Investigation of PFAS Levels in Freshwater Fish at Selected Rivers and Lakes in Massachusetts

Quality Assurance Project Plan

Prepared for:

Massachusetts Department of Environmental Protection Watershed Planning Program

Prepared by

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ACRONYMS

AFFF	aqueous film forming foam
BAF	bioaccumulation factor
BWR	Bureau of Water Resources
CA SWRCB	California State Water Resources Control Board
CASRN	CAS Registry Numbers
COC	chain-of-custody
DFG	Massachusetts Department of Fish and Game
DOD	Department of Defense
DPH	Massachusetts Department of Public Health
DQO	data quality objective
DPH	Department of Public Health
EEA	Executive Office of Energy and Environmental Affairs
EDD	electronic data deliverables
EJ	environmental justice
EPA	United States Environmental Protection Agency
EQuIS	Environmental Quality Information System
ERG	Eastern Research Group, Inc.
Eurofins	Eurofins Lancaster Laboratories Environment Testing
g	gram
HASP	health and safety plan
ITRC	Interstate Technology and Regulatory Council
I	liter
LC-MS/MS	liquid chromatography/mass spectrometry
LCS	laboratory control sample
LLCS	low level laboratory control sample
mL	milliliter
MS	matrix spike
MSD	matrix spike duplicate
MassDEP	Massachusetts Department of Environmental Protection
MassGIS	Massachusetts Bureau of Geographic Information
MassWildlife	Massachusetts Division of Fisheries and Wildlife
MDL	method detection limit
MI EGLE	Michigan Department of Environment, Great Lakes, and Energy
Normandeau	Normandeau Associates, Inc.
ng	nanogram
ppt	parts per trillion
PFAS	per- and polyfluoroalkyl substances
RL	reporting limit
RPD	relative percent difference
SAP	sampling and analysis plan
SOP	standard operating procedures
SFY22	state fiscal year 2022
SFY23	state fiscal year 2023
SERDP	Strategic Environmental Research and Development Program
USGS	United States Geological Survey
QA	quality assurance
QAPP	quality assurance project plan
QC	quality control
WES	Wall Experiment Station
WPP	Watershed Planning Program

Changes to protocols implemented during Phase 1 and Phase 2 of the project are indicated in bold red text; strikethroughs indicate deleted text. These changes were incorporated in March 2023.

1.0 Introduction

The Massachusetts Department of Environmental Protection (MassDEP) is funding a project to measure levels of per- and polyfluoroalkyl substances (PFAS) contamination in fish tissue and surface water in selected lakes and rivers across the Commonwealth. MassDEP selected Eastern Research Group, Inc. (ERG) as the contractor to implement the study. ERG prepared this Quality Assurance Project Plan (QAPP) for the PFAS fish tissue and surface water sampling project.

ERG developed this QAPP following the U.S. Environmental Protection Agency's (EPA's) guidance for QAPPs for the purpose of environmental data collection and analysis (EPA, 2021). ERG also considered additional guidance documents (e.g., ITRC, 2020; MI EGLE, 2018; CA SWRCB, 2020) and QAPPs for other PFAS fish tissue sampling programs.

This QAPP outlines the procedures to be used to ensure that environmental sampling data will be collected and analyzed to meet project requirements and will be of a known and high quality. This QAPP addresses the following main topics:

- Project management, objectives, and approaches (Section 2)
- Methods for generating the data, including methods for field collection of samples and laboratory analysis (Section 3)
- Data validation and assessment of data usability (Section 4)

2.0 Project Management

2.1 Distribution List

The MassDEP Project Lead is Richard Chase (Bureau of Water Resources [BWR]), and he will distribute this approved QAPP and any subsequent revisions to the project personnel listed below. Upon receipt of the QAPP and all revisions, those on the distribution list will be asked to sign the receiving form and return it to the MassDEP Project Lead.

Massachusetts Department of Environmental Protection

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PG Environmental

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Normandeau Associates, Inc.

Corey Francis, Field Crew Lead, cfrancis@normandeau.com

2.2 Project Organization

MassDEP is managing and funding this project. Specifically, the project will be managed out of MassDEP's Watershed Planning Program (WPP) within the BWR. MassDEP WPP officials will also seek input on this project from the Department's Office of Research and Standards and the Department's environmental laboratory, Wall Experiment Station (WES). MassDEP will also consult with state agency partners on project details, including the Massachusetts Department of Public Health (DPH) and the Massachusetts Department of Fish and Game (DFG).

MassDEP has issued a contract to ERG to conduct the field work and summarize the PFAS measurements. ERG has issued subcontracts to PG Environmental (PG) and Normandeau Associates, Inc. (Normandeau), who will conduct sample collection. Dr. Rebecca DeVries (ERG) will serve as Project Manager for the contractor team, with Mr. John Wilhelmi (ERG) as Deputy Project Manager and Ms. Donna Tedder (ERG) as Quality Assurance (QA) Manager. Mr. Kortney Kirkeby (PG) will serve as the Field Sampling Coordinator; he will direct and oversee sample collection, which is to be completed primarily by Normandeau. Mr. Corey Francis (Normandeau) will serve as the Field Crew Lead and Site Safety Coordinator.

MassDEP has issued a separate contract to Eurofins Lancaster Laboratories Environment Testing, LLC (Eurofins), located in Lancaster, PA, to conduct the chemical analysis of environmental samples. Ms. Kerri Sachtleben is the technical point of contact for the analytical laboratory.

Table 1 lists roles and responsibilities of key individuals involved with the project, along with their organization and contact information.

Table 1. Organization	n of Key Project Staff	and Responsibilities
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Staff	Project Role	Project Responsibilities
Richard Chase MassDEP Bureau of Water Resources Email: richard.f.chase@mass.gov	MassDEP Project Lead	Directing all project activities; managing sampling and laboratory analysis contractor support; reviewing, approving, and distributing the QAPP; and coordinating with state agency partners.
Richard Carey	MassDEP	Assuming all Project Lead responsibilities
MassDEP Bureau of Water Resources	Alternate	during times when the MassDEP Project Lead
Email: richard.carey@mass.gov	Project Lead	is not available.

Staff	Project Role	Project Responsibilities
Rebecca DeVries ERG Email: rebecca.devries@erg.com	ERG Project Manager	Managing all sampling support activities, including subcontracts with PG and Normandeau; coordinating with the ERG team to develop the QAPP; leading data analyses; and authoring the project reports.
John Wilhelmi ERG Email: john.wilhelmi@erg.com	ERG Deputy Project Manager	Assisting the ERG Project Manager with her assigned responsibilities; and assuming project management responsibilities during times when the ERG Project Manager is not available.
Anna Stanley-Lee ERG Email: anna.stanley@erg.com	ERG Data Manager	Reviewing, tracking, and compiling laboratory data in the master database.
Kortney Kirkeby PG Environmental Email: kortney.kirkeby@pgenv.com	Field Sampling Coordinator	Contributing to the sampling and analysis plan in the QAPP; scheduling and overseeing field sampling activity; and providing supplemental field sampling crew members, if needed.
Corey Francis Normandeau Associates	Field Crew Lead and Site Safety Coordinator	Managing field sampling crews that collect water samples and collect and process fish tissue samples.
Kerri Sachtleben Eurofins	Laboratory Lead	Analyzing all surface water and fish tissue samples according to specifications in the QAPP; validating chemical measurement results; and reporting validated measurements to MassDEP.

2.3 Problem Definition/Background

PFAS are of nationwide concern for various reasons: PFAS are highly persistent and toxic; they have been found in numerous drinking water supplies, including several in Massachusetts; and these synthetic chemicals are even found in most Americans' blood. In response, environmental and public health agencies at all government levels have investigated the nature and extent of PFAS contamination and its effects on human health and the environment.

Massachusetts agencies have conducted many steps to characterize the nature and extent of PFAS contamination in various environmental media. For instance, the Commonwealth requires public water systems and municipal wastewater facilities to test for PFAS. For surface waters, MassDEP and the U.S. Geological Survey (USGS) recently completed a PFAS river sampling study (USGS, 2021) where PFAS were detected in all 27 of the rivers sampled. The sum of all 24 PFAS at sampling locations ranged between 0.3 and 399 parts-per-trillion (ppt). The highest concentrations were observed downstream of wastewater effluent discharges, but PFAS were also found in rivers upstream of these discharges. Further, DPH recently measured PFAS in surface water collected from 16 lakes and ponds on Cape Cod (DPH, 2021a). At a subset of locations, DPH also collected fish for PFAS analysis. This sampling resulted in DPH issuing fish consumption advisories for all five of the waterbodies where fish were collected, because the measured PFAS levels in fish were greater than "recommended levels for regular consumption" (DPH, 2021b). Though PFAS were detected in surface water at all 16 waterbodies, each

was found safe for recreational activities (e.g., swimming, wading, boating) based on comparison of measured PFAS concentrations to screening levels or a more detailed risk assessment (DPH, 2021a).

Although these various actions have resulted in important advances in understanding environmental PFAS contamination in the Commonwealth, additional work is needed to characterize the nature and extent of PFAS levels in freshwater fish throughout the state. The current project being conducted by MassDEP will help fill this gap.

The principal objective of the current project is to characterize the nature and extent of PFAS contamination in water and edible tissues of freshwater fish from rivers and lakes across the Commonwealth in a manner that will allow assessment of public health risks associated with consuming freshwater fish. This effort will focus on waterbodies with suspected PFAS contamination, though data will also be gathered at several reference locations.

Sampling will be limited to surface waters where people are known to go fishing, including in environmental justice (EJ) communities. Sampling will be conducted both in areas known or suspected to have facilities with the potential to release PFAS into the environment (i.e., "source-impacted areas") and in areas without known PFAS sources (i.e., "reference areas"). And sampling will focus on the freshwater fish species caught from Massachusetts lakes and rivers that are most commonly consumed. Section 3.1 elaborates on the sampling design proposed to meet the project's principal objective.

This project also has multiple secondary objectives and data uses. Secondary uses of the fish tissue and water quality data for PFAS include derivation of species-specific PFAS bioaccumulation factors (BAF) and assessment of interlaboratory differences in PFAS measurements. The surface water PFAS data will also be used to inform public health evaluations due to incidental ingestion during recreational activities. In addition, the surface water PFAS data for freshwater rivers and lakes will enhance WPP's understanding of ambient PFAS levels with respect to assessment of the aquatic life designated use and the potential for development of surface water quality standards. Section 3.1.13.0 explains how sampling locations were selected to inform these data uses.

2.4 Project Tasks

When executing this project, MassDEP and the ERG team will perform a range of tasks that fall into three general categories, listed below. This section presents a high-level summary of the main tasks to be completed under these categories. In the following list, italicized text indicates the project team entity(ies) with primary responsibility for executing the task. Later sections of this QAPP present further detail on these and additional tasks.

Planning

- Developing a comprehensive QAPP (i.e., this document) to guide sample collection, sample analysis, data management, and data analysis (*ERG*).
- Selecting and contracting with an analytical laboratory to measure PFAS concentrations in the surface water and fish tissue samples (*MassDEP*).
- Coordinating with the analytical laboratory that MassDEP selects to determine schedule, logistics of sample transport and delivery, electronic reporting expectations, and all other details for measuring PFAS in water and fish tissue samples (*ERG and MassDEP*).

- Identifying 50 waterbodies for fish and surface water sample collection across the state (ERG).
- Obtaining a "Scientific Collection Permit" from MassWildlife (i.e., the Division of Fisheries and Wildlife) to allow for collecting fish from 50 targeted waterbodies (*Normandeau*).

Sample collection and analysis

- Collecting surface water and fish samples at the 50 targeted waterbodies and using "PFAS-free protocols" to process, package, and transport samples (*Normandeau*).
- Compiling field observations and ancillary data for fish collected and field document management (*PG*, *ERG*).
- Using EPA draft Method 1633 to measure concentrations of the target PFAS in surface water and fish samples and to validate results (*Eurofins*).
- Verifying data reported by the analytical laboratory (ERG and MassDEP).

Data Management, Analysis, and Reporting

- Assembling all project data, including field data sheets, fish identification and measurements, and other ancillary data generated by the project (*ERG*, *PG*).
- Analyzing and summarizing results in an interim and final report (ERG).
- Preparing analytical results for upload into the MassDEP Environmental Quality Information System (EQuIS) database (*ERG*).

Note at the onset of this project, MassDEP intended to conduct an interlaboratory comparison study for a subset of fish tissue and surface water samples using EPA draft method 1633. For various reasons, that study is currently not able to be integrated into this project, though it may be added at a future date. See Attachment D for further detail.

2.4.1 Project Schedule

The project will be conducted in two phases. Phase 1 will be completed in state fiscal year 2022 (SFY22), which ends on June 30, 2022. This phase will include sampling and laboratory analysis of fish and surface water samples collected from five waterbodies. Phase 2 will be completed in state fiscal year 2023 (SFY23), which runs from July 1, 2022, to June 30, 2023. This phase will include sampling and laboratory analysis of fish and surface water samples collected from 45 waterbodies and preparing the final project report. This QAPP covers activities planned for both project phases.

Table 2. Project Schedule

Task	Performance Period
Phase 1 (SFY22)	
Develop initial QAPP for Phase 1	April 2022, updated version
	in May 2022
Sample collection at up to five targeted waterbodies	May/June 2022
Laboratory analysis of samples from up to five waterbodies	June 2022
Update and finalize QAPP for Phase 2 sampling and analysis	June 2022

Task	Performance Period
Prepare data deliverables from Phase 1 sampling	June 2022, pending
	availability of laboratory
	results
Phase 2 (SFY23)	
Prepare draft and final Phase 1 interim brief report	July/August 2022
Sample collection at the remaining 45 waterbodies	July 2022–December 2022
Laboratory analysis of samples from the remaining 45 waterbodies	August 2022–January 2023
Prepare data deliverables with all analytical results	May/June 2023
Prepare draft and final report	May/June 2023

2.5 Quality Objectives and Criteria for Measurement Data

When evaluating public health risks associated with environmental contamination, it is essential to use sampling data that are of known and high quality. Measurements made during this project that meet the published analytical method quality control specifications will be considered suitable for meeting the project's principal objectives. The remainder of this section defines and describes the quality specifications that apply to this project.

2.5.1 Quality Indicators

The following table lists the data quality indicators that apply to this project's PFAS measurements. Some data quality indicators will be evaluated qualitatively and others quantitatively. The table introduces data quality indicators, and later sections of the QAPP provide further detail on topics introduced below.

Data Quality Indicator	Description
Representativeness To ensure the PFAS measurements characterize the range of PFAS levels in freshwater fish commonly consumed throughout Massachusetts.	 Sampling will target MA lakes and rivers that are known to be fished. Sampling will exclude "catch-and-release"-only waterbodies. Field sampling crews will collect fish legally allowed to be kept by recreational fishers and will focus on fish of a defined size range. Sampling will be limited to the fish species that recreational fishers are most likely to keep and consume (see species list). Waterbodies selected for sampling will be informed by locations of known or suspected point and non-point sources of PFAS contamination. Several reference locations will be included.
Comparability To ensure this program's PFAS measurements (1) allow for comparisons of PFAS levels across waterbodies in MA and (2) allow for comparisons of PFAS measurements made by	 To the extent possible, sampling will focus on the same commonly caught fish species across lakes and rivers; and sampling will consider fish from a defined range of sizes. A commercial laboratory will analyze samples according to the specifications of a published analytical method. The laboratory's PFAS measurements will be reviewed to ensure analyses have been conducted according to the

Table 3. Data Quality Indicators

Data Quality Indicator	Description
other parties using similar methods.	 published analytical method and any supplemental data quality requirements in this QAPP. The field sampling crew will use standard and repeatable sampling methodologies.
Completeness To ensure that sufficient data are collected to meet this program's objectives and to minimize the likelihood of missing, invalid, or incomplete data.	 Field sampling crews will reschedule sampling as soon as possible should inclement weather or other unforeseen circumstances interfere with data collection. Field sampling crews will review this QAPP and be trained on proper collection, storage, processing, and tracking of samples. Measurement data reported by the analytical laboratory will be immediately and thoroughly reviewed. The laboratory will be asked to clarify invalid results without explanation and missing data. The target completeness percentage for surface water samples is 90%, meaning more than 90% of the samples is 90%, meaning more than 90% of the samples is 90%, meaning more than 90% of the waterbodies sampled will result in valid measured concentrations for the target PFAS analytes.
Sensitivity To generate PFAS measurements of a known and high quality at concentrations recommended in EPA's draft analytical method. Precision To confirm that this project's PFAS measurements are highly repeatable.	 The analytical laboratory will achieve method detection limits (MDLs) comparable to those shown in Table 6 of EPA draft Method 1633. (Note: The method detection limits will be updated after EPA completes an interlaboratory study.) The project team will review field and lab quality control (QC) samples and data usability criteria. At 10-20% of the 50 waterbodies sampled, the field sampling crew will collect field duplicates for surface water and fish. For PFAS analytes measured at concentrations at least five times the detection limit, the target relative percent difference (RPD), averaged across all duplicate results, if the concentration is ≥ 5 times the MDL, the RPD must be ≤ 40 percent. If the concentration is < 5 times the MDL, RPD must be ≤100 percent.
Accuracy To confirm that this project's PFAS measurements are free from random error or bias.	 percent. The laboratory will use analytical methods documented to be reliable and will employ rigorous QC procedures. The laboratory will report the results of matrix spikes/recoveries and field blanks as indicators of accuracy. The field sampling crew will use PFAS-free best practices for sampling and new, clean sampling materials and supplies at each sampling point to reduce potential for cross contamination.

2.5.2 Criteria for Analytical Parameters

Laboratory analyses of the surface water and fish tissue samples will be conducted using EPA draft Method 1633. The chemical names, CAS Registry Numbers (CAS RNs), reporting limits (RLs), and MDLs for the 40 PFAS to be measured in surface water and fish tissue are presented in Tables 4 and 5. Table 6 summarizes additional details for the sampling that will occur for both environmental media. Refer to Section 4.0 for information on laboratory validation of PFAS measurements and for the project team's data verification procedures.

Note that per MassDEP's request, Eurofins will report non-detect observations at the specified MDLs. Detected results between the MDL and RL will be reported as detected values and "J" qualified.

PFAS Analyte	Acronym	CAS RN	RL (ng/L)	MDL (ng/L)
Perfluorobutanoic acid	PFBA	375-22-4	8.00	2.00
Perfluoropentanoic acid	PFPeA	2706-90-3	4.00	1.00
Perfluorohexanoic acid	PFHxA	307-24-4	2.00	0.500
Perfluoroheptanoic acid	PFHpA	375-85-9	2.00	0.520
Perfluorooctanoic acid	PFOA	335-67-1	2.00	0.640
Perfluorononanoic acid	PFNA	375-95-1	2.00	0.500
Perfluorobutanoic acid	PFBA	375-22-4	8.00	2.00
Perfluorodecanoic acid	PFDA	335-76-2	2.00	0.500
Perfluoroundecanoic acid	PFUnA	2058-94-8	2.00	0.500
Perfluorododecanoic acid	PFDoA	307-55-1	2.00	0.500
Perfluorotridecanoic acid	PFTrDA	72629-94-8	2.00	0.500
Perfluorotetradecanoic acid	PFTeDA	376-06-7	2.00	0.500
Perfluorobutanesulfonic acid	PFBS	375-73-5	2.00	0.300
Perfluoropentansulfonic acid	PFPeS	2706-91-4	2.00	0.400
Perfluorohexanesulfonic acid	PFHxS	355-46-4	2.00	0.570
Perfluoroheptanesulfonic acid	PFHpS	375-92-8	2.00	0.400
Perfluorooctanesulfonic acid	PFOS	1763-23-1	2.00	0.500
Perfluorononanesulfonic acid	PFNS	68259-12-1	2.00	0.400
Perfluorodecanesulfonic acid	PFDS	335-77-3	2.00	0.500
Perfluorododecanesulfonic acid	PFDoS	79780-39-5	2.00	0.900
1H,1H, 2H, 2H-Perfluorohexane sulfonic acid	4:2FTS	757124-72-4	8.00	1.70
1H,1H, 2H, 2H-Perfluorooctane sulfonic acid	6:2FTS	27619-97-2	8.00	2.50
1H,1H, 2H, 2H-Perfluorodecane sulfonic acid	8:2FTS	39108-34-4	8.00	2.60
Perfluorooctanesulfonamide	PFOSA	754-91-6	2.00	0.500
N-methyl perfluorooctanesulfonamide	NMeFOSA	31506-32-8	2.00	0.500
N-ethyl perfluorooctanesulfonamide	NEtFOSA	4151-50-2	2.00	0.500
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9	4.00	1.20
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	2991-50-6	2.00	0.700

Table 4. RLs and	MDLs for Surface	Water Samples
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PFAS Analyte	Acronym	CAS RN	RL (ng/L)	MDL (ng/L)
N-methyl perfluorooctanesulfonamidoethanol	NMeFOSE	24448-09-7	4.00	1.20
N-ethyl perfluorooctanesulfonamidoethanol	NEtFOSE	1691-99-2	20.0	5.00
Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6	8.00	2.00
4,8-Dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4	8.00	1.50
Perfluoro-3-methoxypropanoic acid	PFMPA	377-73-1	4.00	0.500
Perfluoro-4-methoxybutanoic acid	PFMBA	863090-89-5	4.00	1.00
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6	4.00	1.00
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9CI-PF3ONS	756426-58-1	8.00	1.00
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl- PF3OUdS	763051-92-9	8.00	2.10
Perfluoro(2-ethoxyethane)sulfonic acid	PFEESA	113507-82-7	4.00	0.500
3-Perfluoropropyl propanoic acid	3:3FTCA	356-02-5	10.0	1.50
2H,2H,3H,3H-Perfluorooctanoic acid	5:3FTCA	914637-49-3	50.0	10.0
3-Perfluoroheptyl propanoic acid	7:3FTCA	812-70-4	50.0	10.0

*Note that the MDLs/RLs shown in this table are targets, assuming a volume of 250mL. The MDLs and RLs reported for each sample may be slightly higher or lower depending on the sample volume analyzed.

Table 5. RLs	and MDLs	for Fish	Tissue	Samples
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PFAS Analyte	Acronym	CAS RN	RL (ng/g)	MDL (ng/g)
Perfluorobutanoic acid	PFBA	375-22-4	2.00	0.364
Perfluoropentanoic acid	PFPeA	2706-90-3	1.00	0.132
Perfluorohexanoic acid	PFHxA	307-24-4	0.500	0.166
Perfluoroheptanoic acid	PFHpA	375-85-9	0.500	0.119
Perfluorooctanoic acid	PFOA	335-67-1	0.500	0.203
Perfluorononanoic acid	PFNA	375-95-1	0.500	0.153
Perfluorobutanoic acid	PFBA	375-22-4	2.00	0.364
Perfluorodecanoic acid	PFDA	335-76-2	0.500	0.215
Perfluoroundecanoic acid	PFUnA	2058-94-8	0.500	0.129
Perfluorododecanoic acid	PFDoA	307-55-1	0.500	0.0790
Perfluorotridecanoic acid	PFTrDA	72629-94-8	0.500	0.0800
Perfluorotetradecanoic acid	PFTeDA	376-06-7	0.500	0.105
Perfluorobutanesulfonic acid	PFBS	375-73-5	0.500	0.173
Perfluoropentansulfonic acid	PFPeS	2706-91-4	0.500	0.0920
Perfluorohexanesulfonic acid	PFHxS	355-46-4	0.500	0.0770
Perfluoroheptanesulfonic acid	PFHpS	375-92-8	0.500	0.124
Perfluorooctanesulfonic acid	PFOS	1763-23-1	0.500	0.123
Perfluorononanesulfonic acid	PFNS	68259-12-1	0.500	0.0920

PFAS Analyte	Acronym	CAS RN	RL (ng/g)	MDL (ng/g)
Perfluorodecanesulfonic acid	PFDS	335-77-3	0.500	0.202
Perfluorododecanesulfonic acid	PFDoS	79780-39-5	0.500	0.109
1H,1H, 2H, 2H-Perfluorohexane sulfonic acid	4:2FTS	757124-72-4	2.00	0.555
1H,1H, 2H, 2H-Perfluorooctane sulfonic acid	6:2FTS	27619-97-2	3.00	1.39
1H,1H, 2H, 2H-Perfluorodecane sulfonic acid	8:2FTS	39108-34-4	2.00	0.684
Perfluorooctanesulfonamide	PFOSA	754-91-6	0.500	0.0940
N-methyl perfluorooctanesulfonamide	NMeFOSA	31506-32-8	0.500	0.0750
N-ethyl perfluorooctanesulfonamide	NEtFOSA	4151-50-2	0.500	0.102
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9	0.500	0.209
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	2991-50-6	0.500	0.171
N-methyl perfluorooctanesulfonamidoethanol	NMeFOSE	24448-09-7	5.00	0.681
N-ethyl perfluorooctanesulfonamidoethanol	NEtFOSE	1691-99-2	5.00	1.87
Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6	2.00	0.263
4,8-Dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4	2.00	0.400
Perfluoro-3-methoxypropanoic acid	PFMPA	377-73-1	1.00	0.124
Perfluoro-4-methoxybutanoic acid	PFMBA	863090-89-5	1.00	0.200
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6	1.00	0.389
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9CI-PF3ONS	756426-58-1	2.00	0.258
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl- PF3OudS	763051-92-9	2.00	0.250
Perfluoro(2-ethoxyethane)sulfonic acid	PFEESA	113507-82-7	1.00	0.230
3-Perfluoropropyl propanoic acid	3:3FTCA	356-02-5	2.50	0.722
2H,2H,3H,3H-Perfluorooctanoic acid	5:3FTCA	914637-49-3	12.5	2.11
3-Perfluoroheptyl propanoic acid	7:3FTCA	812-70-4	12.5	2.98

Table 6. Additional Sampling and Analysis Details for EPA Draft Method 1633

Analysis	Matrix	Method	Sample Container ¹	Bottle Volume	Minimum Sample Volume	Preservation Technique	Maximum Holding Time before Extraction (Days)
PFAS	Surface Water	EPA Draft 1633	Amber HDPE bottle	2 x 500 mL	2 x 500 mL (w/ headspace)	<6°C (on ice), protected from light or Frozen, ≤ -20°C, protected from light	28 (<6°C) 90 (frozen)

Analysis	Matrix	Method	Sample Container ¹	Bottle Volume	Minimum Sample Volume	Preservation Technique	Maximum Holding Time before Extraction (Days)
PFAS	Fish Tissue	EPA Draft 1633	LDPE bag (PFAS-free)	NA	1 g ²	<6°C (on ice) or frozen at ≤ -20°C, protected from light	90

1. Sample containers (bottles and bags) will be provided by Eurofins.

2. A minimum of 1 gram is needed for analysis; a much larger sample mass will be provided to the lab. *mL=milliliter*

g=gram

Section 4.0 presents further details on the equipment and protocols for sampling and laboratory analysis.

2.5.3 Criteria for Field Measurements

The principal observations and measurements made in the field for fish tissue sampling will be documenting the species of fish collected and recording the length and weight of the fish. Species identification will be performed by field sampling crew members experienced with the taxonomy of freshwater fish in Massachusetts rivers and lakes. Field sampling crew members will use a fish measuring board to measure the fish length, and these measurements will be made to the nearest millimeter; and they will use a digital scale to measure the weight (grams, wet weight). None of these field measurements will be performed in duplicate.

Beyond ensuring that an adequate volume of surface water is collected (i.e., that the bottles provided by the analytical laboratory are filled), no field measurements will be recorded for the surface water samples.

Section 2.8.1 lists other observations (not measurements) that will be recorded by the field sampling crew when collecting surface water and fish samples.

2.5.4 Action Limits

There are currently no federal or Massachusetts aquatic life or health-based standards for PFAS concentrations in surface water or fish. However, DPH has published developed an approach for interpreting the public health implications of exposure to PFAS in surface water and fish tissue. That approach is summarized below and described in a DPH presentation (DPH, 2021c). This project was designed to collect data that DPH can use to assess health risks for the waterbodies that are sampled and to determine if fish consumption advisories are warranted.

An overview of the DPH health evaluation approach follows:

 For a surface water sample from a given waterbody, the concentrations of four PFAS analytes (PFOA, PFNA, PFHxS, and PFOS) are compared to a screening level (23 ng/L). If the individual concentrations are below the screening level for that waterbody's surface water samples, then unlimited swimming in the waterbody is considered safe. If any of these concentrations is greater than the screening level, then a risk assessment would be conducted to evaluate the issue further.

For a fish tissue sample from a given waterbody, the concentrations of the same four PFAS analytes are compared to a different screening level (0.22 µg/kg). If the individual PFAS concentrations are below the screening level for all fish samples from that waterbody, then consuming those fish species caught from the waterbody is considered safe. If any concentration exceeds the screening level, then further analyses of that PFAS compound are conducted to determine whether a fish consumption advisory is warranted and to what fish species that advisory would apply.

The principal outcome of this project will be a database of PFAS concentrations measured in surface water and fish tissue from 50 waterbodies in Massachusetts and a summary report documenting patterns among those data. These PFAS concentration data will be sufficient for determining if fish consumption advisories are needed, but this project's summary report will not make conclusions about fish consumption advisories. DPH will be responsible for the public health interpretations of this project's sampling data. However, as a public health service, ERG will review laboratory analytical results as they are available and immediately inform MassDEP if any samples have PFAS concentrations greater than the screening levels documented above. This will allow MassDEP to notify DPH of such measurements in real time, such that protective public health actions can be taken (if necessary) before waiting for this project's final report to be issued.

2.6 Special Training and Certifications

All personnel supporting the field sampling and laboratory analyses for this project must have the necessary knowledge, qualifications, and experience to ensure that the measured PFAS concentrations are of a known and high quality. Sampling team members will also be required to read this QAPP, as well as the Sampling and Analysis Plan (SAP) included in Attachment A, at least two weeks before being deployed to the field.

Normandeau will provide field sampling crews for this project. Normandeau's staff have extensive prior experience in collecting, processing, storing, and transporting environmental samples; in identifying fish species from Massachusetts waterbodies; in operating the various watercraft types expected to be used in this project; and in using a wide range of fish sampling gear. Their field sampling crew members are fully prepared to collect fish and surface water samples with the methods outlined in this QAPP and in the project's SAP. PG Environmental will coordinate sample collection and provide training to all field sampling crew members on all relevant details in this QAPP, especially steps to take to process fish tissue samples before shipment to the laboratory in a manner that will minimize the likelihood of PFAS cross contamination.

All Normandeau field staff who will support this project have been fully trained in electrofishing procedures. This training includes orientation to the electrofishing equipment, procedures, and risks involved. In addition, all field biologists using electrofishing techniques have read and understand the Electrofishing Safety Guidance provided by the American Fisheries Society (excerpt from the 2008 American Fisheries Society Professional Safety Committee Fisheries Safety Handbook). Furthermore, Normandeau field staff have completed the U.S. Fish and Wildlife Service's course on Principles and Techniques of Electrofishing (CSP2201), offered through the National Conservation Training Center. At

least one field crew member in each two-person sampling team will be certified in CPR, first aid, and AED training.

Eurofins will use EPA draft Method 1633 to measure PFAS concentrations in the surface water samples and fish tissue samples collected in the field. That method does not include certification or specific training requirements, outside of mandatory training on glove removal methods to avoid cross contamination (see Section 5.3.3 of EPA draft Method 1633). Note that Eurofins operates within a written QAPP that meets or exceeds the EPA draft Method 1633 QA/QC requirements. Laboratory personnel performing the analyses described in this QAPP will be required to be qualified to perform the analysis according to the method requirements, according to specifications in this QAPP, and according to the laboratory's internal method competency requirements. This project does not require any mandatory certifications for laboratory chemists, but Eurofins does hold accreditations through the National Environmental Laboratory Accreditation Program, American Association for Laboratory Accreditation, and the Department of Defense Environmental Laboratory Accreditation Program.

2.7 Health and Safety

This QAPP addresses health and safety considerations for field sampling activities only (i.e., collection of surface water and fish tissue samples). Eurofins has its own health and safety plan that must be followed when receiving, handling, analyzing, and discarding environmental samples.

Normandeau field sampling crews will follow Normandeau's corporate "Health and Safety Plan (HASP) for Conducting Fish Collections Using Electrofishing Techniques" (see Appendix H of the SAP). This HASP covers general safety and operational guidelines (e.g., personal protective equipment, first aid, safety equipment); specific safety measures for boating safety, electrical safety, field safety, and hot/cold weather conditions; and emergency procedures for three different types of electrofishing gears: 1) electrofishing boat; 2) towed electrofishing barge; and 3) backpack electrofishing unit.

Once MassDEP approves the sampling locations proposed in this QAPP, ERG will review the health and safety plan with considerations specific to the waterbodies selected for sampling (e.g., avoiding dangerous wildlife, insects, and plants; use of insecticides and other protective measures if sampling waterbodies in areas of concern for mosquito-borne diseases; etc.). The health and safety plan will also address safe use of knives, fish scalers, and other potentially hazardous gear for processing the fish tissue samples. Protections against COVID-19 transmission will also be included if any state advisories apply when sampling occurs.

All field sampling personnel, whether from Normandeau, PG, or ERG, will be required to read and adhere to Normandeau's HASP.

2.8 Documents and Records

This project will generate multiple types of documents and records. These include (1) records generated in the field during sampling activities (see Section 2.8.1); (2) records generated by the laboratory during analysis of samples (see Section 2.8.2); and (3) additional documents and records maintained by the ERG project management team for contract management and other purposes (see Section 3.8.2). Clear, thorough, and complete documentation is required for all three types of records. All documentation and records related to sampling, lab analyses and data will be provided to MassDEP at the end of the project.

2.8.1 Field Documentation

The field sampling effort will generate three types of records, described below.

2.8.1.1 Field forms and Datasheets and Field Logbooks

Field sampling personnel will use river and lake field sheets provided by MassDEP WPP to document general site conditions and other information on the surface water samples collected at each waterbody. They will use MassDEP WPP's fish sampling log to document information on individual fish (e.g., length, weight, sex) and the composite sample that represents those fish. Section 4.0 of the SAP includes detailed information and instructions on how to use those forms.

Prior to every sampling event, Normandeau will assign responsibility for who is to complete the datasheets while the team is in the field. Another team member will be responsible for reviewing the datasheets, and this review will take place as soon as possible after the field sampling event, preferably the same evening. Once Normandeau has finished reviewing the datasheets for a given sampling event, they will scan the forms into PDF and email them to the ERG Project Manager and Deputy Project Manager or upload them to ERG's SharePoint site.

It is our expectation that all field sampling documentation will occur on the project-specific datasheets. However, field personnel will have loose plain paper in an aluminum clipboard with them in case additional space for documentation is needed. Field personnel will follow standard documentation practices for these sheets (e.g., sequentially numbering pages, using legible handwriting in ink, and noting the dates and times of all observations). Due to the potential for PFAS cross-contamination, field sampling crews will not use waterproof/treated paper or field books for additional notes.

2.8.1.2 Photographs

Photographs will be taken during field sampling and at all sampling locations to record activities, general site conditions, and location-specific features. Photographs will be taken in digital format, either using a cell phone or a camera; and they will be taken with date and time stamps embedded in the images. On the same day that photographs are taken, field personnel will upload the electronic files and the photograph log to ERG's SharePoint site.

2.8.1.3 Chain-of-Custody (COC) Forms and Shipping Forms

COC forms will be used to document collection, retention, storage, and transfer of samples. These forms will also contain information on the requested laboratory analyses. A copy of this project's COC forms is included as an appendix to the SAP. Before shipping samples to Eurofins, Normandeau will scan the COC forms and submit them via email to the ERG Project Manager and ERG Data Manager. Eurofins will include the final, completed COC forms in the analytical reports that are submitted to MassDEP. ERG will retain copies of all final COC forms until the project is completed.

2.8.2 Laboratory Documentation

Eurofins will generate two types of records, as described below. Data will also be available for the MassDEP Project Lead, ERG Project Manager, and ERG Data Manager through Eurofins' "myEOL" web portal, available at <u>https://eol.et.eurofinsus.com/myeol/</u>.

Analytical reports (as PDFs) with sample results for all target PFAS analytes.

These reports will include quantitative results, units, RLs, MDLs, dilution factors, and qualifier flags. The reports will also include, as appropriate, case narratives, crosswalks of laboratory and client sample IDs, and all QC parameters (e.g., results from method blank analyses, laboratory control sample analyses, and matrix spike analyses).

Electronic data deliverables (EDDs)

Eurofins will provide EDDs with analytical sample results and QC results in the format specified for this project and including all required fields for WPP's EQuIS database. The data elements listed in Table 7 for sample results are to be kept separate from the data elements for QC samples (i.e., one spreadsheet in an Excel workbook will have results for field samples and another spreadsheet will have results for QC data). Note that fields flagged as "conditional" (e.g., lab qualifiers, results comments) are not required for every sample, and only need to be entered when certain conditions are met (e.g., a laboratory qualifier is only included if the sample result requires one). Note that a crosswalk of the EDD fields listed below and those maintained in Eurofins' "myEOL" web portal is provided in Attachment C, for reference.

Data Elements	Description	Required
LabID	Laboratory name	Yes
LabSNum	Laboratory sample number	Yes
FieldSampNum	Field/client sample number	Yes
Analyte	Analyte name	Yes
Sample Fraction	Fraction associated with analyte	Yes
Result	Result value	Yes*
LabQual	Laboratory qualifier	Conditional
ResComm	Result comments	Conditional
Units	Analyte/Characteristic Units	Yes
MDL	Minimum detection level	Yes*
RL	Reporting limit	Yes*
UQL	Upper Quantification Limit	Conditional*
Analytical Method	Analytical method	Yes
AnalDate	Analysis date	Yes
AnalTime	Analysis time (24-hour format)	Yes
SiteLocator	Site or station locator information	Optional
CollectDate	Sample collection date	Optional
CollectTime	Sample collection time	Optional

Table 7. Data elements to be included in laboratory EDDs with PFAS results

*Results are to be reported as a text field.

Eurofins will send its analytical reports and EDDs via email to MassDEP, and MassDEP will forward results to the ERG Project Manager and ERG Data Manager. Data will be shared with other agencies, as appropriate. For example, as noted previously, draft lab results will be immediately shared with DPH via a shared OneDrive folder. ERG will maintain a master database of analytical results. ERG will make a read-only copy of that database available to MassDEP via SharePoint throughout the project and will deliver the final data to the agency when sample collection is complete.

3.0 Data Generation

3.1 Sampling Design

This section documents multiple decisions made regarding the project's overall sampling design and presents the rationale for those decisions. Sampling design decisions were made to ensure PFAS measurement data will meet this project's principal objective: to characterize the nature and extent of PFAS contamination in water and edible tissues of freshwater fish from rivers and lakes across the Commonwealth in a manner that will allow assessment of public health risks associated with consuming freshwater fish.

3.1.1 Selected Waterbodies

The project team sought to identify freshwater waterbodies in MA with (1) a high likelihood of PFAS contamination and (2) where people are known to collect and consume fish, including in EJ communities. The team used various resources and tools to select 45 waterbodies located in areas with known or suspected releases of PFAS into the environment (i.e., "source-impacted areas") and five waterbodies in areas without known PFAS sources and with low population density (i.e., "reference areas"). Catch-and-release waterbodies, small ponds (<5 acres), waterbodies with marine or brackish water, and waterbodies on Martha's Vineyard and Nantucket were not considered.

This section describes how the waterbodies were selected and then summarizes information on the five Phase 1 waterbodies (approved by MassDEP) and the 45 proposed Phase 2 waterbodies (pending MassDEP approval). The waterbody selection process involved first identifying a universe of candidate waterbodies, then narrowing the universe of candidate locations to a reasonable subset by ranking them based on potential impacts from known and suspected PFAS sources, and finally identifying waterbodies with PFAS sources located upstream of river sampling locations or within the same subbasin as lake or pond sampling locations.

Note that as part of this exercise, ERG also considered the proximity of waterbodies to EJ communities. The Executive Office of Energy and Environmental Affairs (EEA) has developed a GIS map of the Commonwealth that shows all census block groups that are considered EJ communities (MassGIS, 2021a) based on EEA's EJ criteria. However, EEA has not established criteria for designating waterbodies as being in an EJ or non-EJ community. For purposes of this project, any waterbody located within one mile of an EJ block group, as defined by EEA, is considered to be "in an EJ community." According to EEA's EJ criteria, census block groups that meet any of the three criteria listed below are defined as EJ populations, based on data from the 2015-2019 American Community Survey (MassGIS, 2021a):

- Household income: A Census block group with a median household income less than or equal to 65.5 percent of the MA median household income.
- English language isolation: A Census block group with 24.5 percent or more limited Englishspeaking households.
- Percent minority population: A Census block group with 39.5 percent or more minority population or a census block group with a minority population between 24.5 and 39.5 percent and median household income less than 150.5 percent of the state median household income.

The remainder of this section further describes the steps ERG took to select waterbodies for sampling.

There were several adjustments to the waterbodies sampled in Phase 2. The substituted waterbodies, and reasons for substitution, are provided below.

3.1.1.1 Methods for Selecting Phase 1 and Phase 2 Waterbodies

Step 1. Identify the Universe of Waterbodies to Consider

The universe of waterbodies to consider is based on the "Go Fish MA!" application developed by MassWildlife, which includes information on 525 waterbodies (MassWildlife 2022). ERG removed from this list the 36 waterbodies that are designated for "catch-and-release" fishing only. The 489 remaining waterbodies, including 342 lakes or ponds and 147 rivers or streams, were considered for this project.

Step 2: Assign a "PFAS Score" to Each Waterbody

ERG then developed a GIS database of known and suspected PFAS sources to inform the site selection process and used the locations of those sources to assign a "PFAS Score" to each waterbody. The score was calculated based on the total number of sources located within a 2-mile radius of the waterbody, with "known sources" given a weighting factor of three and "suspected sources" given a weighting factor of one. The "PFAS Score" was calculated as the sum of scores from all sources within the 2-mile radius. For instance, if a waterbody had two "known sources" (weighting factor = three) and three "suspected sources" (weighting factor = one) within a 2-mile radius, the PFAS Score would be calculated as $(2 \times 3) + (3 \times 1) = 9$. The PFAS scores were then used to prioritize waterbodies for closer review.

Known and suspected PFAS sources were identified as follows:

- *Known sources*. For this project, the following "known sources" were considered:
 - Sources listed in Appendix G of the Final Report of the PFAS Interagency Task Force, titled *PFAS in the Commonwealth of Massachusetts* and issued on April 20, 2022.
 - Sites or locations with known PFAS contamination from PFAS Analytic Tool¹
 - 26 superfund sites with reported PFAS detections
 - 23 federal agency locations with known or suspected PFAS contamination, including DoD sites with known (sampled) or suspected (no sampling, but activities involving fire suppression) PFAS contamination
 - 10 spill locations reported to the National Response Center referencing aqueous film forming foam (AFFF)
 - 1 facility that reported onsite releases of PFAS to EPA's Toxics Release Inventory
 - Suspected sources. For this project, the following "suspected sources" were considered:
 - The six commercial service airports in the mainland Commonwealth (i.e., Boston, Worcester, Hanscom, Hyannis, Provincetown, and New Bedford).
 - A subset of municipal or combined wastewater treatment plants, specifically the 77 larger grade 6 and grade 7 Massachusetts plants. These sites were obtained from a list

¹ EPA is developing a tool that compiles a variety of place-based PFAS data, tapping into national data systems that can be refreshed in an automated way and to avoid compiling standalone data files or revealing

confidential/sensitive information. While EPA has not yet released the PFAS Analytic Tool, EPA and state officials have access. The list of PFAS considered in scope are those defined by EPA's Office of Research and Development, which may be broader than what would be considered a known or suspected PFAS source for the purposes of this project. As such, only a subset of sources were considered.

of graded wastewater treatment plants published online by Massachusetts DEP in May of 2022 (MassDEP 2022a).

- 113 municipal solid waste landfills. This includes active landfills, as well as closed/inactive landfills that are greater than 20 acres in size. These sites were obtained from a list of solid waste facilities published online by MassDEP in May of 2022 (MassDEP 2022b).
- 51 Massachusetts sites that are accepting diverted food materials (i.e., compost, animal feed, anaerobic digester, and organics processer facilities). These sites were obtained from a map and list of sites accepting diverted rood material published by MassDEP in April of 2022 (MassDEP 2022c).
- Sites or locations with suspected PFAS contamination from the PFAS Analytic Tool
 - One historic and current manufacturer of PFAS
 - 42 facilities generating RCRA waste containing PFAS
 - Two facilities receiving RCRA waste containing PFAS

ERG obtained coordinates for all PFAS sources and used GIS to determine how many and which types of PFAS sources were within a 2-mile radius of each candidate waterbody. This information was then used to calculate the PFAS Score for each waterbody. ERG also created a map of all candidate waterbodies and PFAS sources.

Step 3: Select Lake and Pond Sampling Locations

For lakes and ponds, ERG reviewed each waterbody (by order of decreasing PFAS Score) using the USGS StreamStats web application (https://streamstats.usgs.gov/ss/) to confirm whether any of the PFAS sources located within a 2-mile radius fall within the drainage basin of the waterbody. For this, ERG delineated the drainage basin for each waterbody in StreamStats, downloaded the shapefile for that drainage basin, uploaded the shapefile to ERG's GIS database with the PFAS sources identified in Step 2, and then manually confirmed whether any of the known or suspected PFAS sources fall within the boundaries of the drainage basin. ERG did this for the nearly 150 waterbodies that had a PFAS score greater than zero and found 29 waterbodies with a known or suspected PFAS by DPH in 2021. Eleven additional waterbodies were added, all of which had multiple PFAS sources just outside of the boundaries of their drainage basin. The lakes and ponds were further prioritized by boat accessibility and PFAS score into 30 proposed sites. Backup locations were also identified (not included in this QAPP).

For lakes and ponds and per MassDEP's request, ERG also identified five reference waterbodies. For this, ERG used GIS to estimate the area-weighted sum of the 2020 census block group populations located within a 1-mile radius of each pond and lake that was assigned a PFAS Score of zero. ERG then evaluated the waterbodies (by order of increasing population density) in GIS and with aerial images to ensure that there was nothing else of concern nearby (e.g., potential non-population based sources). ERG selected the first five waterbodies that met these criteria and have a boat ramp, ensuring access for the field sampling crews in these more remote or rural areas.

Step 4: Select River Sampling Locations

For rivers and streams, ERG similarly reviewed candidate sampling locations (by order of decreasing PFAS Score) using the USGS StreamStats web application. For this, ERG also considered sampling locations used in the 2020 MassDEP-USGS study with the highest PFAS measurements. ERG delineated the drainage basin for each river sampling location in StreamStats, downloaded the shape file for that

drainage basin, uploaded the shapefile to ERG's GIS database with the PFAS sources identified in Step 2, and then manually confirmed whether any of the known or suspected PFAS sources fall within the boundaries of the drainage basin. ERG did this for 34 river sampling locations and found 24 with a known or suspected PFAS source in their drainage basin. This list was narrowed down by selecting those with the highest PFAS score and then refining that list to ensure that no more than two sampling locations were selected for given river and to prioritize river sampling locations with boat access.

Step 5: MassDEP Review, Changes and Approval

For proposed lakes/pond and river sampling locations, MassDEP staff reviewed each location, proposed changes based on internal review, and coordinated with ERG to approve the final site list. MassDEP's proposed changes were based on several additional factors for site selection, including:

- adding waterbodies based on known PFAS hot spots that were previously not selected based on the evaluation described in steps 1-4. Any added waterbodies replace draft low-PFAS-score sites and may lie outside the GoFishMA sampling population (i.e., special case).
- Avoiding lake sites in very close proximity to one another.
- enhancing EJ inclusion, where feasible
- minimizing overlap with other agency lake monitoring efforts, including the 2022 DPH PFAS project and the long-running DEP-ORS mercury monitoring project
- shifting site locations further downstream on a given waterbody in order to integrate upstream sources, or shifting further upstream to avoid tidal effects
- excluding very small drainage basin sites (w/o PFAS sources in the basin) in favor of other sites with relatively larger contributory basins
- avoiding lower order streams (with presumably less fishing pressure)
- adjusting the lake/pond list where appropriate to ensure a variety of lake sizes, and
- adding a river reference location for fish tissue (this was not generated in the previous USGS/DEP PFAS-in-water study)

Also, given the ubiquity of PFAS in the environment, additional weight was sometimes given during this final step to higher levels of development in the immediate drainage basin to the sampling location (e.g., highly urbanized areas are generally more likely to have historical PFAS contamination) and/or to larger developed drainages.

MassDEP's proposed changes from step 5 were discussed with ERG as part of finalizing the site list. MassDEP substitutions are flagged in Table 8 for lakes/ponds and Table 9 for rivers.

3.1.1.2 Phase 2 Waterbodies

Based on these criteria, 38 lakes/ponds (including five reference locations) and 12 rivers (including one reference location) were selected (Figure 1). 24 percent are within MassDEP's Northeast region, 24 percent are in the Southeast region, 26 percent are in the Central region, and 26 percent are in the Western region. Four reference lakes are located in the Western region; and one is in the Central region. The reference river is in the Western Region. 64 percent of the waterbodies are within 1-mile of at least one EJ census block. One reference lake and the reference river are located within 1-mile of an EJ census block.

Tables 8 and 9 present the 50 sampling locations selected for this study for lakes/ponds and rivers, respectively. Both tables include waterbody characteristics including location, watershed, boat access, PFAS score, whether PFAS sites fall within or near the boundaries of the waterbody's drainage basin, and whether the waterbody is within one-mile of an EJ community. Additional details are provided below for the Phase 1 locations that were sampled in June 2022 and that set the foundation for the project.

- Connecticut River in Chicopee (West). The Connecticut River is approximately 400 miles long and flows through four New England states. GoFishMA includes coordinates for a location in Chicopee, which is characterized by Massachusetts Division of Wildlife as a "featured site" and has a concrete boat ramp with parking for 10 trailers. At this location, the upstream basin of the Connecticut river includes one federal release site (Westover Air Reserve Base) and one facility generating RCRA waste with a manifest containing PFAS within five miles. Another known PFAS release site (Westfield-Barnes Municipal Airport) falls on the edge of the upstream basin. The Chicopee River flows into the Connecticut River about half a mile downstream of the boat launch; if sampling is conducted downstream of this point, the upstream basin will also include one AFFF spill site reported to the National Response Center within two miles of the sampling location. EJ communities surround this section of the river. Additional information is available here: https://www.ctriver.org/learn/watershed-facts/.
- Lake Boon, Hudson and Stow (Central). Lake Boon is a 180-acre great pond with an average depth of 11 feet and a maximum depth of 23 feet. There is a small boat ramp on the southern end of the lake; the town of Stow maintains a recreational area with shore access, trails, and parking at the north end of the lake. There is a federal release site (Precision Coating), just south of the lake and within the basin of the lake. There is also a Superfund site with known PFAS contamination (the Fort Devens-Sudbury Training Annex) half a mile east of the lake that overlaps with the drainage basin. Additional information is available here: https://www.mass.gov/doc/lake-boon/download
- Ashumet Pond, Mashpee and Falmouth (Southeast). Ashumet Pond is a 220-acre kettlehole pond in Mashpee, located just south of Joint Base Cape Cod. The pond is listed as a "featured site" by the Massachusetts Division of Wildlife on the GoFishMA map and has a paved boat ramp on the east side of the pond with ample parking. Trout are stocked twice a year and the pond is known for smallmouth bass. The majority of Ashumet Pond falls within environmental justice communities. The drainage basin of Ashumet Pond includes one federal PFAS release site (Joint Base Cape Cod). A Superfund site with PFAS contamination (Otis Air National Guard Base/Camp Edwards) is located on the eastern border of the basin. Additional information is available here: https://www.mass.gov/doc/ashumet-pond-0/download
- Flint Pond, Tyngsborough (Northeast). Flint Pond is a shallow 61-acre mill pond with a paved boat ramp and 20 parking spots located on its northeastern shore. The pond has high fishing pressure and is known for warm water fish such as largemouth bass. An environmental justice community lies half a mile to the East. There is one Superfund site with PFAS contamination (the Charles-George Reclamation Trust Landfill) located within the pond's drainage basin, about a half mile away from the pond. Additional information is available here: https://www.mass.gov/files/documents/2016/08/qd/dfwflin.pdf

Upper Spectacle Pond, Otis and Sandisfield (West) (Reference Lake). Upper Spectacle Pond in Otis is a 72-acre pond surrounded by Otis State Forest. The pond has a maximum depth of 22 feet and an average depth of 11 feet. A gravel boat ramp is located off Webb Road on the southeastern bank of the pond. The estimated population within one mile of Upper Spectacle Pond is 84, based on an area-weighted sum of the 2020 census block group populations located within a 1-mile radius of the pond coordinates in the GoFishMA database. No known or suspected PFAS sources are within five miles of the pond or within the drainage basin of the pond. Additional information is available here:

https://www.mass.gov/files/documents/2016/08/qd/dfwuppes.pdf

During Phase 2 sample collection, ERG and MassDEP replaced two waterbodies due to unfavorable fishing conditions identified by the field teams (e.g., low water levels, excessive vegetation). Hardwick Pond was substituted for Delaney Pond and the Ware River was substituted for the Sudbury River.

The field teams did not collect any fish at five of the waterbodies sampled (i.e., Hathaway Ponds, Mossy Pond, Norton Reservoir, Wachusett Reservoir, and the Bungay River) and the lab mistakenly disposed of fish samples prior to analysis from three waterbodies (i.e., Hopedale Pond, Falls Pond, and Nutting Lake). Resources allowed for field teams to sample an additional five waterbodies to fill these gaps. MassDEP and ERG decided to resample two of the waterbodies for which the fish samples lost due to laboratory error (i.e., Hopedale Pond and Falls Pond) as well as three additional waterbodies there were not on the original list (i.e., South Watuppa Pond, Whitman's Pond, and Lake Cochichewick).

Map #	Sampl ing ID	Phase	Waterbody	Lat.	Long.	Region	Watershed	Boat Access	PFAS Score	Known PFAS Source in Basin	Suspected PFAS Source in Basin	PFAS Source just outside of Basin	No PFAS within basin, but large # of PFAS sites within 2 miles	EJ (1- mile)	REF
1	005	1	Ashumet Pond [¶]	41.62998	-70.5371	SE	Cape Cod	Yes*	3	Х				Х	
2	001	1	Flint Pond [¶]	42.67373	-71.43288	NE	Merrimack	Yes*	3	Х				Х	
3	002	1	Lake Boon [¶]	42.40315	-71.50143	CEN	Concord	Yes*	21	Х					
4	004	1	Upper Spectacle Pond [¶]	42.1808	-73.11763	West	Farmington	Yes*	0						x
5	006	2	Asnacomet Pond [±]	42.45626	-71.98327	CEN	Chicopee	Yes*	0						Х
6	007	2	Buck Pond	42.17167	-72.7026	WEST	Westfield	Yes^	8			х	Х	Х	
7	008	2	Congomond Lakes $^{\pm}$	42.02843	-72.75618	WEST	Westfield	Yes*	1		Х			Х	
8	009	2	Crocker Pond [±]	42.57211	-71.88717	CEN	Nashua	Yes	7	Х	х				
9	010-	2	Delaney Pond	42.44438	-71.546	CEN	Concord	¥es^	7	×	×	-	-	-	-
10	011	2	Falls Pond	41.9587	-71.3244	SE	Ten Mile	Yes*	4	Х	Х			Х	
11	012	2	Forge Pond	42.57689	-71.4891	NE	Merrimack	Yes*	3	Х				Х	
12	013	2	Hathaway Ponds [¥]	41.6845	-70.312	SE	Cape Cod	Yes*^	10				Х		
13	014	2	Hopedale Pond	42.14157	-71.557	CEN	Blackstone	Yes*	4	Х	Х			Х	
14	015	2	Jamaica Pond [±]	42.3174	-71.12065	NE	Charles	No§	6					Х	
15	016	2	Lake Attitash	42.84942	-70.9818	NE	Merrimack	Yes*	4			Х			
16	017	2	Lake Cochituate	42.30287	-71.368	NE	Concord	Yes*	6	Х				Х	
17	018	2	Lake Mirimichi	42.02502	-71.292	SE	Taunton	Yes [£]	1		х				
18	019	2	Lake Quannapowitt [±]	42.51866	-71.08069	NE	North Coast	Yes *	1		Х				
19	020	2	Lake Ripple	42.21313	-71.6982	CEN	Blackstone	Yes*	3	Х	Х			Х	
20	021	2	Lake Sabbatia	41.94414	-71.1082	SE	Taunton	Yes*	1		Х		Х	Х	
21	022	2	Lake Winthrop	42.1883	-71.4236	CEN	Charles	Yes*	3	Х					
22	023	2	Long Pond [±]	41.80162	-70.94449	SE	Taunton	Yes*	0		Х				
23	024	2	Long Pond (Yarmouth)	41.66974	-70.1972	SE	Cape Cod	Yes*^	2			х		Х	
24	025	2	Mascuppic Lake [±]	42.6778	-71.3841	NE	Merrimack	Yes*	1			Х		Х	
25	026	2	Moores Pond	42.65688	-72.3476	WEST	Millers	Yes*	0						Х

Table 8. Lake and Pond Sampling Locations

	Sampl ing ID	Phase	Waterbody	Lat.	Long.	Region	Watershed	Boat Access	PFAS Score	Known PFAS Source in Basin	Suspected PFAS Source in Basin	Source just outside of Basin	No PFAS within basin, but large # of PFAS sites within 2 miles	mile)	REF
26	027	2	Mossy Pond [¥]	42.41535	-71.7057	CEN	Nashua	Yes^	5			Х		Х	
27	028-	£	Norton Reservoir	41.99229	-71.2057	SE	Taunton	Yes*	4	×	×	-	-	-	-
28	029	2	Nutting Lake [±] ^Δ	42.53593	-71.26918	NE	Concord	Yes^	1			Х		Х	
29	047	2	Oxbow Pond- Easthampton	42.28487	-72.6295	WEST	Connecticut	Yes*	2	х				х	
30	031	2	Pelham Lake	42.69957	-72.8891	WEST	Deerfield	Yes*	0					Х	х
31	032	2	Pontoosuc Lake	42.48917	-73.2504	WEST	Housatonic	Yes*	3	Х				Х	
32	033	2	Robbins Pond	42.00193	-70.899	SE	Taunton	Yes^	1		Х				
33	034	2	Sandy Pond	42.5619	-71.5556	CEN	Nashua	Yes^	24			Х	х	Х	
34	035	2	Snake Pond	41.68187	-70.5197	SE	Cape Cod	Yes	12	Х				Х	
35	036	2	Studley Pond	42.1198	-70.9203	SE	South Coastal	Yes^	2	х				х	
36	037	2	Wachusett Reservoir [¥]	42.37326	-71.74088	CEN	Nashua	No	7	х	х			х	
37	038	2	Webster Lake $^{\pm}$	42.04051	-71.84415	CEN	French	Yes*	4					Х	
38	039	2	West Lake	42.13127	-73.1625	WEST	Farmington	Yes*^	0						Х

Notes:

-Waterbody:

[±] indicates waterbody was added based on MassDEP review. Criteria for this review are listed in Step 5 of the waterbody selection criteria

[¶] indicates that the waterbody was sampled during Phase 1

-Latitude and longitude coordinates represent the locations of each waterbody as identified in MassWildlife's "Go Fish MA!" web-based interactive map. Coordinates were obtained from Google Maps for waterbodies not within "Go Fish MA!".

-Boat access is based on information contained within MassWildlife's "Go Fish MA!" web-based interactive map, MassDEP Pond Maps, and google searches. Feasibility of access and boat restrictions will be reviewed with Normandeau. If any of the proposed locations are not accessible, a backup location will be substituted.

Types of boat access are marked as:

*Boat access ramp

^Cartop boat access only

§ Possible boat access, depending on ability to use boathouse.

[£] Gated area used by fire department. May need to request access from fire department.

-"PFAS Score" is calculated as the sum of the weighted scores from all PFAS sources within a 2-mile radius of the waterbody. Known sources were assigned a weight of 3 and suspected sources were assigned a weight of 1, as described in the text preceding this table.

-"PFAS Source just outside of Basin" indicates if a PFAS site was very close to the basin, but not within the basin boundaries. This indicator is only recorded for waterbodies that did not have a PFAS source within its basin.

-"No PFAS within basin, but large # of PFAS sites within 2 miles" indicates that the waterbody is in an area with many PFAS sources. This indicator was only recorded for waterbodies that did not have a PFAS source within its basin.

-"Ref" indicates whether waterbodies are assumed to represent reference locations – i.e., not located near any known or suspected land-based PFAS sources.

-"EJ" indicates whether an EJ census tract falls within one mile of the waterbody.

^ANutting Lake was successfully sampled but the fish tissue samples were inadvertently disposed of at the laboratory. Nutting Lake was not resampled due to a limited fish catch during the first sampling event.

[¥]Fish were not caught at Hathaway Ponds, Mossy Pond, or Wachusett Reservoir. Water samples were collected and analyzed from these waterbodies. There were no fish caught at Norton Reservoir and the surface water samples were not sent to the lab.

Sampling ID	Phase	Waterbody	Lat.	Long.	Region	Watershed	Boat Access	PFAS		Sucnoctod DEAS	PFAS Source just outside of Basin	No PFAS within basin, but large # of PFAS sites within 2 miles	EJ (1- mile)	REF
010	2	Hardwick Pond	42.31144	- 72.23854	WEST	Chicopee	Yes	1		x			x	
053	2	Lake Cochichewick	41.66812	- 71.11721	NE	Merrimack	Yes	2		x				
051	2	South Watuppa Pond	41.66812	- 71.11721	SE	Mt Hope Bay	Yes	0					x	
052	2	Whitman's Pond	42.20642	- 70.94267	SE	Weir	Yes	0	X			x	x	

Lake and Pond Sampling Locations added during Phase 2 Sampling

Table 9. River Sampling Locations

Map #	Sampling ID	Phase	Waterbody	Town	Lat.	Long.	Region	Watershed	Boat Access	PFAS Score	Known PFAS Source in Basin	Suspected PFAS Source in Basin	USGS Sampled	EJ (1- mile)	Ref
39	003	1	Connecticut River [¶]	Chicopee	42.15277	-72.62495	WEST	Connecticut	Yes*	4	Х	Х		Х	
40	040	2	Blackstone River [±]	Northbridge	42.1287	-71.63711	CEN	Blackstone	Yes	0	Х	Х			
41	041	2	Bungay River ^{±¥}	Attleboro	41.95085	-71.28372	SE	Ten Mile	Yes^	6				Х	
42	042	2	Charles River [±]	Waltham	42.36252	-71.24494	NE	Charles	Yes*	1	Х	х		х	
43	043	2	Chicopee River	Springfield	42.16085	-72.5012	WEST	Chicopee	Yes^§	2	Х	Х		Х	
44	044	2	Concord River	Lowell	42.6255	-71.2953	NE	Concord	Yes*^	9	Х	Х	Х		
45	045	2	Deerfield River [±]	Florida	42.67908	72.97713	WEST	Deerfield	Yes^	0				Х	Х
46	046	2	Hoosic River	Williamstown	42.72939	-73.2082	WEST	Hoosic	Yes^	2		Х		Х	
47	030	2	Merrimack River	Haverhill	42.75897	-71.0449	NE	Merrimack	Yes^§	5	Х	Х	Х	Х	
48	048	2	Millers River [±]	Orange	42.5885	-72.30611	WEST	Millers	Yes	1		Х		Х	
49	049	2	Nashua River [±]	Groton	42.62747	-71.59306	CEN	Nashua	Yes*	0	Х	Х			
50	050	2	Sudbury River	Ashland	42.26439	-71.4678	NE	Concord	¥es^	3	-	×	-	×	-

Notes:

-Waterbody:

[±] indicates waterbody was added based on MassDEP review. Criteria for this review are listed in Step 5 of the waterbody selection criteria

[¶] indicates that the waterbody was sampled during Phase 1

- Latitude and longitude coordinates represent the locations of each waterbody as identified in MassWildlife's "Go Fish MA!" web-based interactive map.

-Boat access is based on information contained within MassWildlife's "Go Fish MA!" web-based interactive map and google searches. Feasibility of access and boat restrictions will be reviewed with Normandeau. If any of the proposed locations are infeasible, a backup location will be substituted.

Types of boat access are marked as:

*Boat access ramp

^Cartop boat access only

[§]An additional launch site with a boat ramp (not limited to car top) is very close, at South River St next to the yacht club for the Merrimack River in Haverhill and at 56 River Road, Wilbraham for the Chicopee River in Springfield. <u>https://www.cityofhaverhill.com/departments/parks_and_conservation_areas/boating_information.php</u>

-"PFAS Score" is calculated as the sum of the weighted scores from all sources within a 2-mile radius of the waterbody. Known sources were assigned a weight of 3 and suspected sources were assigned a weight of 1, as described in the text preceding this table.

-"PFAS Source just outside of Basin" indicates if a PFAS site was very close to the basin, but not within the basin boundaries. This indicator is only recorded for waterbodies that did not have a PFAS source within its basin.

-"USGS Sampled" indicates that the site is at or close to (within 2 miles) of a site sampled for PFAS by USGS as part of its 2020 study.

⁺Town River does not have identified PFAS sources upstream within their basins. However, this site had a suspected PFAS source approximately 0.5 to 1 mile downstream of the access point and was sampled by USGS downstream of the access sites; if possible, field teams will sample one mile downstream of access point.

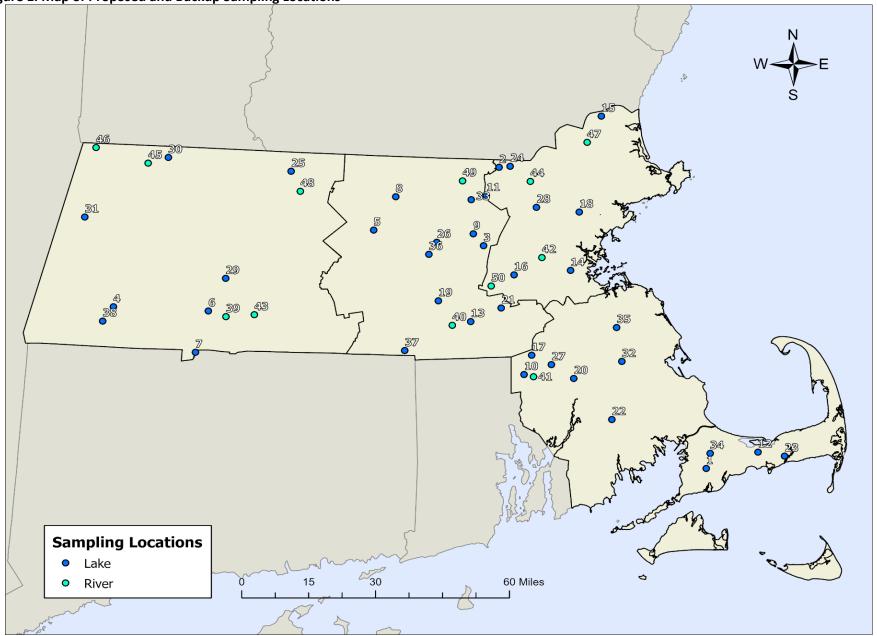
-"EJ" indicates whether an EJ census tract falls within one mile of the waterbody.

[¥]Fish were not caught at the Bungay River. Water samples were collected and analyzed from this waterbody.

River Sampling Locations added during Phase 2 Sample Collection

Sampling ID	Phase	Waterbody	Town	Lat.	Long.	Region	Watershed	Boat Access	PFAS Score	PFAS	Suspected PFAS Source in Basin	USGS Sampled	EJ (1- mile)	Ref
050	2	Ware River	Ware	42.26642	-72.22744	WEST	Chicopee	Yes	0				X	

Figure 1. Map of Proposed and Backup Sampling Locations



Refer to **Error! Reference source not found.** Table 8 (lakes and ponds) and Table 9 (rivers) for additional details on the sampling locations shown in this figure. **Note that waterbodies added during phase 2 are not represented on this map.**

3.1.2 Targeted Fish Species

At every waterbody selected for sampling, the field sampling crew will attempt to collect fish species that people are most likely to consume, while also ensuring that a diversity of species are collected. **Table 10 lists species that were targeted by this project.** Table 10 lists the species that were included in this project's Scientific Collection Permit, which means that these are the only fish species that will be considered for PFAS analysis. The list of fish species was prepared from two sources: Normandeau's professional judgment of freshwater fish commonly caught in Massachusetts for consumption, which is based on more than 20 years of fish tissue sampling in Massachusetts rivers and lakes; and MassWildlife "Pond Maps," which list fish species previously collected in MassWildlife surveys.

The project team will not specify ahead of time which fish species will be targeted for a given waterbody, because the profile of fish species caught in a waterbody cannot be known in advance. The proposed sampling approach for this program will be sampling until the maximum number of fish for a waterbody is collected (see Section 3.1.3) or sampling for four hours, whichever comes first. Some exceptions may occur and the reasons for exceptions will be documented (e.g., for inclement weather).

The maximum number of fish species for PFAS measurements will be three species for lakes and two species for rivers. If field sampling crews collect fish from more than three species shown in Table 10 in a waterbody, the fish species with the greatest numbers of similarly sized adult fish will be selected for PFAS measurement. The rationale for this decision is that the fish species in Table 10 caught in greatest numbers, to first and rough approximation, can be assumed to be the fish species most likely to be consumed. For every waterbody, the field sampling datasheets will document the range of fish species collected, the species selected for analysis (up to three for lakes and up to two for rivers), and the rationale for this selection (which will generally be that these species had the greatest numbers of similarly sized adult fish). This species selection protocol will be applied in Phase 1.

In Phase 2, the field team will continue to collect the species that are most frequently caught at each waterbody, but with additional consideration of species diversity. During this phase, the team will continue to collect sport fish most often caught and kept by recreational anglers (to meet the primary objective of this study) but will also collect other species in order to gather information on both pelagic (including trout) and benthic species. For the latter, the field teams will attempt to collect composite samples at each waterbody for a species that has not been caught at many of the previously sampled waterbodies. At a lake, for example, this might mean that the field crew collects fish for the two species caught in the greatest quantity, and then fish for a third species that has not well represented in the program's previous sampling efforts. This process will be revisited early in Phase 2. The permit was modified in Phase 2 to allow for more than three species to be kept at lakes and more than two species to be kept at rivers in locations with sampling limitations. The maximum number of fish per river or lake, and the maximum number of fish per species remained the same.

The project team also discussed at length whether to include stocked fish (e.g., rainbow trout) in the assessment. Ultimately, the team agreed that stocked fish are commonly consumed and that measuring PFAS in those species is consistent with the projects principal goal – i.e., characterizing the nature and extent of PFAS contamination in water and edible tissues of commonly consumed freshwater fish. Sampling techniques to capture these cold water fish will be applied as needed.

Family Name	Common Name	Scientific Name		
Centrarchidae	Largemouth bass	Micropterus salmoides		
	Smallmouth bass	Micropterus dolomieu		
	Black crappie	Pomoxis nigromaculatus		
	Redbreast sunfish	Lepomis auritus		
	Bluegill	Lepomis macrochirus		
	Pumpkinseed	Lepomis gibbosus		
Moronidae	White Perch	Morone americana		
Percidae	Yellow Perch	Perca flavescens		
Salmonidae	Brook Trout	Salvelinus fontinalis		
	Brown Trout	Salmo trutta		
	Rainbow Trout	Oncorhynchus mykiss		
	Brown Bullhead	Ameiurus nebulosus		
Ictaluridae	Yellow Bullhead	Ameiurus natalis		
	Black Bullhead	Ameiurus melas		
Esocidae	Chain Pickerel	Esox niger		
Cyprinidae	Common Carp	Cyprinus carpio		
Anguillidae	American Eel	Anguilla rostrata		
Catostomidae	White Sucker	Catostomus commersonii		

Table 10. Fish Species Listed on the Scientific Collection Permit

3.1.3 Targeted Fish Size

Field teams will only keep fish that meet the state's minimum size requirements. Of the species listed in Table 10, only chain pickerel (15 inches) and largemouth/smallmouth bass (12 inches) have minimum size requirements. Massachusetts Division of Fisheries and Wildlife regulations prohibit taking fish that do not meet these requirements (see: <u>https://www.mass.gov/info-details/freshwater-fishing-regulations</u>). Note that minimum length is measured for fish as the straight line (not curved over the body) from the tip of the snout to the tip of the tail.

In addition to the legal requirements mentioned above, the field crew will only keep fish that are of the minimum size generally kept by recreational anglers. For example, and as a general guideline, the field crew will collect bluegill, pumpkinseed, yellow perch, and white perch that are at least six inches long. For brown bullhead, the field crew will only keep fish that are minimum of eight inches long.

3.1.4 Number of Species and Fish to be Collected

After the field sampling crew determines the selected fish species for PFAS measurement (using the procedure in Section 3.1.2), the next decision is determining how many similarly sized individual fish of the same species to include in the samples that are sent to the laboratory. This section describes the general rationale regarding the number of fish to include in a sample. As the sampling progresses, MassDEP and the ERG team will coordinate and track progress, and make adjustments as needed. (Note: This section focuses entirely on the primary field samples to be collected. Additional detail on duplicate samples is provided in Section 3.4)

For this study, a composite sample of fish will be generally comprised of between three and five similarly sized fish of the same species that are filleted and analyzed together as one composite sample. However, multiple considerations factor into the number of individual fish to include in a composite sample. First, it is not feasible to prescribe the exact number of fish that can be collected in a given waterbody, as fish catch rates can be unpredictable and beyond the control of the field sampling crew. Second, project resources will allow for no more than three composite samples (Phase 1) and no more than two composite samples (Phase 2) for a given species from a specific waterbody to be sent to the laboratory. Third, the field sampling crew will first prepare as many composites as possible that contain between three and five similarly sized adult fish of the same species. The following decision framework is based on these considerations:

- The field sampling crew will stop sampling in a waterbody if they catch the maximum number of fish for PFAS measurements. For Phase 1, up to three composites could be collected per species. For a given lake this resulted in a maximum number of 45 fish, which would include 15 similarly sized adult fish of three different species. For a given river, the maximum number of fish was 30, which would include 15 similarly sized adult fish of three different species. For a given river, the maximum number of fish was 30, which would include 15 similarly sized adult fish of two different species. In Phase 2, two composites will be collected per species. This means that a maximum of 30 fish will be collected at lake locations and a maximum of 20 in rivers. The field sampling crew will stop sampling if these quantities are caught, even if they have been sampling for less than four hours.
- If the maximum number of fish in a waterbody is not caught, the field sampling crew will continue sampling at that waterbody for four hours. At the end of the four hours, the field sampling crew will number the similarly sized adult fish of a given species and use Table 11 to determine whether fillets will be sent to the laboratory from individual fish or from composites. The strategy behind the approach is to submit as many composite samples as possible within the limits prescribed.
- Criteria for a successful sampling event. A waterbody will be considered successfully sampled if the following criteria are met: (a) for lakes, if at least one sample from each of three different species is sent to the analytical laboratory and (b) for rivers, if at least one sample from each of two different species is sent to the analytical laboratory. If these criteria are not met, ERG will notify MassDEP; proceed with all remaining Phase 1 and Phase 2 sampling; and if sufficient project resources remain after the initial round of sampling at all 50 waterbodies, return to as many waterbodies that project resources allow to collect additional fish. (Note: The field sampling crew will spend at least four hours at every waterbody and catch as much fish as possible, up to the maximum quantities noted earlier. The crew will not stop sampling after the minimum criteria cited above are met. Exceptions may occur for unforeseen reasons, such as inclement weather forcing field sampling crews to leave a waterbody.)

Number of Similarly	Number of Individual Fish for Composite Samples*							
Sized Adult Fish Caught for a Single Species	Composite Sample #1	Composite Sample #2	Composite Sample #3 (Phase 1 only)					
1	Fillet from fish #1 [^]	No sample	No sample					
2	Fillet from fish #1-2	No sample	No sample					
3	Fillets from fish #1-3	No sample	No sample					
4 [¥]	Fillets from fish #1-4	No sample	No sample					
5	Fillets from fish #1-5	No sample	No sample					
6	Fillets from fish #1-3	Fillets from fish #4-6	No sample					

Number of Similarly	Number of Individual Fish for Composite Samples*							
Sized Adult Fish Caught for a Single Species	Composite Sample #1	Composite Sample #2	Composite Sample #3 (Phase 1 only)					
7	Fillets from fish #1-4	Fillets from fish #5-7	No sample					
8	Fillets from fish #1-4	Fillets from fish #5-8	No sample					
9	Fillets from fish #1-3	Fillets from fish #4-6	Fillets from fish #7-9					
10	Fillets from fish #1-4	Fillets from fish #5-7	Fillets from fish #8-10					
11	Fillets from fish #1-4	Fillets from fish #5-8	Fillets from fish #9-11					
12	Fillets from fish #1-4	Fillets from fish #5-8	Fillets from fish #9-12					
13	Fillets from fish #1-5	Fillets from fish #6-9	Fillets from fish #10-13					
14	Fillets from fish #1-5	Fillets from fish #6-10	Fillets from fish #11-14					
15	Fillets from fish #1-5	Fillets from fish #6-10	Fillets from fish #11-15					
>15	Follow the previous row for the first 15 fish and return additional fish to the waterbody							

[^] Up to three composite samples may be collected per species under Phase 1. During Phase 2, a maximum of two composites will be collected per species.

^{*} This program is focused on composite sampling. If insufficient fish are caught to create a composite sample for three different species, an individual fish sample will be collected instead.

^{*} ERG consulted with DEP when four fish of one species were collected from a waterbody. In some cases, these fish were processed into two composites, with the first composite composed of filets from fish #1-2 and the second composite composed of filets from fish #3-4. This determination was made on a case-by-case basis.

3.1.5 Fish Sampling Methods

The previous two sections (a) describe how field sampling crews will select species for sampling and (b) specify the number of fish that will be composited into samples based on the total amount of similarly sized adult fish that are caught. This section provides a high-level summary of the proposed fish sampling activities. Additional detail is provided in Section 3.6.1 (sample collection) and Section 3.6.3 (sample processing) of the SAP.

In brief, Normandeau will conduct sampling with assistance from PG and ERG, as needed. Fish sampling will be conducted primarily via electrofishing from a motorboat, whenever possible. At waterbodies that do not allow for outboard motor use or without a ramp, electrofishing will be considered from a cartop boat or raft. Hook and line and trot lines will be used when conditions do not allow for electrofishing or specific species are sought. For example, at deeper water bodies (i.e., with a maximum depth of greater than around 20 feet), the field crew will begin by using hook and line or trot lines for the first two hours of sampling, after which they will switch over to electrofishing. This will help ensure that the team collects a variety of species, including species from deeper waters.

In the field, sampling crews will collect the fish; batch fish of the same species in live wells based on the criteria laid out in Table 11; remove selected fish of the same species and similar size, pith the fish, and then place them in PFAS-free bags provided by Eurofins; label the bags of whole fish; and return all fish not selected for sampling to the waterbody in a humane manner. After sample collection is complete, the field sampling crew will transport the fish on ice to Normandeau's Bedford facility, where they will be processed. There, field sampling crews will use PFAS-free equipment to measure and weigh the individual fish; skin and fillet the fish; and prepare composite samples using fillets from similarly sized

fish of the same species. Composite samples (i.e., bags with fillets from three to five fish) will be frozen for 24-hours prior to shipment to Eurofins for analysis.

Because of the ubiquitous nature of PFAS in common consumer products and the equipment typically used to collect environmental samples, as well as the low MDLs targeted for this project, special care must be taken throughout sample collection and processing. Section 3.2 of the SAP provides details on the precautions that field sampling crews will take to minimize the potential for cross contamination. Sections 3.6.3 and 3.7 of the SAP further discuss decontamination procedures to be followed during sample collection and sample processing.

3.1.6 Surface Water Sampling Methods

Section 2.3 identifies two data uses for this project's surface water sampling. Two different types of surface water samples will be collected to support those intended uses. This section provides a high-level summary surface water sampling activities, with further details included Section 3.6.2 of the SAP.

The primary surface water data use noted in Section 2.3 is to derive species-specific PFAS bioaccumulation factors. For this data use, one unfiltered surface water grab sample will be collected at each of the 50 waterbodies. At a given waterbody, this "open water" sample will be collected in the immediate vicinity of where the first productive fishing activities occurreAt d (i.e., the surface water sample will be collected at a depth of 1 to 1.5 feet beneath the surface, and sediments will not be disturbed during sample collection. For this data use, only one sample will be collected per waterbody, even if fishing occurs at multiple locations. Note that the air/water boundary will not be included in the sample; sample bottles will be uncapped underwater with no potential for water to enter from the surface layer.

The secondary surface water data use noted in Section 2.3 is to support public health evaluations due to incidental ingestion during recreational activities. Surface water sampling to support this data use will be limited to lakes (not rivers) with large beach areas observed to have frequent recreational use. For purposes of this project, a "beach area" will be considered a public access point at a lake with signage indicating recreational uses of water (e.g., swimming). The field crew will use their judgement when determining whether a "beach area" is sufficiently large to warrant sample collection and will reach out to the ERG Project Manager or Deputy Project Manager if there is any uncertainty. At these waterbodies, "beach area" surface water sample will be collected within 20 feet of the shore at a depth of 0.5 to 1.0 feet. To the extent possible, samples will be collected during early morning hours when the beach areas are likely to be least crowded and be the first activity completed upon arrival to the waterbody. Field sampling crews will wade into the water and collect the grab sample. While this sample collection approach will disturb sediments, the approach may best mimic the water quality conditions that a recreational user might experience.

All surface water samples will be collected in bottles that are immediately placed on ice inside a cooler (<6° C). The field sampling crews will bring the surface water samples to the Normandeau office, document the samples, and ship them on ice (<6° C) with COC forms to Eurofins. Only the "open water" surface water samples will be used to derive species-specific PFAS BAFs. Public health implications (e.g., the need for swimming advisories or other restrictions) will be considered with both the "open water" and "beach area" water samples. For this purpose, data will be shared with DPH.

3.1.7 Field Measurements Methods

In addition to collecting fish and surface water samples, field sampling crews will collect additional measurements at the 50 waterbodies. Following specifications in the SAP, they will:

- Record the GPS coordinates of the two water sample locations. A smartphone application will be used for this purpose.
- Use a fish measuring board to measure fish length and a digital scale to measure fish weight. These measurements will be recorded in Normandeau's Bedford facility for all fish used in the samples sent to the analytical laboratory.
- Use a handheld multimeter to measure water conductivity at all sites where electrofishing is used.

The previous list documents *measurements* that field sampling crews will make. As described earlier, the field sampling crew will identify fish species, take photographs, and document numerous observations on the sampling forms, but none of those activities involves taking measurements.

3.2 Sample Handling and Custody

This program's fish and surface water samples will be handled in a consistent fashion and will only be handled by the field sampling crew, an overnight shipping company, and the analytical laboratory. Immediately after collection at a waterbody, fish collected for analysis will be put in sealable plastic bags provided by Eurofins and placed in coolers and stored on ice. Bottles containing surface water will be placed in separate coolers, also on ice. Field sampling crews will then transport the coolers from the waterbody to Normandeau's Bedford facility, where the collected fish will be processed into composite samples for the laboratory. Frozen samples will be shipped in coolers via overnight delivery to Eurofins. The field sampling crew will be instructed to ship coolers containing samples as soon as possible following sample collection, but not before the fish fillets are completely frozen. ERG will track every shipment to ensure that it arrived at the analytical laboratory and will confirm with the analytical laboratory that samples were, in fact, received.

Another important element of sampling handling is maintaining COC documents to demonstrate that samples have only been handled by designated parties. COC forms will be completed when field samples are collected and when they are transferred from one party to the next. Field sampling crews will place COC forms inside Ziploc bags, which will then be placed in the sampling coolers. Normandeau will make an electronic image of COC forms before shipping sample coolers, and Eurofins will similarly make such images after receiving and analyzing samples. All images will be sent electronically to ERG, who will use COC forms to track any missing samples and who will include all completed COC forms in the final project record. COC forms can be found in the SAP.

3.3 Analytical Methods

Fish tissue composite samples and surface water samples will be analyzed for 40 PFAS using EPA draft Method 1633 (EPA, 2021) by Eurofins. This method was developed by EPA and DOD's Strategic Environmental Research and Development Program (SERDP) to evaluate PFAS compounds in multiple media (i.e., wastewater, surface water, groundwater, soil, biosolids, sediment, landfill leachate, and fish tissue). The method involves preparing and extracting environmental samples and then analyzing the sample extracts by LC-MS/MS in the multiple reaction monitoring (MRM) mode. Sample concentrations are determined by isotope dilution or extracted internal standard quantification using isotopically labeled compounds added to the samples before extraction (EPA, 2021). The method tests for a maximum of 40 PFAS. At the time when this QAPP was developed, EPA draft Method 1633 had been validated by a single-laboratory study (SERDP, 2022). A multi-laboratory validation study is underway and is expected to be completed in 2022.

A high-level overview of laboratory processing and analysis of fish and surface water samples is provided below. Additional details are available in the laboratory's SOPs. The laboratory will document in its reports any deviations from the proposed analytical method. The laboratory will also provide sufficient documentation to allow for an independent validation and verification of the analytical results.

<u>Fish Samples:</u> The laboratory will analyze composite fish samples received from Normandeau. Those samples will arrive at the laboratory on ice as skin-off fillets, which are assumed to represent the edible portions of fish for most populations. The laboratory will homogenize the samples before analysis and then measure 40 PFAS analytes following the protocols in EPA draft Method 1633. Fish tissue concentrations will be reported in units of nanogram PFAS analytes per gram of fish (wet weight). Results will be reported to the MDL.

<u>Surface water samples</u>: The laboratory will analyze surface water samples received from Normandeau. Those samples will arrive at the laboratory in 500mL HDPE sampling bottles, on ice. Two 500mL HPDE sampling bottles will be filled per sample. Analysis of water samples will be for 40 PFAS analytes, and the sampling will follow all specifications in EPA draft Method 1633. Results will be reported in units of nanogram PFAS analytes per liter of sampled water down to MDL.

3.4 Quality Control Procedures

Quality control for this project will be maintained by use of trained and experienced personnel in all aspects of the program, including sample collection and laboratory analysis. Various field and laboratory QC samples will be collected and analyzed to characterize the precision and accuracy of the results.

3.4.1 Field Sampling Quality Control

The field QC samples that will be collected as part of this project are listed below. Prior to the onset of sampling, MassDEP sent decontamination water (DIW - assumed to be PFAS-free, from the MassDEP-WPP-Worcester facility) to Eurofins for confirmatory analysis. None of the 40 PFAS measured under draft EPA method 1633 were detected in these samples. Assuming the MassDEP DIW remains PFAS-free, this water will continue to be used for field blanks and decontamination for the duration of the project. If this situation changes, an alternate source of DIW will be established and tested prior to use.

Field and Equipment Blanks. Field and equipment blanks will be collected and analyzed at 10-20 percent of the sampled waterbodies to assess the potential for PFAS cross contamination introduced during the sampling process. These blanks will be subjected to the same aspects of sample collection, field processing, preservation, transport, and laboratory handling as the environmental samples. Three blanks will be collected for each media during Phase 1. Additional blanks will be collected in Phase 2.

- Surface water. Surface water field blanks will be collected in the field. The field sampling crew
 will fill 500mL HDPE sample bottles at the sampling location using PFAS-free decon water. These
 samples will then be treated in the field and laboratory the same as all other environmental field
 samples and analyzed for the same 40 PFAS.
- *Fish tissue.* Equipment blanks will be collected at Normandaeu's Bedford facility. The field sampling crew will pour PFAS-free water over each piece of equipment and collect the water in

the fish tissue sample collection container (bags provided by the lab), which will be then transferred to a 500mL HDPE sample bottle. The laboratory will analyze the blanks with the same method used for surface water samples.

Field duplicates. A field duplicate is a second sample collected from the source at the same time and place under identical circumstances as the parent field sample, and that is then treated the same throughout laboratory procedures. Field duplicates will be collected to assess reproducibility in both the field collection and laboratory analysis processes. Field duplicates will be collected for fish and surface water at 10 percent of the sampled water bodies. One field duplicate will be collected for both fish and surface water under Phase 1; the rest will be collected at regularly spaced intervals under Phase 2. See Section 6.2 of the SAP for more detail.

Travel or trip blanks will not be collected as part of this project unless a problem is identified with the field blanks. The laboratory will send sample containers that have already been checked for contamination. Transport of unopened bottles is unlikely to introduce contamination.

3.4.2 Laboratory Analysis Quality Control

Laboratory QC data that will be generated for this project are listed below. These analyses will be run at a minimum frequency of one per batch or per twenty (field) samples for larger batches.

- Surrogate recovery
- Method blanks, reagent blanks, and instrument blanks
- Laboratory control samples (LCS) with all compounds of interest and low-level laboratory control samples (LLLCS)
- Laboratory matrix spike (MS) and matrix spike duplicates (MSD)
- Isotopically labeled extraction standards
- Non-extracted internal standards

If QC data fall outside of SOP QC acceptance limits, Eurofins will take corrective actions such as reanalyzing, re-extracting, and flagging outliers. Eurofins will use in-house limits for MS/MSD, LCS/LLLCS, and isotopically labeled extraction standards. For MS, the in-house limit is an RPD greater 30 percent. Preliminary limits for LCS/LLLCS are between 40 percent and 150 percent from the draft method until in-house limits are generated, and preliminary limits for isotopically labeled extraction standards range from 20 percent to 150 percent. The QC acceptance limit for method blanks requires that no analytes are detected at the greater amount of the following: half of the detection limit, one tenth the amount measured in any sample, or one tenth of the regulatory limit.

Instruments will be calibrated as necessary, with frequencies ranging from once a year (mass calibration) to daily or more frequently (instrument blanks).

The laboratory will document any deviations from the proposed analytical method in the laboratory reports. The laboratory will provide sufficient documentation to allow for independent verification of analytical results. Corrective actions for laboratory analytical failures are specified in the laboratory analytical method SOPs.

3.5 Instrument/Equipment Testing and Inspection

Instruments and equipment that the field sampling crew will use during sample collection include conductivity probes and electrofishing units. These devices will be inspected for damage or malfunction

prior to the start of sample collection and when returned from use by the field sampling crew. Needed repairs or operational problems are to be reported to the Normandeau Field Crew Lead. He will also (or instruct appropriate staff to) examine equipment at least quarterly for operational status, even if no sampling using that equipment is immediately planned. All equipment will be checked for operation in accordance with the manufacturer's specifications.

Equipment will be inspected and calibrated at the start of each month when samples are to be collected. The field sampling crew will remove any equipment from service that does not meet calibration requirements or is determined to be defective. The field sampling crew will:

- Read the applicable user's manuals.
- Confirm factory calibration with equipment inspection prior to use in the field.
- Familiarize themselves with the use of all field equipment.
- Follow instructions for calibration and testing of equipment prior to sampling activities each day.
- Ensure that batteries are fully recharged before each day's work.
- Carry extra batteries and back-up equipment (e.g., additional conductivity meter) to the site.

The laboratory will perform instrument calibration consistent with the procedures set forth by the analytical method used for this project and as outlined in the laboratory's SOP (see Attachment C). The laboratory is responsible for ensuring that its equipment functions properly.

3.6 Inspection/Acceptance of Supplies and Consumables

Field supplies are examined for completeness, damage, and suitability for use as they are received and upon use. The Field Crew Lead will be responsible for inspecting supplies for damage and suitability for use. Checks should include the following:

- Sample containers from the laboratory should be appropriately sealed, visibly clean, and intact.
- Gloves, coolers, and ice packs should be checked for condition and integrity before use.
- All supplies should be of appropriate materials (PFAS-free) to avoid contaminating samples. See Section 3.2 of the SAP.

Missing, damaged, or incorrect field supplies will be noted and immediately reported to the PG Field Supervisor or ERG Project Manager, who will then contact the appropriate suppliers or the laboratory to replace damaged or missing items.

The analytical laboratory maintains internal SOPs for inspection and quality checking of supplies.

3.7 Data Management

As described in Section 2.8, this project will generate multiple types of records during field sampling activities and during laboratory analysis of samples. Normandeau will send scanned copies of field data sheets, photographs, and COC forms to the ERG Project Manager and ERG Data Manager or upload them to an ERG password-protected FTP site.

The ERG Data Manager will enter field data into Excel spreadsheets and photographs will be documented in a project photo log. ERG will maintain these records throughout the project and deliver them to MassDEP at the end of SFY22 for Phase 1 activities and at the end of SFY23 for all sample collection activities. ERG will also provide these records to MassDEP at any time upon request.

Laboratory data will be recorded by Eurofins according to their protocols. Eurofins will send analytical reports (as PDFs) to MassDEP along with EDDs containing environmental sample results and QC results in the format specified for this project. Those specifications are necessary to ensure the data can be seamlessly integrated with WPP's EQuIS database (see Section 2.82.8.2). The MassDEP Project Lead will initially receive laboratory data and will forward this information to the ERG Project Manager and ERG Data Manager. ERG will review laboratory reports for completeness and quality concerns (see Section 4.2) and compare results to applicable health-based screening values (see Sections 2.5.4and 4.4) within no more than two business days of receiving the data. If any reporting elements are missing from the laboratory data package, ERG will notify the MassDEP Project lead and follow-up with Eurofins. If any fish tissue or surface water samples exceed screening values, ERG will notify the MassDEP Project Lead, who will then share the draft data with DPH for further review. DPH will determine whether fish consumption or swimming advisories are needed.

After reviewing the laboratory reports, ERG will load the PFAS concentration data into a master Excel database.

3.8 Project Assessment and Oversight

This section describes oversight protocols to ensure that this QAPP is being implemented properly.

3.8.1 Assessments and Response Actions

Field sampling activities will be directed by the Normandeau Field Crew Lead, with oversight by the PG Field Sampling Coordinator. Both have extensive experience collecting environmental samples (particularly fish and surface water) for laboratory analysis and are familiar with the overall objectives and QA/QC goals of this project. They also have a thorough understanding of the procedures needed to eliminate potential for cross contamination when collecting samples for PFAS analysis. The field sampling crew leads will communicate directly with the field staff and will ensure that appropriate response actions are taken in the field to address any problems or issues that may arise.

The PG Field Sampling Coordinator will join the field sampling crew during initial field activities in Phase 1 to confirm that all sample collection procedures are in place and being implemented correctly. He may also oversee sample collection at selected waterbodies in Phase 2 to ensure that the field sampling crew continues to follow the protocols outlined in this QAPP throughout the project.

The ERG Project Manager will perform an on-site performance audit during both Phase 1 and Phase 2 to confirm that the sample collection methods in the field and sample processing methods in Normandeau's Bedford facility are consistent with this QAPP. Also, MassDEP field operations and monitoring staff will observe at least one Normandeau field survey and sample preparation activity during Phase 1, and possibly again during Phase 2.

The analytical laboratory staff will follow their internal procedures, as well as those specified in EPA draft Method 1633, for performing project oversight and instituting appropriate response actions.

3.8.2 Reports to Management

Field and sampling issues will be discussed during routinely scheduled bi-weekly conference calls with the MassDEP Project Lead, ERG Project Manager, Deputy ERG Project Manager, and PG Field Sampling

Coordinator during Phase 1. During Phase 2, bi-weekly conference calls will be attended by the MassDEP Project Lead, ERG Project Manager, and ERG Data Manager. Other members of the project team will be invited to these meetings, as needed.

Early in Phase 2, ERG will submit a brief interim report that summarizes results from Phase 1 of this project. This report will briefly document progress to date. It will describe the sampling program, objectives, and methodologies, and briefly summarize the sampling results collected to date. Throughout Phase 2 and as laboratory results are received, ERG will prepare brief interim data summaries presenting descriptive statistics for selected PFAS analytes by waterbody and fish species. These interim data summaries will also include a presentation of field QC sample results.

ERG will submit a project summary report by the end of SFY23. This final project summary report will be more detailed than the interim report. ERG will describe the project in detail and summarize statistical analyses of data, which may include correlations among concentrations of different PFAS, comparisons to health benchmarks, examination of species differences, and calculation of BAFs. See Section 4.4 for additional details on anticipated statistical analyses for this report.

4.0 Data Review and Usability

The analytical results will be validated and verified before use. The purpose of this review will be to review laboratory documentation regarding the stated methods and acceptability of results. The analytical data review will be conducted according to the standards and criteria set forth in the standard methods and protocols being used by the analytical laboratory. The review process will evaluate the degree to which the analytical laboratory followed the prescribed methods, results of internal QC sample analyses, and implications for data usability or any deviations from the prescribed methods. Additional details on the data validation by the laboratory and data verification by the project team are provided in Sections 4.1 and 4.20, respectively.

4.1 Laboratory Data Validation

Eurofins will be responsible for validating and verifying internal laboratory QA/QC metrics as described in the laboratory's SOPs. LCS will contain all compounds of interest. Eurofins analysts will check method blanks, MS/MSD, LCS/LLLCS, isotopically labeled extraction standards, and non-extracted internal standards results against SOP QC acceptance limits and take corrective actions when QC acceptance limits are not met. Method blanks, MS/MSD, and LCS/LLLCS will be run at a ratio of one per batch or per twenty samples, whichever is smaller. Isotopically labeled extraction standards and non-extracted internal standards will be checked on a per-sample basis.

4.2 Project Team Data Review and Verification

The ERG Project Manager and ERG Data Manager will be responsible for reviewing the data provided by Eurofins prior to conducting any statistical analyses. They will ensure that all required data have been calculated, recorded, and transmitted correctly. For this, the team will confirm that the laboratory provided the items listed below in each data package. If any items are missing, the MassDEP Project Lead or ERG Project Manager will contact Eurofins to request that the laboratory reissue the data package with all necessary elements.

- Chain-of-custody forms
- Data qualifier definitions and legend

- Analytical results summary for all samples included in the chain-of-custody
- Batch QC data summary (recoveries, analytical replicates)
- Case narrative (if needed)
- EDDs with analytical results for the environmental samples and laboratory QC samples in the required format (see Section 2.8.2).

The ERG Project Manager or ERG Data Manager will review analytical results for all field QC samples, including field blanks and field duplicates, as follows:

- Field blanks: The potential for sample contamination will be evaluated based on the results of field blanks. Results will be reviewed to ensure that none of the PFAS analyzed were detected. If PFAS were detected in a field blank, ERG will immediately follow-up with the laboratory and notify the MassDEP Project Lead. The project team will revisit all sampling procedures and ask the laboratory to do the same to identify the source of cross contamination. The field sampling crew will collect another field blank at the next sampling event for confirmation. The ERG Project Manager and MassDEP Project Lead will determine whether the data collected the day of the contaminated blank are "fit for use."
- Field duplicates: Field precision will be evaluated through RPD calculations of surface water and fish sample duplicates, following Equation 1. If a concentration is <5x the laboratory RL, the RPD must be below 40 percent. If the concentration is <5x the RL, the RPD must be below 100%. The project team will evaluate any duplicate data that do not meet these criteria and determine whether the data are deemed "fit for use."</p>

RPD (%) = Absolute value of: $[(x_1 - x_2) / (x_1 + x_2)/2] * 100\%$ [Equation 1]

Where:

 x_1 = Concentration observed in the original sample

 x_2 = Concentration observed in the duplicate sample

The ERG Project Manager or ERG Data Manager team will also review the analytical results for all laboratory QC samples to confirm data qualifiers (e.g., methods blanks, method duplicate samples, MS/MSDs).

4.3 Reconciliation with User Requirements

If samples do not meet lab or method requirements (e.g., failed holding/handling time, exceedance of temperature preservation requirement) or data validation criteria specified above, MassDEP and ERG Project Managers will evaluate whether the analytical data results are appropriate for characterizing PFAS levels in fish and/or surface water and evaluating human health risks.

4.4 Reporting, Analysis, and Use of Project Data

The principal objective of the current project is to characterize the nature and extent of PFAS contamination in water and edible tissues of freshwater fish from rivers and lakes across the Commonwealth in a manner that will allow assessment of public health risks associated with consuming freshwater fish. To meet that goal, the primary analyses of analytical results is a comparison to available health screening values, following DPH's approach (see Section 2.5.4).

In brief, composite fish samples results for four PFAS analytes (PFOA, PFNA, PFHxS, and PFOS) will be compared to a screening level of 0.22 µg/kg to determine whether consumption of fish from a given waterbody is safe or if an advisory may be warranted. In some cases, that comparison may be based on results from a single composite comprised of and represented by up to five fish per species. In other cases, the team may be able to calculate an average based on multiple composite samples, each of which is also comprised of multiple fish. Surface water sample results for the same four PFAS analytes will be compared to a screening level (23 ng/L) to determine whether there is a concern for recreational swimming that warrants additional review (e.g., a risk assessment). For this, the program team will use all available "open-water" and "beach area" surface samples (see Section 3.1.6). The ERG Project Manager will immediately communicate any detections above these screening levels to the MassDEP Project Lead, which will then be passed on to DPH for further review.

Another secondary use of these data is to characterize levels of PFAS present in the edible tissue of the more commonly consumed freshwater fish in selected MA lakes and rivers throughout Massachusetts. To achieve this goal, ERG will complete the analyses listed below – where data permit. Note that it is impossible to predict what species will be collected on a given day at each of the 50 waterbodies and what the final data set for analyses will contain.

- Descriptive Statistics for PFAS concentrations in fish and water. ERG will generate descriptive statistics for each of the PFAS measured in fish by species. Depending on available data quantity, statistics will include frequency of detection, measures of central tendency (e.g., arithmetic means, geometric means), measures of variability (e.g., standard deviation [SD], log SD, range of detected values), percentiles (e.g., 90th percentiles, 95th percentiles), and the percent of results over screening values. Note that a minimum of 10 samples per species will be required to calculate measures of central tendency and that non-detect observations will be substituted with a value equal to the limit of detection divided by two. Depending on available data, these statistics will also be stratified by various factors, such as type of waterbody (e.g., lake versus river), region, and whether the waterbody is an area known or suspected to have PFAS contamination. Similar statistics will also be calculated for surface water sample results across all waterbodies and stratified by type of water and possibly region.
- Statistical comparisons. ERG will use t-tests and Analysis of Variance (ANOVA) tests to compare sample mean PFAS concentrations across fish species, between regions, between areas of suspected PFAS contamination and reference locations, and between lakes and rivers in EJ areas and those not in EJ areas. Similar tests will be run for surface water sample results.
- Comparisons to other benchmarks. ERG will compare results of this study's measured PFAS concentrations in fish and surface water to the DPH screening levels, noted above, as well as other benchmarks (e.g., EPA's draft aquatic life criteria for PFOA and PFOS).

Another secondary use of the data is to derive species-specific PFAS BAFs. To meet this objective, fish and surface samples are collected at the same time and from the same location within a given waterbody. BAFs will be derived using composite fish sample data and "open-water" surface water samples. For each composite sample, BAFs specific to a given sample will be calculated for detected PFAS using Equation 2. BAFs will only be calculated for PFAS analytes that have a sufficient percentage detected results for both surface water and fish to produce meaningful results.

 $BAF\left(\frac{L}{Kg}\right) = C_{fish}/C_{water} \times 1000 \quad [Equation 2]$

Where:

 C_{fish} = the PFAS concentration measured in fish tissue (ng/g) C_{water} = the PFAS concentration measured in the co-located surface water sample (ng/l) Calculated BAFs will be in units of (L/kg). An overall species or trophic-level (TL) BAF will then be calculated for given waterbodies (where multiple composites of a given species are available) or across all waterbodies using the geometric mean of individual BAFs within each category.

To determine the quality of BAF estimates, this study will follow the evaluation criteria for study quality described in a recent review authored by <u>Burkhard et al. (2021</u>). By these criteria, a BAF calculation is determined to be of high, medium, or low quality based on the sum of "criteria quality values" assigned to five factors (shown in the table below). A BAF study of the highest quality would contain more than three water and fish samples (of a single species) collected at the same time and location.

Criteria	Criteria Quality Value				
Criteria	1	2	3		
Number of Water Samples	>3	2-3	1		
Number of Organism Samples	>3	2-3	1		
Temporal coordination	Concurrent Collection	Within 1 year time window	Collection period >1		
Spatial Coordination	Collocated collection	Reasonably close (within 1-2km)	Significantly different locations		
General Experimental Design	Default quality value =0		value =0 Mixed species tissue samples		
BAF study quality	Sum of quality values for the five criteria				
High	4 or 5				
Medium	5 or 6				
Low	7-10				

 Table 12. Evaluation Criteria for BAF Study Quality Reproduced from Burkhard et al. 2021.

Results from these analyses, including a comparison to BAFs calculated in other PFAS studies, will be summarized in the final project report, as described in Section 3.8.2.

5.0 References

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Attachment A – Sampling And Analysis Plan

Attachment B – Laboratory Standard Operating Procedures

Attachment C – Crosswalk of Lab EDD and myEOL Web Portal Fields

Lab variables on myEOL	Notes on myEOL variables	Corresponding data element for WPP's EQuIS database	Description for WPP's EQuIS database	Required for WPP's EQuIS database
Detected	Eurofins reports "N" for no and "Y" for yes			
Sample		LabSNum	Laboratory sample number	Yes
Sample Name		FieldSampNum	Field/client sample number	Yes
Specific Method	Eurofins reports as "1633_DOD5"	Analytical Method	Analytical method	Yes
CAS#				
Matrix				
Project Name	Eurofins reports as "AnalyticalLabSvcs-BWR- 2017-15-BD-17-1045"			
Client Name	Eurofins reports as "Massachusetts Dept of Envir. Protection - Worcester"			
Lab	Eurofins reports as "Eurofins Lancaster"	LabID	Laboratory name	Yes
Lab Section	Eurofins reports as "LCMS"			
Analyte		Analyte	Analyte name	Yes
Result		Result	Result value	Yes
Units		Units	Analyte/Characteristic Units	Yes
Qualifier		LabQual	Laboratory qualifier	Conditio nal
UpperLmt		UQL	Upper Quantification Limit	Conditio nal
LowerLmt				
Reports To	Note that Eurofins is reporting to the LL or MDL (i.e., NDs are <mdl)< td=""><td></td><td></td><td></td></mdl)<>			
UL Type		RL	Reporting limit	Yes
LL Type		MDL	Minimum detection level	Yes
Dilution				
Results Basis	Eurofins reports as "Total"			

Lab variables on myEOL	Notes on myEOL variables	Corresponding data element for WPP's EQuIS database	Description for WPP's EQuIS database	Required for WPP's EQuIS database
Batch				
Sampled		CollectDate and CollectTime	Sample collection date/time	Optional
Prepared				
Analyzed		AnalDate and AnalTime	Sample analysis date/time	Optional
Analysis	Eurofins reports as "Per- and Polyfluoroalkyl Substances by LC/MS/MS"			

Notes:

EDD template also requires (1) sample fraction, (2) ResComm (results comments - linked to qualifiers) and (3) site locater

EDD template separates out sample collection date and time into two fields; same with analysis date and time.

Attachment D – Overview of Future Interlaboratory Study

At the onset of this project, MassDEP had intended to conduct an interlaboratory study of PFAS measurements for potential implementation during this project. The vision for this study was to split a subset of the surface water and fish samples, have two analytical laboratories—MassDEP's Wall Experiment Station (WES) and the contract laboratory (i.e., Eurofins)— measure PFAS concentrations in those samples, and compare the measurements to quantify interlaboratory (and possibly inter-method) variability in PFAS measurements. For various reasons, an interlaboratory study component, comparing results across two laboratories both using draft EPA method 1633, was not able to be integrated into the current project described in this QAPP.

Note that the design of any future interlaboratory study should be based on analytical results from Phase 1 and/or Phase 2 sampling of the current project. For example, the magnitude and variability in measured concentrations for individual PFAS analytes would provide valuable insight on the minimum number of split samples that should be considered.