AFFF contaminated soil and water: risks, remedial options

CRCCARE

A safer, cleaner environmental future

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OUTLINE

- Background and Introduction.
  - Most dangerous contaminants
- Treatability case study for a Project Site
  - AFFF contaminated wastewater using matCARE™
  - AFFF contaminated soil using matCARE™
  - Cost of remediating
- Q & A

matCARE™ : CRC CARE PROVEN TECHNOLOGY FOR AFFF TREATMENT

MOST DANGEROUS CHEMICAL CONTAMINANTS

- Arsenic
- Lead
- Chlorinated hydrocarbons
- PH
- Asbestos- mineral
- Cr(VI)

- Others – recent

  – PFCs

PERFLUORINATED CHEMICALS (PFCS)

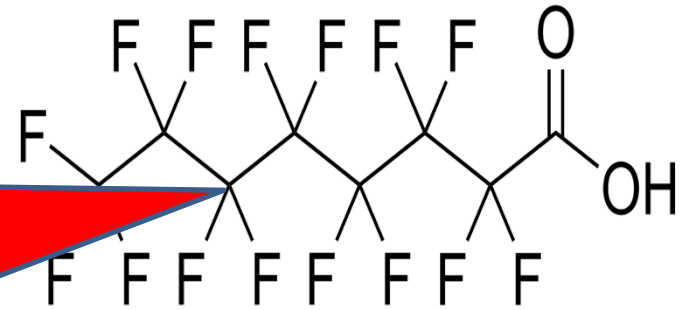
- **Aqueous Film Forming Foam (AFFF)**
  - has been widely used for fire-fighting by the military and many civilian fire departments.
  - comprises a mixture of carbon surfactants, hydrocarbon surfactants, solvents and water. Used to spread over hydrocarbon fuels and extinguish flames
  - The fluorochemistry of AFFF has been described as a complex mixture of fluorinated and non-fluorinated surfactants that results in the formation of persistent fluorochemicals from partially-fluorinated precursors."

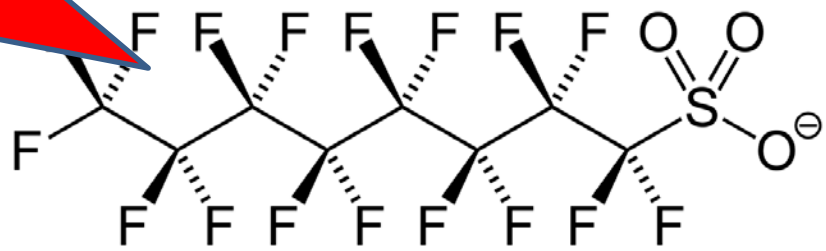
Persistent in the environment. Known to bioaccumulate in the food chain

PERFLUORINATED CHEMICALS (PFCS)

- **Perflurooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS)**
  - Fully
    not
    e
  - Very sta chemicals that have both lipid- and water-repellent properties.

Manufactured since 1940's
Used in aqueous film-forming foams (AFFF), fire suppression systems, hangars, fire trucks





THE PROBLEM

- Issues associated with AFFF containing PFCs
  - Bioaccumulates in higher trophic level organisms through the aquatic food chain (Budakowski et al., 2004)
  - Persistent: very stable chemicals that do not change or break down
- Effects on human health (Key et al., 1997)

  - stay in the human body for many years.
  - toxic to the liver and thyroid gland and
  - may also affect fetal and neonatal development.

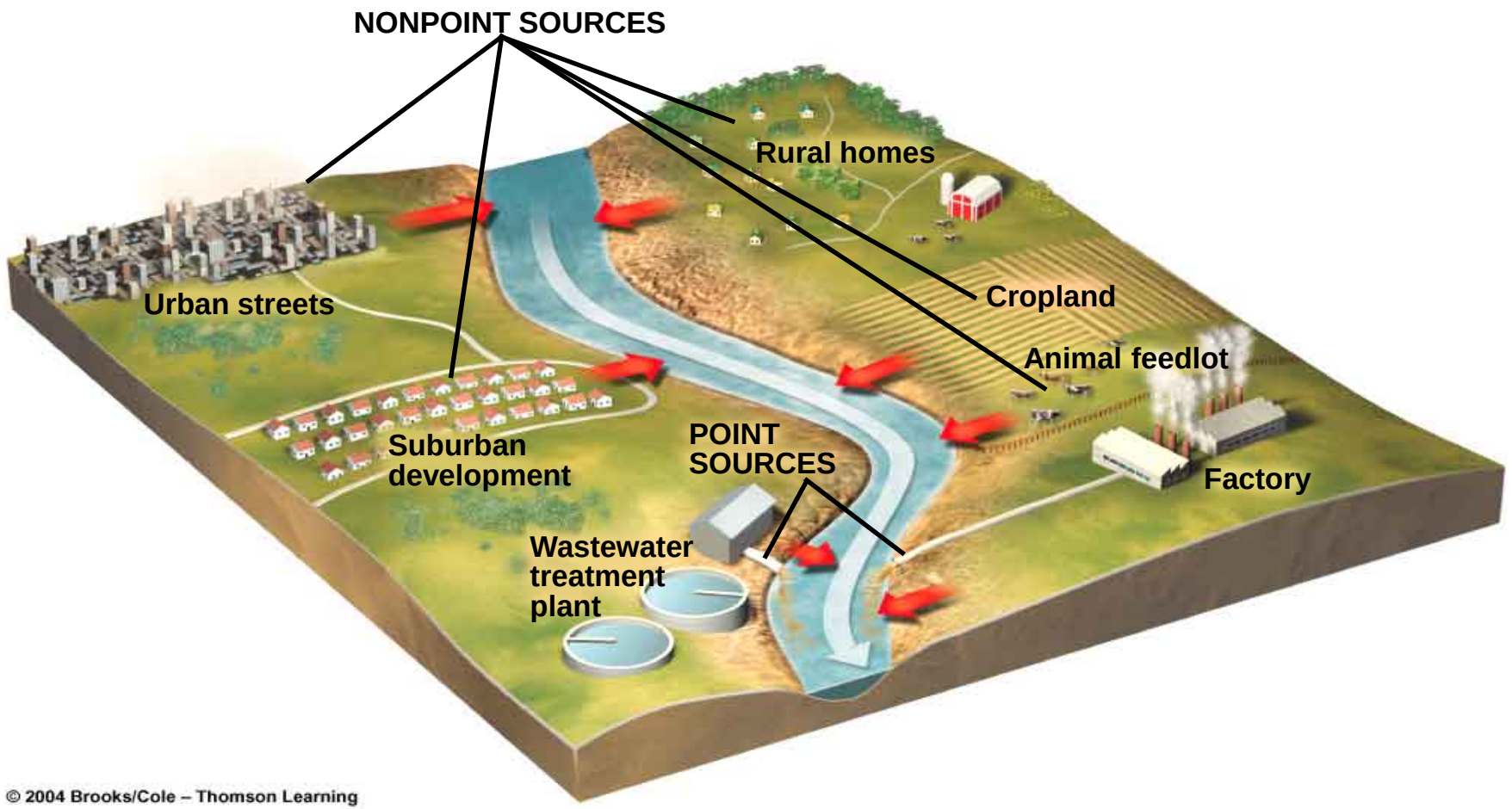
THE PROBLEM

How PFCs reach the environment?

When spilled or disposed of, PFCs found huge exposure into the ground water, soils and sediments around a large number of fire training areas (Johnson et al., 2007).

Once in groundwater PFCs can easily move long distances, potentially affecting nearby water supplies.

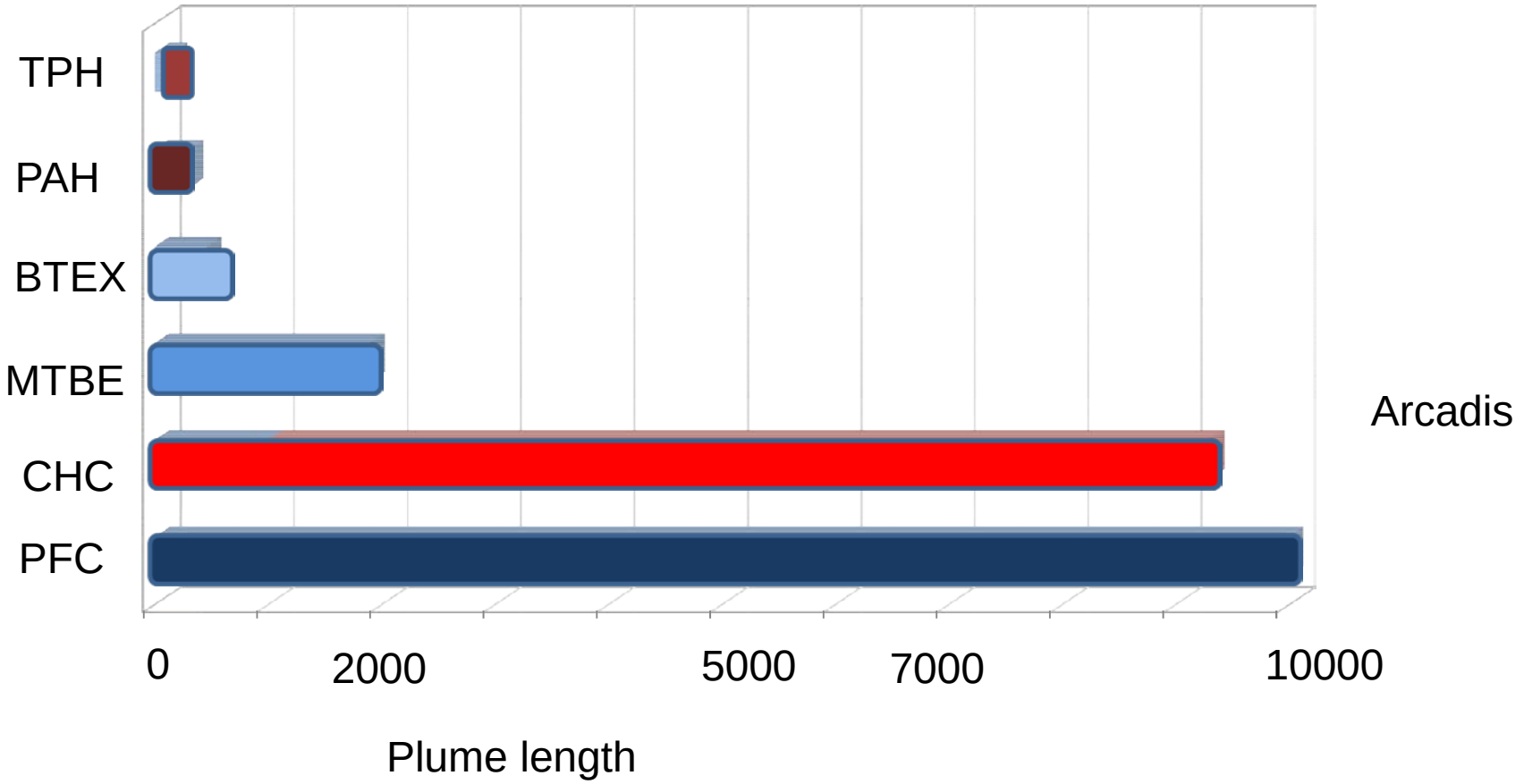
POINT AND NONPOINT SOURCES



FATE AND TRANSPORT OF PFCS

- Much is still unknown about these chemicals- CRC CARE researchers have been researching this using select soils from Australia since 2004
- PFCs are extremely stable
  - Do not hydrolyze, photolyze, or biodegrade under typical environmental conditions
  - Are extremely persistent in the environment
    - » For example the half-life (at 25º C) in water for PFOA and PFOS is > 92 years and > 41 years, respectively
- High potential to absorb to substrates
- Migration depends upon groundwater flow and the charge of the substrate.

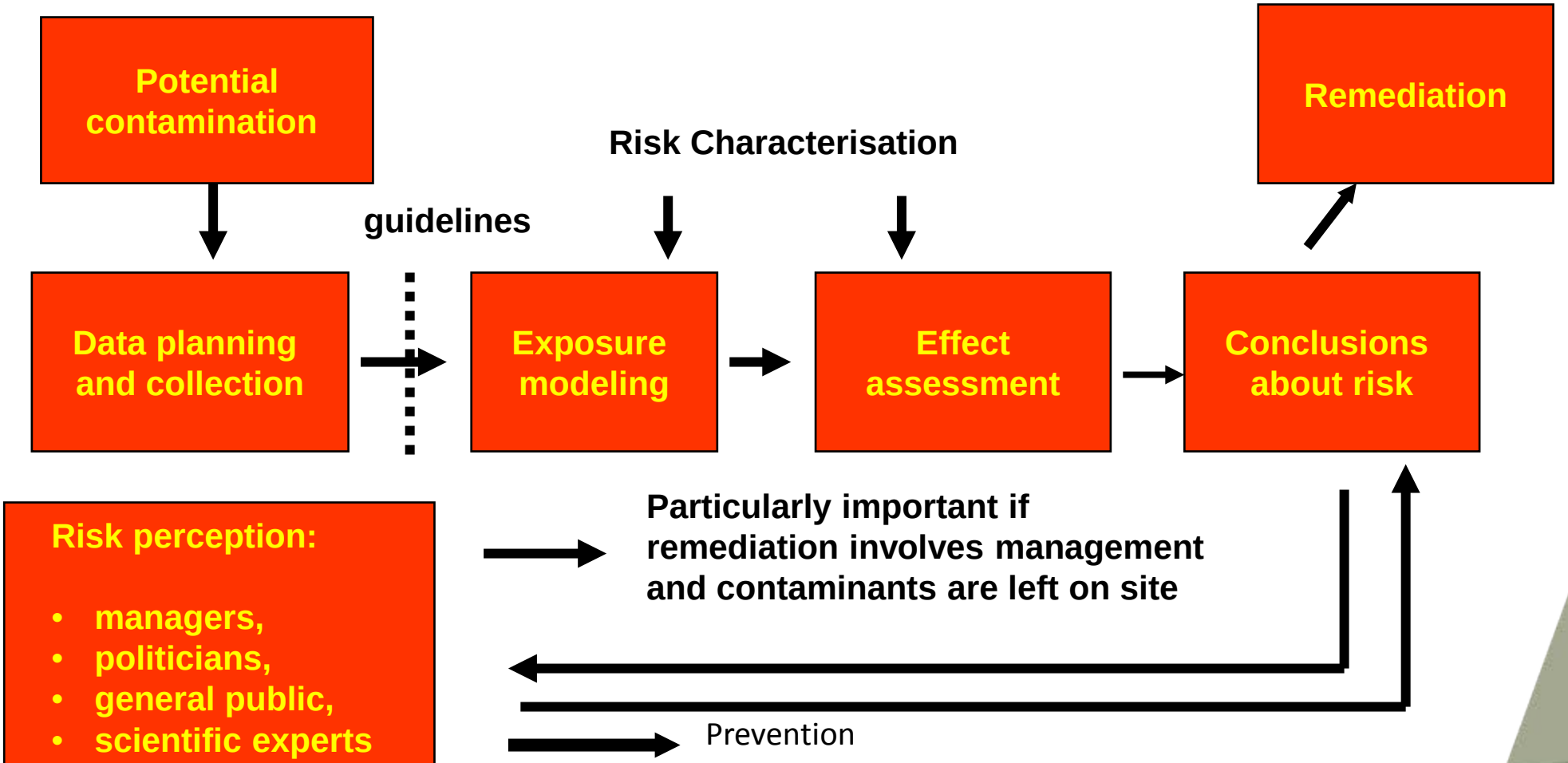
EXTREMELY MOBILE ONCE IN GROUND WATER



PFCS: THRESHOLD VALUES

- US information (List 3 for future water quality regulations)
  - EPA Provisional short-term health guidance
    - PFOA 0.4 µg/L
    - PFOS 0.2 µg/L
- Netherlands National Institute for Public Health and the Environment (RIVM) (2010)
  - MPC of 0.65 nanograms per liter PFOS for freshwater
- No existing NEPM criteria.
- CRC CARE is developing guidance document

Approach to Managing Contamination



Exposure Pathways

- Groundwater to human
- Waste water-soil-crop-human
- Waste water-soil-human
- Waste water-soil-fodder-animal-human
- Waste water-soil-animal-human
- Groundwater-soil-human etc

REMEDIATION: A MAJOR CHALLENGE

Extreme stability of strong carbon-fluorine (C-F) bonds make conventional remediation techniques ineffective (Mak et al., 2009).

- Oxidation/Photo Induced Oxidation
- Thermal Treatment
- Adsorption
- Membrane Filtration
- Sonochemical Treatment
- Chemical immobilization-CARE technology

CASE STUDY COMMENT- Some comments

- Site: Hamilton International Airport- thermal treatment study
  - "Advanced oxidation processes, which utilize the hydroxyl radical,--such as alkaline ozonation, peroxone (i.e., a mixture of 0_3 and H_2Q_2), or Fenton's reagent (i.e., H_20_2 and Fe^{2+} salts)--have been shown to be relatively ineffective for PFOA and PFOS destruction."

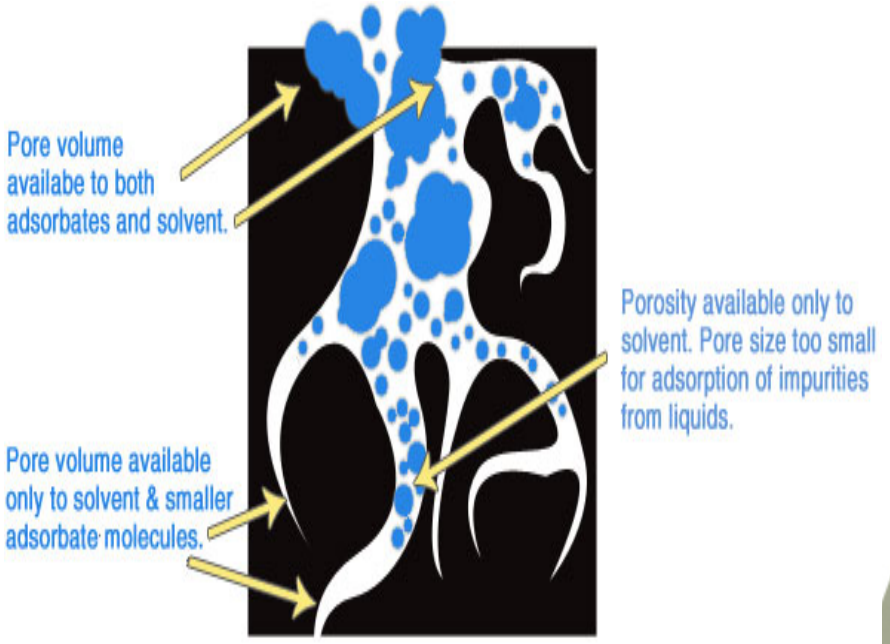
"If Hamilton uses public funds to test Nanozox™ on PFOS/PFOA, Hamilton will become a laughing stock in the scientific community"

Miller (2011)

ADSORPTION

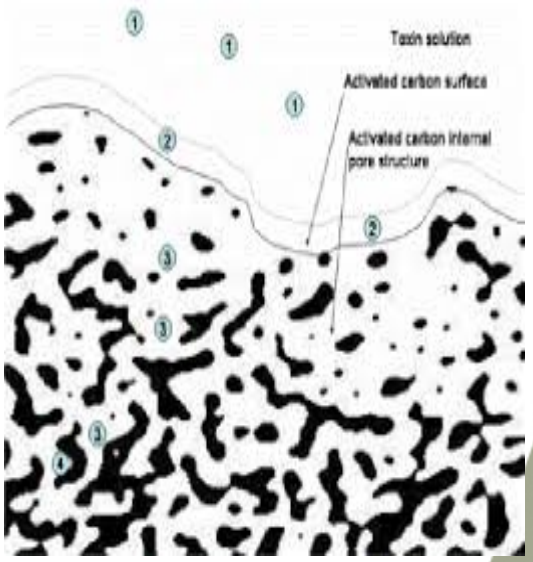
- Adsorption is a surface phenomenon that results in the accumulation of molecules within the internal pores of an activated carbon

- PFOS and PFOA molecules adhere to the surface of an adsorbent (e.g GAC) by partitioning and/or electrostatic interactions.



ADSORPTION

Advantages	Disdvantages
• GAC adsorption technology consistently achieves PFOS removal of > 90% (Ochoa-Herrera and Sierra-Alvarez, 2008).	• GAC can be ineffective at removing PFOA and other PFCs (Oliaei and Kessler, 2006). • Slow kinetics (> 72 hours to reach equilibrium). • For water- may be necessary to operate pump-and-treat systems for many years to meet clean-up goals (Hawley et al., 2012; Paterson, 2012).



Nano materials

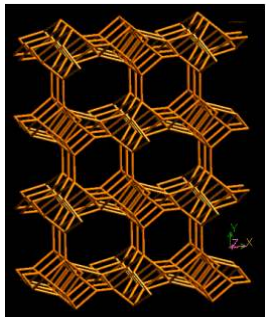
- Used in remediation of contaminated soils
- Inexpensive risk based approach

New materials developed → $$$$$

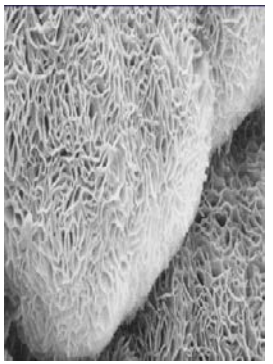
- ❑ Efficient
- ❑ Durable
- ❑ Cheap raw materials
- ❑ Easy regeneration
- ❑ Value added product from natural materials

- ❑ Clay/nano-material based remediation materials can effectively adsorb contaminants both in water and soil environments.
- ❑ Easy to develop catalysts.
- ❑ Potential to develop value added products from the natural clay resources.

AFFF CONTAMINATED WATER REMEDIATION-



- Develop modified natural material with capacity to immobilize PFCs

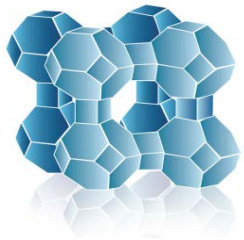


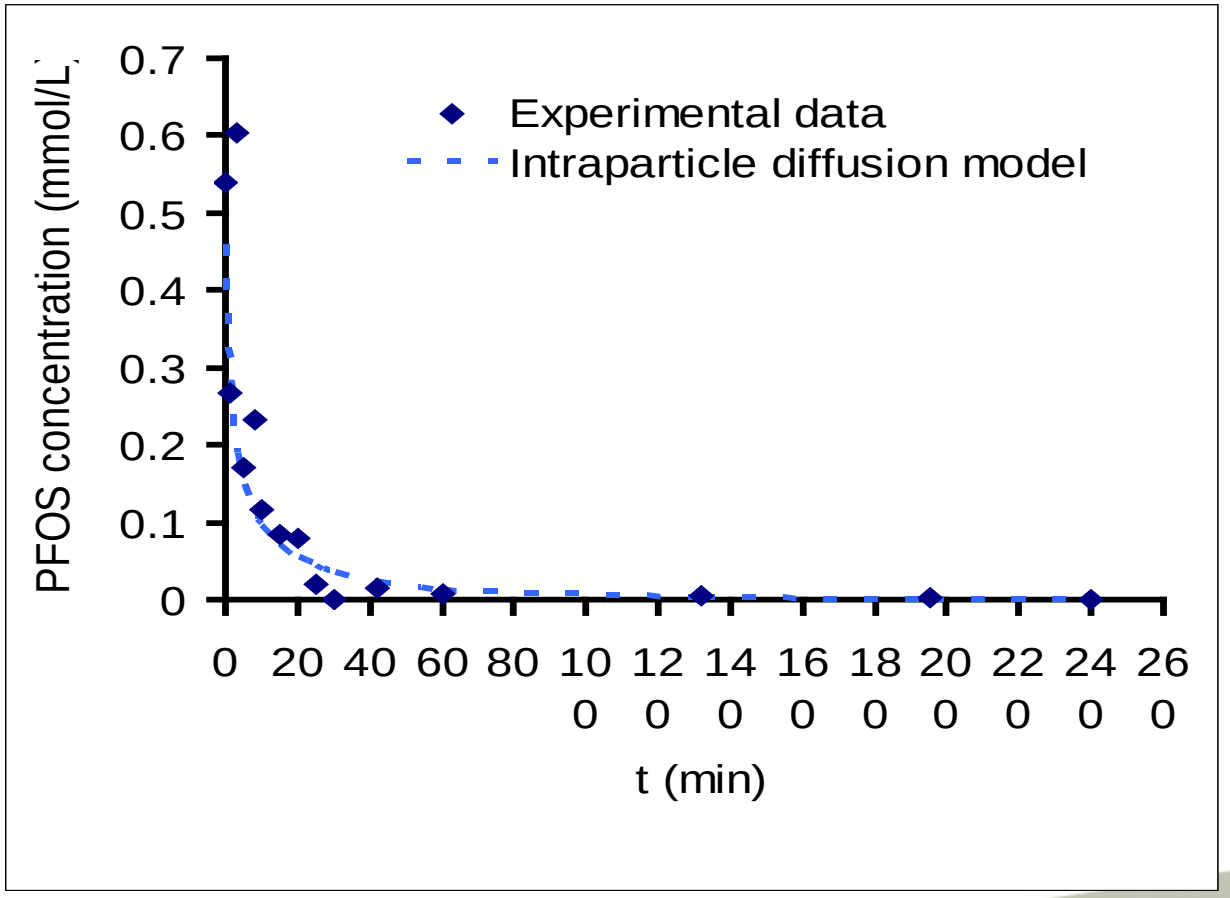
- Asses the ability of modified material to immobilize PFCs - optimization the process
- Scale up the technology

- Transfer to field

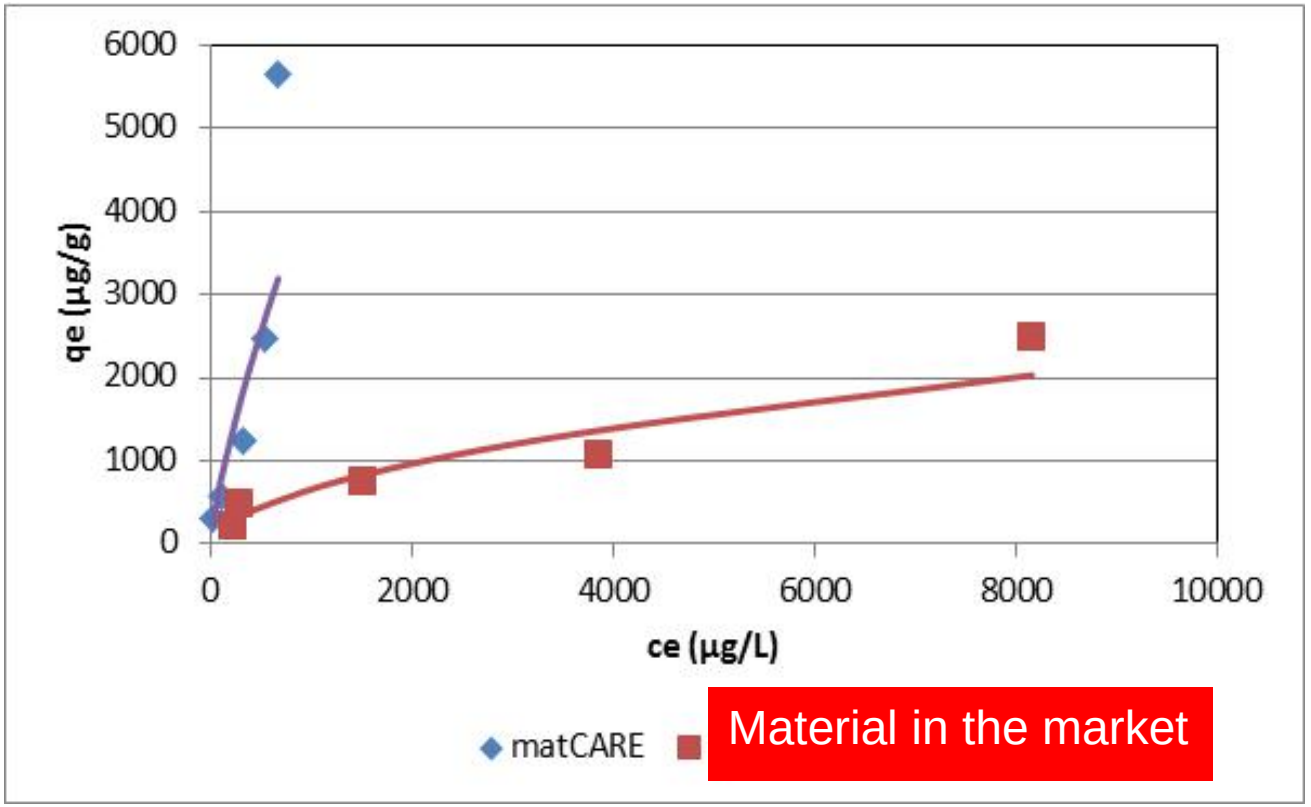
PFOS/PFOA WASTE WATER REMEDIATION

Matcare™





MATCARE is far superior to material commercially available



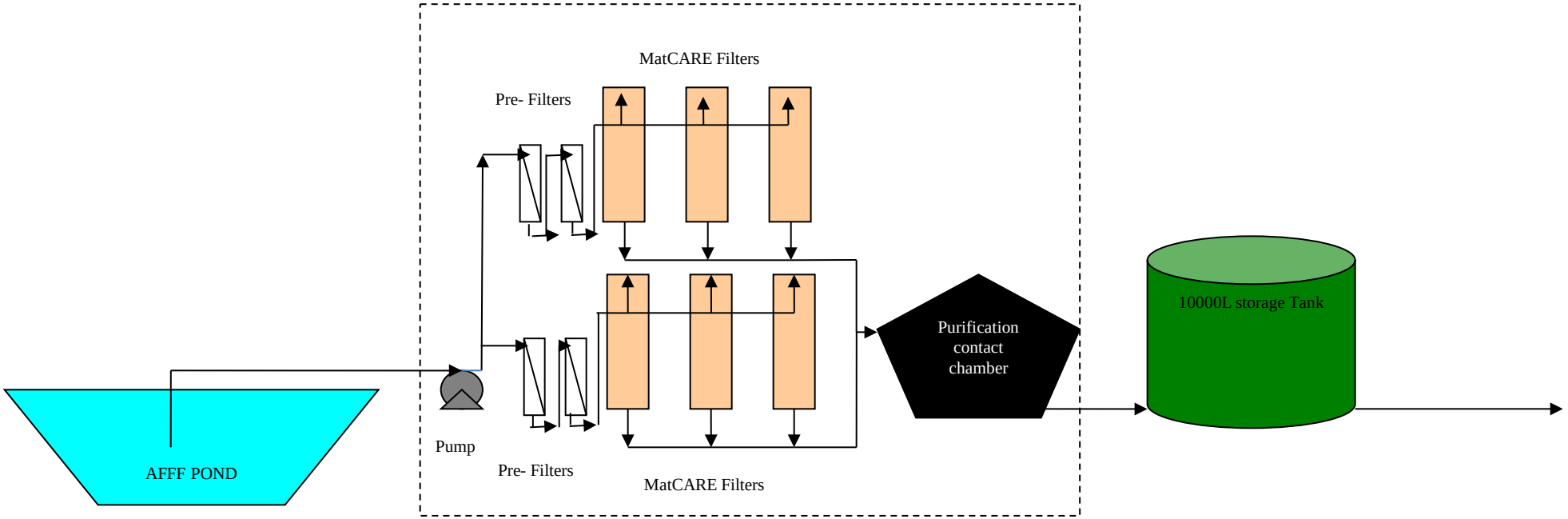
matCARE is reliable, cost effective and superior to other technologies

WASTE WATER TREATABILITY IN LAB

Perfluorinated compounds	Before treatment (µg/L)	After treatment (µg/L)
PFOS	75.8	<0.02
PFOA	2.77	<0.02
6:2 Fluorotelomer sulfonate (6:2 FtS)	508	<0.1
8:2 Fluorotelomer sulfonate	15.2	<0.1
PFOSA	<0.20	<0.02

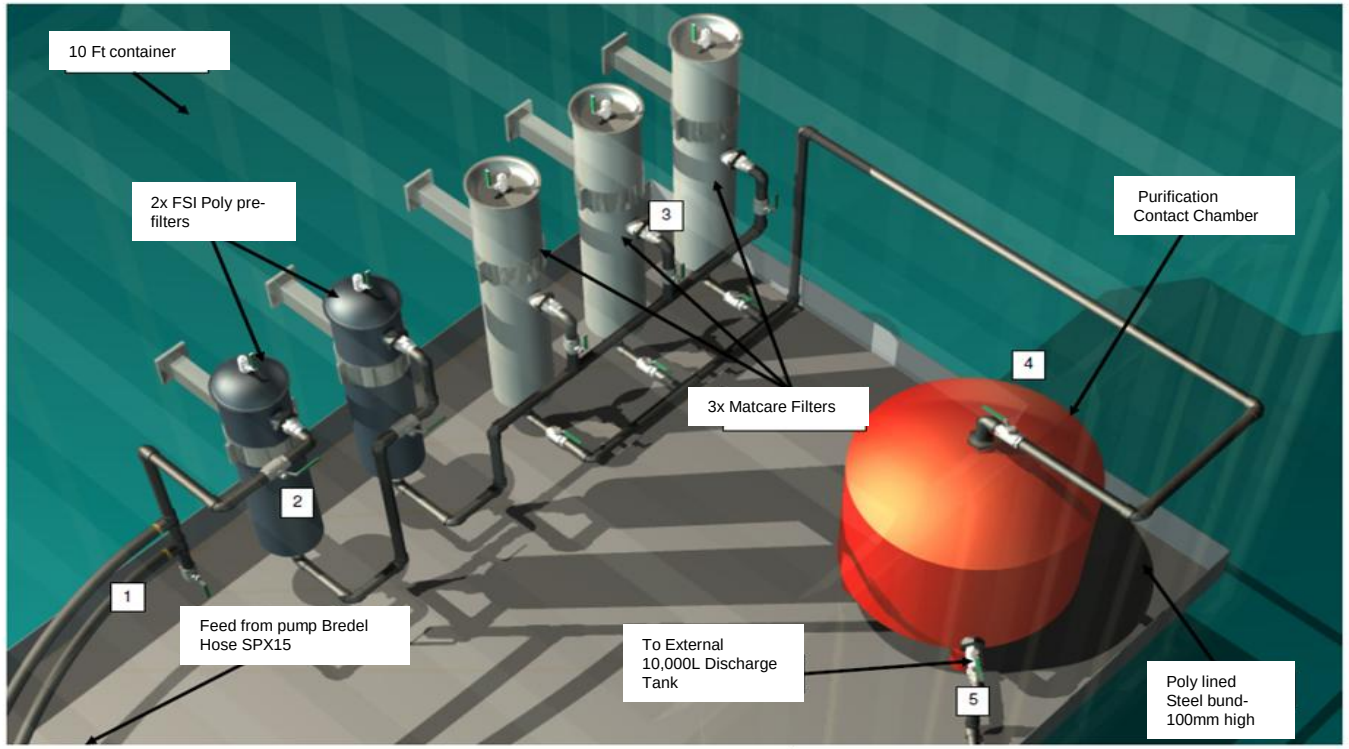
Samples used for batch studies was also tested in column studies.
The data obtained confirmed that four columns in series filled with matCARE™ successfully treated the wastewater to limits below detection for both PFCs and Petroleum Hydrocarbons.

SCHEMATICS OF THE WASTE WATER REMEDIATION TECHNOLOGY



Upgraded AFFF Remediation Plant

WASTE WATER REMEDIATION PLANT



SOIL & GROUNDWATER CONSULTING
207 The Parade Norwood SA 5067
PO Box 3166 Norwood SA 5067
T: 08 8431 7113 F: 08 8431 7115

Remediation AFFF Plant – RAAF Base
Revised 16/06/2011 – MJS – Ingenia

Wastewater remediation (AFFF) – 2.2ML remediated

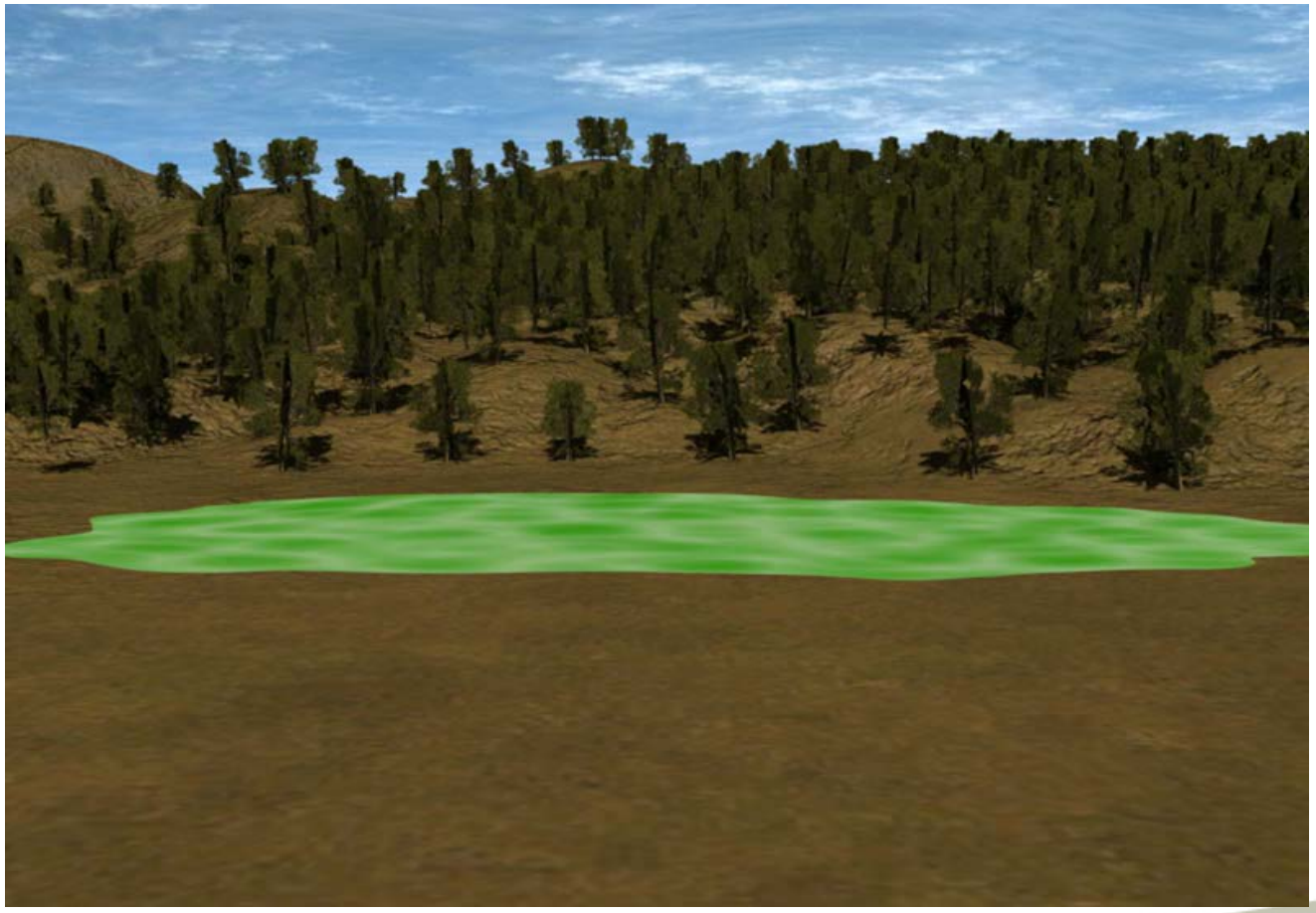
Wastewater pumped into the reactors

Clean water holding tank prior to aquifer injection

Wastewater

Clean water

AFFF WASTEWATER REMEDIATION PLANT ON WHEELS

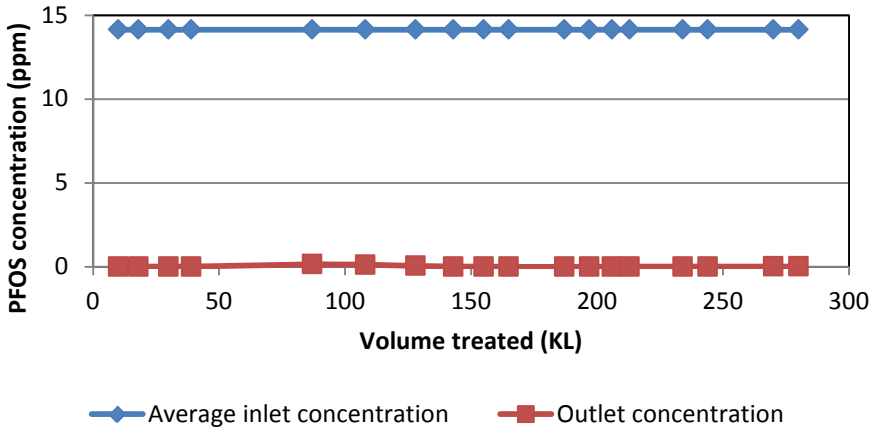


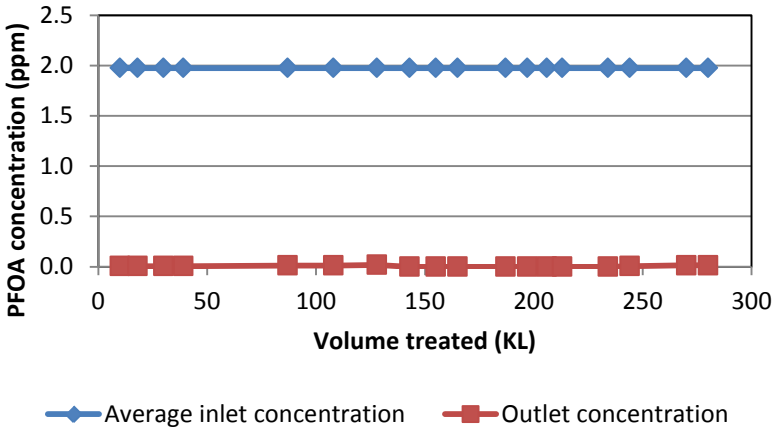
TECHNOLOGY SET UP

- Shipping container is used to set up technology
- Containization presents many advantages including:

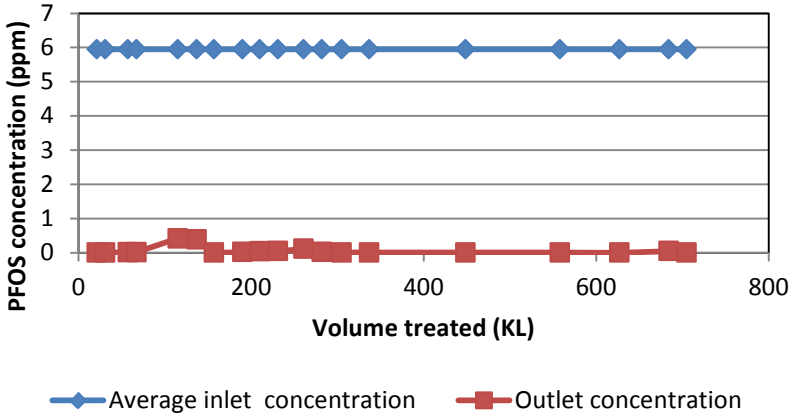
  - Limited civil works (only container foundation is required)
  - Fast implementation, and
  - Mobility

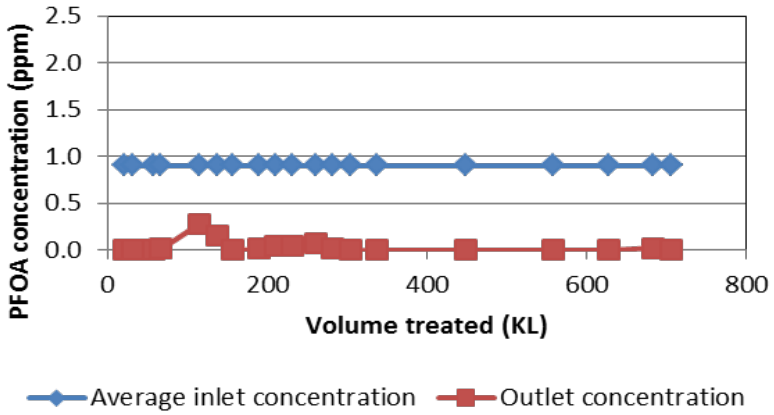
matCARE™ REMEDIATION





2011 data Edinburgh RAAF base AFFF WWTP





2012 data Edinburgh RAAF base AFFF WWTP

AFFF plant performance

Inlet PFOS (mg/l)	Outlet PFOS (mg/L)	PFOS removed (%)	Inlet PFOA (mg/L)	Outlet PFOA (mg/L)	PFOA removed (%)	Volume treated (L)
11.58	<LOR	>99.9>	1.65	<LOR	>99.7	>2,000,000

Note: LOR=Limit of Report (2µg/L); Average values over 2 years were taken.

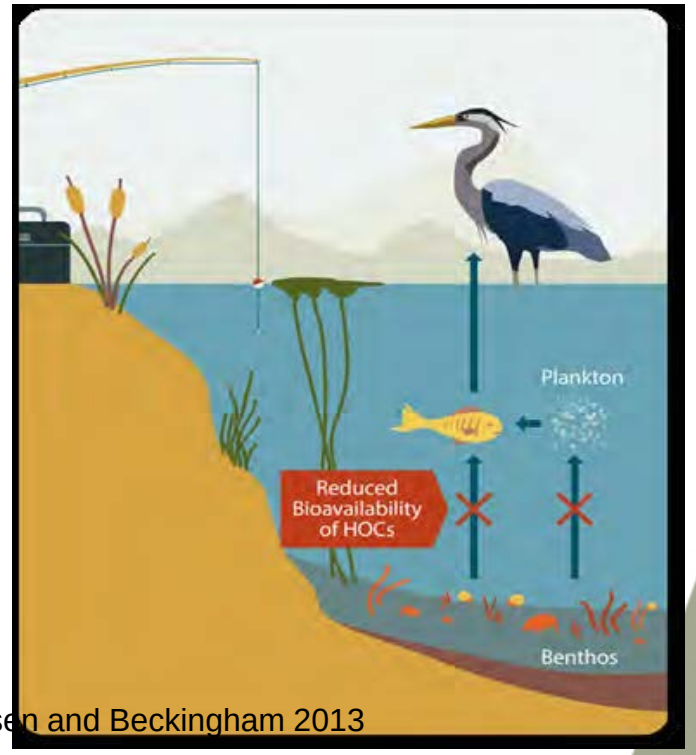
Conclusions

- The AFFF plant built next to the dam containing contaminated waste water has successfully treated in excess of 1,000,000L of contaminated water to a level below the limit of reporting (LOR), which is 2µg/L .
- More than 99% of AFFF (PFOS 99.7% and PFOA 98.8%) has been removed from the wastewater.
- Transportable design presents a number of advantages.

AFFF CONTAMINATED SOIL REMEDIATION

Objective of remediation

- Reduce the actual or potential environmental threat and
- Reduce unacceptable risks to man, animals and the environment to acceptable levels (Wood, 1997)



Janssen and Beckingham 2013

- Removal of risk by physical means (dig and dump) which can be prohibitively expensive and may not ultimately prove effective- leaving for future generations

Alternative: locally change the geochemistry to stabilize and sequester the contaminants and render them biologically unavailable

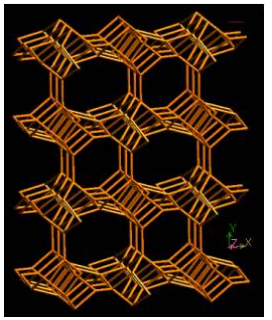
RISK REDUCTION

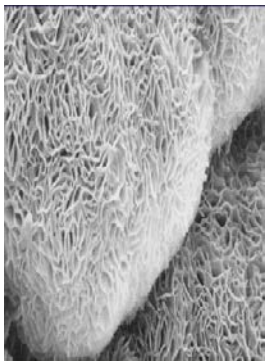
"Could be low cost, in situ management and hence most attractive remediation technique-

Key to risk reduction: development of techniques that enable significant bioavailability reduction and this must be reliable and sustainable over long-term"

Regulator requirement: outcome fulfils NEPM using OECD and other regulatory tests

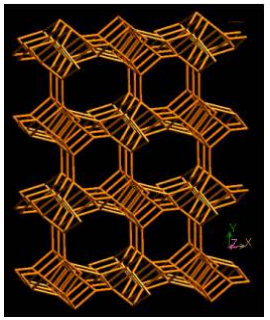
AFFF SOIL AND WATER REMEDIATION- CHEMICAL IMMOBILIZATION: CRC CARE





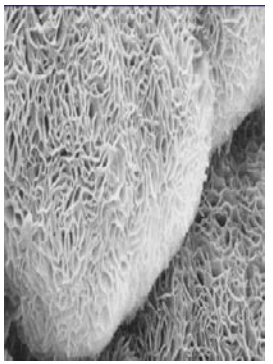
- Develop modified natural material with high capacity to immobilize PFCs
- Assess the ability of modified material to immobilize PFCs- optimization the process
- Investigate the release characteristic of the immobilized PFCs
- Investigate bioavailability of PFCs in treated soils

AFFF SOIL REMEDIATION- BIOAVAILABILITY REDUCTION



Strategies to immobilize PFOS in the impacted soils.

Minimise exposure by reducing contaminant bioavailability,

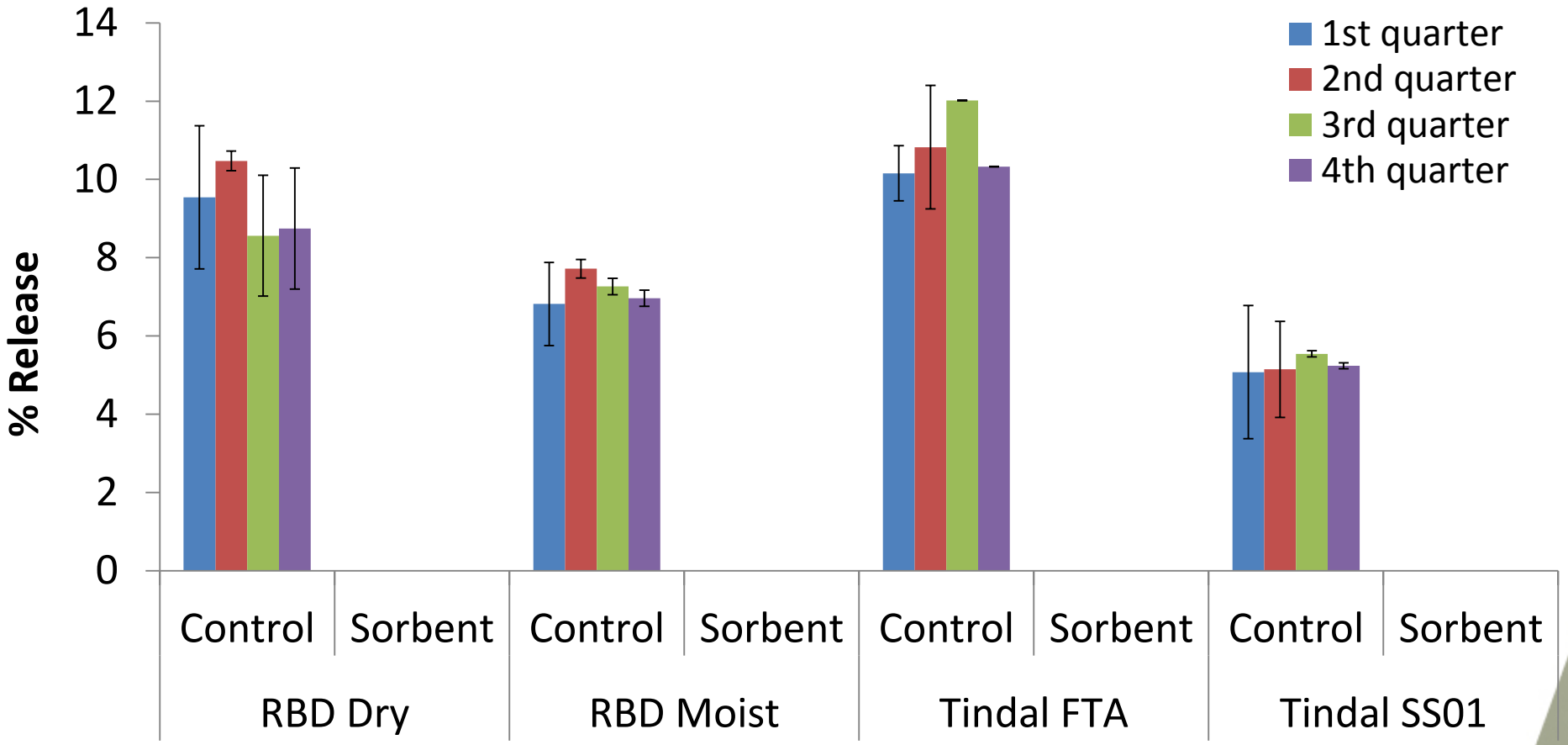


Can this be achieved via immobilisation of PFCs in AFFF contaminated soils? = a risk based approach

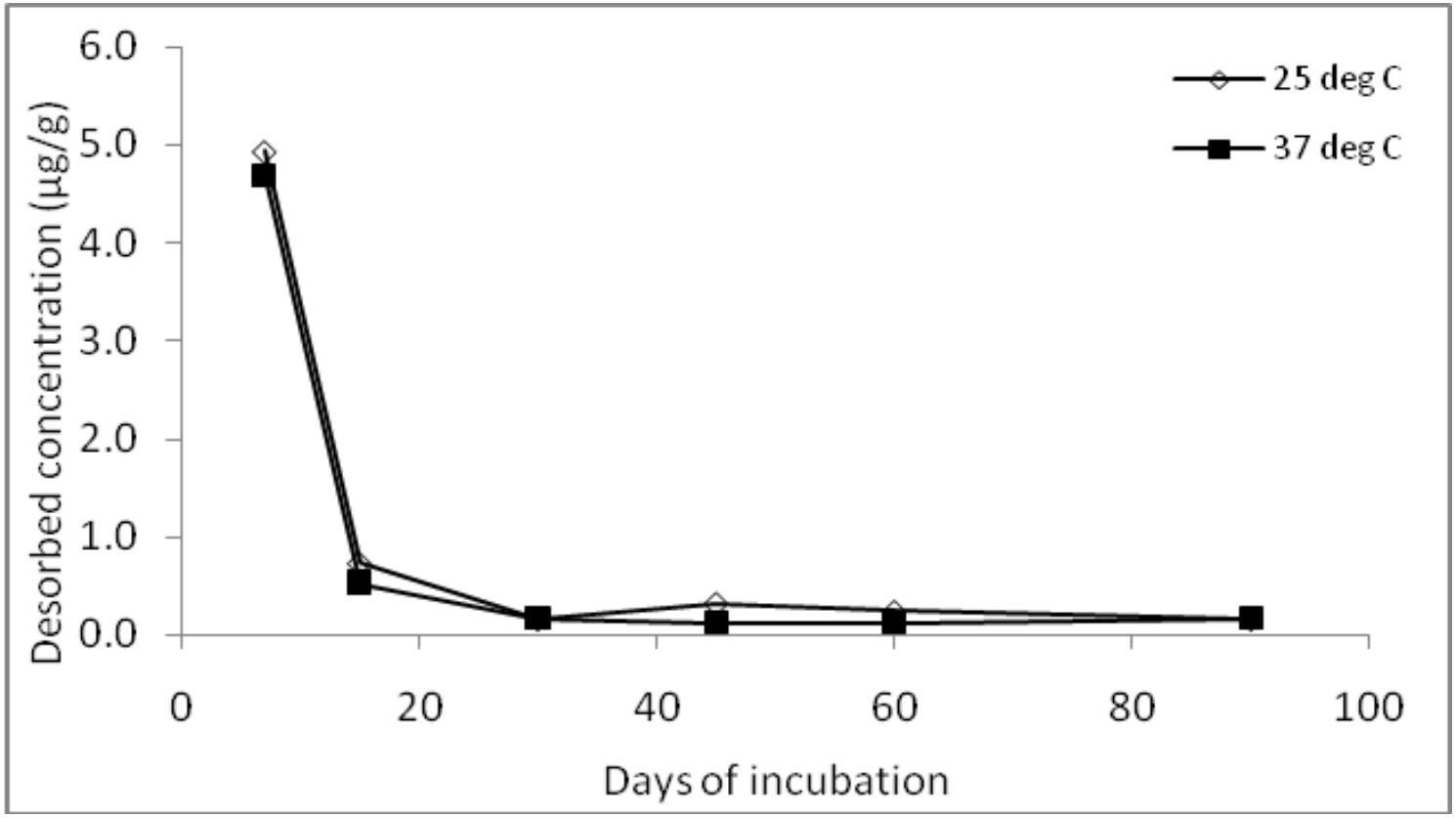
PFOS CONTENT OF SOILS

Soil	PFOS concentration (µg/g dry soil)	
	water extract	solvent extract
Brown (Dry) RBD	0.26	1.83
Brown (Water logged) RBD	10.57	74.38
Red Tindal FTA 064,SB04	2.36	16.17
Black Tindal SS01	0.93	9.26

MODIFIED CLAY TREATABILITY STUDY- FIELD CONTAMINATED SOILS



TIME DEPENDEDNT DESORPTION OF PFOS FROM SOILS TREATED WITH MATCARE



FIELD REMEDIATION- PFOS IN UNTREATED SOILS

Untreated Sample No.	Concentration	
	Aqueous extract (µg/ml)	Soil (µg/g)
1	1.21	5.59
2	2.68	12.33
3	4.43	20.38
4	2.12	9.77
5	1.4	6.42
6	6.09	28.02
7	2.39	11
8	1.63	7.51
9	3.15	14.49
10	2.97	13.68
11	2.01	9.25
12	1.95	8.98

GLIMPSES OF THE FIELD WORK

GLIMPSES OF THE FIELD WORK

FIELD REMEDIATION- PFCs IN TREATED SOILS

Sample No.	Concentration			
	Aqueous extract.(µg/ml)		Soil µg/g	
	one week	Eight weeks	one week	Eight weeks
1	0.02	bdl	0.097	bdl
2	0.01	bdl	0.045	bdl
3	0.04	bdl	0.196	bdl
4	0.03	bdl	0.118	bdl
5	0.01	bdl	0.062	bdl
6	0.02	bdl	0.087	bdl
7	0.01	bdl	0.055	bdl
8	0.01	bdl	0.060	bdl
9	0.02	bdl	0.081	bdl
10	0.02	bdl	0.112	bdl
11	0.02	bdl	0.096	bdl
12	0.02	bdl	0.087	bdl
13	0.02	bdl	0.097	bdl
14	0.02	bdl	0.091	bdl
15	0.04	bdl	0.161	bdl

HPCD extractions

EFFECT OF IMMOBILIZATION ON EARTHWORM SURVIVAL AND UPTAKE IN TREATED SOILS

- Field soils treated with MatCARE allowed to react for 120 days were exposed to worms.
- Weight loss monitored
- Worm tissues solvent extracted

No sign of avoidance in treated soils- no bioaccumulation No mortality

SUMMARY AND CONCLUSIONS

- Remediation technologies investigated have delivered mixed outcomes;
    - Majority of technologies were unsuccessful in remediating of PFCs from waste water;
    - At best tested technologies could remove <90% of PFCs.
    - Ineffectiveness of the technologies were attributed to the extreme stability of strong carbon-fluorine (c-f) bonds

SUMMARY AND CONCLUSIONS

- matCARE™ based technology has successfully remediated >2,000,000 l of waste water in the field at three separate locations;

- Bioavailability reduction- is an attractive strategy for managing PFCs contaminated soils - a risk based approach to managing AFFF contaminated soils.

COST OF REMEDIATION

- Cost varies depending on the contaminant loading, nature of other contaminants in water and soil

“for every complex question there is a simple answer and its wrong”

…….. HL Mencken

ACKNOWLEDGEMENTS

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