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Joint Chemical Engineering Committee (JCEC) New South Wales

‘A chemical engineering perspective on the PFAS problem’

- Peter Nadebaum | Principal and Senior Technical Director - Environment | GHD

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A chemical engineering perspective on the PFAS problem

Peter Nadebaum,
GHD Pty Ltd

Overview

The Australian PFAS situation, drivers, and approach to the problem including

- What are PFAS?
- Where are PFAS found?
- What do we analyse for?
- What criteria do we apply?
- What is the solution?
  - Concepts of source – pathway – receptor: mass flux
  - Remediation technologies and management options
  - The strategy

My perspective

Personal viewpoint

Chemical engineer who has become an environmental engineer

Solving environmental contamination problems

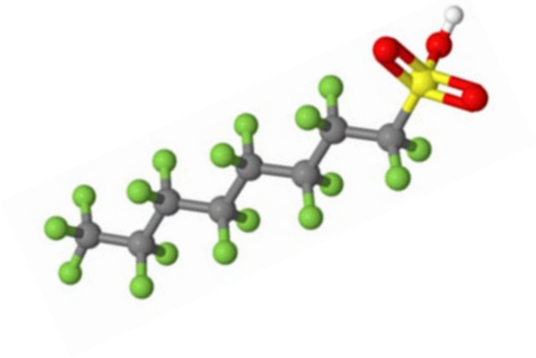
- Land, groundwater, water, wastewater, waste
- Effects: human health, ecological

- Not so much manufacturing

PFAS – what are they?

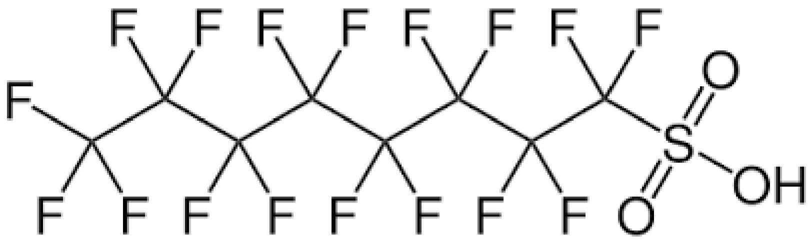
Per and poly Fluoralkyl Substances (PFAS)
Chain of carbon atoms bonded to fluorine atoms

Some have hydrophilic functional group at the end of the chain
Sulphonic acids, carboxylic acids



perfluorooctane sulfonate (PFOS)
perfluorooctanoic acid (PFOA)
perfluorohexane sulfonate (PFHxS).

Very stable – think Teflon



High solubility

FLUOROTECHNOLOGY MAKES IMPORTANT PRODUCTS FOR VITAL INDUSTRIES POSSIBLE

FluoroCouncil member companies voluntarily committed to a global phase-out of long-chain fluorochemistries by the end of 2015, resulting in the transition to alternatives, such as short-chain fluorochemistries that offer the same high-performance benefits, but with improved environmental and health profiles.

ELECTRONICS
Improves insulation, weather-ability, transparency and water-resistance. Provides smooth and smudge-resistant **touch screens.**

FIRST RESPONDERS
Offers life-saving protection in **safety gear** and **firefighting foams** used to fight flammable liquid fires.

OIL AND GAS
Provides reliable equipment to help improve the safety and affordability of oil-field and pipeline operations. Improves the reliability and safety of **fuel system seals** and **hoses, O-rings and downhole** and **field equipment gaskets.**

MILITARY
Enables **apparel** and **equipment** to provide high-barrier skin protection in extreme environments and against chemical warfare agents.

CHEMICAL/ PHARMACEUTICAL MANUFACTURING
Provides sterile, corrosion-resistant **coatings, linings** and **equipment.**

AUTOMOTIVE
Provides every **automotive system** with durability, heat and chemical resistance and vapor barriers. Increases reliability of **engine compartment wirings** and **gauges** and improves auto safety by reducing engine compartment fires. Protects **carpets** and **seats** against stains, soil, oil and water.

AEROSPACE/ DEFENSE
Enables **chemical-resistant tubes, hoses** and **fluid seals**; high and low temperature brake and hydraulic fluids used in **aircraft control systems** and **brakes**; and ultra-high frequency **wire and cable insulation** necessary for navigation, fly-by-wire control and aircraft communications.

HEALTHCARE
Serves as high dielectric insulators in medical equipment that relies on high frequency signals, like **defibrillators, pacemakers** and **CRT, PET** and **MRI imaging devices.** Used to treat **medical garments, drapes** and **divider curtains** to protect against the transmission of diseases and infections.

SEMICONDUCTORS
Creates the ultra-pure manufacturing environments necessary for **micro-electronics.** Used for **plasma machinery, etching materials, cleaning fluids** and **wetting surfactants** for **chemical etchants.**

ALTERNATIVE ENERGY
Enables **lithium batteries, fuel cells** and **solar panels,** which contribute to reduced emissions and energy costs.

OUTDOOR APPAREL/ EQUIPMENT
Creates breathable membranes and long-lasting finishes that provide water repellency, oil repellency, stain resistance and soil release with abrasion-resistant finishes for **apparel** and **equipment.**

BUILDING/ CONSTRUCTION
Enhances durability, UV resistance and anti-corrosive properties to lengthen the lifetime of **infrastructure, facades** and **surfaces.**

FLUORINE — CARBON

FluoroTechnology is the use of fluorine chemistry to create any fluorinated product. When fluorine and carbon atoms join together, they create a powerful chemical bond. The use and manipulation of this bond gives FluoroTechnology its distinct properties of strength, durability, heat-resistance and stability. These properties are critical to the reliable and safe function of myriad products that industry and consumer rely on every day.

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PFAS – why are they a problem?

In 2010, the Stockholm Convention: PFOS is an additional Persistent Organic Pollutant (POP) due to its characteristics as a Persistent, Bioaccumulative and Toxic substance (*PBT).*

- Mobile
- Ubiquitous

The Regulatory Scene in Australia

- PFAS National Environment Management Plan 2020
- National Environment Protection Measure (Assessment of Contaminated Sites)
- CRC CARE Guidance Papers No. 38 (2017), No 43 (2018)
- State guidance
- International agencies

The magnitude of the issue

Initial concern: land, groundwater, surface water affected by PFAS from fire training and fire protection

- Department of Defence (particularly airfields)
- Airport services (particularly fire training)
- City and country fire and rescue (particularly fire training and appliances (trucks)
- Major industry (Major Hazard Facilities – fire protection systems)

Since then – lower concentrations but potentially a problem:

- Landfills, sewage treatment plants, biosolids
- Ubiquitous diffuse sources: widespread; urban waterways, stormwater, groundwater, soil

Potentially $billions to address – depends on policy settings

Ubiquitous

Issue 1: number of compounds

More than 4000 PFAS
Standard analysis: 28 compounds

Recognition - many PFAS compounds present

Depends on product formulations

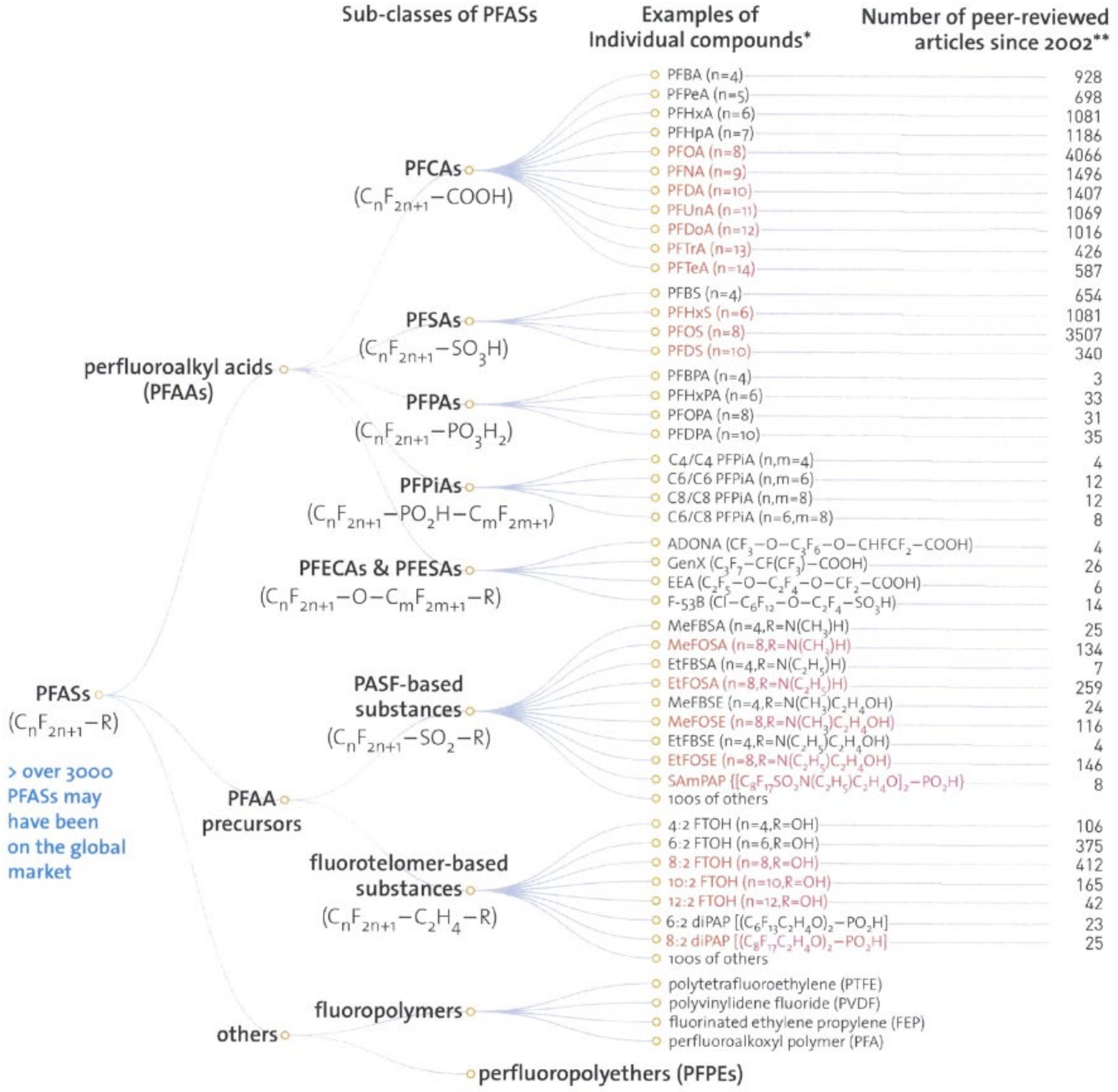
- Older formulations – PFOS main concern
- More recent formulations – low PFOS and PFOA but other fluorinated compounds

Possible transformations:

- Strong oxidation (TOPA) may convert to carboxylates (eg PFOA), but not sulphonates (PFOS)
- Weak oxidation - alkaline hydrolysis may convert to fluorotelomers

Wang, Z et al, 22nd February 2017

Environmental Science & Technology Feature

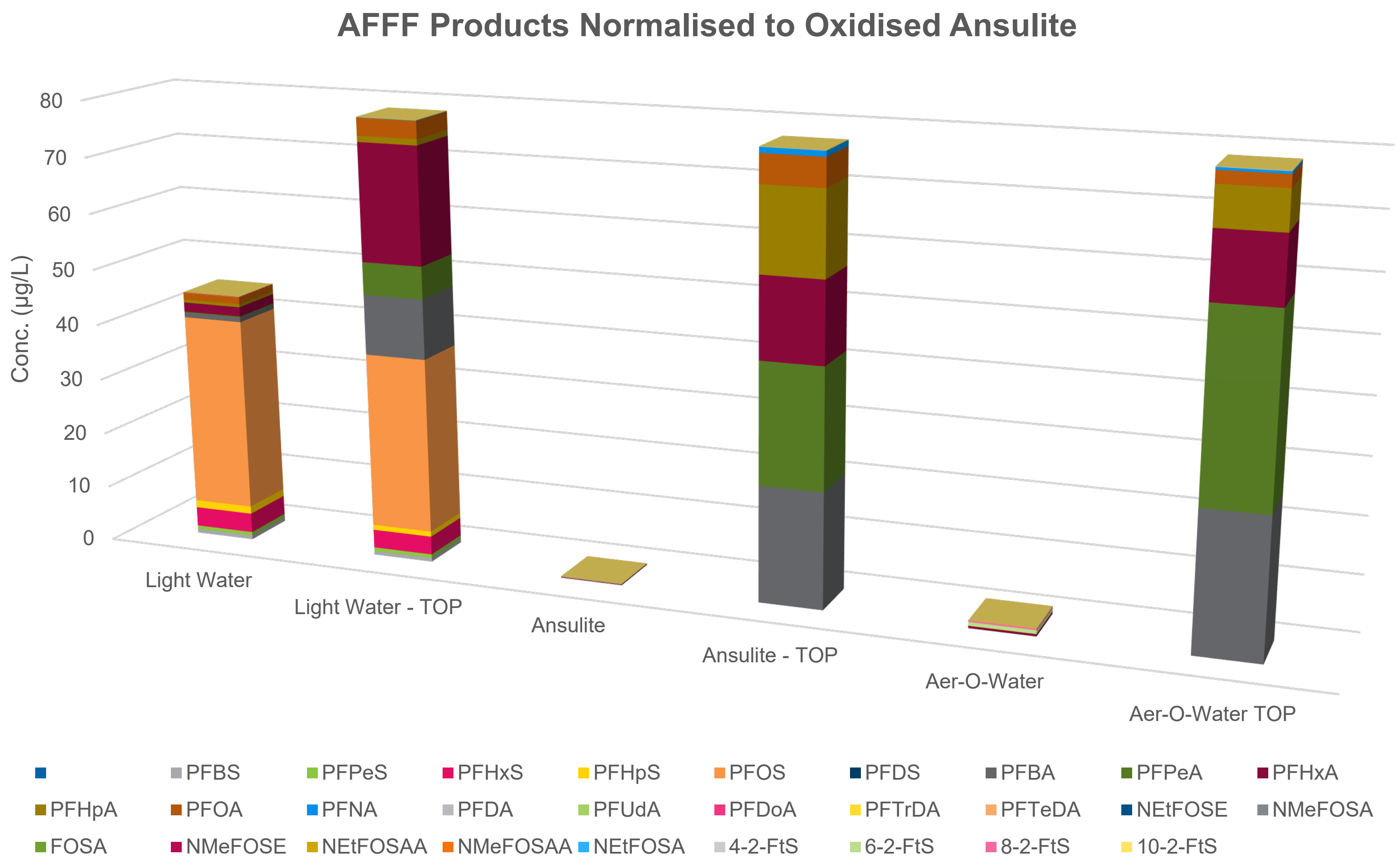


* PFASs in RED are those that have been restricted under national/regional/global regulatory or voluntary frameworks, with or without specific exemptions (for details, see OECD (2015), Risk reduction approaches for PFASs. http://oe.cd/1AN).

** The numbers of articles (related to all aspects of research) were retrieved from SciFinder® on Nov. 1, 2016.

Figure 1. "Family tree" of PFASs, including examples of individual PFASs and the number of peer-reviewed articles on them since 2002 (most of the studies focused on long-chain PFCAs, PFSAs and their major precursors.).

Illustrating the oxidation/transformation issue



Information from
ALS Pty Ltd

The range of PFAS compounds - implications

➡ Composition may change in the environment, with time, leaching (eg PFHxS low in soil, higher in water), location, and treatment

- Concern: “Dark matter”, problem may be worse
- Assessment may ultimately be in terms of PFOS (and PFOA?) equivalents

Issue 2: toxicity

How toxic is PFOS?

Compare some drinking water criteria:

- Mercury: 1 ug/L
- Benzene 1 ug/L
- Dieldrin 0.3 ug/L
- Vinyl chloride 0.3 ug/L
- **PFOS 0.07 ug/**L
- PAHs (BaP) 0.01 ug/L
- Dioxins 6×10^{-7} ug/L (USEPA value for 2,3,7,8 TCDD)

- Toxicity to aquatic organisms: 0.000 23 ug/L

PFOS Health Screening criteria - soils

Land use	PFOS+PFHxS Health Screening Levels (values indicative, range depends on contribution from other sources, and if garden produce is consumed)
Residential	0.01 - 2 mg/kg
Recreation	1 mg/kg
High density residential	2 mg/kg
Industrial (e.g. fire training areas)	20 mg/kg

1: Emphases importance of “direct” vs “indirect” (multi-pathway) exposure
2. PFOA approximately 8 x higher – generally less of a concern
Generally conclude:
- PFOS soil contamination unlikely to pose a health risk at a fire training site
- If off site, or site is to be redeveloped, soil contamination may be a driver

PFOS Health Screening criteria - waters

Water	PFOS+PFHxS Health Screening Levels
Drinking water (DoH)	0.07 ug/L
Finfish/crustaceans (FSANZ 2017)	5.2/65 ug/kg (produce)
Surface water protective of fish consumption	Maybe ≈1 ng/L

Implications – protecting human health

Precautionary policy taken by regulatory agencies to bioaccumulation and persistence

→ extremely low screening soil and water criteria

→ need for clean up/management often depends on off-site impact

→ "**outside in**" approach by EPA NSW

Test plants/fish/eggs and assess consumption by persons

But can be difficult because of variability (house/location/person)

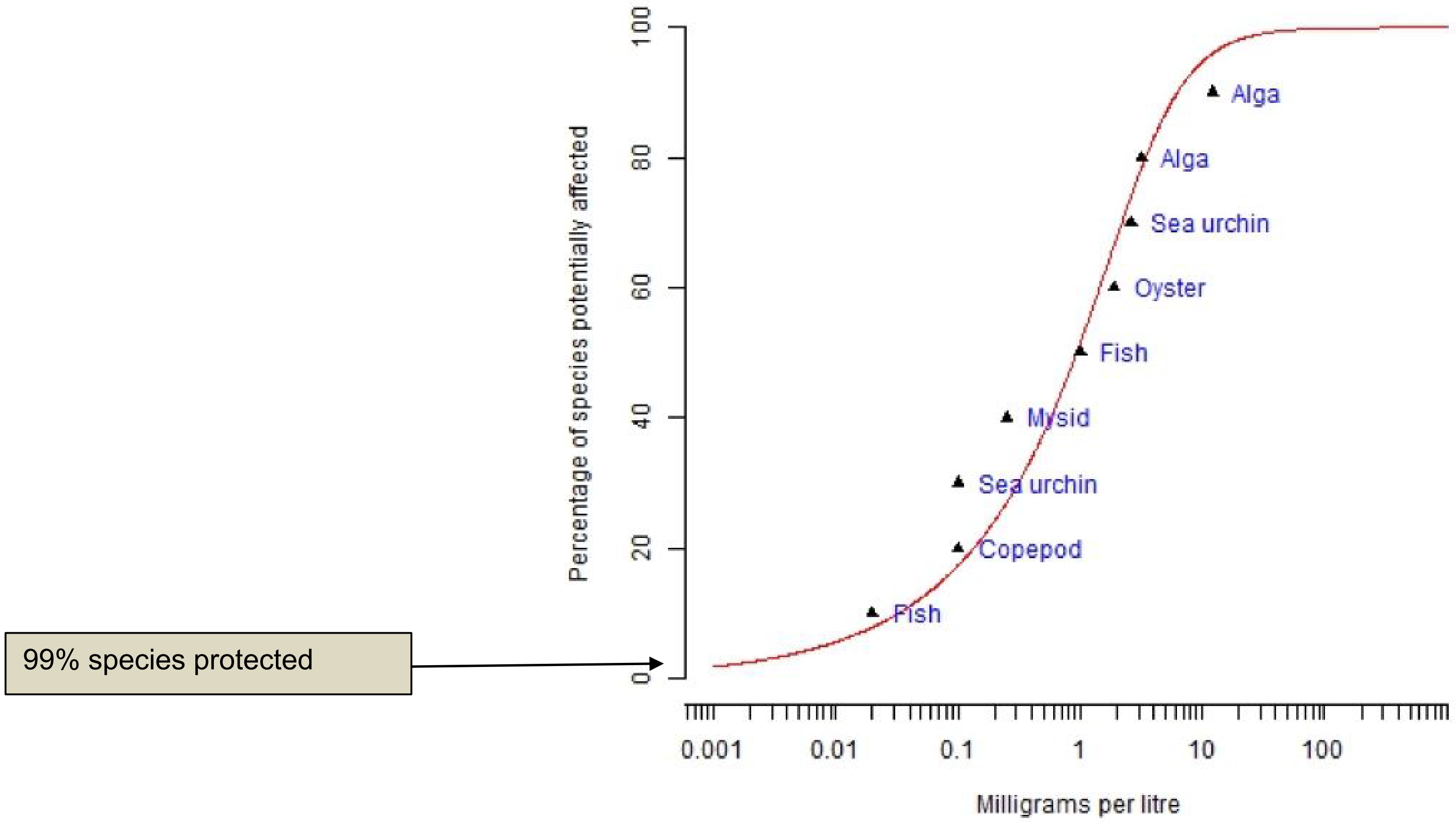
- Water for gardens/irrigation/stock (eg hens/eggs) a concern
- Information/criteria becoming available

Toxicity to ecosystems

Australia:

- Screening criteria based on percentage of organisms protected
- Depends on degree of modification of the ecosystem
- **Water**:
  - For a “slightly to moderately disturbed ecosystem” because of bioaccumulation, require 99% of organisms to be protected
- **Soils**
  - Similar approach (increase percentage of organisms to be protected)

Species Sensitivity Distribution



1. SSD for PFOS in marine waters

Fresh and marine water Screening Levels

PFAS NEMP

Level of species protection	PFOS	PFOA
	(ug/L)	(ug/L)
99%	0.000 23	19
95%	0.13	220
90%	2	632
80%	**31**	1824

Issues:

- 99% values to be used in most situations because of bioaccumulation
- Very high level of uncertainty in 99% freshwater value
- Uncertainty how to use the freshwater value (generally cannot distinguish effects)
- Uncertainty with marine values because tests did not include multi-generational studies (freshwater test results have been used for marine water)
- Consider: only important species? Resilience? Functioning of ecosystem?

Soil Ecological Screening Values

PFAS NEMP

Land Use	PFOS	PFOA
	ESL (mg/kg)	ESL (mg/kg)
Direct Toxicity		
All land uses	1	10
Indirect Toxicity		
All land uses	**0.01**	-

Direct toxicity to terrestrial animals may not be limiting other than in source area

Bioaccumulation in food chain may be limiting consideration

Issue 3: complex to deal with a site with PFAS contamination

PFAS contaminated sites pose a number of risks

Human health:

- Groundwater/water is contaminated with PFAS and cannot be used off site
- Fish, birds, stock accumulate PFAS from contaminated water or soil and present a risk to human health

Ecological:

- Potential for effect on ecological systems (particularly predators)

Financial impact:

- Clean up site/water
- Clean up fire systems
- Works cannot proceed because of contaminated soil
- Litigation/class actions by persons whose health/property values are affected (“you knew and didn’t act”)

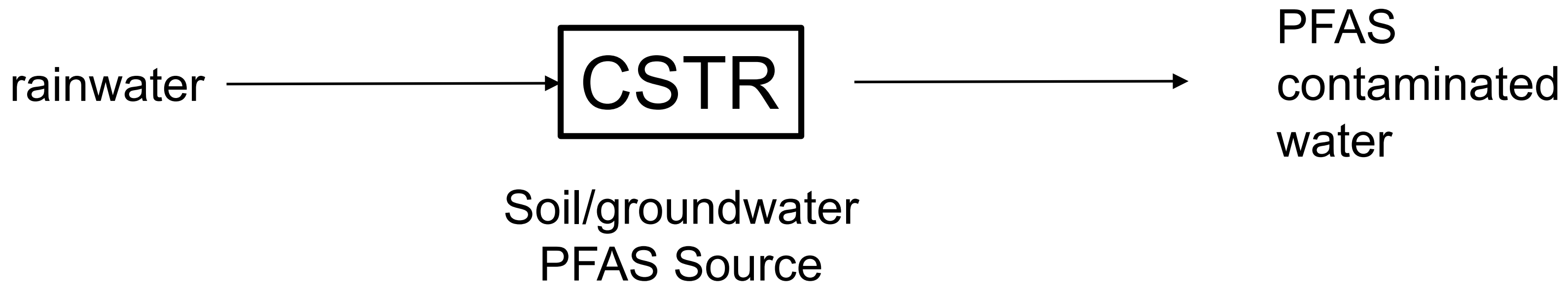
Issue 4: mass flux from source areas is critical

Migration of only traces of PFAS from a source area can pose a high risk

PFAS in soil will leach to groundwater

PFAS in soil will migrate in rainwater

Critical issue: control mass flux



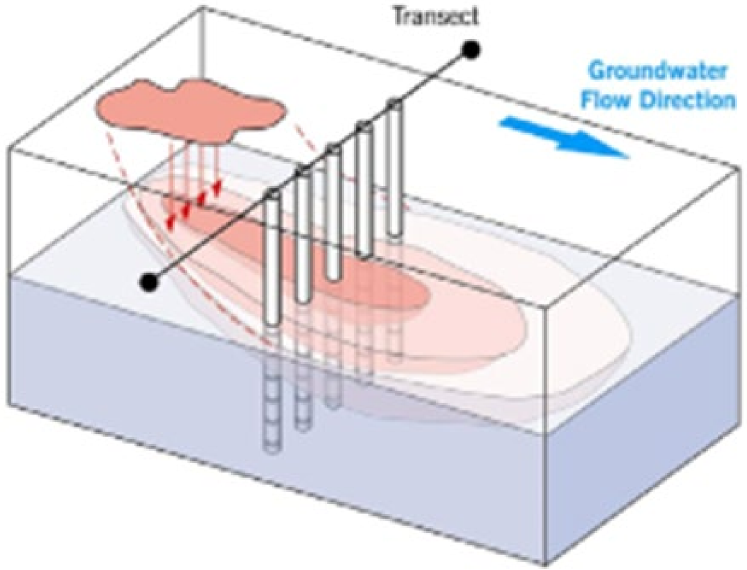
Relativities

Media	Soil	Groundwater	Surface Water
1 mg PFOS in 1 L soil / aquifer / water	0.5 mg/kg	3 mg/L	1 mg/L
Typical Criterion	3 mg/kg (health) 0.01 mg/kg (agriculture)	0.000 07 mg/L (0.07 ug/L) (drinking)	0.000 000 23 mg/L (0.23 ng/L) (toxicity) Also bioaccumulation
Reduction required	~50	~50 000	~5 000 000

Traces of PFAS migrating from source can be high risk

Gradually realised:

- Precautionary screening levels likely to be exceeded!
- May not be able to clean up some sites to comply with screening criteria or confirm that there will not be adverse effects
- Proving a “null hypothesis” (no risk) can be difficult and costly!
- Need to draw on principles of “practicability” and “sustainable remediation”
- Need to minimise mass flux of PFAS moving off site
- Identify mass, minimise mass, and control mass migration



Contamination scenario - soil

Hypothetical site - not to scale

Area	Radius of area (m)	Depth (m)	Average PFOS concentration (mg/kg)	PFOS mass (kg)
A	25	3	17	225
B	100	1	2	90
C	400	0.2	0.04	10

Comment:

- Hypothetical site
- Caution: assumed mass of PFOS in the source area may be higher than for many sites – need estimate

Adapted from paper in ALGA CRONICLE:
Nadebaum, P, Hunt, J W, Smith, G (May, 2017)

Contamination scenario – groundwater/surface water

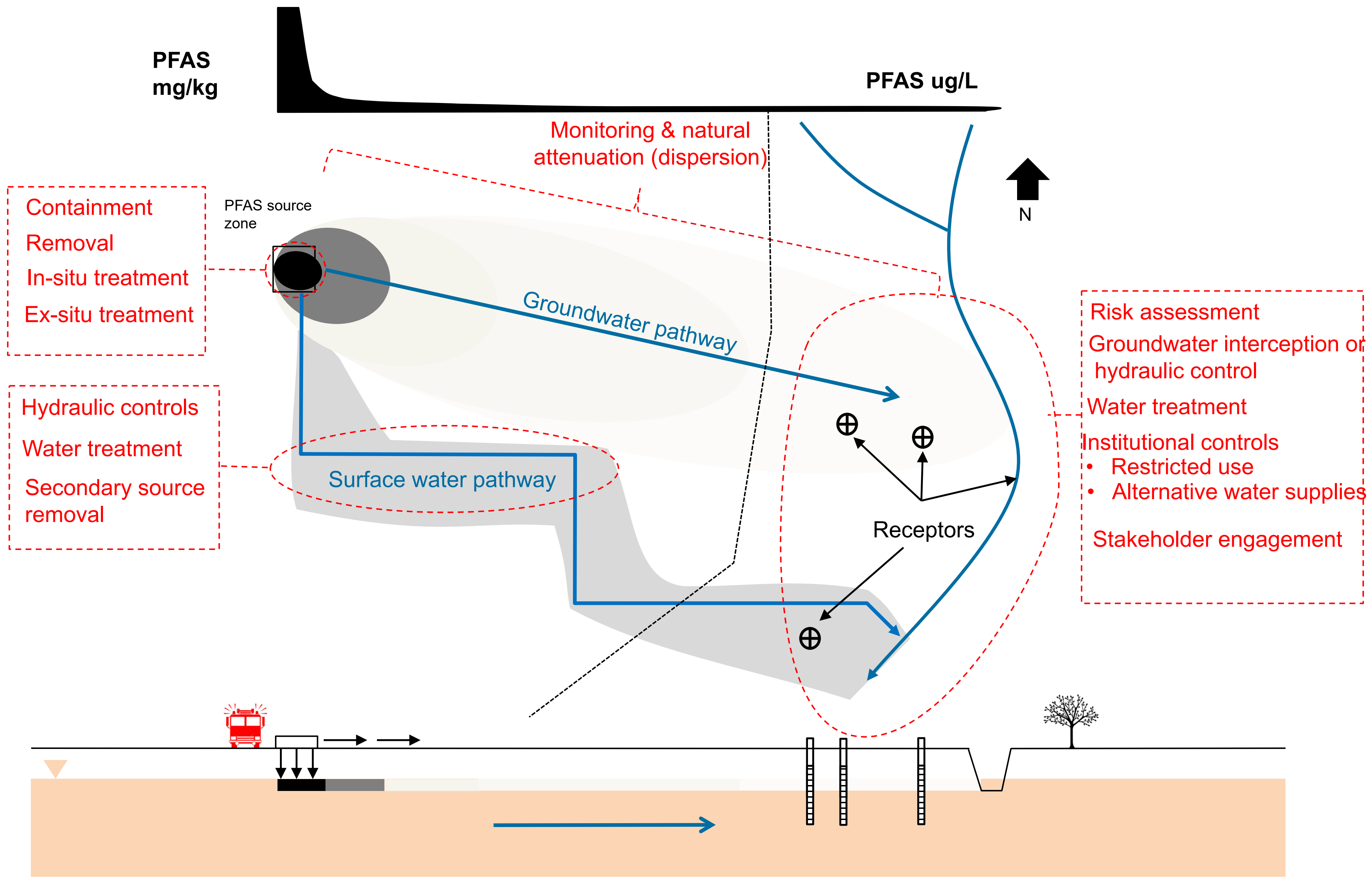
	Area (ha)	Thickness of aquifer contam'd (m)	Average PFOS conc'n (ug/L)	Mass of PFOS (kg)
Area A	2.5	5	29	0.9
Area B	75	2	0.26	0.1
Surface Water	?		<0.1?	<0.1?

Mass of PFOS in groundwater or surface water may be only 0.1 – 1 % of that in soil in the source area

Issue 5: how do we develop a practicable remediation and management strategy?

Overall approach:

1. Establish Conceptual Site Model
2. Determine what must be achieved:
   - Regulatory requirements
   - Risk
3. Estimate distribution of mass and mass flux
4. Evaluate feasible options and combinations of options and technologies
   - Soil
   - Water
5. Determine the most sustainable approach

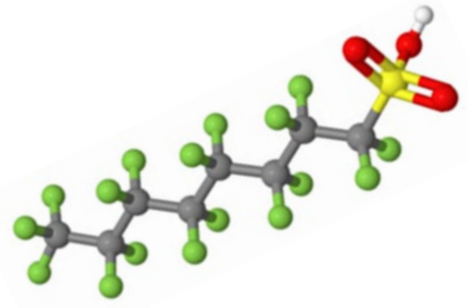


PFAS mg/kg
PFAS ug/L
Monitoring & natural attenuation (dispersion)
N
PFAS source zone
Containment
Removal
In-situ treatment
Ex-situ treatment
Groundwater pathway
Hydraulic controls
Water treatment
Secondary source removal
Surface water pathway
Receptors
Risk assessment
Groundwater interception or hydraulic control
Water treatment
Institutional controls
• Restricted use
• Alternative water supplies
Stakeholder engagement

Source area - soil remediation options

- Challenging due to the strength of carbon-fluorine bonds
- Some treatments involving transformation of PFAS may result in toxic by products that are not yet known or well understood (eg TOPA)
- Cost of field scalable innovative treatment may be prohibitive – seem promising at a trial level but not yet implemented on a commercial scale
- Currently few practicable remediation options available in Australia other than:
  - Capping and containment – may include stabilisation
  - Soil washing
  - Landfill disposal
  - Reuse
  - Excavation and onsite or offsite treatment in a high temperature thermal treatment system

Appears to be the most practicable and effective approach for many sites - limited to source areas where the magnitude of the area and volume are manageable



PFAS Source area considerations

	Technical difficulty	Cost	Sustainability	Risk to the environment during construction	Community acceptance	Regulatory acceptance	Effectiveness in reducing mass flux	Conclusion
Stabilisation	H	$$	M	H	L	L	M	Maybe
Thermal destruction	H	$$$	L	H	H	H	H	Unlikely
Soil washing + water treatment	H	$$$	L	H	H	H	M	Maybe
Landfill	L	$$	L	L	M	L	H	Maybe
On-site engineered containment	L	$	M	L	L	M	H	Preferred?

Contaminated infrastructure

Drains and concrete pads - can be a significant source of PFAS

Concrete - a PFAS sponge and slow release media

Limited feasible options

- Encapsulation – coatings
- Cleaning/decommissioning/replace
- Engineered repository

CONCLUSION: *the clean-up process must also deal with contaminated infrastructure, eg concrete*

GHD

Equipment/system decontamination

Need to consider whether there is a need for decontamination of tanks, pipes, appliances

Need for fire and rescue organisations to protect personnel and environment

Desire to work in fluorine-free environment

But need for effective fire protection!

→ Decontamination criteria, procedures, guidance

Containment

Being applied on many sites

- Resulting in a great many covered stockpiles – necessary, expedient, not a final solution

- Need to consider effectiveness
  - Covered by a structure (road, paving, runway)?
  - Potential for leaching to continue?
  - Dependent on depth to groundwater, lithology

Engineered options – more difficult: regulatory requirements, stakeholder acceptance

Critical consideration: duration – what will be required in the future?




Landfill disposal

Acceptance criteria

	PFOS+PFHxS		
	Total (mg/kg)	ASLP (mg/L)	Total if soluble (mg/kg)
Unlined	20	0.000 07	0.0014
Single liner	50	0.000 7	0.014
Double liner	50	0.007	0.14

Often PFAS in soil quite leachable, ASLP limiting, immobilisation necessary; immobilisation uncertain.
Observed concentrations in landfill leachate can be > these levels

Reuse as fill material

Difficult because of leaching

PFAS NEMP provides guidance on reuse (risk assessment)

No effect on human health, terrestrial ecosystems, groundwater use, receiving waters

May be possible if PFAS very low eg PFOS < 0.002 mg/kg

But leaching may be a concern

0.002 mg/kg = 0.000 1 mg/L = 0.1 ug/L

cf

Drinking water criterion 0.07 ug/L

Maintenance of aquatic ecosystems: 0.000 23 ug/L

Soil management options during construction work[1]

- Practicable solution required whereby contaminated soil can be excavated and managed in a timely manner while minimising risk
- Options include:
  - Reinstatement of soil to the excavation
  - Placement of soil at another location on the site with the same or higher risk contamination profile
  - Containment of soil on-site
  - Offsite disposal or on/offsite treatment

→ Appear to be the most practicable approach for many construction projects, if permitted (some agencies may not allow)

[1]CRC CARE Publication 38

Water management and treatment options

Goal to achieve very low concentrations that are to be discharged to sewer, stormwater or surface waters, or reinjected to an aquifer **AND minimise waste**

- Viable field scalable technologies include:
  - Hydraulic containment; interception
  - Adsorption (e.g. GAC, resins, ion exchange polymers, MyCelx™, MatCARE™, Rembind™); may need pretreatment
  - Surface Active Foam Fractionation (SAFF™)
  - Barrier systems
  - Nanofiltration
  - Reverse osmosis
- Adsorption/separation results in a concentrated PFAS waste that must be treated / disposed of – e.g. high temperature thermal
- May be used as part of a groundwater pump and treat strategy, although much of the mass may remain in source area and within the aquifer
- In-situ destruction – byproduct issues - too difficult

→ Favoured due to lower cost and more manageable waste stream

Diffuse contaminated surface water and sediment

Generally response will be to stop leaching from source and secondary sources

May remove sediment

May provide alternative water supply

Wait

Mass of PFAS - cost and practicability implications

Consider Cost/kg PFAS removed from contaminated soil/groundwater treated

Low concentration: far higher cost/kg than for high concentration

- $10 of millions/kg vs $10s of thousands/kg

Not practicable to treat large areas of diffuse and dilute contamination

Do not continue to use PFAS products!

Issue 6: will a practicable response be acceptable?

Some PFAS will always remain – onsite and off site

Will the concentration become acceptable over time?

No longer use PFAS products – contamination will deplete

Decision process for selecting remedial strategy

Need to consider…..

- Options must comply with regulatory requirements

- Options must have an acceptable risk to stakeholders –

  risk = likelihood x effect

  both remedial works, and condition of the land and water after remediation

  ISO 31000:2009 Risk Management

- Most sustainable option – balance of social, environmental, economic factors – determine through consultative process

  ISO 18504:2017 Sustainable Remediation

Consider economic, social, environmental indicators - eg

(refer to ISO 18504:2017 for more detail on indicators)

[1]Contaminant destruction depends on ultimate disposal option adopted

Technology	Community perception	Contaminant destruction[1]	Waste Generation	Energy Use	Cost	Risk of failure
SOIL						
Landfill off site (maybe with immobilisation)	Unfavourable	Nil	High	Low	Variable	Low
Thermal	Unfavourable	High	Depends on disposal of treated soil	High	High	Low
Containment or encapsulation on site	Unfavourable	Nil	High	Low	Low	High
Soil washing	Favourable	Nil	Moderate	Low	Variable	Medium
GROUNDWATER						
Containment; treat extracted groundwater by sorbent	Favourable	Nil	Moderate	Moderate	High	Low
Permeable Adsorbent Barrier	Favourable	Nil	Moderate	Low	High	Medium

Conclusions

- **Solving the PFAS problem involves chemical engineering concepts:**
  mass balance, mass flux, transport, treatment processes, risk management

- Need to consider concepts of:
  - **Risk – likely/possible**
  - **Practicability**
  - **Proportionate response** to the level of effect/risk
  - **Time frame** for risk minimisation, practicability, sustainability

  A key question: How do we achieve closure?

How can we spend our limited $ most wisely – short term and long term?
Different answers for different stakeholders

The Australian contaminated site system is flexible and risk-based
Strategies for practicably dealing with PFAS contaminated sites are being developed

Acknowledgments

My many colleagues

CRC CARE

www.ghd.com

Thank you for attending this webinar.

Future webinars…

Energy Transition for the Oil & Gas Industry

- presenters from Hatch will share examples of successfully delivering energy transition projects across the globe and how this can be applied specifically to the Oil & Gas industry.
- 16 July, 8:30-9:30PM AEST
- https://www.bigmarker.com/IChemEAust/Singapore-Energy-SIG

PFAS in July: PFAS Diving deeper

- In our second PFAS presentation Mark Clough will expand on the sources and fate and transport of PFAS in the environment and how this is influenced by the chemical properties of PFAS and the physical site setting.
- 28 July, 6:30-7:30PM AEST
- https://www.bigmarker.com/IChemEAust/More-technical-detail-on-PFAS