Northeast Waste Management Officials' Association

WEBINAR

Atmospheric deposition as a source of contamination at PFAS-impacted Sites

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December 13, 2018

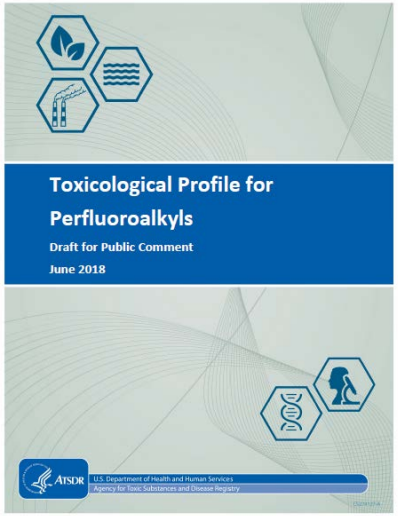
PFAS Health Effects

- PFAS readily absorbed via inhalation or oral exposure and not metabolized in humans or laboratory animals
- Most epidemiological studies focus on PFOA and PFOS
- Provisional Minimum Risk Levels (MRLs) derived for PFOA, PFOS, PFHxS, and PFNA via oral exposure
- Inhalation data limited and considered inadequate for deriving MRLs

Observed Human Health Effects:

- Cancers (kidney, testicular)
- Pregnancy-induced hypertension/pre-eclampsia
- Liver damage
- Increases in serum lipids
- Thyroid disease
- Decreased antibody response to vaccines
- Asthma
- Decreased fertility
- Lower birth weight
- Osteoarthritis

ATSDR
AGENCY FOR TOXIC SUBSTANCES AND DISEASE REGISTRY



Source: ATSDR 2018

PFAS Occurrence - Outdoor Air

- Elevated concentrations observed or expected in urban areas nearest to major emission sources:
  - Industrial facilities producing or using PFAS
  - Areas where Class B firefighting foams used
  - Landfills and wastewater treatment plants
  - Biosolids production and application
- PFOA and PFOS in air typically fall within a range of about 1-20 pg/m^3 (although concentrations as high as 900,000 pg/m^3 observed near large manufacturers)
- Concentrations of volatile PFAS such as FTOHs can be in the hundreds of pg/m^3 in outdoor air

Sources: Ge et al. 2017; Bossi et al. 2016; Lai et al. 2016; Liu et al. 2015; Wang et al. 2015; Ahrens et al. 2011; Cai et al 2012; Goosey and Harrad 2012; Shoeib et al. 2011; Dreyer et al. 2010; Shoeib et al. 2010; Dreyer et al. 2009; Suja et al. 2009; Loewen et al. 2008; Barton et al. 2007; Jahnke et al. 2007; Kim and Kannan 2007; Piekarz et al. 2007; Barton et al. 2006; Shoeib et al. 2004; Stock et al. 2004.

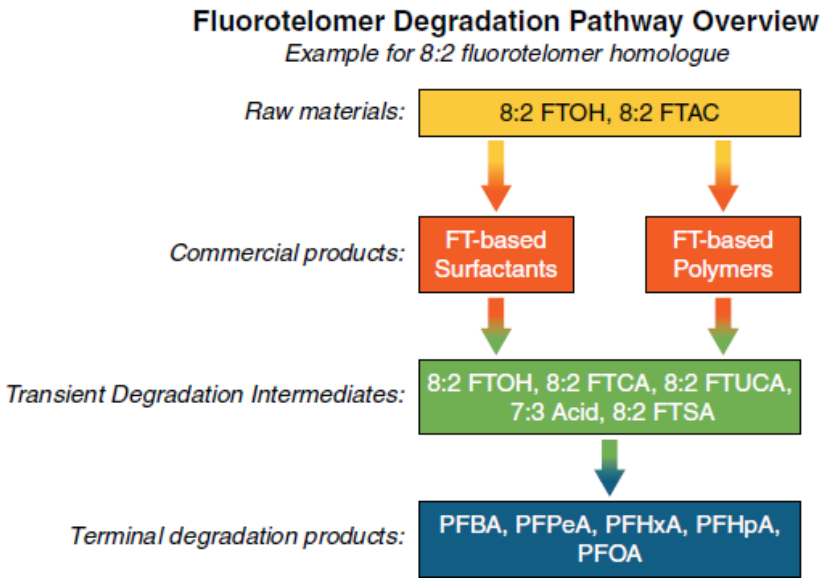
PFAS Species in Outdoor Air

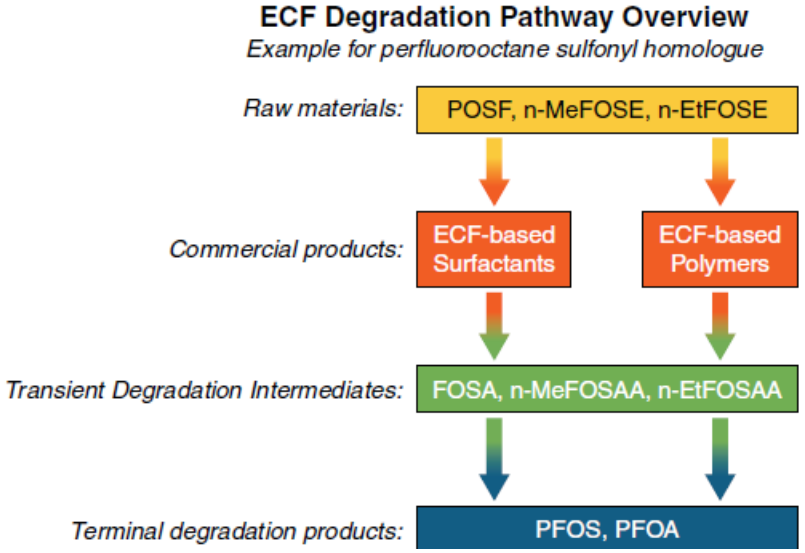
- Wide range of PFAS observed in ambient air, examples include:
  - Perfluoroalkyl acids (PFAAs)
  - Perfluoroalkane sulfonamides (FASAs)
  - Fluorotelomer alcohols (FTOHs)
  - Fluorotelomer carboxylic acids (FTCAs)
  - Perfluoroalkane sulfamido ethanols (FASEs)
- Certain classes of PFAS are volatile or semivolatile and can travel long distances
- Some termed "precursors" can degrade into "terminal degradation products" (PFOA, PFOS, and other PFAAs)

Classification	Examples	Uses
PFAAs	PFOA PFOS PFBA PFHxS PFPeA PFHxA PFHpA PFNA	Surfactants
FASAs	EtFOSA MeFOSA	Intermediate environmental transformation products
FTOHs	6:2 FTOH 8:2 FTOH 10:2 FTOH	Raw material for surfactant and surface protection
FTCAs	8:2 FTCA	Intermediate environmental transformation product
FASEs	EtFOSE MeFOSE	Raw material for surfactant and surface protection

Sources: ITRC 2018; Ge et al. 2017; Bossi et al. 2016; Lai et al. 2016; Liu et al. 2015; Wang et al. 2015; Ahrens et al. 2011; Buck et al. 2011; Cai et al 2012; Goosey and Harrad 2012; Shoeib et al. 2011; Dreyer et al. 2010; Shoeib et al. 2010; Dreyer et al. 2009; Suja et al. 2009; Loewen et al. 2008; Barton et al. 2007; Jahnke et al. 2007; Kim and Kannan 2007; Piekarz et al. 2007; Barton et al. 2006; Shoeib et al. 2004; Stock et al. 2004.

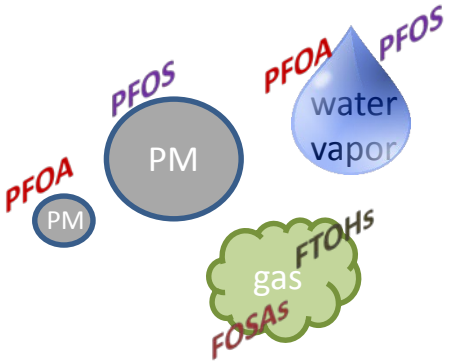
Precursor Degradation Pathways





Sources: ITRC 2018; Buck et al. 2011

Distribution in Air



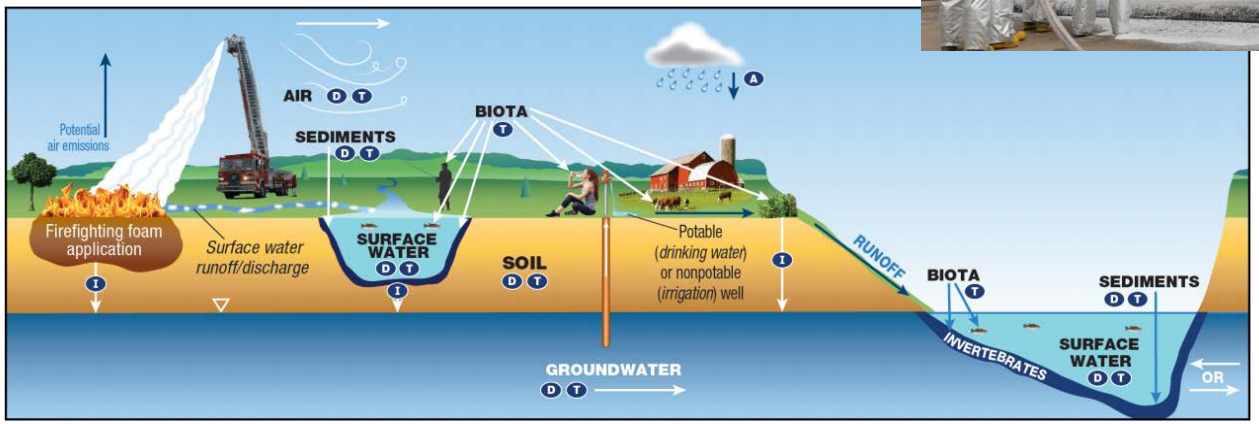
- PFAS occur in gas and particle phases or other aerosols suspended in air (e.g., water vapor)
- Neutral PFAS such as FTOHs often the most dominant PFAS in the gas phase in urban areas, over open ocean, and in remote regions
- Ionic PFAS such as PFOA and PFOS (with low vapor pressure, high solubility) tend to be dominant species in airborne particulate matter
- PFOA associated with smaller, ultrafine particles, while PFOS associated with larger, coarser fractions
- PFAS found in rainwater and marine aerosols (sea spray)

Sources: Ge et al. 2017; Bossi et al. 2016; Lai et al. 2016; Wang et al. 2015; Ahrens et al. 2012; Dreyer et al. 2009

Conceptual Site Models

Considering air emissions when conducting a site investigation

FIRE TRAINING



INDUSTRIAL

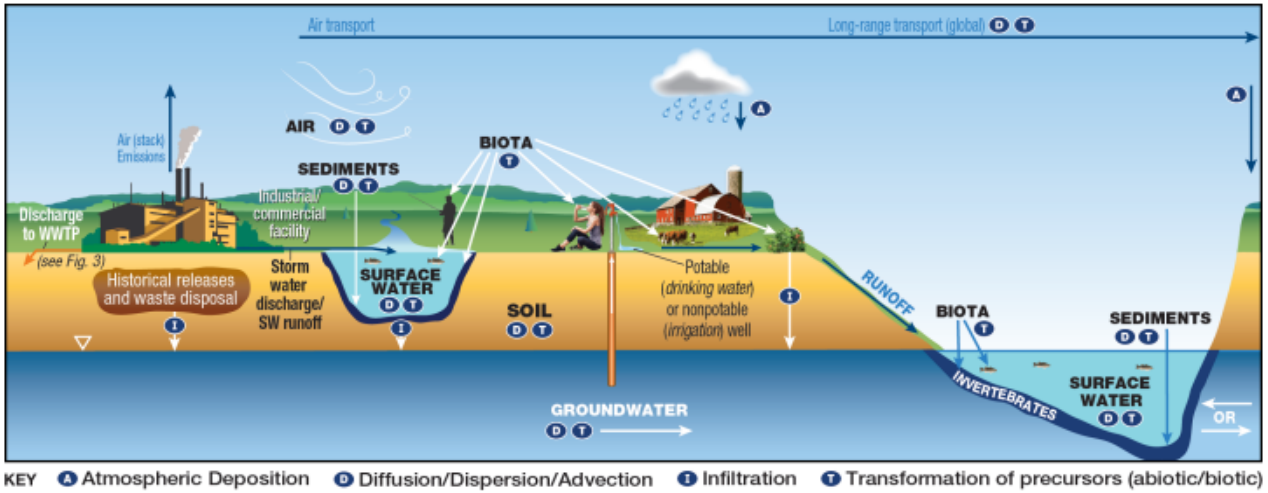


Figure 2. Conceptual site model for industrial sites.

Where to Look for PFAS (MADEP Guidance):

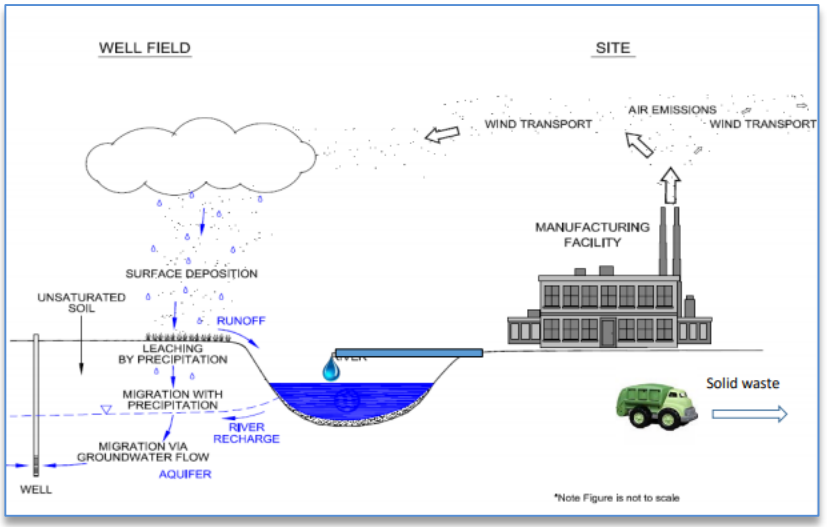
- PFAS manufacturers
- Landfills
- Former and current DoD sites
- Airport hangars, rail yards, petrochemical sites
- Firefighting, training, and equipment areas
- Crash sites (air, rail, motor vehicle)
- Metal coating and plating

Sources: MADEP 2018; ITRC 2018 (L. Trozzolo)

Fate and Transport of PFAS in Air

SHORT-RANGE ATMOSPHERIC TRANSPORT

- PFAS commonly found in precipitation (rain and snow)
- Wet and dry deposition major removal mechanisms from atmosphere, on a timescale of a few days
- Short-range atmospheric transport can result in contamination to terrestrial and aquatic systems near emission sources with multi-media impacts
- Evidence of releases observed miles from source where hydrologic transport unlikely

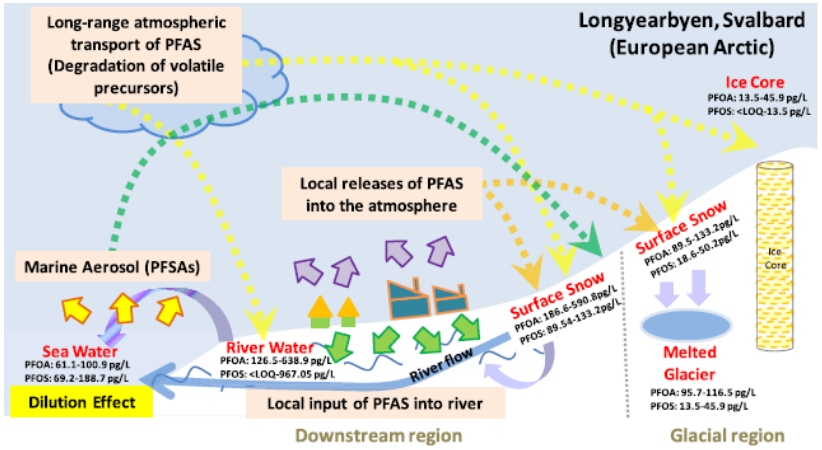


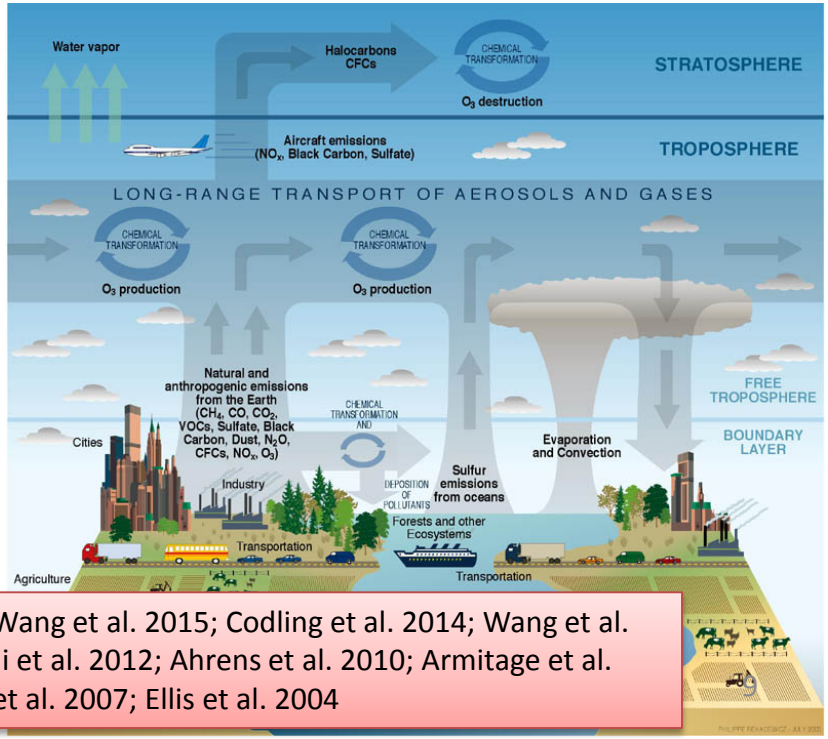
Sources: Liu et al. 2017; NHDES 2017; Chen et al. 2016; NYDOH 2016; Lin et a. 2014; Post 2013; Taniyasu et al. 2013; Zhao et al. 2013; Post 2012; Dryer et al. 2010; Kwok et al. 2010; Frisbee et al. 2009; Barton et al. 2007; Davis et al. 2007; Kim and Kannan 2007; Hurley et al. 2004

Fate and Transport of PFAS in Air

LONG-RANGE ATMOSPHERIC TRANSPORT (LRT)

- LRT responsible for wide distribution of PFAS across earth as evidenced by occurrence in biota, surface snow, ice cores, seawater, and other media as far as the Arctic and Antarctic
- Distribution to remote regions believed to occur from:
  - LRT and subsequent degradation of precursors
  - Transport via ocean currents and release into air as marine aerosols
- Processes and effects similar to atmospheric transport of other recalcitrant compounds





Sources: Bossi et al. 2016; Kirchgeorg et al. 2016; Rankin et al. 2016; Wang et al. 2015; Codling et al. 2014; Wang et al. 2014; Kirchgeorg et al. 2013; Kwok et al. 2013; Benskin et al. 2012; Cai et al. 2012; Ahrens et al. 2010; Armitage et al. 2009; Dasilva et al. 2009; Dryer et al. 2009; Young et al. 2007; Wania et al. 2007; Ellis et al. 2004

PFAS Occurrence - Indoor Air

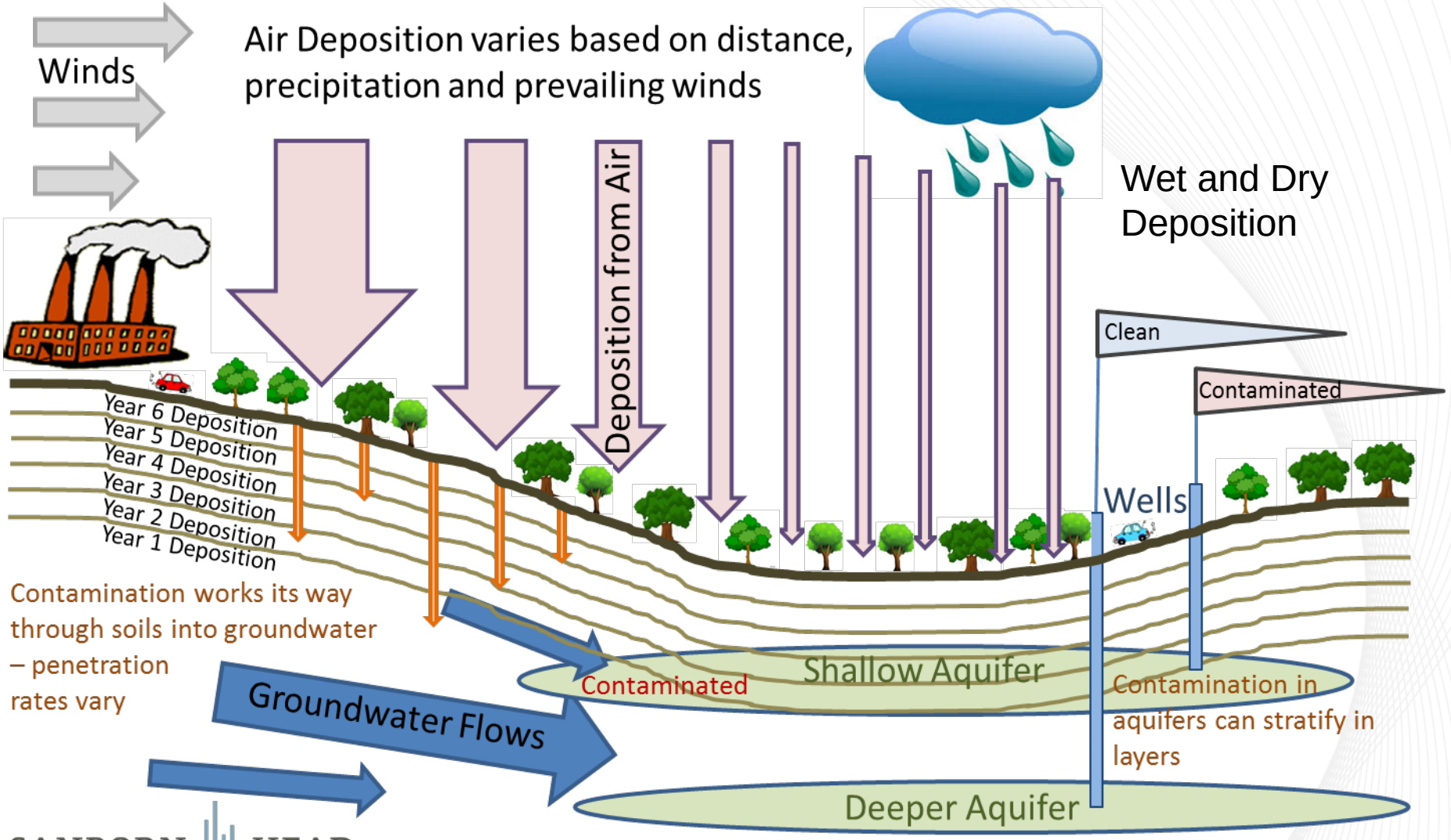
- PFAS can also be present in indoor air
- Indoor concentrations can be higher than outdoors due to the presence of indoor sources
- Most exposures may occur indoors where we spend ~ 90% of our time
- PFAS in indoor air reported in the range of about 1-440 pg/m^3 for PFOA and PFOS
- Volatile PFAS such as FTOHs have been observed on the order of 10,000-50,000 pg/m^3 in schools, homes, and offices and in excess of 300,000 pg/m^3 in commercial buildings

Indoor PFAS Sources:

- **Stain resistant coatings used on carpets and upholstery**
- **Water resistant clothing**
- **Grease-resistant paper**
- **Food packaging**
- **Nonstick cookware**
- **Cleaning products**
- **Personal care products**
- **Cosmetics**
- **Paints, varnishes, and sealants**

Sources: ATSDR 2016; Fromme et al. 2015; Liu et al. 2015; Liu et al. 2014; Fraser et al. 2012; Goosey and Harrad 2012; Shoeib et al. 2011; Fromme et al. 2010; Kaiser et al. 2010; Langer et al. 2010; Gewurtz et al. 2009; Guo et al. 2009; Strynar and Lindstrom 2008; Shoeib et al. 2004

Atmospheric Deposition of Contaminants



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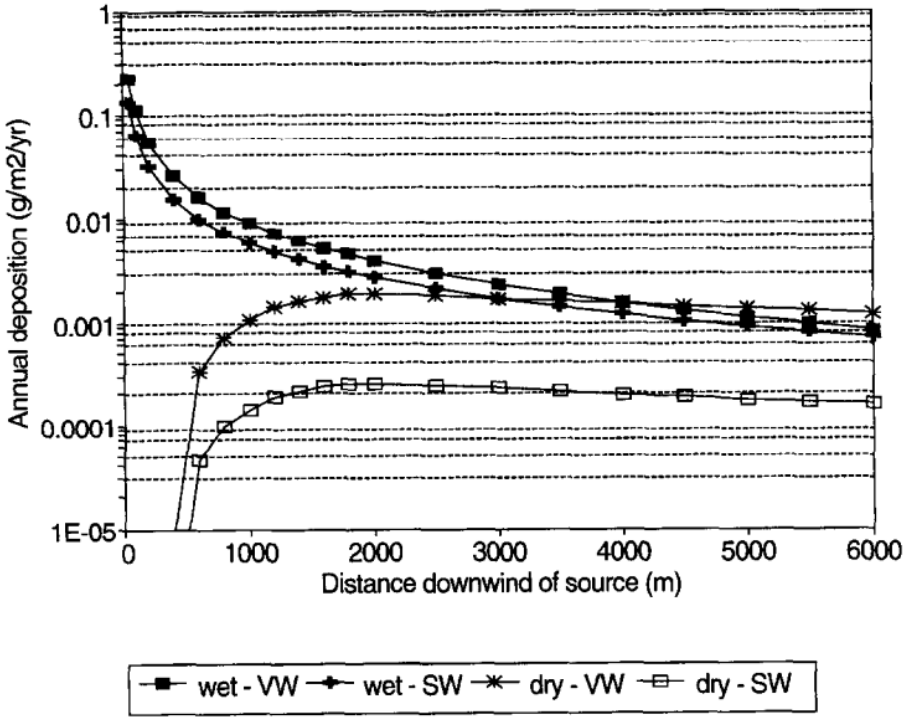
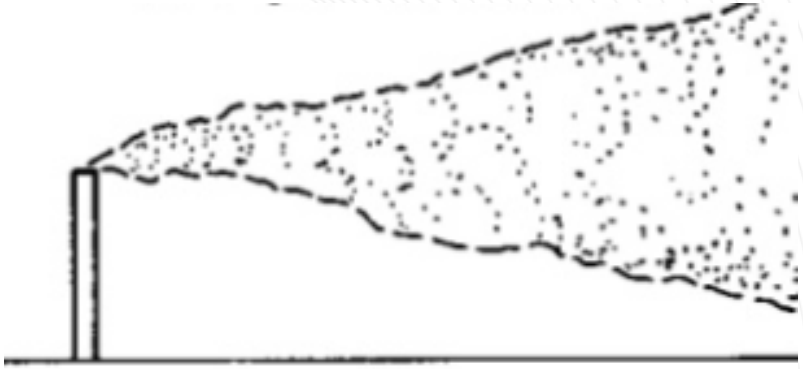
Courtesy of NH Department of Environmental Services

Deposition Factors/Considerations

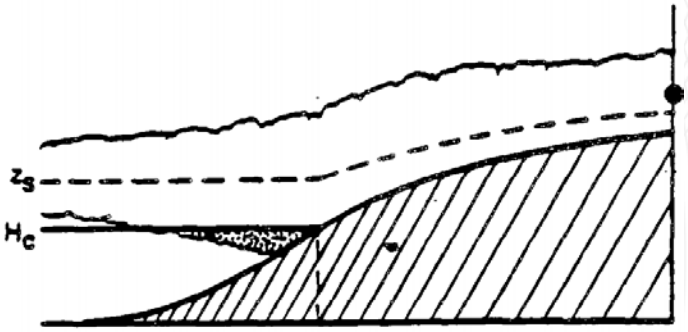
S.G. Zemba et al. / Journal of Hazardous Materials 47 (1996) 229–275





- Dry *v.* Wet
- Dry "Donut Hole"

Plume Impaction



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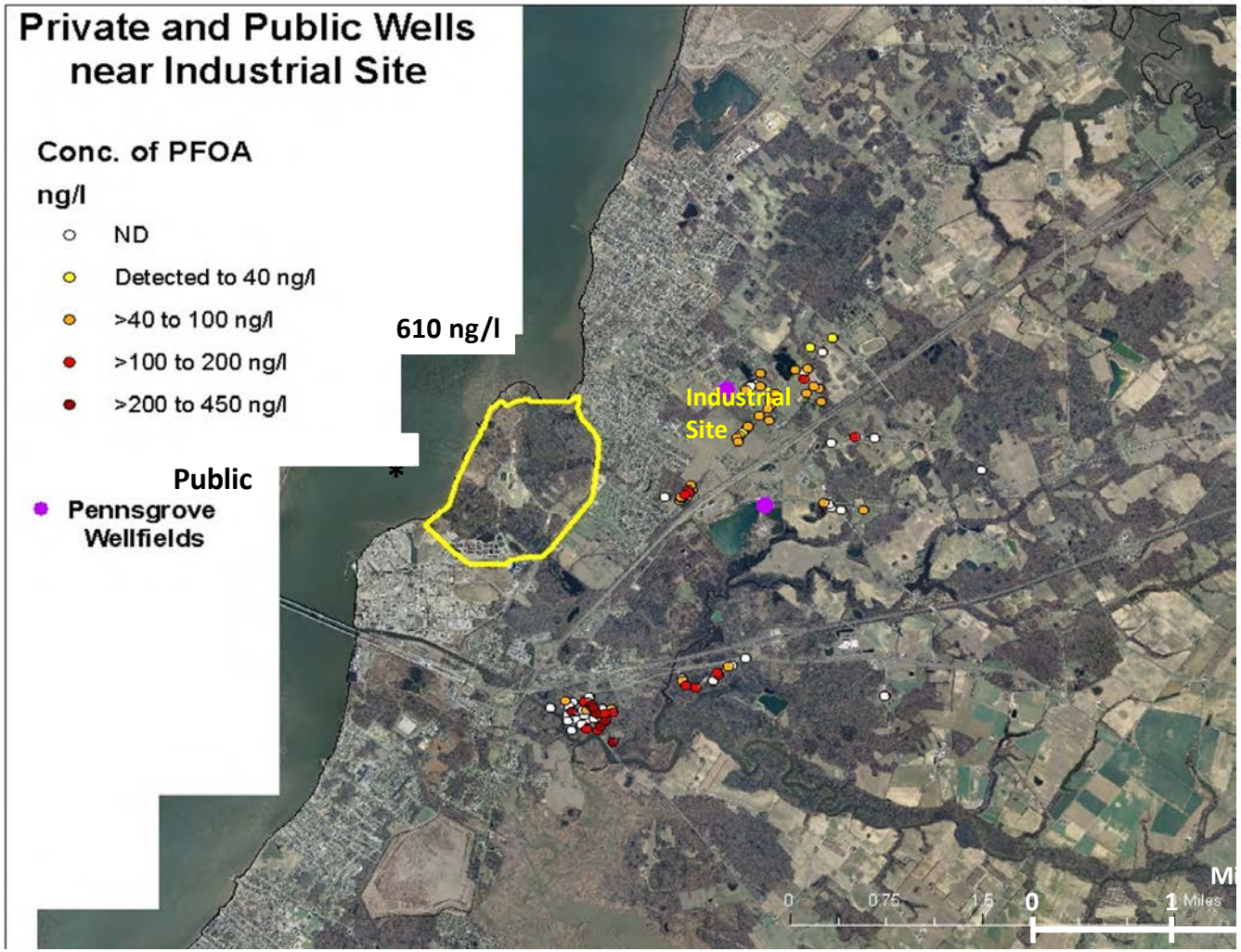
PFAS Airborne Transport Found Near NJ Facility



***Detected in public water supply wells at up to 280 ng/L.**

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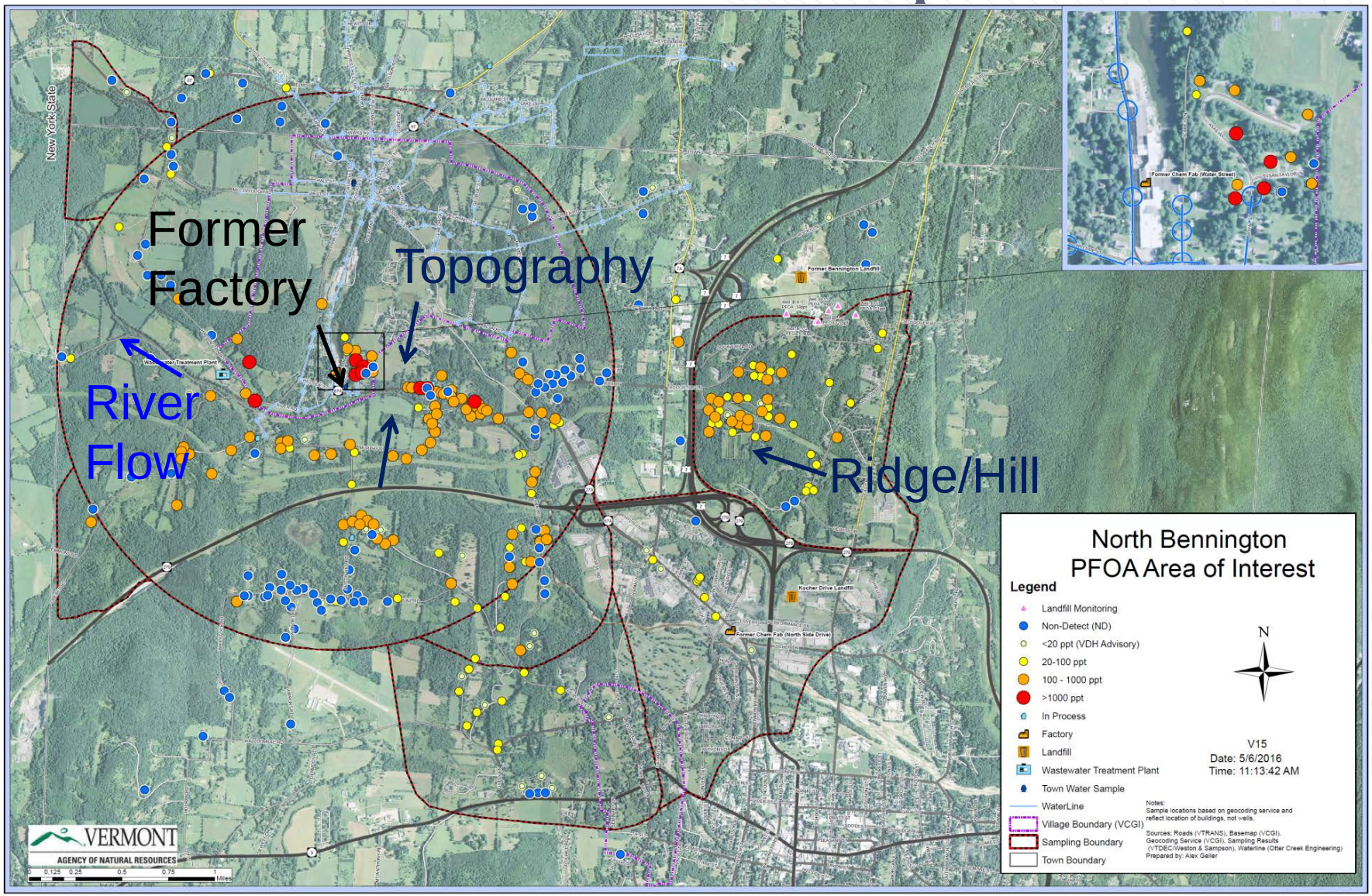
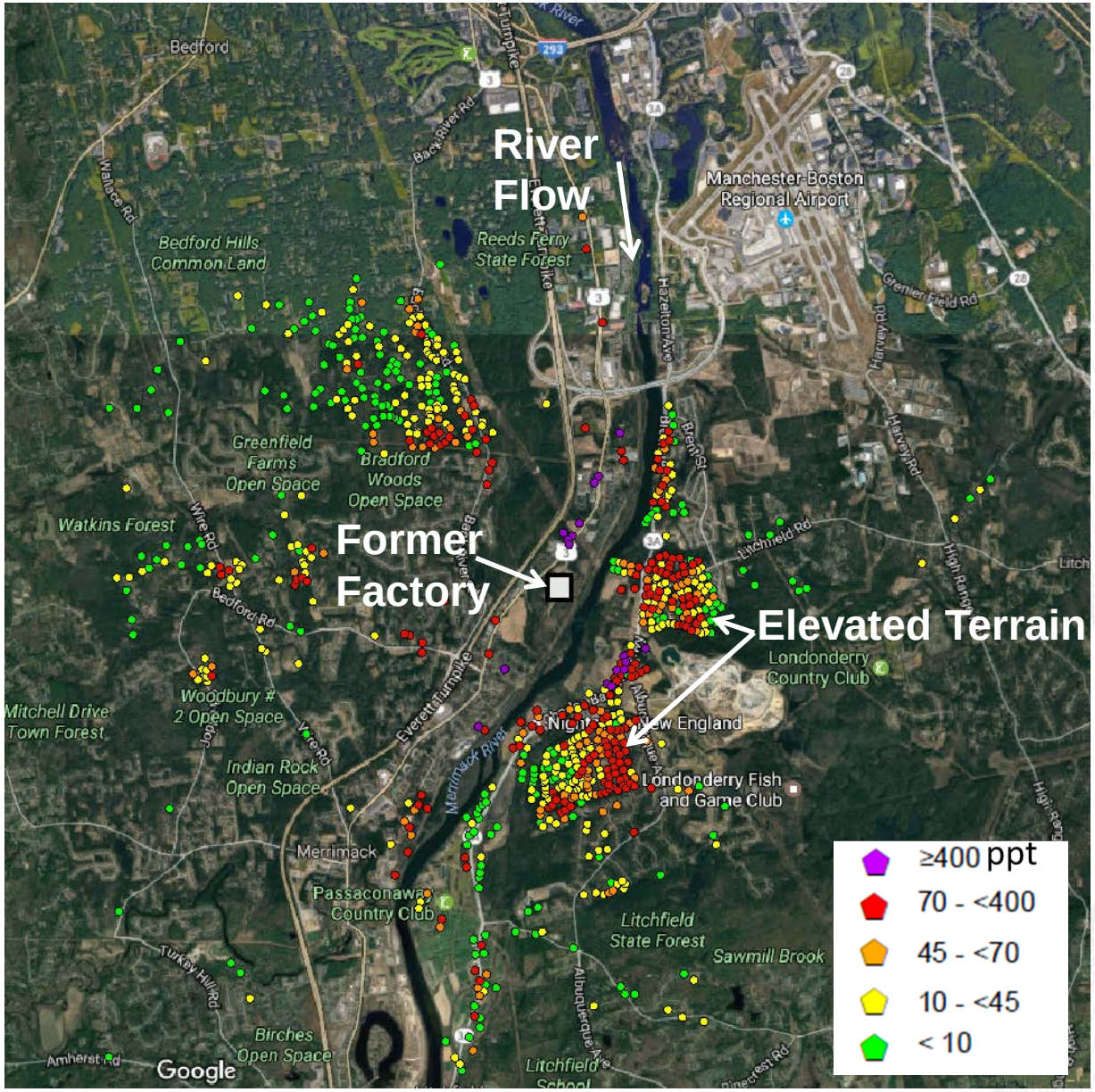
Courtesy of Gloria B. Post, NJDEP, June 5, 2013

PFAS – Airborne Transport in VT



SANBORN HEAD VT Groundwater Standard = 20 ppt

PFAS – Private Well Samples in NH



Courtesy of NH Department of Environmental Services

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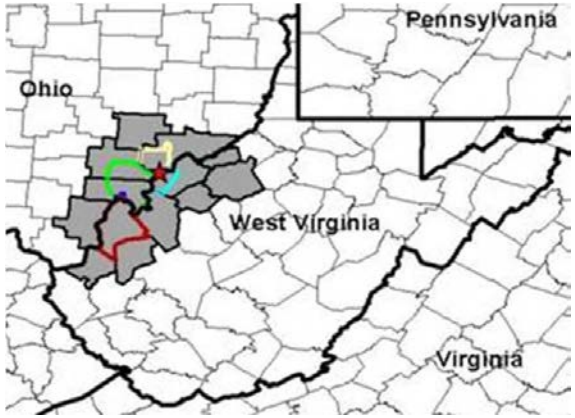
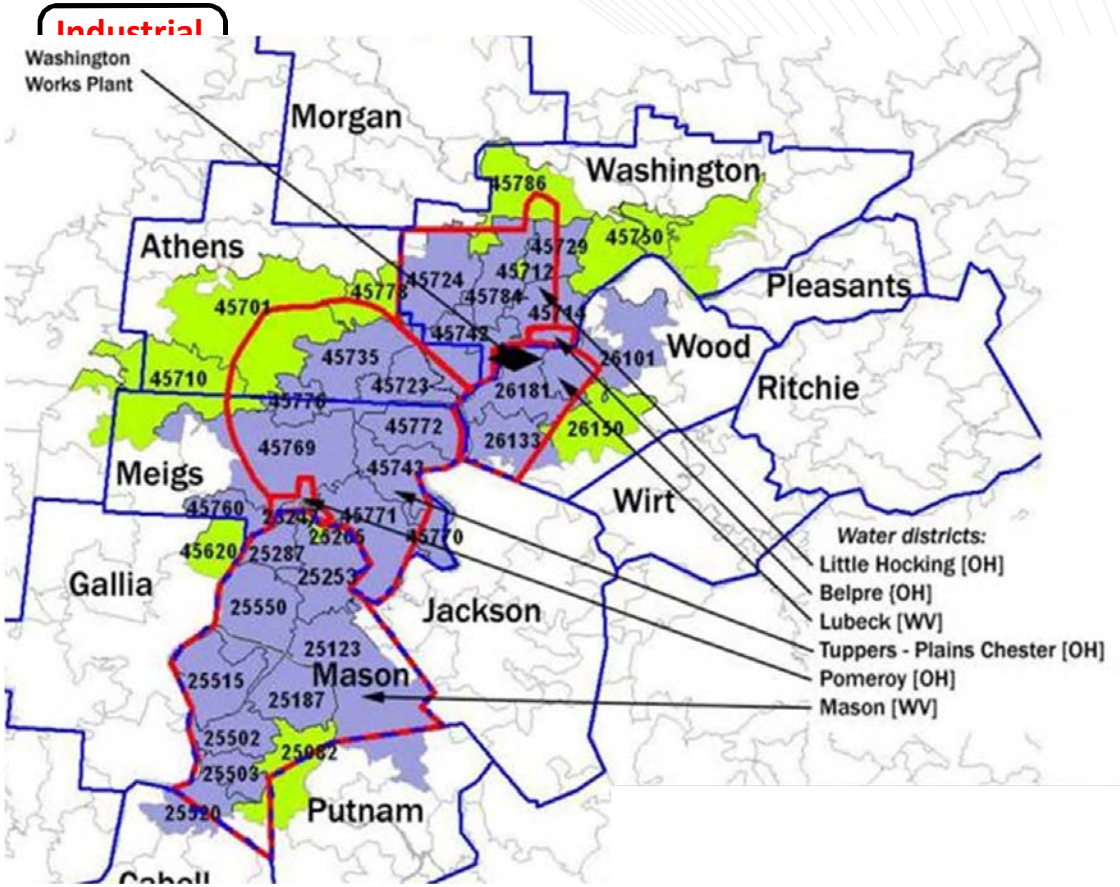
PFAS Investigation Near Manufacturing Plant

Drinking water wells up to ~20 miles from industrial source were contaminated with PFOA through air deposition (WV & Ohio).





Source: S. Frisbee, West Virginia Univ. School of Medicine. 2008.

Courtesy of Gloria B. Post, NJDEP, June 5, 2013

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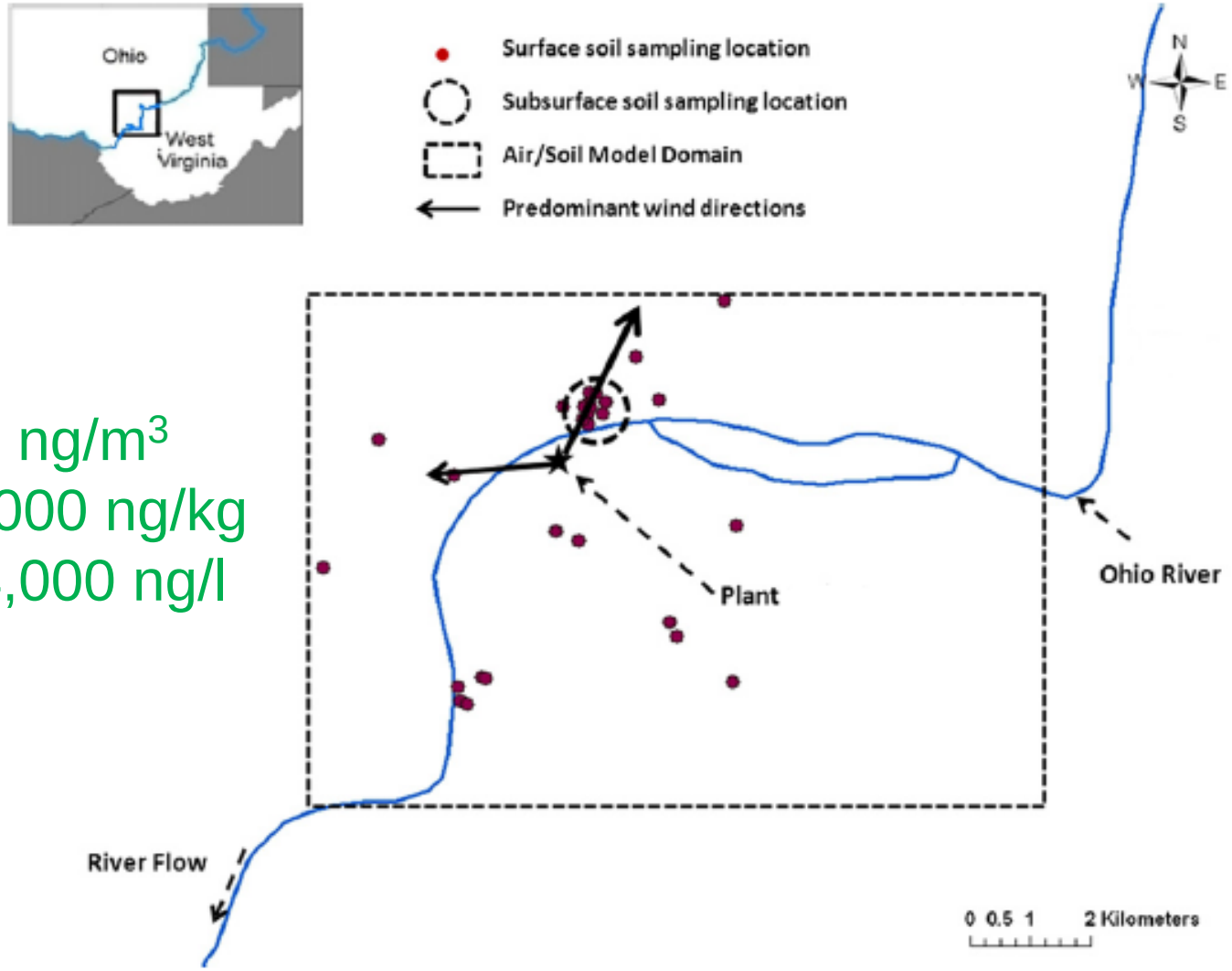
PFAS Modeling Study Example

H.-M. Shin *et al.* (2012), Atmospheric Environment 51 (2012) 67-74



Air: 200 ng/m^3

Soil: 11,000 ng/kg

Water: 4,000 ng/l

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PFAS Modeling Study Example

H.-M. Shin *et al.* (2012), Atmospheric Environment 51 (2012) 67-74

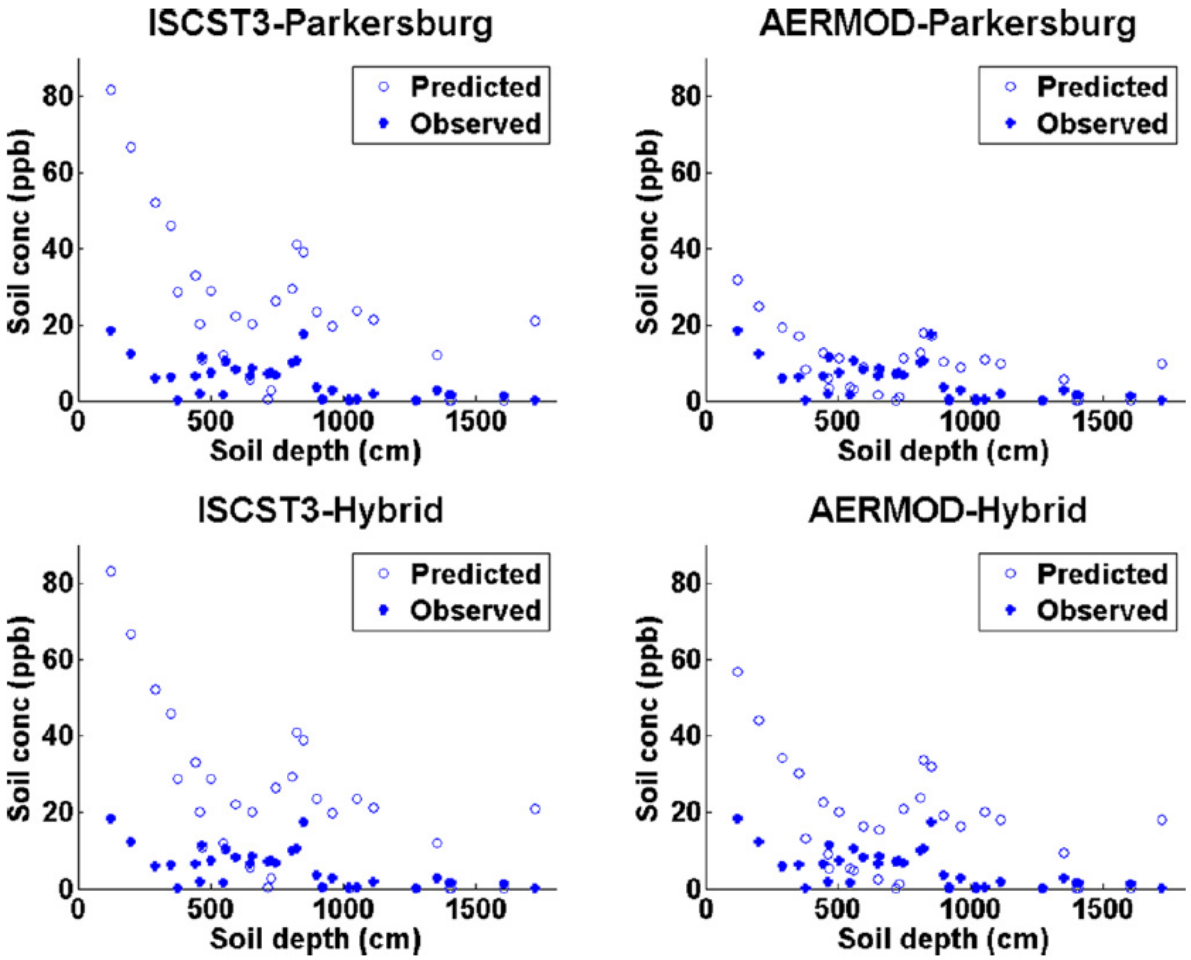

Fig. 4. Scatter plots of cross-sectional subsurface soil concentration prediction profiles by soil depths (cm). Averaged predicted and observed concentrations across sampling locations are shown as filled and blank dots, respectively.

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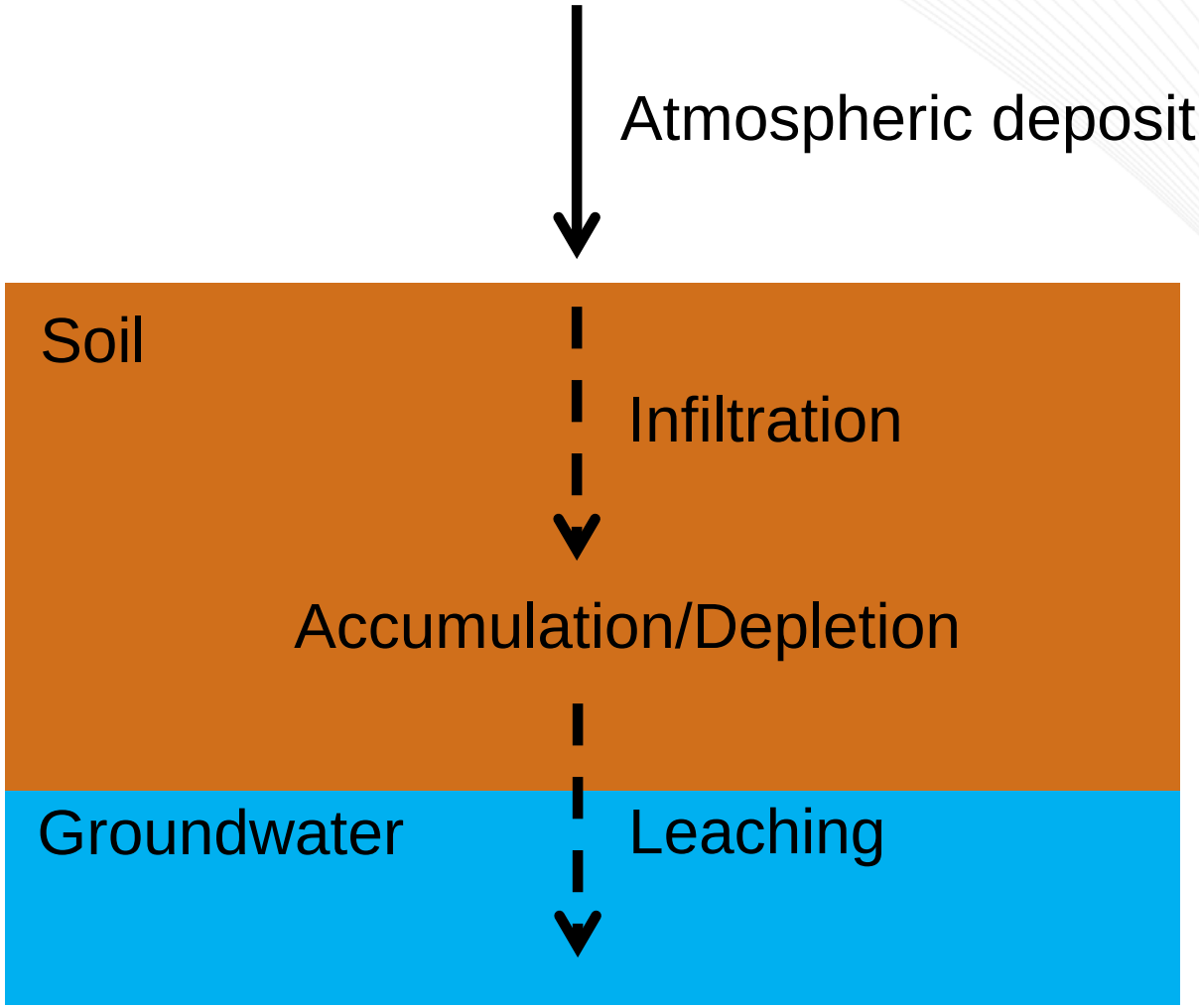
Comments on Modeling

- Basic inputs (*e.g.*, emission rates, particle size distribution, *etc.*) may be unknown or uncertain
- AERMOD deposition models are not fully validated and Method 1/2 options may give varying results
- Coupled air-soil-groundwater models may be difficult to uniquely calibrate
- Hybrid approaches that combine modeling and measurements may be prudent
- Air dispersion/deposition modeling may be useful in predicting expected patterns of PFAS deposition in the vicinity of an air emission source

Soil: The Critical PFAS Reservoir



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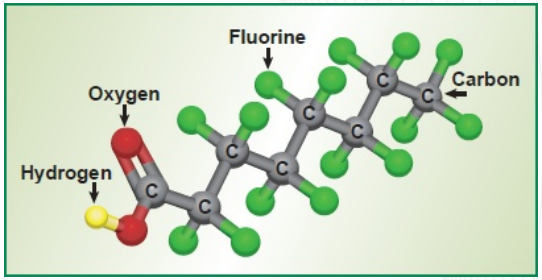
How Much PFAS in Air is Needed to Contaminate Groundwater?

- Assume:
  - PFAS deposits and mixes with precipitation
  - Deposition velocity 1 cm/s
  - 1 m annual precipitation depth
- Find by mass balance:
  - 3.2 ng/m^3 in air produces 1,000 ng/l in water
- Perspective:
  - 70 – 170 ng/m^3 detected in air near Dupont in WV



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PFAS Emissions

- Chromium plating facilities
  - Concentration 4.9 µg/m^3 in vented exhaust corresponds to 1 lb/yr PFOS (1)
  - Lake Calhoun, MN mass balance: 36 lb/yr (2)
- Dupont plant in Washington, WV (3)
  - > 10,000 lb/yr from 1978 through 2002
  - Peaked at 34,000 lb/yr (1999)

(1) NAVFAC TR-2243-ENV, March 2004
(2) https://www.minneapolisparks.org/_asset/0jd11p/water_resources_report_2015.pdf (1.8×10^7 m^3 and 4.2 yr residence)
https://www.pca.state.mn.us/sites/default/files/c-pfc1-02.pdf (average 108 ppt)
(3) Paustenbach et al (2007), *J Toxicol Environ Health* **1**:28-57

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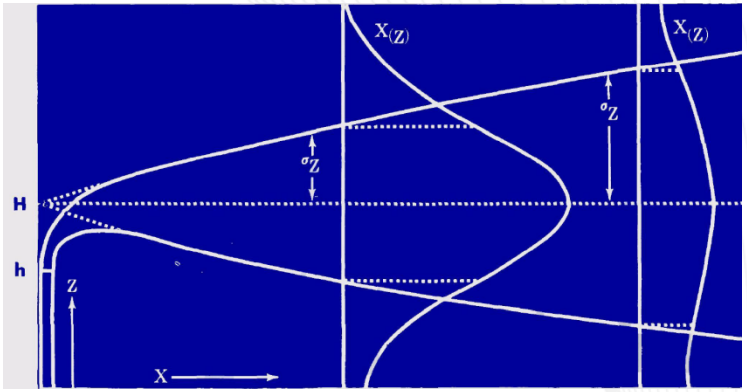
What PFAS Emission Rate Produces Observed Air Levels?

- Ballpark Assumptions:
  - PFAS in air at 10 ng/m^3
  - Emission height ~ 30 m
  - Class D/E stability
  - Wind speed ~5 m/s
  - Transport distance ~1,000 to 1,500 m



- Guesstimate:
  - Impact Cu/Q of 5.0 × 10^{-5} m^{-2} (Turner's Workbook)
  - Implied emission Q = 0.008 lb/hr = 70 lb/yr

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Is Soil a Reservoir for PFAS?

- Estimate 0.014 g/m^2 PFOA/PFOS in soil based on:
  - 10 ng/g of PFOA/PFOS in soil
  - Contaminated depth of 3 ft
  - Soil bulk density of 1,500 kg/m^3
- Annual deposition rate of 0.003 g/m^2-yr based on previous example:
  - Based of 10 ng/m^3 PFOA/PFOS in air
  - Deposition velocity of 1 cm/s

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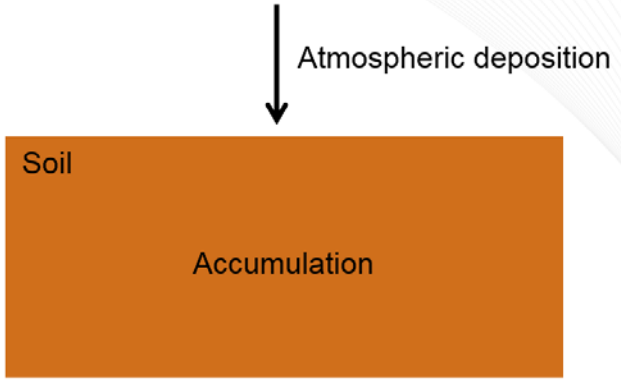
PFAS Background in Soil?

- Ballpark Assumptions:
  - PFAS in air at 10 pg/m^3 = 0.01 ng/m^3
  - Deposition velocity = 1 cm/s
  - Soil depth = 1 ft
  - Deposition time = 30 yrs
  - No loss or removal from soil
  - Soil bulk density = 1500 kg/m^3
- Find
  - Soil concentration = 0.2 ng/g



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Special Thanks!

ITRC PFAS Team: Fate and Transport Sub-team

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THANK YOU !

Discussion

QUESTIONS?

COMMENTS?

DATA GAPS?