Dr Damien Moodie

Overview of the advances in Geocomposites for the containment of PFAS impacted materials.

GEOANZ #1 ADVANCES IN GEOSYNTHETICS
7–9 JUNE 2022 | BRISBANE CONVENTION & EXHIBITION CENTRE

ADE PFAS Team

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Business Unit Manager
(ECTRR)

- Partaken in various State significant and Commonwealth PFAS contaminated land projects
- Key expertise in practical PFAS solutions (development)

ANDREW MITCHELL

Business Unit Manager/PFAS Specialist
NSW Environmental Services

- Defence PFAS Investigation & Management Program
- NSW EPA PFAS Strategy
- Value-add approach to contamination problems

DR. TIMOTHY COGGAN

PFAS Specialist (Water and Wastewater)
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- Guru in method development
- Key expertise in practical PFAS solutions
- Experienced analytical chemist

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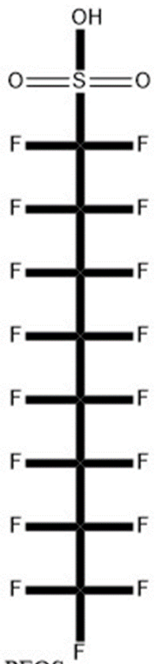
PFAS Specialist – Soils and Solids
(ECTRR)

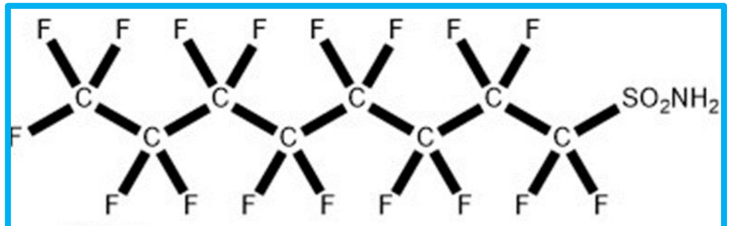
- Specialist experience - PFAS contaminated biosolids
- PFAS bench trials and technical assessments

What are per-and polyfluoroalkyl substances (PFAS)?

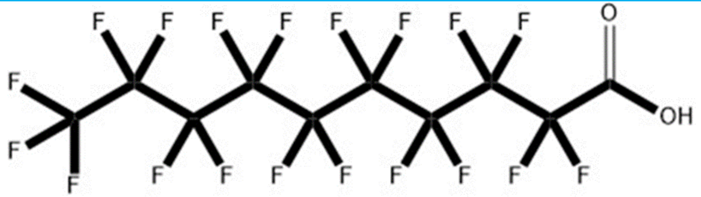


PFOS

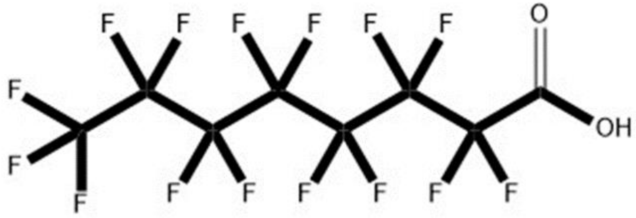
- Produced by electrochemical fluorination and telomerisation processes
- Alkyl chain consisting of –CnF2n+1 (Buck et al. 2011)
- Aliphatic compounds
- Stable terminal degradants (PFCAs & PFSAs)
- Excellent aqueous surface tension lowering properties (surfactants)
- Unique hydrophobic/hydrophilic and lipophobic properties
- Mobile in the environment
- Environmentally persistent and ubiquitous
- (PFOA) Half-life Water >92 years, (PFOS) Half-life Water >42 years
- Able to bioaccumulate
- PFAS prefers to bind to blood and protein
- Mutagenic and potential transgenerational effects (low acute toxicity)



FOSA



PFDA



PFOA

PFAS, a Global Legacy

- 7300 tonnes have been released since inception (UNEP 2012)
- Over 4000 known PFAS compounds have been produced
- Stockholm treaty restricted PFAS is perfluorooctane sulfonic acid (PFOS) and its precursors (UNEP 2012), and PFOA which is listed under annex A for elimination
- Voluntary phase out of longer chain compounds?

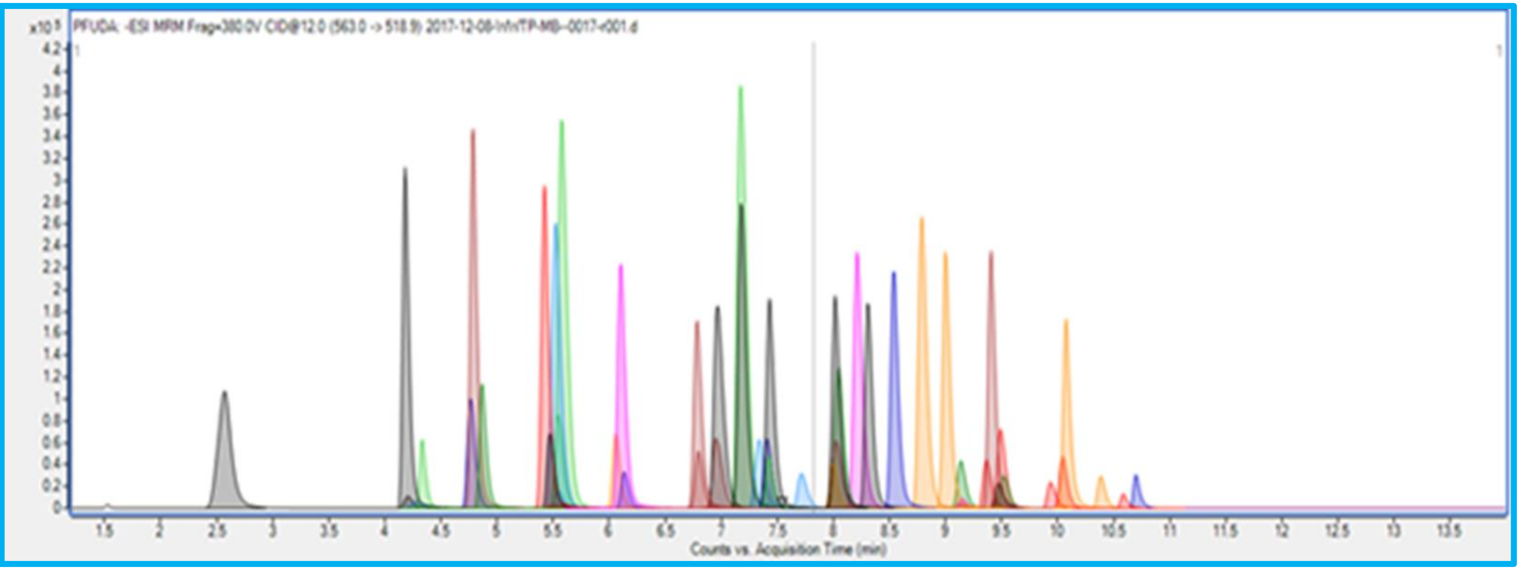
- Some of the Commercial and Consumer Products Containing PFAS:
    - Waste soils and spoils
    - paper and packaging
    - clothing and carpets
    - outdoor textiles and sporting equipment
    - ski and snowboard waxes
    - non-stick cookware
    - cleaning agents and fabric softeners
    - polishes and waxes, and latex paints
    - pesticides and herbicides
    - hydraulic fluids
    - windshield wipers
    - paints, varnishes, dyes, and inks
    - adhesives
    - medical products
    - personal care products (for example, shampoo, hair conditioners sunscreen, cosmetics, toothpaste, dental floss)

Stockholm Convention on persistent organic pollutants (POPs)

Global PFOS contamination of biosolids, maximums

PFAS Chemistry and Analysis

- Nonvolatile PFAS are measured using alkaline extraction methods and LCMS QQQ
- PFAS detection limits may depend on type of environmental matrices, extraction method effectiveness and instrument sensitivity
- Recent analysis methods can now quantify over 50 separate PFAS congeners reliably/affordably
- Total Oxidizable Precursor assay plus PFAS total concentration can give an understanding of total PFAS burden without identifying all PFAS congeners
- PFAS partitioning (compartmentalisation) in a specific environmental matrix may depend on PFAS carbon chain length and attached functional group as well as the physical properties of the matrix and/or solution



PFAS Regulation in Australia

- Currently Australia has a heterogenous approach to PFAS management between states and territories
- NEMP 3.0 is due for release in 2022, may provide a more uniform approach, depends on uptake by each State Authority

Interim position statement on PFAS

EPA VICTORIA | Environment Protection Authority Victoria | VICTORIA State Government

Publication 1669.4* October 2020

** This replaces 1669.3 issued October 2019*

This position statement summarises information about Environment Protection Authority Victoria's (EPA) position on per-and poly-fluorinated alkyl substances (PFAS) and PFAS management. Detailed information about PFAS in Victoria is available on EPA's website, including PFAS and health, PFAS in the environment and PFAS management.

PFAS are a large group of manufactured chemicals that have been used in firefighting foams and other industrial and consumer products for many decades. There are over 4000 individual PFAS substances; the two most well-known are PFOS (perfluorooctane sulphonate) and PFOA (perfluorooctanoic acid), with

EPA's position on PFAS management

EPA uses its statutory powers under the *Environment Protection Act 1970* to hold polluters and landholders to account, issuing remedial notices requiring sites to be investigated and cleaned up. It is EPA's role to investigate potential environmental contamination from substances, including PFAS.

When EPA does not have regulatory authority, EPA will take all regulatory actions available within its powers to manage those impacts effectively. EPA will work collaboratively with other relevant jurisdictions and agencies to address the source(s) of PFAS contamination and any offsite pollution impacts.

VIC EPA interim criterion for the reuse of soil

PFOS	<0.002 mg/kg
PFHxS	<0.001 mg/kg
PFOA	<0.001 mg/kg

Table 7. Landfill acceptance criteria

Landfill type		Interim landfill acceptance criteria [60, 61]		Comments
		Sum of PFOS + PFHxS	PFOA	
Unlined	ASLP leachable concentration (µg/L)	0.07 µg/L	0.56 µg/L	Drinking water x 1 (Department of Health 2017)
	Total concentration (mg/kg)	20 mg/kg	50 mg/kg	Soil - Human health industrial/commercial x 1 Total concentration for PFOA of 50 mg/kg based on the low content limit
Clay/single composite lined	ASLP leachable concentration (µg/L)	0.7 µg/L	5.6 µg/L	Drinking water x 10 (Department of Health 2017)
	Total concentration (mg/kg)	50 mg/kg	50 mg/kg	Soil - Human health industrial/commercial x 10 Total concentration for PFOS + PFHxS and PFOA of 50 mg/kg based on the low content limit
Double composite lined	ASLP leachable concentration (µg/L)	7 µg/L	56 µg/L	Drinking water x 100 (Department of Health 2017)
	Total concentration (mg/kg)	50 mg/kg	50 mg/kg	Soil - Human health industrial/commercial x100

NSW EPA Environment Protection Authority

Addendum to the Waste Classification Guidelines (2014) – Part 1: classifying waste

October 2016

Amendment to Table 2 to include toxicity characteristics leaching procedure (TCLP) and specific contaminant concentration (SCC) values for perfluorooctane sulfonate (PFOS), perfluorohexane sulfonate (PFHxS) and perfluorooctanoic acid (PFOA) chemicals.

Table 2: TCLP and SCC values for classifying waste by chemical assessment

Contaminant[1]	Maximum values for leachable concentration and specific contaminant concentration when used together			
	General solid waste[2]		Restricted solid waste	
	Leachable concentration	Specific contaminant concentration	Leachable concentration	Specific contaminant concentration
	TCLP1 (mg/L)	SCC1 (mg/kg)	TCLP2 (mg/L)	SCC2 (mg/kg)
PFOS + PFHxS	0.05	1.8	0.2	7.2
PFOA	0.50	18.0	2.0	72.0

1. PFOS and PFHxS are to be summed for comparison against the TCLP and SCC values.
2. Values are the same for general solid waste (putrescible) and general solid waste (non-putrescible).

PFAS Containment – Sources

- PFAS contaminated soils (Airports, Military bases, Fire training facilities, PFAS using industries, legacy soils)
- PFAS contaminated concretes and asphalts (Runways, military bases, fire training pads, PFAS using industries)
- PFAS contaminated biosolids (Wastewater treatment plants, Industrial waste (paper and textile mills))
- Municipal solid waste
- Industrial waste
- Receptor linkage pathway = leachates and ground water



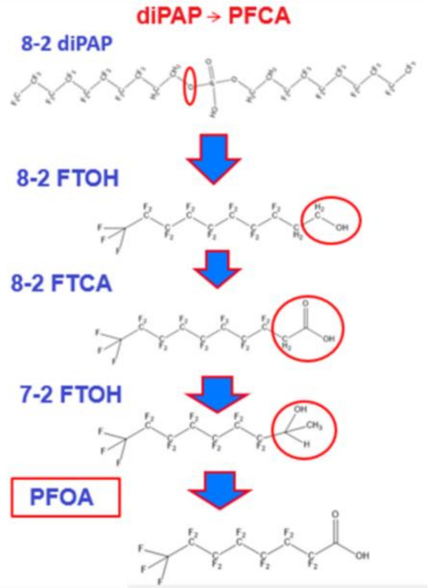

PFAS – Problematic Containment

1. PFAS are a unique water soluble, persistent organic pollutant

- Highly mobile and recalcitrant in the environment, PFAS contained in landfills and stockpiles readily leach and as such can migrate with the leachate and ground/surface waters
- Following saturation of the soil matrix, PFAS may be subsequently transported to either surface waters or groundwater.
- Partitioning in soil horizons is dependent on the PFAS molecules carbon chain length, functional group and the physical conditions present in the matrix (pH, OC, soil type)
- (PFOA) Half-life Water >92 years, (PFOS) Half-life Water >42 years

2. PFAS precursor species may not be detected or considered

- PFAS precursors can transform into stable non degradable PFAS given the right conditions
- Daughter compound types will depend on carbon chain lengths of parent precursor compounds
- PFAS loads may be more considerable if precursor PFAS are included in the overall mass balance
- High diPAP content in paper mill derived biosolids have the potential to transform to less desirable PFCAs including PFHxA and PFOA
- Consider a Total Oxidizable Precursor Assay (TOPA) analysis as part of the initial analysis

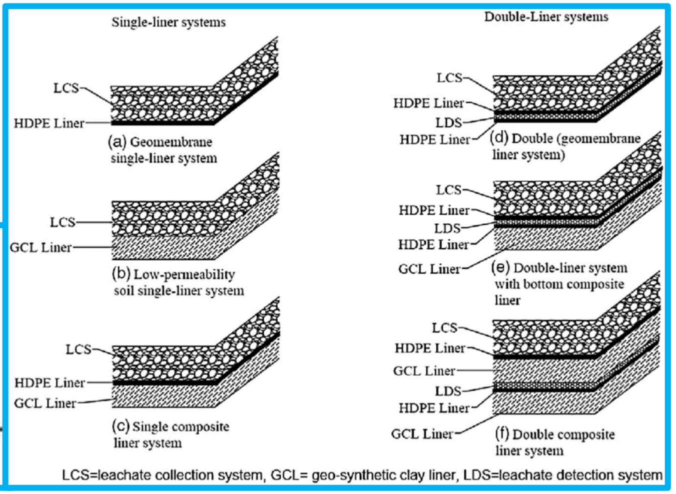


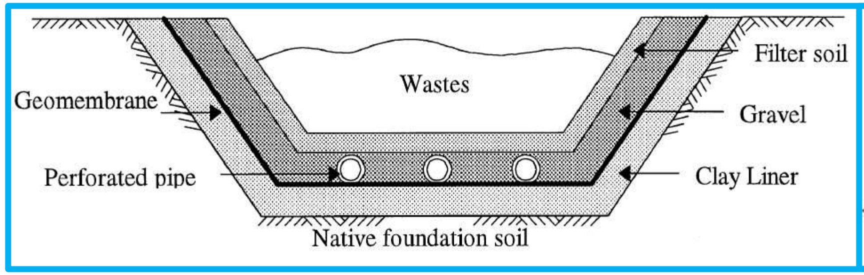
PFAS – Containment

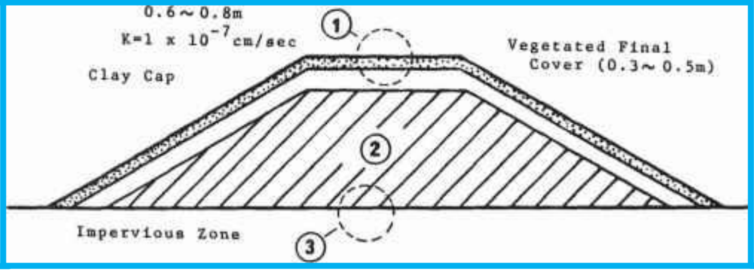
Classic approaches to contaminant mass flux minimization

- **Key tool 1** – Minimise contact with water (capping, run off diversion, dewatering spoils, leachate removal)
- **Key tool 2** – reduce, slow or limit flow of leachate out of cell (various liner systems that prevent leachate access to groundwater – various levels of protection)
- **Key tool 3** – Leachate capture and management

- **These are still useful, but PFAS pose some unique issues**







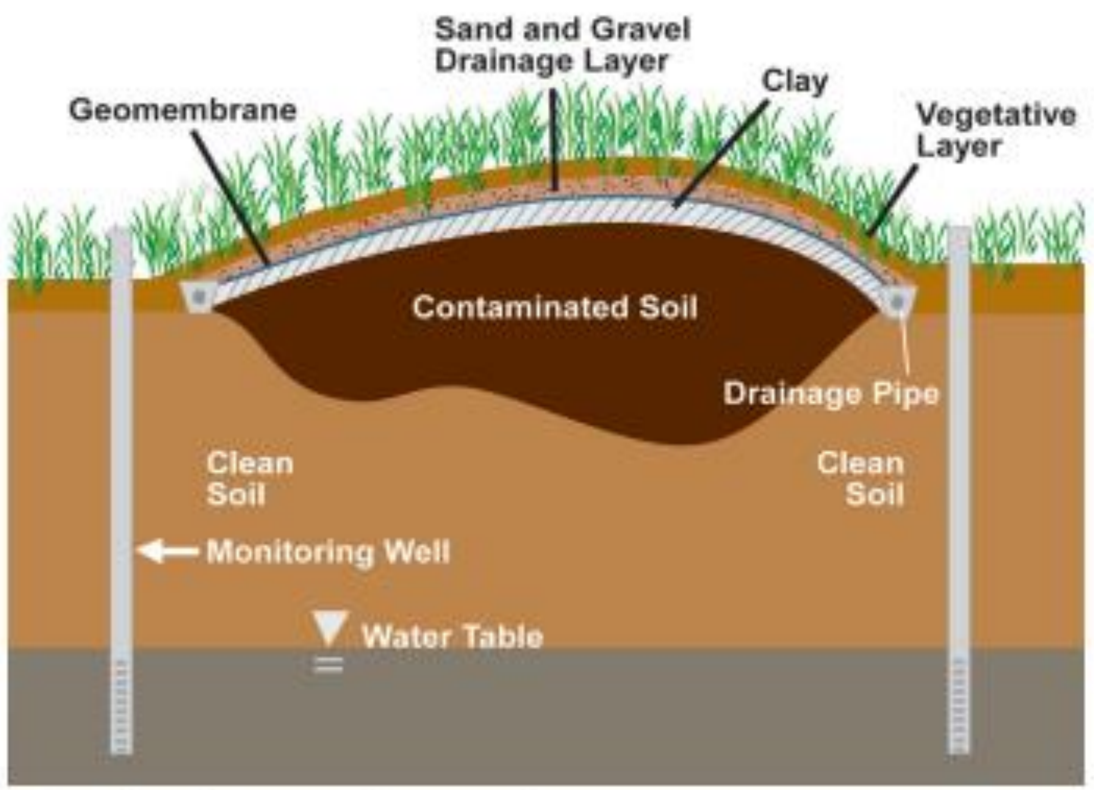
PFAS – Containment

Other approaches to PFAS mass flux minimization in containment cells and landfills

1. **Removal/Reduction –** Remove or limit the mass of PFAS impacted material entering the cell (overall mass reduction in source materials but often not practical and simply transfers the issue to another site/cell)

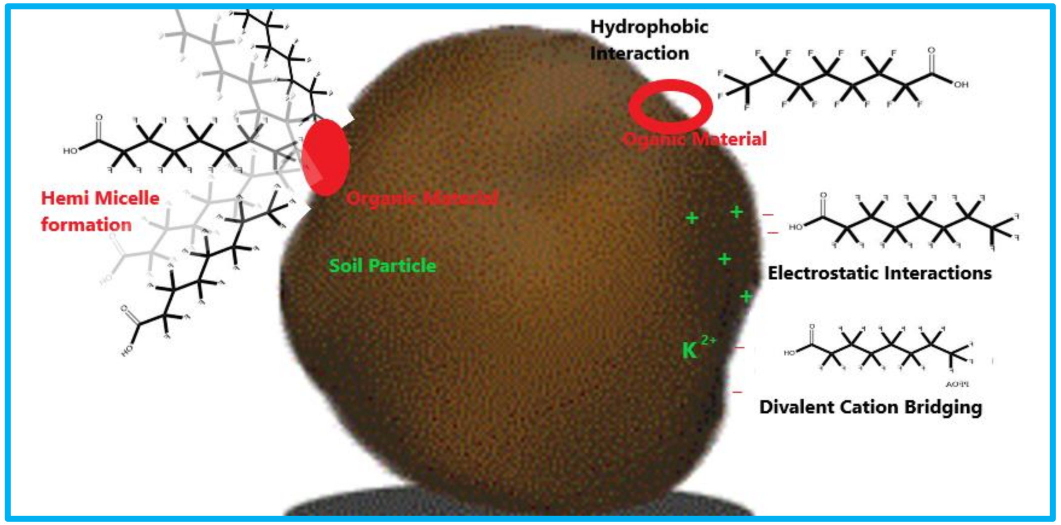
2. **Containment –** Retain PFAS contamination in place (non permeable and permeable liners) – Can the (impermeable) liner keep water out for a long time? What is the retention capacity of the liner (permeable) (how much PFAS can you stick to it!), will other pollutants interfere with PFAS sorption, is it appropriate to just slow down the PFAS?

3. **Dilution -** by the addition of non-PFAS impacted material (reduces concentration but not mass in cell or potential for mass discharge)



PFAS – So how do PFAS behave

- PFAS are weak acids (anionic)
- Sorption is pH dependent, PFAS often desorb at higher pH >7 (depends on matrix)
- Increased salinity (EC) can increase PFAS sorption (PFAS in the aqueous phase are also dissolved salts)
- Unique properties of PFAS lead to increased sorption of longer chain PFAS to organic materials (main interaction is hydrophobic)
- Shorter chain PFAS are less hydrophobic than their longer chain counterparts (C chain length provides insulation distance from sorbent surface and functional group)
- Functional group can affect sorption behaviors (PFCAs are mores soluble than PFSAs)
- Flushes of fresh water can cause desorption (reduced EC, higher pH)



PFAS – Novel mass flux mitigation

Permeable membranes act as PFAS filters, allowing the flow of water through the membrane while retaining the PFAS on a sorbent that utilizes PFAS adsorption properties

- Use the mobility of soluble PFAS and its sorption properties to reduce mass flux (What PFAS/short or long chain?)
- Permeable membranes can utilize the adsorbent properties of some anionic PFAS to retain them on a membrane
- What is the membranes capacity and contact time (How much PFAS can it take?)
- What is the condition of the source material (are there interfering compounds)
- High total concentration/low ASLP concentration – Will there be a steady PFAS concentration at relatively low levels in the leachate for a long time
- Low total concentration/high ASLP concentration – High PFAS levels in leachate will the liner be able to keep up?
- What are the underlying physical conditions (pH, EC)
- Is a bench trial including the impacted material appropriate?
- How do dry membranes preform when compared to a wet membrane (often need to be saturated before optimal efficiency)

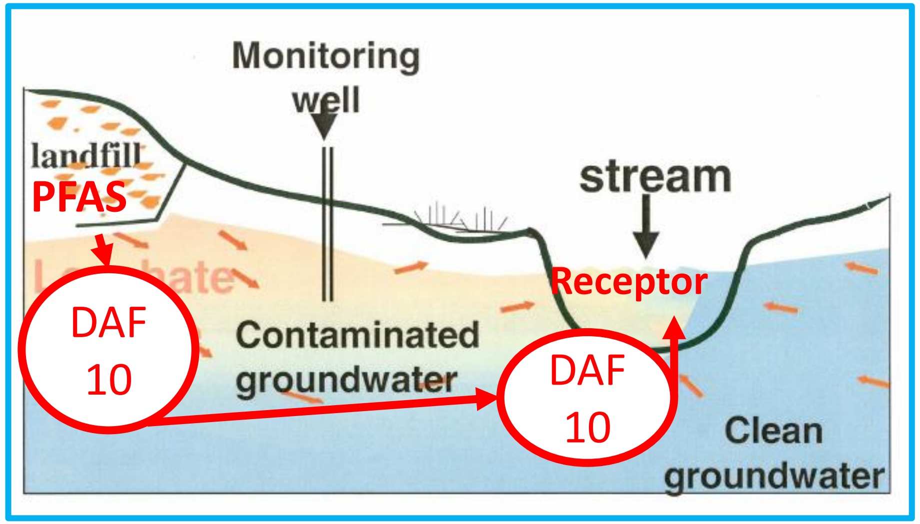
Into the future

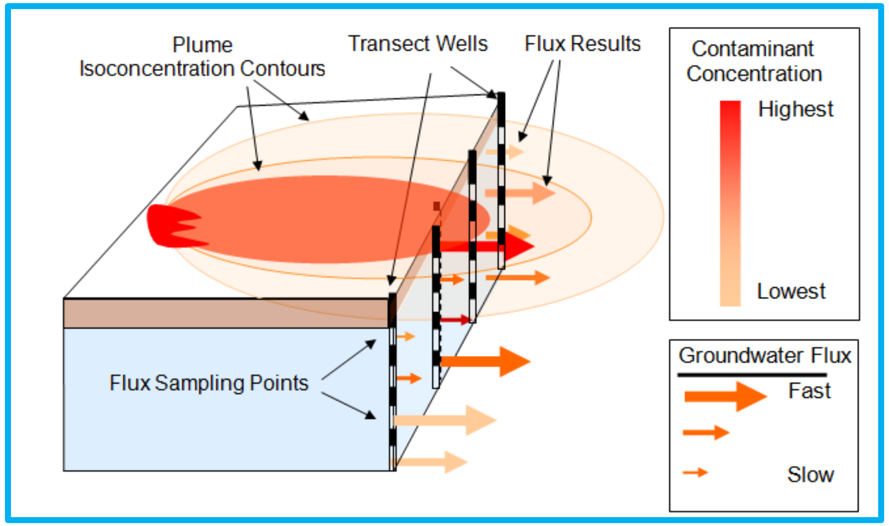
What's the best approach?

- Multimodal systems – high concentration material (sorbents in material, liner, and leachate treatment, maybe a combined approach is best).
- Funnel and gate systems (combinations of impermeable and permeable membranes)
- Elimination is the ultimate key tool, but up to stake holders. (Is elimination practical or economically viable)
- Long term monitoring of retention and filtering systems (how effective are mitigation measures over extended time periods - PFAS have a long half life the mitigation also needs to be durable)
- Should we design for PFAS half-life like we do for elemental toxic metals.
- A clear well defined regulatory framework for PFAS will provide a more stable environment for Geo-membrane manufacturers in the PFAS space

PFAS – Mass flux tools for containment

- Mass flux provides more powerful information than TCLP leaching data and GW data alone.
- Mechanism used to determine acceptance criteria (regulations for landfills, and assess suitability of on-site containment cells)
- Ability to quantify applied method reduction in mass flow out of cell, better diagnostic than static concentration. Makes use of site-specific information such as dilution and attenuation factors.
- Tells us how much is moving where, as opposed to what the concentration is at compliance point. Allows us to determine linkages and estimate impacts at receptors.
- Tool can post-hoc determine if PFAS transport from applied containment mechanism are likely increasing or decreasing (legacy issues.
- Critical for the application of sorbent liners.





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Thank you