MEETING LOGISTICS

• MEETING WEBSITE:
• DNR HOME PAGE: SEARCH ‘PFAS GROUP’
  • HTTPS://DNR.WI.GOV/ TOPIC/CONTAMINANTS/PFASGROUP.HTML
• GOV DELIVERY SUBSCRIPTION
• WISLINE: CALL 1-855-947-8255, CODE: 6612 745#
  • MUTE-THEN-HOLD
• SKYPE NOT AVAILABLE FOR THIS CALL
MEETING LOGISTICS

LUNCH BREAK 12-12:30PM
PURPOSE AND SCOPE

• DNR WILL FACILITATE QUARTERLY MEETINGS THAT WILL FOCUS ON A VARIETY OF TOPICS INCLUDING THE WHAT, WHERE, WHEN AND HOW OF PFAS ASSESSMENT.

• OUR GOAL IS TO:
  • SHARE CONCERNS,
  • IDENTIFY CURRENT AND PROPOSED PRACTICES FOR ASSESSMENT AND TREATMENT, AND
  • STRATEGIZE ON ISSUES REQUIRING SOLUTIONS.

• THIS MEETING WILL FOCUS ON
  • UPDATES SINCE LAST MEETING (LAB CERT, DHS, ETC.)
  • SUBGROUP FORMATION – WATER QUALITY AND WASTE MANAGEMENT
AGENDA

• INTRODUCTION AND PROGRAM UPDATES – BRIDGET KELLY & JUDY FASSBENDER
• LAB CERTIFICATION – TOM TRAINOR
• DRINKING WATER AND GROUNDWATER – STEVE ELMORE
• BROWNFIELDS STUDY GROUP – LAURIE PARSONS & MARK THIMKE
• WASTE AND MATERIALS MANAGEMENT – JOE VAN ROSSUM & KATE STROM HIORNS
• WATER QUALITY – ADRIAN STOCKS
• WATER QUALITY – MEGHAN WILLIAMS & MIKE SHUPRYT
• CLOSING REMARKS
INTRODUCTIONS – WHO ARE WE?

• WHAT IS YOUR NAME?
• WHERE DO YOU WORK?
WHAT IS YOUR INVOLVEMENT WITH PFAS?

- ARE YOU A:
  - Consultant?
  - Municipality/Utility?
  - Environmental Advocacy Group?
  - Attorney?
  - Media Rep?
  - Responsible Party?
  - Regulator?
  - Other?
  - Concerned Citizen?

-HAVE YOU BEEN DIRECTLY INVOLVED IN A SITE WHERE PFAS IS PRESENT?
INTRODUCTION – PROGRAM UPDATES

STAFF UPDATES:

Christine Haag  
RR Program Director

Bridget Kelly  
RR Program Coordinator - EC

Jay Nielsen  
EM Policy Coordinator
MEETING LOGISTICS

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INTRODUCTION – PROGRAM UPDATES

• **SUBGROUP MEETINGS:**

  1) 4.9.19 (HISTORY AND USE)
      ~50 ATTENDEES (IN-PERSON AND REMOTE)
  2) 4.18.19 (FATE AND TRANSPORT)
      ~85 ATTENDEES (IN-PERSON AND REMOTE)

• **ADDITIONAL SUBGROUPS WQ AND WMM – WILL HEAR MORE ABOUT LATER TODAY**
PFAS SUBGROUP - SOURCES

• ITRC FACT SHEETS OVERVIEW
• REGULATORY UPDATE – STATE STANDARDS
• MANUFACTURING HISTORY
• PRIMARY SOURCES
  • AFFF
  • MANUFACTURING
  • WWTP
  • LANDFILLS
• RESOURCE INFORMATION
• EVALUATION METHODS
  • MICHIGAN, MINNESOTA, CALIFORNIA
PFAS SUBGROUP – FATE AND TRANSPORT

• MAJOR SOURCES
  • AFFF
  • INDUSTRIAL
  • LANDFILLS
  • WWTP

• FATE AND TRANSPORT
  • PARTITIONING
  • TRANSPORT
  • PFAS TRANSFORMATION

• PFAS OCCURRENCE BY MEDIUM
  • AIR
  • SOIL AND SEDIMENT
  • GROUNDWATER
  • SURFACE WATER
  • BIOTA AND BIOACCUMULATION
INTRODUCTION – PROGRAM UPDATES

- **MADISON WELL 15/16 STUDY**
  - WELL 15 AND 16 WERE CHOSEN FOR THE STUDY DUE TO RECENT SAMPLING RESULTS BY THE UTILITY SHOWING PFAS IN WELLS 15 AND 16
  - DNR IS CONTRACTING WITH CONSULTANT FOR THIS WORK – CONSULTANT WAS SELECTED THROUGH AN RFP PROCESS CONDUCTED BY RR PROGRAM
  - NO SAMPLING – DESKTOP STUDY

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**Results in parts-per-trillion (ppt)**

<table>
<thead>
<tr>
<th>PFAS Compound</th>
<th>Well 15</th>
<th>Well 16</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfluorobutanoic acid (PFBA)</td>
<td>2.9</td>
<td>PRESENT</td>
</tr>
<tr>
<td>Perfluorobutanesulfonic acid (PFBS)</td>
<td>3.1</td>
<td>PRESENT</td>
</tr>
<tr>
<td>Perfluoropentanoic acid (PFPeA)</td>
<td>5.1 - 5.9</td>
<td>PRESENT</td>
</tr>
<tr>
<td>Perfluoropentane sulfonic acid (PFPeS)</td>
<td>2.7</td>
<td>PRESENT</td>
</tr>
<tr>
<td>Perfluorohexanoic acid (PFHxA)</td>
<td>6.1</td>
<td>2.5</td>
</tr>
<tr>
<td>Perfluorohexanesulfonic acid (PFHxS)</td>
<td>20 - 21</td>
<td>PRESENT</td>
</tr>
<tr>
<td>Perfluoroheptanoic acid (PFHpA)</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Perfluoroheptane sulfonic acid (PFHpS)</td>
<td>PRESENT</td>
<td>PRESENT</td>
</tr>
<tr>
<td>Perfluorooctanoic acid (PFOA)</td>
<td>5.4 - 5.7</td>
<td>PRESENT</td>
</tr>
<tr>
<td>Perfluorooctanesulfonic acid (PFOS)</td>
<td>5.3 - 5.8</td>
<td>PRESENT</td>
</tr>
<tr>
<td>Perfluorooctanesulfonamide</td>
<td>not detected</td>
<td>not detected</td>
</tr>
<tr>
<td>N-Ethyl perfluorooctane sulfonamide</td>
<td>not detected</td>
<td>not detected</td>
</tr>
<tr>
<td>Combination PFOA + PFOS</td>
<td>11 - 12</td>
<td>2.3* - 2.7*</td>
</tr>
</tbody>
</table>

PRESENT: Substance detected at levels too low to accurately quantify

* estimated concentration (ppt)
INTRODUCTION – PROGRAM UPDATES

• MADISON WELL 15/16 STUDY
  • PILOT STUDY TO DEVELOP METHODOLOGY
  • INVENTORY CURRENT AND HISTORICAL INDUSTRIAL AND COMMERCIAL ACTIVITIES TO HELP DETERMINE POSSIBLE SOURCES OF PFAS IN TWO DRINKING WATER WELLS
  • RESULTS AVAILABLE MID-SUMMER
INTRODUCTION – PROGRAM UPDATES

GOVERNOR EVERS INTRODUCED PFAS BILL ON MAY 23, 2019

CHEMICAL LEVEL ENFORCEMENT AND REMEDIATION (CLEAR) ACT

LRB-2292-2

THE BILL (IF ENACTED) WOULD ALLOW DNR TO ESTABLISH, BY RULE, THE FOLLOWING:

• ACCEPTABLE LEVELS AND STANDARDS;
• MONITORING REQUIREMENTS;
• REQUIRED RESPONSE ACTIONS FOR ANY PFAS DETECTIONS.
• APPLIES TO ALL MEDIA:
  • DRINKING WATER, GROUNDWATER, SURFACE WATER,
  • AIR, SOLID WASTE, BEDS OF NAVIGABLE WATERS, AND SOIL AND SEDIMENT
• PROVIDES DNR AND DHS WITH STAFF AND FUNDING SUPPORT TO CARRY OUT THESE INITIATIVES.

Governor Evers and Secretary Cole, announced the bill; Senators Hansen and Miller; Representatives Sargent, Gruszynski, and Taylor; leaders in introducing this bill
EPA’S PFAS ACTION PLAN

JUDY FASSBENDER, SECTION CHIEF

DNR REMEDIATION AND REDEVELOPMENT PROGRAM
EPA’s Per- and Polyfluoroalkyl Substances (PFAS) Action Plan
STATUS OF PFAS ANALYTE RECOMMENDATIONS FROM DHS

JUDY FASSBENDER, SECTION CHIEF
DNR REMEDIATION AND REDEVELOPMENT PROGRAM
• DHS continues to work through process of recommending NR 140 Standards
• Cycle 10 contaminants expected mid-2019 (PFOS and PFOA)
• Cycle 11 contaminants expected end of 2020 (34 other PFAS)
BUREAU OF DRINKING WATER AND GROUNDWATER: THE MAKING OF A NR 140 STANDARD

STEVE ELMORE, PROGRAM DIRECTOR
DRINKING WATER AND GROUNDWATER
WDNR
PFAS Regulation in WI – Drinking Water

**What is Next**
- Groundwater standard for PFOA and PFOS
- Additional Municipal sampling
  - UCMR5 in 2022
- Additional private well sampling in relation to new PFAS remediation cases

**Other Possibilities**
- US EPA Maximum Contaminant Level?
- More Voluntary sampling?
- Department led sampling effort?
- Other types of state standards?
PFAS Regulation in WI – Drinking Water

• Drinking Water Monitoring for PFAS

Unregulated Contaminant Monitoring Rule (UCMR) Monitoring
  • Detections: La Crosse (PFOS), West Bend (PFOA), Rhinelander (PFHxS)
  • All < 70 ppt in most recent report
  • Additional monitoring will be done in subsequent UCMR

VOLUNTARY MUNICIPAL MONITORING
  • Madison, Marinette, Peshtigo

PRIVATE WELL MONITORING – REMEDIATION SITES (NR 700 series)
  • JCI/TYCO – 160 wells
  • MIRO Plant - Manitowoc
  • General Mitchell International Airport
PFAS Regulation in WI – Drinking Water

• **What is Next**
  - Groundwater standard for PFOA and PFOS
  - Additional Municipal sampling
    - UCMR5 in 2022
  - Additional private well sampling in relation to new PFAS remediation cases

• **Other Possibilities**
  - US EPA Maximum Contaminant Level?
  - More Voluntary sampling?
  - Department led sampling effort?
  - Other types of state standards?
NR 149 LABORATORY CERTIFICATION PROGRAM

TOM TRAINOR
What has been completed since the last meeting

- The list of PFAS that Wisconsin is offering certification for has been finalized
- Certification will be available for drinking water, aqueous and non-aqueous (solid) matrices
- TNI codes for the “WI PFAS SOP” and for all WI PFAS have been established so that PT samples can be uploaded to our database
- Drinking water samples will require analysis by EPA Method 537.1
- A draft list of requirements housed in the “WI PFAS SOP” has been generated and is available for comment until June 7, 2019
- The “WI PFAS SOP” has been sent to 17 different laboratories for input
What is left to do before Wisconsin starts accepting PFAS applications

• Finalize the “WI PFAS SOP” based on comments received [target 6.14.19]

• Update the Laboratory Certification Application Form to allow labs to request PFAS certification [target 7.8.19]

• Inform laboratories that Wisconsin is accepting PFAS applications [target 7.8.19]

• Update the Laboratory Certification Website with the required PFAS information needed for certification [target 7.8.19]

• Update the Laboratory Certification Database (6 tables, 300+ rows, 2000+ fields) to handle PFAS certification [target 7.19.19]
# WISCONSIN PFAS CERTIFICATION LIST

## 36 COMPOUNDS

### 13 Carboxylic Acids
- PFBA
- PFPeA
- PFHxA
- PFHpA
- PFOA
- PFNA
- PFDA
- PFUnA
- PFDoA
- PFTriA
- PFTeA
- PFHxDA
- PFODA

### 12 Sulfonic Acids
- PFBS
- PFPeS
- PFHxS
- PFHpS
- PFOS
- PFNS
- PFDS
- PFDoS
- 4:2 FTSA
- 6:2 FTSA
- 8:2 FTSA
- 10:2 FTSA

### 4 Replacement Chemicals
- HFPO-DA
- DONA
- 9Cl-PF3ONS
- 11Cl-PF3OudS

### 3 Sulfonamides
- FOSA
- NMeFOSA
- NEtFOSA

### 2 Sulfamidoacetic acids
- NMeFOSAA
- NEtFOSAA

### 2 Sulfamidoethanols
- NMeFOSE
- NEtFOSE
The purpose of the “WI PFAS SOP” is to indicate the minimum requirements that need to be met to perform PFAS analysis on non-drinking water matrices for Wisconsin compliance samples.

The laboratory is to follow the requirements of EPA method 537.1 listed in this SOP along with the other additional requirements listed in this SOP.

\{F\} = when this is listed after a requirement and the requirement is not met then the associated results must be qualified on the test report. The qualifier can direct the data user to a narrative where the detail is provided to indicate what was the non-conformance and what were the possible effects on the sample results.
Sample Handling

1. HDPE sample containers must be used. {F}
2. Samples must be single bagged at a minimum as well as the ice. {F}
3. All samples must be assessed for free chlorine using free chlorine strips with a detection capability of 0.1 mg/L or lower. Trizma preservative is not required if the samples do not contain free chlorine.
4. When equipment is used in the field to collect samples, an equipment blank must be collected.
   - The equipment blank does not need to be analyzed unless the associated samples contain detections greater than the Method Reporting Limit (MRL). {F} [537.1] The MRL is set to the lowest concentration standard (or a higher concentration standard) in the initial calibration, and sample results are reported to the MRL.
5. Site-specific field blanks must be collected at the same time samples are collected.
   - The field blank does not need to be analyzed unless the associated samples contain detections greater than the MRL. {F} [537.1]
6. Ship samples at 0 – 10 °C. The temperature at sample receipt must be measured and documented. {F}
7. Store samples in the laboratory at 0 – 6 °C.
8. Extracted internal standards (exact labeled analogs of the target analytes) must be used where commercially available.
9. 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, from the same functional group as the target analyte, and must span the same water solubility range as the target analyte.
1. Holding time is 14 days to extraction and 28 days from extraction to analysis. {F} [537.1]
2. The entire sample received in the sample bottle must be extracted. {F}
   • An exception is made if the sample received is at extremely high concentrations; subsampling is then allowed, but the data must be qualified.
   • Another exception is made if more sample volume is received than what can be extracted through the solid phase extraction (SPE) cartridge; subsampling is then allowed, but the data must be qualified.
3. Fortify the sample, in the sample bottle it was received in, by adding the extracted internal standards. Cap, invert, and mix.
   • 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 what were the possible effects on the sample results. {F}
4. If particulates in the sample (samples with > 1% solids) need to be removed before using SPE, centrifuge the sample and use the supernatant as the sample. Do not use filters to separate the solids from the liquid phase.
5. Determine sample volume by marking the bottle level or by weighing. Do not measure sample volume with a graduated cylinder. [537.1]
6. Use an appropriate SPE cartridge for the matrix analyzed and the analytes reported.
7. Rinse the sample bottle and cap with elution solvent using two separate rinses, pour the solvent from each rinse through the SPE cartridge, and collect the filtrate for analysis.
8. Concentrate the extract to near dryness unless a technology is employed that allows for a non-concentrated extract.
9. Bring to a quantitative final volume with the final injection solvent and vortex.
Solid (Non-aqueous) Sample Extraction

1. HDPE sample bottles that do not have Teflon lids must be used. [F]
2. Extraction hold time is 28 days from collection, and analysis hold time is 28 days from extraction. When updated information exists from the EPA that indicates that different holding times are appropriate, those will be required. [F]
3. The entire sample received must be homogenized prior to subsampling.
4. Fortify the subsampled portion by adding the extracted internal standards. Let the fortification solvent dry before adding the extraction solvent.
5. Solid sample extractions are performed by using one of the two options presented in this SOP.

**Extraction A**

a. Add enough basic digestion solution to wet and cover the sample. Record the volume used.
b. Sonicate the samples in a heated water bath for at least 30 minutes.
c. Let the samples sit at room temperature for at least 12 hours.
d. Neutralize the basic solution by adding an equivalent number of moles of acid and vortex. At this point the sample has been digested and the solution neutralized.
e. Add an appropriate extraction solvent to the sample.
f. Shake the mixture for a minimum of 1 hour and then centrifuge.
g. Decant and save the supernatant.
h. Repeat steps (e, f, and g).
i. After the extracts have been combined, check the pH of the diluted extract to make sure it is at the appropriate pH for the SPE cartridge being used and the target analytes.
j. Sonicate the mixture for a minimum of 30 minutes.
k. Cleanup the extract using an appropriate SPE cartridge.

**Extraction B**

l. Add enough basic digestion solution to wet and cover the sample. Record the volume used.
m. The extraction process takes place by using a combination of shaking the sample and sonication of the sample.
n. A minimum total extraction time of 4 hours is required. The amount of time used for the shaking and sonication are up to each laboratory as long as the total adds up to a minimum of 4 hours (i.e. 1-hour shake, 3-hour sonication...).
o. After the shaking/sonication step, adjust the pH of the extraction solution so it is appropriate for the SPE cartridge used and the target analytes.
p. Cleanup the extract using an appropriate SPE cartridge.
1. Each analyst must generate an acceptable initial demonstration of capability (IDC) before performing the analysis.
2. Analyze all target analytes to determine the retention time of the linear and branched isomers (where commercially available).
3. Analyze a method blank. The results must be less than ½ MRL or the IDC must be repeated.
4. Initial precision and recovery – analyze 4 extracted spikes (midrange). The average recovery must be 70-130% and the RSD < 20% or the IDC must be repeated. [537.1]
5. Analyze a QCS (ICV) – 2nd source. The recoveries must be 70-130% or the IDC must be repeated. [537.1]
6. Analyze a lab control sample fortified at the MRL. The recoveries must be 50-150% or the IDC must be repeated. The lab control sample is prepared the same as samples. This is a one-time requirement per analyst.
Ongoing QC

1. An extraction batch is a set of one to 20 environmental samples of the same matrix (aqueous or non-aqueous) extracted in a continuous 24-hour period.

2. **Method blank** (1/batch) – results must be $< \frac{1}{2}$ MRL, $< 1/10$ the sample concentration or $< 1/10$ the regulatory limit to pass. Method blank concentration is determined by extrapolating below the low standard, unlike samples. [F]

3. **Lab control sample** (1/batch) – spike with all target analytes. Recoveries must be 70-130%. [F]

4. **Extracted internal standards (labeled target analogs)** – the EIS peak area in any injection must be within 50-150% from the most recent CCC peak area and not more than 50%-150% from the average peak area from the initial calibration (ICAL). [537.1] [F]

5. **Field blank** – analysis is only required if a sample contains a method analyte at or above the MRL. Results must be $< \frac{1}{2}$ MRL, $< 1/10$ the sample concentration, or $< 1/10$ the regulatory limit to pass. Field blank concentration (and equipment blank concentration when used) is determined by extrapolating below the low standard, unlike samples. [F] [537.1]

6. **QCS (ICV)** – required with each new ICAL. Recovery must be 70-130%. Samples may not be analyzed if this fails.

7. **CCV** – required at the beginning and end of each analysis batch and after every 10 field samples. The first CCV on non-ICAL days must be at or below the MRL and recover at 50-150%. All other CCV’s require 70-130% recovery. Samples may only be reported if bracketed by passing CCVs. [537.1]

8. **Retention Time Windows** – the laboratory must establish a policy of defining how retention time windows will be set.

9. The MDL must be less than the MRL.
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 the peak. [537.1]
2. Sample results for all analytes will be calculated using isotope dilution. 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, from the same functional group as the target analyte, and must span the same water solubility range as the target analyte.
3. Branched and linear isomers must be used as quantitative calibration standards where commercially available. [537.1]
4. A qualitative calibration standard for branched isomers must be used to identify retention times where quantitative standards are not commercially available. [537.1]
5. A valid mass calibration must be established before any analysis.
6. Mass calibration must bracket the ion masses of interest.
7. Perform an appropriate tune for the precursor ion.
8. Perform an appropriate tune for the product ions.
9. Absolute retention times are set using the midpoint standard from the ICAL on ICAL days, and on non-ICAL days, absolute retention times are set using the beginning CCV of each run.
10. ICAL is required at instrument setup or after ICV/CCV failure – samples may not be analyzed with a failing ICAL.
    a. For calibration factors, the RSD must be <20%.
    b. For linear regression, the $r^2$ must be > 0.99, and a minimum of 5 non-zero concentration standards must be used.
    c. For quadratic regression, the $r^2$ must be > 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.
    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%.
11. All sample results reported must be from a response that is within the initial calibration’s lowest and highest response. Results for samples below the low standard are not allowed. Report non-detections as < MRL. MDL samples and blanks can be extrapolated below the lowest standard response. [537.1] {F}
12. All analytes that have two transitions will require two transition ions (precursor ion to quantitation ion and precursor ion to confirmation ion). The confirmation ion is used for positive analyte detections.

13. The relative abundance of the primary and secondary ions (where applicable) in the samples shall match the observed abundance to within 50-150% from the midpoint standard in the ICAL on ICAL days or from the beginning CCV on non-ICAL days. {F}

14. The primary to secondary ion transition ratios must 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}

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

15. Documentation of the primary and confirmation transitions and the ion ratio are required.

16. The extracted internal standards used in the samples must be added to the initial calibration standards, ICV, and CCVs at a single concentration.

17. 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.

18. Signal to Noise (S/N) must be ≥ 3:1 for quantitation ions and confirmation ions.

19. Utilize these transitions 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:

- PFOA 413-369
- PFOS 499-80
- PFHxS 399-80
- PFBS 299-80
- 4:2 FTS 327-307
- 6:2 FTS 427-407
- 8:2 FTS 527-507
- NETFOSAA 584-419
- NMeFOSAA 570-419
20. Target analytes and their exact labeled analog must elute within 0.1 min. If there is no exact labeled analog then the alternate labeled analyte analog must be within 0.3 min of the target analyte. [F]
21. HDPE/PPE autosampler vials are single use only. [537.1]
22. The laboratory must follow and have a written procedure to demonstrate that the analytical run is back in control after a sample with a high concentration is analyzed. Analyzing one or two instrument blanks after the high sample is not sufficient corrective action due to the delayed release of the analyte in the system.
23. Report results in acid form.
24. Blank values may not be subtracted from sample values. [537.1]
25. Calibration standards purchased as salts must be mass corrected for the salt content. [537.1]
26. Any analytes in the samples that contain multiple peaks due to linear and branched isomers must be integrated in the same manner as the standards.
27. The laboratory SOP must include at a minimum:
   • which extracted internal standards are used to calculate the result of each analyte reported,
   • which mass is used for the precursor ion for each analyte reported,
   • which mass is used for the product quantitation ion for each analyte reported,
   • which mass is used for the product confirmation ion for each analyte,
   • specific instructions for conditioning and elution of the SPE,
   • indicate which branched isomers are calculated using a quantitative calibration standard and which are calculated using the linear isomer standard.
28. Where PT samples are available for the individual analytes, and the laboratory wants to be certified on a PFAS analytes basis then each analyte must include a passing PT.
29. Where PT samples are available for the individual analyte, and the laboratory wants to be certified for the PFAS analyte group then 80% of the spiked analytes in the PT provider sample must pass.
30. Requirements in NR 149 still apply to this analysis, unless otherwise specified in this SOP.
Recommendations – not requirements

1. Additional clean-up of each sample, method blank, LCS, and field blank using granular activated carbon is highly recommended. The laboratory should be prepared to demonstrate that this additional clean-up is not necessary by meeting extracted internal standard recoveries.

2. Use weighted regressions.

3. Proof all reagents, materials, and equipment as sources of contamination.

4. Taurodeoxycholic Acid (TDCA) and some of its isomers, including tauroursodeoxycholic acid and taurochendeoxycholic acid, are known interferences which may overestimate or yield a false positive result for perfluoro-octanesulfonic acid (PFOS), while 5-pregn-3,20-diol-3-sulfate and 34S-3-hydroxy-5-pregn-20-one sulfate may interfere with perfluorohexanesulfonic acid (PFHxS). The laboratory should have protocols for ensuring chromatographic separation of PFOS from TDCA and for detecting interferences by monitoring secondary multiple reaction transitions. The 499 > 80 transition is prominent in all TDCA isomers and in PFOS. However, the 499 > 99 transition for PFOS is not affected by the TDCA. In the absence of chromatographic separation of TDCA from PFOS, the 499 > 80 transition will result in significant bias in PFOS concentrations. Therefore, both transitions must be monitored for PFOS and results must agree within 20% to ensure accurate quantification of PFOS. Similarly, analysis for PFHxS can be biased by co-eluting interferences. In this case, the 399 > 80 and the 399 > 99 transitions may both be affected, and therefore, a third transition, 399 > 119, also must be monitored to demonstrate that there is not a bias from co-eluting interferences.

5. Matrix effects manifest as either high or low extracted internal standard recovery. If the labeled extracted internal standard recoveries do not meet acceptance criteria, then the laboratory should determine whether a matrix effect is the cause. One diagnostic test is to dilute the sample extract and reanalyze it. Another diagnostic test is to further cleanup the sample, or lastly, to repeat the extraction using a smaller sample size.

6. Prior to daily use, flush the LC column with elution solvents.

7. Each individual standard and labeled standard should be validated by analysis to confirm its identity and the absence of significant impurities.

8. 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.

9. 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.
10. In order to be used for cleanup of sample extracts, the performance of the SPE cartridges should be checked at least once for each manufacturer’s lot of cartridges. This performance check is accomplished by processing a spiked reagent water sample through the extraction procedure and analyzing the extract. Labeled compounds are not added to these check samples before extraction because the recovery correction inherent in isotope dilution will mask problems with the cartridges. Cartridge performance is acceptable if the recoveries of the native analytes are within the QC acceptance criteria for the LCS.

11. Prior to any analyses, optimize the following instrumental conditions: mass calibration, MRM acquisition parameters, scans per peak, chromatographic resolution, retention time calibration, sensitivity, and instrument background elimination. Actual tuning parameters are instrument-specific and should be optimized according to manufacturer’s specifications.

12. The mass spectrometer system must undergo mass calibration according to manufacturer’s specifications to ensure accurate assignments of m/z values by the instrument. Mass calibration is performed at least annually, after performing major maintenance, or as required to maintain routine instrument sensitivity and stability performance.

13. To determine if background concentrations of PFAS significantly impact this analysis, a 40 part per trillion (ppt) standard containing all of the target analytes in 0.3% NH4OH (v/v) in methanol should be analyzed three times, with alternating instrument solvent (methanol) blank measurements. If the peak area from the standards is not greater than that of the solvent blank using a Student’s t-test (95% confidence), then it may be necessary to modify the “plumbing” of the analytical system. This test should be performed prior to any analysis, at least annually, and after major instrument maintenance.

14. To establish retention times, analyze individual solutions of each of the target compounds using the LC gradient and acquisition parameters determined above. Analyze a mixed solution of all target compounds to confirm their separation and identification.

15. Consider setting minimum separation requirements between the linear and branched isomers of an analyte.

16. Consider utilizing the peak asymmetry check in EPA 537.1 to diagnose acceptable peak shape.

17. Mass calibration should be verified to be within 0.5 amu of the true value.

18. Use the DOD sampling guidelines for sample collection.
BROWNFIELD STUDY GROUP – DEVELOPING SITE INVESTIGATION RESOURCES

LAURIE PARSONS, OBG & BSG MEMBER

MARK THIMKE, FOLEY & LARDNER, BSG CO-CHAIR
PER- AND POLY-FLUORINATED ALKYL SUBSTANCES (PFAS) IN PHASE I ESAS:

AN UPDATE ON DEVELOPING INTERIM SCREENING PROCEDURES AND BEST PRACTICES
PFAS IN PHASE I ESAS

• THE PFAS DILEMMA BEGINS AT THE DUE DILIGENCE STAGE

• BECOMING A BARRIER TO PROGRESS FOR REDEVELOPMENT AT SOME BROWNFIELD SITES IN WISCONSIN (NOT ALL)

• NO REQUIREMENTS OR STANDARD OF CARE FOR ASSESSING PFAS IN ASTM-COMPLIANT PHASE I ESAS, WILL TAKE AT LEAST A YEAR TO DEVELOP

• BSG PFAS SUBGROUP WAS FORMED IN THE INTERIM (APRIL 2019)

• PURPOSE: ESTABLISH SCREENING PROTOCOLS AND BEST PRACTICE FOR INITIAL DUE DILIGENCE STAGE THAT FACILITATE FORWARD PROGRESS FOR BROWNFIELD REDEVELOPMENT

• DRAFT ISSUE STATEMENT PRESENTED AT BSG MAY 10, 2019 MEETING, INPUT RECEIVED
BROWNFIELD STUDY GROUP – PFAS SUBGROUP

- SNEJANA KARAKIS, RAMBOLL
- NICHOLAS JOHNSON, FOLEY & LARDNER
- MARITA STOLLENWERK, TRC
- Kristin Kurzka, Sigma
- LAURIE PARSONS, RAMBOLL OBG
Proposition

• Augment the ASTM process by generating supplemental due diligence screening procedures and best practices

• Interim usage until ASTM supplements the existing Phase I ESA standard, ASTM E 1527-13

• Primary scope:
  ➢ Supplemental “State” of Practice Review – asking for input external to WI
  ➢ Develop a site evaluation checklist specific to known characteristics, history, manufacture and usage of PFAS at facilities/properties
  ➢ Create a companion document with peer reviewed and agency endorsed references outlining manufacturing activities typically associated with PFAS, product types, chronology of usage and potential to occur
  ➢ Allow for stakeholder involvement and reviews, incorporating WDNR ESA Phase I guidance
TARGET TIMELINE

MILESTONE DATES (UPDATED 5/31):

• MAY 31, 2019 COMPLETE DRAFT OUTLINE CHECKLIST

• JUNE 15, 2019 SUPPLEMENTAL COMPANION DOCUMENT DRAFTED FOR STAKEHOLDER REVIEW

• JULY 31, 2019 FINAL DRAFT INTERIM GUIDANCE FOR DISTRIBUTION
WASTE MATERIALS AND MANAGEMENT – PFAS PROGRAM DEVELOPMENT

JOE VAN ROSSUM, PROGRAM DIRECTOR & KATE STROM HIORNS, SECTION CHIEF
WDNR
FOCUS FOR THE WMM PROGRAM:

• IF PFAS-CONTAINING MATERIALS ARE DISPOSED OF IN LANDFILLS, AT COMPOST SITES, OR BY LANDSPREADING, WHAT IS THE POTENTIAL IMPACT TO GROUNDWATER, SURFACE WATER, AND DRINKING WATER?
  • LIST WASTES THAT COMMONLY CONTAIN PFAS
  • DETERMINE CLOSED AND ACTIVE LANDFILLS THAT LIKELY HAVE THOSE WASTES, WHAT ENGINEERING FEATURES ARE PRESENT, AND POTENTIAL FOR IMPACT
  • WORK WITH WW PROGRAM TO DETERMINE ACCEPTABLE PFAS LEVELS AT WASTEWATER TREATMENT PLANTS AND POTENTIAL FOR LEACHATE TREATMENT
  • DEVELOP BEST MANAGEMENT PRACTICES FOR DISPOSAL OF PFAS-CONTAINING WASTE

• INFORMATION GATHERING
WHAT ARE YOUR CONCERNS RELATED TO PFAS AND WASTE MANAGEMENT?

• REQUESTING FEEDBACK TODAY FROM ATTENDEES
• WHAT HAVE YOU LEARNED FROM OTHER STATES OR YOUR RESEARCH?
• DEVELOPING A WORKPLAN

• WASTE SUBGROUP MEETING ON JULY 18
  • MORE INFORMATION WILL BE POSTED ON THE PFAS TECHNICAL ADVISORY GROUP WEBPAGE
WATER QUALITY – PFAS PROGRAM DEVELOPMENT

ADRIAN STOCKS, PROGRAM DIRECTOR
WDNR WATER QUALITY BUREAU
FOCUS FOR THE WQ PROGRAM:

• DEVELOP WQS
• DEVELOP SOURCE REDUCTION STRATEGIES AND/OR PERMIT REQUIREMENTS FOR FACILITIES WHERE NECESSARY
• DETERMINE APPROVED ANALYTICAL METHOD FOR BIO-SOLIDS
• GAIN A BETTER UNDERSTANDING OF THE POTENTIAL FOR GW CONTAMINATION AND PRIVATE WELL IMPACTS FROM LAND SPREADING.
• DEVELOP PFAS CONTAMINANT LEVELS IN CONJUNCTION WITH EPA FOR 503 REQUIREMENTS AND NR 204 LAND SPREADING CONTAMINANT LEVELS.
• INFORMATION GATHERING
SURFACE WATER QUALITY STANDARDS

• WI CURRENTLY DOES NOT HAVE SURFACE WATER QUALITY STANDARDS (WQS) FOR PFAS
• WQS APPLY IN WATERBODIES
• WQS ARE USED TO CALCULATE EFFLUENT LIMITATIONS
SURFACE WATER QUALITY STANDARDS

• TRIENNIAL STANDARDS REVIEW

A: Antidegradation
   - Bacteria Criteria Revision
   - Biocriteria
   - Chloride Variance Streamlining
   - Designated Uses Process Revision
   - P Assimilative Capacity in GLs
   - P Site Specific Criteria
   - Wetlands Floristic Assessment
   - Numeric Benchmarks

B: Cyanobacteria
   - Human Health Criteria Revisions
   - PFOS/PFOA
   - Outstanding/Exceptional Resource
   - Water Process Revision
   - Mercury MDV

C: Aquatic Life
   - Criteria Revisions

D: Ammonia
   - Arsenic
   - Chloride
   - Total Suspended Solids (TSS)
   - Copper
   - Nitrate/Nitrogen

E: P Criteria for
   - 2-Story Lakes
   - Arsenic Variance
   - Process

A: In Progress
B: New Priorities
C: Priorities, but limited progress expected
D: Barriers to progress
E: Not Priorities
WATER QUALITY STANDARDS
DEVELOPMENT PROCESS

0.02 kg / day

Bioaccumulation factor

70 kg

RfD

Relative source contribution

Human Health
Surface Water
Quality Criteria

2 liters / day
WHAT IS DNR DOING NOW?

• WORKING TO ESTABLISH LONG-TERM STRATEGY
  • SURFACE WQS (TRIENNIAL STANDARDS REVIEW)
  • SOLICITATION OF DHS’S EVALUATION FOR GW STANDARDS
  • SCOPING - SURFACE WATER MONITORING
  • BIOSOLIDS
  • COLLABORATION WITH UW ON STUDY IN MARINETTE TO DETERMINE THE IMPACTS OF PFAS-CONTAINING BIOSOLIDS ON AGRICULTURAL FIELDS IN WISCONSIN RECEIVING LAND-SPREAD BIOSOLIDS.

• ADDRESSING KNOWN PFAS CONTAMINATION WITH REGULATORY TOOLS AVAILABLE + PERMITTEE COOPERATION
  • PROTECT HUMAN HEALTH AND THE ENVIRONMENT
EXAMPLES

- HUSKY REFINERY POST-"INCIDENT"
- TYCO FIRE TECHNOLOGY CENTER
- DEWATERING PROJECTS
- POTW BIOSOLIDS
- OTHERS
WHAT ARE YOUR CONCERNS RELATED TO PFAS AND WPDES PERMITTING?

• Water Quality Subgroup Meeting (Late June)
• Requesting Feedback from Attendees
• What Have You Learned from Other States or Your Research?
• Developing a Workplan

• More information will be posted on the PFAS Technical Advisory Group Webpage
PREVIOUS FISH TISSUE SAMPLING EFFORTS

- 2006-2012 – SUBSET OF CONTAMINANT MONITORING SAMPLES ANALYZED FOR PFAS, COMBINED WITH PFAS DATA FROM EPA
  - WDNR SAMPLED FISH SAMPLED FROM RIVERS WITH HIGH INDUSTRIAL USE, GREAT LAKES AOCS
  - PFOS FOUND IN >99% OF SAMPLES
  - OTHER PFAS DETECTED (BESIDES PFOS) VARIED BY LOCATION*
  - PFOS VARIATION:
    - SPECIES: HIGHEST IN FILLETS OF WHITE BASS, CRAPPIE, AND BLUEGILL
    - LOCATION: HIGHEST IN FILLETS FROM MISSISSIPPI RIVER, LOWEST IN FILLETS FROM LAKE SUPERIOR

*May be an artifact of analysis method
FISH CONSUMPTION ADVISORIES

• LOCATIONS WITHIN THE MISSISSIPPI RIVER HAVE PFOS-BASED ADVISORIES
  • POOL 3 – BLUEGILL, CRAPPIE
  • POOL 4 – BLUEGILL
  • POOLS 5, 5A, AND 6 – BLUEGILL, CRAPPIE

• PFAS LEVELS DETECTED IN FISH FROM OTHER LOCATIONS WERE NOT HIGH ENOUGH TO SUPERSEDE ADVISORIES ALREADY IN PLACE FOR PCBs
  • PCB LEVELS GENERATED MORE RESTRICTIVE ADVICE
Recent/Future Fish Tissue Sampling Efforts

• 2017-2018: Green Bay and Menominee River up to the 1st Dam

• 2019: All samples taken during routine contaminant monitoring will be analyzed for PFAS

• Preliminary results from 2017
  • PFAS levels consistent with levels observed in previous samples
  • PCBs are still the contaminant that drive the advisory
2019 WATER QUALITY MONITORING PLANS

• PROJECT OBJECTIVE 1: DESCRIBE PFAS CONCENTRATIONS AT SITES WITH KNOWN OR SUSPECTED CONTAMINATION

• PROJECT OBJECTIVE 2: COLLECT PAIRED FISH TISSUE AND SURFACE WATER CHEMISTRY TO AID DEVELOPMENT OF A WATER QUALITY STANDARD

• TIMEFRAME: MID TO LATE SUMMER
  • INTENDED TO CHARACTERIZE LOCAL CONDITIONS
  • MAXIMIZES THE CHANCE THAT RESIDENT FISH ARE CAPTURED
  • WILL ENSURE, TO THE EXTENT PRACTICABLE, THAT WATER CHEMISTRY AND FISH TISSUE ARE REPRESENTATIVE OF LOCAL CONDITIONS
## 2019 Water Quality Monitoring Plans

### Study Locations

<table>
<thead>
<tr>
<th>Waterbody</th>
<th>Source known?</th>
<th>Known contamination</th>
<th>Number of sample sites</th>
<th>Sample types</th>
</tr>
</thead>
<tbody>
<tr>
<td>Menominee River from Scott Flowage to mouth</td>
<td>Y</td>
<td>Groundwater wells, surface water</td>
<td>3-5</td>
<td>Fish &amp; water</td>
</tr>
<tr>
<td>Starkweather Creek from headwaters to Lake Monona</td>
<td>Y</td>
<td>Groundwater wells</td>
<td>4</td>
<td>Fish &amp; water</td>
</tr>
<tr>
<td>La Crosse River and Silver Creek</td>
<td>Y</td>
<td>Groundwater wells</td>
<td>4</td>
<td>Water</td>
</tr>
<tr>
<td>Wisconsin River, middle reach</td>
<td>N</td>
<td>Groundwater wells, bald eagle plasma</td>
<td>3</td>
<td>Fish &amp; water</td>
</tr>
<tr>
<td>Mississippi River Pools 3, 4, 6, &amp; 8</td>
<td>Y</td>
<td>Surface water, fish tissue</td>
<td>4</td>
<td>Fish &amp; water</td>
</tr>
</tbody>
</table>
HOW WILL MONITORING DATA BE USED?

• FISH FILLET DATA: USED TO ISSUE FISH CONSUMPTION ADVISORIES

• FISH FILLET & WATER DATA: USED IN DERIVING SURFACE WATER QUALITY STANDARDS

Acceptable Daily Exposure

Relative source contribution

0.02 kg / day

Bioaccumulation factor

2 liters / day

Images: https://www.alsglobal.eu/media-general/images/dioxins/pops/pfas-2.png
SUMMARY

• WDNR ANALYZED FISH FILLETS FOR PFAS IN 2006-2012 AND ISSUED PFOS-BASED ADVISORIES FOR LOCATIONS WITHIN THE MISSISSIPPI RIVER

• PRELIMINARY 2017 PFAS DATA FROM GREEN BAY AND MENOMINEE RIVER FISH SHOWS SIMILAR LEVELS TO PREVIOUS SAMPLING EFFORTS

• ALL 2019 FISH CONTAMINANT SAMPLES WILL BE ANALYZED FOR PFAS

• 2019 WATER QUALITY MONITORING EFFORTS WILL FOCUS ON LOCATIONS WITH KNOWN CONTAMINATION

• MONITORING DATA WILL BE USED TO ISSUE FISH CONSUMPTION ADVISORIES AND IN THE DEVELOPMENT OF SURFACE WATER STANDARDS
QUESTIONS?

FISH CONTAMINANT MONITORING & ADVISORIES:
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608-220-4769

WATER QUALITY MONITORING:
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WATER QUALITY STANDARDS:
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SHARING EXPERIENCES

• A FORUM TO SHARE KNOWLEDGE AND EXPERIENCE WITH PFAS
REVIEW OF MEETING

• WHAT WAS HELPFUL
• WHAT WAS NOT HELPFUL
• RECOMMENDATIONS FOR IMPROVEMENT
NEXT QUARTER MEETING

SEPTEMBER 20TH FROM 10-2
THANKS FOR PARTICIPATING