Battelle Symposium 2023

What Are the Knowledge Gaps for Fate and Transport at Complex Sites?

Moderators

- Charles Newell, Ph.D., P.E. (GSI Environmental)
- John Wilson, Ph.D. (Scissortail Environmental)

Panelists

- Tamzen Macbeth, Ph.D., PE (CDM Smith)
- Hunter Anderson, Ph.D. (U.S. Air Force)
- Curt Stanley, P.G., CPGS (GSI Environmental)
- Natalie Capiro, Ph.D. (Auburn University, Cornell University)

Photo Courtesy of Dr. Fred Payne, Arcadis

Kick Off Discussion: *Knowledge gaps at complex sites based on the type of contaminant & hydrogeologic setting*

What is the biggest knowledge gap for:

1. **Curt Stanley:** Petroleum hydrocarbon sites?
2. **Natalie Capiro:** Chlorinated solvent sites from a basic science, R&D perspective?
3. **Tamzen MacBeth:** Chlorinated solvent sites from a field applications, practitioner perspective?
4. **Hunter Anderson:** PFAS + dioxane sites?

Mr. Curt Stanley
A Historical Perspective on Petroleum Hydrocarbon Sites

Evolution of Petroleum Investigations in Groundwater
Solving the Knowledge Gaps over Time

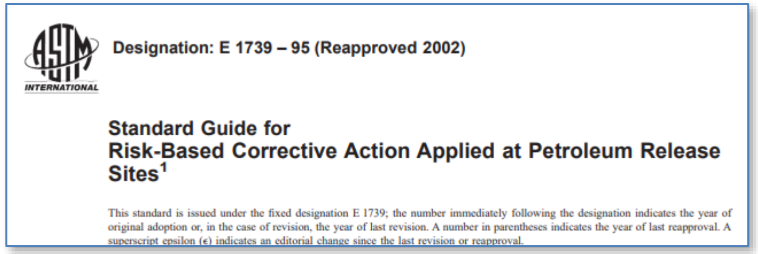
GSI ENVIRONMENTAL

It all started in the 80's with API 1628 "Guide to the Assessment & Remediation of Underground Petroleum Releases.

Timeframe	Natural Attenuation	LNAPL/*NSZD*	Oxygenates	PFAS
1980s	API	API		
1990s	Plume Studies BIOSCREEN, API ASTM RBCA, USEPA, Wiedemeier, et. al.		API	
2000s	EPA, USGS	*Johnson Paper* API, ITRC, *ITRC,* ASTM	API, EPA, HRSC/Mass Flux	
2010s	Shell GWSDAT	*Garg et al. NSZD Paper,,* ASTM, ITRC	API, Plume Studies CA Low Threat	
2020's	GWSDAT V3.1, EPA (IEc) HRSC Rpt	ITRC, CONCAWE EPA Clarification		PFAS/LNAPL Relationships?

Critical Management Milestones That Addressed Key Data Gaps

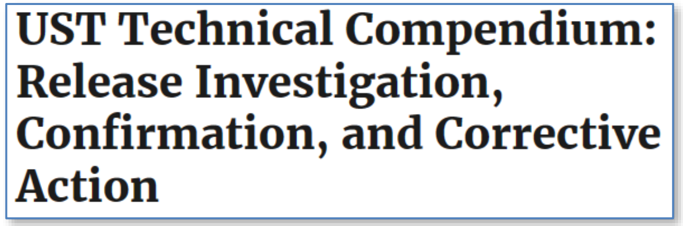
- **2006 ASTM RBCA** – utilizes a tiered approach to risk management including MNA
- **2012 CA Low Threat Closure Policy** – Establishes general & media specific closure criteria
- **2000s Oxygenate High Resolution Site Characterization** – Oxygenate properties push need for 3-D characterization
- **2023 USEPA High Resolution Site Characterization**– Quantify the costs and benefits of HRSC at UST sites
- **2023 EPA LNAPL Clarification** - “EPA does not consider that 40 CFR 280.64 requires removal of all measurable free product. **EPA considers that the objective is the removal of free product to prevent migration.”**



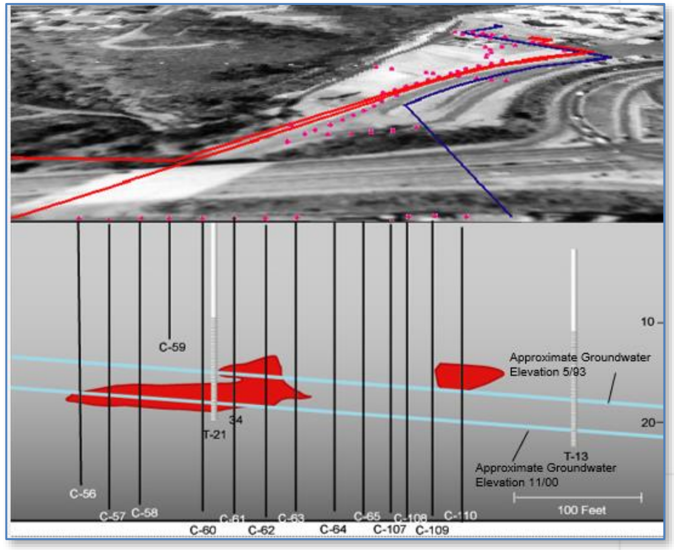
Designation: E 1739 – 95 (Reapproved 2002)

Standard Guide for
Risk-Based Corrective Action Applied at Petroleum Release Sites[1]

This standard is issued under the fixed designation E 1739; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.



UST Technical Compendium: Release Investigation, Confirmation, and Corrective Action

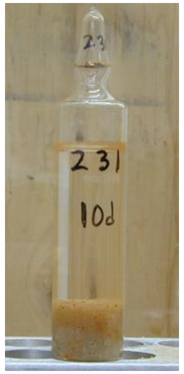


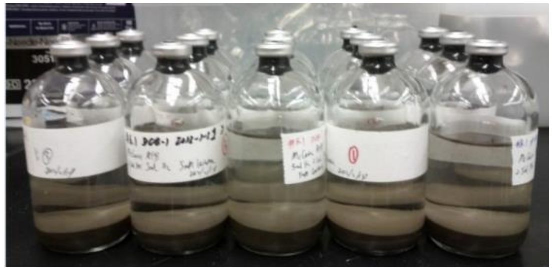
Dr. Natalie Capiro
Chlorinated Solvent R&D

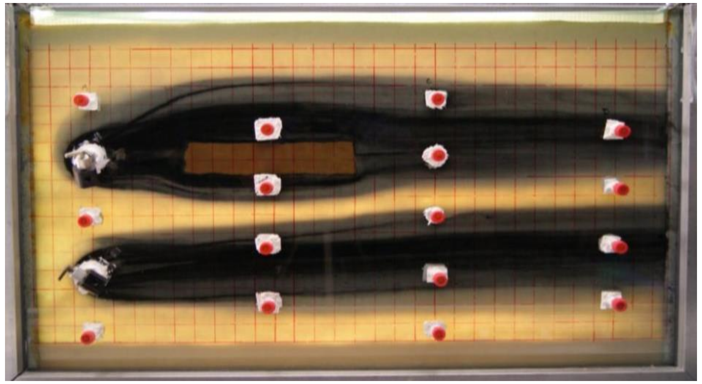
Chlorinated Solvents Research Challenges: Scale

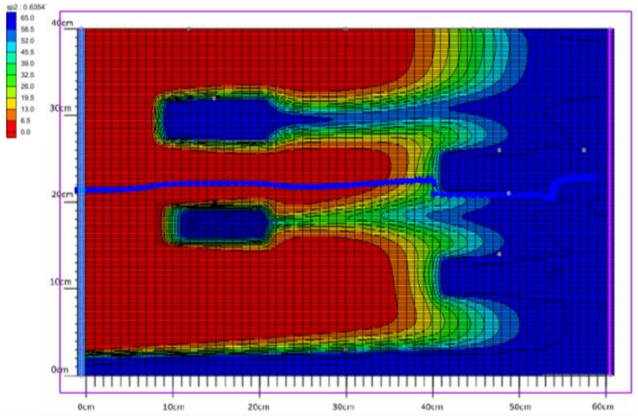
Translating lab results to field process: Balancing micro- to macro-scales

- Transport and reactivity in heterogeneous systems
- Multi-dimensional storage and release of reactive contaminants
- Temporal and spatial distributions of chemical and biological metrics





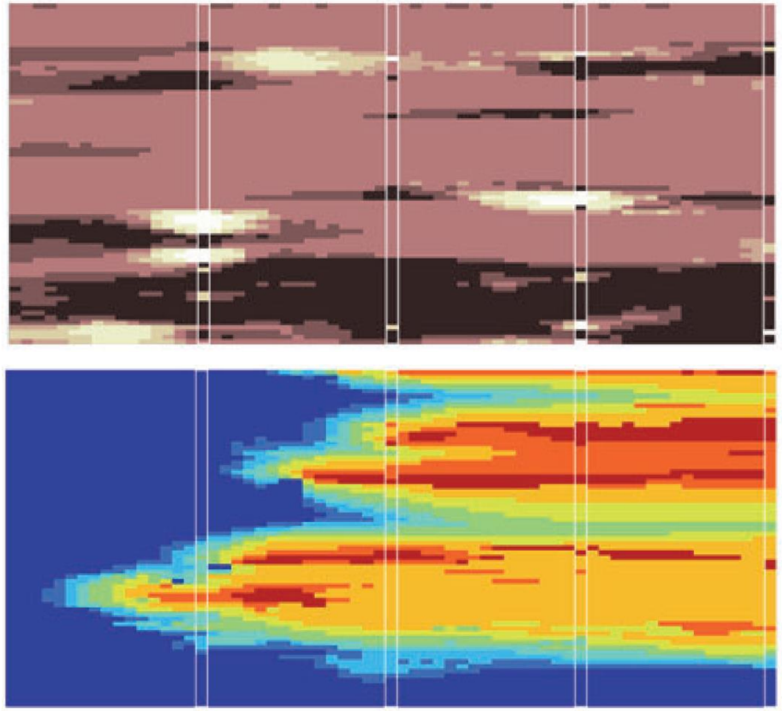




There is currently a paucity of laboratory experiments in multi-dimensional flowing systems that could help guide the development and validation of mathematical modeling tools addressing groundwater remediation issues.

Chlorinated Solvents Research Challenges: Mathematical Modeling

Using mathematical models to account for combined physical-chemical-biological processes

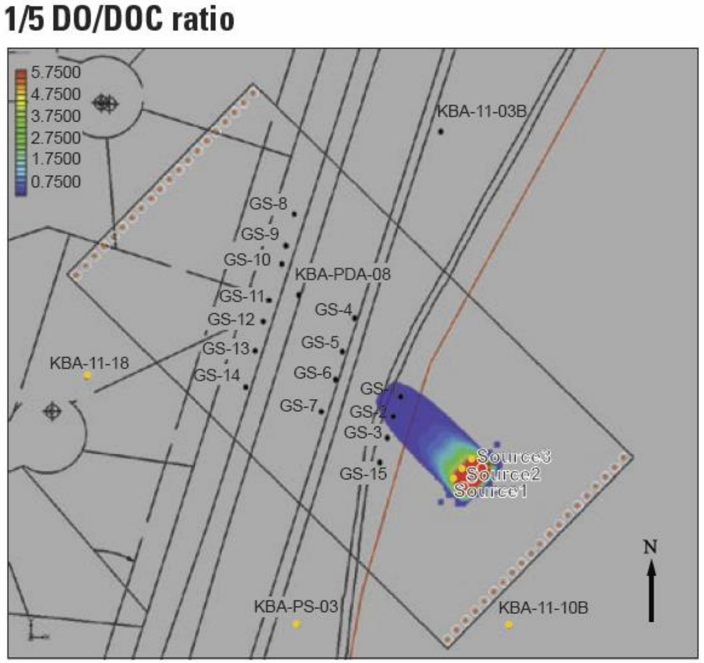


SEAM3D Transport/Reaction Model

- Biodegradation Package – spatially-varying redox zones
- Reductive Dechlorination Package – rates linked to Bio Package
- NAPL Dissolution and Reaction Packages – rate-limited mass transfer and plume persistence

PHT3D Transport/Reaction Model

- PHREEQC-2 geochemical model – abiotic reduction and oxidation of chlorinated ethenes



1/5 DO/DOC ratio

Computational models are useful tools in assessing MNA; however, no single model is ideally suited to quantify natural attenuation capacity at sites and to evaluate when it is appropriate to transition from active to passive treatment. Ensuring translation from “academic” models to field-applicable models is critical.

Chlorinated Solvents Research Challenges: Heterogeneity

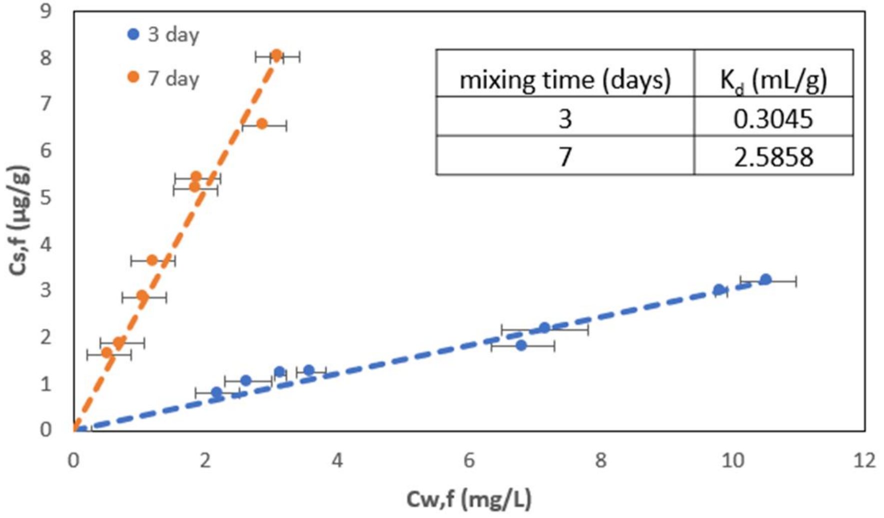
Understanding the contribution of adsorption/desorption behavior to back diffusion from low-permeability soils

Rate and extent of PCE and TCE sorption-desorption:

- Non-ideal sorption-desorption behavior (i.e., isotherm hysteresis).
- Role of non-linear adsorption on contaminant release.
- Rate-limited (non-equilibrium) desorption from laboratory- and field-aged soils.

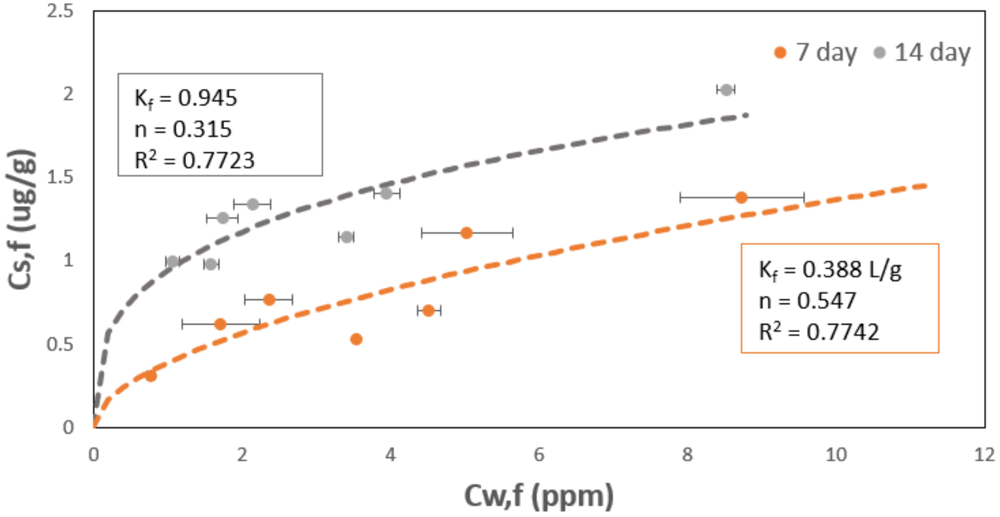
Appling Soil: OC =0.6%, Permeability = 1.20 x 10^{-11} m^2, SA= 3.50 m^2/g

Hudson Soil: OC =1.0%, Permeability = 5.13 x 10^{-14} m^2, SA= 10.47 m^2/g



mixing time (days)	K_d (mL/g)
3	0.3045
7	2.5858

Linear Soil-Water Partitioning



Freundlich Soil-Water Partitioning

Courtesy of Kurt Pennell's Lab, Brown U

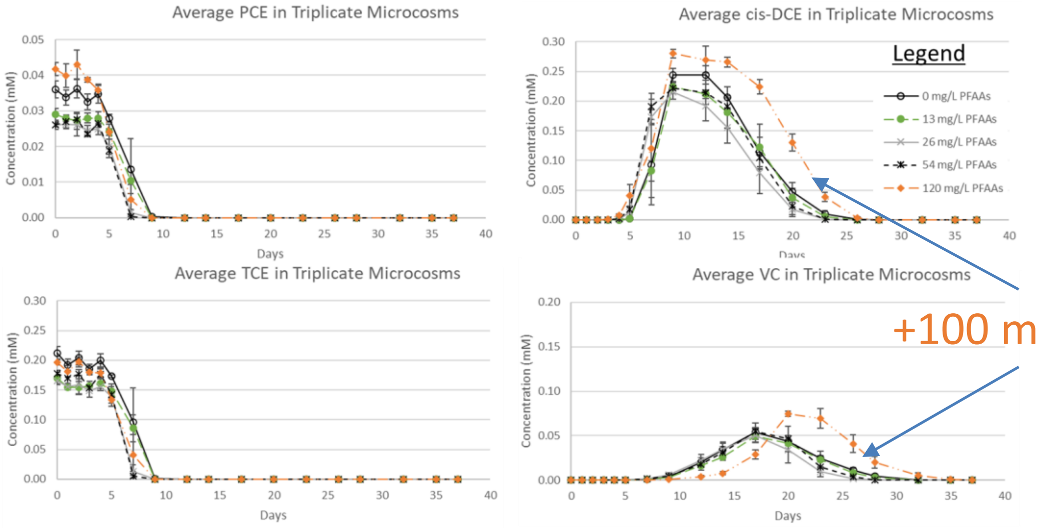
Chlorinated Solvents Research Challenges: Biological Transformations

Quantifying rates of microbial reductive dechlorination and influence of biotic transformations on contaminant mass transfer

Select impacting factors:

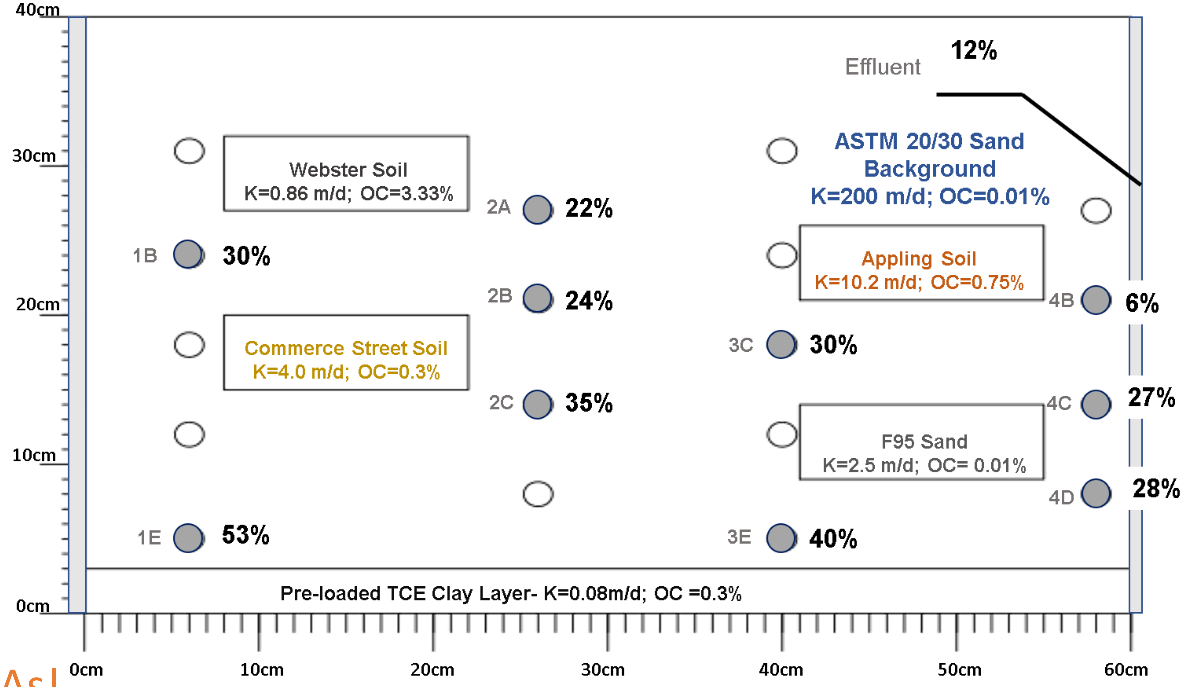
- Contaminant mixtures (co-contaminants)
- Specific microbial strains (e.g., *Dhc* RDase genes)
- Soil permeability and hydraulic conductivity
- Soil organic carbon content
- Water chemistry (pH, ionic strength, DO/redox conditions, etc.)

Transformation of chlorinated ethenes in the presence of PFAAs in microcosms (w/ soil) *Hnatko et al. ES&T (in press)*



+100 mg/L PFAAs!

Bio-enhancement (%) of Trichloroethene (TCE) Mass Transfer Relative to Abiotic Flushing Alone *Hnatko et al. Chemosphere 2020*



Chlorinated Solvents Research Challenges: Abiotic Transformations

Evaluating the relative contribution of biologically-mediated abiotic degradation (BMAD) processes

Iron Species	Transform PCE	Transform TCE	Redox condition
Magnetite	Yes[1,2]/No (after 150 days)[3]	Yes[1,2]/Very Slow[3]	Anoxic
Fe (II) +magnetite	Yes[3]	Yes[3]	Anoxic
Fe (II)	??	Yes[4]	Oxic and anoxic
Fe(II) +sulfate	Yes[5]	Yes[5]	Anoxic

[1] Wilson et al. 2018;
[2] Lee and Batchelor 2002;
[3] Culpepper et al. 2018;
[4] Schaefer et al. 2018
[5] Fan et al. 2017

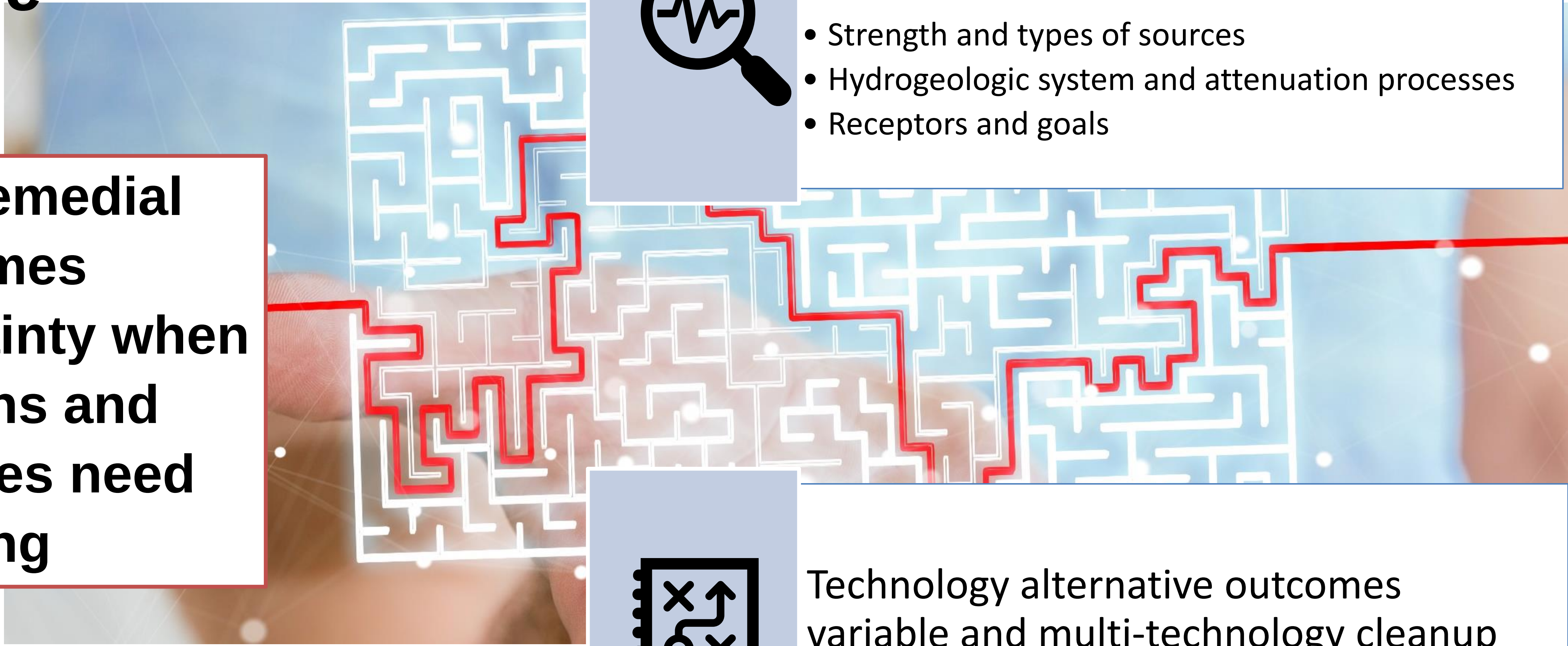
Discrepancies in BMAD results and the influence of reactive minerals have resulted in unreliable kinetic mass transfer data. In the field, the BMAD reactions might be missed due to selection of an analytical method that does not account for products in the reductive-elimination pathway (e.g., acetylene).

Dr. Tamzen MacBeth

Chlorinated Solvents – Site Scale Perspective

Chlorinated Solvent Sites: Knowledge Gap

Expectations for Closure



1. **Long remedial timeframes**
2. **Uncertainty when decisions and outcomes need validating**

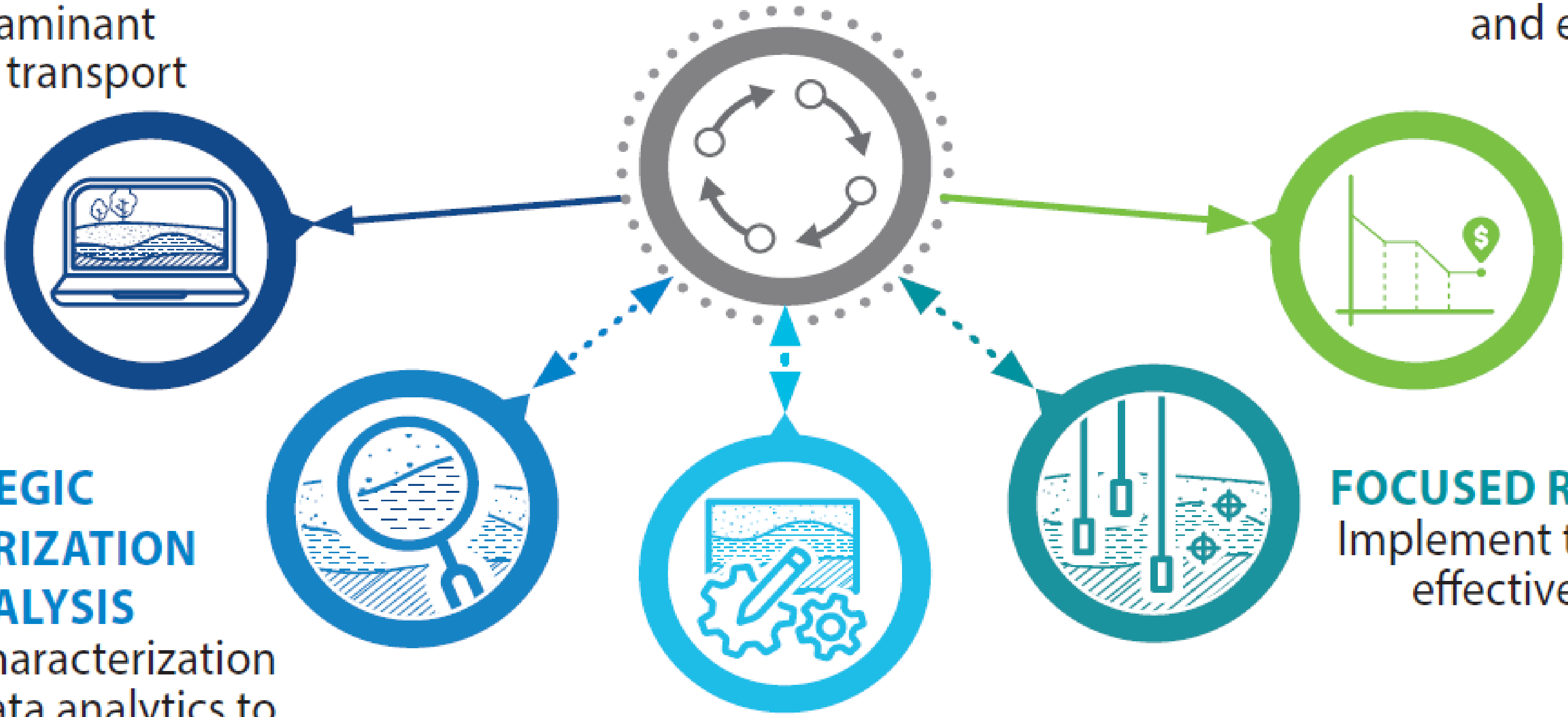
Uncertainties in Conceptual Site Model drive predictions of remediation success

- Strength and types of sources
- Hydrogeologic system and attenuation processes
- Receptors and goals

Technology alternative outcomes variable and multi-technology cleanup approaches likely

CONCEPTUAL SITE MODEL

Foundation that drives remediation decision-making



HYDROGEOLOGIC MODEL

Establish hydrogeologic model at appropriate scale to understand contaminant distribution, fate and transport

STRATEGIC CHARACTERIZATION AND ANALYSIS

Apply focused characterization and advanced data analytics to support remedy selection, design and implementation

OPTIMIZED REMEDY

Utilize data analytics and predictive analysis to optimize technology selection, design and implementation

FOCUSED REMEDIATION

Implement targeted, cost-effective remedies

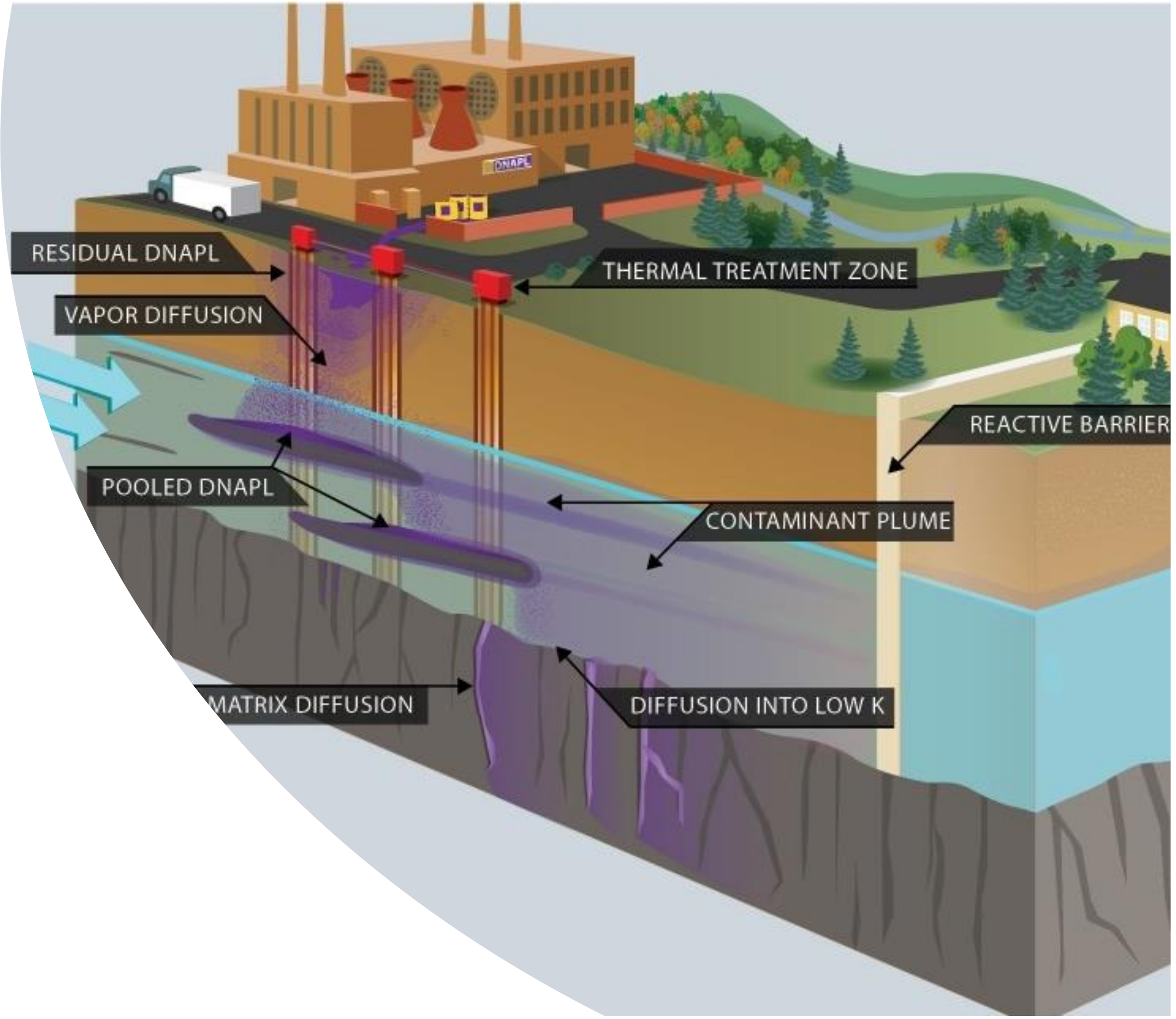
PREDICTABLE RESULTS

Achieve objectives with improved certainty, lower cost, and expedited delivery

Chlorinated Solvent Sites: Knowledge Gap

How do challenges affect outcomes?

1. Hidden sources
2. Complex environmental conditions
3. Emerging contaminants



DEFINE GOALS AND SELECT DATA ANALYTICS

Analytics

- ESS
- Statistics
- 3D Model
- Geochemical Model
- Hydraulic Model
- Fate and Transport Model
- Dashboards
- Reports
- Chemical forensics

MINE EXISTING DATA AND BUILD DATA LIBRARY

Source Data

+

Data Library

+

Data Linkages

ANALYZE AND VISUALIZE

Chemical Fingerprinting

Statistics and Predictive Modeling

Background (e.g. PFAS)

Environmental Sequence Stratigraphy

Attenuation Mechanisms

REMEDIAL DECISION-MAKING

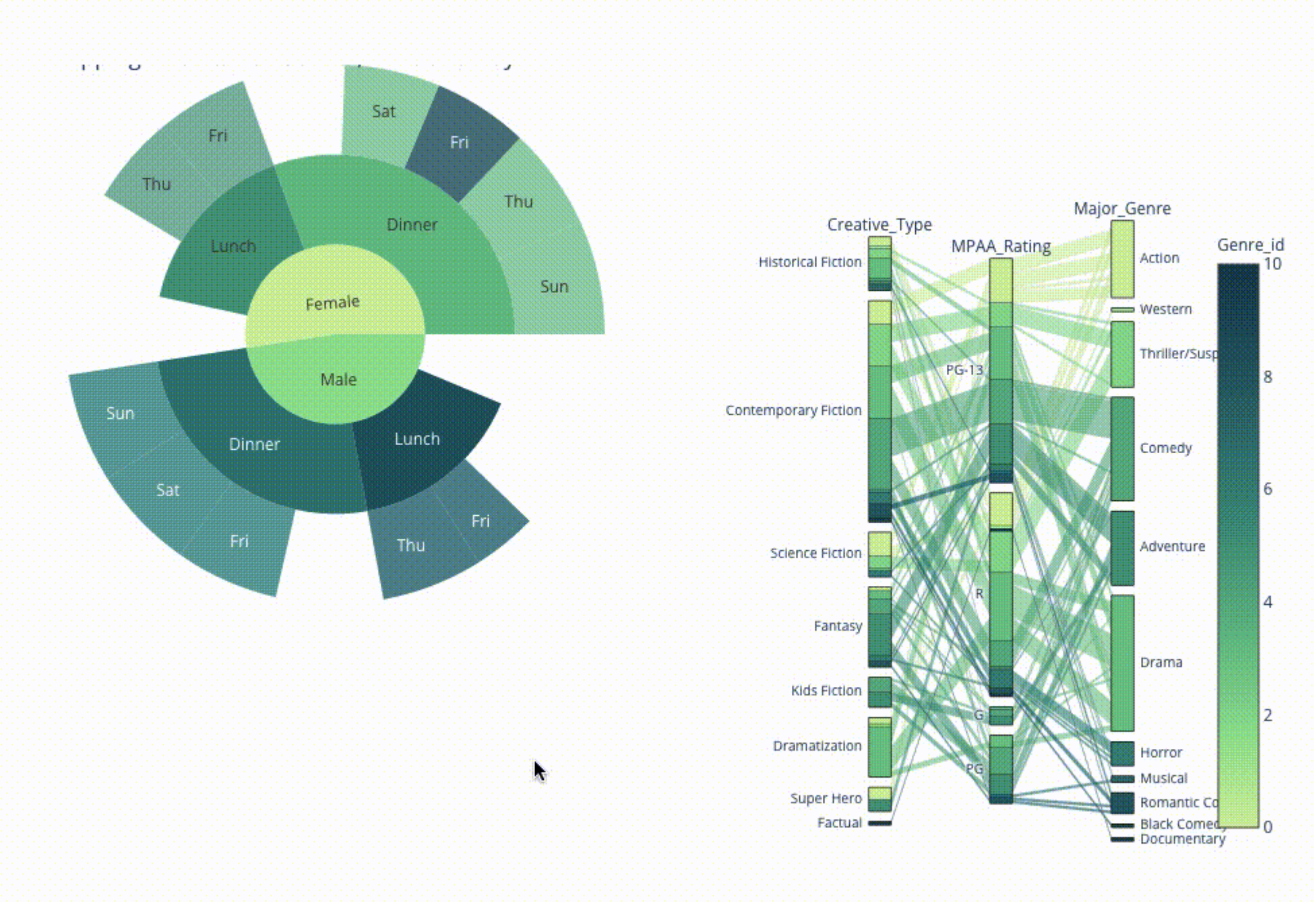
Select Remedial Technologies

Evaluate treatment performance

Optimize existing treatment systems

Predict treatment timeframe

The Future: Leverage Metadata Analysis



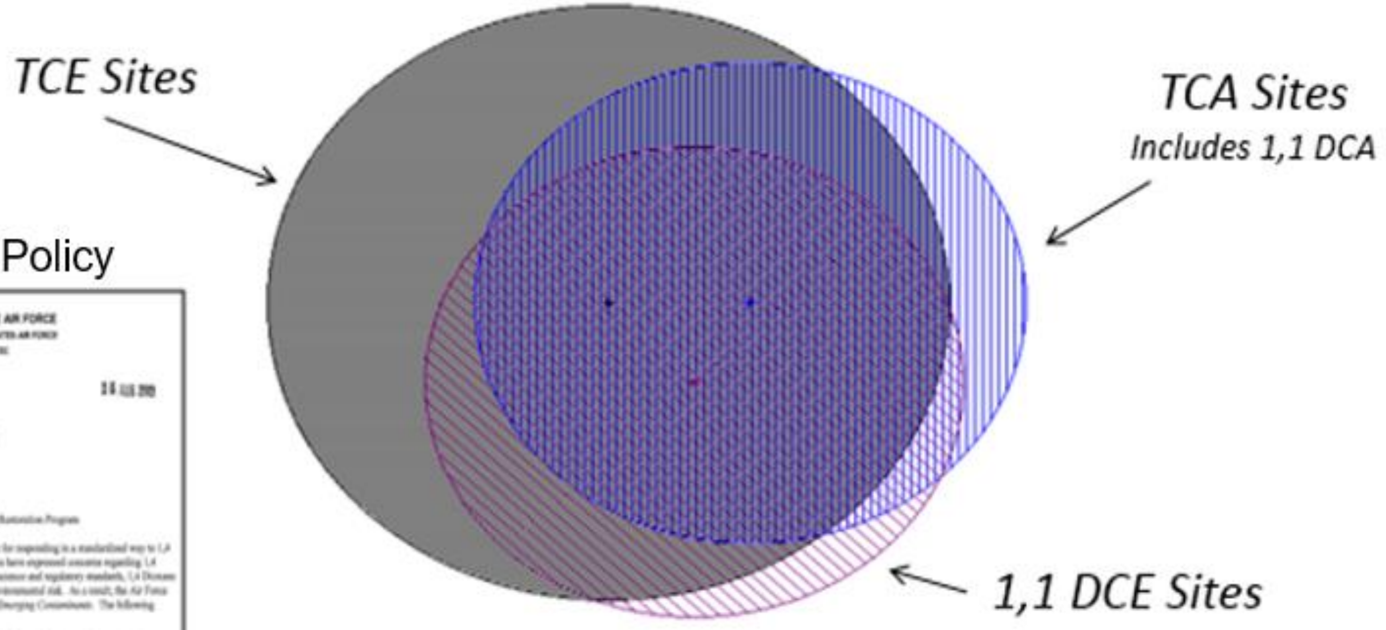
- Comprehensive programs have been implemented and a tremendous amount of data acquired
- We need integrative databases
- Rapid evaluation of problems, trends, correlations, and outcomes
- Machine Learning

Dr. Hunter Anderson
PFAS and 1,4-Dioxane

1,4-Dioxane: Current Challenges Still Related to Inventory of Occurrence

Groundwater Sites (pre-RC) with TCA and/or TCE Past/Present Sources

(Emphasis on Waste Solvent Disposal Sites)



2013 AF Policy

DEPARTMENT OF THE AIR FORCE
HEADQUARTERS UNITED STATES AIR FORCE
WASHINGTON, DC

MEMORANDUM FOR SEE DISTRIBUTION LIST

FROM: HQ USAF/A7C
1260 Air Force Pentagon
Washington, DC 20330-1260

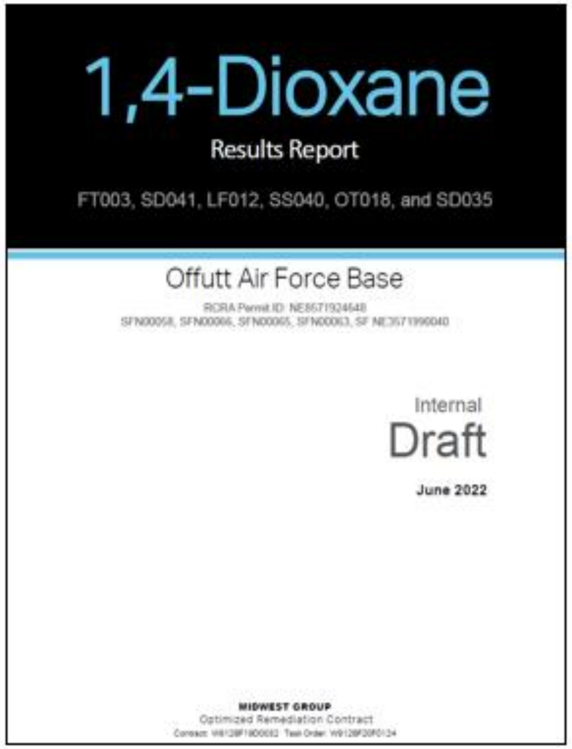
SUBJECT: Guidance on 1,4 Dioxane, Environmental Restoration Program

MARK A. CORRELL, SES, P.E.
The Deputy Civil Engineer
DCS/Logistics, Installations & Mission Support

Phased Execution Approach:

1. Confirmation Sampling
2. Full-Scale Delineation
3. Remedy Evaluation

Example Report



1,4-Dioxane
Results Report
FT003, SD041, LF012, SS040, OT018, and SD035

Offutt Air Force Base
RCRA Permit ID: NE8571924648
SFN00058, SFN00066, SFN00065, SFN00063, SF NE3571990040

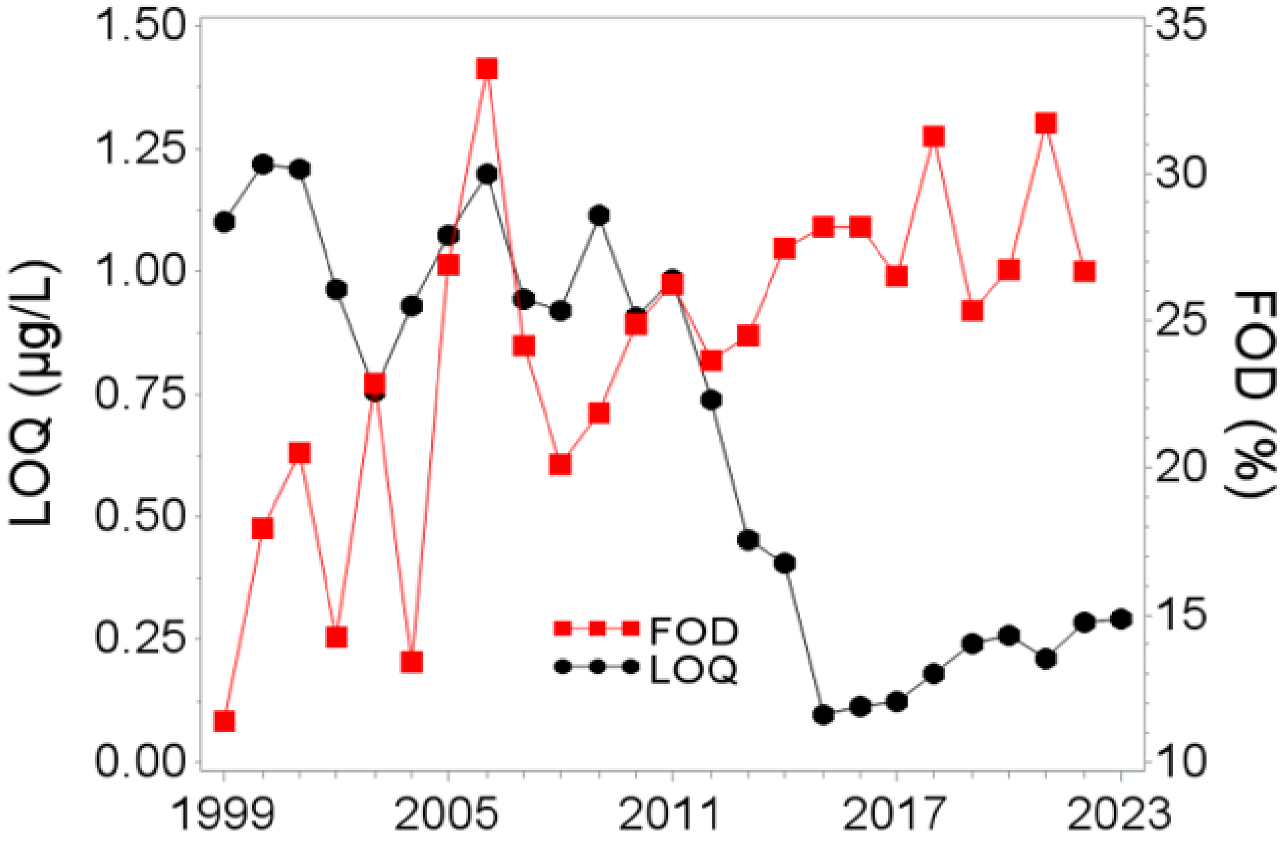
Internal
Draft

June 2022

MIDWEST GROUP
Optimized Remediation Contract
Contract: W9128F19D0032 Task Order: W9128F20F0124

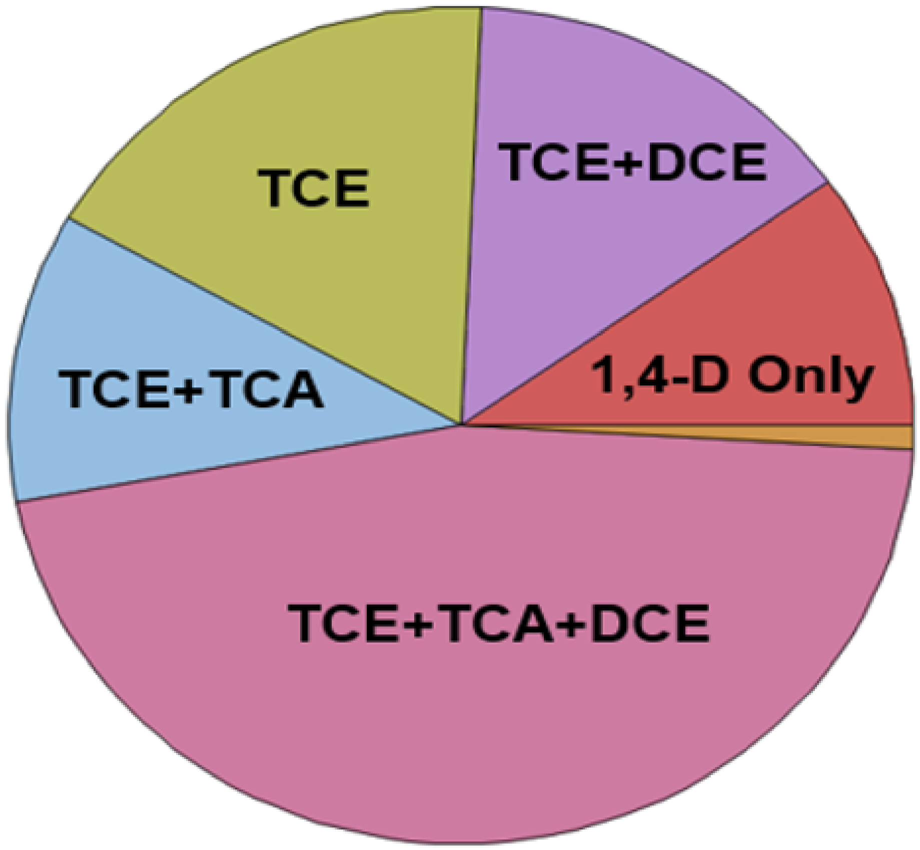
1,4-Dioxane Profile – Status Quo…

AFCEC Occurrence Profile



FOD – Frequency of Detection
LOQ – Limit of Quantification

Co-Occurrence Profile



TCE: TCE and/or 1,2-DCE and/or VC
TCA: 1,1,1-TCA and/or 1,1-DCA
DCE: 1,1-DCE

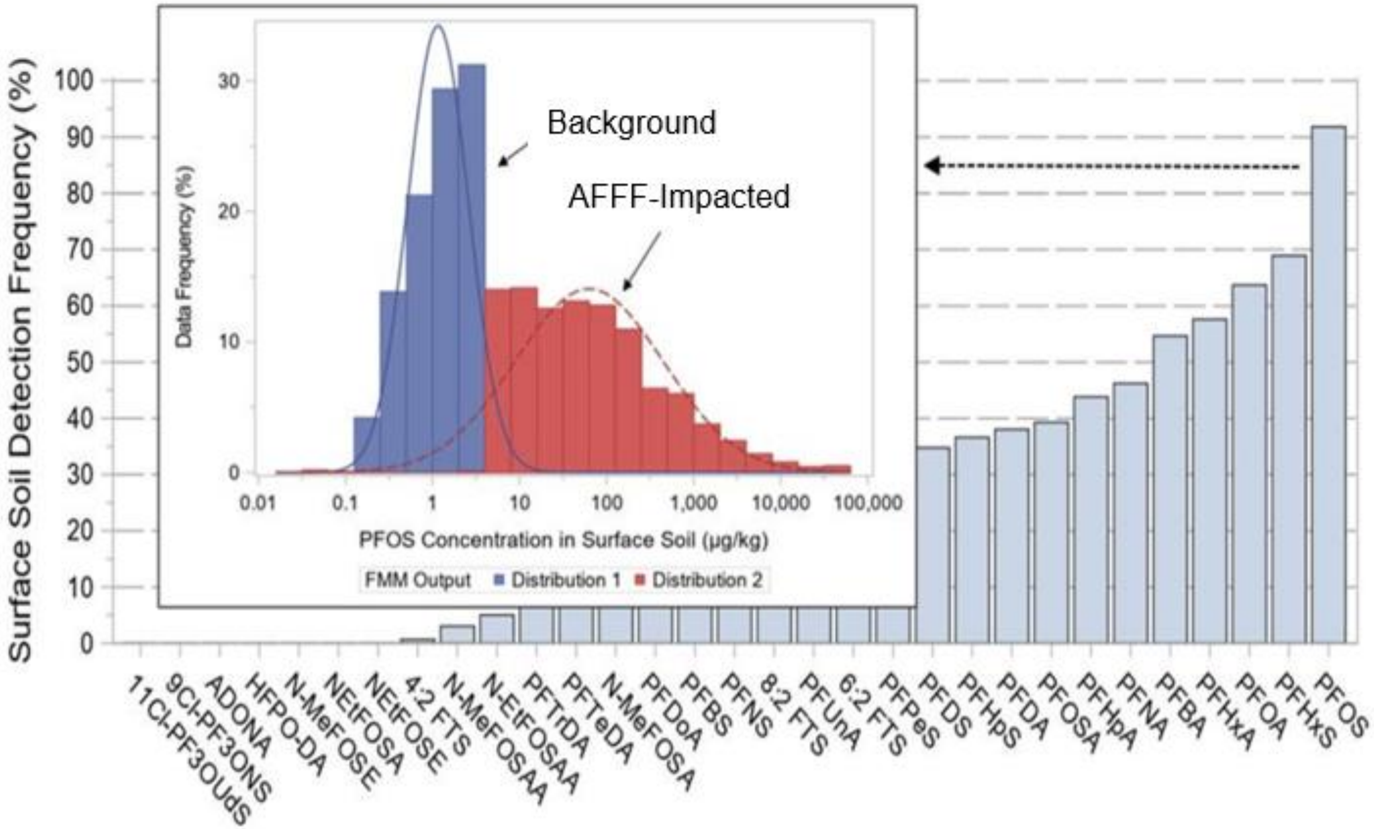
PFAS: Challenges Require a Whole New Paradigm of Remedial Practice

- **How “dirty” is “dirty”**
  - Thousands of AFFF-impacted source areas
    - How best to prioritize?
    - When is remediation required?
  - Novel retention mechanisms with focus on vadose zone transport
    - Universal surface soil releases
    - Bulk of mass in near surface soil
  - Background contamination from decades of atmospheric deposition
    - Resurgence in forensic chemistry
- **How “clean” is “clean”**
  - What are realistic remedial goals in the context of current regulatory criteria?
  - Legal requirements are highly variable
  - Long-chain vs short-chain physical properties

PFAS: "Background" is Real….

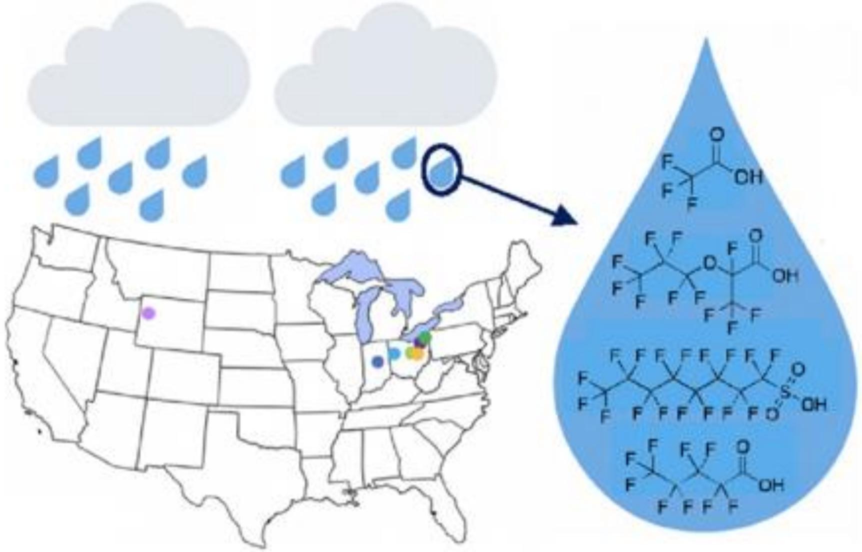
- **Global atmospheric deposition (i.e., background contamination)**
  - Mostly surface soil and surface water issue but could affect groundwater

All AFCEC Data: Finite Mixture Model (FMM) Results



Pike et al. 2020

- 100% PFAS detection frequency
- Total PFAS ΣPFAS = 50-850 ηg/L (ppt)
- PFOA = 0.2-30 ppt
- PFOS = 2-50 ppt



Focus Topic 1: What are the key challenges?

- What is the most difficult site challenge with complex sites: regulatory, technical, or cost issues?
- If you could change one factor about regulations, what would you do?
- If you could modestly improve a key technology (e.g., characterization, modeling, remediation) what would you improve?
- Can we do better at finding sources?
- How about knowledge gaps for unconsolidated versus fractured rock?

Focus Topic 2: Complex sites in 2000 vs 2023?

- What are key technologies/practices we no longer use?
- What are the key innovations since the turn of the century?
- Which subfield has progressed the most since 2000:
  - Site characterization;
  - Understanding fate and transport processes
  - Remedial technology?
- What is the most impactful paper, guidance document, regulation written in our field since 2000?

Focus Topic 3: Discuss specific knowledge gaps.

- Is the *Advection Dispersion* model still useful or should we focus on *Advection Diffusion* transport models?
- How do we recognize and characterize the features of the geology that carry groundwater plumes?
- What techniques do we have to get inexpensive, high resolution values for **K** that can go into transport models?
- What is the best place to look for sources, and what is the best tool to use?
- What would a perfect groundwater remediation model look like?

QR CODE For References