Partitioning and Storage of Per- & Polyfluoroalkyl Substances at Fire Training Areas Considering Supramolecular Assemblies

Vision, Initiatives and Paradigm Shift

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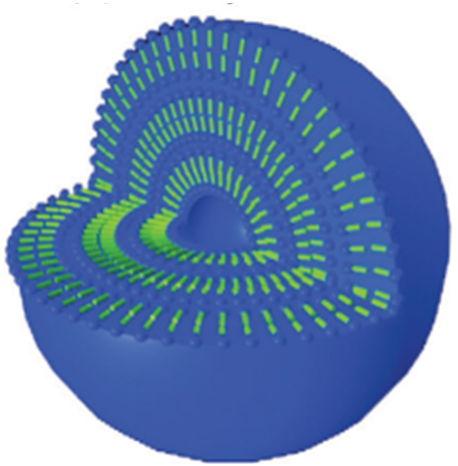
Overview

- Potted History of PFAS and Foams
- Source Zones PFAS storage –current thinking
- Cations, Zwitterions as less mobile ongoing source of PFAAs
- PFAS Physical Chemistry
- Fluorinated Amphiphile Self Assembly
- Supramolecular Assemblies
- PFAS storage at interfaces
- AFFF Foam Chemistry
- Langmuir-Blodgett multilayers as vadose zone storage repositories
- Concrete microporous structures
- Summary



Ramanathan, 2013

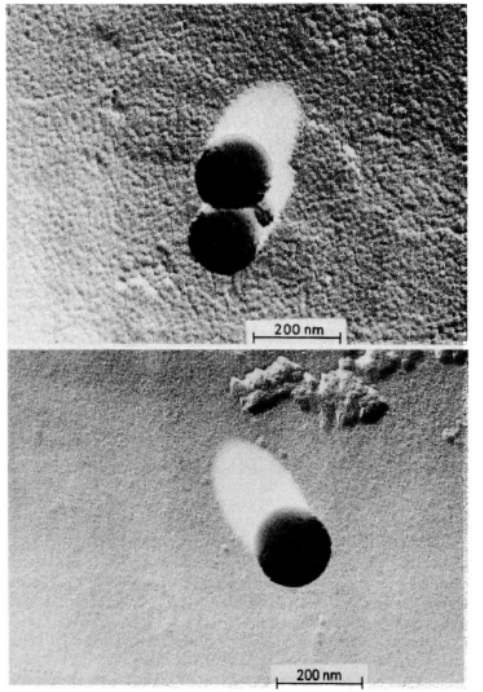
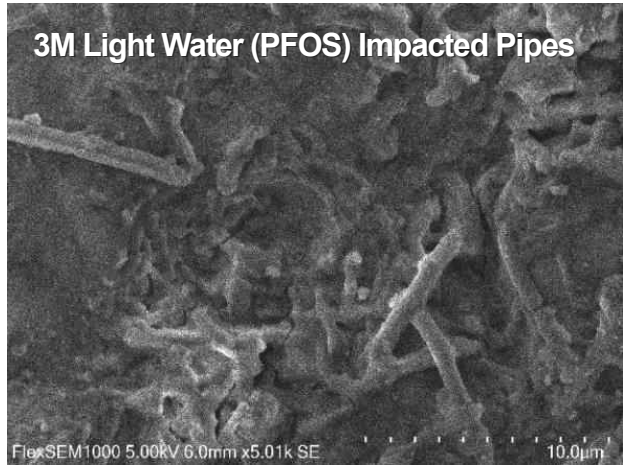


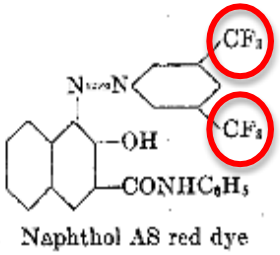
Figure 6. Electron micrograph of liposomes from **6**: (a) monomeric, (b) polymeric (after 15 min of UV irradiation).

Elbert et. al., 1984



Images Courtesy of Bjorn Bonnet, Swedish University of Agricultural Sciences (SLU)

History of PFAS, Fluorinated and Fluorine Free Firefighting Foams



Naphthol AS red dye

1922 Swarts synthesizes trifluoracetic acid (TFA) first PFAA synthesized

1930's PFAS mass production (>100 tonnes p.a.) of azo dye TFA precursors

1949 J. H. Simons describes environmental persistence of fluorocarbons

Summer **1962** 3M field tests PFAS foams at Marinette, WI

1967 3M AFFF supplied to five US Naval stations

15th May **1970**; US DoD QPL lists 3M Light Water FC-106

3rd June **1976**; US DoD QPL lists Ansul AFFF

1985 Fluorine free training foams developed

1997 Fluorosurfactants described in groundwater associated with use of AFFF

2002 3M formulated F3 foam with comparable performance to PFOS-based AFFF foams meeting the ICAO Level B specification

2009 The Stockholm Convention establishes restriction on PFOS uses

2010: First observations of PFAS in Swedish drinking water resulting in the closure of 3 water supply wells

2014 Solberg Rehealing F3 Foam wins USEPA Presidential Designing Greener Chemicals Award

2014 PRESIDENTIAL GREEN CHEMISTRY CHALLENGE AWARD winner

RE-HEALING™ FOAM AUTHENTIC FLUORO-FREE

1890 Moissan reports CF_4 synthesis

1943 R. D. Fowler reports extreme unreactivity of perfluorocarbons & no evidence of alkaline hydrolysis

29th July **1967** USS Forrestal Fire

1968 Dr. Donald Taves, New York, finds PFOS in blood samples from humans, including in his own blood.

24th October **1973** US DoD QPL lists National Foam Aer-O-Water 6

1986 AFFF Product Environmental Datasheet states that '*AFFF is biodegradable*' & '*if AFFF products were pure chemicals instead of mixtures, OECD guidelines would classify them as "readily biodegradable"*'

2001 High Molecular Weight Fluoropolymers introduced to AFFF to replace fluorosurfactants

2003 3M phases out sales of PFOS, PFOA and PFHxS chemistries

2010 USEPA PFOA Stewardship program starts

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

2014 Testing of Danish groundwater finds elevated PFAS at multiple locations

2016 National Foam F3 Jetfoam ICAO B wins Green Apple Award

INTEGRITY

GREEN APPLE AWARD WINNER 2016

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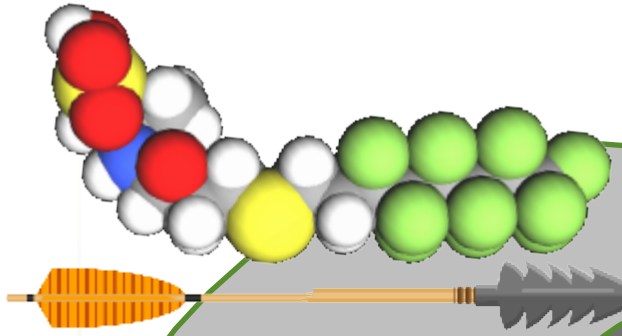
Per- & Polyfluoroalkyl Substances

>7 Million PFAS – OECD Definition



Poly-

Polyfluoroalkyl
- precursors

Sulphonamides

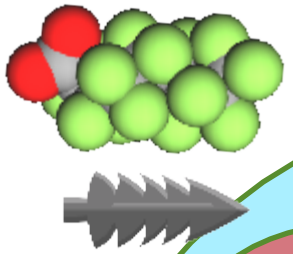
Polyfluoroalkyl ethers

Fluorotelomers

Side Chain Fluoropolymers

Transformation

Biological treatment or chemical oxidants promote transformation



Per-

Perfluoroalkyl

Long Chain
PFOS PFDA
PFOA PFNA
PFHxS PFTDA

Short Chain
PFBS PFPeA
PBA PFPeS
PFHxA PFHpA

Ethers
GenX
F53B
EE-NH_4

Cyclics
PFECHS

Ultra Short Chains
TFA PFPrA

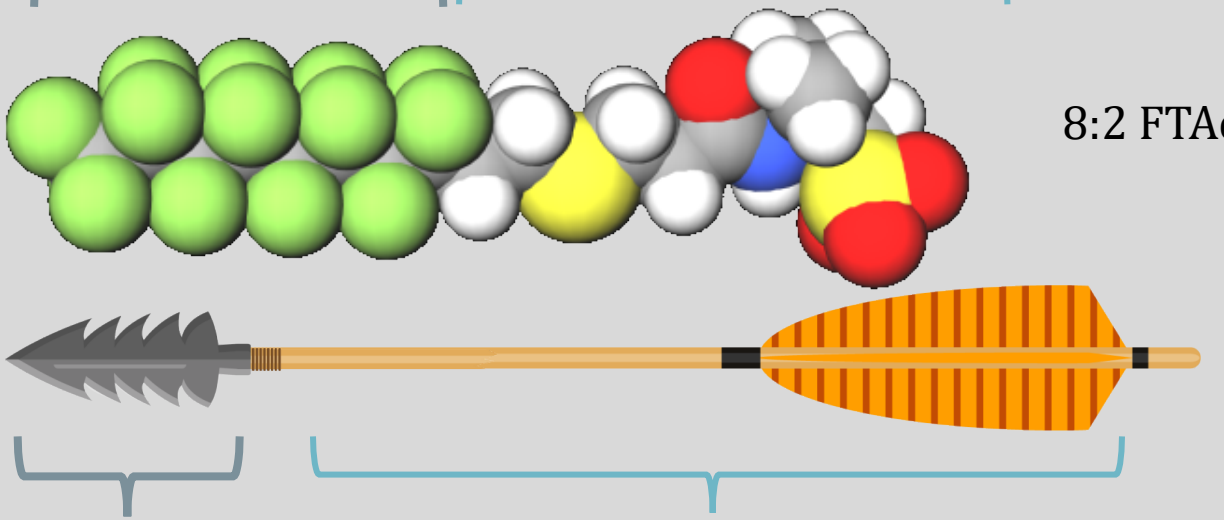
Per- & Polyfluoroalkyl Substances

Poly-

(Precursors)

Persistent perfluorinated

Non-fluorinated - Biologically/Chemically removed



8:2 FTAoS

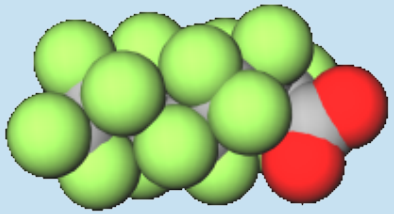
Stone arrowhead, like perfluorinated section of molecule, persists forever

Wooden shaft, like non-fluorinated section of molecule, is degraded so rots away in ground / in vivo

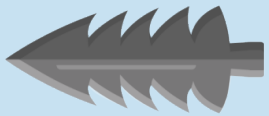
Biotransformation / Abiotic Oxidation

Per-

(Terminal products)



PFOA



Stone arrowhead

Perfluoroalkly acid formed from precursor persists indefinitely as "chemical rocks", like stone arrowheads that last forever in the environment

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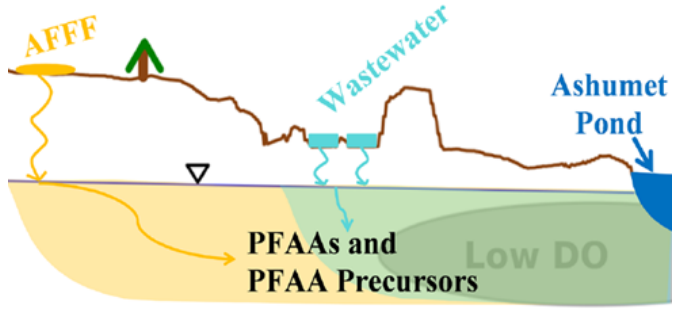
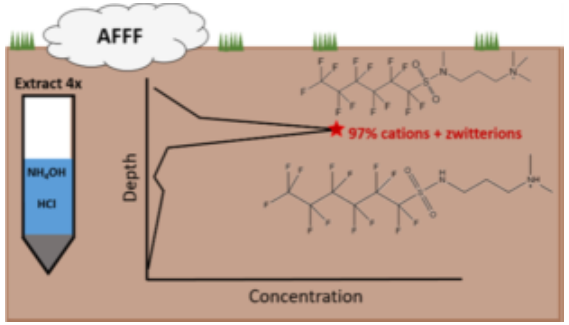
Sources of PFAAs long lasting – Cationic/Zwitterionic precursors?

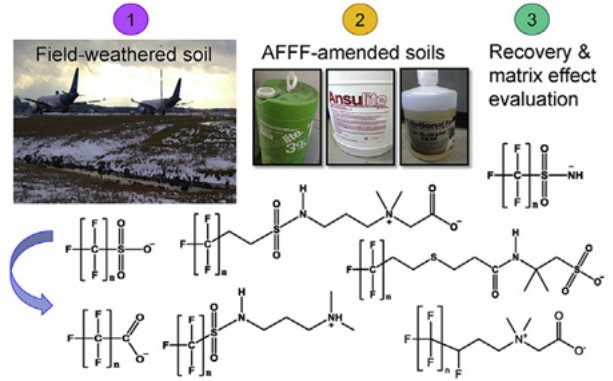
- The unsaturated zones continue to be a source of PFASs to the groundwater after **18 years** (FTA-1) and **20 years** (infiltration beds) of inactivity –Weber et al., 2017
- Cationic precursor loading in AFFF impacted soils revealed using low pH extractions –Munoz et al., 2018
- Sequential base-acid soil extractions reveals cations and zwitterions which represent 97% of PFAS – Nickerson et al., 2020
- Estimated conversion rate of precursors to PFAAs less than 2% annually. 82% of total PFAS mass was encountered in lower-permeability soils. –Adamson et al., 2020



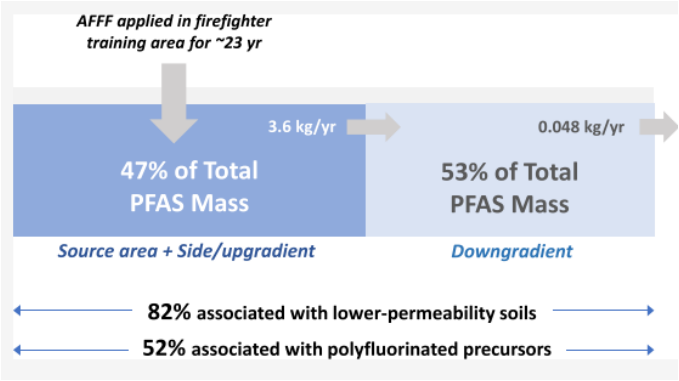
Weber et al., 2017



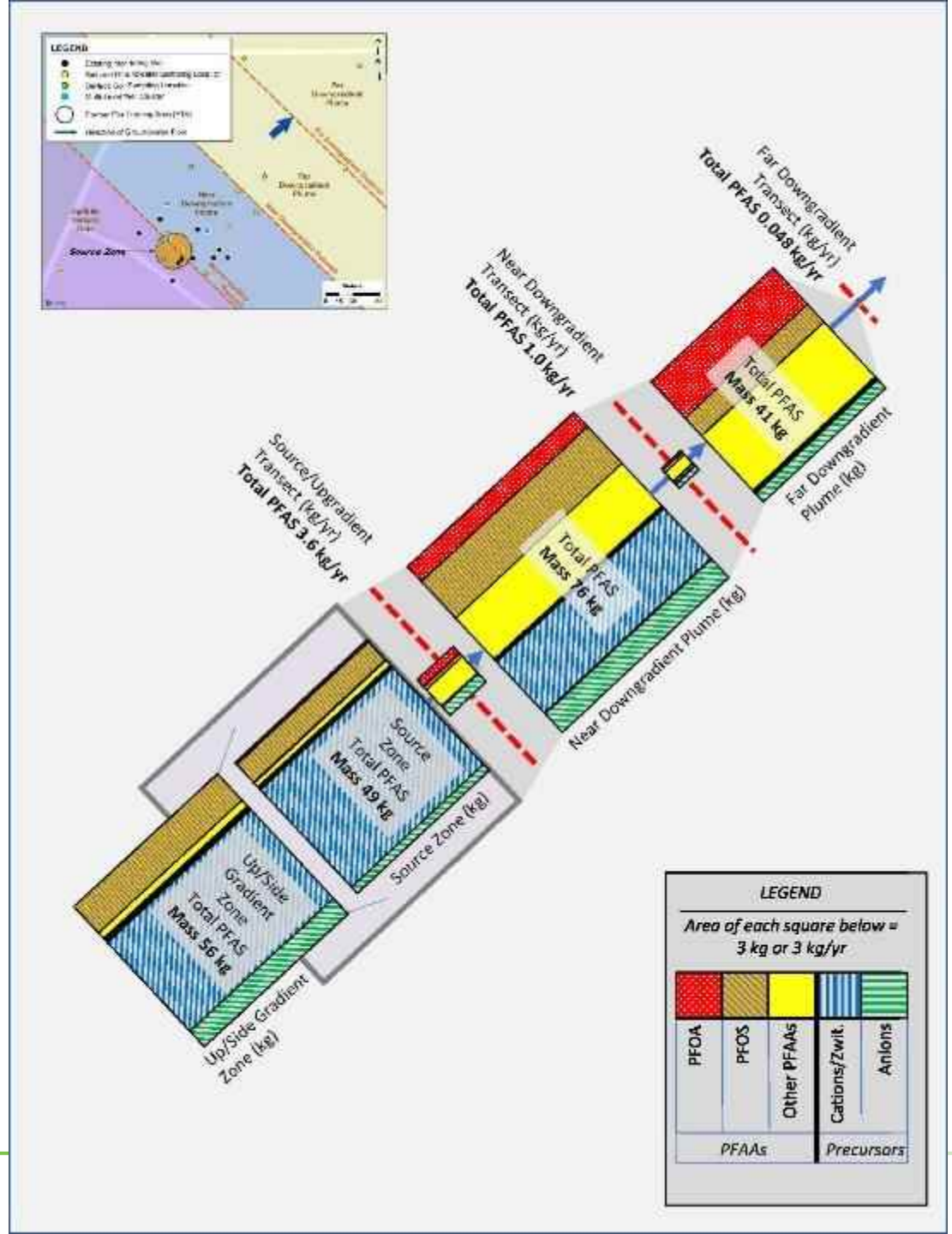
Nickerson et al., 2020

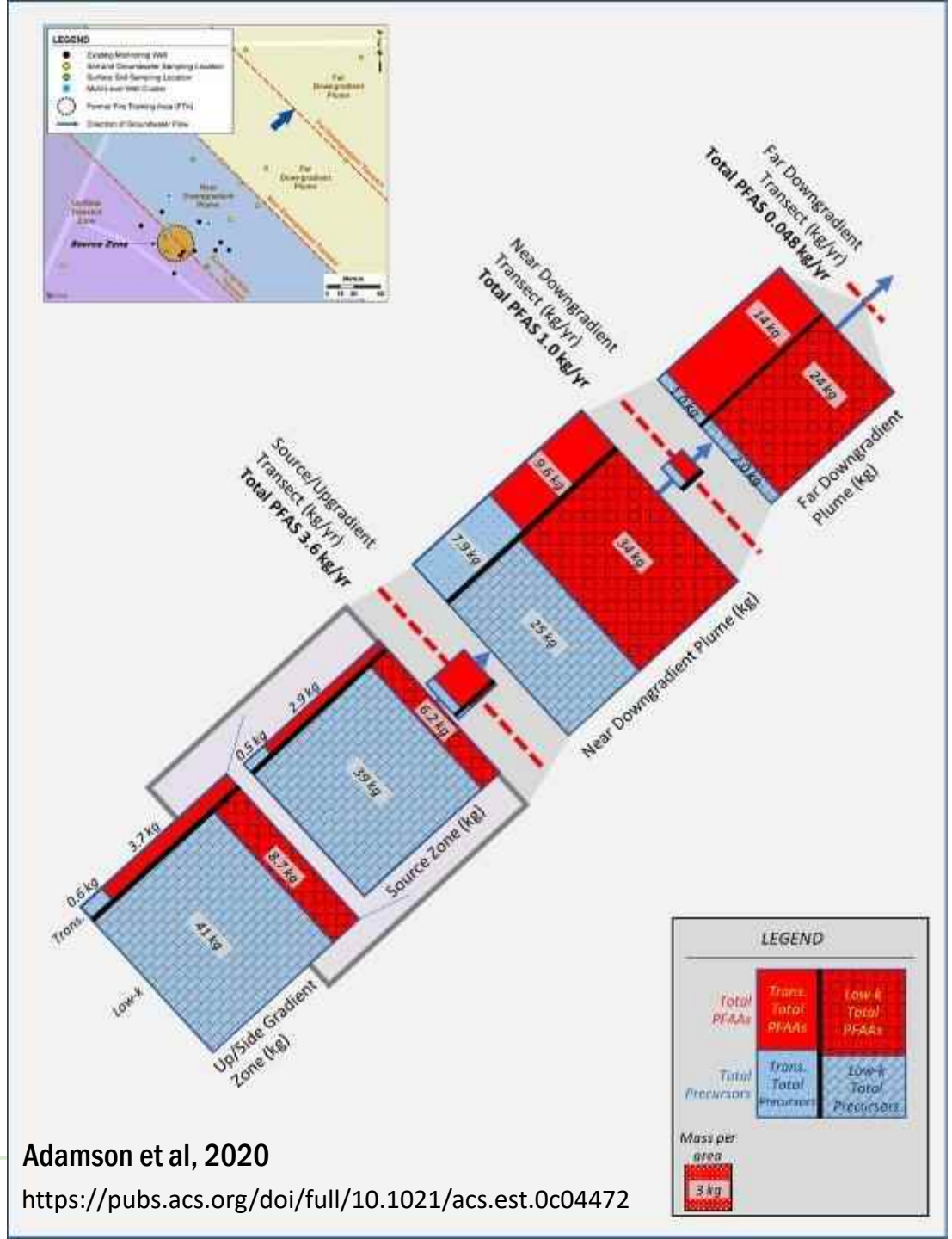


Munoz et al., 2018



Adamson et al., 2020



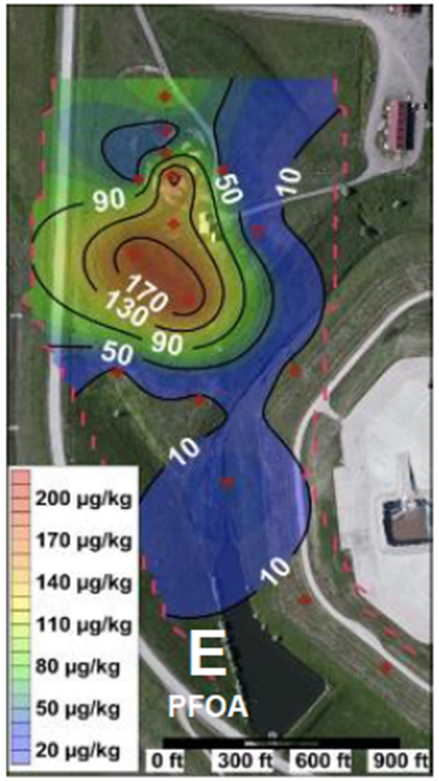


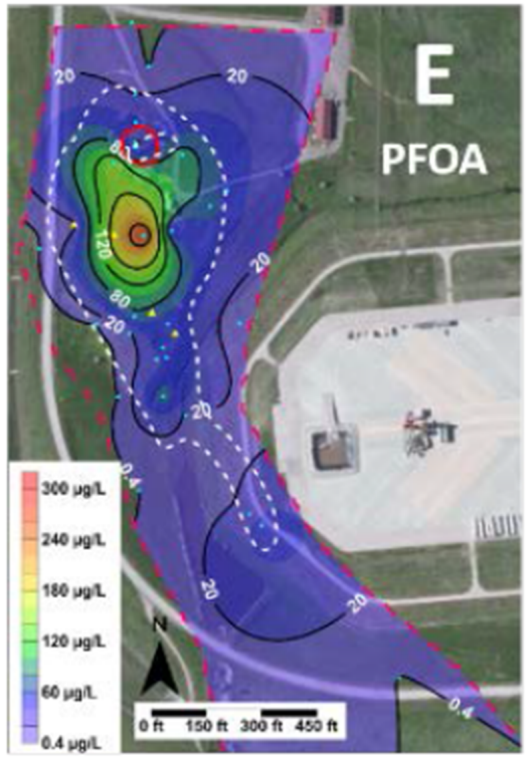
Adamson et al, 2020

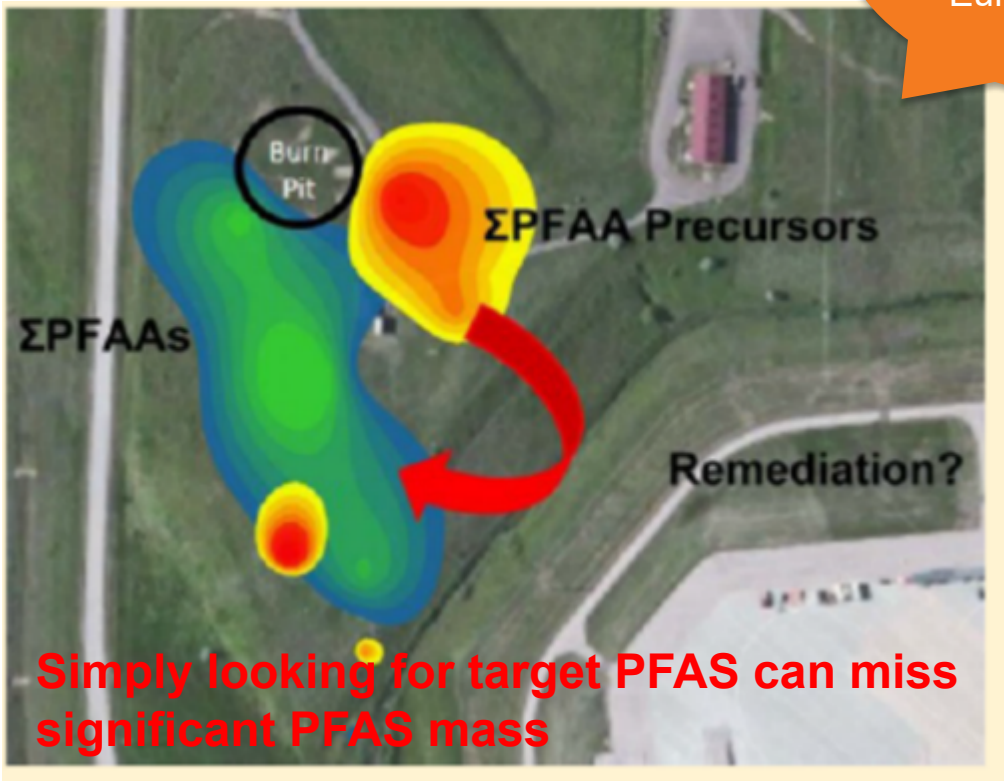
https://pubs.acs.org/doi/full/10.1021/acs.est.0c04472

Non target analysis (e.g. TOP assay) required to find PFAS impacted soils, which contain PFAA-precursors

Base Acid (Nickerson) Soil extractions commercially available via ALS or Eurofins to apply prior to TOP assay







McGuire et al., 2014

https://pubs.acs.org/doi/10.1021/es5006187

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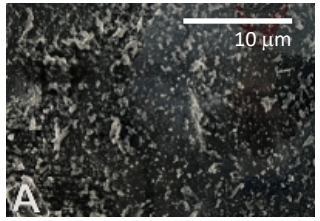
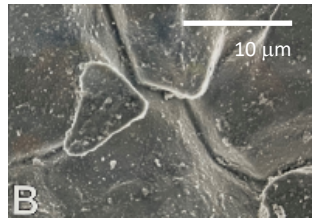
PFAS retained on surfaces

- Observed excessive and prolonged retention of PFAAs originating from AFFF within fire suppression systems, in surficial soils and pavements. What are the causes?
- Sorption of amphiphilic PFAS (fluorosurfactants) on surfaces often does not conform to conventional sorption theories.
- Insufficient credible mechanisms for PFAA retention within fire suppression systems, on concrete surfaces and in soils

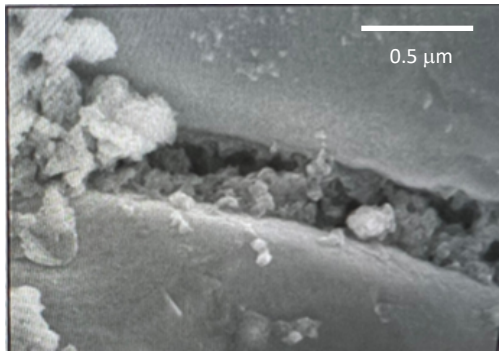
PFAS supramolecular assemblies detected on interior walls of fire suppression systems



Pipe Interior

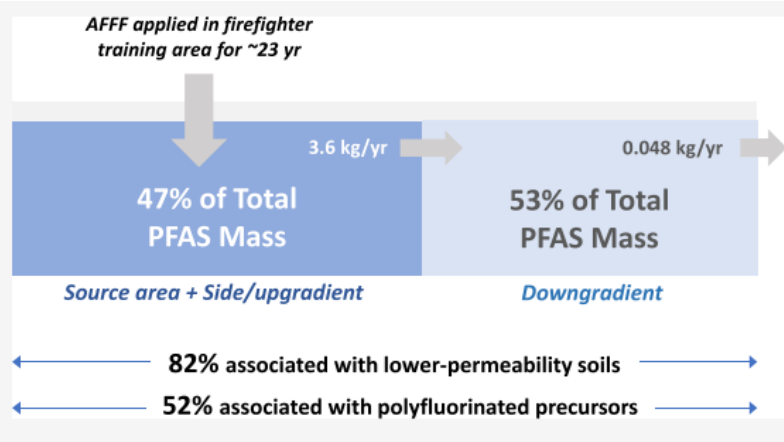


Pipe Exterior



PFAS aggregates on the interior of fire suppression system pipework (Lang et al., Chemosphere, 308, (2), 2022)

Significant retention of PFAS by soil



Adamson et al., 2020, *ES&T* 54, 15768-15777

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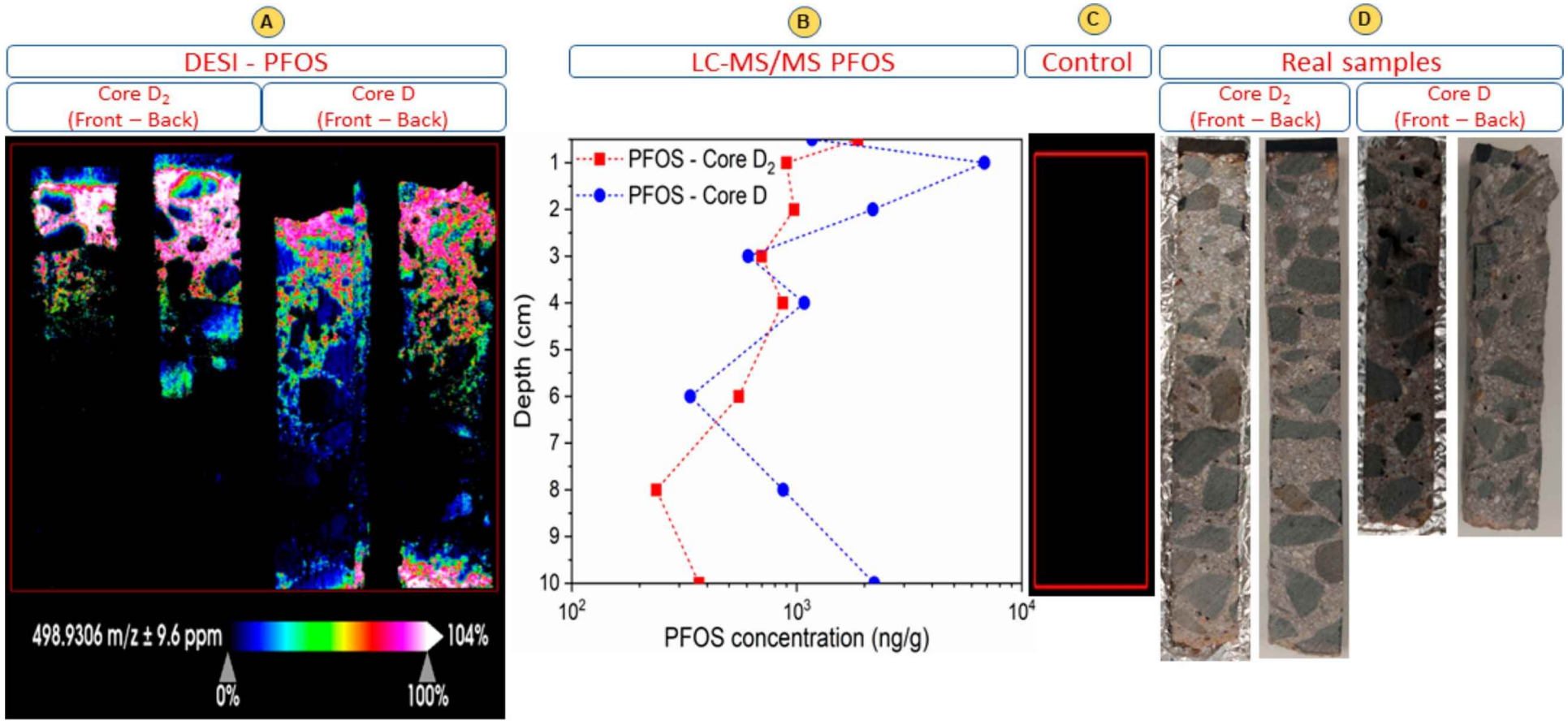
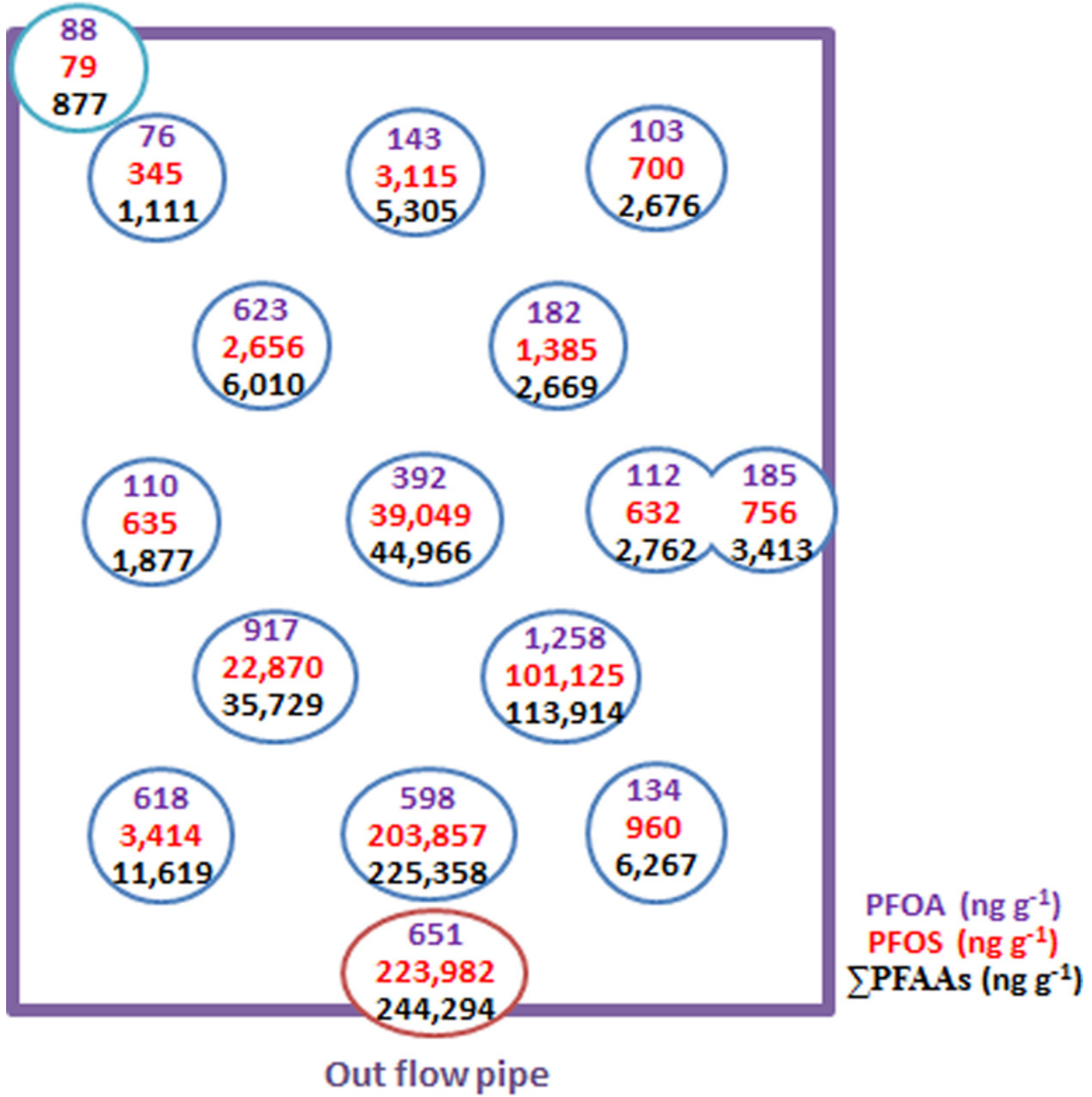
DESI MSI Visualization of PFOS Distribution In Concrete Core



Visualization of the Distribution of PFOS and PFHxS in Concrete by DESI MSI Vo et. Al., Environmental Science & Technology Letters 2023 10 (5), 446-451

Target PFAS on concrete surfaces

- PFOS concentrations vary by 4 orders of magnitude
- Highest concentrations where AFFF has run towards drain repeatedly
- Retention on the surface as a result of repeat deposition of stable supramolecular assemblies in Langmuir Blodget films?
- Wicking?



Baduel et. al., 2015

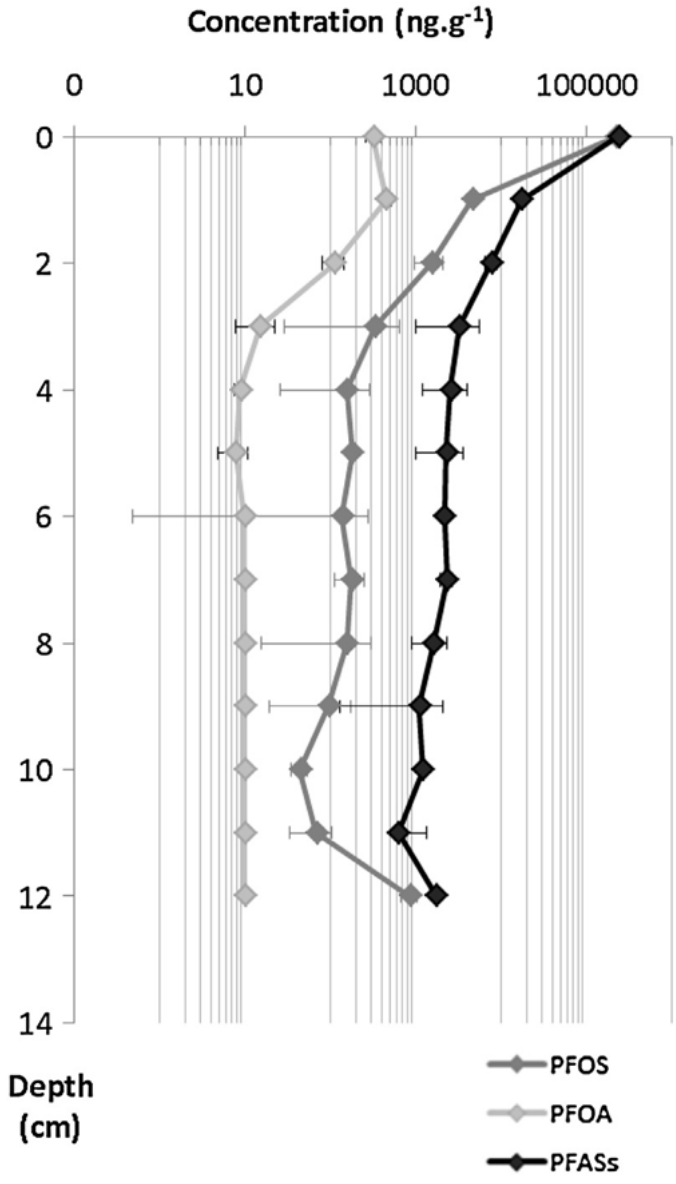
Longer PFAA chains retained at surface of concrete –how?

	PFBA		PFPA		PFHxA		PFHA		PFOA		PFNA		PFDeA		PFUnA		PFDoA		PFTriA		PFTeA	
	Profile 1	Profile 2	Profile 1	Profile 2	Profile 1	Profile 2	Profile 1	Profile 2	Profile 1	Profile 2	Profile 1	Profile 2	Profile 1	Profile 2	Profile 1	Profile 2	Profile 1	Profile 2	Profile 1	Profile 2	Profile 1	Profile 2
0 ± 0.2	69	80	82	98	443	534	78	97	280	365	339	579	3,621	3,107	2,275	2,422	1,675	1,814	300	298	376	370
0.8 - 1.2 cm	661	627	569	652	3,520	4,851	461	672	408	507	<6	<6	<12	<12	<3	4	<10	<10	<3	<3	<5	<5
1.8 - 2.2 cm	503	359	407	326	2,274	2,260	238	234	137	91	<6	<6	<12	<12	<3	4	<10	<10	<3	<3	<5	<5
2.8 - 3.2 cm	333	117	339	116	1,739	698	72	31	21	<10	<6	<6	<12	<12	6	<3	<10	<10	<3	<3	<5	<5
3.8 - 4.2 cm	255	135	302	121	1,272	645	35	13	8	<10	<6	<6	<12	<12	<3	5	<10	<10	<3	<3	<5	<5
4.8 - 5.2 cm	278	113	287	113	961	425	17	11	6	<10	<6	<6	<12	<12	<3	4	<10	<10	<3	<3	<5	<5
5.8 - 6.2 cm	204	196	310	207	360	680	<2	7	<10	<10	<6	<6	<12	<12	<3	<3	<10	<10	<3	<3	<5	<5
6.8 - 7.2 cm	201	225	287	240	629	524	5	4	<10	<10	<6	<6	<12	<12	6	4	<10	<10	<3	<3	<5	<5
7.8 - 8.2 cm	177	144	238	125	414	215	4	<2	<10	<10	<6	<6	<12	<12	5	<3	<10	<10	<3	<3	<5	<5
8.8 - 9.2 cm	25	190	25	233	79	257	2	<2	<10	<10	<6	<6	<12	<12	3	<3	<10	<10	<3	<3	<5	<5
9.8 - 10.2 cm	136	160	152	186	144	146	<2	<2	<10	<10	<6	<6	<12	<12	<3	3	<10	<10	<3	<3	<5	<5
10.8 - 11.2 cm	14	139	11	165	11	112	<2	3	<10	<10	<6	<6	<12	<12	<3	4	<10	<10	<3	<3	<5	<5
11.8 - 12.2 cm	120	109	142	127	108	76	7	5	<10	<10	<6	<6	<12	14	12	7	<10	<10	<3	<3	<5	<5

	PFBS		PFHxS		PFOS		PFDS		62FTS 1	
	Profile 1	Profile 2	Profile 1	Profile 2	Profile 1	Profile 2	Profile 1	Profile 2	Profile 1	Profile 2
0 ± 0.2	164	153	540	729	217,587	237,409	416	531	17	26
0.8 - 1.2 cm	2,231	3,007	3,163	3,825	4,427	4,893	<10	<10	458	<13
1.8 - 2.2 cm	1,328	1,325	1,452	1,088	1,937	1,147	<10	<10	242	<13
2.8 - 3.2 cm	1,130	401	503	168	558	120	<10	<10	152	<13
3.8 - 4.2 cm	1,050	527	346	96	249	64	<10	<10	63	<13
4.8 - 5.2 cm	1,235	451	226	59	167	195	<10	<10	43	<13
5.8 - 6.2 cm	1,186	868	10	64	41	238	<10	<10	<13	<13
6.8 - 7.2 cm	1,159	900	58	29	228	131	<10	<10	20	<13
7.8 - 8.2 cm	971	554	36	14	258	57	<10	<10	15	<13
8.8 - 9.2 cm	93	1,054	24	9	151	42	<10	<10	<13	<13
9.8 - 10.2 cm	721	670	10	9	51	37	<10	<10	<13	<13
10.8 - 11.2 cm	39	586	<5	17	44	95	<10	<10	<13	<13
11.8 - 12.2 cm	504	461	33	43	725	997	<10	<10	<13	<13

Concentration interval (ng g^{-1})

- C < LOQ
- LOQ< C < 100
- 100< C < 1000
- 1,000< C < 10,000
- 10,000< C <100,000
- 100,000< C <1,000,000



Baduel, et al., 2015

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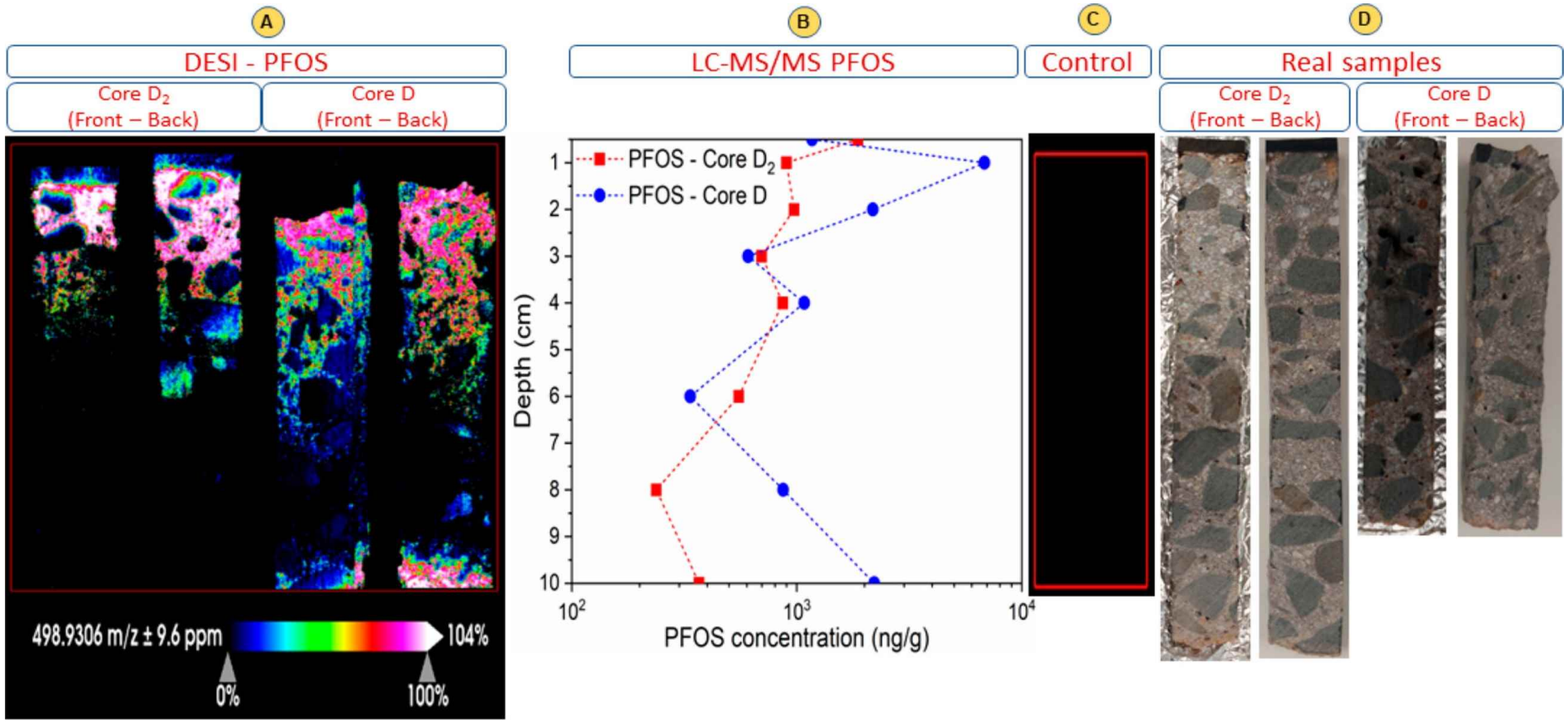


Visualization of the Distribution of PFOS and PFHxS in Concrete by DESI MSI Vo et. Al., Environmental Science & Technology Letters 2023 10 (5), 446-451

PFAA Distribution in concrete

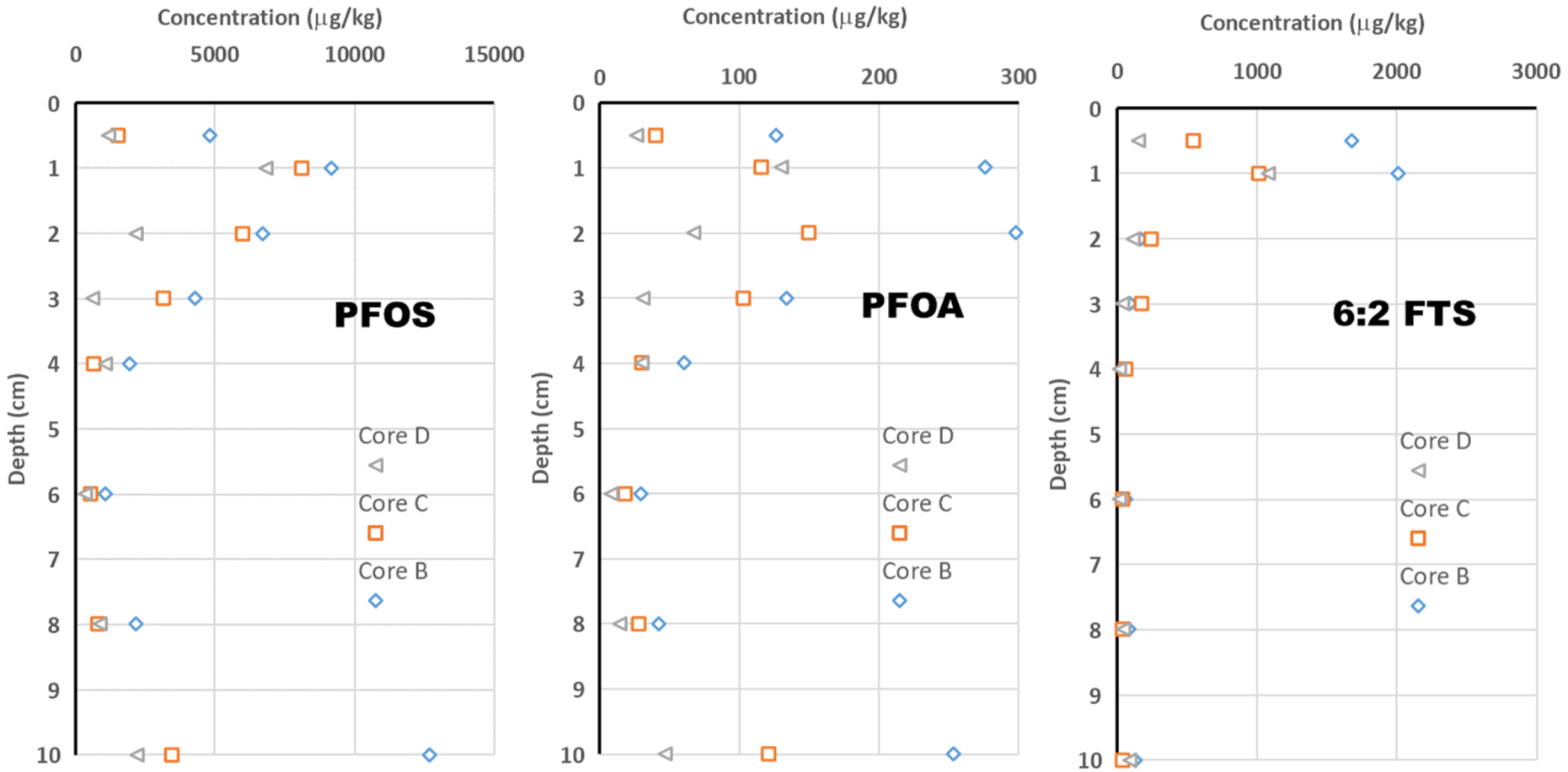


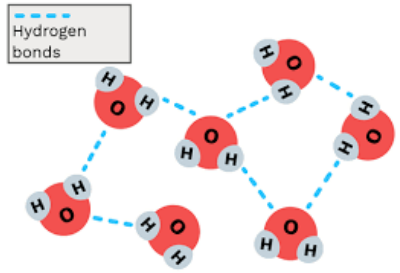
Fig. 1. Vertical profiles of PFOS, PFOA, and 6:2 FTS in three different concrete cores (note the different scales of the x axis).

Thai, et al., 2021

Bulky and Rigid Perfluoroalkyl Chains

- Linear fluoroalkyl chains have a 50% larger cross-section area than an alkyl chain
- The "hydrophobic“ effect of the chain is roughly proportional to its area in contact with water
- Fluoroalkyl chain have diminished association with water as a result of reduced van der Waals interactions – imparting increased hydrophobicity

Punches a larger hole in water which increases surfactant properties



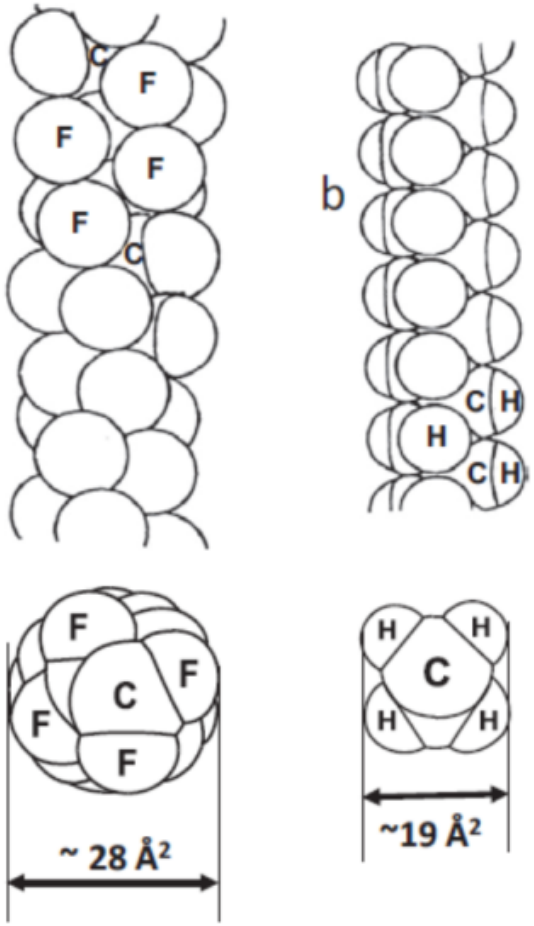


Fig. 1. Comparative hard-sphere model representations of *F*-alkyl and alkyl chains and their cross-sections. Adapted from Krafft and Riess (2009).

		Fluorine	Hydrogen
Electronegativity		3.98	2.2
Ionisation potential	kJ/mol	1676	1312
Electron affinity	kJ/mol	328	73
Covalent radius	Å	0.57	0.31
van der Waals radius	Å	1.35-1.47	1.2

		F-alkyl chain	Alkyl chain
Cross-section area	Å2	27–30	18–21
Van der Waals diameters	Å2	5.6	4.2

		F-alkly chain	Alkyl chain
Volumes Occupied	Å3	CF2 ~38	CH2 27
	Å3	CF3 ~92	CH3 54

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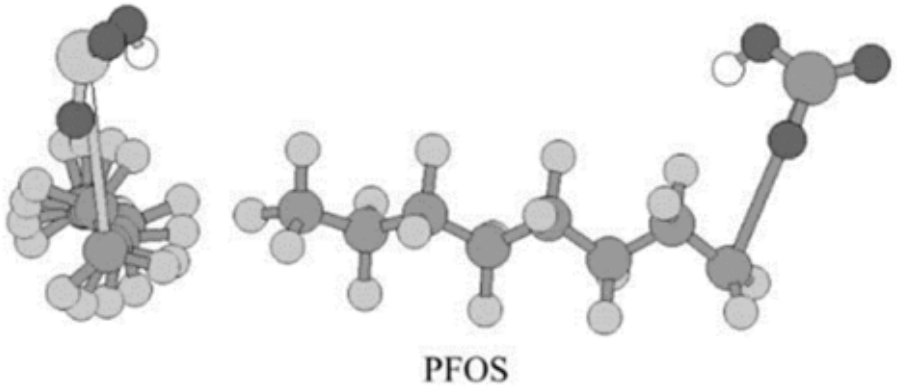
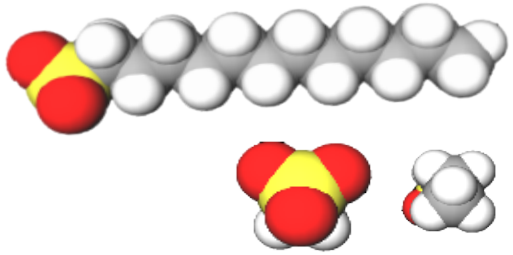
Surfactant Tail Shape Determines Critical Packing Parameters

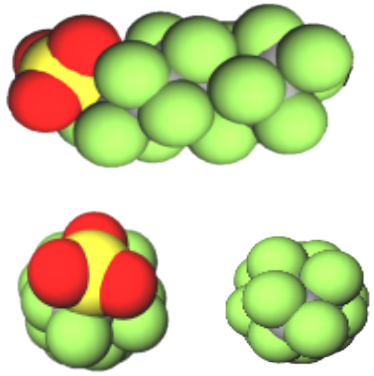


Erkoc et al., 2001 Journal of Molecular Structure (Theochem) 549 (2001) 289-293

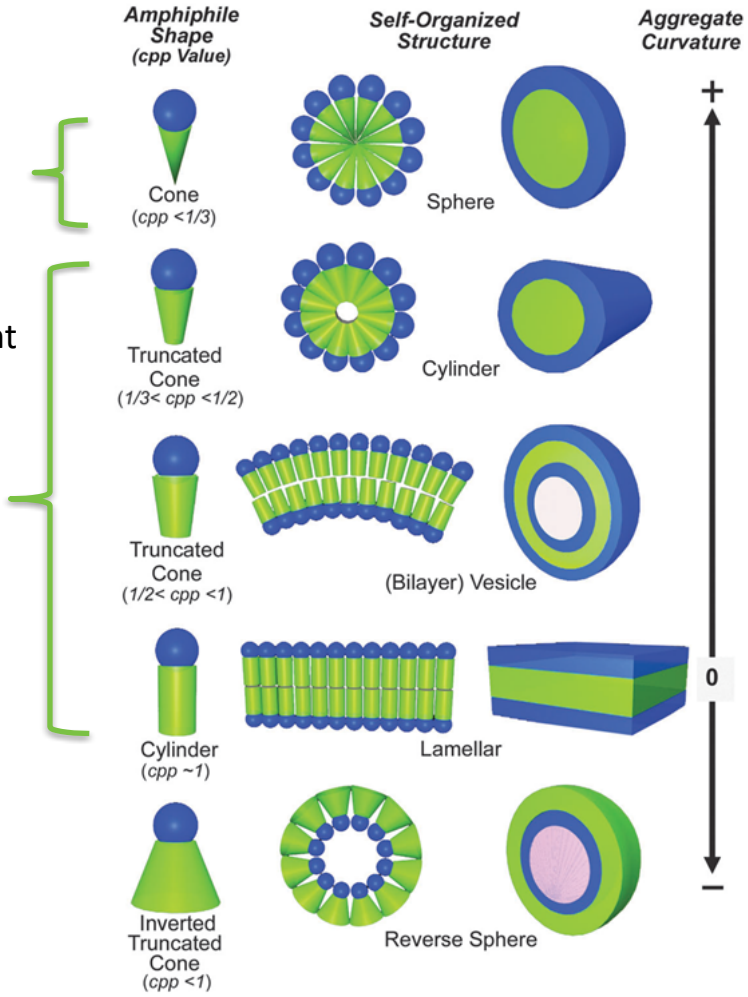
- Fluorine has high electronegativity which imparts a **rigid** helical fluorocarbon structure to perfluoroalkyl groups leading to the formation of **bulky, rigid, rod-shaped fluorosurfactant tails**
- The bulky, rigid, rod shape of the fluoroalkyl chains tends to decrease the curvature of the aggregates they form in solution
- This results in a strong tendency to form vesicles and lamellar phases rather than micelles



SDS – C12 hydrocarbon surfactant



PFOS C8 fluorosurfactant



Ramanathan et al., Phys.Chem.Chem.Phys., 2013, 15, 10580

Gladysz, Curran, Horváth 2004 DOI:10.1002/3527603905

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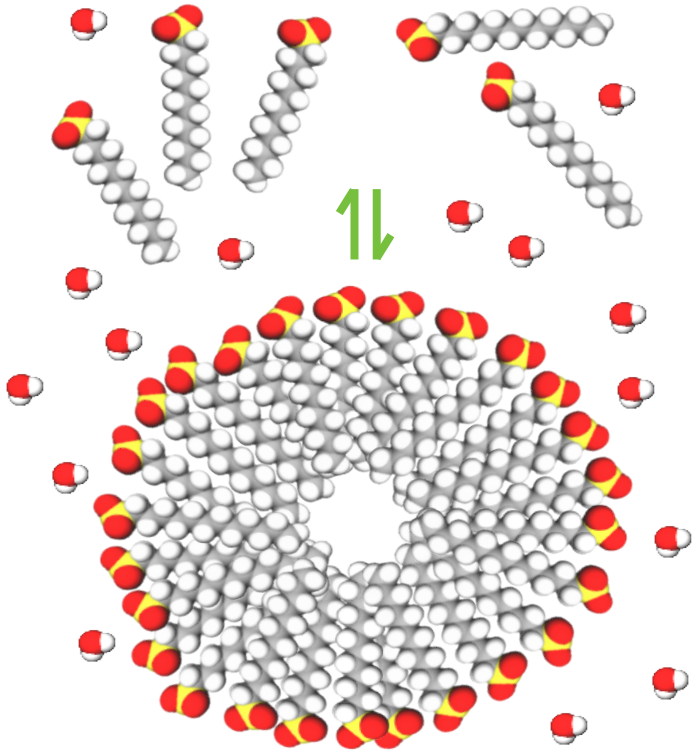
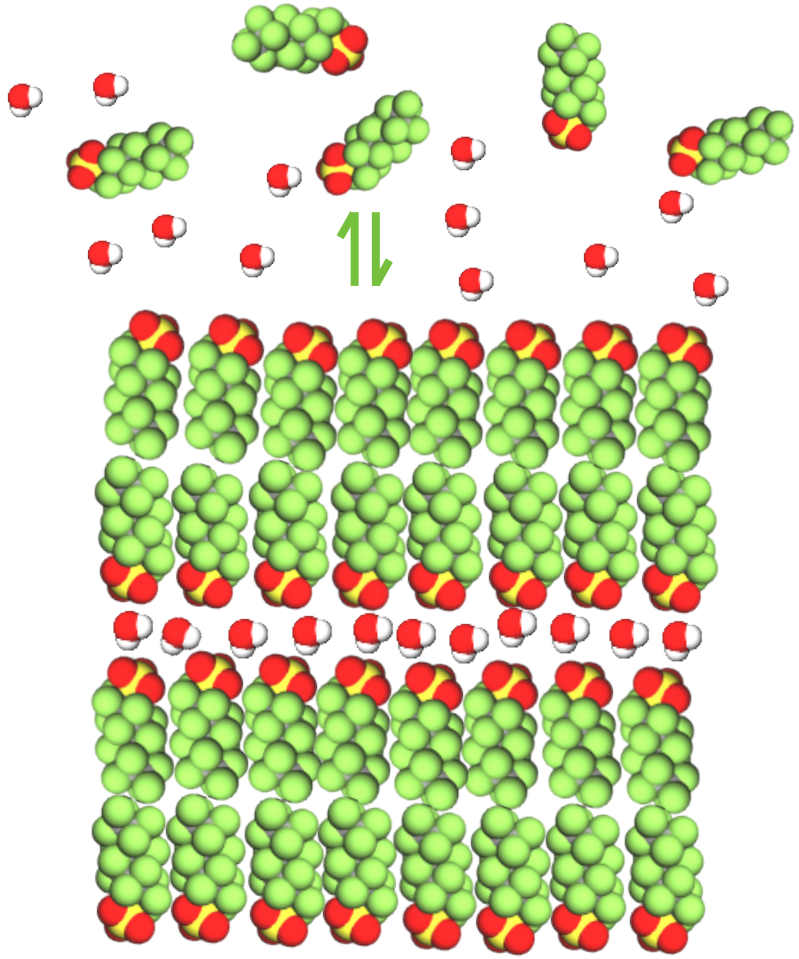
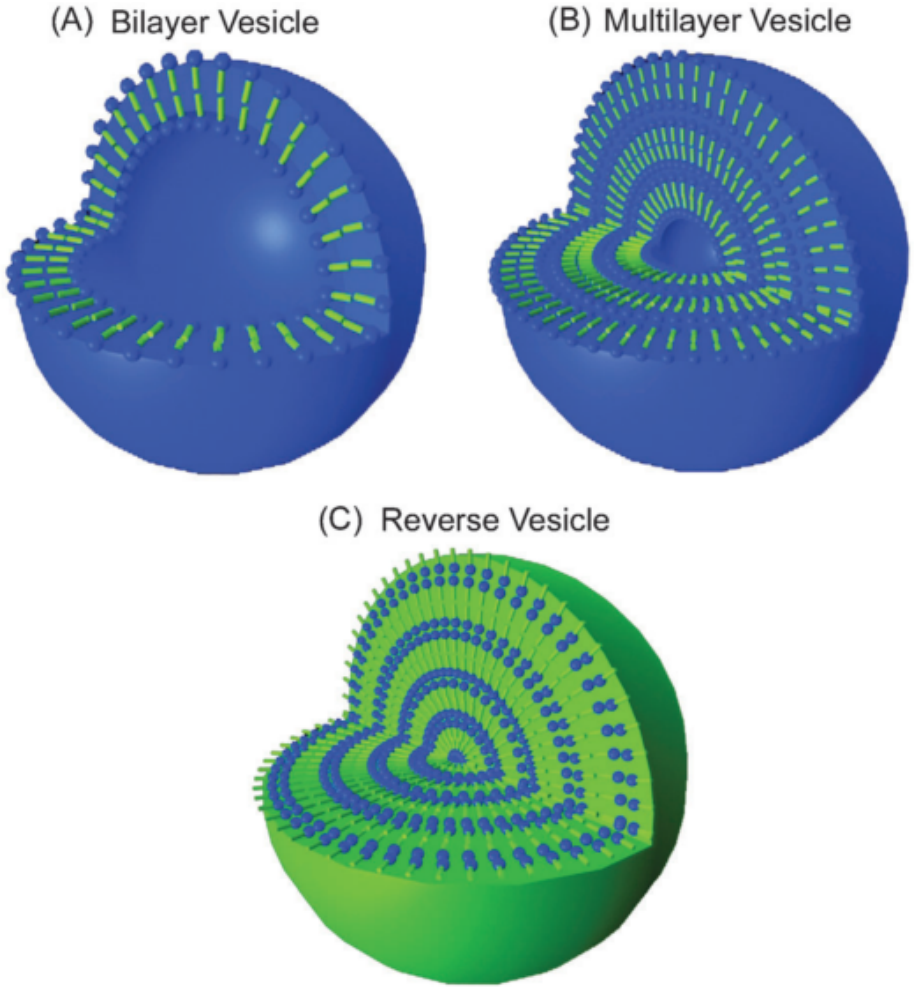
Hydrocarbon surfactants form micelles



Fluorosurfactants form vesicles & lamellar phases



Supramolecular Assemblies



Ramanathan et. al., 2013

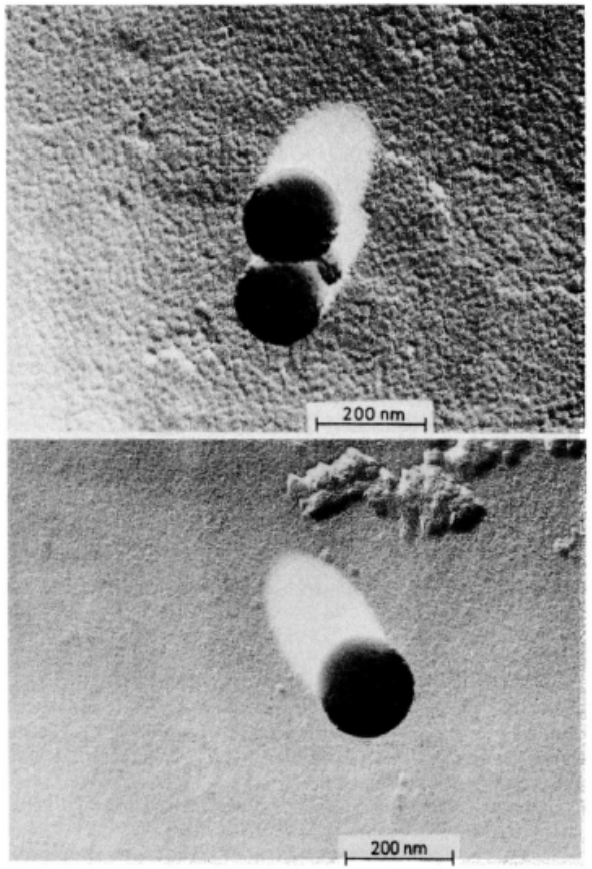


Figure 6. Electron micrograph of liposomes from **6**: (a) monomeric, (b) polymeric (after 15 min of UV irradiation).

Elbert et. al., 1984

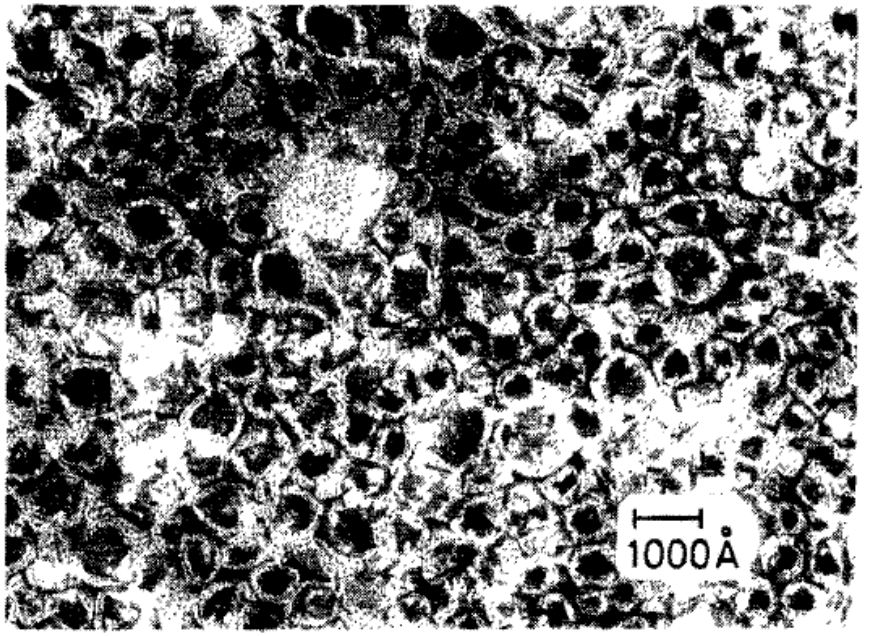


Figure 1. Electron micrograph of fluoroalkyl vesicles (20_{10}^{F}-L-Glu-C_1-N^+ (**1**), 10 nM); stained by uranyl acetate; magnification × 13 333.

Kunitake et al., 1982

Self Assembly of Fluorosurfactants

- Once a molecule is fitted with a perfluoroalkyl functional group (>C4) they are likely to become amphiphilic
- Fluorosurfactants are susceptible to adsorption at interfaces, self-association into colloidal systems, including spherical and worm-like micelles, vesicles and hollow fibers, emulsions, microemulsions or other more or less complex self-assemblies
- Vesicles made from F-amphiphiles are characterized by higher organization of their bilayer and improved stability
- Some vesicles withstood heat sterilization and showed only little changes in particle size distribution after 3 months at 40 °C.

"very large aggregates of micrometers in size"

"micelles formed by fluorosurfactants tend to be rodshaped"

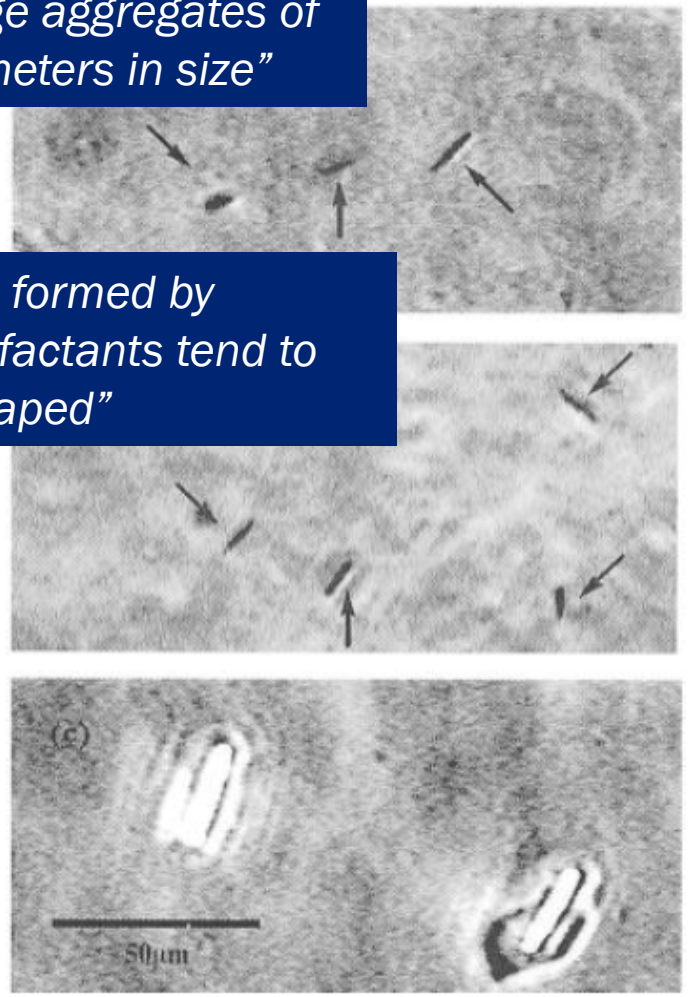
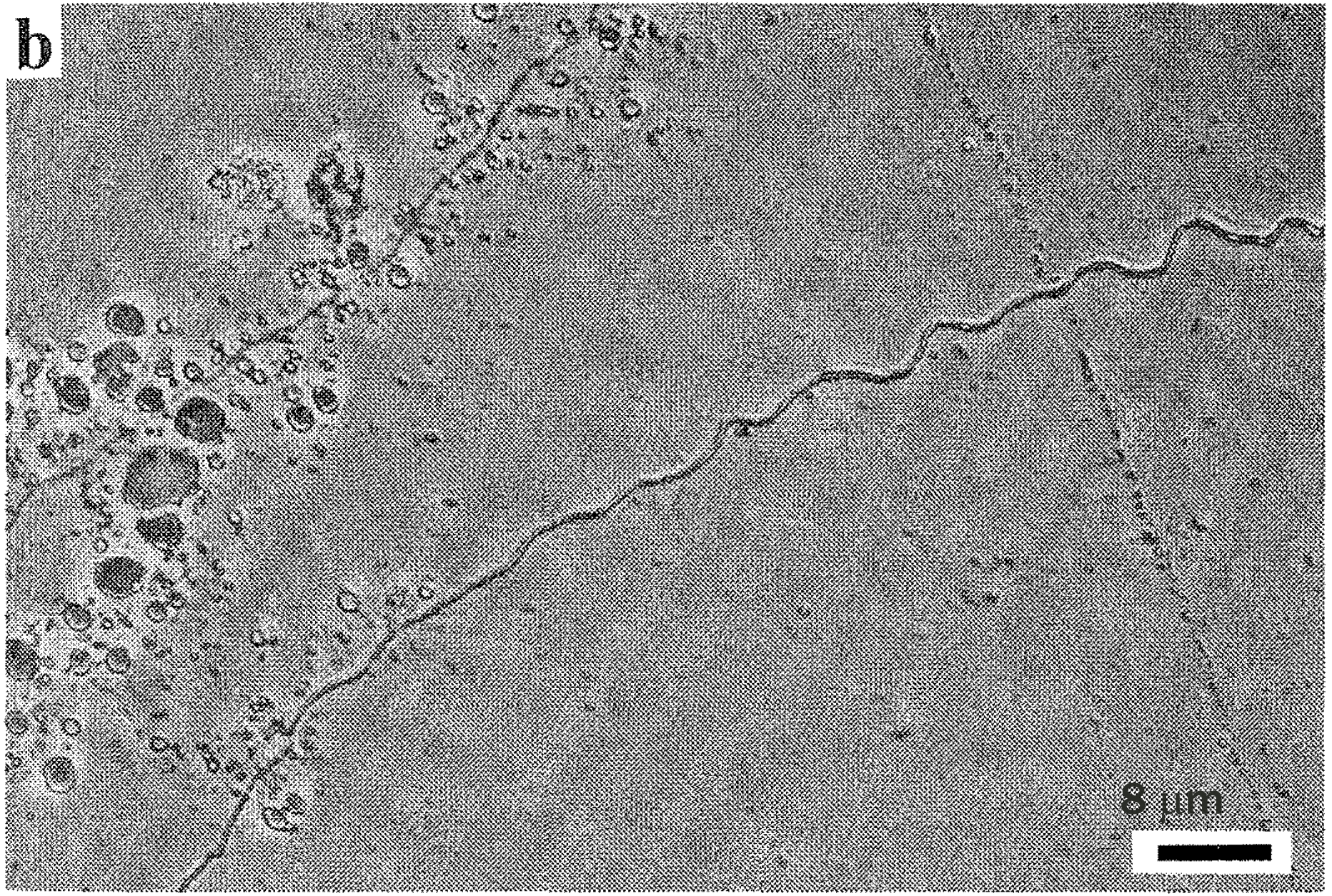


Figure 8. Phase contrast micrograph of Ch4Cf11; the concentrations are 1.1 mmol kg^{-1} (a) and 3.4 mmol kg^{-1} (b, c).

Furuya et al., 1996



Giulieri et al., 1994

6% dispersion of PFAS at room temperature leads to spontaneous formation of stable cylindrical aggregates

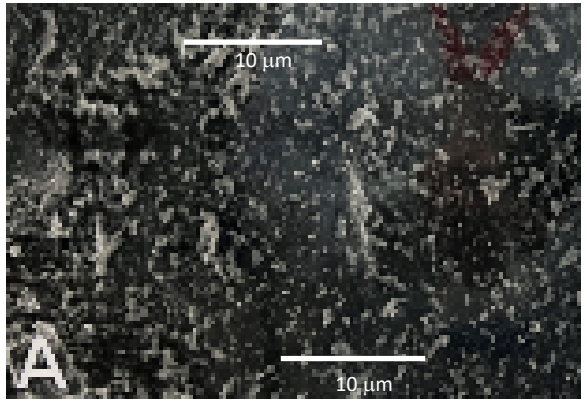
- flexible long fibers
- rigid hollow tubules

50 µm long (0.1 to 0.5 µm wide) within 2 weeks

Supramolecular Assemblies - PFAS retained on surfaces

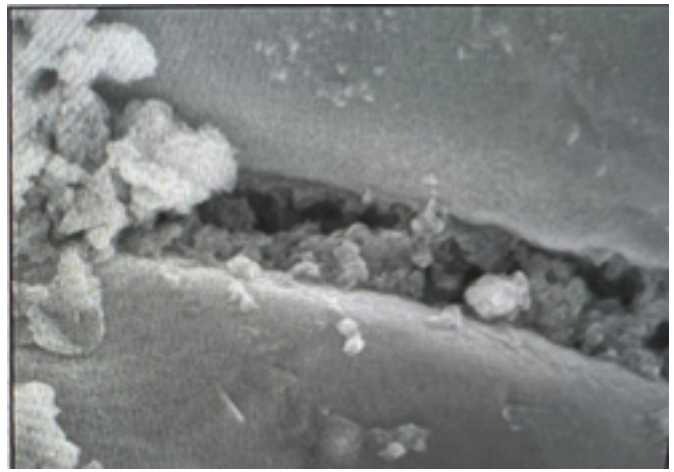
- Storage of AFFF within fire suppression systems causes a significant mass of PFAS to be retained on the inner surfaces of fire suppression system.
- Sorption of amphiphilic PFAS (fluorosurfactants) on surfaces often does not conform to conventional sorption theories.
- Formation of supramolecular assemblies is predicted and has been observe and provides a credible mechanism for PFAS retention within fire suppression systems.

PFAS supramolecular assemblies detected on interior walls of fire suppression systems



Pipe Interior

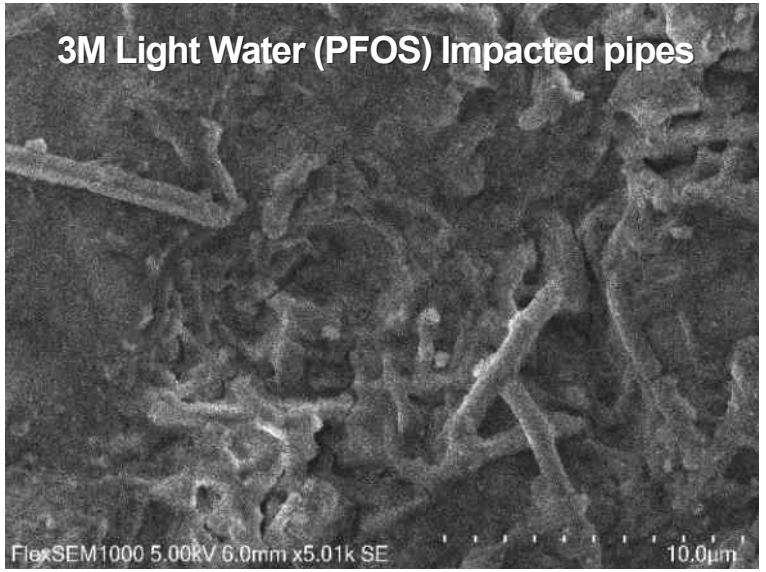
Pipe Exterior

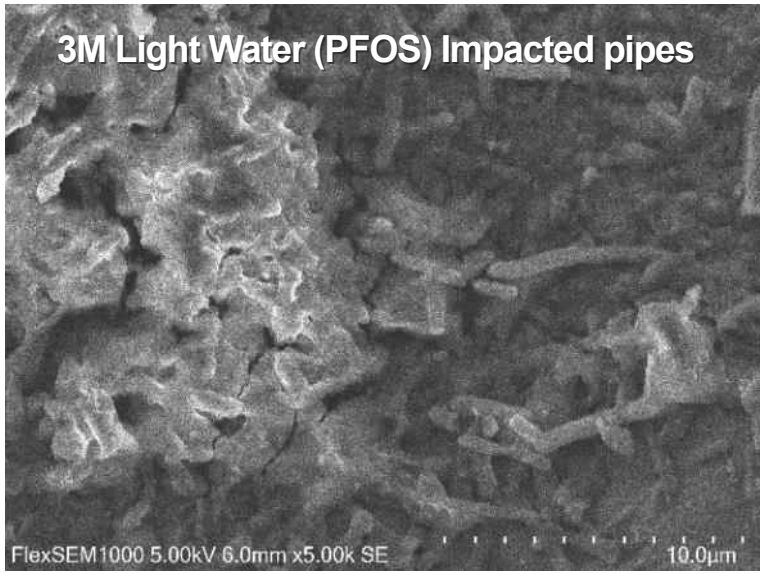


PFAS aggregates on the interior of fire suppression system pipework (Lang et al., Chemosphere, 308, (2), 2022)

PFAS Retained on Surfaces

Images Courtesy of Dave Megson, Manchester Metropolitan University





Images Courtesy of Bjorn Bonnet, Swedish University of Agricultural Sciences (SLU)

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Foaming behaviour of fluorocarbon surfactants used in firefighting –viscosity impacted by self-assembled structures

- Zwitterionic fluorocarbon surfactant (FC1157) foaming behaviour related to solution viscosity and turbidity
- Turbidity comes from the formation of large aggregates in bulk
- FC1157 molecules tend to self-assemble in solution into vesicles, with formation of single lamellar vesicles, multi-layered vesicles and fusion vesicles

Yu et al., 2020

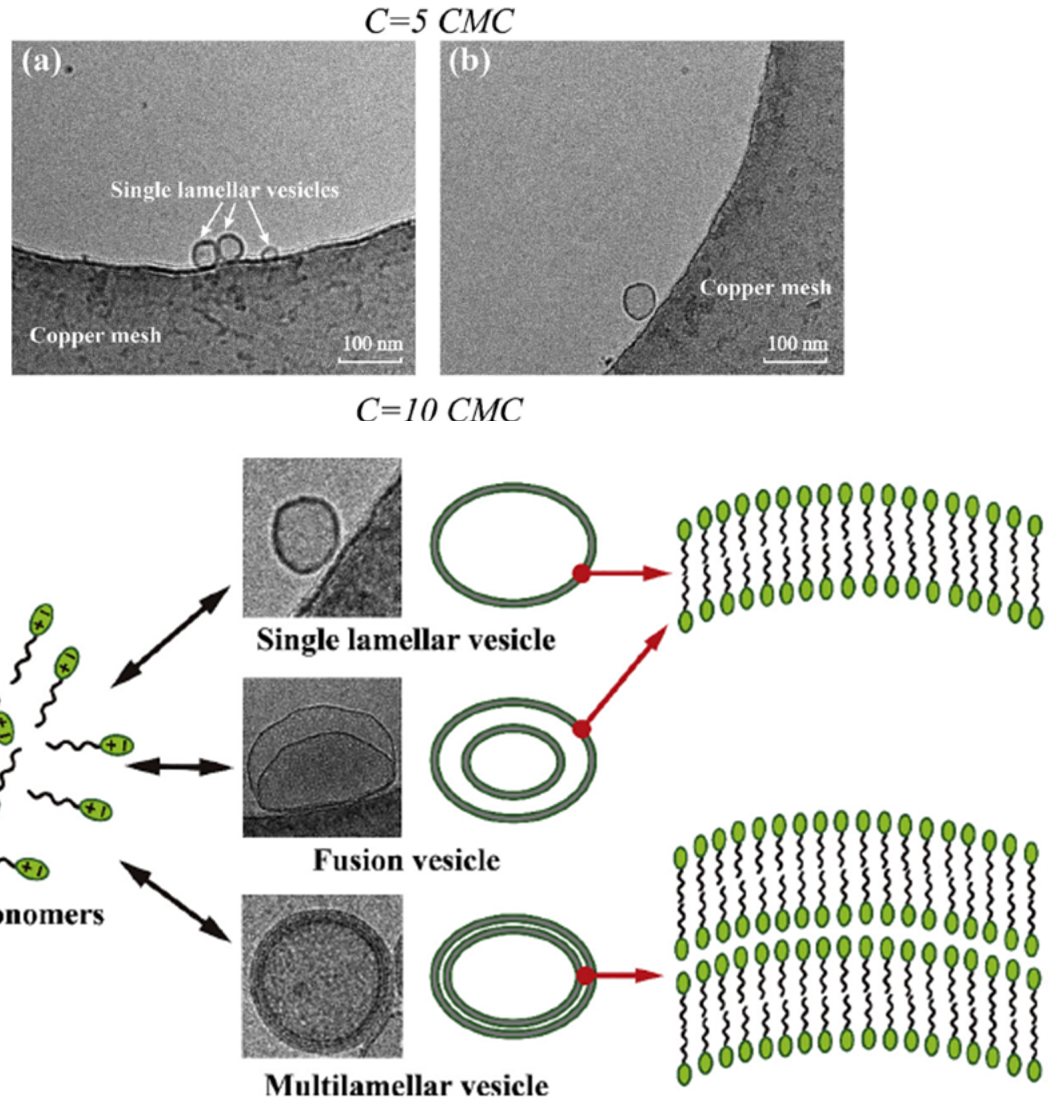
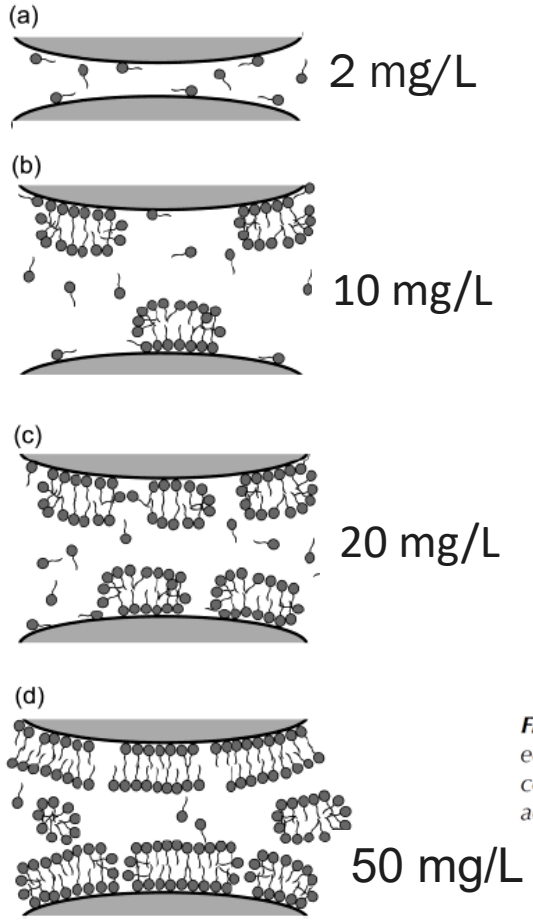


Fig. 14. A schematic illustration on the possible self-assembly structures of FC1157.

Surfactants increase concentrations at interfaces



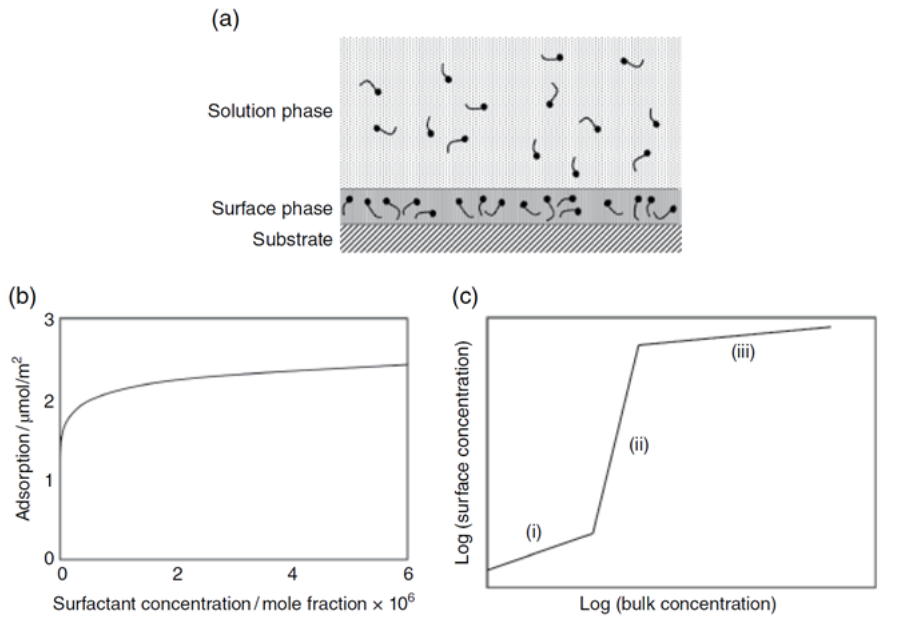


Figure 8.1 *(a) In describing adsorption the surface is regarded as a separate phase in equilibrium with the solution. (b) The surfactant concentration in the surface phase versus the concentration in the solution phase is termed the adsorption isotherm. (c) Plotting the adsorption isotherm on a log-log scale reveals features at low surfactant concentrations*

- Kronberg et al. 2014 - Surface adsorption driven by two factors:
  1. Energy gained on exchanging a surface-water contact to a surface-surfactant contact
  2. The hydrophobic effect –the escaping tendency of the fluorosurfactants perfluoroalkyl moiety from the aqueous environment
- Hemi-micelles can form at liquid-solid surfaces at concentrations in the range of 0.001 to 0.01 of the CMC (Schwarzenbach 2003)
- Perfluorooctylsulphonamide forms bilayers structure at 10-50 mg/L (Rojas et al., 2002)

Potential ingredients in a foam concentrate

Glycols / Alcohols

Propylene glycol
Propylene glycol t-Butyl ether
Polyethylene glycol
Tetraethylene glycol dimethyl ether
Diethylene glycol monobutyl ether
Tetraethylene glycol dimethyl ether
Propylene glycol t-Butyl ether
1,4-Dioxane
2-Butoxyethanol
N-Propanol
Hexylene glycol
1,2-Propanediol
Ethylene glycol

Surfactants (<15%)

Fluorosurfactants (2-15 %)
Hydrocarbon surfactants
Protein-based surfactants
Synthetic detergent mixtures
and others

Polymers (for select types)

Polysaccharide gums
Xanthan gums
Fluorinated polymers

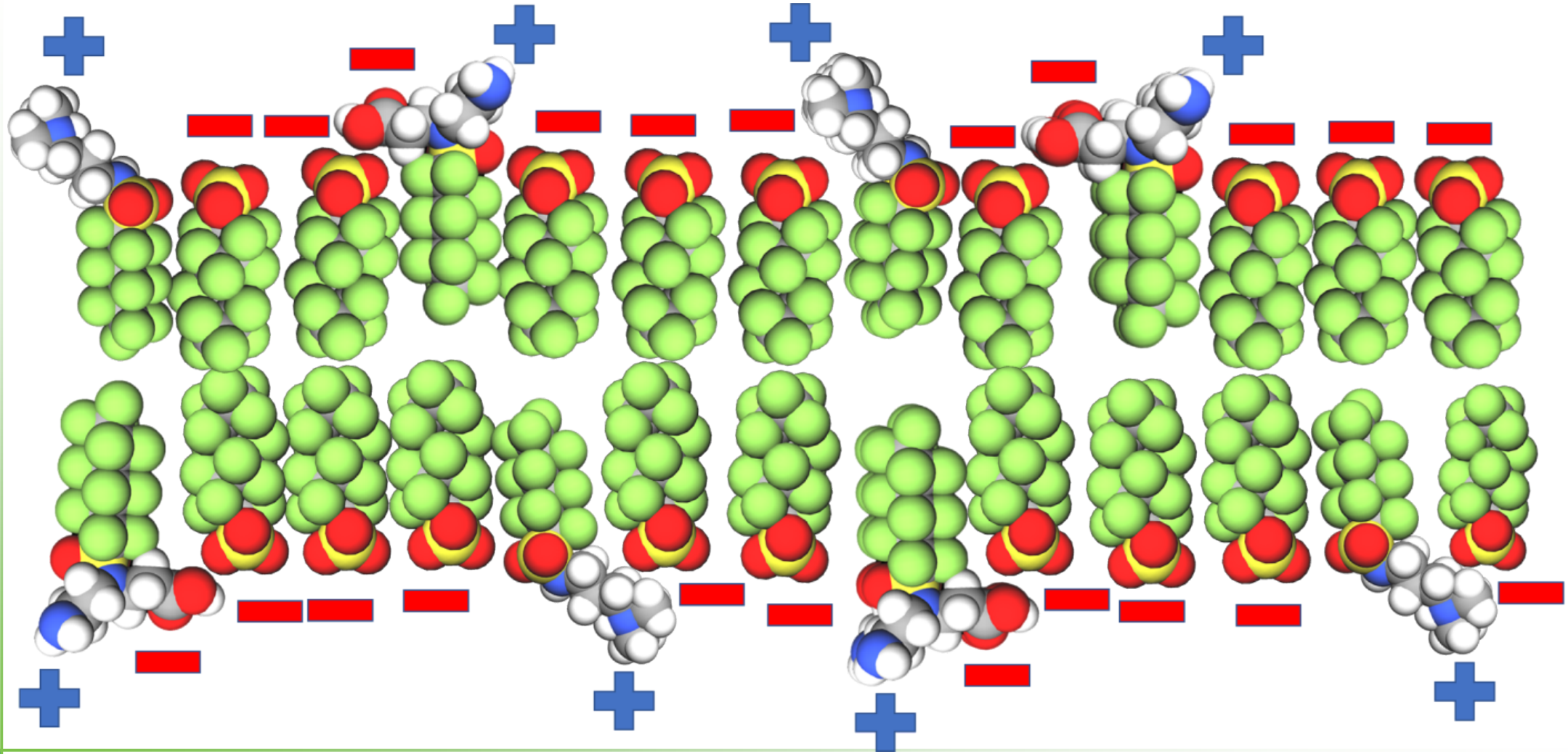
Additives/modifiers

Acetic acid
Sodium chloride
1H-Benzotriazole
Triethanolamine
Sucrose
Dichlorephene
EDTA
Zinc oxide
Ferrous sulfate
Sucrose
Dichlorephene
EDTA
Zinc oxide
Ferrous sulfate
Magnesium sulfate
2-Biphenylol
Nonylphenol ethoxylate

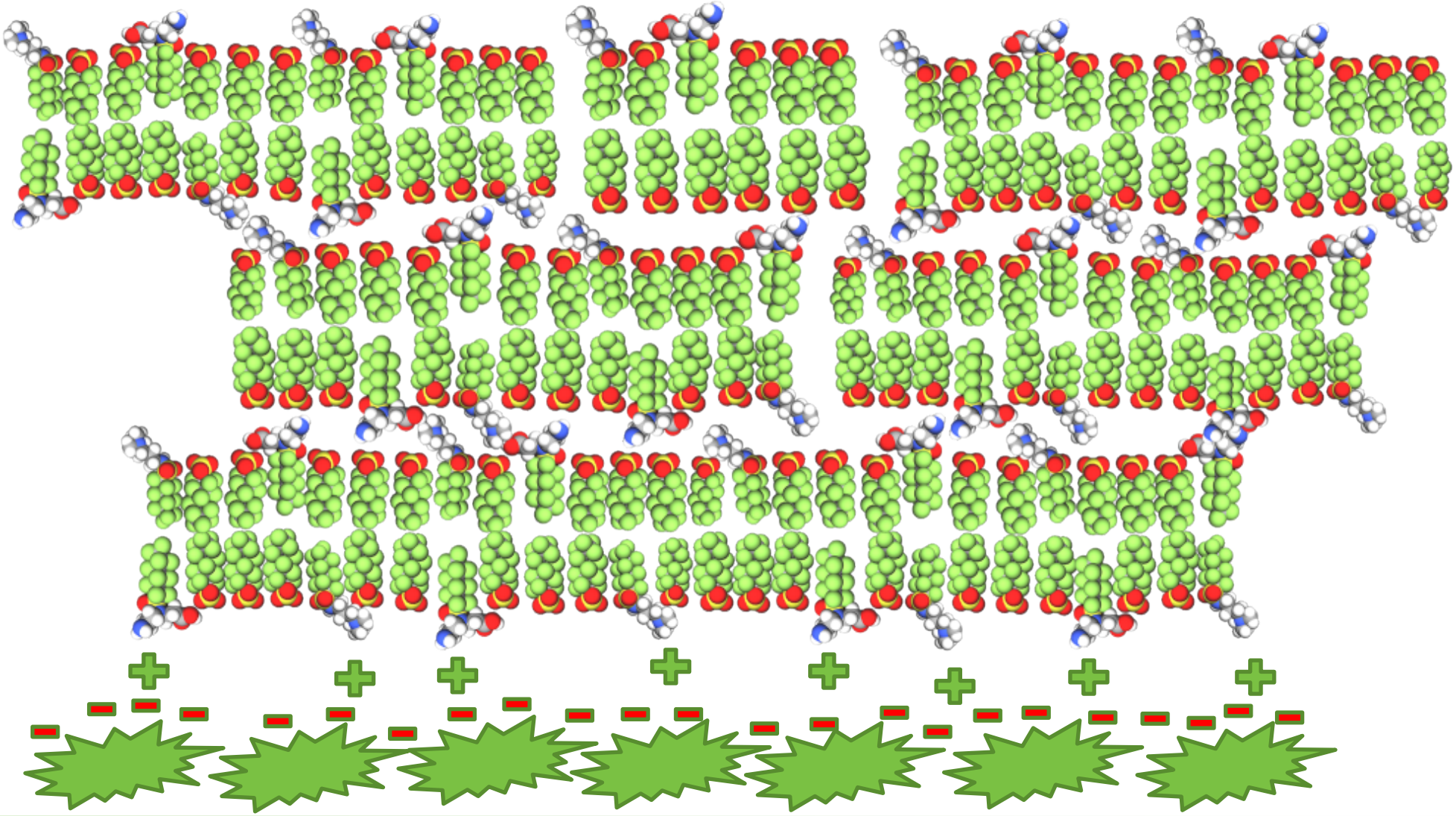
Water as Diluent (>60%)

Adapted from Korzeniowski et al, 2019

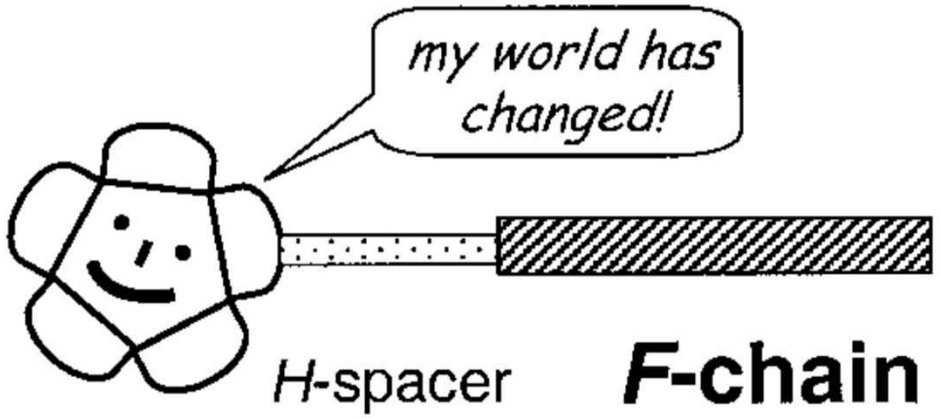
Mixtures of anions, cations and zwitterions can facilitate the formation structures and strengthen them



Cations and zwitterions anchor multi-bilayered structures to surfaces?



FnHm Diblocks



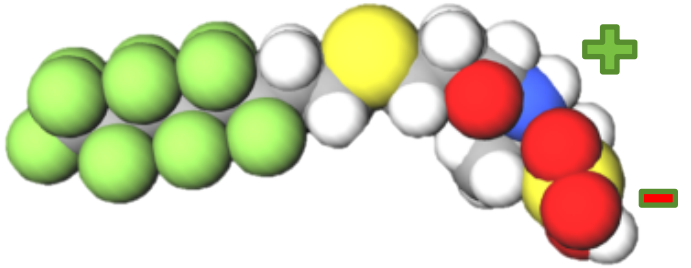
The Molecule

Gladysz et al., 2004

hydrophillic oleophillic fluorophillic

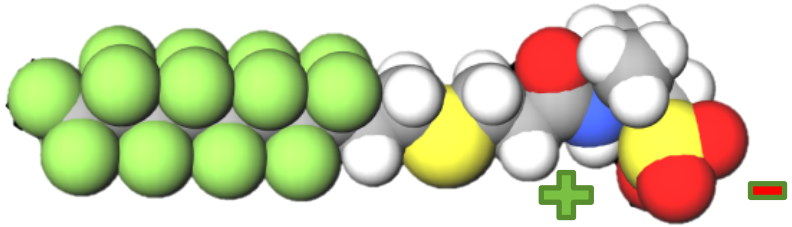
Significant Antipathy

- a deep-seated feeling of dislike; aversion.



6:2FTSAS

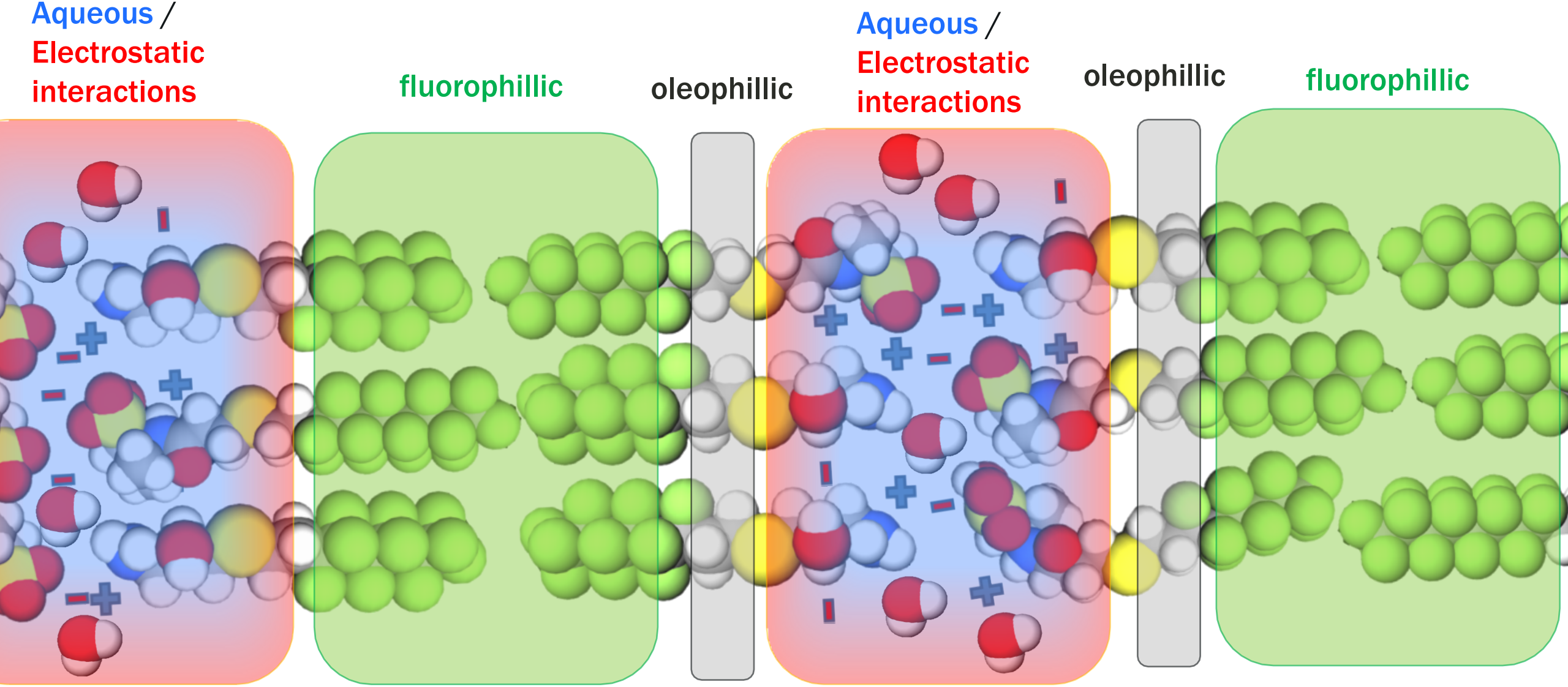
6:2FTTHN



8:2FTAoC

6:2FTAB

Fluorotelomer Phases Within Supramolecular Assemblies



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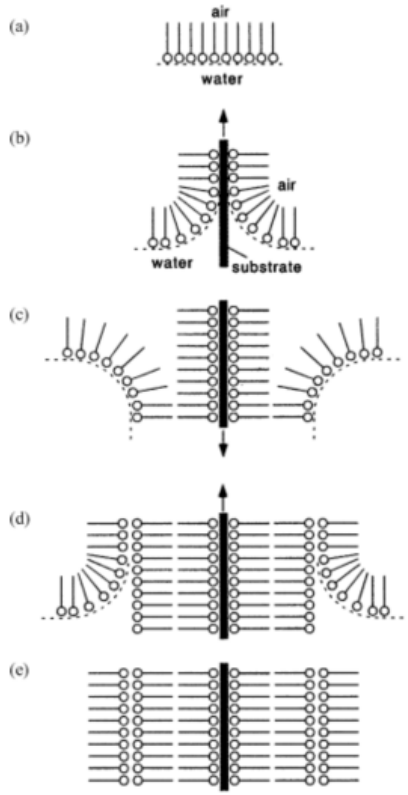
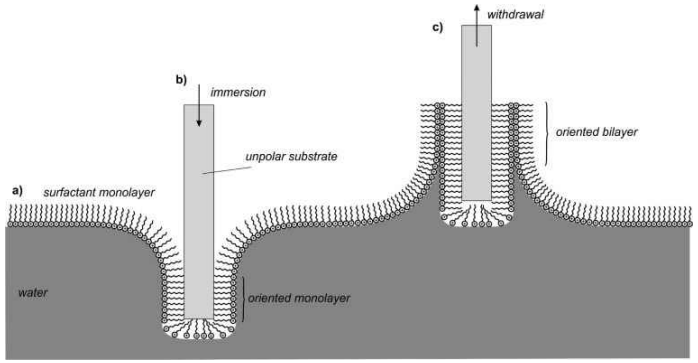
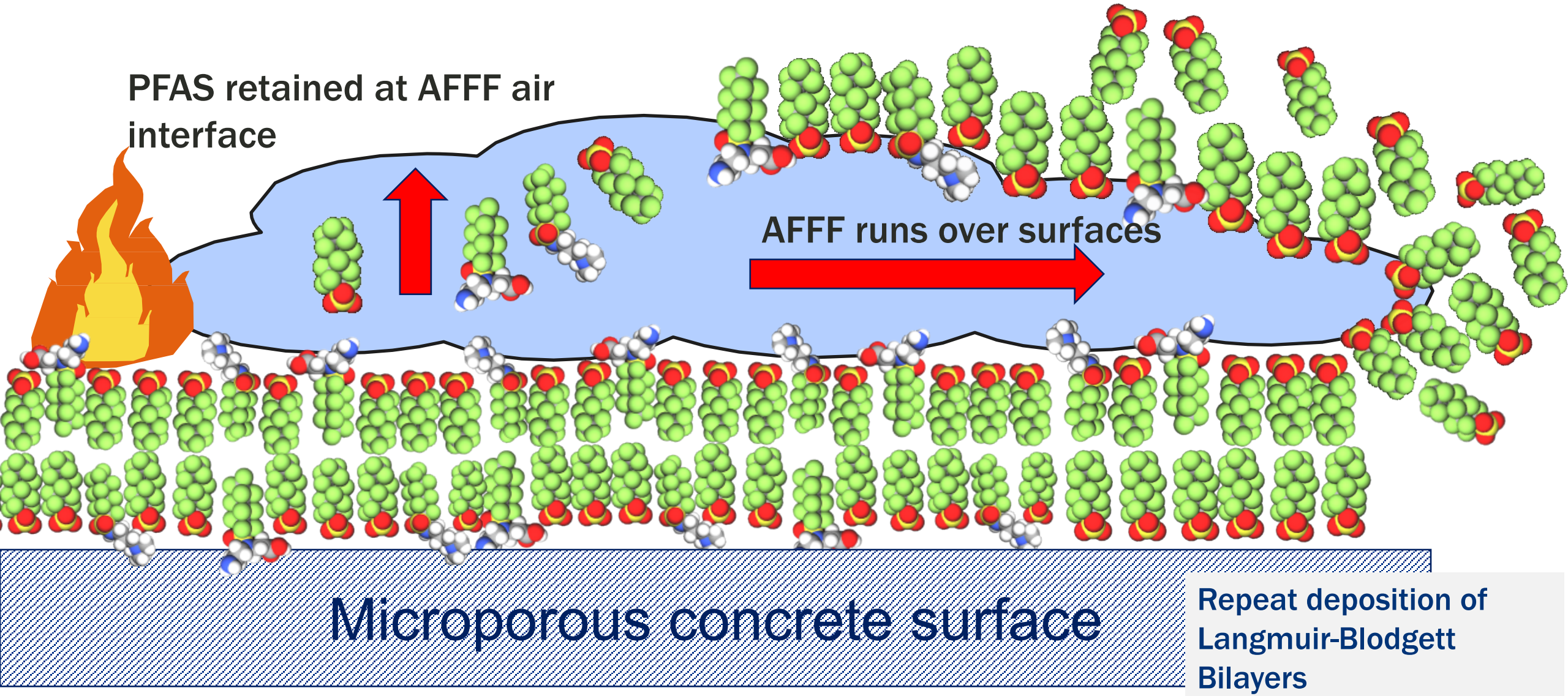
Langmuir-Blodgett Film Multilayers – Deposition on Surfaces

- Langmuir monolayers can be transferred onto solid supports for the formation of multilayer Langmuir-Blodgett (LB) films
- Langmuir monolayers of fluorinated molecules show higher crystallinity than those formed by hydrocarbon surfactants
- Fluorocarbon multibilayers have been reported on surfaces
- Many bilayers of LB films could be formed on top of one another via repeat fire training
- Cationic and zwitterionic PFAS will facilitate layer formation and stabilise layers





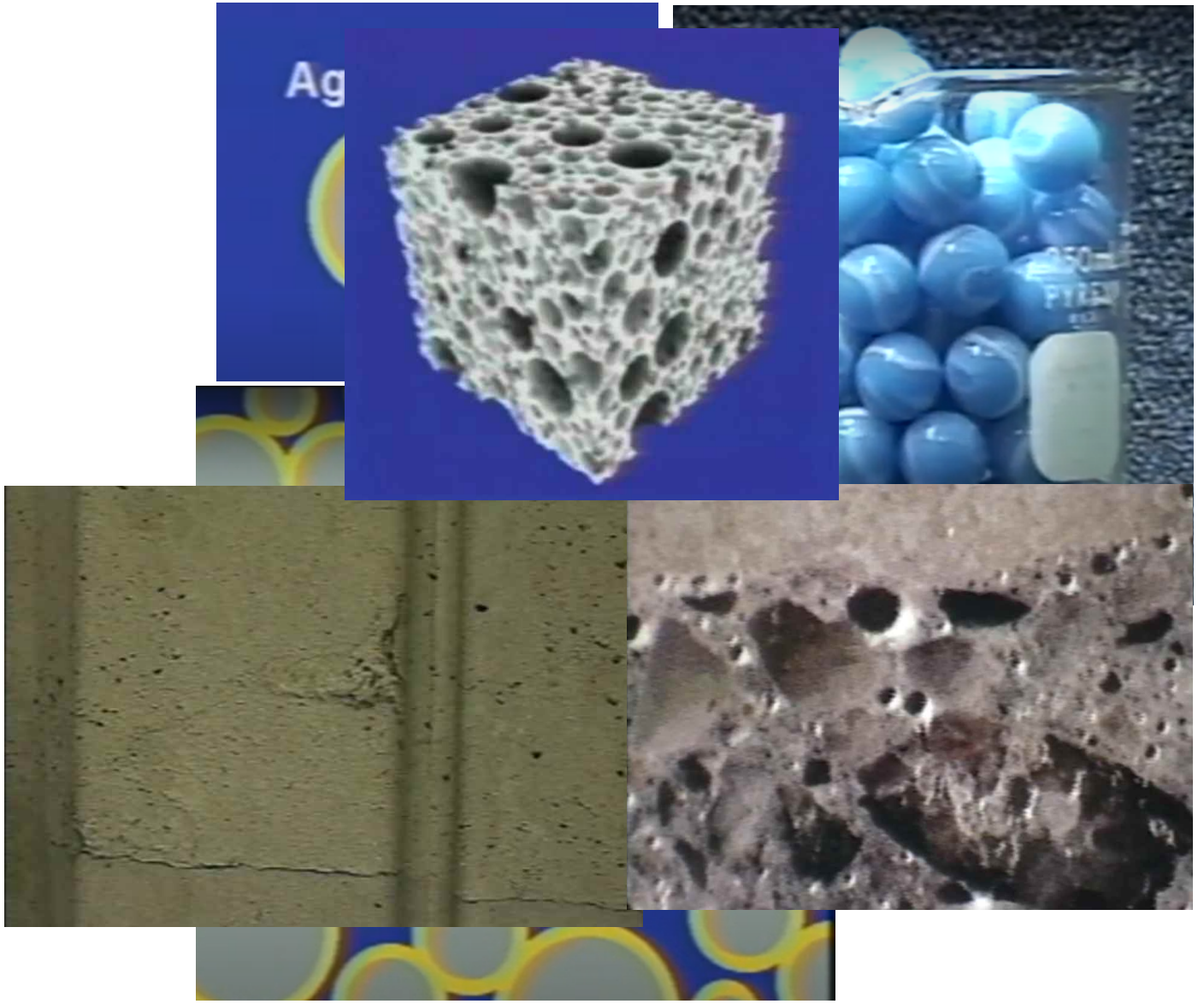
PFAS Deposition on surfaces as AFFF is dispensed



Repeat deposition of Langmuir-Blodgett Bilayers

Concrete - PFAS Storage

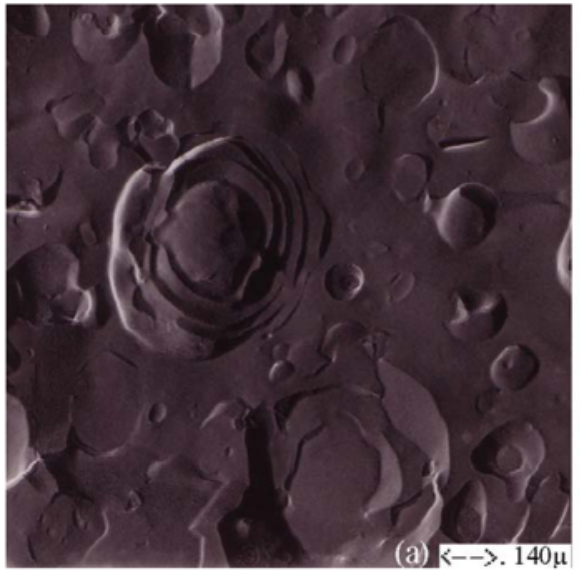
- Interfacial transition zones –greater porosity at surface of aggregates (sand and gravel)
- Disconnected capillaries in porosity
- Microcracking common at surface
- Air entrainment for frost protection creates 10- 500 μm voids (surfactant added to create bubbles)
- Disconnected Capillaries and void spaces become grouted with PFAS LB-films? Water entry prevented?



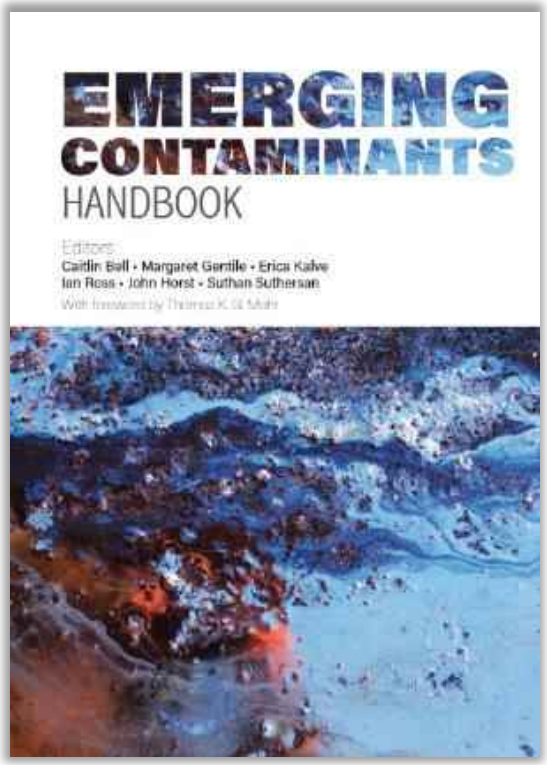
Implications

Prof. Jinxia Liu – McGill University

- Fate and transport
  - Storage of SA-PFAS in porous matrices exposed to dispensed AFFF e.g. concrete
  - SA-PFAS forming at NAPL:water, air:water interfaces?
- Water treatment
  - Sorbent media –IX Resins, GAC, membrane filtration
- Decontamination of fire suppression systems
  - Removal of SA-PFAS that contain anionic, cationic and zwitterionic PFAS
- PFAA destruction vs self-assembly
  - evidence of self assembly, as opposed to fluorinated amphiphile destruction, thinking that branched are a more recalcitrant target



Song et al., 2005



2 Fluorine Free Foams
Transitioning Guide

Ian Ross
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Peter Storch
Arcadis, Australia

Ted Schaefer
Energy and Resources Institute, Charles Darwin University, Australia

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ENRg Consultants, Monks Risborough, United Kingdom

CONTENTS

How clean is clean?

by Ian Ross

The ongoing detection of multiple types of per- and polyfluoroalkyl substances (PFAS) in drinking water is leading to increased public awareness of the potential impact of this class of extremely persistent anthropogenic chemicals on public health.

In December 2023, Sweden's Supreme Court announced the final judgment in a case that has been litigated for the last 10 years. The Supreme Court ruled that more than 150 residents in the village of Ronneby, who were exposed to elevated levels of PFAS in drinking water, suffered personal injury, as a result of the use of firefighting foams and reported elevated levels of PFAS in their blood[1]. Prior court rulings in 2021 determined that an elevated level of PFAS in blood equated to personal injury, which was overturned in 2022 with the court of appeal maintaining that personal injury had to be proven. The Supreme Court's decision sets a precedent in Sweden and may impact litigation progressing in other countries. Human biomonitoring (HBM) values for perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) for which (1) no adverse health effects are expected to occur in humans and (2) may lead to human health impairment were published in 2021[2]

PFAS comprise a broad group of over 7 million extremely persistent synthetic chemicals[3]. Many of these compounds transform in the environment over time, from one form, termed polyfluoroalkyl substances (partially fluorinated) to another, termed perfluoroalkyl substances (fully fluorinated) as the non-fluorinated parts of the polyfluoroalkyl substances are subject to microbial or abiotic attack.

The extreme environmental persistence of fluorocarbon compounds has been well known since at least 1950[4]. Therefore, it is not surprising that PFAS are being discovered in drinking water above safe levels in many countries, and it is clear that PFAS (C6 and C8) in firefighting foams will soon be curtailed by advancing regulations.

Regulations in Europe and Australia address both bulk polyfluoroalkyl PFAS (e.g. C8) and target perfluoroalkyl PFAS (e.g. PFOA). Methods to detect both types of PFAS have been commercially available for almost a decade, but decontamination approaches for fire suppression systems often fail to attempt to measure the regulated PFAS, meaning the data provided to support successful decontamination is not trustworthy. This article aims to explain the essential scientifically validated lines of evidence required to demonstrate fire suppression system decontamination, to assist with assessing the credibility of decontamination approaches.

Pragmatism During Foam Transition

The maximum contaminant levels (MCLs) of 4 parts per trillion (ppt) or nanograms per litre (ng/L) for PFOS and PFOA and hazard indices for four additional PFAS, proposed in drinking water by USEPA could lead to several thousand US drinking water systems being impacted[5]. These proposed, very low, target concentrations of PFOS and PFOA may lead to the need to treat significant volume of drinking water, with the American Water Works Association (AWWA) pointing out that roughly 98 percent of drinking water utilities in the country, have maximum PFOA and PFOS levels below 10 ppt[6]. With US rainfall containing up to 50 ppt of PFOS and 30 ppt of PFOA[6], the potential for widespread detections of PFAS below 10 ppt in surface water and groundwater appears possible[7]. When examining a broader array of PFAS in US rainfall, some 16,400 ppt of PFAS has been reported[8] with many sources of PFAS having to potential to impact surface waters[9].

Taking the existing low-level background (ambient) PFAS concentrations in the environment into account can be critical when considering the concentrations deemed as targets by regulators. This is also the case when managing potential high-concentration sources of PFAS such as from use of fluorinated firefighting foams. With increasing number of individual PFAS facing regulations in drinking water and groups of PFAS already regulated in firefighting foam and other products, a detailed understanding of how to measure PFAS to comply with regulations and prove effective treatment is essential. The likely pace of regulatory focus on additional PFAS, beyond those regulated in drinking water, needs to be considered, with some pragmatism required when balancing costs to manage PFAS, attempts to future proof treatment approaches and existing ambient 'background' PFAS concentrations.

'Dark Matter' Fluorosurfactants as PFAA-Precursors

The perfluoroalkyl substances are collectively termed perfluoroalkyl acids (PFAAs) and these include the 'C8' molecules, such as PFOS and PFOA and 'C6' replacements such as perfluorohexanoic acid (PFHxA). Modern firefighting foams are dominated by polyfluoroalkyl substances, termed PFAA-precursors and regulations addressing their concentrations in firefighting foams came into force in the UK and Europe Union in July 2020[10-12]. The fluorosurfactants added to modern fluorinated firefighting foams are termed polyfluoroalkyl substances or PFAA-precursors as they transform in the environment, over time, to generate "dead end" perfluorinated daughter products (PFAAs) as ultra-persistent terminal products[13].

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