290 Elwood Davis Road, Suite 340
Liverpool, New York 13088
315.453.9009

ANCHOR QEA

November 30, 2020

Mr. Scott Inman (via email)
Project Manager
Wisconsin Department of Natural Resources
Remediation and Redevelopment Program
3911 Fish Hatchery Road
Fitchburg, Wisconsin 53711

Re: Final PFAS Special Study Report
Milwaukee Estuary Area of Concern
Milwaukee, Milwaukee County, Wisconsin
EPA GLRI Grant No. GL-00E02392

Dear Mr. Inman:

Anchor QEA, LLC is pleased to submit the attached *Final PFAS Special Study Report* for the Milwaukee Estuary Area of Concern (MKE AOC), Milwaukee County, Milwaukee, Wisconsin. This PFAS Special Study Report describes the results of a surface water and sediment sampling event conducted within the MKE AOC and incorporates final comments received on November 13, 2020 and discussed on November 30, 2020.

If you have any questions regarding this report, please contact me (315-414-2014; kpowell@anchorqea.com) at your convenience.

Sincerely,

Kim Powell

Kimberly Powell
Project Manager
Anchor QEA, LLC

cc: Christopher Dietrich, DNR
Brennan Dow, DNR
Judy Fassbender, DNR

November 2020

Final PFAS Special Study Report

Prepared for the Wisconsin Department of Natural Resources

November 2020
Milwaukee Estuary Area of Concern PFAS Sampling

Final PFAS Special Study Report

Prepared for
Wisconsin Department of Natural Resources
3911 Fish Hatchery Road
Fitchburg, Wisconsin 53711

Prepared by
Anchor QEA, LLC
290 Elwood Davis Road, Suite 340
Liverpool, New York 13088

TABLE OF CONTENTS

TABLES (IN TEXT)

TABLES (ATTACHED)

FIGURES

APPENDICES

ABBREVIATIONS

AFFF	aqueous film-forming foam
BUI	beneficial use impairment
CEC	Coleman Engineering Company
COPEC	contaminant of potential ecological concern
DNR	Wisconsin Department of Natural Resources
EPA	U.S. Environmental Protection Agency
FSP	*Field Sampling Plan*
FTS	fluorotelomer sulfonate
GEL	GEL Laboratories, LLC
GLLA	Great Lakes Legacy Act
GLRI	Great Lakes Restoration Initiative
GLWQA	Great Lakes Water Quality Agreement
HQ	hazard quotient
IDW	investigation-derived waste
IGLD85	International Great Lakes Datum of 1985
KK	Kinnickinnic
K_{OC}	organic carbon partition coefficient
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
LWD	low water datum
MDEQ	Michigan Department of Environmental Quality
mg/kg	milligrams per kilogram
MKE AOC	Milwaukee Estuary Area of Concern
MS	matrix spike
MSD	matrix spike duplicate
N-EtFOSA	n-ethyl perfluoro-1-octanesulfonamide
N-EtFOSAA	n-ethyl perfluorooctane sulfonamidoacetic acid
NEtFOSE	2-(n-ethyl perfluoro-1-octane sulfonamido ethanol
ng/g	nanograms per gram
ng/L	nanograms per liter
N-MeFOSAA	n-methylperfluorooctane sulfonamidoacetic acid
N-MeFOSE	2-(n-methyl perfluoro-1-octanesulfonamidoethanol
PFAA	perfluoroalkyl acid
PFAS	perfluoroalkyl and polyfluoroalkyl substances
PFBA	perfluorobutanoate
PFBS	perfluorobutane sulfonate

PFCA	perfluoroalkyl carboxylic acid
PFDoA	perfluorododecanoate
PFDS	perfluorodecane sulfonate
PFHpA	perfluoroheptanoic acid
PFHpS	perfluoroheptanesulfonic acid
PFHxA	perfluorohexanoate
PFHxDA	perfluorohexadecanoic acid
PFHxS	perfluorohexane sulfonate
PFNA	perfluorononanoic acid
PFNS	perfluorononane sulfonate
PFOA	perfluorooctanoate
PFODA	perfluorooctadecanoic acid
PFOS	perfluorooctane sulfonate
PFOSA	perfluorooctane sulfonamide
PFPeA	perfluoropentanoic acid
PFPeS	perfluoropentanesulfonic acid
PFSA	perfluorosulfonic acid
PFTeDA	perfluorotetradecanoic acid
PFTrDA	perfluorotridecanoic acid
PFUnA	perfluoro-n-undecanoic acid
PID	photoionization detector
PPE	personal protective equipment
QA	quality assurance
QAPP	*Quality Assurance Project Plan*
QC	quality control
RAP	*Remedial Action Plan*
RV	research vessel
Sigma	The Sigma Group
SM	Standard Method
SMC	South Menomonee Canal
Study Area	Portions of MKE AOC
TCLP	Toxicity Characteristic Leaching Procedure
TSS	total suspended solids
UWM	University of Wisconsin – Milwaukee

1 Introduction

This *PFAS Special Study Report* describes the results of a surface water and sediment sampling event conducted within the Milwaukee Estuary Area of Concern (MKE AOC). The objective of this program was to screen sediments and surface water for perfluoroalkyl and polyfluoroalkyl substances (PFASs), a class of compounds over which there is emerging concern with respect to human and environmental health. This report has been prepared for the Wisconsin Department of Natural Resources (DNR) under a U.S. Environmental Protection Agency (EPA) Great Lakes Restoration Initiative (GLRI) grant (EPA GLRI Grant No. GL-00E02392).

1.1 Background

1.1.1 Site Description

The MKE AOC is one of five Great Lakes Areas of Concern in Wisconsin. In August 2020, Wisconsin delisted its first AOC, the Menominee River AOC, leaving four Areas of Concern remaining in Wisconsin. The MKE AOC comprises portions of three rivers—Milwaukee, Menomonee, and Kinnickinnic (KK)—and the inner harbor, outer harbor, and nearshore areas of Lake Michigan, bounded by a line extending north from Sheridan Park to the City of Milwaukee's Linnwood water intake. The MKE AOC was initially listed in 1987 under the Great Lakes Water Quality Agreement (GLWQA). This AOC was later expanded in 2008 to include legacy contaminated sediments in the Little Menomonee River located in the upper portion of the Menomonee River, along with Lincoln Creek and Cedar Creek located in the upper portion of the Milwaukee River.

The PFAS Special Study Area, comprising the lower estuary portion of the MKE AOC, is depicted in Figure 1 and includes the following specific areas:

- Milwaukee River Reach 4
- Menomonee River Reaches 4 and 5
- South Menomonee Canal (SMC)
- KK River Reaches 2, 3 (including SkipperBud's Slip), and Reach 4 (particularly the Connection Channel)
- Outer harbor
- Lake Michigan outside of the breakwater

These areas have been identified to provide a general characterization of PFAS within the MKE AOC, and include areas where contaminated legacy sediments are targeted for future removal actions. A general description of each portion of the Study Area is provided below.

Milwaukee River Reach 4 is 2.3 miles long, beginning upstream at the former North Avenue Dam and continuing downstream to the Menomonee River confluence. The river passes through downtown

Milwaukee, with a shoreline consisting primarily of sheetpile bulkheads and includes 17 bridge crossings. The banks are urbanized with a mix of residential and commercial properties. Water depths in this reach range from 6 to 23 feet (NOAA 2020).

Menomonee River Reach 4 extends from the 25th Street Bridge to the 16th Street Bridge and is approximately 0.6 miles long, while Menomonee River Reach 5 begins at the 16th Street Bridge and extends 1 mile downstream to the confluence with the Milwaukee River. This portion of the river consists of mixed industrial and commercial use (CH2M 2016). The shoreline is mostly sheetpile bulkhead walls and a few portions of concrete bulkhead. These reaches include the Federal Navigation Channel, authorized to a project depth of 21 feet below low water datum (LWD), or International Great Lakes Datum of 1985 (IGLD85) elevation of 556.5 feet (NOAA 2020). Current water depths vary from 8 to 25 feet within the navigational channel and generally increase further downstream (CH2M 2016).

The KK River downstream of West Becher Street to the KK River/Milwaukee Bay Connection Channel encompasses KK River Reaches 2 through 4. KK River Reach 2 is defined as West Becher Street Bridge downstream to the South Kinnickinnic Avenue Bridge. KK River Reach 2 is a mixture of industrial and commercial use. The shoreline consists mostly of sheetpile bulkhead walls with some docks, piers, and slips. Water depths in Reach 2 range from 2 to 21 feet (NOAA 2020). In 2009, an estimated 170,000 cubic yards of sediment was dredged as part of a Great Lakes Legacy Act (GLLA)-funded project, followed by the placement of a 1- to 4-foot sand cover over most of the remediated area (CH2M Hill 2011).

KK River Reach 3 is defined as the KK River immediately downstream of the South Kinnickinnic Avenue Bridge to the end of the Municipal Mooring Basin (Turning Basin). KK River Reach 3 also includes the SkipperBud's Slip, the Car Ferry Slip, and the Municipal Slip. KK River Reach 3 is a mixture of industrial and commercial uses. The shoreline is primarily sheetpile bulkhead wall with portions of natural shoreline at the SkipperBud's Slip. Water depths in Reach 3 range from 12 to 27 feet (NOAA 2020). The Federal Navigation Channel within the KK River begins downstream of the South Kinnickinnic Avenue Bridge in Reach 3 and continues to the confluence with the Milwaukee River. The authorized channel elevation in this section is 21 feet below LWD (556.5 feet IGLD85).

Following Reach 3, Reach 4 of the KK River includes the Turning Basin from the upstream mouth, two slips (Washington Slip and Greenfield Slip) before the confluence with the Milwaukee River, and the KK River/Milwaukee Bay Connection Channel. The shoreline consists of steel sheetpile walls, concrete bulkheads, and minimal amounts of natural shoreline. Both small watercraft and large vessel traffic occur in Reach 4.

The outer harbor begins after the area from the confluence of the KK River and Milwaukee River at the Daniel Hoan Memorial Bridge (Connection Channel) out to the boundaries of the breakwater.

This portion of the harbor includes industrial, commercial, and public park space. The shoreline consists of a mix of sheetpile bulkhead wall, concrete bulkhead, armor stone revetment, and sand beach. Water depths in the outer harbor range from 7 to 32 feet (NOAA 2020).

Lake Michigan immediately outside of the breakwater is open lake, with water depths ranging from 30 to 50 feet near the harbor (NOAA 2020). The breakwater consists of sheetpile bulkhead wall, armor stone revetment, and concrete bulkhead. The navigation channel is maintained approximately 500 feet east of the harbor entrance.

1.1.2 Site History

Under the GLWQA, the DNR completed the initial *Milwaukee Estuary Stage 1 Remedial Action Plan* (RAP) in 1991 (DNR 1991). Updates to the RAP have been periodically performed, with the most recent update in August 2020 (DNR 2020). In April 2020, DNR updated the targets and status for 9 of 11 of the established Beneficial Use Impairments (BUIs). The RAP identifies the project areas as requiring additional sediment characterization.

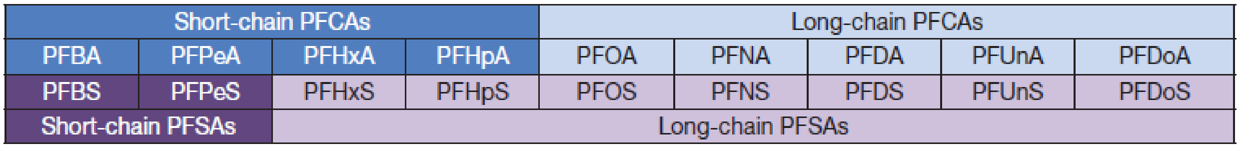
Historical sampling in the MKE AOC has identified various contaminants of concern, including metals, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons resulting from historical industrial discharge. There are multiple Superfund sites, GLLA sites, and other known contaminated sites within the MKE AOC. This is the first report regarding the presence of PFAS in water and sediment within the MKE AOC.

1.1.3 Introduction to PFAS

PFASs are a class of manmade compounds first developed in the 1930s and widely marketed since the 1950s. They have had a wide variety of uses in consumer products and industrial applications: food packaging, clothing and carpet protectant coatings, non-stick cookware, chrome-plating operations, and aqueous film-forming foams (AFFFs) used to extinguish fuel fires. Many short-chain PFAS compounds are still in use, while most long-chain PFAS compounds have been phased out.

The PFAS class comprises thousands of compounds. However, the focus of toxicological research and regulatory attention has largely been on a group of PFAS called perfluoroalkyl acids (PFAAs). PFAAs are chemicals structurally similar to each other. Each is composed of a chemically functional, ionic head group and a carbon tail, which has all its available bond sites occupied by fluorine atoms. PFAAs differ in the type of head group and length of the carbon tail. Perfluorocarboxylic acids (PFCAs) have a carbonate head group, while perfluorosulfonic acids (PFSAs) have a sulfonate head group. Compounds within both of these groups can be identified using the number of carbons in their carbon tail. For example, the PFSA compound with a four carbon tail (C4) is called perfluorobutane sulfonate (PFBS). The compounds that have been the subject of the most attention are the eight carbon (C8) PFCA and PFSA compounds: perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS), respectively. These C8 compounds are considered long-chain compounds. With some exceptions, long-chain compounds are more likely to be bioaccumulative and have a greater tendency to adsorb (i.e., attach) to sediments. The definition of long-chain versus short-chain is different for the PFCA and PFSA compounds (Conder et al. 2008). Table 1 provides classifications of short-chain and long-chain PFCAs and PFSAs. Sediment adsorption characteristics, represented as organic carbon partition coefficients (K_{oc} values), are provided in Table 2 (attached).

Table 1
Comparison of Short- and Long-Chain PFCAs and PFSAs



Short-chain PFCAs				Long-chain PFCAs				
PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA
PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS	PFUnS	PFDoS
Short-chain PFSAs		Long-chain PFSAs						

Note:
Taken from ITRC (2020).

In addition to PFAAs, recent research has included compounds known to transform to PFAAs (precursor compounds) and compounds designed to replace PFAAs in consumer and industrial applications (replacement chemistries). A number of these compounds were analyzed as part of this study.

1.1.4 Overview of PFAS Regulatory and Guidance Values

Several agencies in other states have set regulatory and/or guidance values for concentrations of PFAS in groundwater, drinking water, surface water, soil, and biota such as fish, waterfowl, and deer. To date, the focus of these efforts has been on the most well-researched compounds such as PFOA and PFOS in water. However, some regulatory programs have identified threshold values[1] for more compounds (e.g., Texas has set regulatory limits on 16 PFASs). Still, nearly all the threshold values set are confined to PFAAs. Exceptions include North Carolina and Ohio, which have set guidance values for 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-propanoic acid (GenX), and Canada and Denmark, which have set threshold values for one or two fluorotelomer sulfonate compounds. In comparison to other media, very little attention has been given to studying and setting threshold values on PFAS in sediment. Regulatory and/or guidance values are rapidly being developed and refined across the nation and beyond.

Differences in PFOS and PFOA characteristics result in different criteria assessed to develop standards for various water types (e.g., drinking water, surface water), protected receptors (e.g., human health,

---

[1] The term threshold value is used within this report to generically refer to a comparative value or screening level for assessing chemical concentrations. When this value is a specific regulatory criterion or an official recommendation, the appropriate term is applied.

ecological toxicity), and regulatory limits (e.g., notification level, action level, enforcement level). Therefore, it is difficult to directly compare threshold values for water between regulatory programs. However, in the absence of specific water threshold values (e.g., surface water), comparisons to values across water types is necessary even though not ideal. General values for PFOS and PFOA are on the order of double digit nanogram per liter (ng/L) in drinking water and groundwater. In 2016, EPA set health advisories for PFOS and PFOA in drinking water at 70 ng/L for each compound, as well as the sum of the two. Wisconsin has proposed Enforcement Standard Recommended Values for PFOA and PFOS in groundwater at 20 ng/L for each compound, as well as the sum of the two. In addition, it has proposed a Preventive Action Limit Recommended Value at 2 ng/L for the individual and sum of the two compounds. A rulemaking effort is underway in Wisconsin where the DNR is working collaboratively with the Department of Health Services to develop standards for additional substances.[2]

1.2 Objectives

The objectives of this study were to document the presence, if any, of PFAS in surface water (collected at two-thirds the water column depth) and the top 4 feet of sediments within the MKE AOC and to identify where these concentrations in the rivers may be above Lake Michigan background concentrations and/or threshold values established by regulatory agencies in other states, since Wisconsin did not have established levels at the time of this study.

Fourteen sampling locations in the target Study Area were identified by DNR and incorporated into the *Field Sampling Plan* (FSP; Anchor QEA 2020a). These locations were selected taking into consideration: 1) existing chemical conditions in sediment; 2) the location of former industrial operations; 3) areas that may be identified for dredging in the future for navigational or remedial purposes; and 4) providing overall spatial coverage within the Study Area.

---

[2] https://dnr.wisconsin.gov/topic/SurfaceWater/NR105.html

2 Site Investigation

This section summarizes PFAS sampling activities performed in November 2019. This site investigation collected environmental data to document the presence, if any, of PFAS in sediments and surface water in targeted areas of interest within the MKE AOC and addressed data quality objective 5 as presented in the approved *Quality Assurance Project Plan* (QAPP; Anchor QEA 2020b).

2.1 Sampling Methodology

Sediment and water samples were collected from 14 locations in the targeted PFAS sampling areas within the MKE AOC (Figure 2). Specifically, the locations were placed in six target areas and include the following:

- Milwaukee River – four locations in Reach 4
- Menomonee River – two locations, including one location in Reach 4 and one location in Reach 5
- SMC – one location
- KK River – four locations, including one location in Reach 2, one location in Reach 3 near SkipperBud's Slip, one location in the Reach 3 navigation channel, and one location at the confluence of the Milwaukee River, KK River, and inner and outer harbors near the I-794 bridge in the Connection Channel
- Outer harbor – two locations, including one location near the inner harbor entrance and one location near the Jones Island Confined Disposal Facility
- Lake Michigan – one background location outside the breakwater

Samples were collected from November 18 through November 22, 2019, using Anchor QEA's drilling subcontractor Coleman Engineering Company's (CEC's) sampling vessel and the University of Wisconsin – Milwaukee's (UWM's) *research vessel* (R/V) *Neeskay*. The sampled locations, along with water depths, core penetration and recovery, and laboratory testing performed are summarized in Table A-1 (Appendix A). During field activities, field personnel followed the procedures described in the FSP (Anchor QEA 2020a), which were based on the Michigan Department of Environmental Quality (MDEQ) General PFAS Sampling Guidance (MDEQ 2018) and approved by DNR, to minimize the potential for cross-contamination during sample collection, processing, packaging, and shipment.

2.1.1 Water Sampling

Site water sample locations were co-located with sediment sampling locations. At each of the 14 sample locations, surface water samples were collected prior to the initiation of sediment sampling activities to minimize the potential effects from bottom disturbance of sediment during sediment sampling. In the Milwaukee River, Menomonee River, KK River, and the river confluence area, 11 samples were collected using CEC's sampling vessel. To collect samples in the outer harbor and Lake Michigan (locations MKE-19-12, MKE-19-13, and MKE-19-14), higher wind and waves necessitated the use of the larger *R/V Neeskay* vessel.

Water quality data, including dissolved oxygen, temperature, pH, and turbidity, were recorded at each location using a sampling sonde. These water quality measurements were made at two-thirds of the water depth (as measured from the water's surface). Water depth was determined prior to sampling using a weighted tape measure from CEC's sampling vessel. From the *R/V Neeskay*, water depth was determined from the onboard depth sounder, as the deck height of the vessel prohibited visual readings from a weighted tape measure. Water quality measurements are summarized in Table A-2 (Appendix A). Water samples were collected from two-thirds of the water column depth using a Kemmerer Bottle sampler. The Kemmerer Bottle was retrieved, and the water sample was distributed directly to pre-labeled sample containers supplied by the analytical laboratory. The water samples were placed on wet ice and transported to shore for logging and packaging prior to being shipped to GEL Laboratories, LLC (GEL), in Charleston, South Carolina, for PFAS and total suspended solids (TSS) analysis.

2.1.2 Sediment Sampling

Following water sampling, sediment samples were collected as either a sediment core or a sediment surface grab. Sediment cores were collected from 11 locations from the Milwaukee River, Menomonee River, KK River, and the river confluence areas by Anchor QEA's drilling subcontractor CEC. Surface grab samples of sediment were collected from three locations in the outer harbor and Lake Michigan areas from the UWM's *R/V Neeskay*.

Sediment cores for PFAS analysis targeted recovery of the upper 4 feet of sediment. Sediment cores were collected using direct-push methods with a piston corer. This method involved a piston seal attached to a cable that was inserted into the core tube. The polycarbonate core tube was then attached to a drive head. Threaded drive rods were then attached to the drive head and the assembly lowered through the water. Upon reaching the sediment surface, the piston cable was secured such that the piston remained stationary as the core tube was advanced to create a suction. The core tube was advanced using a hydraulic ram mounted to the sampling vessel that pushed the drive rods and core tube into the sediment to the target depth of 4 feet. All samples were collected to that depth except MKE-19-11. After three attempts at location MKE-19-11, the best attempt was only able to penetrate 2 feet into the sediment before encountering refusal with a recovery of 1.8 feet. It is suspected that at MKE-19-11, coring attempts encountered refusal at native material and only minimal soft sediment was present potentially due to periodic maintenance dredging of the navigation channel in this area.

Sediment samples from the outer harbor and Lake Michigan were collected with a surface grab sampler (Ponar) to target surface (top 3 to 5 inches) sediment. At each location, sediments recovered from the Ponar were placed into a stainless-steel pan, photographed, and then a visual description of the recovered sediment was documented on the field collection log. The recovered sediments from a location were then homogenized to a uniform consistency and color using a stainless-steel spoon, and then distributed directly to pre-labeled sample containers supplied by the analytical laboratory. The sediment samples were placed on wet ice and transported to shore for logging and packaging prior to being shipped to GEL. Sampling and processing equipment were decontaminated between locations in accordance with the FSP.

The horizontal position of each sampled location was recorded using a GPS with submeter accuracy. The actual sampled locations are depicted in Figure 2. On occasion, sampling locations were offset from the targeted location, either due to field conditions or identified utility crossings. As noted above, water depth was determined at each location by manually measuring the distance from the water surface to the sediment surface (mudline), using a weighted tape measure. Measurements were recorded to the nearest tenth of a foot. Water depth associated with surface grab samples collected from the *R/V Neeskay* were measured using the vessel's electronic depth sounder. The date and time of the water depth measurements were as recorded in the field. The mudline elevation at each location was then estimated based on the water surface elevation from the nearest gauging station, using the same date and time as the water depth measurement.

In addition to local U.S. Geological Survey and National Oceanic and Atmospheric Administration gauging stations identified in the FSP, a temporary gauging station was installed on the SMC prior to sampling efforts at the request of DNR during the investigation. This temporary gauging station was installed at the Milwaukee Metropolitan Sewer District dock located on the SMC and consisted of a piezometer that recorded pressure head every 15 minutes throughout the duration of the field effort. The elevation of the piezometer was surveyed by Anchor QEA's subcontractor The Sigma Group (Sigma), using real-time kinematic global positioning system surveying techniques to determine the elevation. Piezometer readings were then translated into a water surface elevation. Figure 3 depicts a hydrograph of the water surface elevation observed throughout the field effort. Table A-1 (Appendix A) summarizes the samples and includes horizontal position, sample date, water depth, mudline elevation estimates, core penetration, and recovered sediment core lengths. Photographs of sediment sampling activities are presented in Appendix A.

2.2 Sediment Sample Processing

Collected sediment cores were transported to a landside core processing area to facilitate concurrent core processing during field activities. Sediment cores were processed in a dedicated space within Sigma's building located at 300 West Canal Street, Milwaukee, Wisconsin 53233. Each core was processed by experienced core sample processing staff in accordance with procedures outlined in the FSP.

Prior to opening each core, cores were weighed. Bulk density was calculated using the weight of the sediment within the core, recovered sediment volume (based on the inner diameter of the core tube), and total length of recovered sediment. The calculated field bulk density is presented in Table A-1 (Appendix A) for each core. Sediment cores were then split longitudinally, screened with a photoionization detector (PID), logged using the Unified Soil Classification System to describe the observed soil type, color, consistency, odors, and visible evidence of discoloration or sheens, and then photographed. Photographs of core processing are presented in Appendix A. The strength parameters of fine-grained (e.g., silts and clays) sediments were assessed using a handheld pocket penetrometer for compressive strength and torvane for shear strength, where appropriate. A minimum of one set of strength tests were performed on a representative portion of sediment from a given sample depth interval. The sediment core logs, in Appendix A, present the lithology, sampled depth intervals, PID, torvane, and pocket penetrometer readings.

After the lithologic logging was completed, sediment cores were subsampled. Subsampling targeted depth intervals from 0 to 1.0 foot, 1.0 to 2.5 feet, and 2.5 to 4.0 feet. Representative portions of sediment were transferred from each sample interval into a stainless-steel bowl using stainless-steel utensils, and then transferred to the appropriate container provided by the analytical laboratory. All reusable material and equipment used for homogenizing sediment were decontaminated between sediment samples in accordance with the FSP.

Field Scribe, a data collection application created by Anchor QEA, was used for on-site sample management. Sampling coordinates, sample IDs, core penetration, core recovery, lithology, and analytical testing requirements for each sample from each core were entered at the time of core processing, and sample labels and chain-of-custody forms were printed on site to provide information to the laboratory.

2.3 Sample Analysis

Both water and sediment samples were sent to GEL in Charleston, South Carolina. Sediment samples were analyzed for PFAS by EPA Method 537[3] Modified, total organic carbon by EPA Method 9060 Modified, and total solids by Standard Method (SM) 2540G. Water samples were analyzed for PFAS by EPA Method 537 Modified and TSS by SM 2540D.

---

[3] Analyses followed DNR performance-based guidance (https://dnr.wi.gov/news/input/documents/guidance/draft/EA-19-0001-D.pdf)

2.4 Decontamination

Standard and PFAS decontamination practices were implemented throughout the investigation, as detailed in the FSP, to minimize the potential for PFAS cross-contamination. When practicable, PFAS-free disposable equipment was used for sampling, homogenizing, and subsampling procedures (e.g., core liners, bowls, spoons, pans). However, when equipment was reused, decontamination steps specified in the FSP were followed to ensure that samples would not be cross-contaminated.

Products suspected to contain PFAS were not permitted in the sampling or processing areas during the PFAS Special Study. Prior to the investigation, field crews screened clothing, personal protective equipment (PPE), equipment, and personal items for the possibility of PFAS-containing materials based upon the MDEQ's PFAS sampling guidance (MDEQ 2018).

Sampling vessels used in field sampling activities were also inspected, and if necessary, cleaned to remove oil, grease, mud, or other foreign matter, including vegetation, prior to sampling and leaving the site.

2.5 Investigation-Derived Waste

Potentially contaminated sediment, water, PPE, and other investigation-derived waste (IDW) materials generated during the PFAS field investigation were collected, segregated, and disposed of in accordance with the FSP. Excess sediment not used for sample analysis and decontamination liquids generated during core processing were collected in separate 55-gallon (closed top) drums. Non-sediment waste, such as PPE, disposable sampling equipment, used core liners, caps, and plastic sheeting were collected and disposed of as municipal solid waste. Grossly contaminated non-sediment waste that could not be effectively decontaminated was placed with the excess sediment into 55-gallon drums. In total, three drums of sediment and one drum of liquid waste were generated during the investigation, including IDW generated during the SMC investigation. One composite sample of sediment and one composite sample of water was submitted for analysis of metals and semivolatile and volatile organic compounds using the Toxicity Characteristic Leaching Procedure (TCLP). TCLP results are presented in Appendix A.

2.6 Quality Control

2.6.1 Field Deviations

Deviations from the approved FSP were sometimes necessary as a result of conditions encountered in the field. For six sampling locations, the targeted position was offset by more than 10 feet as specified in the Standard Operating Procedure (SOP 01 – Field Records), due to utility crossings, unsafe field conditions (e.g., ice sheets), or vessel drift. Because the intent of the sampling program was to obtain an overall understanding of the presence and concentrations of PFAS within select portions of the MKE AOC, these offsets did not impact data usability or interpretations. Specific deviations associated with sample locations are as follows:

- MKE-19-02 – Offset approximately 25 feet upstream from targeted location due to buried utility crossing
- MKE-19-07 – Offset approximately 50 feet from targeted location due to ice sheet in SMC at time of sampling
- MKE-19-09 – Offset approximately 85 feet from targeted location due to ice sheet at SkipperBud's Slip at time of sampling
- MKE-19-12 – Offset approximately 440 feet northeast from targeted location to capture sediment outside of navigation channel while avoiding a buried utility crossing
- MKE-19-13 – Offset approximately 90 feet from targeted location due to vessel drift during sampling (*R/V Neeskay* did not anchor to avoid disturbing sediments for water sampling)
- MKE-19-14 – Offset approximately 90 feet from targeted location due to vessel drift during sampling (*R/V Neeskay* did not anchor to avoid disturbing sediments for water sampling)

2.6.2 Laboratory QA/QC

The laboratory followed the specified analytical methods, and all requested sample analyses were completed within recommended holding times with one exception. After all analyses were completed and reported, a laboratory sequencing error was discovered, and PFAS results reported for water sample MKE-19-02-SW-201911201522 were determined to be the incorrect sample, and the correct results could not be determined. Three additional samples—MKE-19-12-SW-201911201024, MKE-19-13-SW-201911200935, and MKE-19-14-SW-201911200844—were analyzed in the same group, and consequently, their results were also unknown.

The laboratory conducted the required quality control (QC) analyses at the frequencies specified in the QAPP. Precision was acceptable as demonstrated by the laboratory control sample (LCS)/laboratory control sample duplicate (LCSD), matrix spike (MS)/matrix spike duplicate (MSD), and laboratory and field duplicate relative percent difference values, with one exception. Accuracy was acceptable as demonstrated by the calibration, labeled standard, LCS/LCSD, and MS/MSD recovery values with a few exceptions. Quality assurance (QA)/QC results that were outside of control limits listed in the QAPP were qualified "J" or "UJ" to indicate they are estimated, and two results were rejected. Appendix B provides additional information regarding QA/QC results and qualifiers. Perfluorooctadecanoic acid (PFODA) results were rejected in samples MKE-19-07-SC-02-3.8-191120 and MKE-19-12-SG-201911201024, due to zero percent recovery in the MS and MSD analyses. Most results were not qualified, however, completeness was 94%, which is less than the 95% goal listed in the QAPP, largely due to the laboratory sequencing error for the four water samples whose results were consequently not reportable.

3 Results

Concentration summary statistics for all analyzed PFAS compounds in surface water and sediment are presented in Table 3 (attached). Within the table and in the results below, the descriptions are organized by PFCAs, PFSAs, and precursors and replacement chemistries, with the length of the carbon chain noted in parentheses (e.g., C14). The full set of raw data files can be found in Appendix B.

3.1 Surface Water

Concentrations above the detection limit were found in surface water (collected at two-thirds the water column depth) for 65% of PFAA compounds. For the PFCAs, the compounds with short carbon chains (C4 through C7) as well as C8 were detected in 100% of the samples. The relatively longer chain compounds (C9 through C18) ranged from all non-detect to a 50% detection rate in perfluorotetradecanoic acid (PFTeDA; C14). The highest concentration PFCA compound found in surface water was perfluorohexanoate (PFHxA; C6) at 24.9 ng/L in one sample.

For the PFSAs, all but the longest chain compounds analyzed (C9 and C10) were detected in at least some samples. The highest concentration PFSA was also the C6 compound (perfluorohexane sulfonate [PFHxS]) at 44.4 ng/L. The only detected precursor or replacement chemistry compound in surface water was 6:2 fluorotelomer sulfonate (FTS), which was detected in 50% of samples, with a maximum concentration of 19.8 ng/L. No replacement chemistry compounds (GenX, F53B minor, F53B major, or ADONA) were found in MKE AOC surface water samples.

Across all compounds, locations, and replicates sampled, 68% of reported[4] water measurements were non-detect.

3.2 Sediment

Less than half of the tested PFCA compounds were detected in the MKE AOC sediments. The most frequently detected PFCA compound was perfluorobutanoate (PFBA; C4), which was found in 57% of samples, with a maximum concentration of 0.8 nanogram per gram (ng/g). The longer chain compounds (C11 through C16) were detected more frequently in the sediments than the shorter chain compounds, with a maximum concentration of 1.5 ng/g for both perfluorododecanoate (PFDoA; C12) and PFTeDA (C14).

---

[4] Water samples at stations MKE-19-02, MKE-19-12, MKE-19-13, and MKE-19-14 are not reported due to laboratory sequencing analytical error.

Three PFSA compounds were detected in some sediment samples: PFHxS (C6), PFOS (C8), and perfluorodecane sulfonate (PFDS; C10). The maximum rate of detection and concentration was found for PFOS, with an 86% detection rate and a maximum concentration of 9.1 ng/g.

Eight of the fifteen precursor and replacement chemistry compounds were detected in several of the MKE AOC sediment samples. The majority of the detections were for the PFOS precursor compounds, namely perfluorooctane sulfonamide (PFOSA), n-ethyl perfluoro-1-octane sulfonamide (N-EtFOSA), n-methylperfluorooctane sulfonamidoacetic acid (N-MeFOSAA), n-ethyl perfluorooctane sulfonamidoacetic acid (N-EtFOSAA), 2-(n-methyl perfluoro-1-octanesulfonamidoethanol (N-MeFOSE), and 2-(n-ethyl perfluoro-1-octane sulfonamido ethanol (NEtFOSE). There were also two detected fluorotelomer compounds (6:2 and 10:2 FTS), which are PFCA precursors. The highest detected concentration of all precursor compounds was 6:2 FTS at 25.2 ng/g. This compound had a 50% detection rate. Like the water samples, none of the replacement chemistry compounds on the analyte list were detected in the sampled locations of the MKE AOC sediments.

Across all compounds, locations, replicates, and depths sampled, 80% of reported sediment measurements were non-detect.

4 Trends and Interpretations

The results of the PFAS Special Study were evaluated in several ways. First, overall trends by analyte were assessed by media (sediment and surface water) using detection trends presented in Table 3 (attached). Next, the spatial trends by media were evaluated for each of the target areas. Screening level threshold values were then compiled from literature and results from the MKE AOC sampling were compared to these values and other sediment sites. Finally, additional background information is provided on 6:2 FTS, a compound detected in the sampled MKE AOC surface water and sediments.

4.1 Trends by Analyte

As shown in Table 3, the PFCA concentrations in surface water throughout the MKE AOC appear to decrease with increasing chain length. This trend is consistent with the increasing tendency for higher chain lengths to partition to sediments based on a higher K_{oc}, particularly with the collection of surface water samples at two-thirds the water column depth. Table 2 presents the published K_{oc} values for each PFAS compound. Furthermore, the longer chain compounds (C10 through C18) were generally not detected in surface water (with the exception of PFTeDA [C14] and perfluorohexadecanoic acid [PFHxDA; C16], which have a few samples just above the detection limit). These longer chain compounds were also detected in sediments.

PFSA concentrations across the Study Area are highest for PFHxS and PFOS in surface water and PFOS and PFDS in sediment. Like the PFCA compounds, the shorter chain compounds were detected more frequently in surface water, while the longer chain compounds were detected more frequently in sediments.

The only precursor compound found in surface water above detection limits in the Study Area was 6:2 FTS. This compound's main degradation products are perfluoropentanoic acid (PFPeA) and PFHxA (Wang et al. 2011). In addition to 6:2 FTS, 10:2 FTS and a number of PFOS precursor compounds were detected in sediment samples.

As mentioned above, no replacement chemistry compounds (GenX, F53B minor, F53B major, or ADONA) were found in MKE AOC surface water or sediment samples.

4.2 Spatial Trends

Spatial trends were assessed by targeted areas. Spatial trends in surface water concentrations were assessed using bar plots of each analyte (Figures 4a through 4jj). For sediment, stacked bar plots with the surface sample on the top row followed by samples at each decreasing depth interval (e.g., 0 to 0.5 foot, 0.5 to 1.0 foot, 1.0 to 2.0 feet, and 2.0 to 4.0 feet) are shown by analyte in Figures 5a through 5jj. Results are organized by PFCAs, PFSAs, and precursors and replacement chemistries.

4.2.1 Outer Harbor and Lake Michigan

Sediment and surface water samples were collected at three locations in Milwaukee Bay—two in the outer harbor (locations MKE-19-12 and MKE-19-13) and one in Lake Michigan (location MKE-19-14; Figure 2). Due to an error at the analytical laboratory, PFAS concentrations from all three background surface water samples are not reportable. The sediment data at these locations showed detected concentrations for only PFBA (MKE-19-12 and MKE-19-14; Figure 5a), PFOS (MKE-19-14; Figure 5r), and N-EtFOSAA (MKE-19-13; Figure 5z). All detected concentrations (which ranged from 0.2 to 0.7 ng/g) were slightly above the detection limit.

4.2.2 Menomonee River (Including SMC)

Sediment and surface water samples were collected at three Menomonee River locations (Figure 2), specifically one each in Reach 4 (MKE-19-05), Reach 5 (MKE-19-06), and the SMC (MKE-19-07). There do not appear to be any large spatial differences in the surface water between or within these stretches of the Study Area. All PFAS surface water concentrations were similar between locations MKE-19-05, MKE-19-06, and MKE-19-07. With the exception of changes in concentration seen at depth at locations MKE-19-06 and MKE-19-07, the sediment concentrations also did not vary appreciably between or within these stretches of the Study Area.

4.2.2.1 PFCAs

Several PFCAs were detected in the surface water of the Menomonee River and the SMC. The short-chain compounds had the highest surface water concentrations, with PFBA (C4) and PFPeA (C5) concentrations the highest, ranging from approximately 6 to 9 ng/L. Detected PFOA concentrations ranged from 2.8 to 3.7 ng/L. Longer chain PFCAs (perfluorononanoic acid [PFNA], PFTeDA, and PFHxDA) were detected in surface water just above their detection limits (0.7 to 1.3 ng/L).

Despite having higher detected surface water concentrations, all PFBA sediment concentrations were below 1 ng/g and did not show discernable trends with depth of sediment. The only other detected concentrations in the sediments for these areas were for the long-chain compounds PFDoA (Figure 5i), perfluorotridecanoic acid (PFTrDA; Figure 5j), and PFTeDA (Figure 5k). All of these had detected sediment concentrations under 1 ng/g and did not show discernable trends with depth of sediment. PFOA was not detected in any Menomonee River sediment sample.

4.2.2.2 PFSAs

Of the PFSA compounds, PFBS, PFHxS, and PFOS were detected in surface water at 2.8 to 8 ng/L (see Figures 4n, 4p, and 4r, respectively). The remainder of the PFSAs were non-detect in surface water, with the exception of PFPeS, which had detected concentrations just over the detection limit (0.6 to 0.8 ng/L; Figure 4o).

In sediment, the only detected compounds were PFOS and PFDS (Figures 5r and 5t, respectively). All of these concentrations were below 2 ng/g with the exception of PFDS in the deepest sampling intervals (2 to 4 feet) at locations MKE-16-06 and MKE-19-07, which showed somewhat higher concentrations (3.1 to 5.9 ng/g) as compared to other locations within MKE AOC.

4.2.2.3 PFAS Precursors

The only precursor compound detected in the surface water of Menomonee River and SMC was 6:2 FTS at concentrations slightly higher than the detection limit (Figure 4dd).

Similar to surface water, the sediments also show detected concentrations of 6:2 FTS (1.3 to 5.4 ng/g) at locations MKE-19-05 and MKE-19-06, but there is no apparent trend with sediment depth (Figure 5dd). In addition, the PFOS precursors PFOSA, N-MeFOSAA, and N-EtFOSAA show increasing sediment concentrations with depth at locations MKE-19-06 and MKE-19-07 (Figure 5v, 5y, and 5z).

4.2.3 Milwaukee River

Sediment and surface water samples were collected at four locations within Reach 4 of the Milwaukee River (Figure 2). Due to an error at the analytical laboratory, the surface water PFAS concentrations at location MKE-19-02 are not reportable. As described below, there were no apparent spatial trends in concentrations between the analyzed three surface water locations or any of the sediment locations.

4.2.3.1 PFCAs

Several PFCAs were detected in the Milwaukee River. Similar to the Menomonee River and the SMC, the short-chain compounds had the highest surface water concentrations, with PFBA concentrations the highest, ranging from approximately 5.6 to 6.2 ng/L (Figure 4a). PFPeA, PFHxA, perfluoroheptanoic acid (PFHpA), and PFOA were detected in surface water at all stations, with reportable data at concentrations from 1.2 to 4.0 ng/L (Figures 4b through 4e). Besides PFOA, the only long-chain PFCA found in surface water in the Milwaukee River was PFTeDA at locations MKE-19-01 and MKE-19-04, with concentrations of 0.7 to 0.8 ng/L, just over the detection limit (Figure 4k). No spatial trends were evident for PFCAs in the surface water and no PFCAs were detected in the sediments of the Milwaukee River.

4.2.3.2 PFSAs

The PFSAs detected in surface water of the Milwaukee River were PFBS, PFHxS, and PFOS at concentrations of 1.7 to 3.5 ng/L (Figures 4n, 4p, and 4r, respectively). Similar to PFCAs, no spatial trends were evident for PFSAs in surface water.

The only detected PFSA compounds in the Milwaukee River sediments were PFOS and PFDS (Figures 5r and 5t, respectively). The depth profiles for these two compounds are similar when compared by location. They show slight increases in concentration (1.1 to 2.0 ng/g) of both compounds at depth in the cores at locations MKE-19-02 and MKE-19-03. Small increases in concentration of both compounds (1.5 to 2.0 ng/g) were also found at mid-depth (0.5 to 2 feet) at locations MKE-19-01 and MKE-19-04.

4.2.3.3 PFAS Precursors

No precursor or replacement compounds were detected in the Milwaukee River surface water samples.

In sediments of the Milwaukee River, there were some detected precursor compounds, namely N-MeFOSAA and N-EtFOSAA (Figures 5y and 5z, respectively). These show increasing concentrations with depth at locations MKE-19-02, MKE-19-03, and MKE-19-04, with a maximum concentration of 10.3 ng/g. Additionally, there was a detection of PFOSA at the 0.5- to 1-foot depth interval of MKE-19-04 , a detection of 6:2 FTS at the deepest section of MKE-19-02, and detections of N-MeFOSE in two sections of MKE-19-04 (Figures 5v, 5dd, and 5aa, respectively). All concentrations of these last three compounds were just above the detection limit.

4.2.4 Kinnickinnic River

Sediment and surface water samples were collected at three locations in the KK River, including one location in Reach 2 (MKE-19-08), one location in Reach 3 near SkipperBud's Slip (MKE-19-09), and one location in the Reach 3 navigation channel (MKE-19-10). Samples were also collected at one location in the Connection Channel where the Milwaukee and KK rivers join (MKE-19-11; Figure 2). The samples from the KK River showed the highest PFAS levels of the entire Study Area. Of the samples in this waterway, the most upstream location (MKE-19-08) frequently resulted in the highest surface water (44.4 ng/L PFHxS; 32.7 ng/L PFOS; 7.1 ng/L PFOA; 19.8 ng/L 6:2 FTS) and sediment (9.1 ng/g PFOS at segment 0.5 to 1 feet) concentrations. These higher surface water and sediment concentrations decreased when proceeding downstream, with a potential second peak of select compounds in surface water (16.9 ng/L PFHxS; 14.2 ng/L PFOS; 4.2 ng/L PFOA; 9.5 ng/L 6:2 FTS) and sediment (7.5 ng/g PFOS at segment 1 to 2 feet) at MKE-19-10.

4.2.4.1 PFCAs

Of the PFCA compounds, the short-chain compounds and PFOA were detected in surface water at all locations ranging from 1.7 to 24.9 ng/L (Figures 4a through 4e). There were also low-level detections (0.8 to 1.3 ng/L) of PFNA, PFTeDA, and PFHxDA at location MKE-19-08 (Figures 4f, 4k, and 4l, respectively).

The only short-chain PFCA compound detected in sediments of the KK River was PFBA. This compound was found at 1- to 2-foot and 2- to 4-foot depth intervals at all locations except at the farthest downstream location (MKE-19-11; Figure 5a). Perfluoro-n-undecanoic acid (PFUnA) was found in three sediment samples across two locations (MKE-19-08 and MKE-19-10; Figure 5h) and PFHxDA was found at depth at location MKE-19-08 at concentrations just over the detection limit (Figure 5l). The C12-C14 compounds (PFDoA, PFTrDA, and PFTeDA) each had multiple, low-level detections in the sediments of the KK River (Figures 5i, 5j, and 5k, respectively). The detected concentrations at locations MKE-19-09 and MKE-19-11 remained at or just above the detection limit (maximum value of 0.7 ng/g). Detections of these C12-C14 compounds at the remaining two locations (MKE-19-08 and MKE-19-10) were more frequent, but did not exceed 1.6 ng/g. There do not appear to be any depth trends to the PFCA sediment data in this reach of the MKE AOC.

4.2.4.2 PFSAs

Of the PFSA compounds in surface water, the C4-C8 compounds were all detected and only perfluoroheptanesulfonic acid (PFHpS) was not detected at all four sampling stations (Figures 4n through 4r). Surface water concentrations of these compounds ranged from 0.6 to 44.4 ng/L. PFHxS displayed the highest concentrations, ranging from 7.5 to 44.4 ng/L (Figure 4p), with the highest concentration located at MKE-19-08. PFOS displayed the second highest concentrations, ranging from 6.8 to 32.7 ng/L (Figure 4r), with the highest concentration located at MKE-19-08. Perfluorononane sulfonate (PFNS) and PFDS were not detected (Figures 4s and 4t).

In sediment samples, only PFHxS, PFOS, and PFDS were detected (Figures 5p, 5r, and 5t, respectively). PFHxS had only two detections, both were samples in the top two depth intervals (0- to 0.5-foot and 0.5- to 1-foot sections) of MKE-19-08 and just above the detection limit (Figure 5p). PFOS, however, was detected at all stations and at all core depths, with a maximum concentration of 9.1 ng/g in the 0.5- to 1-foot depth interval of the core at location MKE-19-08 (Figure 5r). While not being detected at all in the surface water of this reach, PFDS was detected in all but two sediment samples in this reach (Figure 5t). Instead of having the highest concentrations upstream at location MKE-19-08, like PFOS in sediment and all the detected PFSAs in surface water, PFDS concentrations at MKE-19-08 were near the detection limit and then peaked at location MKE-19-10 (7.6 ng/g in the 1- to 2-foot depth interval) and MKE-19-09 (6.3 ng/g in the 0.5- to 1-foot depth interval). Like the PFCAs in the KK River, the data for the PFSAs do not show obvious trends with depth.

4.2.4.3 PFAS Precursors

The sole precursor compound found in the surface water of this river of the MKE AOC was 6:2 FTS (Figure 4dd). The data show a maximum concentration of 19.8 ng/L upstream at location MKE-19-08 with lower concentrations at downstream locations (non-detect to 9.5 ng/L).

6:2 FTS was also found in all but one sediment sample, which was the surface sample at location MKE-19-08 (Figure 5dd). The highest sediment concentration (19.8 ng/g) was at the surface of location MKE-19-10. With the exception of the non-detect sample, the results indicate a downward trend of 6:2 FTS concentrations with depth in the KK River.

Additional precursor compounds were found in the sediment samples of the KK River, but not the surface water. PFOSA was found at depth up to a concentration of 3.5 ng/g at locations MKE-19-09, MKE-19-10, and MKE-19-11 (Figure 5v). N-MeFOSAA and N-EtFOSAA were detected, sometimes at higher concentrations, in 80% and 87% of sediment samples, respectively. The highest of these concentrations were from deeper intervals of the cores, especially the 1- to 2-foot section at locations MKE-19-09, MKE-19-10, and MKE-19-11, which had a concentration range of 1.9 to 13.9 ng/g (see Figures 5y and 5z). The surface sediment samples (0 to 0.5 foot) for these compounds had generally lower concentrations than the deeper sections.

Other precursor compounds found at low levels were N-EtFOSA and N-EtFOSE (Figures 5x and 5bb). These were detected at concentrations just above the detection limit at location MKE-19-09. 10:2 FTS was detected in the three deepest samples at location MKE-19-08, with concentrations ranging from just above the detection limit to 1.4 ng/g (Figure 5ff).

4.3 Comparison to Selected Threshold Values for Surface Water

In addition to trend evaluations, the surface water PFAS dataset from MKE AOC was compared to selected threshold values for each compound obtained from literature. In this context, a threshold value was a regulatory criterion or an official recommendation. A representative threshold value was selected using three decision criteria.

1. Threshold values that are surface water and non-drinking water source values (as opposed to groundwater, drinking water, or surface water drinking water source threshold values) were selected because the Study Area samples were collected in surface waters that are non-drinking water sources[5].
2. Geography was used to select threshold values (i.e., applicable jurisdiction for states located near Wisconsin).
3. If no threshold values for either criteria were available, other (e.g., groundwater, drinking water, or geographically distant) threshold values were used, as available.

For some compounds, no threshold values were found (e.g., PFHxDA). Table 4 presents selected threshold values for each compound (where available) along with the reason for choosing the threshold value. These selected threshold values obtained from the literature were then compared to the maximum concentration of each PFAS.

---

[5] Note that Lake Michigan water is treated and used as drinking water from two locations outside of the Study Area, as reported on the City of Milwaukee's Milwaukee Water Works site (https://city.milwaukee.gov/water/about/WaterTreatment). The Linnwood Water Treatment Plant is located on the north side of the bay. The Linnwood intake is 1.25 miles from the shore at a depth of 60 feet. The Texas Avenue intake supplying the Howard Avenue Water Treatment Plant on the south side is 2.5 miles from shore, also at a depth of 60 feet.

Across all PFAS with threshold values, only PFOS and the sum of PFOS and PFOA were identified as exceeding the selected threshold values. PFOS exceeded a state-wide Michigan surface water, human noncancer value for non-drinking water sources published in 2014 as the threshold value. Michigan's water quality values are rules (not recommendations) setting minimum water quality standards for the protection of public health and natural resources. With both Michigan and Wisconsin bounding Lake Michigan, this PFOS threshold value is relevant to this Study because Wisconsin does not have a surface water standard, while Michigan does. Michigan's threshold value of 12 ng/L applies to non-drinking water sources, while the threshold value of 11 ng/L applies to drinking water sources. The maximum (32.7 ng/L; MKE-19-08) and second highest (14.2 ng/L; MKE-19-10) measured concentrations of PFOS were both found in the KK River, as shown on Figure 6. Both of these PFOS values are above Michigan's threshold value of 12 ng/L.

The Wisconsin Groundwater Enforcement Standard Recommended Value was used in the analysis in Table 4 for the sum of PFOS and PFOA but not for the individual compounds because more relevant surface water numbers were available. The maximum surface water concentrations of PFOA (7.1 ng/L) and PFOS (32.7 ng/L) that were observed in MKE AOC samples were both found in the KK River at MKE-19-08. By using the substitution of the Wisconsin threshold values (20 ng/L for each compound) instead of the Michigan water quality values, PFOS still exceeds the threshold value. However, PFOA does not exceed the threshold value of 20 ng/L at any locations as shown on Figure 7. Similarly, when combining results of PFOA and PFOS, MKE-19-08 continues to be the only location within the dataset that exceeds the 20 ng/L value (39.8 ng/L; see Figure 4u for combined PFOA and PFOS results). If the Preventive Action Limit Recommended Values (2 ng/L for each compound) were used, both compounds would exceed the recommend value at all locations with reportable results.

4.4 Sediment Concentrations as Compared to Other Sediment Sites

A review of the literature and other readily available sources did not identify any sediment PFAS concentration threshold values from jurisdictions in geographic proximity to the MKE AOC. One source, an Australian Ecological Risk Assessment, has published soil/sediment toxicity values for the protection of terrestrial organisms, plants, and invertebrates (Coffey Environments Australia Pty Ltd 2018). The lowest of these values is 1 milligram per kilogram (mg/kg) (1,000 ng/g) for both PFOS and PFOA. The MKE AOC sediment sample concentrations are all far below 1 mg/kg.

In the absence of a more complete suite of threshold values, a comparison of MKE AOC sediment concentrations to published PFAS sediment concentrations was completed. Codling et al. (2014) and Codling et al. (2018) published PFAS concentration values for several compounds in sediment samples taken in 2010 and 2011 from locations in Lake Michigan. A comparison of the MKE AOC concentrations to these published values is presented in Table 5. As is represented by the blue highlights in the table, some of the longer chain PFAAs (PFDoA, PFTrDA, PFHxDA and PFDS) and two precursors compounds (PFOSA and N-EtFOSA) may have higher concentrations in the MKE AOC than those reported in the Codling papers, although all harbor and bay stations were non-detect. Additionally, many of the shorter chain PFAAs (C5 through C10 PFCAs, PFBS, and PFHxS) have concentrations below those reported by Codling.

4.5 Background on 6:2 Fluorotelomer Sulfonate (6:2 FTS)

6:2 FTS was detected in the upper reaches of the KK River at higher concentrations than the other areas of the MKE AOC. While not much is known about this compound in comparison to the much more researched PFOS and PFOA, it is known that this compound has been manufactured since the 1970s. More recently, it has also been considered as a “replacement” for PFOS (Field and Seow 2017). It is found in a variety of consumer products, AFFFs (a fire suppressant), and chrome-plating mist suppressants. In analytical studies, 6:2 FTS was the dominant fluorotelomer sulfonate found in certain formulations of AFFFs, with 4:2 and 8:2 FTS also found at lower concentrations (Backe, Day, and Field 2013; Schultz, Barofsky, and Field 2004). 6:2 FTS has been found at very high concentrations (up to 14,600,000 ng/L in groundwater) at Air Force Bases that have conducted firefighting training operations using AFFFs (Backe, Day, and Field 2013; Schultz, Barofsky, and Field 2004). Ambient concentrations of 6:2 FTS have been detected in a New York Lake (non-detect to 1.46 ng/L) and in Lake Superior (non-detect to 0.055 ng/L) (Kim and Kannan 2007; Scott et al. 2010).

5 Overall Observations and Recommendations

In summary, the majority of samples taken in the MKE AOC had PFAS concentrations below the method detection limit. Across all compounds, locations, replicates, and depths sampled, 68% of reportable surface water and 80% of reportable sediment measurements were non-detect. In addition, 10 of the analyzed PFAS compounds were not detected in any sample.

Of the PFAS compounds that were detected, the highest levels were generally found in the KK River. Concentrations within the Menomonee River and SMC were lower than KK River but similar to each other. The Menomonee River and SMC had a slightly higher percentage of total samples above the detection limit (22% of all sediment and surface water samples) than the Milwaukee River (10%). Of the samples in the KK River, the most upstream location (MKE-19-08) showed the highest surface water and sediment concentrations of PFAS compounds. There was a noticeable downward trend in concentrations in the KK River when proceeding downstream toward Milwaukee Bay, but some compounds displayed a potential second peak at location MKE-19-10. There did not appear to be any obvious upstream to downstream spatial trends of samples collected in the other waterways of the MKE AOC.

The PFAA compounds with shorter carbon chains (all of the classified 'short chain' compounds as well as the C6-C8 compounds) were detected more frequently in surface water, while the longer chain compounds (C10 and larger) were detected more frequently in sediments. This trend could be explained by the chemical nature of PFAAs, which have an increasing tendency to partition to sediments (higher K_{oc}) with increasing chain length.

Some of the precursor compounds found in the sediments of the MKE AOC (e.g., PFOSA, the sulfonamides, the sulfonamidoacetic acids, the sulfonamido ethanols, and 6:2 FTS) have been shown to degrade to final products also found in the MKE AOC sediments (e.g., PFOS, PFPeA, and PFHxA) (Benskin et al. 2013; Zhang et al. 2017; Wang et al. 2011).[6] Although these precursors were found at low concentrations, their presence suggests that they may act as a historical and ongoing source of PFOS and other final products. None of the replacement chemistry compounds on the analysis list (GenX, F53B minor, F53B major, and ADONA) were detected in the MKE AOC.

Representative threshold values were selected for each compound and compared to the surface water results from the MKE AOC. Two surface water samples within the KK River (MKE-19-08 and MKE-19-10) contained the <u>only</u> concentrations found to be above the selected PFOS threshold value. The same surface water sample (MKE-19-08) also contained the <u>only</u> concentration above the sum of the selected PFOS and PFOA threshold value. An important component of this analysis is the threshold values available and chosen for comparison. For compounds where there were multiple

---

[6] 10:2 FTS, found in the deeper sections of sediment samples at station MKE-19-08 in the Kinnickinnic River, is also a likely precursor of one or more PFCAs, but this has not been established in the scientific literature.

threshold values available, the most relevant values were used in the analysis. No threshold values were available for 17 PFAS compounds.

In the absence of available threshold values for sediment PFAS concentrations, a comparison to relevant published sediment concentrations was done. A total of six compounds (PFDoA, PFTrDA, PFHxDA, PFDS, PFOSA, and N-EtFOSA) in the MKE AOC riverine samples were above the Lake Michigan concentrations reported in the literature.

Additional research should be completed in the upstream reaches of the KK River to discern sources of PFAS from entering the waterway. Fish contaminant monitoring should also be considered in the KK River to determine if fish found in the KK River carry higher levels of PFAS as found in this Study.

6 References

Anchor QEA (Anchor QEA, LLC), 2020a. *Field Sampling Plan*. Characterization of Sediments in Kinnickinnic River and Milwaukee Bay of the Milwaukee River Estuary Area of Concern. August 2020.

Anchor QEA, 2020b. *Quality Assurance Project Plan*. Characterization of Sediments in Kinnickinnic River and Milwaukee Bay of the Milwaukee River Estuary Area of Concern. August 2020.

Backe, W.J., T.C. Day, and J.A. Field, 2013. "Zwitterionic, Cationic, and Anionic Fluorinated Chemicals in Aqueous Film Forming Foam Formulations and Groundwater from U.S. Military Bases by Nonaqueous Large-Volume Injection HPLC-MS/MS." *Environ. Sci. Technol.* 47:5226−5234.

Benskin, J.P., M.G. Ikonomou, F.A.P.C. Gobas, T.H. Begley, M.B. Woudneh, and J.R. Cosgrove, 2013. "Biodegradation of N-Ethyl Perfluorooctane Sulfonamido Ethanol (EtFOSE) and EtFOSE-Based Phosphate Diester (SAmPAP Diester) in Marine Sediments." *Envion Sci & Technol* 47:1381-1389.

CH2M Hill, 2011. *Final Remedial Action Report, Kinnickinnic River Sediment Removal Project, Milwaukee, WI*. Remedial Action WA No. 049-RARA-1508, Contract No. EP-S5-06-01. March 2011.

CH2M, 2016. *Final Site Characterization Report – Menomonee River Sediment Investigation, Milwaukee Estuary Area of Concern, Milwaukee, Wisconsin*. July 2016.

Codling, G., A. Vogt, P.D. Jones, T. Wang, P. Wang, Y.-L. Lu, M. Corcoran, S. Bonina, A. Li, N.C. Sturchio, K.J. Rockne, K. Ji, J.-S. Khim, J.E. Naile, and J.P. Giesy, 2014. "Historical trends of inorganic and organic fluorine in sediments of Lake Michigan." *Chemosphere* 114: 203-209.

Codling, G., S. Hosseini, M. Corcoran, S. Bonina, T. Lin, A. Li, N.C. Sturchio, K.J. Rockne, K. Ji, H. Peng, and J.P. Giesy, 2018. "Current and historical concentrations of poly and perfluorinated compounds in sediments of the northern Great Lakes - Superior, Huron, and Michigan." *Environmental Pollution* 236: 373-381.

Coffey Environments Australia Pty Ltd, 2018. *Department of Defense RAAF Base Tindal: Ecological Risk Assessment*. Prepared for Australian Department of Defense. Available at: https://www.defence.gov.au/Environment/PFAS/docs/Tindal/Reports/Tindal%20ERA%20Final%20Report_V3.pdf. November 12, 2018.

Conder, J.M., R.A. Hoke, W. de Wolf, M.H. Russell, and R.C. Buck, 2008. "Are PFCAs Bioaccumulative? A Critical Review and Comparison with Regulatory Criteria and Persistent Lipophilic Compounds." *Environmental Science & Technology* 42(4):995-1003. doi: 10.1021/es070895g.

DNR (Wisconsin Department of Natural Resources), 1991. *Milwaukee Estuary Stage 1 Remedial Action Plan*. Contract No. PUBL-WR-276-91.

DNR, 2017. *Draft Remedial Action Plan Update for the Milwaukee Estuary Area of Concern*. December 2017.

Field, J.S., and J. Seow, 2017. "Properties, Occurrence, and Fate of Fluorotelomer Sulfonates." *Critical Reviews in Environmental Science and Technology* 47(8):643-691.

ITRC (Interstate Technology Regulatory Council), 2020. *Naming Conventions and Physical and Chemical Properties of Per- and Polyfluoroalkyl Substances (PFAS)*. Available at: https://pfas-1.itrcweb.org/fact-sheets/.

Kim, S-Y., and K. Kannan, 2007. "Perfluorinated Acids in Air, Rain, Snow, Surface Runoff, and Lakes: Relative Importance of Pathways to Contamination of Urban Lakes." *Environ. Sci. Technol.* 41:8328-8334.

MDEQ (Michigan Department of Environmental Quality), 2018. *Michigan Department of Environmental Quality General PFAS Sampling Guidance*. Revised October 16, 2018.

NOAA (National Oceanic and Atmospheric Administration), 2020. Chart 14924, Milwaukee Harbor. Provided by NOAA Office of Coast Survey, nauticalcharts.noaa.gov.

Schultz, M.M., D.F. Barofsky, and J.A. Field, 2004. "Quantitative Determination of Fluorotelomer Sulfonates in Groundwater by LC MS/MS." *Environ. Sci. Technol.* 38:1828-1835.

Scott, B.F., A.O. De Silva, C. Spencer, E. Lopez, S.M. Backus, and D.C.G. Muir, 2010. "Perfluoroalkyl acids in Lake Superior water: Trends and sources." *Journal of Great Lakes Research* 36:277-284.

Wang, N., J. Liu, R.C. Buck, S.H. Korzeniowski, B.W. Wolstenholme, P.W. Folsom, and L.M. Sulecki, 2011. "6:2 Fluorotelomer sulfonate aerobic biotransformation in activated sludge of waste water treatment plants." *J. Chemosphere* 82(6):853-858. doi: 10.1016/j.chemosphere.2010.11.003.

Zhang, L., L.S. Lee, J. Niu, and J. Liu, 2017. "Kinetic analysis of aerobic biotransformation pathways of a perfluorooctance sulfonate (PFOS) precursor in distinctly different soils." *Environmental Pollution* 229:159-167.

Tables

Table 2
Published Log K_{oc} Values for PFAS

Analyte	Length of Carbon Chain	Log K_{oc} (reference)
Perfluorocarboxylic Acids (PFCAs)		
Perfluorobutanoate (PFBA)	C4	1.88 (1) -0.8-1.3 (2)
Perfluoropentanoate (PFPeA)	C5	1.37 (1) 0.7-1.7 (2) 1.7-2.1 (3)
Perfluorohexanoate (PFHxA)	C6	1.31 (1) 0.2-1.8 (2)
Perfluoroheptanoate (PFHpA)	C7	-0.2-0.17 (4) 1.63 (1) 1.1-2.1 (2) 1.7-2.1 (3)
Perfluorooctanoate (PFOA)	C8	2.06-2.11 (5) 1.98 (6) 0.04-0.63 (4) 2.2-2.6 (7) 1.89 (1) 1.7-2.9 (2) 2.77-3.21 (8) 2.1-2.2 (3)
Perfluorononanoate (PFNA)	C9	2.39-2.50 (5) 0.62-1.26 (4) 2.36 (1) 2.4-3.9 (2) 2.4-2.5 (3)
Perfluorodecanoate (PFDA)	C10	2.76-2.92 (5) 1.48-1.90 (4) 2.96 (1) 3.7-5.5 (2) 2.8-3.2 (3)
Perfluoroundecanoate (PFUnA)	C11	3.30-3.47 (5) 3.56 (1) 3.9-5.8 (2)
Perfluorododecanoate (PFDoA)	C12	3.8-5.5 (2) 3.7-3.8 (3)
Perfluorotridecanoic acid (PFTrDA)	C13	
Perfluorotetradecanoic acid (PFTeDA)	C14	3.7-5.2 (2)
Perfluorohexadecanoic acid (PFHxDA)	C16	
Perfluorooctadecanoic acid (PFODA)	C18	

Table 2
Published Log K_{oc} Values for PFAS

Analyte	Length of Carbon Chain	Log K_{oc} (reference)
Perfluorosulfonic Acids (PFSAs)		
Perfluorobutane sulfonate (PFBS)	C4	1.2 (6) -0.39- -0.70 (4) 1.79 (1) -0.7-2.2 (2) 1.8-2.1 (3)
Perfluoropentane sulfonate (PFPeS)	C5	
Perfluorohexane sulfonate (PFHxS)	C6	2.05 (1) 1.7-4.1 (2) 2.0-2.1 (3)
Perfluoroheptane sulfonate (PFHpS)	C7	
Perfluorooctane sulfonate (PFOS)	C8	2.57-2.68 (5) 2.4-2.6 (9) 2.85 (6) 3.13 (10) 1.18-1.60 (4) 3.0-4.2 (7) 2.80 (1) 3.9-5.3 (2) 2.7-2.8 (3)
Perfluorononane sulfonate (PFNS)	C9	
Perfluorodecane sulfonate (PFDS)	C10	3.53-3.66 (5)
Precursors and Replacement Chemistries		
Perfluorooctane sulfonamide (PFOSA)	--	3.7-5.0 (7) 4.3-6.0 (2)
N-methyl perfluoro-1-octanesulfonamide (N-MeFOSA)	--	
N-ethyl perfluoro-1-octanesulfonamide (N-EtFOSA)	--	
N-methyl perfluorooctanesulfonamidoacetic acid (N-MeFOSAA)	--	3.11-3.35 (5)
N-ethyl perfluorooctanesulfonamidoacetic acid (N-EtFOSAA)	--	3.23-3.49 (5)
2-(N-methyl perfluoro-1-octanesulfonamido)-ethanol (N-MeFOSE)	--	
2-(N-ethyl perfluoro-1-octanesulfonamido)-ethanol (N-EtFOSE)	--	
4:2 fluorotelomer sulfonate (4:2 FTS)	--	
1H,1H,2H,2H-perfluorooctanesulfonic acid (THPFOS) (6:2 FTS)	--	
1H,1H,2H,2H-perfluorodecanesulfonic acid (8:2 FTS)	--	
10:2-fluorotelomer sulfonate (10:2 FTS)	--	
2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-propanoic acid (GenX)	--	

Table 2
Published Log K_{oc} Values for PFAS

Analyte	Length of Carbon Chain	Log K_{oc} (reference)
11-chloroeicosafluoro-3-oxaundecane-1-sulfonate (PF3OUdS) (F53B minor)	--	
9-chlorohexadecafluoro-3-oxanonnane-1-sulfonate (PF3ONS) (F53B major)	--	
Sodium dodecafluoro-3H-4,8-dioxanonanoate (ADONA)	--	

Note:

All Log K_{oc} values were laboratory derived.

Abbreviation:

K_{oc}: organic carbon partition coefficient

References:

1. Guelfo, J.L., and C.P. Higgins, 2013. "Subsurface Transport Potential of Perfluoroalkyl Acids at Aqueous Film-Forming Foam (AFFF)-Impacted Sites." *Environmental Science and Technology* 47:4164-4171.

2. Pereira, H.C., M. Ullberg, D.B. Kleja, J.P. Gustafsson, and L. Ahrens, 2018. "Sorption of perfluoroalkyl substances (PFASs) to an organic soil horizon--Effect of cation composition and pH." *Chemosphere* 207:183-191.

3. Zhao, L., L. Zhu, L. Yang, Z. Liu, and Y. Zhang, 2012. "Distribution and desorption of perfluorinated compounds in fractionated sediments." *Chemosphere* 88(11):1390-1397.

4. Enevoldsen, R., and R.K. Juhler, 2010. "Perfluorinated compounds (PFCs) in groundwater and aqueous soil extracts: using inline SPE-LC-MS/MS for screening and sorption characterization of perfluorooctane sulphonate and related compounds." *Analytical and Bioanalytical Chemistry* 398:1161-1172.

5. Higgins, C.P., and R.G. Luthy, 2006. "Sorption of Perfluorinated Surfactants on Sediments." *Environmental Science and Technology* 40:7251-7256.

6. Milinovic, J., S. Lacorte, M. Vidal, and A. Rigol, 2015. "Sorption behavior of perfluoroalkyl substances in soils." *Science of the Total Environment* 511:63-71.

7. Ahrens, L., L.W.Y. Yeung, S. Taniyasu, P.K.S. Lam, and N. Yamashita, 2011. "Partitioning of perfluorooctanoate (PFOA), perfluorooctane sulfonate (PFOS) and perfluorooctane sulfonamide (PFOSA) between water and sediment." *Chemosphere* 85:731-737.

8. Xiang, L., T. Xiao, P.F. Yu, H.M. Zhao, C.H. Mo, Y.W. Li, H. Li, Q.Y. Cai, D.M. Zhou, and M.H. Wong, 2018. "Mechanism and Implication of the Sorption of Perfluorooctanoic Acid by Varying Soil Size Fractions." *Agricultural and Food Chemistry* 66:11569-11579.

9. Johnson, R.L, A.J. Anschutz, J.M. Smolen, M.F. Simcik, and R.L. Penn, 2007. "The Adsorption of Perfluorooctane Sulfonate onto Sand, Clay, and Iron Oxide Surfaces." *Journal of Chemical Engineering Data* 52:1165-1170.

10. Chen, H., S. Chen, X. Quan, Y. Zhao, H. Zhao, 2009. "Sorption of perfluorooctane sulfonate (PFOS) on oil and oil-derived black carbon: Influence of solution pH and [Ca2+]." *Chemosphere* 77:1406-1411.

Table 3
PFAS Concentration Summary Statistics by Analyte

Analyte	Length of Carbon Chain	Percent of Locations Detected (Range of Detections) Surface Water (ng/L)	Percent of Locations Detected (Range of Detections) Sediment (ng/g)
Perfluorocarboxylic Acids (PFCAs)			
Perfluorobutanoate (PFBA)	C4	100% (5.6 - 12)	57% (0.3 - 0.8)
Perfluoropentanoate (PFPeA)	C5	100% (2.8 - 17.9)	All ND
Perfluorohexanoate (PFHxA)	C6	100% (2.9 - 24.9)	All ND
Perfluoroheptanoate (PFHpA)	C7	100% (1.2 - 4.4)	All ND
Perfluorooctanoate (PFOA)	C8	100% (2.3 - 7.1)	All ND
Perfluorononanoate (PFNA)	C9	40% (0.7 - 0.9)	All ND
Perfluorodecanoate (PFDA)	C10	All ND	All ND
Perfluoroundecanoate (PFUnA)	C11	All ND	14% (0.3 - 0.3)
Perfluorododecanoate (PFDoA)	C12	All ND	50% (0.3 - 1.5)
Perfluorotridecanoic acid (PFTrDA)	C13	All ND	43% (0.3 - 0.7)
Perfluorotetradecanoic acid (PFTeDA)	C14	50% (0.7 - 0.9)	50% (0.4 - 1.5)
Perfluorohexadecanoic acid (PFHxDA)	C16	30% (1.2 - 1.3)	7% (0.6)
Perfluorooctadecanoic acid (PFODA)	C18	All ND	All ND
Perfluorosulfonic Acids (PFSAs)			
Perfluorobutane sulfonate (PFBS)	C4	100% (1.7 - 8.9)	All ND
Perfluoropentane sulfonate (PFPeS)	C5	70% (0.6 - 7.7)	All ND
Perfluorohexane sulfonate (PFHxS)	C6	100% (2.8 - 44.4)	7% (0.4 - 0.6)
Perfluoroheptane sulfonate (PFHpS)	C7	20% (0.6 - 1.7)	All ND
Perfluorooctane sulfonate (PFOS)	C8	100% (2.4 - 32.7)	86% (0.2 - 9.1)
Perfluorononane sulfonate (PFNS)	C9	All ND	All ND
Perfluorodecane sulfonate (PFDS)	C10	All ND	79% (0.4 - 7.6)

Table 3
PFAS Concentration Summary Statistics by Analyte

Analyte	Length of Carbon Chain	Percent of Locations Detected (Range of Detections)	
		Surface Water (ng/L)	Sediment (ng/g)
Precursors and Replacement Chemistries			
Perfluorooctane sulfonamide (PFOSA)	--	All ND	43% (0.3 - 3.5)
N-methyl perfluoro-1-octanesulfonamide (N-MeFOSA)	--	All ND	All ND
N-ethyl perfluoro-1-octanesulfonamide (N-EtFOSA)	--	All ND	7% (0.6 - 0.7)
N-methyl perfluorooctanesulfonamidoacetic acid (N-MeFOSAA)	--	All ND	79% (0.7 - 8.7)
N-ethyl perfluorooctanesulfonamidoacetic acid (N-EtFOSAA)	--	All ND	79% (0.6 - 13.9)
2-(N-methyl perfluoro-1-octanesulfonamido)-ethanol (N-MeFOSE)	--	All ND	7% (0.7 - 0.9)
2-(N-ethyl perfluoro-1-octanesulfonamido)-ethanol (N-EtFOSE)	--	All ND	7% (1.0)
4:2 fluorotelomer sulfonate (4:2 FTS)	--	All ND	All ND
1H,1H,2H,2H-perfluorooctanesulfonic acid (THPFOS) (6:2 FTS)	--	50% (1.7 - 19.8)	50% (0.7 - 25.2)
1H,1H,2H,2H-perfluorodecanesulfonic acid (8:2 FTS)	--	All ND	All ND
10:2-fluorotelomer sulfonate (10:2 FTS)	--	All ND	7% (0.7 - 1.4)
2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-propanoic acid (GenX)	--	All ND	All ND
11-chloroeicosafluoro-3-oxaundecane-1-sulfonate (PF3OUdS) (F53B minor)	--	All ND	All ND
9-chlorohexadecafluoro-3-oxanonnane-1-sulfonate (PF3ONS) (F53B major)	--	All ND	All ND
Sodium dodecafluoro-3H-4,8-dioxanonanoate (ADONA)	--	All ND	All ND

Abbreviations:
ND: non-detect
ng/g: nanograms per gram
ng/L: nanograms per liter

Table 4
Regulatory and Threshold Values for PFAS Surface Water Concentrations

Chemical	CAS RN	Units	Frequency of Detection (%)	Maximum Detected Concentration[1]	Maximum Non-Detected Concentration[1]	Maximum Concentration[1,2]	Basis for Maximum (D/ND)	Threshold Value	Threshold Value Source[3]	Guidance Value Decision Criteria Category[4]
Carboxylates										
Perfluorobutanoate (PFBA)	375-22-4	ng/L	100	12.0	N/A	12.0	D	7,000	MN (DW/GW1)	B
Perfluoropentanoate (PFPeA)	2706-90-3	ng/L	100	17.9	N/A	17.9	D	93	TX (GW)	C
Perfluorohexanoate (PFHxA)	307-24-4	ng/L	100	24.9	N/A	24.9	D	93	TX (GW)	C
Perfluoroheptanoate (PFHpA)	375-85-9	ng/L	100	4.4	N/A	4.4	D	300,000	OR (SW)	A
Perfluorooctanoate (PFOA)	335-67-1	ng/L	100	7.1	N/A	7.1	D	12,000	MI (SW1)	A
Perfluorononanoate (PFNA)	375-95-1	ng/L	40	0.9	0.6	0.9	D	1,000	OR (SW)	A
Perfluorodecanoate (PFDA)	335-76-2	ng/L	0	N/A	0.7	0.7	ND	370	TX (GW)	C
Perfluoroundecanoate (PFUnA)	2058-94-8	ng/L	0	N/A	0.6	0.6	ND	290	TX (GW)	C
Perfluorododecanoate (PFDoA)	307-55-1	ng/L	0	N/A	0.6	0.6	ND	290	TX (GW)	C
Perfluorotridecanoic acid (PFTrDA)	72629-94-8	ng/L	0	N/A	0.6	0.6	ND	290	TX (GW)	C
Perfluorotetradecanoic acid (PFTeDA)	376-06-7	ng/L	50	0.9	0.7	0.9	D	290	TX (GW)	C
Perfluorohexadecanoic acid (PFHxDA)	67905-19-5	ng/L	30	1.3	5.7	5.7	ND	NA	N/A	
Perfluorooctadecanoic acid (PFODA)	16517-11-6	ng/L	0	N/A	0.6	0.6	ND	NA	N/A	
Sulfonates										
Perfluorobutane sulfonate (PFBS)	375-73-5	ng/L	100	8.9	N/A	8.9	D	7,000	MN (DW/GW1)	B
Perfluoropentane sulfonate (PFPeS)	2706-91-4	ng/L	70	7.7	0.6	7.7	D	NA	N/A	
Perfluorohexane sulfonate (PFHxS)	355-46-4	ng/L	100	44.4	N/A	44.4	D	47	MN (DW/GW2)	B
Perfluoroheptane sulfonate (PFHpS)	375-92-8	ng/L	20	1.7	0.6	1.7	D	NA	N/A	
Perfluorooctane sulfonate (PFOS)	1763-23-1	ng/L	100	32.7	N/A	32.7	D	12	MI (SW2)	A

Table 4
Regulatory and Threshold Values for PFAS Surface Water Concentrations

Chemical	CAS RN	Units	Frequency of Detection (%)	Maximum Detected Concentration[1]	Maximum Non-Detected Concentration[1]	Maximum Concentration[1,2]	Basis for Maximum (D/ND)	Threshold Value	Threshold Value Source[3]	Guidance Value Decision Criteria Category[4]
Perfluorononane sulfonate (PFNS)	68259-12-1	ng/L	0	N/A	0.6	0.6	ND	NA	N/A	
Perfluorodecane sulfonate (PFDS)	335-77-3	ng/L	0	N/A	0.6	0.6	ND	NA	N/A	
Sum PFOS + PFOA		ng/L	100	39.8	N/A	39.8	D	20	WI (GW)	B
Precursors and Replacement Chemistries										
Perfluorooctane sulfonamide (PFOSA)	754-91-6	ng/L	0	N/A	0.6	0.6	ND	200	OR (SW)	A
N-methyl perfluoro-1-octanesulfonamide (N-MeFOSA)	31506-32-8	ng/L	0	N/A	1.2	1.2	ND	NA	N/A	
N-ethyl perfluoro-1-octanesulfonamide (N-EtFOSA)	4151-50-2	ng/L	0	N/A	0.6	0.6	ND	NA	N/A	
N-methyl perfluorooctanesulfonamidoacetic acid (N-MeFOSAA)	2355-31-9	ng/L	0	N/A	1.2	1.2	ND	NA	N/A	
N-ethyl perfluorooctanesulfonamidoacetic acid (N-EtFOSAA)	2991-50-6	ng/L	0	N/A	1.2	1.2	ND	NA	N/A	
2-(N-methyl perfluoro-1-octanesulfonamido)-ethanol (N-MeFOSE)	24448-09-7	ng/L	0	N/A	0.6	0.6	ND	NA	N/A	
2-(N-ethyl perfluoro-1-octanesulfonamido)-ethanol (N-EtFOSE)	1691-99-2	ng/L	0	N/A	0.6	0.6	ND	NA	N/A	
4:2 fluorotelomer sulfonate (4:2 FTS)	757124-72-4	ng/L	0	N/A	6.1	6.1	ND	NA	N/A	
1H,1H,2H,2H-perfluorooctanesulfonic acid (THPFOS) (6:2 FTS)	27619-97-2	ng/L	50	19.8	5.9	19.8	D	200	CAN (DW)	C
1H,1H,2H,2H-perfluorodecanesulphonic acid (8:2 FTS)	39108-34-4	ng/L	0	N/A	1.2	1.2	ND	200	CAN (DW)	C
10:2-fluorotelomer sulfonate (10:2 FTS)	120226-60-0	ng/L	0	N/A	1.2	1.2	ND	NA	N/A	
2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-propanoic acid (GenX)	13252-13-6	ng/L	0	N/A	0.6	0.6	ND	700	OH (DW)	B
11-chloroeicosafluoro-3-oxaundecane-1-sulfonate (PF3OUdS) (F53B minor)	763051-92-9	ng/L	0	N/A	1.2	1.2	ND	NA	N/A	
9-chlorohexadecafluoro-3-oxanonnane-1-sulfonate (PF3ONS) (F53B major)	73606-19-6	ng/L	0	N/A	0.6	0.6	ND	NA	N/A	
Sodium dodecafluoro-3H-4,8-dioxanonanoate (ADONA)	919005-14-4	ng/L	0	N/A	0.6	0.6	ND	NA	N/A	

Table 4
Regulatory and Threshold Values for PFAS Surface Water Concentrations

Notes:
1: Values are rounded to two significant figures.
2: Maximum concentration is the maximum detected concentration unless all non-detect, then maximum non-detect concentration is the maximum concentration.
3: Threshold value sources
  MI (SW1): Michigan Surface Water, Human Noncancer Value (HNV) for non-drinking water source (2011)
  MI (SW2): Michigan Surface Water, Human Noncancer Value (HNV) for non-drinking water source (2014)
  MN (DW/GW1): Minnesota Drinking Water/Groundwater Chronic Health Risk Limit (HRL) (2009/2011/2018)
  MN (GW/GW2): Minnesota Drinking Water/Groundwater Chronic Health-Based Value (HBV, not promulgated) (2017/2019)
  TX (GW): Texas Groundwater Tier 1 Protective Concentration Level (PCL) (2016)
  OR (SW): Oregon Surface Water Initiation Level (IL)(2011)
  WI (GW): Wisconsin Groundwater Enforcement Standard Recommended Value (2020)
  CAN (DW): Canada Drinking Water Screening Value (DWSV) (2019)
  OH (DW): Ohio Drinking Water Action Level (2019)
4: Guidance Value Decision Criteria Categories:
  A) Surface water values (non drinking water source, if specified)
  B) Geographically co-located drinking water or groundwater values (where multiple values were available, chronic values were chosen over subchronic values and promulgated values were chosen over non-promulgated or values in development
  C) The only guidance value available for the compound
CAS RN: Chemical Abstracts Service Registry Number
D: detect (Basis for Maximum [D/ND] column)
N/A: not applicable
NA: not available
ND: non-detect (Basis for Maximum [D/ND] column)
ng/L: nanogram per liter

Table 5

Comparison of MKE AOC Sediment PFAS Concentrations to Published Values

Analyte	Length of Carbon Chain	Range of Concentrations (ng/g)			
		Lake Michigan Sediments 2010^{a,b}	Lake Michigan Sediments 2011^{a,b}	MKE AOC Sediments – Harbor and Bay Stations^{c} 2019	MKE AOC Sediments – Riverine Stations^{d} 2019
Perfluorocarboxylic Acids (PFCAs)					
Perfluorobutanoate (PFBA)	C4	ND - 1.32	All ND	*0.26* - 0.34	*0.36* - 0.79
Perfluoropentanoate (PFPeA)	C5	ND - 1.30	0.2 - 2.2	All ND (*0.29*)	All ND (*0.29*)
Perfluorohexanoate (PFHxA)	C6	--	0.2 - 1.7	All ND (*0.36*)	All ND (*0.36*)
Perfluoroheptanoate (PFHpA)	C7	--	0.0 - 46.7	All ND (*0.29*)	All ND (*0.29*)
Perfluorooctanoate (PFOA)	C8	ND - 3.7	0.1 - 3.3	All ND (*0.36*)	All ND (*0.36*)
Perfluorononanoate (PFNA)	C9	--	0.1 - 3.0	All ND (*0.29*)	All ND (*0.29*)
Perfluorodecanoate (PFDA)	C10	--	0.4 - 11.0	All ND (*0.66*)	All ND (*0.66*)
Perfluoroundecanoate (PFUnA)	C11	--	0.7 - 0.9	All ND (*0.29*)	*0.29* - 0.35
Perfluorododecanoate (PFDoA)	C12	All ND	All ND	All ND (*0.29*)	*0.29* - 1.5
Perfluorotridecanoate (PFTrDA)	C13	--	All ND	All ND (*0.29*)	*0.29* - 0.70
Perfluorotetradecanoate (PFTeDA)	C14	ND - 0.3	0.0 - 1.7	All ND (*0.36*)	*0.36* - 1.5
Perfluorohexadecanoate (PFHxDA)	C16	--	All ND	All ND (*1.11*)	*1.11* - 0.59
Perfluorosulfonic Acids (PFSAs)					
Perfluorobutane sulfonate (PFBS)	C4	ND - 7.9	0.3 - 9.0	All ND (*0.29*)	All ND (*0.29*)
Perfluorohexane sulfonate (PFHxS)	C6	--	0.3 - 2.9	All ND (*0.29*)	*0.29* - 0.57
Perfluorooctane sulfonate (PFOS)	C8	ND - 12.8	0.1 - 8.2	0.21 - 0.25	*0.36* - 9.1
Perfluorodecane sulfonate (PFDS)	C10	--	0.1 - 1.9	All ND (*0.29*)	*0.29* - 7.6
Precursors and Replacement Chemistries					
Perfluorooctane sulfonamide (PFOSA)	--	ND - 0.78	All ND	All ND (*0.29*)	*0.29* - 3.5
N-methyl perfluoro-1-octanesulfonamide (N-MeFOSA)	--	All ND	--	All ND (*0.77*)	All ND (*0.77*)
N-ethyl perfluoro-1-octanesulfonamide (N-EtFOSA)	--	All ND	--	All ND (*0.79*)	*0.79* - 0.73
2-(N-methyl perfluoro-1-octanesulfonamido)-ethanol (N-MeFOSE)	--	ND - 0.98	All ND	All ND (*0.69*)	*0.69* - 0.94
2-(N-ethyl perfluoro-1-octanesulfonamido)-ethanol (N-EtFOSE)	--	ND - 0.86	All ND	All ND (*0.70*)	*0.70* - 1.0

Notes:

Italicized and underlined values are equal to the average MDL for MKE AOC sediments. In some instances the average MDL is greater than the detected concentrations.

Lake Michigan 2010 sediment PFAS concentrations obtained from: Codling et al., 2014. "Historical trends of inorganic and organic fluorine in sediments of Lake Michigan." *Chemosphere 114* : 203-209.

Lake Michigan 2011 sediment PFAS concentrations obtained from: Codling et al., 2018. "Current and historical concentrations of poly and perfluorinated compounds in sediments of the northern Great Lakes - Superior, Huron, and Michigan." *Environmental Pollution 236* : 373-381.

Blue highlights indicate compounds where the MKE AOC river locations may be above published concentrations found in Lake Michigan.

Green highlights indicate MKE AOC river concentrations below those found in Lake Michigan.

a. Lake Michigan samples are reported as a range of both ponar and sediment core samples.

b. Detection and limit of quantitation values were not given in Codling et al. 2014 or Codling et al 2018.

c. Harbor and bay stations are stations MKE-19-12, MKE-19-13, and MKE-19-14.

d. River stations are stations MKE-19-01 through MKE-19-11.

Abbreviations:

MDL: method detection limit

MKE AOC: Milwaukee River Estuary Area of Concern

ng/g: nanograms per gram

PFAS: perfluoroalkyl and polyfluoroalkyl substances

Figures

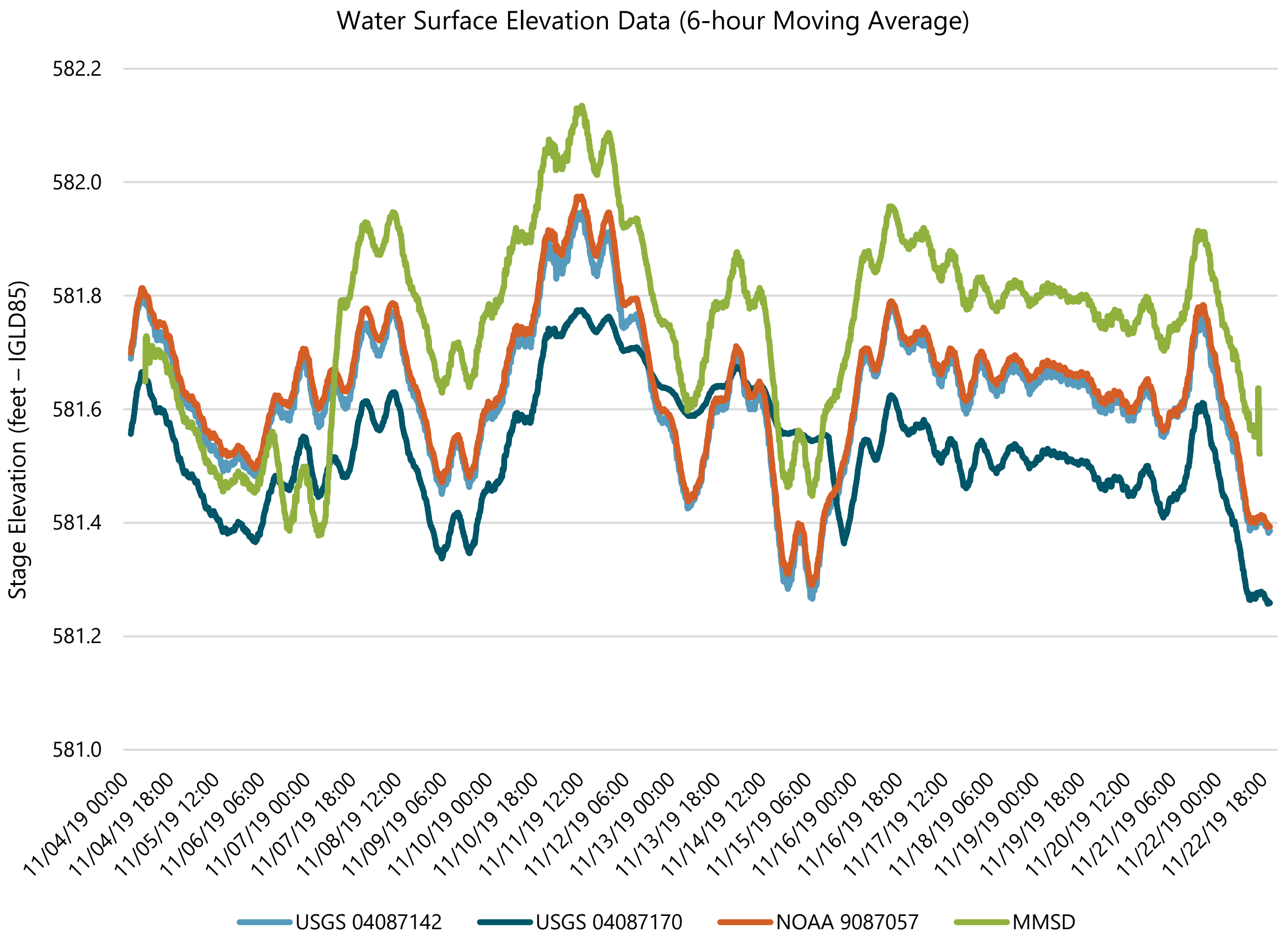
Publish Date: 2020/08/14, 3:47 PM | User: bhurry
Filepath: Q:\Jobs\WisconsinDNR_1779\Requests\Maps\Figures\AQ_Figure01_WIDNR_PFAS_SpecialStudy_SiteLocation.mxd

ANCHOR QEA

Figure 1
Study Area

Publish Date: 2020/10/30, 11:13 AM | User: jquinley
Filepath: \\orcas\GIS\Jobs\WisconsinDNR_1779\Milwaukee_1779\Maps\PFOS_PFOA\AQ_WIDNR_PFOS_PFAS_Figure2_SiteSamplingLocations.mxd

Figure 2
Sampling Locations

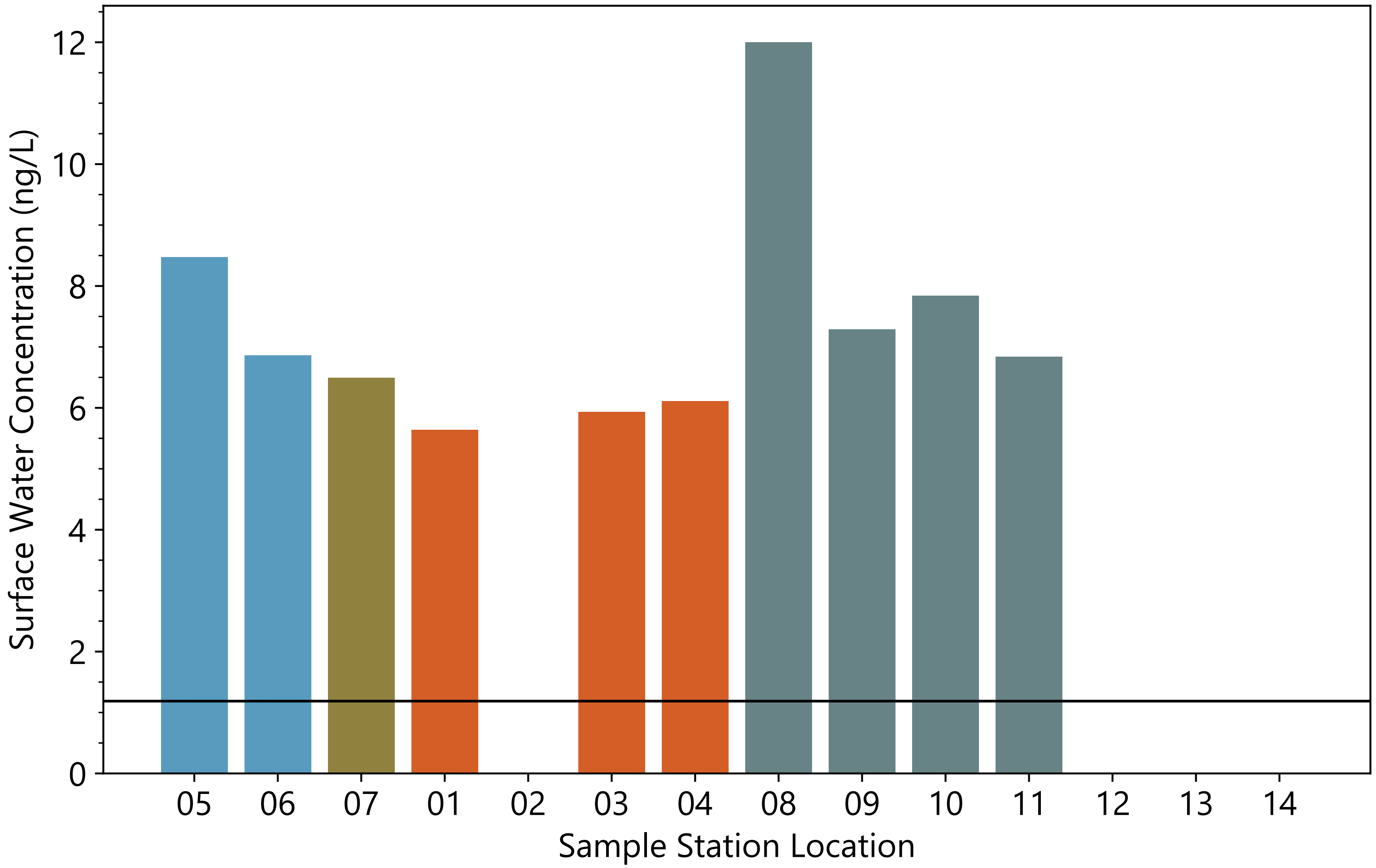


Notes:

1. Water levels were obtained from USGS Station 4087142, USGS Station 04087170, NOAA Station 9087057, and the project specific station temporarily installed at the MMSD dock
2. Stage elevations are in IGLD85 feet.
3. Average water levels are averaged on a 6-hour scale.

IGLD85: International Great Lakes Datum 1985
MMSD: Milwaukee Metropolitan Sewer District
NOAA: National Oceanic and Atmospheric Administration
USGS: U.S. Geological Survey

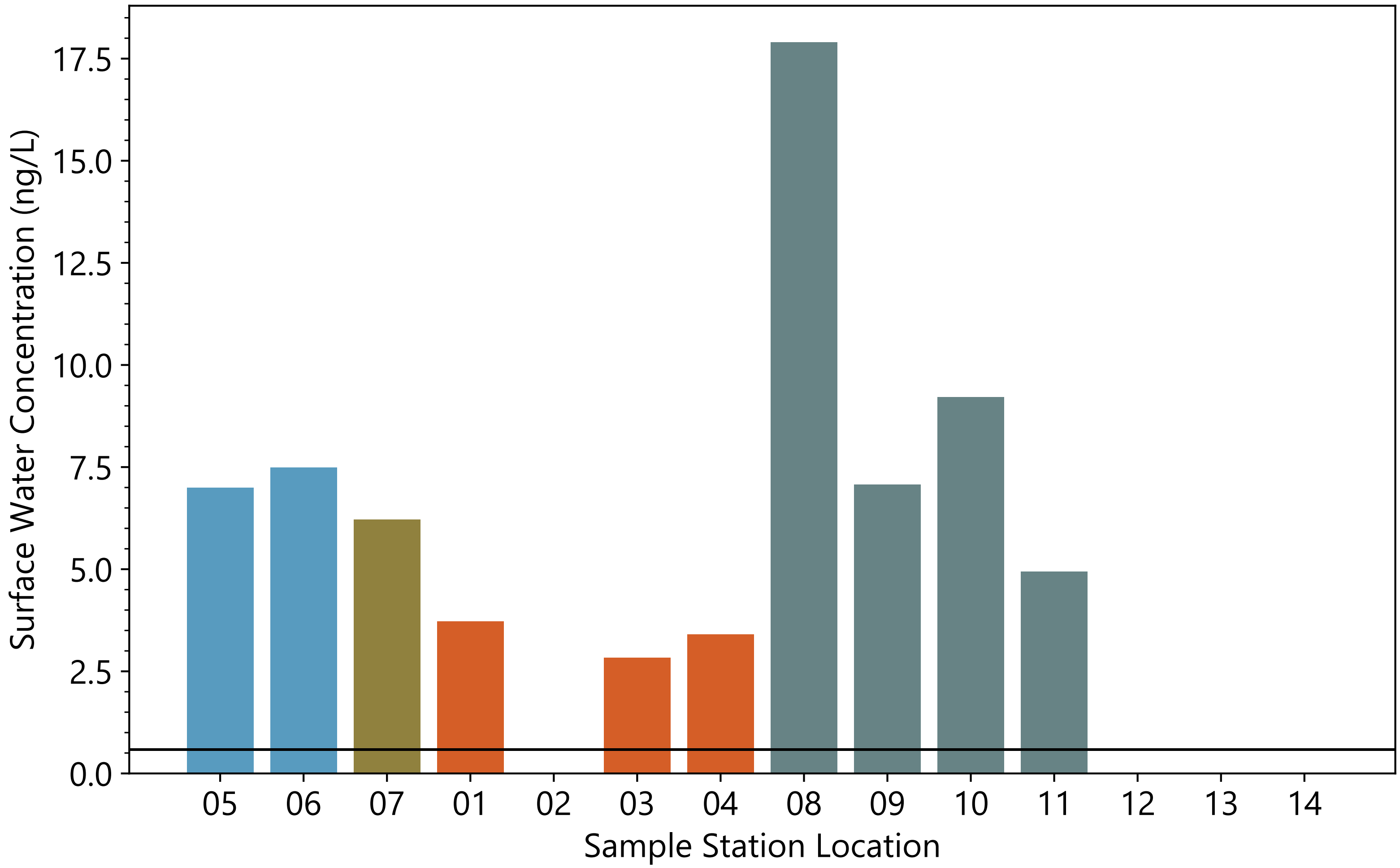
Figure 3
Surface Water Elevation Hydrograph
PFAS Special Study Report



Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

🟦 Menomonee River	■ Kinnickinnic River
🟨 South Menomonee Canal	🟫 Harbor
🟧 Milwaukee River	🟪 Lake Michigan

Figure 4a
Perfluorobutanoate (PFBA) Concentrations for MKE AOC



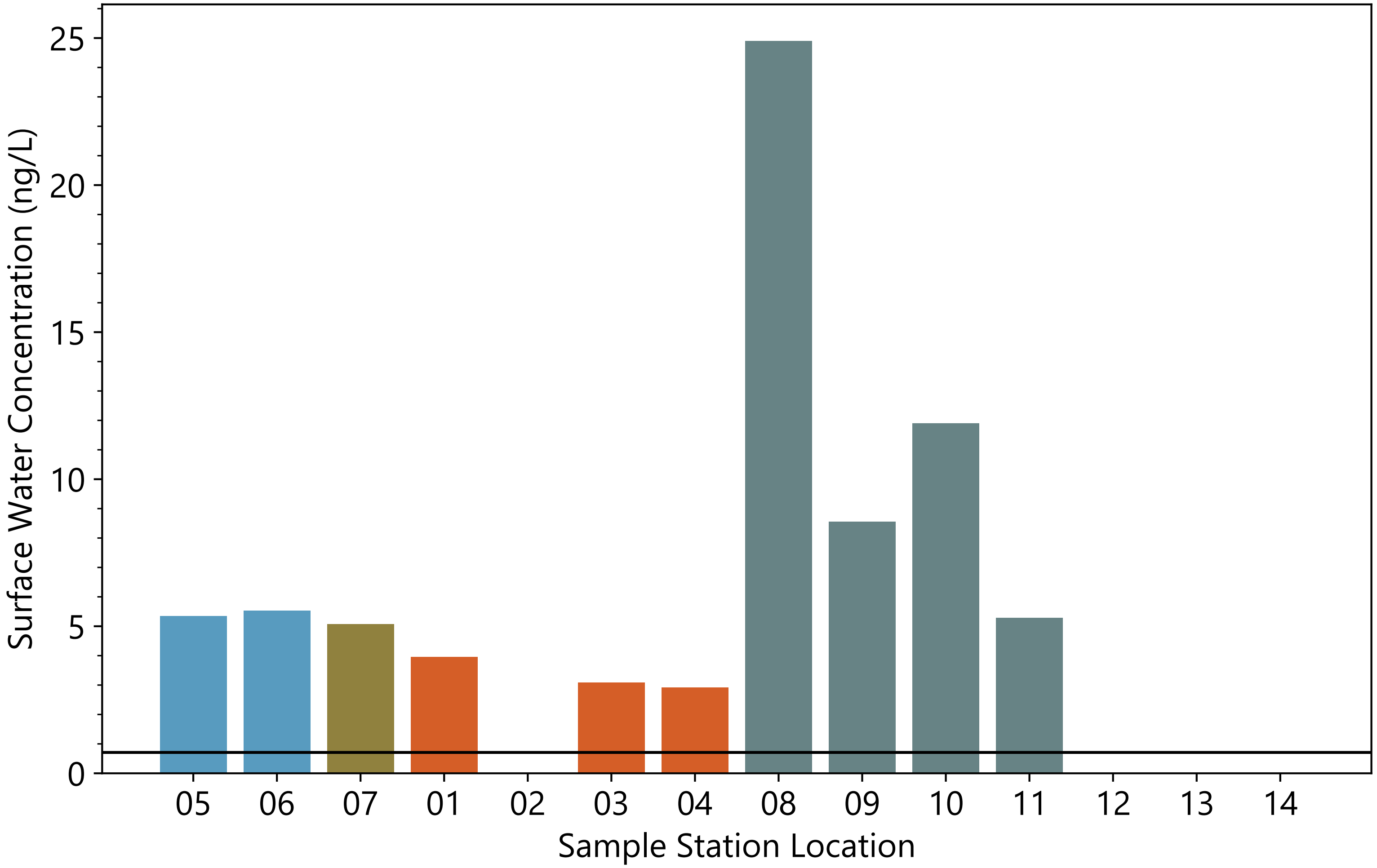
Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

- 🟦 Menomonee River
- 🟫 South Menomonee Canal
- 🟧 Milwaukee River
- ⬛ Kinnickinnic River
- 🟫 Harbor
- 🟪 Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 4b
Perfluoropentanoate (PFPeA) Concentrations for MKE AOC



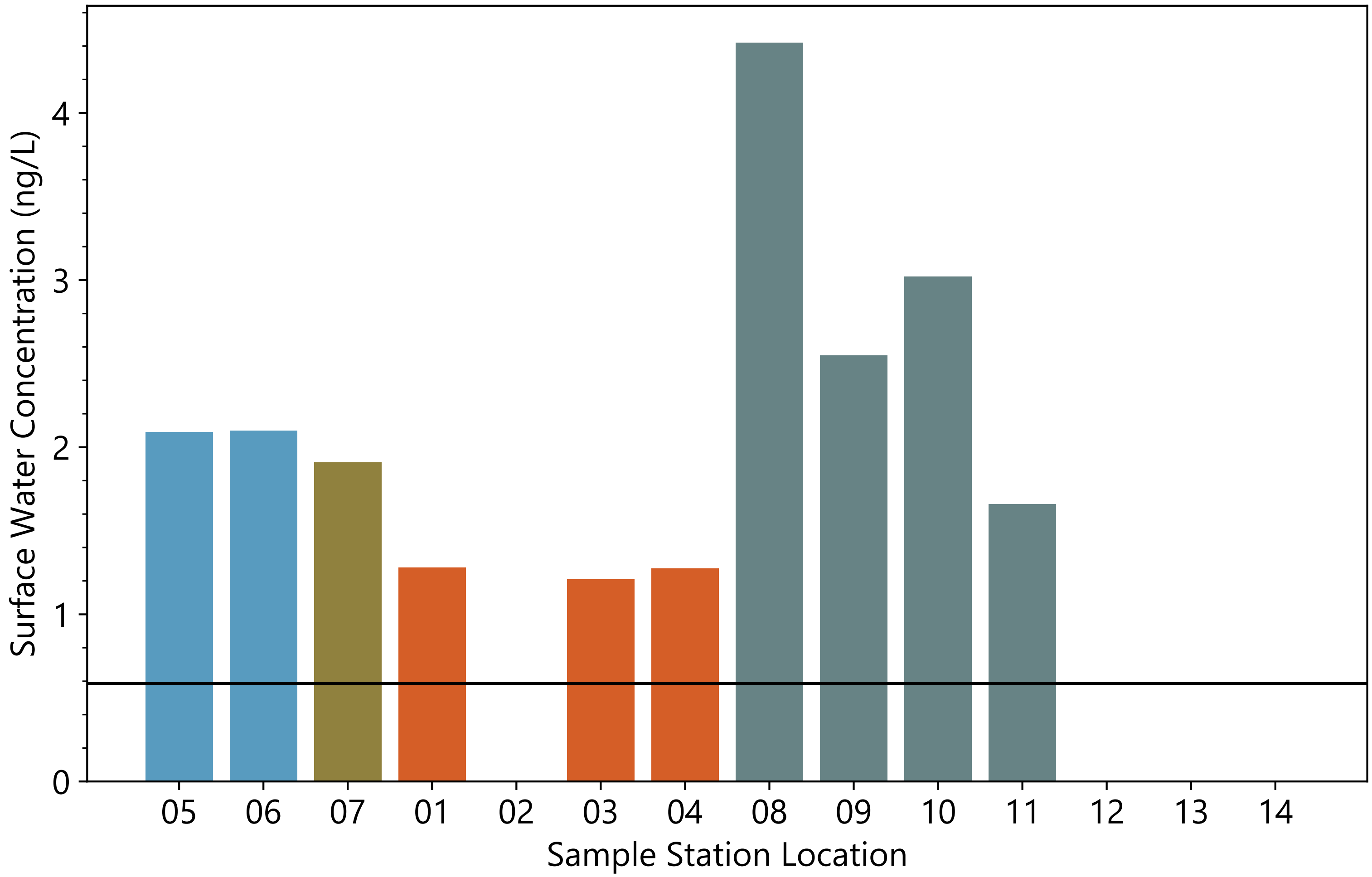
Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

■ Menomonee River
■ South Menomonee Canal
■ Milwaukee River
■ Kinnickinnic River
■ Harbor
■ Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 4c
Perfluorohexanoate (PFHxA) Concentrations for MKE AOC



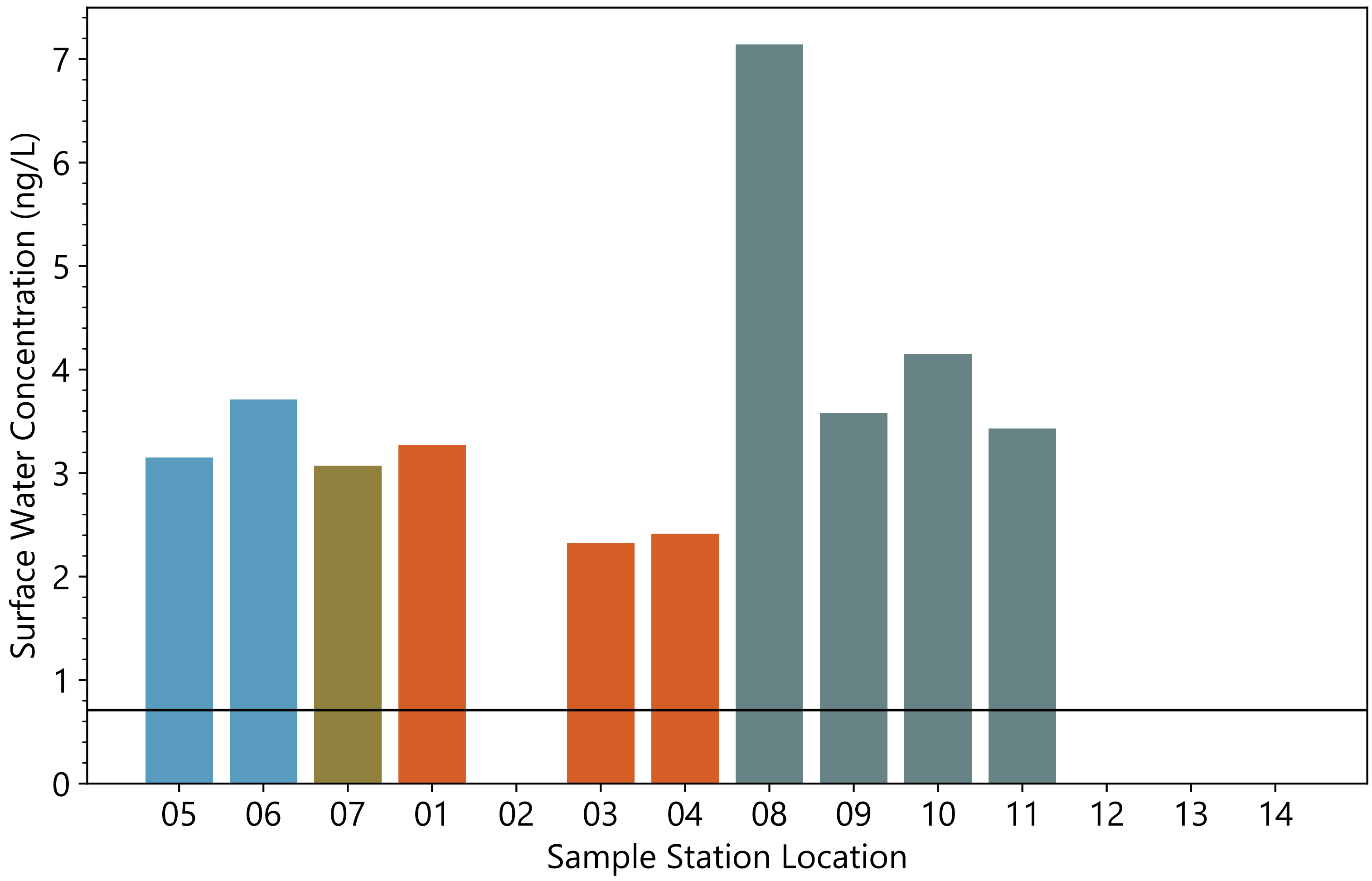
Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

🟦 Menomonee River
■ South Menomonee Canal
🟧 Milwaukee River
■ Kinnickinnic River
🟫 Harbor
🟪 Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 4d
Perfluoroheptanoate (PFHpA) Concentrations for MKE AOC

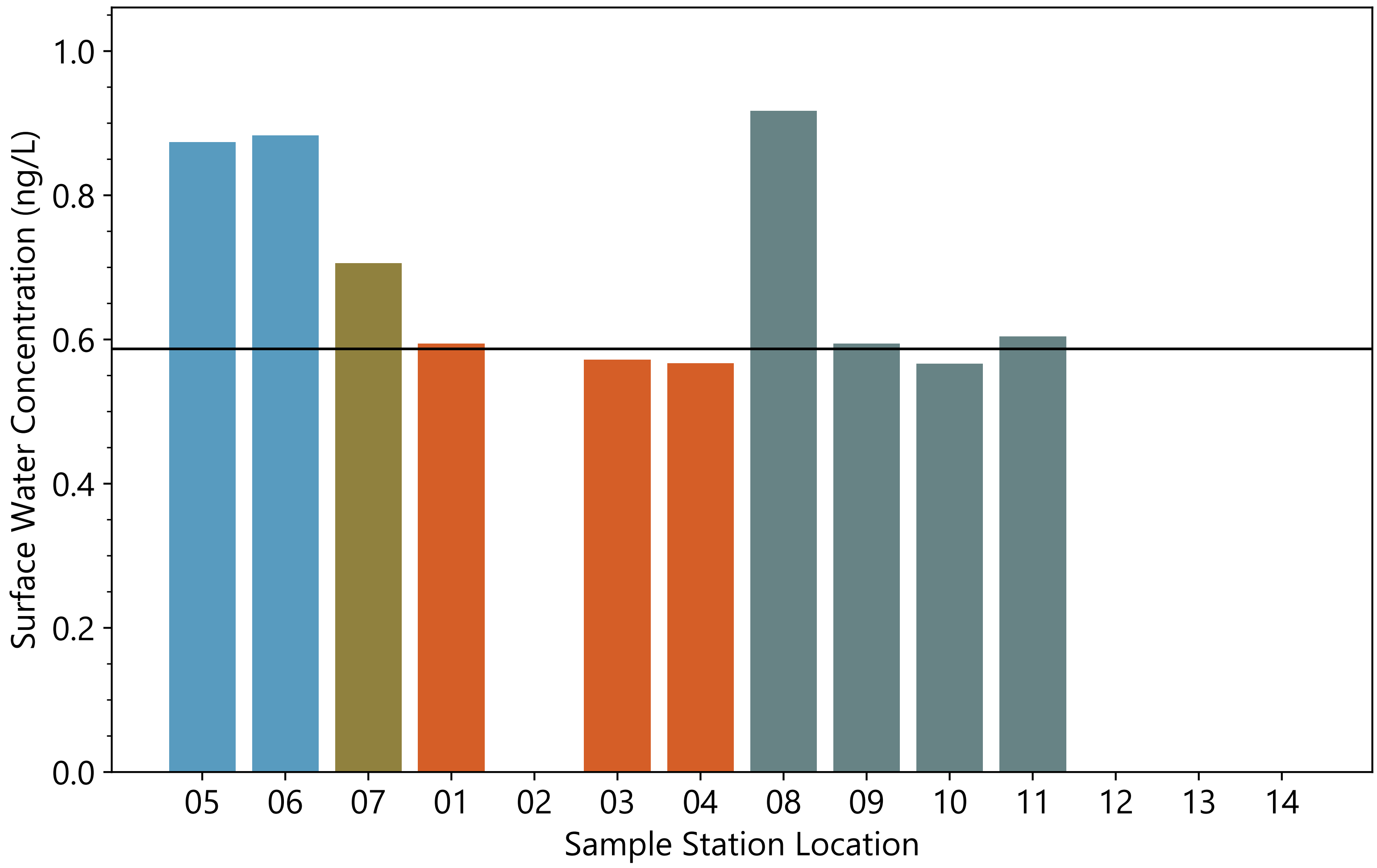


Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 4e
Perfluorooctanoate (PFOA) Concentrations for MKE AOC



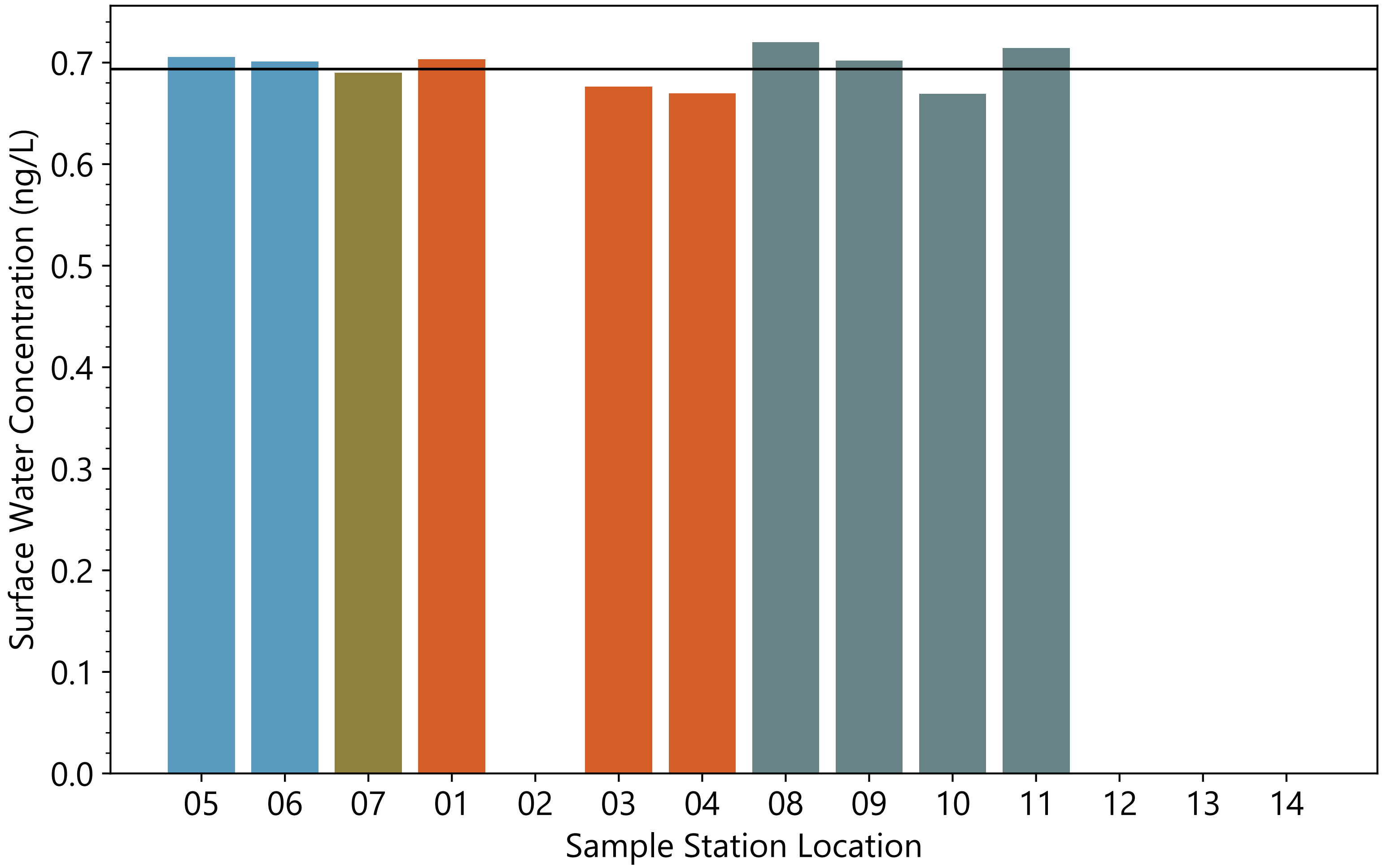
Notes:

1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

🟦 Menomonee River	🟦 Kinnickinnic River
🟫 South Menomonee Canal	🟫 Harbor
🟧 Milwaukee River	🟪 Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

Figure 4f
Perfluorononanoate (PFNA) Concentrations for MKE AOC



Notes:

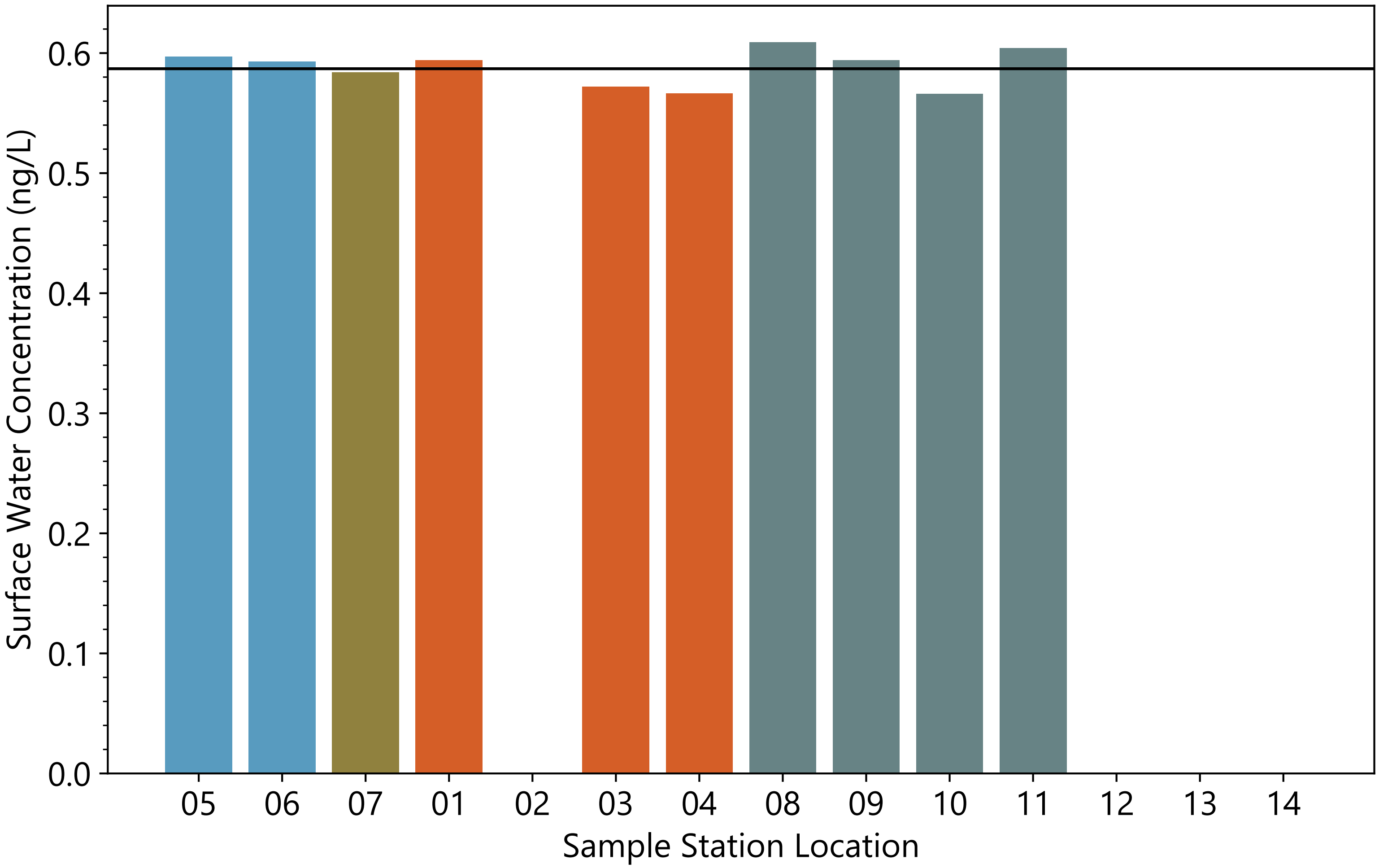
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

🟦 Menomonee River
🟨 South Menomonee Canal
🟧 Milwaukee River
⬛ Kinnickinnic River
🟫 Harbor
🟪 Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

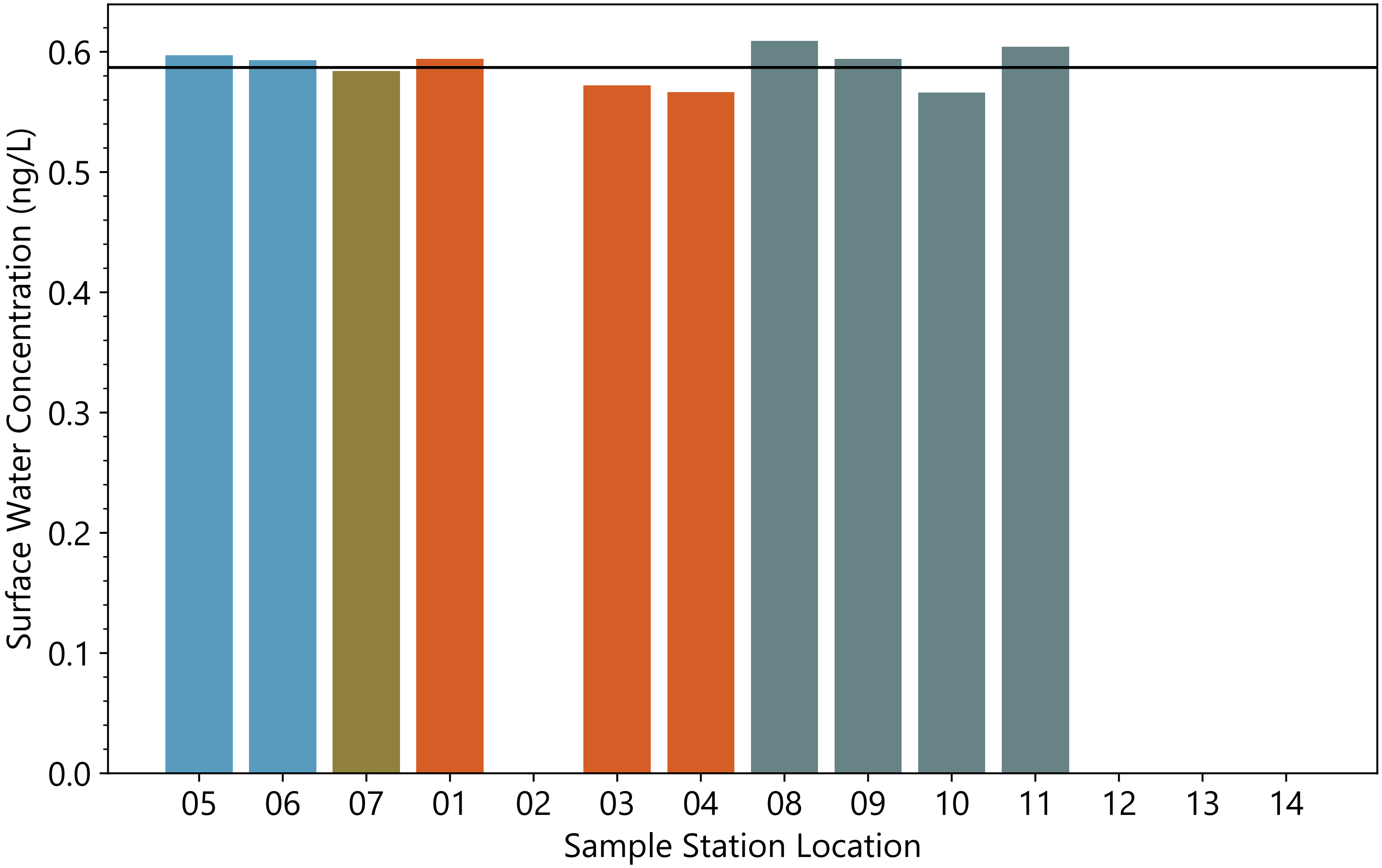
ANCHOR QEA

Figure 4g
Perfluorodecanoate (PFDA) Concentrations for MKE AOC



Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

Figure 4h
Perfluoroundecanoate (PFUnA) Concentrations for MKE AOC



Notes:

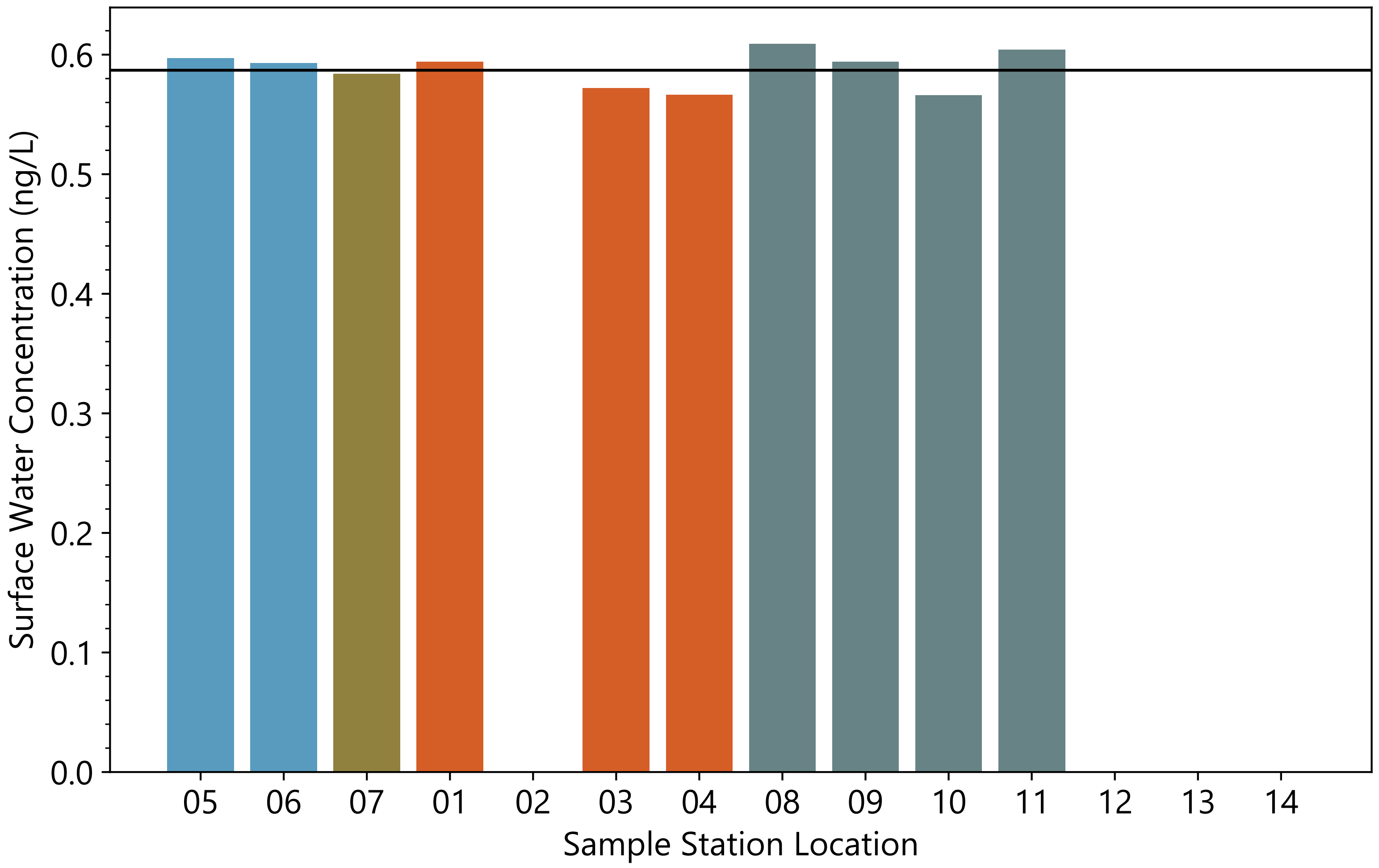
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

🟦	Menomonee River	🟦	Kinnickinnic River
🟫	South Menomonee Canal	🟫	Harbor
🟧	Milwaukee River	🟪	Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

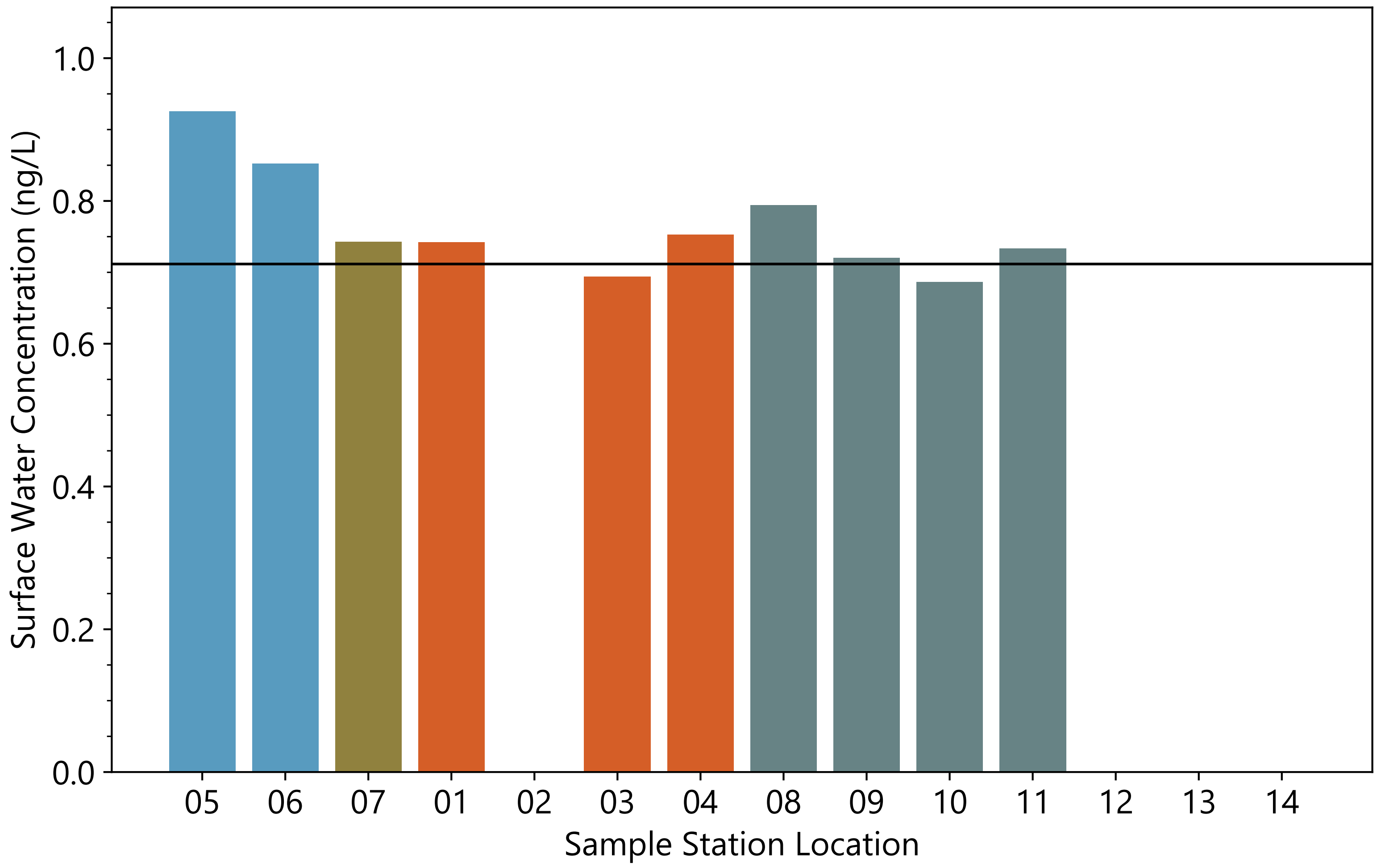
Figure 4i
Perfluorododecanoate (PFDoA) Concentrations for MKE AOC



Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

■ Menomonee River
■ South Menomonee Canal
■ Milwaukee River
■ Kinnickinnic River
■ Harbor
■ Lake Michigan

Figure 4j
Perfluorotridecanoic acid (PFTrDA) Concentrations for MKE AOC



Notes:

1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

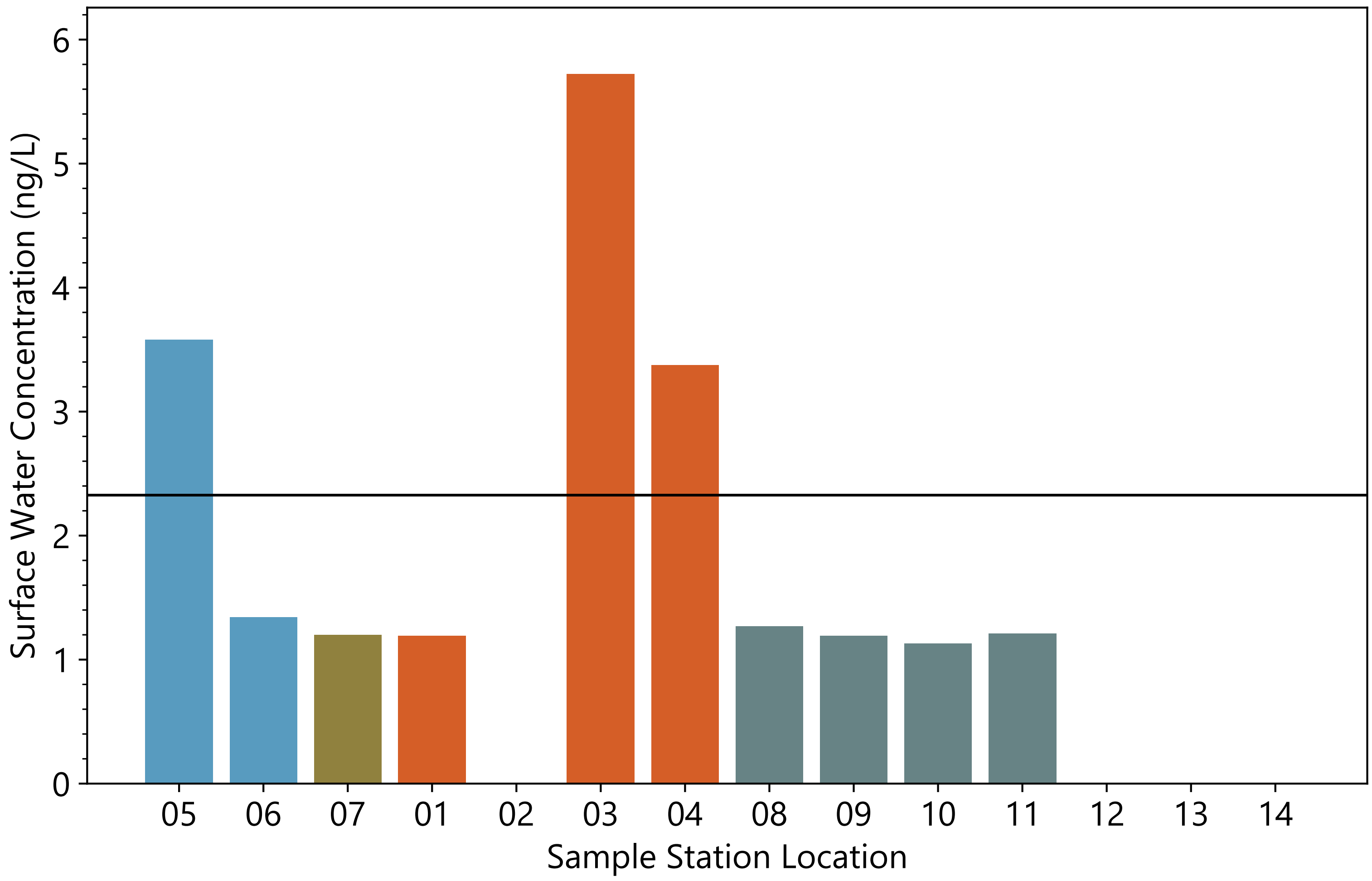
■	Menomonee River	■	Kinnickinnic River
■	South Menomonee Canal	■	Harbor
■	Milwaukee River	■	Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 4k

Perfluorotetradecanoic acid (PFTeDA) Concentrations for MKE AOC



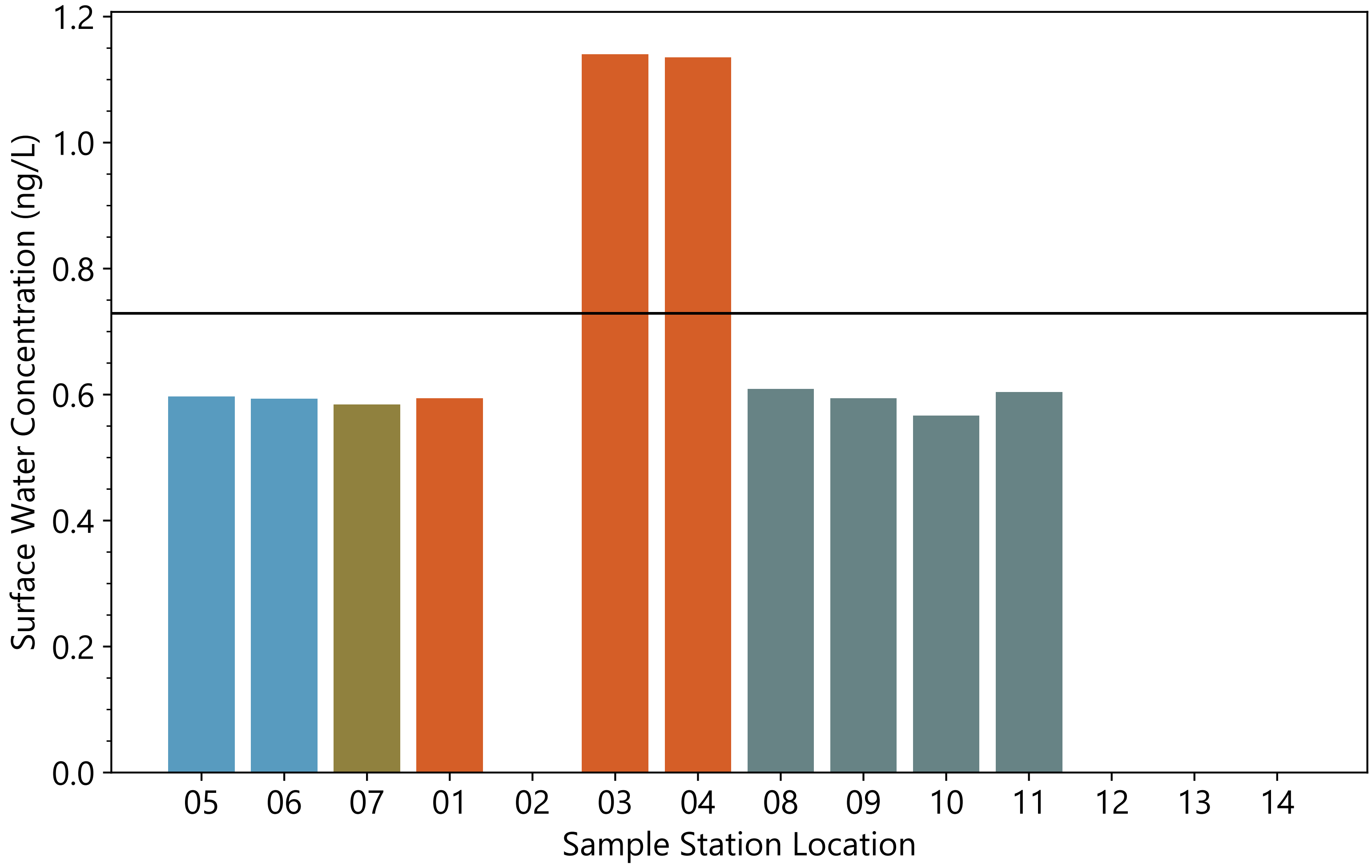
Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

■	Menomonee River	■	Kinnickinnic River
■	South Menomonee Canal	■	Harbor
■	Milwaukee River	■	Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

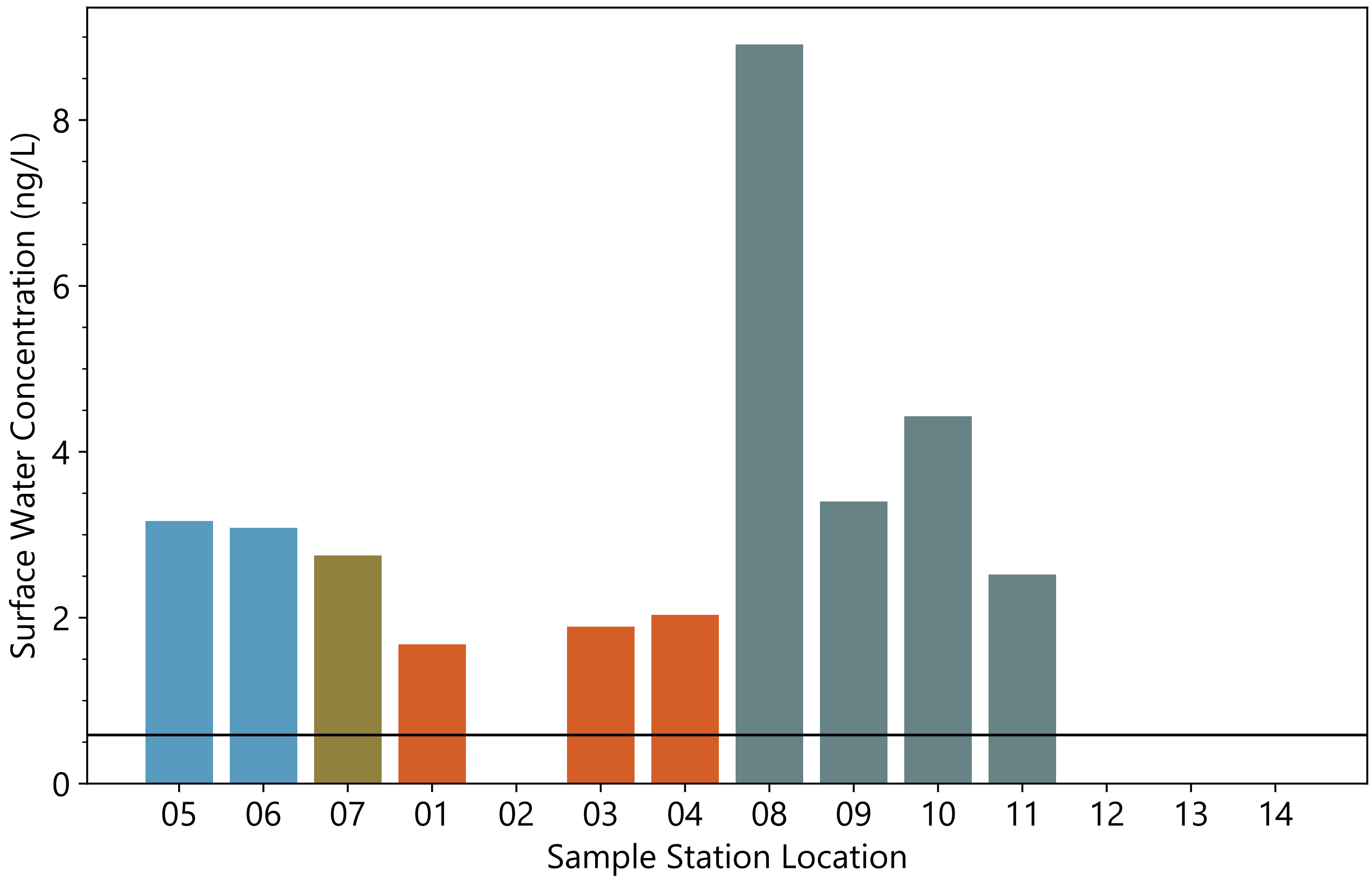
ANCHOR QEA

Figure 4l
Perfluorohexadecanoic acid (PFHxDA) Concentrations for MKE AOC



Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

Figure 4m
Perfluorooctadecanoic acid (PFODA) Concentrations for MKE AOC



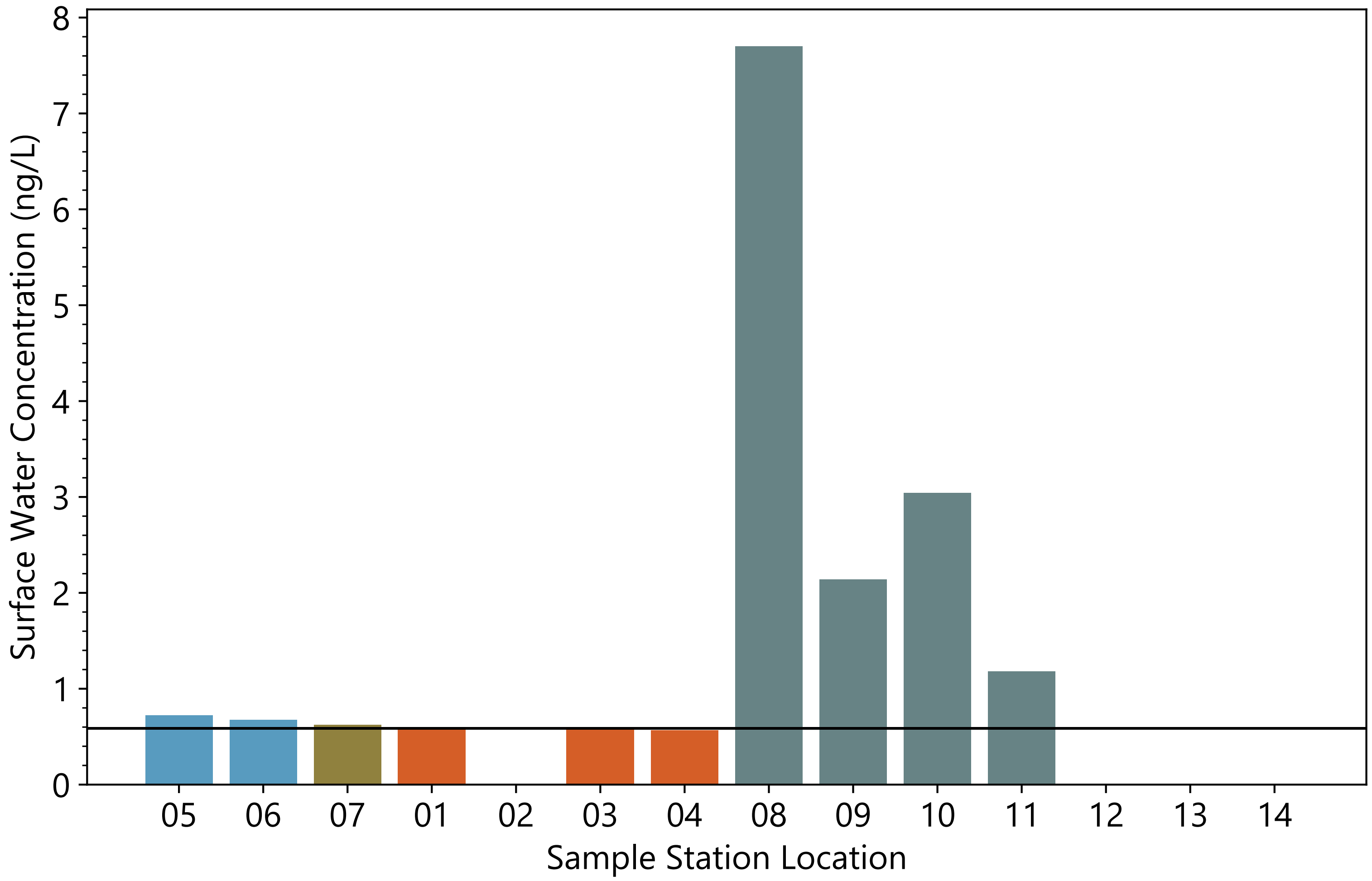
Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

🟦 Menomonee River
■ South Menomonee Canal
🟧 Milwaukee River
■ Kinnickinnic River
🟫 Harbor
🟪 Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 4n
Perfluorobutane sulfonate (PFBS) Concentrations for MKE AOC

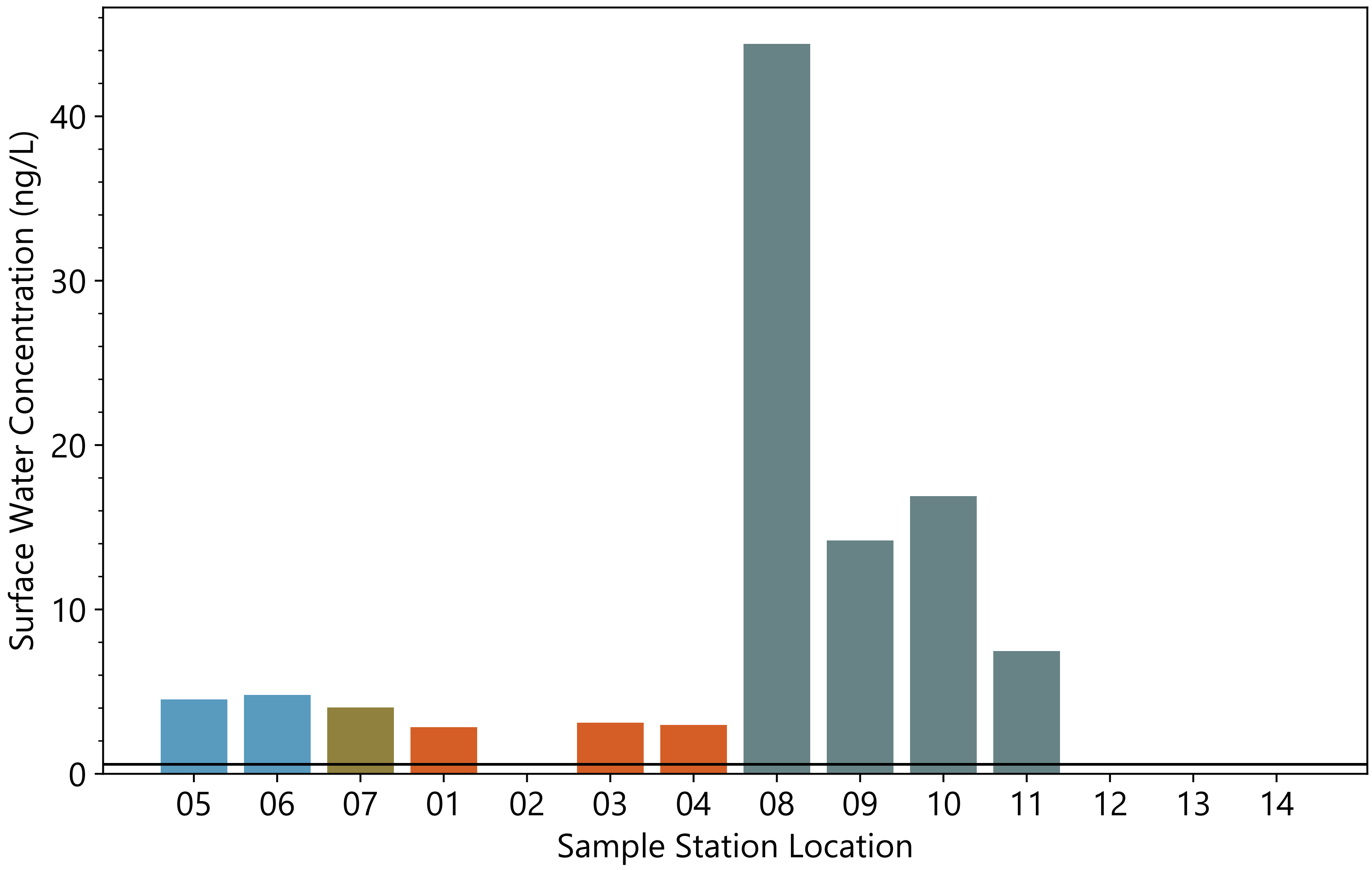


Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

■ Menomonee River
■ South Menomonee Canal
■ Milwaukee River
■ Kinnickinnic River
■ Harbor
■ Lake Michigan

ANCHOR QEA

Figure 4o
Perfluoropentane sulfonate (PFPeS) Concentrations for MKE AOC

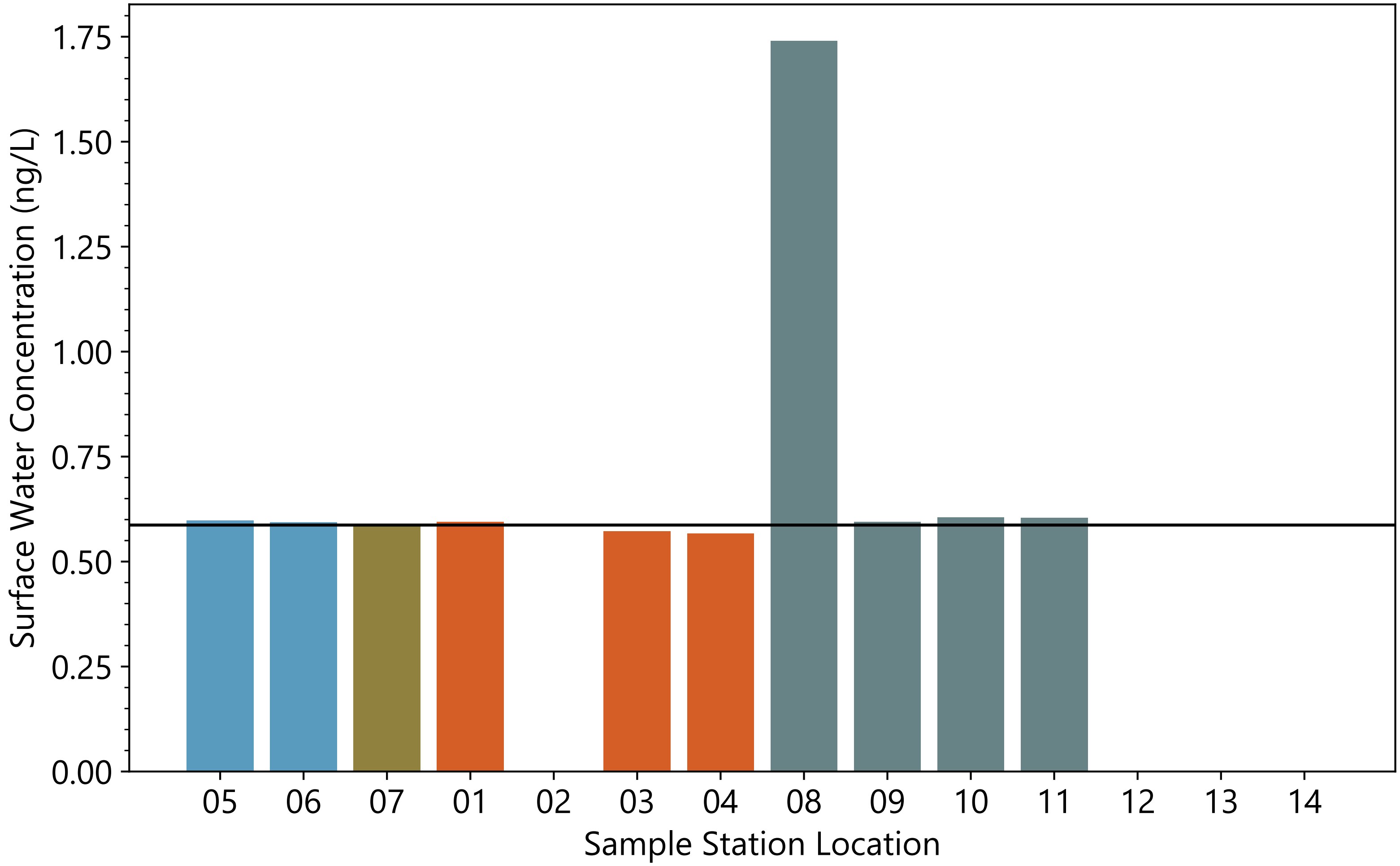


Notes:

1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

Figure 4p
Perfluorohexane sulfonate (PFHxS) Concentrations for MKE AOC

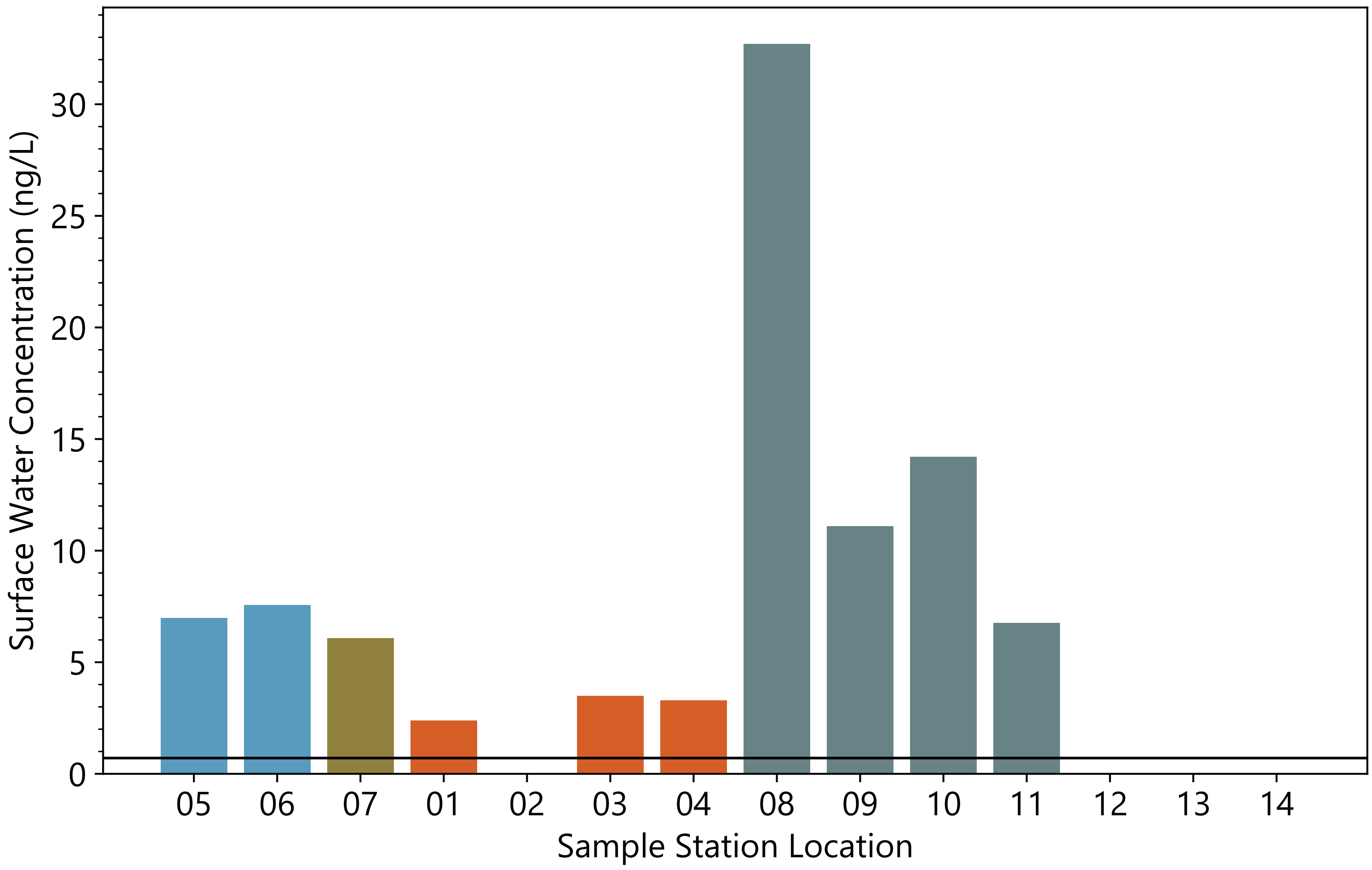


Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

🟦 Menomonee River
🟨 South Menomonee Canal
🟧 Milwaukee River
⬛ Kinnickinnic River
🟫 Harbor
🟪 Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

Figure 4q
Perfluoroheptane sulfonate (PFHpS) Concentrations for MKE AOC



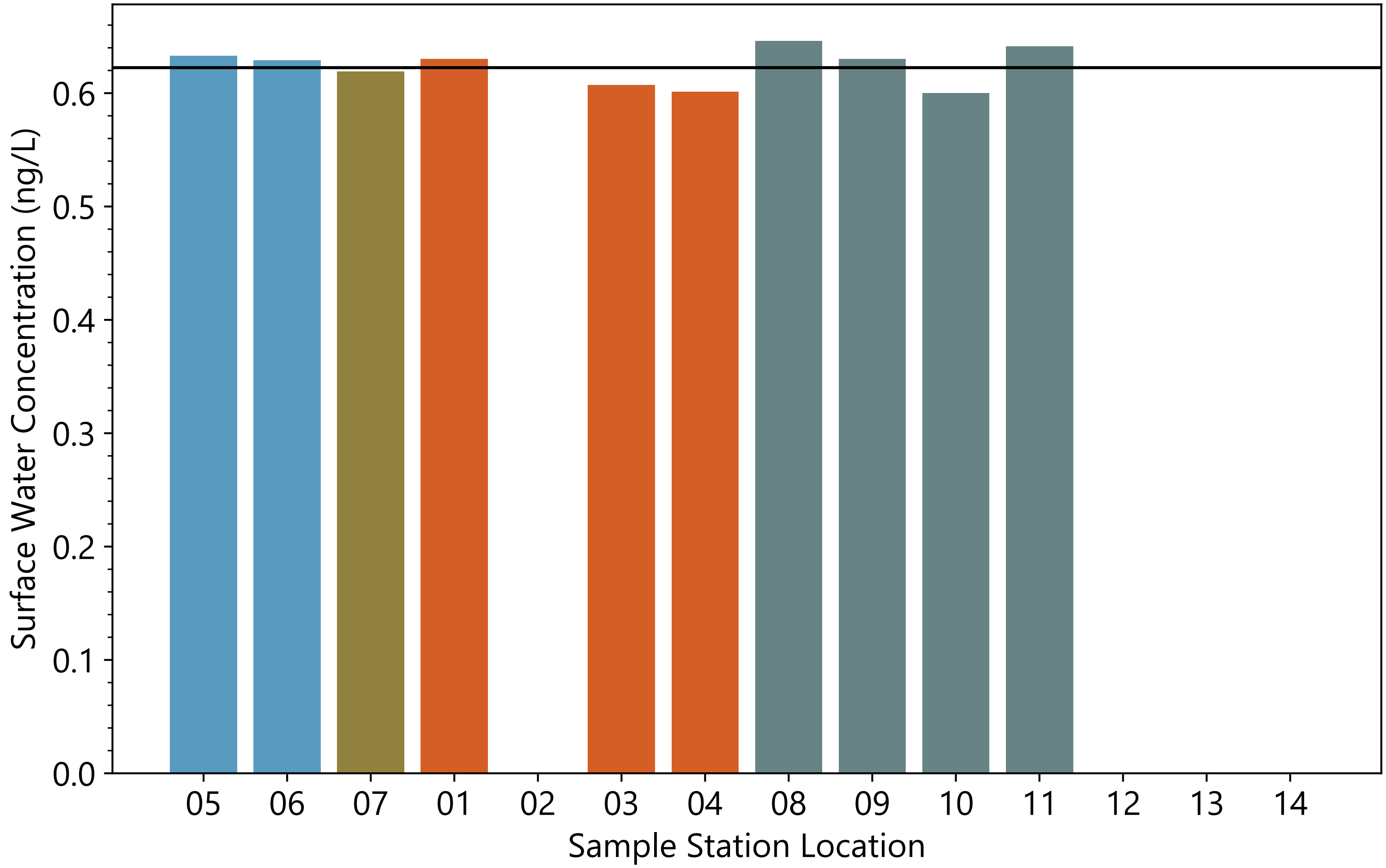
Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

■	Menomonee River	■	Kinnickinnic River
■	South Menomonee Canal	■	Harbor
■	Milwaukee River	■	Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 4r
Perfluorooctane sulfonate (PFOS) Concentrations for MKE AOC

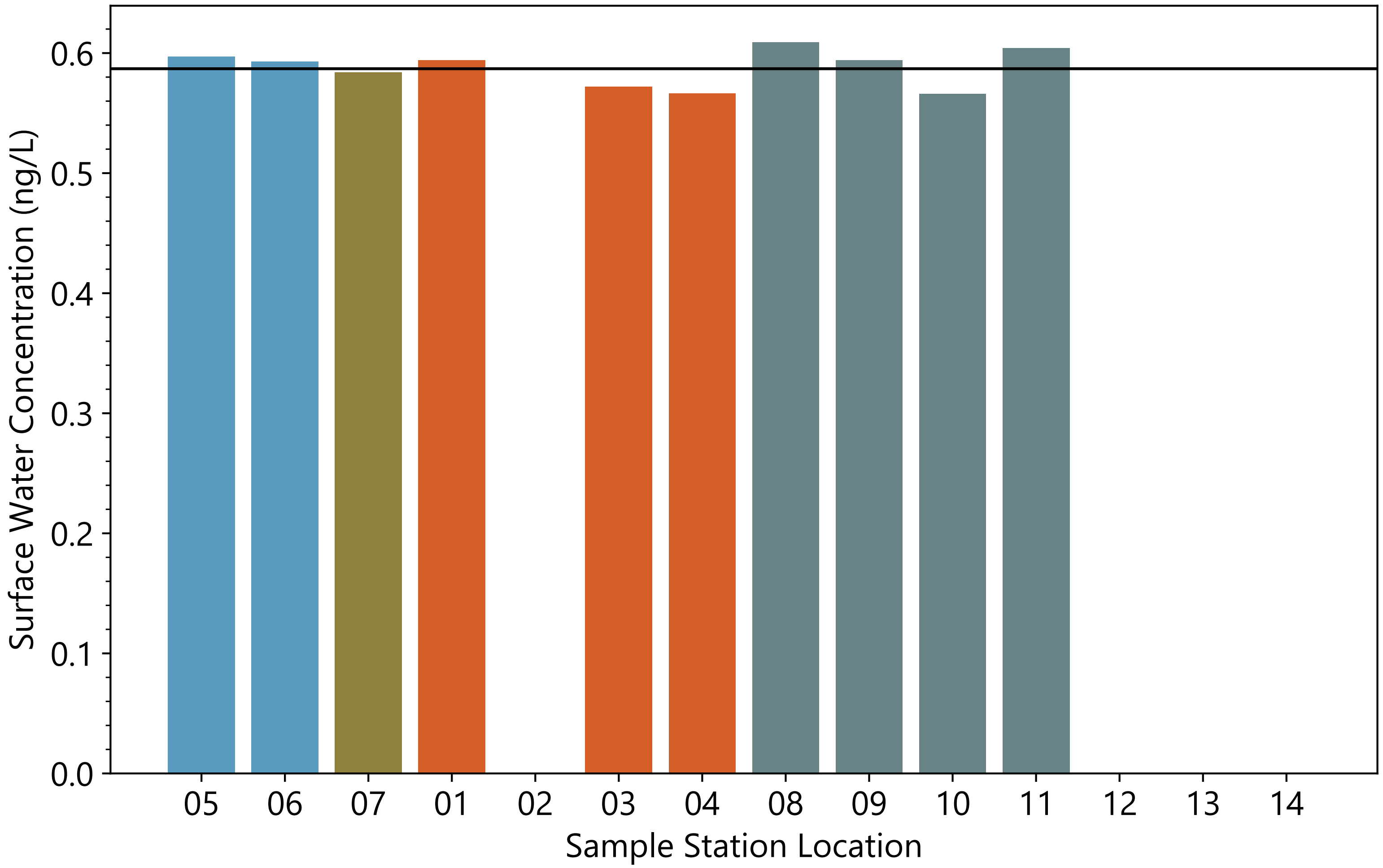


Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

🟦	Menomonee River	■	Kinnickinnic River
■	South Menomonee Canal	■	Harbor
🟧	Milwaukee River	🟪	Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

Figure 4s
Perfluorononane sulfonate (PFNS) Concentrations for MKE AOC

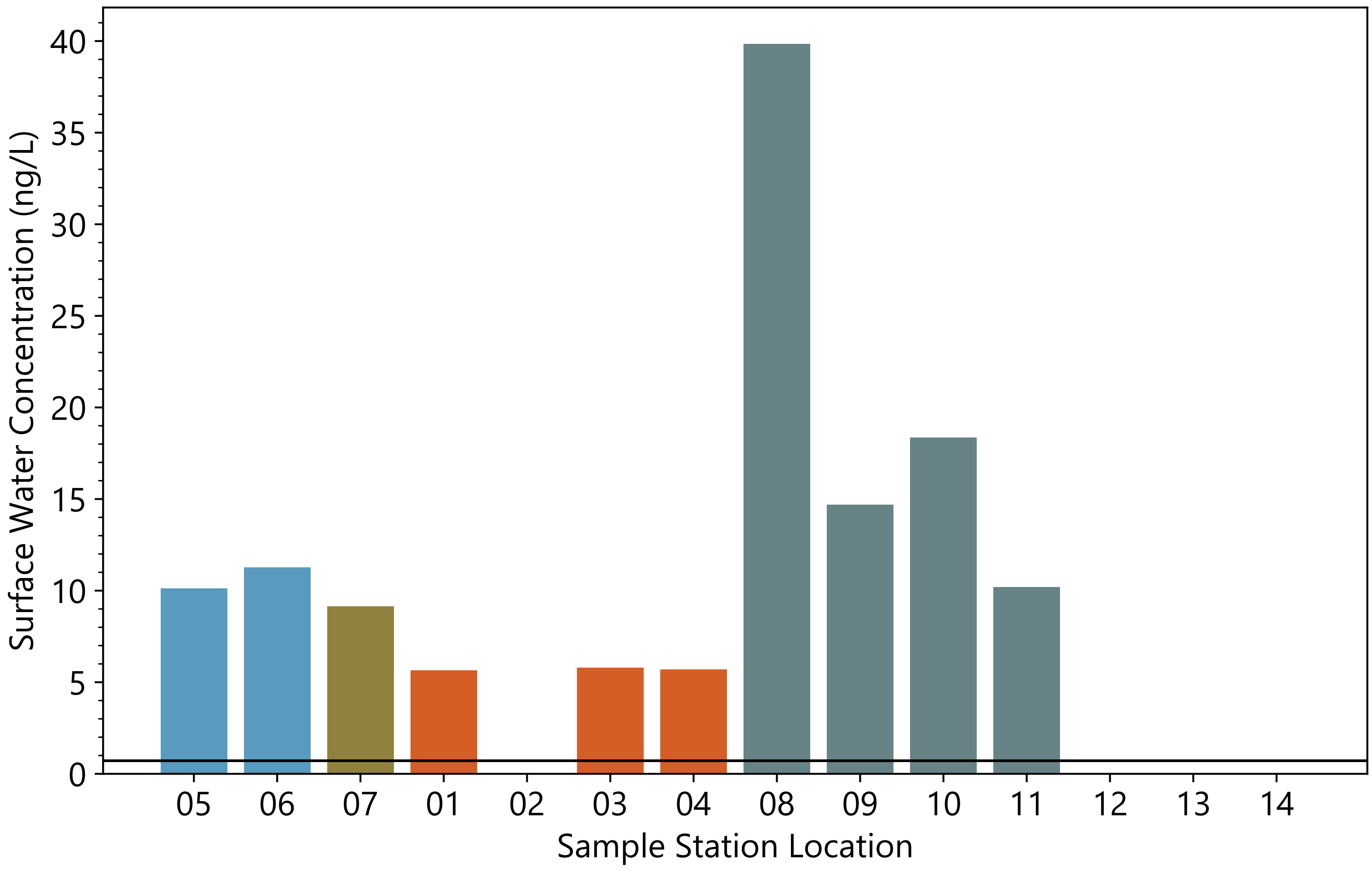


Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

🟦 Menomonee River	⬛ Kinnickinnic River
🟨 South Menomonee Canal	🟫 Harbor
🟧 Milwaukee River	🟪 Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

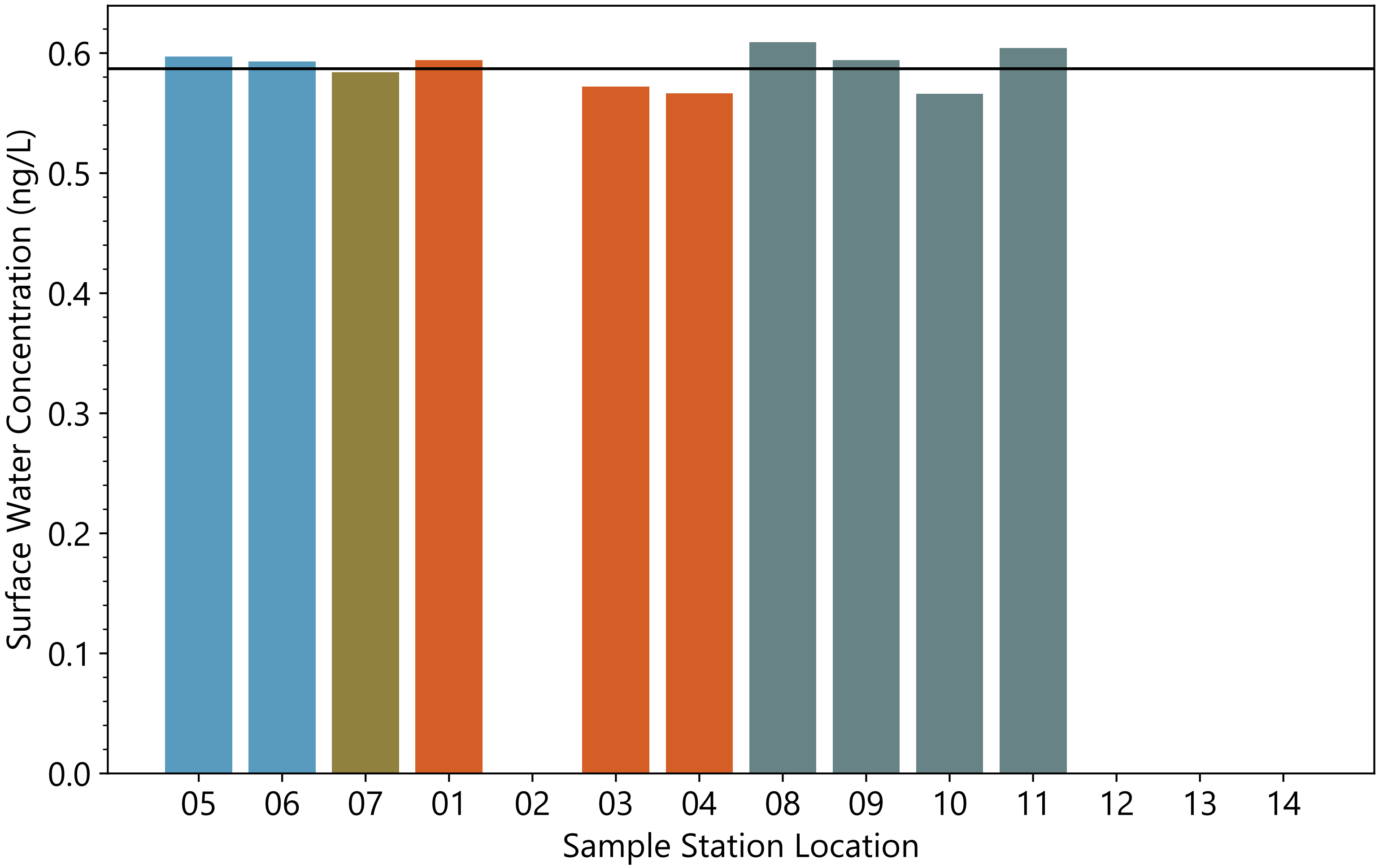
Figure 4t
Perfluorodecane sulfonate (PFDS) Concentrations for MKE AOC



Notes:
1. If both samples were detects, their values were directly summed. If both samples were non-detect, the value shown is the average method detection limit. Hatching represents sample groups that were both non-detect.
2. Horizontal line represents the average method detection limit for the analytes.
3. Blank values were classified as not reportable after data validation.
4. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

ANCHOR QEA

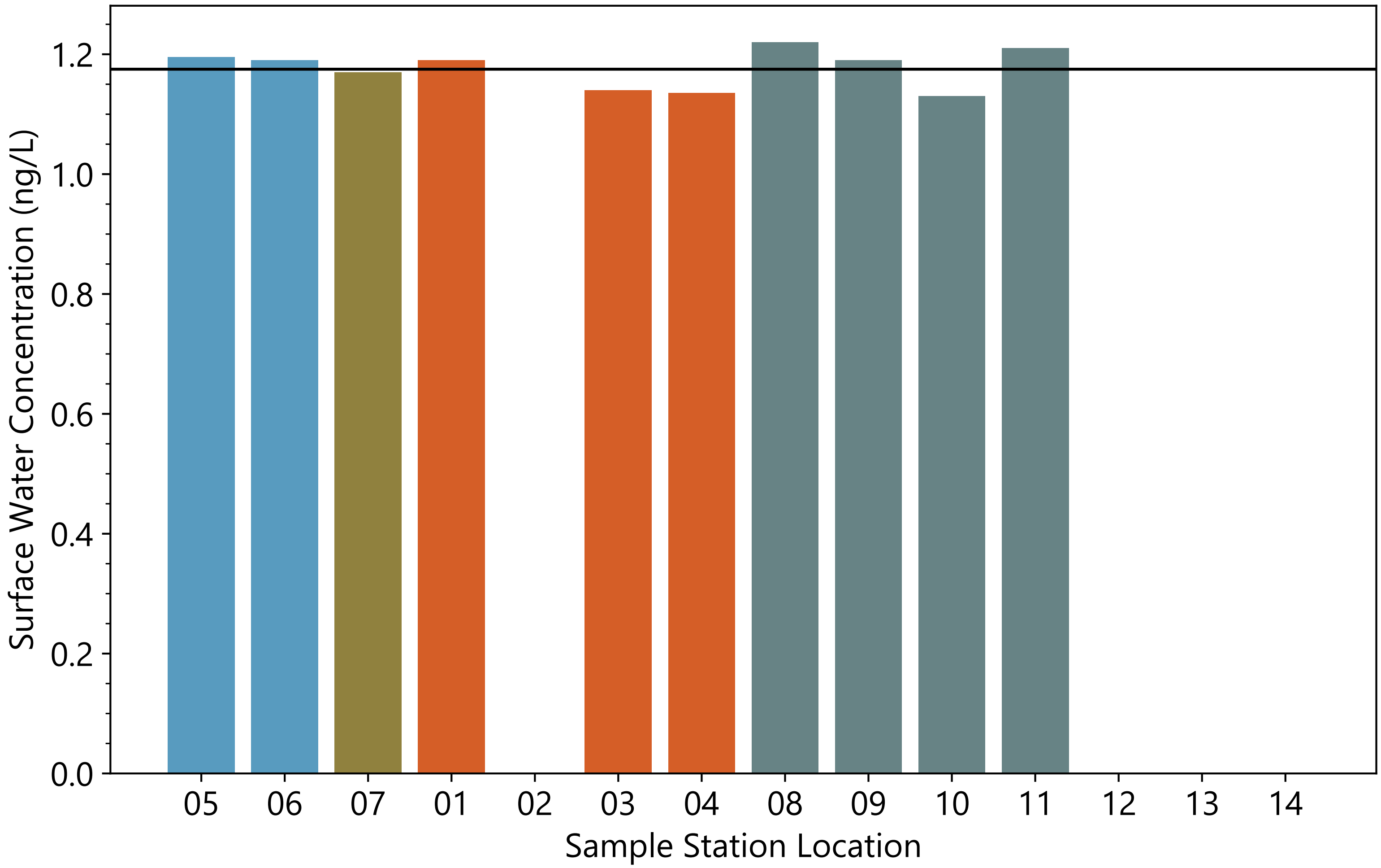
Figure 4u
Combined Perfluorooctanoate (PFOA) and Perfluorooctane sulfonate (PFOS) Concentrations for MKE AOC



Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

■ Menomonee River
■ South Menomonee Canal
■ Milwaukee River
■ Kinnickinnic River
■ Harbor
■ Lake Michigan

Figure 4v
Perfluorooctane sulfonamide (PFOSA) Concentrations for MKE AOC

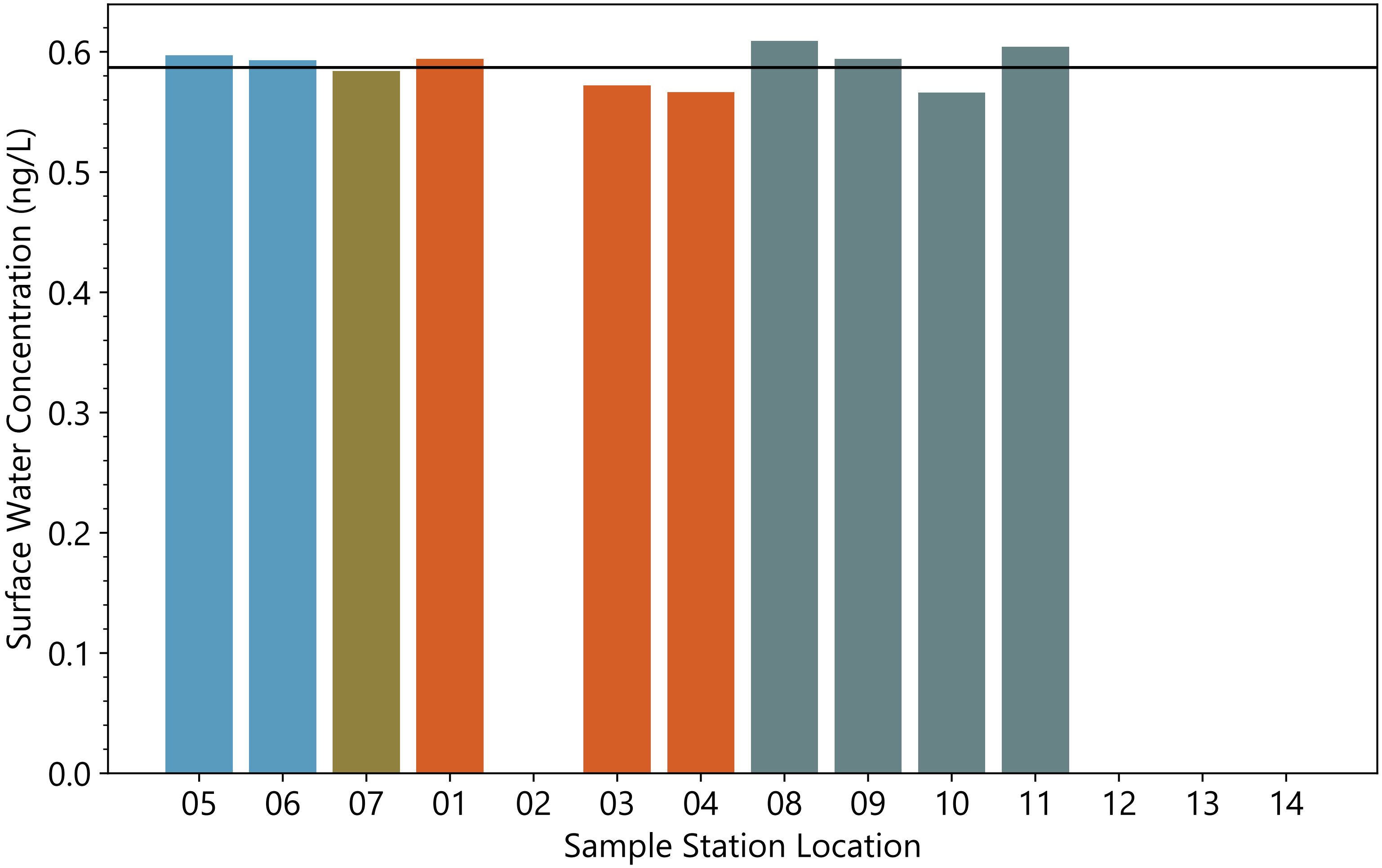


Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 4w
N-methyl perfluoro-1-octanesulfonamide (N-MeFOSA) Concentrations for MKE AOC

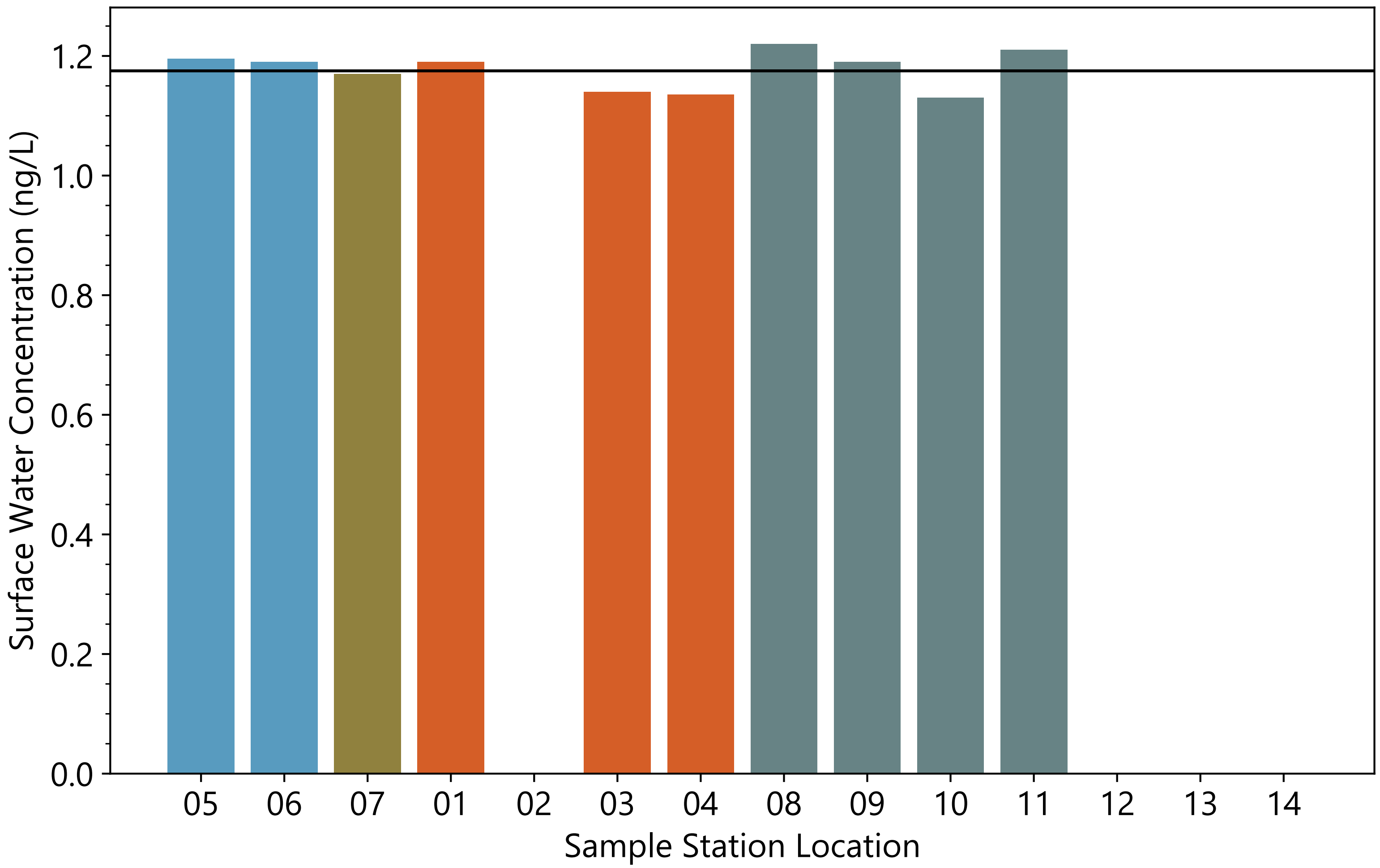


Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 4x
N-ethyl perfluoro-1-octanesulfonamide (N-EtFOSA) Concentrations for MKE AOC



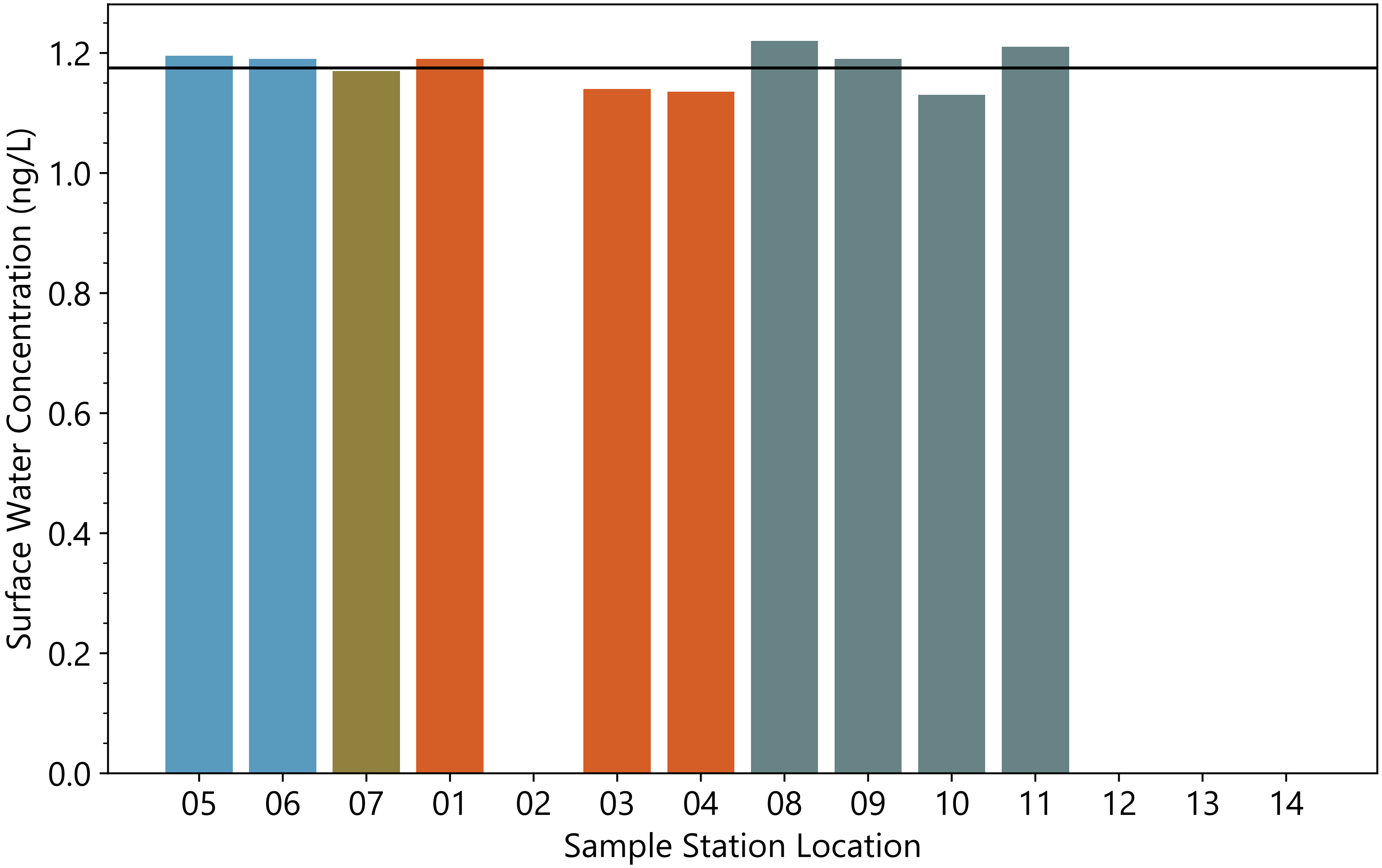
Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

🟦 Menomonee River
🟫 South Menomonee Canal
🟧 Milwaukee River
⬛ Kinnickinnic River
🟫 Harbor
🟪 Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 4y
N-methyl perfluorooctanesulfonamidoacetic acid (N-MeFOSAA) Concentrations for MKE AOC

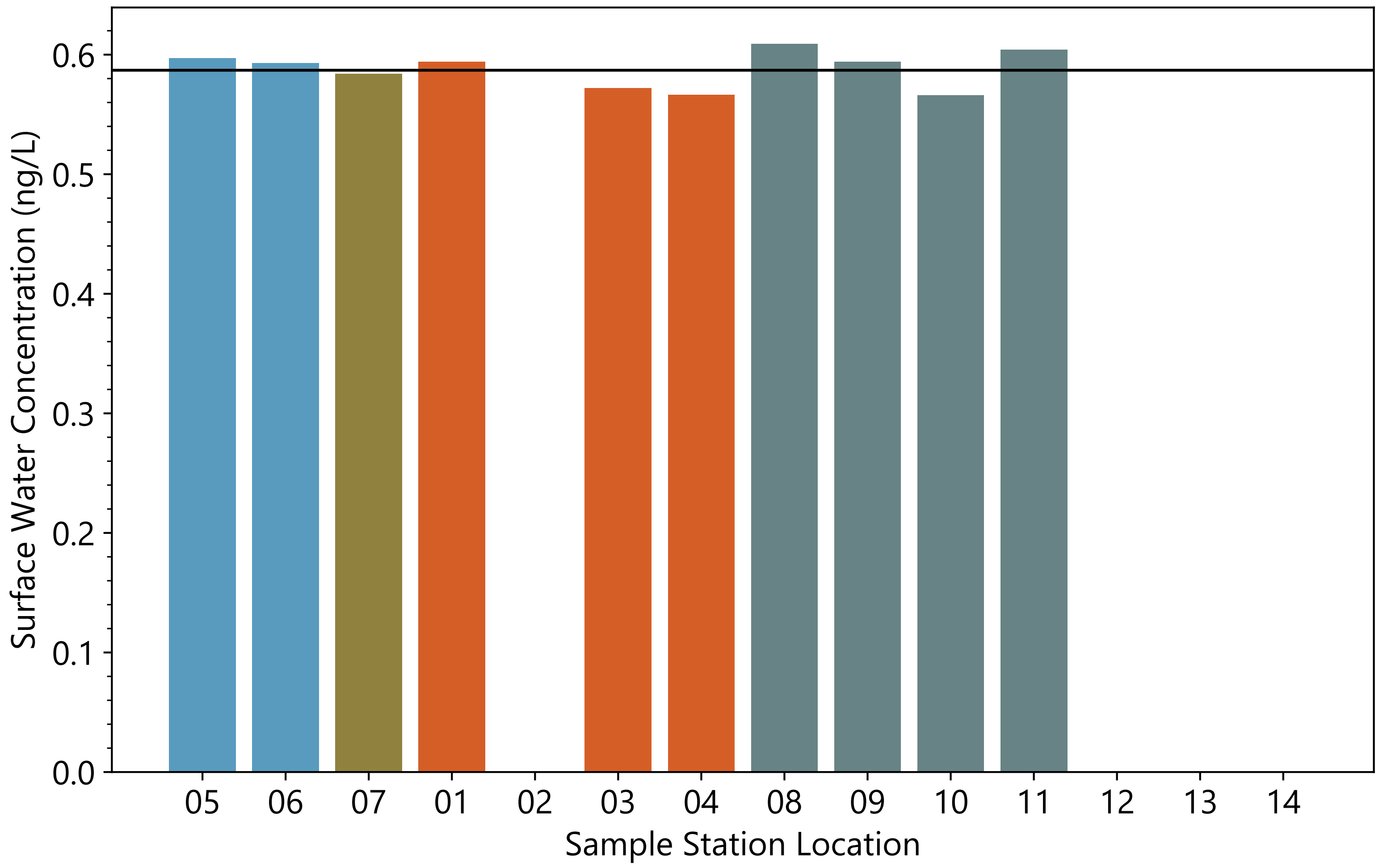


Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

- ■ Menomonee River
- ■ South Menomonee Canal
- ■ Milwaukee River
- ■ Kinnickinnic River
- ■ Harbor
- ■ Lake Michigan

ANCHOR QEA

Figure 4z
N-ethyl perfluorooctanesulfonamidoacetic acid (N-EtFOSAA) Concentrations for MKE AOC



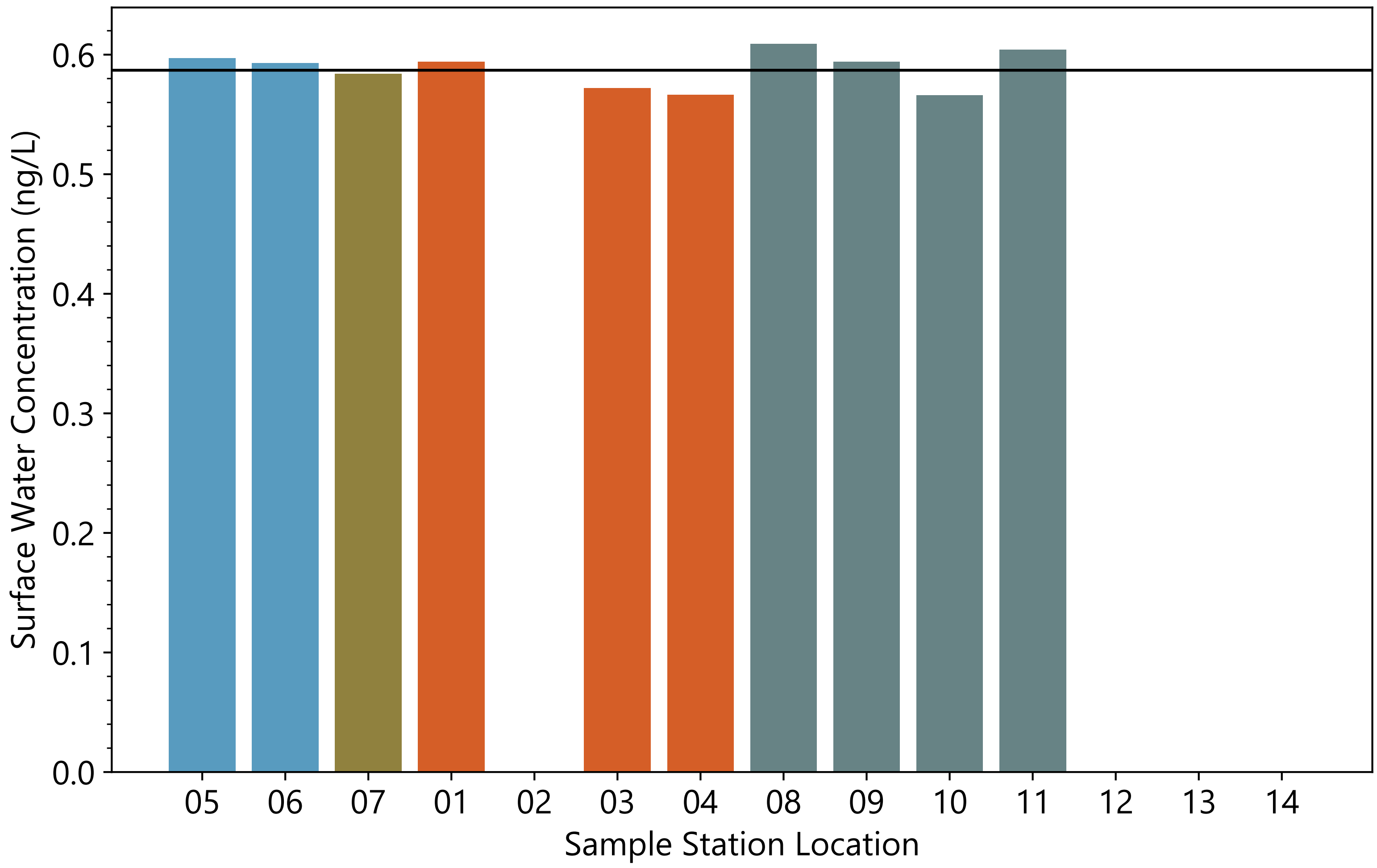
Notes:

1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 4aa
2-(N-methyl perfluoro-1-octanesulfonamido)-ethanol (N-MeFOSE) Concentrations for MKE AOC



Notes:

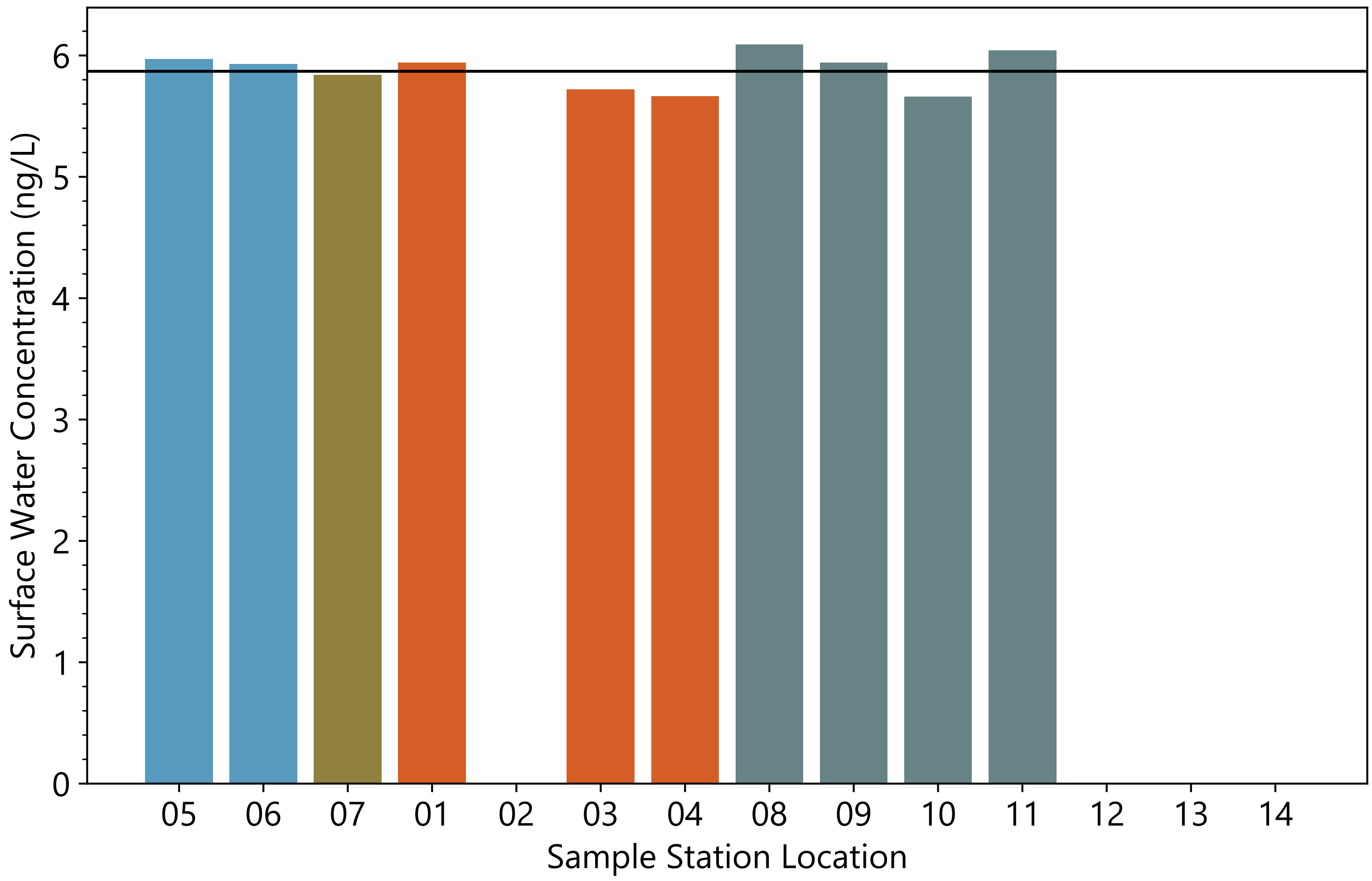
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

🟦 Menomonee River	■ Kinnickinnic River
■ South Menomonee Canal	■ Harbor
🟧 Milwaukee River	🟪 Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

Figure 4bb

2-(N-ethyl perfluoro-1-octanesulfonamido)-ethanol (N-EtFOSE) Concentrations for MKE AOC



Notes:

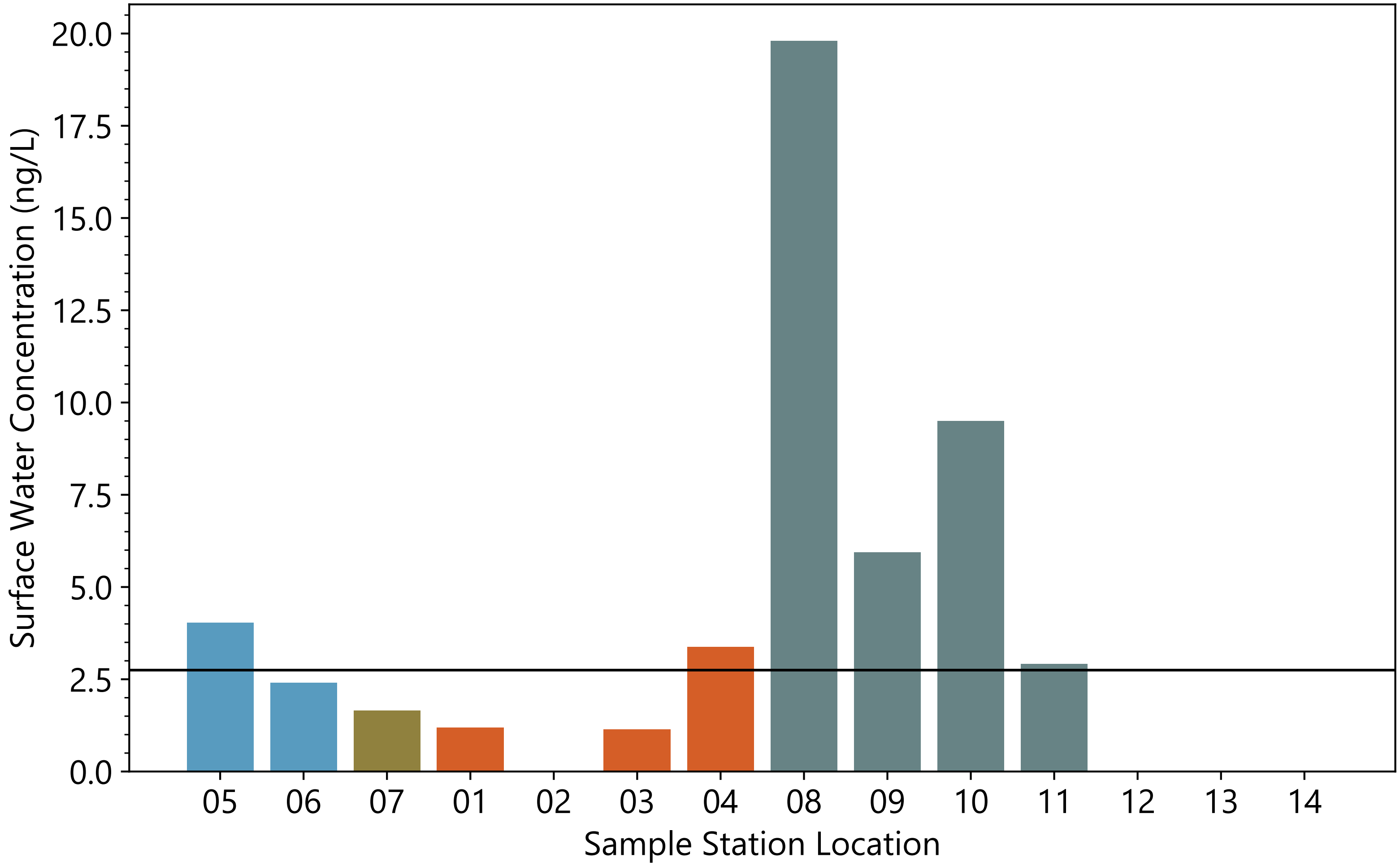
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

■ Menomonee River
■ South Menomonee Canal
■ Milwaukee River
■ Kinnickinnic River
■ Harbor
■ Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 4cc
4:2 fluorotelomer sulfonate (4:2 FTS) Concentrations for MKE AOC



Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

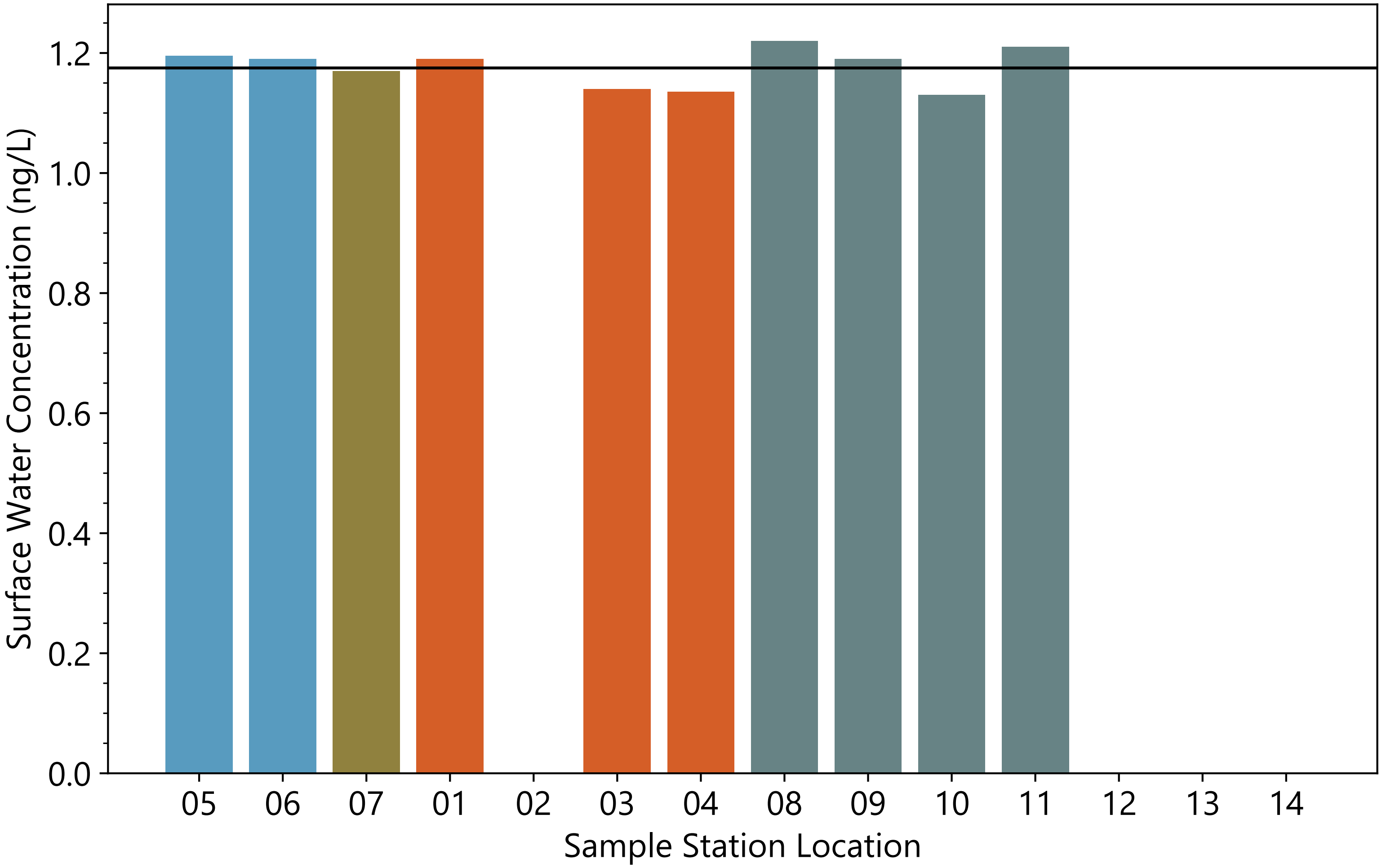
🟦 Menomonee River	■ Kinnickinnic River
■ South Menomonee Canal	■ Harbor
🟧 Milwaukee River	🟪 Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 4dd

1H,1H,2H,2H-perfluorooctanesulfonic acid (THPFOS) (6:2 FTS) Concentrations for MKE AOC



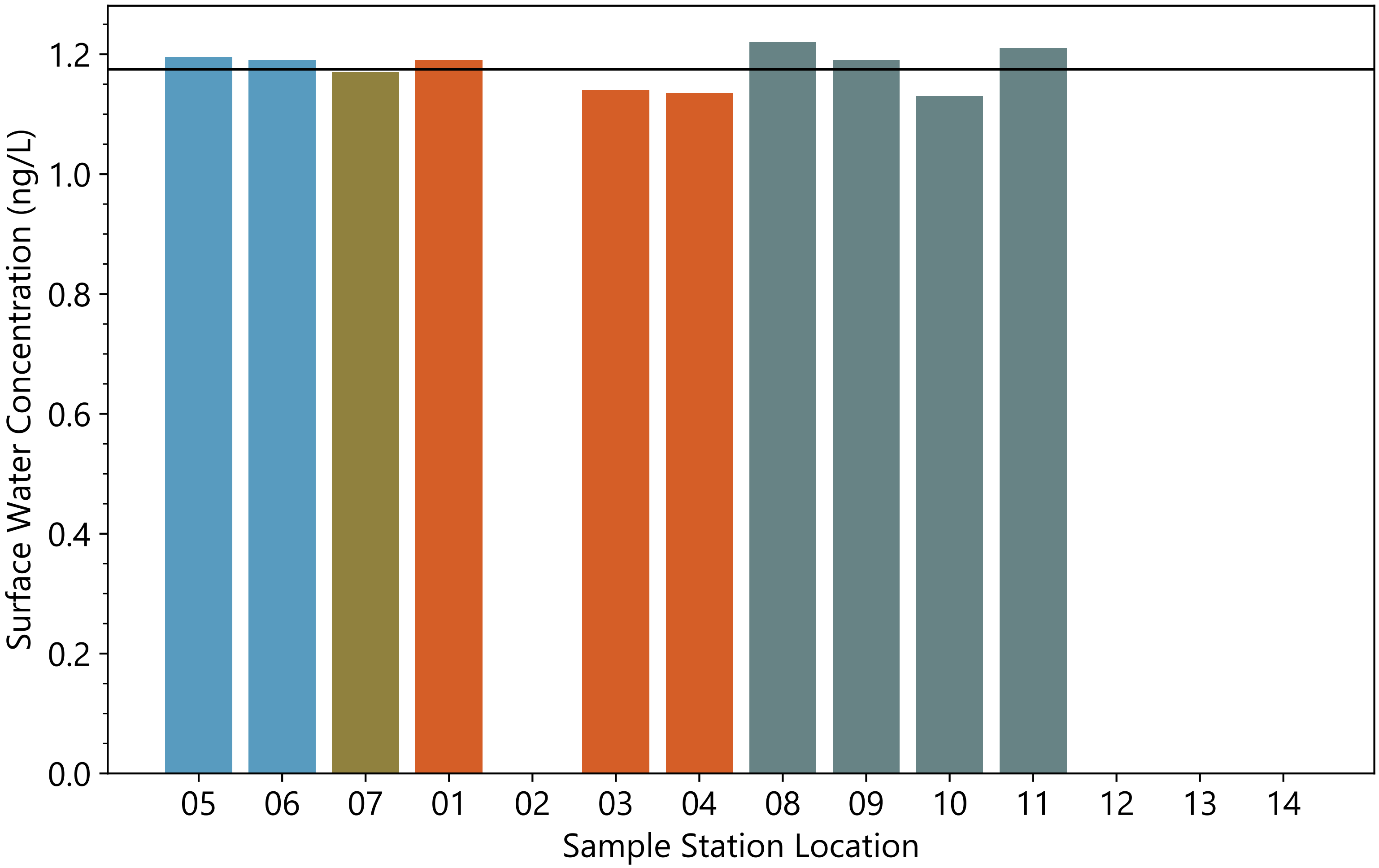
Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

🟦 Menomonee River	■ Kinnickinnic River
■ South Menomonee Canal	■ Harbor
🟧 Milwaukee River	🟪 Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

Figure 4ee

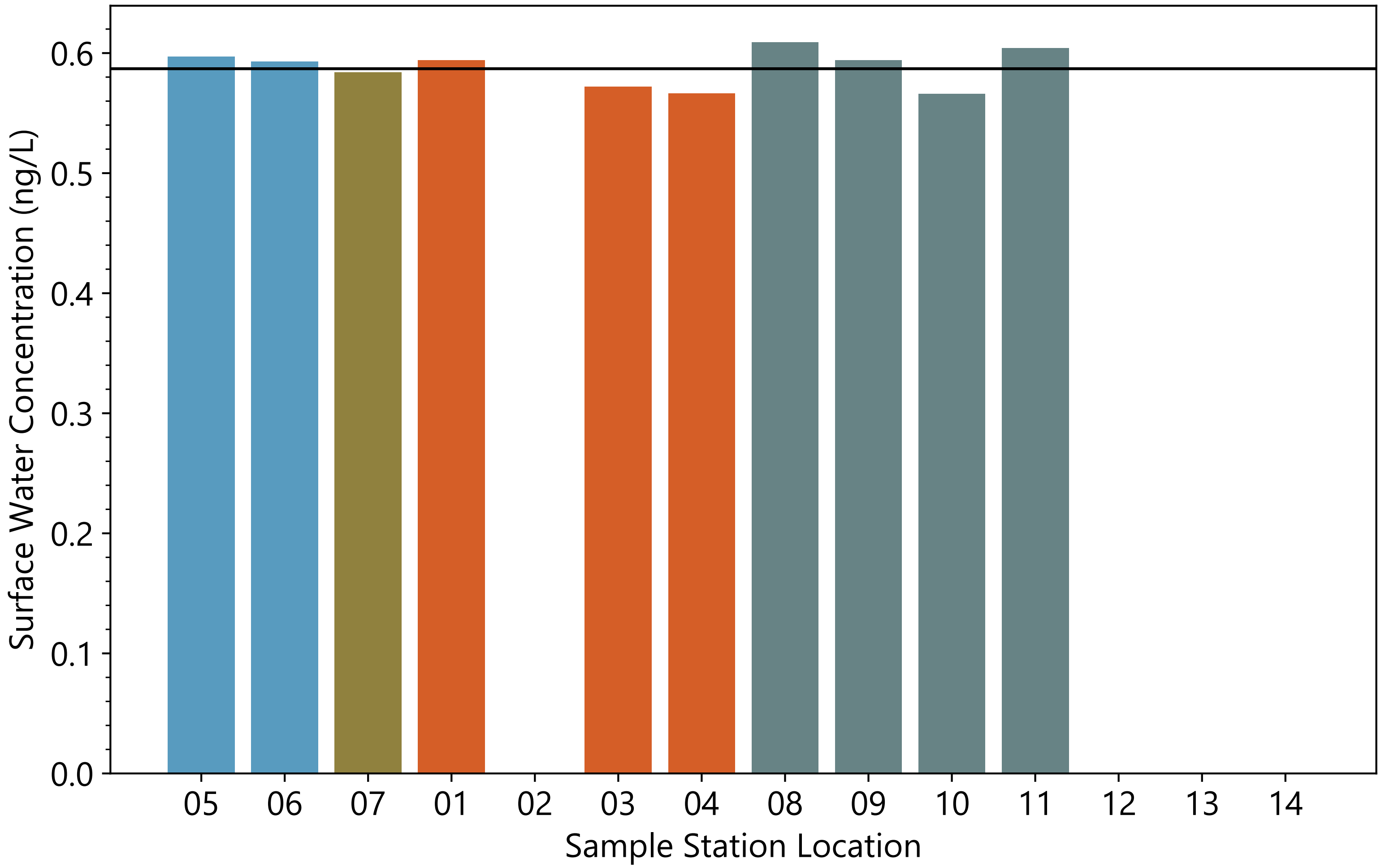
1H,1H,2H,2H-perfluorodecanesulphonic acid (8:2 FTS) Concentrations for MKE AOC



Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

ANCHOR QEA

Figure 4ff
10:2-fluorotelomer sulfonate (10:2 FTS) Concentrations for MKE AOC



Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

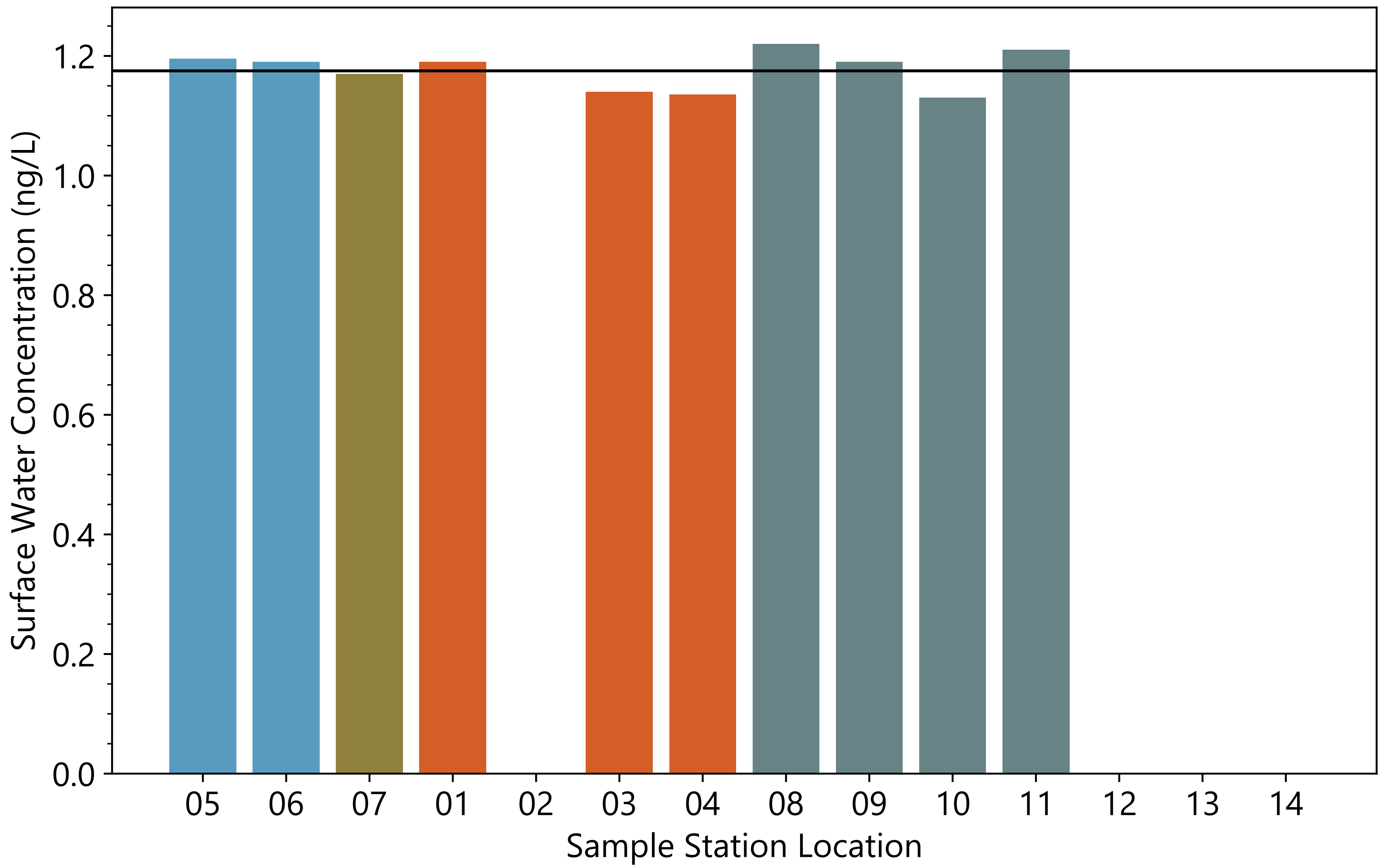
■ Menomonee River
■ South Menomonee Canal
■ Milwaukee River
■ Kinnickinnic River
■ Harbor
■ Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 4gg

2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-propanoic acid (GenX) Concentrations for MKE AOC



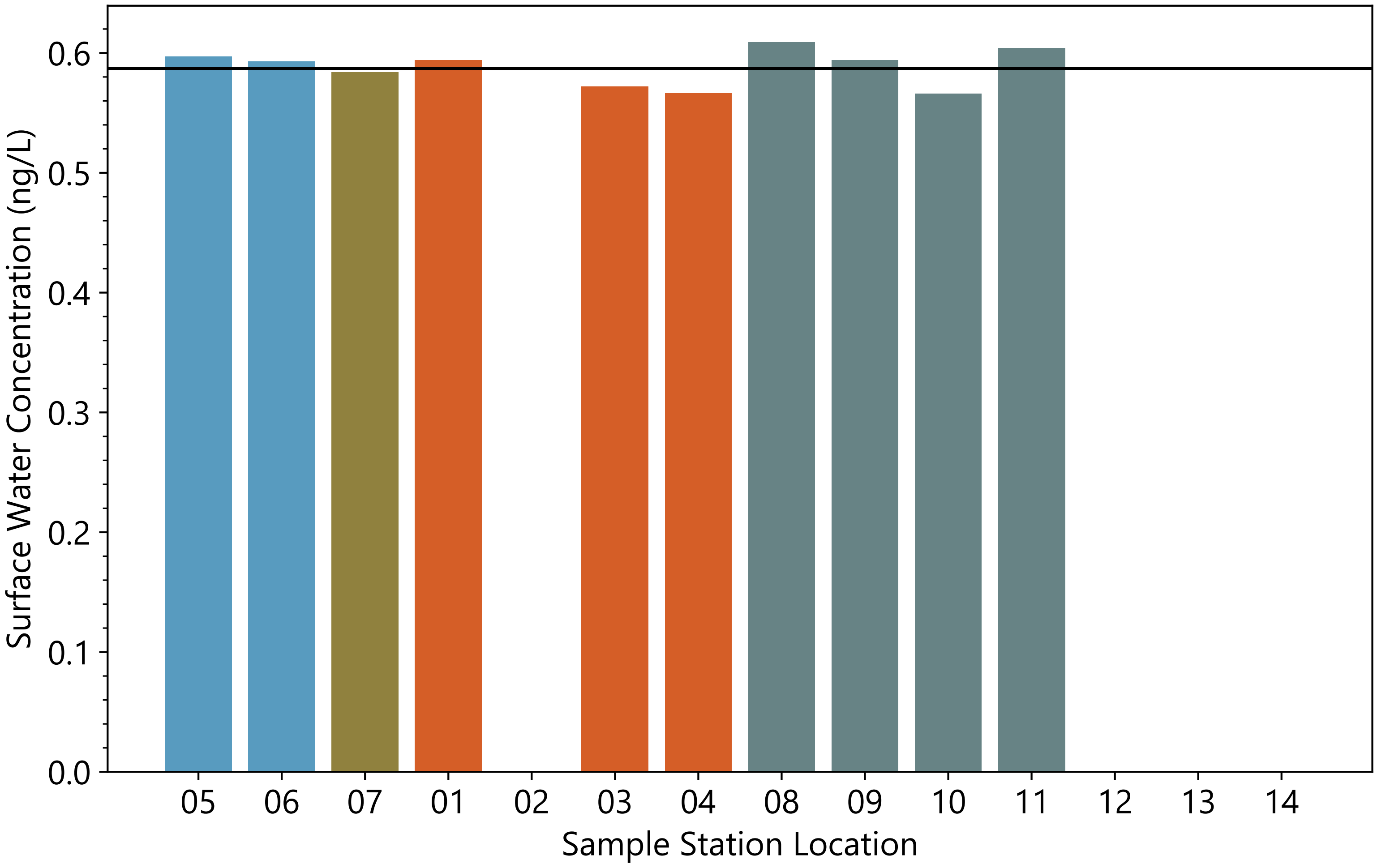
Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

■ Menomonee River
■ South Menomonee Canal
■ Milwaukee River
■ Kinnickinnic River
■ Harbor
■ Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 4hh
11-chloroeicosafluoro-3-oxaundecane-1-sulfonate (PF3OUdS) (F53B minor) Concentrations for MKE AOC



Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

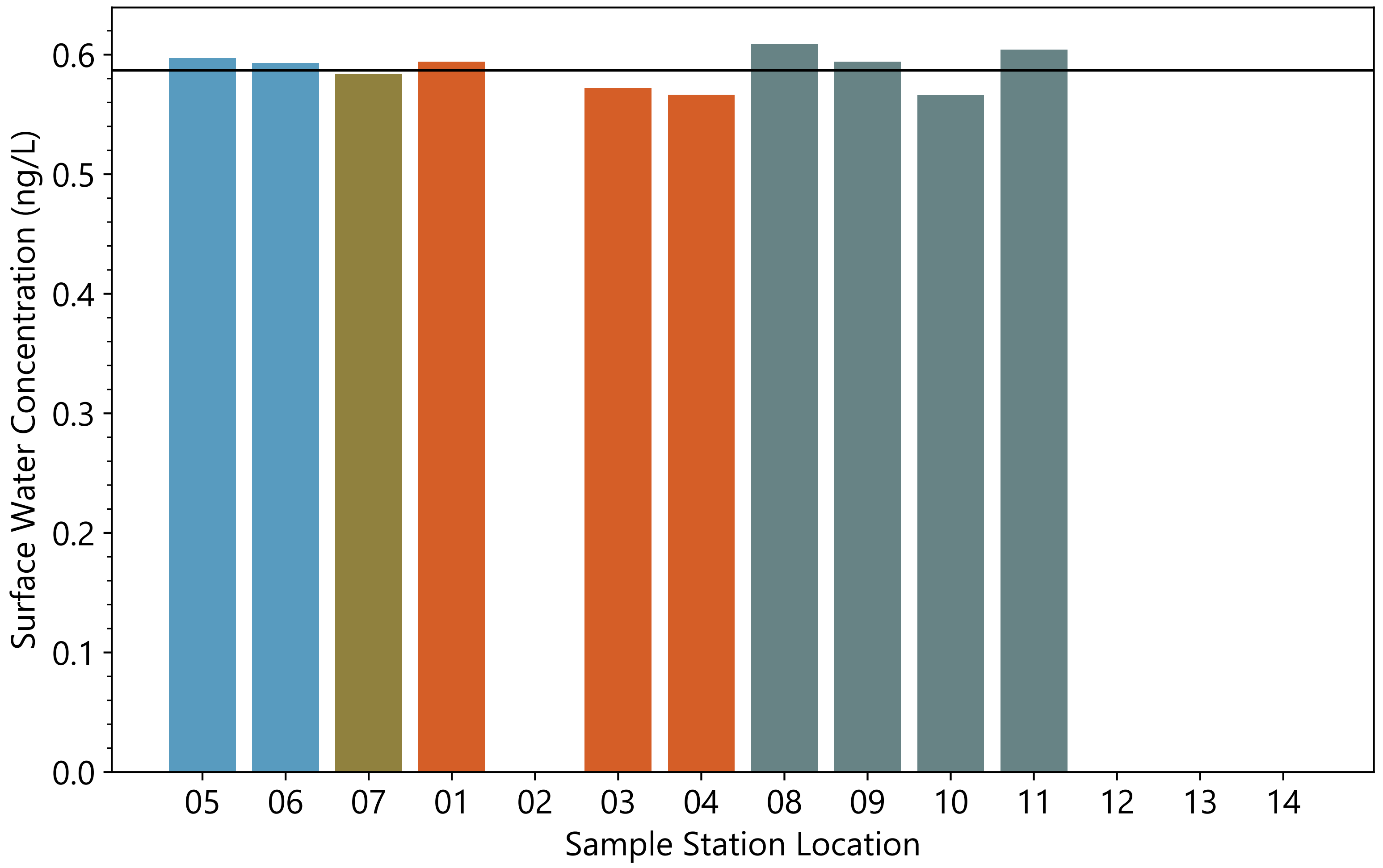
🟦 Menomonee River	■ Kinnickinnic River
■ South Menomonee Canal	■ Harbor
🟧 Milwaukee River	🟪 Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 4ii

9-chlorohexadecafluoro-3-oxanonnane-1-sulfonate (PF3ONS) (F53B major) Concentrations for MKE AOC



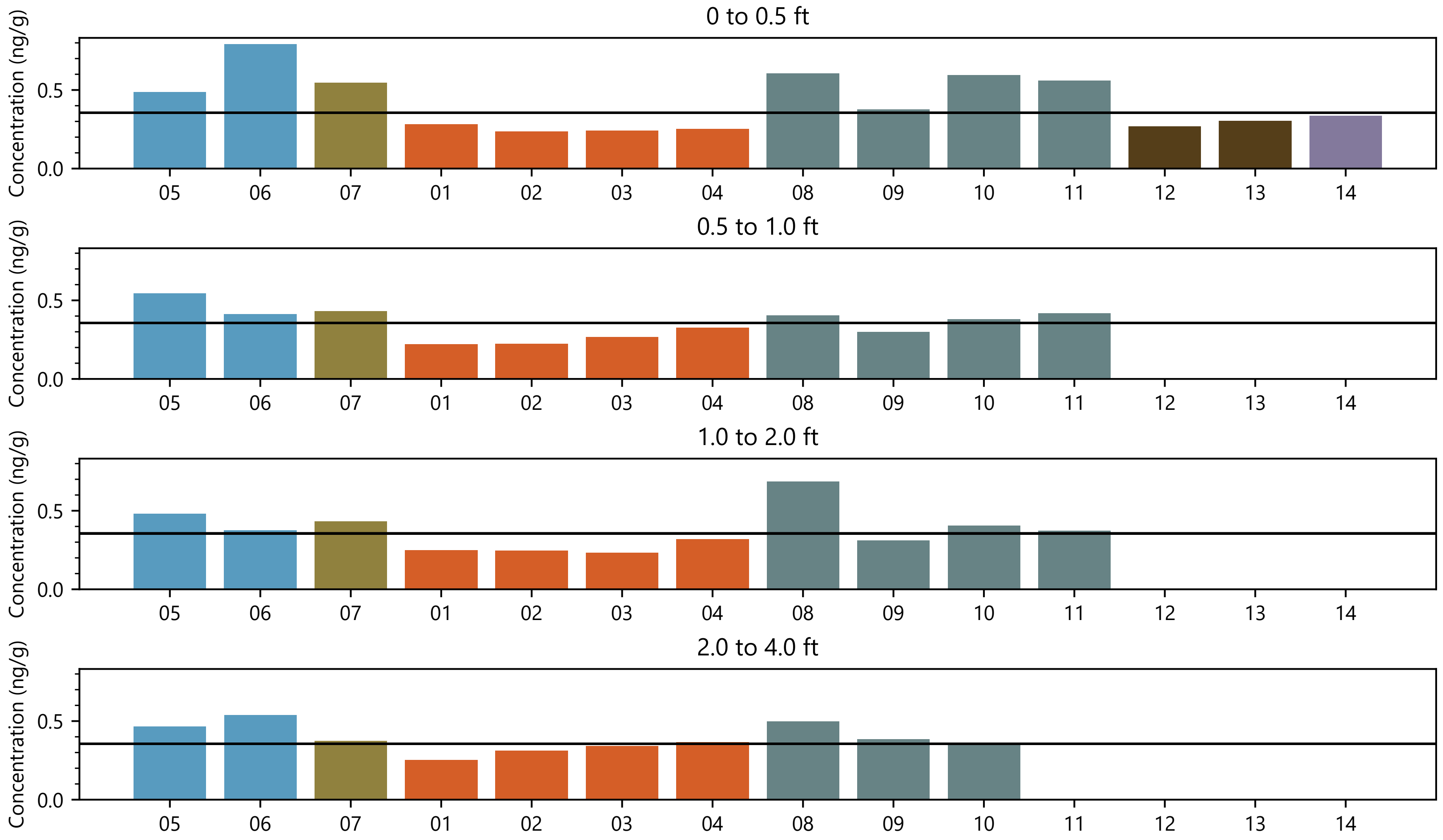
Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. Blank values were classified as not reportable after data validation.
5. Harbor samples were at locations 12 and 13. Lake Michigan sample was at location 14.

- 🟦 Menomonee River
- 🟨 South Menomonee Canal
- 🟧 Milwaukee River
- ⬛ Kinnickinnic River
- 🟫 Harbor
- 🟪 Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 4jj
Sodium dodecafluoro-3H-4,8-dioxanonanoate (ADONA) Concentrations for MKE AOC

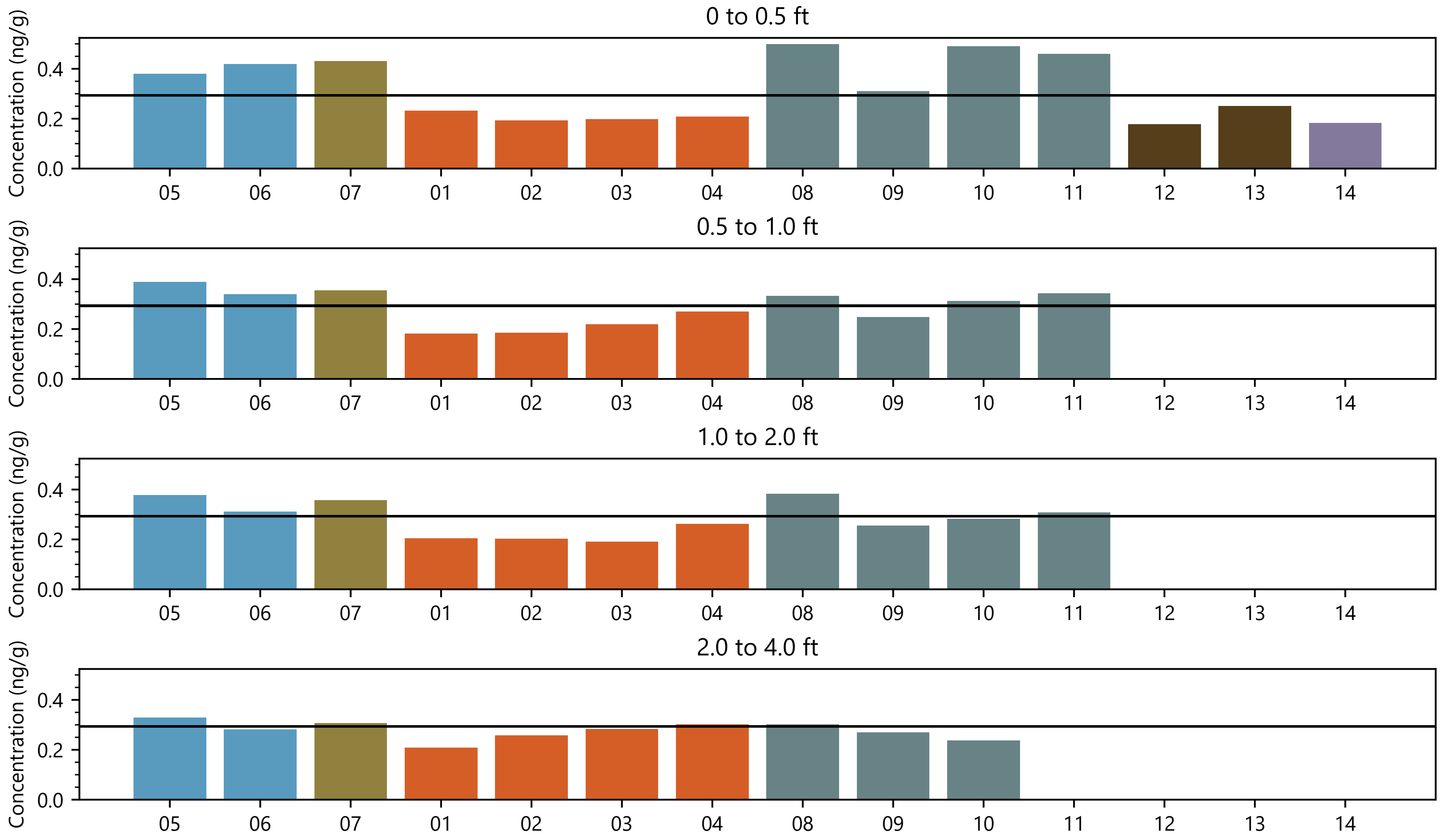


Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only). All other blank values were classified as not reportable after data validation.

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 5a
Perfluorobutanoate (PFBA) Concentrations for MKE AOC Sediment



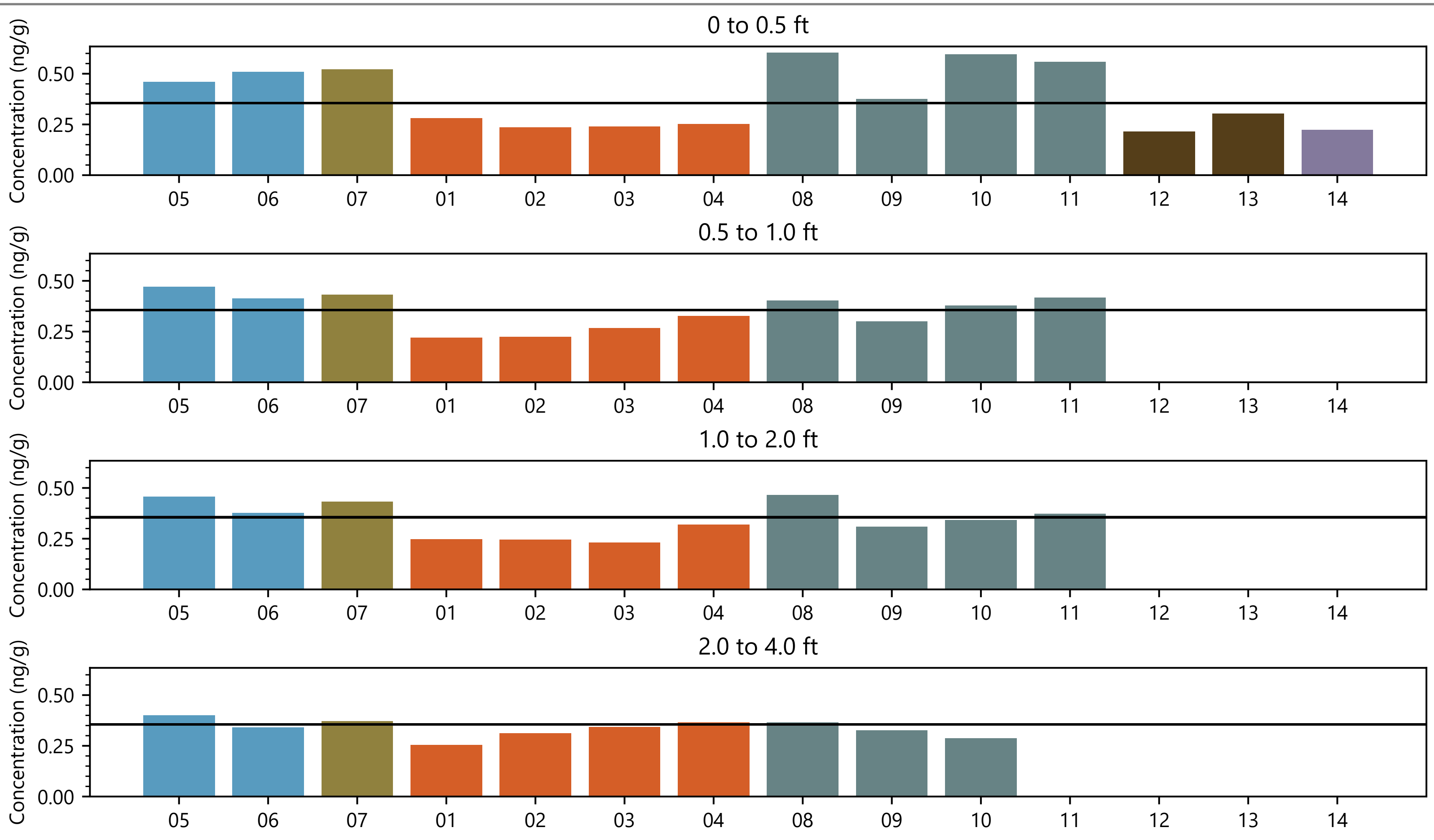
Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only). All other blank values were classified as not reportable after data validation.

■ Menomonee River
■ South Menomonee Canal
■ Milwaukee River
■ Kinnickinnic River
■ Harbor
■ Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

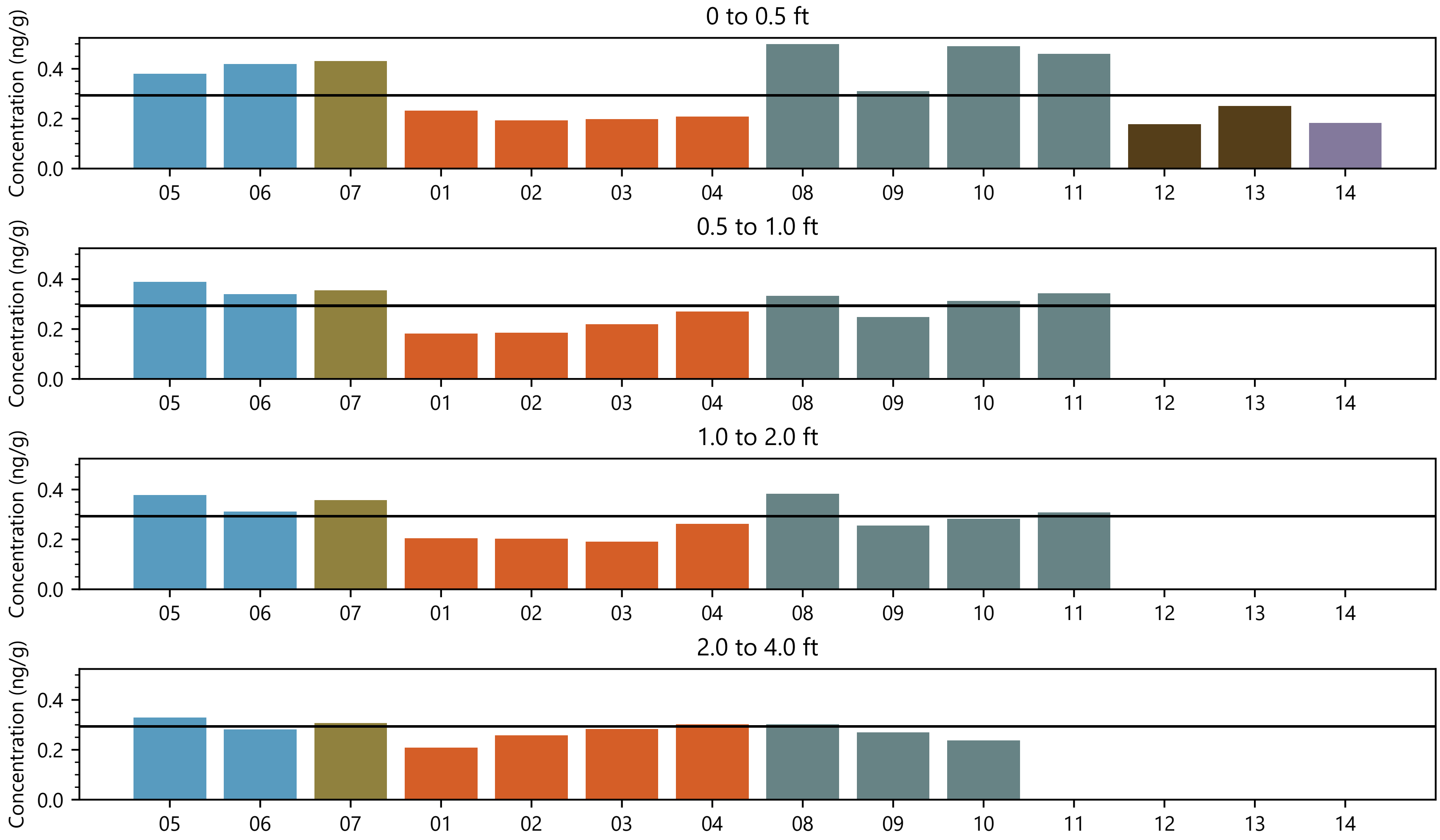
Figure 5b
Perfluoropentanoate (PFPeA) Concentrations for MKE AOC Sediment



Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only). All other blank values were classified as not reportable after data validation.

■ Menomonee River	■ Kinnickinnic River
■ South Menomonee Canal	■ Harbor
■ Milwaukee River	■ Lake Michigan

Figure 5c
Perfluorohexanoate (PFHxA) Concentrations for MKE AOC Sediment



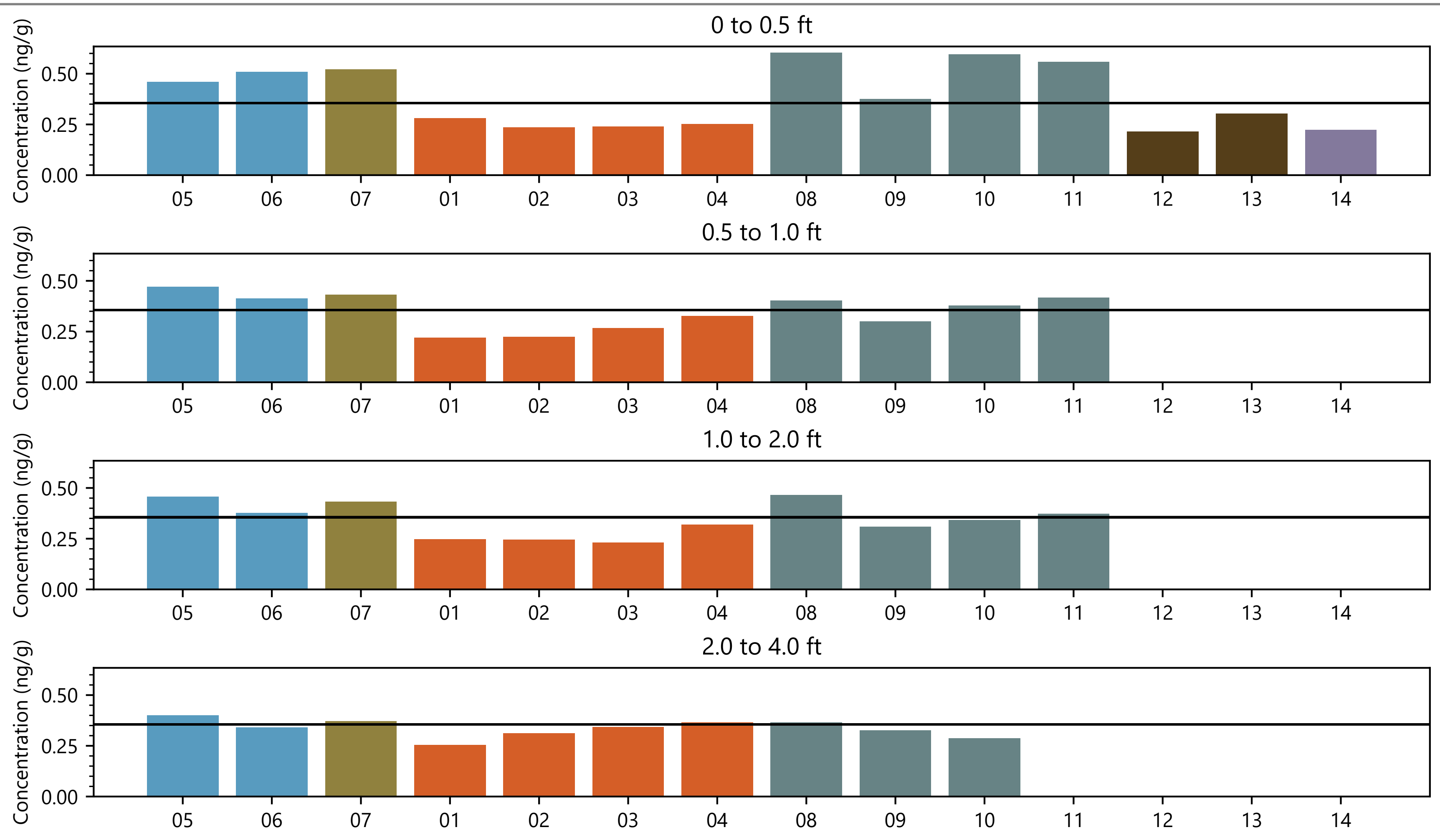
Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only).
   All other blank values were classified as not reportable after data validation.

■ Menomonee River
■ South Menomonee Canal
■ Milwaukee River
■ Kinnickinnic River
■ Harbor
■ Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

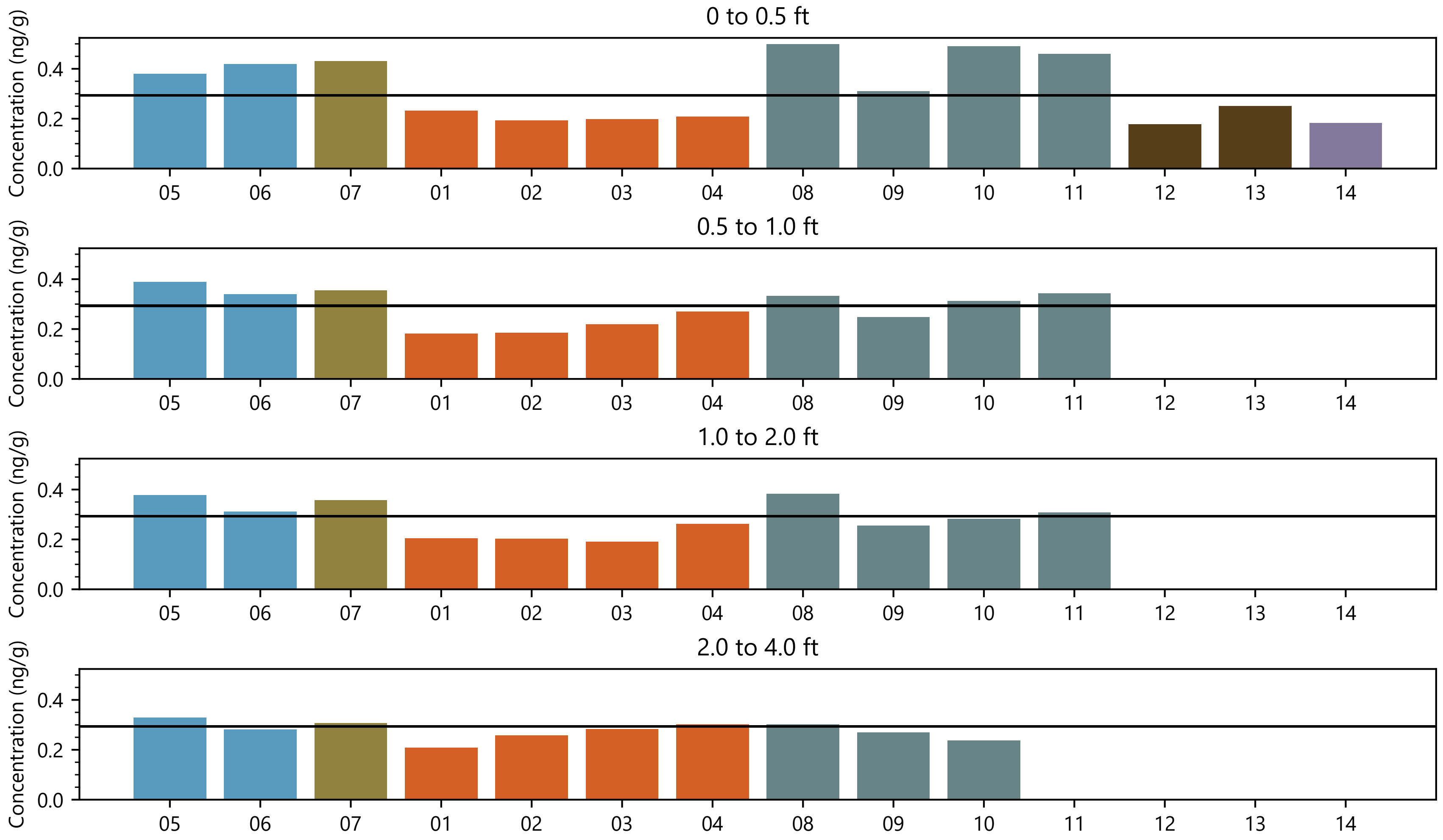
Figure 5d
Perfluoroheptanoate (PFHpA) Concentrations for MKE AOC Sediment



Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only).
All other blank values were classified as not reportable after data validation.

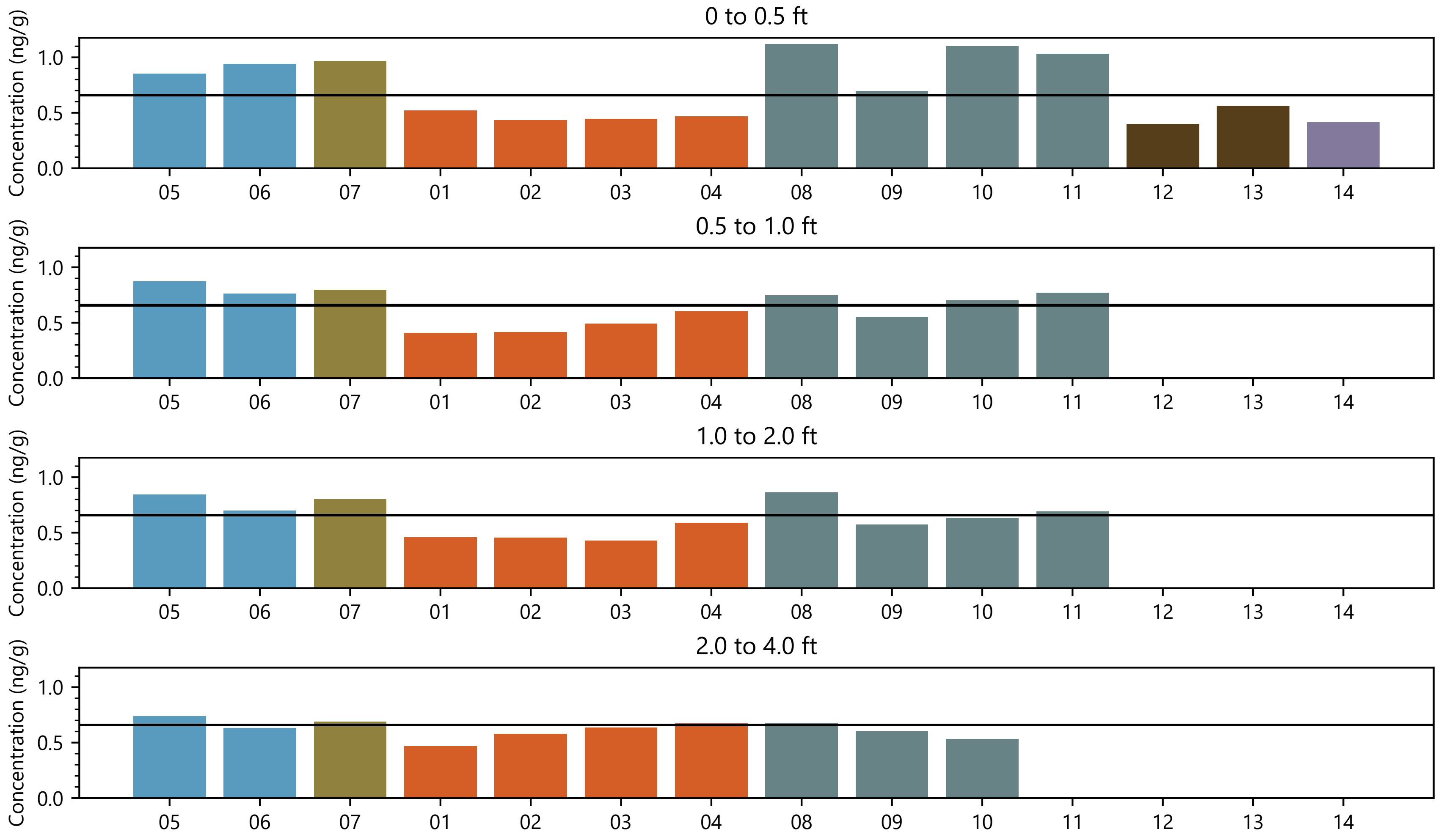
🟦 Menomonee River
🟨 South Menomonee Canal
🟧 Milwaukee River
⬛ Kinnickinnic River
🟫 Harbor
🟪 Lake Michigan

Figure 5e
Perfluorooctanoate (PFOA) Concentrations for MKE AOC Sediment



Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only).
   All other blank values were classified as not reportable after data validation.

Figure 5f
Perfluorononanoate (PFNA) Concentrations for MKE AOC Sediment



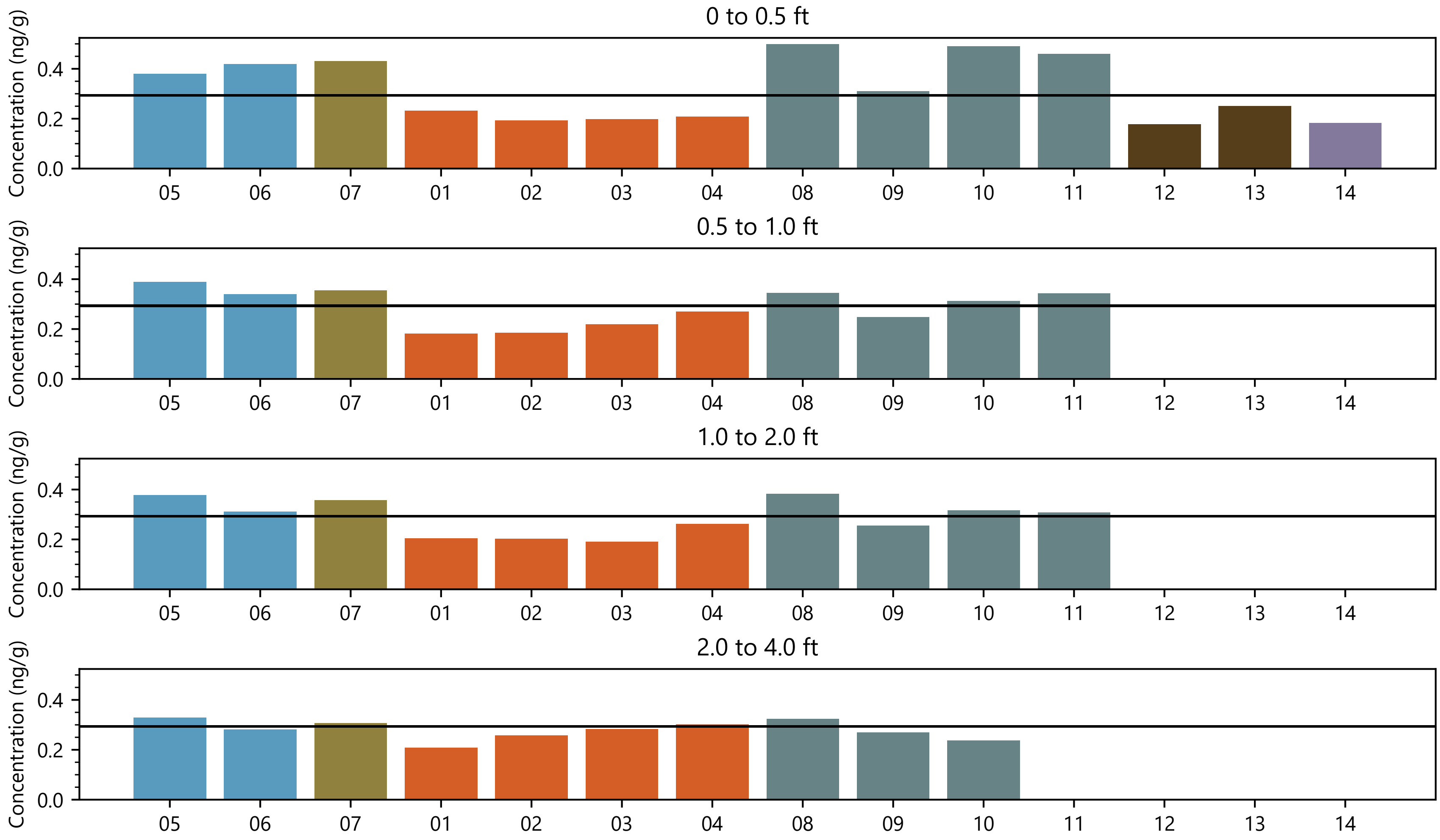
Notes:

1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only).
   All other blank values were classified as not reportable after data validation.

■ Menomonee River
■ South Menomonee Canal
■ Milwaukee River
■ Kinnickinnic River
■ Harbor
■ Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

Figure 5g
Perfluorodecanoate (PFDA) Concentrations for MKE AOC Sediment

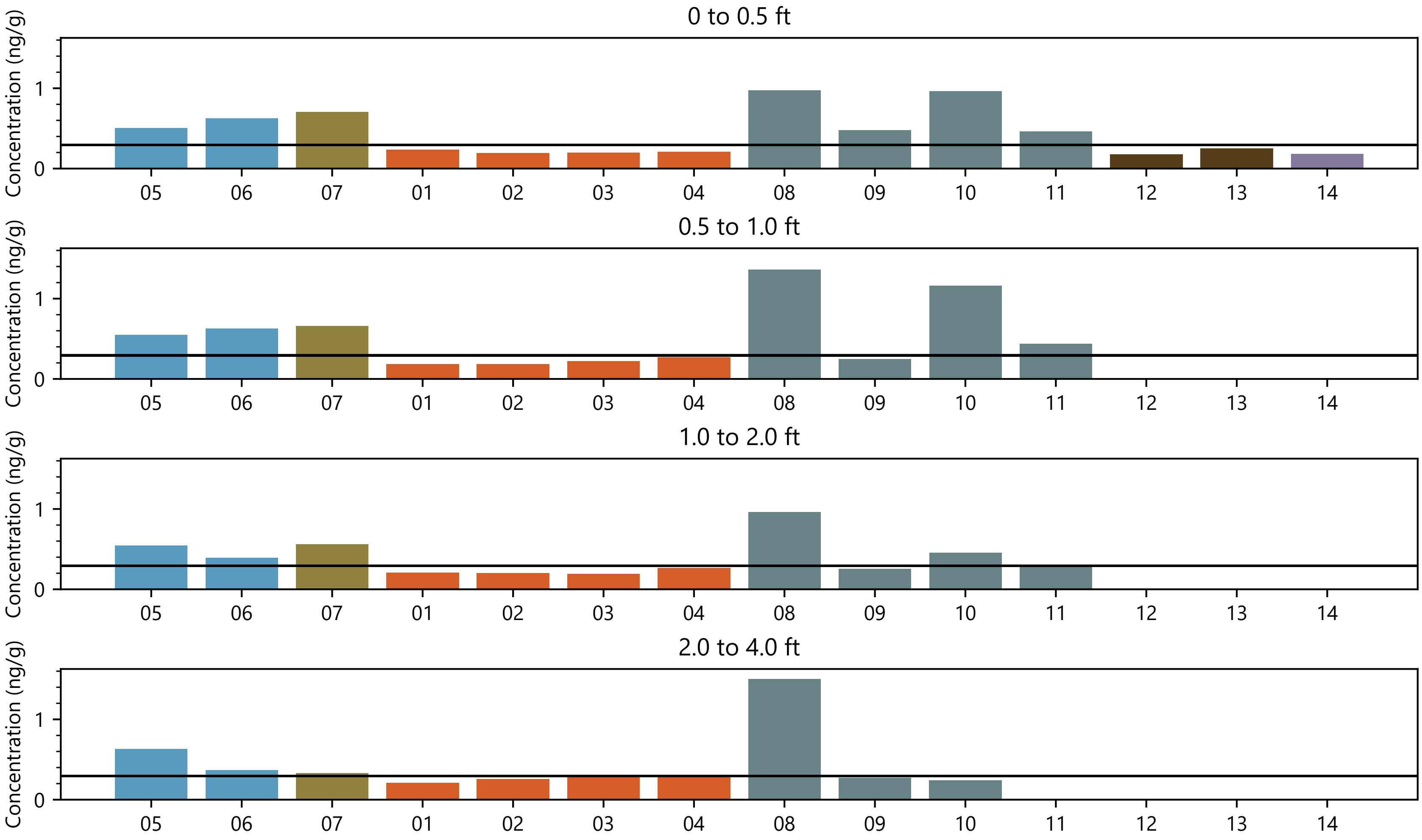


Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only).
   All other blank values were classified as not reportable after data validation.

🟦 Menomonee River	■ Kinnickinnic River
■ South Menomonee Canal	🟫 Harbor
🟧 Milwaukee River	🟪 Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

Figure 5h
Perfluoroundecanoate (PFUnA) Concentrations for MKE AOC Sediment



Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only).
   All other blank values were classified as not reportable after data validation.

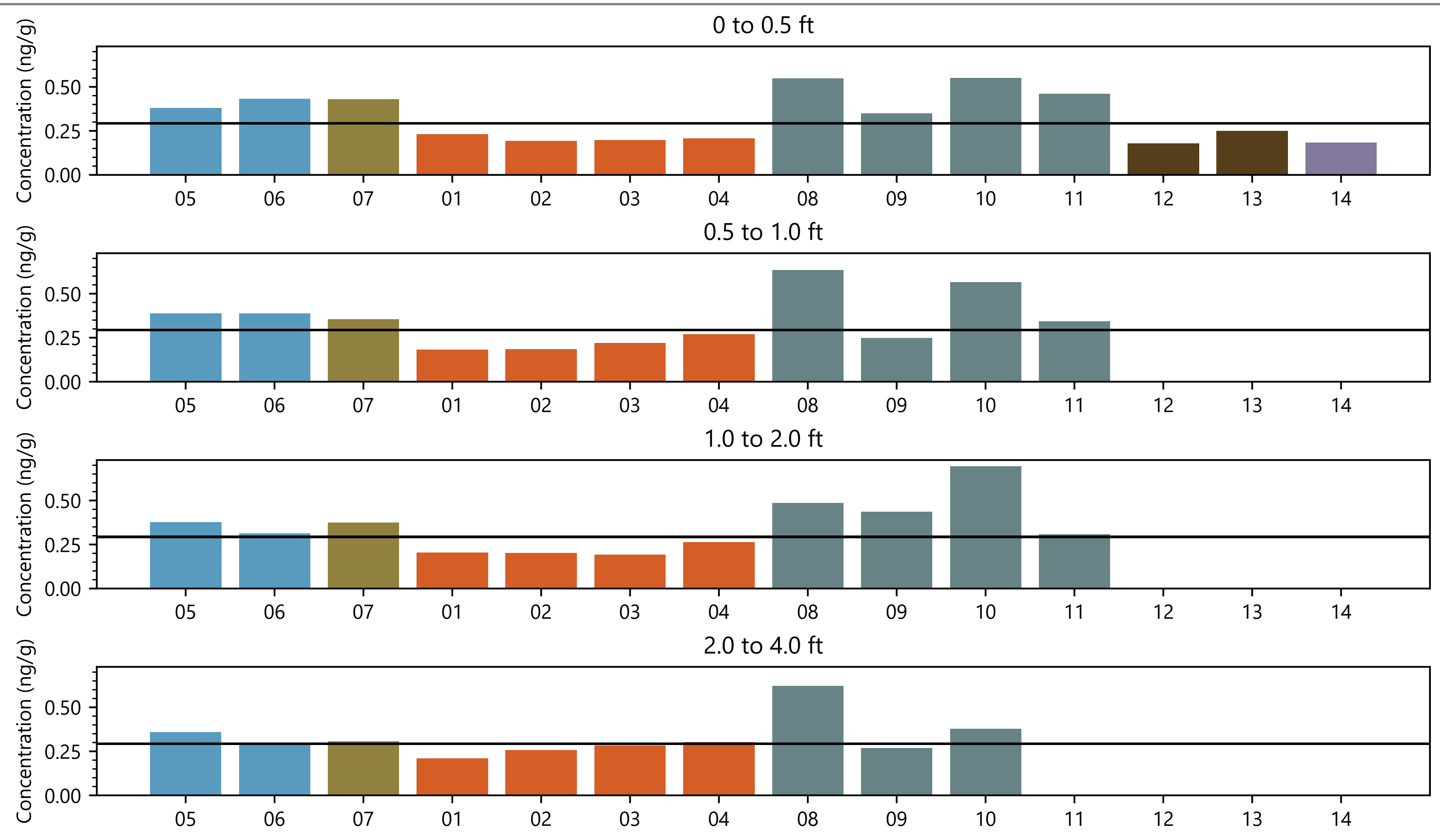
■ Menomonee River
■ South Menomonee Canal
■ Milwaukee River
■ Kinnickinnic River
■ Harbor
■ Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 5i

Perfluorododecanoate (PFDoA) Concentrations for MKE AOC Sediment

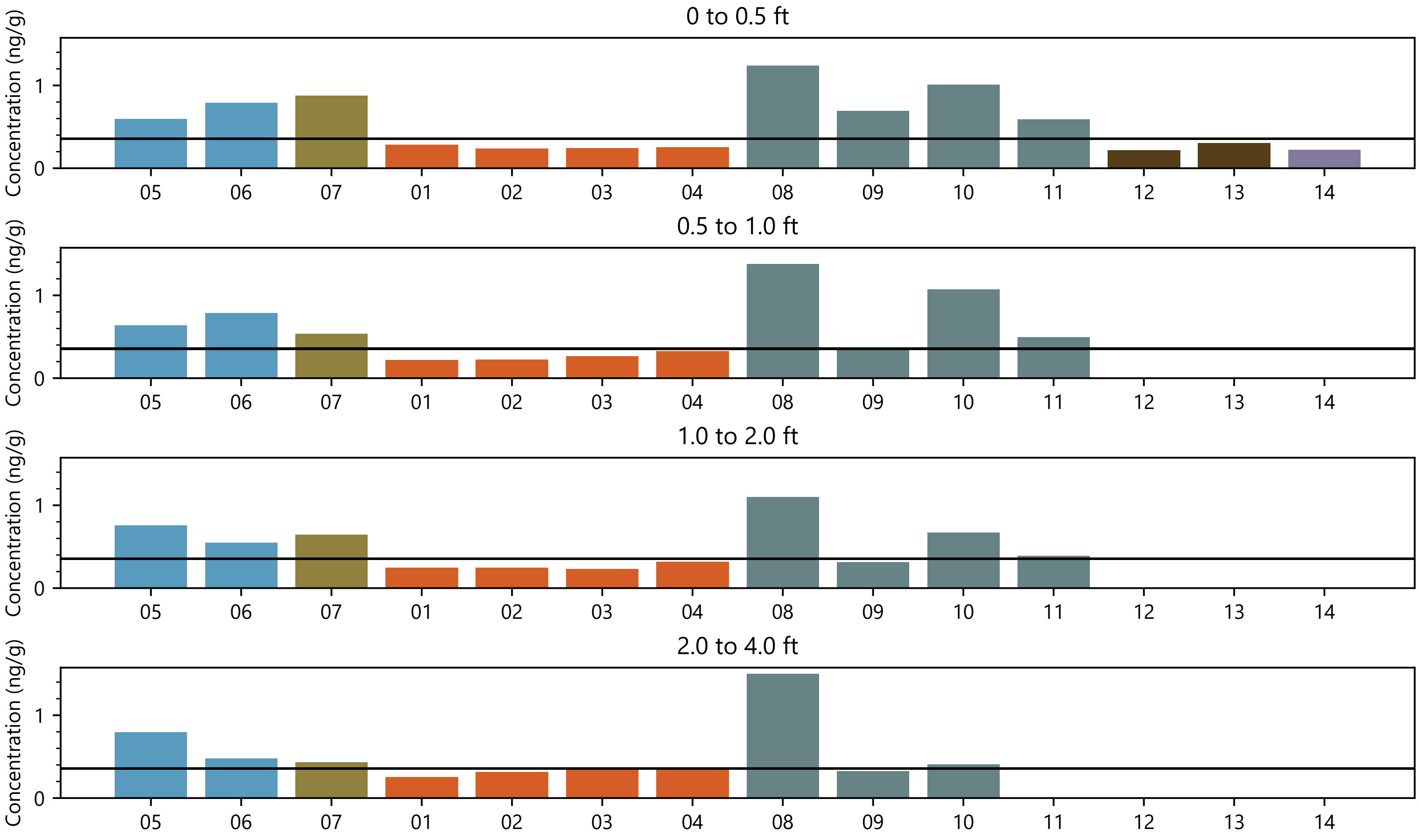


Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only). All other blank values were classified as not reportable after data validation.

■ Menomonee River
■ South Menomonee Canal
■ Milwaukee River
■ Kinnickinnic River
■ Harbor
■ Lake Michigan

Figure 5j

Perfluorotridecanoic acid (PFTrDA) Concentrations for MKE AOC Sediment

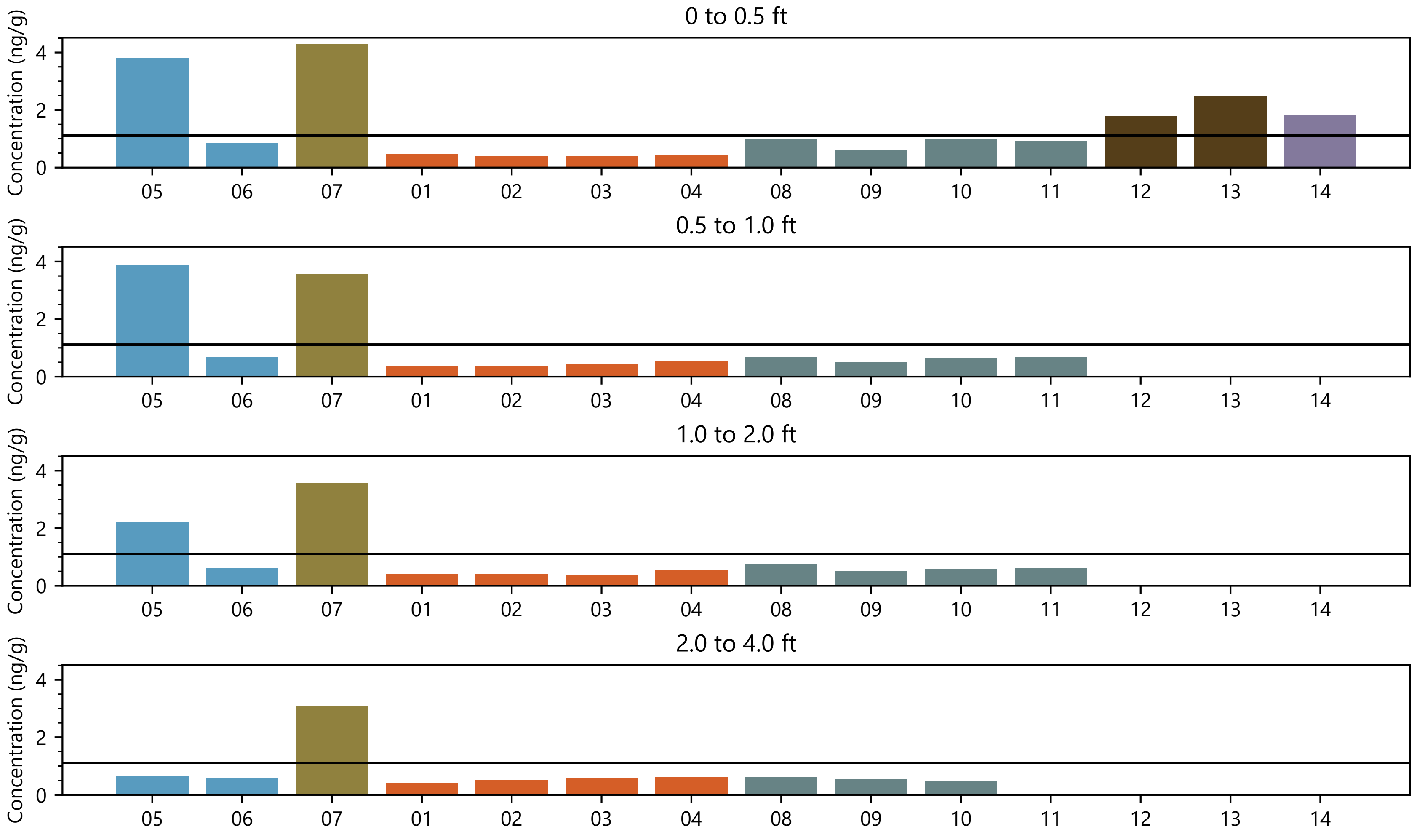


Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only).
   All other blank values were classified as not reportable after data validation.

■ Menomonee River	■ Kinnickinnic River
■ South Menomonee Canal	■ Harbor
■ Milwaukee River	■ Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

Figure 5k
Perfluorotetradecanoic acid (PFTeDA) Concentrations for MKE AOC Sediment



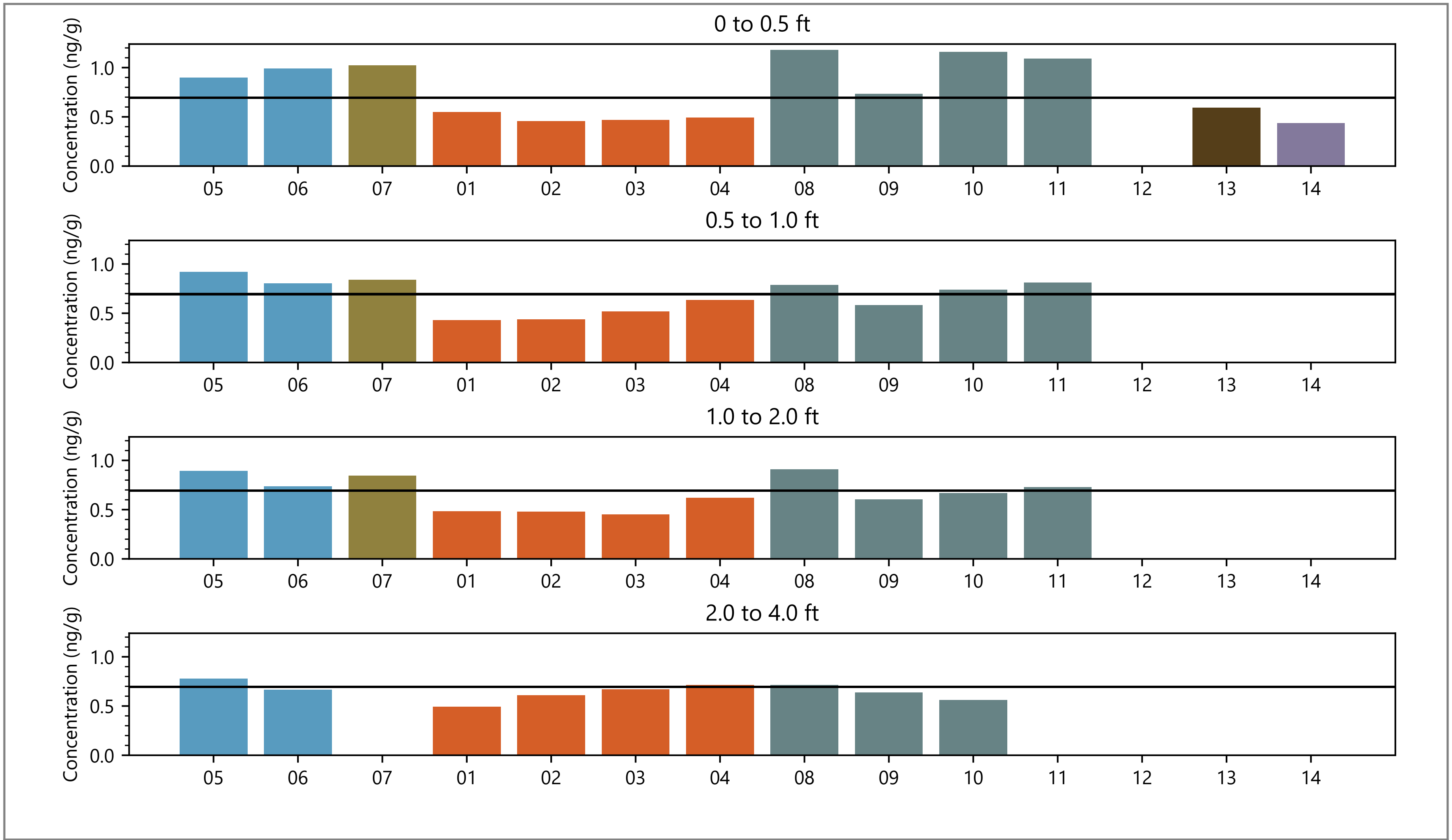
Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only).
   All other blank values were classified as not reportable after data validation.

■	Menomonee River	■	Kinnickinnic River
■	South Menomonee Canal	■	Harbor
■	Milwaukee River	■	Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

Figure 5l

Perfluorohexadecanoic acid (PFHxDA) Concentrations for MKE AOC Sediment



Notes:

1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only). All other blank values were classified as not reportable after data validation.

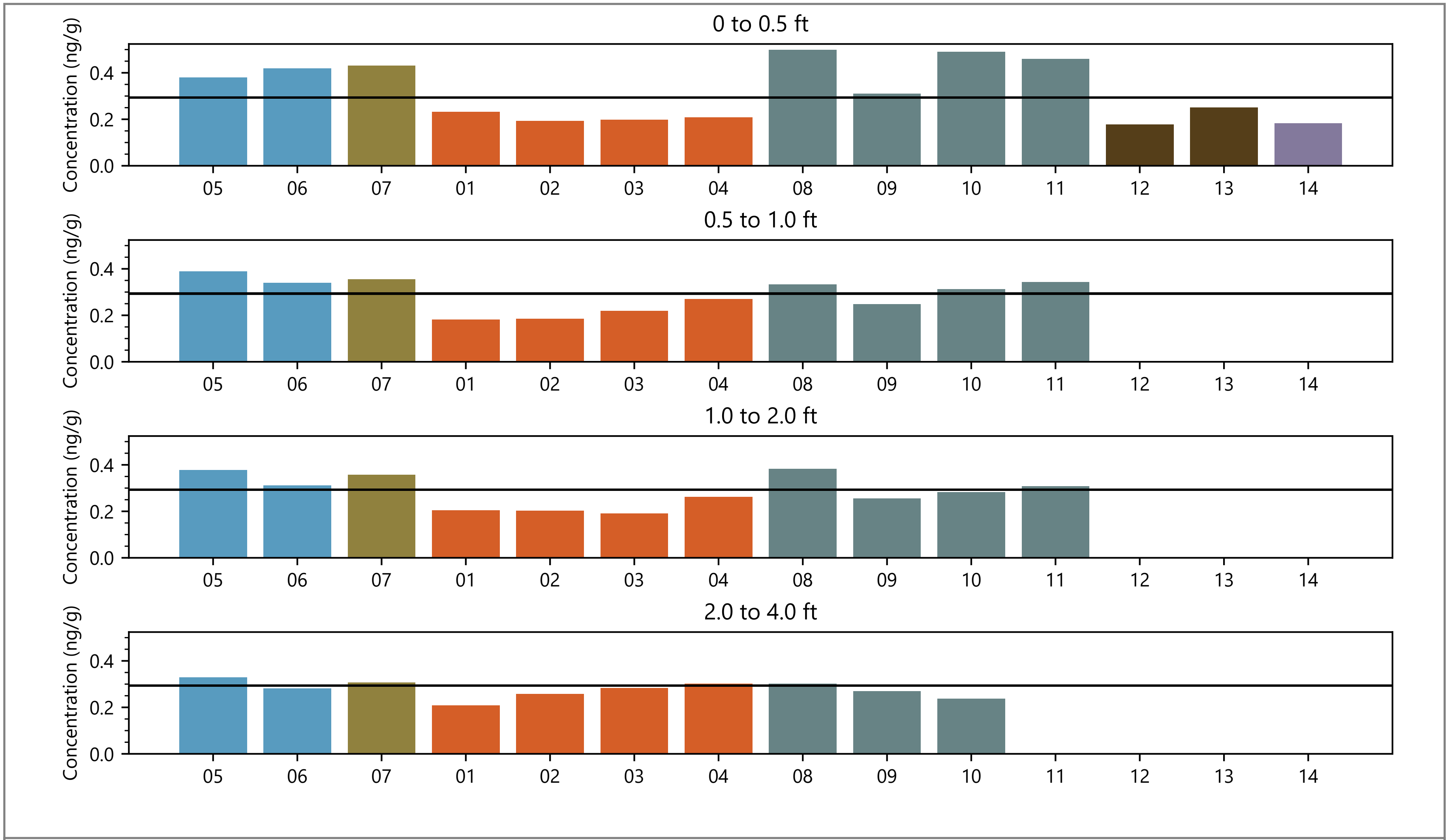
■ Menomonee River
■ South Menomonee Canal
■ Milwaukee River
■ Kinnickinnic River
■ Harbor
■ Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 5m

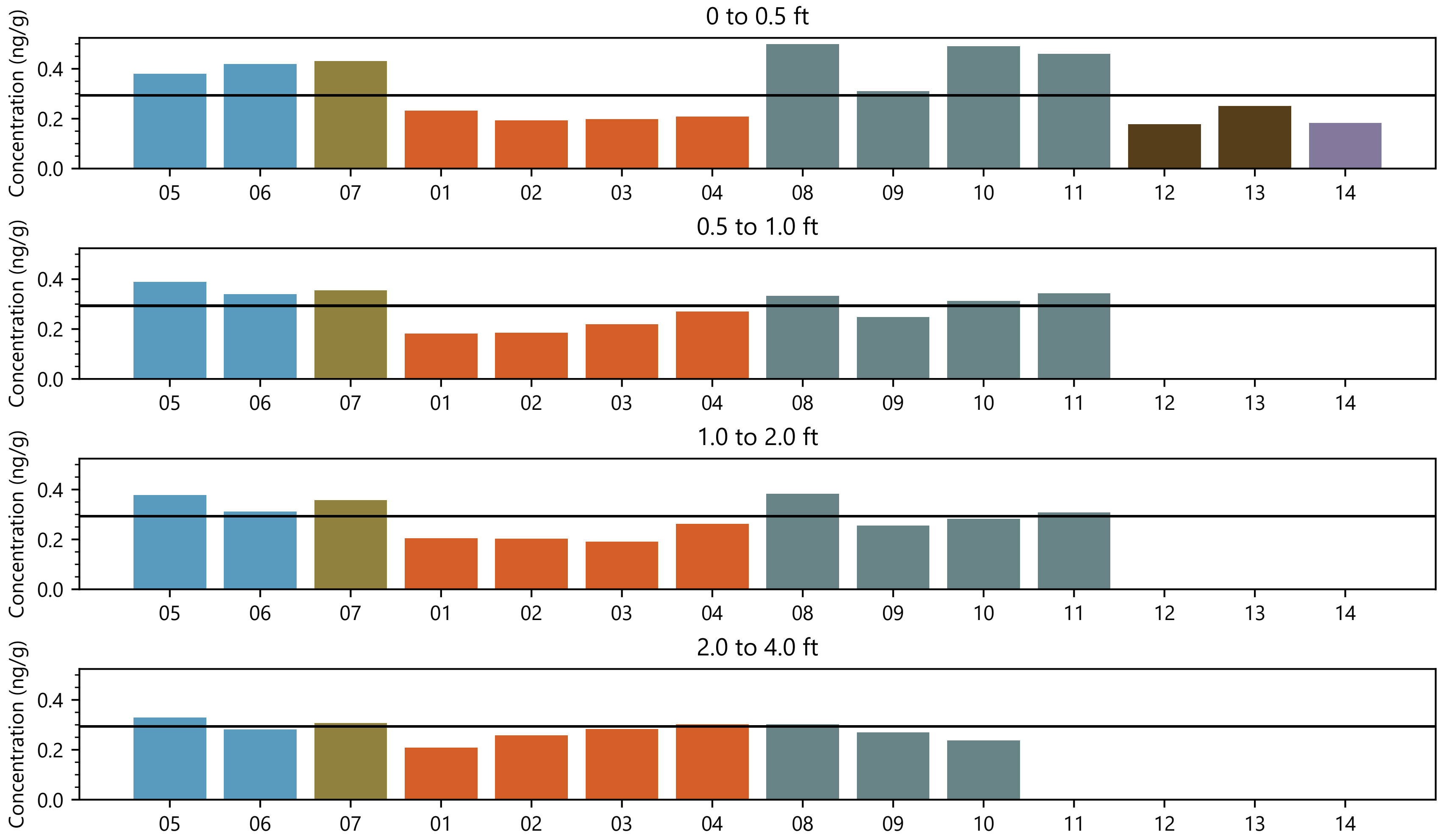
Perfluorooctadecanoic acid (PFODA) Concentrations for MKE AOC Sediment



Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only).
   All other blank values were classified as not reportable after data validation.

🟦 Menomonee River
🟫 South Menomonee Canal
🟧 Milwaukee River
⬛ Kinnickinnic River
🟫 Harbor
🟪 Lake Michigan

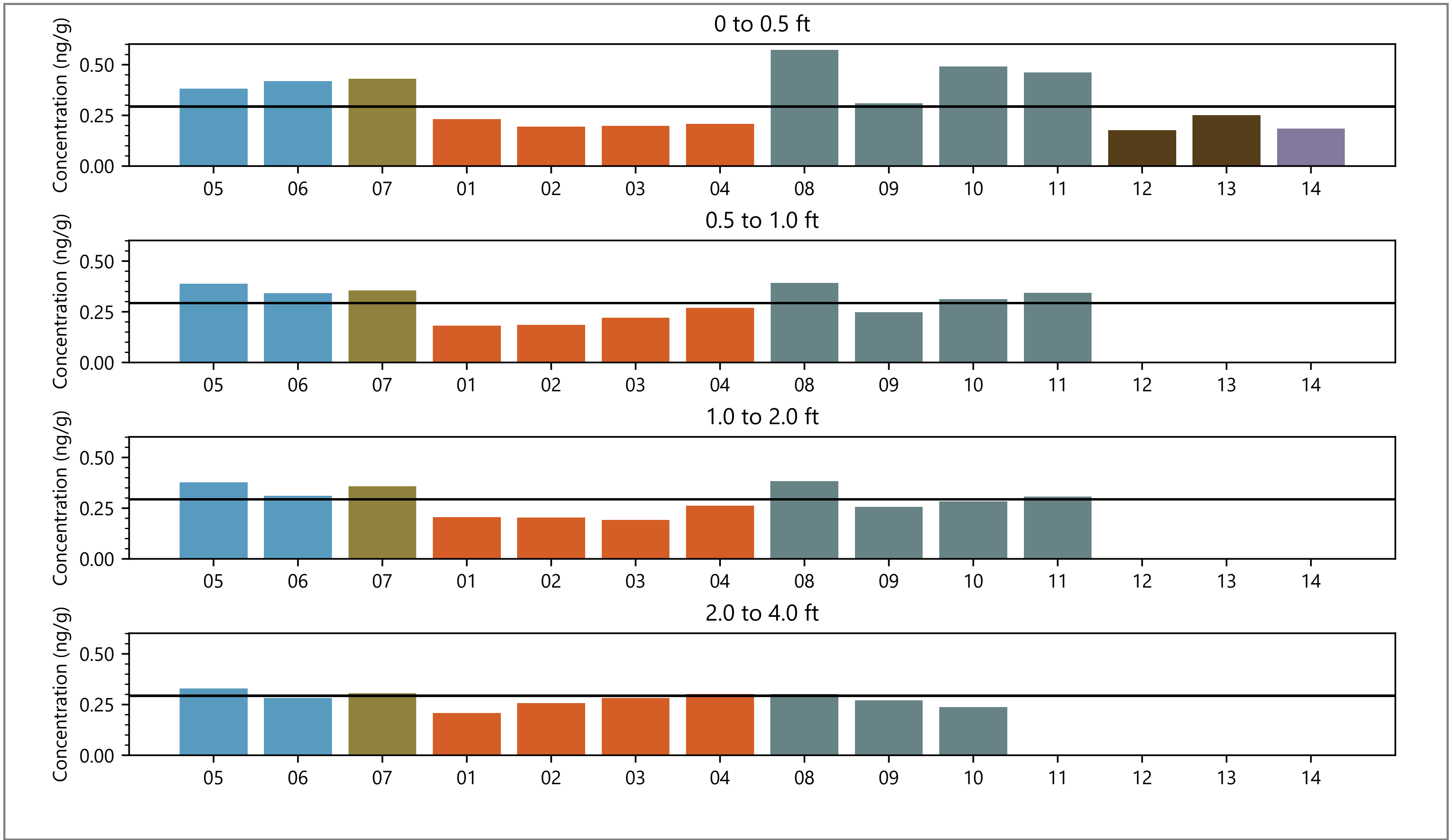
Figure 5n
Perfluorobutane sulfonate (PFBS) Concentrations for MKE AOC Sediment



Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only).
All other blank values were classified as not reportable after data validation.

■ Menomonee River
■ South Menomonee Canal
■ Milwaukee River
■ Kinnickinnic River
■ Harbor
■ Lake Michigan

Figure 5o
Perfluoropentane sulfonate (PFPeS) Concentrations for MKE AOC Sediment



Notes:

1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only). All other blank values were classified as not reportable after data validation.

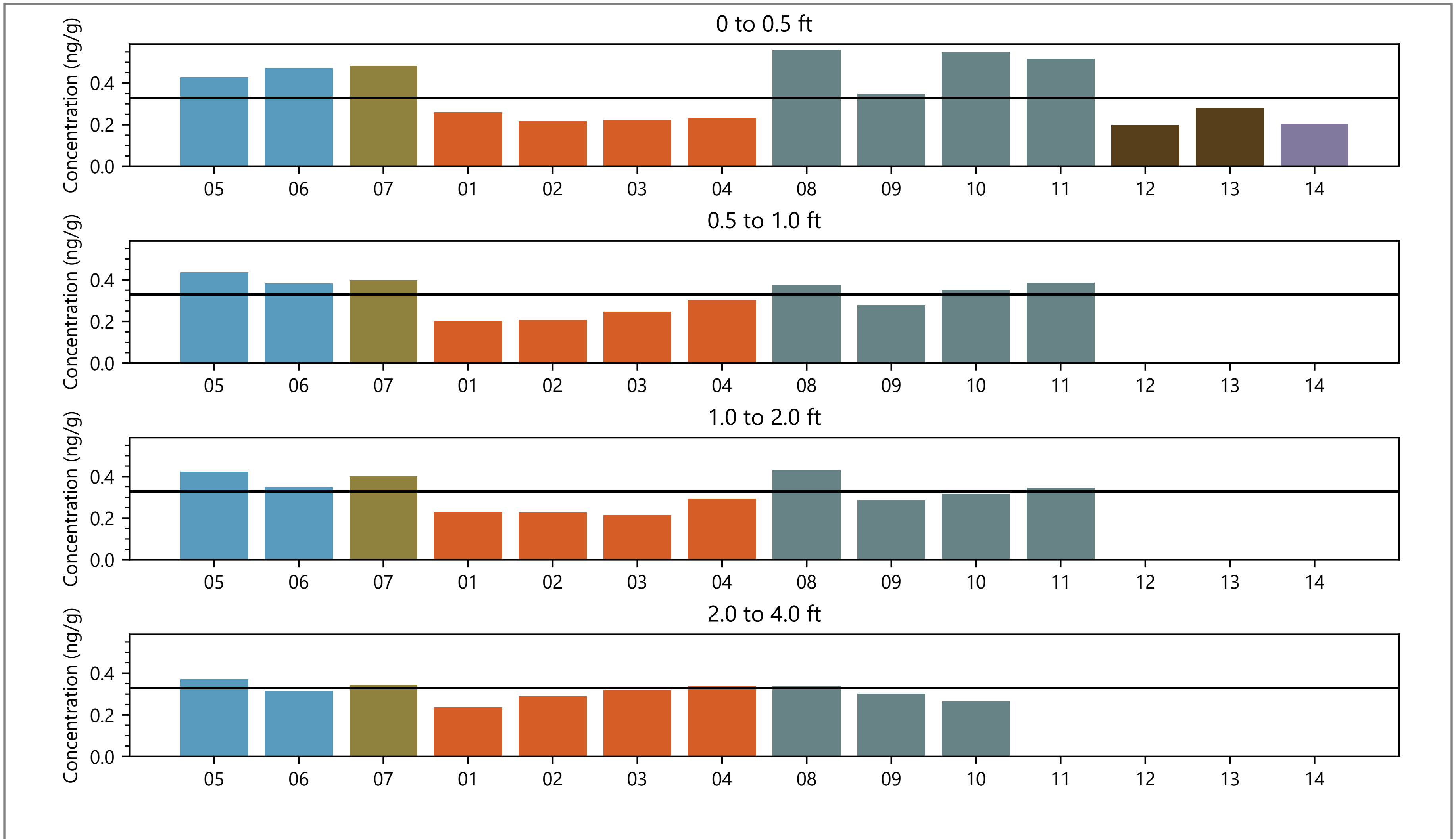
🟦	Menomonee River	■	Kinnickinnic River
■	South Menomonee Canal	🟫	Harbor
🟧	Milwaukee River	🟪	Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 5p

Perfluorohexane sulfonate (PFHxS) Concentrations for MKE AOC Sediment



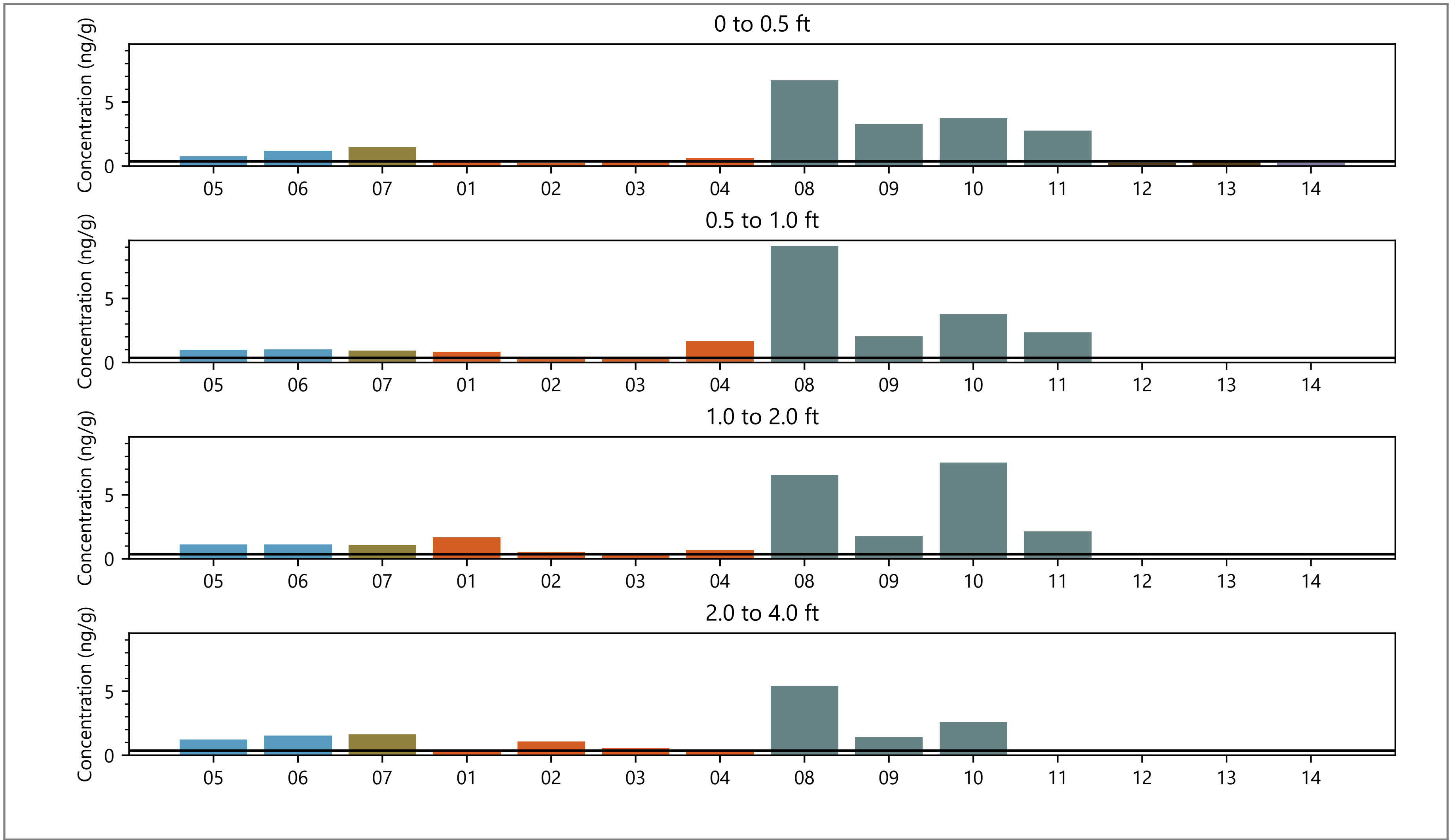
Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only).
All other blank values were classified as not reportable after data validation.

🟦 Menomonee River	🟩 Kinnickinnic River
🟨 South Menomonee Canal	🟫 Harbor
🟧 Milwaukee River	🟪 Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 5q
Perfluoroheptane sulfonate (PFHpS) Concentrations for MKE AOC Sediment



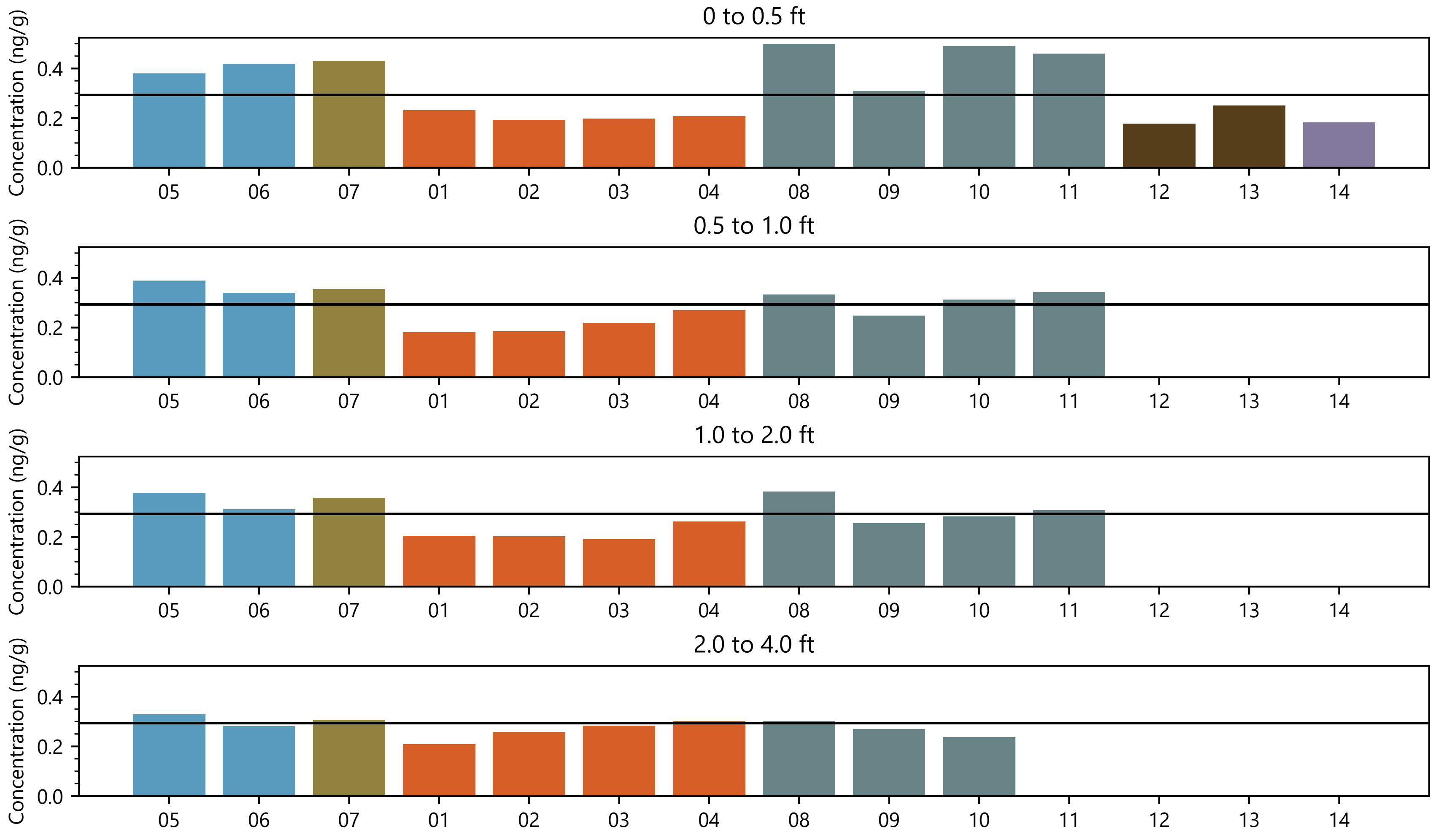
Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only). All other blank values were classified as not reportable after data validation.

🟦	Menomonee River	■	Kinnickinnic River
■	South Menomonee Canal	■	Harbor
🟧	Milwaukee River	🟪	Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 5r
Perfluorooctane sulfonate (PFOS) Concentrations for MKE AOC Sediment



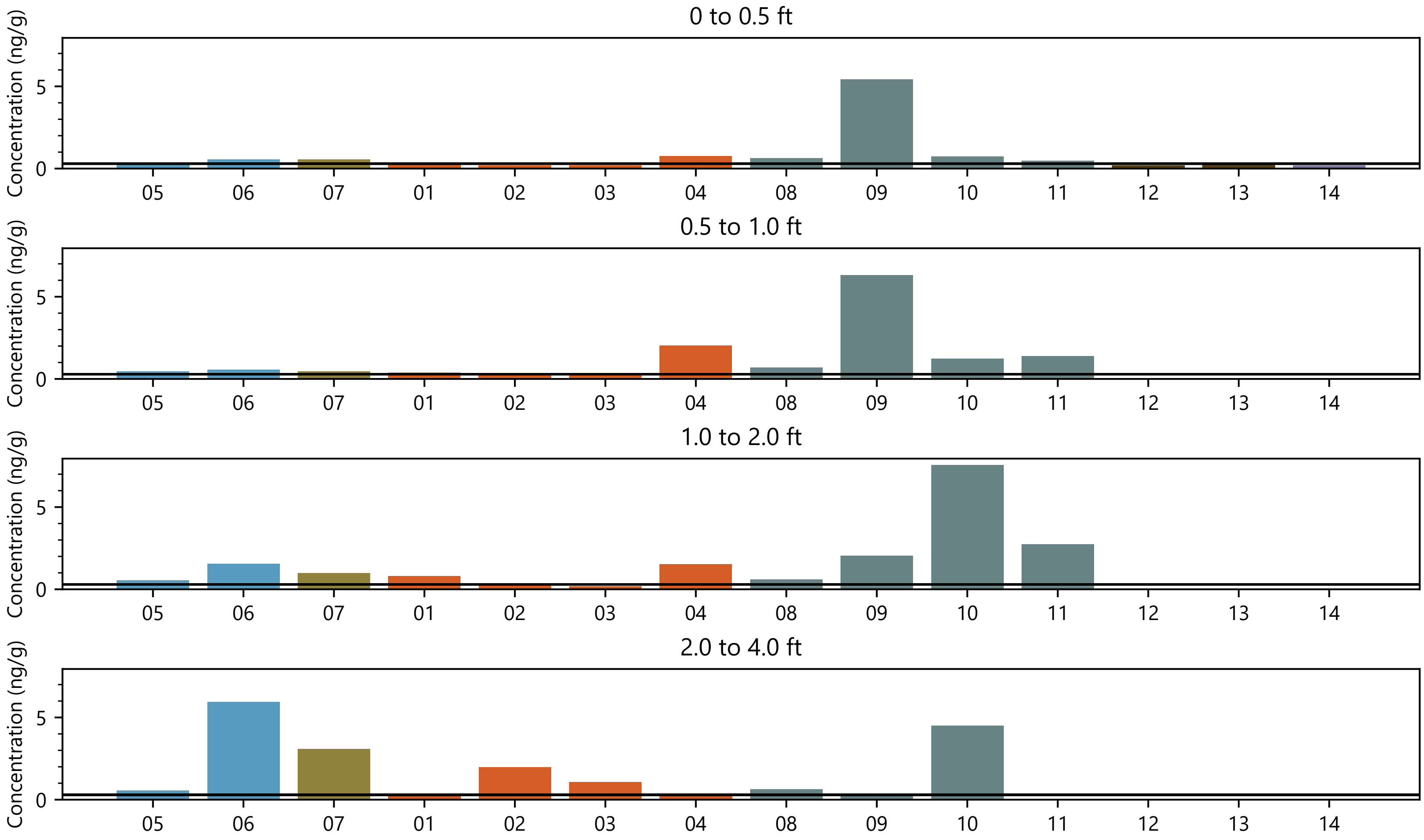
Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only). All other blank values were classified as not reportable after data validation.

■ Menomonee River
■ South Menomonee Canal
■ Milwaukee River
■ Kinnickinnic River
■ Harbor
■ Lake Michigan

ANCHOR QEA

Figure 5s

Perfluorononane sulfonate (PFNS) Concentrations for MKE AOC Sediment



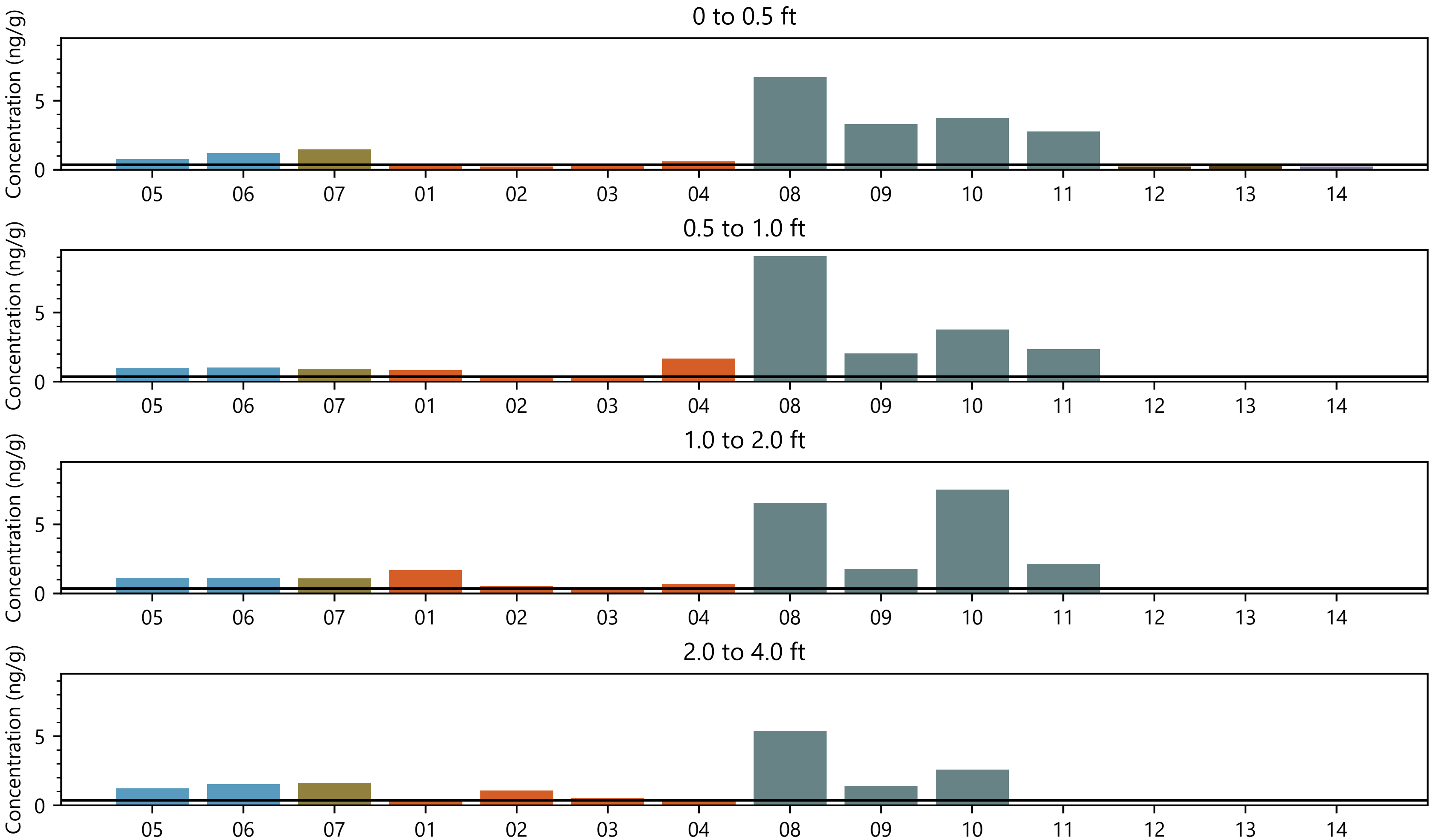
Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only). All other blank values were classified as not reportable after data validation.

🟦 Menomonee River	■ Kinnickinnic River
■ South Menomonee Canal	■ Harbor
🟧 Milwaukee River	🟪 Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 5t
Perfluorodecane sulfonate (PFDS) Concentrations for MKE AOC Sediment



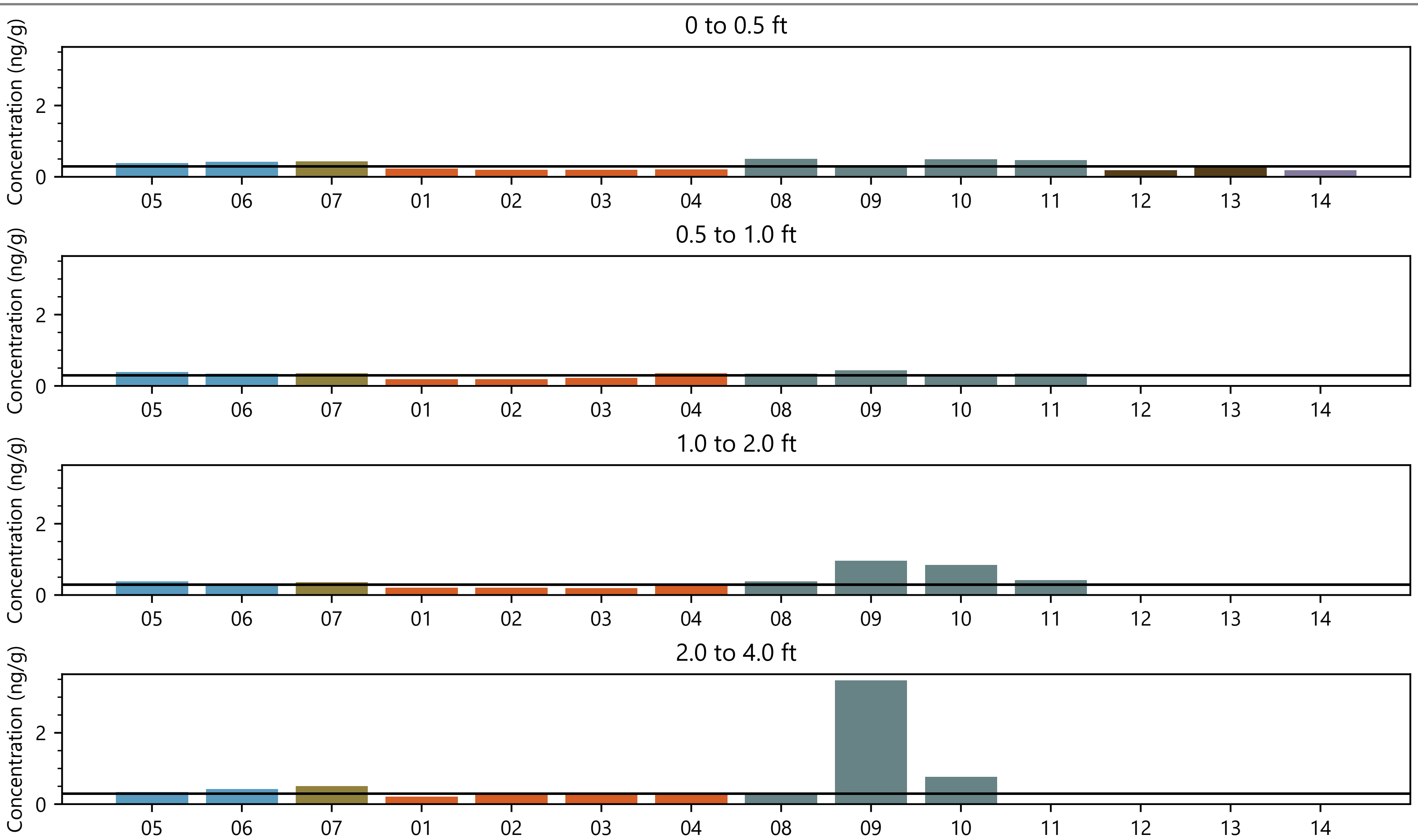
Notes:
1. If only one sample was detected, the non-detect was treated as 0. All PFOA samples were non-detect.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only). All other blank values were classified as not reportable after data validation.

🟦 Menomonee River	■ Kinnickinnic River
■ South Menomonee Canal	■ Harbor
🟧 Milwaukee River	🟪 Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

Figure 5u

Combined Perfluoroocatanoate (PFOA) and Perfluorooctane sulfonate (PFOS) Concentrations for MKE AOC Sediment



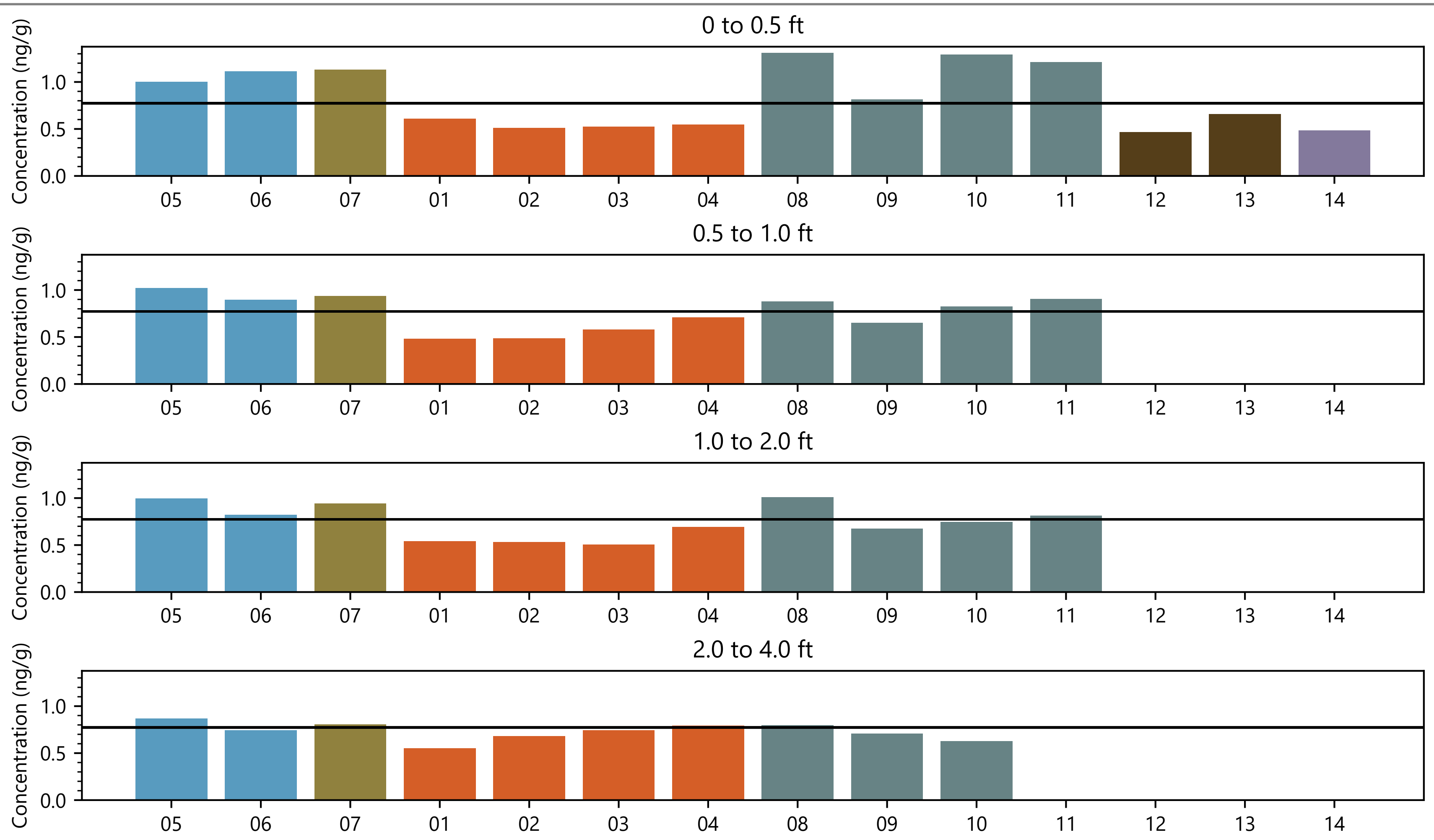
Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only).
   All other blank values were classified as not reportable after data validation.

🟦	Menomonee River	■	Kinnickinnic River
■	South Menomonee Canal	■	Harbor
🟧	Milwaukee River	🟪	Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 5v
Perfluorooctane sulfonamide (PFOSA) Concentrations for MKE AOC Sediment



Notes:

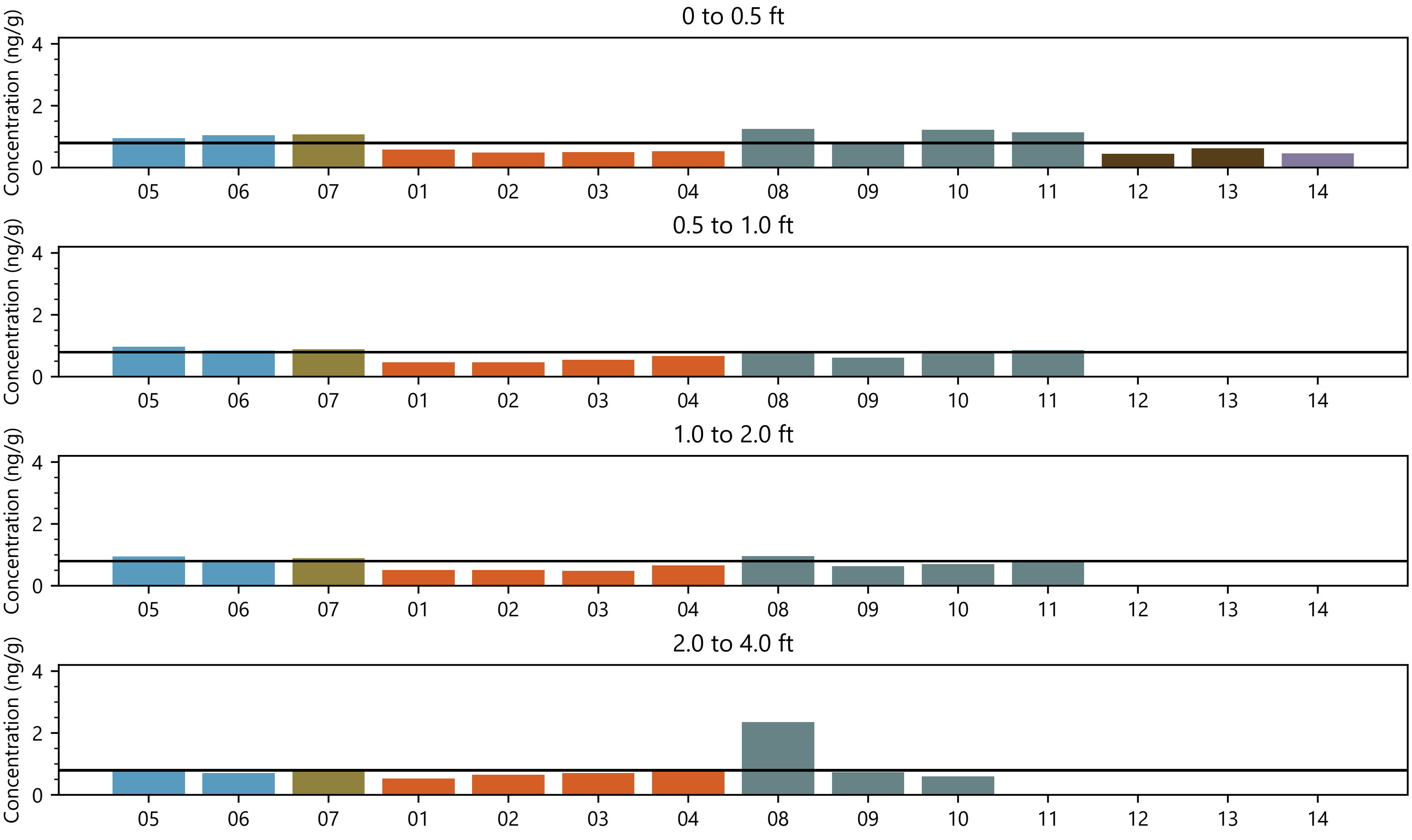
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only). All other blank values were classified as not reportable after data validation.

■ Menomonee River
■ South Menomonee Canal
■ Milwaukee River
■ Kinnickinnic River
■ Harbor
■ Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 5w
N-methyl perfluoro-1-octanesulfonamide (N-MeFOSA) Concentrations for MKE AOC Sediment



Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only). All other blank values were classified as not reportable after data validation.

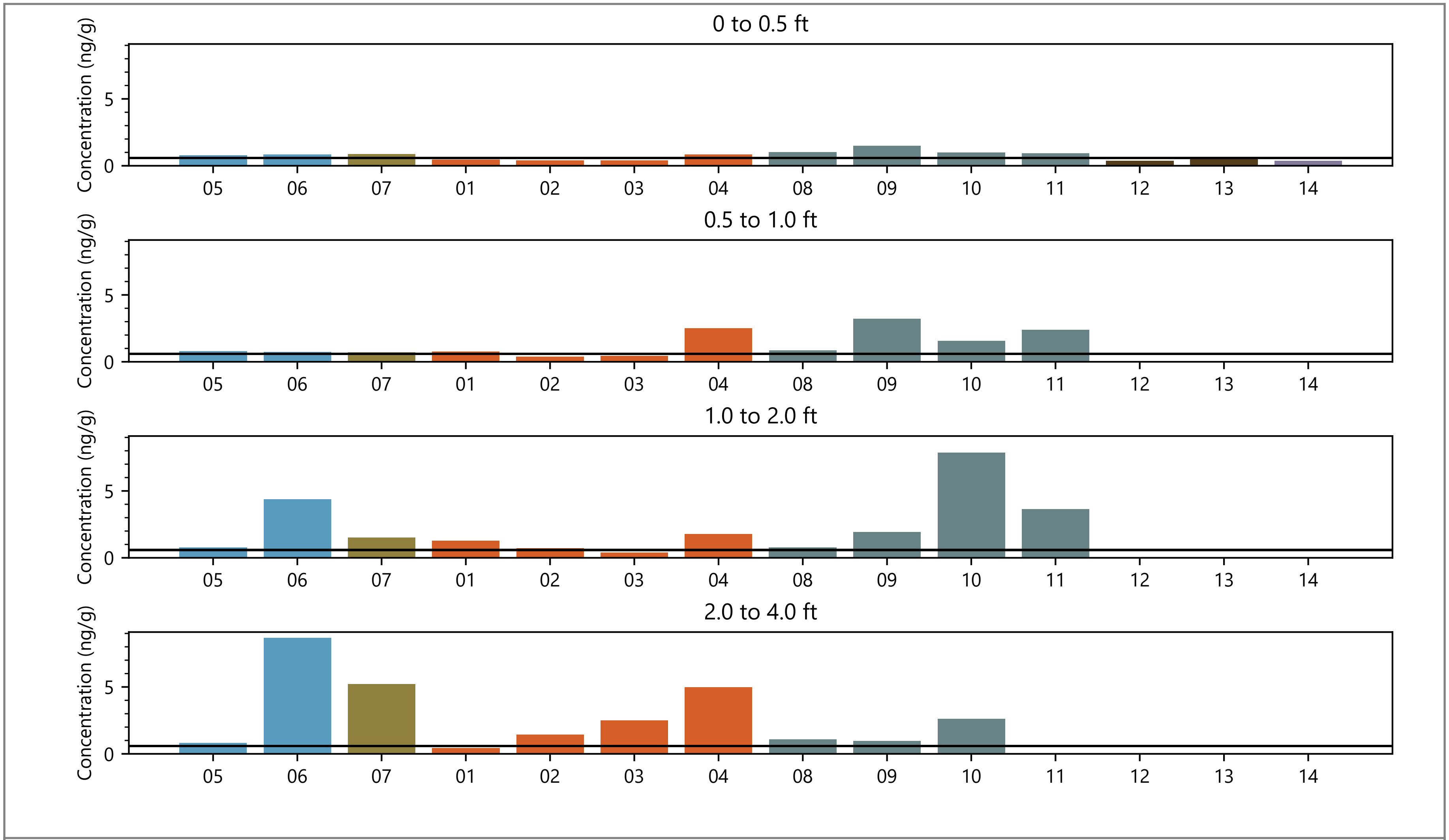
■	Menomonee River	■	Kinnickinnic River
■	South Menomonee Canal	■	Harbor
■	Milwaukee River	■	Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 5x

N-ethyl perfluoro-1-octanesulfonamide (N-EtFOSA) Concentrations for MKE AOC Sediment



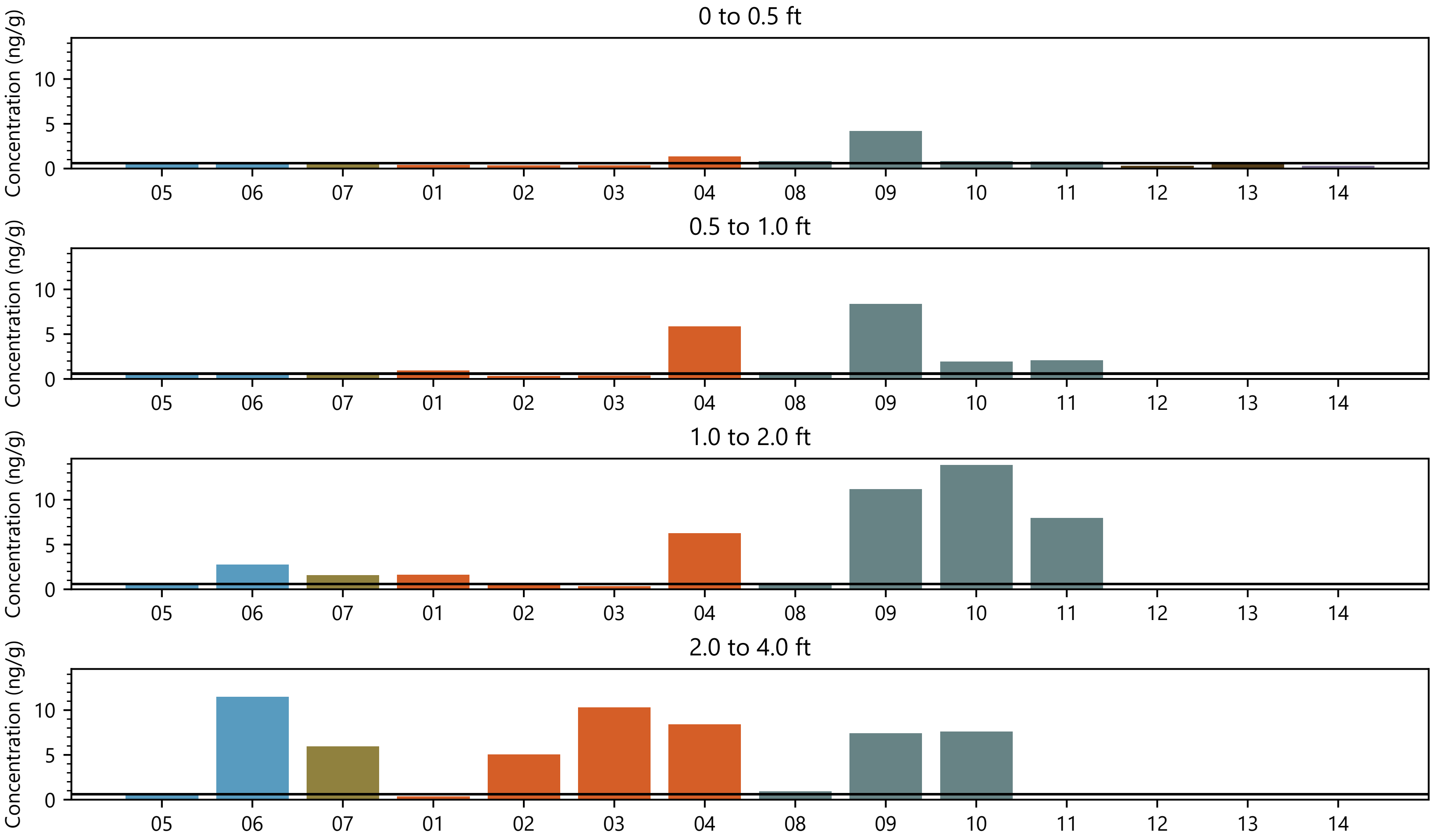
Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only). All other blank values were classified as not reportable after data validation.

🟦	Menomonee River	■	Kinnickinnic River
■	South Menomonee Canal	■	Harbor
🟧	Milwaukee River	🟪	Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

Figure 5y

N-methyl perfluorooctanesulfonamidoacetic acid (N-MeFOSAA) Concentrations for MKE AOC Sediment



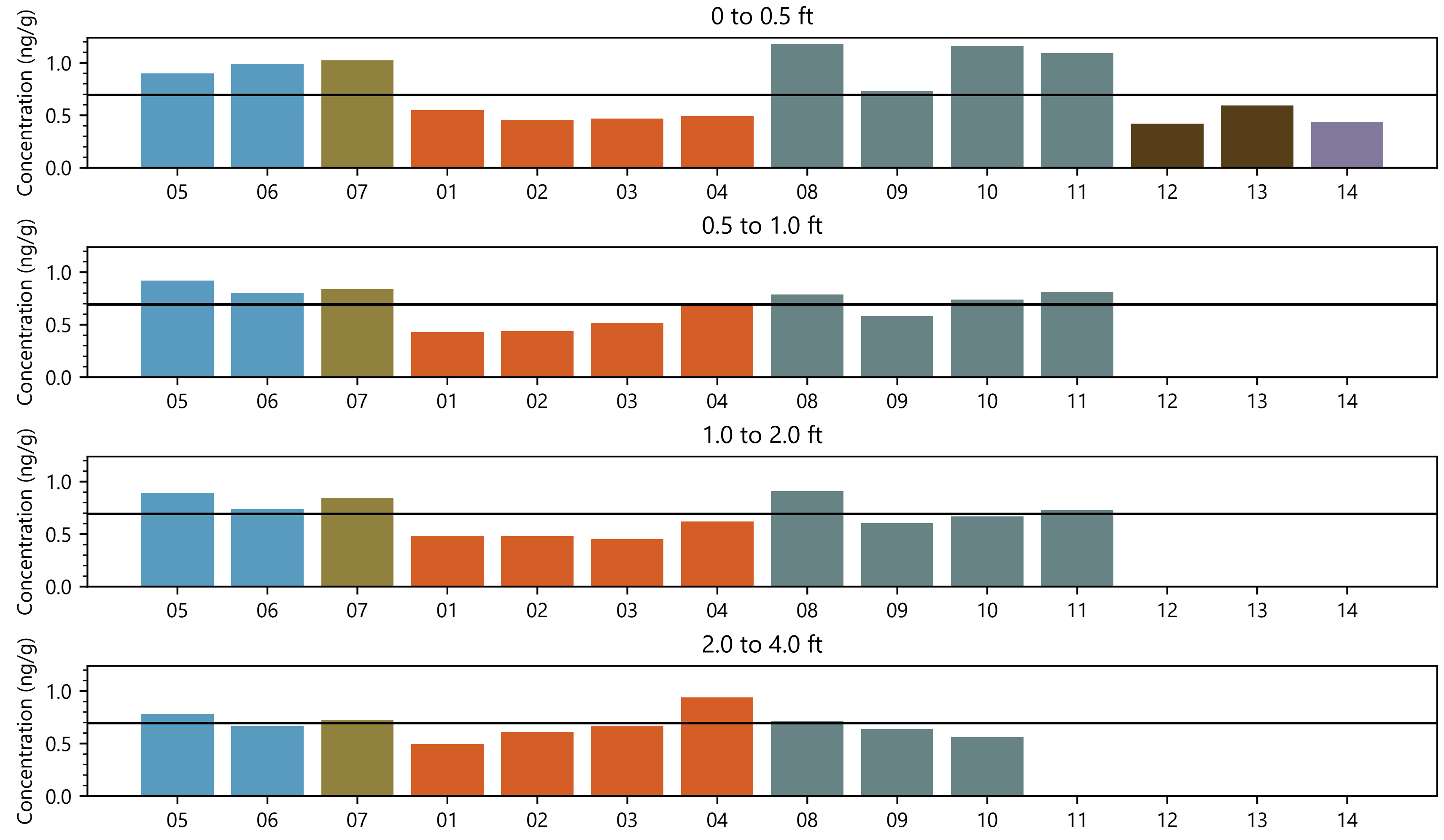
Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only). All other blank values were classified as not reportable after data validation.

■ Menomonee River	■ Kinnickinnic River
■ South Menomonee Canal	■ Harbor
■ Milwaukee River	■ Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

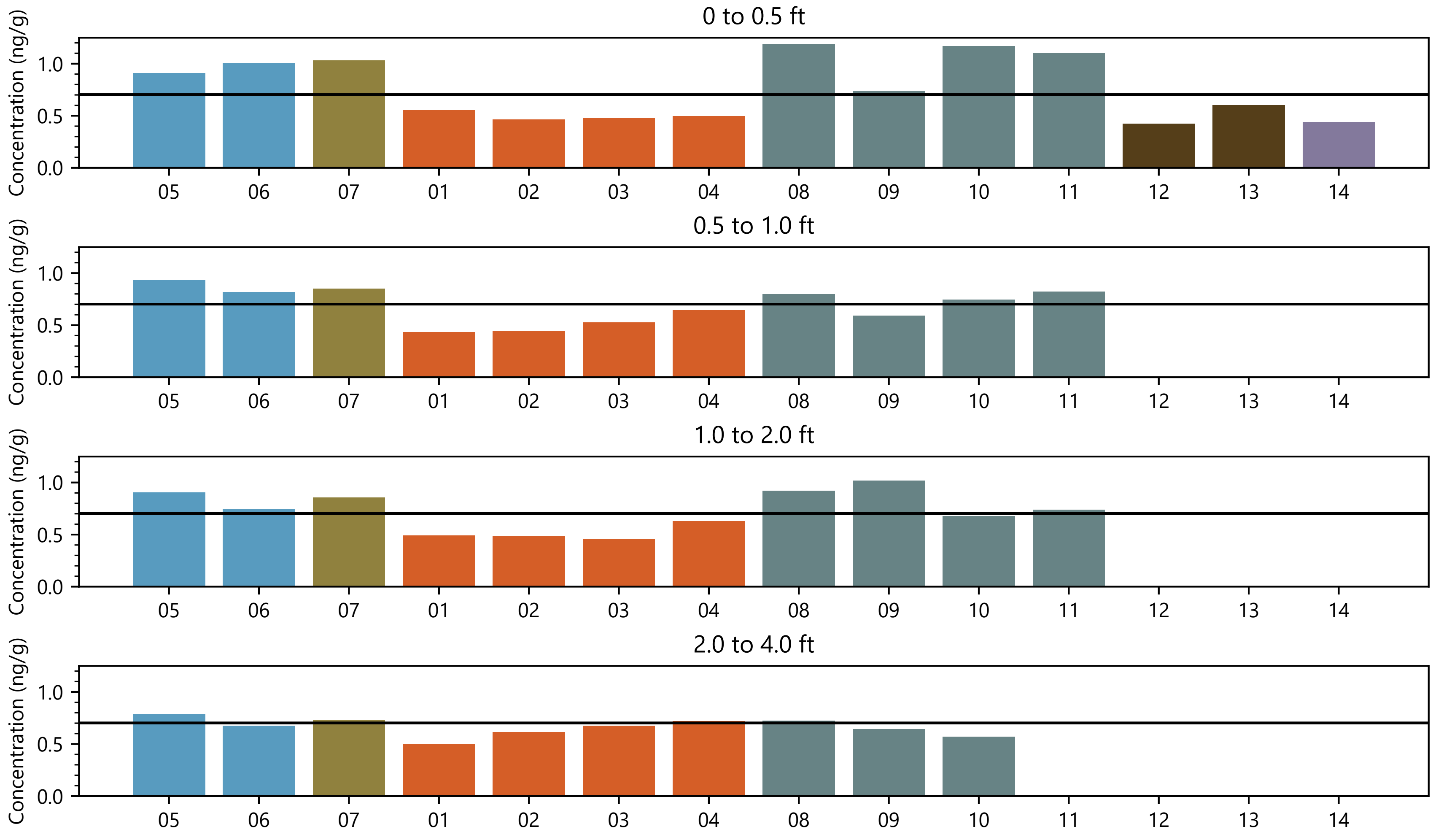
Figure 5z
N-ethyl perfluorooctanesulfonamidoacetic acid (N-EtFOSAA) Concentrations for MKE AOC Sediment



Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only).
All other blank values were classified as not reportable after data validation.

■ Menomonee River
■ South Menomonee Canal
■ Milwaukee River
■ Kinnickinnic River
■ Harbor
■ Lake Michigan

Figure 5aa
2-(N-methyl perfluoro-1-octanesulfonamido)-ethanol (N-MeFOSE) Concentrations for MKE AOC Sediment



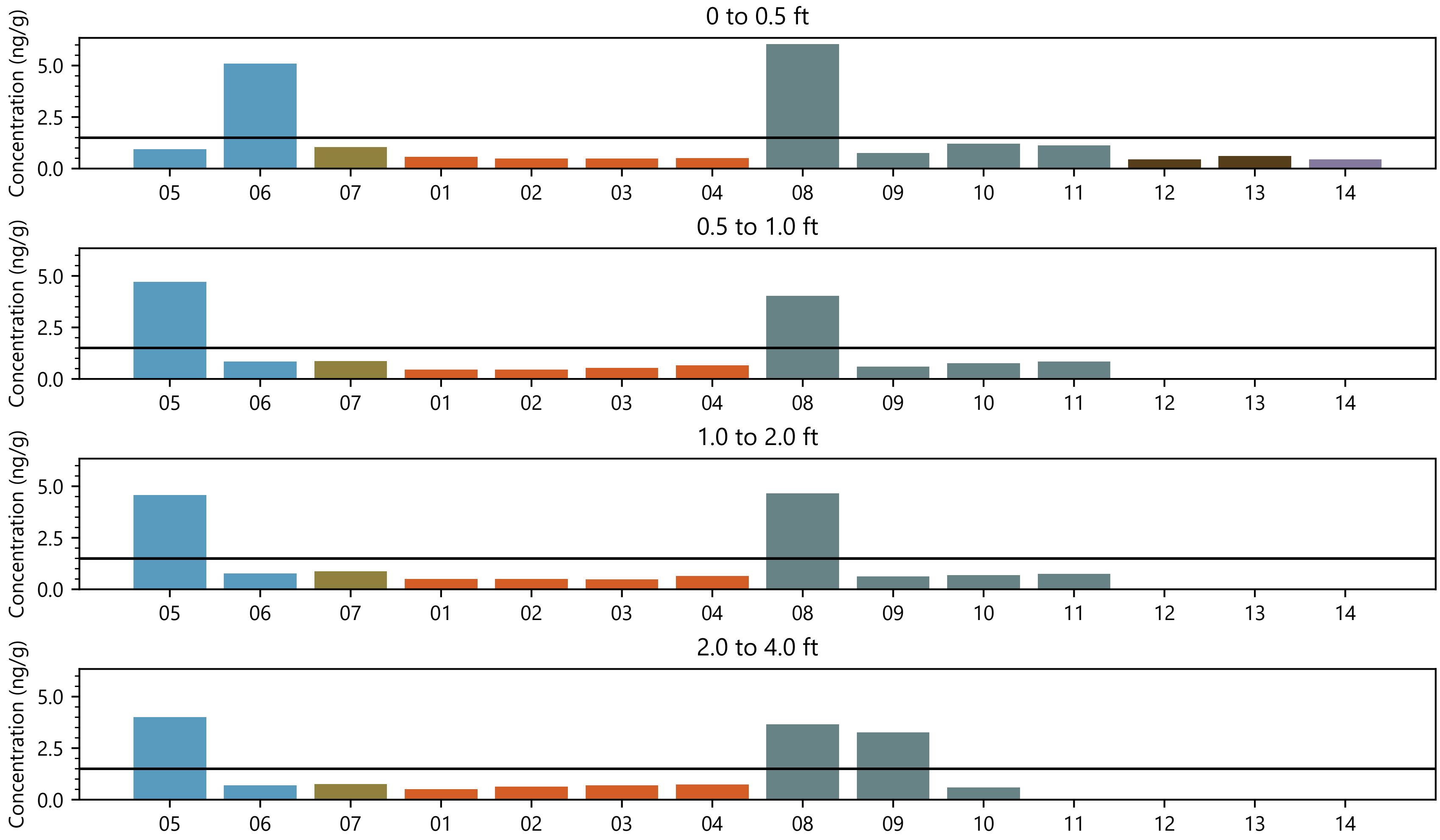
Notes:

1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only). All other blank values were classified as not reportable after data validation.

■ Menomonee River
■ South Menomonee Canal
■ Milwaukee River
■ Kinnickinnic River
■ Harbor
■ Lake Michigan

Figure 5bb

2-(N-ethyl perfluoro-1-octanesulfonamido)-ethanol (N-EtFOSE) Concentrations for MKE AOC Sediment

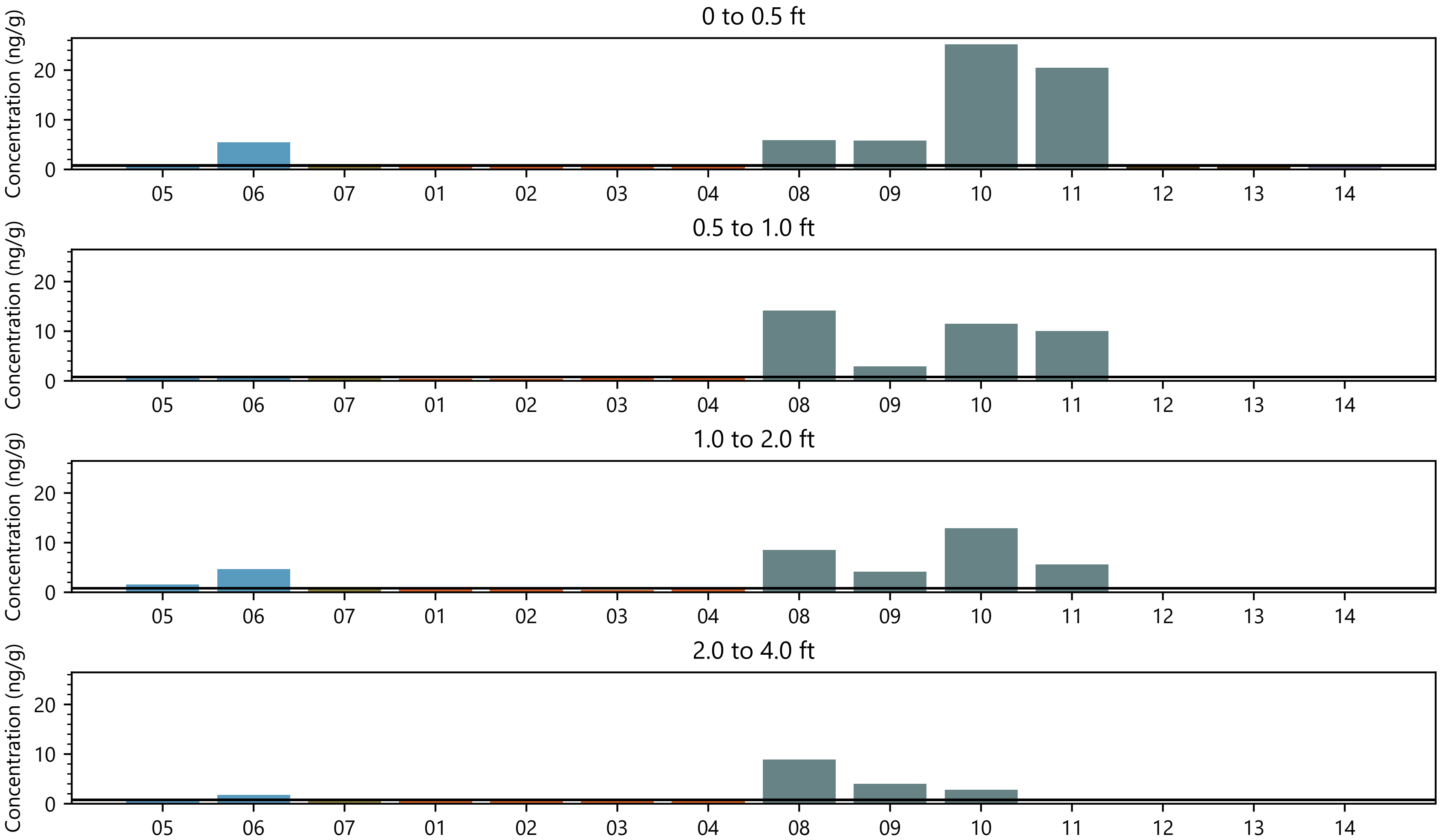


Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only).
   All other blank values were classified as not reportable after data validation.

■ Menomonee River
■ South Menomonee Canal
■ Milwaukee River
■ Kinnickinnic River
■ Harbor
■ Lake Michigan

Figure 5cc

4:2 fluorotelomer sulfonate (4:2 FTS) Concentrations for MKE AOC Sediment



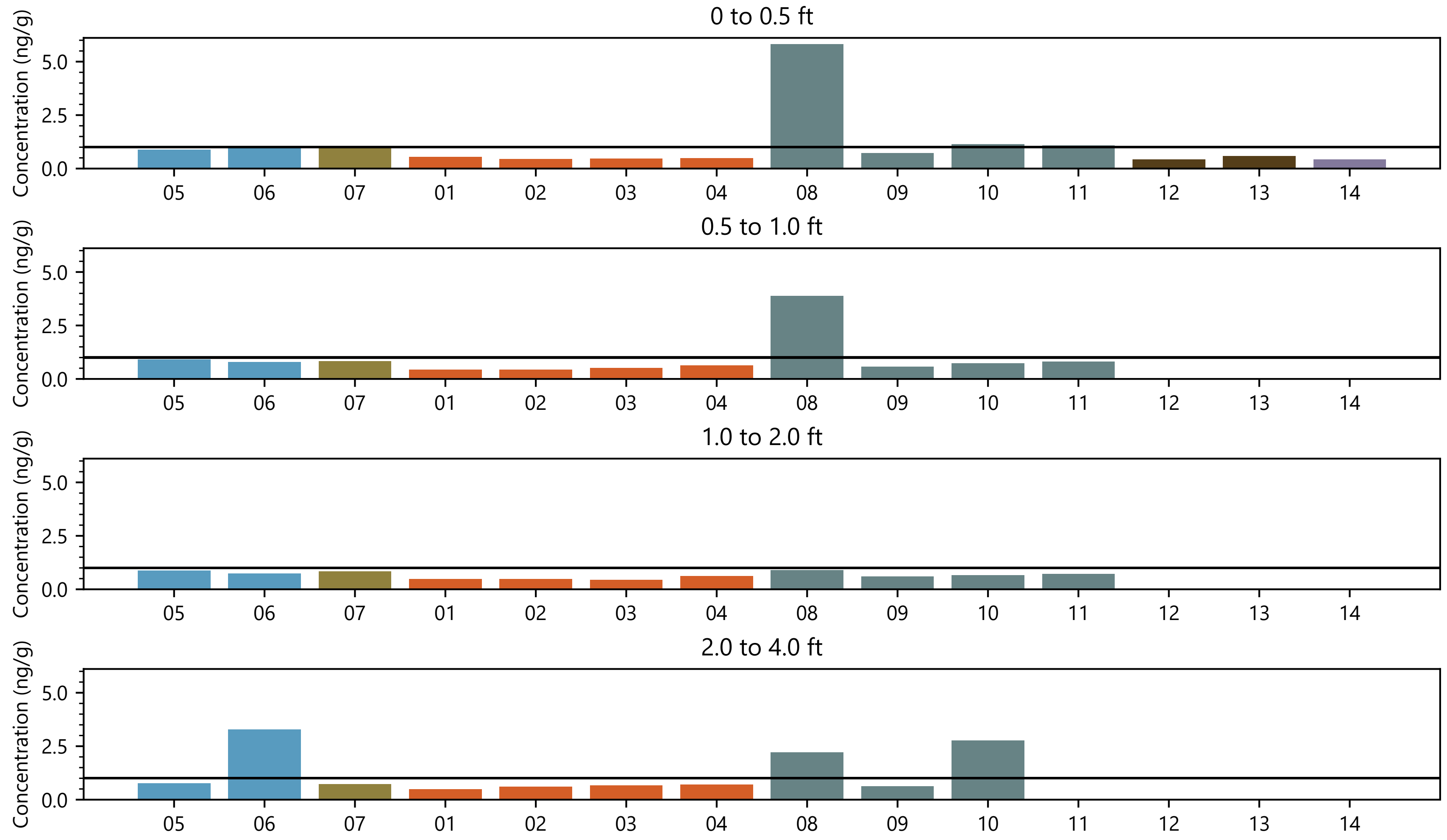
Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only). All other blank values were classified as not reportable after data validation.

🟦 Menomonee River
🟨 South Menomonee Canal
🟧 Milwaukee River
⬛ Kinnickinnic River
🟫 Harbor
🟪 Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 5dd
1H,1H,2H,2H-perfluorooctanesulfonic acid (THPFOS) (6:2 FTS) Concentrations for MKE AOC Sediment



Notes:

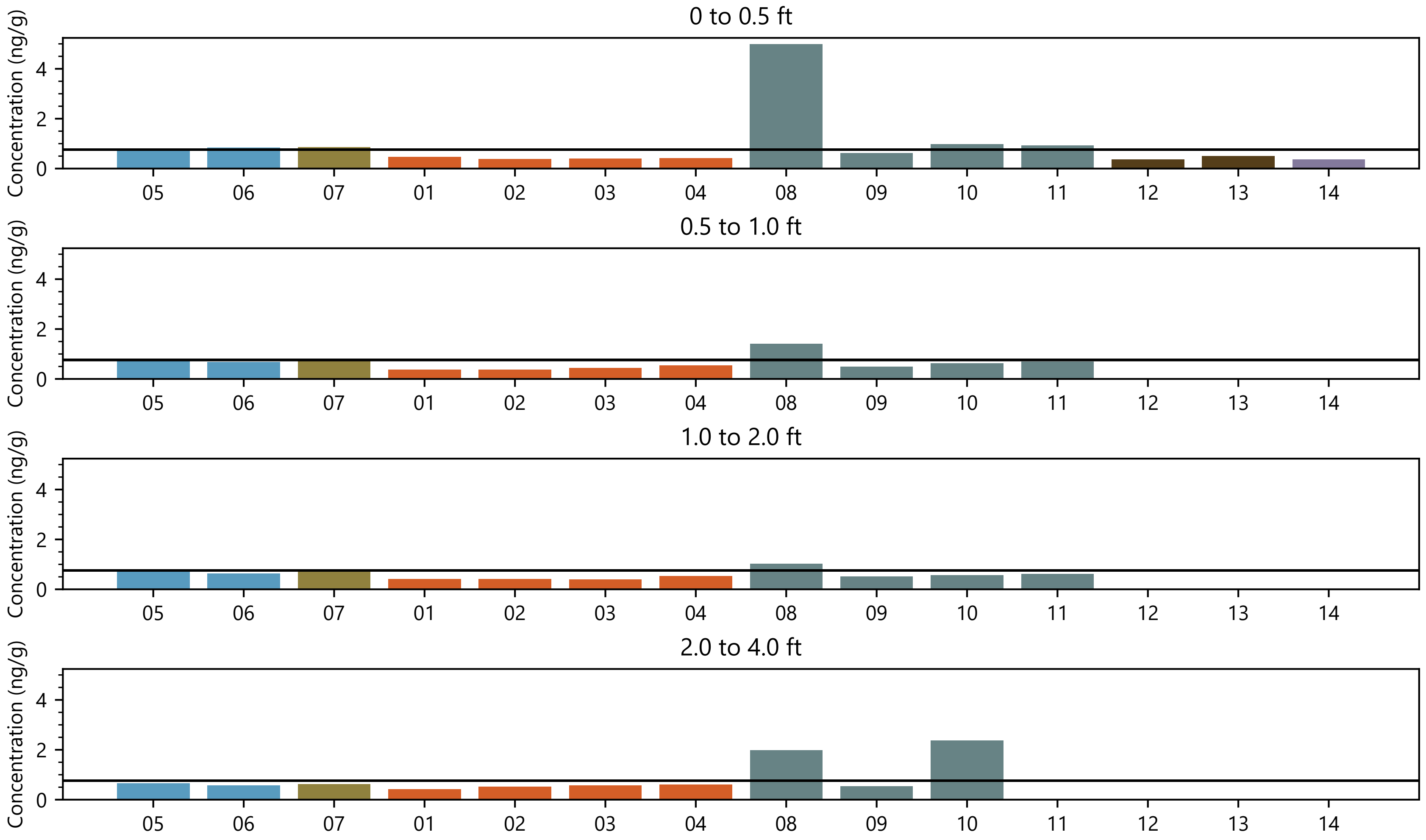
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only). All other blank values were classified as not reportable after data validation.

■ Menomonee River
■ South Menomonee Canal
■ Milwaukee River
■ Kinnickinnic River
■ Harbor
■ Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

Figure 5ee

1H,1H,2H,2H-perfluorodecanesulphonic acid (8:2 FTS) Concentrations for MKE AOC Sediment

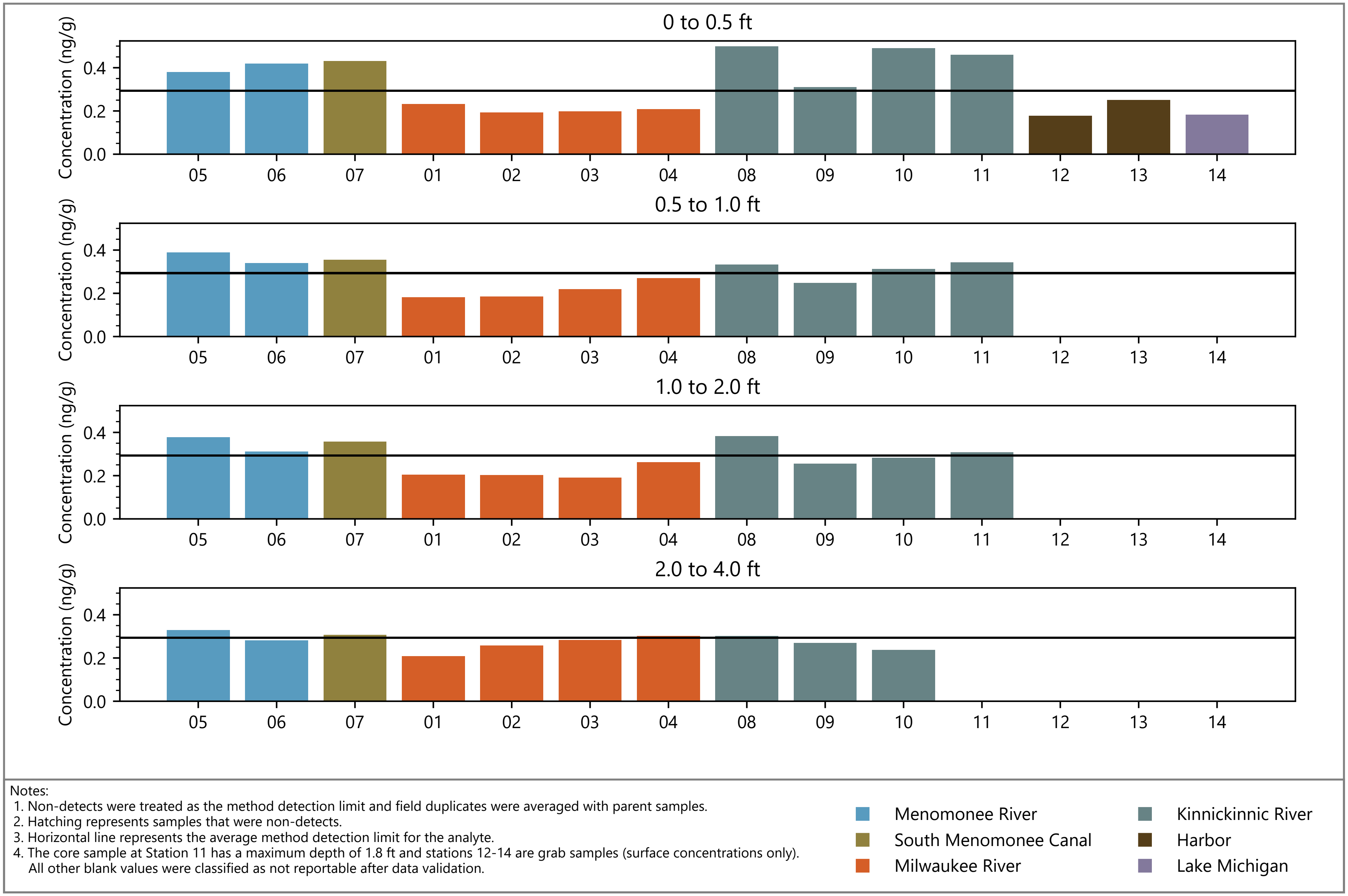


Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only).
All other blank values were classified as not reportable after data validation.

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 5ff
10:2-fluorotelomer sulfonate (10:2 FTS) Concentrations for MKE AOC Sediment

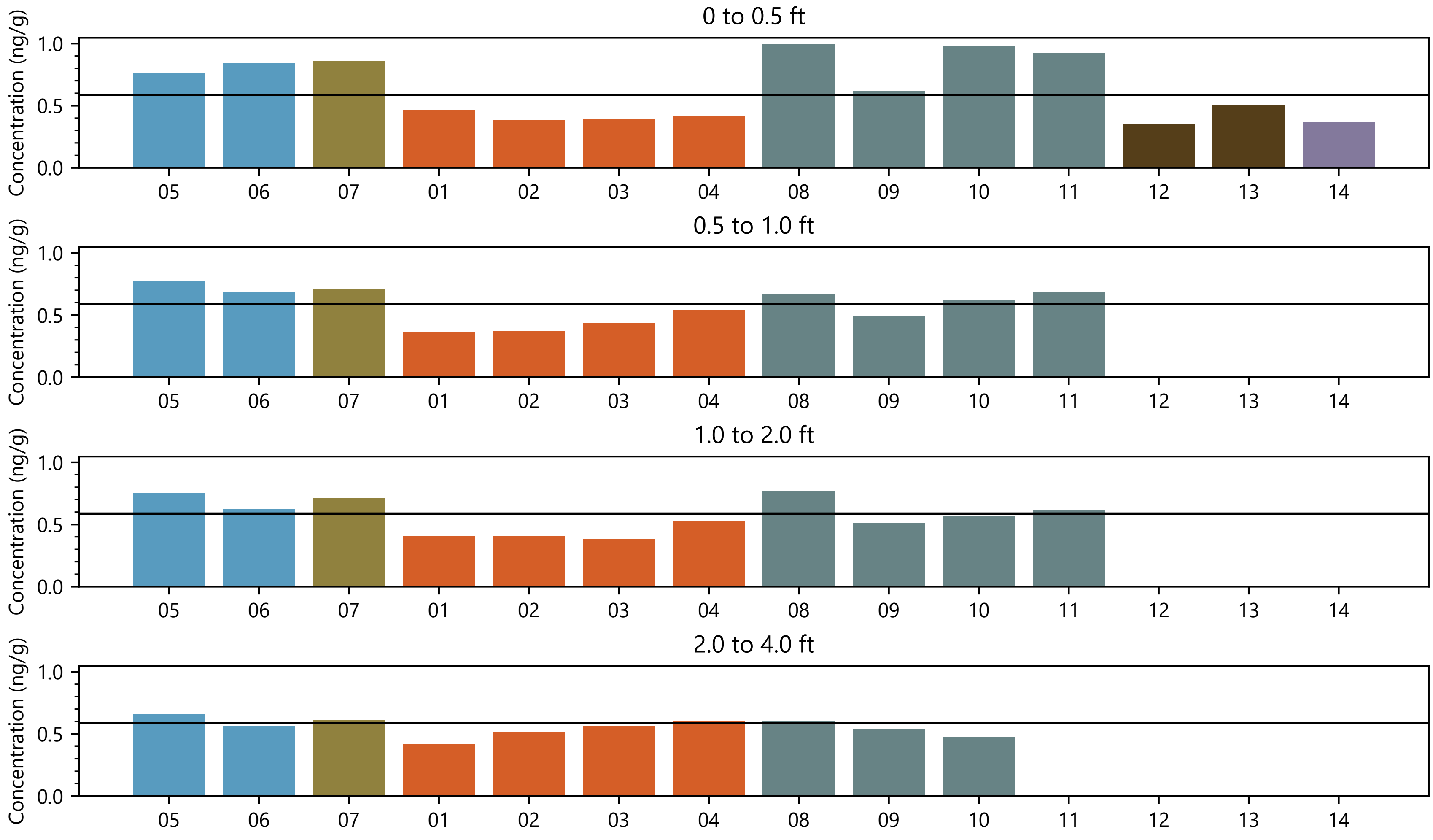


Notes:

1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only).
   All other blank values were classified as not reportable after data validation.

Figure 5gg

2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-propanoic acid (GenX) Concentrations for MKE AOC Sediment



Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only).
All other blank values were classified as not reportable after data validation.

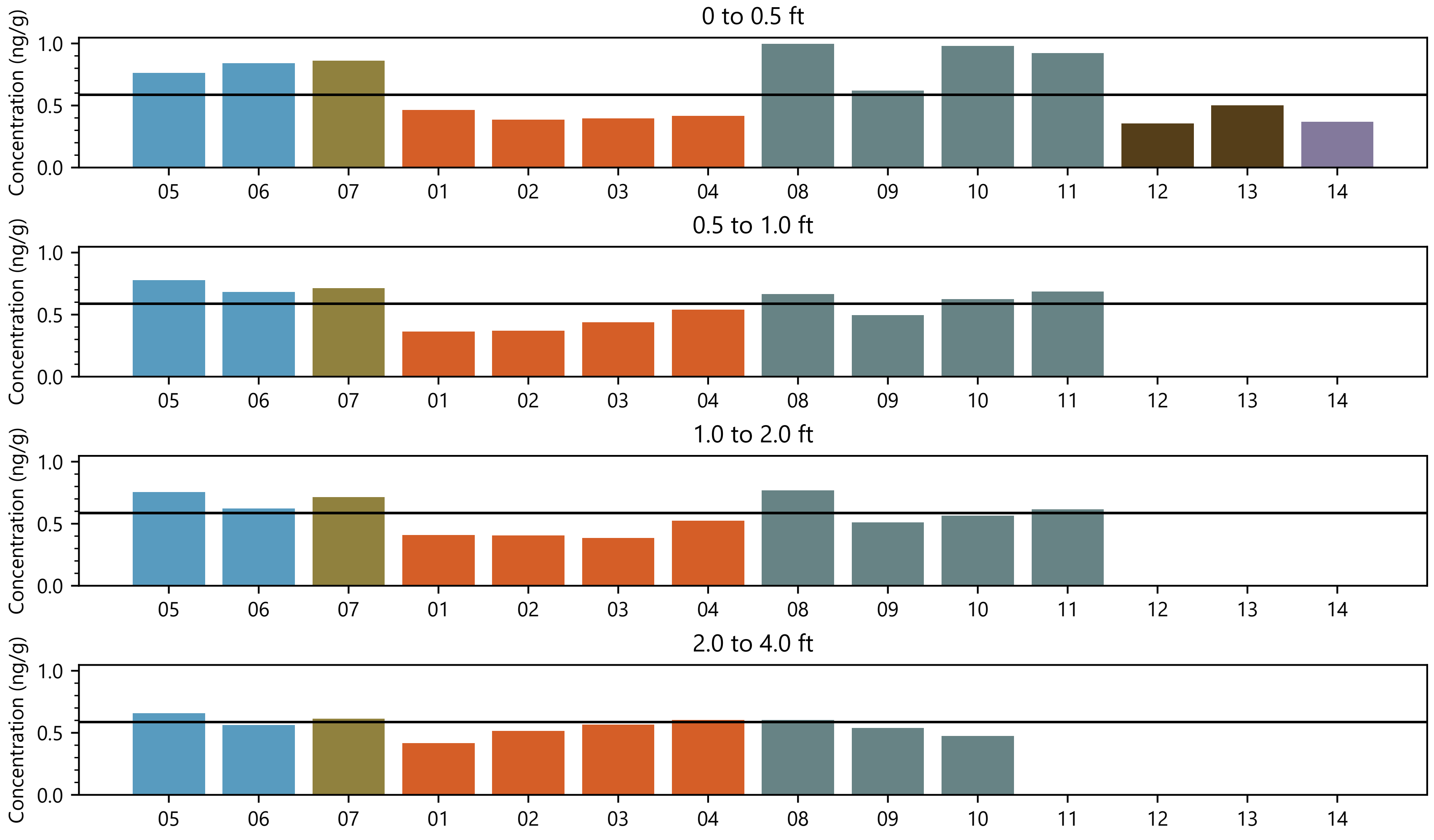
■ Menomonee River
■ South Menomonee Canal
■ Milwaukee River
■ Kinnickinnic River
■ Harbor
■ Lake Michigan

Publish Date: 05/06/2020 17:05 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 5hh

11-chloroeicosafluoro-3-oxaundecane-1-sulfonate (PF3OUdS) (F53B minor) Concentrations for MKE AOC Sediment

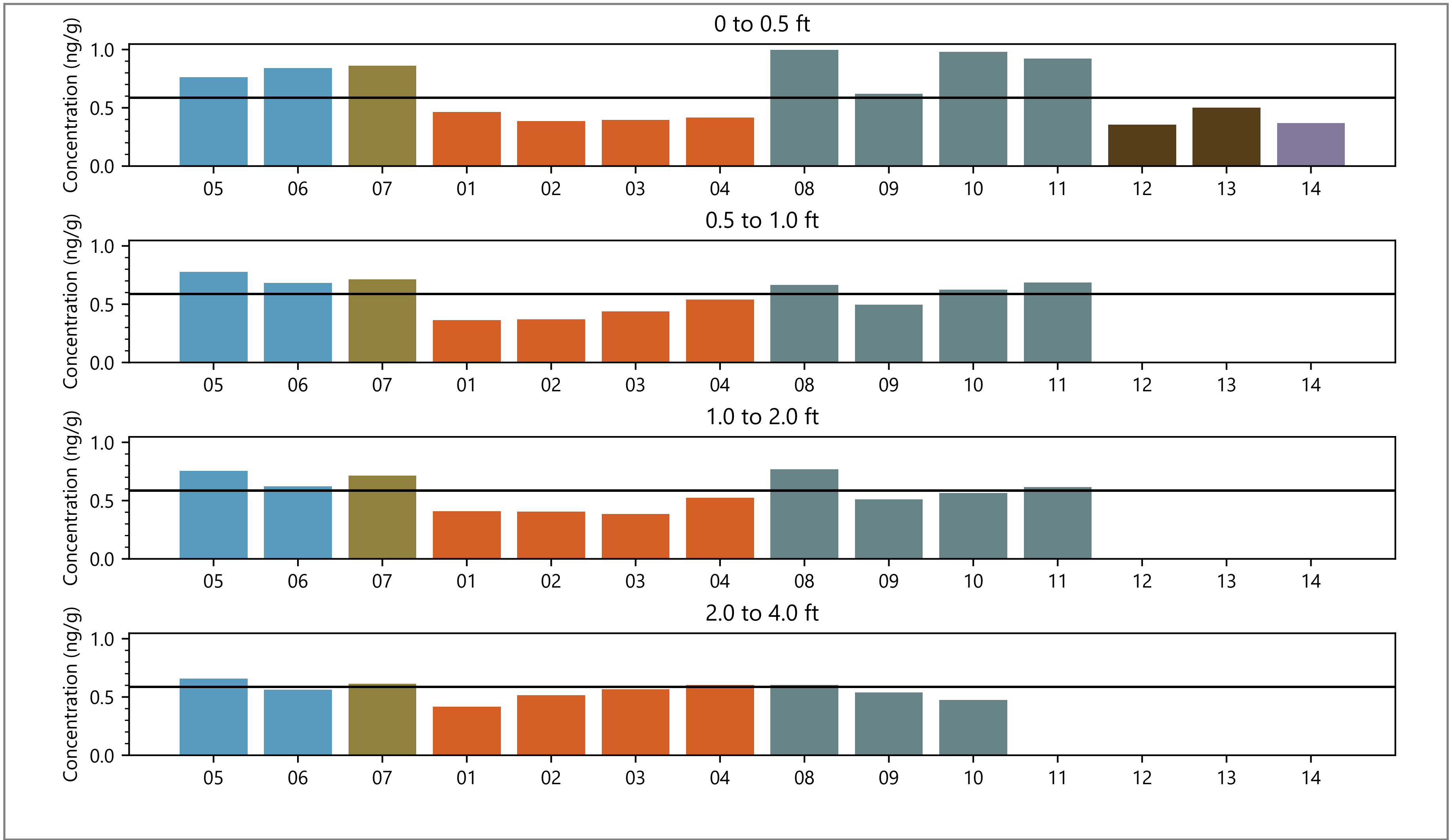


Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only).
   All other blank values were classified as not reportable after data validation.

🟦 Menomonee River	■ Kinnickinnic River
■ South Menomonee Canal	🟫 Harbor
🟧 Milwaukee River	🟪 Lake Michigan

Figure 5ii

9-chlorohexadecafluoro-3-oxanonnane-1-sulfonate (PF3ONS) (F53B major) Concentrations for MKE AOC Sediment



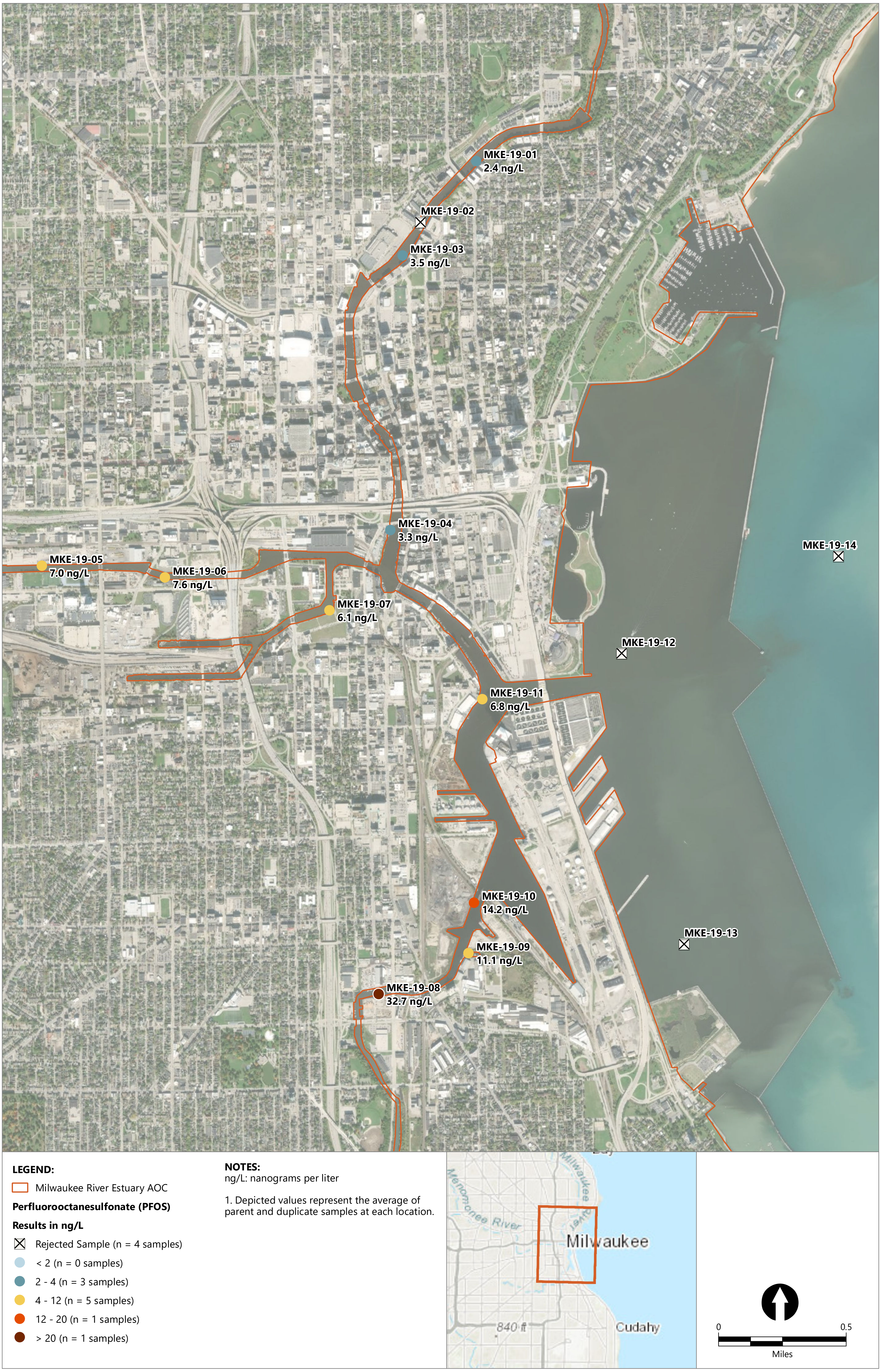
Notes:
1. Non-detects were treated as the method detection limit and field duplicates were averaged with parent samples.
2. Hatching represents samples that were non-detects.
3. Horizontal line represents the average method detection limit for the analyte.
4. The core sample at Station 11 has a maximum depth of 1.8 ft and stations 12-14 are grab samples (surface concentrations only).
All other blank values were classified as not reportable after data validation.

🟦 Menomonee River
🟨 South Menomonee Canal
🟧 Milwaukee River
⬛ Kinnickinnic River
🟫 Harbor
🟪 Lake Michigan

Publish Date: 05/06/2020 17:06 PM | User: SYR-SPARE2
File Path: \\helios\aq\D_Drive\Projects\WI_DNR\Milwaukee_AOC\Design_Analysis\PFAS\Barplots\PFAS_barplots.py

ANCHOR QEA

Figure 5jj
Sodium dodecafluoro-3H-4,8-dioxanonanoate (ADONA) Concentrations for MKE AOC Sediment



LEGEND:

▭ Milwaukee River Estuary AOC

Perfluorooctanesulfonate (PFOS)

Results in ng/L

☒ Rejected Sample (n = 4 samples)

● < 2 (n = 0 samples)

● 2 - 4 (n = 3 samples)

● 4 - 12 (n = 5 samples)

● 12 - 20 (n = 1 samples)

● > 20 (n = 1 samples)

NOTES:
ng/L: nanograms per liter

1. Depicted values represent the average of parent and duplicate samples at each location.

Publish Date: 2020/10/30, 11:12 AM | User: jquinley
Filepath: \\orcas\GIS\Jobs\WisconsinDNR_1779\Milwaukee_1779\Maps\PFOS_PFOA\AQ_WIDNR_PFOS_PFAS_Figure6_PFOSConcentrations.mxd

ANCHOR QEA

Figure 6
Perfluorooctanesulfonate (PFOS) Values at Sampling Locations

LEGEND:

▭ Milwaukee River Estuary AOC

Perfluorooctanoate (PFOA)

Results in ng/L

☒ Rejected Sample (n = 4 samples)

● < 2 (n = 0 samples)

● 2 - 4 (n = 8 samples)

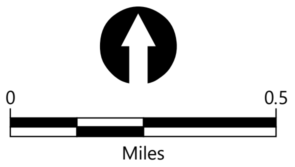
● 4 - 12 (n = 2 samples)

● 12 -20 (n = 0 samples)

● > 20 (n = 0 samples)

NOTES:
ng/L: nanograms per liter

1. Depicted values represent the average of parent and duplicate samples at each location.



Publish Date: 2020/10/30, 11:15 AM | User: jquinley
Filepath: \\orcas\GIS\Jobs\WisconsinDNR_1779\Milwaukee_1779\Maps\PFOS_PFOA\AQ_WIDNR_PFOS_PFAS_Figure7_PFASConcentrations.mxd

ANCHOR QEA

Figure 7
Perfluorooctanoate (PFOA) Values at Sampling Locations

Milwaukee AOC PFAS Special Study