Overview of PFAS Technical Issues

Rula A. Deeb, Ph.D., BCEEM, PMP
Senior Principal

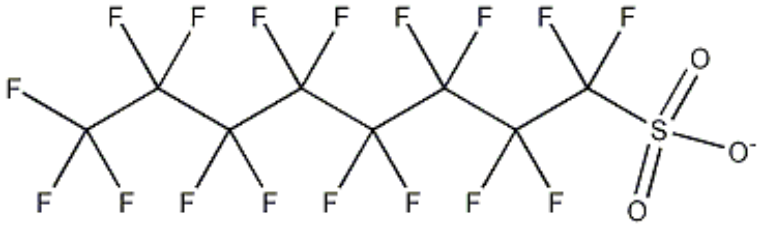
Geosyntec consultants

Outline

- Overview of PFAS
  - Nomenclature
  - Uses
  - Sources to the environment
- Key technical issues
  - Occurrence
  - Fate and transport
  - Toxicology
  - Regulations and drivers
  - Treatment
- Summary

Nomenclature

- Per- and polyfluoroalkyl substances (PFAS)
  - A family of synthetic organic compounds that contain multiple fluorine (F) atoms
- Incorrectly referred to as "PFCs"
  - PFCs are greenhouse gases regulated by the Kyoto Protocol
  - PFCs are one of the families of PFASs (all PFCs are PFASs, but not all PFASs are PFCs)
- Most well-known compounds
  - Perfluorooctanoic acid (PFOA)
  - Perfluorooctane sulfonic acid (PFOS)



PFOS

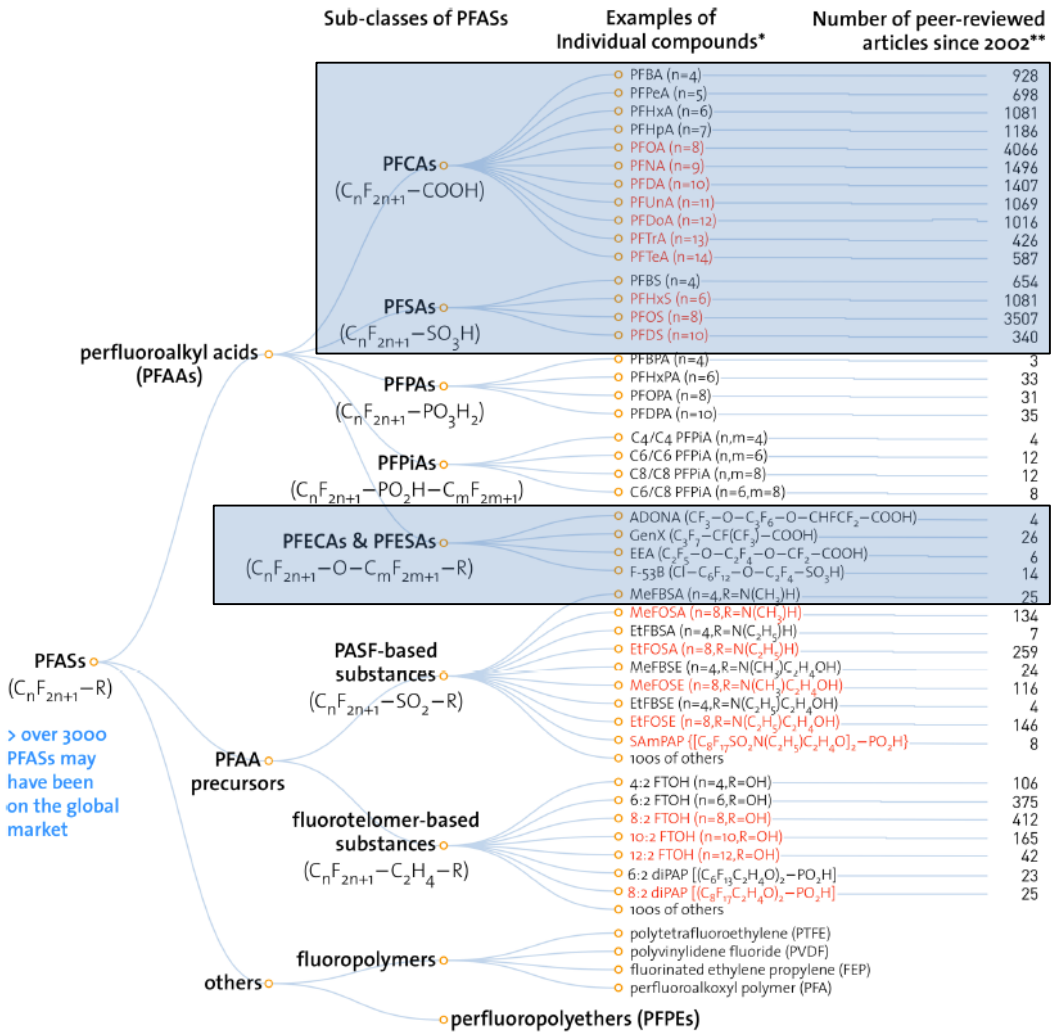
Chemistry

Geosyntec consultants

- C-F bond is shortest and strongest bond in nature
- Perfluoroalkyl substances
  - Compounds for which all hydrogens on all carbons (except for carbons associated with functional groups) have been replaced by fluorines
  - e.g., perfluoroalkyl acids (e.g., PFOA, PFOS)
- Polyfluoroalkyl substances
  - Compounds for which all hydrogens on at least one (but not all) carbons have been replaced by fluorines
  - e.g., fluorotelomer-based compounds
  - Carbon-hydrogen linkages allow for biotic and abiotic degradation

Chemistry

- PFCAs and PFSAs are a small fraction of PFASs
- Short-chain PFASs and fluorinated alternatives are replacing long-chain PFASs
  - Perfluoroalkyl ether carboxylic acids (PFECAs) found in the Cape Fear River in NC



Source: Dr. Detlef Knappe, NCSU

Uses

Geosyntec consultants

Surface treatments/coatings

- Carpet and upholstery
- Apparel
- Paper and packaging
- Non-stick cookware

Performance chemicals

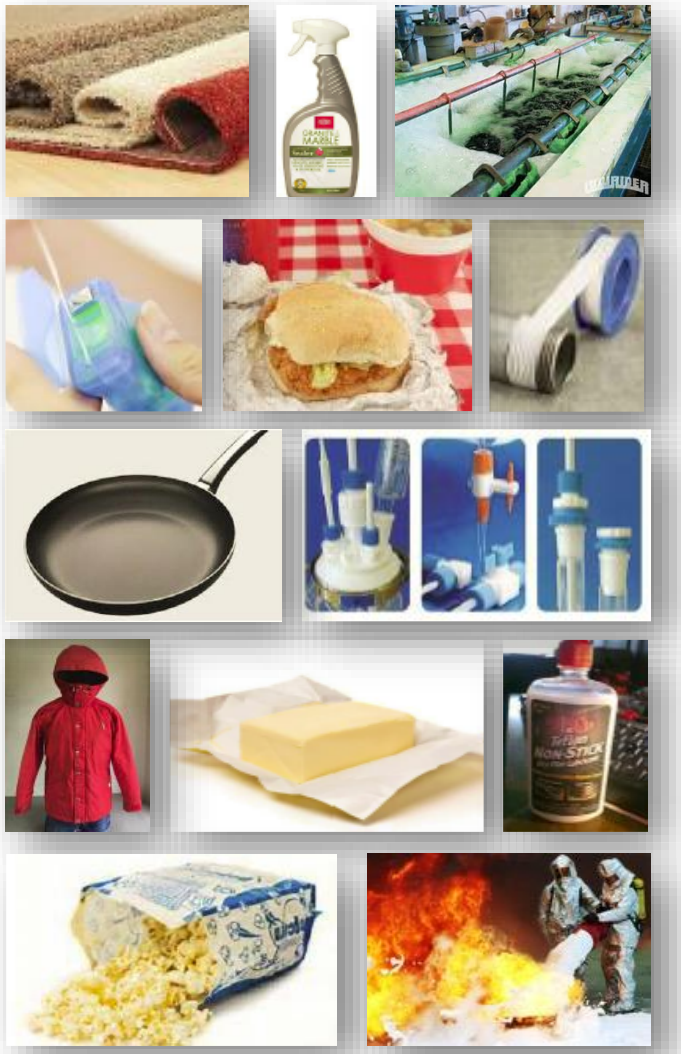
- Chromium plating (mist suppression)
- Insecticides
- Lubricants
- AFFF

- AFFF = aqueous film forming foam
  - Proprietary mixtures of fluorinated and hydrocarbon surfactants, water, corrosion inhibitors, solvents, few % PFASs
  - Only 3% of fluorochemicals produced are used in AFFF
  - 75% of AFFF produced used by military, and 25% used by oil refineries, municipal airports and fire stations, and tank farms
  - History
    - Mid 1960s-1970: 3M sole source supplier of AFFF
    - 1973: National Foam
    - 1976: Ansul
    - 1994 to present: Angus, Chemguard, Fire Service Plus
  - Multiple AFFFs likely used at most sites

Environmental Sources

Geosyntec consultants

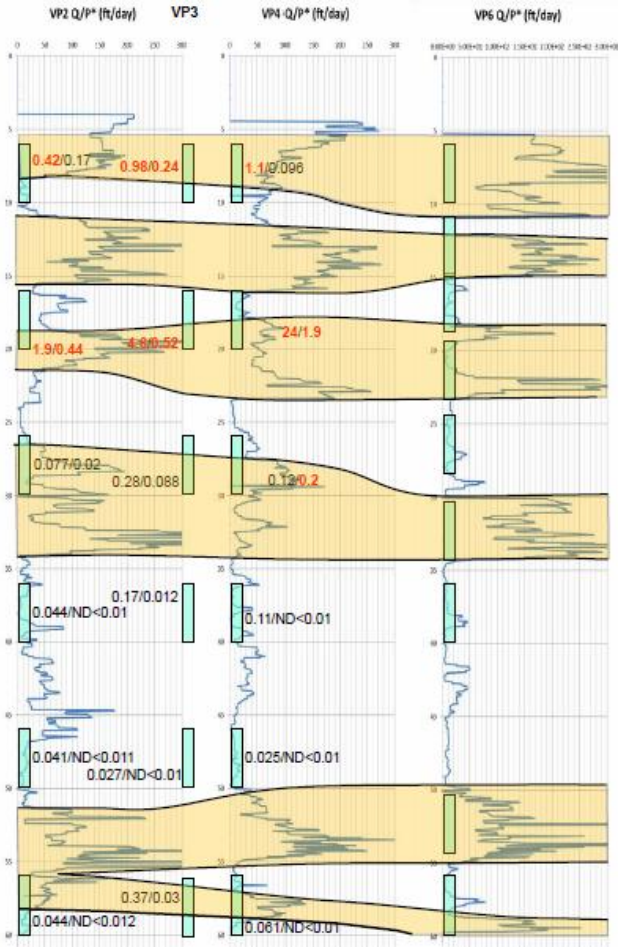
- Private industry
  - Chemical manufacturing processes
  - Textiles and carpets
  - Heavy industry (chrome plating)
  - Petrochemical industry (AFFF systems)
  - Aerospace industry
  - Airports
  - Prop 65 and other product challenges (food packaging, clothing, carpeting)
- Military
  - AFFF
- Municipalities
  - Fire-fighting areas, airports, drinking water systems, landfills, wastewater treatment plants



Why PFASs are Emerging Now

Geosyntec consultants

- PFASs are not detectable using conventional analytical tools for environmental contaminants (e.g., gas chromatography)
- Commercially-available measurement techniques only recently available (last 10 years)



Occurrence in Stormwater, Biosolids and Landfills

Geosyntec consultants

Release of Per- and Polyfluoroalkyl Substances (PFASs) from Carpet and Clothing in Model Anaerobic Landfill Reactors

Johnsie R. Lang[†], B. McKay Allred[‡], Graham F. Peaslee[§], Jennifer A. Field[∥], and Morton A. Barlaz[†]*
[†] Department of Civil, Constructional, and Environmental Engineering, North Carolina State University, Box 7908, Raleigh, North Carolina 27695-7908, United States
[‡] Department of Chemistry, Oregon State University, 153 Gilbert Hall, Corvallis, Oregon 97331-4003, United States
[§] Department of Chemistry, Hope College, 35 E. 12th St., Holland, Michigan 49423-3605, United States
[∥] Department of Environmental and Molecular Toxicology, Oregon State University, 1007 ALS Bldg. 2750 Campus Way, Corvallis, Oregon 97331-4003, United States

Environ. Sci. Technol., **2016**, *50* (10), pp 5024–5032
DOI: 10.1021/acs.est.5b06237
Publication Date (Web): April 20, 2016

Environmental Science & Technology

Occurrence and Fate of Perfluorochemicals in Soil Following the Land Application of Municipal Biosolids

Jennifer G. Sepulvado†, Andrea C. Blaine†, Lakhwinder S. Hundal‡, and Christopher P. Higgins*†
Colorado School of Mines, Golden, Colorado 80401, United States
Metropolitan Water Reclamation District of Greater Chicago, 6001 West Pershing Road, R&D Department, Se
Cicero, Illinois 60804, United States

Environ. Sci. Technol., **2011**, *45* (19), pp 8106–8112
DOI: 10.1021/es103903d
Publication Date (Web): March 29, 2011

Oxidative Conversion as a Means of Detecting Precursors to Perfluoroalkyl Acids in Urban Runoff

Erika F. Houtz and *David L. Sedlak*
Environ. Sci. Technol., 2012, *46* (17), pp 9342-9349
Publication Date (Web): August 17, 2012 (Article)
DOI: 10.1021/es302274g
A new method was developed to quantify concentrations of difficult-to-measure and unidentified precursors of perfluoroalkyl carboxylic (PFCA) and sulfonic (PFSA) acids in urban runoff. Samples were exposed to hydroxyl radicals generated by thermolysis of …

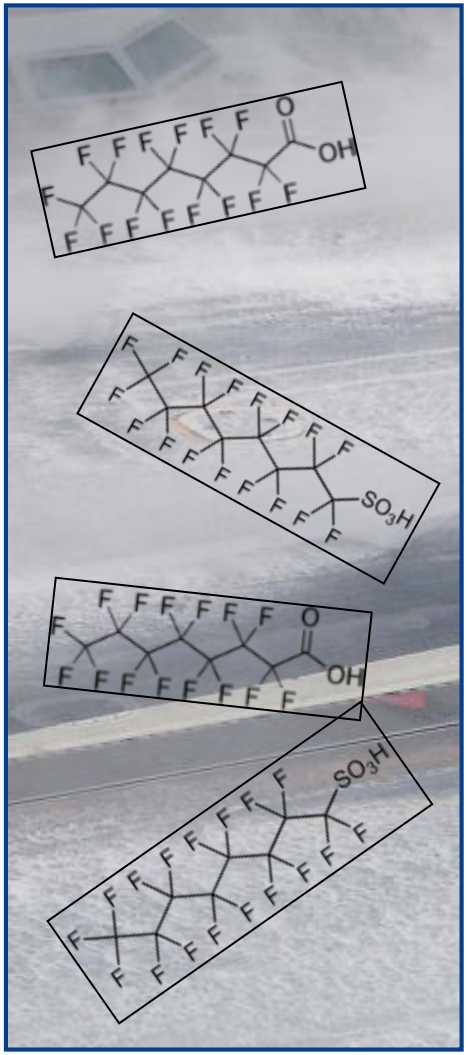
Perfluorinated Acids in Air, Rain, Snow, Surface Runoff, and Lakes: Relative Importance of Pathways to Contamination of Urban Lakes

Seung-Kyu Kim and *Kurunthachalam Kannan*
Environ. Sci. Technol., 2007, *41* (24), pp 8328-8334
Publication Date (Web): November 13, 2007 (Article)
DOI: 10.1021/es072107t

Fate and Transport

Geosyntec consultants

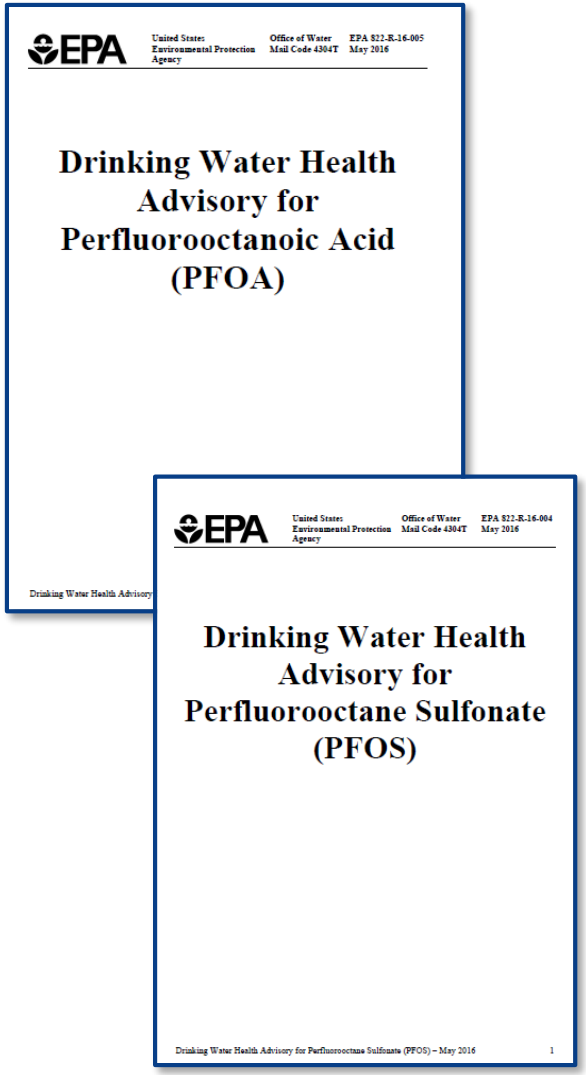
- Sorption generally increases with number of carbons
- Transport related to charged state of PFASs
  - Anions > zwitterions > cations
  - Shorter chain lengths generally move faster
- Polyfluorinated substance
  - Potential to form PFSAs and PFCAs (abiotically and biotically)
  - Variable transport properties
- PFSAs and PFCAs
  - Not readily biodegradable
  - Not readily transformed abiotically
  - Generally high mobility



→ Mobile and persistent

Toxicology

- Best toxicity data coverage for PFOA and PFOS
  - USEPA reference doses for human health
    - PFOS: reduced birth weight
    - PFOA: developmental effects in bones, accelerated puberty
  - Wildlife effects
    - Effects on liver and kidney
    - Reproduction
  - Aquatic toxicity data (fish, invertebrates) for some compounds
- Other PFASs
  - Limited information in peer-reviewed literature and chemical registration information (REACH dossiers, TSCA submittals)



Biological Fate

- Detectable in nearly any biological tissue
- Partitions to protein (proteinophilic), not fat/lipid
- Not metabolized, or metabolizes to persistent PFASs
- Bioaccumulates in animals and plants (uptake and water evaporation)

B10MONITORING CALIFORNIA
10TH ANNIVERSARY

Chemical Group: Perfluorochemicals (PFCs)
› **Measured in:** Serum

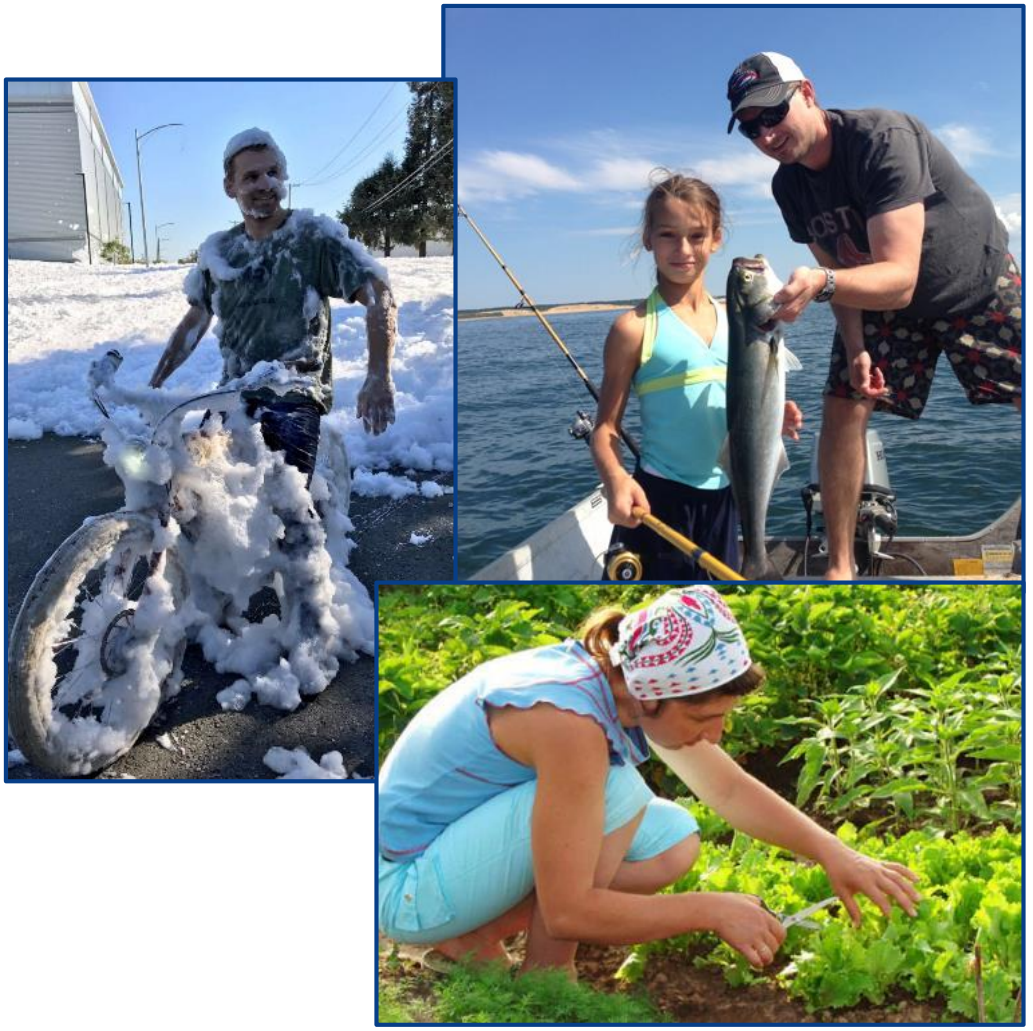
A+

Project: California Teachers Study (CTS)
› **Study Group:** All
› **Sample Collection Date:** 2011

Human Exposure Pathways

Geosyntec consultants

- Major[1,2]
  - Drinking water
  - Incidental soil/dust ingestion
  - Diet (bioaccumulation)
    - Fish and seafood
    - Homegrown produce
- Usually insignificant or minor
  - Dermal absorption
  - Inhalation



[1] Oliaei et al., 2013. Environ. Sci. Pollut. Res. Manag. 20:1977-1992
[2] Domingo, 2012. Environment International 40:187-195

Risk Assessment Challenges

Geosyntec consultants

- It's not just PFOA and PFOS
  - For example, dozens to hundreds of other PFASs in AFFF
  - Toxicity of other PFASs?
- Background exposure for humans
- No standard guidance of models for risk assessment (conceptual site models, sampling approaches, uptake factors, toxicity values)



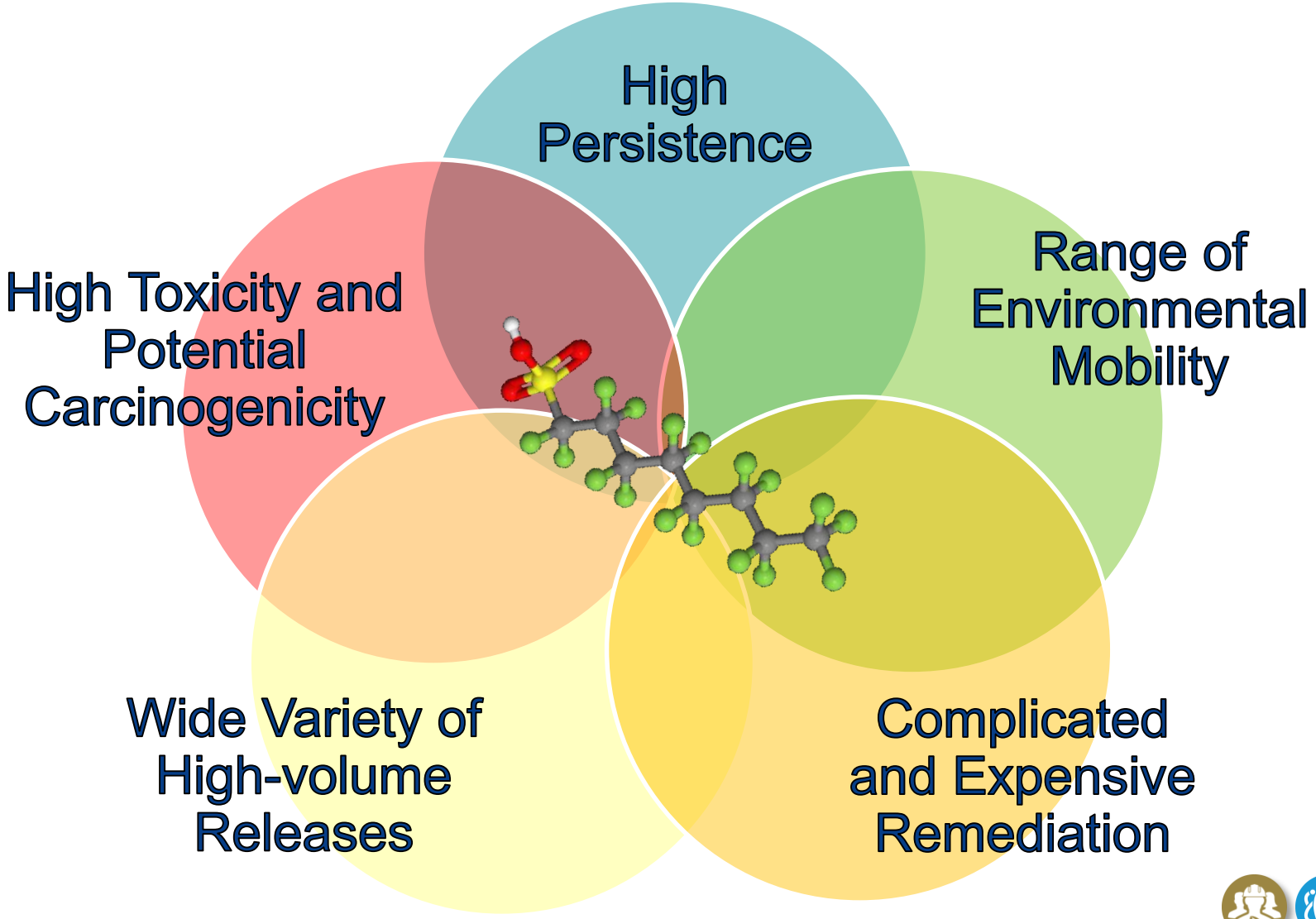

Treatment

Geosyntec consultants

- Challenging and costly due to stability of PFOS and complexity of PFAS mixtures
- No destruction technologies currently available
  - "New era" of pump-and-treat
- Lack of proven (demonstrated) in situ treatment methods
- Available technologies do not address sorbed PFASs and precursors

Perfect Storm of Environmental Challenges

Geosyntec consultants



Summary

Geosyntec consultants

- PFAS is more than PFOS and PFOA
- PFAS chemistry is complicated and mixtures are complex
- PFASs produced for decades and used in large volumes = potential for reopening closed sites or creating new sites
- Multiple states have issue standards/guidance for PFOS and PFOA (and other PFASs) in the absence of enforceable cleanup standards
- Treatment is challenging and costly
- This is not just a U.S. issue
- The state of knowledge continues to evolve

Contact information

Geosyntec consultants

Rula A. Deeb
Phone: 510.285.2676
Mobile: 510.932.9110
rdeeb@geosyntec.com