SUBSURFACE FATE AND TRANSPORT OF POLY- AND PERFLUOROALKYL SUBSTANCES (PFAS)

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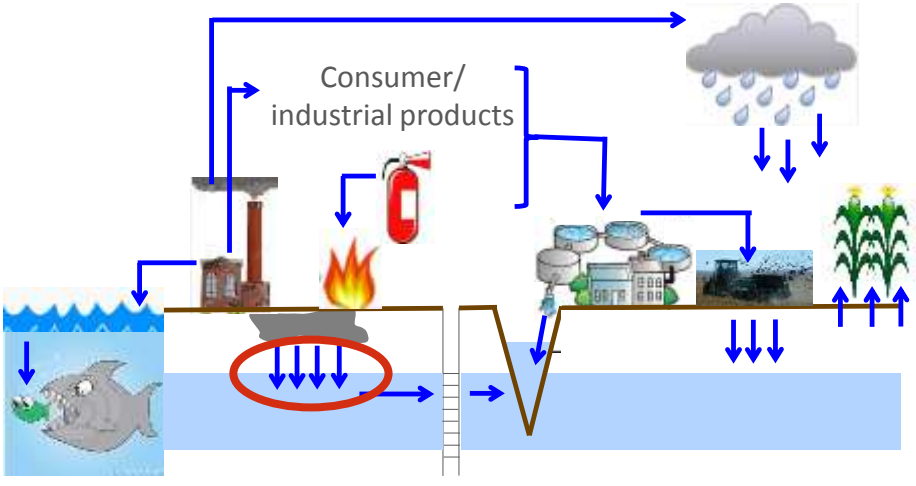
INTRODUCTION: ENVIRONMENTAL DISTRIBUTION



OVERVIEW

- Key sources and pathways
- Ideal subsurface transport
- Factors impacting ideal transport
- Conceptual model considerations

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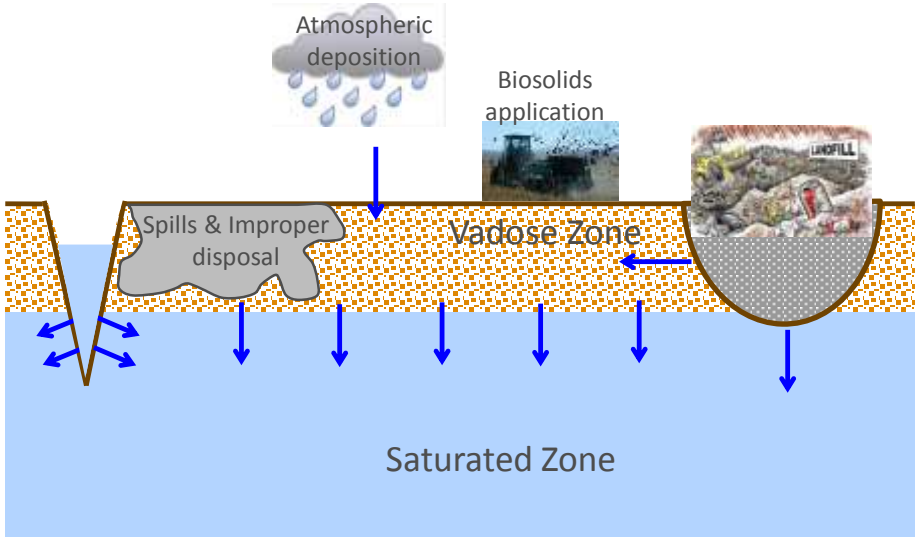
PFAS GROUNDWATER SOURCE/PATHWAY OVERVIEW



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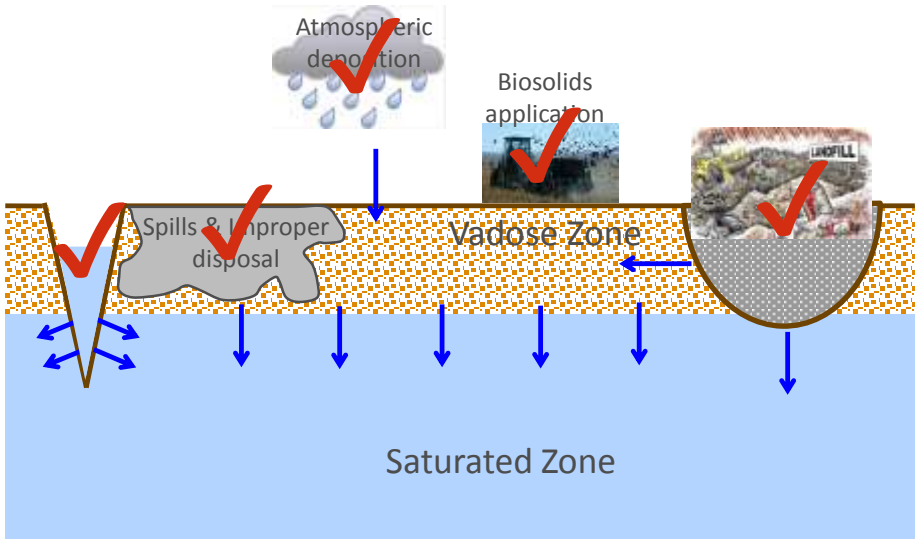

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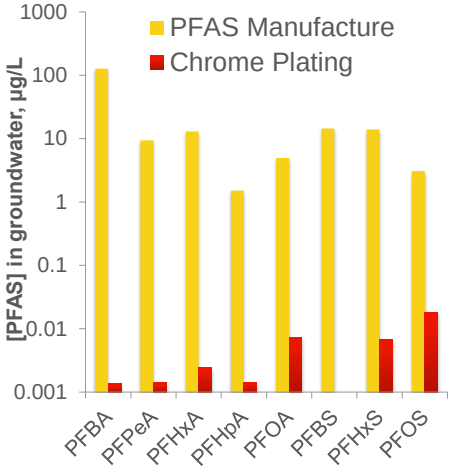
SOURCE/PATHWAY: SPILLS, 'IMPROPER' DISPOSAL[2,3]



- [PFAS] in groundwater 0.0013-126 µg/L
- Manufacturing max = 126 µg/L PFBA
- Plating max = 0.018 µg/L PFOS
- Data from other secondary industrial (e.g. textiles, paper)?

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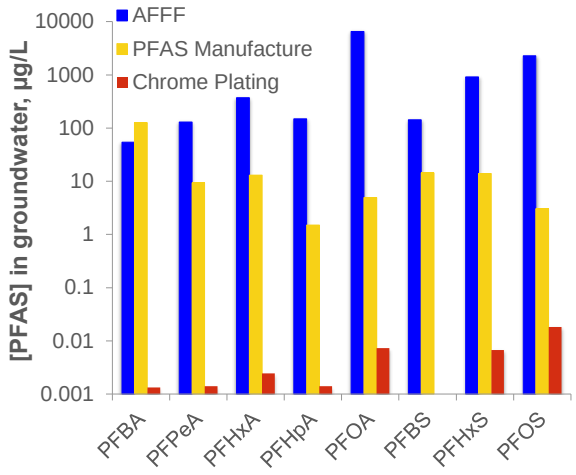
SOURCE/PATHWAY: SPILLS, 'IMPROPER' DISPOSAL[4-7]

A closer look at AFFF groundwater impacts



- Most groundwater [PFAS] greater in AFFF vs. manufacture, plating

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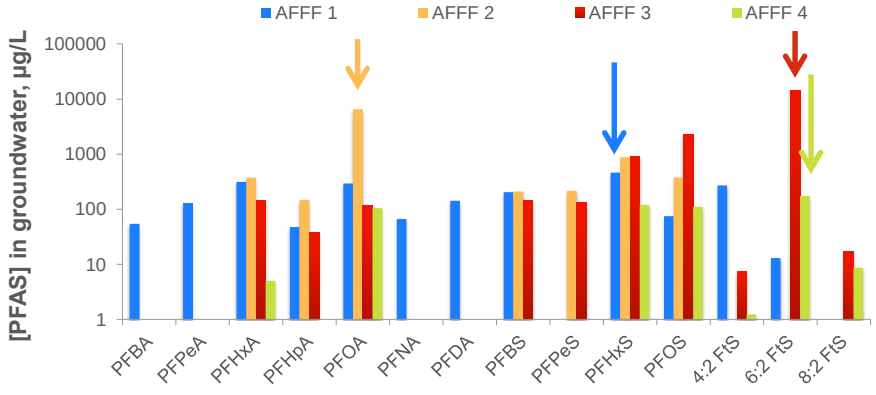
SOURCE/PATHWAY: SPILLS, 'IMPROPER' DISPOSAL[4-7]

A special look at AFFF groundwater impacts



- Max AFFF 1 = PFHxS, 462 µg/L
- Max AFFF 2 = PFOA, 6570 µg/L
- Max AFFF 3= 6:2 FtS, 14600 µg/L
- Max AFFF 4 = 6:2 FtS, 173 µg/L

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SOURCE/PATHWAY: SPILLS, 'IMPROPER' DISPOSAL[4-7]

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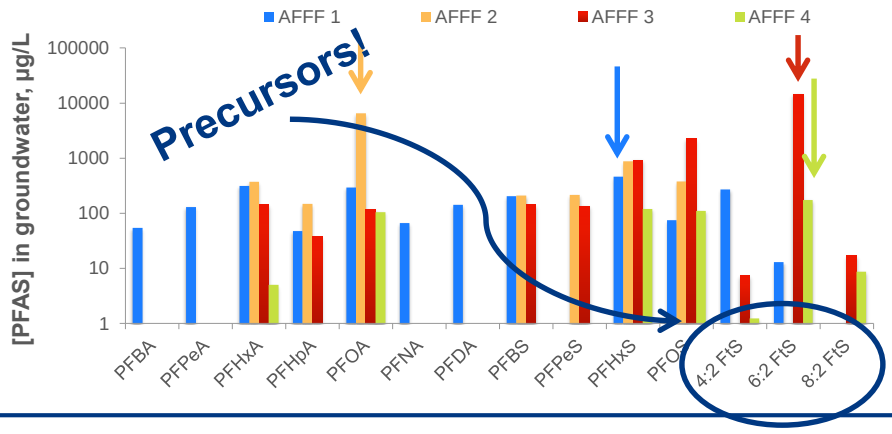

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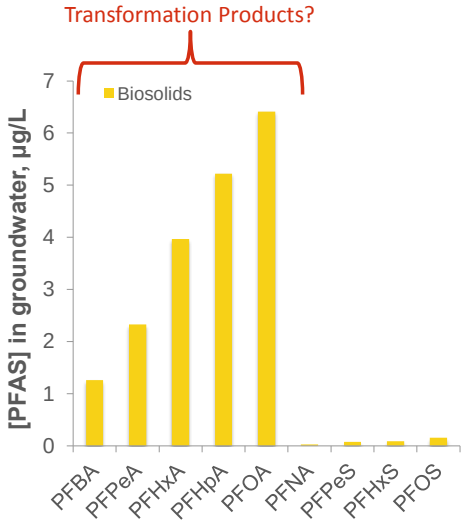
SOURCE/PATHWAY: BIOSOLIDS APPLICATION[8,9]



- WWTP received industrial effluent incl. ECF, telomer
- Present in municipal biosolids, potential to leach but…
- No documented impact to GW

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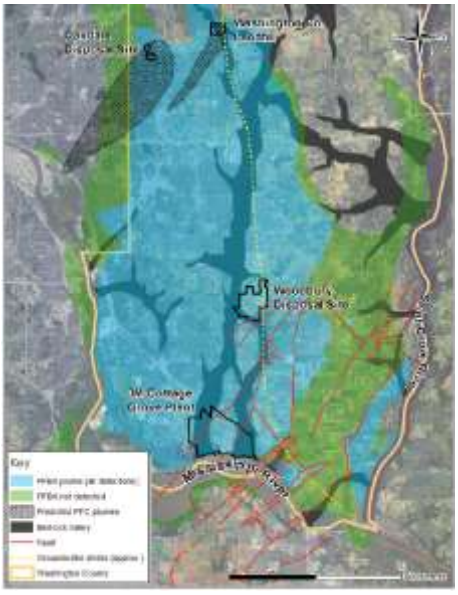
SOURCE/PATHWAY: SURFACE WATER – GROUNDWATER[10]



- GW-SW interactions in MN aid in spread of PFBA plume
- ~100 square miles
- [PFAS] near GW-SW exchange:
  - PFBA: 0.29-3.4 µg/L
  - PFOA: 0.067-3 µg/L
  - PFOS: 0.058-3.3 µg/L

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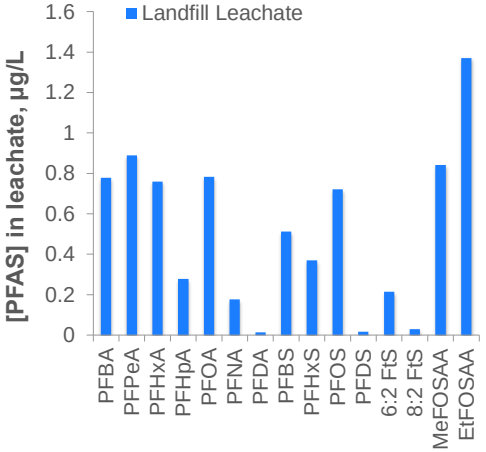
SOURCE/PATHWAY: LANDFILLS[11-14]

PFAS in municipal landfill **leachate**



Additional landfill data:

- Near 3M in MN, **GW [PFAS]** near landfill:
  - PFOA = 65 µg/L
  - PFOS = 30 µg/L
- Near 3M in MN, landfill **leachate PFAS**:
  - PFHxA = 29 µg/L
  - PFOA = 82 µg/L
  - PFOS = 31 µg/L

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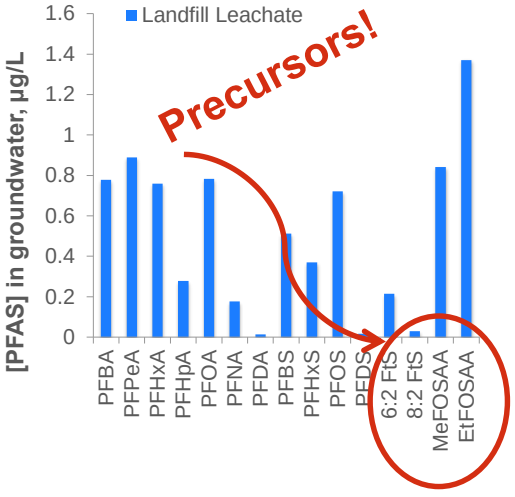
SOURCE/PATHWAY: LANDFILLS[11-14]

PFAS in municipal landfill **leachate**



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SOURCE/PATHWAY: ATMOSPHERIC DEPOSITION[15-19]

Media	Value	Units	Constituent	Reference
Rural air	0.000125	µg/m³	6:2 FTOH	Jahnke et al., 2007
Urban air	0.000275	µg/m³	8:2 FTOH	Jahnke et al., 2007
Manufacturing air	0.9	µg/m³	PFOA (only)	Davis et al., 2007
WWTP Air	12.29	µg/m³	6:2 FTOH	Ahrens et al., 2011
Landfill Air	17.38	µg/m³	8:2 FTOH	Ahrens et al., 2011
Urban Rain	0.042	µg/L	PFOA	Eschauzier et al., 2010
Urban Snow	0.0196	µg/L	PFOA	Kim and Kannan, 2007
GW from atm. dep.	78	µg/L	PFOA (only)	Davis et al., 2007

Considerations:

- Proximity to sources: manufacturing, WWTP, landfill
- How to separate atmospheric vs. other impacts at these sites?
- May contribute to background in soils, surface water

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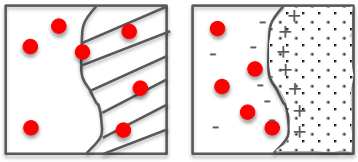
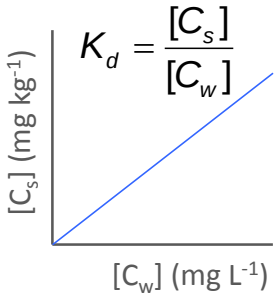
TRANSPORT: IDEAL

Sorption: accumulation of a chemical from a fluid phase into and/or onto a non-fluid phase





- Measured in laboratory (equilibrium) scenarios
- Isotherms not always linear, PFAS slightly nonlinear
- Primary process impacting perfluoroalkyl acids, once released

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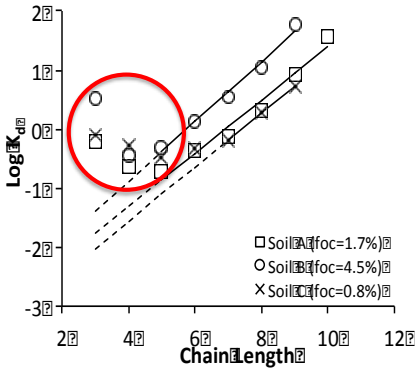
TRANSPORT: IDEAL[20-21]



Analyte Name	Tail Length[a]	Average Log K_{oc}	±	n[b]
PFBA	3	1.88	0.11	3
PFPeA	4	1.37	0.46	3
PFHxA	5	1.31	0.29	3
PFHpA	6	1.63	0.15	3
PFOA	7	1.89	0.02	3
PFNA	8	2.36	0.04	3
PFDA	9	2.96	0.15	3
PFUnA	10	3.56		1
PFBS	4	1.79	0.10	3
PFHxS	6	2.05	0.08	3
PFOS	8	2.80	0.08	3

- Primary impacts on sorption: f_{oc}, chain length (some exceptions)
- Other factors: functional group, pH, Ca^{2+}

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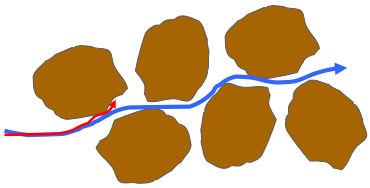
TRANSPORT: IDEAL



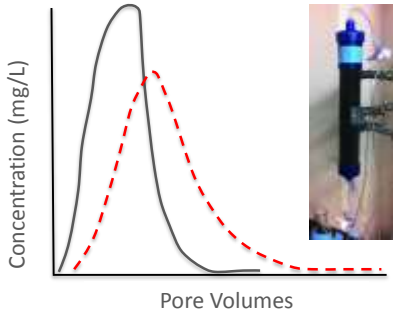
$$R\frac{\partial C}{\partial t} = D_L\frac{\partial^2 D}{\partial x^2} - v_x\frac{\partial C}{\partial x}$$

sorption dispersion advection

Sorption and Retardation

- The velocity of water relative to velocity of contaminant
- Retardation factor (R):

$$R = 1 + \frac{\rho_b}{\phi}K_f n C_w^{n-1}$$



- ↑ R leads to ↓ transport

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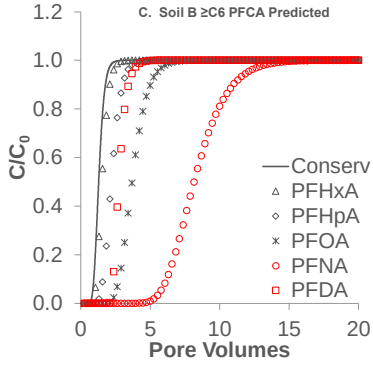
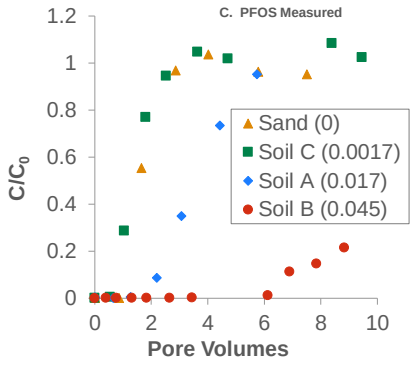
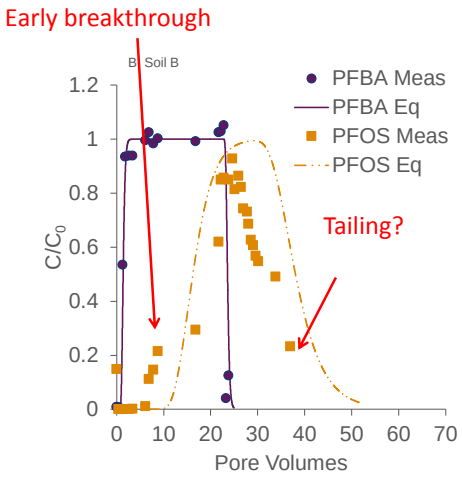
TRANSPORT: IDEAL[In Prep]





- Chain length dependent breakthrough
- Increased f_{oc} = slower transport

TRANSPORT: NON-IDEAL[In Prep]



- Short chain: equilibrium
- Long chain: Early breakthrough, tailing = rate-limited (kinetic) effects
- Most relevant for longer chains, higher f_{oc}
- Particularly pumping scenarios

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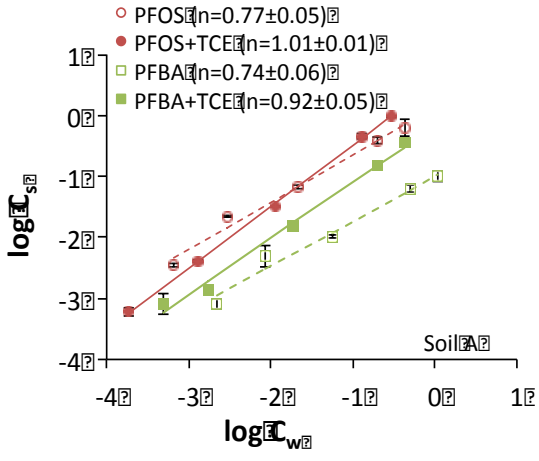
PATHWAY: NON-IDEAL TRANSPORT[21]



Co-Contaminant effects:

- Multiple PFAS – competitive sorption?
- AFFF sites
  - Other AFFF components
  - Hydrocarbon constituents
  - Chlorinated solvents
  - NAPL
- Other types of sites?

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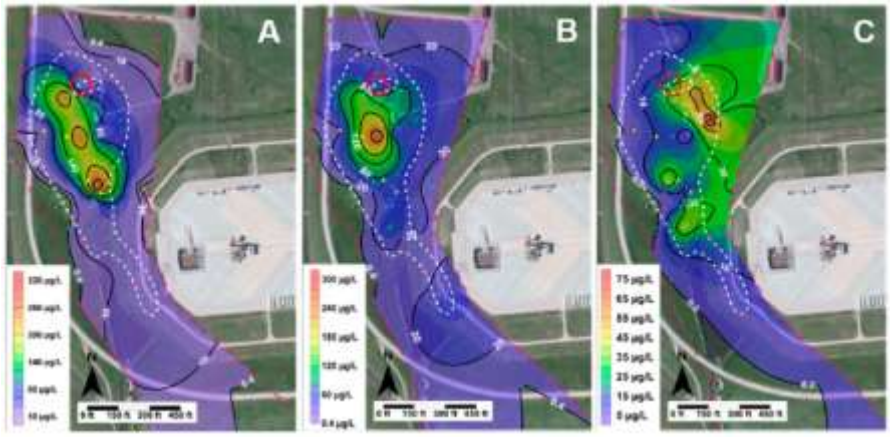
PATHWAY: NON-IDEAL TRANSPORT[4]

PFHxA PFOA PFOS



No evidence of differential transport.

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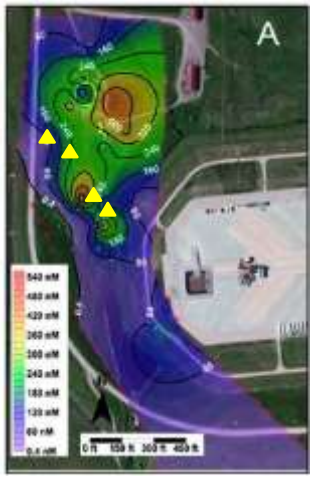
TRANSPORT: NON-IDEAL[4]

Total Precursors in groundwater:



- Oxygen infusion wells
- [Precursor] elevated *outside* of oxygen infusion areas
- Elevated precursors = areas for potential [PFAA] ↑

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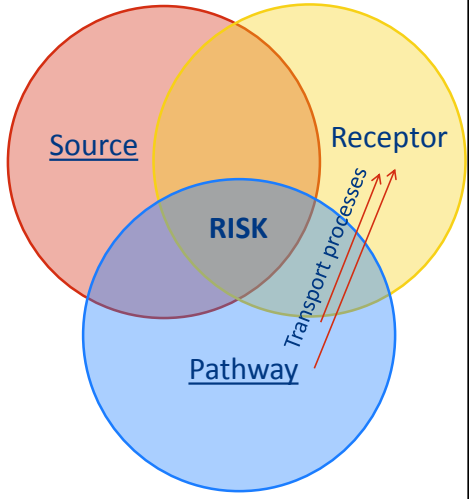
CONCEPTUAL MODEL CONSIDERATIONS

Source/Pathway:

- Max [PFAS] of mg/L (AFFF) to low µg/L (bisolids, GW-SW)
- Target PFAS vary by source
- PFOA/PFOS not always max
- Precursors indirect source of PFCAs/PFSAs

Transport:

- Non-ideal transport likely: kinetics, co-contaminants, transformation
- Plume lengths of miles possible



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