# Perfluorinated Compounds (PFCs) Forum

Environment Institute
of Australia and
New Zealand Inc.

# Overview

- Introduction of Speakers
- Introduction of PFCs – what are they and why are they a problem?
- PFCs and current relevant environmental legislation
- PFCS risk assessment in Australia
- Regulation of PFCs
- Laboratory Analysis of PFCs and current limitations
- PFCs water and soil treatment - current and promising technologies

# Are you Certified?

- After 1 July 2017 any reports submitted to the EPA to comply with the requirements of the CLM Act must be prepared, or reviewed and approved, by a *certified consultant*.

- EIANZ has a Certified Environmental Practitioner Scheme including speciality certification for Contaminated Land Assessment Specialist which is endorsed by the EPA

- More information go to:
  - Cenvp.org
  - www.epa.nsw.gov.au/clm/selectaclmcons.htm

# Upcoming Events - EIANZ

# Upcoming Events - EIANZ

- 18 May, 15 June – *"Learning to Adapt"* Climate Change Adaptation Professional Development Course, Canberra
- 6 June – EIANZ NSW Division Open Meeting – come along and see how the committee works and give back to the profession

# NSW - Perfluorinated Compounds (PFCs) Forum

Current Status on Understanding of Legal Risk, NSW Regulation, Health Risk, Lab Analysis Limitations, Current and Promising Treatments.

# Today's Presentation

- Outline
  1. Introduction of Speakers and PFCs – What Are They and Why are They a Problem? (Michael Nicholls)
  2. PFCs and current relevant environmental legislation (H&H - Maureen Peatman)
  3. PFCS risk assessment in Australia (Enrisks - Jackie Wright)
  4. Regulation of PFCs (NSW EPA – Andrew Mitchell)
  5. Laboratory Analysis of PFCs and current limitations (ALS – Marc Centner)
  6. PFCs water and soil treatment - current and promising technologies (Michael Nicholls)
  7. Questions

This event will count as 2 points per hour towards your Certified Environmental Practitioner CPD Log.

# Presenter Biographies

## Maureen Peatman (Partner – Hunt & Hunt)

- National Leader of H&H's Environment and Planning Law business (former Chair of Board)
- Re-established and is current Chair of the Australian Environment & Planning Committee of the Legal Practice Section, Law Council of Australia
- Established the Australian Young Environmental Lawyer of the year award (now "Mahla Pearlman Young Environmental Lawyer of the Year" award)
- Highly commended, and has been invited to address various Federal and State Government bodies on Environmental Law matters

## Andrew Mitchell (Manager Hazardous Incidents at EPA NSW)

- Manager of NSW EPA's Hazardous Incidents Division – developing systems and training internally to improve NSW EPA's incidents and emergency response
- Previous Deputy State Environmental Services Functional Area Coordinator focussed on stronger links with other agencies in the emergency management space
- Coordinated NSW's vapour Intrusion Guidelines and NSW Asbestos Emergency Plan
- Previous worked with Olympic Coordination Committee developing EMS for the games.
- Former Environmental Engineer (URS Corp)

# Therese Manning (Principal at EnRiskS)

- 25 years' experience in human health and ecological risk assessment in Australia as a regulator (NSW EPA) and as a consultant (enRiskS).
- Extensive experience in the fate, transport and toxicology of persistent organic pollutants, in particular
- Risk assessment approaches for chemicals; assessment of fate, transport and toxicology of hazardous chemicals; regulation of chemicals management; communication of risks and chemical processes; chemical science promotion
- Member of the NSW Government Williamtown Expert Panel providing advice on the assessment of perfluorinated compounds (risk and toxicology

# Marc Centner (National Technical Manager – ALS)

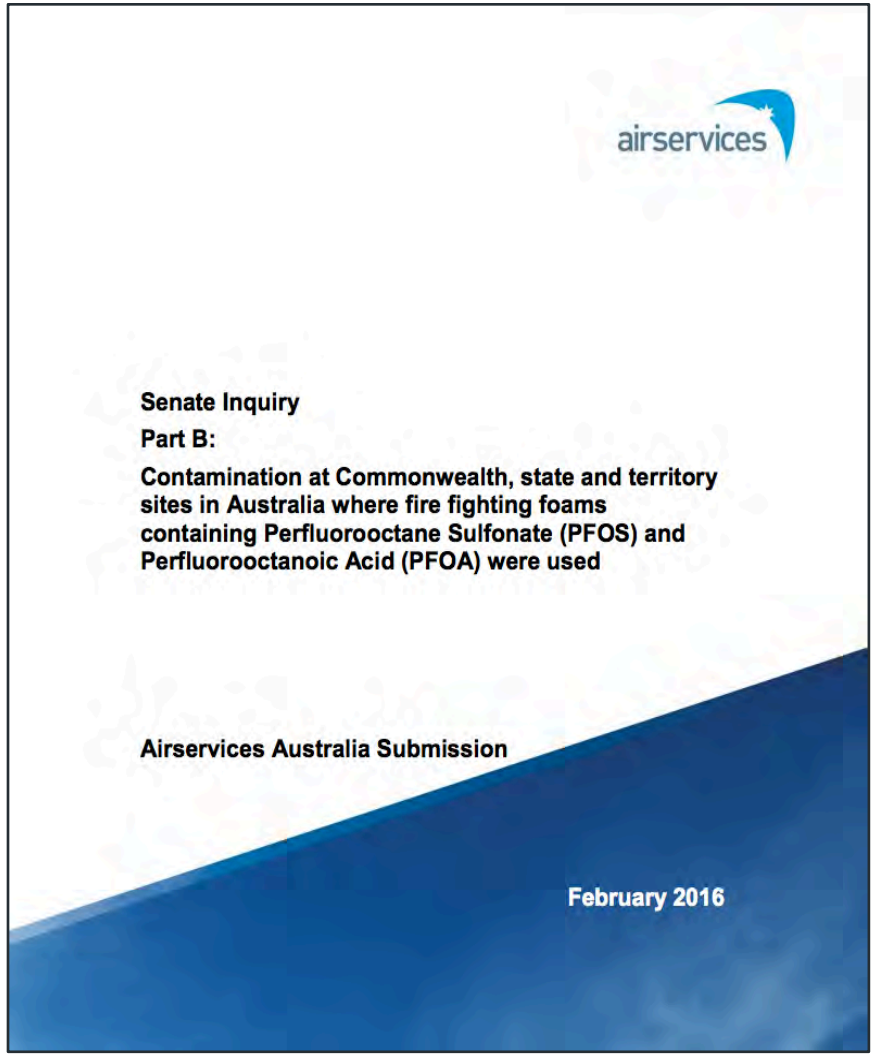
- Technical leader for PFC analysis at Australia's largest laboratory with involvement in PFCs since 2008
- Assisted with technical development of NEPM guidelines
- Research / Papers on Topics such as "Challenges in the measurement of PFOS in environmental samples: are the numbers meaningful to environmental toxicologists and regulators ", "Simultaneous Accumulation and Derivatization of Volatiles Using the Dynamic Solvent Effect" and "Trace analysis of complex organic mixtures using capillary gas-liquid chromatography and the dynamic solvent effect"
- Masterclass presenter / NATA technical assessor and Standards Australia Technical Committee

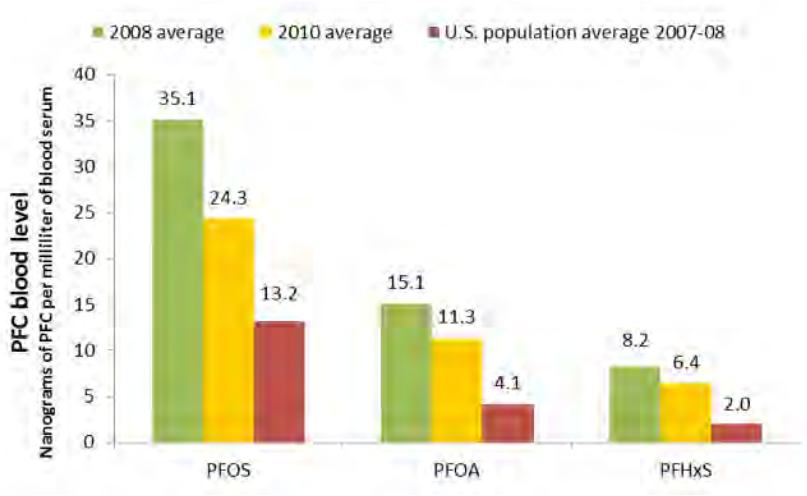
# Michael Nicholls (Director/Principal – iEnvironmental)

- 18 Years contaminated land consulting experience in Australia, China, Middle East
- Presented to China Ministry of Environmental Protection on PFCs and POPs in 2012
- PFC enthusiast; currently running a PFC R&D program on treatment for PFC leaching from cement (KiStrategies)

# This Presentation

- Outline
  1. PFCs – what are they and why are we worried?
  2. PFCs – how much do we really know?
  3. PFCs – what can we do about them once they are out?





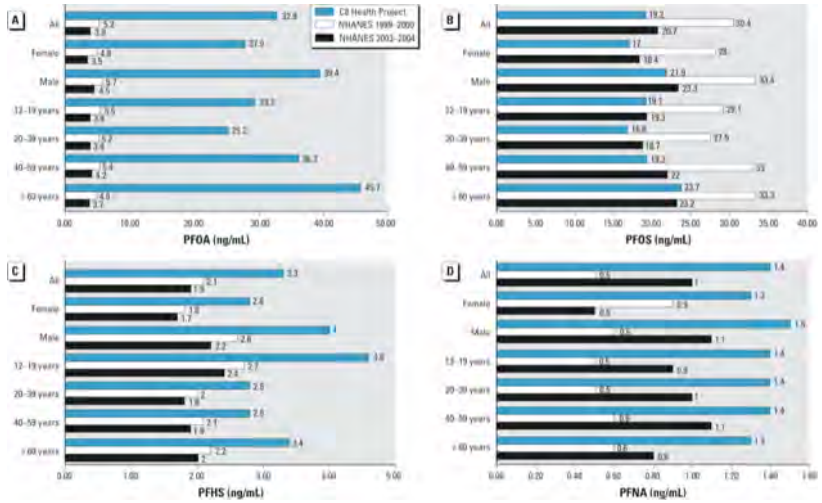




FIGURE 2.

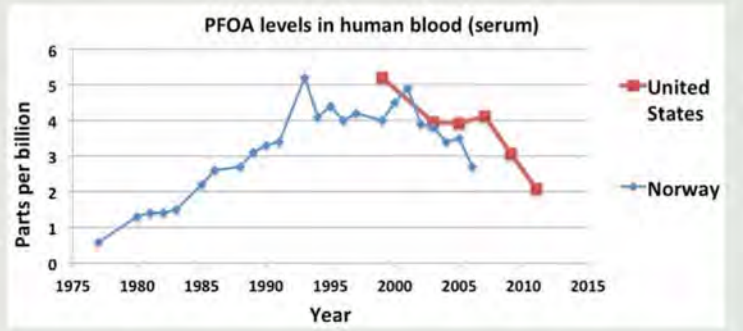
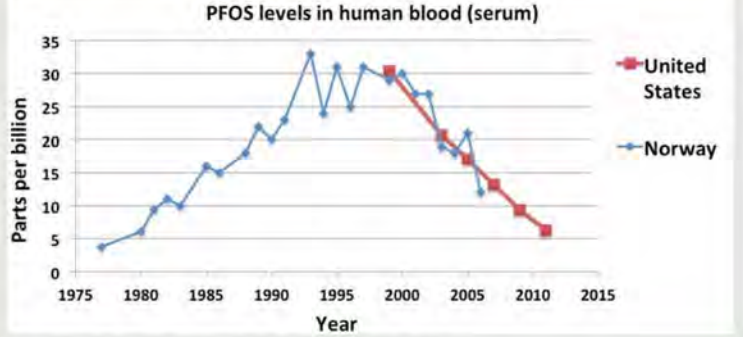



FIGURE 3.



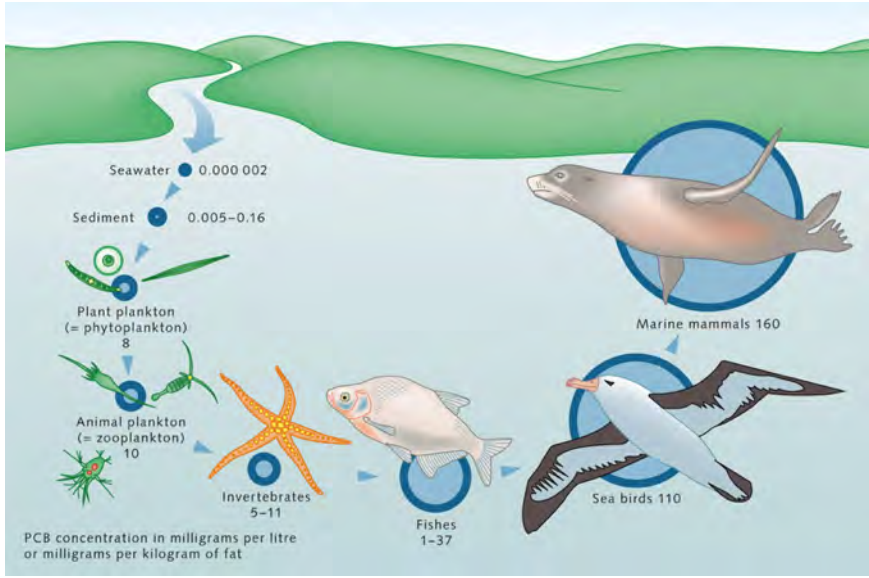

*Source: Environmental Working Group, from NHANES 2015.*

# 1. PFCs – what are they and where?

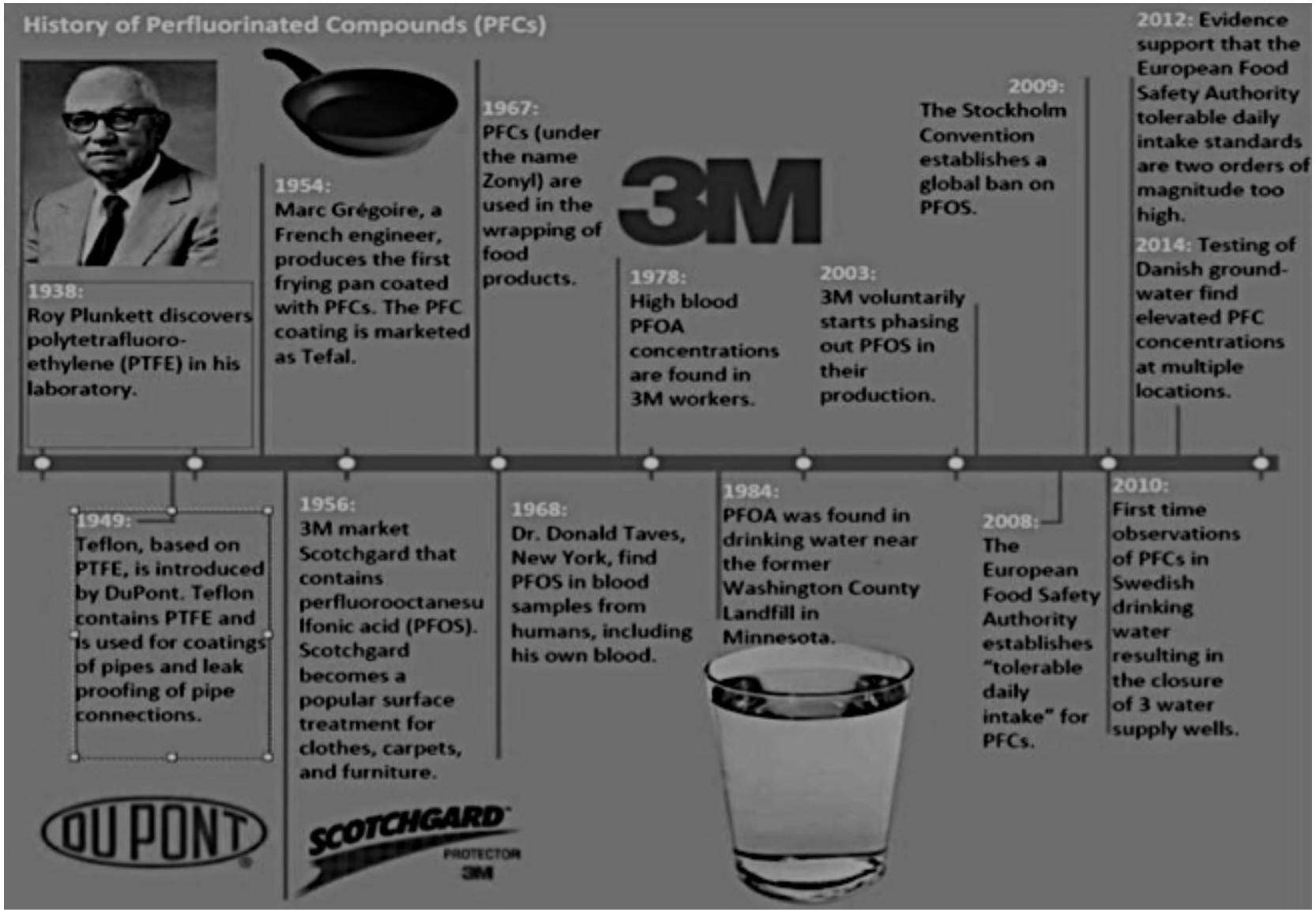
*Per- and poly-fluorinated alkyl substances (PFASs), are also commonly known as PFCs (per- and poly-fluorinated chemicals)*

# PFCs – what are they and where?

- Fully fluorinated compounds that are synthetic substances and not naturally found in the environment
- Very stable chemicals that have both lipid- and water-repellent properties, and bioaccumulate
- Carbon chains >=$C_8$ are more persistent in the environment than those with <=$C_7$
- There are two main groups of perfluorinated chemicals used in industry (from NICNAS):
  - perfluoroalkyl sulfonic acids **(PFSA)** group, including chemicals such as perfluorooctane sulfonate **(PFOS)**
  - perfluorocarboxylic acid **(PFCA)** group, including chemicals such as perfluorooctanoic acid **(PFOA)**

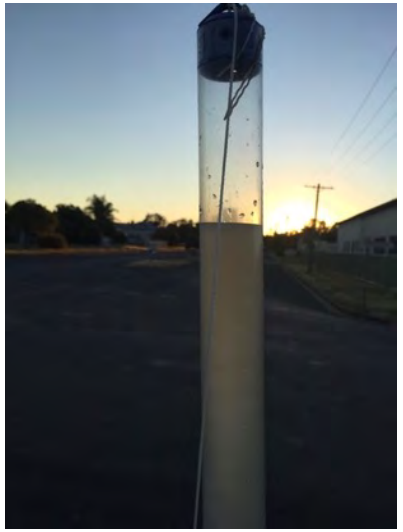


# PFCs


History of Perfluorinated Compounds (PFCs)
1938: Roy Plunkett discovers polytetrafluoro-ethylene (PTFE) in his laboratory.
1949: Teflon, based on PTFE, is introduced by DuPont. Teflon contains PTFE and is used for coatings of pipes and leak proofing of pipe connections.
DUPONT
1954: Marc Grégoire, a French engineer, produces the first frying pan coated with PFCs. The PFC coating is marketed as Tefal.
1956: 3M market Scotchgard that contains perfluorooctanesulfonic acid (PFOS). Scotchgard becomes a popular surface treatment for clothes, carpets, and furniture.
SCOTCHGARD PROTECTOR 3M
1967: PFCs (under the name Zonyl) are used in the wrapping of food products.
1968: Dr. Donald Taves, New York, find PFOS in blood samples from humans, including his own blood.
3M
1978: High blood PFOA concentrations are found in 3M workers.
1984: PFOA was found in drinking water near the former Washington County Landfill in Minnesota.
2003: 3M voluntarily starts phasing out PFOS in their production.
2008: The European Food Safety Authority establishes "tolerable daily intake" for PFCs.
2009: The Stockholm Convention establishes a global ban on PFOS.
2010: First time observations of PFCs in Swedish drinking water resulting in the closure of 3 water supply wells.
2012: Evidence support that the European Food Safety Authority tolerable daily intake standards are two orders of magnitude too high.
2014: Testing of Danish ground-water find elevated PFC concentrations at multiple locations.

# PFCs – what are they and where?

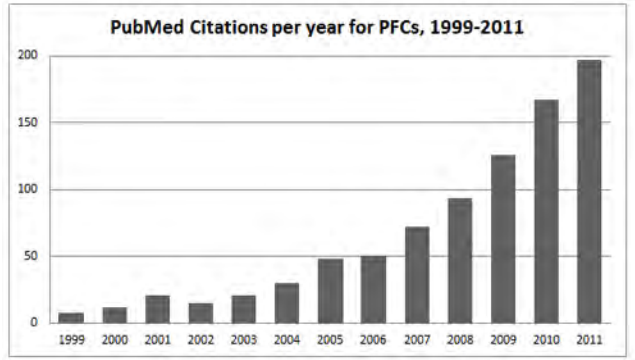
- The are/were found in the following products:
  - > Fire Fighting Foams (60 tonnes estimated as stockpiled in Australia), Grease and Lubricant
  - > Carpeting and Carpet Care
  - > Treated clothing, upholstery, textiles, medical and garments.(i.e. gortex applied membranes or waterproofing sprays)
  - > Food contact (i.e. popcorn bag liner) and PTFE Cookware, Dental Floss
  - > Sealants for stone, tile and wood; (Teflon products ->bailers!)
- 2008 NICNAS Survey Australian import of PFCs ->
  - > PFOS = mist suppressant for chrome plating (99%), and Aviation industry for hydraulic fluid (1%) , and photography industry surfactants (0.002%)
  - > PFAS = metal plating, mist suppressants, fire fighting foams, carpet treatments, curatives, industrial coatings and printing inks
- Present in all of our blood!

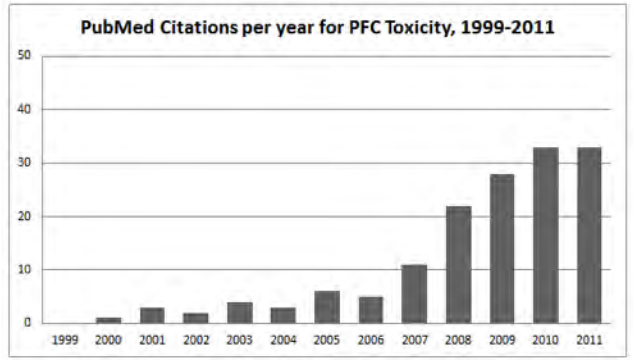


# PFCs – what are they and where?

- No manufacture in (or export from) Australia (NICNAS Senate Enquiry 2014)
- Approx. 7.4 tonnes and 13.6 tonnes of PFAS (as technical grade and in products) were reported imported into Australia in 2006 and 2007, respectively
- Approx. 160,000 litres of class B fire fighting foam products containing between 0.1-7% PFOS formulations (7.6 tonnes) were held in stock (2007) for emergency use
- How to dispose safely?

# 2. PFCs – how much do we really know?



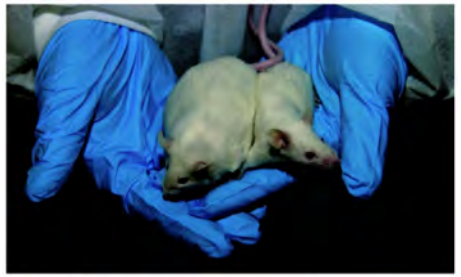

**All Studies MeSH String:** (perfluorinated[All Fields] AND compounds[All Fields]) OR PFCs[All Fields]
**Toxicity Studies MeSH String**: (perfluorinated[All Fields] AND compounds[All Fields]) OR PFCs[All Fields] AND (("toxicity"[Subheading] OR "toxicity"[All Fields]) OR ("epidemiology"[Subheading] OR "epidemiology"[All Fields] OR "epidemiology"[MeSH Terms]))

Total citation counts for all time are as follows:

- PFC Citations: 1046 (863 for 1999-2011). Earliest citation: 1973
- PFC Toxicity Citations: 180 (151 for 1999-2011). Earliest citation: 1982

# PFCs – how much do we really know?

- Limited evidence of health effects on humans
- Number of studies showing PFCs effects on animals
- Chemicals are extremely stable
- Do not hydrolyse, photolyse, or biodegrade under typical environmental conditions
- Are extremely persistent in the environment – i.e. half-life (at 25$^{o}$ C) in water for PFOA and PFOS is > 92years and > 41 years respectively
- High potential to absorb to substrates



Fiskville CFA training facility permanently closed after toxic chemicals found

By Alison Savage

Updated 26 Mar 2015, 5:15pm

**The Country Fire Authority's Fiskville training centre, which was at the centre of a cancer cluster investigation, will be closed permanently after toxic chemicals were found at the site earlier this month.**

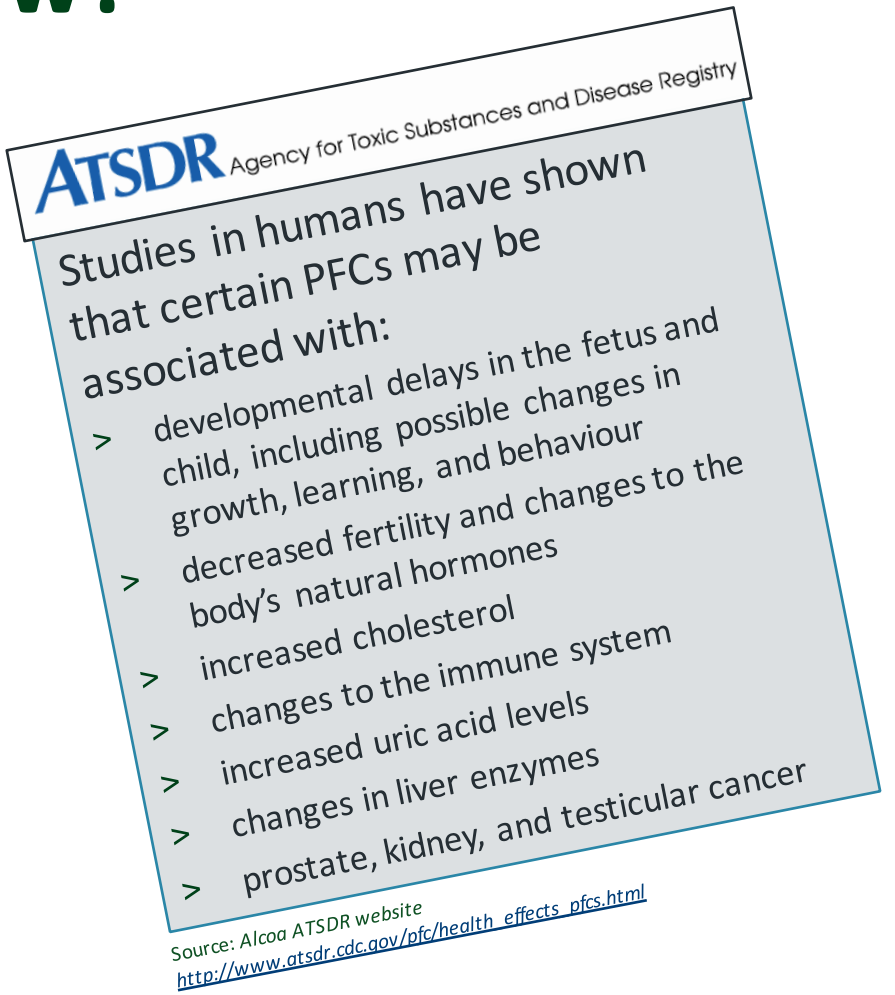
The centre near Ballan, north-west of Melbourne, was temporarily closed in early March when tests found the toxic chemical PFOS in mains water stored in tow large tanks.

Authorities conducted 550 new tests on the site and found some areas had levels of PFOS more

PHOTO: CFA firefighters at a graduation ceremony at the

# PFCs – how much do we really know?

- ATSDR:
  - > Scientists are not sure about the possible health effects of human exposure to PFC
  - > PFOS, PFOA, PFHxS and PFNA have been more widely studied than other PFCs
  - > Animals exposed to some PFCs at high levels have shown changes in the function of the liver, thyroid, pancreas, and hormone levels
  - > PFCs behave differently in humans than they do in animals
  - > PFCs build up and remain in the human body and the amount reduces very slowly over time
  - > More research is needed to confirm or rule out possible links between health outcomes and exposure to PFCs and to quantify the associated dose-response relationships



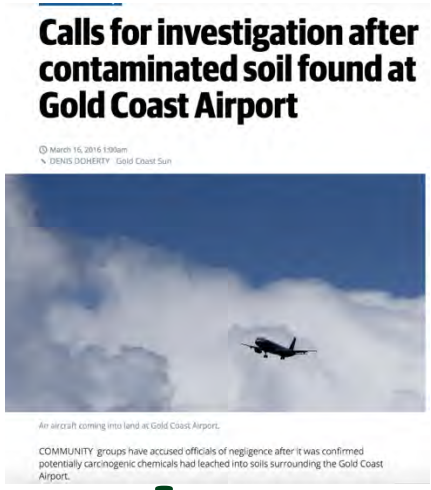

Source: Alcoa ATSDR website
http://www.atsdr.cdc.gov/pfc/health_effects_pfcs.html


CANCER CLUSTER

Cancer cluster: EPA considers testing water at Coakley Landfill

Community meeting in Rye on Thursday

The Environmental Protection Agency is considering a local lawmaker's request to test waters around the now closed Coakley landfill in Greenland and North Hampton, seen at the upper left, for perfluorochemicals contamination. Photo by Joanna Raptis/Seacoastonline


Calls for investigation after contaminated soil found at Gold Coast Airport

An aircraft coming into land at Gold Coast Airport.

COMMUNITY groups have accused officials of negligence after it was confirmed potentially carcinogenic chemicals had leached into soils surrounding the Gold Coast Airport.


Herald Sun

Common camping gear found to house toxic chemicals

Chemicals in waterproofing tents has Greenpeace hopping mad.

CAMPERS and other lovers of the outdoors are being urged to s products that contain harmful chemicals used in waterproofing.


Queensland town in Defence water contamination scare

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October 1 2015

Amy Remeikis

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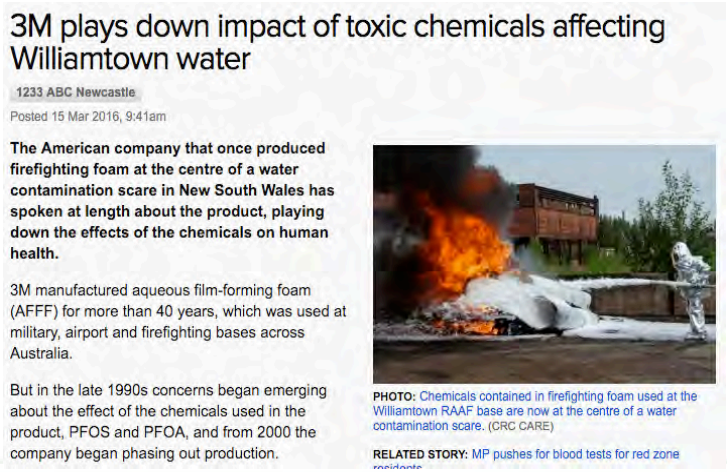
Residents of a Queensland town face living with potential health time bombs after chemicals used for decades at an army aviation base were found to have leached into the ground and contaminated part of the ground water supply.

It has left some residents with chemical levels 44 times the national average in their blood.

# 2. PFCs – what can we do about them once they are out?


3M plays down impact of toxic chemicals affecting Williamtown water

1233 ABC Newcastle

Posted 15 Mar 2016, 9:41am

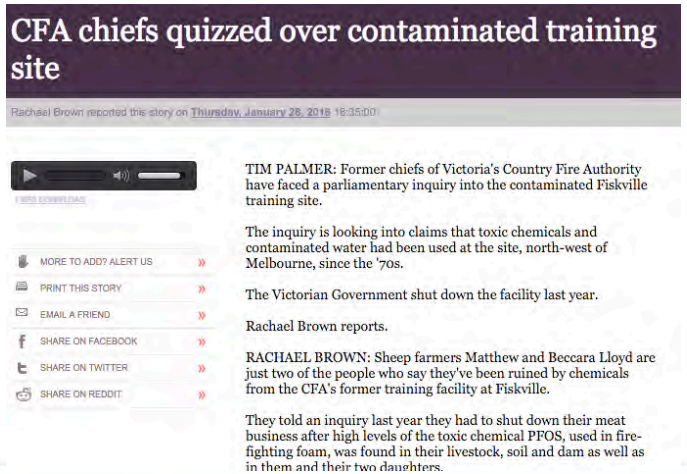
**The American company that once produced firefighting foam at the centre of a water contamination scare in New South Wales has spoken at length about the product, playing down the effects of the chemicals on human health.**

3M manufactured aqueous film-forming foam (AFFF) for more than 40 years, which was used at military, airport and firefighting bases across Australia.

But in the late 1990s concerns began emerging about the effect of the chemicals used in the product, PFOS and PFOA, and from 2000 the company began phasing out production.

PHOTO: Chemicals contained in firefighting foam used at the Williamtown RAAF base are now at the centre of a water contamination scare. (CRC CARE)

RELATED STORY: MP pushes for blood tests for red zone


CFA chiefs quizzed over contaminated training site

Rachael Brown reported this story on Thursday, January 28, 2016 18:35:00

MORE TO ADD? ALERT US

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TIM PALMER: Former chiefs of Victoria's Country Fire Authority have faced a parliamentary inquiry into the contaminated Fiskville training site.

The inquiry is looking into claims that toxic chemicals and contaminated water had been used at the site, north-west of Melbourne, since the '70s.

The Victorian Government shut down the facility last year.

Rachael Brown reports.

RACHAEL BROWN: Sheep farmers Matthew and Beccara Lloyd are just two of the people who say they've been ruined by chemicals from the CFA's former training facility at Fiskville.

They told an inquiry last year they had to shut down their meat business after high levels of the toxic chemical PFOS, used in fire-fighting foam, was found in their livestock, soil and dam as well as in them and their two daughters.


NSW EPA to investigate 'historical legacy' of perfluorinated compounds

Lucy Carter reported this story on Monday, February 22, 2016 12:31:00

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ELEANOR HALL: The New South Wales environment watchdog has joined Queensland and Victoria in announcing an investigation into perfluorinated compounds in the water supply.

The chemicals have been widely used but their impact on human health is unknown.

The six-month investigation in New South Wales will be specifically looking at airports, industrial sites and fire-fighter training facilities where the chemicals may have leeched into water supplies, as Lucy Carter reports.

LUCY CARTER: From Teflon non-stick coatings to fire-fighting foam, the chemicals known as perfluorinated compounds or PFC's have had a wide range of speciality uses over the past few decades.

IAN MUSGRAVE: Because of the fluorine atoms on them, that makes them very resistant to breakdown and it also makes them very water repellent.

# What can we do about them once they are out?

- **Detection** – accuracy is developing – *more later*
- **Risk threshold** – understanding of group of contaminants & human and ecological health risk (3 generations exposed). C8 Science Panel ; www.**cfa**.vic.gov.au/about/**fiskville**-investigation/ – *more later*
- **Regulation** – use overseas regs or develop our own? – *more later*
- **Treatments** – some promising PFC-impacted soil, water and concrete (yes concrete) treatments – *more later*
- New firefighting foams developed / replacement technologies
- **Legal** – where do we stand with all the uncertainty? – *more now*

# Contact

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# Environment Institute of Australia and New Zealand (EIANZ)

# PFCs Seminar

**27 April 2016, 5.30 pm**
**The Grace Hotel, 77 York Street, Sydney**

Maureen Peatman

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Perfluorooctanoic acid, or PFOA for short, is part of a group of chemicals called perfluorochemicals. They have become quite widely used in the last 50 years or so, because they are very effective at repelling things like oil, water, grease and heat. It makes them ideal for non-stick coatings for cookware, flame-resistant and waterproof clothing, and stain-resistant carpets and paint.



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Perfluorinated compounds (PFCs) (fire fighting foams and others) – associated acronyms AFFFs (fire fighting foams), PFOS, PFOA – can lead to contamination in groundwater, soil, waterways and other contamination at and surrounding Defence airfields, airports, fire fighting training facilities and other industrial sites that have used fire fighting foams or produced PFC products ie Teflon and Scotchgard etc.



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# Prosecutions

Prosecutions will be brought by the Environment Protection Authority of NSW under the provisions of the *Protection of the Environment Operations Act 1997*(POEO Act). There are several provisions under the POEO Act which enable the EPA to prosecute in relation to this type of pollution. The most likely type of prosecution would be for the pollution of waters.



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**Section 116(1)** relevantly provides:

*116. Leaks, spillages and other escapes*

*(1) If a person wilfully or negligently causes any substance to leak, spill or otherwise escape (whether or not from a container) in a manner that harms or is likely to harm the environment:*

*(a) the person, and*

*(b) if the person is not the owner of the substance, the owner, are each guilty of an offence.*

**Section 120**

A person who pollutes any waters is guilty of an offence.



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Water pollution or pollution of waters is defined the dictionary.

If the matter would, had it been placed in any waters, have polluted or have been likely to pollute those waters.

"**Waters**" means the whole or any part of:

a) any river, stream, lake, lagoon, swamp, wetland, unconfined surface water, natural or artificial watercourse, dam or tidal waters (including the sea), or

b) any water stored in artificial works, any water in water mains, water pipes or water channels, or any underground artisian water.

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**Question:** ***What does the case law tell us?***

Prosecutions for contamination fall within the Class 5 jurisdiction of the Land and Environment Court of New South Wales. We will examine some of the cases which demonstrate the risks but also the most appropriate way to deal with a contamination incident.



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## *Environment Protection Authority v Austar Coalmine Pty Limited* [2011] NSWLEC 252 a decision dated 12 December 2011 by Preston CJ.

- Austar pleaded guilty to having committed an offence against 120(1) of the *POEO Act* of polluting waters.
- The offence involved an unknown amount of water containing two pollutants, a detergent and effluent from a bathhouse, escaping on 29 July 2010 into a creek called Bellbird Creek. The pollutants travelled about 2 kilometres downstream to the Doyle Street Dam. All the land was owned by Austar.
- Austar operated an underground coalmine at Wollombi Road, Pelton.



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**Question:** ***What did the Court do?***

The maximum penalty for a corporation for the offence is $1m. The Court considered:

a) Objective harmfulness of offence - environmental harm
b) Foreseeability of risk of harm
c) Practical measures to prevent risk of harm (241(1)(b) POEO Act)
d) Control over causes
e) Complying with orders (241(1)(e) POEO Act)
f) State of mind of the offender



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# Subjective Circumstances

a) Prior criminality
b) Plea of guilty
c) Contrition and remorse
d) Assistance to authorities
e) Synthesising the objective and subjective circumstances

Held:

Austar was ordered to pay a penalty in the sum of $100,000 to be reduced by 25% for the early plea of guilty – therefore $75,000, coupled with publication of the fine and payment of the Prosecutor's costs in the sum of just under $40,000.

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## *Environment Protection Authority v Coggins* [2003] NSWLEC 111, a decision by Cowdroy J on 20 June 2013

The EPA charged Coggins under Section 116(1) and 120(1) of the *Protection of the Environment Operations Act 1997*. Coggins pleaded guilty to the offence under section 116(1) and the EPA dropped the offence for polluting waters.

Coggins was the Course Superintendent at Warringah Golf Club Limited and on 9 February 2001 used a pesticide in an area in close proximity to Brookvale Creek which resulted in pollution of the Creek and Manly Dam.



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Again, the judge took into account:

a) the extent of the harm caused (death of more than 10,000 fish - 4.16 tonnes);
b) the evidence showed:
   - no long term damage;
   - prior to the pollution event, the lagoon had poor quality water, making the pollution event more severe;
   - it was not reasonable to attribute the entire biological effects of the fish kill to the escape of the pesticide on 12 January 2001.



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The Court held that the degraded quality of the lagoon did not mitigate the defendant's conduct and it took into account:

a) practical measures to prevent or control, abate or mitigate such harm;
b) foreseeability of harm caused or likely to be caused to the environment;
c) the extent to which the defendant had control over the offence;
d) plea of guilty.



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# Deterrence

**Defendant's character**

The Court must determine whether the defendant is of otherwise good character and if established take it into account as a mitigating factor in the sentencing process. The defendant is, and has been, a person of excellent character. He has no criminal record. He has an unblemished employment record.



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## Consequences of the offence

The defendant had incurred expenses in the sum of $220,000 for legal advice and expert evidence. He had been obliged to sell his house in Sydney and to relocate his family to less expensive accommodation near Coffs Harbour with financial assistance provided by relatives.



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The Court acknowledged that the defendant and his family had to alter their lives as a result of the offence. However, such changes do not constitute extreme and exceptional hardship, see *R v T* (1990) A Crim R 29 at 40 where Gleeson CJ said (at 40) that:

> "*The hardship must be so extreme – going so far beyond the sort of hardship which inevitably results to a family when the breadwinner is imprisoned*"

to warrant a sentencing judge to be more lenient. His Honour gave an example of such hardship being:

> "*where a wife is mentally ill and is at risk of suicide unless supported by the companionship of the offender*".



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## The extent of the defendant's cooperation

Initially the defendant gave a false account of the circumstances leading to the offence. The Court was satisfied that the defendant provided the false account because of his fear of the consequences of his actions. To his credit, he confessed within a matter of days that the account was not true.

## Penalty

Offences against section 116 of the POEO Act are considered by the legislature to be within the tier of most serious environmental pollution offences. The defendant's counsel requested a section 10 which the Court rejected. The Court ordered that the defendant should serve, by way of penalty, community service (maximum would be 500 hours) and the Court ordered 250 hours of community service.



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# HUMAN HEALTH RISK ISSUES ASSOCIATED WITH PFAS

**Jackie Wright, Therese Manning and Ruth Jarman**

**Environmental Risk Sciences Pty Ltd (enRiskS)**

**Environment Institute of Australia and New Zealand**

**27 April 2016**

# OVERVIEW

- Overview of toxicity for PFOS/PFOA
  - Exposure pathways
  - Toxicokinetics – what happens in the body when exposed
  - How do we measure toxicity in humans?
  - Elimination half-lives and differences between animals and humans
  - Toxicity of PFOS/PFOA to animals and humans
- How does this translate to guidelines?

# EXPOSURE PATHWAYS

- At environmental pH PFOS / PFOA will exist primarily as an anion in water
- Vapour inhalation pathway not applicable: PFOS / PFOA are not volatile at environmental pH
- Blood data shows most people have been exposed to low levels
- Potential exposure pathways:
  - Oral.
  - Dermal.
  - Inhalation of dust.
  - Secondary uptake e.g. transfer of PFOS into the food chain following accumulation of PFOS in crops, livestock or fish.



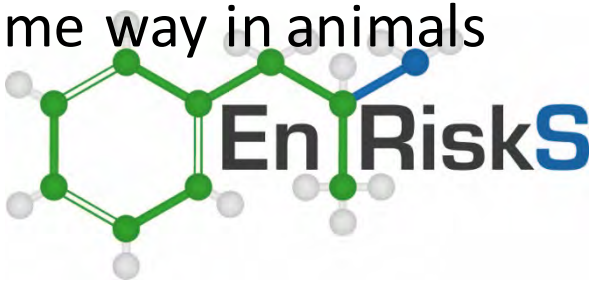



## TOXICOKINETICS

- Rapidly absorbed following oral exposure.
- PFAS has a high affinity for serum albumin/protein so easily distributed throughout the body - different to other POPs which accumulate in fatty tissue.
- These chemicals are not readily metabolised in most organisms including mammals.
- Excretion is the only means where toxicity is reduced – not much excreted.
- Can be species and gender dependent.

# How Do We Measure Toxicity in Humans?

- Human (Occupational/Epidemiological) Studies:
  - Small number of participants.
  - High occupational exposure.
  - May not be able to tell what the adverse effect is due to confounding factors.
- Animal studies:
  - Doses/exposure concentrations usually much higher than the general population is exposed to.
  - Smaller animals are cheaper to study however may not reproduce effects in humans.
  - Assumes the chemical behaves the same way in animals and humans.
  - Animal ethics is limiting.



# ELIMINATION HALF-LIFE: ANIMALS VS HUMANS

| Chemical | Human | Monkey | Rat | Mouse |
|---|---|---|---|---|
| PFOS (male) | 4-8 years | 100-200 days | 40-50 days | 40 days |
| PFOS (female) | 4-8 years | 100-200 days | 45-65 days | 34 days |
| PFOA (male) | 2.3 years | 20 days | 12 days | 16 days |
| PFOA (female) | 2.3 years | 20 days | Few hours | 16 days |

- Toxicity can be inferred based on elimination half-life.
- The longer the residence time in the body the greater the potential for adverse health effects?
- Similar residence time for men and women but huge differences between humans and animals...

EnRiskS

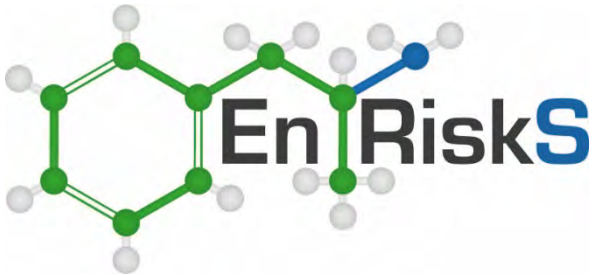
# TOXIC EFFECTS

| Animal studies | Human studies (Epi studies) |
|---|---|
| Liver damage | Increased serum cholesterol |
| Changes in serum cholesterol | Increase in uric acid |
| Decreased pup survival (PFOS) | Liver damage |
| Developmental neurotoxicity (PFOS) | Reduced foetal growth |
| Multigenerational effects on liver and kidney | Serum cholesterol |
| | Increase in liver enzymes |
| Tumours (PFOA) (non-genotoxic) | Decreased bilirubin |
| Reduced foetal growth (PFOA) | Kidney disease |
| Weight loss | Early menopause |
| Endocrine disruption | |
| Potential for impaired immune function | |
| Decreased immunoglobulin | |
| Changes in spleen, thymus and liver | |

*ATSDR Draft Toxicological Profile for Perfluoroalkyls (Aug 2015):*

*Humans and rodents react differently to PFOA and PFOS, and not all of the effects observed in rats and mice may occur in humans. The liver appears to be the most sensitive target in animals ingesting perfluoroalkyls.*

**Some effects in animals are relevant to humans**

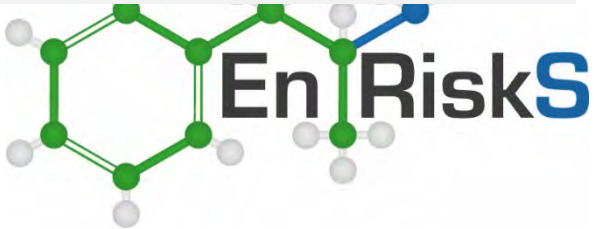


# RECENT ENHEALTH GUIDANCE

- "Human exposure should be minimised as a precaution due to persistence.
- The ingestion of contaminated food is the major human exposure pathway – specific foods may be important.
- The significant health benefits of breast feeding are well established and far outweigh any potential health risks from PFOS/PFOA transferred through breast milk.
- No accepted clinical treatment to reduce levels in the human body.
- Blood testing has no current value in informing clinical management."

enHealth currently reviewing the data and will provide guidance on appropriate TRV to adopt for evaluating human health issues

http://www.health.gov.au/internet/main/publishing.nsf/Content/A12B57E41EC9F326CA257BF0001F9E7D/$File/PFC-guidance-statements-15March2016.pdf



# WHAT TRVS CURRENTLY AVAILABLE

| | PFOS | | | PFOA | | |
|---|---|---|---|---|---|---|
| | POD (mg/kg/d) | UF | TRV (ng/kg/d) | POD (mg/kg/d) | UF | TRV (ng/kg/d) |
| **EFSA 2008** | 0.03 | 200 | 150 | 0.3 | 200 | 1500 |
| **USEPA 2014** | 0.00088# | 30 | 30 | 0.0045# | 300 | 20 |
| **ATSDR 2015** | 0.00252# | 90 | 30 | 0.00154# | 90 | 20 |
| **Danish EPA 2015** | 0.033 | 1230 | 30 | 0.003# | 30 | 100 |
| **USEPA 2009 (DWG)** | 0.03 | 390 | 80 | 0.46 | 2430 | 190 |
| **Minnesota 2009** | 0.0025# | 30 | 80 | 0.0023# | 30 | 77 |
| **Germany 2006** | 0.025 | 300 | 100 | 0.1-1.0 | 1000 | 100 |

# based on human equivalent dose (calculated assuming steady state)

EFSA – currently adopted by FSANZ

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# SCREENING GUIDELINES

- Once we have agreed TRV, we have standard approaches that can be used for determining screening guidelines

Soil

- Water solubility of these compounds means they are easily leached
- Direct contact with soil results in much lower exposure than could occur if groundwater/surface waters nearby are affected
- Instead of soil guidelines based on direct contact it is more appropriate to assess leachability from soil and compare ASLP results to water guidelines for screening

# SCREENING GUIDELINES

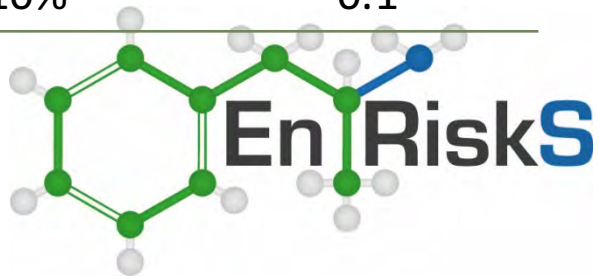
## Water

- Drinking
  - NHMRC drinking water guidelines provides standard calculation to use
  - Assumes 10% of daily intake may come from water we drink (cook, clean, shower etc)
  - Assumes we drink 2 L per day and weigh 70 kg
- Recreational
  - NHMRC guidance indicates that screening guidelines protective for secondary water contact are 10 times the drinking water guideline (effectively means assuming we ingest 200 mLs instead of 2 L per day every day for lifetime and that we only permit 10% of TDI via this pathway)

# DRINKING WATER GUIDELINES – VALUES?

- PFOA not commonly found most Australian sites
- Not large difference between values for PFOS given use of trace level techniques (sampling variability and measurement error)

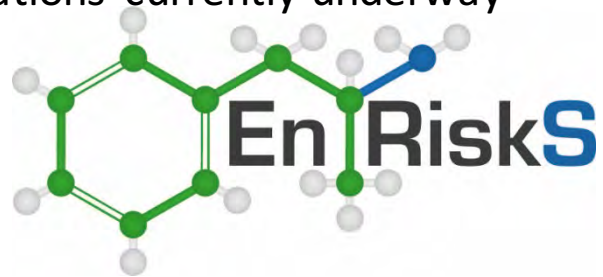
| TRV (µg/kg bw/d) | Ingestion Rate (L/day) | Body Weight (kg) | Relative Source Contribution | Proposed DWG (µg/L) |
|---|---|---|---|---|
| **EFSA 2008** | | | | |
| PFOS – 0.15 | 2 | 70 | 10% | 0.5 |
| PFOA – 1.5 | 2 | 70 | 10% | 5 |
| **USEPA 2014/ATSDR 2015** | | | | |
| PFOS – 0.03 | 2 | 70 | 10% | 0.1 |
| PFOA – 0.02 | 2 | 70 | 10% | 0.1 |



# SCREENING GUIDELINES

## Food

- Seafood
  - Major food group where screening guidelines are needed
  - Can be calculated using TDI and relevant assumptions about how much seafood we eat
  - Median intake for those who regularly eat fish is 110 g/day
  - Can assume 10% of TDI could be obtained via seafood consumption
  - Also assume people weigh 70 kg in line with NHMRC and ASC NEPM recommendations
- Other foods
  - May need to estimate screening guidelines for other types of food – meat, milk, eggs – this will be determined once more information is available from some of the large site investigations currently underway

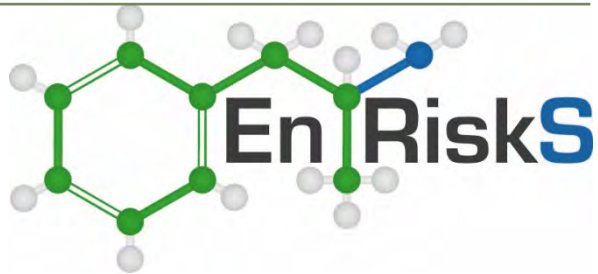


# SEAFOOD SCREENING GUIDELINES – VALUES?

- FSANZ are the normal body who determine these things
- Based on advice provided by them to NSW could calculate following

| TRV (µg/kg bw/d) | Ingestion Rate (kg ww/day) | Body Weight (kg) | Relative Source Contribution | Proposed Screening (µg/kg ww) |
|---|---|---|---|---|
| **EFSA 2008** | | | | |
| PFOS – 0.15 | 0.11 | 70 | 10% | 10 |
| PFOA – 1.5 | 0.11 | 70 | 10% | 100 |
| **USEPA 2014/ATSDR 2015** | | | | |
| PFOS – 0.03 | 0.11 | 70 | 10% | 2 |
| PFOA – 0.02 | 0.11 | 70 | 10% | 1 |

- PFOS will be the driver



# CONCLUSIONS

- We know that PFOS/PFOA cause adverse health effects in animals.
- We do not have a lot of data on the effects of PFOS/PFOA in humans however this is normal - we use animal data to infer toxicity to humans, or lack there of, for many chemicals.
- Some of the effects in animals are relevant to humans and these should also be considered.
- We know that the residence time of PFOS/PFOA in the body is different for animals and humans (significantly longer in humans).
- While there are things we don't fully understand yet, toxicity reference values are available and can be considered for protecting human health.
- Can use the toxicity reference values to develop appropriate screening guidelines.
- enHealth is working on providing advice – coming soon !!

## THANKYOU – QUESTIONS?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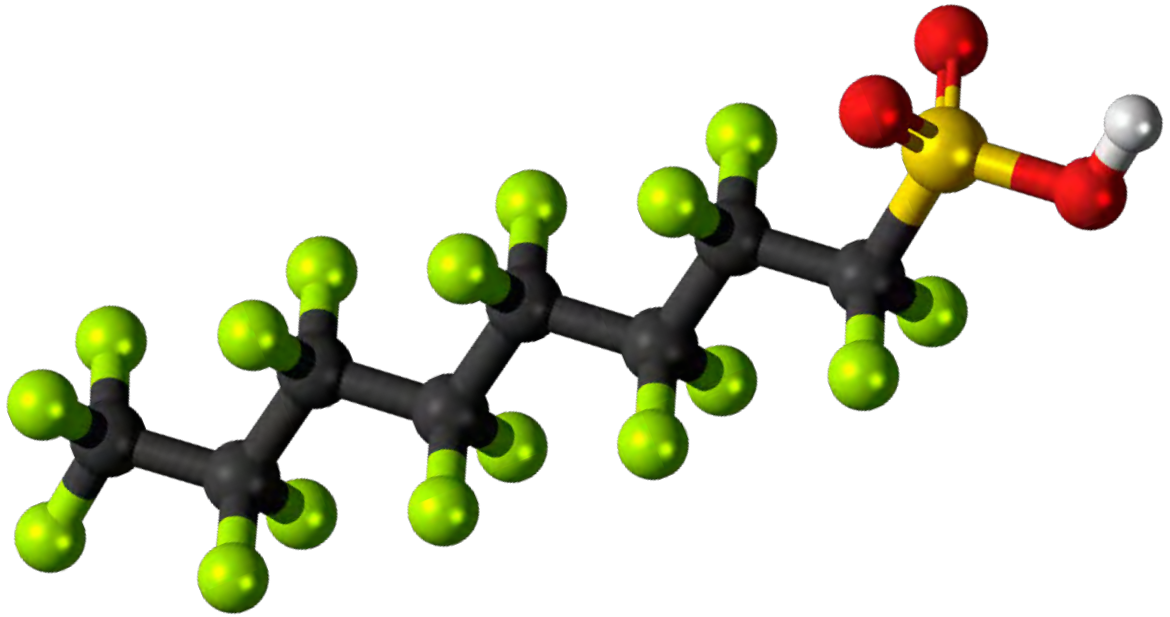
# Forward Strategy on Perfluorinated Compounds (Poly- and Per-Fluorinated Alkyl Substances)



Andrew Mitchell
Manager Hazardous Incidents

# What is the EPA doing?

- Seeking to identify significant current and historical releases to the environment of PFCs.
- Working with the owners or occupiers of sites that may be contaminated.
- Screening these sites to prioritise for further investigation.
- Using appropriate regulatory tools to ensure appropriate remedial outcomes, with regard to risk.
- Communicating about it.

# Where is the EPA looking?

- Firefighting training sites:
  - Fire & Rescue NSW
  - Rural Fire Service
  - Airports
  - Power stations
  - Petrochemical manufacturing and storage
  - Ports
- Foam deluge systems
- Metal plating

# How do we assess risk?

- Emerging contaminant
- Lack of agreed and formal guidance
- Precautionary approach towards a ubiquitous modern chemical
- EnRiskS Decision Tree
  - Neither “made” nor “approved”
  - Prioritises sites for further investigation
  - Allows low risk sites to be ruled out
  - Must be applied consistent with made and approved guidelines

# Decision Tree

- Preliminary samples of surface water and/or groundwater:
  - Onsite:
    - > 10 µg/L → investigate further now
    - > 0.05 µg/L → investigate further in due course
  - Offsite:
    - > 0.1 µg/L → investigate further now
    - > 0.05 µg/L → investigate further in due course
  - Onsite or offsite < 0.05 µg/L → no further investigation warranted (at this stage)

# Decision Tree

- Soils – subject to ASLP leaching rather than total concentration:
  - Leachate > 100 µg/L → investigate further now
  - Leachate > 1 µg/L → investigate further in due course
  - Leachate < 1 µg/L→ no further investigation warranted (at this stage)
- Screening levels are interim subject to further consultation
- Further research needed into PFC partitioning in soils:
  - TOC
  - Clay content
  - Other?

# What is the regulatory role for the EPA?

- Significant contamination – Contaminated Land Management Act
- Pollution – Protection of the Environment Operations Act
- Scheduled premises
- Disposal options – solid and liquid waste
- Contextualisation with other emerging and trace contaminants

# Questions

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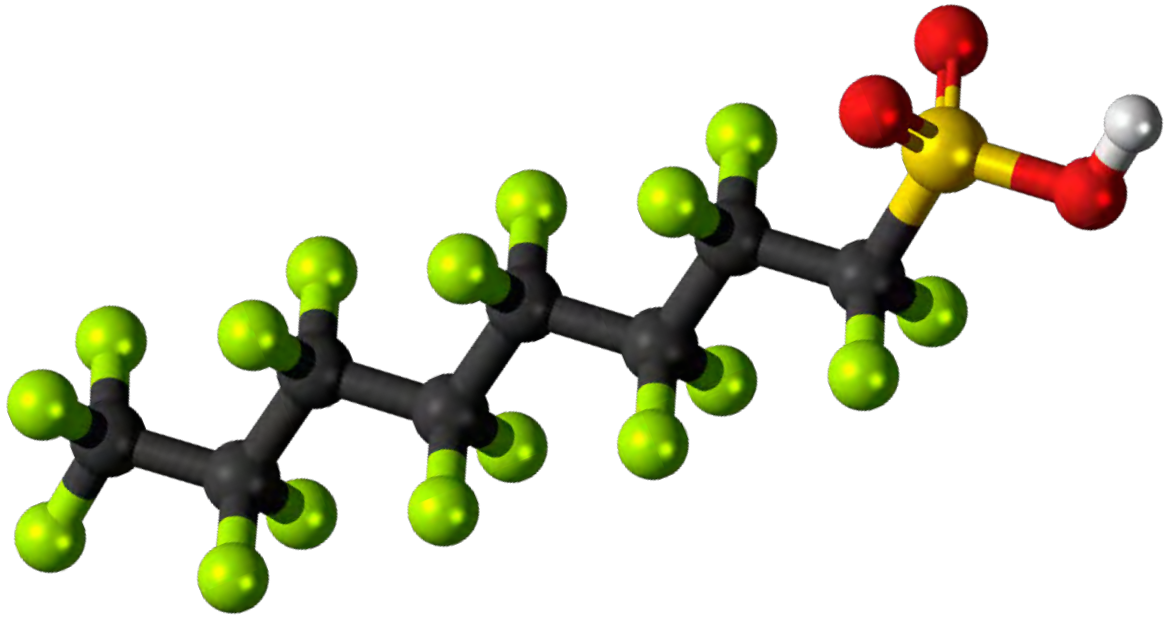

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# Questions

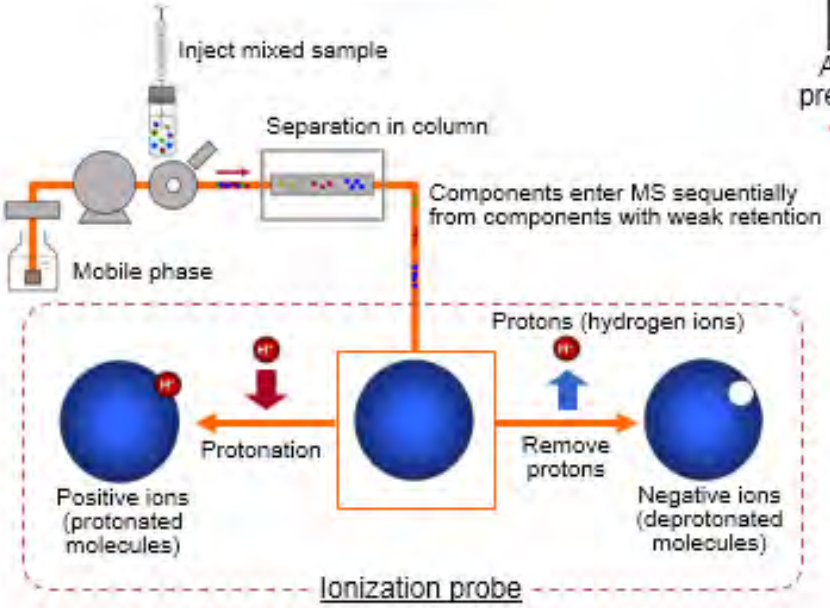
# Laboratory Analysis of PFAS

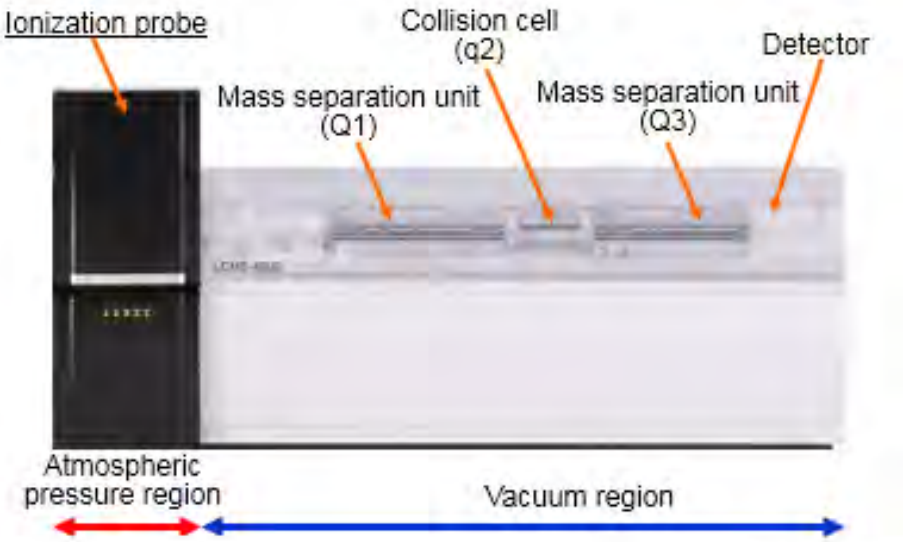
Marc Centner, National Manager, Environmental, ALS Life Sciences, Australia

# Analytical Process

- Extraction
  - none – “direct injection”
  - liquid/liquid,
  - liquid/solid
- Clean Up
  - column cleanup (liquid/solid)
  - dispersive(liquid/solid)
  - liquid partition
- Instrumental Analysis - LCMSMS.

# HPLC-MSMS Analysis

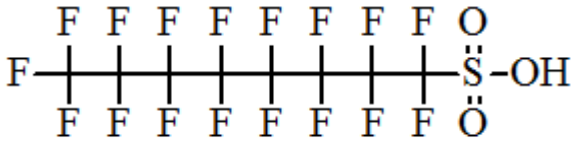



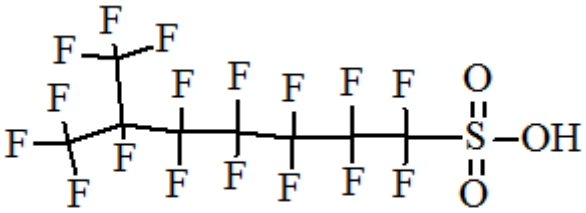


Thanks to Shimadzu Australasia for Images

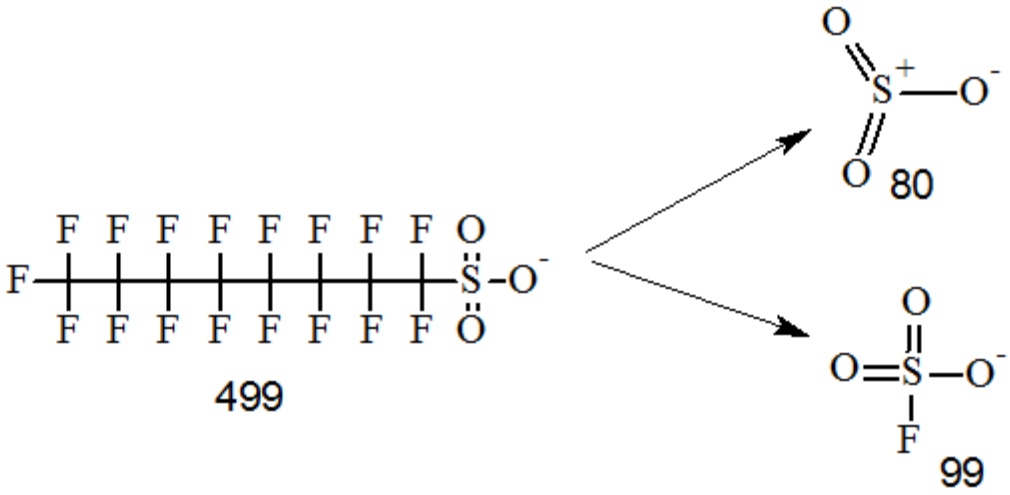
# LCMSMS - PFOS



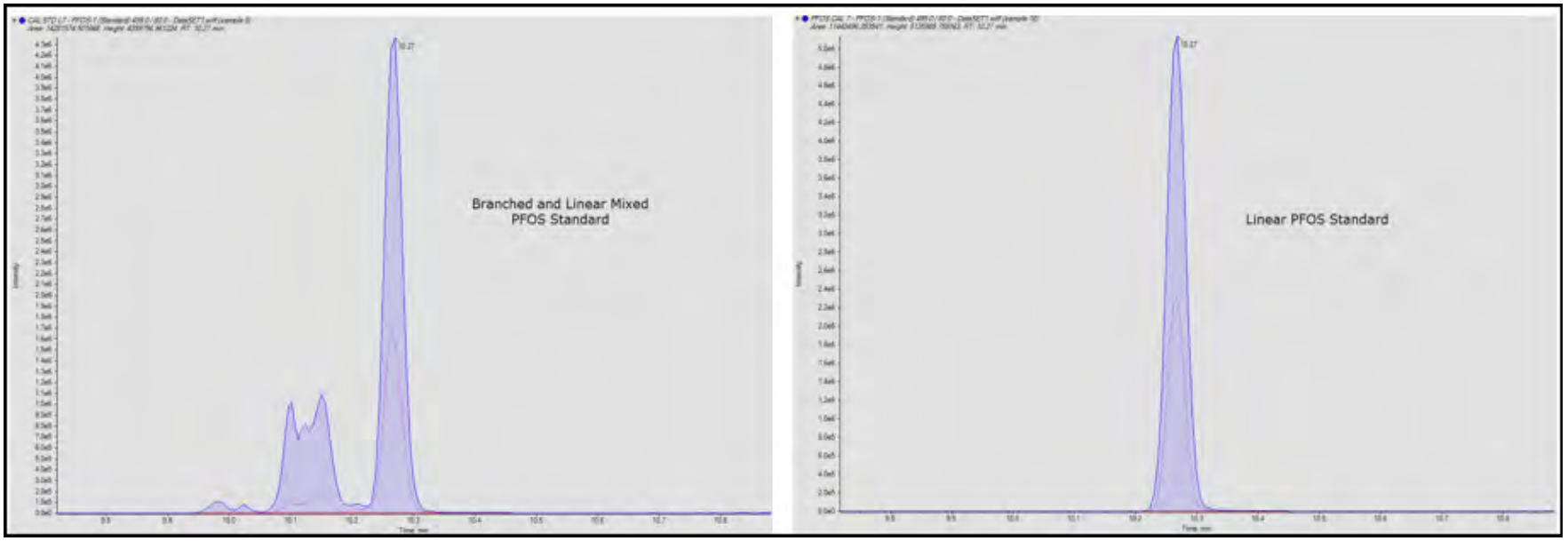
Linear



Branched

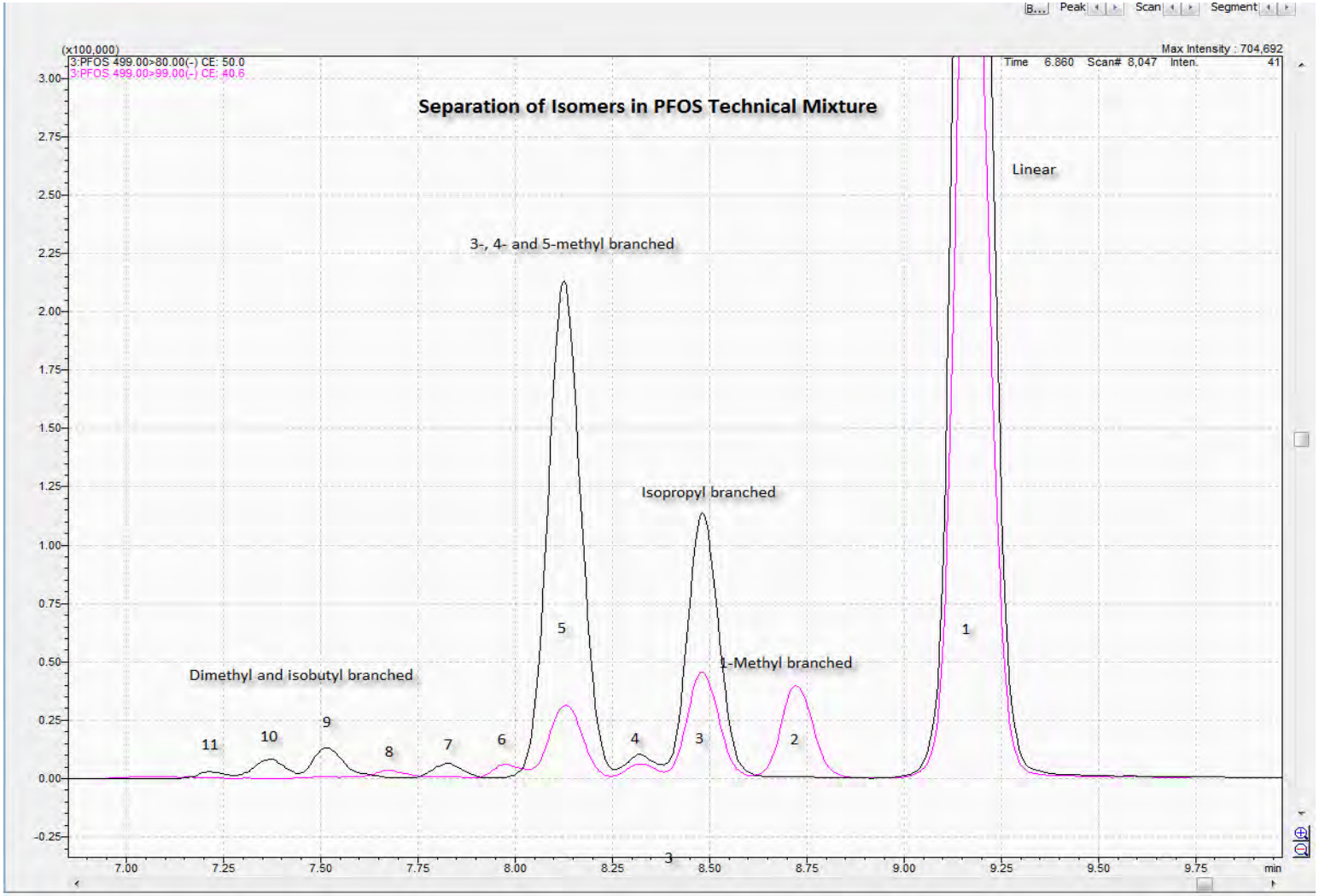


# PFOS – Chromatogram

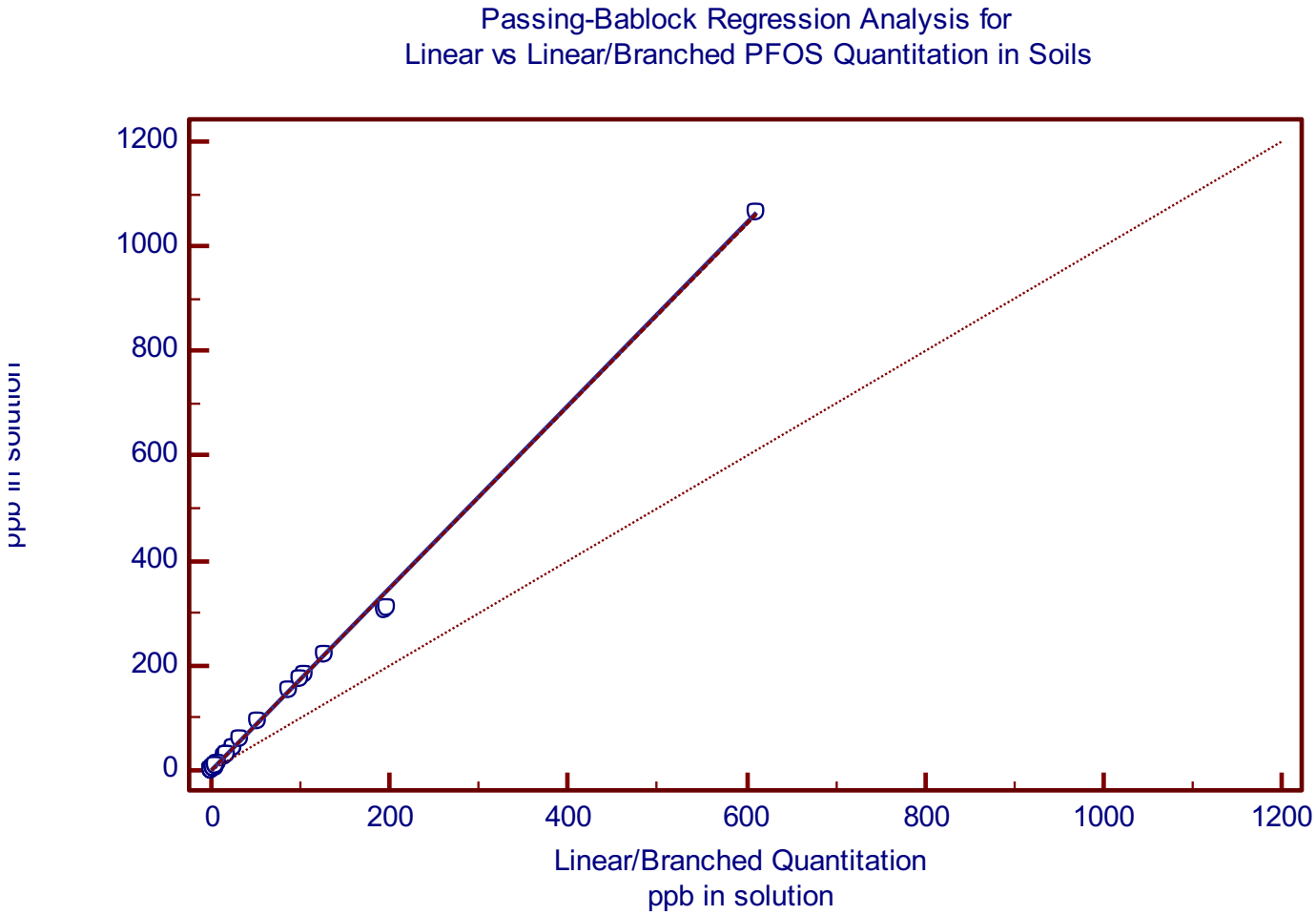



Blue trace is 499 > 80
Pink trace is 499 > 99

# LCMSMS PFOS Full Separation

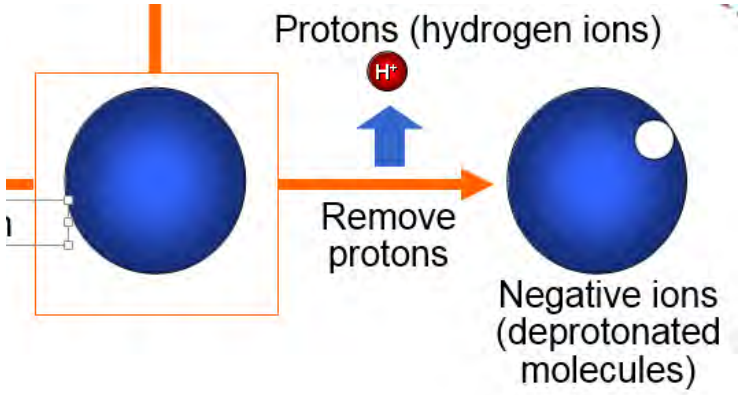


# Quantitation – Which Standard



# Sample Clean-up - 1

- "Soft" ionisation mechanism is prone to matrix induced interferences:
  - Enhancement
  - Suppression




- Extra steps in analytical process provide for increased opportunities for contamination – the simpler the better - avoid by standardisation ("isotope dilution") and sample dilution

# Sample Clean-up - 2

- Clean-up relies on differences between chemistry of target compounds and interferences, e.g. acids vs bases, polar vs non polar.
- Clean-up and extraction can be simultaneous processes by exploiting specificity in extraction. Sometimes possible but difficult multiple target compounds have slightly different chemistries.
- For PFAS, Fluorophilicity represents an interesting approach to sample cleanup – “like dissolves like”

# Sample Preparation - Waters

- "Direct Injection" – a sample is mixed 1:1 with methanol, filtered and analysed.
- A sample is passed through a column containing a solid phase medium that retains target compounds – typically an ion exchange process that retains carboxylic and sulfonic acids – what of other PFAS in products?
- Alternative – ion pairing onto non-polar medium – mixed functionality.
- Analytes eluted with basified methanol.
- Samples filtered prior to analysis – what about PFAS entrained on sediments?

# Sample Preparation - Soils

- Extraction with a polar solvent usually – basified methanol – suitable for sulfonic and carboxylic acids and not specific to PFAS.
- Ion pairing extraction into relatively non-polar solvent suitable for broader range of analytes. Will also extract a broader range of co-extracted interferences
- Generally because of the nature of the work in Australia, many sites highly impacted and dilution (together with standardisation) is the most practical solution.

# PFAS and Good Laboratory Practice

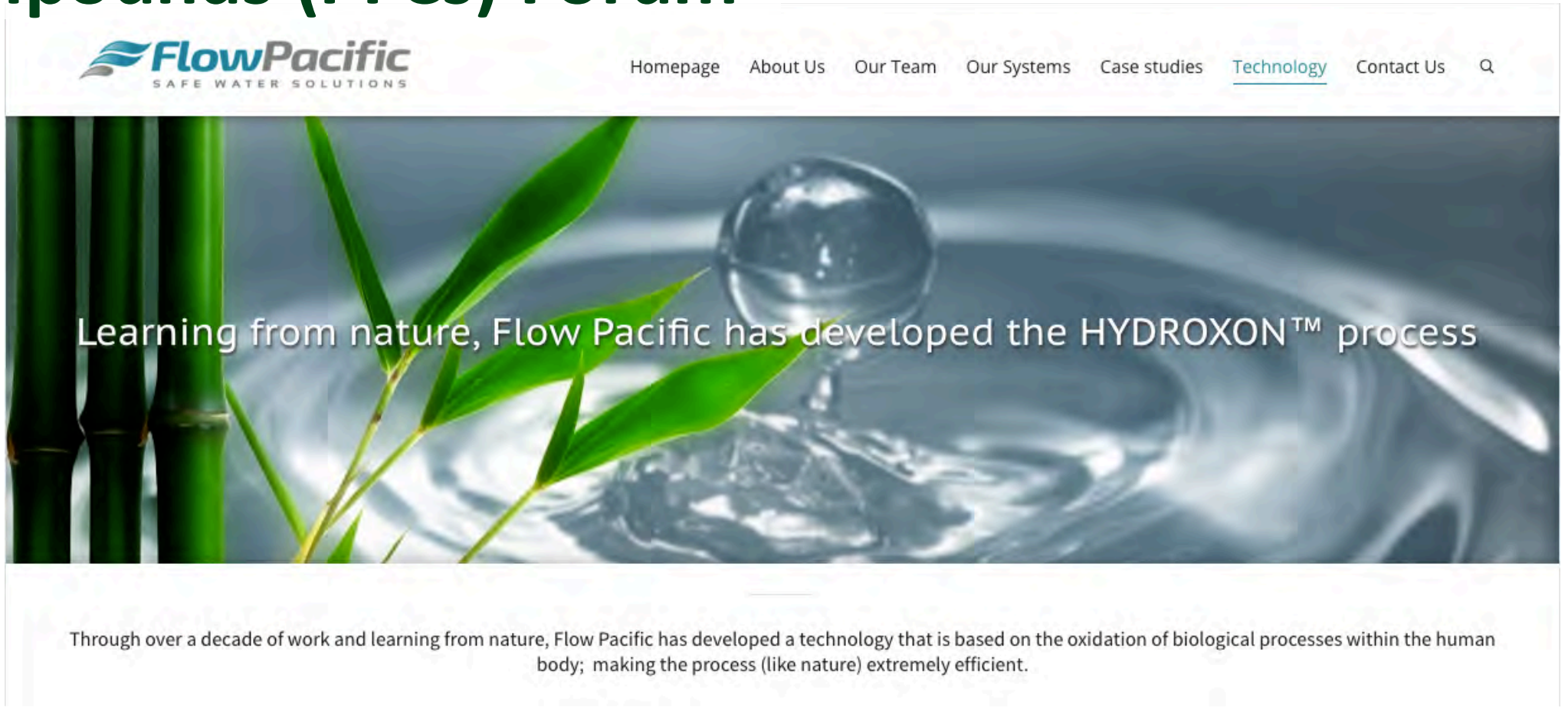
- Test all reagents, glassware and processes for contamination
- Use disposable labware wherever possible.
- Simplify process and eliminate multiple steps in preparation if possible – consider automation.
- Thoroughly decontaminate after highly impacted samples – good client information on potential impact is invaluable.
- Consider isolation of clean waters, from impacted soils, spatially or temporally in preparation laboratory.
- Understand analytical context – do results make sense?

# Thank You – Suggested Reading

The literature is extensive:

- Anything by Jennifer Field and co-workers – discusses what actually is in AFFFs.
- J. P. Benskin, J.P, A. O, Da Silva and J. W. Martin, 2010, Isomer Profiling of Perfluorinated Substances as a Tool for Source Tracking: A Review of Early Findings and Future Applications, in *Reviews of Environmental Contamination and Toxicology,* 208.

# NSW - Perfluorinated Compounds (PFCs) Forum




Current and Promising Treatment Technologies

# This Presentation

- Outline
  1. Development of PFC contamination treatments
  2. Current Promising Water Treatments
  3. Current Promising Soil Treatments
  4. Current Promising Concrete Treatments

# 1. Development of PFC contamination treatments

# Development of PFC contamination treatments

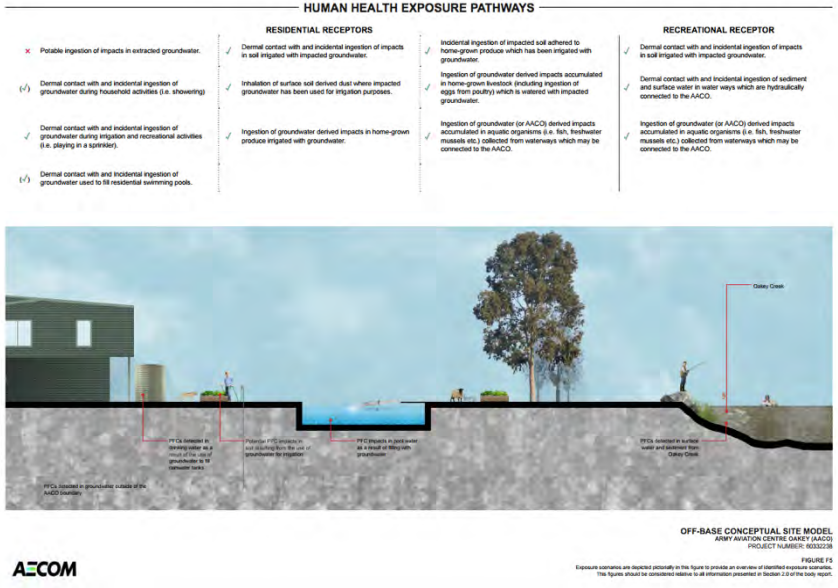
- What needs to be treated:
  - **Drinking water**
  - **Surface water** and sediment
  - **Groundwater**
  - **Soil**
  - **Landfill leachate**
  - **Concrete impacted with PFCs**
  - Water treatment biosolids - *USEPA notes that "incineration of the concentrated wastes would be needed for the complete destruction of PFCs"(Emerging Contaminant Fact Sheet –PFOS and PFOA2014).*
  - Waste (various)

# Development of PFC contamination treatments

- Studies are still being undertaken on how various PFCs of different chain lengths are distributed throughout the body and excreted
- Previously thought due to lower persistence, that small chain PFCs are likely less toxic, and thus short chain PFCs have been used as PFOS replacements.
- However toxicity of short chain PFCs is not understood, and conventional treatments do not adsorb short chain PFCs http://www.ewg.org/research/poisoned-legacy/how-safe-are-alternatives-long-chain-pfcs
  - November 2014 - a group of prominent international scientists published the Helsingør Statement - discussion paper raising concerns about the transition from long-chain PFCs to alternatives with fewer carbon atoms.
  - May 2015 – Madrid Statement - group of prominent scientists – concerned with continued PFAS production, and seek prevention of use of fluorinated alternatives

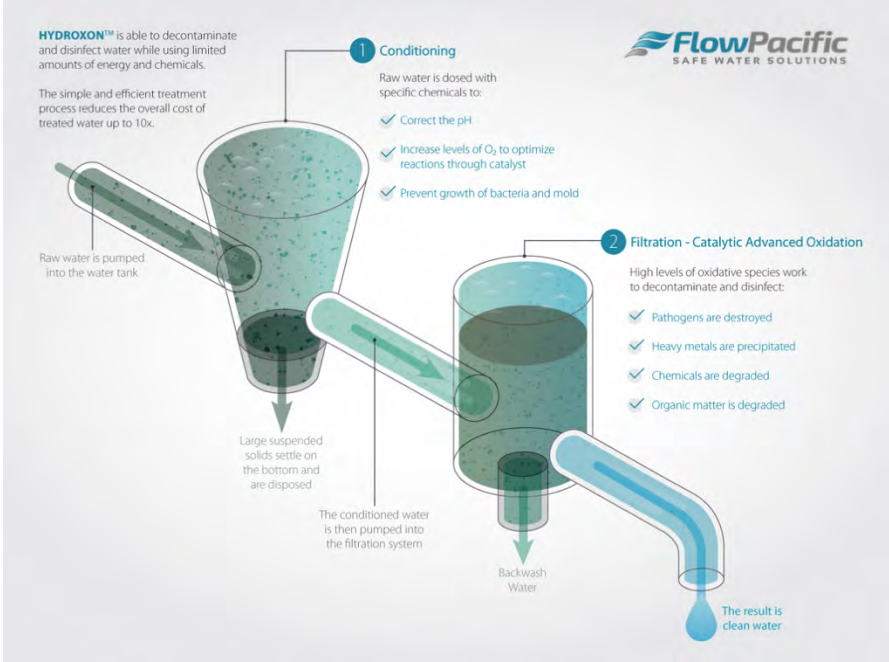
# Development of PFC contamination treatments

- Case Study: Dept of Defence Oakey (AECOM July 2015 Source Study) - Active and Depleting Sources of PFCs
  - > Sources:
    - Current stocks of AFFF
    - PFCs impregnated base infrastructure (concrete of fire training ground)
    - Residual contamination in fire fighting vehicles and equipment
    - Residual soil, groundwater and infrastructure in the former and current Fire Training Area, former Fire Station, and former AFFF USTs
  - > Potential Receptors:
    - Domestic irrigators extracting water for crops / livestock
    - Agricultural irrigators (crops and livestock production)
    - Agricultural users of biosolids
    - Recreational users of Oakey Creek and sporting fields
    - Regional terrestrial and creek ecologies
    - Domestic human use of bore water presumed no longer used based on community advice



# Development of PFC contamination treatments

- Reviews:
  - > New Jersey Drinking Water Quality Institute 2015:
    - Review of case studies of efficacy of drinking water treatments for PFCs (PFNA, PFOA, PFOS)
    - Granular Activated Carbon – most common treatment for long chain PFCs. Competition for adsorption with other contaminants. Thermal regeneration of GAC is effective.
    - Powdered Activated Carbon – high concentration needed, and useful for spill response. Challenge for disposal of waste products.
    - Membrane Filtration (i.e. R.O. and nanofiltration) - Multi-contaminant removal. Rejection rate can be high. Waste/ byproducts must be managed. Mineral addition may be necessary.
    - Anion Exchange - Competition with common ions forbinding sites on resins can impact effectiveness. Organics, total dissolved solids, minerals can clog resins and reduce efficiency
    - Advanced Oxidation – can destroy pollutants, other organic compounds may compete for hydroxyl radicals and reduce efficiencies

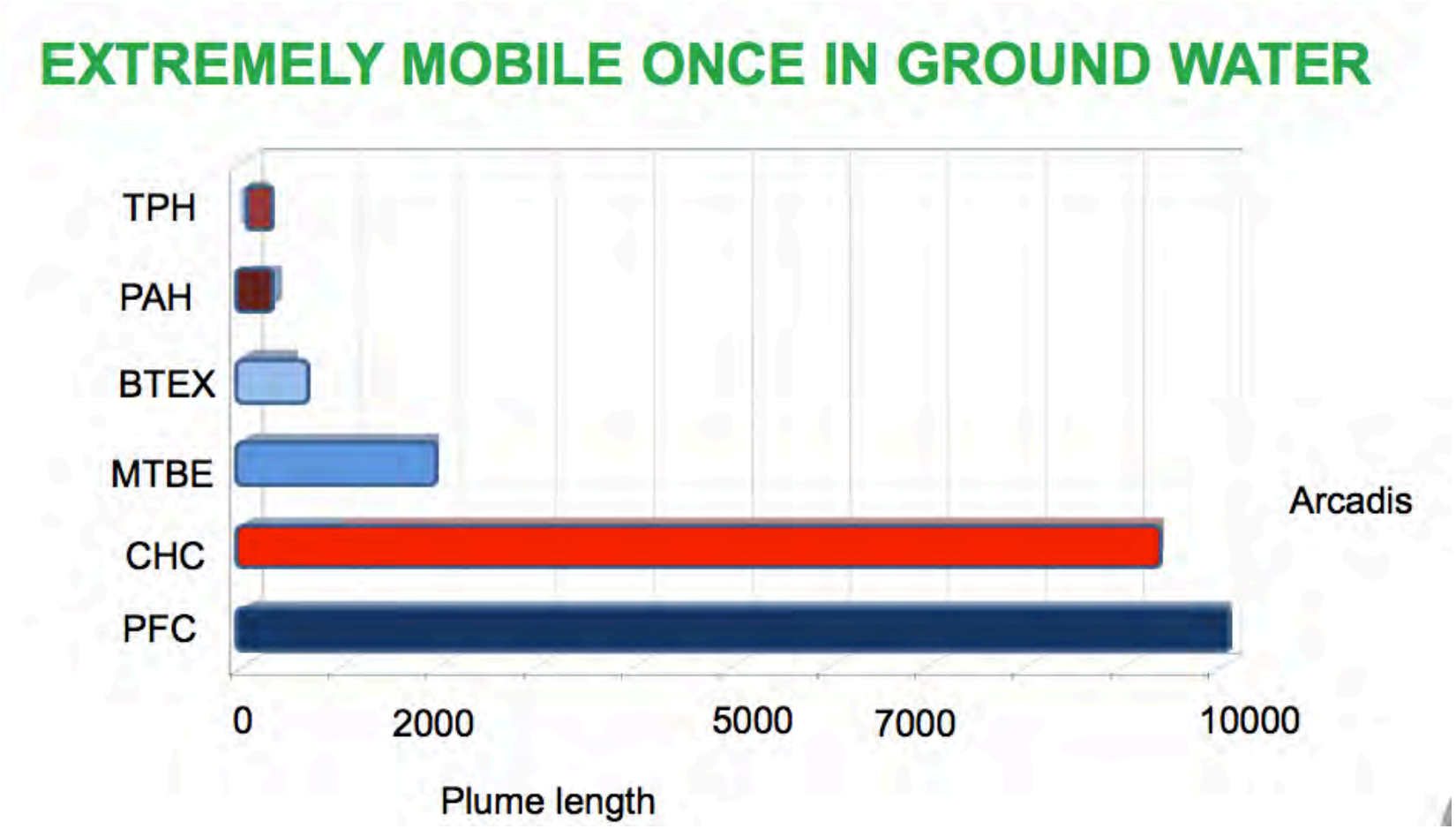


# Development of PFC contamination treatments

- Reviews:
  - Association of State and Territorial Solid Waste Management Officials (ASTSWMO) 2015:
    - Groundwater, the most common treatment is extraction and filtration through granular activated carbon (GAC). This technology has been shown to consistently remove PFOS at µg/L concentrations with an efficiency of 90%; however, it is not as efficient at removing PFOA and other PFCs .
    - Other treatments are experimental and more costly than GAC.
    - Soil – most common treatment is excavation and disposal to landfill. Expensive and inefficient (transfer).
    - Soil – high temperature incinerators destroy PFOS and PFOA.
    - Activated persulfate have significant potential for soil and groundwater insitu treatment.
    - Fungus degradation of PFOA and PFOS promising.

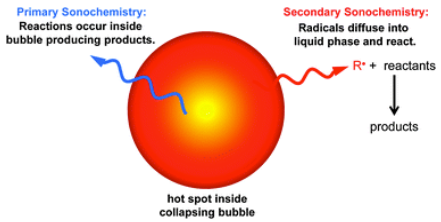
# 2. Current Promising Water Treatments

# Current Promising Water Treatments



# Current Promising Water Treatments

| Technology / Company | Treatment Description | Weaknesses | Strength |
|---|---|---|---|
| Hydroxon Water Treatment / FlowPacific (water) | Catalytic Advanced Oxidation combined with Photocatalytic Process. Produces hydroxyl radicals. | New technology, only proven in trials for PFCs short chain and long chain and my be less effective with competing organic contaminants (but extremely successful, and very exciting results in one of the few technologies that destroy / denature PFCs). | Less expensive and much more effective than other treatment technologies; will denature and treat many other contaminants in the same process. Very small chemical use, low energy use due to small retention time needed for treatment. |
| Sonolysis (water) | Expanding and compressing gas bubbles produced by ultrasound with frequencies of 20–1,000 kHz. Produces hydroxyl radicals. | High energy demand and thus expensive operation | Probably robust technique (experiments only), no additional chemicals are needed |
| Incineration Treatment (water and soil) | Useful for prior sorption – i.e. membrane filtration liquid, and solids | High energy demand due to high temperature (1100C) and energy loss when heating water or sorbent, and thus expensive operation. Unknown toxicology of gases from incinerated PFCs. | Will destroy PFCs / transform into gases. High temperature thermal treatment needed. |
| Reed Bed Treatment / Oceans-ESU (water, sludge) | Proven (real world airport projects) technology that has treated PFCs in surface water runoff at airports in UK. Treatment occurs at mycorrhizal zone – is actually fungal and bacterial treatment and fixation of PFCs. | Needs large area for reed bed. Still not fully understood – but not to be binding to soil (treatment is related to fungus reactions and not adsorption as primary mechanism). | Proven at Airports in UK to remove PFCs continuously for more than 15 years. Can be used pumped groundwater, and also treat surface water runoff for multiple contaminant feeds. Low cost, eco-friendly habitat outcome. Will treat arrange of contaminants in the process. |
| SCISOR / Arcadis (water, soil wash) | Confidential insitu chemical oxidation combination. Treatment of groundwater / soil washing | Not the cheapest options, but proven in real world projects, however still in development stage. Recent new trials have been very successful. | Well developed by large company with real world examples in USA and Europe. Recent trials showing success. |
| Rembind Plus / Ziltec (Water and Soil) | I have only had discussions and reviewed experimental evidence. Appears to be useful for S/S binding of soil and water treatment. | GAC content means PFCs adsorb, which persistent longer term risk unless thermally treated | Appears to remove long and short chain PFCs in water treatment, but takes several iterations. |
| GAC / Activated Carbon / Various (water) | Common treatment used in water treatment or soil wash treatment. | Adsorb PFCs, so they remain a POP in the environment and ongoing liability. Will not treat shorter chain PFCs which may be more toxic | Readily available, proven in real world. |
| matCARE (water and soil) by CRC Care | Modified clay that adsorbs PFCs to clay (Al and Fe) minerals. | Long term leachability from matCARE unknown / does not destroy PFCs | Has been shown to work in full scale applications |




# 2. Current Promising Soil Treatments

# Current Promising Soil Treatments

| Technology / Company | Treatment Description | Weaknesses | Strength |
|---|---|---|---|
| Incineration Treatment (water and soil) | Useful for prior sorption – i.e. membrane filtration liquid, and solids | High energy demand due to high temperature (1100C) and energy loss when heating water or sorbent, and thus expensive operation. Unknown toxicology of gases from incinerated PFCs. | Will destroy PFCs / transform into gases |
| Excavation and offsite disposal | Excavation of impacted soils and removal from site to a licensed accepting landfill | Some landfills not accepting PFC impacted materials. Transfers problem to a new location. Can be expensive for transport. Waste regulation unclear. | Fast and effective way of removing secondary source material. |
| Reed Bed Treatment / Oceans-ESU (water, sludge) | Proven (real world airport projects) technology that has treated PFCs in surface water runoff at airports in UK. Treatment occurs at mycorrhizal zone – is actually fungal and bacterial treatment and fixation of PFCs. | Needs large area for reed bed. Still not fully understood – but not to be binding to soil (treatment is related to fungus reactions and not adsorption as primary mechanism). | Proven at Airports in UK to remove PFCs continuously for more than 15 years. Can be used pumped groundwater, and also treat surface water runoff for multiple contaminant feeds. Low cost, eco-friendly habitat outcome.<br>Will treat arrange of contaminants in the process. |
| SCISOR / Arcadis (water, soil wash) | Confidential insitu chemical oxidation combination. Treatment of groundwater / soil washing | Not the cheapest options, but proven in real world projects, however still in development stage. Recent new trials have been very successful. | Well developed by large company with real world examples in USA and Europe. Recent trials showing success. |
| Rembind Plus / Ziltec (Water and Soil) | I have only had discussions and reviewed experimental evidence. Appears to be useful for S/S binding of soil and water treatment. | GAC content means PFCs adsorb, which persistent longer term risk unless thermally treated | Appears to remove long and short chain PFCs in water treatment, but takes several iterations. |
| matCARE (water and soil) by CRC Care | Modified clay that adsorbs PFCs to clay (Al and Fe) minerals. | Long term leachability from matCARE unknown / does not destroy PFCs | Has been shown to work in full scale applications |

# 3. Current Promising Concrete Treatments

# Current Promising Concrete Treatments

| Technology / Company | Treatment Description | Weaknesses | Strength |
|---|---|---|---|
| PFC-Impacted Cement Treatment XXXXX (under R&D confidentiality) (solids, soil) | Embeds and crystalizes into cement matrix, reducing leachability for disposal, and reducing leachability during rainfall on surfaces or broken stockpiles | This is currently only the trial stage – KiStrategies have designed trials, and in process of getting regulator review | Treatment product has been used for more than 40 years, but never in the environmental space until now. Historically has shown significant long term prevention of leaching or moisture entry into cementous products. Also running trials to reduce leachability of solidified/stabilized PFC impacted soils and ash. Extremely promising potential. Likely use as solidifying agent (being tested) for PFC impacted soils. |

- Recent understanding that PFCs continue to leach from concrete affected by PFCs in rainfall, over a long period:
  - Recent evidence of concrete at a defence airbase leaching PFCs under neutral conditions in the AECOM 2016 Defence Oakey airbase report, Table 3
    http://www.defence.gov.au/id/_Master/docs/Oakey/0207AACOakey2015PFCBackgroundReviewAndSourceStudyJul2015.pdf
  - Recent University of Queensland study - penetration of PFCs into concrete was studied, and leachability from the concrete pad (fire training area of Airport) was also studied, showing PFCs significantly penetrated the concrete, and continued to be a significant source of release of PFOS and PFOA, likely to keep emitting from the concrete pad for several decades.
    http://www.ncbi.nlm.nih.gov/pubmed/25966923

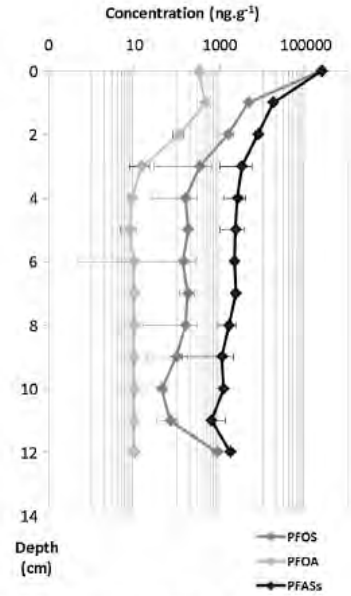



Fig. 3. Vertical profile contamination (ng g$^{-1}$) of PFOS, PFOA and ∑PFASs in the concrete at site #14 close to the out flow pipe. The concentration is an average of the two core profiles and the error bars represent the standard variation between these two values. More compounds are presented in Supplementary material S3(b).

# QUESTIONS?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