PFAS Technical Group

December 17, 2021

Agenda

- Welcome and Introductions
- EPA Method 1633 – Adrian Hanley, EPA
- Minnesota Landfill Study – Laura Marti, MPCA
- Conclusions & Next Steps

USEPA Draft Method 1633 for Per- and Polyfluorinated Alkyl Substances (PFAS) and the NPDES Method Approval Process

The 10,000-foot view

What is PFAS?

- If you don't know, and you work in the environmental sector, you've been hiding under a rock for the last few years. I won't bore everyone else who has seen hundreds of "What is PFAS" slides.
- Below are two points one needs to keep in mind when discussing how to analyze environmental samples for PFAS compounds:
  - Thousands of PFAS compounds have been used in industry and released into the environment
  - Many PFAS compounds are known to degrade and form new compounds

Method 1633: DoD-EPA Collaboration

- Because of the multiple Federal and State players in investigation and remediation activities, DoD sought a unified approach to a PFAS analysis method and approached the Administrator for the Office of Water in 2019 to start a collaborative effort to develop, validate, and give formal EPA approval to a PFAS method that would be useful for DoD and various EPA Programs.
- DoD agreed to pay for the method validation effort, and follow direction provided through EPA review of each step of the validation process.
- EPA is responsible for drafting and revising Method 1633 and drafting portions of the validation study reports.
- OLEM is using the data for a parallel SW-846 method validation.

OW's CWA Method Validation Process

- Methods are approved by EPA for nationwide NPDES use via a process that includes:
  - Identifying a promising technique or procedure based on internal (EPA) or external development efforts (e.g., literature review, lab SOPs, or Voluntary Consensus Standard Body procedures)
  - Formal study planning documentation (e.g., QAPP and/or study plan)
  - Drafting an actual method in EPA format
  - Single-laboratory validation with at least 9 different water and wastewater matrices
  - Refinement of any issues identified in the single-laboratory validation study
  - Multi-laboratory validation targeting 9 laboratories running 9 wastewater matrices
  - Development of QC acceptance criteria that reflect the real-world performance of the method in the multi-laboratory validation study

OW's CWA Method Approval Process

- The method and all the supporting documentation are included in a rulemaking docket, typically for proposal at 40 CFR Part 136.
- Following the proposal, EPA:
  - Reviews and responds to all public comments received
  - Makes any needed revisions to the method based on the comments
- The method gains final approval through a final rule that promulgates the method for use in Clean Water Act NPDES compliance monitoring.
- **No method is formally approved until that rulemaking process is complete**, but unapproved methods may still be useful to EPA and other organizations.

Generic OW/Wastewater Method Schedule

- Method validation
  - Single-laboratory validation: 1-2 years
  - Multi-laboratory validation: 1 year
- Rulemaking
  - Proposal: 6 months to 1 year
  - Comment response and finalization: 1-2 years

Note: *Once a method has been multi-lab validated, we usually post it on our website. Many states will immediately start using these methods in permits, which is their right if they operate their own NPDES program.*

Due to high demand from stakeholders, Method 1633 was posted after single lab validation.

Method 1633 Overview

The draft method uses liquid chromatography (LC) with tandem mass spectrometry detection (MS/MS) to target 40 specific PFAS analytes representing:

- Perfluoroalkyl carboxylic acids (11 analytes, including PFOA)
- Perfluoroalkyl sulfonic acids (8 analytes, including PFOS)
- Fluorotelomer sulfonic acids (3 analytes)
- Perfluorooctane sulfonamides (3 analytes)
- Perfluorooctane sulfonamidoacetic acids (2 analytes)
- Perfluorooctane sulfonamide ethanols (2 analytes)
- Per- and Polyfluoroether carboxylic acids (5 analytes, including ADONA)
- Ether sulfonic acids (3 analytes)
- Fluorotelomer carboxylic acids (3 analytes)

- The draft method employs 24 isotopically labeled standards to quantify the 40 analytes by isotope dilution.

Single-laboratory Validation

- DoD selected a procedure developed by SGS-Axys Analytical in British Columbia.
- DoD developed a formal study plan for a single-laboratory validation study.
- OW and OLEM reviewed the study plan and offered recommendations to DoD for steps and matrices of interest to EPA.
- SGS-Axys performed the single-laboratory validation study under the direction of DoD.
- DoD provided OW and OLEM with all the results for our review.
- OW agreed to draft some materials for the DoD study report.

Summary of Single-laboratory Validation

- The DoD single-laboratory study tested:
  - 3 groundwaters
  - 3 surface waters
  - 3 landfill leachates
  - 7 wastewaters from different industries
  - 3 sediments
  - 3 tissues (fish and clams)
  - 3 biosolids
  - 7 soils
- Results were generally good, with some issues related to the landfill leachates, which are very complicated samples.

Single-laboratory Validation MDLs

- The reported MDLs from the single-laboratory study varied by analyte and matrix, as summarized below:
  - Aqueous sample MDLs ranged from about 0.12 to 5.94 ng/L, with all but 4 of the 40 analytes having MDLs between 0.12 and 1.5 ng/L
  - Soil sample MDLs ranged from about 0.014 to 0.348 ng/g (dry weight)
  - Tissue sample MDLs ranged from about 0.032 to 9.98 ng/g (wet weight) with all but 1 of the 40 analytes having MDLs between 0.032 and 1.5 ng/g
- The MDLs for the 40 analytes were often MDL_b values, driven by background levels of those analytes in the laboratory and in various supplies and reagents used in the procedure.

Single-laboratory Validation Labeled Compound Recoveries

- As with the MDLs, recoveries of the 29 labeled compounds varied by analyte and matrix.
- The average recoveries of most of the labels were between:
  - 46 and 148% in wastewater samples
  - 48 and 90% in surface water samples
  - 65 and 111% in groundwater samples
  - 42 and 131% in landfill leachates
- The ^{13}C-labels generally exhibited higher minimum recoveries than the deuterium-labeled compounds in the aqueous samples, likely due to the potential exchange of deuterium with hydrogen from water.
- Recoveries in the solid samples were generally higher than in aqueous samples.

Next Steps

- DoD is completing the report on the single-laboratory study.
- EPA will review the draft report and provide comments to DoD before the report is widely released.
- DoD is starting the multi-laboratory validation study using at least 9 laboratories and multiple matrices.
  - DoD's study will validate the draft method as currently written, without an option for the labs to make any modifications.
  - This will provide a baseline of method performance.
  - Expected to be complete in 2022
- OW will use the study results to develop formal multi-laboratory performance specifications for the final method and prepare the method for proposal.

Another PFAS Method Option

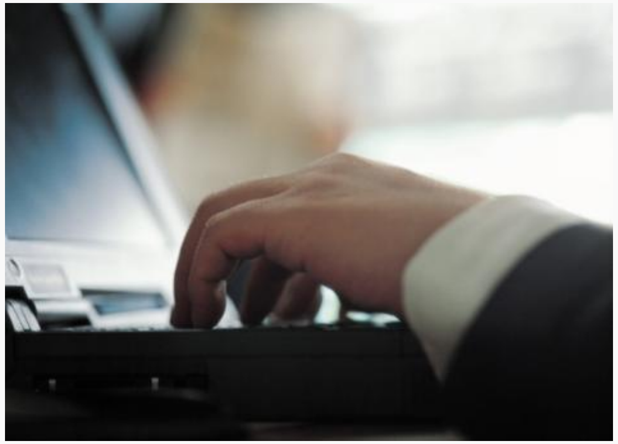
- Adsorbable organic fluorine (AOF) by combustion ion chromatography (CIC)
  - Adsorbs sample onto activated carbon or other sorbent and wash out inorganic halides (including inorganic Fluorine)
  - Combust in a furnace
  - Exhaust is bubbled through a basic solution that captures fluorine as the fluoride ion (F^-)
  - Analyze the solution by ion chromatography to detect the fluoride ion
  - Detects the fluoride from any organofluorine compounds (including any PFAS, but also some pharmaceuticals and pesticides)
  - Does not detect inorganic fluorine
- OW is currently working with ORD and a commercial laboratory to flesh out and test a draft procedure from ASTM.

AOF Considerations

- Similar to EPA Method 1650 for adsorbable organic halides (AOX) that was used in the pulp and paper effluent guideline
- Different PFAS compounds have different affinities for the activated carbon sorbent, making the use of spiked samples for QC purposes more challenging.
  – Which spike compounds should you use? The “good” ones or the poorer performers?
- Because AOF is not a specific compound, but an aggregate measure of organic fluorine content, it may be most useful as a screening procedure or for range-finding efforts.

Contact Information

For more information or additional feedback, please contact:



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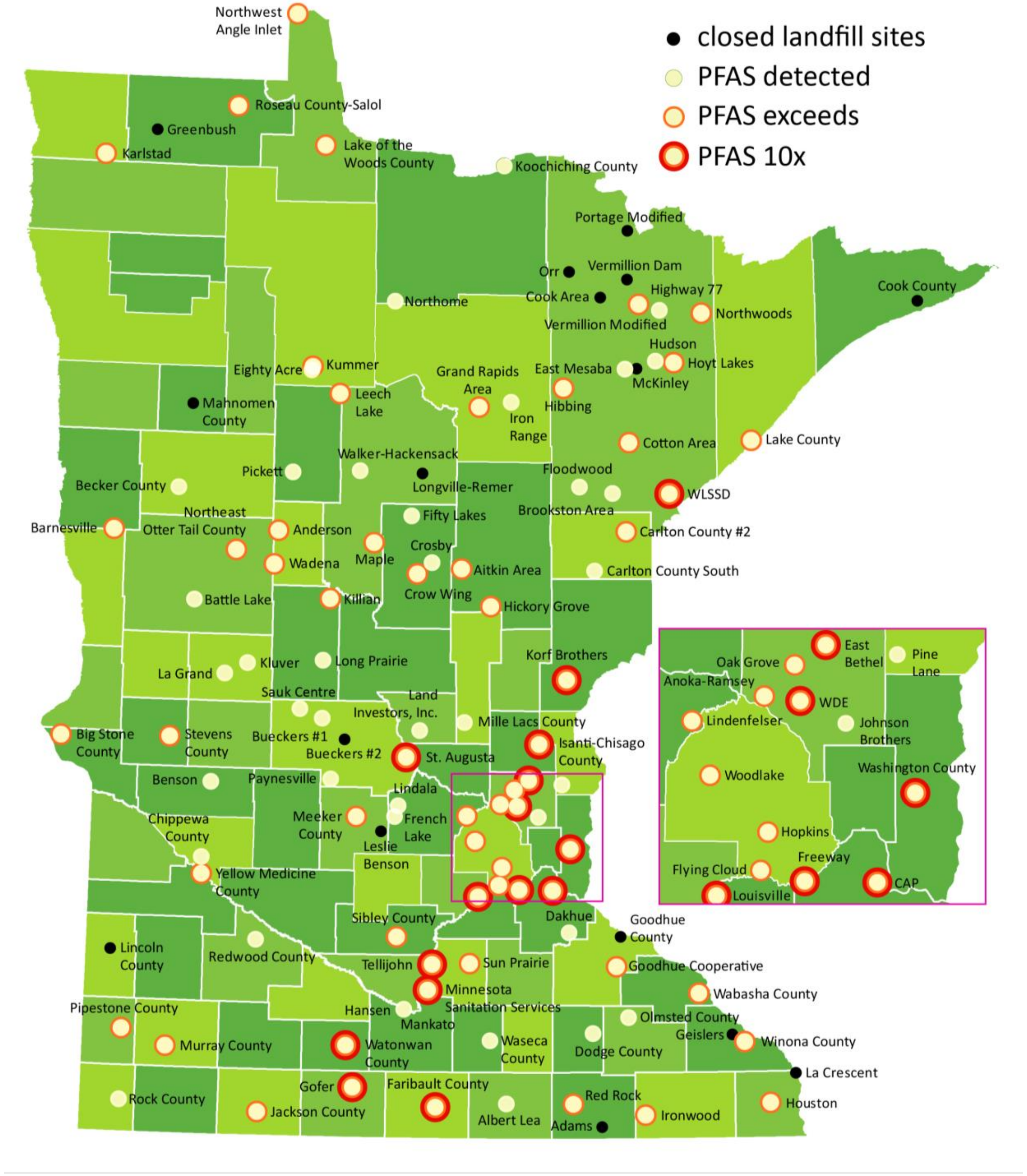
Managing PFAS in Minnesota Closed Landfills

MINNESOTA

Closed Landfill Program - CLP

- 1994 Landfill Cleanup Act
- Created CLP – manage mixed municipal waste LFs
- Landfill responsibility transferred to state
- 110 landfills throughout Minnesota
- Funding sources: tax dollars, CLIF
- Total program cost: ~ $480 million through FY20
    - Estimated need: $309 million over next 30 years
- Link to CLP website



97% of assessed closed landfills have PFAS contamination

- 60 landfills exceed state guidelines, with 80% located outside the metro area
- 15 sites with PFAS found at 10x the health-based guidance values
- Highest level of PFAS in groundwater is at Gofer Landfill in SW Minnesota

Minnesota PFAS Water Guidance

MDH health-based guidance values evolve over time as additional research becomes available

- Surrogate values used when widespread detection of chemical in drinking water, but insufficient toxicological data to set an HBV
- Dec 2021 – HBV for PFHxA
  - 0.2 ug/L

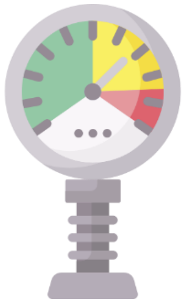
Values noted in parts per billion (ppb)

	PFOA	PFOS	PFBA	PFBS	PFHxS
2002	7	1			
2006	1	0.6	1		
2007	0.5	0.3	7		
2009	0.3	0.3	7	7	
2013	0.3	0.3	7	7	0.3
2016	0.07	0.07	7	7	0.07
2017	0.035	0.027	7	3 or 2	0.027
2020	0.035	0.015	7	3 or 2	0.047

Blue = HRL; Red = HBV; Green = Surrogate

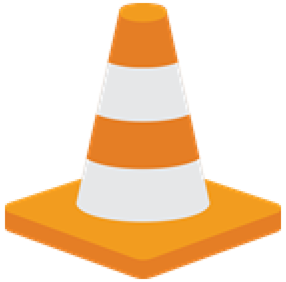
Priorities for managing PFAS at landfills

Drinking water wells



Determine extent of contamination

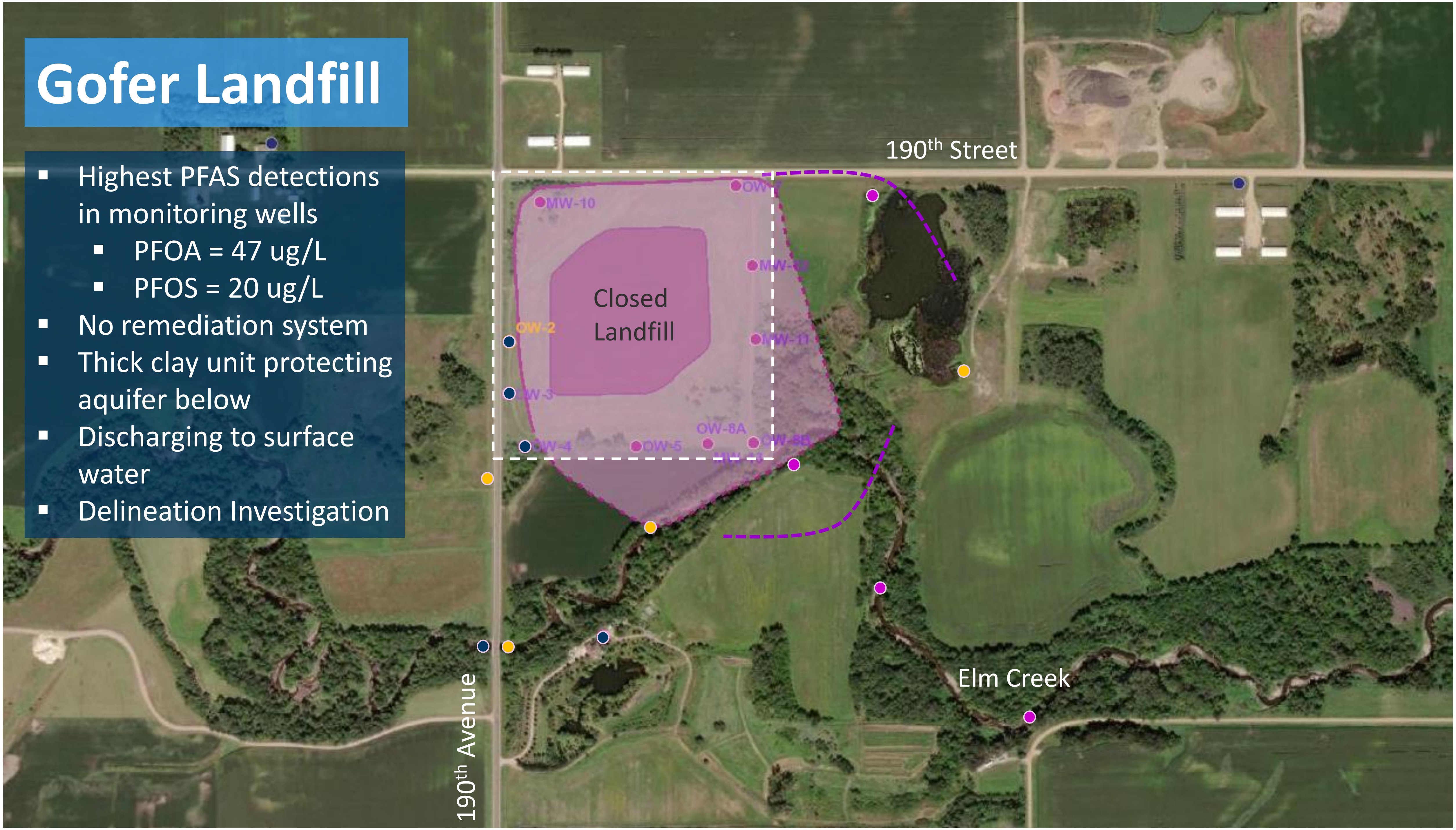
Leachate and groundwater treatment



Fund rapid emergency response

Gofer Landfill

- Highest PFAS detections in monitoring wells
  - PFOA = 47 ug/L
  - PFOS = 20 ug/L
- No remediation system
- Thick clay unit protecting aquifer below
- Discharging to surface water
- Delineation Investigation



Washington County Landfill

Large PFAS plume mixed with other disposal site plumes = over 150 sq. mi.
Affected:

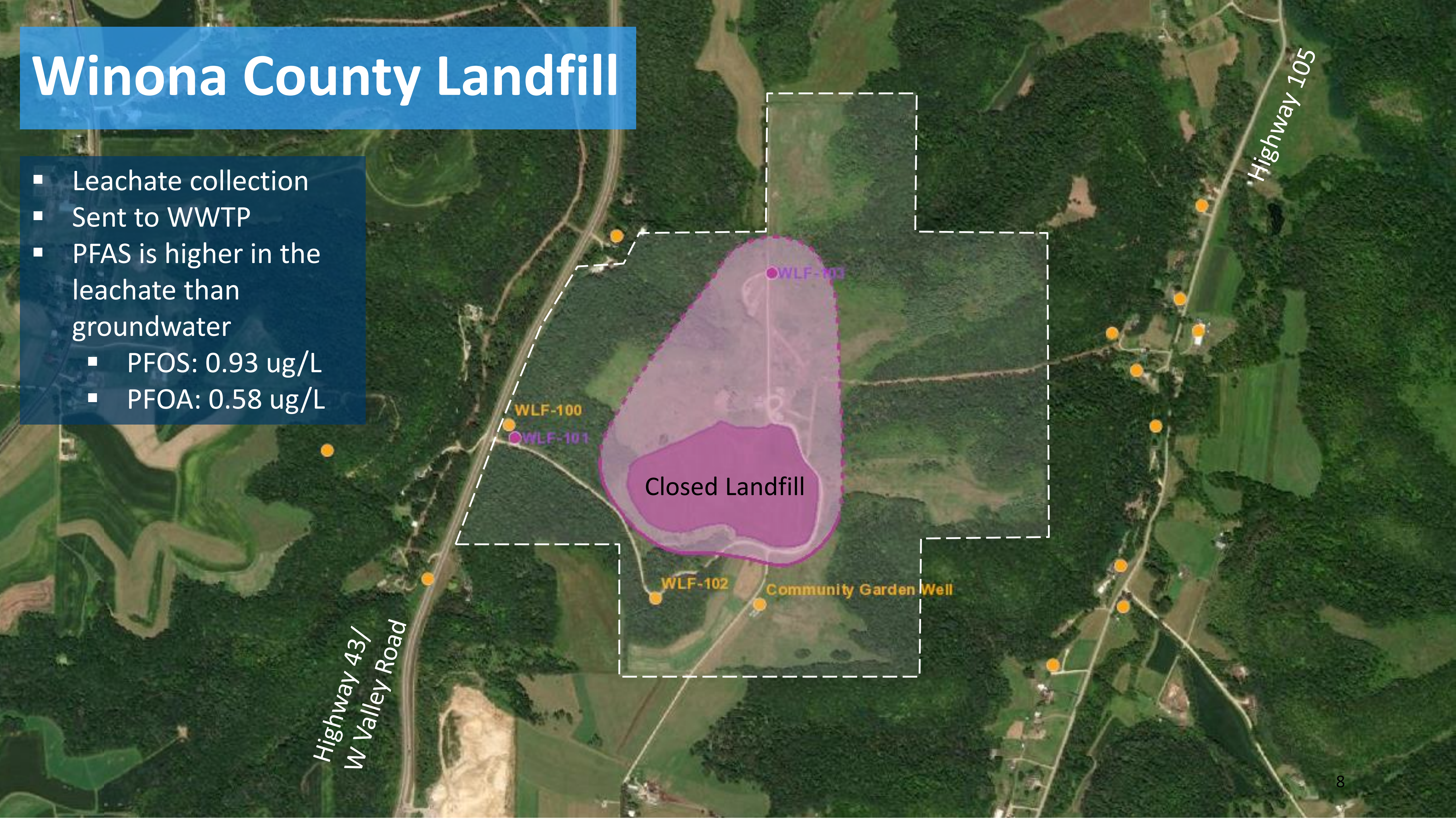
- 4 major aquifers
- 14 East Metro communities
- 1000s of private wells

Source - 3M Waste
2009 – 2M yd^3 waste excavated, placed in containment cells
2018 - $850M settlement with 3M
Still finding contamination in monitoring wells
- continue to monitor

https://www.pca.state.mn.us/waste/pfas-waste-sites

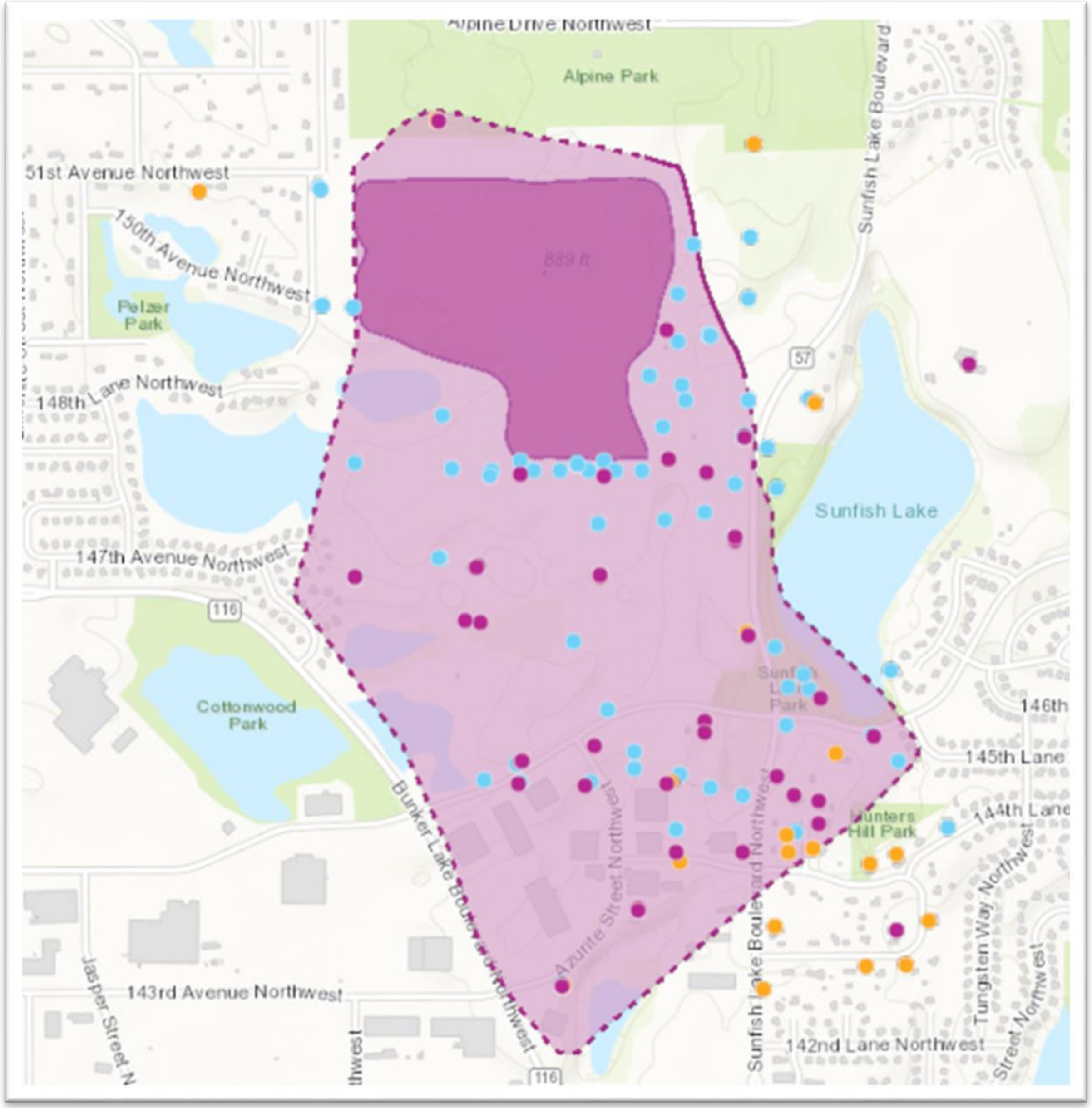
Winona County Landfill

- Leachate collection
- Sent to WWTP
- PFAS is higher in the leachate than groundwater
    - PFOS: 0.93 ug/L
    - PFOA: 0.58 ug/L



Communication tools

- [Groundwater Contamination Atlas]
- PFAS media event in March 2021
- Sign up for Gov Delivery emails
- Public meetings (virtual & in person)



Minnesota's PFAS Blueprint

- Released in February 2021
- Provides information about PFAS toxicity and their occurrence in Minnesota
- Identifies the state's approach to managing and addressing PFAS in our environment
- Proposes strategic path forward
- Full Blueprint
- Blueprint Summary

Monitoring Plan

- Planned release in 2022
- Lays out a path forward for PFAS monitoring at sites
- Systematic approach to monitoring

Closed Landfill Program
Next Steps

- Receptor monitoring
- Drinking water treatment
- Delineation investigations
- Leachate feasibility study

DNR Updates, Conclusions & Next Steps