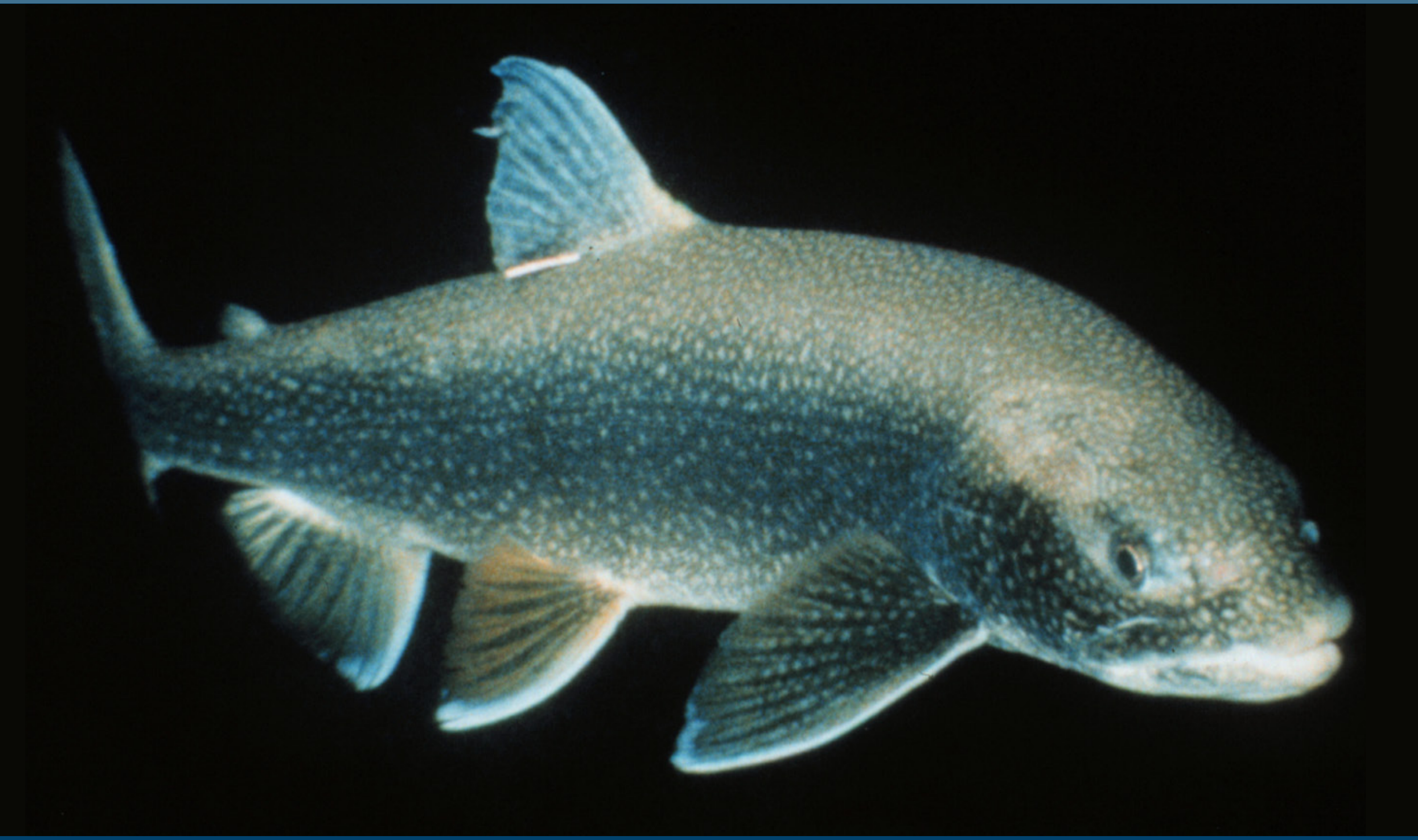
GREAT LAKES FISH MONITORING AND SURVEILLANCE PROGRAM

TECHNICAL REPORT

Status and Trends of Contaminants in Whole Fish through 2016



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Great Lakes RESTORATION

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

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 fish , 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, and other organochlorine pesticides (OCPs). An assessment of data through 2016 shows that concentrations of several contaminants are decreasing in Great Lakes top predator fish. These trends may be attributed to pollution reduction and clean-up efforts within the Great Lakes watershed. Key highlights from the 1992-2016 monitoring show that the:

- Mean total PCB concentrations in fish declined at all sites since 1992;
- Mean total PBDE concentrations in fish declined at all sites since 2002; and
- Mercury concentrations in fish declined at the Rockport, Lake Huron and Apostle Islands, Lake Superior sites since 2006.

The GLFMSP collects fish at one of two long-term monitoring stations in each of the Great Lakes, in the late summer to fall of each year, with stations alternating within each lake annually. In support of the 2016 Lake Superior Cooperative Science and Monitoring Initiative (CSMI), fish and other samples (e.g., benthic invertebrates, water samples) were also collected at both GLFMSP collection sites in Lake Superior. Analytical results are made publicly available approximately 18 to 22 months after field collection, following biological data collection, homogenization, chemical analysis, and data quality review. In 2016, samples were collected between June and November at GLFMSP even-year sites within each lake.

This report summarizes the field sample and biological data collection results (e.g., species, number of fish, length, weight, gender, age) from all 2016 GLFMSP collection efforts and presents the analytical results from five classes of contaminants (PCBs, PBDEs, mercury, HBCDD, and PFAS) in Lake Trout (*Salvelinus namaycush*) and Walleye (*Sander vitreus*) collected for the GLFMSP Base Monitoring Program. The analytical results from 2016 are placed into the context of long-term trends beginning when each contaminant was first subjected to routine monitoring.

PCBs: Trend data show that mean total PCB concentrations at each site continue to show a statistically significant decline over the short term (2006-2016) and the long term (1992-2016).

PBDEs: Mean total PBDE concentrations showed a statistically significant decline at all Lake Trout sites in Lakes Superior, Michigan, Huron, and Ontario in the short term (2006-2016) and in the long term (2002-2016). The decline in mean total PBDE concentrations in Walleye at the Middle Bass Island, Lake Erie site was significant in the long term, but not in the short term.

Mercury: Mean mercury concentrations continue to show a statistically significant decline over the past decade(2006-2016) at the Rockport, Lake Huron site and the Apostle Islands, Lake Superior site; however, concentrations show a statistically significant increase at the Saugatuck, Lake Michigan site, and no long-term change was observed at the Middle Bass Island, Lake Erie site or the Oswego, Lake Ontario site. The overall increase in mercury concentration observed at Saugatuck was small, and the analysis does not include age-corrected fish data. When evaluated across a longer time period beginning when mercury was first subjected to monitoring at these sites (2000-2016), only the Apostle Islands, Lake Superior site had a statistically significant decline; no statistically significant change was observed for Saugatuck, Rockport, Middle Bass Island, or Oswego sites.

HBCDD and PFAS: There are currently not enough years of data to evaluate temporal trends for HBCDD or PFAS. In 2016, mean total HBCDD was highest at the Rockport, Lake Huron site and lowest at the Middle Bass Island, Lake Erie site. In 2016, mean total PFAS and mean perfluorooctanesulfonic acid (PFOS) (a PFAS compound) concentrations tended to be highest at the Middle Bass Island, Lake Erie site and the Oswego, Lake Ontario site and lowest at the Apostle Islands, Lake Superior site.

CECs: This report also presents the results of Contaminants of Emerging Concern (CEC) screening analyses performed on Base Monitoring Program samples. The most abundant CEC compound class found in this screening was halomethoxyphenols.

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 fish , 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).

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 *et seq*.) 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). 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).

This report summarizes sample and biological data collection results for the 2016 Base Monitoring Program and CSMI/Special Studies collection efforts and presents the 2016 Base Monitoring Program analytical results in context with long-term trends. This report focuses on analytical results from five classes of contaminants (polychlorinated biphenyls [PCBs], polybrominated diphenyl ethers [PBDEs], mercury, hexabromocyclododecane [HBCDD], and per- and polyfluoroalkyl substances [PFAS]) which have been designated as binational chemicals of mutual concern through the GLWQA Chemicals of Mutual Concern Annex (Annex 3) (GLWQA 2012) and also includes results from Contaminants of Emerging Concern (CEC) screening analyses.

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) and deliver fish to a homogenization laboratory after collection. A total of seven sampling teams collected fish for the Base Monitoring Program and CSMI/Special Studies components in 2016 between June and November:

- Great Lakes Indian Fish & Wildlife Commission
- Michigan Department of Natural Resources, Alpena Fisheries Research Station
- Michigan Department of Natural Resources, Charlevoix Fisheries Research Station
- Ohio Department of Natural Resources, Division of Wildlife Sandusky Fisheries Research Station
- U.S. Geological Survey Lake Ontario Biological Station
- U.S. Geological Survey Lake Superior 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) for the Base Monitoring Program. Collection sites are intended to be representative of offshore conditions in each Lake. Lake Trout (*Salvelinus namaycush*) are collected in all lakes and Walleye (*Sander vitreus*) are collected at one site located in the western basin of Lake Erie which is too shallow to support lake trout. Lake trout in the size range of 600-700 mm are targeted 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 represented 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).

3.1.2 Cooperative Science and Monitoring Initiative (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 2016, the CSMI lake was Lake Superior. 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, phytoplankton, zooplankton/seston, and water samples in the CSMI lake aboard the R/V *Lake Guardian*. Detailed collection and site information for the GLFMSP CSMI/Special Studies component is provided in the GLFMSP QAPP (EPA 2012a).

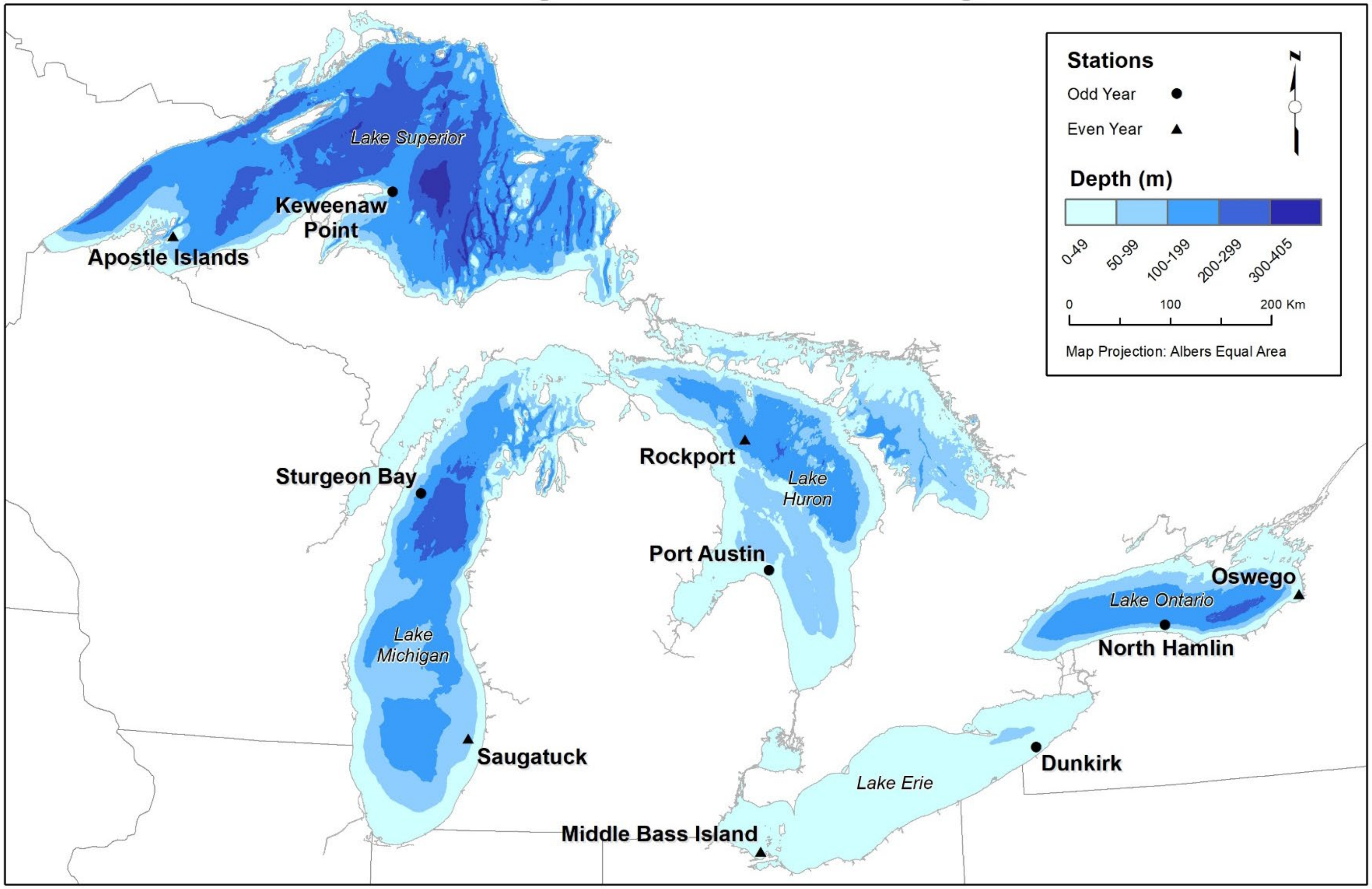

Figure 1: GLFMSP Collection Sites.

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 2016, the homogenization laboratory was Aquatec Biological Sciences, Inc. (Aquatec). Aquatec follows approved GLFMSP specific SOPs (Aquatec 2016) 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, otoliths, maxillae, coded wire tags [CWTs]), and aged the fish. In 2016, lake trout age was determined based on annuli enumeration of maxillae and otoliths[1]. Fish age is an important variable when assessing contaminant trends and as such, the GLFMSP compositing scheme was revised in 2013 to group fish according to age (rather than by length) prior to homogenization and chemical analysis. CWTs were also used to age lake trout when available. Walleye age was determined based on annuli enumerations of otoliths. EPA reviewed the ages 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 Apostle Islands site, a total of 46 lake trout were collected, so nine composites of five fish and one composite of one fish were created. At the Oswego site, a total of 19 fish were collected. Low sample numbers could result in more variable site means because they are based on less data owing to: 1) decreased sample sizes as a smaller number of composites are created for the site; and/or 2) fewer than the target of five fish comprised the composites. Because of this, composites including fewer fish were created for Oswego to minimize within-composite age variability among fish.

After grouping fish into composites based on EPA's criteria noted above, the homogenization laboratory processed the whole fish and prepared composites of these samples. In addition, a mega-composite was prepared (i.e., tissue from all composites from a single site) where applicable for screening of contaminants of emerging concern. The single fish composite from Apostle Islands was not included in the mega-composite for this site in 2016. 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 collection year. The analytical laboratory cooperators that analyzed the 2016 collected fish tissue were Clarkson University, State University of New York (SUNY) Oswego, and SUNY Fredonia. The 2016 Base Monitoring Program analytical data sets are presented in Table 1. All analytical data generated to support the GLFMSP are prepared in accordance with an approved QAPP and SOPs (Clarkson University 2016).

Upon sample receipt, the analytical laboratory cooperator analyzed the homogenate tissue for different classes of contaminants including PCBs, PBDEs, mercury, HBCDD, PFAS, toxaphene, chlordanes, 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 of this report).

[1] After the 2016 field season, the GLFMSP concluded a four-year, inter-laboratory comparison study of multiple age enumeration structures to allow for a more rapid, accurate, and precise measurement of age prior to homogenization (Murphy et al. 2018). Refer to Section 6 *Future Reporting* for more information.

Table 1: 2016 Base Monitoring Program Analytical Data Sets

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

Results generated by all analytical methods were reported on a wet weight basis in accordance with SOPs (Clarkson University 2016). No mathematical adjustments based on lipid content or fish age were performed on the 2016 results or as part of the trend analyses presented in this report. Long-term analytical data in the GLFMSP presented in this report have not been corrected to adjust for fish age -- the reason being 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 GLFMSP are reported as contaminant concentrations for each composite for a given sampling year at each collection site. Age-corrected data from the GLFMSP are presented in Pagano et al. (2018) and Zhou et al. (2018).

4 QUALITY ASSURANCE AND QUALITY 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). 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.

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.

To date, no major QA/QC issues have been identified through 2016.

5 RESULTS

This section summarizes results from 2016 sample collection, biological data collection, and analysis and presents the 2016 Base Monitoring Program analytical results in context with long-term trends.

5.1 SAMPLE COLLECTION

5.1.1 Base Monitoring Program

A total of 165 lake trout were collected in Lakes Superior, Huron, Michigan, and Ontario and a total of 50 Walleye were collected in Lake Erie in 2016 (Table 2). Due to low availability of lake trout in the target size range at two collection sites, a total of 19 lake trout were collected at Oswego and a total of 46 lake trout were collected at Apostle Islands instead of the target 50. Low fish availability at the Oswego site may have been caused by strong winds at the site during the collection, which can shift the thermocline and tend to scatter fish.

Table 2: 2016 Base Monitoring Program Field Data

Lake	Site	Species	Date	Depth (m)	Collection Method	Field Length Range (mm)	Field Weight Range (g)
Erie (n=50)	Middle Bass Island	Walleye	November 2016	3.5-4	Gillnet	382-516	494-1501
Huron (n=50)	Rockport	Lake Trout	October, November 2016	2.7-5.6	Gillnet	598-855	2052-6995
Michigan (n=50)	Saugatuck	Lake Trout	September 2016	30	Gillnet	574-743	1490-5085
Ontario (n=19)	Oswego	Lake Trout	September, November 2016	15-37	Gillnet	569-767	1940-5356
Superior (n=46)	Apostle Islands	Lake Trout	October 2016	6-15	Gillnet	577-714	1558-3258

5.1.2 Cooperative Science and Monitoring Initiative (CSMI)/Special Studies

In 2016, 10 additional lake trout were collected in Lake Superior, from Keweenaw Point (Table 3). Additional lake trout were not collected from Apostle Islands due to low availability of samples in the target size range. A total of 356 forage fish were collected from Keweenaw Point and Apostle Islands (Table 4). Sediment, benthic invertebrates, phytoplankton, zooplankton/seston, *Mysis* and water samples were also collected from both Lake Superior sites during a dedicated Research Vessel (R/V) *Lake Guardian* CSMI survey (Table 5).

Table 3: 2016 CSMI Lake Trout Field Data

Lake	Site	Date	Depth (m)	Collection Method	Field Length Range (mm)	Field Weight Range (g)
Superior (n=10)	Keweenaw Point	October, November 2016	8	Gillnet	551-683	1400-2850

Table 4: 2016 CSMI Forage Fish Field Data

Lake	Site	Species Collected	Date	Depth (m)	Collection Method
Superior	**Apostle Islands**	• Rainbow Smelt (n=78) • Bloater (n=60) • Ninespine Stickleback (n=52) • Cisco (n=30) • Deepwater Sculpin (n=30) • Lake Whitefish (n=30) • Slimy Sculpin (n=12) • Spoonhead Sculpin (n=5)	June 2016	35-135	Bottom Trawl
Superior	**Keweenaw Point**	• Round Whitefish (n=23) • Bloater (n=13) • Kiyi (n=12) • Longnose Sucker (n=10) • Burbot (n=1)	June 2016	15-146	Gillnet

Table 5: 2016 CSMI R/V *Lake Guardian* Collected Field Data

Lake	Site	Sample Type and Sampling Depth (m)	Date	Collection Method
Superior	**Apostle Islands**	Water (3 m)	June 2016	Pump
		Zooplankton/Seston/*Mysis* (whole water tow from 68 m)	June 2016	Nested net (153 µm for zooplankton/seston and 500 µm for *Mysis*)
		Sediment (69 m)	June 2016	Ponar
		Benthic invertebrates (69 m)	June 2016	Benthic sled (500 µm net) & Ponar grab (separated through 253 µm sieve)
Superior	**Keweenaw Point**	Water (3 m)	June 2016	Pump
		Zooplankton/Seston/*Mysis* (whole water tow from 53 m)	June 2016	Nested net (153 µm for zooplankton/seston and 500 µm for *Mysis*)
		Sediment (54 m)	June 2016	Ponar
		Benthic invertebrates (~50 m)	June 2016	Benthic sled (500 µm net) & Ponar grab (separated through 253 µm sieve)

5.2 BIOLOGICAL DATA COLLECTION AND HOMOGENIZATION

Tables 6 and 7 provide a summary of biological data measurements (excluding age results which are included in Table 8) as recorded by the homogenization laboratory for the 2016 Base Monitoring Program and CSMI/Special Studies samples.

Table 6: 2016 Base Monitoring Program Biological Data

Lake	Site	Species	Lab Length Range (mm)	Lab Weight Range (g)	Gender Count (M, F)	Dominant Maturity Stage [a, b]
Erie (n=50)	Middle Bass Island	Walleye	381-519	489-1490	31, 19	Mature (62%)
Huron (n=50)	Rockport	Lake Trout	552-846	2017-6892	23, 27	Mature (46%), Ripe (52%)
Michigan (n=50)	Saugatuck	Lake Trout	558-738	1466-5027	30, 20	Mature (62%)
Ontario (n=19)	Oswego	Lake Trout	533-742	1902-5327	9, 10	Gravid (42.1%), Mature (47.4%)
Superior (n=46)	Apostle Islands	Lake Trout	423-702	1528-3220	40, 6	Mature (87%)

[a] *Mature = fish is sexually mature (egg deposition status is either unknown, unimportant, or nonapplicable); Ripe = ovary is full of eggs that are ready for deposition and fertilization (ovary wall structure weakened or broken, eggs escape upon external palpation); Gravid = ovary is full of eggs that are not yet ready for deposition or fertilization (eggs still contained within ovary wall structure)*
[b] *% = percent of total number of fish collected at each site*

Table 7: 2016 CSMI/Special Studies Lake Trout Biological Data

Lake	Site	Species	Lab Length Range (mm)	Lab Weight Range (g)	Gender Count (M, F)	Dominant Maturity Stage
Superior (n=10)	Keweenaw Point	Lake Trout	560-669	1308-2716	10, 0	Mature (100%) [a, b]

[a] *Mature = fish is sexually mature (egg deposition status is either unknown, unimportant, or nonapplicable)*
[b] *% = percent of total number of fish collected at each site*

Table 8 provides a summary of age data for 2016 Base Monitoring Program and CSMI/Special Studies lake trout samples. Age results included in the table were determined based on annuli enumeration of otoliths and on CWTs. The dominant aging method used to obtain the final age for each fish is listed. Final age was determined based on CWT where available and then based on annuli enumeration of otolith if no CWT was present. No Walleye from Middle Bass Island exceeded the target age range of 4-5 years. The majority of Lake Trout exceeded the target age range of 6-8 years in Rockport (70%) and Apostle Islands (60%), while 40% exceeded the age range in Keweenaw Point, 22% exceeded the age range in Saugatuck, and 11% exceeded the age range in Oswego. 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.

Table 8: 2016 Age Data (Base Monitoring Program and CSMI/Special Studies Lake Trout)

Lake	Site	Species	Age Range (years)	Dominant Aging Method	Percent of Fish Exceeding Target Age Range
Erie (n=50)	Middle Bass Island	Walleye	2-4	Otolith	0%
Huron (n=50)	Rockport	Lake Trout	5-18	Otolith	70%
Michigan (n=50)	Saugatuck	Lake Trout	4-16	Otolith, CWT	22%
Ontario (n=19)	Oswego	Lake Trout	4-11	CWT	11%
Superior (n=46)	Apostle Islands	Lake Trout	6-22	Otolith	60%
Superior (n=10)	Keweenaw Point	Lake Trout	8-11	Otolith	40%

Lake Trout age was also determined based on annuli enumeration of maxillae as part of the four-year, inter-laboratory comparison study of multiple age enumeration structures described in Section 3.2 (Murphy et al. 2018). Information on maxilla age results for 2016 samples as well as 2013-2015 samples is presented 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).

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 2016, places these results in context with long-term trends, and present results from the CEC screening analyses performed on these samples. The 2016 CSMI/Special Studies Program analytical results will be presented in future GLFMSP reports.

Due to low sample numbers at Oswego, as stated in Section 3.2, the number of fish assigned to composites varied to minimize age variability. The calculation of abundance weighted means (i.e., weighted based on the number of fish per composite) and standard errors for the 2016 Oswego data mitigates the impact of the varying number of fish per composite; however, there could still be some comparability concerns when evaluating composite results across years at this site.

As stated in Section 3.2, one composite from Apostle Islands contained only one fish instead of the target five. This composite was analyzed for all contaminants but was not included in site means presented in this report.

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 even year sites from 1992– 2016 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 136 to 628 ng/g across the five sites (Table 9) in 2016. 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. In general, mean total PCB concentrations have exhibited a decreasing trend at all sites over both the 2006 – 2016 (Table 9) and 1992-2016 (Table 9 and Figure 2) time frames.

Estimated declines since 2006 are statistically significant at all sites and range from 30% at Saugatuck to 76% at Apostle Islands. Estimated PCB declines since 1992 are statistically significant and range from 65% at Middle Bass Island to 81% at Rockport.

Table 9: Summary of 2016 Total PCB Site Means and Temporal Trends

Lake	Site	# Composites	Species	2016 Site Means Total PCB Concentration (standard error) (ng/g)	Estimated % Decline 1992-2016 (95% CI LL- UL)[d]	Estimated % Decline 2006-2016 (95% CI LL-UL)
Erie	Middle Bass Island	10	Walleye	488 (40.0)	65 (57 - 72)	33 (17 - 45)
Huron	Rockport	10	Lake Trout	355 (70.4)	81 (77 - 84)	57 (38 - 70)
Michigan	Saugatuck	10	Lake Trout	610 (118)	80 (75 - 83)	30 (6 - 49)
Ontario	Oswego	6 [a]	Lake Trout	628 (101)[c]	81 (78 - 83)	46 (30 - 58)
Superior	Apostle Islands	9 [b]	Lake Trout	136 (24.7)	77 (68 - 84)	76 (65 - 83)

[a] *Composites included 2-4 fish each to minimize age variability within a composite*
[b] *Based on 9 composites of 5 fish (single fish composite not included)*
[c] *Site mean is weighted based on number of fish per composite*
[d] *CI LL-UL indicates confidence interval lower level-upper level*

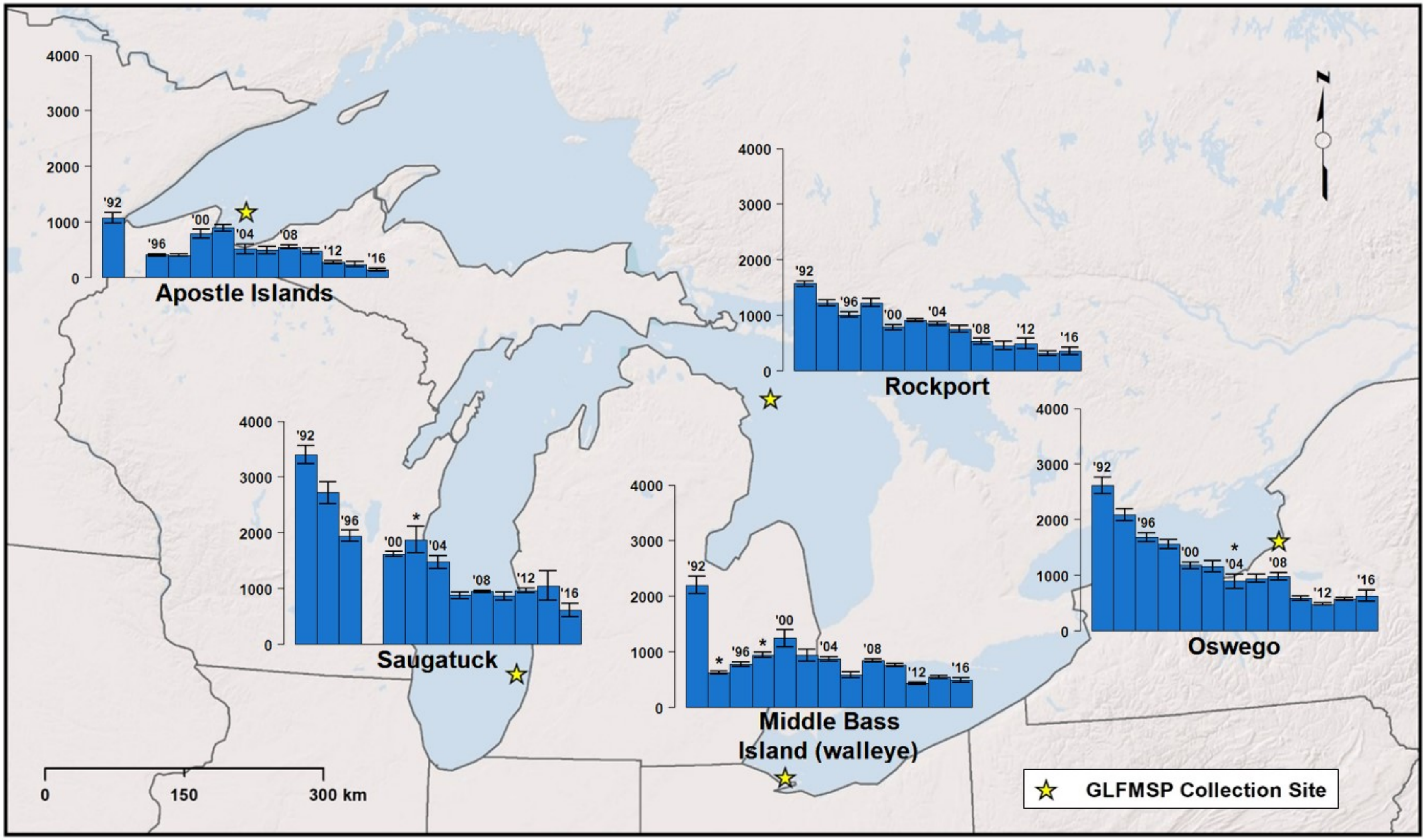

Figure 2. Mean Total PCB Concentration (ppb) in Lake Trout/Walleye 1992-2016.

Notes: *1) Stations are not representative of the entire lake.*
2) A missing bar = samples not collected for that site/year.
3) An asterisk (*) indicates less than 5 composites are included in the sampling period.
4) Lake Trout were collected in all lakes except Lake Erie.
5) The last two digits of collection years are displayed above corresponding bars as 'XX.

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 2002.

Site mean total PBDE concentrations ranged from 9.75 to 45.1 ng/g across the five sites (Table 10) in 2016. 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. 2017). 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 sites over the 2006-2016 time series (Table 10) and range from 20% at Middle Bass Island to 58% at Apostle Islands.

Estimated total PBDE concentration declines over the 2002-2016 time series (Table 10 and Figure 3) are statistically significant at all Lake Trout sites and range from 48% at Apostle Islands to 66% at Saugatuck. The 16% decline in PBDE concentration in Walleye at Middle Bass Island since 2002 is not statistically significant.

Table 10: Summary of 2016 Total PBDE (5 congeners) Site Means and Temporal Trends

Lake	Site	# Composites	Species	2016 Total PBDE Site Mean Concentration (standard error) (ng/g)	Estimated % Decline [d] 2002-2016 (95% CI LL-UL)[e]	Estimated % Decline 2006-2016 (95% CI LL-UL)
Erie	Middle Bass Island	10	Walleye	9.75 (0.931)	16 (-4 - 31)	20 (2 - 34)
Huron	Rockport	10	Lake Trout	32.0 (6.20)	59 (41 - 72)	40 (6 - 61)
Michigan	Saugatuck	10	Lake Trout	41.9 (8.51)	66 (52 - 76)	41 (19 - 58)
Ontario	Oswego	6 [a]	Lake Trout	45.1 (12.4)[c]	51 (33 - 64)	40 (18 - 56)
Superior	Apostle Islands	9 [b]	Lake Trout	37.7 (8.70)	48 (24 - 64)	58 (38 - 72)

[a] *Composites included 2-4 fish each to minimize age variability within a composite*
[b] *Based on 9 composites of 5 fish (single fish composite not included)*
[c] *Site mean is weighted based on number of fish per composite*
[d] *A negative percent decline of –X% corresponds to a percent increase of X%*
[e] *CI LL-UL indicates confidence interval lower level-upper level*

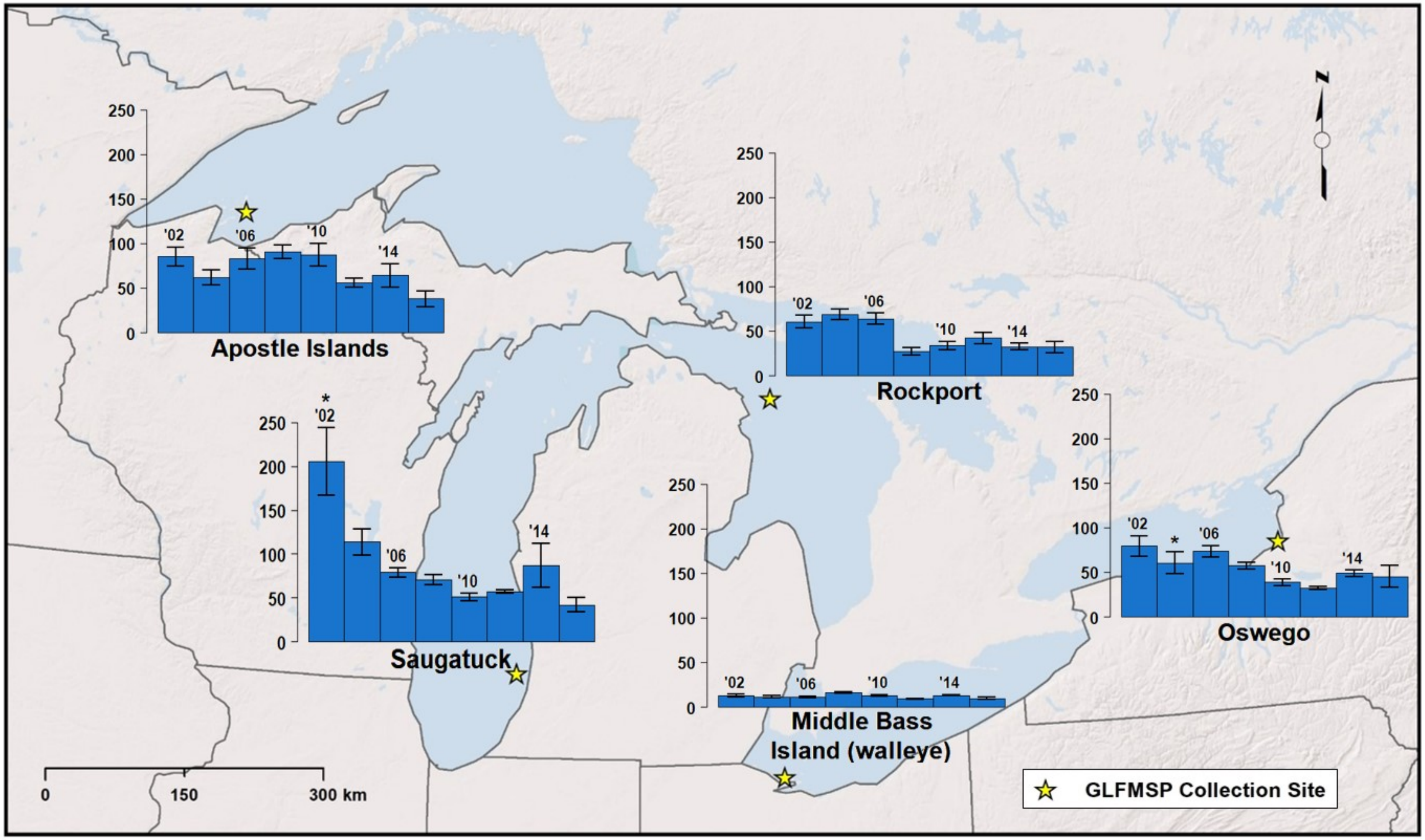

Figure 3. Mean Total PBDE (5 Congeners) Concentration (ppb) in Lake Trout/Walleye 2002-2016.

Notes: *1) Stations are not representative of the entire lake.*
2) A missing bar = samples not collected for that site/year.
3) An asterisk (*) indicates less than 5 composites are included in the sampling period.
4) Lake Trout were collected in all lakes except Lake Erie.
5) The last two digits of collection years are displayed above corresponding bars as 'XX.
6) Total PBDE = sum of congeners 47, 99, 100, 153, and 154.

5.3.3 Mercury

The GLFMSP began monitoring for total mercury in 1999. Mean total mercury concentrations are shown at all even-year sampling sites from 2000-2016 in Figure 4.

Site mean mercury concentrations ranged from 93 to 170 ng/g across the five sites (Table 11) in 2016. In general, mean mercury concentrations showed a statistically significant decline over the 2006-2016 time series (Table 11) at Rockport and Apostle Islands. At Saugatuck, a statistically significant increase of 24% was exhibited from 2006 – 2016. Mercury concentrations in 2006 at Saugatuck were the lowest reported for the time series, which could explain the increasing trend observed from 2006-2016. Since 2000, only Apostle Islands had a statistically significant decline in mercury concentrations (56%). No statistically significant changes in the concentrations of mercury have been detected for Middle Bass Island or Oswego since 2006. While the other four sites, i.e., Middle Bass Island, Rockport, Saugatuck, and Oswego, exhibited an increase in mercury concentrations for the 2000-2016 time frame (ranging from 1% at Middle Bass Island to 6% at Rockport), none were statistically significant (Table 11). Increasing age of Lake Trout collected at Saugatuck and Rockport may explain the lack of trends over the entire time period (Zhou et al. 2017). Refer to section 5.2 for discussion of correlation between fish age and contaminant concentrations.

Table 11: Summary of 2016 Total Mercury Site Means and Temporal Trends

Lake	Site	# Composites	Species	2016 Total Mercury Site Mean Concentration (standard error) (ng/g)	Estimated % Decline [d] 2000-2016 (95% CI LL-UL)[e]	Estimated % Decline [d] 2006-2016 (95% CI LL-UL)
Erie	Middle Bass Island	10	Walleye	93 (5.0)	-1 (-15 to 11)	5 (-9 to17)
Huron	Rockport	10	Lake Trout	170 (14)	-6 (-32 to 15)	35 (17 to 49)
Michigan	Saugatuck	10	Lake Trout	170 (11)	-5 (-25 to 11)	-24 (-44 to -6)
Ontario	Oswego	6 [a]	Lake Trout	150 (23)[c]	-4 (-22 to 11)	-12 (-37 to 8)
Superior	Apostle Islands	9 [b]	Lake Trout	130 (6.4)	56 (46 to 65)	51 (39 to 61)

[a] *Composites included 2-4 fish each to minimize age variability within a composite*
[b] *Based on 9 composites of 5 fish (single fish composite not included)*
[c] *Site mean is weighted based on number of fish per composite*
[d] *A negative percent decline of –X% corresponds to a percent increase of X%*
[e] *CI LL-UL indicates confidence interval lower level-upper level*

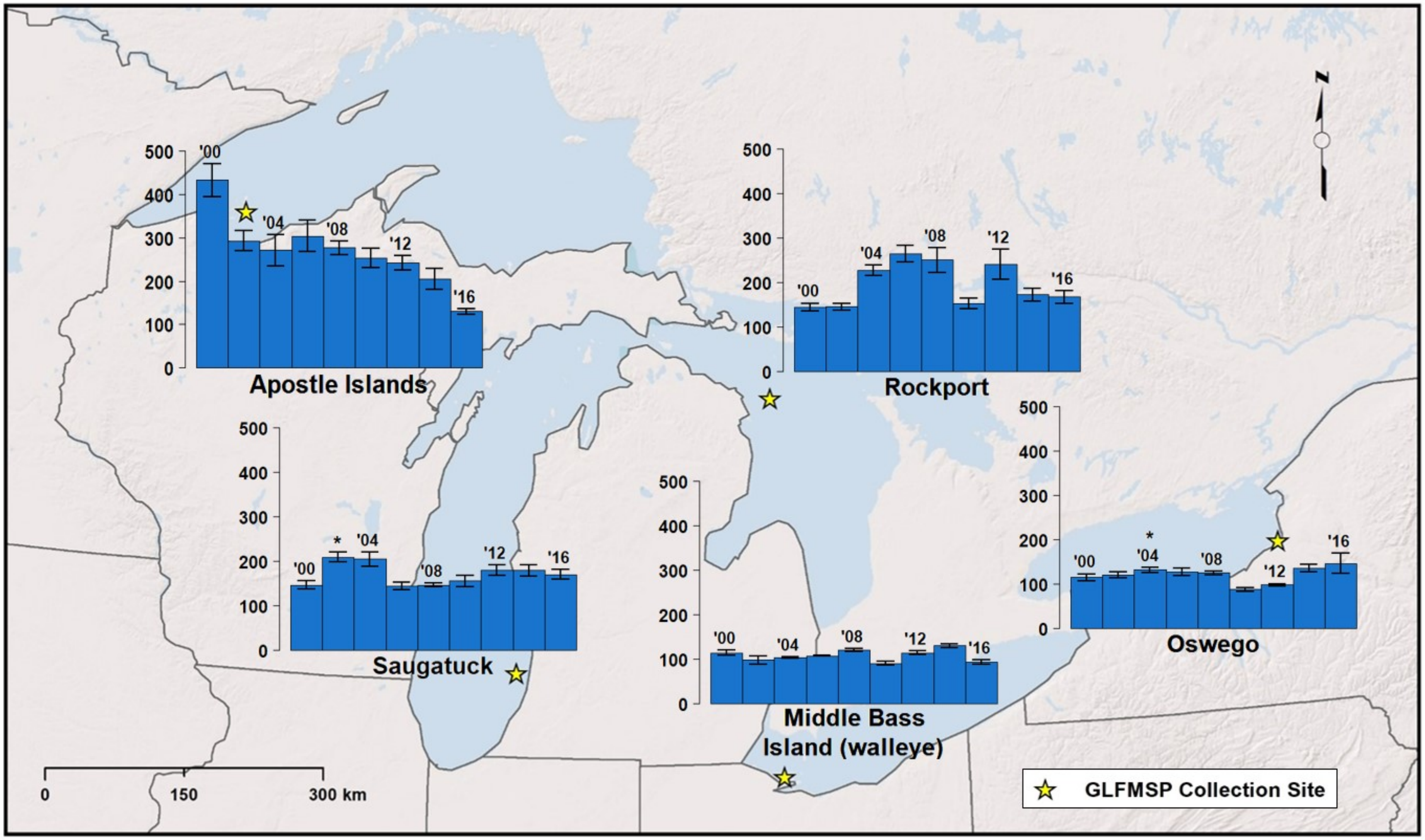

Figure 4. Mean Total Mercury Concentration (ppb) in Lake Trout/Walleye 2000-2016.

Notes: 1) *Stations are not representative of the entire lake.*
2) *A missing bar = samples not collected for that site/year.*
3) *An asterisk (*) indicates less than 5 composites are included in the sampling period.*
4) *Lake Trout were collected in all lakes except Lake Erie.*
5) *The last two digits of collection years are displayed above corresponding bars as 'XX.*

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 that were originally collected in 2010. Four years of data (2010, 2012, 2014, and 2016) are available for even-year sites. Because the six-year 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. Total HBCDD mega-composite means range from 3.34 ng/g at Middle Bass Island to 7.15 ng/g at Saugatuck (Table 12) in 2016. 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. Mean total HBCDD concentration was highest at Rockport and lowest at Middle Bass Island.

Table 12: Summary of 2016 Total HBCDD Mega-composite Means

Lake	Site	# Replicates [a]	Species	2016 Total HBCDD Mega-composite Concentration (standard error) (ng/g)
Erie	Middle Bass Island	3	Walleye	3.34 (0.05)
Huron	Rockport	3	Lake Trout	10.3 (0.08)
Michigan	Saugatuck	3	Lake Trout	7.15 (0.04)
Ontario	Oswego	3	Lake Trout	6.11 (0.44)
Superior	Apostle Islands	3	Lake Trout	6.50 (0.10)

[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)

5.3.5 PFAS

The GLFMSP began monitoring PFAS compounds in 2011. The list of analyzed PFAS compounds has varied since 2011. In 2016, monitored PFAS compounds included 26 perfluorinated carboxylic acids and sulfonates with 4 to 13 carbons, including 10 branched isomers. In recent years, including 2016, the method used to quantify PFAS was modified to improve reproducibility in complex biological tissues (Point et al. 2019). Due to the evolving analytical methodology and smaller number of composites analyzed, it is not appropriate at this time to assess temporal trends for PFAS compounds. Table 13 shows total PFAS and Perfluorooctanesulfonic acid (PFOS) site mean concentrations and their associated standard errors for the composites that were analyzed at each site. Because the PFAS analysis scheme was generally consistent across sites, the mean concentrations can be compared to each other, even if each one is a low-biased estimate. As seen in Table 13, total PFAS and PFOS concentrations are generally highest at Middle Bass Island and Oswego, and lowest at Apostle Islands. Mean total PFAS concentrations were calculated based on the 16 PFAS compounds that were analyzed, excluding branched isomers. Measured results were not censored based on reporting or detection limits and all reported results were included in the totals.

Table 13: Summary of 2016 Total PFAS and PFOS Composite Means

Lake	Site	# Composites	Species	2016 Total PFAS Mega-composite Concentration (standard error) (ng/g)	2016 PFOS Composite Mean (standard error) (ng/g)
Erie	Middle Bass Island	3	Walleye	69.5 (12.7)	61.0 (11.9)
Huron	Rockport	3	Lake Trout	30.5 (4.9)	18.8 (2.8)
Michigan	Saugatuck	3	Lake Trout	32.0 (2.1)	27.5 (1.7)
Ontario	Oswego	3	Lake Trout	69.7 (2.0)	63.4 (1.9)
Superior	Apostle Islands	3	Lake Trout	11.4 (0.77)	5.5 (0.39)

5.3.6 Contaminants of Emerging Concern (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 atom. Historically, organic chemicals containing carbon bonded to chlorine or bromine have been found to be bioaccumulative and to potentially exhibit adverse effects on lake biota (e.g., PCBs, OCPs, PBDEs) (Howard and Muir 2010).

The most abundant compound class identified in the CEC screenings performed on the 2016 samples is the halomethoxyphenols. This class of compounds accounts for more than 60% of the total halogenated compound concentration in top predator fish from all five Great Lakes. The halomethoxyphenols represent a greater contribution to the total body burden of halogenated species than legacy PCBs (Figure 6). Methoxyphenols are also known as guaiacols. As a compound class, halomethoxyphenols include chlorinated guaiacols, as well as methoxyphenols containing other halogens such as bromine and iodine. Little is known about the effects of this class of compounds in fish.

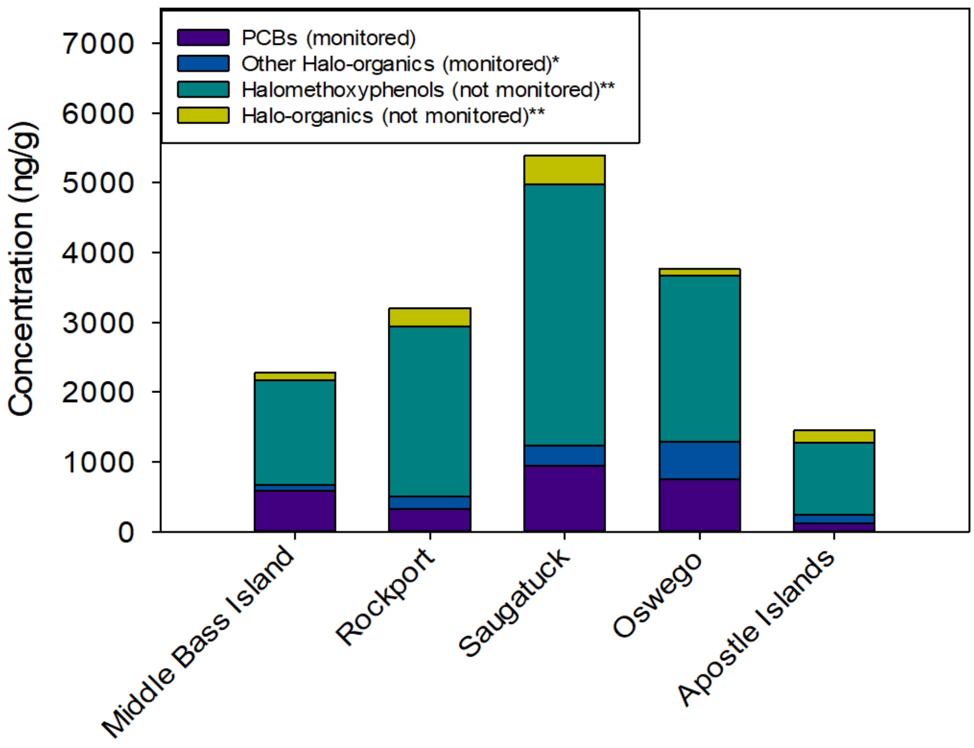

Figure 5. Concentrations of Halogenated Compound Classes in GLFMSP Mega-composite Samples from 2016. * Includes PBDEs and OCPs. ** Compound classes not currently on the Base Monitoring Program analyte list but discovered via screening for CECs. Concentrations were determined using reference standards where available or structurally similar compounds.

6 FUTURE REPORTING

A decreasing rate of decline for total PCB concentrations in Lake Huron Lake Trout was observed beginning in 2000. Upon further assessment, the slowing decline was found to be related to fish age. In 2013, the GLFMSP revised its compositing scheme to ensure fish were group according to age, rather than by length, prior to homogenization and chemical analysis. The revised age assignment procedure was warranted in the face of observed changes in Great Lakes food web structure. These changes can drive declines in fish growth rates and thus impact bioaccumulation potential of contaminants in top predator species such as Lake Trout and Walleye (Zhou et al. 2018). A four-year, inter-laboratory comparison of multiple age enumeration structures was completed in 2017 to select the best measurement of fish age (Murphy et al. 2018). The maxilla bone was determined to be the most precise, accurate, and rapidly assessed structure for fish age determinations for the GLFMSP, based on comparisons between age enumeration structures and the known fish age from the CWT. Use of Lake Trout and Walleye maxilla for GLFMSP aging commenced in 2017, and fish ages presented in subsequent GLFMSP technical reports will be based on this aging estimation method. Additional CSMI/Special Studies analytical results will also be presented in future GLFMSP technical reports.

7 SUMMARY

The 2016 GLFMSP Technical Report details sampling information from the 2016 Base Monitoring Program and 2016 CSMI, assesses data and trends through 2016, and shows that concentrations of several contaminants are decreasing in Great Lakes top predator fish. Key highlights include:

- Mean total PCB concentrations in fish declined at all sites since 1992;
- Mean total PBDE concentrations in fish declined at all sites since 2002; and
- Mercury concentrations in fish declined at the Rockport, Lake Huron and Apostle Islands, Lake Superior sites since 2006, but increased at the Saugatuck, Lake Michigan site.

Declines in mean total PCB concentrations are shown to be statistically significant in both short-term (2006-2016) and long-term (1992-2016) timeframes. Declines in mean total PBDE concentrations are shown to be statistically significant in both short-term (2006-2016) and long-term (2002-2016). However, the short-term decline in mean total PBDE concentrations at Middle Bass Island, Lake Erie was not statistically significant. Declines in mean total mercury concentrations are shown to be statistically significant over the past ten years (2000-2016) at the Rockport, Lake Huron site, and the Apostle Islands, Lake Superior site. Increases in mean total mercury concentrations are shown to be statistically significant at the Saugatuck, Lake Michigan site, and no statistically significant changes were observed at the Middle Bass Island, Lake Erie site or the Oswego, Lake Ontario site. Currently, there are not enough years of data to evaluate trends for HBCDD or PFAS.

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APPENDIX A – LIST OF RECENT GLFMSP PUBLICATIONS

The following is a list of GLFMSP publications produced between 2016 and 2019.

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.

Crimmins, B.S., McCarty, H.B., Fernando, S., Milligan, M.S., Pagano, J.J., Holsen, T.M., Hopke, P.K., 2018. Commentary: Integrating Non-targeted and Targeted Screening in Great Lakes Fish Monitoring Programs. Journal of Great Lakes Research. 44, 1127-1135.

Dupree, E.J., Crimmins, B.S., Holsen, T.M., Darie, C.C., 2019. Developing Well-Annotated Species-Specific Protein Databases Using Comparative Proteogenomics. Advances in Experimental Medicine and Biology: Advancements of Mass Spectrometry in Biomedical Research. 1140, 389-400.

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