VI CONGRESSO INTERNACIONAL DE
MEIO AMBIENTE SUBTERRÂNEO

18 e 19 de novembro de 2019
Belo Horizonte • MG

TÍTULO DO TRABALHO APROVADO PARA APRESENTAÇÃO NO VI CONGRESSO INTERNACIONAL DE MEIO AMBIENTE SUBTERRÂNEO

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Belo Horizonte, XX de Novembro de 2019

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Groundwater Remediation Options for Emerging Contaminants

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Presentation Objectives

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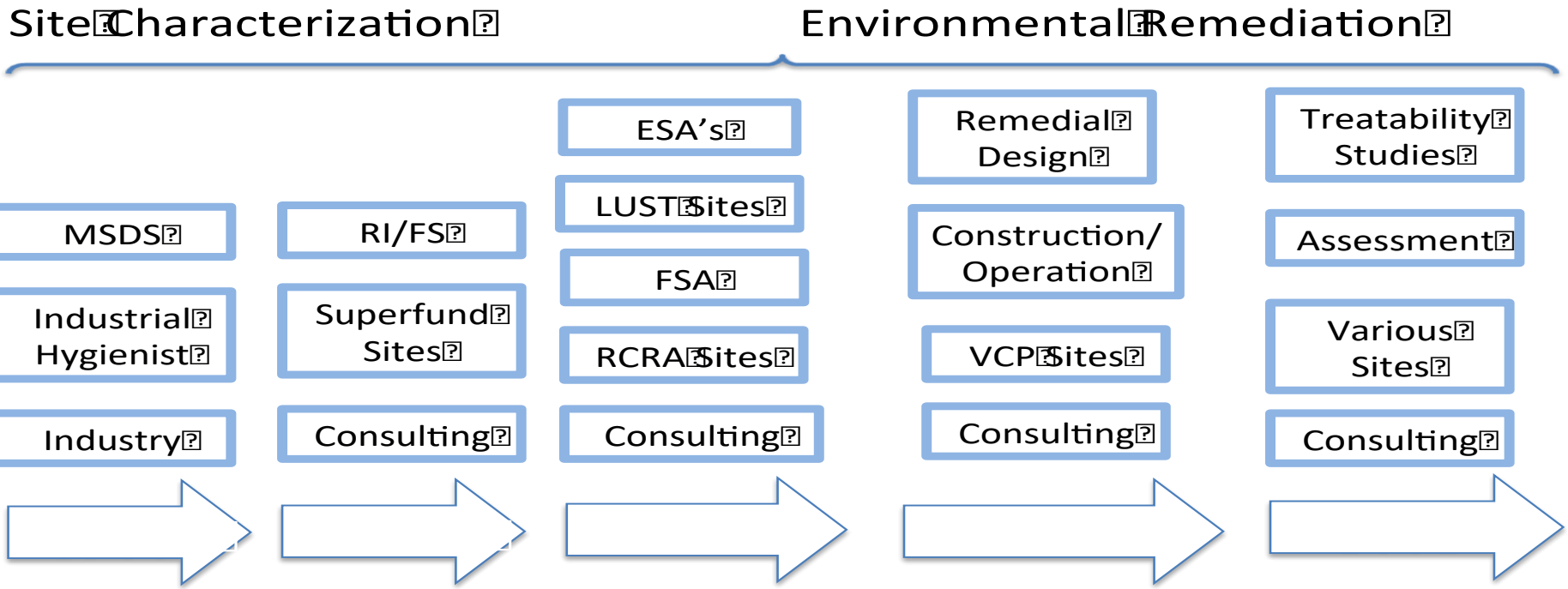
Presentation Outline

- The Last 30 Years
- Contaminants of Concern/Emerging
- Conceptual Site Model
- Remediation Technologies
- In-Situ Chemical Oxidation (ISCO)
- Delivery Methods
- PFAS Compounds/Sulfluramid
- Concluding Remarks

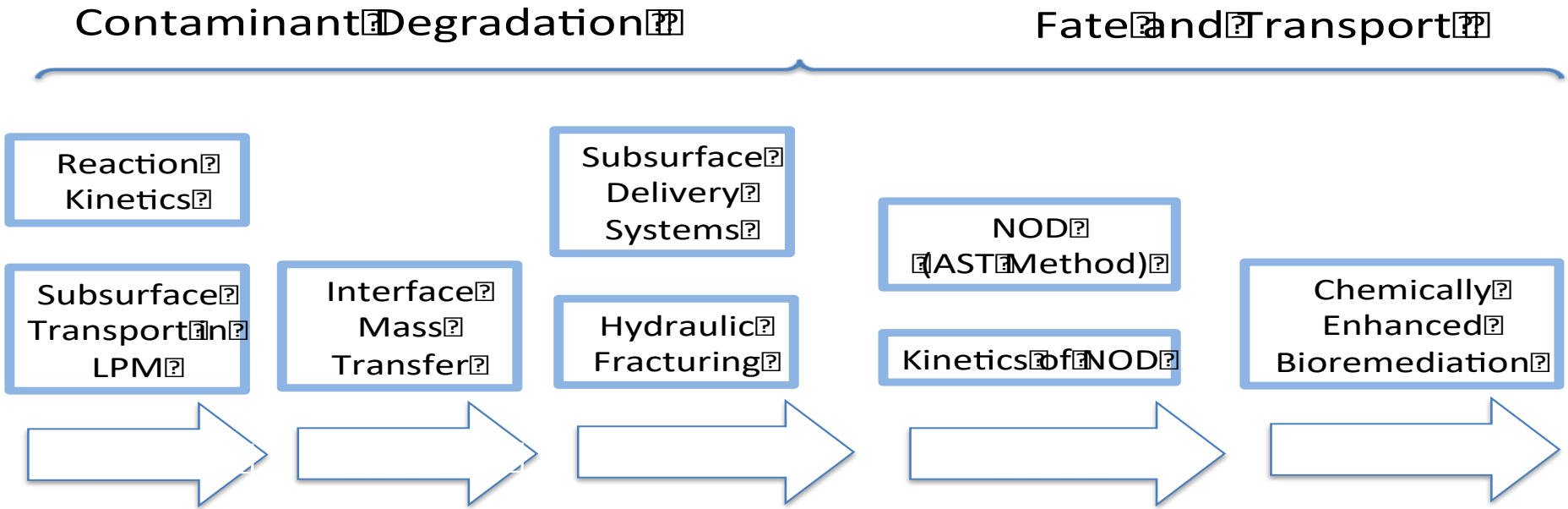
The Last 30 Years

(Consulting)



The Last 30 Years

(Research and Development)



Contaminants of Concern

Contaminant of concern	Priority as a COC at U.S. hazardous waste sites (ATSDR ranking)[a]	Prevalence at U.S. NPL sites[b]		U.S. drinking water standards (µg/L)[c]
		Number of NPL sites with COC present	Sites with COC present as a % of total NPL sites	
Arsenic	1	1,149	68%	10
Lead	2	1,272	76%	15
Mercury	3	714	49%	2
Vinyl chloride	4	616	37%	2
Polychlorinated biphenyls	5	500	31%	0.5
Benzene	6	1,000	59%	5
Cadmium	7	1,014	61%	5
Polycyclic aromatic hydrocarbons	8	600	42%	–
Benzo(a)pyrene	9	–	–	0.2

Contaminants of Concern

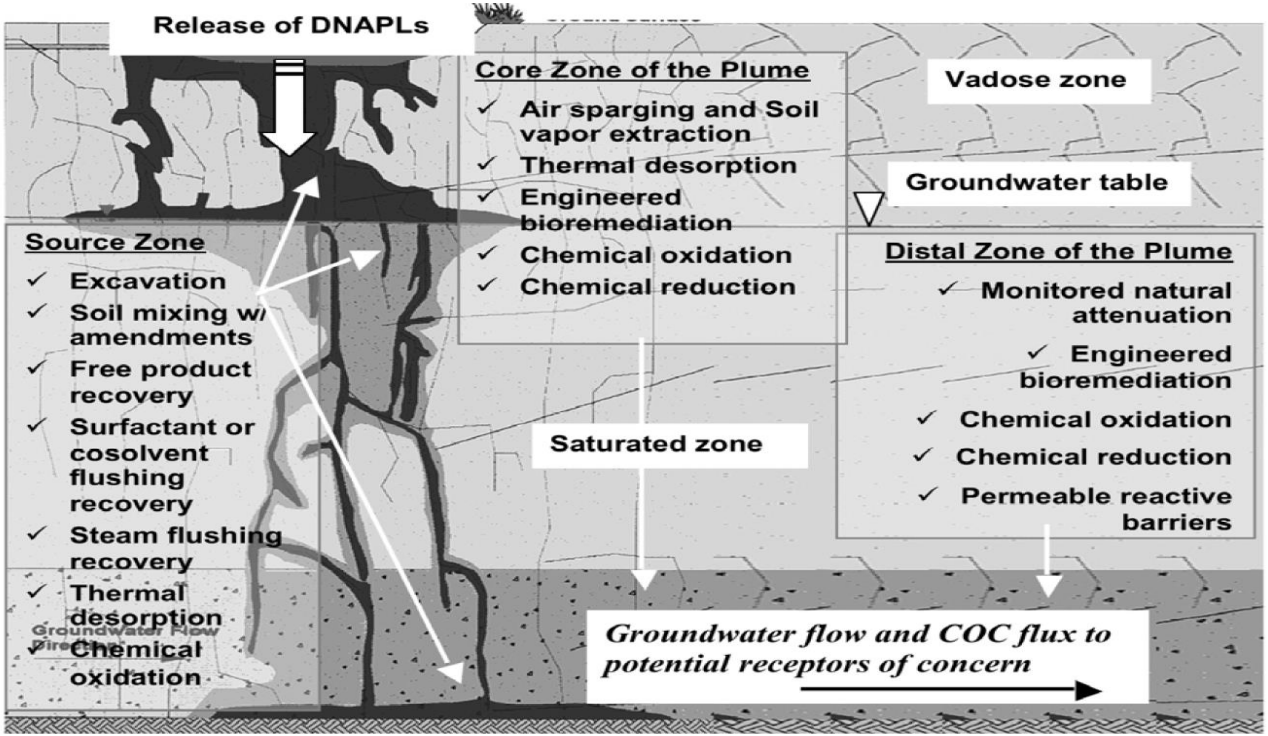
- MTBE
- Perchlorate
- 1,4-Dioxane
- Munitions Compounds
- 1,2,3-Trichloropropane

Emerging Contaminants???

- Pharmaceuticals
- Personal Care Products
- Lifestyle Products
- Microplastics
- Nanomaterials
- Disinfectants and Household Cleaners
- Disinfection By-Products
- Plasticizers
- Pesticides (Sulfluramid)
- Flame Retardants (PFAS Compounds)

Site Conceptual Model

Remediation Technologies



Remediation Technologies

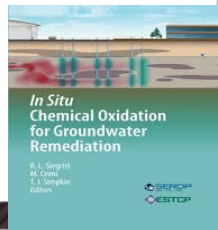
- Thermal Remediation Technologies
- Biological Remedies
- Monitored Natural Attenuation
- In Situ Chemical Oxidation (ISCO)
- In Situ Chemical Reduction (ISCR)
- Zero Valent Iron (ZVI)
- Electroenhanced Technologies
- Heat Enhanced Remediation
- Injectable Activated Carbon Amendments
- Surfactant Enhanced Remediation
- Phytoremediation

In Situ Chemical Oxidation

In Situ Chemical Oxidation is a recent application of a relatively old technology.

Water and Wastewater Treatment:

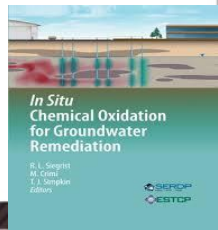
- Removal of soluble iron and manganese
- Color removal
- Taste and odor removal
- Disinfection



In Situ Chemical Oxidation

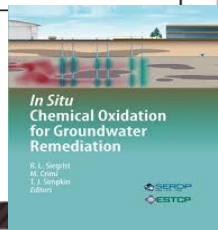
- In Situ Chemical Oxidation is a soil and/or groundwater remediation technology that uses oxidants to react with contaminants, resulting in their conversion into less harmful products.

- Key considerations for designing ISCO remediation projects include contaminant type, geochemical conditions, and the chemical delivery method.



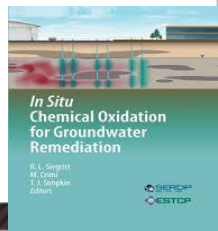
In Situ Chemical Oxidation

Oxidant	Oxidant	Commercial Form	Activator	Reactive Species
Permanganate	$KMnO_4$ or $NaMnO_4$	Powder, liquid	None	MnO_4^-
Hydrogen peroxide	H_2O_2	Liquid	None, Fe(II), Fe(III)	$OH\cdot$, $O_2^{\cdot-}$, $HO_2\cdot$, HO_2^-
Ozone	O_3 (in air)	Gas	None	O_3, $OH\cdot$
Persulfate	$Na_2S_2O_8$	Powder	None, Fe(II), Fe(III), heat, H2O2, high pH	SO_4^{2-}, $SO_4^{\cdot-}$
Peroxone	H_2O_2 plus O_3 (in air)	Liquid, gas	O_3	O_3, $OH\cdot$
Percarbonate	$Na_2CO_3 \cdot 1.5\ H_2O_2$	Powder	Fe(II)	$OH\cdot$
Calcium peroxide	CaO_2	Powder	None	H_2O_2, $HO_2\cdot$,



In Situ Chemical Oxidation

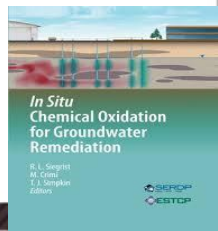
Reactive species	Formula	Standard reduction potential (V)
Hydroxyl radical	$OH\cdot$	+2.8
Sulfate radical	$SO_4^{\cdot-}$	+2.6
Ozone	O_3	+2.1
Persulfate anion	$S_2O_8^{2-}$	+2.1
Hydrogen peroxide	H_2O_2	+1.77
Permanganate anion	MnO_4^-	+1.7
Perhydroxyl radical	$HO_2\cdot$	+1.7
Oxygen	O_2	+1.23
Hydroperoxide anion	HO_2^-	-0.88
Superoxide radical	$O_2^{\cdot-}$	-2.4



In Situ Chemical Oxidation

Advantages include:

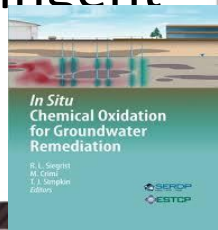
- Robust treatment method
- Can be implemented quickly
- Variety of oxidants and activation approaches
- Variety of delivery approaches
- Applicable to a range of subsurface conditions
- Relatively low mobilization costs
- Ability to couple with pre- and post-treatment methods
- Generally well-accepted by the regulatory community



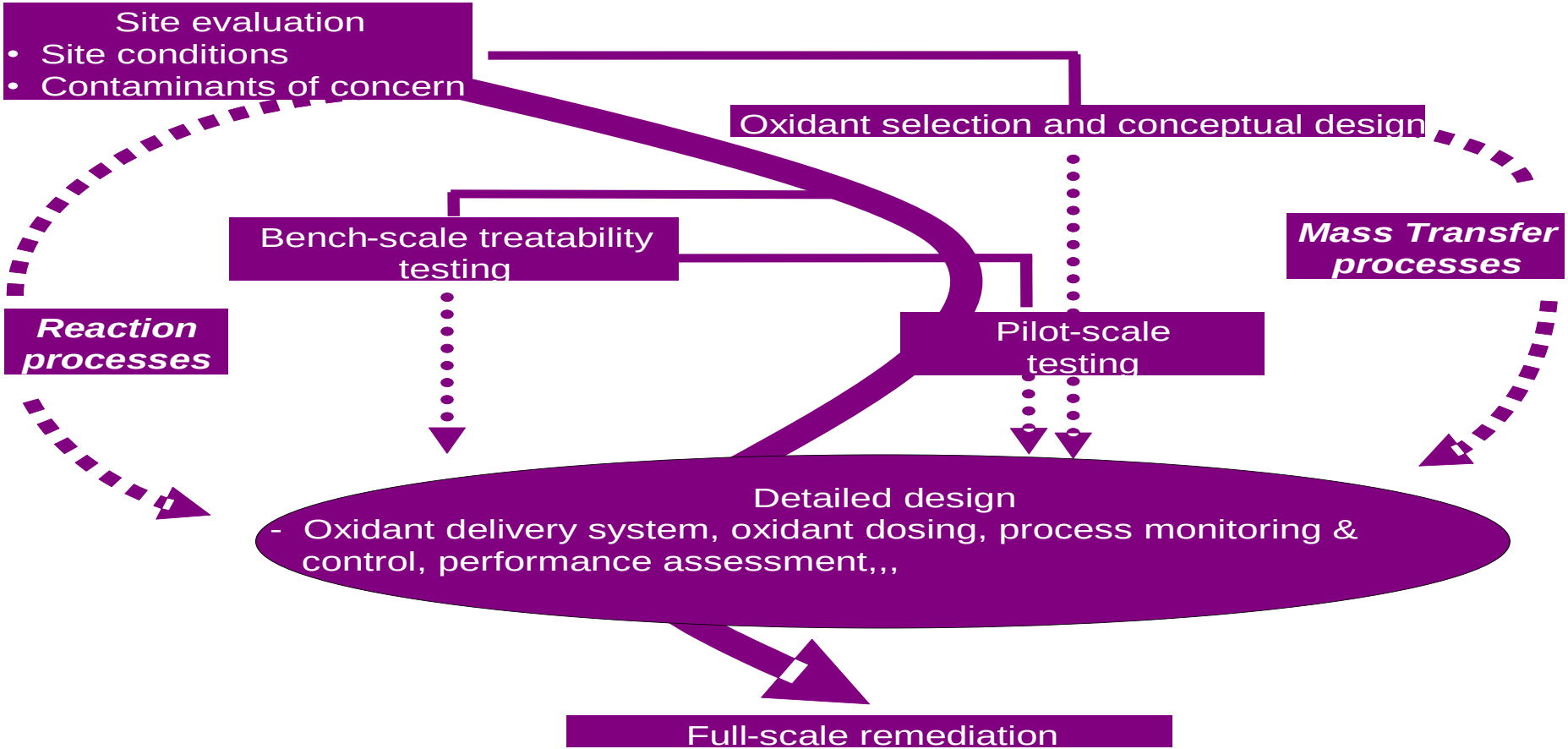
In Situ Chemical Oxidation

Potential disadvantages include:

- Potential need for large amounts of chemical
- Resistance of some contaminants to oxidation
- Limited ability to penetrate low permeability soil and groundwater zones
- Potential for ISCO-induced effects (e.g., gas evolution, permeability reduction, secondary water quality effects)
- Potential for rebound of target contaminants
- Inability to treat contaminant source zones to the most stringent goal levels (e.g., MCLs)



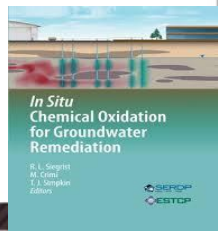
In Situ Chemical Oxidation



Delivery Methods

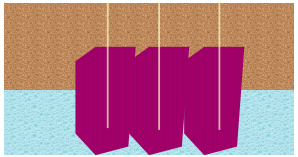
Delivery Methods must overcome transport limitations and natural oxidant demand (NOD).

- Heterogeneity
- Low Permeability Media (LPM)
- NOD >> contaminants
- Kinetics

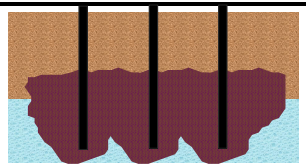


Delivery Methods

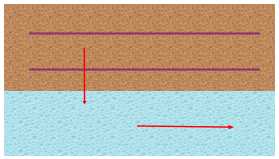
Liquid | **Gas** | **Solid**



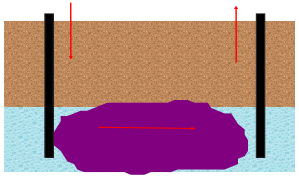
Permeation



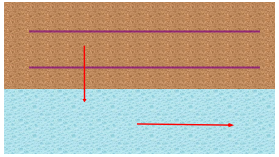
Sparging



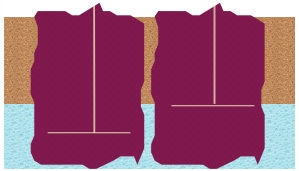
Hydraulic Fractures



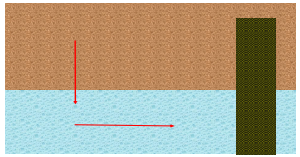
Flushing



Pneumatic Fracture

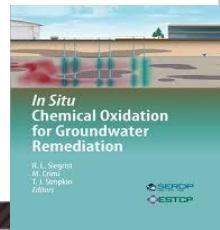


Mixing

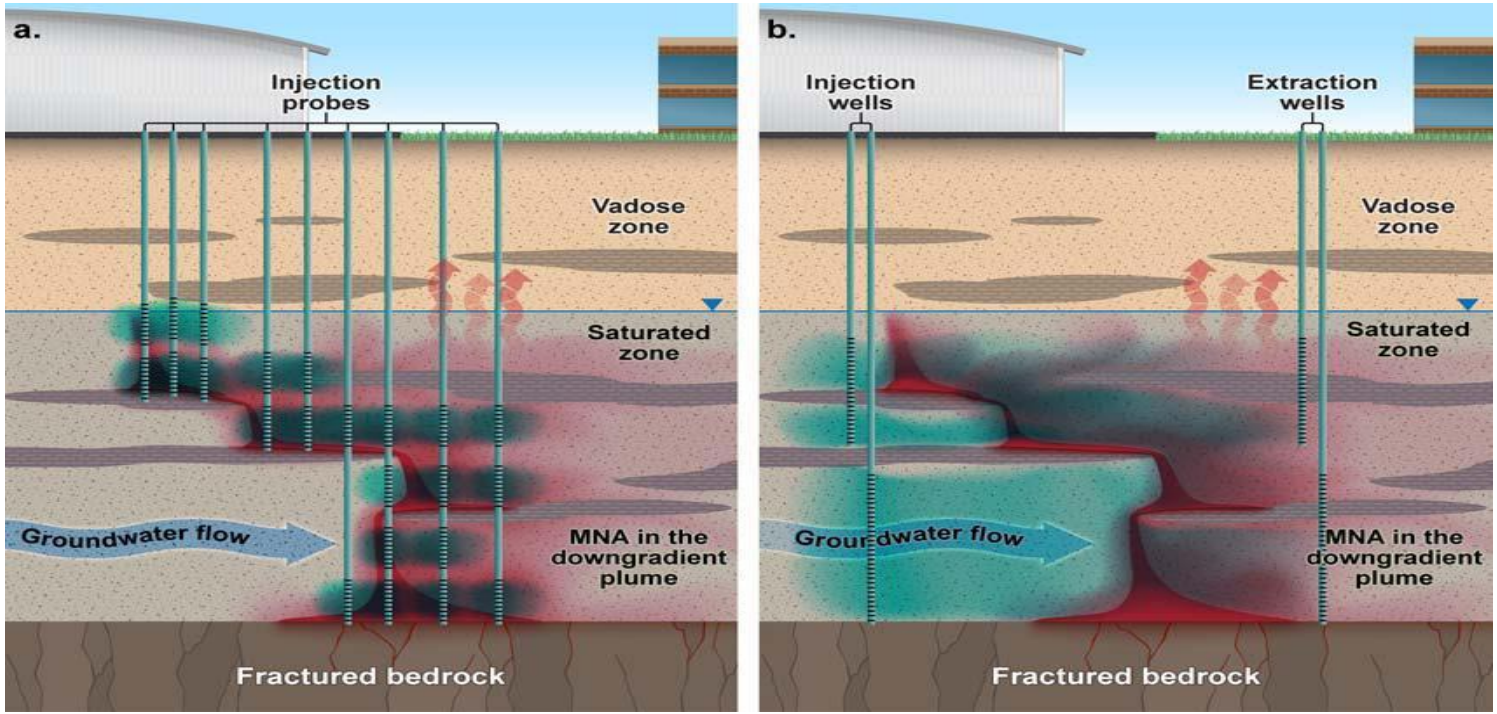


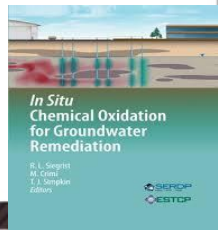
Treatment walls

Delivery Method (n = 181)	%
Injection wells	40
Direct push	23
Sparge points (ozone)	14
Infiltration	10
Injectors	7
Recirculation	7
Fracturing	6
Mechanical mixing	2
Horizontal wells	1



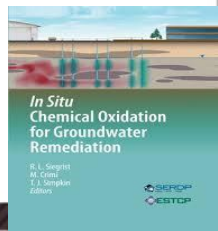
Delivery Methods





Delivery Methods

Parameters Monitored for Injection
• Groundwater Level or Piezometric Head • Injection Pressure and Flow Rate • Injectate Concentration • Volume of Oxidant Injected



Delivery Methods

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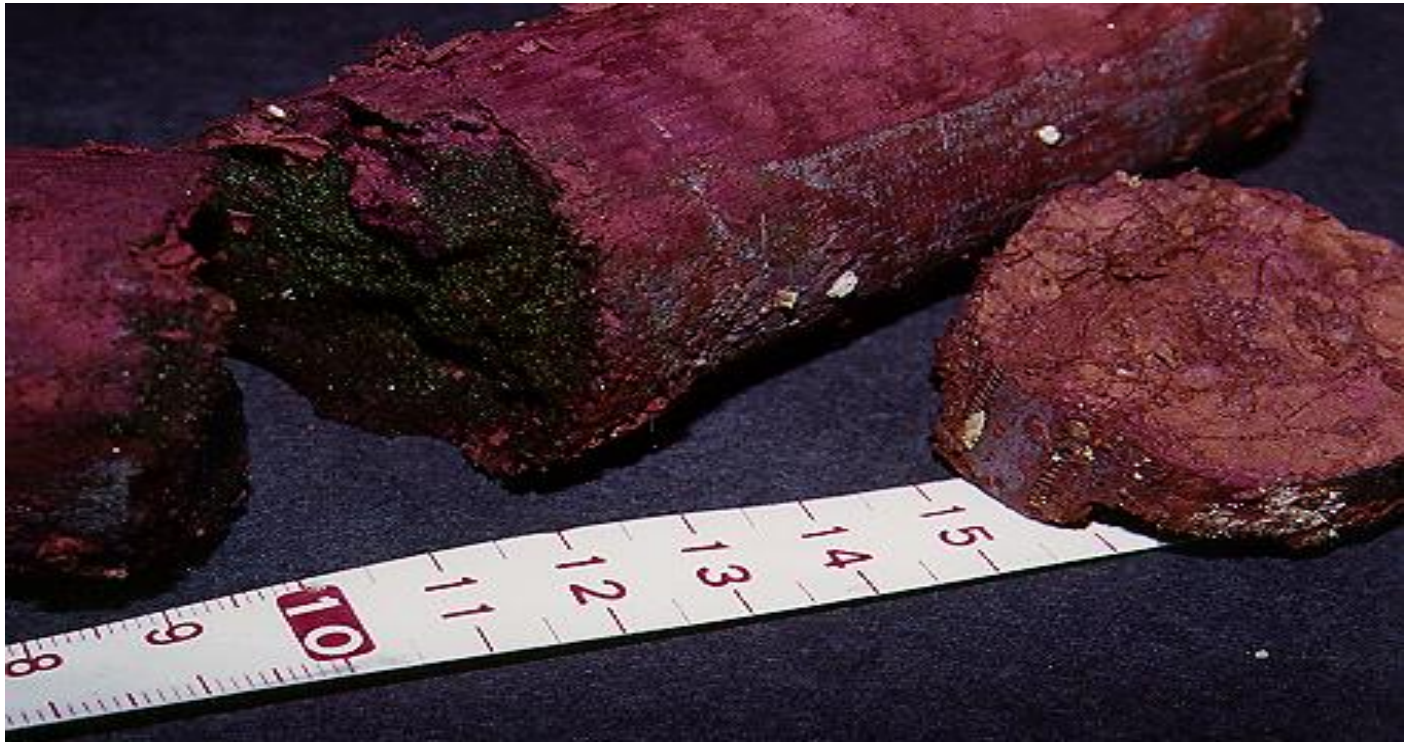
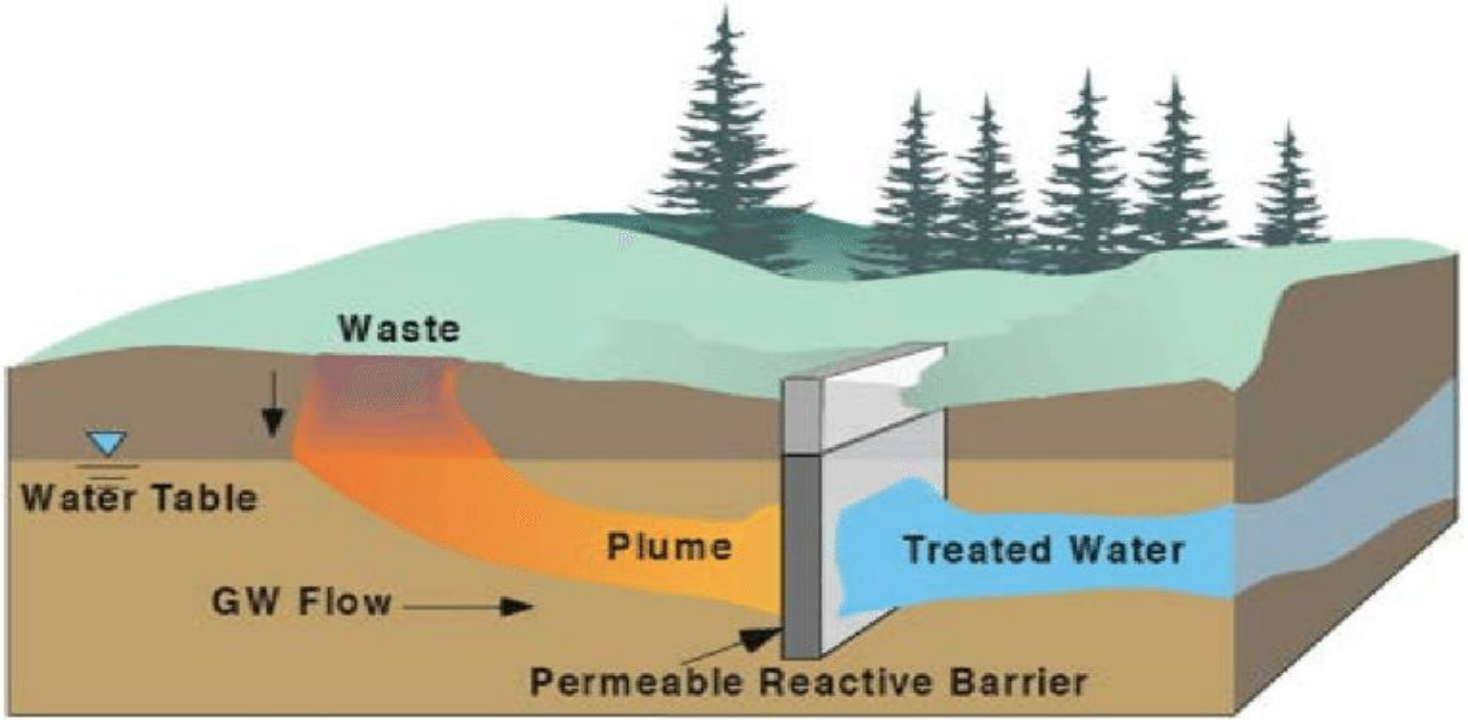
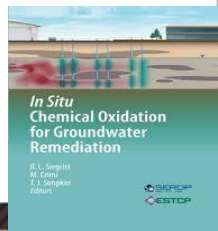


Delivery Methods



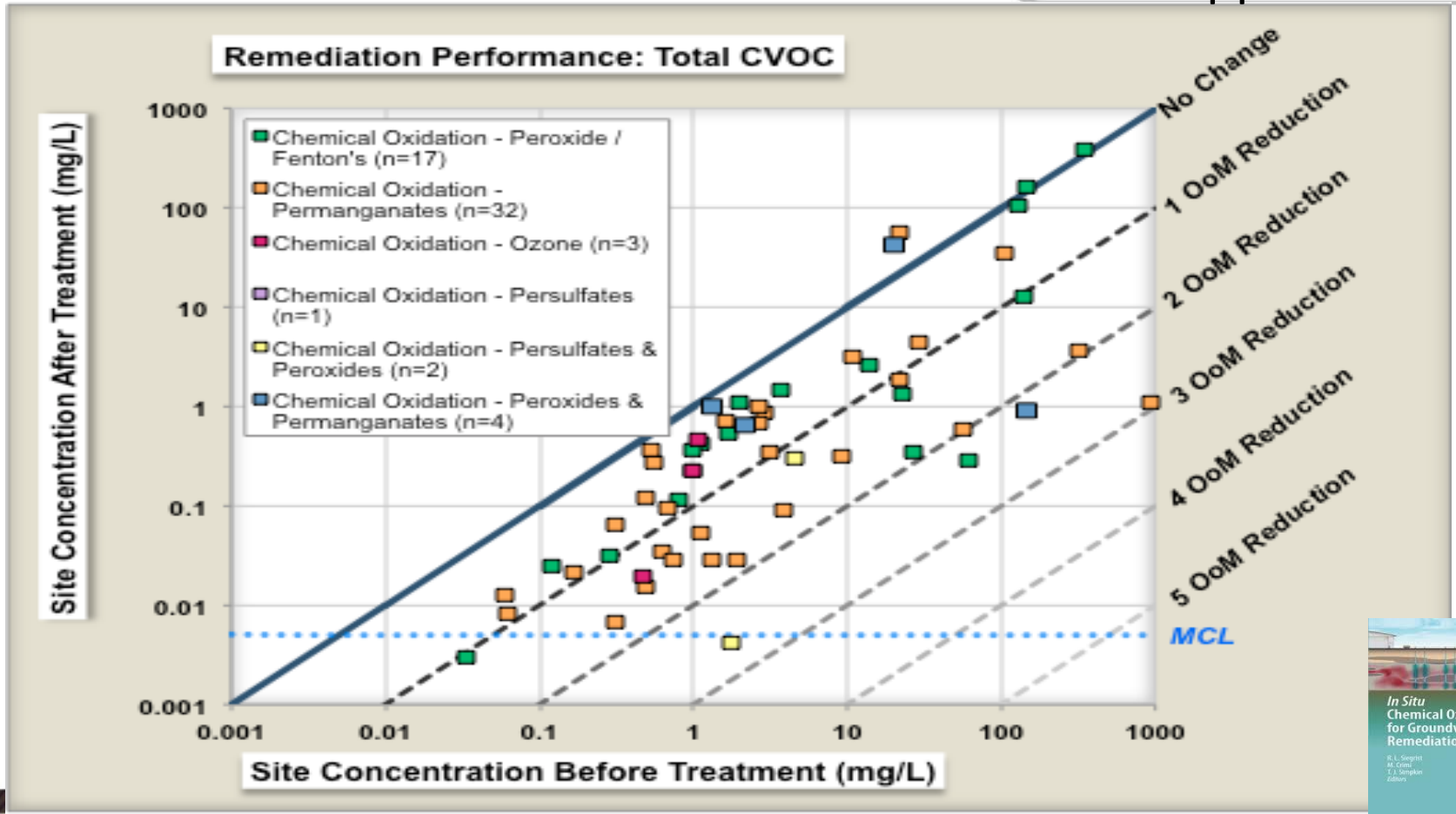
Delivery Methods

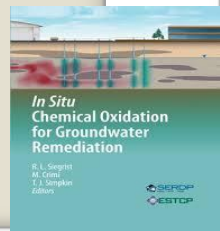
Parameters Monitored for Performance
• Color; Temperature; Dissolved Oxygen • Oxidation-reduction potential • pH • Specific Conductance
• Contaminants – aquifer solids and groundwater • Alkalinity; Manganese; Potassium or Sodium • Sulfate; Chloride • Iron; Site-specific redox-sensitive metals



Delivery Methods

5 ppm to < 5 ppb





PFAS Compounds

- Per- and polyfluoroalkyl substances (PFAS) are a group of man-made chemicals that includes PFOA, PFOS, GenX, and many other chemicals.
- PFAS have been manufactured and used in a variety of industries around the globe, including in the United States since the 1940s.
- There is evidence that exposure to PFAS can lead to adverse human health effects

PFAS Compounds

Industrial / Commercial Sources

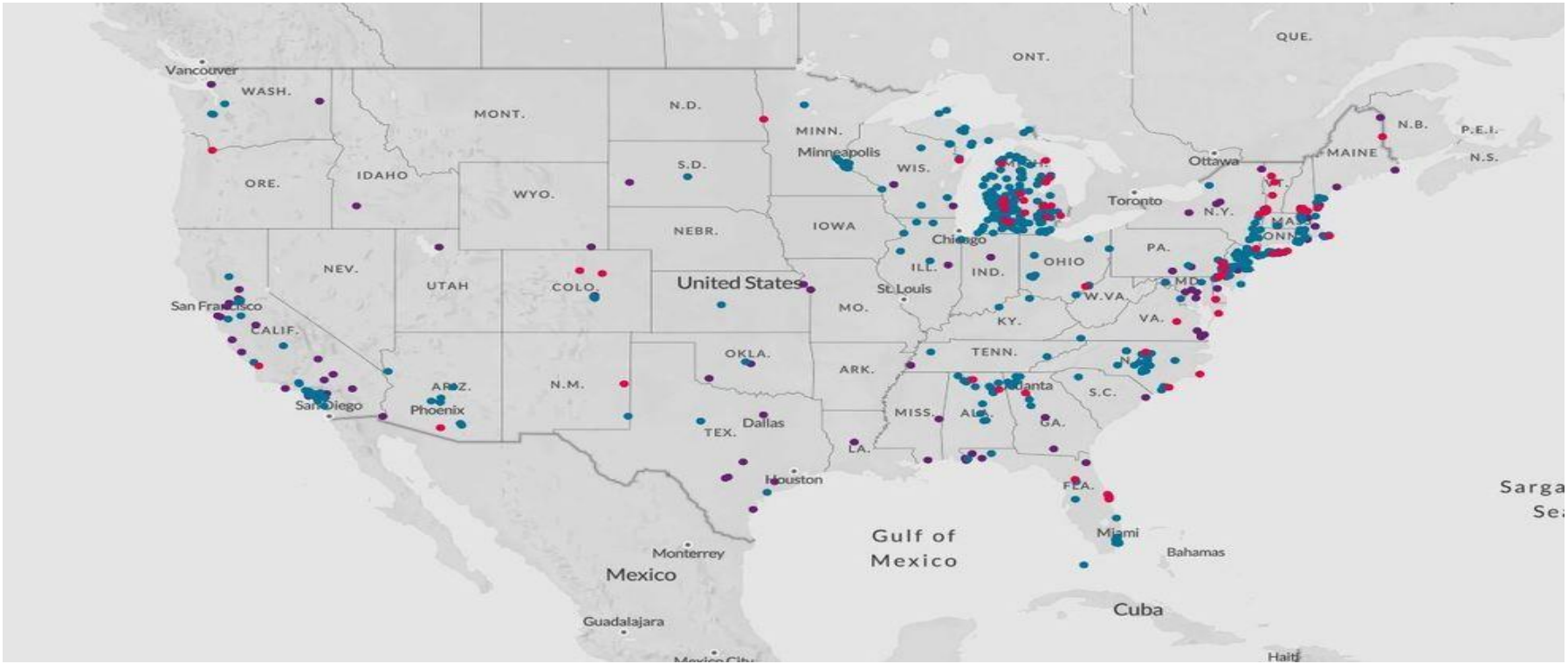
- Aqueous Film Forming Foam (AFFF)
  - Military installations
  - Civilian airports
  - Petroleum refineries
  - Fire fighting training area
- Production and Manufacturing
  - Surfactants, resins, molds, plastics
  - Textiles/leather/paper products
  - Chrome plating
- Landfills
  - Consumer products
  - Industrial waste
  - Biosolids applied as cover
- Waste Water Treatment Plants
  - Influent may not be treated (or may be transformed) and end up in effluent
  - Biosolids created in treatment process may contain PFAS

PFAS Compounds

Residential/Consumer Products

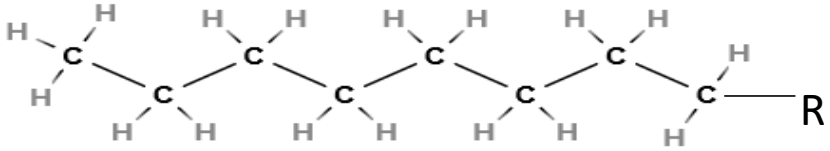
- Cosmetics
  - Make-up
  - Sunscreen
  - Floss
- Consumer products
  - Teflon
  - Gore-tex
  - Scotchguard
  - Any stain- or water-resistant fabrics, furniture, or carpets
- Food
  - Pathway to food contamination is unclear; could be from biosolids, contaminated water, aerosols etc
- Food wrappers/containers
  - Microwave popcorn bags
  - Take out containers
  - Pizza boxes

PFAS Compounds



PFAS Compounds

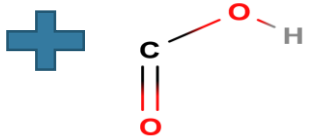
PFAS = Poly- and perFluoroAlkyl Substances



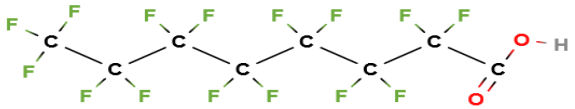
PFAS Compounds

Alkyl chain + Functional group = Compound

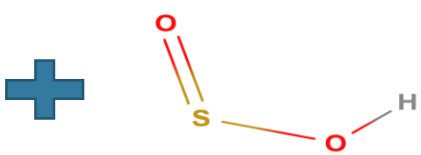
Perfluoroalkyl chain



Carboxylic acid



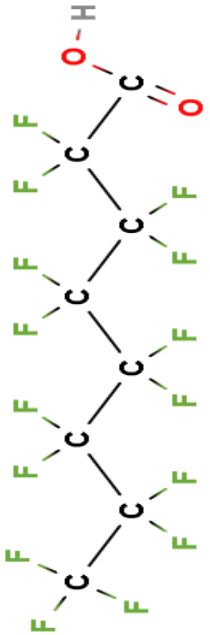
Perfluoroalkyl carboxylic acid (PFCA)



Sulfonic acid

Perfluoroalkyl sulfonic acid (PFSA)

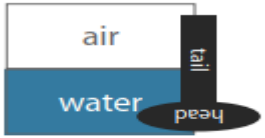
PFAS Compounds

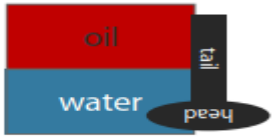


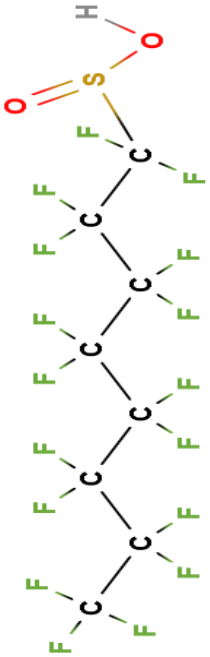
Most PFAS are surfactants

Hydrophilic

Hydrophobic

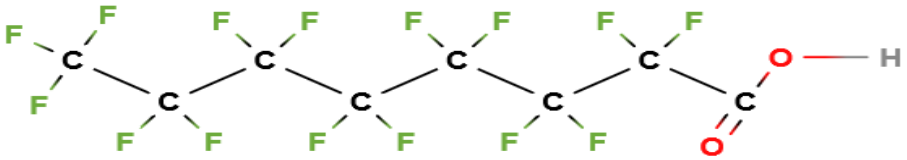


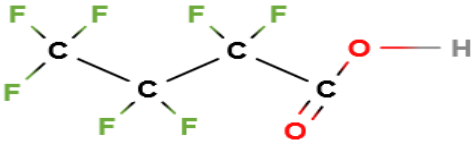




PFAS Compounds

PFAS Comp0unds are very persistent in the environment and in the human body – meaning they don’t break down and they can accumulate over time.





Longer-chained PFAS:

- Less mobile
- More bioaccumulative
- More data

Shorter-chained PFAS:

- More mobile
- Less bioaccumulative
- Less data

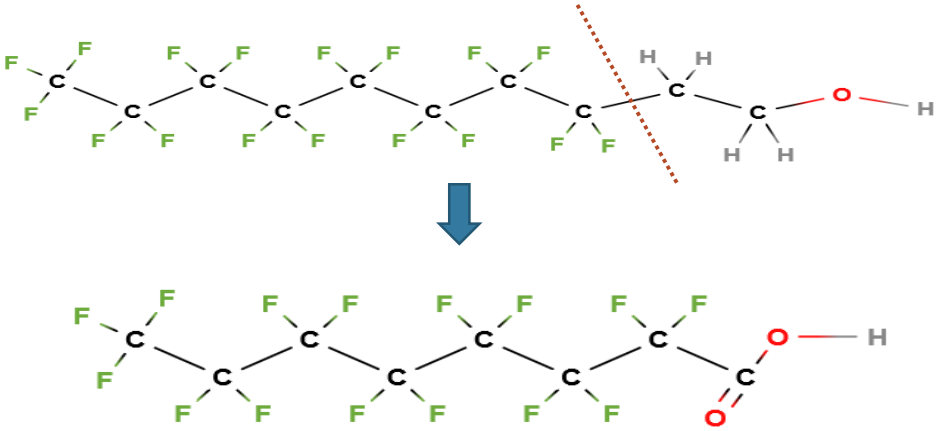
PFAS Compounds

Regulations:

- EPA Health Advisory = 70 ppt PFOS+PFOA
- Not an MCL
- Not enforceable
- Regulated at state level
- Future potential MCL, designation as hazardous substances, potential site re-opener

PFAS Compounds

Polyfluoroalkyl substances are precursors to perfluoroalkyl substances!



8:2 fluorotelomer alcohol, a polyfluoroalkyl substance

Perfluorooctane carboxylic acid (PFOA)

Sulfluramid

- **Sulfluramid is a pesticide that used to be made by Dupont in the U.S.**
- **It breaks down into PFAS and several other chemicals within weeks.**
- **Ongoing production and use of sulfluramid in Brazil despite widespread knowledge of its dangers.**

Remediation Technologies

- ISCO is NOT a proven destruction technology
- However, some defluorination technologies show promise in pilot scale demos

Remediation Technologies

- Separation technologies also show promise.
- Separation is a function of hydrophobicity
- Requires regeneration or destruction of spent GAC/IX resin → treatment trains
- Novel adsorbents in development

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Thank you!