- The webinar will start promptly at 12:00 EST There will be a Q&A session during the last 10 - 15 minutes of the webinar
- All participants will be on mute
- One day after the webinar has been concluded an email will be sent that will allow you to download a copy of the webinar

- The webinar is being recorded and will also be made available via email
- Please use the “Chat” (see the icon to ask questions for the presenters. Questions will be answered at the end of the webinar. If any questions are missed due to a lack of time, we will follow-up via email after the webinar.

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Do it Right, Do it once

Treatability Testing for Remedial Applications

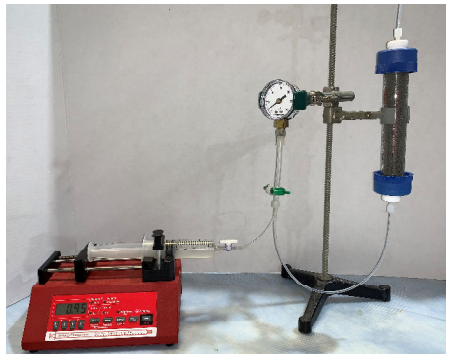
Presented by

Laurel Crawford
Treatability Laboratory Manager

September 8, 2021

Who is XDD?

- Focused on remediation since early 1980's
  - Solve difficult design problems
  - Involved in early development of remediation technologies:
    - Soil vapor extraction (SVE)
    - Air (AS) and oxygen sparging / biosparging
    - In situ chemical oxidation (ISCO) and reduction (ISCR)
    - Aerobic and anaerobic bioremediation
    - Thermally enhanced remediation
    - Vapor intrusion mitigation
- Treatability testing for end-users, consultants, and contractors
- Integrated remedial strategies



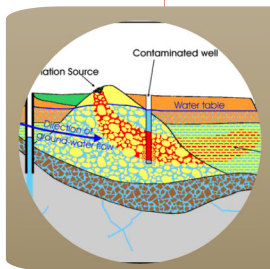
Integrated Remedial Strategies

Define Objective

- Depends on sensitivity of receptors, regulations, etc.
- Site Closure

Remedial Design

- Choosing technology (or hybrids) to meet goals
- May be non-remediation approaches



Define Criteria

- Set reasonable criteria to achieve goals
- Incorporate non-remediation approaches

Incorporate end goal of site closure into every phase of RI/FS

Feasibility/Treatability Studies

- Field data to support design, bench, pilot study

Remedial Investigation

- Focus RI to get data that support goal / criteria

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Why Conduct Treatability Studies?

- Select right site-specific technology
  - Determine potential failure mechanisms e.g., ISCO
    - Oxidant selection
    - Adverse reactions between oxidant and soil / groundwater
  - Determine field design parameters e.g., Bio
    - Need food (electron donor), nutrients, electron acceptor, correct bacteria?
    - Correct geochemistry?
  - Secondary effects (e.g., metals mobilization, unwanted by-products)
  - Site logistics (e.g., facility redevelopment, downgradient receptors)
- Certainty of success / appropriate remedial design
  - Remedial events are expensive!
  - Treatability studies typically cost less than 1/10th of field applications
  - Scale-up to field implementation

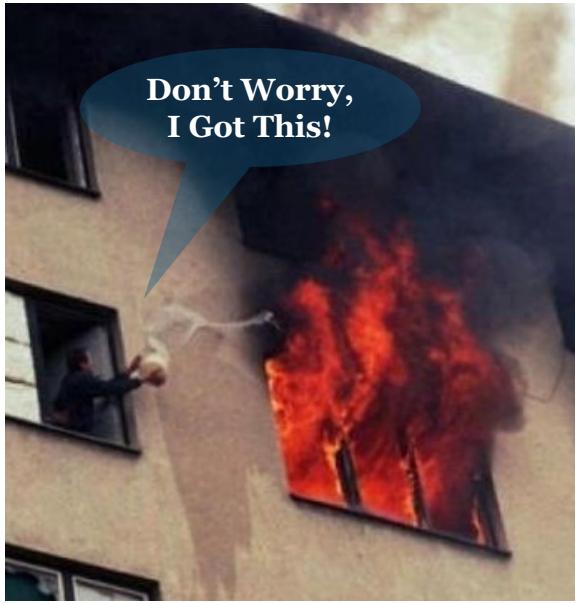
Cost Savings

Why Conduct Treatability Studies?

- Determine correct amount of reagents applied in field
  - "under-dosing" avoided, which can often result in apparent "failure" and subsequent mobilization events

You Needed This:

But What You Got Was…

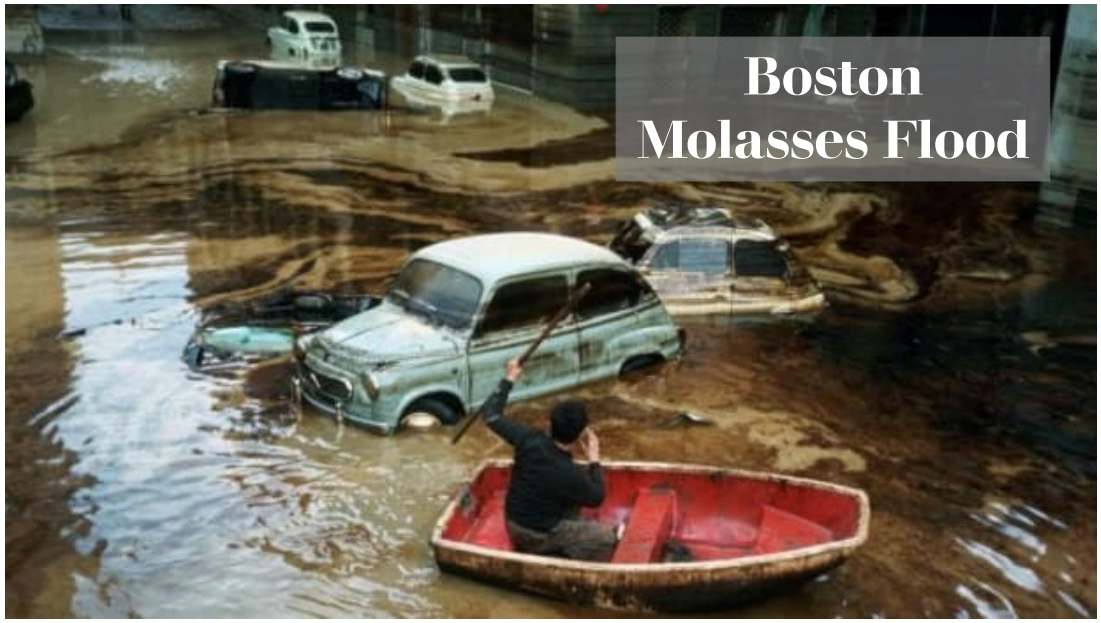


Why Conduct Treatability Studies?

- Determine correct amount of reagents applied in field
  - "over-dosing" less likely

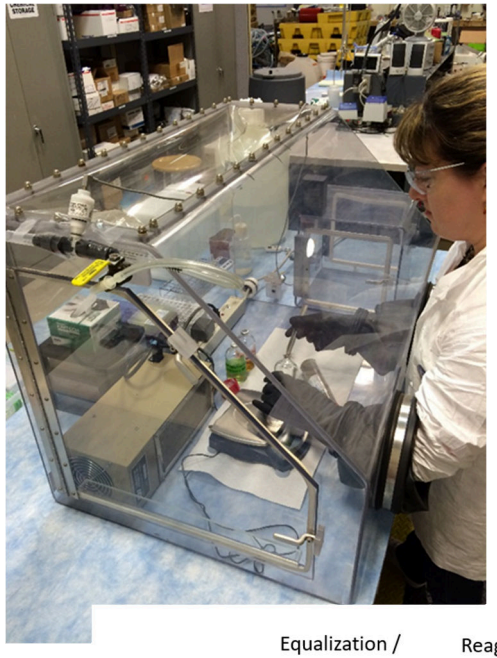
You Needed This:

But What You Got Was…

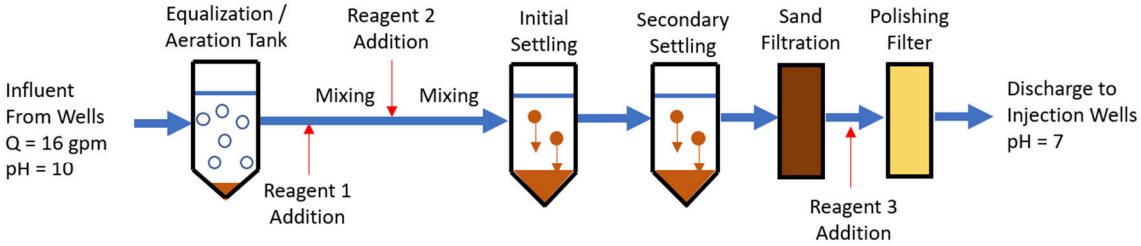


XDD Treatability Services

- Chemical Oxidation
  - Catalyzed Hydrogen Peroxide
  - Activated Persulfate
  - Solid Phase Oxidants
  - Permanganate
  - Ozone
- Chemical Reduction
  - Zero Valent Iron (ZVI)
  - Metal Sulfides
  - Mixed Reagents (e.g., EHC)
- In Situ Stabilization / Solidification (ISS)
  - Metals, VOCs, SVOCs
- Surfactant Enhanced Product Recovery



- Bioremediation:
  - Aerobic
  - Anaerobic
- Thermal Enhancements
  - SVE
  - Bioremediation
- Combined Technologies
  - ISS – ISCO
  - Treatment train approach



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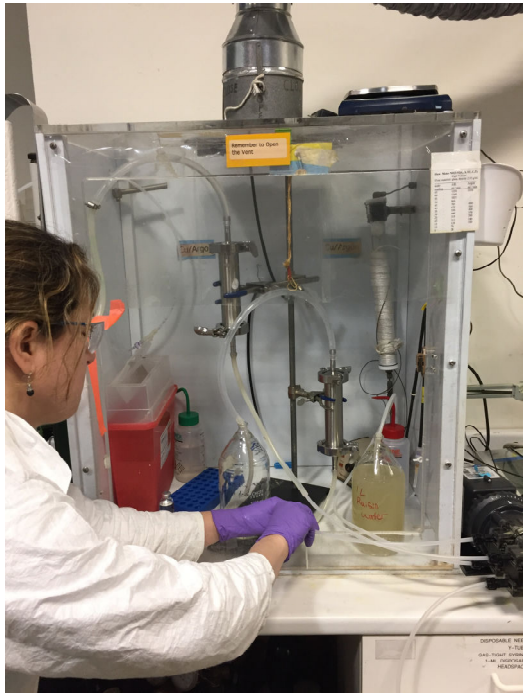
XDD Treatability Services



- In-House analytical capabilities
  - Geochemical parameters
  - Volatile Organic Compounds
  - Dissolved Gases
    - Methane, ethane, ethene
    - Acetylene
    - Oxygen, carbon dioxide
- Permitted to receive / test international soils
- Research-funded testing
  - SERDP metals immobilization during ISCO
  - PFAS
- Customized testing

State of the Practice vs. State of the Art

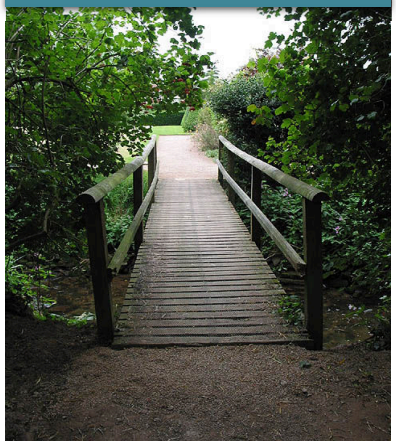
Complex Remediation Concepts are Being Packaged in Easy to Use Products, Still Need to Apply With Care

State of the Practice

- Initial low cost
- Limited or “rule of thumb” design
- Lower certainty of success
- Ultimately higher cost?

Short-Term Cost Pressures

State of The Art



- Potentially initial higher cost
- Appropriate testing and design
- Higher certainty of success
- Ultimately lower cost?

Common State of the Practice

"Testing is a Design Tool. Not R&D"

- Remedial design steps often skipped
  - Treatability / pilot testing
    - Determine site-specific design parameters (TOD)
    - Confirm dosing
    - Identify interferences (COD, BOD, abiotic reactions)
    - Site geology / hydrogeology
    - Heterogeneity in COCs, geology
- Remedial design using dosing spreadsheets?
  - Usually minimum dosing / application recommended
  - Good start…provides starting point
  - Additional evaluation often recommended by vendors
  - ….and often ignored….

	A	B	C	D	E
1	OXIDANT/REAGENT VOLUME CALCULATIONS - This sheet takes the soil / groundwater volumes and contaminant mass estimat				
2	Site:	<Enter Site Name>			
3	Revision Date:	<Enter Data>			
4					
5					
6	Area 1				Eff. Pore Vol. (Gal) (from 'Site Info" Tab) =
7					Soil Mass (LBs) (from 'Site Info" Tab) =
8					
9	Peroxide (CHP) Injection Volume Estimates - Requirement for Contar				
10	Contaminant Demand (LBs H_2O_2) (from "Ox_Mass" Tab)				
11	Stock Peroxide Solution Calculations:				27% Stock Soln.
12	Peroxide Mass (LBs H_2O_2)				14,158
13	Peroxide Stock Soln. Volume (Gal)				1,542
14	Dilution Water Required to Yield Field Strength (Gal)				Dilutic
15					27% Stock Soln.
16					4.84
17					7,465
18	Total Diluted Peroxide Volume (Gal) (total volumes differ slightly due to minor rounding error)				9,007
19	Injection Pore Volumes Req'd to Emplace Oxidant Mass For Contaminant Demand [1]				0.15
20	Citric Acid, Monohydrate (LBs $C_6H_8O_7{*}H_2O$)		Molar Concentration (mM)>>>	100	1,580
21	Straight Pore Volume Dosing Calculation - Assumes Full Pore Volume at Desired Field Concent				
22					27% Stock Soln.
23	Total Peroxide Volume (Gal) to Dose Desired Pore Volume (copied from Row 13 above)				1,542
24	Total Dilution Water Volume (Gal) to Dose Desired Pore Volume				28,754
25	Total Injection Volume (Gal) at Desired Field Concentration =				30,296
26	Injection Pore Volumes Req'd to Emplace Oxidant Mass For Contaminant Demand				0.5
27	Required Oxidant Concentration to Emplace Oxidant Mass For Contaminant Demand				1.51%
28	Citric Acid, Monohydrate (LBs $C_6H_8O_7{*}H_2O$)		Molar Concentration (mM)>>>	100	5,314

Steps are Critical for Accurate Cost and Performance Assessment

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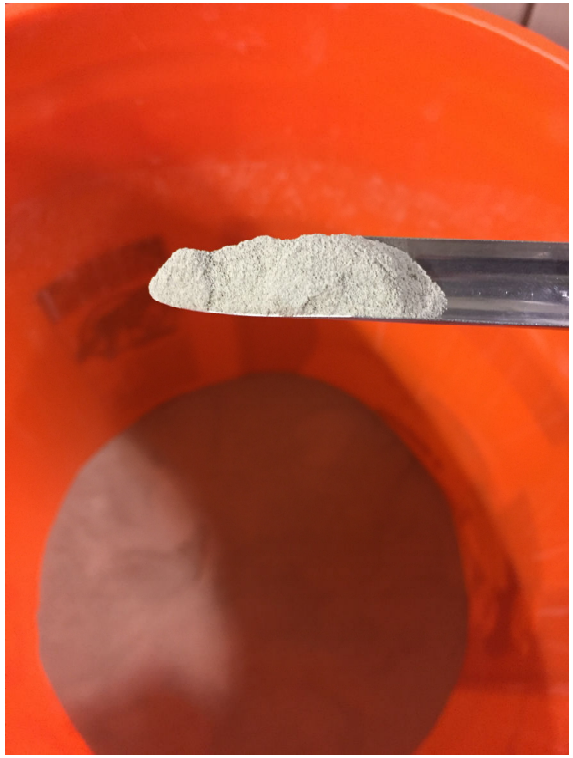
Case Study 1: Oxygen Release Compound Mass Loading

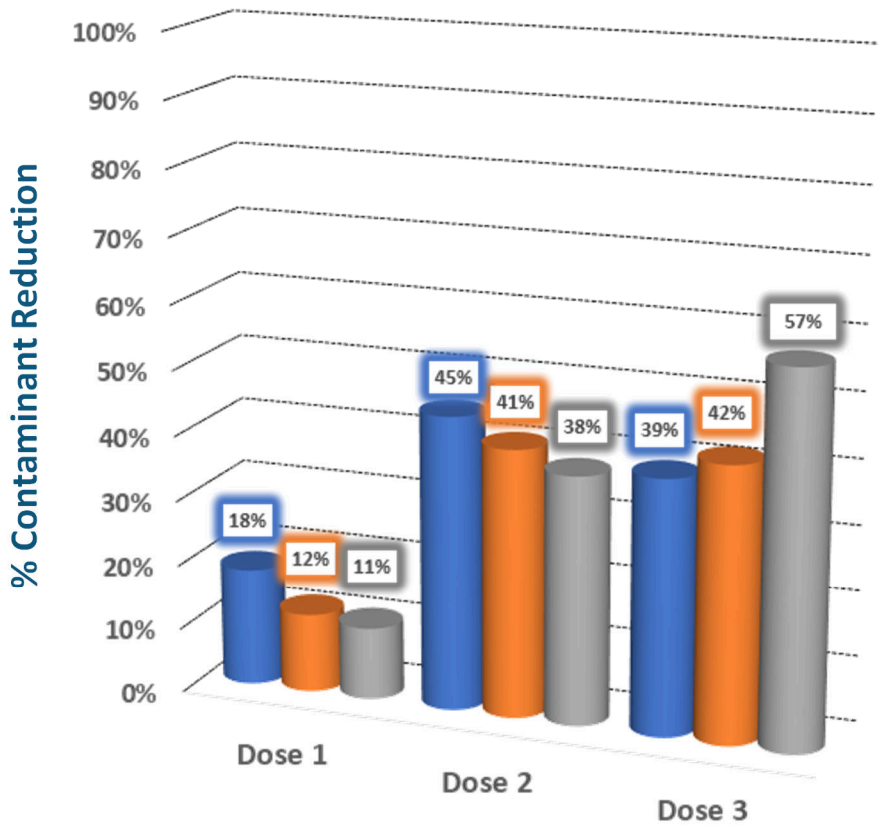
- Superfund site
  - Multiple source/plume
  - chlorinated solvents, petroleum hydrocarbons
- Comparison of oxygen release products
  - Evaluated 3 oxygen release compounds
  - Requested dosing recommendations from each product vendor to hit goals
  - Tested 3 products at highest recommended dosage out of the 3 products*

* Some of above vendors recommended treatability testing to validate dosage assumptions



Case Study 1: Oxygen Release Compound Performance

Vendor Design Estimated >90% Reduction with Single Dose

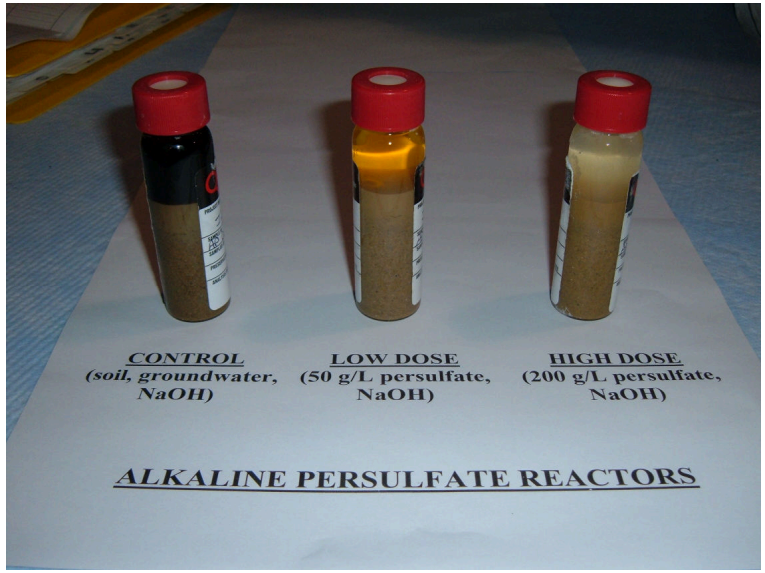


All Products Failed Even After 3 Applications at the Maximum Recommended Dosage

A Little More About the Details

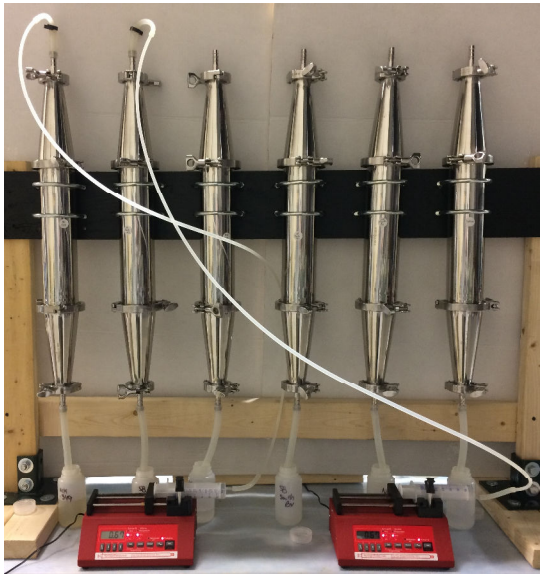
Treatability Test Details

- Controls
  - Bio: killed control
  - ISCO: no oxidant (site media only)
- Duplicate or triplicate reactors
- Test Duration
  - ISCO, ISCR, ISS: 2 days to 8 weeks
  - Bio: 2 to 6 months
- Media Requirements
  - Soil: 2 to 30 pounds
  - Groundwater: 1 to 20 liters
  - NAPL (if spiking necessary)
  - From area of interest
- Costs
  - $2,000 to $50,000 or greater (function of scope, technology, number of samples, etc.)



Treatability Test Details

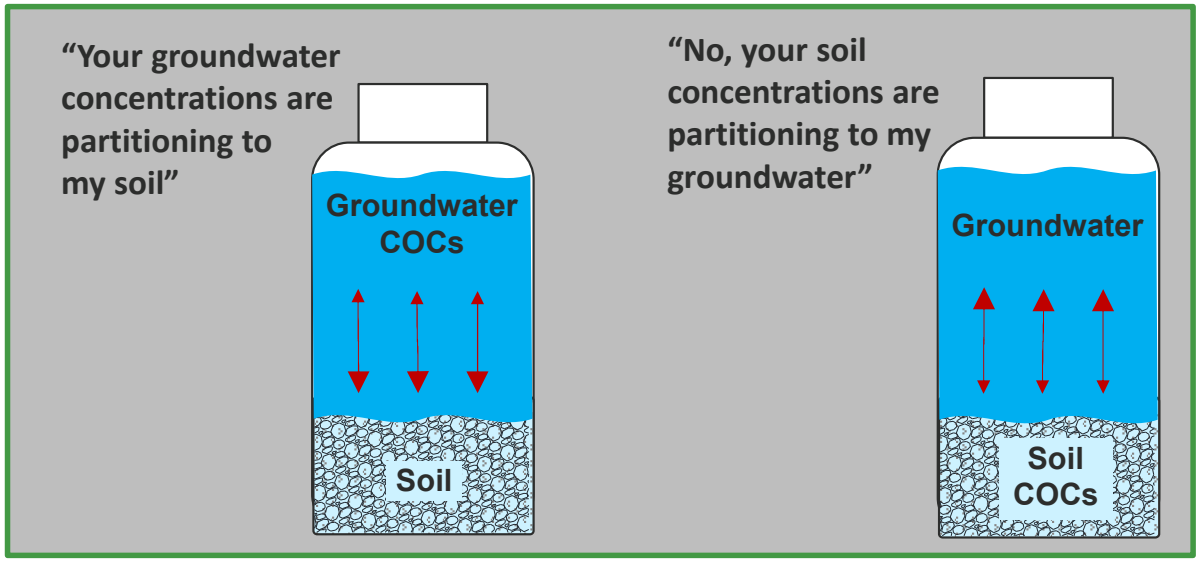
- Phased approach / Multiple technologies
  - Screening tests for emerging contaminants (e.g., PFAS)
  - ZVI, Bio
    - Batch reactors – determine approximate kinetics, dosage, product
    - Columns – select appropriate product to refine kinetics and dosage
  - ISCO
    - Phase I - determine failure mechanisms
      - test multiple oxidants for TOD, pH buffering, stability
    - Phase II – contaminant destruction evaluation
      - select best oxidant based on Phase I



- Test to approximate field conditions!
  - Groundwater to soil ratio (typically 1 to 2 pore volumes of reagents)
  - Groundwater temperature
  - Samples from area of interest and native condition

Treatability Test Details

- Incorporate / analyze both soil and groundwater
  - Mass Balance
  - Need to account for partitioning effects – highly variable
    - Koc (soil sorption coefficient)
    - Foc site-specific (soil organic carbon fraction)



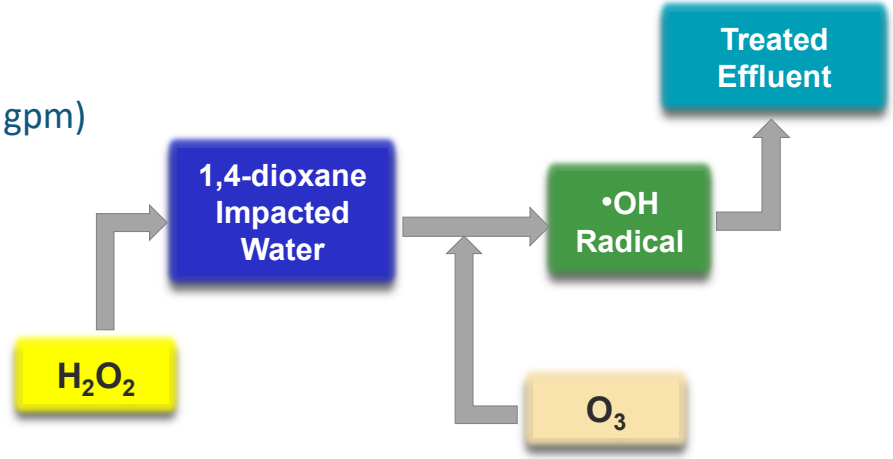
Case Study 2: Oxidant Stability Issue

- Chlorobenzenes in weathered bedrock and soil
- Catalyzed hydrogen peroxide (CHP) selected by USACE
- Bench tested CHP and persulfate to verify feasibility
  - CHP worked well….but short half-life
  - Activated persulfate worked well, and more stable…
  - Recognized advantages of persulfate system, but…..
- Required to conduct side by side pilot tests to prove:
  - CHP failure (minimal effective ROI / instability)
  - Persulfate successful due to enhanced stability / contact
- Persulfate applied successfully full-scale
- Saved $100,000's on a failed application

Northeast Superfund Site

Case Study 3: Ex Situ Advanced Oxidation

- Landfill site w/ suite of COCs
  - Existing leachate / groundwater extraction system (50-100 gpm)
  - Powdered activated carbon (PAC) / sand filtration
  - 1,4-dioxane up to 322 µg/L - not treated by PAC / filtration
- Advanced Oxidation Process (AOP)
  - H_2O_2 plus O_3 produces hydroxyl free radical (•OH)
    - proven effective on emerging contaminants (e.g., 1,4-dioxane)
  - Bench evaluated various concentrations of H_2O_2 and O_3



- Goal: treat 1,4-dioxane to criteria while maintaining by-products within regulatory standard
  - Complication: Bromate (BrO_3^-) is a common disinfection by-product formed during water treatment processes (e.g., chlorination, direct ozonation, AOP, etc.)
  - Bromide at site (up to 1,300 µg/L) pre-curser to bromate formation
  - MCL for bromate - 10 µg/L in drinking water

Case Study 3: AOP Effects on 1,4-Dioxane and Bromate

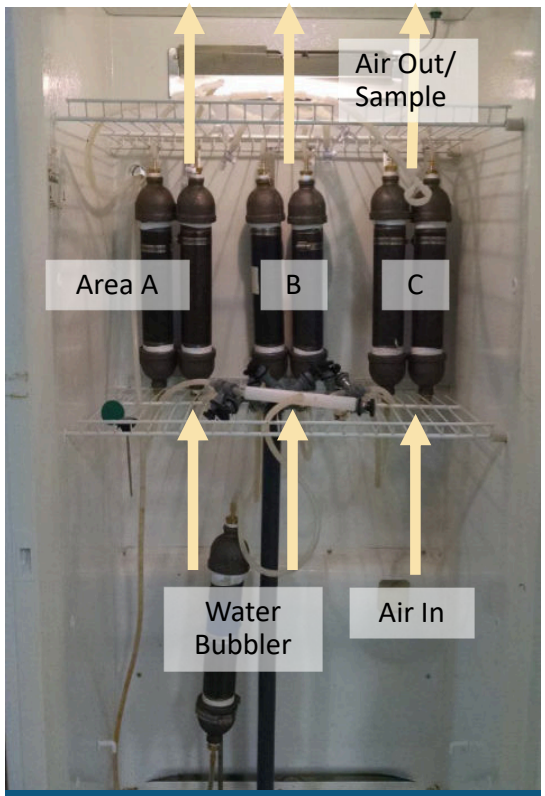
240 µg/L 1,4-dioxane baseline			
Test Scenarios		Impact on 1,4-Dioxane	Impact on Bromate
H_2O_2 (mg/L)	O_3 (mg/L)	Final 1,4-dioxane (µg/L)	Final Bromate (µg/L)
3.6	5	48	64
7.1	10	6.6	190
9.2	13	1	290
14.2	20	1	430
H_2O_2:O_3 Molar Ratio = 1		1,4-dioxane decreased as O_3 dose increased	Bromate increased as O_3 dose increased

Conclusions:

H_2O_2:O_3 molar ratio required optimization to reduce bromate formation.

Case Study 4: Thermal SVE / BV - Bench

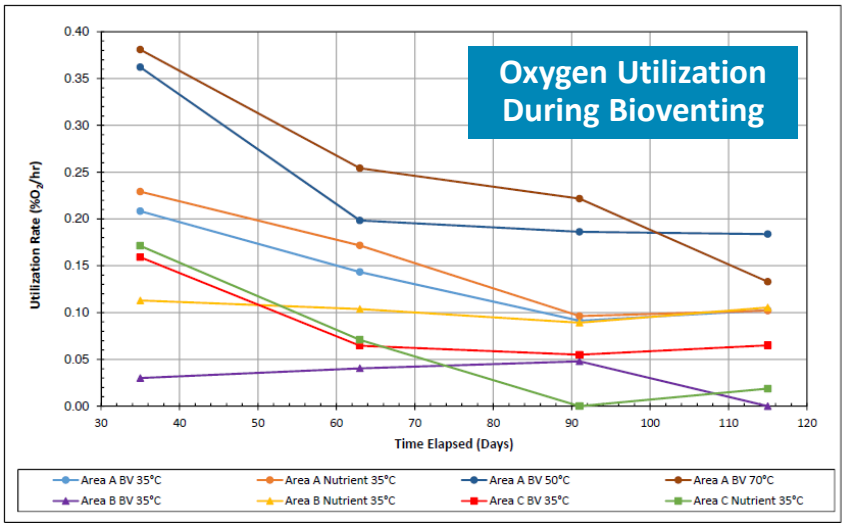
- Former manufacturing facility
  - VOCs, SVOCs
  - Heterogeneous, low permeability soils
  - Groundwater treatment system
- Treatability to evaluate thermally enhanced SVE / bioventing (BV)
  - Columns
  - Three soils: Test Areas A, B, and C
  - Three temperatures: 35 °C, 50 °C, 70 °C
  - Transition several columns to bioventing phase
    - decreased flow rates
    - measured oxygen utilization
  - Nutrients added to select test conditions



35 °C Incubator

Case Study 4: Thermal SVE / BV - Bench & Field

- Majority of treatment during bioventing phase
  - Total COC reductions from 76% to 99%
  - High oxygen utilization in the more impacted columns
  - Oxygen utilization decreased due to dwindling contaminant source (electron donor)
  - Biological population increase
  - Nutrient addition had limited additional benefit
  - Increased temperature accelerated contaminant reductions
    - > 35 °C limited additional benefit (50 °C and 70 °C columns)

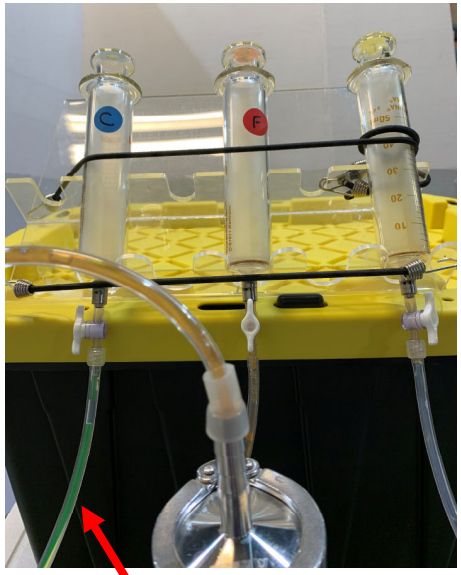


Full-Scale	VOCs (lb)	SVOCs (lb)	Total (lb)
Baseline	39,500	2,100	41,600
8-Month Operation	16,600	550	17,150
% Reduction	58%	73%	59%

- Full-scale
  - Heterogeneous soils incorporated into SVE design
- ~86% mass reduction via biodegradation (21,080 lbs)
  - Validated through oxygen utilization / COD measurements
- 12 months post-operation
  - 90% of system shut down, site closure pending

Case Study 5: Phased ZVI Treatability

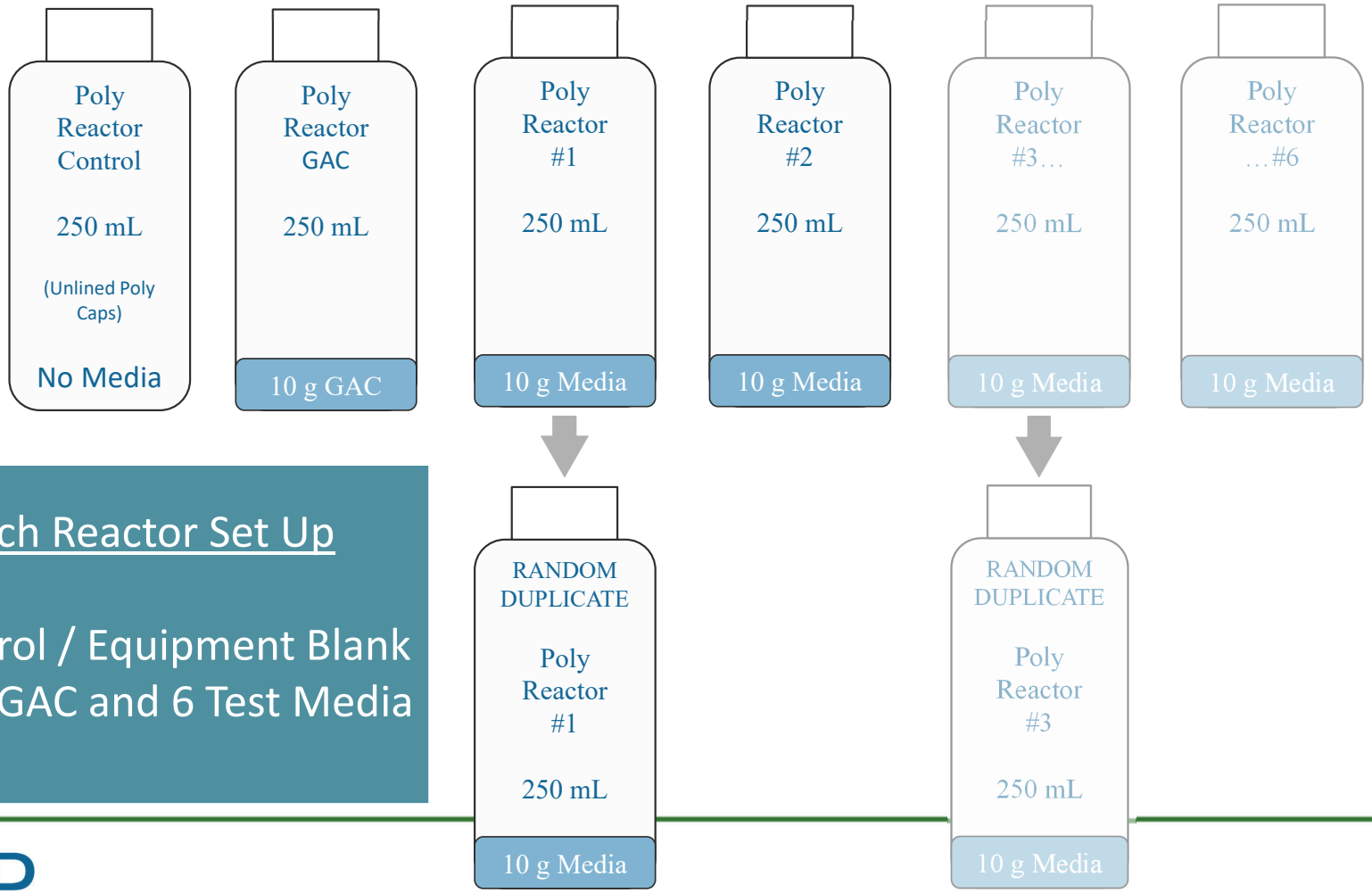
- Former landfill
  - CVOCs in groundwater in weathered bedrock
  - Goal - 80% reduction in total COCs
  - PRB proposed remedy using ZVI
- Bench testing ZVI dose/ product
  - Batch – Phase I
    - 3 products tested from Hepure
      - Ferox Flow
      - Ferox Target
      - Ferox Plus Emulsified [eZVI])
    - 2 dosages each product (1% and 5%)
  - Columns – Phase II
    - Confirm ZVI product(s) / dose from Phase I
    - Tested Ferox Flow and Target at 5%
    - 4-ft and 8-ft treatment zone simulations (i.e., column length / PRB width)



Fluorescein tracer to confirm velocity (2 ft/day)

- Results
  - Batch – Phase I
    - 80% reduction goal met
      - Flow - by day 25
      - Target - by day 13
  - Columns – Phase II
    - Flow – up to 66% reduction
    - Target – 91% reduction
- Conclusions
  - Minimum PRB width of 4 ft
  - Cost-benefit analysis recommended
    - Wider trench vs product costs
      - Ferox Flow – lower $/lb, greater longevity, slower kinetics
      - Ferox Target – higher $/lb & kinetics

Case Study 6: Phased PFAS Treatability



Batch Reactor Set Up

- Control / Equipment Blank
- One GAC and 6 Test Media

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Case Study 6: PFAS Batch Test Results

Compound	Carbon Length	Average Baseline	Control	Synthetic Media	Natural Media	Pre-Treatment	Commercial Resin	Organic Modified #1A	Organic Modified #1B	GAC	Surfactant Modified
PFOA	8	534	556	504	483	82	329	34	450	40	ND <1.9
PFOS		6	5	4	3	ND <2	ND <2	ND <1.9	15	ND <2	ND <1.9
PFHpA	7	56	58	53	52	51	46	15	54	3	ND <1.9
PFHpS		ND<2	ND <2	ND <2	ND <1.9	ND <2	ND <2	ND <1.9	0	ND <2	ND <1.9
PFHxA	6	17	18	16	16	17	17	12	18	ND <2	ND <1.9
PFHxS		4	5	2	4	4	2	ND <1.9	3	ND <2	ND <1.9
PFPeA	5	7	7	7	7	7	7	7	7	ND <2	ND <1.9
PFPeS		ND<2	ND <2	ND <2	ND <1.9	ND <2	ND <2	ND <1.9	0	ND <2	ND <1.9
PFBA	4	4	4	4	4	4	4	ND <1.9	4	ND <2	ND <1.9
PFBS		3	3	3	3	3	3	3	3	ND <2	ND <1.9
Total PFAS		630	656	593	572	498	408	71	557	45	ND <1.9
Reduction		**--**	**--**	**9.6%**	**12.8%**	**24.1%**	**37.8%**	**89.2%**	**11.5%**	**93.1%**	**100%**

Selected for Column Flushing Study

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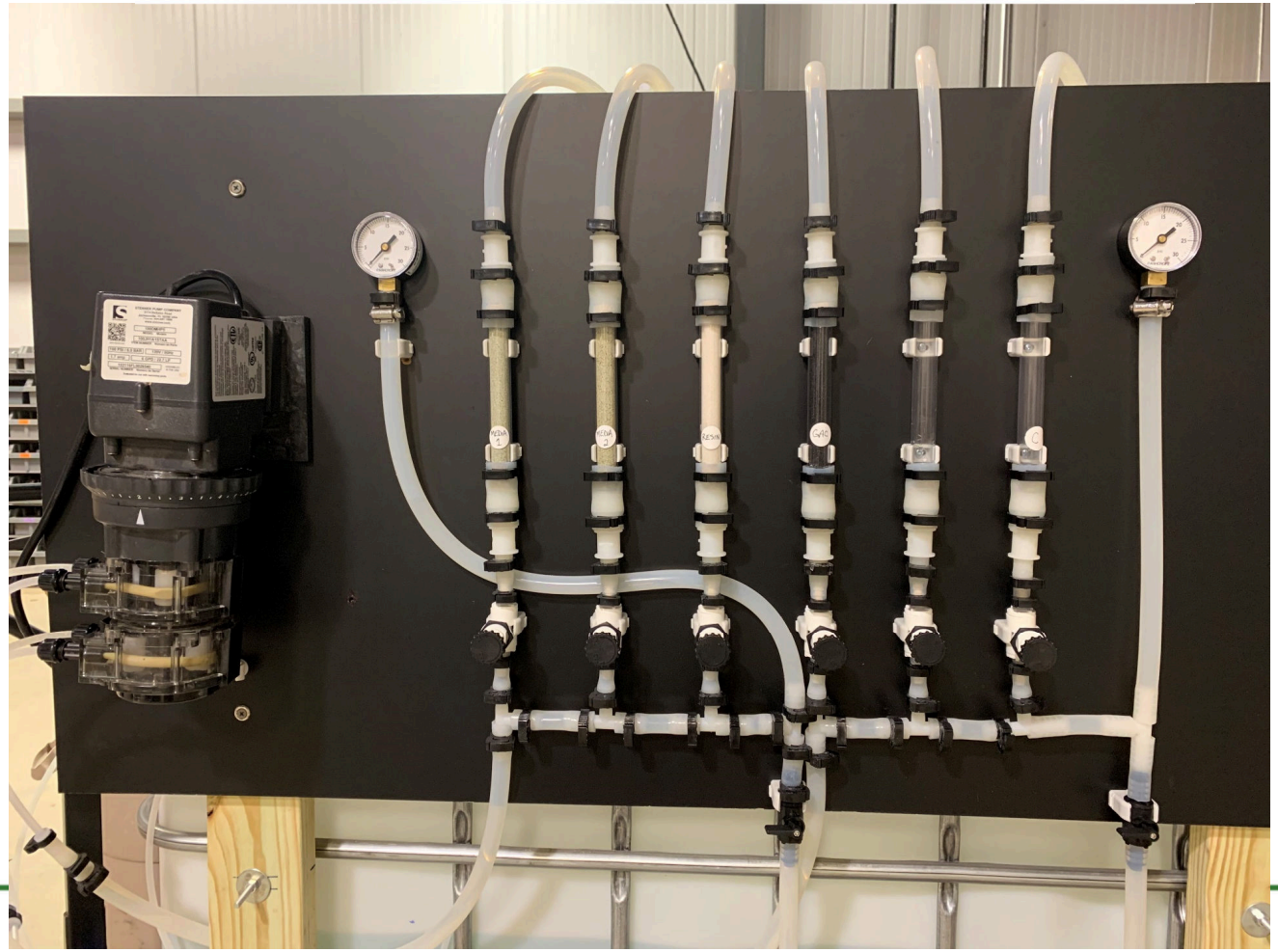
Case Study 6: PFAS Column Apparatus



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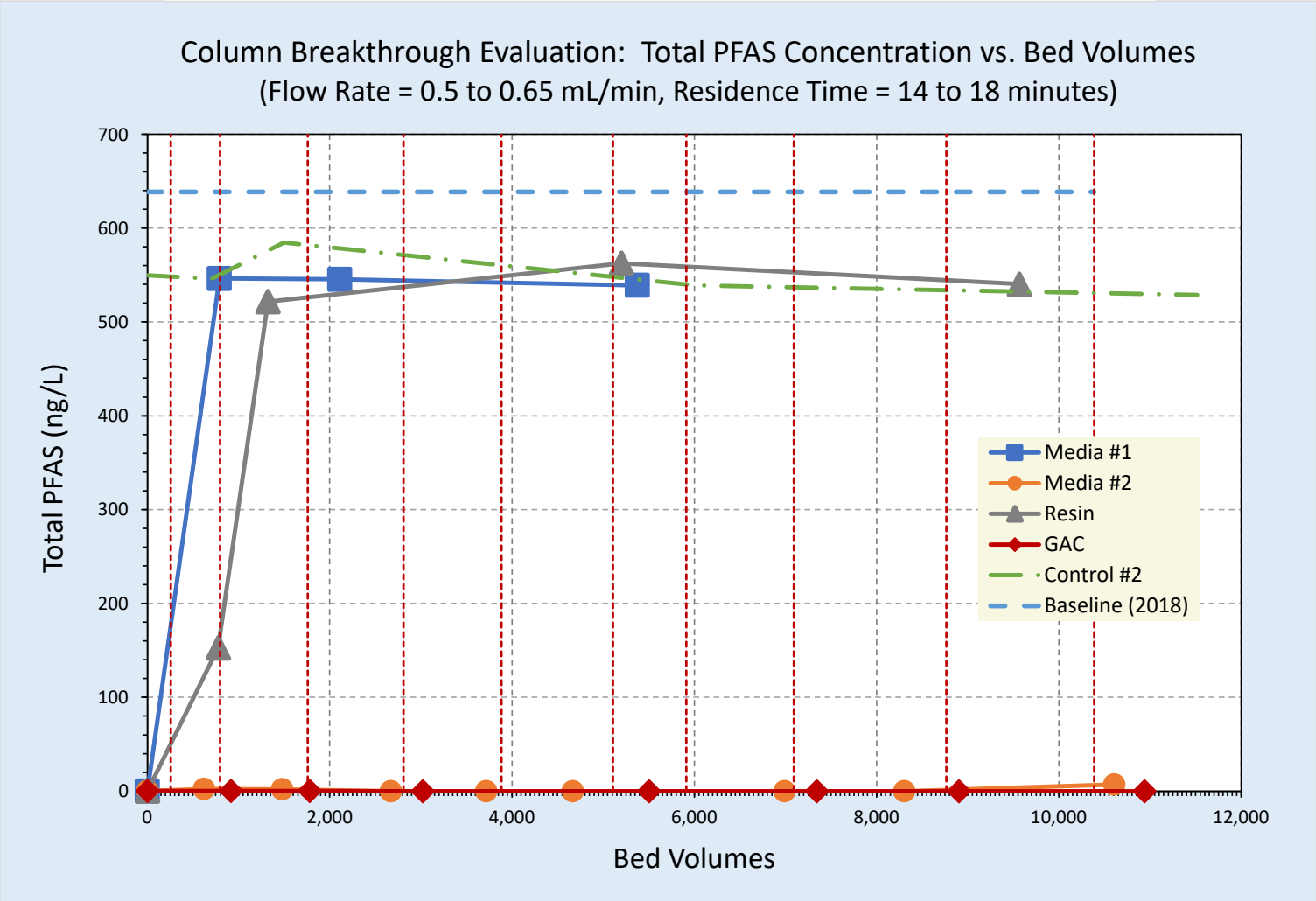
Case Study 6: PFAS Column Test Results



Case Study 7: Ex Situ TOD/COD Removal

- Large industrial site
  - Surface cap with P&T system
  - High iron, TOC / COD
- Treatability and field support for pretreatment processes
  - Pre-GAC treatment included:
    - Coagulation / flocculation and settling
    - pH adjustment
    - TOC / COD removal via modified sorbent
- Pretreatment steps saved client $56k/year

Case Study 8: Enhanced Bioremediation, ME

- Site background
  - Chlorinated solvents in fractured bedrock
  - Metals mobilization a concern
  - P&T for hot spot area
- Evaluated bioremediation in treatability study
  - Limited food / electron donor
  - Limited nutrients
  - No appropriate bacteria
  - pH not ideal

- Full-scale remedy
  - Pull-push approach using treatability determined reagents and dosage
  - Two applications over 12-month period
- Remedy successful: the P&T system evaluation permitted shutdown

Questions?

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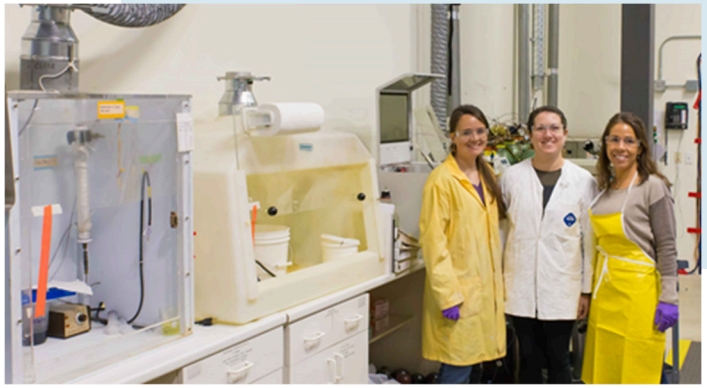

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