100, 153, 154; 5) Data were collected from both Lake Erie sites in 2008, but values are approximately equal (Dunkirk: 15.0 ppb; Middle Bass Island: 15.8 ppb) and partially overlap on the plot. 5) Error bars represent standard error.*

5.3.3 Mercury

The GLFMSP began monitoring for total mercury in 1999. Figure 4 shows changes in mean total mercury concentrations over time at collection sites for all years where mercury was analyzed. This includes data from 1999-2019 for odd-year sites except Dunkirk, for which data are presented from 2008-2019 as explained in [Section 5.3,](#page-15-0) and data from 2000-2018 for even-year sites.

Site mean mercury concentrations ranged from 66 to 241 ng/g across the five sites in 2018 and ranged from 104 to 181 ng/g across the five sites in 2019 [\(Table 11\)](#page-22-1). Mean mercury concentrations showed a statistically significant decline over the 2008-2018 time series at the Middle Bass Island and Apostle Islands sites, with estimated ten-year declines of 34% and 33%, respectively. In 2019, no site showed a statistically significant decrease over the 2009-2019 time series [\(Table 11\)](#page-22-1). However, the mean mercury concentration showed a statistically significant increase of 19% at the Sturgeon Bay site over this time period.

Since 1999 at odd-year sites and 2000 at even-year sites, statistically significant decreases in mercury concentrations were detected at the Middle Bass Island and Apostle Islands sites only. While six of the other sites did exhibit an estimated increase over this period, with the largest increase of 14% at the Port Austin and Keweenaw Point sites [\(Table 11\)](#page-22-1), none were statistically significant.

Lake	Year	Site	# Composites	Species	2018/2019 Total Mercury Site Mean Concentration <i>(standard)</i> error) (ng/g)	Estimated % Decline ^a 2000- 2018 or 1999- 2019 (95% CI LL-UL) b	Estimated % Decline Over Ten Years (95% CI LL- UL
Superior	2018	Apostle Islands	10		241 (24.63)	50 $(38 \text{ to } 60)$	33 (15 to 48)
	2019	Keweenaw Point	9	Lake Trout	181 (33.3)	-14 (-43 to 9)	-19 (-59 to 10)
Michigan	2018	Saugatuck	10	Lake Trout	123 (9.82)	11 $(-5 \text{ to } 25)$	$9(-9 to 25)$
	2019	Sturgeon Bay	10		136(7.84)	-4 (-21 to 10)	-19 (-38 to -2)
Huron	2018	Rockport	10	Lake Trout	199(22.37)	-6 (-31 to 14)	16 $(-9 \text{ to } 35)$
	2019	Port Austin	10		177(15.08)	-14 (-33 to 3)	15 (-5 to 31)
Erie	2018	Middle Bass Island	10	Walleye	66(3.11)	$23(10 \text{ to } 34)$	34 (22 to 44)
	2019	Dunkirk	10	Lake Trout	104(9.84)	N/A ^c	-5 (-17 to 5) ^d
Ontario	2018	Oswego	10	Lake Trout	108(9.66)	-2 (-14 to 16)	-13 (-38 to 7)
	2019	North Hamlin	$10\,$		120(3.91)	2 $(-8 \text{ to } 11)$	-7 (-20 to 5)

Table 11: Summary of 2018 and 2019 Total Mercury Site Means and Temporal Trends

a A negative percent decline of –X% corresponds to a percent increase of X%.
^{*b*} CI LL-UL indicates confidence interval lower level-upper level.
^{*c*} Lake Trout were not collected at Dunkirk until 2008.

d Dunkirk estimated % decline is for the 2008-2019 period.

LAKE SUPERIOR

LAKE ERIE

 $\mathbf 0$

LOS $\sqrt{\mathcal{P}_{\mathcal{O}}}$ 1 203 b 2005

LAKE MICHIGAN

1209 BIN -2019 BIS $\mathcal{P}_{\mathcal{P}_{\mathcal{A}}}^{\mathcal{P}_{\mathcal{A}}}$ **12019**

LAKE ONTARIO

, 2001.

Sturgeon Bay (Lake Trout)

2015 2011 **2019**

O Saugatuck (Lake Trout)

LAKE HURON

Figure 4. Mean total Mercury concentration (ppb) in Lake Trout/Walleye 1999-2019 (even and odd-year sites).

Notes: 1) Stations are not representative of entire lake; 2) Missing dot = samples not collected for that site/year; 3) Asterisk () indicates less than 5 composites are included in the sampling period; 4) Data were collected from both Lake Erie sites in 2010, but values are approximately equal (Dunkirk: 94.5 ppb; Middle Bass Island: 90.4 ppb) and partially overlap on the plot.5) Error bars represent standard error.*

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5.3.4 HBCDD

The GLFMSP added analysis of three HBCDD isomers in mega-composite samples to the program in 2012, beginning with analysis of samples collected in 2010. HBCDD was added to the GLFMSP due to its designation as a chemical of mutual concern under the GLWQA. Five years of data are available for each even-year (2010, 2012, 2014, 2016, and 2018) and odd-year (2011, 2013, 2015, 2017, and 2019) site, each include five data points per site. Because this time period is not sufficient to allow for a meaningful evaluation of trends, temporal trends for total HBCDD concentration are not evaluated in this report. However, each mega-composite sample was analyzed for three HBCDD isomers in triplicate, such that site means and associated analytical variability could be calculated. Mean total HBCDD concentrations were calculated based on the three analyzed HBCDD isomers. Measured results were not censored based on reporting or detection limits and all reported results were included in the totals.

Total HBCDD mega-composite means across the 2018-2019 period range from 1.58 ng/g at Middle Bass Island to 9.33 ng/g at Port Austin [\(Table 12\)](#page-24-1). Total HBCDD concentrations were highest at Apostle Islands and lowest at Middle Bass Island in 2018. Total HBCDD concentrations were highest at Port Austin and lowest at Dunkirk in 2019. Variation among the two sampling sites was greatest in Lake Superior, with a mean concentration from Apostle Islands more than two times greater than samples from Keweenaw Point.

[Figure 5](#page-25-1) shows changes in HBCDD concentration over time at collection sites for all years where HBCDD was analyzed. Because only five years of data covering only an eight-year period are available for each site, temporal trends were not evaluated statistically, and the data are only presented over time for illustrative purposes.

Lake	Year	Site	# Replicates ^a	Species	Total HBCDD Mega-composite Mean Concentration (standard error) (ng/g)
Superior	2018	Apostle Islands	3	Lake Trout	9.12(0.21)
	2019	Keweenaw Point	3		4.12(0.28)
Michigan	2018	Saugatuck	3		6.26(0.30)
	2019	Sturgeon Bay	3	Lake Trout	7.12(0.10)
Huron	2018	Rockport	3	Lake Trout	7.39(0.13)
	2019	Port Austin	3		9.33(0.22)
Erie	2018	Middle Bass Island	3	Walleye	1.58(0.20)
	2019	Dunkirk	3	Lake Trout	1.86(0.07)
Ontario	2018	Oswego	3	Lake Trout	4.22(0.09)
	2019	North Hamlin	3		3.4(0.14)

Table 12: Summary of 2018 and 2019 Total HBCDD Mega-composite Means

^a Single mega-composite samples were analyzed in triplicate (so variability estimates include analytical variability but not sampling variability, which is included in the calculated standard errors for other analyte classes presented in this report).

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1-2018 B-2019

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2018-2019

Figure 5: HBCDD concentration (ppb) in Lake Trout/Walleye 2010-2019 (even and odd-year sites)

Notes: 1) Stations are not representative of entire lake; 2) Error bars represent stand error. 3) Single mega-composite samples were analyzed in triplicate (so variability estimates include analytical variability but not sampling variability, which is included in the calculated

standard errors for other analyte classes presented in this report).

5.3.5 PFAS

The GLFMSP began monitoring PFAS compounds in 2011. The list of analyzed PFAS compounds has varied since 2011. In 2018 and 2019, monitored PFAS compounds included 26 perfluorinated carboxylic acids and sulfonates with 4 to 13 carbons, including 10 branched isomers. Starting with data collected in 2013, the analytical method used to quantify PFAS was modified to improve reproducibility in complex biological tissues [\(Point et al. 2019\)](#page-32-4). This method utilizes ultra-high-performance liquid chromatography with tandem mass spectrometry (UPLC-MSMS) to analyze for the targeted PFAS compounds. There have also been changes to the number and type (e.g., age-based versus size-based, changes in median age) of composites analyzed over the years. All composites for each site were analyzed in 2011 and 2012, and after 2012, the data only include five composites per site. In most cases, the first five composites (i.e., the youngest fish based on age-compositing) were used, but in 2013, a different subset of five composites was used (i.e., not only the youngest five) for each site.

The analyses presented in this report focus on Perfluorooctanesulfonic acid (PFOS), which is one of the most widely used and studied chemicals in the PFAS group [\(EPA 2022\)](#page-32-5), is frequently detected in GLFMSP fish samples, and has the highest concentration among the PFAS compounds in GLFMSP fish samples on average. [Table 13](#page-26-1) shows PFOS site mean concentrations and their associated standard errors for the composites that were analyzed from each site sampled in 2018 and 2019. Because the PFAS analysis scheme was generally consistent across sites, the mean PFOS concentrations can be compared to each other. As seen in [Table 13,](#page-26-1) PFOS concentrations across the 2018-2019 period range from 3.6 ng/g at Keweenaw Point to 66.8 ng/g at Dunkirk. PFOS concentrations were highest at Oswego and lowest at Apostle Islands in 2018, and highest at Dunkirk and lowest at Keweenaw Point in 2019.

[Figure 6](#page-27-1) shows changes in PFOS concentration over time at collection sites for all years where PFOS was analyzed. Due to the evolving analytical methodology and differences in composites analyzed over the years, temporal trends were not evaluated statistically, and the data are only presented over time for illustrative purposes. The current scheme of analyzing only the first five composites for PFAS compounds was not fully implemented until 2014, and therefore, only the three most recent sampling years per site can be considered fully comparable.

Figure 6: PFOS concentration (ppb) in Lake Trout/Walleye 2011-2019 (even and odd-year sites)

Notes: 1) Stations are not representative of entire lake; 2) 2011 and 2012 data include all composites for each site and a different analytical method was used, which is not comparable to the current method; 3) After 2012, data only include 5 composites per site. Since 2014, the first five composites (the youngest fish based on age-compositing) were used. In 2013, a different subset of five composites was used (not only the youngest five) for each site. 4) Error bars represent standard error.

5.3.6 CECs

Since 2014, Base Monitoring Program mega-composites samples have been screened for CECs. Initial screening studies have been focused on detecting organic compounds that contain one or more chlorine or bromine atoms. Historically, organic chemicals containing carbon bonded to chlorine or bromine have been found to be bioaccumulative and potentially exhibit adverse effects on lake biota (e.g., PCBs, OCPs, PBDEs) (Howard [and Muir 2010\)](#page-31-10).

[Figure 7](#page-28-1) summarizes the total concentration of all halogenated organic chemicals observed in fish collected from even-year sites in 2018. Middle Bass Island exhibited the highest total concentration followed by Apostle Islands, Rockport, with Saugatuck, and Oswego exhibiting similar concentrations. [Figure 8](#page-29-0) summarizes the total concentration of all halogenated organic chemicals observed in fish collected from odd-year sites sampled in 2019. The highest total concentration of halogenated compounds was observed at North Hamlin, followed by Port Austin and Sturgeon Bay which exhibited similar concentrations, followed by Dunkirk and Keweenaw Point, which exhibited similar concentrations. Similar to observations in the Great Lakes Fish Monitoring and Surveillance Program Technical Report: Status and Trends of Contaminants in Whole Fish through 2016 [\(EPA 2021a\)](#page-32-1) and the Great Lakes Fish Monitoring and Surveillance Program Technical Report: Status and Trends of Contaminants in Whole Fish through 2017 [\(EPA 2021b\),](#page-32-2) halomethoxyphenols were the dominant class of compounds observed in all of the lakes, followed by PCBs and other halogenated components on the routine monitoring schedule (i.e., organochlorine pesticides).

^{} Includes PBDEs and OCPs.*

*** Concentrations were determined using reference standards where available or structurally similar compound.*

Figure 8. Concentrations of halogenated compounds and PCBs in GLFMSP mega-composite samples from 2019.

- ** Includes PBDEs and OCPs.*
- *** Concentrations were determined using reference standards where available or structurally similar compound.*

6 SUMMARY

The 2019 GLFMSP Technical Report details sampling information for the Base Monitoring Program and CSMI/Special Studies, assesses Base Monitoring Program trends through 2018 for even-year sites and 2019 for odd-year sites, and shows that various legacy contaminant concentrations are decreasing in Great Lakes top predator fish. Key highlights include:

- Mean total PCB concentrations in Lake Trout at all sampling sites including Rockport and Port Austin (Lake Huron), Saugatuck and Sturgeon Bay (Lake Michigan), Apostle Islands and Keweenaw Point (Lake Superior), and Oswego and North Hamlin (Lake Ontario), and in Walleye at Middle Bass Island (Lake Erie), have declined significantly since 1991/1992. Concentrations have also significantly declined at the Dunkirk sampling site in eastern basin of Lake Erie since monitoring of Lake Trout began in 2008.
- Mean total PCB concentrations have exhibited a statistically significant decreasing trend at all sites over the ten-year (2008-2018 or 2009-2019) timeframe (2008-2019 for Dunkirk).
- Mean total PBDE concentrations in Lake Trout at Rockport (Lake Huron), Saugatuck (Lake Michigan), Apostle Islands (Lake Superior), and Oswego (Lake Ontario), and in Walleye at Middle Bass Island (Lake Erie), have declined significantly since 2002. Mean Total PBDE concentrations in Lake Trout have also declined significantly at Sturgeon Bay (Lake Michigan), North Hamlin (Lake Ontario), and Keweenaw Point (Lake Superior) since 2001.
- Mean total PBDE concentrations showed a statistically significant decline at Apostle Islands (Lake Superior), Saugatuck (Lake Michigan), Middle Bass Island (Lake Erie), and Oswego (Lake Ontario) over the 2008-2018 timeframe. Mean total PBDE concentrations also showed a statistically significant decline at the North Hamlin (Lake Ontario) and Port Austin (Lake Huron) sites over the 2009-2019 time frame.
- Mean mercury concentrations in Lake Trout at Apostle Islands (Lake Superior) and Walleye at Middle Bass Island (Lake Erie) have declined significantly since 2000.
- Mean mercury concentrations showed a statistically significant decline over the 2008-2018 timeframe at Middle Bass Island (Lake Erie) and Apostle Islands (Lake Superior). At Sturgeon Bay (Lake Michigan), a statistically significant increase in mean mercury concentration was exhibited from 2009-2019.

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APPENDIX A – LIST OF RECENT GLFMSP REPORTS

The following is a list of GLFMSP publications produced between 2018 and 2022.

- Crimmins, B.S., Holsen, T.M., 2019. Non-targeted Screening in Environmental Monitoring Programs. *Advances in Experimental Medicine and Biology: Advancements of Mass Spectrometry in Biomedical Research. 1140*, 731-741. DOI: https://doi.org/10.1007/978-3-030-15950-4_43
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