# FATE AND TRANSPORT MODELING OF PFOS IN A FRACTURED CHALK AQUIFER TOWARDS A LARGE SCALE DRINKING WATER ABSTRACTION

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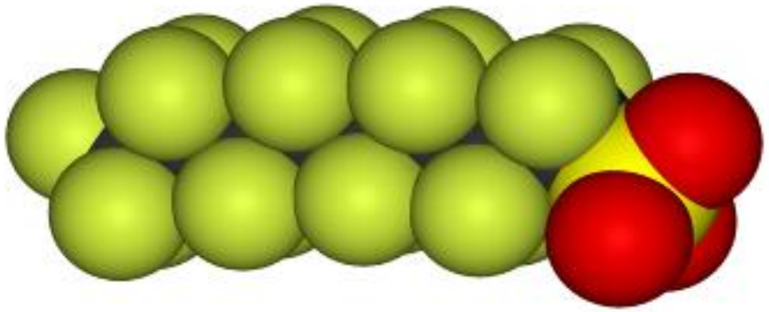


# PFAS Introduction

PFAS comprises many thousands of compounds –multiple sources

PFAS are impacting drinking water worldwide

Some PFAS are classed as persistent organic pollutants

Advanced analytical methods are being adopted to measure PFAS

None of the PFASs biodegrade, some biotransform to daughter compounds that are extremely persistent

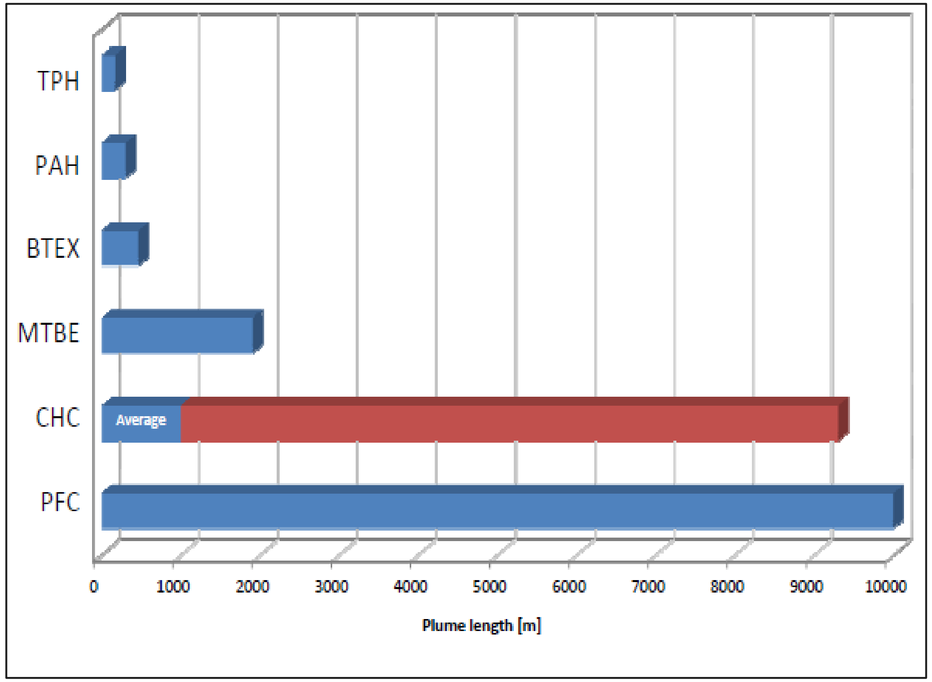
Dramatically increasing regulatory concern

# PFAS - Properties and Implications

PFAS plumes are generally longer as PFAS are generally:

- Highly soluble
- Low $K_{OC}$
- Recalcitrant – extreme persistence
- Mostly Anionic

| Chemical Properties | PCB (Arochlor 1260) | PFOA | PFOS | TCE | Benzene |
|---|---|---|---|---|---|
| Molecular Weight | 357.7 | 414.07 | 538 | 131.5 | 78.11 |
| Solubility (@20-25°C), mg/L | 0.0027 | 3400 – 9500 | 519 | 1100 | 1780 |
| Vapor Pressure (@25°C), mmHg | $4.05 \times 10^{-5}$ | 0.5-10 | $2.48 \times 10^{-6}$ | 77.5 | 97 |
| Henry's Constant, atm-$m^3$/mol | $4.6 \times 10^{-3}$ | $1.01 \times 10^{-4}$ | $3.05 \times 10^{-9}$ | 0.01 | 0.0056 |
| Log Koc | 5 – 7 | 2.06 | 2.57 | 2.473 | 2.13 |



# Perfluorinated compounds (PFCs)

- Perfluorinated Compounds (PFCs) generally are the **Perfluoroalkyl acids (PFAAs)**
- PFAAs include:
  - Perfluoralkyl carboxylates (PFCAs) e.g. PFOA
  - Perfluoroalkyl sulfonates (PFSAs) e.g. PFOS
  - Perfluoroalkyl phosphinic acids (PFPiS); perfluoroalkyl phosphonic acids (PFPAs)
- There are many PFAAs with differing chain lengths, PFOS and PFOA have 8 carbons (C8) - octanoates

C1 **M**ethane
C2 **E**thane
C3 **P**ropane
C4 **B**utane
C5 **Pe**ntane
C6 **Hex**ane
C7 **Hep**tane
C8 **O**ctane
C9 **N**onane
C10 **D**ecane
C11 **U**nodecane
C12 **Do**decane
C13 **Tr**idecane
C14 **Te**tradecane

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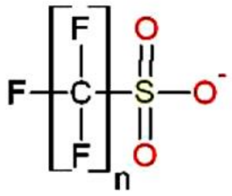
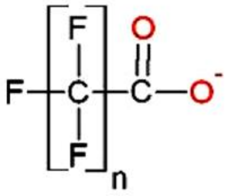
Perfluoroalkyl Sulfonates[L]




| | |
|---|---|
| PFBS | n = 4 |
| PFPeS * | n = 5 |
| PFHxS | n = 6 |
| PFHpS | n = 7 |
| PFOS | n = 8 |
| PFNS * | n = 9 |
| PFDS | n = 10 |

Perfluoroalkyl Carboxylates[L]




| | |
|---|---|
| PFBA | n = 4 |
| PFPeA | n = 5 |
| PFHxA | n = 6 |
| PFHpA | n = 7 |
| PFOA | n = 8 |
| PFNA | n = 9 |
| PFDA | n = 10 |
| PFUdA | n = 11 |
| PFDoA | n = 12 |
| PFTrA | n = 13 |
| PFTeA | n = 14 |

Zwitterionic, Cationic, and Anionic Fluorinated Chemicals in Aqueous Film Forming Foam Formulations and Groundwater from U.S. Military Bases by Nonaqueous Large-Volume Injection HPLC-MS/MS
Will J. Backe,† Thomas C. Day,† and Jennifer A. Field*,‡

**PFAAs totally resist biodegradation & biotransformation so are extremely persistent**

# Let‘s start with three key concepts

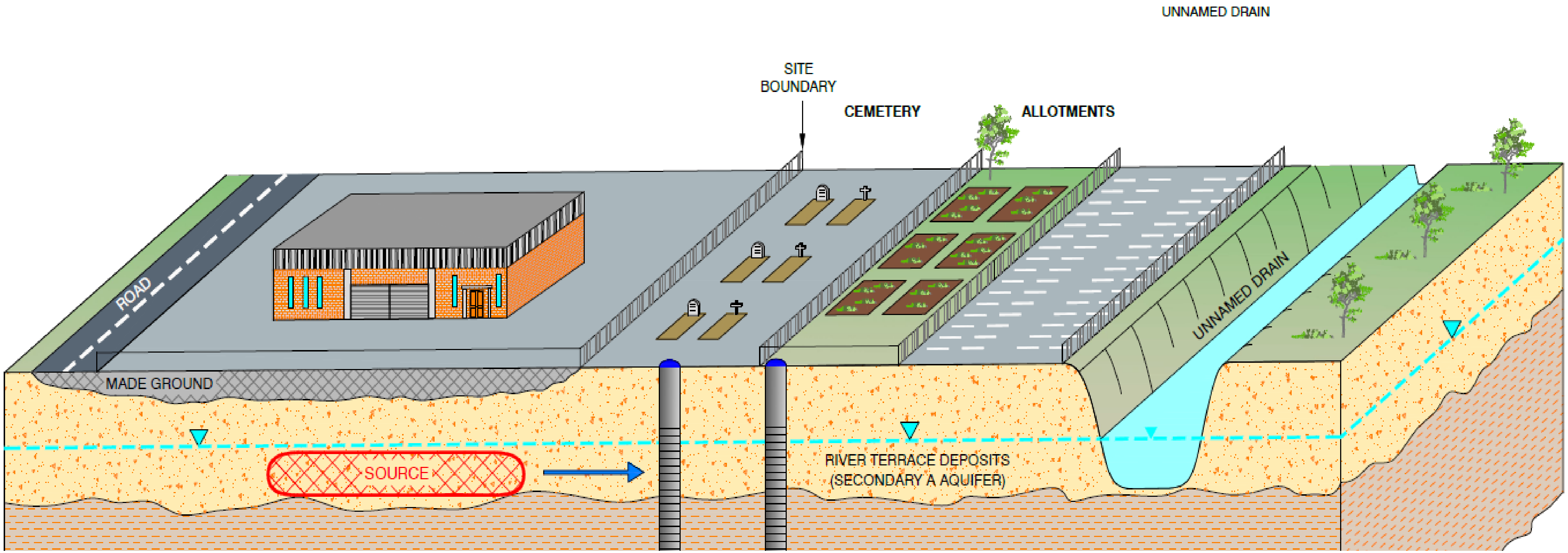
1. What is Risk?


x


2. Suitable for Use


3. Source-Pathway-Receptor linkages

# Conceptual Site Model



# Buncefield

- Explosion measured at 2.4 on the richter scale
- 786,000 litres of foam concentrate used
- 53 million litres of 'clean water' applied to fire
- 15 million litres of water recycled and reapplied to fire
- 10 million litres of water moved on site to protect the environment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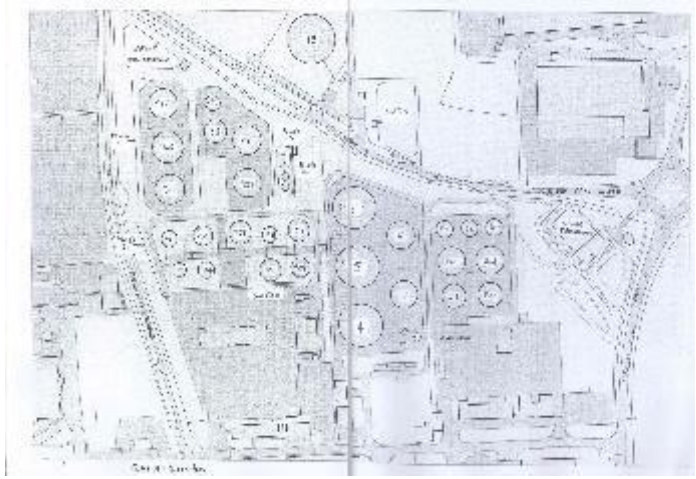
# Buncefield Environmental Project

- Immediate clean-up operation to uplift 50 million litres liquid –trucked to London, stored 18 months and treated with reverse osmosis
- PFOS to be present in approximately 12,000m$^3$ of shallow soils (<2m below ground level)
- Prevent infiltration through to the underlying Principal Aquifer
- Concentrations ranged from 0.005 to 3.5mg/kg with an average concentration of 0.82mg/kg
- Key SPR linkages identified
  - Sources
    - Fuel
    - Firewater (PFOS)
  - Pathways
  - Infiltration
    - Offsite migration
  - Receptors
    - Shallow soils
    - Chalk Aquifer
    - Drinking Water Abstraction (3.5km east)

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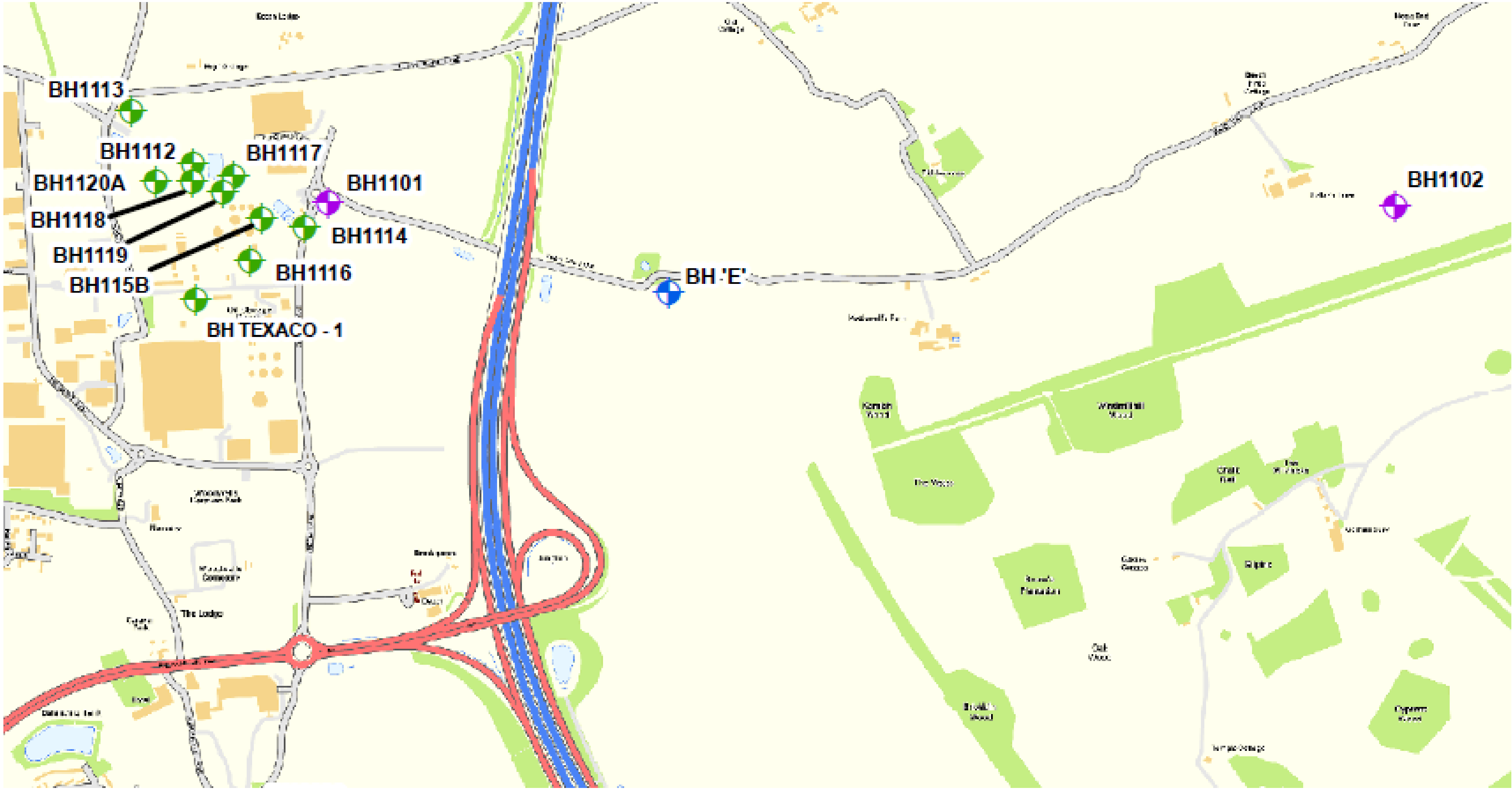
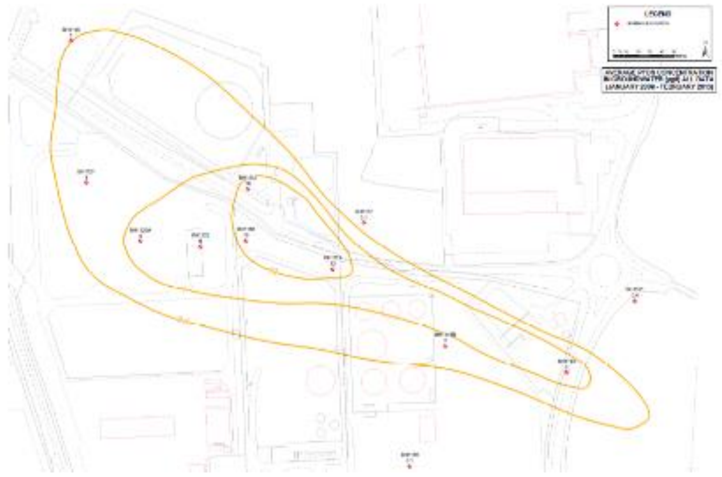
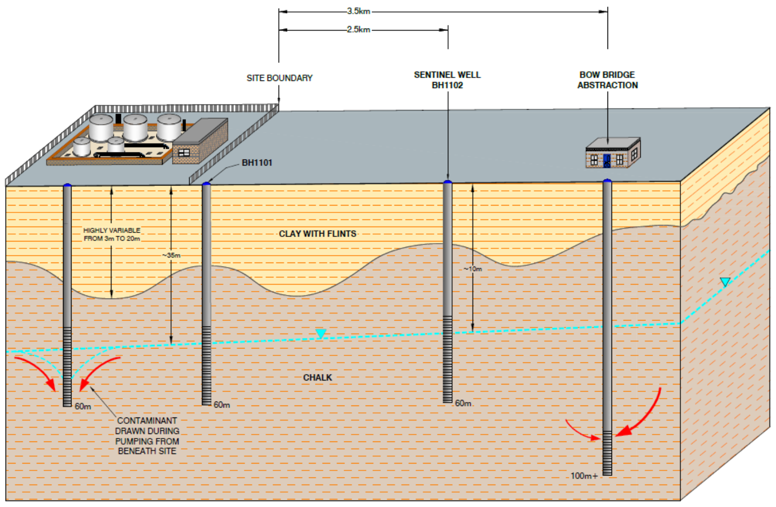


# Buncefield CSM



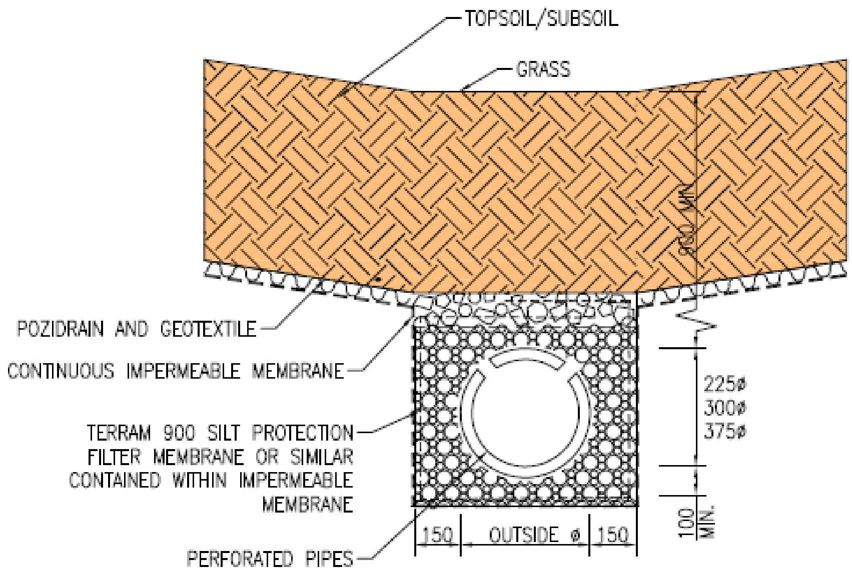
- Majority of Fire water recovered
- Soak away for adjacent road excavated through overlying clay layer which protects the underlying chalk aquifer
- Protecting clay layer punctured
- Soak away dimensions small so limited volume of firewater entered aquifer
- Site Specific Acceptance Criteria (SSAC) were developed for PFOS based on the Environment Agency compliance criteria of 0.3ug/l and 1ug/l at receptor to yield SSACs



# Agreed Risk Management Strategies

- Shallow Soil
  - Removal of LNAPL/heavily impacted soils
  - Cut infiltration pathway to the underlying aquifer
    - capping project
    - terminal rebuild project
- Chalk Aquifer
  - Recovery of LNAPL from groundwater
  - Removal of contaminant mass from centre of Site *via* groundwater pumping
  - Monitored Natural Attenuation


**56,000 m3 of water extracted ~1kg of PFOS.**

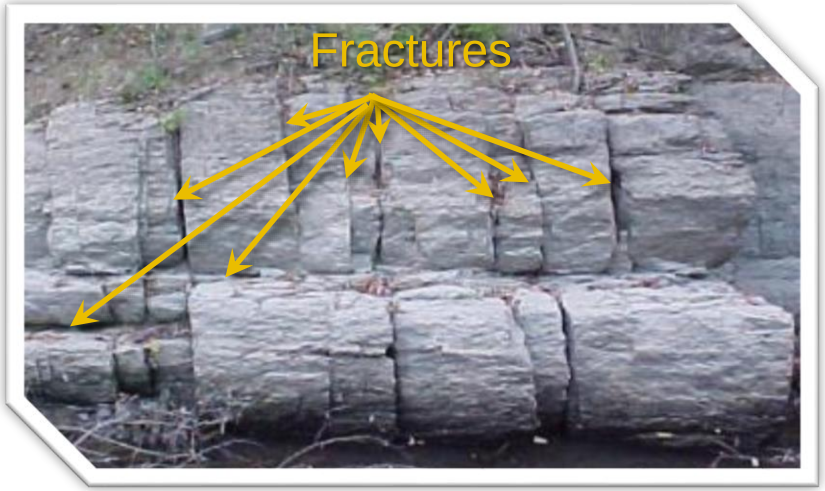


TOPSOIL/SUBSOIL
GRASS
900 MIN.
POZIDRAIN AND GEOTEXTILE
CONTINUOUS IMPERMEABLE MEMBRANE
TERRAM 900 SILT PROTECTION FILTER MEMBRANE OR SIMILAR CONTAINED WITHIN IMPERMEABLE MEMBRANE
PERFORATED PIPES
225ø
300ø
375ø
150
OUTSIDE ø
150
100 MIN.

# Dual-Porosity Conceptual Model

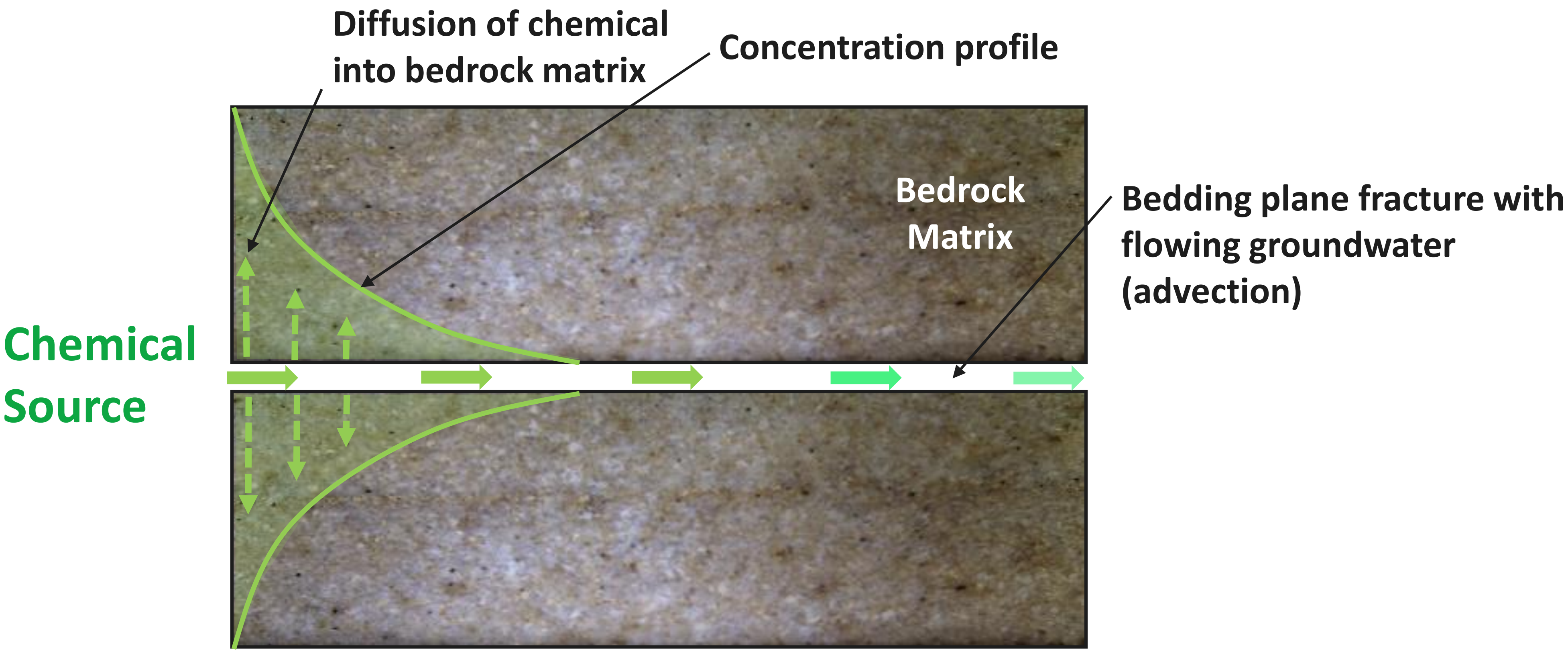
**Primary Porosity**
- Also known as immobile porosity
- Porosity within the bedrock matrix

**Secondary Porosity**
- Also known as mobile porosity
- Porosity within bedrock fractures


**Site Information**
- Immobile porosity: 35%
- Mobile porosity: 0.1%
- Implication: the bedrock matrix can store about 350 times more groundwater and chemicals than the bedrock fractures.

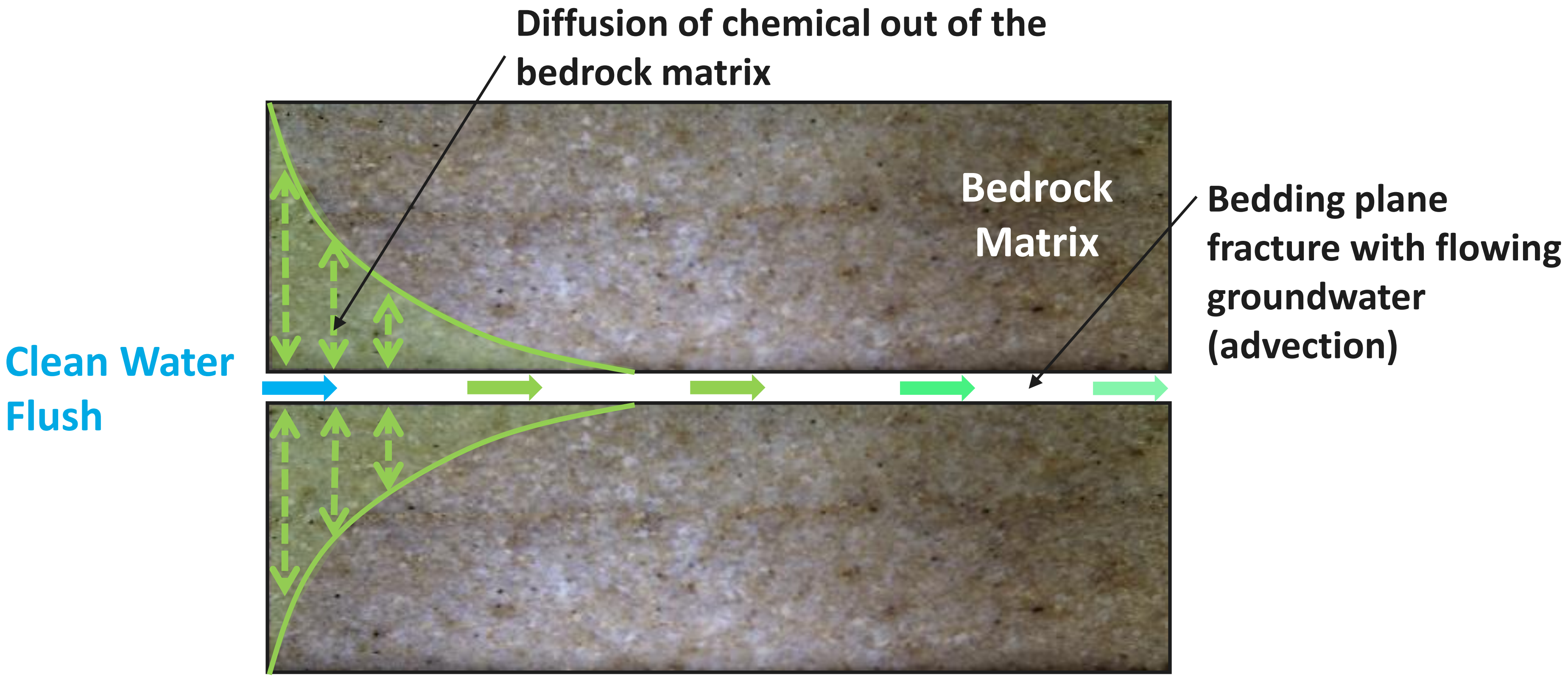
# Dual-Porosity Conceptual Model




When a chemical source is introduced at an open, flowing bedrock fracture:

- Chemical is transported along the fracture via advection and dispersion
- A concentration gradient is created between the fracture and the bedrock matrix
- Chemical is transported into the bedrock matrix via diffusion
- The matrix diffusion process results in slower plume velocity (i.e. retardation)

# Dual-Porosity Conceptual Model

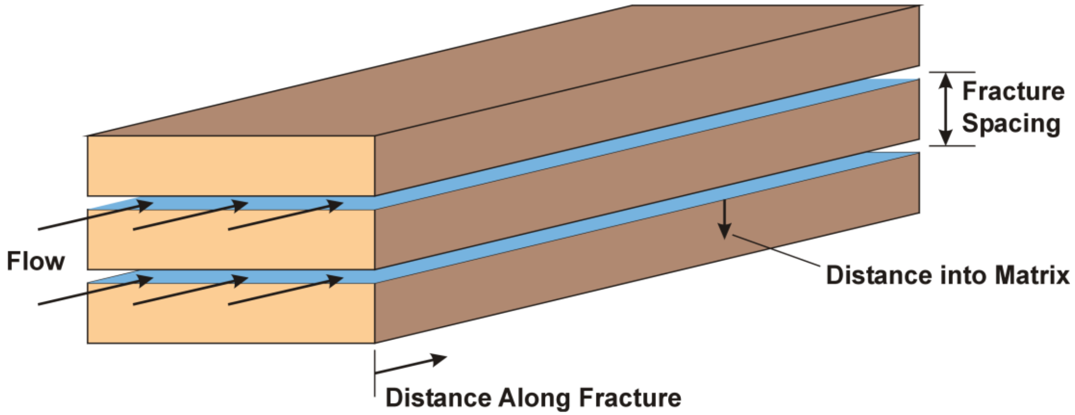


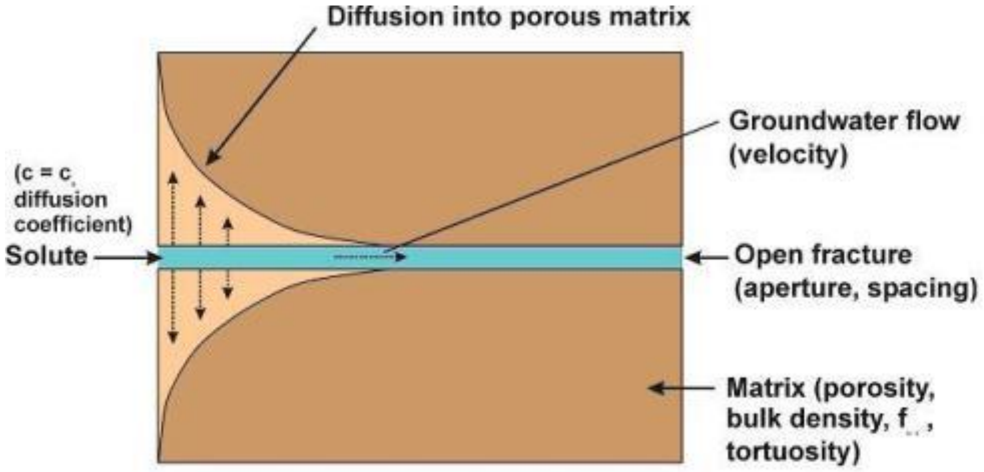

When a clean water flush (i.e. remediation) is attempted in a bedrock fracture:

- Clean water is transported along the fracture via advection
- A chemical concentration gradient develops from the bedrock matrix to the fracture
- Chemical is transported via diffusion from the bedrock matrix into the fracture (i.e., "reverse diffusion")
- The reverse diffusion process can cause rebound during remediation efforts

# Modeling Approach
# Dual-Porosity Conceptual

- Parallel plate model simulates groundwater flow in a series of open, flowing fractures
- Solutes are transported in fractures via advection and dispersion
- Solutes are transported to and from the bedrock matrix via diffusion



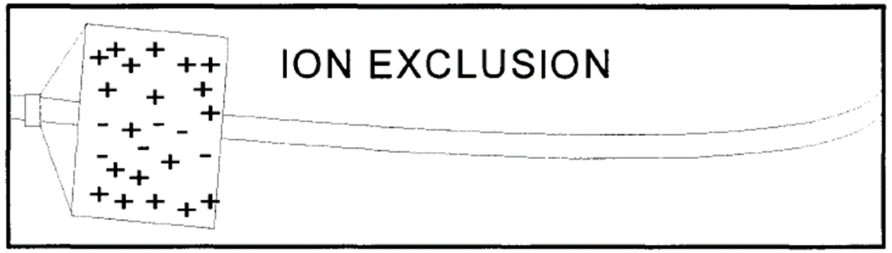

(Single Fracture in Bedrock)

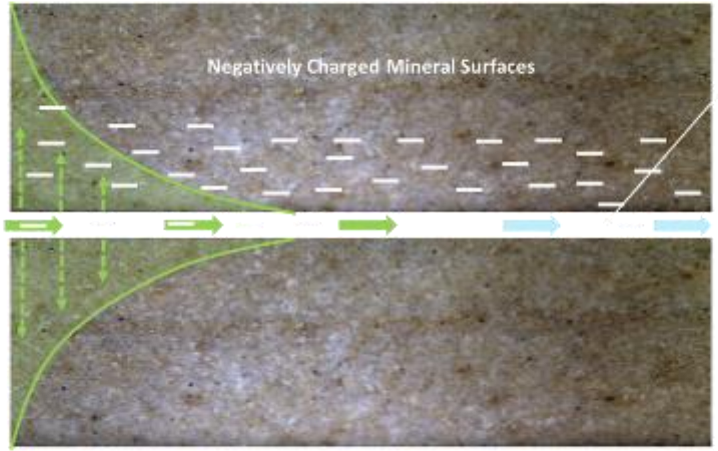
# Anion Exclusion Hypothesis

- Comparing transport of PFOS and MTBE allowed us to gain insight into factors controlling PFOS transport
- PFOS Diffusion Coefficient Estimates

| | |
|---|---|
| Standard estimation value: | $3.3 \times 10^{-6}$ cm2/sec |
| Measured value: | $4.1 \times 10^{-7}$ cm2/sec |

- Dual-Porosity-Derived Retardation Factor
  - PFOS: 221 -equates to plume progressing 29 m/y
  - MTBE: 378 -equates to plume progressing 17 m/y
- PFOS transport velocity was significantly lower than the average linear groundwater velocity (6,497 m/y)
- The dual-porosity retardation factor for PFOS was lower than MTBE, indicating PFOS is more mobile than MTBE in this setting
- Additional mechanisms impeding PFOS diffusion into the Chalk suggested



# Investigation, Risk Assessment and Remediation of Multiple PFAS Source Zones at an Airport to Safeguard an at Risk Water Supply

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- Conceptual site models
- Risk based and sustainable contaminated land management
- PFOS Distribution
- Regulations
- Guernsey Case study
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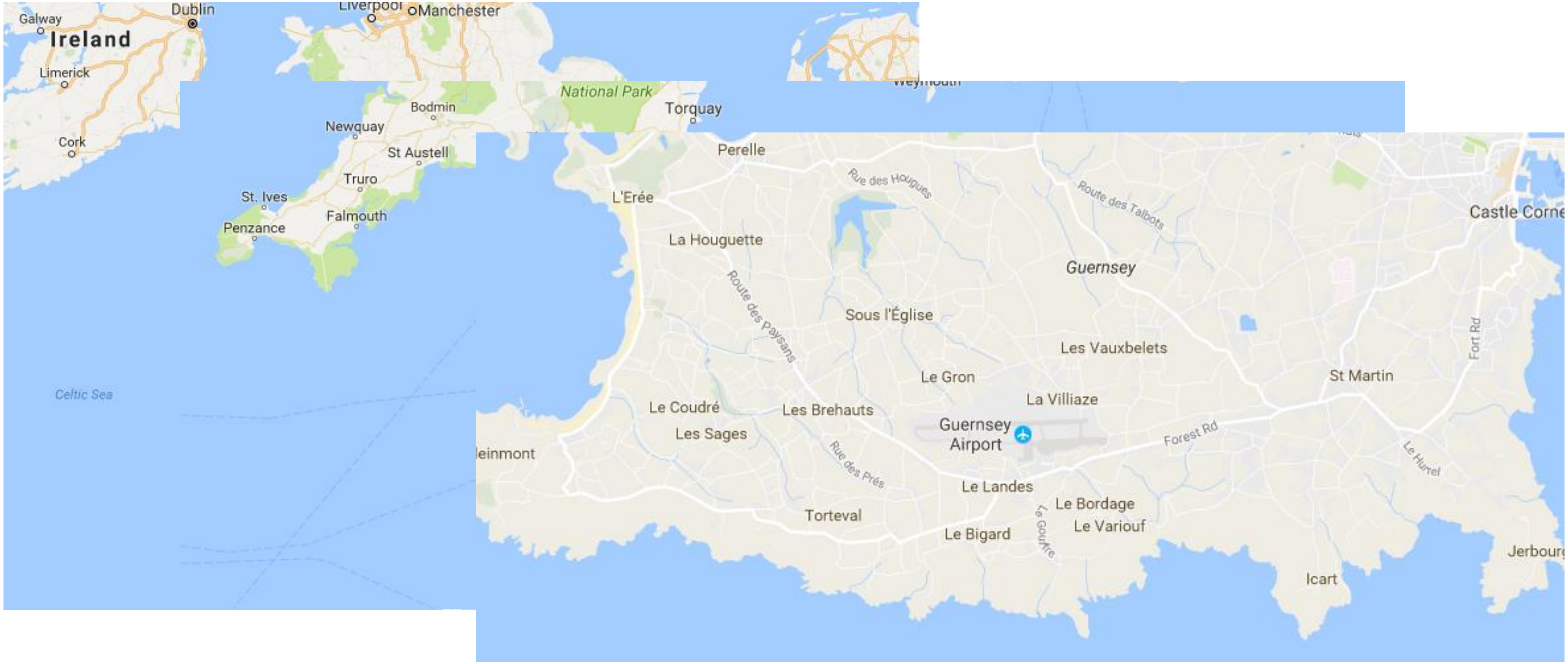
  - Approach
  - Risk Assessment
  - CALM Modelling
  - Remediation
  - Outcome

# Guernsey




**Drinking water derived principally from surface water**

# UK Drinking Water Inspectorate

| Item | Regulatory requirement | Guidance value (concentration) | Minimum action to be taken |
|---|---|---|---|
| **Perfluorooctane sulphonate (PFOS)** | | | |
| Tier 1 | Regulation 27 (Risk assessment) | potential hazard | • ensure considered as part of statutory risk assessment |
| Tier 2 | Regulation 10 (Sampling: further provisions) | > 0.3µg/l | • consult with local health professionals; • monitor levels in drinking water. |
| Tier 3 | Regulation 4(2) (Wholesomeness) | > 1.0µg/l | As tier 2 plus: • put in place measures to reduce concentrations to below 1.0µg/l as soon as is practicable. |
| Tier 4* | Water Industry (Suppliers' Information Direction) 2009 (Notification of events) | > 9.0ug/l | As tier 3 plus: • ensure consultation with local health professionals takes place as soon as possible; • take action to reduce exposure from drinking water within 7 days. |
| *Note - notification to the Inspectorate under the Information Direction may also be triggered at lower levels due to Tier 1, 2 or 3 activities | | | |
| **Perfluorooctanoic acid (PFOA)** | | | |
| Tier 1 | Regulation 27 (Risk assessment) | potential hazard | • ensure considered as part of statutory risk assessment |
| Tier 2 | Regulation 10 (Sampling: further provisions) | > 0.3µg/l | • consult with local health professionals; • monitor levels in drinking water. |
| Tier 3 | Regulation 4(2) (Wholesomeness) | > 5.0µg/l | As tier 2 plus: • put in place measures to reduce concentrations to below 5.0µg/l as soon as is practicable. |
| Tier 4* | Water Industry (Suppliers' Information Direction) 2009 (Notification of events) | > 45.0µg/l | As tier 3 plus: • ensure consultation with local health professionals takes place as soon as possible; • take action to reduce exposure from drinking water within 7 days. |
| *Note - notification to the Inspectorate under the Information Direction may also be triggered at lower levels due to Tier 1 2 or 3 activities | | | |

guardians of drinking water quality

(October 2009)

**Guidance on the Water Supply (Water Quality) Regulations 2000[1] specific to PFOS (perfluorooctane sulphonate) and PFOA (perfluorooctanoic acid) concentrations in drinking water**

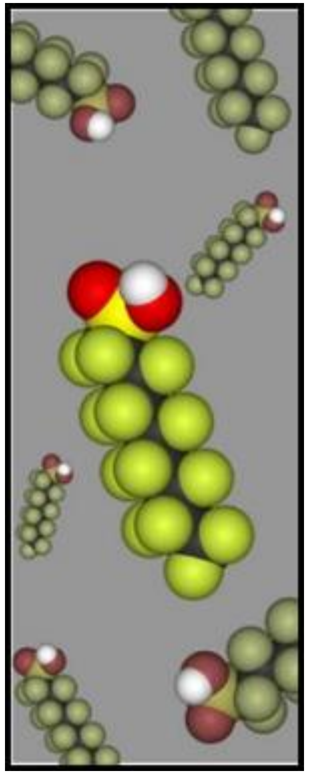
Water supply companies must risk assess potential sources of PFOA/PFOA which might affect their supply system and undertake monitoring.

While 0.3ug/L are the trigger, target guidance levels are 1.0ug/L PFOS & 5.0ug/L PFOA.

# Strategy for Managing PFOS in Guernsey

Arcadis have been working with Guernsey since 2008. The work included the following:

- Desk Based Review & Preliminary Risk Assessment
- Intrusive Assessments and Monitoring
- Fate & Transport Modelling (Quantitative Risk Assessment)
- Management/Remediation Strategy
- Interim Emergency Response Measures
- Implementation of Remedial Management Strategies



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# Guernsey Site Setting


# Initial Objectives

- Quantify the extent of PFOS impacts in soil and water within the airport boundaries;
- Determine whether the identified PFOS impacts represent a significant risk to the potable water supply;
- Identify the most cost effective and pragmatic method of managing any on-going PFAS impacts within the reservoirs and water catchment areas

# Channel Island Airport
# Site Setting and Drivers

**Setting**

- Densely populated island communities
- Surface water dominated drinking water supply
- Airport – topographical high point within water supply catchments
- Shallow water table (<0.5m bgl)

**Source**

- Fire fighting foam usage

**Drivers**

- To provide a sustainable solution which would protect drinking water sources and the wider environment in the short, medium and longer terms

# Guernsey Incidents & Foam Usage

Eleven locations were identified where AFFF has been used. Following investigations by Arcadis, 7 main areas were found to be impacted with PFOS:

- Fire Training Area (GAFT)
- G-BNCY crash site 1997 (GAFC)
- Fire Tender Incident 2002 (GAFE)
- Fire Station Area and Old Fire Training Area (GAFS)
- Central Area Site (Herald Crash - 1984) (GAHD)
- Runway End (GARE)
- Forest Road Crash Site 1999 (GAPP)


**Four of the above locations were considered priority and were subject to remediation.**

# Incidents & Foam Usage

- 11 locations were identified where airport firefighting foam containing PFAS had been used
- 7 of these areas were found to be impacted with PFAS.
- 4 locations were then prioritised and were subject to further investigations and remediation, including:
  - Fire Training Area
  - Fire Tender Incident
  - Fire Station Area
  - 1999 Crash Site
- Interim Emergency Response Measures
  - Sampling adjacent to fire station revealed elevated PFOS concentrations entering drainage
  - Localised dewatering quickly established to prevent ongoing migration of PFOS

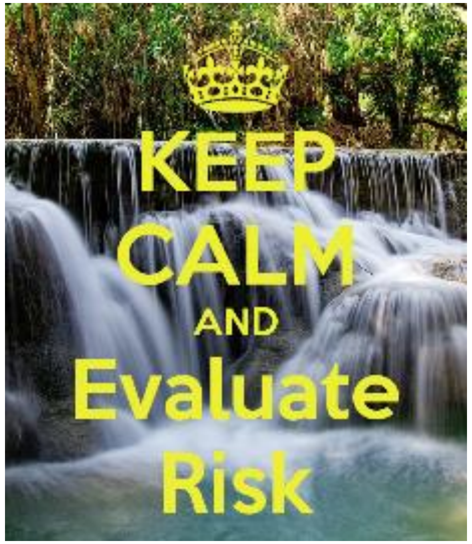

# Fate & Transport Modelling – Site Specific Detailed Quantitative Risk Assessment

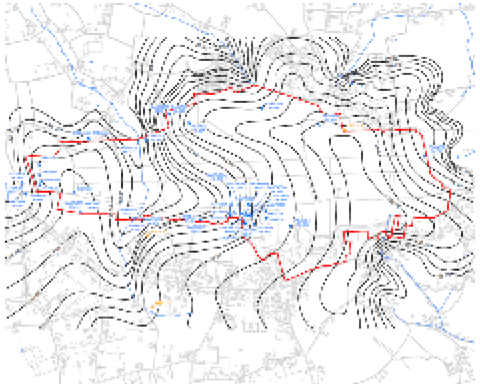
- Site Detailed quantitative risk assessment (DQRA) of the delineated PFOS soil and water impacts
- Modelling for alternative locations and likely volumes of PFOS impacted material that would be moved during any airport redevelopment works.
- Site specific model in order to model accurately the anticipated migration of the PFOS

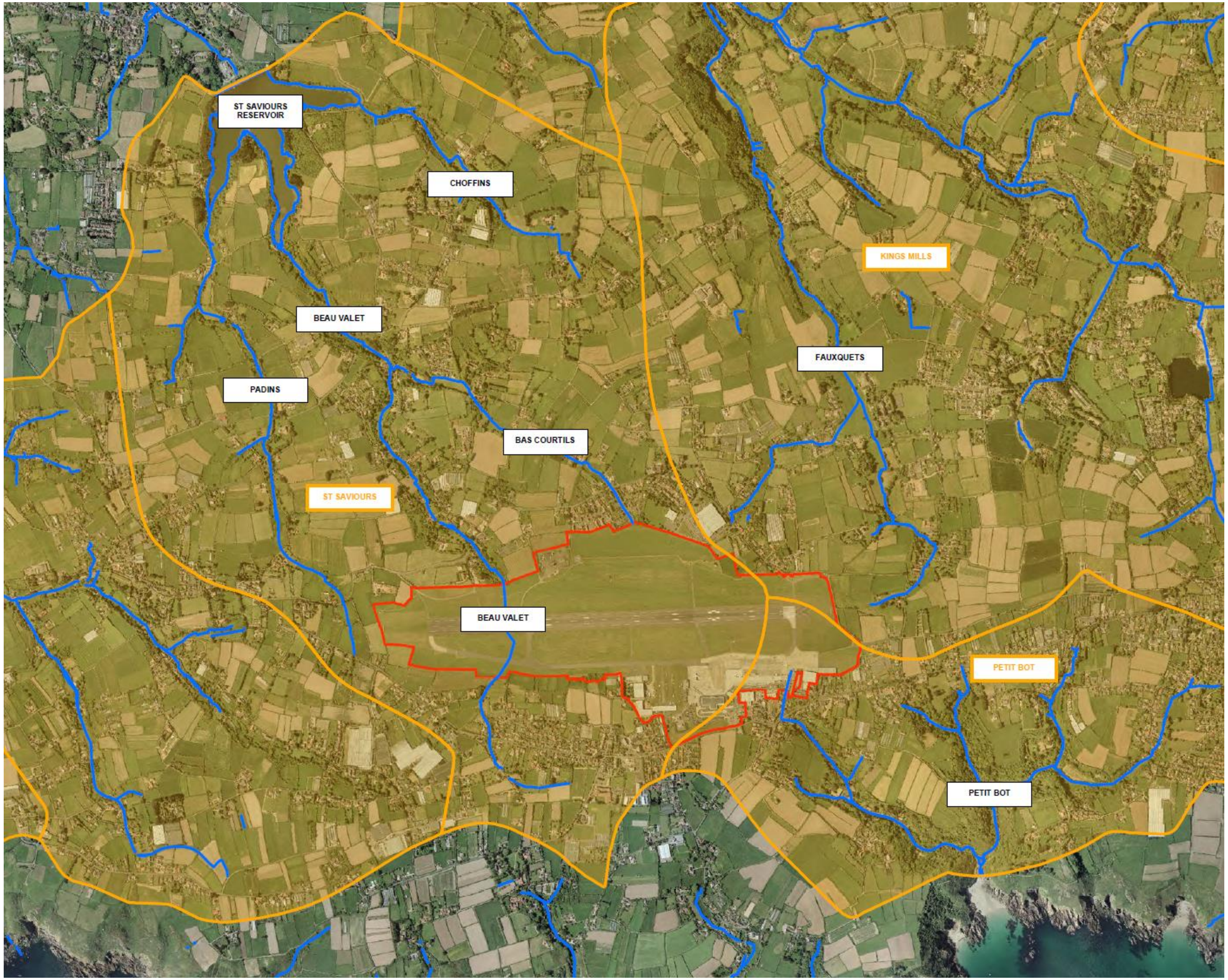
# Calculating Attenuation Linkage Model (CALM)

To assess fate and transport processes of identified PFOS concentrations a numerical was compiled with the primary interlinking elements:

- PFOS within soils beneath the airport, leaching into groundwater and migrating into surface water
- PFOS within the surface water system, mixing and diluting as it flows to the reservoir
- PFOS within the reservoir, entering, mixing and diluting via the streams and being abstracted



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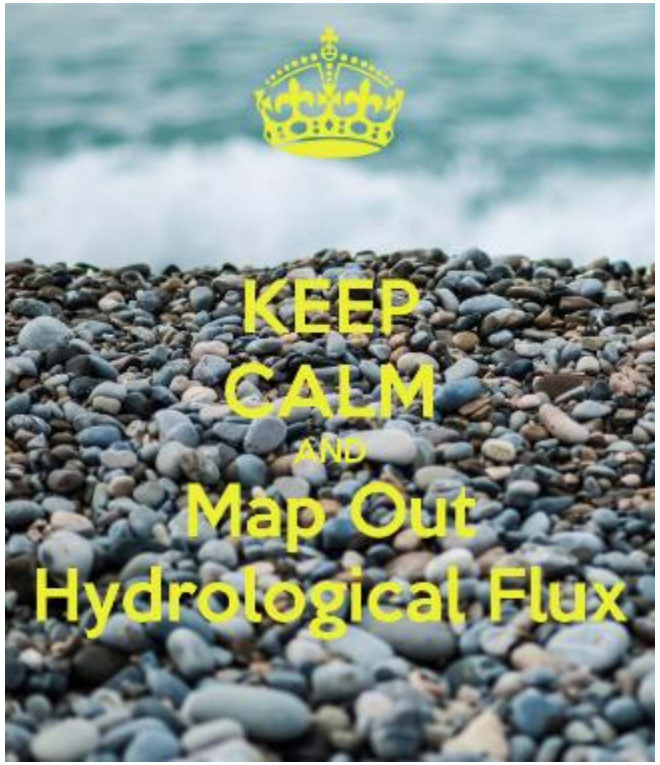

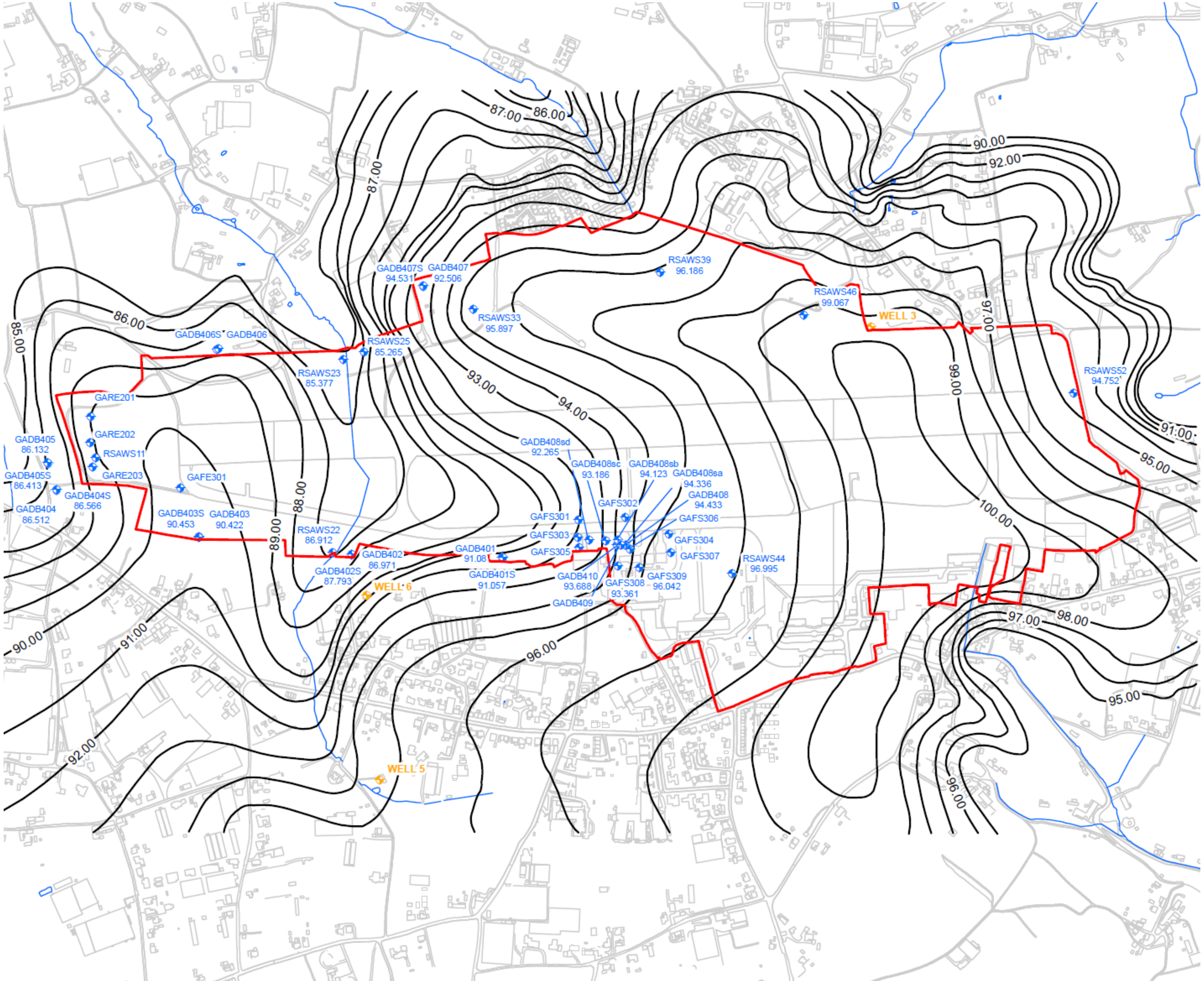

RSAWS39
96.186
GADB407S
94.531
GADB407
92.506
RSAWS33
95.897
RSAWS46
99.067
WELL 3
RSAWS25
85.265
RSAWS23
85.377
GADB406S
GADB406
GARE201
GARE202
RSAWS11
GARE203
GADB405
86.132
GADB405S
86.413
GADB404S
86.566
GADB404
86.512
GAFE301
GADB403S
90.453
GADB403
90.422
RSAWS22
86.912
GADB402
86.971
GADB402S
87.793
WELL 6
GADB401
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GAFS308
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RSAWS52
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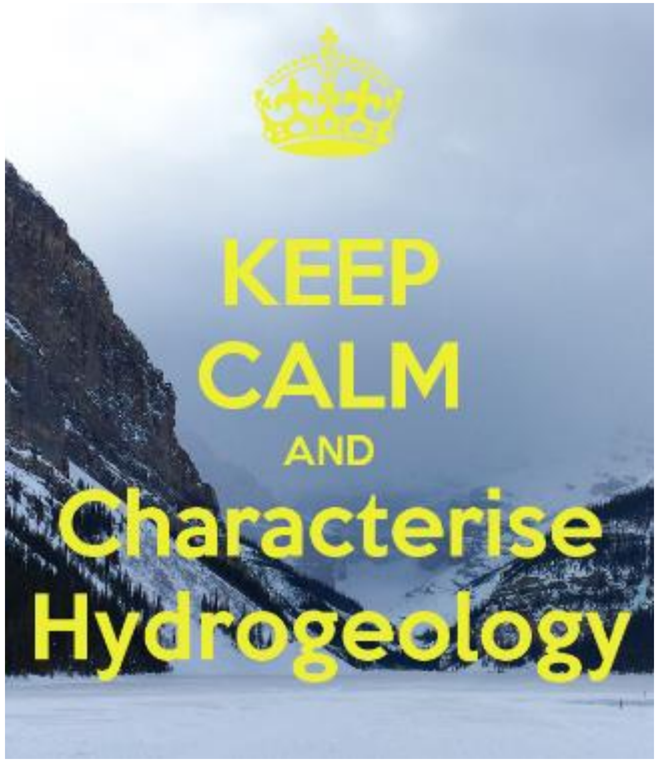
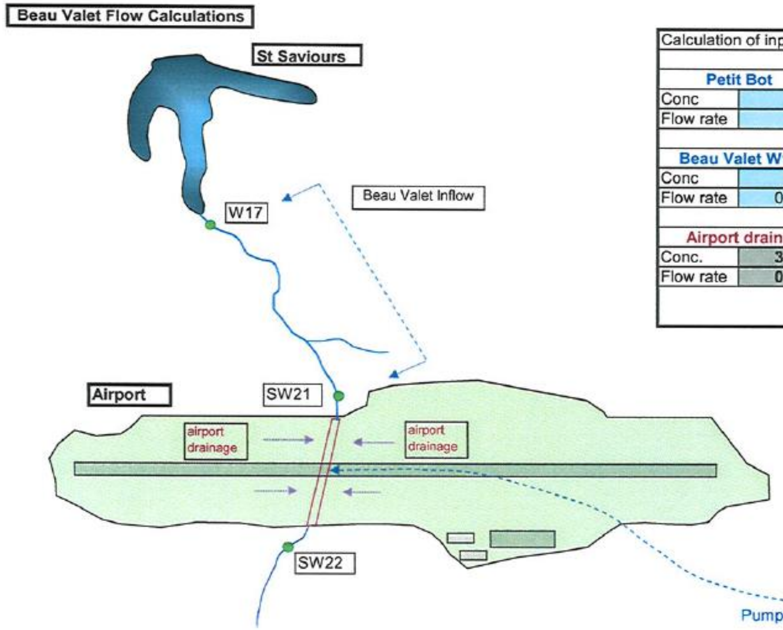


KEEP
CALM
AND
Characterise
Hydrogeology

# Calculating Attenuation Linkage Model (CALM)
# Reservoir Inlet Flow Model




Calculation of input from drainage system

| Petit Bot | |
|---|---|
| Conc | 0 |
| Flow rate | 0 |

| Beau Valet W17 | |
|---|---|
| Conc | 3.42 |
| Flow rate | 0.016 |

| Airport drains | |
|---|---|
| Conc. | 30.90 |
| Flow rate | 0.002 |

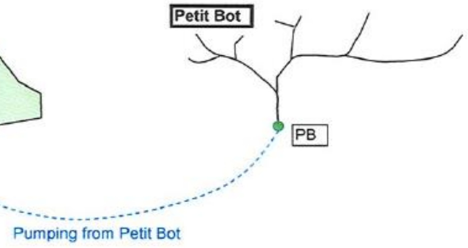
| Beau Valet SW22 | |
|---|---|
| Conc | 0 |
| Flow rate | 0.004 |

| Inflow to culvert (SW22+PB) | |
|---|---|
| Conc | 0.00 |
| Flow rate | 0.004 |

| Beau Valet SW21 | |
|---|---|
| Conc | 10.3 |
| Flow rate | 0.006 |

| Beau Valet Inflow | |
|---|---|
| Flow rate | 0.012 |
| | 0.01 |

| W17 check | |
|---|---|
| Conc | 2.57 |
| Flow rate | 0.018 |




Variations in "output" from beneath airport

| Petit Bot | |
|---|---|
| Conc | 0 |
| Flow rate | 0 |

| Beau Valet SW22 | |
|---|---|
| Conc | 0 |
| Flow rate | 0.006 |

| Airport drains | |
|---|---|
| Conc. | 30.90 |
| Flow rate | 0.002 |

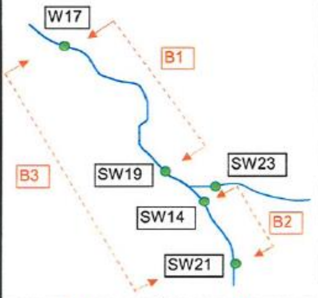
| Calculated output (SW21) | |
|---|---|
| Conc | 7.73 |
| Flow rate | 0.008 |

Effect on flow into resevoir

| Beau Valet Inflow | |
|---|---|
| Flow rate | 0.012 |

| Resulting W17 | |
|---|---|
| Conc | 3.08 |
| Flow rate | 0.020 |

Beau Valet Baseflow calculation




| W17 | |
|---|---|
| Flow rate | 0.016 |

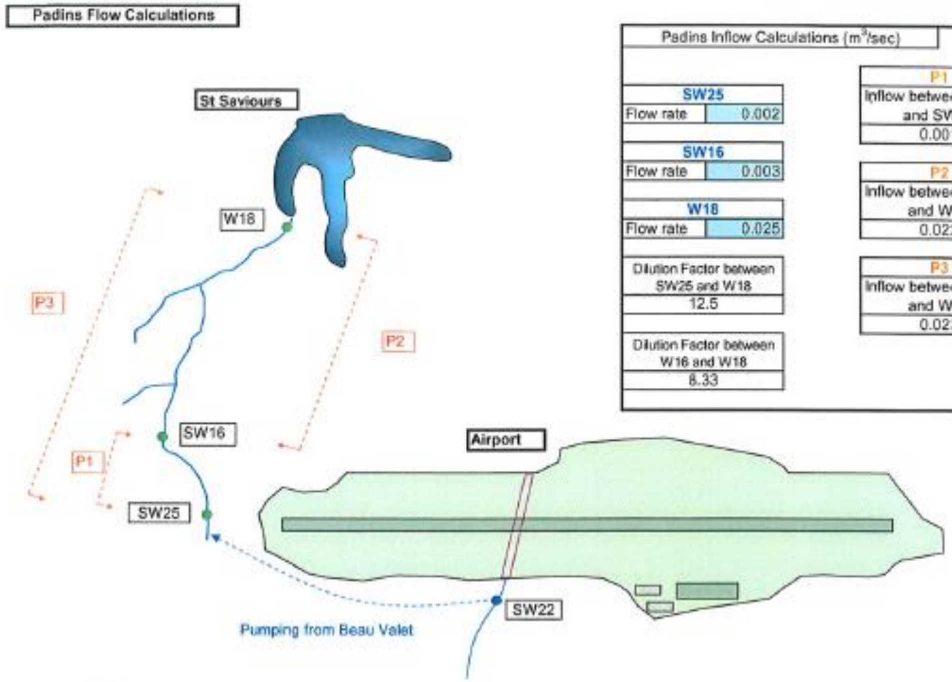
| SW19 | |
|---|---|
| Flow rate | 0.045 |

| SW23 | |
|---|---|
| Flow rate | 0.003 |

| SW14 | |
|---|---|
| Flow rate | 0.028 |

| SW21 | |
|---|---|
| Flow rate | 0.006 |

| B1 | B2 | B3 |
|---|---|---|
| Baseflow between SW19 and W17 | Baseflow between SW21 and SW14 | Baseflow between SW21 and W17 |
| -0.029 | 0.022 | 0.007 |




Padins Inflow Calculations ($m^3/sec$)

| SW25 | |
|---|---|
| Flow rate | 0.002 |

| SW16 | |
|---|---|
| Flow rate | 0.003 |

| W18 | |
|---|---|
| Flow rate | 0.025 |

| Dilution Factor between SW25 and W18 |
|---|
| 12.5 |

| Dilution Factor between W16 and W18 |
|---|
| 8.33 |

| P1 |
|---|
| Inflow between SW25 and SW16 |
| 0.001 |

| P2 |
|---|
| Inflow between SW16 and W18 |
| 0.022 |

| P3 |
|---|
| Inflow between SW25 and W18 |
| 0.023 |

PFOS concentrations based on SW25

| Pumping from Beau Valet | |
|---|---|
| Conc | 0 |
| Flow rate | 0.002 |

| SW25 | |
|---|---|
| Conc | 11 |
| Flow rate | 0.002 |

| Resulting SW16 | |
|---|---|
| Conc | 4.40 |
| Flow rate | 0.005 |

| Resulting W18 | |
|---|---|
| Conc | 0.81 |
| Flow rate | 0.027 |

PFOS concentrations based on SW16

| Pumping from Beau Valet | |
|---|---|
| Conc | 0 |
| Flow rate | 0 |

| SW16 | |
|---|---|
| Conc | 0.89 |
| Flow rate | 0.003 |

| Resulting W18 | |
|---|---|
| Conc | 0.11 |
| Flow rate | 0.025 |

PFOS concentrations based on W18

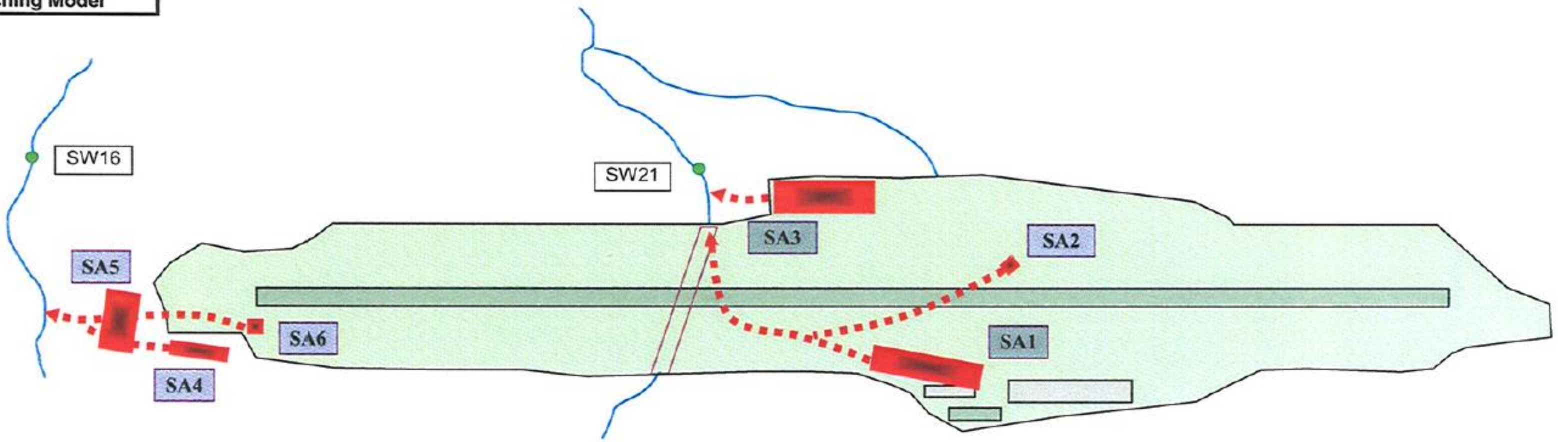
| Pumping from Beau Valet | |
|---|---|
| Conc | 0 |
| Flow rate | 0.002 |

| W18 | |
|---|---|
| Conc | 0.64 |
| Flow rate | 0.025 |

| Resulting W18 | |
|---|---|
| Conc | 0.59 |
| Flow rate | 0.027 |

# Calculating Attenuation Linkage Model (CALM) Soil Source Leaching Model

**Soil Source Leaching Model**




| | SA1 | SA2 | SA3 | SA4 | SA5 | SA6 |
|---|---|---|---|---|---|---|
| Initial conc. (mg/kg) | 5.03 | 0.63 | 0.009 | 0.531 | 0.02 | 9.985 |
| kd | 1 | 1 | 1 | 1 | 1 | 1 |
| k (m/day) | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| I | 0.02 | 0.01 | 0.03 | 0.02 | 0.03 | 0.02 |
| Width (m) | 55 | 20 | 75 | 25 | 100 | 20 |
| Length (m) | 125 | 20 | 150 | 85 | 45 | 25 |
| Ne | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| Comp. Distance (m) | 655 | 810 | 180 | 110 | 38 | 290 |
| L2 conc. (µg/l) = | 1.70E+03 | 2.52E+02 | 3.90E+00 | 2.12E+02 | 6.40E+00 | 3.49E+03 |
| L3 conc. (µg/l) = | 1.42E+03 | 3.47E+00 | 3.31E+00 | 1.23E+02 | 6.40E+00 | 2.96E+02 |
| Q ($m^3$/sec) | 2.55E-04 | 2.17E-05 | 5.21E-04 | 1.16E-04 | 3.65E-04 | 3.51E-05 |
| SSAC (mg/kg) = | [redacted] | [redacted] | [redacted] | [redacted] | [redacted] | [redacted] |

**Beau Valet flow data (see Beau Valet tab)**

| Measured flow & conc. at SW22 | |
|---|---|
| Conc. | 0.00 |
| Flow rate | 0.004 |

| Measured flow & conc. at SW21 | |
|---|---|
| Conc. | 10.30 |
| Flow rate | 0.006 |

| Calculated Inflow to Beau Valet | |
|---|---|
| Conc. | 30.90 |
| Flow rate | 0.002 |

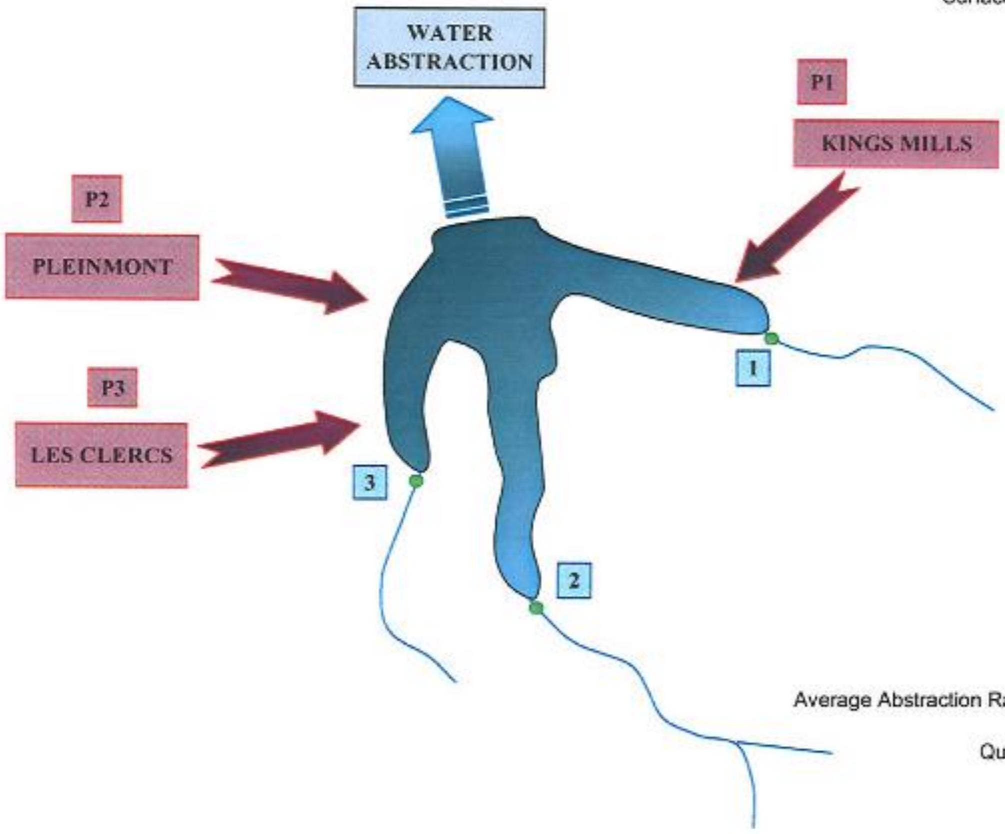
| Baseflow between SW21 and W17 |
|---|
| 0.007 |

| Inflow from Bas Courtils (SW23) |
|---|
| 0.003 |

# Calculating Attenuation Linkage Model (CALM) Reservoir Mixing Model

ARCADIS Design & Consultancy for natural and built assets

**Reservoir Mixing Model**




| | |
|---|---|
| Surface Area of Reservoir ($m^2$) | 126908 |
| Maximum capacity of reservoir (litres) | 7.20E+08 |
| Initial PFOS concentration in reservoir (µg/l) | 0.74 |
| Initial quantity of water in reservoir (litres) | 7.20E+08 |
| Initial mass of PFOS in reservoir (kg) | 0.53 |

| Stream 1 (Choffins) | |
|---|---|
| PFOS conc (µg/l) | 0.00 |
| Flow rate ($m^3$/sec) | 0.011 |

| Stream 2 (Beau Valet) | |
|---|---|
| PFOS conc (µg/l) | 3.42 |
| Flow rate ($m^3$/sec) | 0.041 |

| Stream 3 (Padins) | |
|---|---|
| PFOS conc (µg/l) | 0.00 |
| Flow rate ($m^3$/sec) | 0.031 |

| Pumping P1 (Kings Mills) | |
|---|---|
| PFOS conc (µg/l) | |
| Flow rate ($m^3$/sec) | |

| Pumping P2 (Pleinmont) | |
|---|---|
| PFOS conc (µg/l) | |
| Flow rate ($m^3$/sec) | |

| Pumping P3 (Les Clercs) | |
|---|---|
| PFOS conc (µg/l) | |
| Flow rate ($m^3$/sec) | |

| Direct Precipitation |
|---|
| Average Precipitation (mm/year) |
| 869.54 |

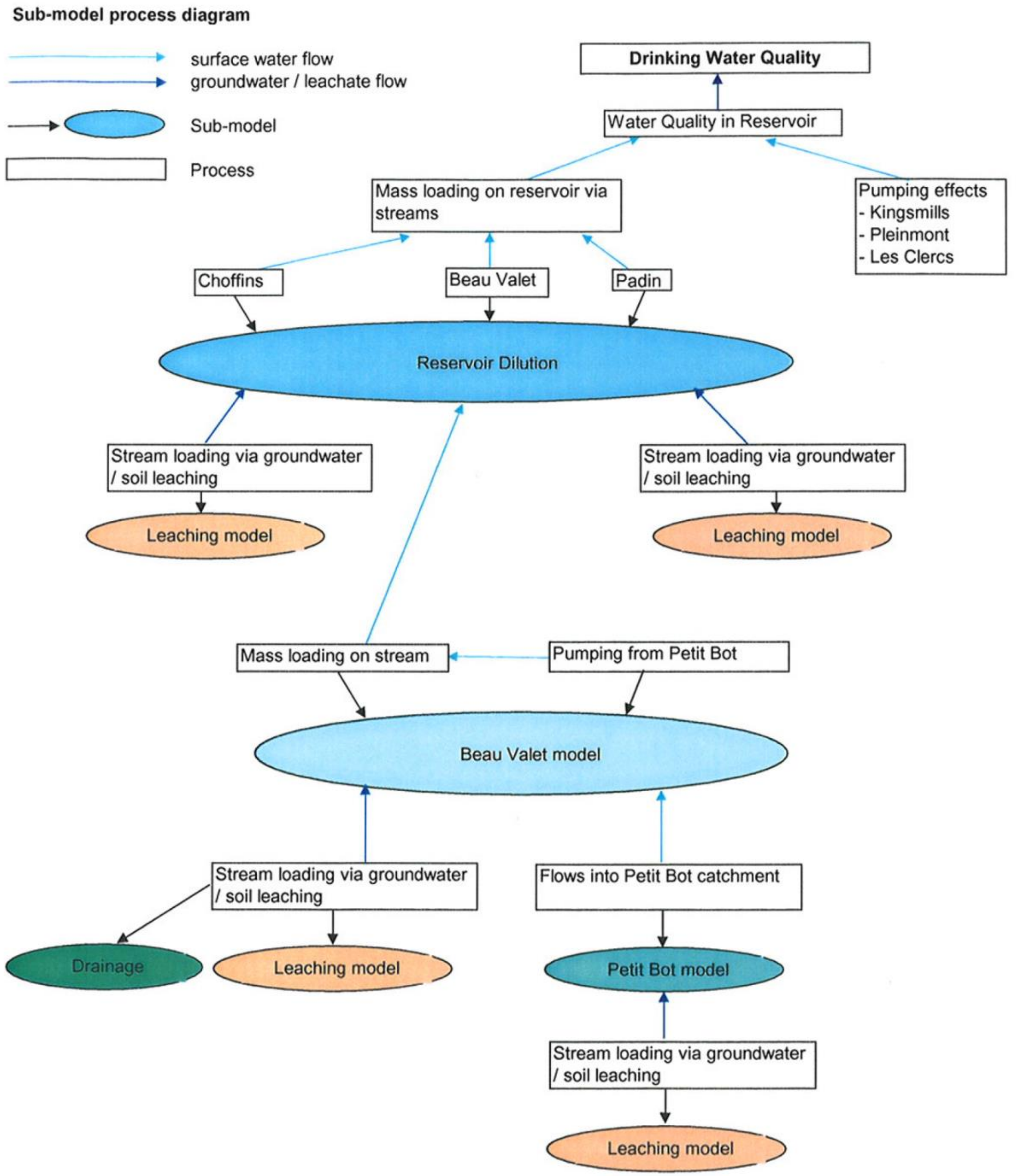
Calculated precipitation flow rate 0.0035

| | |
|---|---|
| Average Abstraction Rate over period ($m^3$/sec) | 0.058 |
| Quantity Abstracted (litres) | 1.83E+09 |
| Time Period (days) | 365 |
| Inflow concentration (µg/l) | 1.62 |
| Inflow flow rate ($m^3$/sec) | 0.086 |
| Quantity of inflow over time period (litres) | 2.73E+09 |
| Inflow mass of PFOS (kg) | 4.42 |

| RESERVOIR OVERTOPPING | Resulting concentration of PFOS (µg/l) | 1.62 |
|---|---|---|
| | Reduction in reservoir water quality | |
| | Resulting mass of PFOS in reservoir (kg) | 1.167 |
| | Resulting quantity of water in reservoir (litres) | 7.20E+08 |

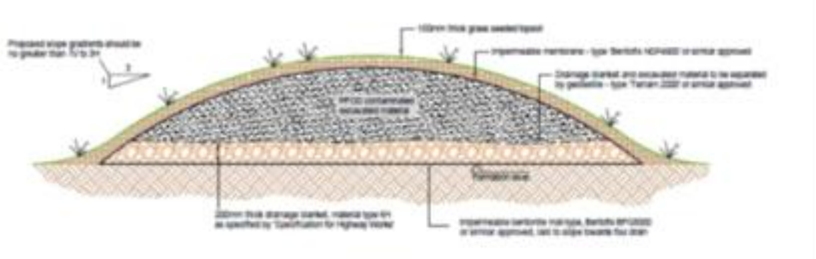
This model does not account for overland runnoff into the reservoir, although this are likely to be of comparatively low significance.

# Calculating Attenuation Linkage Model (CALM)




# PFOS Mass Removal & Containment

- Removal of the PFOS impacted soil that was considered to act as a PFOS source into the groundwater
- Excavations of impacted soils carried out at 4 locations
- All excavated material was then isolated in a specifically designed bund to the front of the airport terminal building
- 15,000 tons of PFOS contaminated soils within a dedicated waste management cell, which also acted as a sound barrier.



Typical Indicative Section Through PFOS Contaminated Material Containment Bund

# Groundwater Treatment

- Designed in 2009 by Arcadis
- Capacity 20L/s
- Capture of water leaving airport towards reservoir, treatment and discharge away from reservoir
- Treatment of 200 million $m^3$ of water containing up to 300 $\mu$g/L (ppb) PFOS
- Consistent treatment performance using granulated activated carbon to less than UK regulatory standards

# Results

- Systematic and robust approach with the aim of efficiently and cost effectively assessing the risks
- Development of short, medium and long term solutions to protect the population’s drinking water supply
- Within 9 months of assessment a solution was developed and implemented which reduced PFOS concentrations in the drinking water supply by 75%
- Further reductions in PFOS concentrations were ensured in the medium and longer term

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# PFOS levels in Guernsey drinking water safe, finds report


Soil contaminated by an overturned fire truck was removed in March 2012

**Guernsey and Alderney tap water is safe to drink despite containing traces of a firefighting chemical, says a report.**

# Guernsey Water works to cut levels of Pfos in raw water

## Improved monitoring shows levels are well within UK guidance

by **Paul Ainsworth**
painsworth@guernseypress.com

ACTION is being taken to reduce Pfos levels within raw water, Guernsey Water's annual water quality report has said.

The utility said it had been working with the Director of Environmental Health and Pollution Regulation and other States departments to reduce levels of the firefighting foam chemical Pfos, through the treatment of stream water from affected catchments and the removal and containment of contaminated soil.

The utility's water quality risk manager, Margaret McGuinness, said affected catchments had also been closely monitored and measures put in place, such as stream diverts, to minimise levels in raw water.

'This has been successful and we have seen a drop in the maximum detected Pfos concentration recorded,' she said.

Over the year Pfos has been monitored on a fortnightly basis both in the raw water in St Saviour's and treated water leaving the parish's water treatment works.

The maximum result detected in the treated drinking water analysis was 0.049µg/l (parts per billion) which is well within tier 1 of the guidance issued by the UK Drinking Water Inspectorate on Pfos.

There has also been a drop in the maximum detected Pfos concentration recorded at St Saviour's Reservoir, falling from 0.19µg/l in 2014 to 0.077µg/l recorded in 2015.

There was a further decrease in the maximum Pfos concentration detected in samples from streams, from 20µg/l to 14µg/l a year later in 2015.

'This was due to a combination of factors including the removal of contaminated soil from the catchment and natural variation in rainfall amounts.'

Water quality customer enquiries rose by 110 to 226 in 2015, with 78 of these related to the taste and odour of drinking water, which was a direct consequence of algal 'die off' in the St Saviour's and Longue Hougue reservoirs.

Guernsey Water said this was being dealt with through improved water quality monitoring and proactive selection of raw water sources which helps dilute or avoid supplying taste-affected water.

Overall, the utility said, its annual water quality report showed it had achieved all its 2015 water quality targets with 100% compliance recorded at the service reservoirs and water treatment works for the second year running.

The utility provided 4,527 megalitres of safe and high-quality water to its customers and, when analysed, 99.84% of the water met all national and European Union Standards.

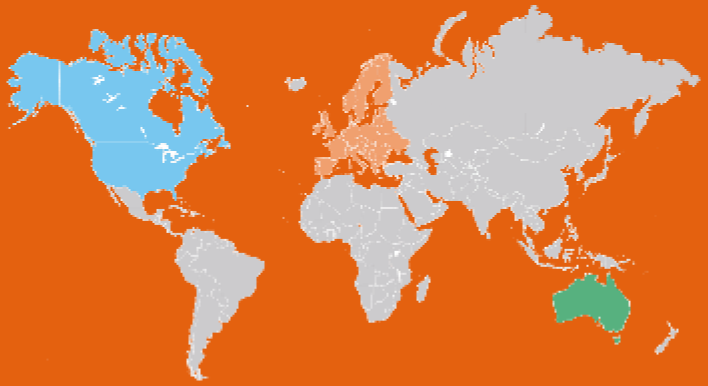
Director of water services Stephen Langlois said it continued to provide water that was safe and good to drink.

'These excellent figures are due to the diligence and technical expertise of our staff who are constantly striving to improve what we do and ensure our customers always value the quality of the drinking water we supply.'

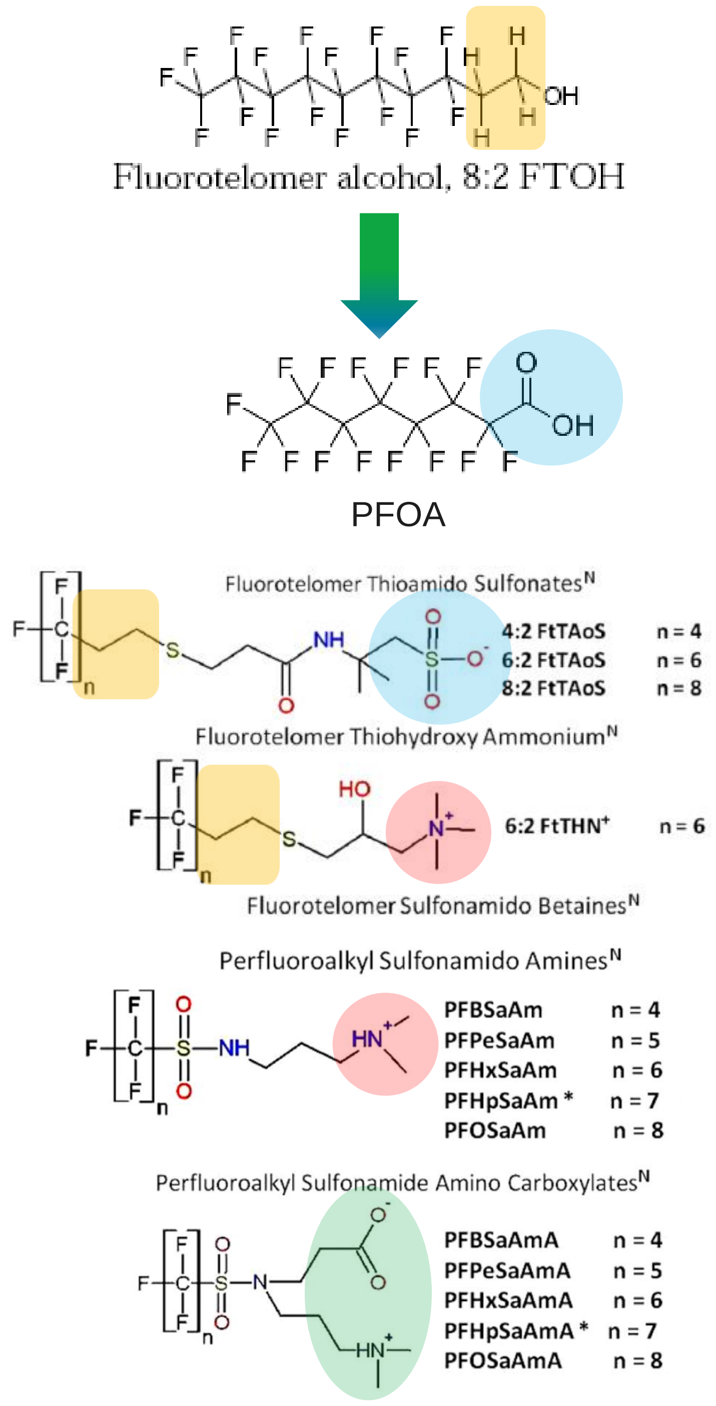

**Director of water services at Guernsey Water Stephen Langlois has said the utility continued to provide water that is safe and good to drink.** **(Picture by Tom Tardif, 15570564)**

# PFC’s to PFASs / REGULATORY CLIMATE / PFAS DISTRIBUTION

Evolution of regulatory understanding globally and global distribution



# Polyfluorinated Compounds -Precursors




Thousands of polyfluorinated precursors to PFAAs have been commercially synthesized for bulk products

The common feature of the precursors is that they will **biotransform** to make PFAA's as persistent "dead end" daughter products

PFAS do not biodegrade i.e. mineralise

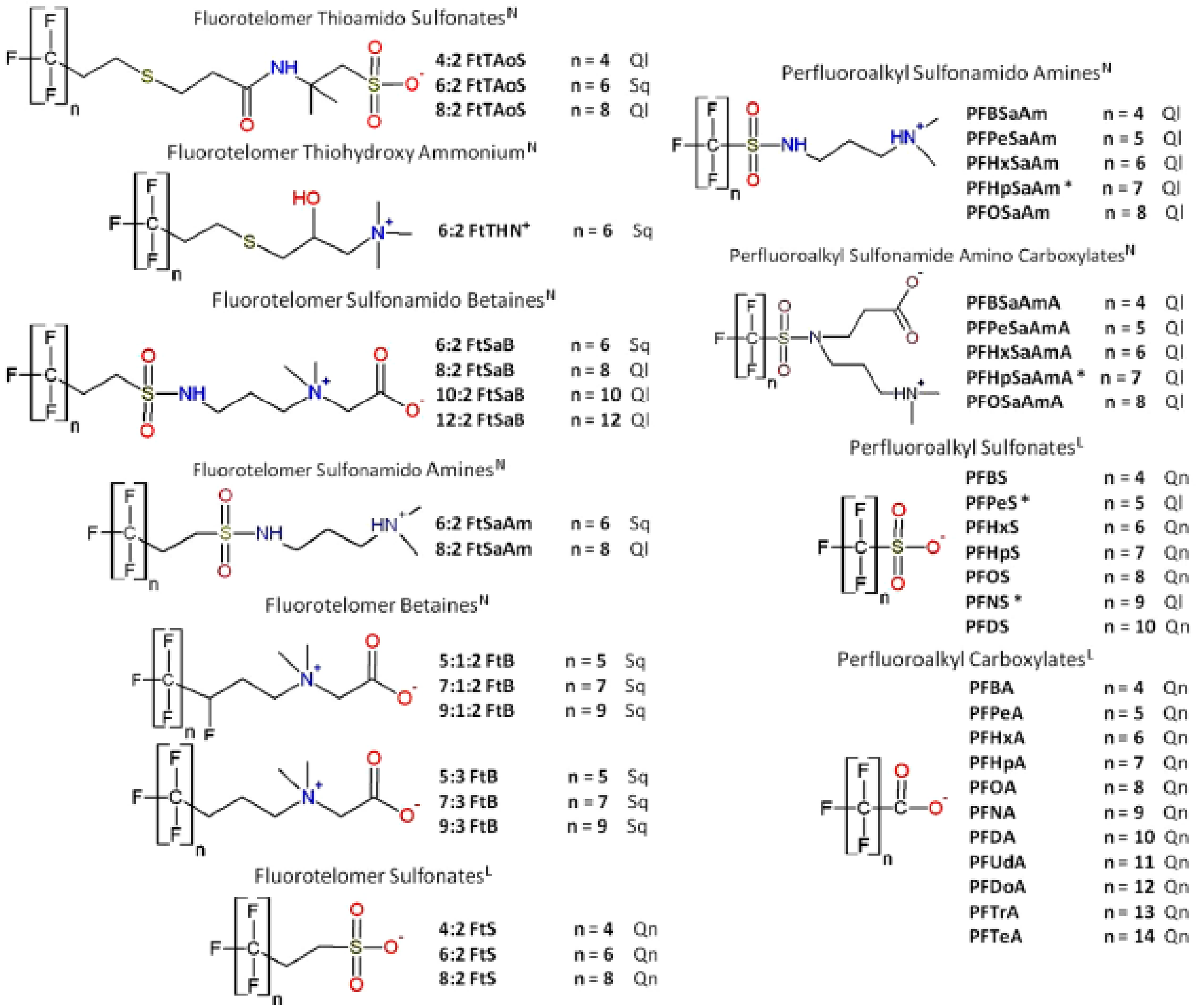
Some precursors are fluorotelomers

Some are cationic (positively charged) or zwitterionic (mixed charges) –this influences their fate and transpor in the environment

Cationic / zwitterionic PFAS tend to be less mobile than anionic PFAAs and so can potentially be retained longer in "source zones"

Environmental fate and transport will be complex as PFAS comprise multiple chain lengths and charges

# Diversity of PFAS Characterised in AFFF




**Zwitterionic, Cationic, and Anionic Fluorinated Chemicals in Aqueous Film Forming Foam Formulations and Groundwater from U.S. Military Bases by Nonaqueous Large-Volume Injection HPLC-MS/MS**

Will J. Backe,[†] Thomas C. Day,[†] and Jennifer A. Field*[,‡]

[†]153 Gilbert Hall, Department of Chemistry, Oregon State University, Corvallis, Oregon 97331-4003, United States
[‡]1007 Agricultural and Life Science Building, Department of Molecular and Environmental Toxicology, Oregon State University,

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Article

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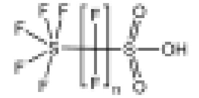
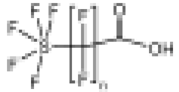
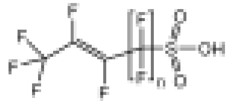
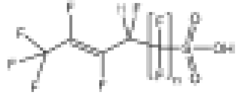
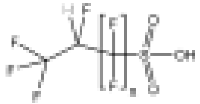
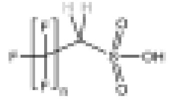
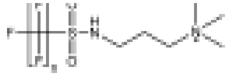
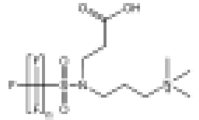
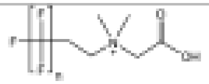
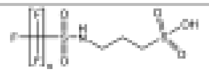
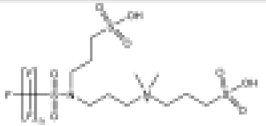
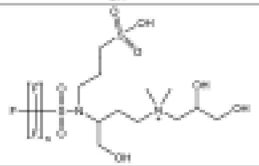
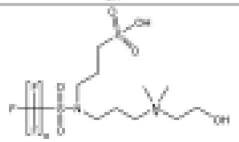
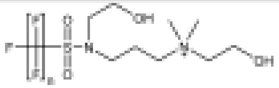
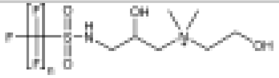
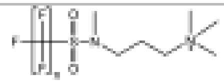
# Discovery of 40 Classes of Per- and Polyfluoroalkyl Substances in Historical Aqueous Film-Forming Foams (AFFFs) and AFFF-Impacted Groundwater

Krista A. Barzen-Hanson,[†] Simon C. Roberts,[∇,‡] Sarah Choyke,[§] Karl Oetjen,[‡] Alan McAlees,[||] Nicole Riddell,[||] Robert McCrindle,[⊥] P. Lee Ferguson,[§] Christopher P. Higgins,[*,‡] and Jennifer A. Field[*,#]

| Class Number | Structure | $n^{a,b}$ | Acronym[c] | Confidence Level[d,e] | AFFF/CP Found In |
|---|---|---|---|---|---|
| 21 |  | 3-9 | n-F5S-PFAS | 2b | A, B, C, D, E, G, M, N |
| 22 |  | 6-8 | n+/-F5S-PFAA[f] | 3 | M, N |
| 23 |  Multiple isomers possible | 1-10 | UPFAS[g,h] | 3 | A, B, C, D, E, M, N, P |
| 24 |  Multiple isomers possible | 1-6 | H-UPFAS[g,h] | 3 | A, B, C, D, E, F, G, M |
| 25 |  Multiple isomers possible | 0[i]-8 | H-PFAS[g,h] | 3 | A, B, C, D, E, F, G, M, N, P |
| 26 |  Multiple isomers possible | 5, 7 | x:1 PFAS[i] | 3 | A, B, C, D, E, F, G, M, N, P |

| Class Number | Structure | $n^{a,b}$ | Acronym[c] | Confidence Level[d,e] | AFFF/CP Found In |
|---|---|---|---|---|---|
| 13 |  | 3-8 | N-TAmP-FASA | 3 | A, B, C, D, E, F, G |
| 14 |  | 3-6 | N-TAmP-FASAP | 3 | D, E, F, G |
| 15 |  | 4-6 | N-CMAmP-FASAP | 2b | D, E, F, G |
| 16 |  | 3-6 | N-CMAmP-FASA | 2b | D, E, F, G |
| 17 |  | 6, 8, 10 | CMAmE-FA | 2b | L |
| 18 |  | 4, 6, 8 | CMAmB-FA | 3 | L |
| 19 | $C_{n+8}H_{18}O_3SN_2F_{2n+1}$ | 6, 8, 10 | Not applicable | 4 | I, J |
| 20 | $C_{n+11}H_{20}O_2SN_2F_{2n+1}$ or $C_{n+10}H_{18}O_3SN_2F_{2n+1}$ | Unknown | Not applicable | 5 | I, J |

| Class Number | Structure | $n^{a,b}$ | Acronym[c] | Confidence Level[d,e] | AFFF/CP Found In |
|---|---|---|---|---|---|
| 1 |  | 3-6 | N-SP-FASA | 2b | B, C |
| 2 |  | 3-8 | N-SPAmP-FASA | 2b | A, B, C, F |
| 3 |  | 3-9 | N-SHOPAmP-FASA | 3[f] | C, D, E, F, G |
| 4 |  | 4-6 | N-SPHOEAmP-FASA | 3 | B, C |
| 5 |  | 3-8 | N-SPAmP-FASAPS | 2b | A, B, C |
| 6 |  | 3-6 | N-diHOPAmHOB-FASA | 3 | B, C, O |
| 7 |  | 2-6 | N-diHOPAmHOB-FASAPS | 3 | A, B, C |
| 8 |  | 2-8 | N-HOEAmP-FASAPS | 2b | A, B, C |
| 9 |  | 2-8 | N-HOEAmP-FASE | 2b | A, B, C, D, E |
| 10 |  | 4-6 | N-HOEAmHOP-FASA | 3 | B, C |
| 11 |  | 2-8 | N-HOEAmP-FASA | 2b | A, B, C, D, E |
| 12 |  | 4-8 | N-TAmP-N-MeFASA | 3 | B |

# Aerobic Biotransformation Funnel –Precursors converted to PFAAs

# Human Exposure to PFAS

**Drinking water**

**Food**

Main exposure

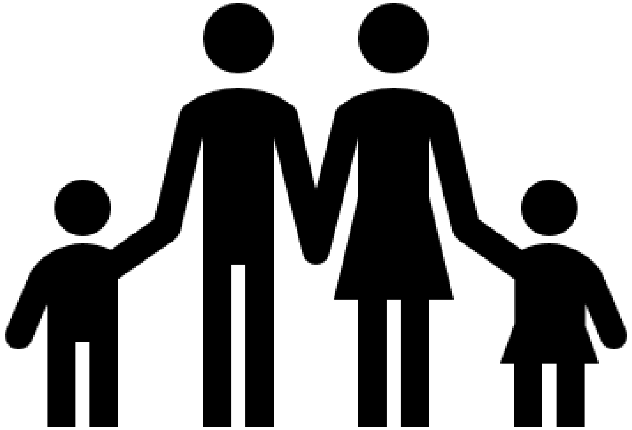
House dust

Indoor air

Outdoor air

Consumer products

- Fluoropolymers inc. side chain polymers
- Fluorosurfactants
- Performance chemicals
- Product residuals



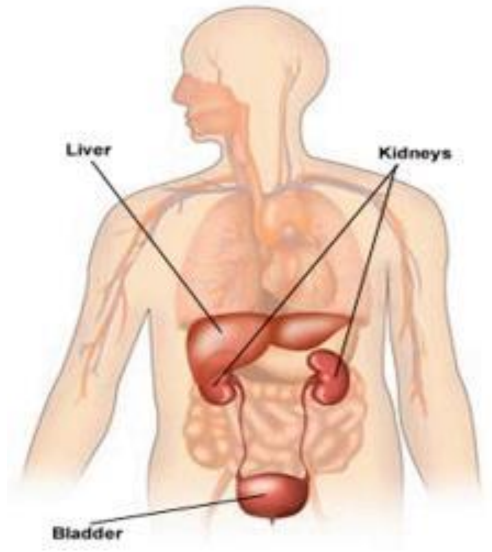
Precursor

PFAA

# PFAS Exposure, Distribution, and Elimination in Humans

| EXPOSURE | DISTRIBUTION | ELIMINATION |
|---|---|---|
| • **Most exposure** is likely from ingestion of contaminated food or water<br>• Exposure can also comes from:<br>  • Breast milk<br>  • Air<br>  • Dust (especially for children)<br>  • Skin contact with various consumer products | • PFAS bind to proteins, not to fats.<br>• Highest concentrations are found in blood, liver, kidneys, lung, spleen and bone marrow.<br>• Long chain PFAS such as PFOS, PFHxS and PFOA have bioaccumulative properties.<br>• Shorter chain PFAS generally have a lower bioaccumulation potential, although there may be some exceptions. | • Elimination of PFOS, PFHxS and PFOA from the human body takes some years, whereas elimination of shorter chain PFAS are in the range of days<br>• Apart from chain length, blood half-lives of PFAS are also dependent on gender, PFAS-structure (branched vs. straight isomers), PFAS-type (sulfonates vs. carboxylates) and species.<br>• Elimination mainly by urine. |

# Toxicity for Humans



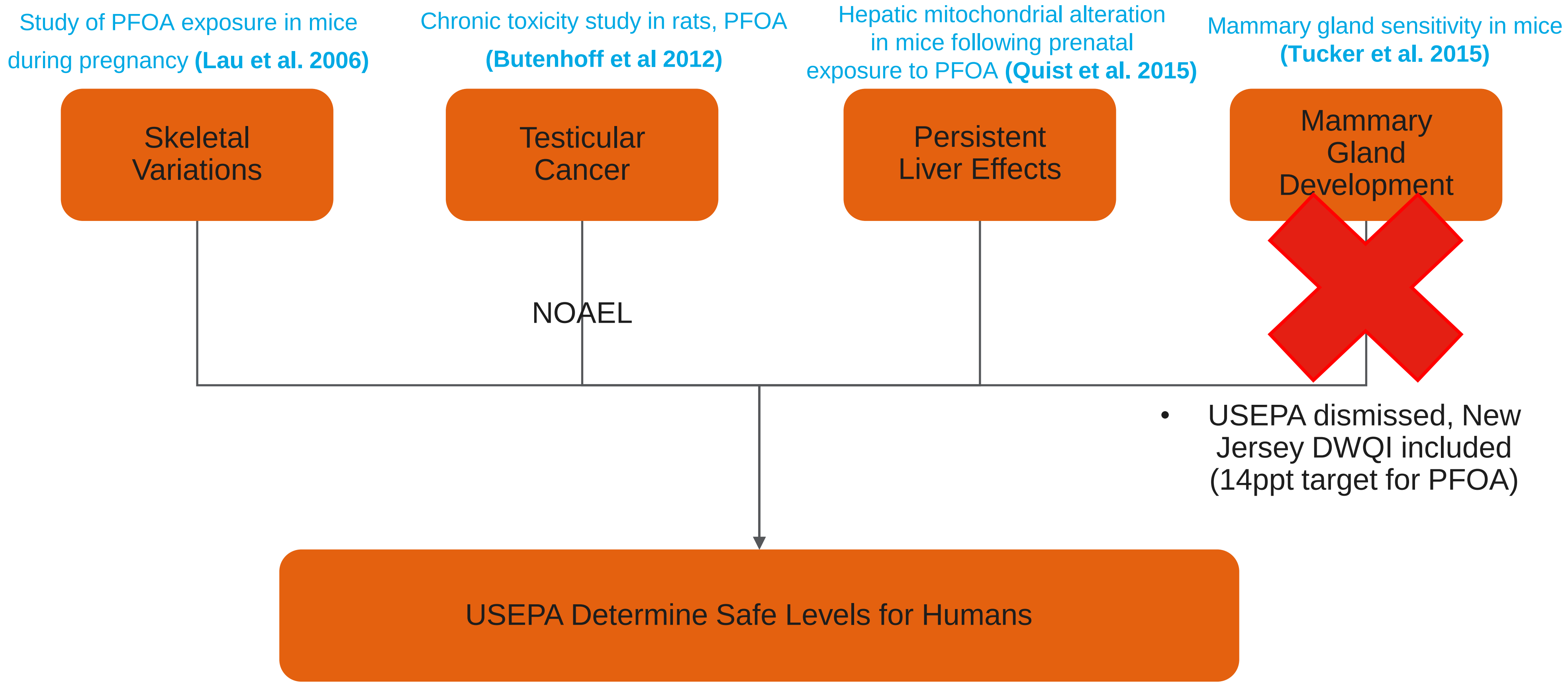

- Exposure mainly by ingestion
- PFAS bind to proteins (not to lipids / fats) and are mainly detected in blood, liver and kidneys
- PFOS: carcinogenity “suggestive” (US EPA, 2014). PFOA: “possibly carcinogenic” (International Agency for Research on Cancer, IARC, 2014)
- Study with 656 children demonstrated elevated exposure to PFOS & PFOA are associated with reduced humoral immune response [1]
- Large epidemiological study of 69,000 persons found probable link between elevated PFOA blood levels and the following diseases: high cholesterol, ulcerative colitis, thyroid disease, testicular cancer, kidney cancer and preeclampsia – C8 science panel [2]
- European Food Safety Authority (2008) established a TDI for PFOS and PFOA of **150** ng/kg bw/day and **1.500** ng/kg bw/day
- USEPA has selected a Reference Dose for PFOS and PFOA of **20** ng/kg bw/day (May 2016)

[1] Grandjean, P.; Andersen, E. W.; Budtz-Jørgensen, E.; Nielsen, F.; Mølbak, K.; Weihe, P.; Heilmann, C. Serum vaccine antibody concentrations in children exposed to perfluorinated compounds. *JAMA* **2012**, 307, 391–397.

[2] http://www.c8sciencepanel.org/

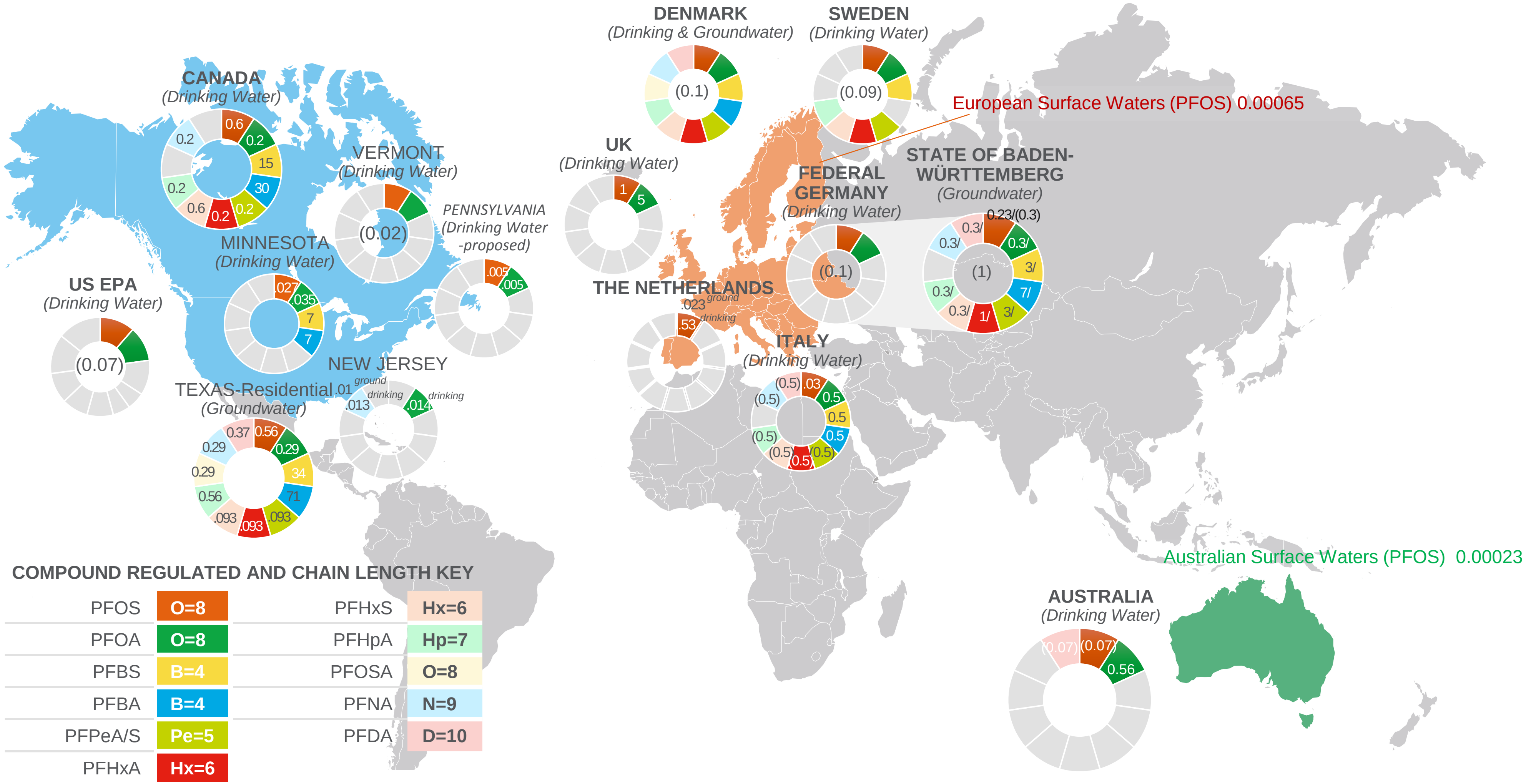
# Perfluorinated Compounds: Reproductive Toxicity

- Pregnant/breastfeeding mothers are the primary sensitive populations.
  - Detected in breastmilk, umbilical cord blood, and amniotic fluid
- At birth infants have roughly equivalent serum levels as mothers.
  - Levels in infants increases further after birth from breast milk or from water in formulae



# Evolving Regulatory PFAS Values – Overview

## Drinking, Surface and Ground Water (μg/l)




**COMPOUND REGULATED AND CHAIN LENGTH KEY**

| | | | |
|---|---|---|---|
| PFOS | O=8 | PFHxS | Hx=6 |
| PFOA | O=8 | PFHpA | Hp=7 |
| PFBS | B=4 | PFOSA | O=8 |
| PFBA | B=4 | PFNA | N=9 |
| PFPeA/S | Pe=5 | PFDA | D=10 |
| PFHxA | Hx=6 | | |

# PFAS in European Surface Waters

| River | PFOS (ng/l) | Flow($m^3/s$) |
|---|---|---|
| Scheldt (Be, NL) | 154 | - |
| Seine (Fr) | 97 | 80 |
| Severn (UK) | 238 | 33 |
| Rhine (Ge) | 32 | 1,170 |
| Krka (Sl) | 1,371 | 50 |

Environmental Pollution 157 (2009) 561–568

Contents lists available at ScienceDirect

Environmental Pollution

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

ELSEVIER

EU-wide survey of polar organic persistent pollutants in European river waters

Robert Loos*, Bernd Manfred Gawlik, Giovanni Locoro, Erika Rimaviciute, Serafino Contini, Giovanni Bidoglio

*European Commission, Joint Research Centre, Institute for Environment and Sustainability, Via Enrico Fermi, 21020 Ispra, Italy*

*More than 100 river water samples from 27 European Countries were analysed for 35 selected polar organic contaminants.*

# European Surface Water Distribution

Environmental Pollution 157 (2009) 561–568

Contents lists available at ScienceDirect

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**Table 1**

Summary of analytical results of polar pollutants in EU Rivers

| Chemical | CAS No. | RL [ng/L] | Freq [%] | Max [ng/L] | Average [ng/L] | Med [ng/L] | Per90 [ng/L] | Limit [ng/L] |
|---|---|---|---|---|---|---|---|---|
| ***Perfluorinated acids*** | | | | | | | | |
| PFHxA; perfluorohexanoate | 68259-11-0 | 1 | 39 | 109 | 4 | 0 | 12 | 30 |
| PFHpA; perfluoroheptanoate | 375-85-9 | 1 | 64 | 27 | 1 | 1 | 3 | 30 |
| PFOA; perfluorooctanoate | 335-67-1 | 1 | 97 | 174 | 12 | 3 | 26 | 30 |
| PFNA; perfluorononanoate | 375-95-1 | 1 | 70 | 57 | 2 | 1 | 3 | 30 |
| PFOS; perfluorooctansulfonate | EDF-508 | 1 | 94 | 1371 | 39 | 6 | 73 | 30 |
| PFDA; perfluorodecanoate | 335-76-2 | 1 | 40 | 7 | 1 | 0 | 1 | 30 |
| PFUnA; perfluoroundecanoate | 2058-94-8 | 1 | 26 | 3 | 0 | 0 | 1 | 30 |
| 4-Nitrophenol | 100-02-7 | 1 | 97 | 3471 | 99 | 16 | 95 | 100 |
| 2,4-Dinitrophenol | 51-28-5 | 1 | 86 | 174 | 18 | 10 | 40 | 100 |
| Bentazone | 25057-89-0 | 1 | 69 | 250 | 14 | 4 | 31 | 100 |
| 2,4-D (Dichlorophenoxyacetic acid) | 94-75-7 | 1 | 52 | 1221 | 22 | 3 | 35 | 100 |
| Ketoprofen | 22071-15-4 | 3 | 14 | 239 | 10 | 0 | 17 | 100 |
| Naproxen | 22204-53-1 | 1 | 69 | 2027 | 38 | 4 | 47 | 100 |
| Bezafibrate | 41859-67-0 | 1 | 55 | 1235 | 32 | 4 | 56 | 100 |
| Mecoprop | 7085-19-0 | 1 | 43 | 194 | 15 | 0 | 54 | 100 |
| Ibuprofen | 15687-27-1 | 1 | 62 | 31,323 | 395 | 6 | 220 | 200 |
| Diclofenac | 15307-86-5 | 1 | 83 | 247 | 17 | 5 | 43 | 100 |
| Gemfibrozil | 25812-30-0 | 1 | 35 | 970 | 29 | 0 | 17 | 100 |

# Groundwater Risks to Receptors

Landfill Leachate
Municipal / Domestic WWTP
Industry & Manufacturing
Agricultural Land
Commercial / Domestic Products
Metal Plating
ASTs –Fuel storage (FFFP / FP)

?

**Diffuse**
Ground level impacts and ground/surface water

?

AFFF / FFFP / FP
Fire training
Incident Response

?

**Source – Pathway – Receptor**
High concentration, spill site, route via groundwater to receptor e.g. drinking water well

**Grasshopper effect**

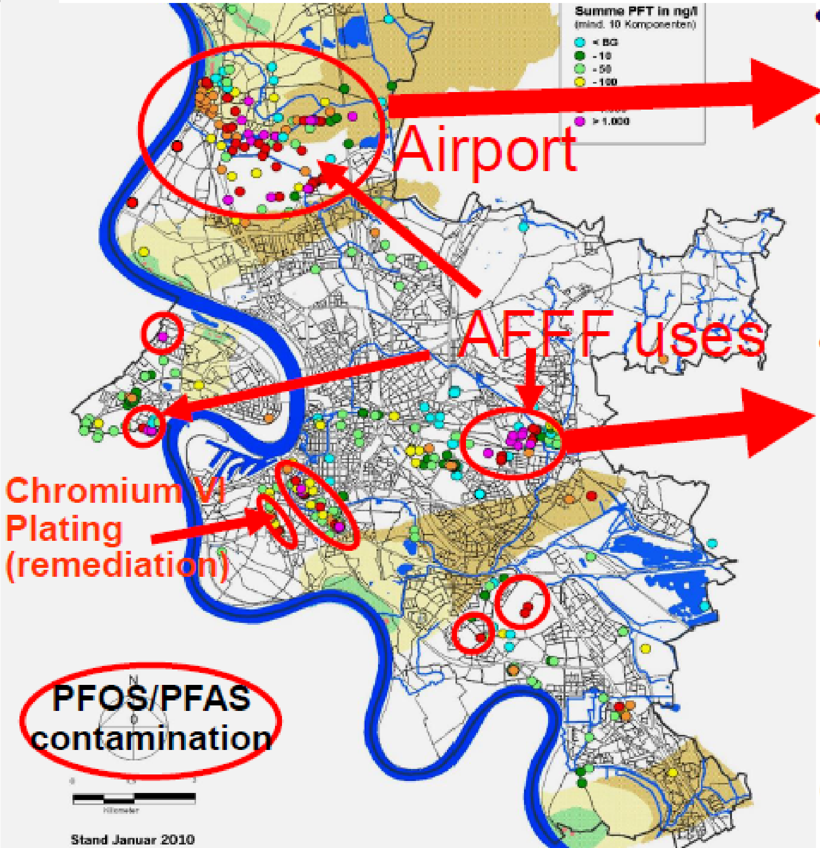
via widening of source zones

e.g. concentrated plume intercepts crop spray irrigation to make secondary wider source area for more dilute plume

# Excessive Costs

Octob

## PFOS/PFAS contaminated sites ?
## Groundwater screening in Düsseldorf city




Weber R, Bantz et al. 30th Intern. Symposium on Halogenated Organic Pollutants (*DIOXIN 2010*) , San Antonio 12-17.09. 2010.

- Cost of three wells controlling the point sources were 2 million €.
- Total remediation estimate for the airport: might reach 100 million €. http://www.derwesten-recherche.org/2013/10/pft-alarm-am-flughafen-dusseldorf-verseuchung-noch-extremer-sanierung-konnte-100-millionen-kosten/
- Remediation cost of a fire were 42 m3 AFFF were used:
  - 1 million Euro assessment.
  - >10 million Euro remediation.
- Ongoing case Baden-Württ. Soil exchange estimate 1-3 billion €. http://www.faz.net/aktuell/wissen/baden-wuerttemberg-chemische-abfaelle-auf-dem-acker-14419295.html

Lesson learned 6: Remediation of PFAS from groundwater/soil is challenging and expensive. No natural degradation!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Schwäbisch Gmünd, Germany
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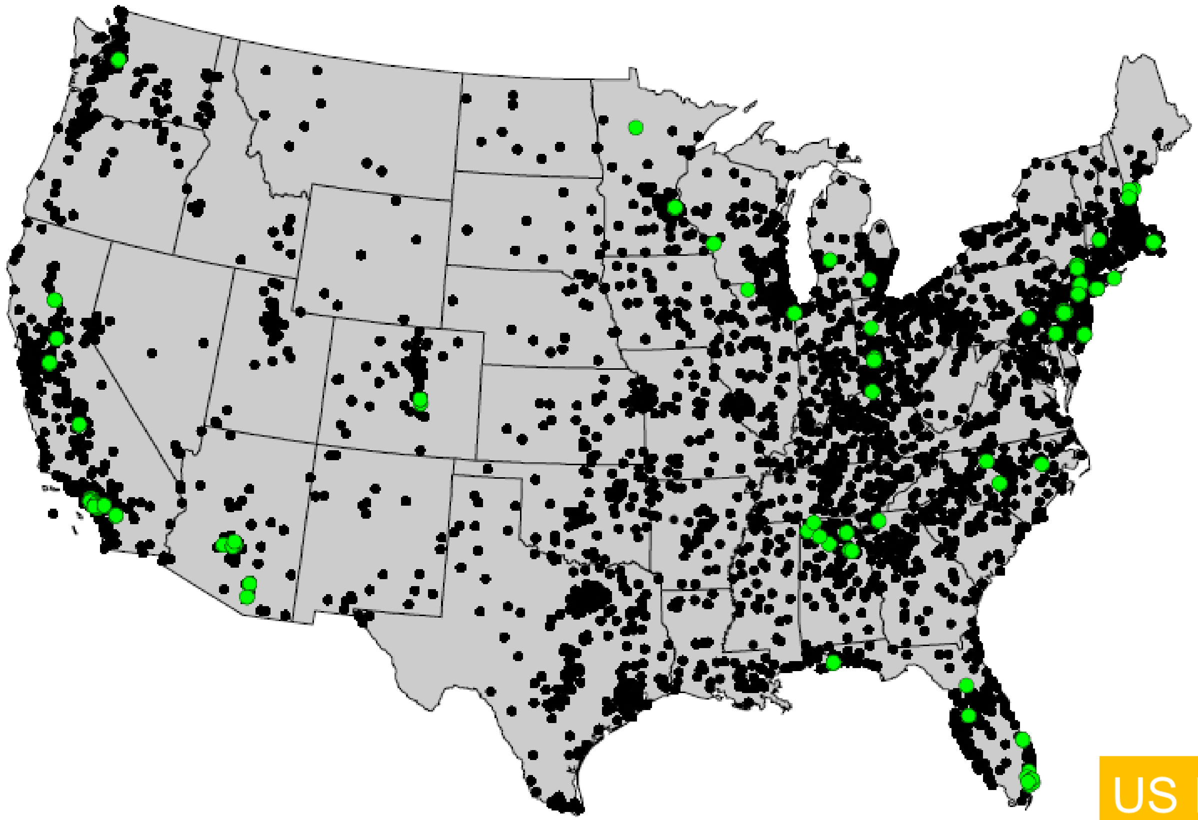
http://greensciencepolicy.org/wp-content/uploads/2016/09/Rolland-Weber-PFOS-PFAS-German-activities-Final.pdf



**Risk based approaches not adopted in Germany**

# PFAS in US Public Water Supplies



USEPA UMCR 3, May 2016

INDEPENDENT News Voices Culture Lifestyle Tech Sport Daily Edition

News › World › Americas

## Six million Americans drinking water containing unsafe levels of unregulated chemicals, study finds

In one Delaware town, the levels of one such chemical in the water supply were 25 times higher than the EPA deems safe

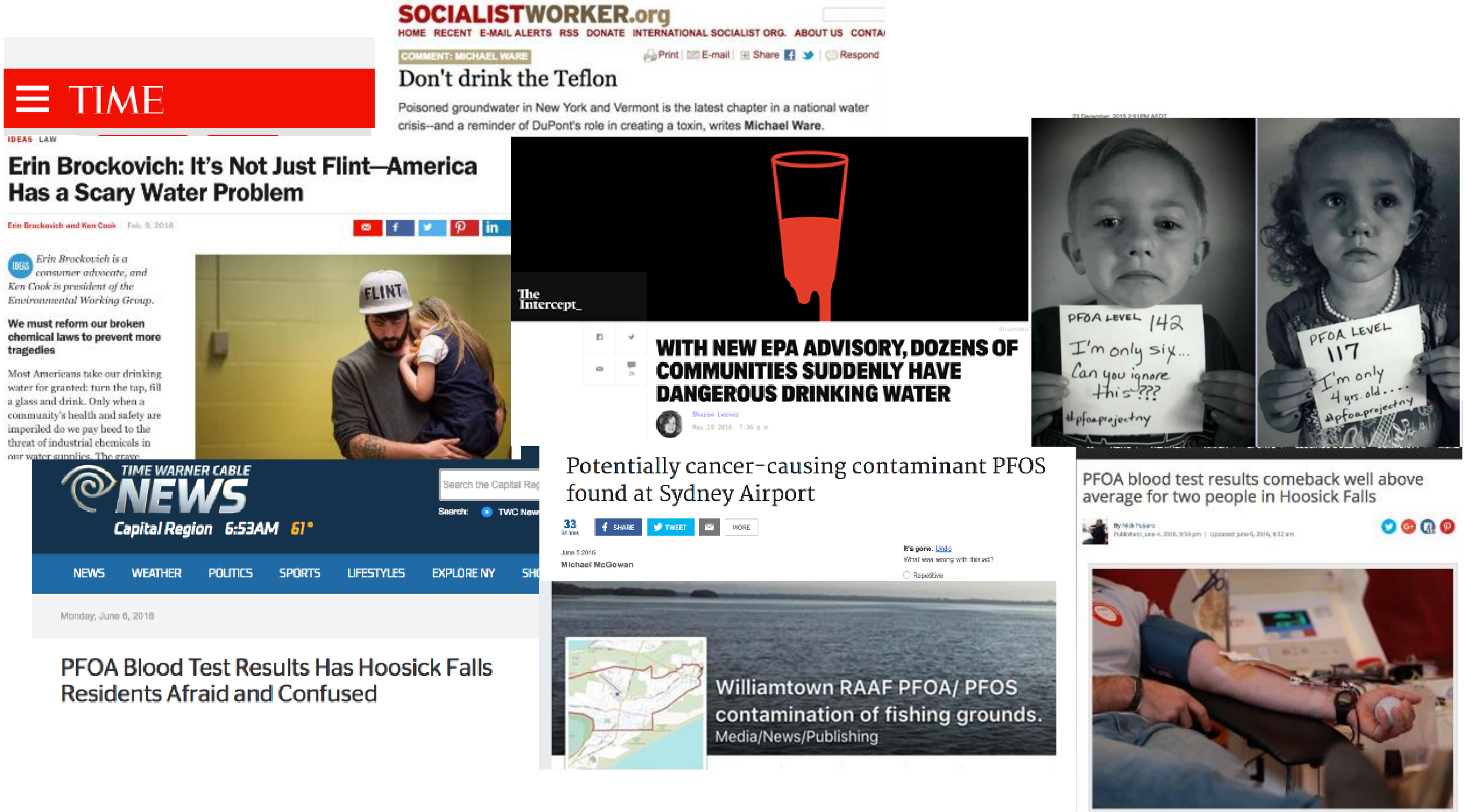
Tim Walker US Correspondent | @timwalker | Tuesday 9 August 2016 22:57 BST |


US EPA has established the drinking water health advisory levels at 70 ng/L for PFOA/PFOS 19th May 2016

https://www.epa.gov/ground-water-and-drinking-water/drinking-water-health-advisories-pfoa-and-pfos

**Detected in ~ 2% of large public water supplies**

# PFAS News 2016



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Don't drink the Teflon

Poisoned groundwater in New York and Vermont is the latest chapter in a national water crisis--and a reminder of DuPont's role in creating a toxin, writes **Michael Ware**.

TIME

IDEAS LAW

**Erin Brockovich: It's Not Just Flint—America Has a Scary Water Problem**

Erin Brockovich and Ken Cook | Feb. 9, 2016

*Erin Brockovich is a consumer advocate, and Ken Cook is president of the Environmental Working Group.*

**We must reform our broken chemical laws to prevent more tragedies**

Most Americans take our drinking water for granted: turn the tap, fill a glass and drink. Only when a community's health and safety are imperiled do we pay heed to the threat of industrial chemicals in our water supplies. The grave...

The Intercept_

**WITH NEW EPA ADVISORY, DOZENS OF COMMUNITIES SUDDENLY HAVE DANGEROUS DRINKING WATER**

Sharon Lerner

May 19 2016, 7:36 p.m.

PFOA LEVEL 142

I'm only six... Can you ignore this???

#pfoaprojectny

PFOA LEVEL 117

I'm only 4 yrs. old....

#pfoaprojectny

PFOA blood test results comeback well above average for two people in Hoosick Falls

TIME WARNER CABLE NEWS

Capital Region 6:53AM 61°

NEWS WEATHER POLITICS SPORTS LIFESTYLES EXPLORE NY

Monday, June 6, 2016

PFOA Blood Test Results Has Hoosick Falls Residents Afraid and Confused

Potentially cancer-causing contaminant PFOS found at Sydney Airport

SHARE TWEET MORE

June 5 2016

Michael McGowan

Williamtown RAAF PFOA/ PFOS contamination of fishing grounds.

Media/News/Publishing

# PFAS News

ABC NEWS

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## Oakey residents begin class action against Defence Department over toxic firefighting foam

By Elly Bradfield, Kirrin McKechnie and Nick Wiggins

Updated 11 Jul 2017, 4:36am

**PHOTO:** Lead Plantiff Brad Hudson with his 16-year-old daughter Megan and younger daughter Amber. (ABC News: Elly Bradfield)

About 450 residents are seeking up $200 million in damages from the Defence Department over the contamination of soil and water by toxic firefighting foam used at the

**RELATED STORY:** Breastfed child records high levels of firefighting foam toxins

**RELATED STORY:** Army firefighting chemical exposure levels revised down

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## Oakey breastfed child records high levels of firefighting foam toxins

By Elly Bradfield

Updated 7 Apr 2017, 2:45am

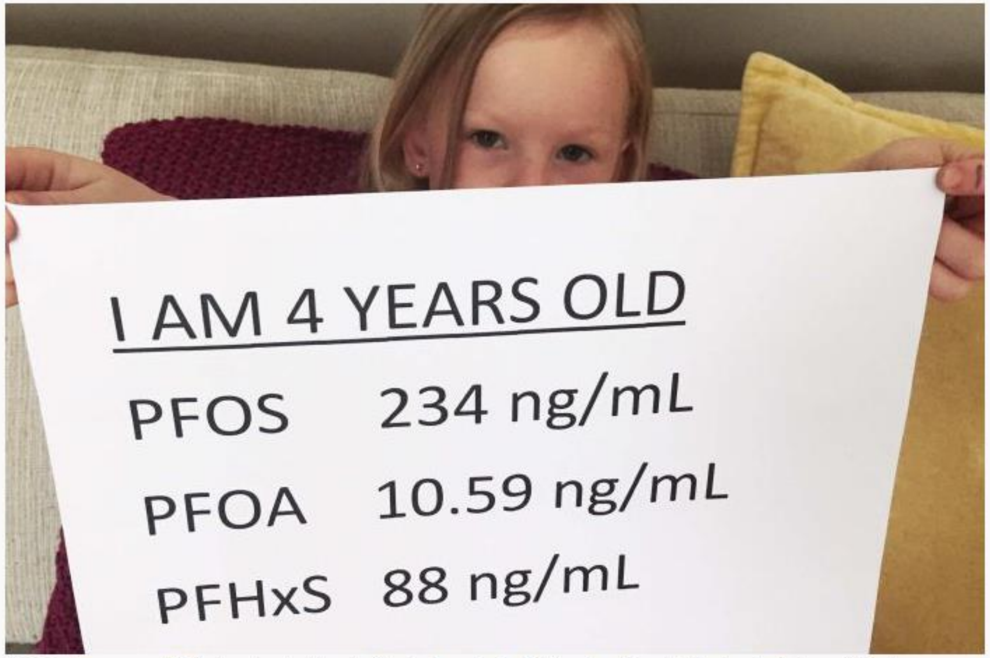
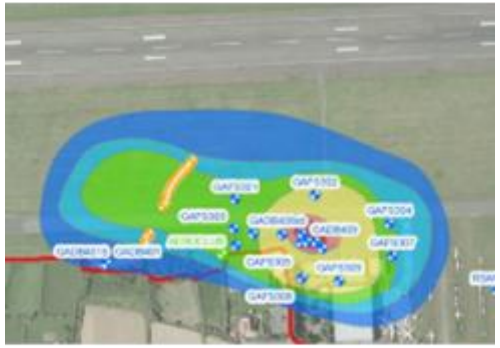



**PHOTO:** Four-year-old Evie has elevated levels of toxins found in firefighting foam found at the Army's Oakey aviation base. (ABC News: Elly Bradfield)

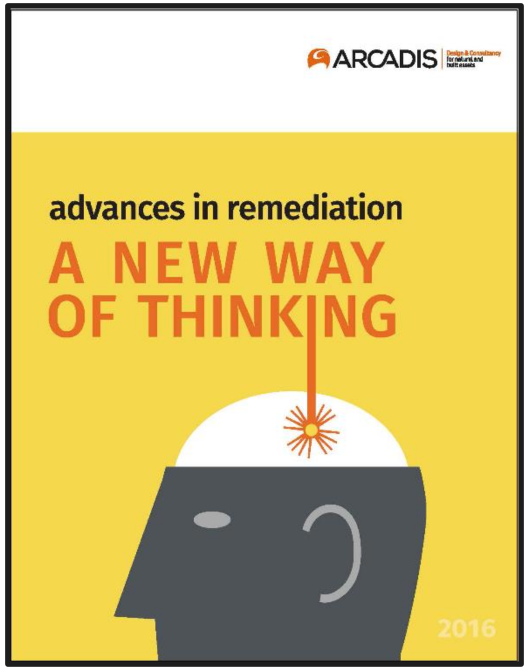
# Summary - PFAS Management..

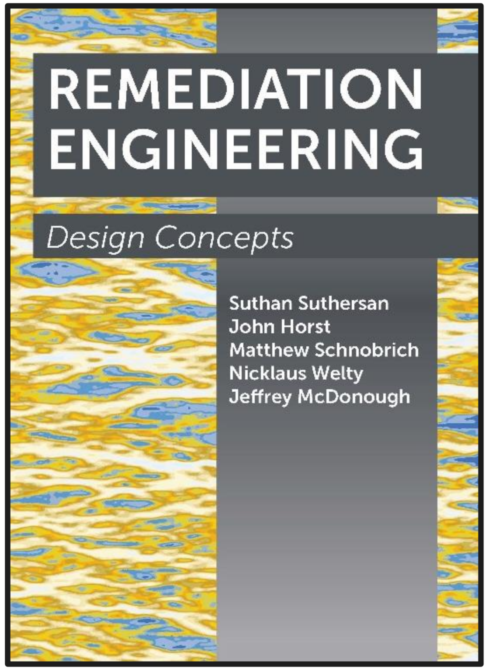
- Better site characterisation
- Assess contaminants comprehensively – TOP assay
- Develop intelligent CSM
- Use of detailed site specific quantitative risk assessment
- Consider more sustainable risk management solutions
- Address public risk perception
- Emerging remedial technologies provide ingenious solutions for PFAS

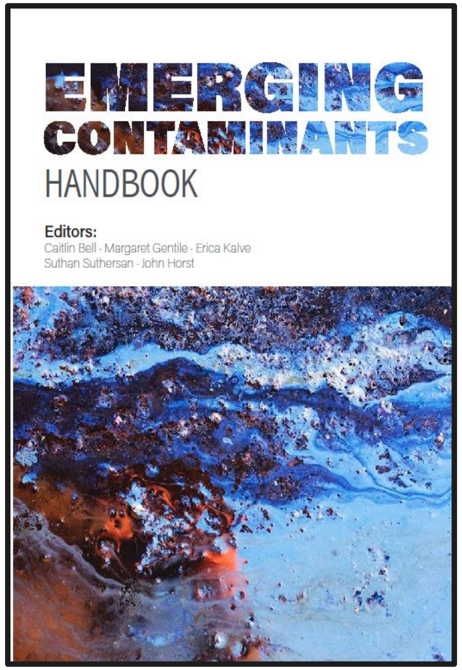


ARCADIS Design & Consultancy for natural and built assets

# Publications..





Download at:
https://www.concawe.eu/publications/558/40/Environmental-fate-and-effects-of-poly-and-perfluoroalkyl-substances-PFAS-report-no-8-16