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SERDP and ESTCP Webinar Series

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    - Required webinar ID: 944-040-092
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Treatment Options for the Emerging Contaminants 1,2,3-Trichloropropane and 1,2-Dibromoethane

May 23, 2019

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Welcome and Introductions

Michael Kavanaugh, Ph.D.
Webinar Facilitator

SERDP DOD • EPA • DOE | ESTCP

Webinar Agenda

- **Webinar Logistics** (5 minutes)
  Dr. Michael Kavanaugh, Geosyntec Consultants
- **Overview of SERDP and ESTCP** (5 minutes)
  Dr. Andrea Leeson, SERDP and ESTCP
- **Reactive Gas Process for In Situ Treatment of 1,2,3-Trichloropropane (TCP) in Vadose Zone Soils** (25 minutes + Q&A)
  Dr. Paul Hatzinger, APTIM Federal Services
- **Natural Attenuation and In Situ Treatment of 1,2-Dibromoethane (EDB) at a Complex Field Site** (25 minutes + Q&A)
  Dr. Paul Koster van Gross, APTIM Federal Services
- **Final Q&A session**

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- Use a compatible browser (Firefox, IE or Edge)
- If material is not showing on your screen or if screen freezes
  - Key in Ctrl + F5 to do a hard refresh of your browser
- If connecting to computer audio
  - Click the arrow next to the "*Join Audio*" button
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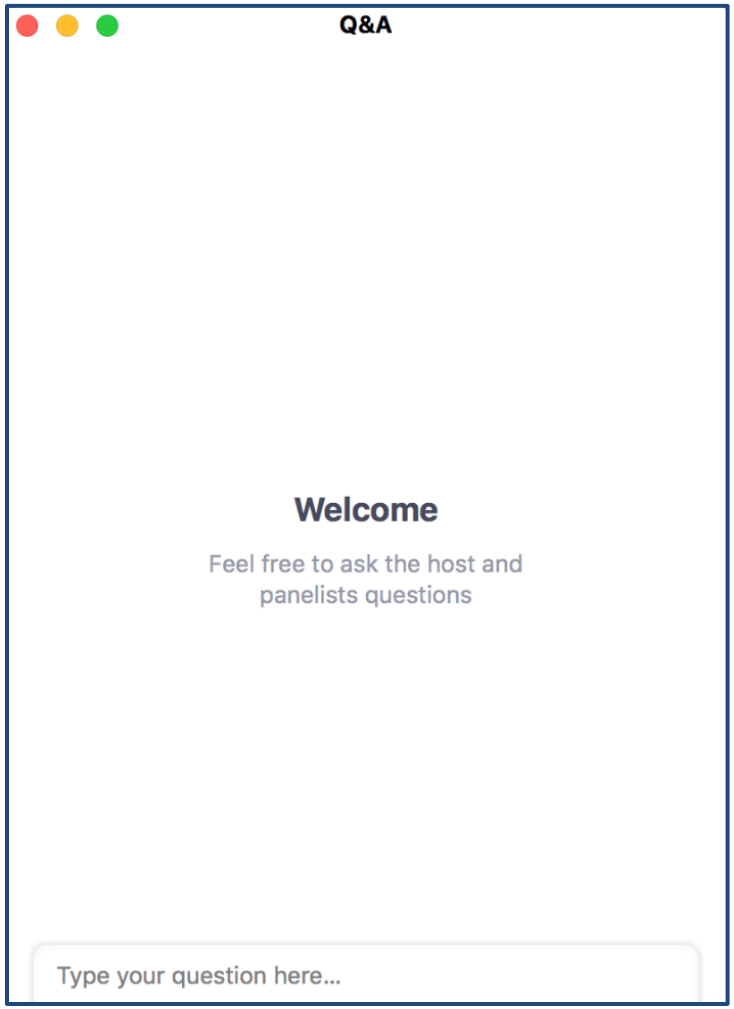
- Find the Q&A button on your control bar and type in your question(s)
- Make sure to add your organization name at the end of your question so that we can identify you during the Q&A sessions



SERDP and ESTCP Overview

Andrea Leeson, Ph.D.
SERDP and ESTCP

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DoD's Environmental Technology Programs

Science and Technology

- Statutory program established 1991
- DoD, DOE, EPA partnership
  - Advanced technology development to address near-term needs
  - Fundamental research to impact real world environmental management

Demonstration and Validation

- Demonstrate innovative cost-effective environmental and energy technologies
  - Transition technology out of the lab
  - Establish cost and performance
  - Partner with end user and regulator
  - Technology transfer
    - Accelerate commercialization or broader adoption
    - Direct technology insertion

Environmental Drivers

Sustaining Ranges, Facilities and Operations

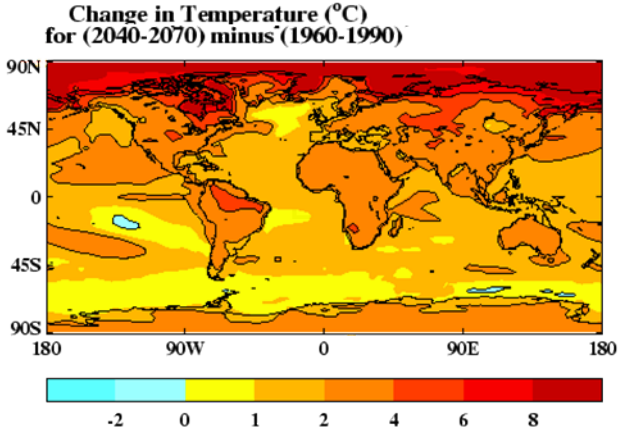
Maritime Sustainability
Threatened and Endangered Species

Toxic Air Emissions and Dust

UXO and Munitions Constituents

Noise

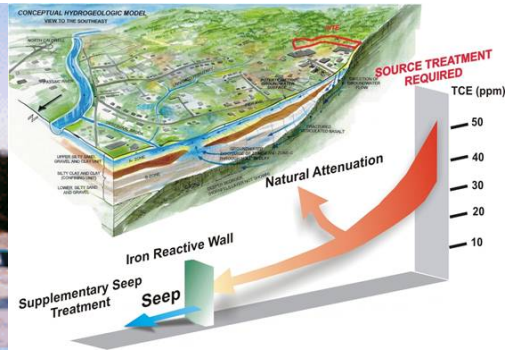
Sustainable FOB



Environmental Drivers

Reducing Current and Future Liability

Contamination from Past Practices



- Groundwater, soils and sediments
- Large UXO liability
- Emerging contaminants

Pollution Prevention to Control Life Cycle Costs

- Elimination of pollutants and hazardous materials in manufacturing, maintenance, and operations
- Achieve compliance through pollution prevention

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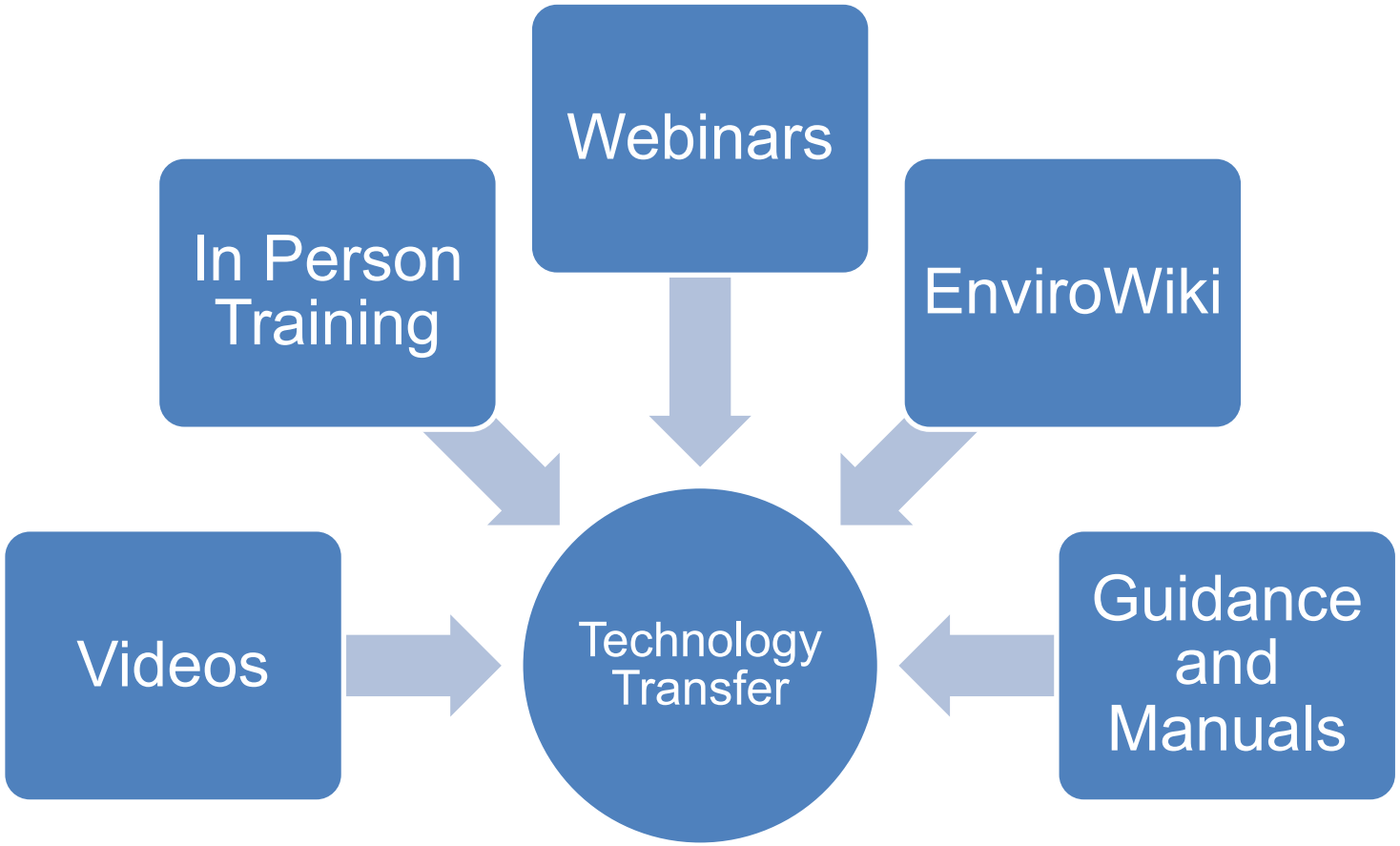

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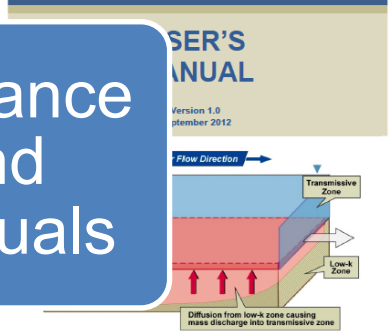
Webinars

In Person Training

EnviroWiki

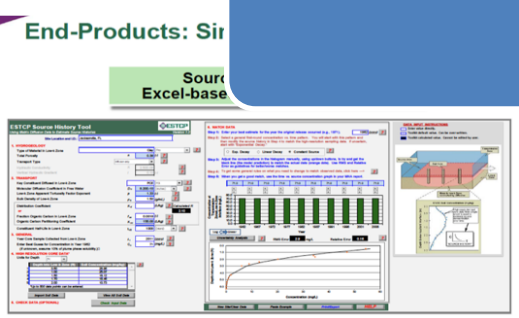
Matrix Diffusion Toolkit



Videos

Technology Transfer

Guidance and Manuals



SERDP and ESTCP Webinar Series

Date	Topic
June 6, 2019	Developing and Demonstrating Non-Toxic Paints for Corrosion Protection
June 20, 2019	Developing Adaptation Strategies to Address Climate Change and Uncertainty
July 11, 2019	Vapor Intrusion: Modeling Tools and Cost Effective Mitigation
July 25, 2019	Understanding Underwater Munitions Mobility and Behavior on the Beach Face and in Shallow Muddy Environments

For upcoming webinars, please visit

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Save the Date!

SERDP • ESTCP
SYMPOSIUM

A three-day symposium showcasing the latest technologies that enhance DoD's mission through improved environmental and energy performance

December 3-5, 2019

Washington Marriott Wardman Park

Registration open

Reactive Gas Process for In Situ Treatment of 1,2,3-Trichloropropane (TCP) in Vadose Zone Soils

Paul B. Hatzinger, Ph.D.
APTIM

SERDP DOD • EPA • DOE | ESTCP

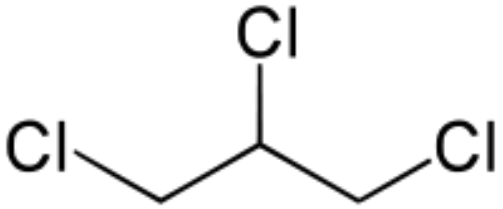
Agenda

- Problem statement
- Background information
  - 1,2,3-TCP
  - Reactive gas process
- Laboratory study results
- Field investigation data
- Field demonstration design
- Conclusions

Image Source: G. Lavorgna, APTIM

Problem Statement

- 1,2,3-TCP is a carcinogen
  - No Federal MCL
  - California MCL – 0.005 µg/L



- Presence at DoD sites
  - Solvent for cleaning, degreasing, varnish removal
  - Aircraft tank sealers
  - Contaminant in common soil fumigant (D-D)
  - Groundwater at >45 bases
    - 1,400 wells, 17% rate
  - Soils at 27 bases
    - 850 boreholes, 7% rate
- Resistant to biodegradation
- Difficult to treat abiotically

Characteristics of TCP

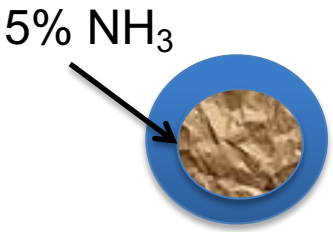
Property	TCP	CT	TCE
Vapor Pressure (torr)	3	99	132
Henry's Law Constant	3	286	94
Solubility (grams/liter)	1.8	0.8	1.1
Log K_{oc}	2.5	2.6	2.4

- Non-reactive with many conventional amendments
- Difficult to air strip/volatilize
- Resistant to biodegradation – long half lives (years)
  - Evidence of reductive dechlorination and cometabolism
  - Reactive with strong oxidants (activated persulfate)
- Subject to alkaline hydrolysis

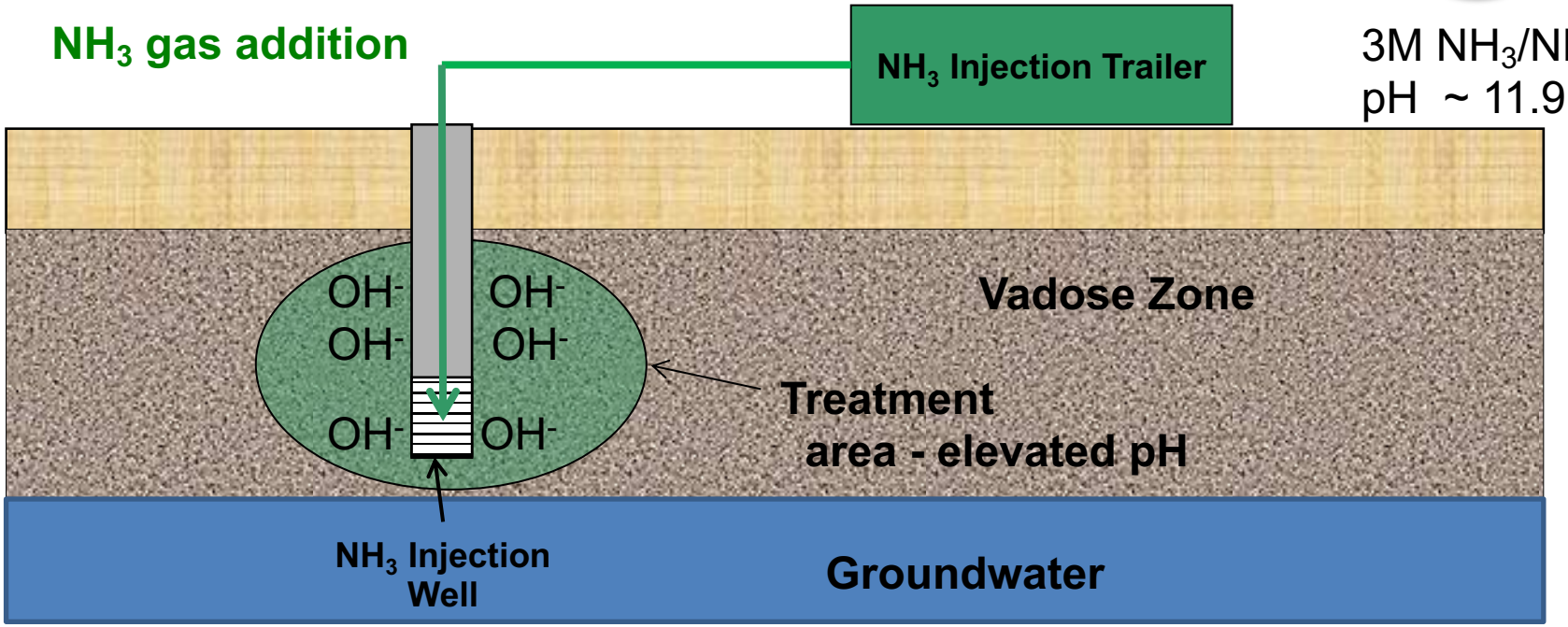
Reactive Gas Process

Gaseous ammonia (NH_3) injection to vadose zone soils → higher pH; alkaline hydrolysis

$$NH_3 + H_2O \longleftrightarrow NH_4^+ + OH^-$$



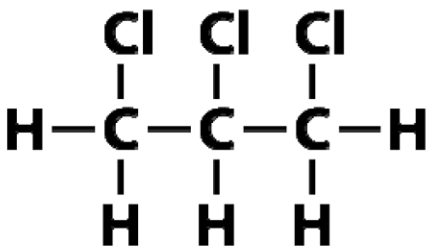
3M NH_3/NH_4^+
pH ~ 11.9



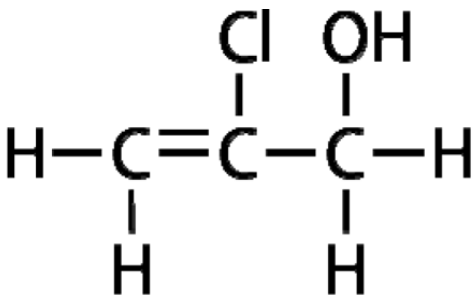
Notes: M = molar; NH_4^+ = ammonium; OH^- = hydroxide

TCP Hydrolysis

1,2,3-trichloropropane



-HCl



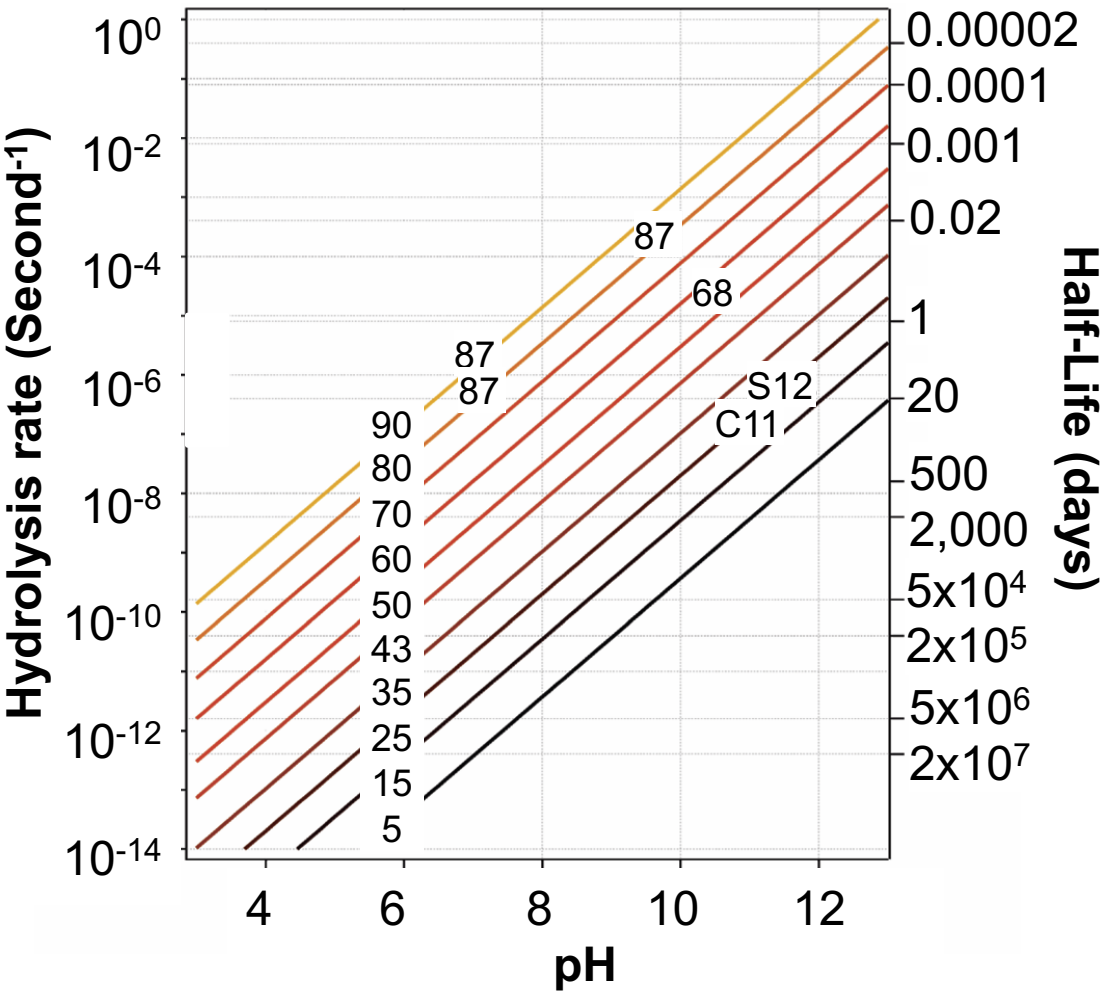
2-chloro-2-propen-1-ol
or 3-chloro-2-propen-1-ol

(2-chloroallylalcohol)

Readily biodegradable under aerobic conditions

TCP Half-Life Hydrolysis

Influence of pH, Temperature

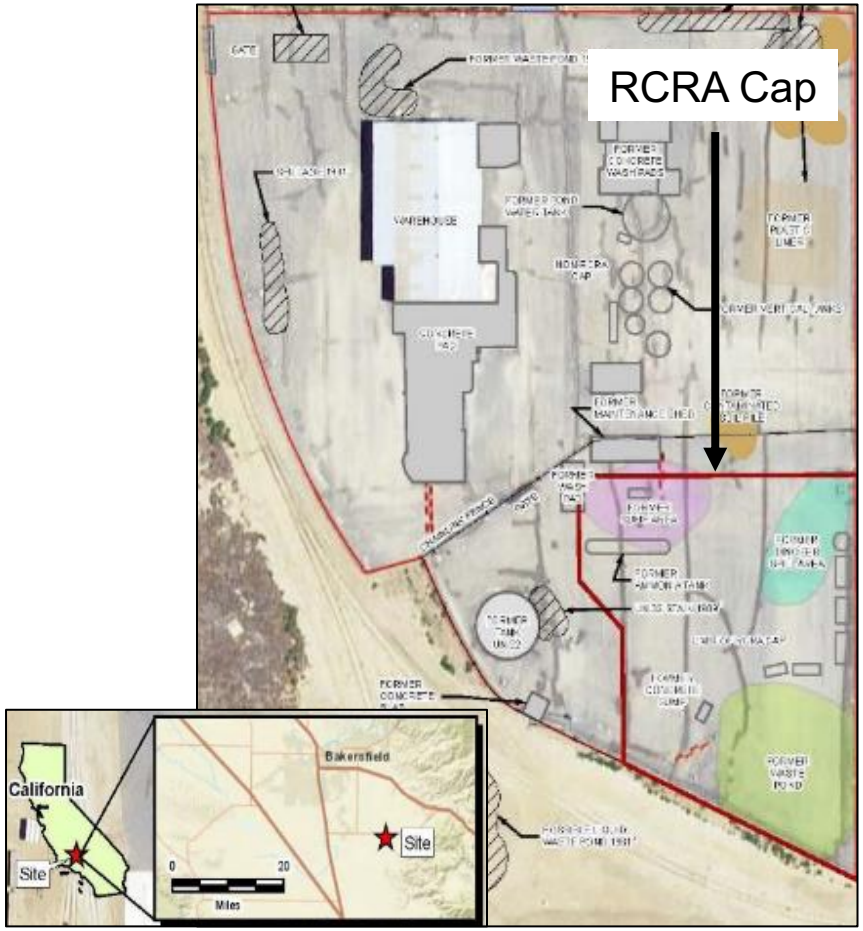


TCP half-life decreases with increasing pH and increasing temperature

Demonstration Site

Brown and Bryant Superfund Site (B&B)

- Arvin, California (San Joaquin Valley)
- Pesticide re-formulator (1960-1989)
- Added to NPL in 1989
- 1,2,3-TCP and other contaminants
- RCRA cap in southeast
  - High 1,2,3-TCP in north eastern capped area, vadose zone

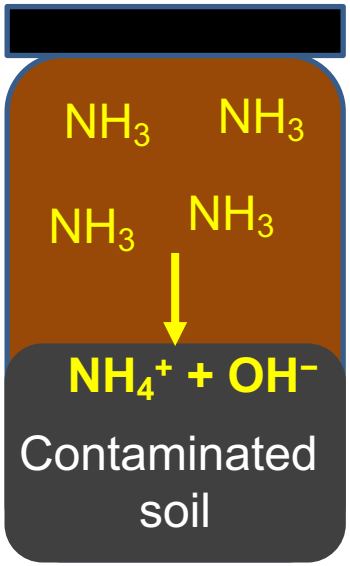


Notes: NPL = National Priorities List; RCRA = Resource Conservation and Recovery Act

Laboratory Studies

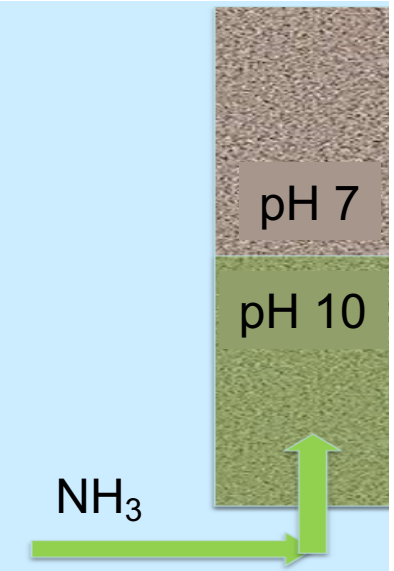
Batch and Column

Batch studies



TCP and DCP (vadose soils, B&B); explosives (surface soil; UMCD)

Column studies



Determine reaction extent under different conditions (B&B)

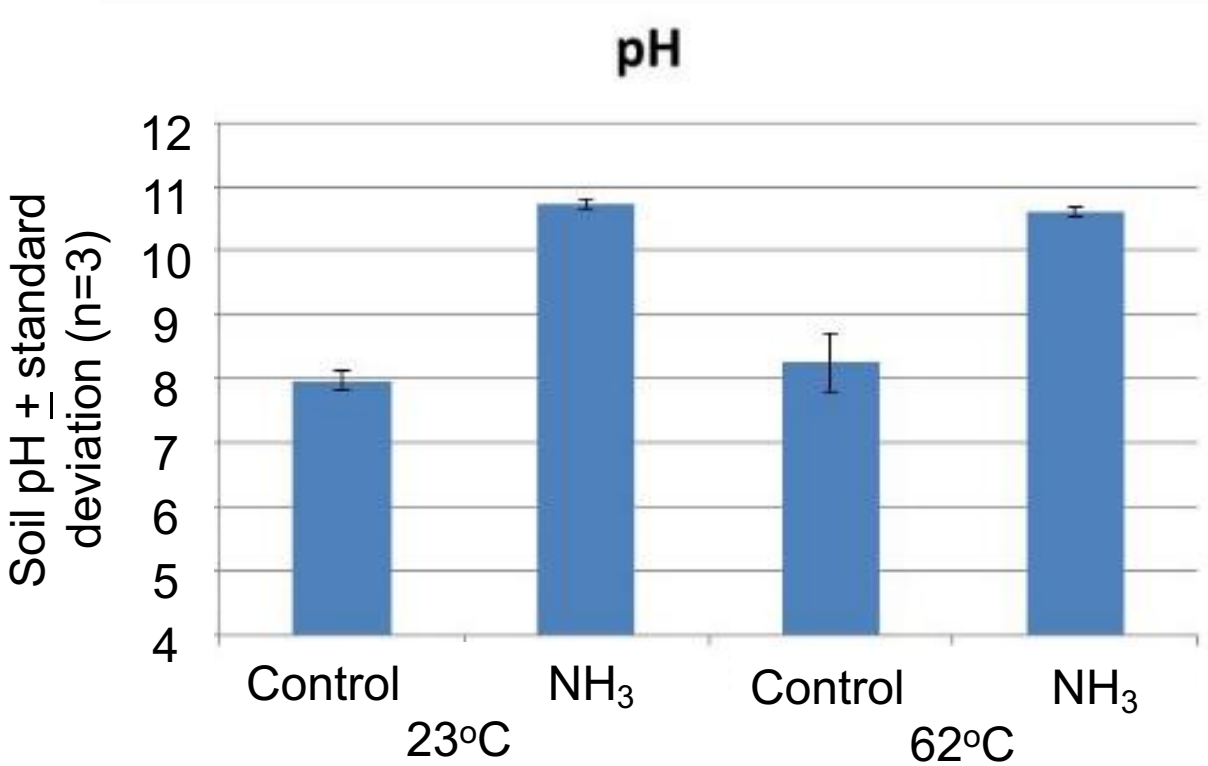
Notes: DCP = dichloropropanes; UMCD = Umatilla Chemical Depot

TCP Hydrolysis – Batch Results

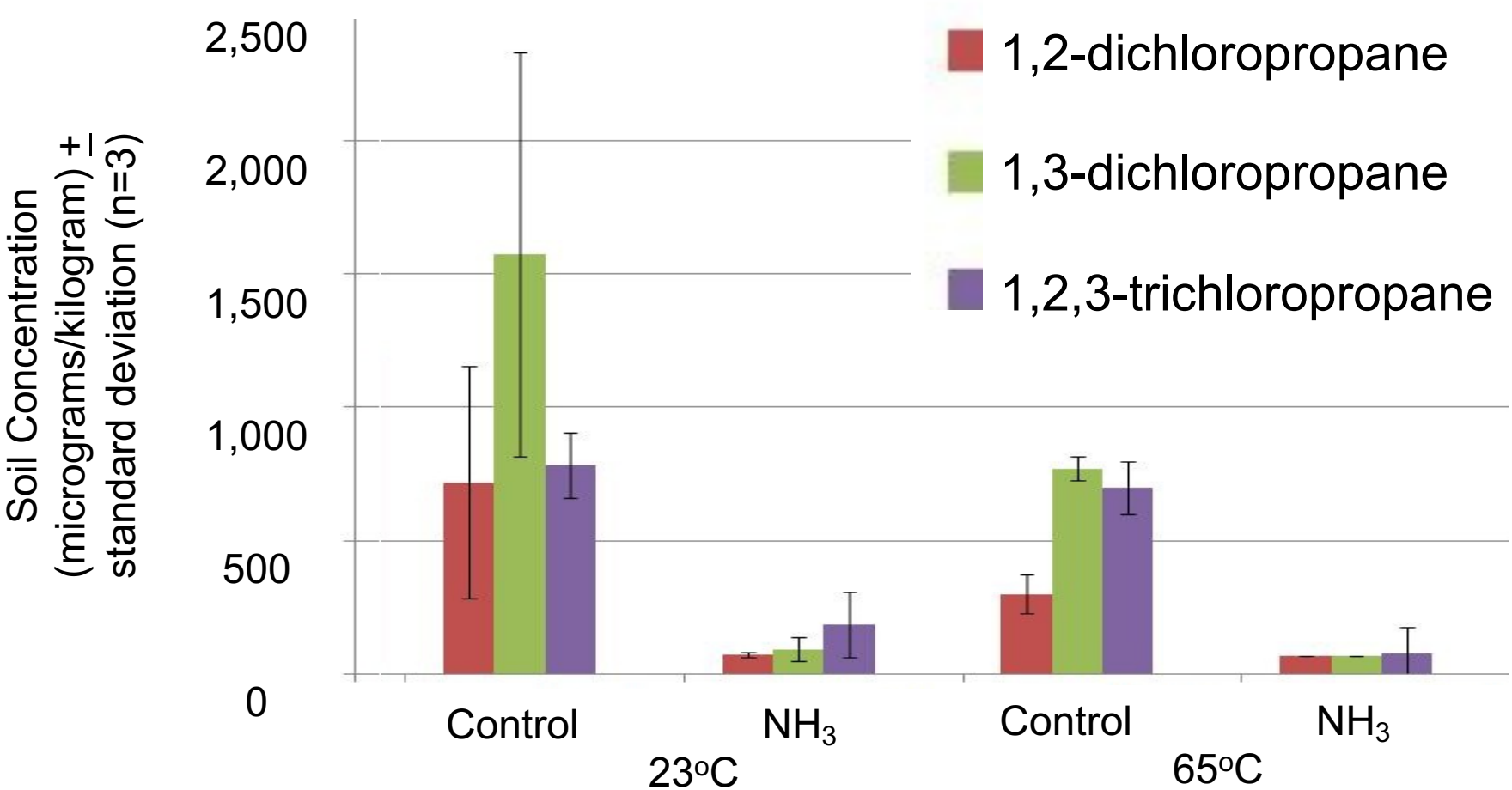
NH_3 Reaction Study

- Gaseous ammonia and chloropropane contaminated soil
  - Room temperature (23°C), and 62°C for 5 days

Image Source: Scott Waisner, USACE



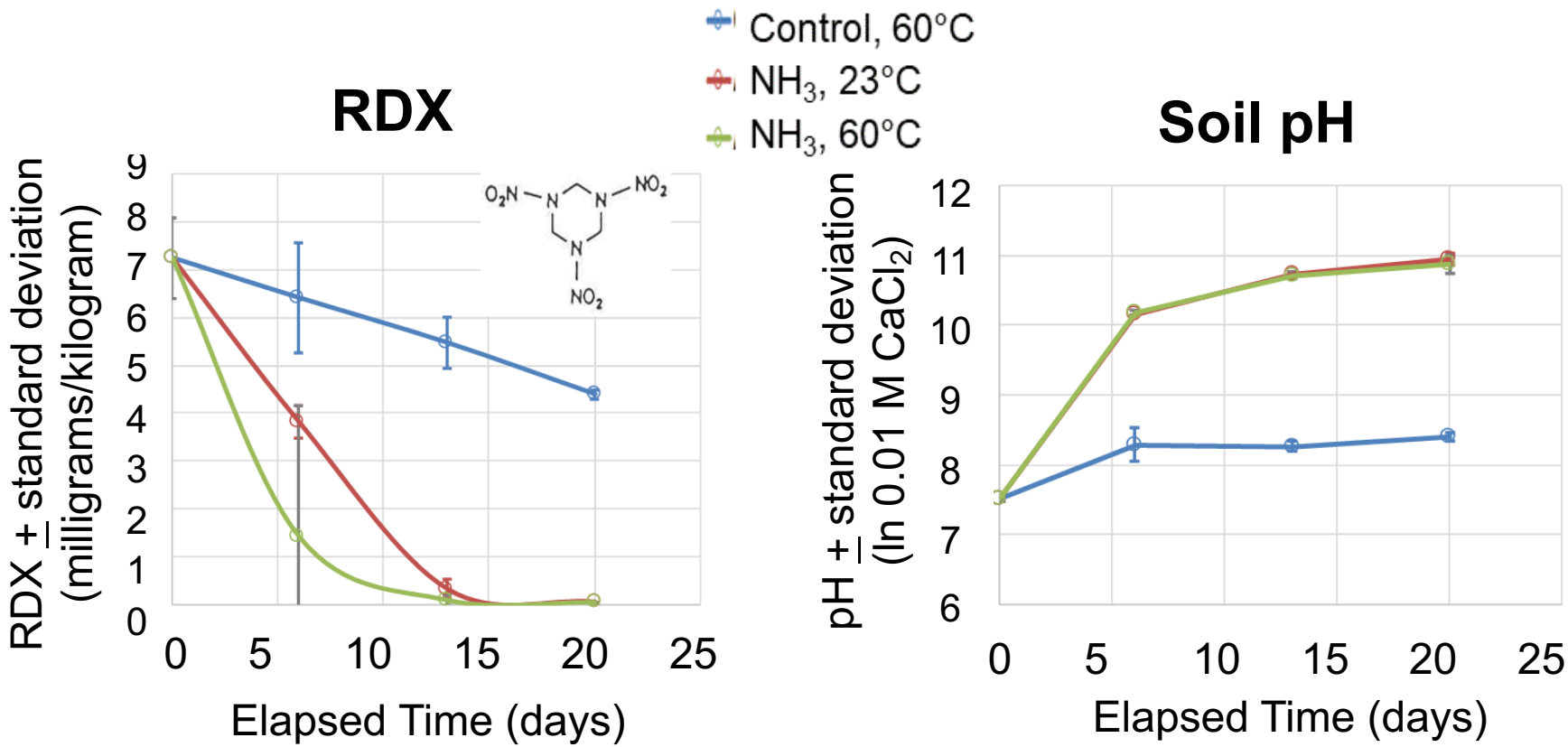
TCP Hydrolysis – Batch Results



TCP and DCP degradation apparent at 23°C and 65°C after 5 days

RDX Hydrolysis

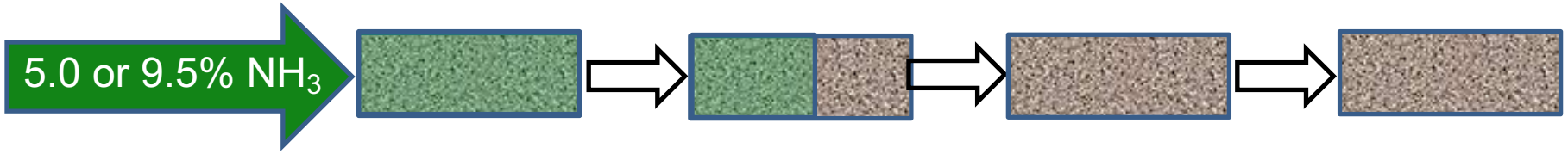
Soil Batch Results – Umatilla Chemical Depot (OR)



Notes: $CaCl_2$ = calcium chloride; ln = natural log; RDX = hexahydro-1,3,5-trinitro-1,3,5-triazine

Column Studies – NH_3 Transport

- Supply NH_3 gas to site soils; measure pH change with distance
  - Gas concentration; flow rate
  - Soil moisture



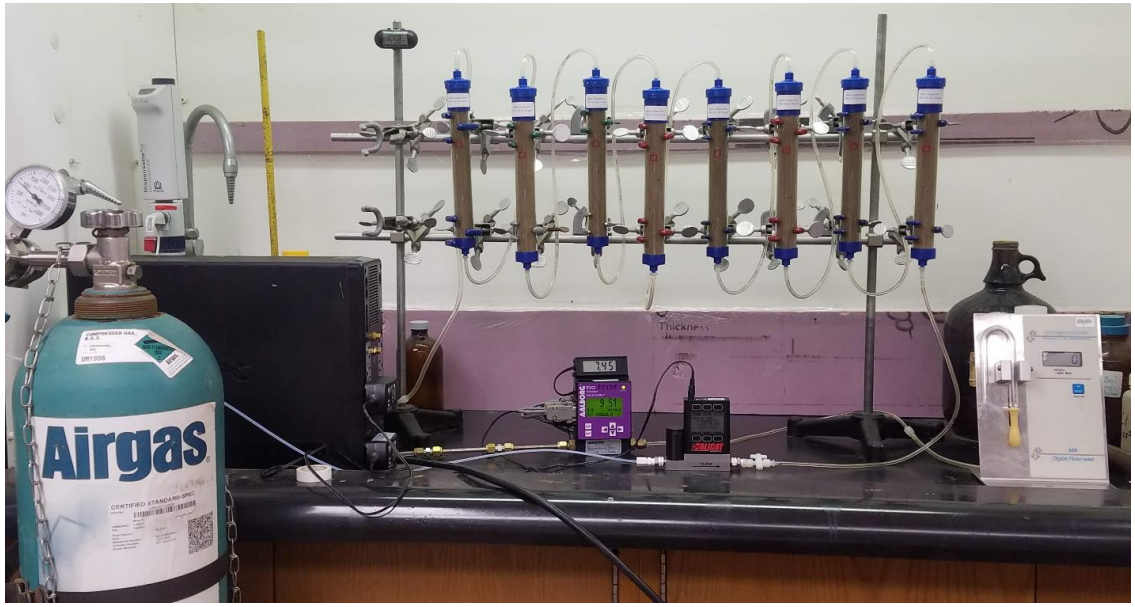


Image Source: Scott Waisner, USACE

Column Studies – NH_3 Transport

Effect of gaseous NH_3 concentration, soil moisture, and gas flow on soil pH and residual NH_3

	Conditions		
Column Test	**NH_3 in Air (%)**	**Flow (sccm)**	**Moisture Content (%)**
#2	9.5	5	16.9%
#3	5.0	10	16.3%
#4	9.5	10	15.9%
#5	9.5	10	5.5%

Notes: sccm = standard cubic centimeters per minute

Column Studies – NH_3 Transport

Results

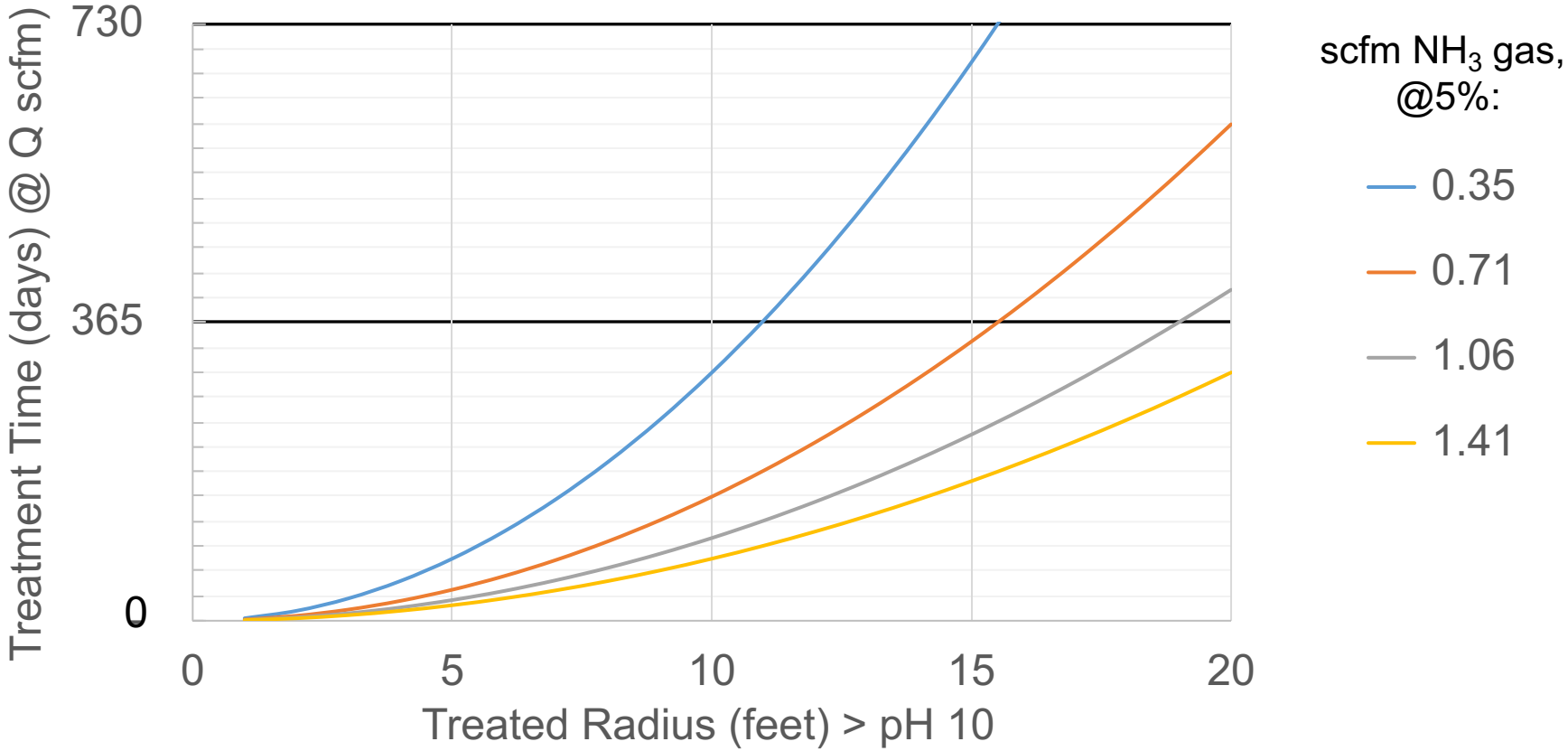
Column Test	Ammonia		Total Soil Treated pH 10 (g $soil_{dry}$)	Soil pH at Saturation		Distance NH_3 front (cm)
	Residual (NH_3-N mg/kg $soil_{dry}$)	Total Injected (mg NH_3-N)		DI	$CaCl_2$	
#2	7,996	5,007	400	10.4	10.2	66
#3	4,999	5,949	721	10.3	10.1	106
#4	9,923	6,176	438	10.6	10.4	63
#5	4,384	6,117	1,129	10.3	10.0	168

- Soil pH > 10 all conditions
- 5% vs 9.5% NH_3
  - Small difference in resultant soil pH
  - Significant difference in NH_3 residual
- Lower soil moisture → greater treatment area and lower residual

Notes: DI = deionized water; $CaCl_2$ –calcium chloride

Column Studies

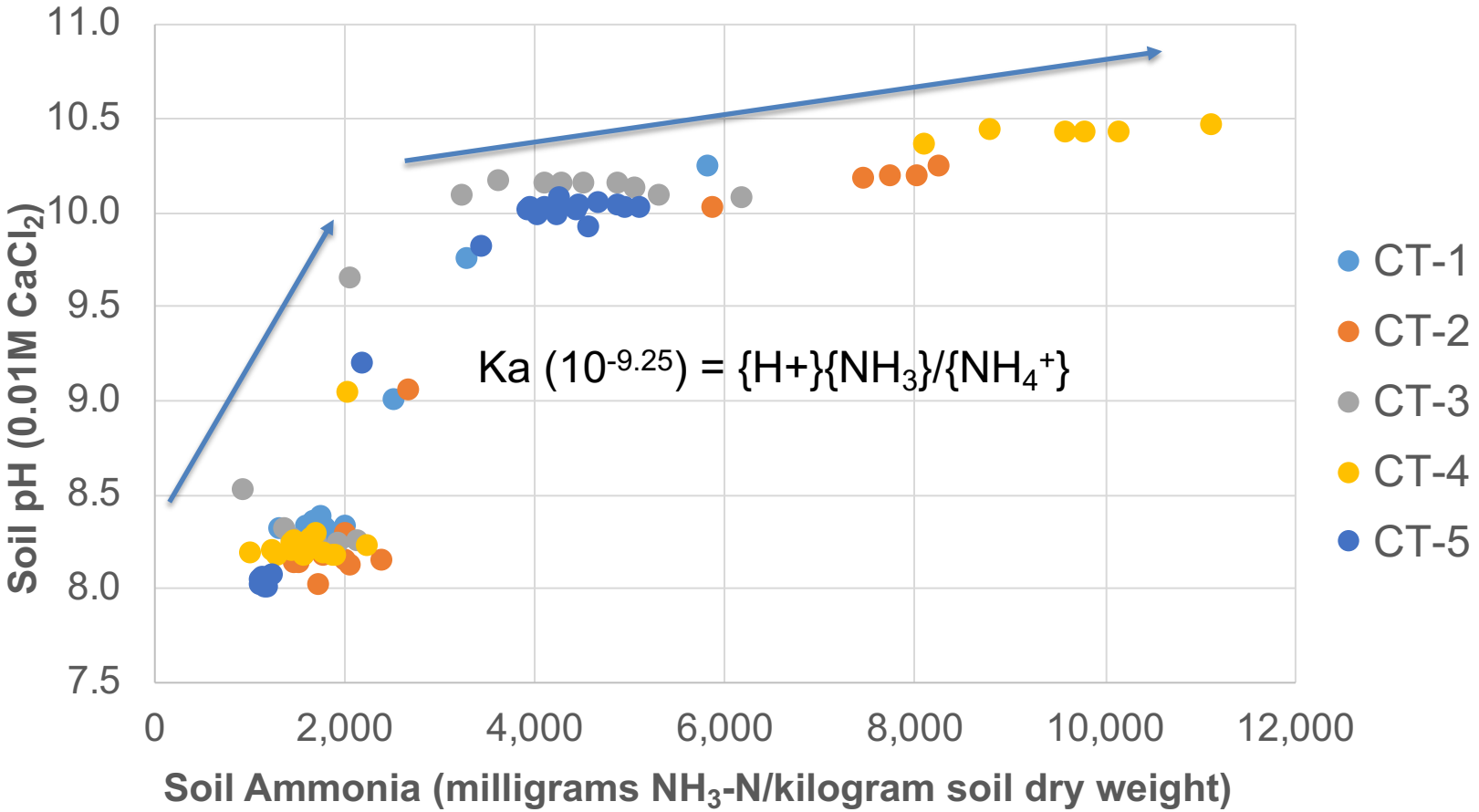
Modeled Treatment Radius (Column #3 Data)



Notes: scfm = standard cubic feet per minute

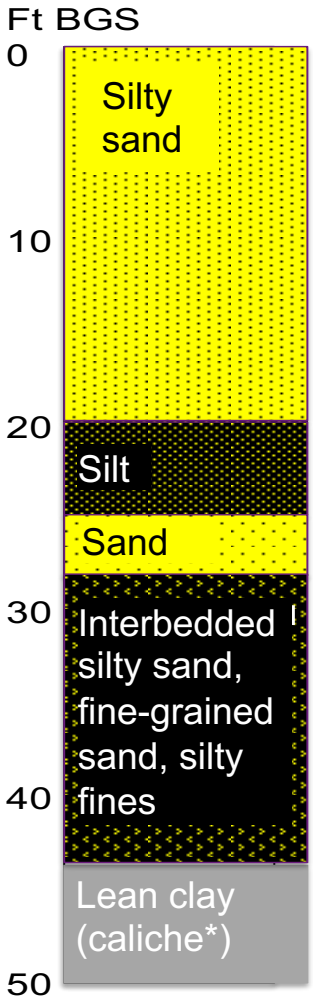
Column Studies

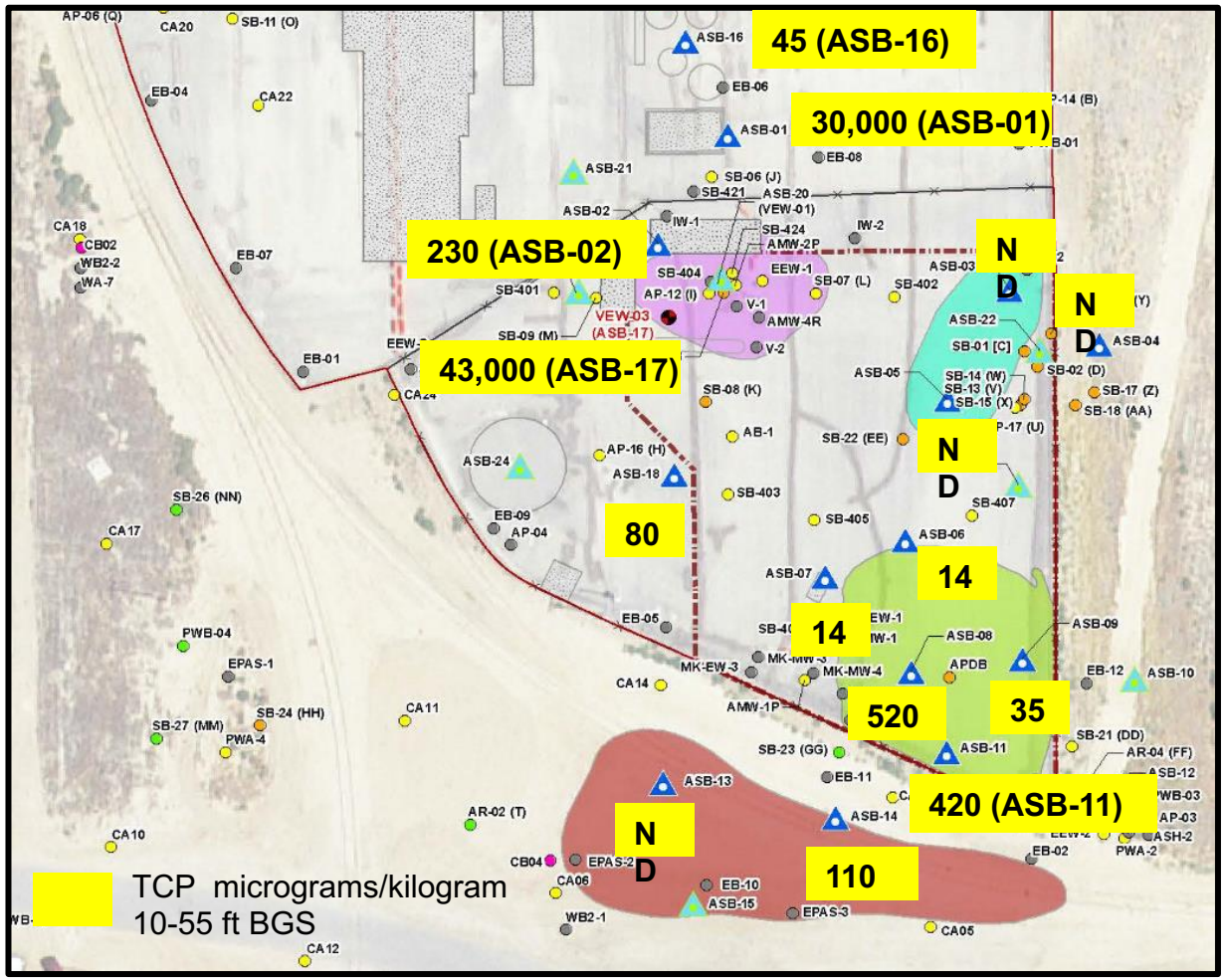
pH vs. Extractable NH_3 on Soil



Maximum soil pH at B&B is influenced by high initial soil NH_4^+

B&B Site Investigation – TCP

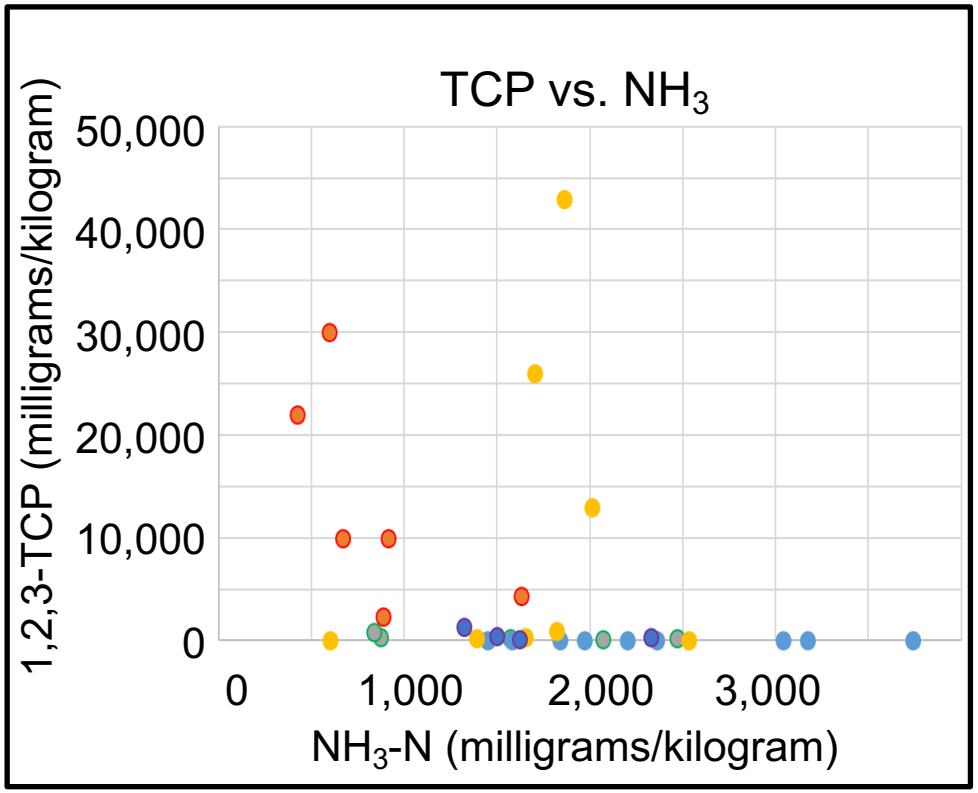


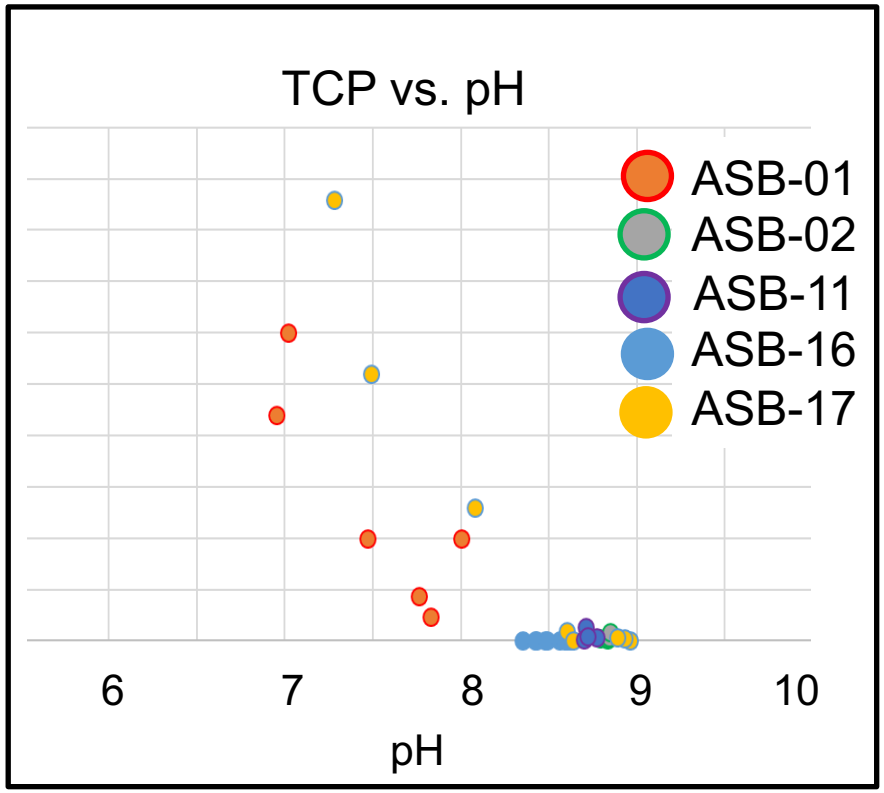


Notes: ft BGS = feet below ground surface; ND = non-detect

B&B Site Investigation

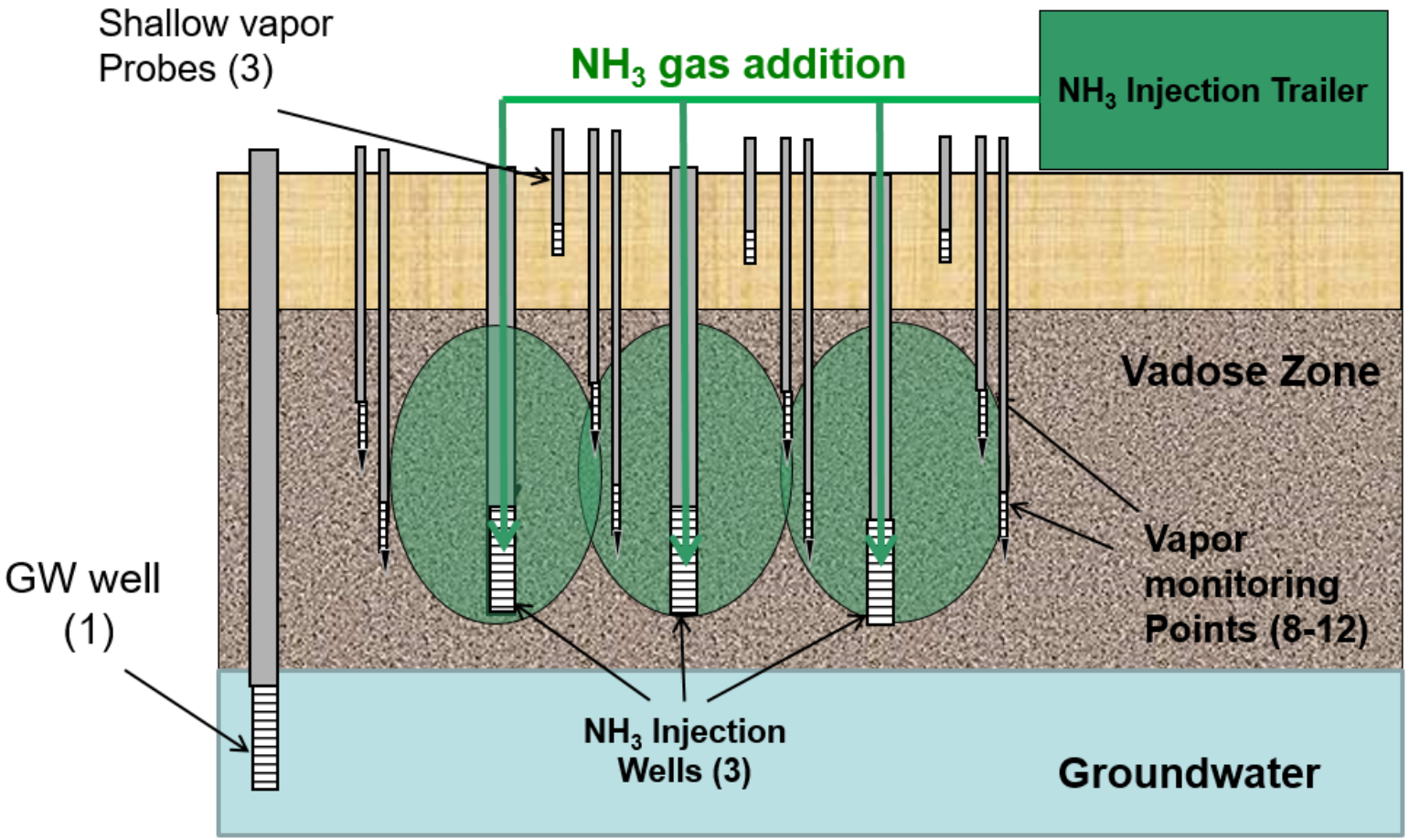
Five Soil Borings





- Inverse relationship (TCP vs pH; TCP vs NH_4^+)
- No similar relationship(s) with Dinoseb

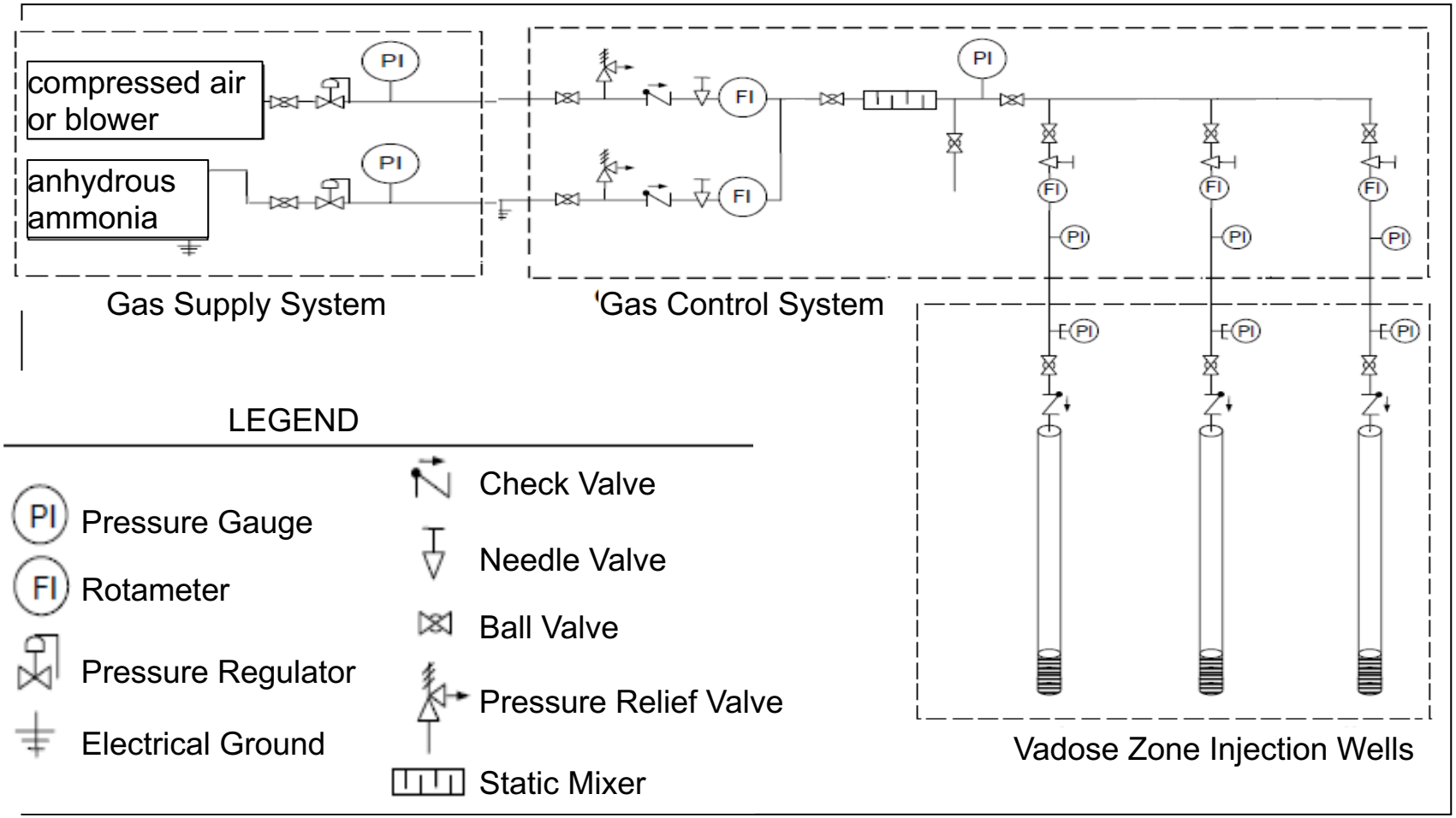
Field Demonstration Design



Not to scale

Field Demonstration Design

Generalized Process Flow Diagram



Generalized process flow diagram for field deployment – Full design not yet complete

Field Demonstration Schedule

- Phase I: Baseline Sampling (3 Months)
  - Monthly soil gas sampling, 3 initial soil cores*
  - Baseline NO_3^- groundwater sampling
- Phase II: Active Treatment (8 Months)
  - Monthly soil gas sampling, 3 soil cores*
- Phase III: Post Treatment Monitoring (4 months)
  - 2 rounds soil gas sampling (bi-monthly), 3 soil cores*
  - Groundwater sampling for post-treatment NO_3^- (1-2 wells)
- Phase IV: Decommissioning (1 month)

Field Demonstration Phases and Timeline (months)

Phase I Phase II Phase III Phase IV

Conclusions

- NH_3 gas increases soil pH
  - Promote contaminant alkaline hydrolysis
  - Unsaturated zones
- Effective for DoD contaminants in vadose and surface soils
  - TCP
  - DCP
  - Explosives

References Cited

- Hunter, P.G., I. May, and K. Brown. 2006. DoD-Wide Occurrence of Emerging COCs in Groundwater and Soil. U.S. Air Force. http://www.denix.osd.mil/cmrmd/upload/2B_HUNTERFINAL.PDF
- Sarathy, V., A. J. Salter, J.T. Nurmi, G. O'Brien Johnson, R.L. Johnson, and P.G. Tratnyek. 2010. Degradation of 1,2-3-trichloropropane (TCP): Hydrolysis, elimination, and reduction by iron and zinc. Environ. Sci. Technol. 44:787-793
- Coyle, C.G., V.F. Medina, S.A. Waisner, C.S. Griggs. 2017. Use of dilute ammonia gas for treatment of 1,2,3-trichloropropane and explosives-contaminated soils. J. Environ Management. 204:775-782

For additional information, please visit

https://serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Persistent-Contamination/ER-201632

Speaker Contact Information

paul.hatzinger@aptim.com; 609-895-5356

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Q&A Session 1

Natural Attenuation and In Situ Treatment of 1,2-Dibromoethane (EDB) at a Complex Field Site

Paul Koster van Groos, Ph.D.
APTIM Federal Services

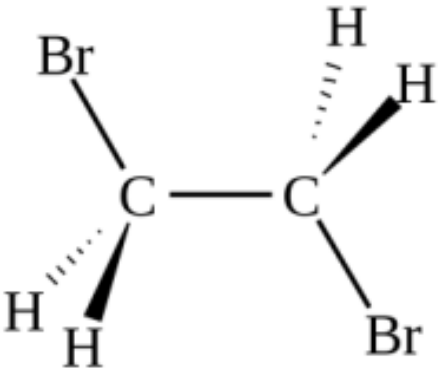
SERDP DOD • EPA • DOE | ESTCP

Agenda

- Project background
- Laboratory isotope studies
- Natural attenuation at Kirtland Air Force Base (AFB)
- Anaerobic biostimulation at Kirtland AFB
- Conclusions
- Benefits to DoD

Background – EDB

- Ethylene dibromide (EDB) or 1,2-dibromoethane
  - "Emerging" contaminant
- 1920s
  - Large quantities used as lead scavenger in gasoline
- Early 1980s
  - Fumigant use ends
- Late 1980s
  - EDB use falls with decrease in leaded gasoline use
- 1992
  - 2nd Lowest EPA MCL (0.05 µg/L)



1,2-dibromoethane (EDB)

Steve Snodgrass
https://www.flickr.com/photos/stevensnodgrass/4385045639

Background – EDB

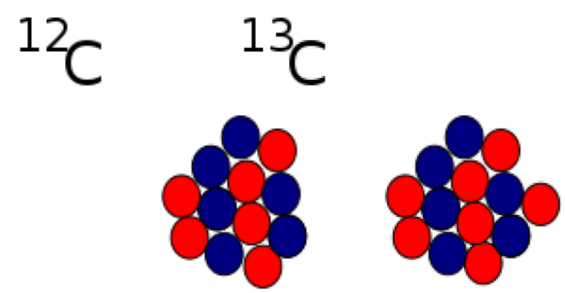
- Leaded fuels are still in use (e.g., Aviation Gasoline)
- ~7 x 10^8 L/year AvGas used in US (2008)
- ~500 mg/L EDB in AvGas
- ~75 g EDB in 40 gal tank of Cessna 172
- ~500 Olympic sized pools to EPA MCL

https://www.kadena.af.mil/News/Photos/igphoto/2000651518/

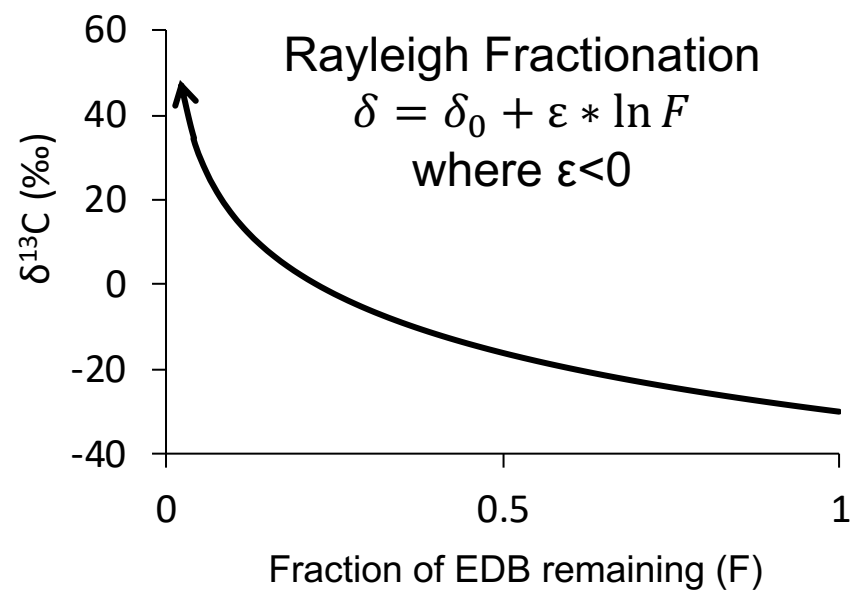
Ramon Velasquez
https://commons.wikimedia.org/wiki/File:IbaAirportjf9319_15.JPG

Background – Isotopes

- Compound-Specific Isotope Analysis (CSIA)
- ^{12}C = 98.9%
  ^{13}C = 1.1%
- ^{13}C EDB degrades slower (kinetic isotope effect)
- Change in isotope composition → evidence of degradation

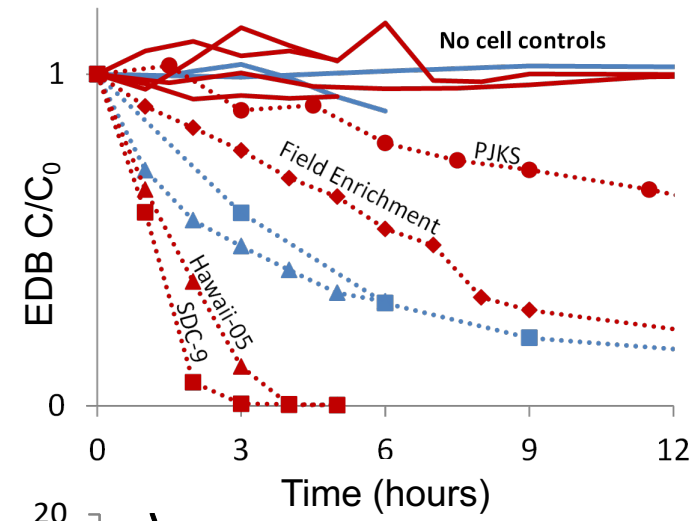


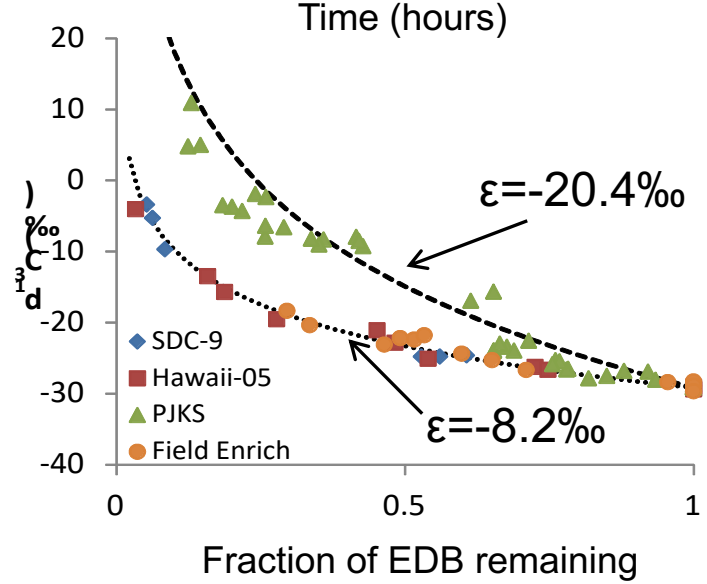
https://commons.wikimedia.org/wiki/File:Carbon-12.svg
https://commons.wikimedia.org/wiki/File:Carbon-13.svg



Lab Isotope Studies – CSIA Calibration

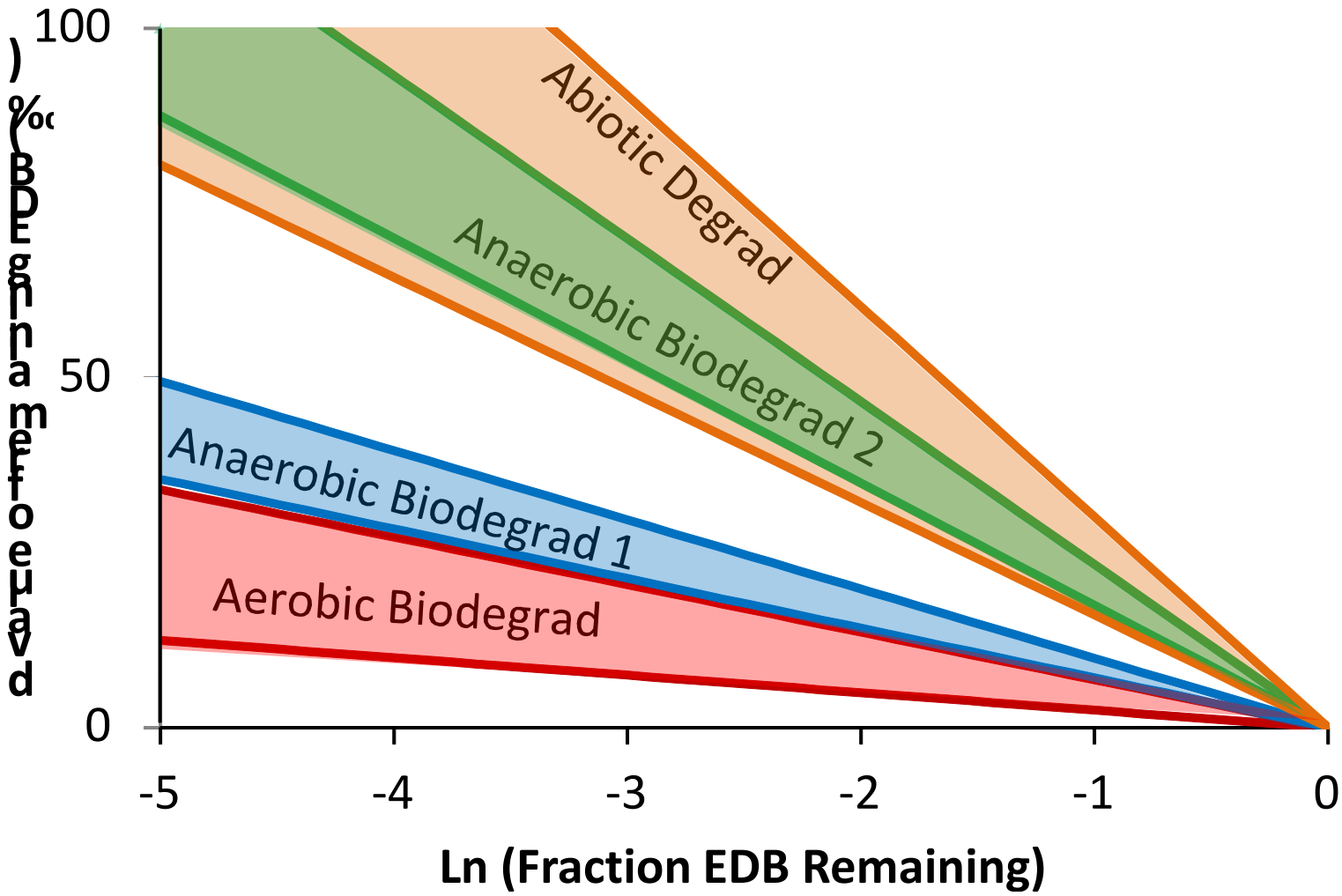
- EDB biodegradation can occur aerobically and anaerobically
- Anaerobically
  - EDB biodegrades to ethene/ethane and Br^-
- Anaerobic isotope fractionation with at least two levels apparent
  - ε = -8.2‰ and ε = -20.4‰





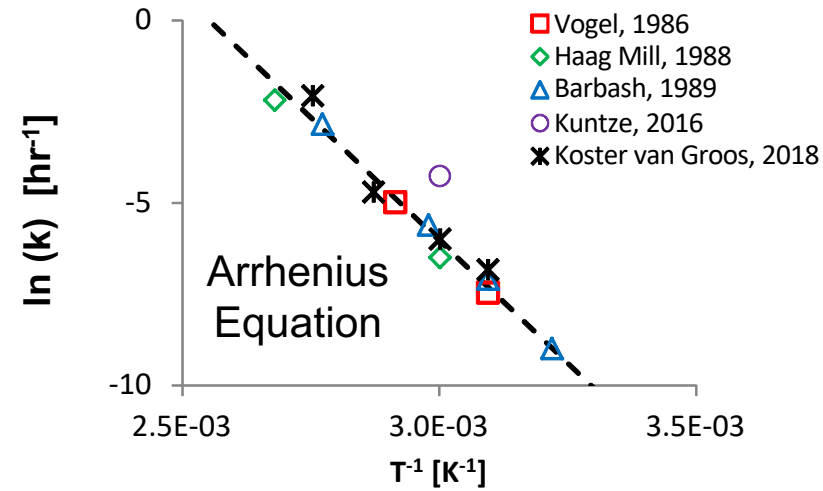
Notes: C = concentration; C_0 = initial concentration; Br^- = bromide

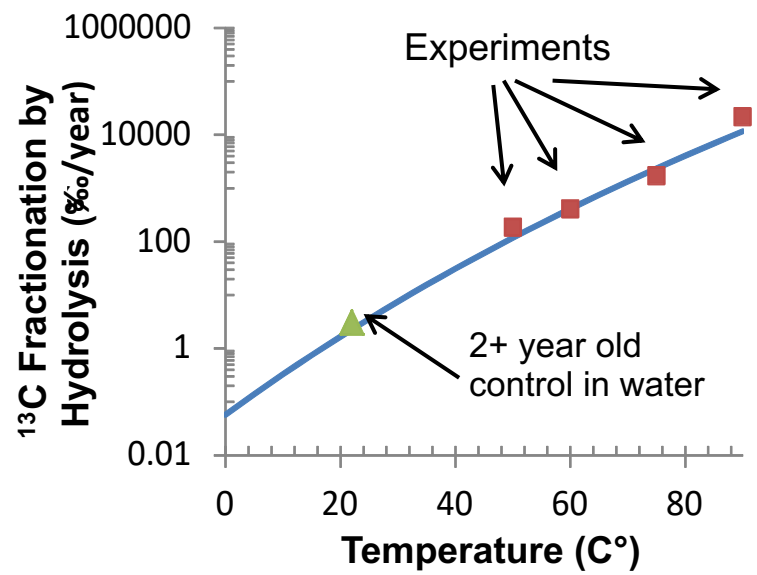
Lab Isotope Studies – CSIA Calibration



Lab Isotope Studies – Hydrolysis

- Hydrolysis
  - Ubiquitous in water
  - Half lives ~decade at field temperatures
  - Kinetics + consistent isotope fractionation provides some timing information

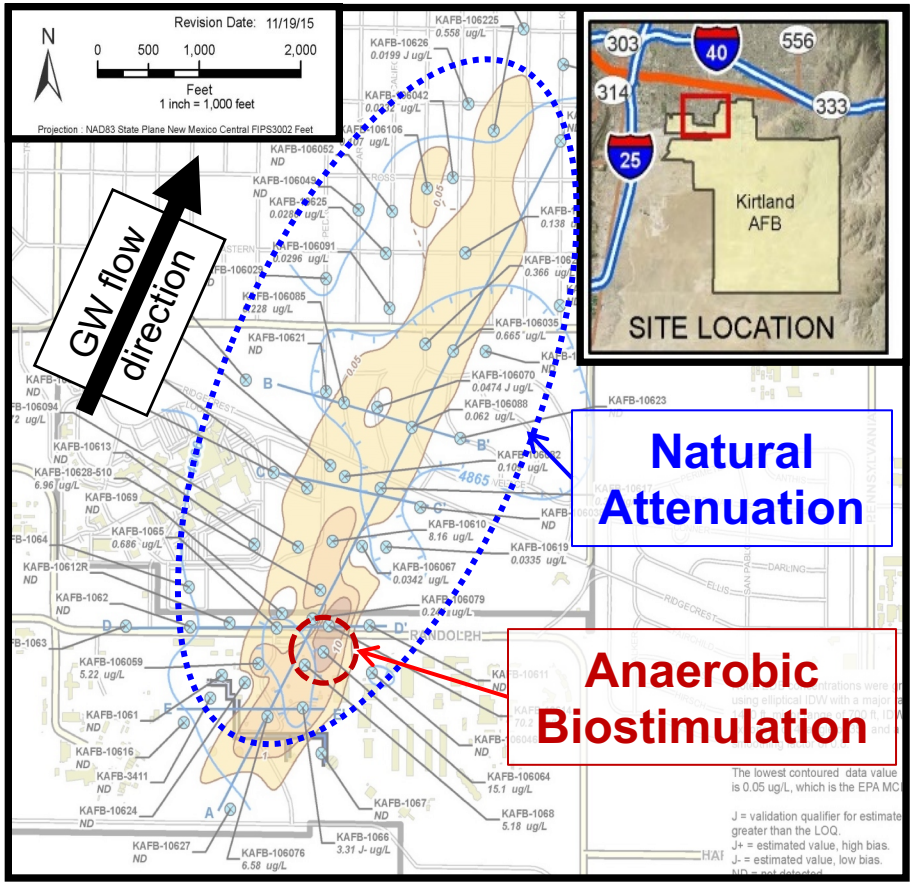




EDB Natural Attenuation

Kirtland AFB, New Mexico

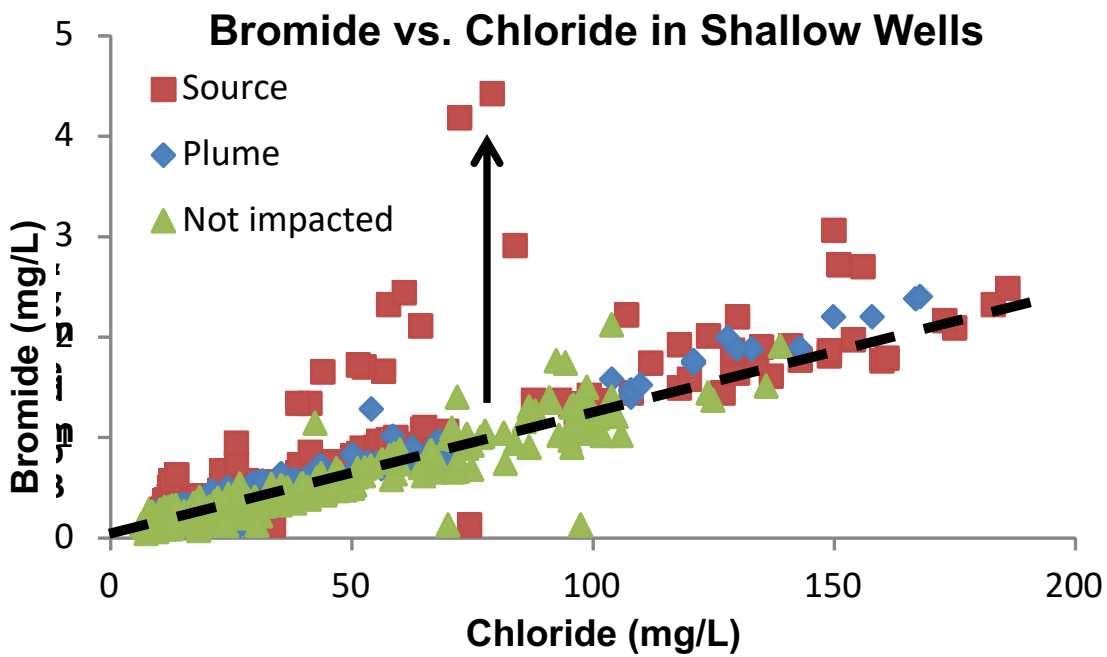
- Historic Leak of AvGas, JP-4, JP-8
- AvGas used until mid 1970s
- EDB > 100 µg/L
- ~500 ft to groundwater

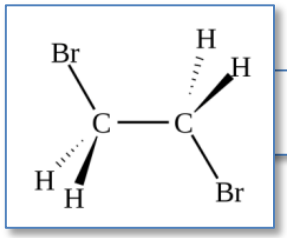


Basemap from USACE, 2015
https://hwbdocuments.env.nm.gov/Kirtland%20AFB/KAFB4345.pdf

EDB Natural Attenuation

Br^- and Ethene Suggest EDB Degradation





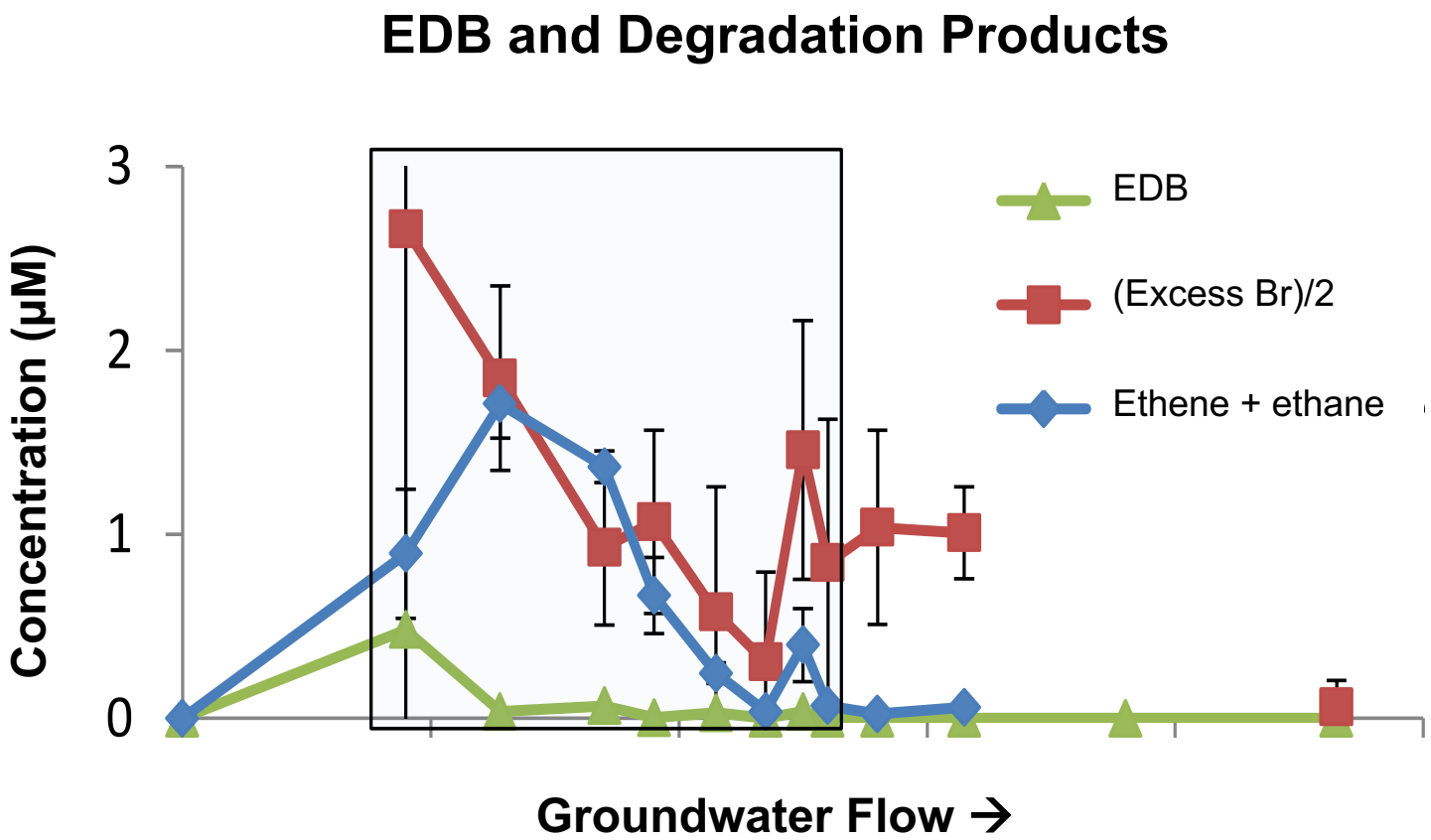
Reductive dehalogenation / dihaloelimination

EDB → Ethene/Ethane + 2 Br^-

$$Br_{excess} = Br_{meas} - \left(Br/_{Cl}\right)_{bkg} x\ Cl_{meas}$$

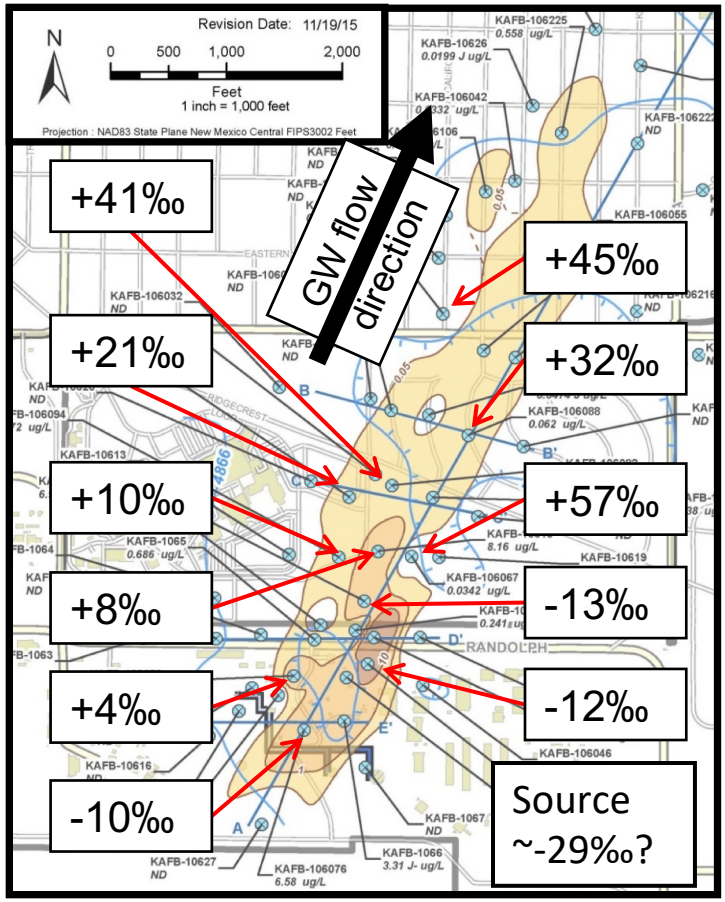
EDB Natural Attenuation

Br^- and Ethene Suggest EDB Degradation

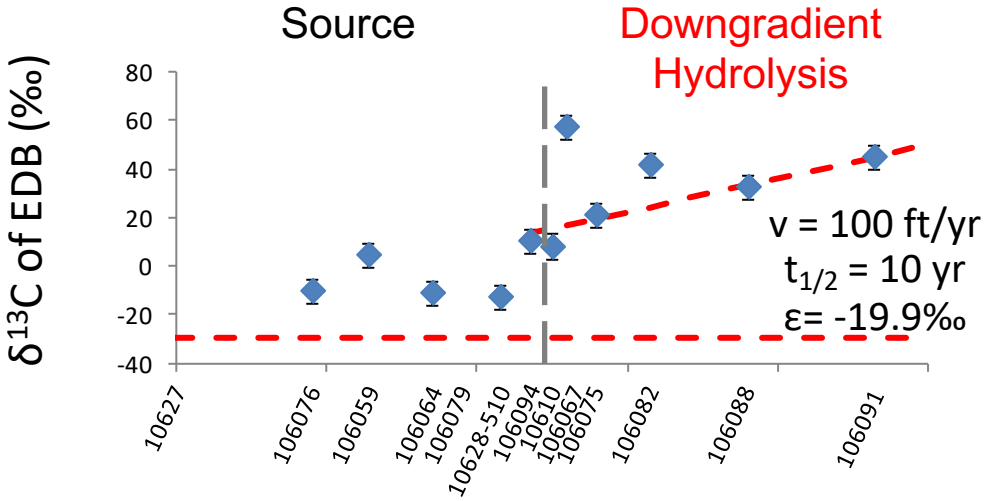


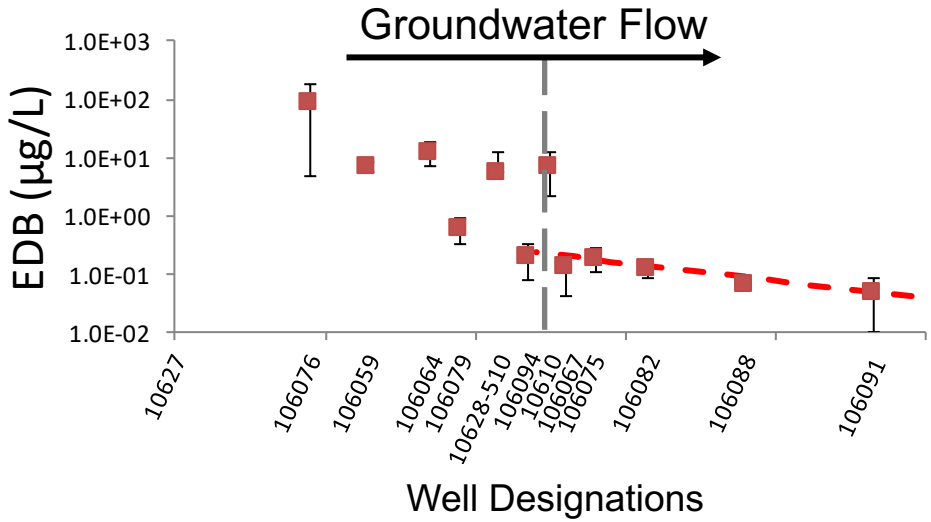
EDB Natural Attenuation

EDB Carbon Isotope Results



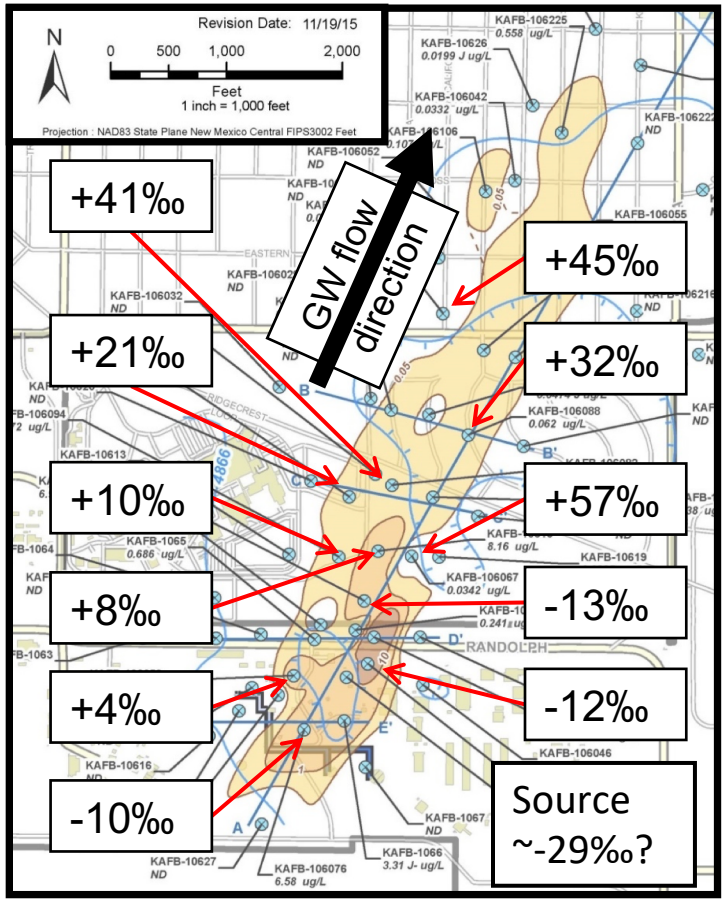
Basemap from USACE, 2015
https://hwbdocuments.env.nm.gov/Kirtland%20AFB/KAFB4345.pdf



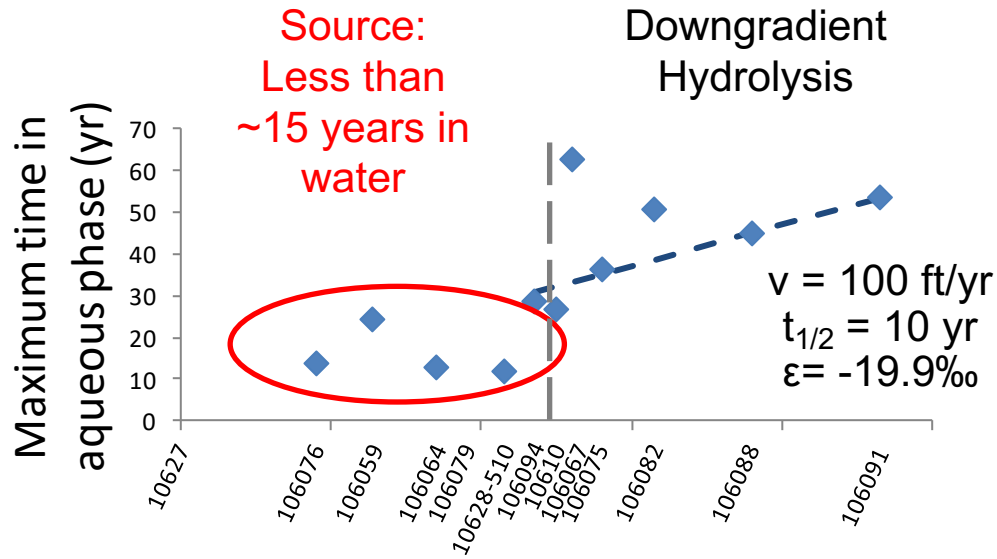


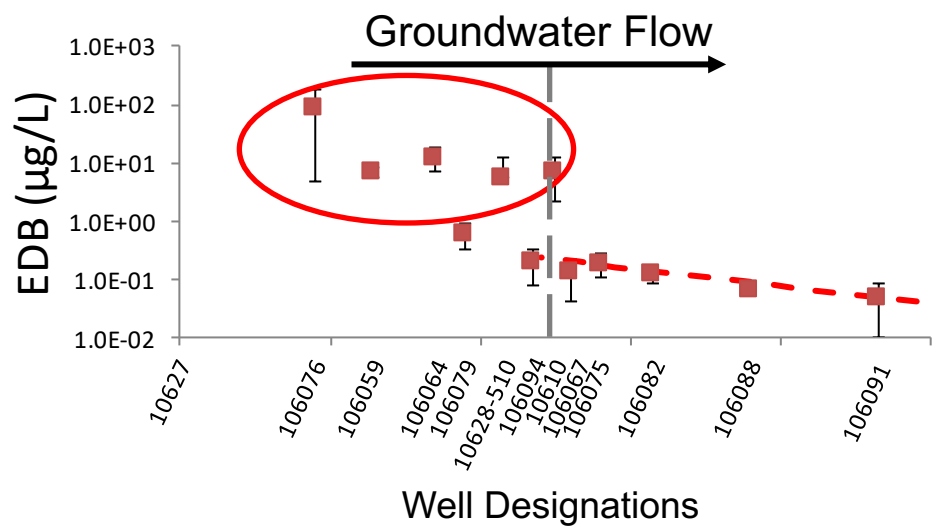
EDB Natural Attenuation

EDB Carbon Isotope Results



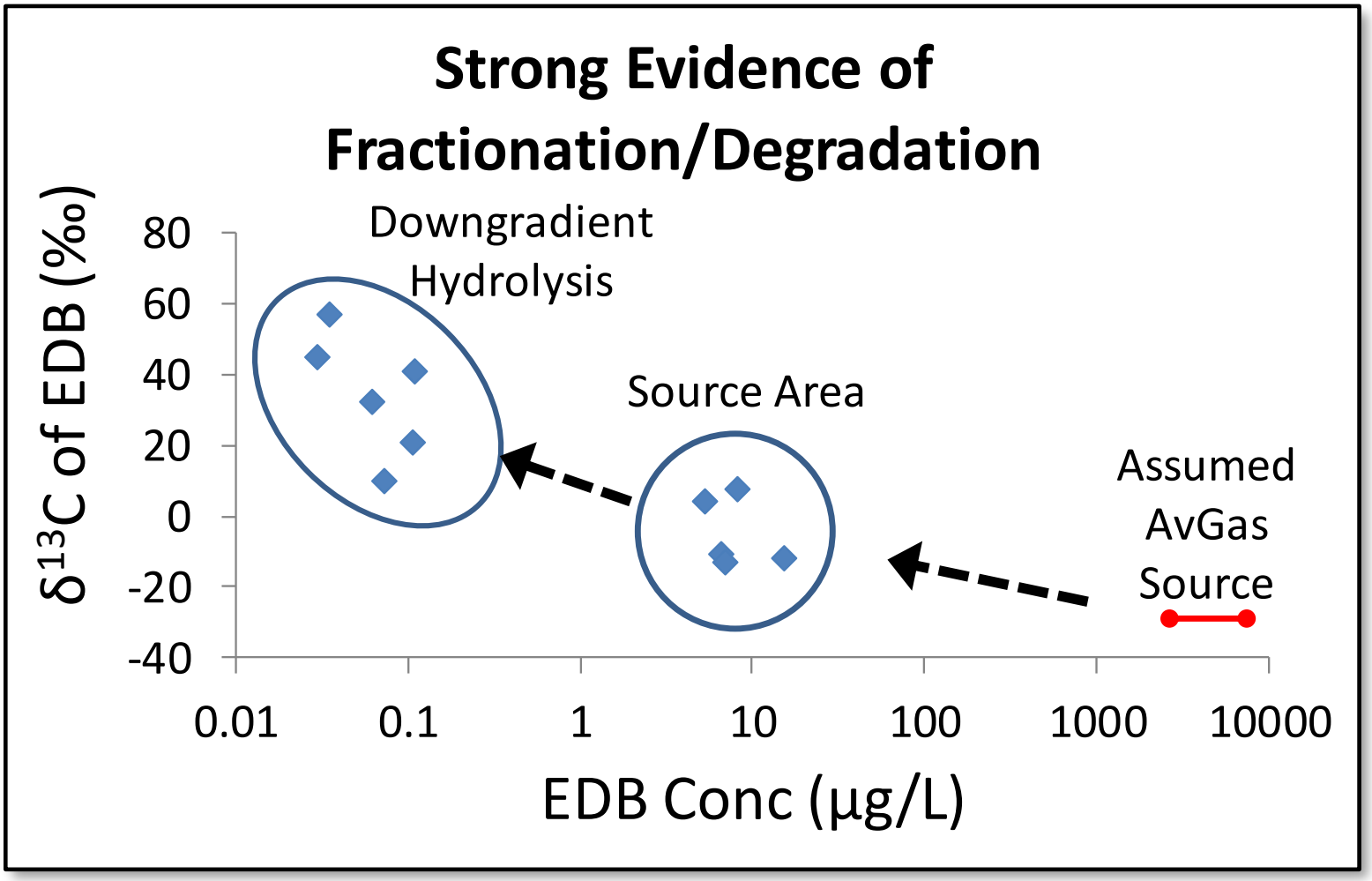
Basemap from USACE, 2015
https://hwbdocuments.env.nm.gov/Kirtland%20AFB/KAFB4345.pdf



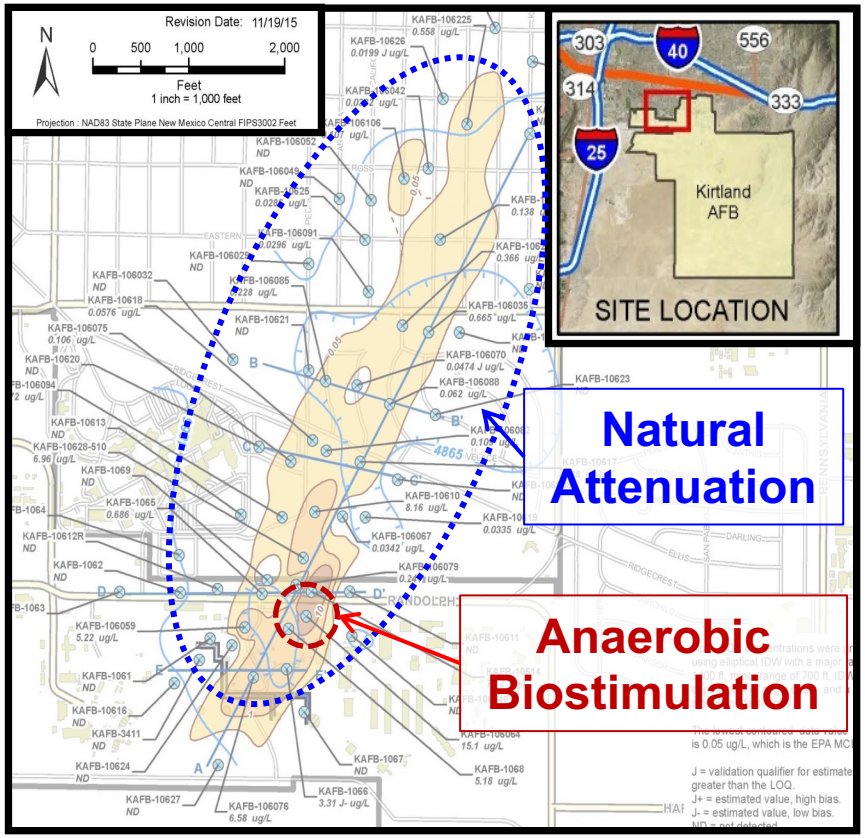


EDB Natural Attenuation

EDB Carbon Isotope Results

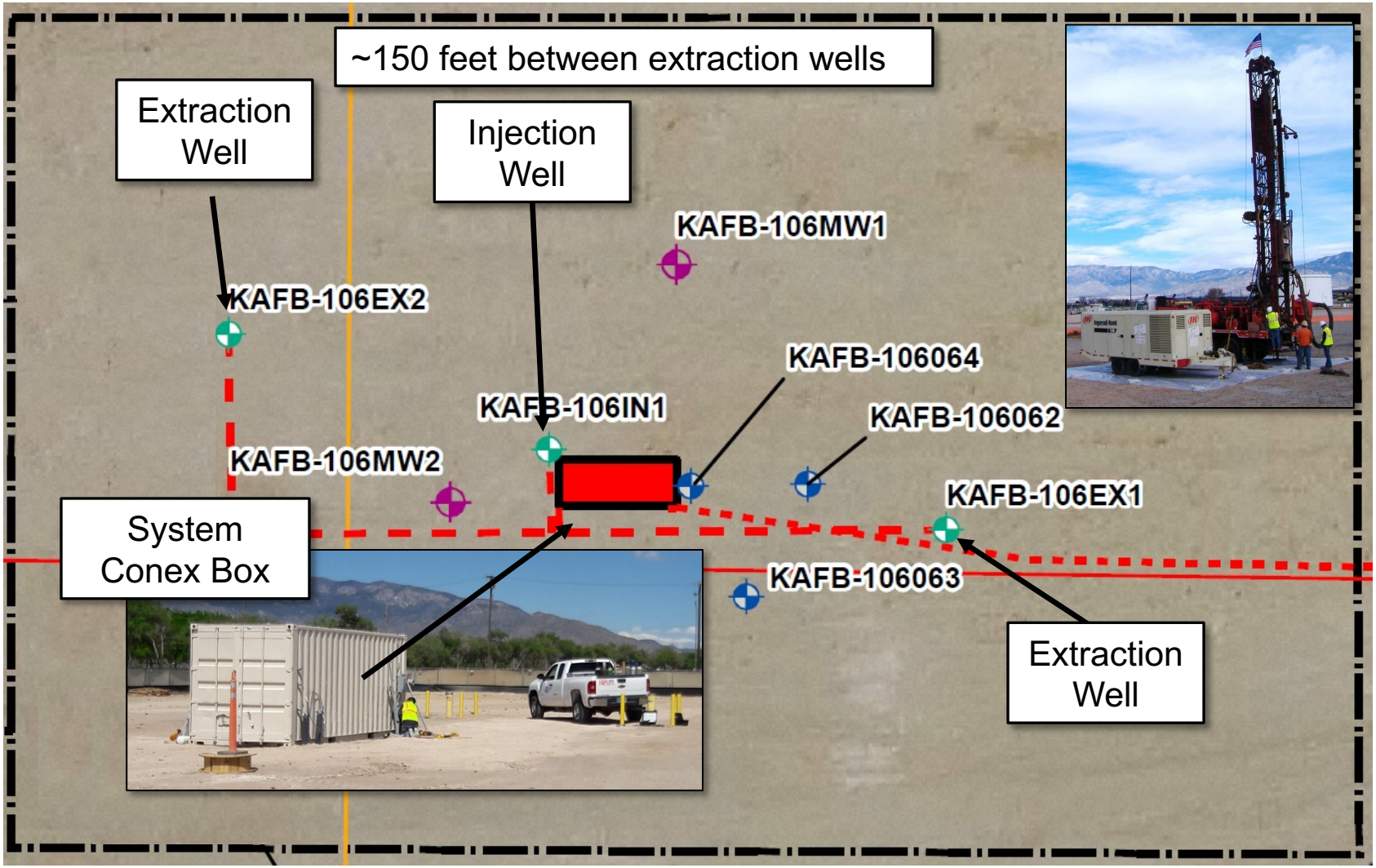


Anaerobic Biostimulation



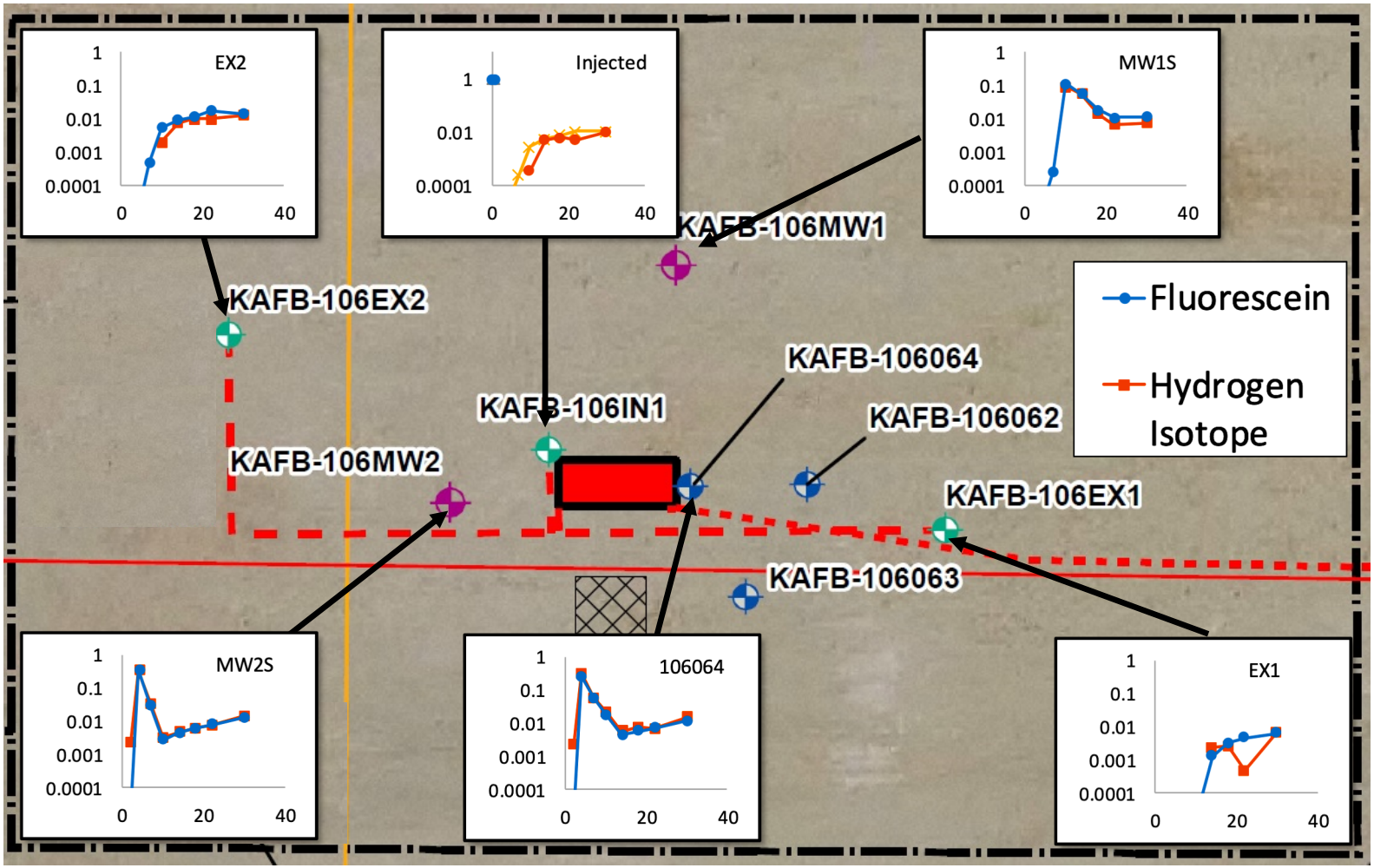
- Work with Kirtland AFB and US Army Corps of Engineers
- Recirculation system
- Phase 1: Evaluate baseline conditions and distribution of water
- Phase 2: Evaluate biostimulation with lactate and nutrients
- Phase 3: Evaluate biostimulation/ bioaugmentation
- Continued monitoring

Pilot Demonstration Site

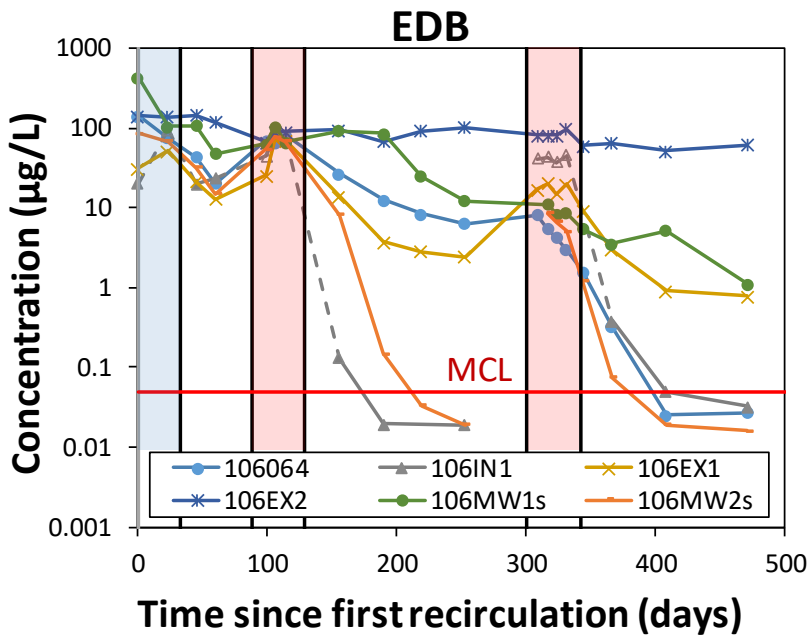


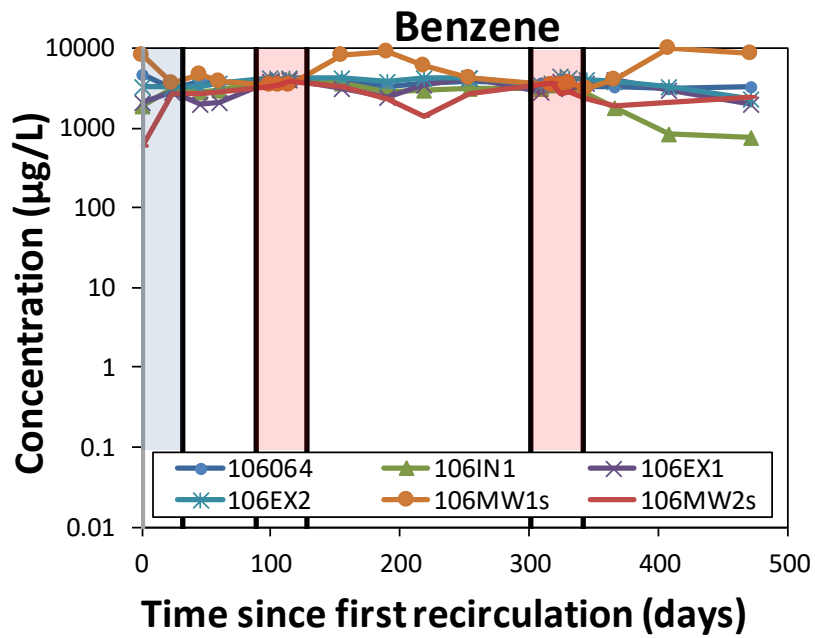
Phase 1: Water Distribution

Fraction of 24-hr Tracer Slug Concentration vs. Time (days)



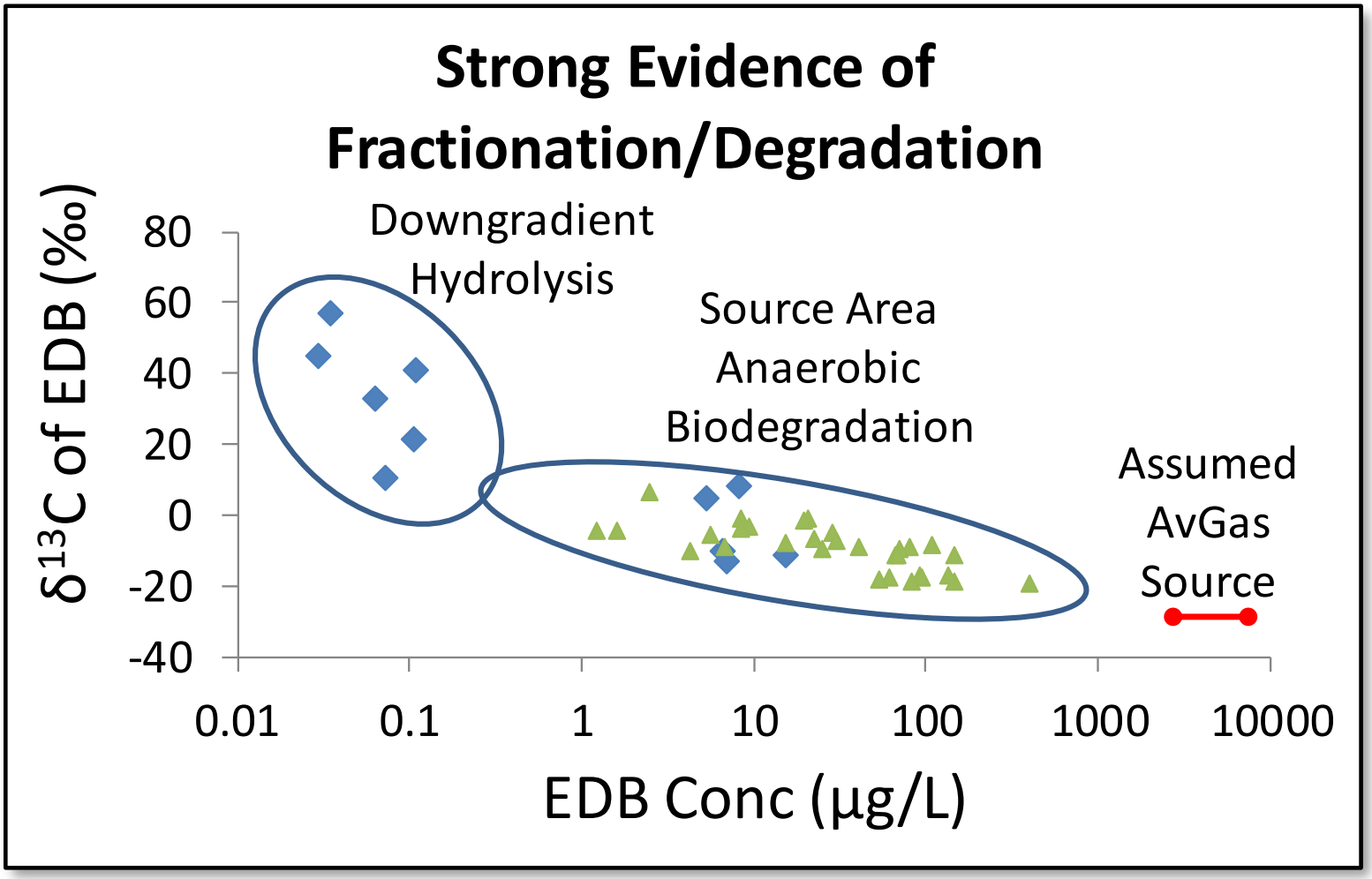
EDB Degradation after Biostimulation





- 99.7%+ reduction in EDB from baseline at 4 monitoring locations after mixing amendments (red zones)
- 3 wells below EPA MCL of 0.05 µg/L

EDB Carbon Isotope Results



Conclusions

- EDB degradation results in isotope fractionation
- Natural attenuation of EDB was apparent at field site
- Hydrolysis can be relevant
  - Half-life time ~ decade
- Anaerobic biostimulation effective for EDB
  - 99%+ reduction in most wells

Benefits to DoD

- Better tools to evaluate EDB natural attenuation
- Better knowledge of degradation mechanisms related to AvGas leaks
- Demonstration that anaerobic in-situ bioremediation is effective
- EDB is an “emerging” contaminant still widely used in leaded fuels (AvGas)

For additional information, please visit

https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Emerging-Issues/ER-201331

Speaker Contact Information

paul.kostervangroos@aptim.com; 609-895-5367

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Q&A Session 2

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ESTCP

The next webinar is on June 6, 2019

Developing and Demonstrating Non-Toxic Paints for Corrosion Protection

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Survey Reminder

Please take a moment to complete the survey that will pop up on your screen when the webinar ends

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