2020 Sampling Plan and Results for Upper Harpswell Cove/Mare (Mere) Creek to Monitor PFAS in Ribbed Mussels.

Date: 11/30/2020
Prepared by: David S. Page[1] for Brunswick Area Citizens for a Safe Environment

INTRODUCTION

This sampling program was conducted to determine whether certain Per- and Polyfluoroalkyl substances (PFAS) associated with operations at the former Brunswick Naval Air Station (BNAS) are present in biological receptors in upper Harpswell Cove, Brunswick, Maine. Upper Harpswell Cove receives fresh water input from Mare (Mere) Creek[2], which drains portions of the former Brunswick Naval Air Station (BNAS) (see Figure 1). To do this, we use mussels as *in situ* biological samplers by expanding on prior mussel sampling in Harpswell Cove by the Maine Department of Environmental Protection (MEDEP). This sampling plan uses field methods similar to those used by MEDEP with added PFAS-specific sampling procedures described for mussel sampling at the former Pease Airforce Base (AMEC Foster Wheeler, 2020). Shown below are those PFAS species analyzed by MEDEP, including species (PFOS, PFOA, PFOSA) related to the use of aqueous film-forming fire-fighting foam at the former BNAS:

Table 1. PFAS species and their Abbreviations	
PFBS	Perfluorobutane Sulfonate
PFBA	Perfluorobutanoate
PFDA	Perfluorodecanoate
PFDoA	Perfluorododecanoate
PFHpA	Perfluoroheptanoate
PFOA	Perfluorooctanoate
PFHxS	Perfluorohexane Sulfonate
PFHxA	Perfluorohexanoate
PFNA	Perfluorononanoate
PFOS	Perfluorooctane Sulfonate
PFOSA	Perfluorooctane Sulfonamide
PFPeA	Perfluoropentanoate
PFUnA	Perfluoroundecanoate

The following description of the use of mussels as pollutant monitoring is taken from the Maine Department of Environmental Protection (MEDEP) 2016 Surface Water Ambient Toxic (SWAT) monitoring program final report.[3]

[1] dpage@bowdoin.edu
[2] Both Mare Creek (Brook) and Mere Creek (Brook) are in use.
[3] https://www.maine.gov/dep/publications/reports/2016-SWAT-Report.pdf

"Blue mussels (*Mytilus edulis*) have been relied upon extensively by the SWAT program (since 1986) and other monitoring programs as an indicator of exposure of marine environments to chemical pollutants. Mussels are ubiquitous and readily collected across the coast of Maine, as well as throughout the entire Gulf of Maine. Published information about contaminants in mussels provides some historical context and allows comparisons between geographic areas and over time. Since blue mussels are consumed as food by humans, they can be used to understand potential human exposure to contaminants. Mussels are sessile, allowing attribution of their contaminant burdens to the environment where they were collected. Mussels filter large volumes of water as they feed, allowing them to concentrate many chemicals from the water column or from sediments suspended in the water column. This allows detection in mussel tissue of contaminants that may be present below detection limits in particulate matter, sediment, or water. Use of mussels also provides insight into the biologically available portion of contaminants, which may not readily be discerned from background sediment or water concentrations."

In the present study, ribbed mussels, *Geukensia demissa*, were sampled. This mussel generally occurs in the mid to lower part of the vegetated salt marsh zone in the lower reaches of tidal creeks. Ribbed mussels are more tolerant of low salinity than blue mussels, *Mytilus edulis*. Both species are widely used in mussel sampling programs for pollution monitoring (e.g., Smalling et al., 2015).

Blue mussels from Harpswell Cove were tested for PFCs in 2014 and 2016 as part of the MEDEP SWAT program. Harpswell Cove receives fresh water from Mare Creek, which receives drainage from the former Brunswick Naval Air Station. For the 2014 and 2016 MEDEP SWAT program, sample-specific detection limits for individual PFCs were approximately 3 to 7 parts per billion (ng/g) in mussel tissue on a dry weight basis. PFOSA levels detected in tissue from ~ 1.5 miles south of Mare Brook in 2014 ranged from 4.51 to 5.32 ng/g dry wt. across the three spatial replicates where it was detected. For 2016, PFOSA levels detected in tissue from ~ 1 mile south Mare Brook ranged from 3.052 to 4.05 ng/g dry wt. across the two spatial replicates where it was detected. Other PFCs were below detection limits[3]. The 2016 MEDEP sampling sites were at least 1 mile south of the mouth of Mare Creek. The 2014 sites are at least 1.6 miles south of the mouth of Mare Creek. Both sets of MEDEP blue mussel sites were in the marine portion of Harpswell Cove where blue mussels occur and where there would be significant dilution of any fresh water inputs from Mare Creek. For the 2020 study, the plan was to sample ribbed mussels that are more directly exposed to water from Mare Creek.

Shellfish were also collected and analyzed for PFAS at the former Pease Airforce Base (AMEC Foster Wheeler, 2020) in Portsmouth, New Hampshire. PFOS was detected in 9 of 14 blue mussel tissue samples from the five target locations. Detected concentrations ranged from 0.000391 mg/kg (ppm wet wt.) to 0.00165 mg/kg (ppm wet wt.). Comparison with MEDEP values is made difficult by the fact that the Pease Report gives values in mg/kg (ppm) on a wet tissue weight basis. MEDEP gives results in ng/g (ppb) on a dry tissue weight basis, preferred for monitoring studies because of the variability of water content in tissues. Converting the Pease mussel tissue results to ng/g (ppb) gives 0.391-1.65 ppb, wet tissue wt. Assuming the water content of mussel tissue is about 85%, gives a dry tissue weight of 0.15 g per gram of wet tissue. Using this to estimate dry weight values for the Pease data gives an approximate range of 2.6 to 11.1 ppb PFAS on a dry tissue wt basis.

PFOS, PFOA and PFBS were not detected in the nine blue mussel tissue samples collected from the three reference locations in the Pease study.

METHODS

Sample site selection.

The sampling sites are shown in Figure 2. The 3 upper Harpswell Cove/Mare Creek sites are shown as H1, H2 and H3. There are 2 control sites. Both are at Wharton Point at the head of Maquoit Bay, Brunswick and have similar demographic elements to the Harpswell Cove sites, but are well removed from the former BNAS. Control site (C1) is east of the boat ramp at Wharton Point and C2 is west of the boat ramp. Table 2 gives the location and coordinates of the sampling sites.

Table 2. Sampling site locations, showing head stake coordinates.

Site	Date Sampled	Time on Site	Lat	Long
H1	9/10/2020	0925 hr	N43° 51.817’	W069° 55.952’
H2	9/10/2020	0952 hr	N43° 51.811’	W069° 56.092’
H3	9/10/2020	1044 hr	N43° 51.582’	W069° 56.261’
C1	9/11/2020	1040 hr	N43° 52.029’	W069° 59.532’
C2	9/11/2020	1129 hr	N43° 52.037’	W069° 59.648’

Field Sampling

The field sampling methods follow those described in the MEDEP 2015/2016 SWAT Report[1] and the AMEC former Pease AFB mussel sampling (AMEC, 2020)

Ribbed mussels were collected during the low tide period on September 10, 2020 along the shoreline from 3 distinct sampling sites based on an earlier field survey (D.S. Page, March, 2020) where the northern-most limit of ribbed mussel occurrence was identified. The 2 control sites at Wharton Point, Brunswick were sampled similarly on September 11, 2020.

Sampling commenced 2 hours prior to low tide. Hand methods were used to dig mussels out of the marsh substrate using stainless steel tongs. The center of each sampling site was identified by a head stake and the GPS lat./long. coordinates recorded. Duplicate mussel samples were taken randomly within a 30 meter radius of the head stake and placed in labelled high density polyethylene (HDPE) mesh bags. Ribbed mussels within a size range of 6-10 cm were sampled for analysis. 18-20+ mussels (depending on size) were collected randomly in duplicate within each intra-site sampling area.

Mussel replicates in the labelled HDPE mesh bags were transported to the laboratory in coolers over ice. Mussels were washed in clean water in the mesh bags in an open bucket at the laboratory to remove external debris and attached sediments. The sampling plan gives 10 duplicate samples for PFAS analysis from 5 locations. The designation for each set of duplicate samples for a given site is the site code, with 1 or 2 appended (i.e. H1 site, H11; H12 duplicates).

Tissue sample processing was done on the same day as field collections at all sites. For each sample for PFAS analysis, all soft tissue from each mussel in a sample were removed using stainless steel implements and combined with the soft tissue from mussels within the same replicate in a pre-labelled HDPE USEPA-Certified sample jar. Total soft tissue wet weight per replicate was recorded. Filled jars were stored at - 10 deg. C until shipped with an appropriate Chain of Custody form for chemical analysis by overnight express to Battelle Laboratories in Norwell, MA on September 15, 2020. Laboratory records show that the samples were received in good condition in a frozen state within 24 hours of shipment.

PFAS Field Sampling Guidelines

FIELD CLOTHING and PPE
- No clothing or boots containing Gore-Tex®
- No materials containing Tyvek®
- Do not use fabric softener on clothing to be worn in field
- Do not used cosmetics, moisturizers, hand cream, or other related products the morning of sampling

FIELD EQUIPMENT
- Must not contain Teflon® (aka PTFE) or LDPE materials
- All sampling materials must be made from stainless steel, HDPE, acetate, silicon, or polypropylene
- No waterproof field books can be used
- No plastic clipboards, binders, or spiral hard cover notebooks can be used
- Sharpies and permanent markers not allowed; regular ball point pens are acceptable
- Keep PFC samples in separate cooler, away from sampling containers that may contain PFAS
- Coolers filled with regular ice

Tides

Harpswell Harbor, Maine TIDES
43.7667° N, 70.0000° W

September 2020

Day	Low
Wed 09	10:12 AM EDT 1.7 ft
Thu 10	11:01 AM EDT 1.9 ft
Fri 11	11:54 AM EDT 2.0 ft
Sat 12	12:52 PM EDT 1.9 ft
Sun 13	1:52 PM EDT 1.5 ft
Mon 14	2:50 PM EDT 1.0 ft

Chemical Analysis

Mussel samples were analyzed for PFAS species by the Battelle, Norwell Operations Analytical Chemistry Services, 141 Longwater Drive, Suite 202, Norwell, Massachusetts 02061. Table 3 gives the PFAS species analyzed for and the detection limit parameters. At our request, Battelle increased the sample size and lowered the dilution for analysis to increase the sensitivity of the analytical method to detect PFAS species. For example, the LOD for PFOS in Table 3 of 0.15 ng/g wet wt corresponds to 1.0 ng/g dry wt assuming 85% water content.

Table 3. PFAS Target Species for Chemical Analysis with detection limit parameters (all wet wt. basis). The DL (detection limit) is the lowest concentration that can be detected. The LOD (limit of detection) is the lowest concentrations that can be distinguished from the blank value with a stated confidence level (generally 99%). The LOQ is the lowest concentration at which the analyte can not only be reliably detected but at which some predefined goals for bias and imprecision are met.

PFAS Specie	Abbreviation	DL	LOD	LOQ
Perfluorobutane Sulfonate	PFBS	0.021	0.050	0.500
Perfluorobutanoate	PFBA	0.060	0.200	0.500
Perfluorodecanoate	PFDA	0.053	0.150	0.500
Perfluorododecanoate	PFDoA	0.076	0.200	0.500
Perfluoroheptanoate	PFHpA	0.049	0.100	0.500
Perfluorooctanoate	PFOA	0.047	0.100	0.500
Perfluorohexane Sulfonate	PFHxS	0.084	0.200	0.500
Perfluorohexanoate	PFHxA	0.076	0.200	0.500
Perfluorononanoate	PFNA	0.057	0.200	0.500
Perfluorooctane Sulfonate	PFOS	0.051	0.150	0.500
Perfluorooctane Sulfonamide	PFOSA	0.042	0.100	0.500
Perfluoropentanoate	PFPeA	0.064	0.200	0.500
Perfluoroundecanoate	PFUnA	0.036	0.100	0.500

Analytical Method Summary (From Battelle Data Report; See Appendix 1)

Sample Preparation

Tissue homogenate samples were aliquoted into extraction tubes and fortified with surrogates prior to the addition of solvent. The sample was extracted on the Geno/Grinder with methanol and extraction salts ($MgSO_4$ and NaCl). Post centrifugation, the entire extract was suspended in Millipore water and processed through Weak-anion exchange (WAX) solid phase extraction (SPE) cartridges. Target analytes are eluted from the WAX SPE using 0.5% NH_3 in methanol. Extracts were further refined using Envi-carb to remove co-extracted interferences. Extracts were concentrated to approximately 500 µL under nitrogen with a water bath set between 50°C and 60°C, reconstituted with methanol/water and fortified with internal standard. Extracts were transferred for LC-MS/MS analysis in 80:20 methanol/water (V/V). The pH of all samples prior to SPE extraction was verified between 6 and 8.

Analysis

Battelle Standard Operating Procedure 5-369 - Analysis of Perfluoroalkyl Substances in Environmental Samples by Liquid Chromatography and Tandem Mass Spectrometry (LC-MS/MS:

PFAS were measured by liquid chromatography tandem mass spectrometry (LC- MS/MS) in the multiple reaction monitoring (MRM). An initial calibration consisting of representative target analytes, labelled analogs, and internal standards was analyzed prior to analysis to demonstrate the linear range of analysis. Calibration verification was performed at the beginning and end of 10 injections and at the end of each sequence. Target PFAS were quantified using the isotope dilution method. Samples are reported in ng/g concentrations on a wet weight basis.

The analytical protocol included full Quality Assurance/Quality Control (QA/QC) procedures (See Battelle Data Report Appendix 1)

RESULTS

The results for all PFAS species analyzed are given in Table 4. For each sample site, 2 field duplicate samples were collected. For example, for Mare Creek/Harpswell Cove site H1 (Fig. 2), samples H11 and H12 are the field duplicates for that site. The field duplicate Wharton Point control sites' samples are numbered similarly. Two PFAS species were reliably quantified, PFBA (Perfluorobutanoate) and PFOS (Perfluorooctane sulfonate and one, PFBS (Perfluorobutane sulfonatate) in trace amounts.

TABLE 4. Brunswick Area Citizens for a Safe Environment (BACSE) September, 2020 Mussel PFAS Sampling Results

All values given as ng/g (PPB) wet wt or dry wt as indicated.
Data Quality Qualifier Abbreviations:
J: Analyte detected below the Limit of Quantitation (LOQ)
U: Taken as non-detect (ND) Analyte not detected or detected below the DL value, LOD reported.

Site		H11		H12		H21		H22		H31		
Analyte	Qual H1, H2	PPB wet	PPB Dry	PPB wet	PPB Dry	PPB wet	PPB Dry	PPB wet	PPB Dry	Qual H3	PPB wet	PPB Dry
PFBA		0.68	4.73	0.61	4.53	0.58	4.69	0.51	4.85	J	0.43	3.70
PFPeA	U	ND	ND	ND	ND	ND	ND	ND	ND	U	ND	ND
PFHxA	U	ND	ND	ND	ND	ND	ND	ND	ND	U	ND	ND
PFHpA	U	ND	ND	ND	ND	ND	ND	ND	ND	U	ND	ND
PFOA	U	ND	ND	ND	ND	ND	ND	ND	ND	U	ND	ND
PFNA	U	ND	ND	ND	ND	ND	ND	ND	ND	U	ND	ND
PFDA	U	ND	ND	ND	ND	ND	ND	ND	ND	U	ND	ND
PFUnA	U	ND	ND	ND	ND	ND	ND	ND	ND	U	ND	ND
PFDoA	U	ND	ND	ND	ND	ND	ND	ND	ND	U	ND	ND
PFOSA	U	ND	ND	ND	ND	ND	ND	ND	ND	U	ND	ND
PFBS	J	0.02	0.14	0.03	0.22	0.02	0.16	0.03	0.29	J	0.03	0.26
PFHxS	U	ND	ND	ND	ND	ND	ND	ND	ND	U	ND	ND
PFOS		0.81	5.63	0.98	7.27	0.86	6.96	0.54	5.14	J	0.23	1.98

Site		H32		C11			C12		C21		C22	
Analyte	Qual H3	PPB wet	PPB Dry	Qual C1, C2	PPB wet	PPB Dry	PPB wet	PPB Dry	PPB wet	PPB Dry	PPB wet	PPB Dry
PFBA	J	0.42	2.97	J	0.45	3.63	0.50	4.35	0.43	3.63	0.42	3.95
PFPeA	U	ND	ND	U	ND	ND	ND	ND	ND	ND	ND	ND
PFHxA	U	ND	ND	U	ND	ND	ND	ND	ND	ND	ND	ND
PFHpA	U	ND	ND	U	ND	ND	ND	ND	ND	ND	ND	ND
PFOA	U	ND	ND	U	ND	ND	ND	ND	ND	ND	ND	ND
PFNA	U	ND	ND	U	ND	ND	ND	ND	ND	ND	ND	ND
PFDA	U	ND	ND	U	ND	ND	ND	ND	ND	ND	ND	ND
PFUnA	U	ND	ND	U	ND	ND	ND	ND	ND	ND	ND	ND
PFDoA	U	ND	ND	U	ND	ND	ND	ND	ND	ND	ND	ND
PFOSA	U	ND	ND	U	ND	ND	ND	ND	ND	ND	ND	ND
PFBS	J	0.03	0.21	J	0.03	0.24	0.02	0.17	0.03	0.25	0.02	0.19
PFHxS	U	ND	ND	U	ND	ND	ND	ND	ND	ND	ND	ND
PFOS	J	0.34	2.41	U	ND	ND	ND	ND	ND	ND	ND	ND

PFBA and the closely related PFBS are ubiquitous breakdown product of stain- and grease-proof coatings on food packaging, upholstery, carpets, etc. PFBA and PFBS are present in similar detectable amounts in both the Mare Creek and Control site mussels.

PFOS, associated with the use of firefighting foam at the former Brunswick Naval Air Station, was detected in ribbed mussels from Sites H1 and H2 at and near the mouth of Mare Creek at levels exceeding those detected in blue mussels by MEDEP in 2014 and 2016 at sites 1 to 1.5 miles south of the creek mouth in marine waters. The concentration of PFOS in the 2020 ribbed mussels was lowest for sample H3, farthest from the creek mouth, indicating a gradient of dilution of PFOS in creek water going from north to south. PFOS was not detected in control site mussels. (For summary, see Table 5, Figure 4)

Table 5. September, 2020 Mere Creek Mussel Sampling PFOS Results

Data are ng/g (PPB) dry tissue wt basis		n=2 for all sites
Location	Sample ID	**PFOS SITE MEAN ± SD**
H1 Mouth Mere Creek	H11, H12	6.45 ± 1.16
H2 Near Mouth Mere Creek	H21, H22	6.05 ± 1.29
H3 0.4 mi south of mouth of Mare Creek	H31, H32	2.19 ± 0.30
C1 Wharton Point Control	C11.C12	ND
C2 Wharton Point Control	C21, C22	ND

These results indicate that chronic inputs of PFOS from historic PFOS deposits remaining at the former Brunswick Naval Air Station are continuing to reach biological communities downstream from the facility on an ongoing basis. The concentrations of PFOS in Mere Creek mussels are comparable to those found in mussels at the former Pease Air Force Base. (AMEC, 2020).

REFERENCES

Amec Foster Wheeler. 2020. Final Expanded Site Inspection Report Per- and Polyfluoroalkyl Substance Release Program Former Pease Air Force Base Portsmouth, New Hampshire NHDES Site #: 198404025, Project Number: 34346. Prepared By: Amec Foster Wheeler, 511 Congress Street, Suite 200 Portland, ME 04101 USA. 1565 pp. http://www4.des.state.nh.us/IISProxy/IISProxy.dll?ContentId=4834752

MEDEP-SWAT, 2015/2016. Maine Department of Environmental Protection Bureau of Land and Water Quality, Surface Water Ambient Toxics Monitoring Program 2015/2016, Report to the Joint Standing Committee on Environment and Natural Resources 128th Legislature, First Session, October 2017. https://www.maine.gov/dep/publications/reports/2016-SWAT-Report.pdf

Smalling, K.L., Deshpande, A.D., Blazer, V.S., Galbraith, H., Dockum, B.W., Romanok, K.M., Colella, K., Deetz, A.C., Fisher, I.J., Imbrigiotta, T.E., Sharack, B., Sumner, L, Timmons, D., Trainor, J., Wieczorek, D., Samson, J., Reilly, T.J., and Focazio, M.J., 2015, Chemical and ancillary data associated with bed sediment, young of year bluefish (Pomatomus saltatrix) tissue, and mussel (Mytilus edulis and Geukensia demissa) tissue collected after Hurricane Sandy in bays and estuaries of New Jersey and New York, 2013–14: U.S. Geological Survey Data Series 956, 18 p.

FIGURES

Figure 1. Overall study area showing relationship of upper Harpswell Cove to Mare Creek and former Brunswick Naval Air Station.

Figure 2. Outline map of sampling sites showing locations of MEDEP mussel sampling sites.

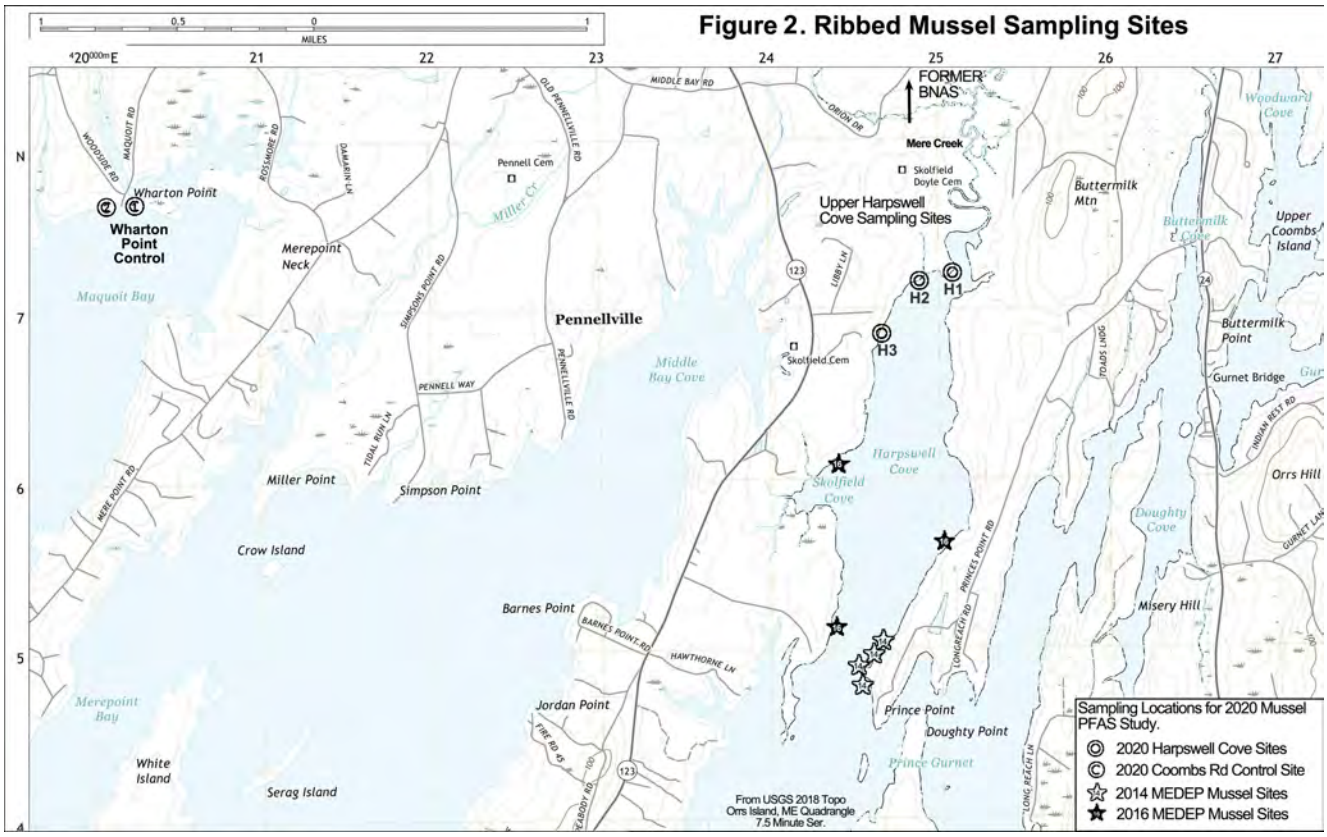
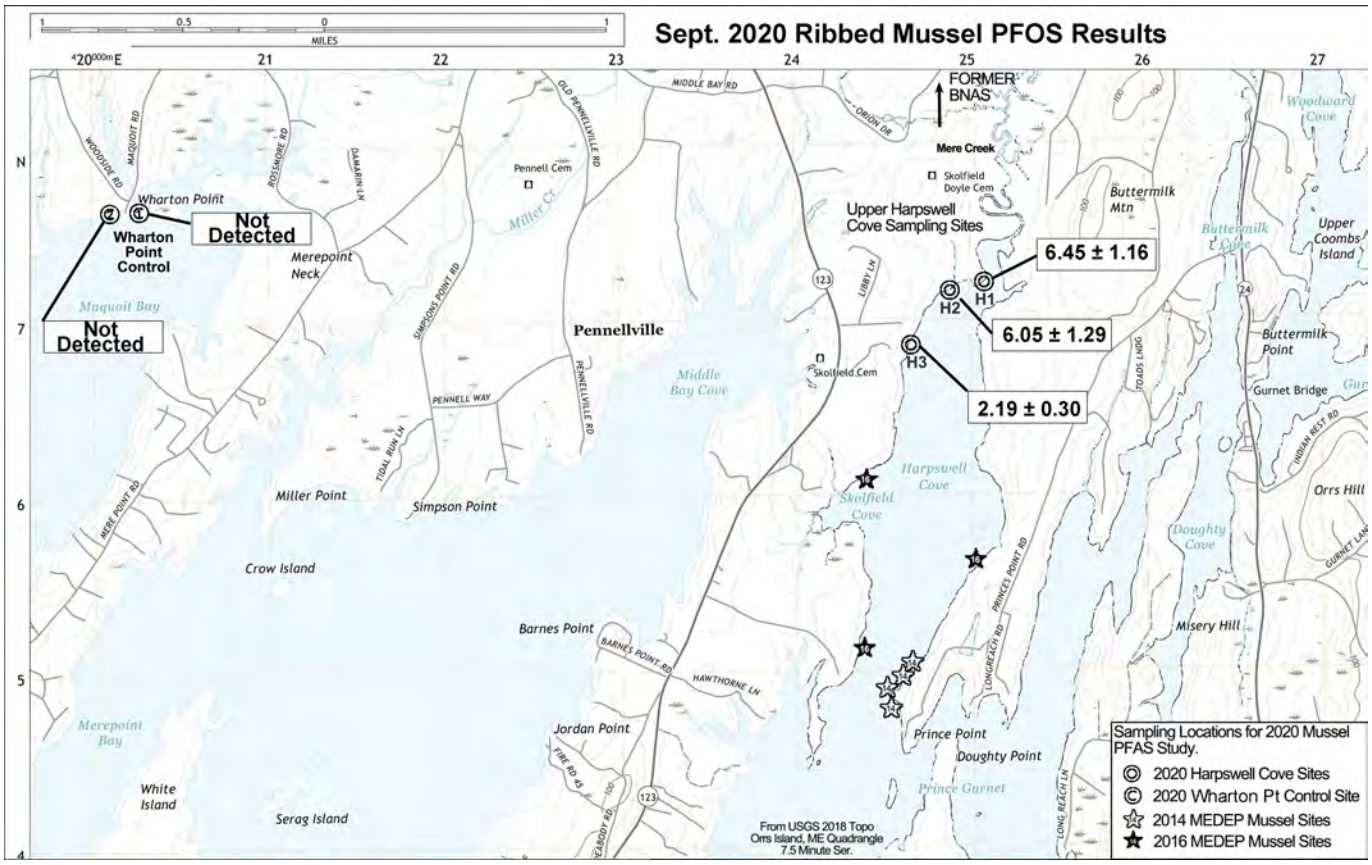


Figure 3. Harpswell Cove/Mare Creek Sites Detail

Figure 4. Map summary of 2020 PFOS results for Mare Creek and Control sites.



APPENDIX 1.

Full Laboratory Data Report, including COC and QA/QC documents, presented as separate pdf file.

APPENDIX 2.

Field Notes presented as separate pdf file.

APPENDIX 3.

Field Photos presented as separate pdf file.