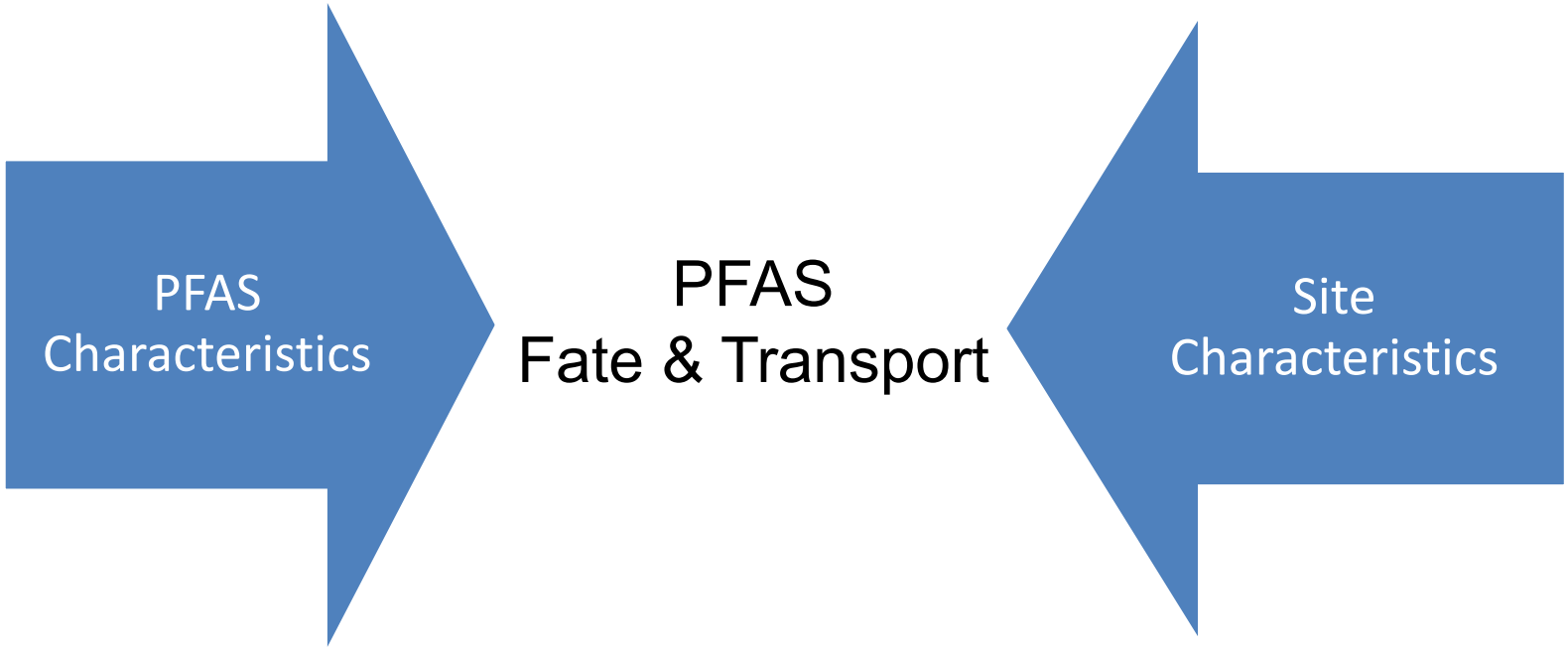
Fate –Biotransformation

Jennifer Field, PhD
Oregon State University

What is Fate and Transport?

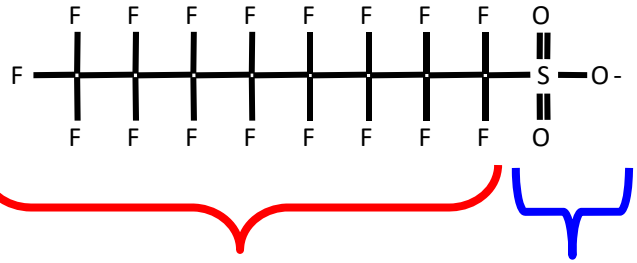
- Fate and Transport describes the behavior of PFAS following their release to the environment and encompasses ***physical, chemical, and biological processes*** that influence distribution, chemical transformation, and migration

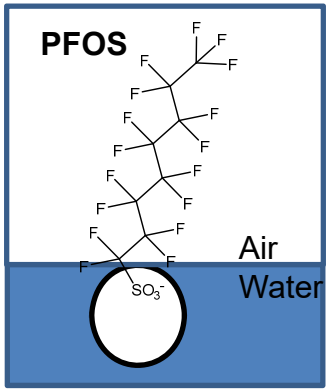

PFAS
Characteristics
PFAS
Fate & Transport
Site
Characteristics

The Heads and Tails of PFAS

Perfluorooctane sulfonate (PFOS)
$C_8F_{17}SO_3^-$

Lipo- & hydrophobic tail





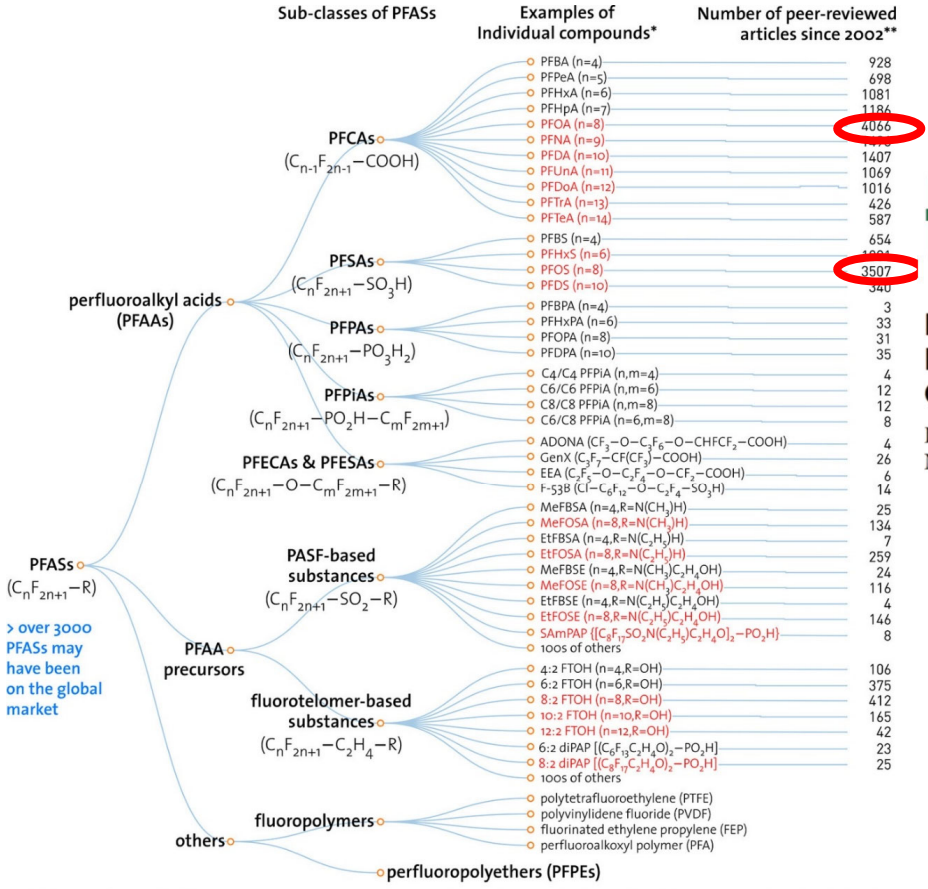
Good news: C-F bond is one of the strongest chemical bonds known

Bad news: C-F bond is one of the strongest chemical bonds known

PFAAs are extremely persistent in the environment

Images used with permission from Jennifer Field, Oregon State University

PFAS Family Tree: It's not just PFOS and PFOA



* PFASs in **RED** are those that have been restricted under national/regional/global regulatory or voluntary frameworks, with or without specific exemptions (for details, see OECD (2015), Risk reduction approaches for PFASs. http://oe.cd/1AN).
** The numbers of articles (related to all aspects of research) were retrieved from SciFinder® on Nov. 1, 2016.

Environmental Science & Technology
Article
pubs.acs.org/est

Discovery of 40 Classes of Per- and Polyfluoroalkyl Substances in Historical Aqueous Film-Forming Foams (AFFFs) and AFFF-Impacted Groundwater

Krista A. Barzen-Hanson,[†] Simon C. Roberts,[∇,‡] Sarah Choyke,[§] Karl Oetjen,[‡] Alan McAlees,[∥] Nicole Riddell,[∥] Robert McCrindle,[⊥] P. Lee Ferguson,[§] Christopher P. Higgins,[*,‡] and Jennifer A. Field[*,#]

Total PFAS high resolution mass spectrometry (HRMS) suspect list now ~1500 compounds

- HRMS library now includes ~325 PFAS
- ~120 homologous series: - $(CF_2)_n$ - where n = 1 to 18
  - 14 classes are *truly* perfluorinated (all C-H are C-F)
  - ~50 classes are ECF-derived, while ~70 are FT-derived
- To date, most sites have ~10 to 100 different PFAS

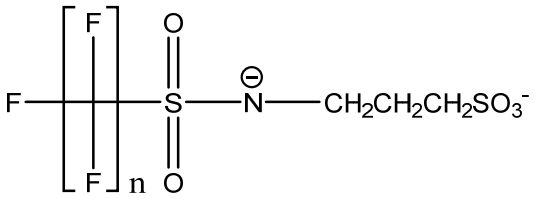
Wang *et al.* 2017, *ES&T*.

Barzen-Hanson *et al.*, 2017, *ES&T*.

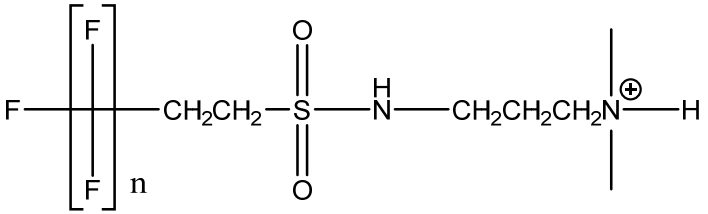
Reprinted with permission from Wang et al. 2017. A never-ending story of per- and poly-fluoroalkyl substances (PFASs)? Env. Sci. & Tech., 51:2508-2518. Copyright 2017 American Chemical Society.

Structural Implications

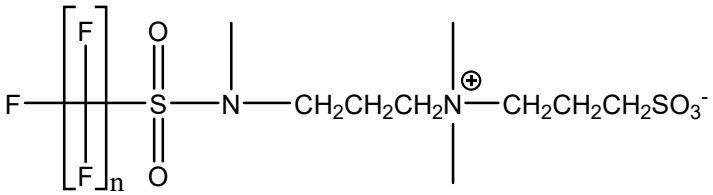
- Diversity of PFAS structures has important implications for fate and transport processes



*Poly*fluorinated anion



*Poly*fluorinated cation



*Poly*fluorinated zwitterion

Images used with permission from Jennifer Field, Oregon State University

Transformation of PFAA Precursors

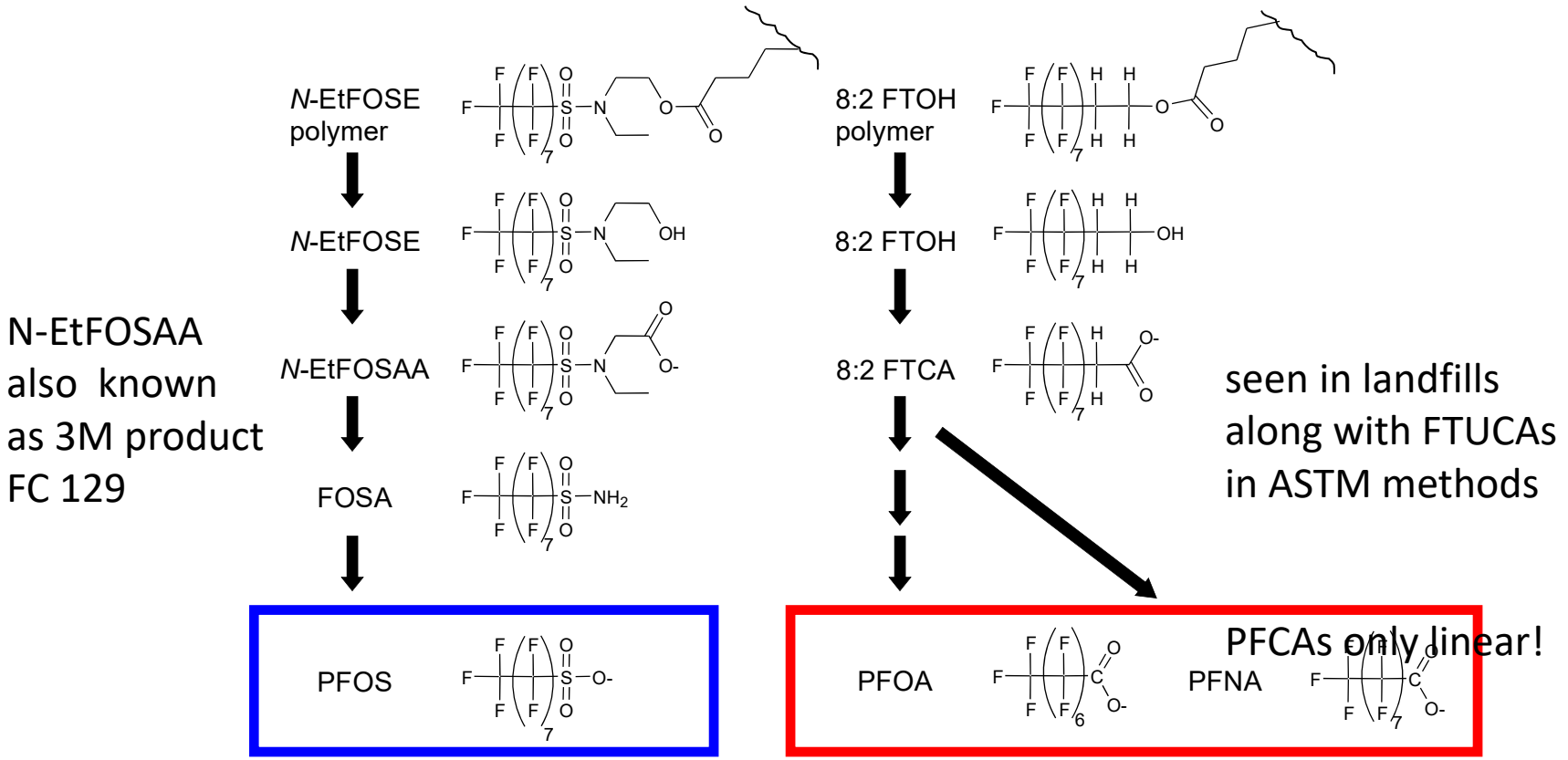
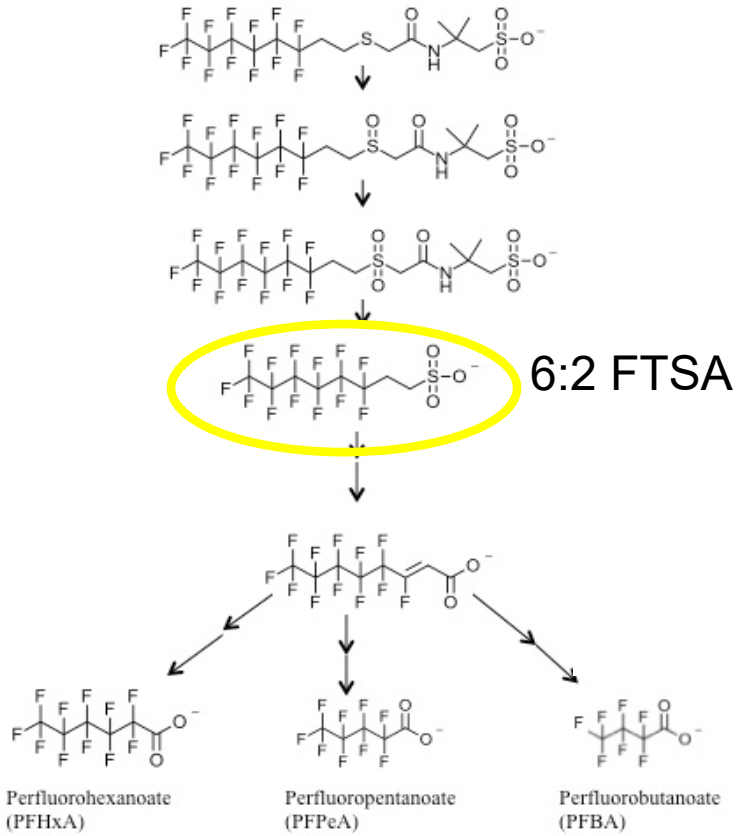


Figure courtesy of C. Higgins

Biotransformation of PFAS[1,2]

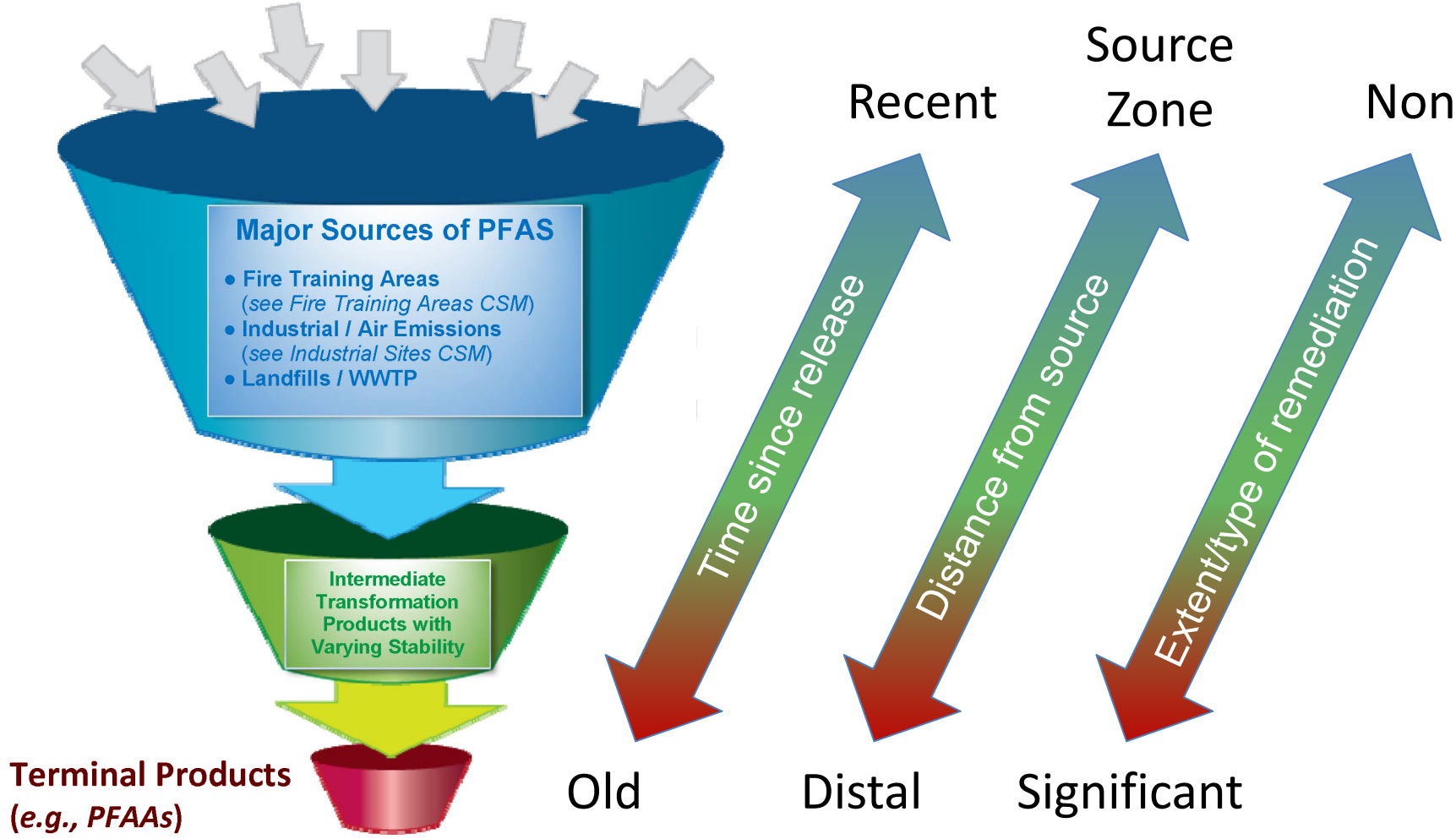
- Ansul transformation to FTSA (aerobic) explains high FTSA levels[3]
- Polyfluorinated ECF consumer product (primarily) PFAS biotransform to PFOS and other PFAS[4]
  - No published studies on polyfluorinated ECF AFFF-derived PFAS
- PFAAs not expected to degrade
  - Enzyme-based humification lab study[5] suggests potential PFCA transformation



[1]Weiner et al., 2013. Environ Chem; [2]Harding-Marjanovic et al., 2015 *ES&T*; [3]Backe et al., 2012. *ES&T* ; [4]Rhoads et al., 2008. *ES&T* ; [5]Luo et al., 2015. *ES&T* Letters

Reprinted with permission from Harding-Marjanovic, et al. 2015. Aerobic biotransformation of fluorotelomer thioether amido sulfonate (lodyne) in AFFF-amended microcosms. Env. Sci. & Tech., 49(13):7666-7674. Copyright 2015 American Chemical Society

Complexity Varies with Time, Space, and History



Source: Adapted from figure by L. Trozzolo, TRC, used with permission

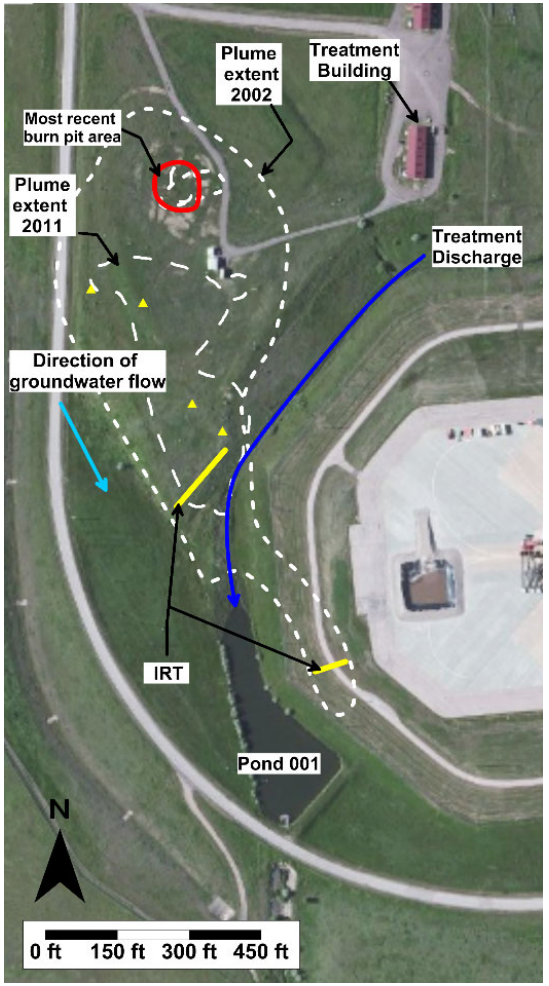
Case Study: The Mystery at Ellsworth

Investigated former firefighter training area (OU-1)

- "Bermed pit" in use from 1942-1990
- VOCs, SVOCs, pesticides, and chlorinated solvents in groundwater
- Typical depth to groundwater ~ 5 m

Remediation (1996-2011)

- Soil Vapor Extraction
- Groundwater Pump and Treat (extensive)
- Oxygen Infusion Wells



McGuire *et al.*, 2014 *ES&T.*

Reprinted with permission from McGuire et al., 2014. Evidence of remediation-induced alteration of subsurface poly- and perfluoroalkyl substance distribution at a former firefighter training area. *Env. Sci. & Tech.,* 48(12):6644–6652. Copyright 2014 American Chemical Society

Field Sampling and Analysis

- Samples collected Oct 2011 and Aug 2012:
  - 2011: 17 temporary wells drilled (soil, aquifer solids, groundwater)
  - 2012: 22 additional groundwater samples and 34 additional soils
- Analyzed for PFAAs and known AFFF components or suspected transformation products
- All groundwater samples also subjected to TOP assay

Photo courtesy C. Higgins

Surface Soil Contamination

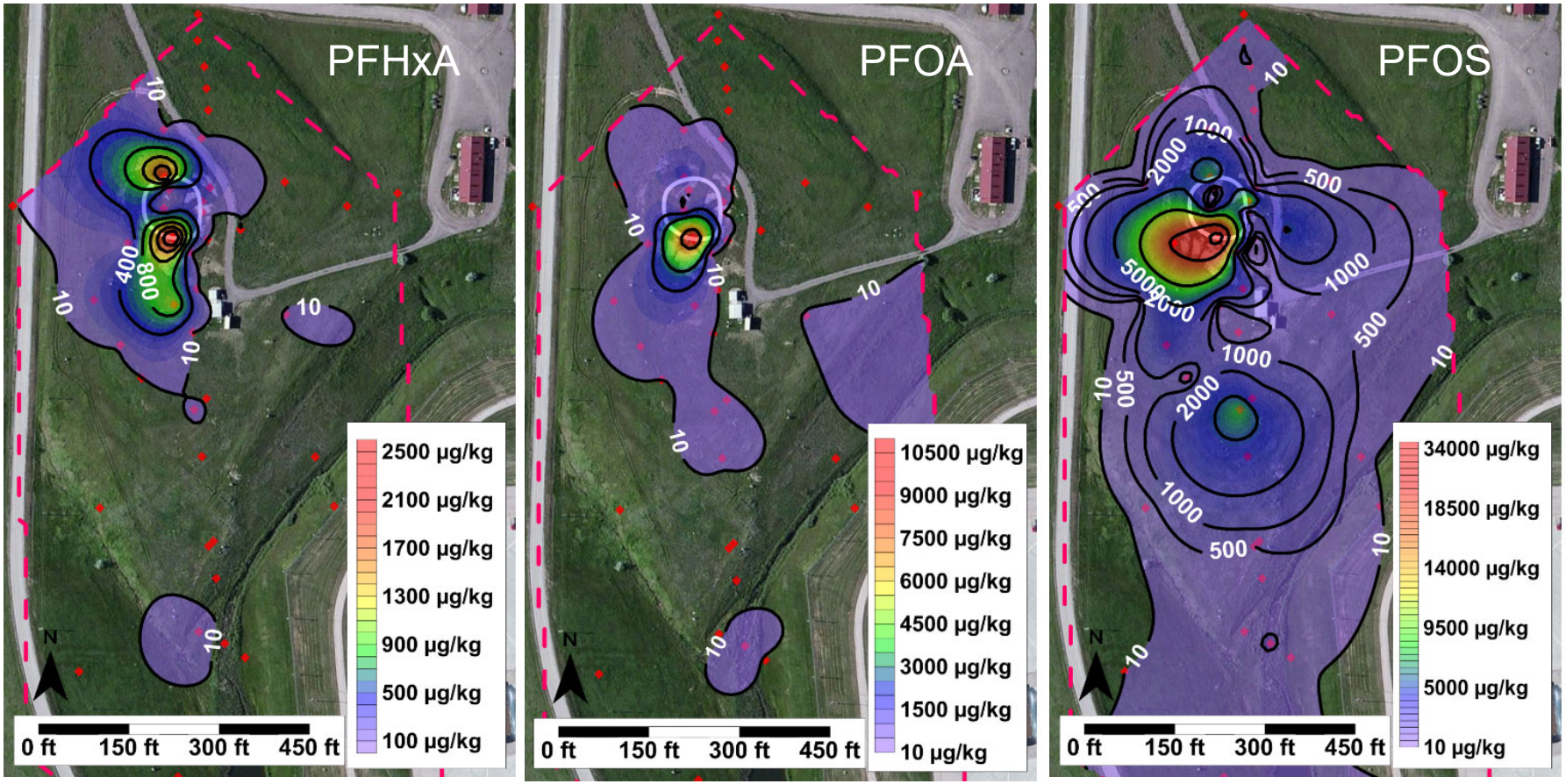


Figure 2 from McGuire et al 2014

Reprinted with permission from McGuire et al., 2014. Evidence of remediation-induced alteration of subsurface poly- and perfluoroalkyl substance distribution at a former firefighter training area. *Env. Sci. & Tech.,* 48(12):6644–6652. Copyright 2014 American Chemical Society

Groundwater Contamination

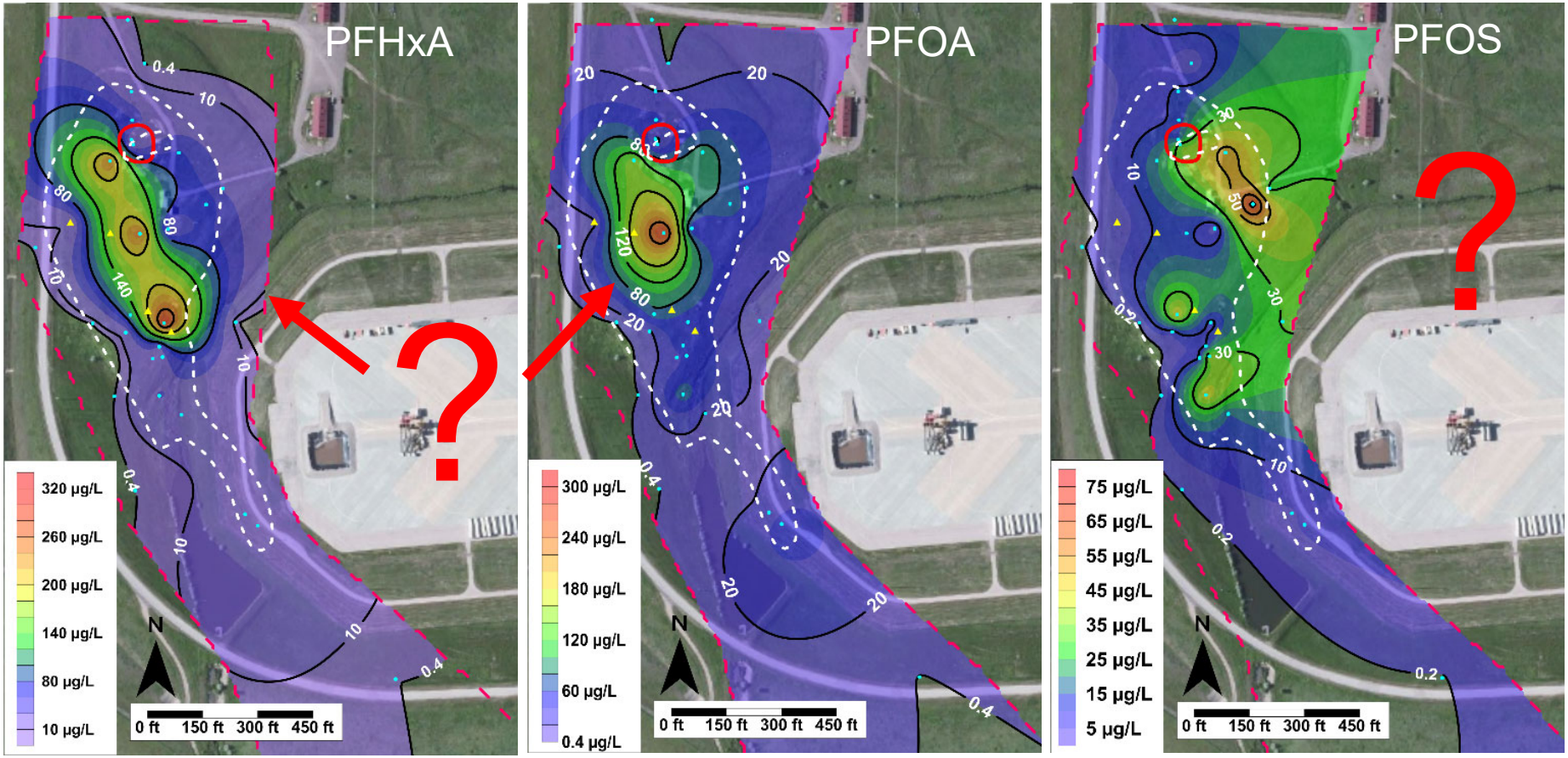
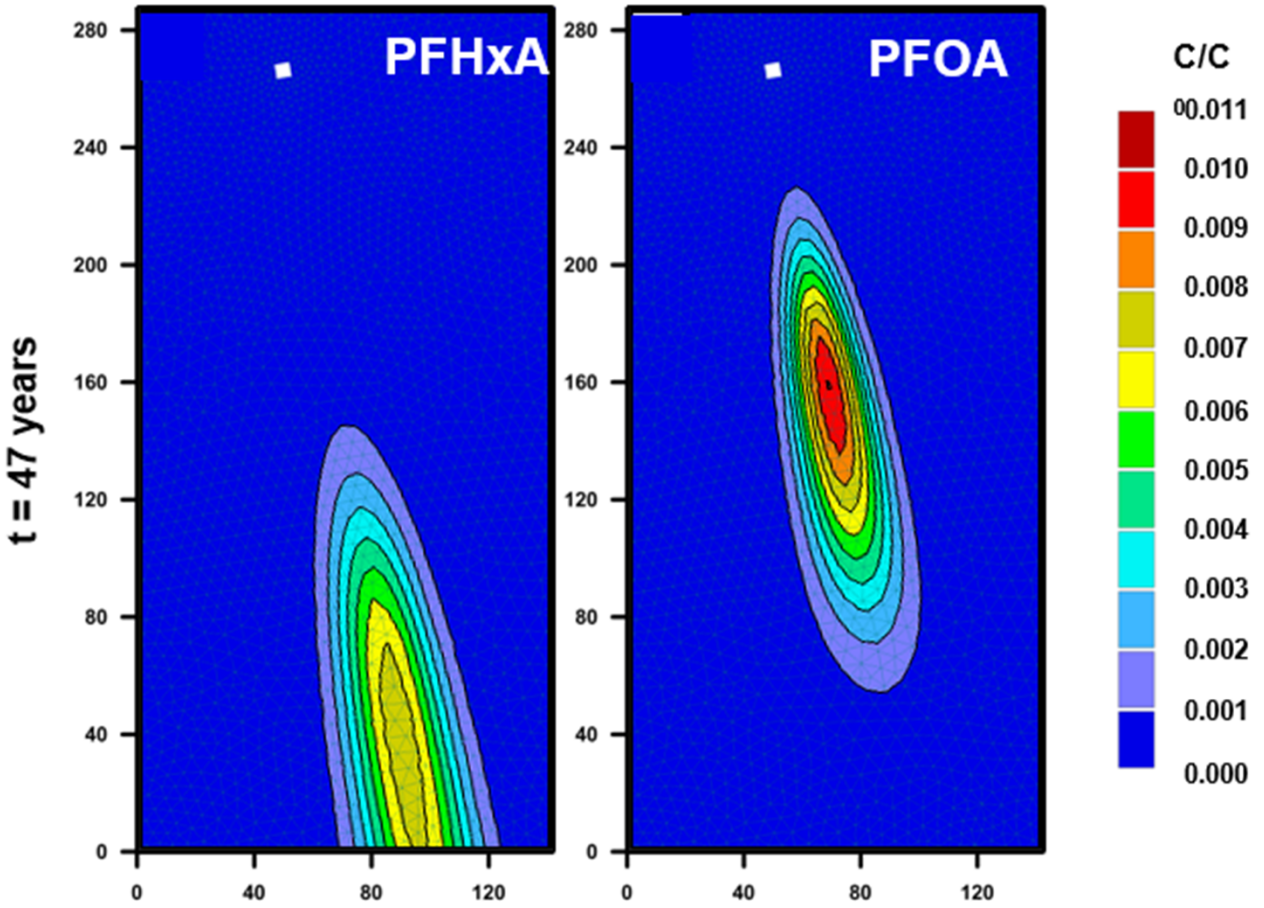


Figure 3 from McGuire et al 2014

Reprinted with permission from McGuire et al., 2014. Evidence of remediation-induced alteration of subsurface poly- and perfluoroalkyl substance distribution at a former firefighter training area. *Env. Sci. & Tech.,* 48(12):6644–6652. Copyright 2014 American Chemical Society

2-D Modeling



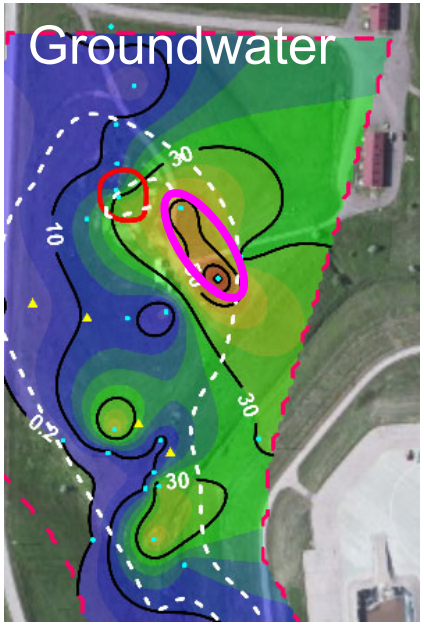
Much greater differential transport would be expected

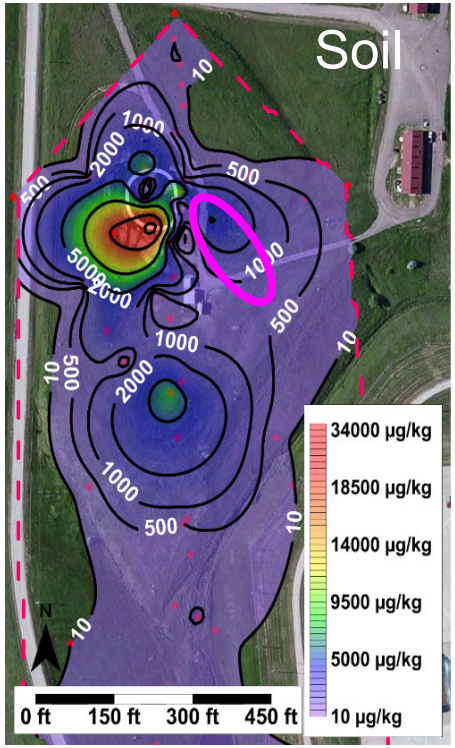
- Release ongoing?

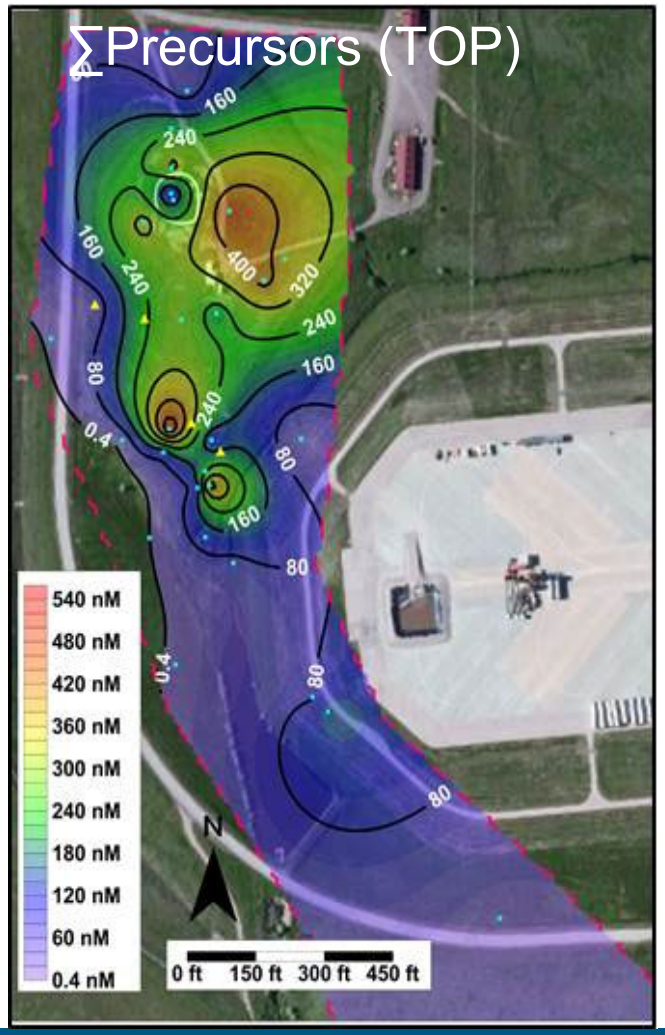
Figure S8 from McGuire et al 2014

Reprinted with permission from McGuire et al., 2014. Evidence of remediation-induced alteration of subsurface poly- and perfluoroalkyl substance distribution at a former firefighter training area. *Env. Sci. & Tech.*, 48(12):6644–6652. Copyright 2014 American Chemical Society

What's up with PFOS?







Additional surface source?

Groundwater pumping?

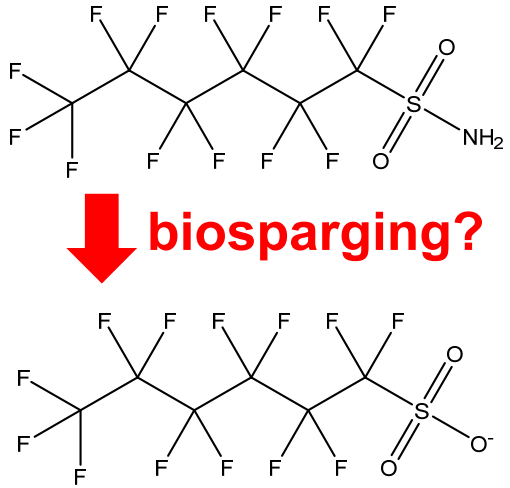
…but why are PFCAs still present in "historical" plume?

Figures 2C, 3C, and 4A from McGuire et al 2014

Reprinted with permission from McGuire et al., 2014. Evidence of remediation-induced alteration of subsurface poly- and perfluoroalkyl substance distribution at a former firefighter training area. *Env. Sci. & Tech.,* 48(12):6644–6652. Copyright 2014 American Chemical Society

Effect of biosparging?

- PFHxS: PFOS ratio ~ 0.1 in AFFF
- If co-released, would expect ratio to ↑ (continually) downgradient
- PFHxS produced in situ?
  - Highest ratios (~ 50) near biosparging wells



Houtz et al. 2013 *ES&T.*

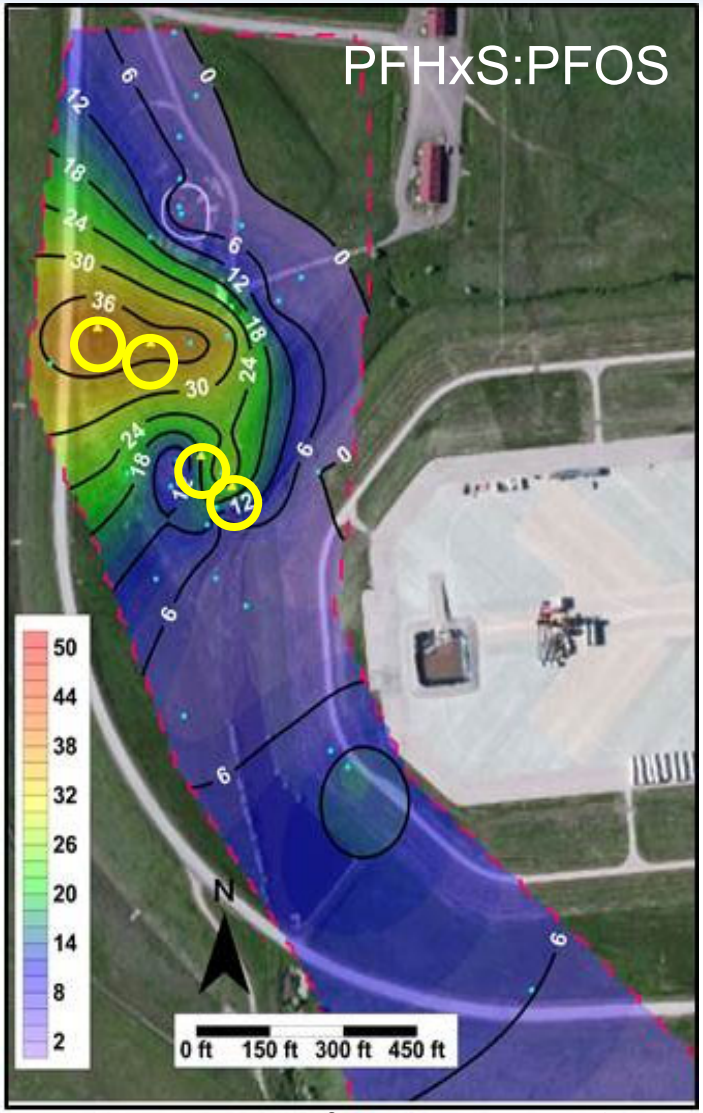


Figure 4C from McGuire et al 2014

Reprinted with permission from McGuire et al., 2014. Evidence of remediation-induced alteration of subsurface poly- and perfluoroalkyl substance distribution at a former firefighter training area. *Env. Sci. & Tech.,* 48(12):6644–6652. Copyright 2014 American Chemical Society


Questions?