From: Rozeboom, David B - DNR
Sent: Monday, October 21, 2019 5:12 AM
To: John Storlie
Cc: Steve Osesek
Subject: RE: BRRTS # 02-32-000065 - Wells 23 & 24, La Crosse
Attachments: WDNR_SurfaceWater_PFAS_SOP_Draft.pdf; Proposed - WI PFAS Aqueous (Non-Potable Water) and Non-Aqueous Matrices Method Criteria 9.11.2019.pdf

Follow Up Flag: Follow up
Flag Status: Completed

Hi John,

I have attached two documents pertaining to PFAS sample collection and analysis:

1) **WDNR_SurfaceWater_PFAS_SOP.** This documents describes the sampling procedures used by DNR staff collecting surface water samples.
2) **Proposed – WI PFAS Aqueous (Non-Potable Water) and Non-Aqueous Matrices Method Criteria 9.11.19.** This document was recently out for public comment and will be finalized in the coming weeks. The final version will likely be less stringent in some areas, so in the interim labs can use this proposed document. Laboratories will be certified against the final document as applications are received. Keep in mind there will be some changes to this document before it is finalized.

The DNR recommends the following lab methods for sample analysis:

1) Method 537.1 for drinking water.
2) Modified 537 for soil, groundwater and surface water. We are allowing laboratories to use their own in-house developed method as long as the criteria specified in the WI guidance document (described above) for PFAS are met.

For sampling considerations you can follow Michigan's PFAS Sampling Guidance linked below.

https://www.michigan.gov/pfasresponse/0,9038,7-365-86510_87154-469832--,00.html

Let me know if you have any questions.

Thank You

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Dave Rozeboom
West Central Region Team Supervisor

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From: John Storlie <john.storlie@theosgrp.com>
Sent: Friday, October 18, 2019 4:57 AM
To: Rozeboom, David B - DNR <David.Rozeboom@wisconsin.gov>
Cc: Steve Osesek <steve.osesek@theosgrp.com>
Subject: Re: BRRTS # 02-32-000065 - Wells 23 & 24, La Crosse

Thanks, is there a method for soils?

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From: Rozeboom, David B - DNR <David.Rozeboom@wisconsin.gov>
Sent: Friday, October 18, 2019 4:42:58 AM
To: John Storlie <john.storlie@theosgrp.com>
Cc: Steve Osesek <steve.osesek@theosgrp.com>
Subject: RE: BRRTS # 02-32-000065 - Wells 23 & 24, La Crosse

Agreed. I'll talk to our surface water quality folks and get back to you.

Dave Rozeboom
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From: John Storlie <john.storlie@theosgrp.com>
Sent: Thursday, October 17, 2019 5:53 PM
To: Rozeboom, David B - DNR <David.Rozeboom@wisconsin.gov>
Cc: Steve Osesek <steve.osesek@theosgrp.com>
Subject: RE: BRRTS # 02-32-000065 - Wells 23 & 24, La Crosse

Dave - What lab method the Department use for the recent Surface Water sample analyses? Is that the method you want us to use for the Black River sampling? Did they have an SOP for sample collection? We should try to be consistent with their Mississippi R sampling, I would think.
Thanks,
John

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From: Rozeboom, David B - DNR <David.Rozeboom@wisconsin.gov>
Sent: Wednesday, September 25, 2019 2:49 PM
To: John Storlie <john.storlie@theosgrp.com>
Cc: Steve Osesek <steve.osesek@theosgrp.com>; Randy Turtenwald (Turtenwaldr@cityoflacrosse.org) <Turtenwaldr@cityoflacrosse.org>; 'Lenz, Bernard' <LenzB@cityoflacrosse.org>
Subject: RE: BRRTS # 02-32-000065 - Wells 23 & 24, La Crosse

Hi John,

Do you have an ETA on the SI work plan for this site?

Thank You

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From: Rozeboom, David B - DNR
Sent: Friday, July 19, 2019 2:49 PM
To: John Storlie <john.storlie@theosgrp.com>
Cc: Steve Osesek <steve.osesek@theosgrp.com>; Randy Turtenwald (Turtenwaldr@cityoflacrosse.org) <Turtenwaldr@cityoflacrosse.org>; 'Lenz, Bernard' <LenzB@cityoflacrosse.org>
Subject: RE: BRRTS # 02-32-000065 - Wells 23 & 24, La Crosse

John,

Thank you for the notice. I look forward to a Site Investigation Workplan in mid-September.

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From: John Storlie <john.storlie@theosgrp.com>
Sent: Friday, July 19, 2019 9:26 AM
To: Rozeboom, David B - DNR <David.Rozeboom@wisconsin.gov>
Cc: Steve Osesek <steve.osesek@theosgrp.com>; Randy Turtenwald (Turtenwaldr@cityoflacrosse.org)

<Turtenwaldr@cityoflacrosse.org>; 'Lenz, Bernard' <LenzB@cityoflacrosse.org>
Subject: BRRTS # 02-32-000065 - Wells 23 & 24, La Crosse

Dear Dave:
As we discussed this morning, I am writing to formally request an extension of the deadline for submittal of the Site Investigation Work Plan (SIWP). The OS Group, LLC, (OSG) has been engaged to complete the SIWP, but between vacation schedules for both City and OSG staff, we are unable to schedule a project kick off meeting until mid-August. The REP letter states that the SIWP is due July 10, 2019, and the City's RFP requests its submittal by August 16, 2019. I assume they already requested an extension. As this is a complex case, we request an additional month to September 16, 2016.
Please reply via with your concurrence should you concur. Thank you.
We look forward to working with you on this project.
Sincerely,

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PROPOSED - Wisconsin PFAS Aqueous (Non-Potable Water) and Non-Aqueous Matrices Method Criteria
- Version 9.11.2019 -
Per- and Polyfluorinated Alkyl Substances (PFAS) Analysis Using Isotope Dilution by LC/MS/MS

The purpose of this document is to provide the criteria specified by the department that is considered suitable for analysis of PFAS in aqueous (non-potable water) and non-aqueous matrices for Wisconsin. The criteria specified in this document is pursuant to NR 149.41 (2) and provides criteria until the EPA has published their 1600 series isotope dilution method. Potable water samples need to follow EPA 537.1 instead of this document.

{F} = when this is listed after a criterion, and the criteria is not met, then the associated results must be qualified (flagged) on the test report. The qualifier used can refer the data user to the narrative where detail is provided to indicate what the non-conformance was and the possible effects on the sample results.

Sample Handling

1. Grab samples are collected in high density polyethylene (HDPE) or polypropylene (PPE) containers. {F} Polytetrafluoroethylene (PTFE, Teflon) containers and contact with PTFE surfaces must be avoided.

   Note: Surface binding of target compounds to sample collection containers is known to occur in water samples. The entire water sample volume must be extracted. Removing an aliquot of water sample from the sample collection container is not recommended and can result in significant loss of longer-chain PFAS compounds (e.g. carboxylic acids ≥ C9, sulfonic acids ≥ C7). If a smaller aliquot must be used (high sediment, high PFAS levels, etc.), it must be noted on the test report along with the reason why. This is addressed in the Aqueous Sample Extraction Section 1a and 1b.

2. When equipment is used in the field to collect samples, an equipment blank must be collected. {F} For samples that are collected over multiple days, it may not be easily apparent to the laboratory as to whether this has been met or not. This shall be determined by the data users when there are multiple collection days.

3. Ship samples at above their freezing point to 6 °C, except tissues which are to be shipped frozen. The temperature at sample receipt must be measured and documented, except frozen samples which can be documented as frozen. {F}

   Note: If the site where samples are being collected is considered a “newer” spill and source apportionment is one of the data quality objectives, the samples should be shipped with dry ice. Compound transformation can occur if the samples are not frozen.

4. Samples and extracts shall be stored in a freezer at the laboratory. {F}

   Note: Sample containers are not to be filled completely.

5. Holding time is 28 days from collection to extraction and 30 days from extraction to analysis, except tissue which is 1 year from collection to analysis. {F}

6. Sample containers and extract vials must be quantitatively rinsed with polar solvent to remove any adsorbed PFAS compounds. PFAS loss to container walls can occur if sample or extracts sit in their container for more than as little as one hour. Samples must be vortexed well before transfer, subsampling or injection. Insufficient vortexing can lead to compound loss.

Initial Demonstration of Capability (IDC)

1. Analyze all target analytes to determine the retention time of the linear and branched isomers (where commercial standards are available). As of September 2019, the following branched isomer standards are commercially available: PFHxS, PFOS, NMeFOSAA, NEtFOSAA, and PFOA (qualitative).

2. Analyze a method blank. The results must be less than one-half the method reporting limit (MRL) or the IDC must be repeated.

3. For initial precision and recovery, analyze 4 extracted spikes (midrange concentration). The average recovery must be 65-135% and the RSD must be < 30% or the IDC must be repeated.

4. Extracted internal standard recoveries must be 50 – 150% or the IDC must be repeated.

Ongoing QC

1. **Extraction batch** – defined as a set of one to 20 environmental samples of the same matrix extracted in a continuous 24-hour period.

2. **Method blank** (1/batch) – results must be less than the highest of the following or associated detections in the samples must be qualified:

    a. 1/2 the MRL
    b. 1/10 the sample concentration

    Note: detections in the method blank between the MDL and 1/2 the MRL do not need to be qualified.

3. **Laboratory control sample** (1/batch) – spike with all target analytes. The LCS shall be spiked at a low range (1 – 2x MRL) in each batch, or the laboratory may rotate spike concentrations between batches alternating low range, medium range, and high range. Recoveries must be 65-135%, except for the low range (1 – 2x MRL) spike where recoveries must be 50-150%. {F}

4. **Extracted internal standards (exact isotopically labeled analogs of the target analytes)** – these are isotopically labeled internal standards that are added to the sample at the very beginning of the procedure, before any extraction, centrifuging, filtering or phase separation takes place. A minimum ten minute equilibrium time must be allowed from the time these internal standards are added to the samples to the time the samples are further processed. These labeled internal standards undergo the same extraction as the other compounds in the sample. The Department of Defense refers to these as extracted internal standards (EIS). Except for the neutral EIS (FOSA, NMeFOSA, NEtFOSA, NMeFOSE, and NEtFOSE) acceptable recoveries are 25-150%. For the neutral EIS the laboratory shall start with 10% - 150% limits and develop their own statistical limits once enough data points have been collected. If any recovery is outside of these limits, reinject. If the EIS recovery fails again, the data may be reported with a qualifier. A minimum EIS signal to noise ratio of 10:1 must be achieved to use the EIS to report results. {F}

    Extracted internal standards will be used where commercially available. As of September 2019, at least 25 of the 36 compounds Wisconsin is offering certification for are available as isotopically labeled analogs of the target analytes.

    Where there are no commercially available extracted internal standards of the target analyte, an alternate extracted internal standard must be used. The alternate extracted internal standard must be isotopic and either from the same functional group as the target analyte, elute close to the target analyte, or have the same chain length as the target analyte (whichever gives better performance). The same extracted internal standard can be used for more than one target analyte.

5. **Field blanks**

Calibration (Initial and Continuing)

1. Standards must be brought to room temperature and vortexed immediately prior use.

2. Initial calibration is performed at setup and after ICV or CCV failure.

    a. If calibration factors are used, the RSD must be less than 20%.
    b. If linear regression is used, the coefficient of determination must be greater than 0.99, and a minimum of 5 non-zero concentration standards must be used.
    c. If quadratic regression is used, the coefficient of determination must be greater than 0.99, and a minimum of 6 non-zero concentration standards must be used.
    d. If linear or quadratic regressions are used, they may not be forced through zero. (The department is aware that this is a requirement of EPA 537.1, but it is not acceptable for non-potable water analyses.)
    e. All standards in the initial calibration must recover within 70-130% of the theoretical value, except for the MRL standard which must recover within 50-150%.

3. Branched and linear isomers must be used as quantitative calibration standards where commercially available (PFHxS, PFOS, NMeFOSAA, and NEtFOSAA are currently available).

4. A qualitative calibration standard for branched isomers must be used to identify retention times where quantitative standards are not commercially available (PFOA is currently available).

5. Absolute retention times are set using the midpoint standard from the initial calibration (ICAL) on ICAL days. If needed, absolute retention times may be updated using the first CCV retention times on non-ICAL days.

6. **QCS (ICV – 2nd source)** – perform with each new initial calibration and before sample analysis. Recovery must be 70-130%. Samples may not be analyzed if the QCS fails.

7. **CCV** – perform at the beginning and end of each analysis batch and after every 10 field samples.

    a. The first CCV on non-initial calibration days must be at or below the MRL and recover at 50-150%.
    b. All other CCVs must achieve 70-130% recovery.
    c. Samples may only be reported if bracketed by passing CCVs unless the recovery failure is high and there are no detections of that compound in the associated samples.

8. **CCB** – analyze after each CCV to demonstrate the instrument is free from levels of contaminants that would bias results. If method blanks or reagent blanks need to be analyzed, they may take the place of the CCBs. The results of the CCBs must be less than one-half the MRL.

9. **Extracted internal standards** used in samples must be added to the initial calibration standards, ICV and CCVs and CCBs at the same concentration. Since there is no matrix effect in these samples, the EIS must recover 50 – 150%.

Aqueous Sample Extraction

1. The laboratory must prepare the entire sample in a sample container unless the exceptions listed below apply. The entire sample received in the sample bottle must be extracted. {F}

    a. If the sample received is at extremely high concentrations, then subsampling is allowed but the data must be qualified.
    b. If more sample volume is received than what can be extracted through the SPE, then subsampling is allowed but the data must be qualified.

2. Fortify the sample, in the sample bottle it was received in, by adding the extracted internal standards. Cap, invert and mix. A minimum ten minute equilibrium time must be allowed from the time these internal standards are added to the samples to the time the samples are further processed. The extracted internal standards are to be added before any extraction, centrifuging, filtering or phase separation takes place.

   Note: Biphasic and problematic sample matrices may require a different procedure for fortification. In these events, the narrative shall include the detail as to why fortification in the sample bottle was not possible, what was done instead, and the possible effects on the sample results. {F}

3. If particulates in the sample need to be removed before using solid phase extraction (SPE), centrifuge the sample and use the supernatant as the sample. Reminder: the EIS must be spiked into the sample before the centrifuging or filtering takes place and a minimum ten minute equilibrium time is achieved. Do not use filters to separate the solids from the liquid phase unless there is data to demonstrate that the filters used do not result in contamination greater than one-half the MRL and that they do not cause loss of compounds. The data quality objectives from the data user should determine whether the solids portion of the sample needs to be extracted. Not analyzing the solids portion may lead to a low bias in total sample concentration.

   Note: If the percent solids are greater than one percent and a total sample concentration is required, then both phases must be extracted and analyzed. If the percent solids are less than one percent, then extraction and analysis of the aqueous phase is generally adequate.

4. Determine sample volume by marking the sample level on the bottle or by weighing. Do not measure sample volume with a graduated cylinder.

   Note: When the sample has significant solids, the weight or volume displaced by the solids must be accounted for in the initial sample volume determination.

5. Use an appropriate SPE cartridge for the matrix analyzed and the analytes reported. A weak anion exchange cartridge has been shown to work with the compounds for which Wisconsin is offering certification.

6. Using three separate rinses, rinse the sample bottle and cap with elution solvent, pour the solvent from each rinse through the SPE cartridge, and collect the filtrate for analysis. If a filter was used, the filter must be rinsed as well. Quantitative transfers can be achieved by solvent-rinsing with the elution solvent.

7. Bring to a quantitative final volume with the final injection solvent and vortex well.

Non-Aqueous Sample Extraction

1. The laboratory must homogenize the entire sample received, except for tissues where the tissue area of concern is homogenized.

2. Fortify an aliquot of sample by adding the extracted internal standards directly onto the sample. A minimum of ten minutes must be allowed for the solvent carrier to evaporate prior to addition of the extraction solution.

3. Non-aqueous samples must be extracted with a solution before SPE clean-up.

4. Use an appropriate SPE cartridge for the matrix analyzed and the analytes reported. A weak anion exchange cartridge has been shown to work with the compounds for which Wisconsin if offering certification.

5. A clean-up cartridge must be used for fish tissue analysis to eliminate known interferences with PFOS (e.g. bile acids such as taurodeoxycholic acid (TDCA).)

6. Quantitative transfers must be achieved by solvent-rinsing using the elution solvent.

7. Bring to a quantitative final volume with the final injection solvent and vortex well.

Sample Analysis

1. The LC/MS/MS must be capable of negative ion ESI, produce unique product ions within retention time windows, and be able to provide a minimum of 10 scans across each peak.

2. Mass calibration must be performed such that the range of masses associated with all precursor and product ions is bracketed for both the primary and confirmation transitions. Documentation must be available to demonstrate that the mass calibration covers this range.

3. Sample results for analytes with isotopically labeled analogs commercially available will be calculated using isotope dilution. Sample results for analytes without isotopically labeled analogs available will be calculated using extracted labeled internal standard analytes and internal standard quantitation recovery correction.

4. Quantitative standards containing both branched and linear isomers must be used when commercially available and the peak areas summed to calculate the sample result. Where quantitative standards are not available for the branched isomers, qualitative standards will be used to identify retention times, and the peak areas will be summed and calculated using the quantitative linear isomer response.

5. Target analytes and their exact labeled analog must elute within 0.1 min. {F}

6. The laboratory must a written policy of defining how retention time windows will be set.

7. The method reporting limit (MRL) must not be set at a concentration below the lowest standard concentration in the initial calibration. The MDL must be less than the MRL.

8. Sample and quality control blank results are reported to the MDL and the MRL is included with each result. The MDL for PFOS and PFOA, each, in potable and non-potable waters shall be no higher than 2 ng/L. Results reported between the MDL and MRL shall be qualified as estimated concentrations.

   Example 1: MDL = 0.6, MRL = 2, sample result = 0.4. Report as

Result	MDL	MRL
<0.6	0.6	2.0

   Example 2: MDL = 0.6, MRL = 2, sample result = 0.8. Report as

Result	MDL	MRL
0.8 J	0.6	2.0

9. All samples need to be brought to room temperature and vortexed prior to aliquoting into the instrument sample vial.

10. HDPE/PPE autosampler vials are single use only unless they are immediately recapped.

11. All sample results reported must be from a response that is no higher than the highest response in the initial calibration, except for samples that saturate the instrument.

    a. Sample results may be reported with “E” flags for samples that saturate the instrument and the responses are above the response of the highest calibration standard.
    b. Non-detections are reported as < MDL but the MRL is also reported for quantitative reference.

12. All analytes that have two transitions must include two transitions ions (precursor ion to quantitation ion and precursor ion to confirmation ion). The confirmation ion is used for positive analyte detections. The department will provide a list of analytes and confirmation ions on our website.

13. The primary and secondary ion transition ratios must be assessed and be within 50 – 150% of the value calculated from the midpoint standard in the ICAL on ICAL days or from the beginning CCV on non-ICAL days. {F}

    The transition ratio = $\frac{\text{quantitation ion abundance}}{\text{confirmation ion abundance}}$

    Note: When the ion ratio fails, be sure to report the compounds as detections but qualify them as failing the ion ratio.

14. Document the primary and confirmation transitions and the ion ratio.

15. The Signal to Noise (S/N) ratio must be greater than or equal to 3:1 for quantitation ions and confirmation ions.

16. The following transitions will be used for quantitation for the following analytes [precursor – product] unless a technically justified reason is used to choose an alternate transition to avoid interference and any known bias:

    a. PFOA 413-369
    b. PFOS 499-80
    c. PFHxS 399-80
    d. PFBS 299-80
    e. 4:2 FTS 327-307
    f. 6:2 FTS 427-407
    g. 8:2 FTS 527-507
    h. NEtFOSAA 584-419
    i. NMeFOSAA 570-419

17. The laboratory must determine at what concentration the instrument has carryover at concentrations greater than one-half the MRL. The laboratory must have a documented procedure to bring the instrument back in control after a sample with carryover is encountered. PFAS compounds have demonstrated a delayed release in the system.

18. Report results in acid form.

19. Calibration standards purchased as salts must be mass corrected for the salt content.

20. When aqueous samples contain solids that will interfere with the SPE procedure, the aqueous phase is separated from the solid phase and only the aqueous phase is analyzed. In these cases, the results will be noted as a liquid concentration result and not a total sample concentration result, and the weight of the solid phase not prepared should be reported. This can be noted in the narrative. If the data quality objective is to obtain a total concentration, then both phases need to be extracted and analyzed.

21. Blank values may not be subtracted from sample values.

22. Analytes in the samples that contain multiple peaks due to linear and branched isomers must be integrated in the same manner as the standards.

23. The laboratory SOP must include at a minimum:

    a. The extracted internal standards are used to calculate the result of each analyte reported.
    b. The mass used for the precursor ion for each analyte reported.
    c. The mass used for the product quantitation ion for each analyte reported.
    d. The mass used for the product confirmation ion for each analyte reported.
    e. Instructions for conditioning and elution of the SPE.
    f. Specify which branched isomers are calculated using the linear isomer standard.

21. PFOA and PFOS WS PT samples are required for potable water certification of PFOA and PFOS. To obtain the 18-compound group potable water certification from Wisconsin, a PT with a minimum of 6 PFAS compounds must be analyzed, that includes PFOA and PFOS, and 80% of the spiked analytes must pass.

22. PFOA and PFOS WP PT samples are required for aqueous (non-potable) certification of PFOA and PFOS. To obtain the 36-compound group aqueous (non-potable water) certification from Wisconsin, a PT with a minimum of 6 PFAS compounds must be analyzed, that includes PFOA and PFOS, and 80% of the spiked analytes must pass.

23. Requirements in NR 149 still apply to this analysis, unless otherwise specified in this document.

AS NEW INFORMATION IS PROVIDED BY THE EPA THIS DOCUMENT WILL BE UPDATED AND DISTRIBUTED.

Recommendations

1. Perform solid and fish tissue PT samples.
2. Additional clean-up using granular activated carbon is highly recommended.
3. Evaluate all bottles, water, reagents, materials, and equipment as sources of contamination and be able to demonstrate that they are “PFAS-free.”
4. Each individual standard and labeled standard should be validated by analysis to confirm its identity and the absence of significant impurities.
5. Certified standards have been known to vary by as much as 20% between vendors for these compounds. Be sure to be able to demonstrate that the standards being used are of known and defensible quality.
6. Perfluorocarboxylic acid standards in methanol solution may undergo esterification to the methyl esters. Most purchased perfluorocarboxylic acid standard solutions are received in methanol containing 4 mole equivalents of NaOH. Basic methanol (0.3% NH4OH v/v in methanol), rather than straight methanol, is used for all standard dilutions to avoid this potential problem.
7. Homogenize the entire sample in the original sample container by shaking samples that are pourable liquids or by stirring solids in their original container with a clean spatula, glass stirring rod, or other suitable implement.
8. To determine if background concentrations of PFAS significantly impact this analysis, solvent blanks analyzed after a standard should contain less than one-half the MRL.
9. To establish retention times, analyze individual solutions of the each of the target compounds. Analyze a mixed solution of all target compounds to confirm their separation and identification.
10. MS/MSDs will help with assessing measurement bias for those target analytes that do not have exact labeled isotope analogs.

WISCONSIN LABORATORY ACCREDITIATION PROGRAM PFAS CERTIFICATION OFFERINGS - 5.1.19					
#	**Acronym**	**Name**	**CAS #**	**# carbons**	**Acronyms (other)**
Carboxylic Acids					
1	PFBA	Perfluorobutanoic acid	375-22-4	4	
2	PFPeA	Perfluoropentanoic acid	2706-90-3	5	
3	PFHxA	Perfluorohexanoic acid	307-24-4	6	
4	PFHpA	Perfluoroheptanoic acid	375-85-9	7	
5	PFOA	Perfluorooctanoic acid	335-67-1	8	
6	PFNA	Perfluorononanoic acid	375-95-1	9	
7	PFDA	Perfluorodecanoic acid	335-76-2	10	
8	PFUnA	Perfluoroundecanoic acid	2058-94-8	11	PFUdA, PFUnDA
9	PFDoA	Perfluorododecanoic acid	307-55-1	12	PFDoDA
10	PFTriA	Perfluorotridecanoic acid	72629-94-8	13	PFTrA, PFTrDA
11	PFTeA	Perfluorotetradecanoic acid	376-06-7	14	PFTeDA
12	PFHxDA	Perfluorohexadecanoic acid	67905-19-5	16	
13	PFODA	Perfluorooctadecanoic acid	16517-11-6	18	
Sulfonic Acids					
14	PFBS	Perfluorobutanesulfonic acid	375-73-5	4	
15	PFPeS	Perfluoropentanesulfonic acid	2706-91-4	5	
16	PFHxS	Perfluorohexanesulfonic acid	355-46-4	6	
17	PFHpS	Perfluoroheptanesulfonic acid	375-92-8	7	
18	PFOS	Perfluorooctanesulfonic acid	1763-23-1	8	
19	PFNS	Perfluorononanesulfonic acid	68259-12-1	9	
20	PFDS	Perfluorodecanesulfonic acid	335-77-3	10	
21	PFDoS	Perfluorododecanesulfonic acid	79780-39-5	12	PFDoDS
22	4:2 FTSA	4:2 Fluorotelomer sulfonic acid	757124-72-4	6	
23	6:2 FTSA	6:2 Fluorotelomer sulfonic acid	27619-97-2	8	
24	8:2 FTSA	8:2 Fluorotelomer sulfonic acid	39108-34-4	10	
25	10:2 FTSA	10:2 Fluorotelomer sulfonic acid	120226-60-0	12	
Sulfonamides, Sulfomidoacetic acids, Sulfonamidoethanols					
26	FOSA	Perfluorooctane sulfonamide	754-91-6	8	PFOSA
27	NMeFOSA	N-Methyl perfluorooctane sulfonamide	31506-32-8	9	MeFOSA
28	NEtFOSA	N-Ethyl perfluorooctane sulfonamide	4151-50-2	10	EtFOSA
29	NMeFOSAA	N-Methyl perfluorooctane sulfonamidoacetic acid	2355-31-9	11	MeFOSAA
30	NEtFOSAA	N-Ethyl perfluorooctane sulfonamidoacetic acid	2991-50-6	12	EtFOSAA
31	NMeFOSE	N-Methyl perfluorooctane sulfonamidoethanol	24448-09-7	11	MeFOSE
32	NEtFOSE	N-Ethyl perfluorooctane sulfonamidoethanol	1691-99-2	12	EtFOSE

Replacement Chemicals					
33	HFPO-DA	Hexafluoropropylene oxide dimer acid [1]	13252-13-6	6	PFPrOPrA
34	DONA	4,8-Dioxa-3H-perfluorononanoic acid [2]	919005-14-4	7	
35	9Cl-PF3ONS	9-chlorohexadecafluoro-3-oxanonane-1-sulfonic acid [3]	756426-58-1	8	F-53B Major
36	11Cl-PF3OUdS	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid [4]	763051-92-9	10	F-53B Minor
	1 - Also referred to as "GenX"				
	2 - Also available as the ammonium salt = ADONA (Ammonium 4,8-dioxa-3H-perfluorononanoate) # 958445-44-8				
	3 - Also available as the potassium salt = Potassium, 9-chlorohexadecafluoro-3-oxanone-1-sulfonate # 73606-19-6				
	4 - Also available as the potassium salt = Potassium, 11-chloroeicosafluoro-3-oxaundecane-1-sulfonate # 83329-89-9				

Scope

This method pertains to the collection of surface water chemistry samples for per- and polyfluoroalkyl substances (PFAS), sometimes referred to as for per- and polyfluorinated compounds (PFC). PFAS refer to a group of ~3,000 synthetic fluorinated chemicals that are comprised of a chain of carbon atoms attached to a fluorine atom, plus a variety of other atoms. The Wisconsin State Lab of Hygiene (WSLH) currently analyzes approximately 15-20 compounds of some of the most common PFAS in surface waters, and many more compounds may be added in the future (method OC12731 [OC16200 coming soon from WSLH]). PFAS have unique chemical properties in that they repel both oil and water, as a result they have been used in many industrial processes and commercially available products. As PFAS are found in many common products, this SOP -especially the Approved and Prohibited Materials Table (page 5)- must be closely followed to prevent cross contamination.

The following compounds and reporting limits are listed below for this analytical method, these may be updated based on laboratory protocols at the WSLH without subsequent changes to this field sampling SOP:

Analyte	Report Limit (ng/L)
Perfluoro-1-octanesulfonate (PFOS)	0.2
Perfluoro-1-butanesulfonate (PFBS)	0.8
Perflioro-1-hexanesulfonate (PFHxS)	0.2
Perfluoro-1-heptanesulfonate (PFHpS)	0.2
Perfluoro-1-decanesulfonate (PFDS)	0.8
Perfluoro-n-octanoic acid (PFOA)	0.4
Perfluoro-n-pentanoic acid (PFPA)	20.0
Perfluoro-n-hexanoic acid (PFHxA)	4.0
Perfluoro-n-heptanoic acid (PFHpA)	0.4
Perfluoro-n-nonanoic acid (PFNA)	0.2
Perfluoro-n-decanoic acid (PFDA)	0.2
Perfluoro-n-undodecanoic acid (PFUnDA)	0.8
Perfluoro-n-dodecanoic acid (PFDoDA)	0.8
Perfluoro-n-tridecanoic acid (PFTrDA)	2.0
Perfluoro-n-tetradecanoic acid (PFTeDA)	2.0

Ordering Equipment From the WSLH

PFAS bottles and certified PFAS-free DI water can be ordered by any DNR staff directly from the WSLH organics lab. Ordering equipment for up to three sampling sites can fit into one cooler from the WSLH. Staff may need to indicate the number of coolers and sites they need when ordering. For example, if you are sampling two sites on three different dates (six total samples) you will want to order bottles for six sites in three coolers. The WSLH needs approximately one week notice to assemble the bottles plus shipping time, staff should order supplies at a minimum two weeks, ideally three weeks before the planned sampling event. PFAS-free DI water is available in 2.5-gallon containers, other size containers may be available but DNR will need to pay for analysis cost to certify that any new container is PFAS-free. The contact for ordering PFAS supplies is Erin Mani (erin.mani@slh.wisc.edu, 608-224-6269) the ESS Organics Lab Supervisor.

Sample Preservation

Samples must be iced or refrigerated at 4°C for transport and storage and shielded from light from the time of collection until analysis. PFAS have been shown to be stable for several months under these conditions. However, the holding time for PFAS analysis is currently set at **28 days** for WSLH analysis.

Summary of Method

Contamination is a major concern with PFAS samples due to their ubiquity and persistence in the environment. All sample bottles must come pre-cleaned directly from the WSLH to prevent contamination (or directly from any other certified lab that is conducting the analysis). Any other sample equipment that may come in contact with the sample water must be thoroughly rinsed with deionized water and source water. In wadeable stream systems, the sampler should wade into the water moving upstream and sample near the thalweg making sure that the area is free of recently disturbed sediments. Samples should be collected 3-6 inches below the surface of the water to avoid any surface scums or particles. Samples collected from nonwadeable rivers or lakes should be made upstream of the watercraft, in lakes off the bow of the boat. The step-by-step methods listed below offer detailed instructions on how to collect a single surface water sample.

Standard QA/QC practices

In general, a field blank and a duplicate sample is recommended at the rate of one for every ten samples (i.e. 10% rule). However, given the high chance for PFAS contamination it is recommended that one field blank is taken at every site visit regardless of the number of samples taken. For a field blank, WSLH certified PFAS-free DI water is transported into the field in a separate “PFAS-free” labeled container. While in the field, a crew member fills a sample bottle with DI water and transports it on ice with the other samples. If conducting a field duplicate, a sample is taken in the field in the same location as the

previous sample. Certified PFAS-free water and containers must be replaced every year, and in some cases more frequently if many samples are being collected. In general, a field blank is used to determine if there is any cross contamination or interference in the sample collection methods and preservation. A duplicate is used to determine how interferences in laboratory analysis or inherent variability in the concentrations in the waterbody.

Safety

Safety precautions of a general nature should be recognized. Life jackets should be worn if sampling from a boat or in areas of swift current. Collecting samples in cold weather, especially around cold waterbodies, carries the risk of hypothermia, and collecting samples in extremely hot and humid weather carries the risk of dehydration and heat related illness. A first aid kit should always be carried with the field crew for general safety considerations. All pertinent WDNR safety SOPs must be followed when sampling for PFAS.

Equipment

- Three (3) 500mL polypropylene (PP) bottles from WSLH per sample
- Cooler provided by WSLH
- 2.5-gallon container of PFAS-free certified DI water from WSLH
- Powderless nitrile gloves
- "Wet" ice
- PVC waders
- Sharpie® and/or pencil
- Organic lab slip(s) printed on standard non-recycled printer paper

Collection procedures

1. Wearing powderless nitrile gloves label the three (3) bottles with the appropriate field number and sampling location using only approved materials (i.e. Sharpie® brand permanent markers).
    a. Three (3) bottles equals one sample, so the bottles should be labeled identically, but should include a 1 of 3, 2 of 3 or 3 of 3 tag at the end of the label. Only one lab slip is needed for one sample if sending to the WSLH, even though there will be three bottles.

2. Locate a sampling location that is at least 10 to 20 feet upstream from a bridge crossing, in the middle of the stream channel, and is at least knee deep if possible. In cases where stream depth is shallow it is more important to collect the sample in an area of sufficient flow than the deepest location. Walk upstream to the sampling location to ensures the sample is not contaminated by sediment that has been dislodged from the substrate.

3. Facing upstream, using a polypropylene PFAS bottle dip the inverted bottle into the surface water 3 to 6 inches below the water surface and then invert to collect the sample. Avoid collecting any surface films which may contain debris or residue.

4. Do not touch the inside of the bottle or inside of the cap with anything besides sample water.

5. Fill each of the bottles to the "shoulder" leaving minimal headspace.

6. With dry hands fill out the organic lab slip form WSLH, check the box for Perfluorinated Compounds under the Halogenated Compounds header.

7. Store the samples on wet ice in the WSLH provided cooler and ship or deliver to the WSLH. There is a 28-day holding time and substantial prep-work that needs to be done by the lab. Ship within a few days to give adequate time for sample prep and chemical analysis.

8. If conducting a QAQC sample, on-site fill another three (3) bottles with certified PFAS-free DI water and complete a separate organic lab slip selecting the Field QC-Blank checkbox.

Sampling at Non-wadeable systems

When sampling at depth is performed it is very easy to compromise the cleanliness of a sample as more hardware is involved in obtaining a sample (lake, nonwadeable river, etc.). The sampler must be certain that all materials used to collect a sample must be on the approved materials list. If using collection equipment when sampling be sure to triple rinse equipment with certified PFAS-free DI water and then conduct a second triple rinse with source water. After each rinse, be sure to manually inspect equipment and wipe of any adhered dirt or debris using an approved material.

Approved Materials	Prohibited Materials
Sample Containers and Gear	

▪ High-density polyethylene (HDPE)
▪ Polypropylene
▪ Silicone
▪ Stainless steel
▪ Polyethylene[1]
▪ Decontamination:
  ○ Alconox®
  ○ Liquinox®
▪ "Wet" ice
	▪ Flouropolymers used in:
	▪ Teflon®
	▪ Neoflon®
	▪ Tefzel®
	▪ Hostaflon®
	▪ Kynar®
	▪ Includes PTFE, PVDF, PCTFE, ETFE and FEP[2]
	▪ Glass
	▪ "Blue" ice, gel or other synthetic

Field Documents	
▪ Printer paper (non-recycled) ▪ Rite in the Rain® paper[3] ▪ Aluminum clipboards ▪ Pencils ▪ Sharpie® markers	▪ Other brands of waterproof paper or notebooks ▪ Paper products with adhesive backing ▪ Plastic or composite clipboards ▪ Recycled paper products ▪ Other permanent marker brands
Personal Protective Equipment	

▪ Nitrile gloves (powderless)
▪ Waders made from Polyvinyl chloride (PVC)
▪ Uncoated rubber or neoprene products
▪ Polyurethane
	▪ Latex gloves
	▪ Fabric softeners
	▪ Gore-Tex®, DWR or other water-resistant synthetic fibers or coatings
	▪ Tyvek® (non-coated may be allowable)
	▪ Materials listed as:
	  ○ Water or stain resistant
	  ○ Chemical UV protection
	  ○ Insect resistant

Personal Care Products	

▪ Insect repellents:
  ○ OFF Deep Woods
  ○ Sawyer Permethrin
▪ Banana Boat Sport Performance Lotion SPF 30
▪ Neutrogena Ultra-Sheer Dry-Touch Sunscreen SPF 30
▪ Coppertone Sunscreen Lotion Ultra Guard SPF 50
	▪ Any brand not listed as allowable
	▪ No disposable food containers or wrappers

1 – LDPE and Polyethylene (e.g. Ziploc®) may be used as long as they do not come into direct contact with the sample.
2 - Polytetrafluoroethylene, polyvinylidene, polychlorotrifluoroethylene, ethylene tetrafluoroethylene, fluorinated ethylene propylene.
3 – Should not come into direct contact with sample, other brands have not been tested.

References

Bartlett, S.A. and Davis, K.L. 2018. Evaluating PFAS contamination issues. *Remediation*. 28:53-57.

MI DEQ. 2018. General PFAS sampling guidance: Michigan Department of Environmental Quality.

Mueller, R. and Yingling, W. 2018. Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods for Per- and Polyfluoroalkyl Substances (PFAS). Fact Sheet, Interstate Technology and Regulatory Council.

NHDES. 2016. Sampling for Per- and Polyfluoroalkyl Substances/Perfluorinated Chemicals (PFAS/PFC) at Contaminated Sites. State of New Hampshire Department of Environmental Services

Updates and Tracking

Version Number	Date	Sections	Name	Approval
1.0 DRAFT	06/24/2019	All	Shupryt, Amrhein, Bruhn, Giblin, Hudak, Klosiewski	

This document is available electronically on the WDNR's website. [CLICK HERE]

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