Environmental Management of Firefighting Foam

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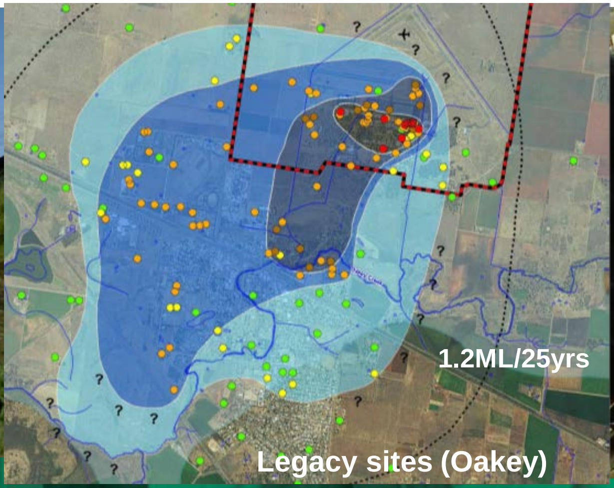
August 2016

Firefighting foam management overview

- Life and safety have always been paramount considerations
- Foam types & impacts
- Emerging worldwide concerns for FOCs
- Queensland risk review and Policy
- Risk reduction measures
- Practical transition to Best Practice

Bruce Highway - CQ



Legacy sites (Oakey)

Coode Island (Vic) 1991

Firefighting foam users

- Qld Fire & Emergency Services
  (Fluorine-free, non-persistent foams since 2003)
- Bulk fuels & chemicals facilities
- Defence facilities (air bases & vessels)
- Airports & transport (often close to wetlands & waterways)
- Maritime (wharves, ships, fire-fighting tugs, stockpiles)
- Mining sector (large vehicles, currently uncontained releases)
- Offshore platforms (over water, uncontained)
- Foam hand extinguishers (waste disposal issues)


Tanker fire Dubai 2009


Adelaide 2016


Buncefield UK 2005

Foam types

Penetrates & wets solids

Layer on top of liquid fuels

CLASS A
Solids fires (3D)
(timber, tyres, bushfires)
Fluorine-free

CLASS B
Liquid fuel fires (2D)
(hydrocarbons, solvents)

AFFF, FFFP, FP, etc.
Fluoro-surfactants

FFF
Fluorine-free foam

FOAMS
Cool the fuel
Exclude oxygen
Suppress fuel vapor
Prevent (re)ignition

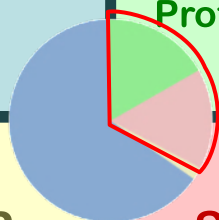
FOAM USE IS HIGHLY DISPERSIVE

Fire fighting foam composition

FOAM CONCENTRATE

WATER ~65%

SURFACTANTS ~17%
HC surfactants
Fluorosurfactants
Protein based, etc.



MODIFIER ~1-2%
Polysaccharide gum
Salts/oxides
Biocides, EDTA etc.

SOLVENTS ~16%
Glycol ethers
Alcohols
Carbitol, etc.

CONCERNS

- AQUATIC BIOTA
- WATER POLLUTION
- SOIL CONTAMINATION
- HUMAN HEALTH

IMPACT MECHANISMS

SHORT-TERM

- O_2 DEPLETION IN WATERWAYS
- ACUTE TOXICITY (low & short-term)

LONG-TERM

- PERSISTENCE
- BIOACCUMULATION
- CHRONIC TOXICITY (long-term)

FOAM USE IS HIGHLY DISPERSIVE

Firefighting Foams
CHARACTERISTICS

FOAM USE IS HIGHLY DISPERSIVE

- Difficult to contain
- High solubility (dissolve & move in water)
- High mobility in soils (to groundwater)

FLUORINATED SURFACTANTS

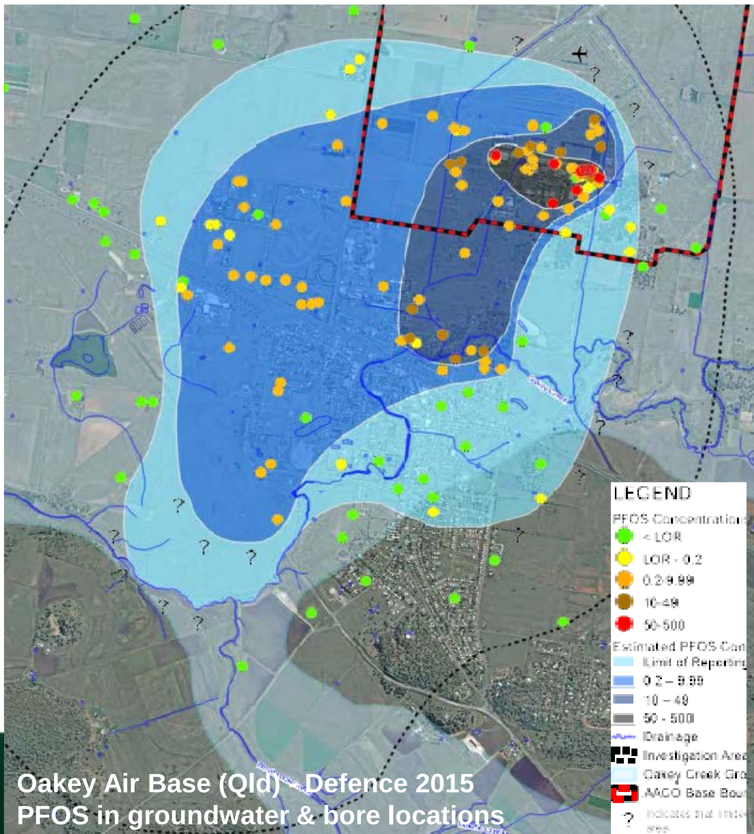
- Developed in 1960s
- Toxic compounds that do not degrade
- Many bioaccumulate
- Previously regarded as benign
- Worldwide dispersal, highly mobile
- Alternatives available since 2003-2005
- CHRONIC (long-term) EFFECTS

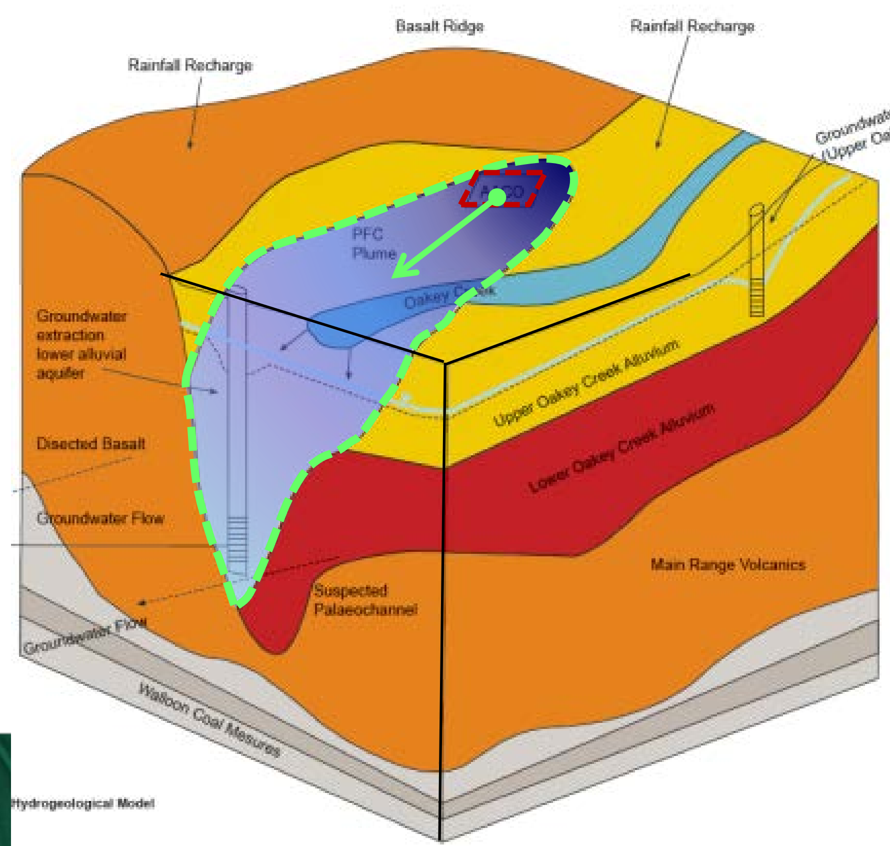
PROBLEMS FROM INTENSIVE USE SITES

- e.g. Oakey 1.2ML AFFF foam released over 25 years.

FOAM USE IS HIGHLY DISPERSIVE

- High solubility (dissolve & move in surface & ground water)
- High mobility in soils (to waterways and groundwater)



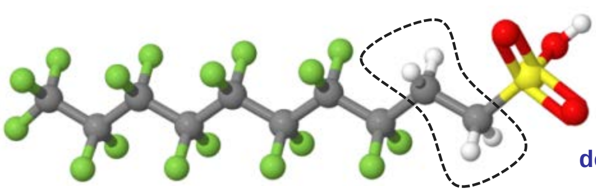


Short-chain C4-C6 plume likely to be well ahead of C8 PFOS extent

Fluorinated Organic Compounds (FOCs/PFCs)

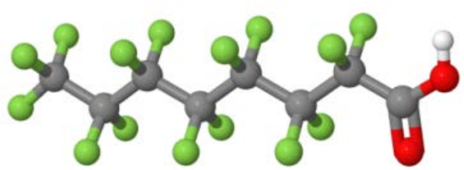
P
B
T

- **Persistence** is extreme (non-degradable)
- **Bioaccumulative** for many compounds
- **Toxicity** (mostly chronic long-term effects concerns)
- Environmental & health concerns known since ~2000
- 100s of fluorinated compounds in foams
- No alternatives to PFCs for foam until ~2002-2006
- **All** fluorinated organics are toxic and problematic
- Many are precursors to PFOS and PFOA or similar

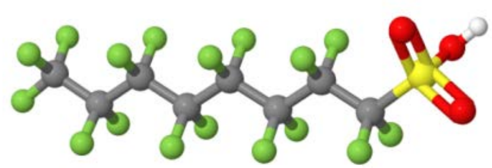


8:2 Fluorotelomer sulfonate (8:2FtS)

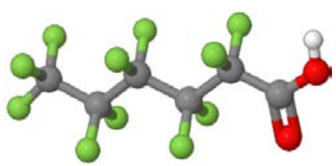
Partial degradation



(C8) PFOA



(C8) PFOS



(C6) Perfluorohexanoic acid

Why now? - Pollutants of emerging concern

(e.g. Asbestos – Ozone-depleting CFCs - DDT pesticide - Leaded petrol - Diesel particulates – etc.)

- **Persistent toxic fluorinated organics used in some foams.**
- **Rapidly emerging indications of long-term adverse effects for human health & wildlife worldwide.**
- **Numerous legacy contaminated sites (& ongoing releases).**
- **Very high cleanup costs (e.g Airport A$150M, truck fire A$1.2M).**

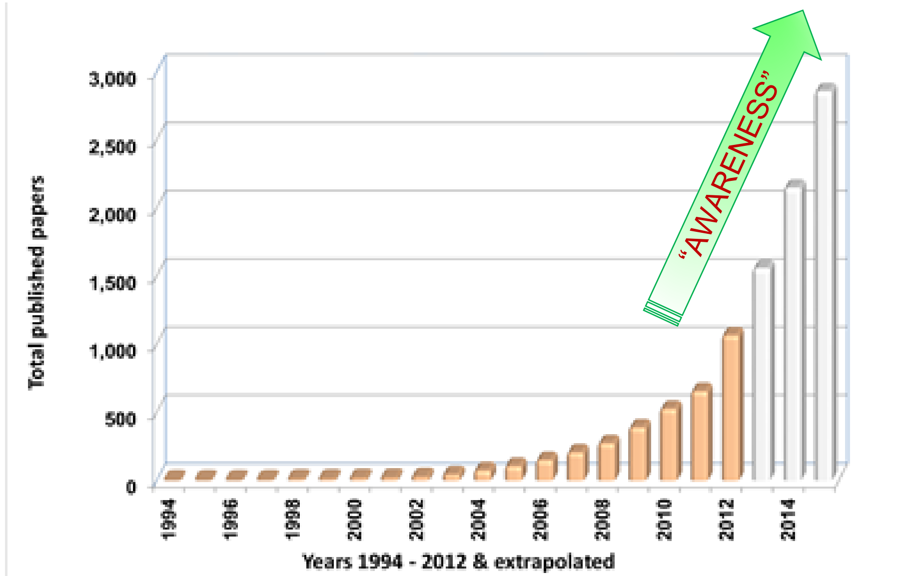


Figure 2.1 A – Number of published papers on perfluoroalkyl substances 1994 onwards (Trojanowicz & Koc [8] & Buck *et al* [9])

Rapidly growing (public) information on fluorinated compounds in peer-reviewed scientific publications since 2008. *Grandjean & Clapp 2015*

>2,500 papers on PFASs from 2001-2011
Trojanowicz & Koc 2013

Industry knowledge (cancer) since 1997
US (Ohio) PFOA compensation trial evidence in 2015

Why now? - Pollutants of emerging concern

(e.g. Asbestos – Ozone depleting - DDT pesticide - Leaded petrol - Diesel particulates – etc.)

- PFOS and PFOA are only 2 of ~200 compounds of concern.
- Hundreds of FOCs in or resulting from fluorinated foam.
- Plus numerous unknown transformation products.
- New analysis method for detecting hidden compounds.

Table 2.1 B – Fluorinated organic compounds (FOCs) in samples of firefighting foams, groundwater & surfactants

Place & Field (2012)–FOCs in MilSpec AFFF [31]

Perfluorobutane sulfonamide amine* (C4)	6:2 fluorotelomer thioether amido sulfonic acid
Perfluoropentane sulfonamide amine* (C5)	4:2 fluorotelomer sulfonamide betaine
Perfluorohexane sulfonamide amine* (C6)	5:1:2 fluorotelomer betaine
Perfluorobutane sulfonamide amino carboxylic acid* (C4)	5:3 fluorotelomer betaine
Perfluoropentane sulfonamide amino carboxylic acid* (C5)	7:1:2 fluorotelomer betaine
Perfluorohexane sulfonamide amino carboxylic acid* (C6)	7:3 fluorotelomer betaine
Perfluorohexane sulfonamide ammonio dicarboxylic acid*	8:2 fluorotelomer sulfonamide amine
Perfluoropentane sulfonamide ammonio dicarboxylic acid*	8:2 fluorotelomer sulfonamide betaine
(* Perfluorosulfonamides are precursors for sulfonate compounds)	8:2 fluorotelomer thio hydroxy ammonium
Perfluorohexane sulfonic acid (C6 PFHxS)	8:2 fluorotelomer thioether amido sulfonic acid
Perfluoroheptane sulfonic acid (C7 PFHpS)	8:2 fluorotelomer thioether amino carboxylic acid
Perfluorooctane sulfonic acid (C8 PFOS)	9:1:2 fluorotelomer betaine
6:2 fluorotelomer sulfonamide amine	9:3 fluorotelomer betaine
6:2 fluorotelomer sulfonamide betaine	10:2 fluorotelomer sulfonamide betaine
6:2 fluorotelomer thio hydroxy ammonium	10:2 fluorotelomer thioether amino carboxylic acid
6:2 fluorotelomer thioether amido amino carboxylic acid	

Table 2.1 A – Fluorinated organic compounds (FOCs) in samples of firefighting foams, groundwater & surfactants

Backe, Day & Field (2013)–FOCs in AFFF and groundwater [32]

4:2 fluorotelomer thioamido sulfonate (PFBA precursor)	Perfluoroheptyl carboxylate (C7 PFHeA) (End point)
6:2 fluorotelomer thioamido sulfonate (PFHxA precursor)	Perfluorooctyl carboxylate (C8 PFOA) (“ “)
8:2 fluorotelomer thioamido sulfonate (C8 PFOA precursor)	Perfluorononyl carboxylate (C9 PFNA) (“ “)
4:2 fluorotelomer sulfonate (4:2FtS) (PFBA precursor)	Perfluorodecyl carboxylate (C10 PFDA) (“ “)
6:2 fluorotelomer sulfonate (6:2FtS))(PFHxA precursor)	Perfluoroundecyl carboxylate (C11 PFUnDA) (“ “)
8:2 fluorotelomer sulfonate (8:2FtS) (C8 PFOA precursor)	Perfluorododecyl carboxylate (C12 PFDoDA) (“ “)
Perfluoroheptly sulfonamido amine (C7 PFHeS precursor)	Perfluorotridecyl carboxylate (C13 PFTriDA) (“ “)
Perfluorooctyl sulfonamido amine (C8 PFOS precursor [47])	Perfluorotetradecyl carboxylate (C14 PFTeDA) (“ “)
Perfluorheptyl sulfonamide amino carboxylate (C7)	(Fluorinated organic compounds common to both studies)
Perfluoroctyl sulfonamide amino carboxylate (PFOS prec.)	(6:2 fluorotelomer thio hydroxy ammonium)
Perfluorobutyl sulfonamido amine (C4 PFBS precursor)	(6:2 fluorotelomer sulfonamido betaine)
Perfluoropentyl sulfonamido amine (C5 PFPeS precursor)	(8:2 fluorotelomer sulfonamido betaine)
Perfluorohexyl sulfonamido amine (C6 PFHxS precursor)	(10:2 fluorotelomer sulfonamido betaine)
Perfluorbutyl sulfonamide amino carboxylate (C4)	(12:2 fluorotelomer sulfonamido betaine)
Perfluorpentyl sulfonamide amino carboxylate (C5)	(5:1:2 fluorotelomer betaine) (PFPeA precursor)
Perfluorohexyl sulfonamide amino carboxylate (C6)	(7:1:2 fluorotelomer betaine) (PFSepA precursor)
Perfluorobutyl sulfonate (C4 PFBS) (End point compound)	(9:1:2 fluorotelomer betaine) (PFNA precursor)
Perfluoropentyl sulfonate (C5 PFPeS) (“ “)	(5:3 fluorotelomer betaine) (PFPeA precursor)
Perfluorononyl sulfonate (C9 PFNS) (“ “)	(7:3 fluorotelomer betaine) (PFSepA precursor)
Perfluorodecyl sulfonate (C10 PFDS) (“ “)	(9:3 fluorotelomer betaine) (PFNA precursor)
Perfluorobutyl carboxylate (C4 PFBA) (“ “)	(Perfluorohexyl sulfonate (C6 PFHxS))
Perfluoropentyl carboxylate (C5 PFPeA) (“ “)	(Perfluoroheptyl sulfonate (C7 PFHepS))
Perfluorohexyl carboxylate (C6 PFHxA) (“ “)	(Perfluorooctyl sulfonate (C8 PFOS))

Table 2.1 C – Fluorinated organic compounds (FOCs) in samples of firefighting foams, groundwater & surfactants.

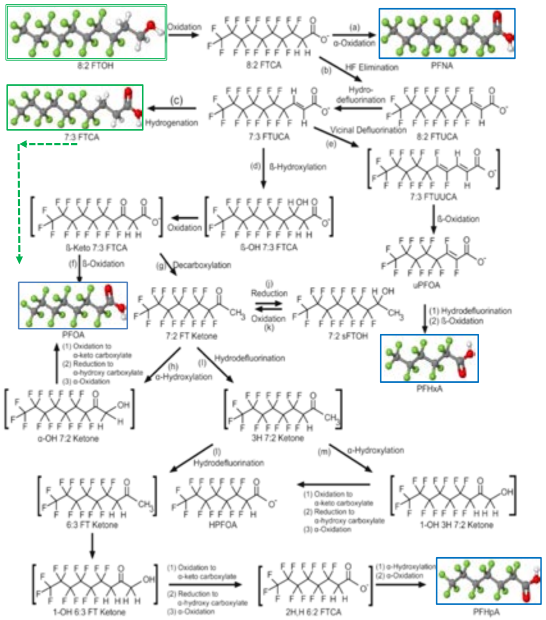
D'Agostino and Mabury (2014)–Novel FOCs in 10 AFFF concentrates and 2 commercial fluorinated surfactants. [34]

Groups and classes of PFASs	Dominant form	Number of compounds	Total
Perfluoroalkylamido betaine (PFAAB)-related (A, B, C)			
n=3, 4, 5, 6 7, 8, 9, 10,11, 12, 14	n=8, $C_{14}H_{14}ON_2F_{17}{}^{+1}$	(11 compounds)	
n=6, 7, 8, 9, 10,11, 12, 14	n=8, $C_{16}H_{16}O_3N_2F_{17}{}^{+1}$	(8 compounds)	
n=8, 10, 12	n=8, $C_{19}H_{22}O_3N_2F_{17}{}^{+1}$	(3 compounds)	**(22 compounds)**
Fluorotelomerthioalkylamido betaine (FTSAB)-related (D, E, F, G, H)			
n=4, 6, 8, 10	n=6, $C_{10}H_6O_2SF_{13}{}^{-1}$	(4 compounds)	
n=4, 6, 8, 10, 12	n=6, $C_{15}H_{20}ON_2SF_{13}{}^{+1}$	(5 compounds)	
n=4, 6, 8, 10, 12, 14	n=6, $C_{17}H_{22}O_3N_2SF_{13}{}^{+1}$	(6 compounds)	
n=6, 8, 10	n=6, $C_{16}H_{22}ON_2SF_{13}{}^{+1}$	(3 compounds)	
n=6	n=6, $C_{16}H_{22}O_2N_2SF_{13}{}^{+1}$	(6 compounds)	**(19 compounds)**
Fluorotelomermercaptoalkylamido sulfonate (FTSAS)-related (I, J, K)			
n=4, 6, 8, 10, 12, 14	n=6, $C_{15}H_{17}O_4NS_2F_{13}{}^{-1}$	(6 compounds)	
n=4, 6, 8, 10	n=6, $C_{15}H_{17}O_5NS_2F_{13}{}^{-1}$	(4 compounds)	
n=4, 6, 8	n=6, $C_{11}H_8O_2SF_{13}{}^{-1}$	(3 compounds)	**(13 compounds)**
Fluorotelomersulfonamide alkylbetaine (FTAB)-related (L, M)			
n=6, 8, 10, 12, 14	n=6, $C_{15}H_{20}O_4N_2SF_{13}{}^{+1}$ [48]	(5 compounds)	
n=6, 8, 10	n=6, $C_{13}H_{18}O_2N_2SF_{13}{}^{+1}$	(3 compounds)	**(8 compounds)**
Fluorotelomer betaine (FTB) (N, O)			
n=5, 7, 9, 11, 13	n=5, $C_{12}H_{15}O_2NF_{11}{}^{+1}$	(5 compounds)	
n=5, 7, 9, 11, 13, 15	n=5, $C_{12}H_{14}O_2NF_{12}{}^{+1}$	(6 compounds)	**(11 compounds)**
Fluorotelomerthiohydroxyl ammonium (FTSHA) (P, Q)			
n=6, 8, 10	n=6, $C_{14}H_{19}ONSF_{13}{}^{+1}$	(3 compounds)	
n=6, 8	n=6, $C_{14}H_{19}O_2NSF_{13}{}^{+1}$	(2 compounds)	**(6 compounds)**
Perfluoroalkylsulfonamido-based surfactants (PFASA-) (R/S, T, U, V) (Likely C3-C9 sulfonate precursors)			
n=3, 4, 5, 6, 7, 8 (branched)	n=6, $C_{14}H_{18}O_4N_2SF_{13}{}^{+1}$	(6 compounds)	
n=3, 4, 5, 6	n=6, $C_{14}H_{18}O_4N_2SF_{13}{}^{+1}$	(4 compounds)	
n=3, 4, 5, 6, 7, 8	n=6, $C_{11}H_{14}O_2N_2SF_{13}{}^{+1}$	(6 compounds)	
n=3, 4, 5, 6 (branched)	n=6, $C_{17}H_{22}O_6N_2SF_{13}{}^{+1}$	(4 compounds)	
n=6, 7, 8, 9	n=8, $C_{17}H_{22}O_6N_2SF_{13}{}^{+1}$	(4 compounds)	**(24 compounds)**
n = perfluorinated carbon chain lengths of C3 to C15. (For **A** to **V** refer to original paper).			**Total 103 compounds**

Table 2.1 D

Herzke, Olsson and Posner (2012)–PFASs in consumer products in Norway (results for 2 current AFFF) [35].

Perfluorobutanoate	PFBA	(C4)	Perfluoroctane sulfonamide	PFOSA (PFOS precursor)
Perfluoropentanoate	PFPA	(C5)	6:2 fluorotelomer sulfonate	6:2 FtS
Perfluorohexanoate	PFHxA	(C6)	6:2 fluorotelomer alcohol	6:2 FtOH
Perfluorooctanoate	PFOA	(C8)	8:2 fluorotelomer alcohol	8:2 FtOH (PFOA precursor)
Perfluorodecanoate	PFDA	(C10)	10:2 fluorotelomer alcohol	10:2 FtOH (PFDA precursor)
Perfluorododecanoate	PFDoA	(C12)		



Tables of the main known FOCs. (Explanatory Notes)

E.g. one compound can result in 16 transformation and 5 end-products.

Queensland Government

Regulatory position (the Qld Policy)

The *Precautionary Principle* *(in decision making)*

Obligation in legislation triggered by:

- ✓ threat of serious or irreversible environmental damage; and
- ✓ scientific uncertainty as to the nature and scope of the threat of environmental damage.

Justice Preston (2006) clarified considerations and stated:
"The function of the precautionary principle is, therefore, to ***require the decision-maker to assume that there is, or will be, a serious or irreversible threat of environmental damage*** *and to take this into account, notwithstanding that there is a degree of scientific uncertainty about whether the threat really exists."*

Chief Judge of the NSW Land and Environment Court, Justice Preston in Telstra Corporation Limited v Hornsby Shire Council [2006] NSWLEC

PFCs exposure poses real threats

Elimination in humans ($t_{1/2}$):

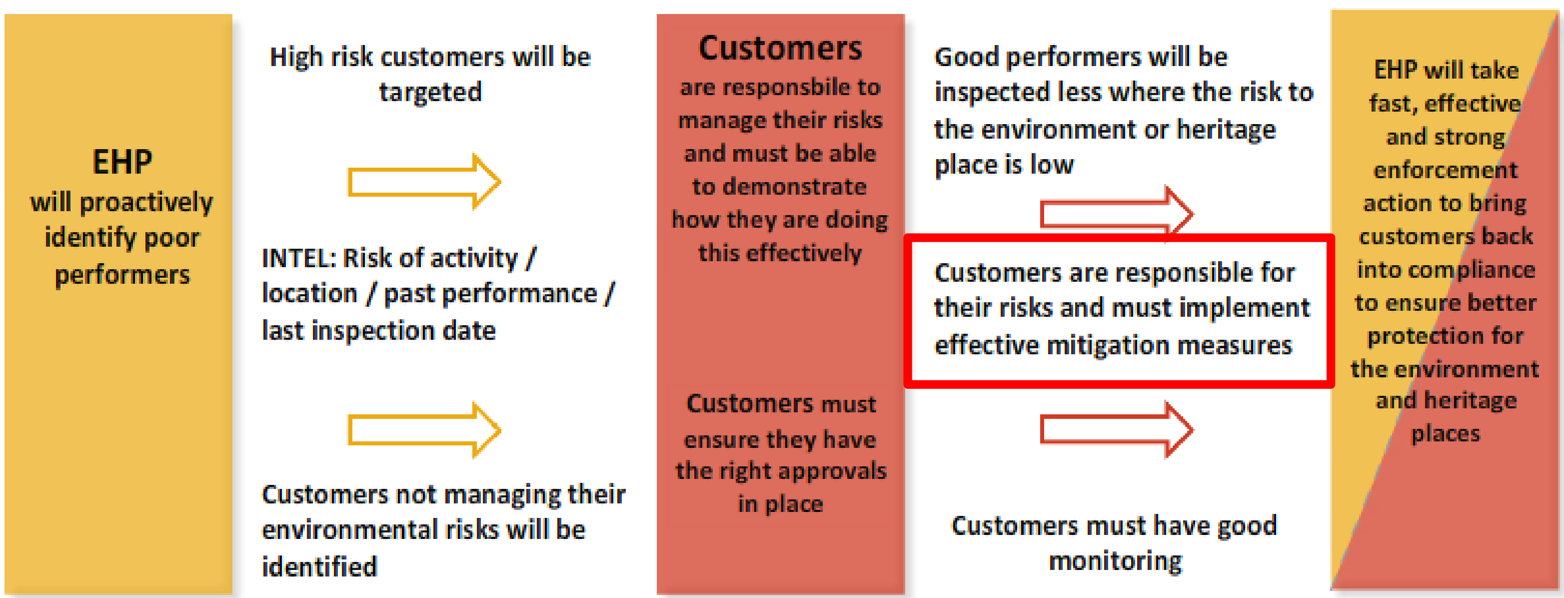
- C8, PFOS – 5.4 years
- C8, PFOA – 2.3 to 3.8 yrs
- C6, PFHxS – 8.5 years (≈C8)

  (! x 5 half lives [↓] 15-40 years)

- ~200 similar compounds.
- Extensive information now published about adverse effects and behaviour.
- Adverse effects of increasing exposure to combinations emerging.

Environmental Management of Foam

- Review of issues & Policy development (2013-16)
- Foam industry has not self-regulated
- Regulatory Strategy (Policy) model to address
- Prompt, staged implementation needs to occur



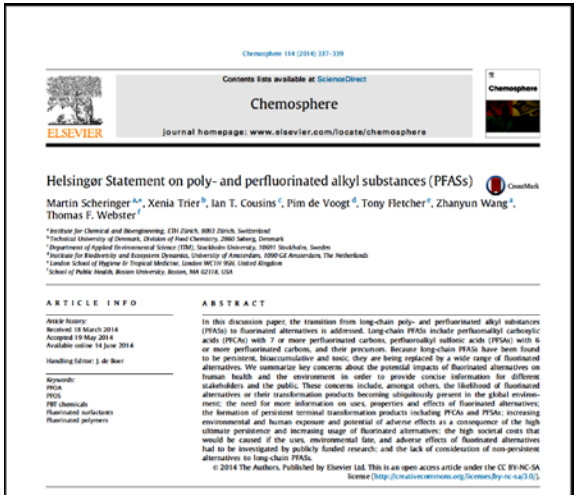
END-USER RESPONSIBILITY

Worldwide concerns about <u>all</u> FOCs

Helsingør & Madrid Statements 2014 - (177 scientists signed)

Scientific community concerns:

- Health & environmental impacts of FOCs
- Widespread occurrence of fluorinateds
- Extreme persistence
- Lack of decline & increasing exposure
- Impacts of fluorinated alternatives
- Lack of info & testing for 100s of FOCs
- Lack of transparency by manufacturers
- Synergistic effects likely but unknown
- World-wide & tighter regulation needed
- Problematic & costly waste disposal
- Strongly suggest cease use of all FOCs
- Develop non-toxic alternatives



Chemosphere 114 (2014) 337–339

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Helsingør Statement on poly- and perfluorinated alkyl substances (PFASs)

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ARTICLE INFO

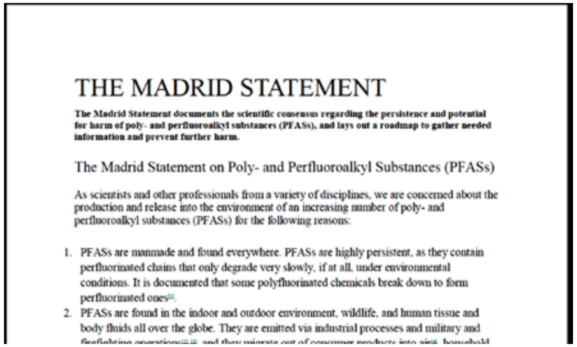
Article history:
Received 18 March 2014
Accepted 19 May 2014
Available online 14 June 2014

Handling Editor: J. de Boer

Keywords:
PFOA
PFOS
PBT chemicals
Fluorinated surfactants
Fluorinated polymers

ABSTRACT

In this discussion paper, the transition from long-chain poly- and perfluorinated alkyl substances (PFASs) to fluorinated alternatives is addressed. Long-chain PFASs include perfluoroalkyl carboxylic acids (PFCAs) with 7 or more perfluorinated carbons, perfluoroalkyl sulfonic acids (PFSAs) with 6 or more perfluorinated carbons, and their precursors. Because long-chain PFASs have been found to be persistent, bioaccumulative and toxic, they are being replaced by a wide range of fluorinated alternatives. We summarize key concerns about the potential impacts of fluorinated alternatives on human health and the environment in order to provide concise information for different stakeholders and the public. These concerns include, amongst others, the likelihood of fluorinated alternatives or their transformation products becoming ubiquitously present in the global environment; the need for more information on uses, properties and effects of fluorinated alternatives; the formation of persistent terminal transformation products including PFCAs and PFSAs; increasing environmental and human exposure and potential of adverse effects as a consequence of the high ultimate persistence and increasing usage of fluorinated alternatives; the high societal costs that would be caused if the uses, environmental fate, and adverse effects of fluorinated alternatives had to be investigated by publicly funded research; and the lack of consideration of non-persistent alternatives to long-chain PFASs.



THE MADRID STATEMENT

The Madrid Statement documents the scientific consensus regarding the persistence and potential for harm of poly- and perfluoroalkyl substances (PFASs), and lays out a roadmap to gather needed information and prevent further harm.

The Madrid Statement on Poly- and Perfluoroalkyl Substances (PFASs)

As scientists and other professionals from a variety of disciplines, we are concerned about the production and release into the environment of an increasing number of poly- and perfluoroalkyl substances (PFASs) for the following reasons:

1. PFASs are manmade and found everywhere. PFASs are highly persistent, as they contain perfluorinated chains that only degrade very slowly, if at all, under environmental conditions. It is documented that some polyfluorinated chemicals break down to form perfluorinated ones[1].
2. PFASs are found in the indoor and outdoor environment, wildlife, and human tissue and body fluids all over the globe. They are emitted via industrial processes and military and

Operational Policy content

(Other contaminants considered separately)

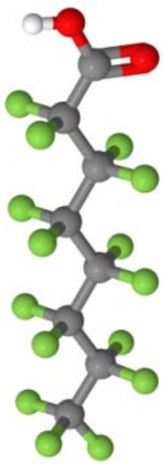
Non-persistent foams (e.g. fluorine-free)

- BOD & acute toxicity concerns for waterways
- Contain wastes on site if possible
- Treat or biodegrade wastes on site is possible
- Disposal to trade waste or sewer (WWTP) OK
- Biodegradable and largely self remediating
- Emergency direct releases tolerable
- No significant restriction on dispersed rural firefighting or limited essential testing of critical systems (e.g. dockside to waterways)

Operational Policy content

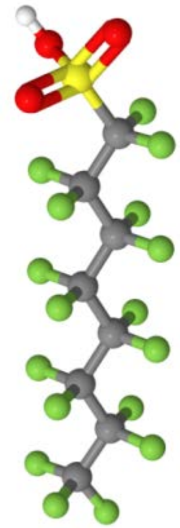
(Other contaminants considered separately)

<u>Persistent foams</u> (e.g. all fluorinated, AFFF, FP FFFP…)



(C8) PFOA

- Know what you have in stocks, asses the risk
- PFOS not acceptable, take out of service now
- ≥C7 foams – Put in place interim containment measures & phase out (ASAP <u>within</u> 3 yrs)
- Fully contain wastes in impervious bunding
- C6-<u>PURE</u> foam OK (99.5% certified) <u>BUT</u> wastes must be fully contained in impervious bunding
- Persistent foams not to be used for testing
- High temperature destruction of wastes



(C8) PFOS

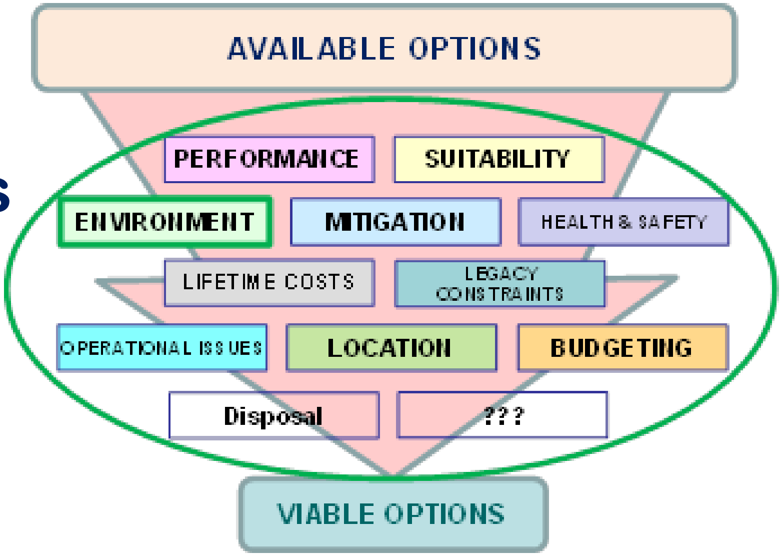
VALUES AT RISK & COSTS

- Human health (long-term)
- Aquatic ecosystems (short and long-term)
- Primary produce contamination & food chain
- Adjacent/downstream users of land and waters
- Economic, land & amenity values (already evident)
- Land contamination – very high cleanup costs
- Cost recovery? Industry, insurers, community…?

Challenges for transition to best practice

Balanced decisions based on ALL considerations:

- Life and safety are paramount
- Re-engineering systems
- Interim containment measures
- *Decontamination of fluorinated systems
- Whole-of-life costs (incl. wastes)
- Long-term containment & management
- Land contamination assessment & remediation



Cross-contamination of replacement foam by fluorinated residues has already emerged as a very significant and costly problem overseas.

Managing foam use

Life & Safety Considerations are PARAMOUNT

Environmental considerations need to be taken seriously in balanced decision making

Forward planning:

Facilities and contingency planning for containment.

Incident management:

Contain and manage firewater & wastewater.

Waste disposal:

Wastewater disposed of as regulated waste.

Managing foam use

Foam end-user activities:

- Legislative provisions have applied since 1995.
- Policy provides guidance on compliance & priorities.
- Transition to non-persistent foam ASAP for direct releases.
- User need to assess risks & compliance.
- Alternative products certified & demonstrated effective.
  (high-end users – airports, oil platforms, fuel terminals, brigades, IMO, etc.)
- All fluorinated foam including C6 must be fully contained.

Management measures:

- Choice of suitable C6-PURE or non-persistent product.
- Procedures to prevent releases (contingency plans).
- Containment of firewater and wastewater.
- Disposal of firewater as regulated waste.

Photo TMR Qld

Mythbusting – *"Foam can be contained by floating booms"* (recent US industry guideline).

Foams are soluble and dissolve into the water column !