



# REGENESIS<sup>®</sup>

Technology-Based Solutions for the Environment




## Estimation of Sorbed-Phase Biodegradation Rate in Activated Carbon Barriers

Microbial Diagnostics – CSIA – *in situ* Microcosms

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# Contents

- Injectable Activated Carbon Barriers
  - plume management without pumping
- Coupling Sorption with Biodegradation
  - bioregeneration of capture capacity
- Field Validation and Rate Measurement
  - calibration for engineering control

# The Challenge

*In situ* remediation performance is typically tracked using groundwater samples

So what to do when concentrations are non-detect within a colloidal carbon barrier?

How can we *quantify* net destruction rate to improve engineering control?

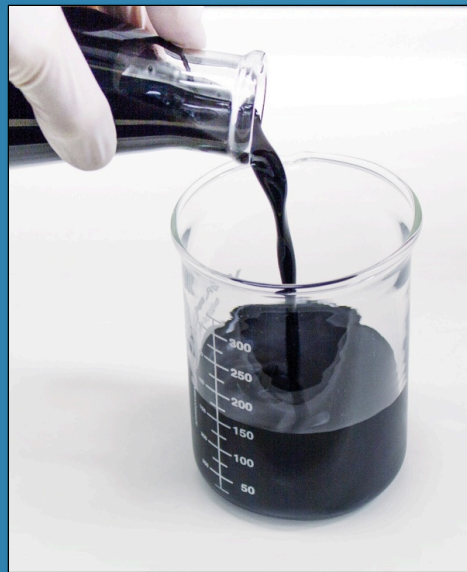


# This talk

Estimation of post-sorption degradation rates using *in situ microcosms* (ISM)s)

# Injectable activated carbon – fundamentals

**PLUME STOP™**  
Liquid Activated Carbon



 **REGENESIS**

**Booth # 134/6**

# Fundamentals



# Plume Management – Barrier

Keeping it simple...

## Configuration

Bioregeneration of sorption sites extends barrier longevity



# Fundamentals

- **The carbon quantity is tiny**
  - Groundwater flow is not affected
- **The capture efficiency is high**
  - Contaminant advection is slowed significantly
- **The groundwater may flow through the barrier in days**
  - The contaminants may take years to pass through
- **Biodegradation in the barrier extends its performance**
  - If the rate is fast enough the extension is indefinite

# Key parameters

Barrier performance is the interplay of two modelling parameters:

- **Contaminant Retardation Factors**
- **Contaminant Degradation Rates**

Retardation splices more treatment time into a shorter distance

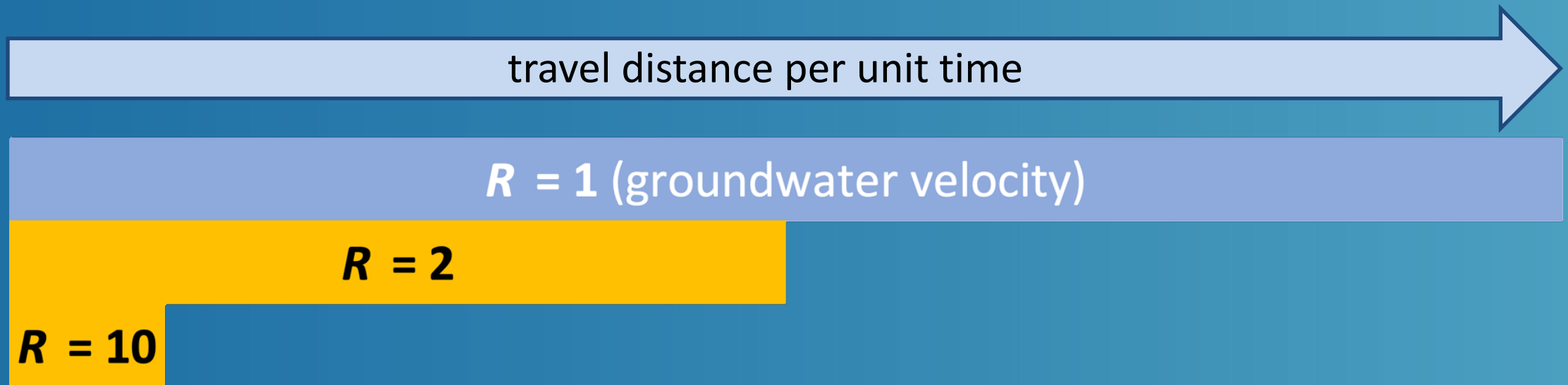
Degradation rate determines if breakthrough will ever occur

# Retardation-Factors



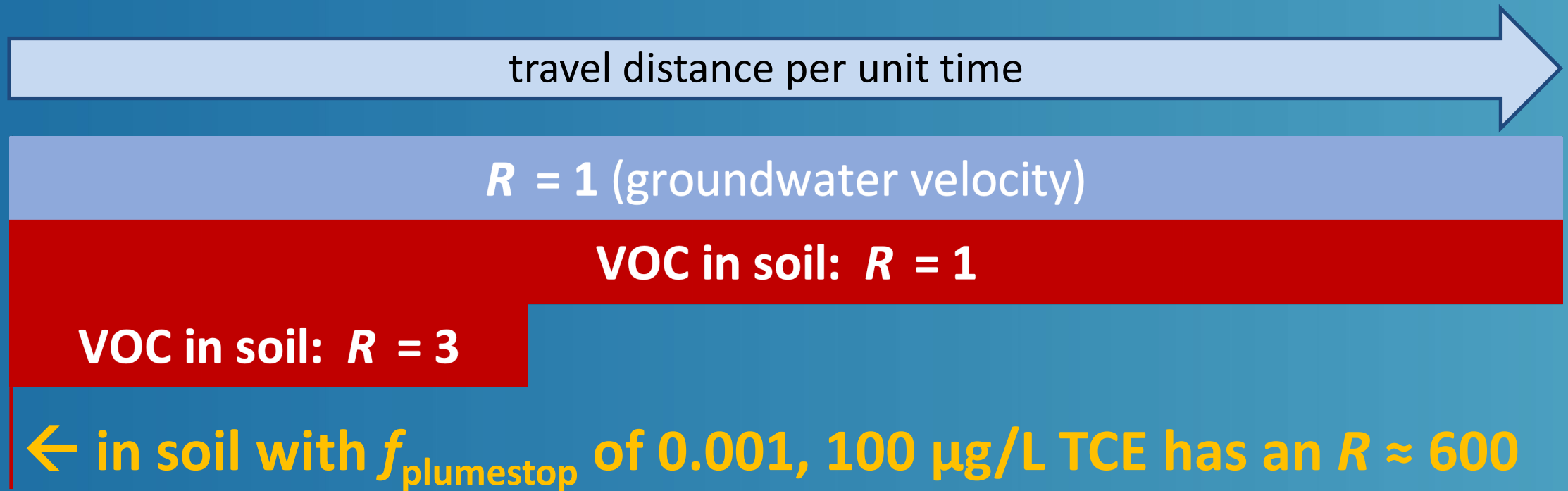
# Managing plumes via the retardation factor $R$

- The Retardation Factor ( $R$ ) determines how fast a contaminant moves relative to the groundwater.



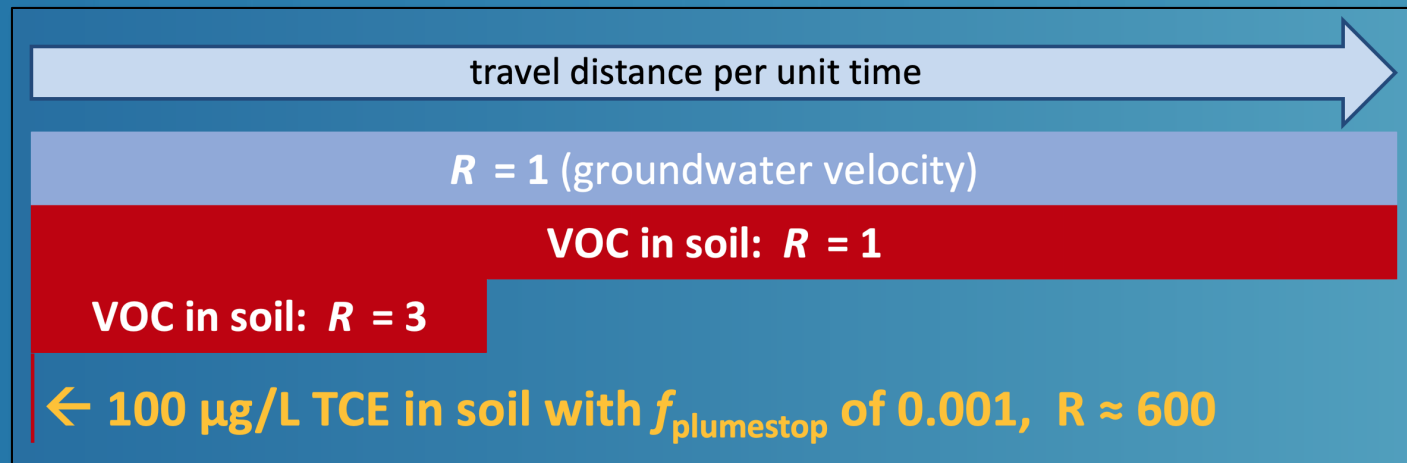
# Managing plumes via the retardation factor $R$

- The Retardation Factor ( $R$ ) determines how fast a contaminant moves relative to the groundwater.



# Managing plumes via the retardation factor $R$

- The TCE may therefore have **one month** to degrade in a bio-only barrier
- But it will have **16 years** to degrade over the same distance if PlumeStop<sup>®</sup> is added
- This translates to better performance and greater security



# Field Validation and Rate Measurement

- $R$  as installed can be validated through soil cores or tracer tests

## Challenge:

- But how to determine bio rates if the dissolved phase is non-detect?
- Solution – *in situ* microcosms (ISMs)
- Key – data resolution sufficient for purpose





# In Situ Microcosms

60



collect and dry saturated soils

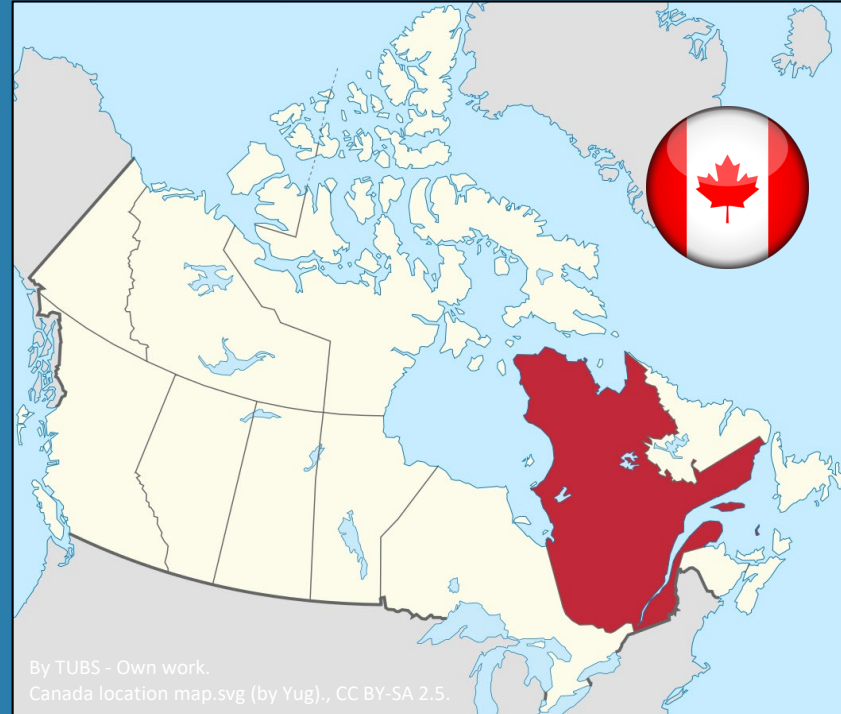


place soil into screened housings



deploy before amendment application

# ISM Usage Example



By TUBS - Own work.  
Canada location map.svg (by Yug), CC BY-SA 2.5.

**Quebec, Canada  
Rail Yard, VOCs**

# Implementation



Matt Burns

November 2017

## Amendments

- PlumeStop: 1,900 L
- AquaZVI: 800 L
- HRC Pimer: 250 L
- HRC: 250 L
- Augment: 18 L

## Dilution/Chase Water

- Potable Water: 25,000L

## Total Fluids:

- Wast + Amendment: 28,000
- Aproximately 10% of mobile porosity within treatment zone

## Observations

- Pressure: 20 to 40 psi
- Some back pressure
- Amendment observed and some geochemical shifts in wells within treatment area



# ISM Usage Example – Quebec Rail Yard

Chlorinated ethenes / ethanes

- $\sum$  Tri – 4,500  $\mu\text{g/L}$
- $\sum$  Di – 13,000  $\mu\text{g/L}$

Soil type

- Heterogeneous silt and sand

Treatment

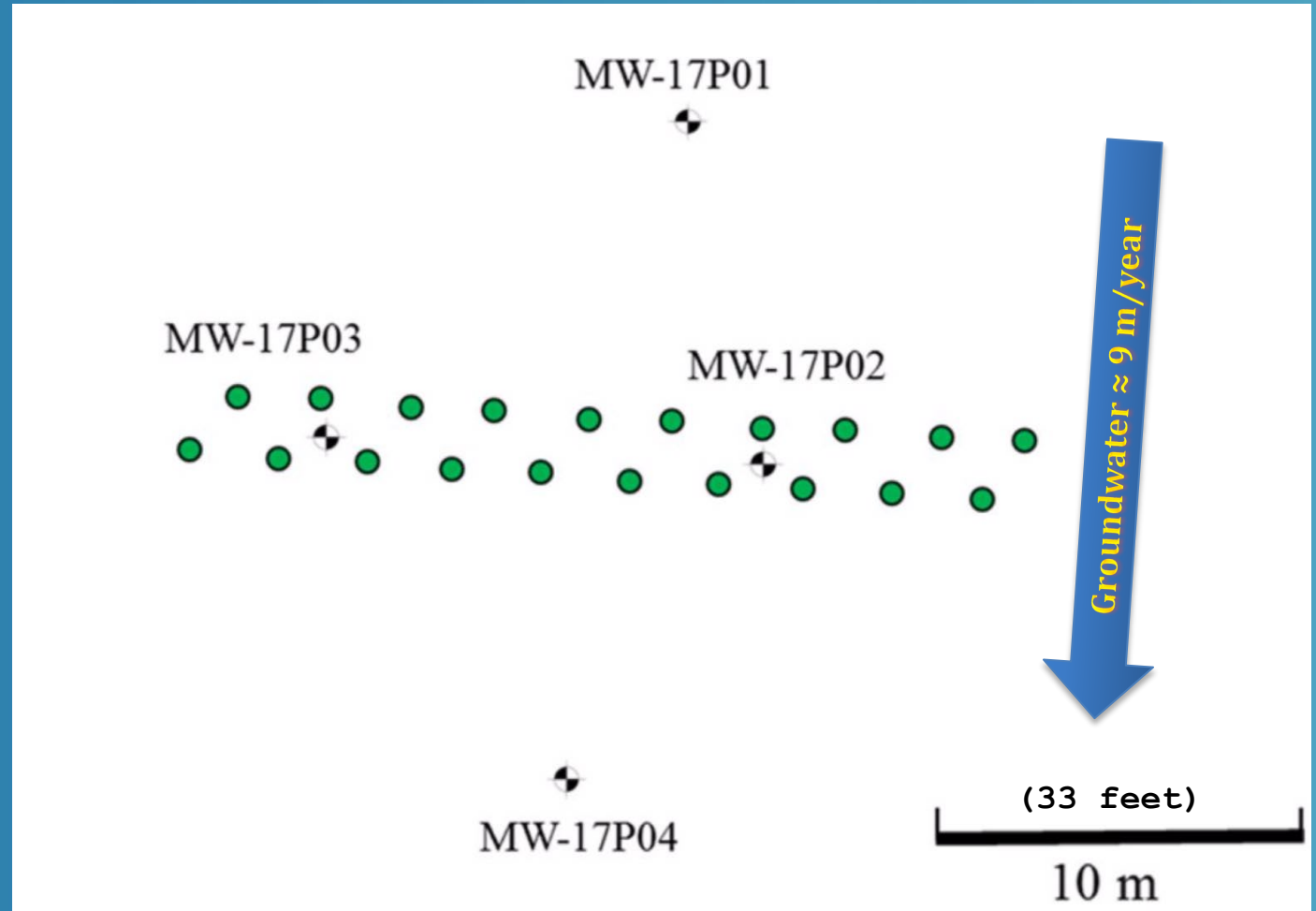
- 26' – 46' bgl (8 – 14 m)

Seepage velocity

- 30 ft/year (9 m/year)

Barrier

- 16' x 100' x 20' d
- 5 m x 30 m x 6 m d



# Design Model - Quebec Rail Yard

(Post LAC™ Application)

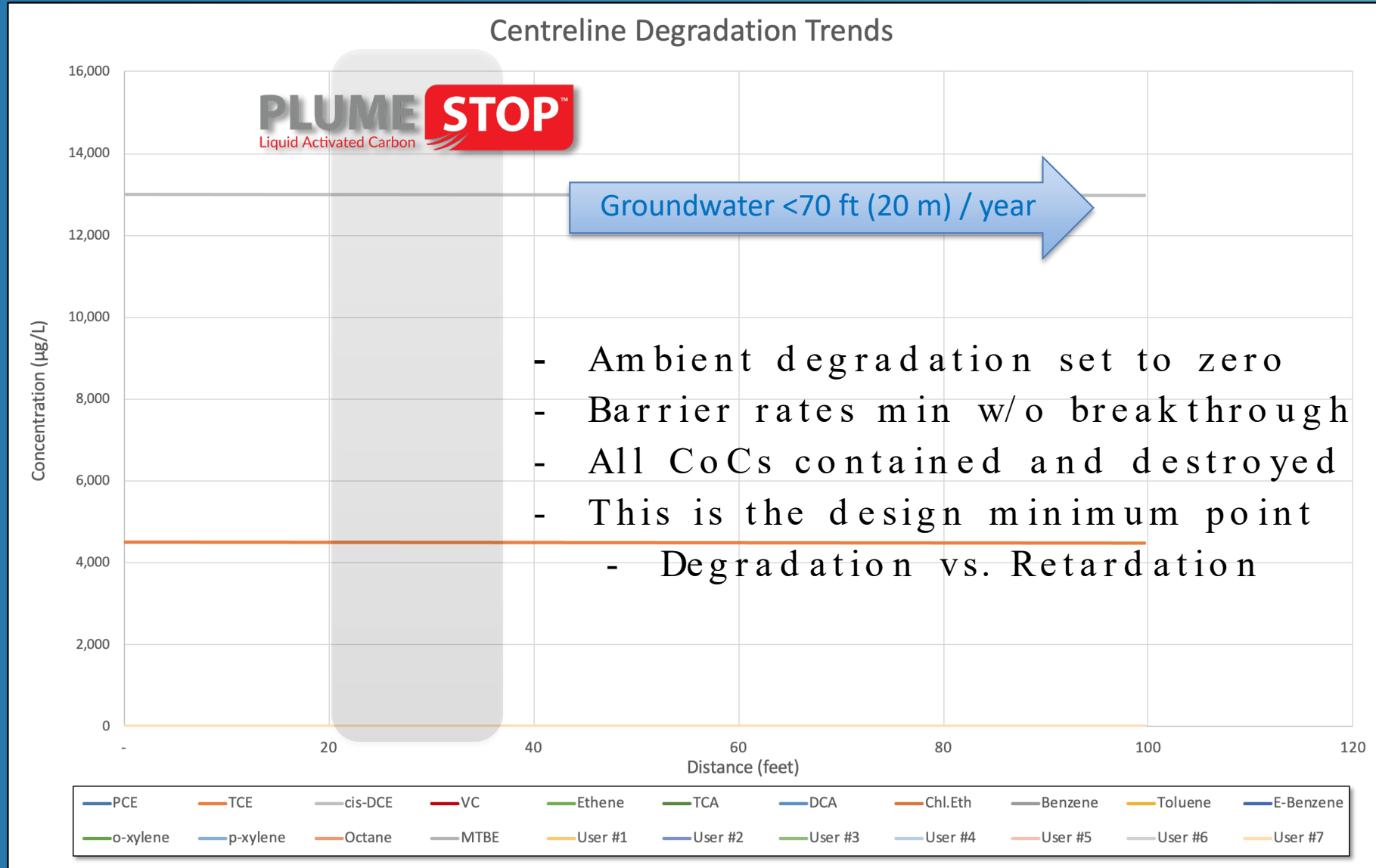
Deg. Rates  $k$  (as  $t_{1/2}$ )  
 100 days (TCE, DCE)  
 30 days (VC, ethene)

Retardation Factors ( $R$ )

- dynamically variable
- convex isotherms
- competitive sorption
- range 10's to 1000's

$f_{oc} = 0.001$   
 $f_{PlumeStop} = 0.0003$

LAC™ Emplaceable Range:  
 ~0.0001 - 0.02 (:0.0003 ≈ 1.5%)



# Design Model - Quebec Rail Yard

(No LAC™ Application)

Deg. Rates  $k$  (as  $t_{1/2}$ )

100 days (TCE, DCE)

30 days (VC, ethene)

- (all unchanged)

Retardation Factors ( $R$ )

- TCE = 1.81

- DCE = 1.53

- VC = 1.02

$f_{oc}$  = 0.001

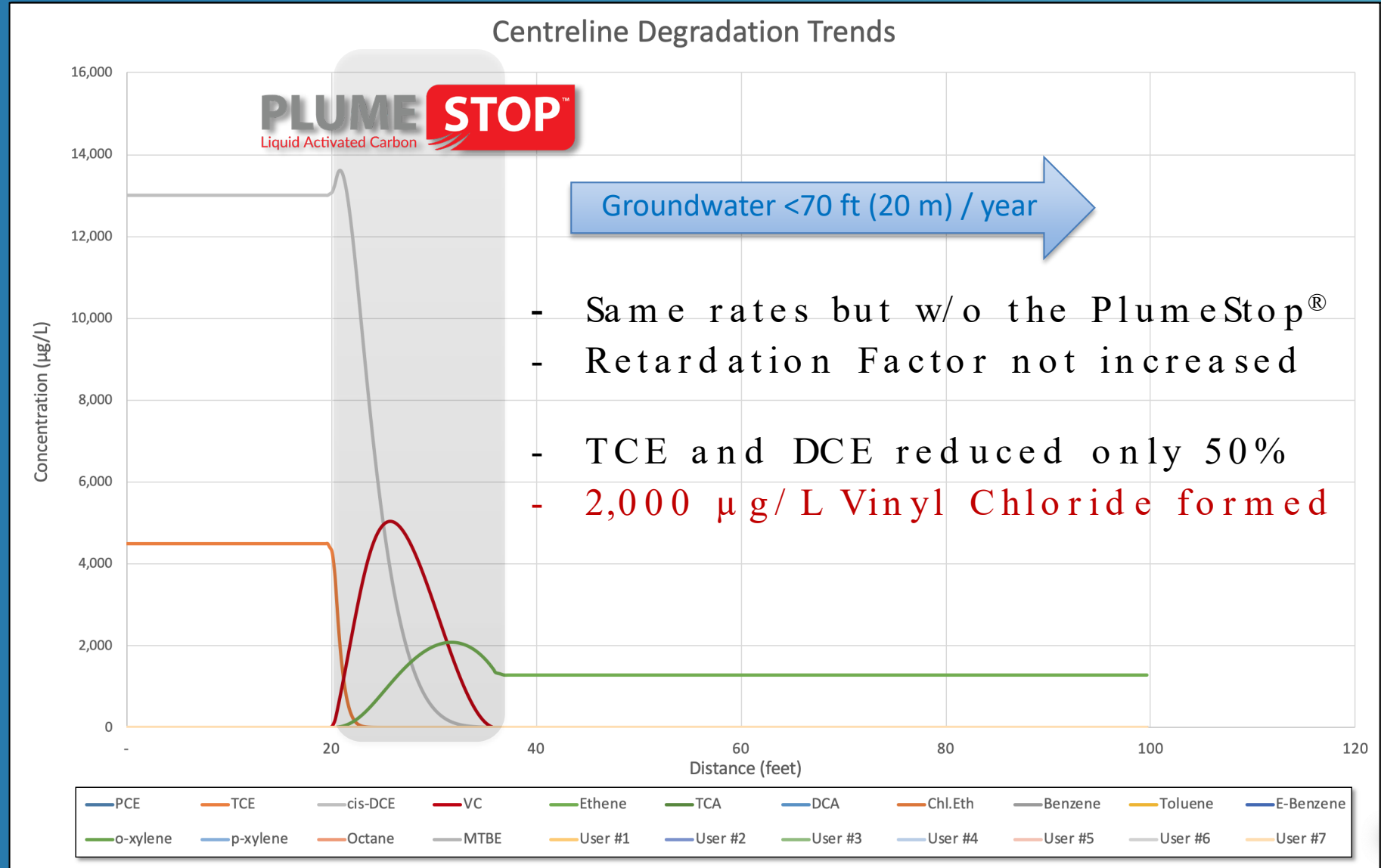
$f_{PlumeStop}$  = **zero**

Bio rates would have to be  
< 10 days (TCE, DCE)

< 3 days (VC)

for compliance w/o retardation

(in the Quebec winter)



# Design Model - Quebec Rail Yard

(i.e. Post LAC™ Application)

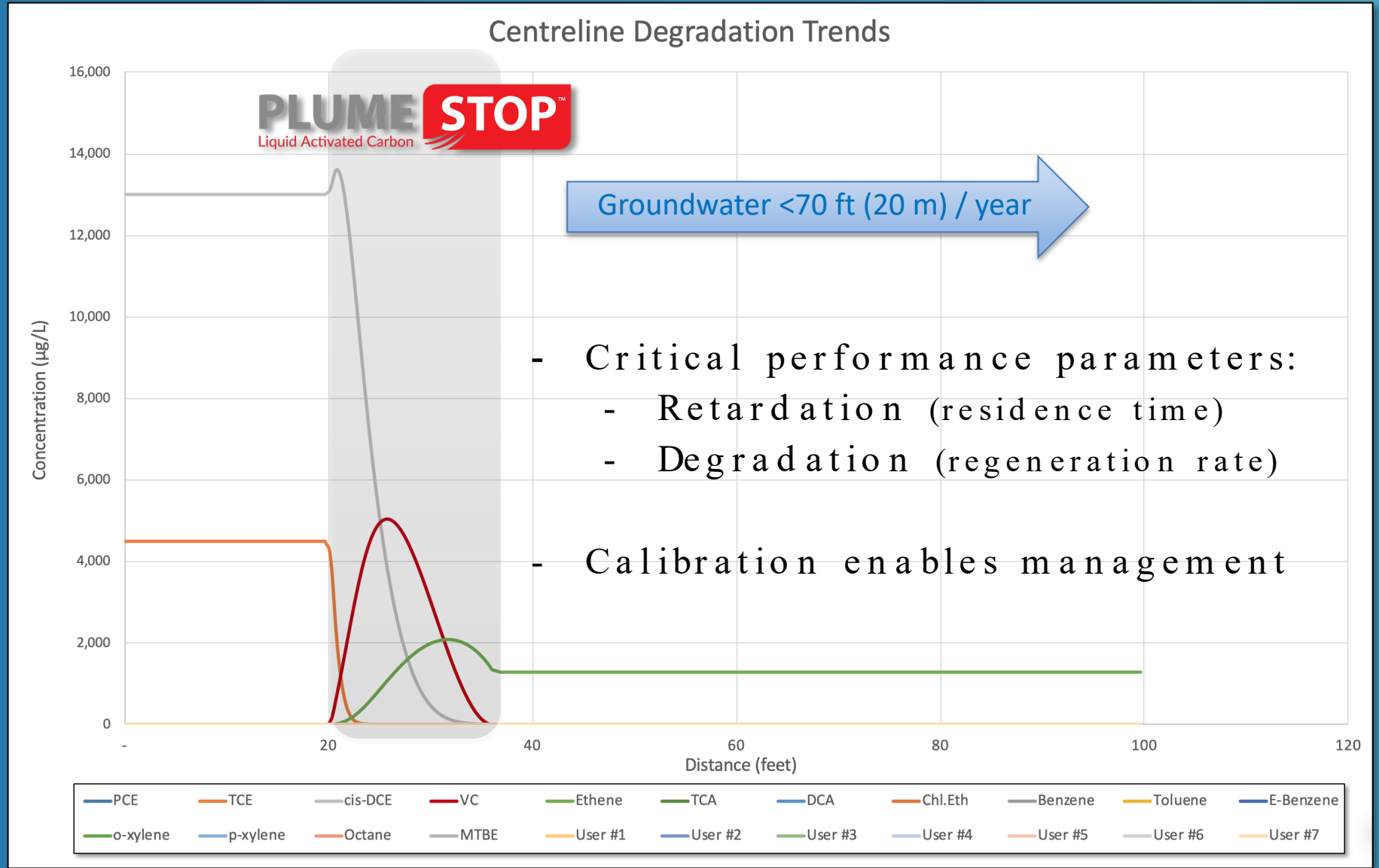
Deg. Rates  $k$  (as  $t_{1/2}$ )  
 100 days (PCE, TCE, DCE)  
 30 days (VC, ethene)

Retardation Factors ( $R$ )

- dynamically variable
- convex isotherms
- competitive sorption
- range 10's to 1000's

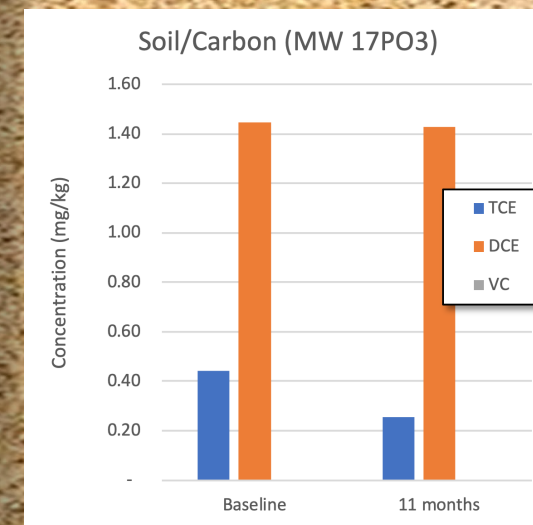
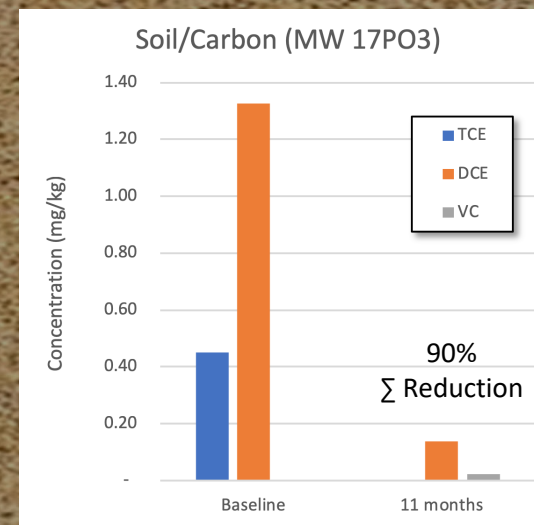
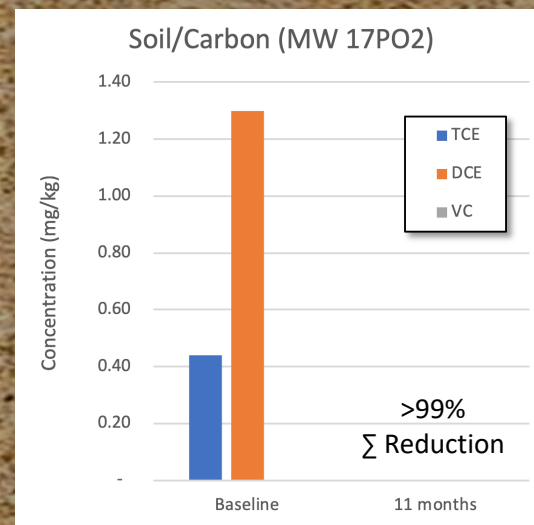
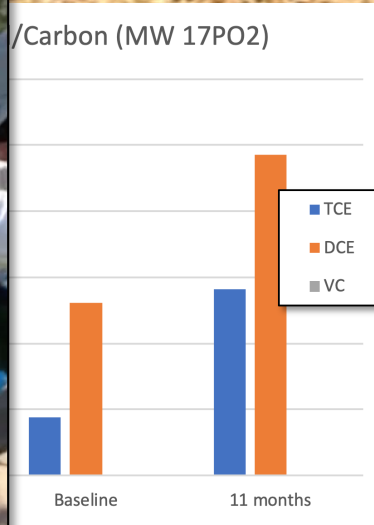
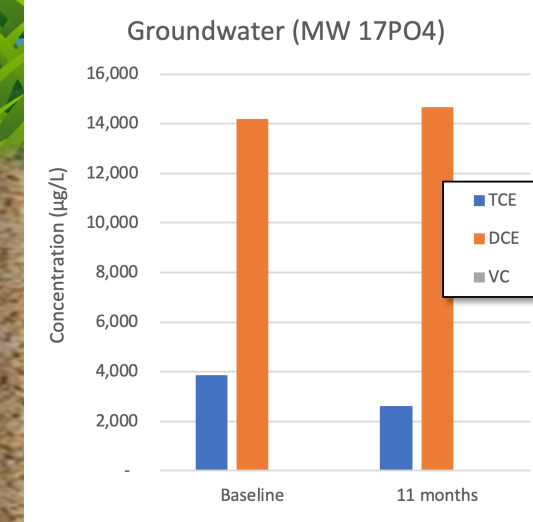
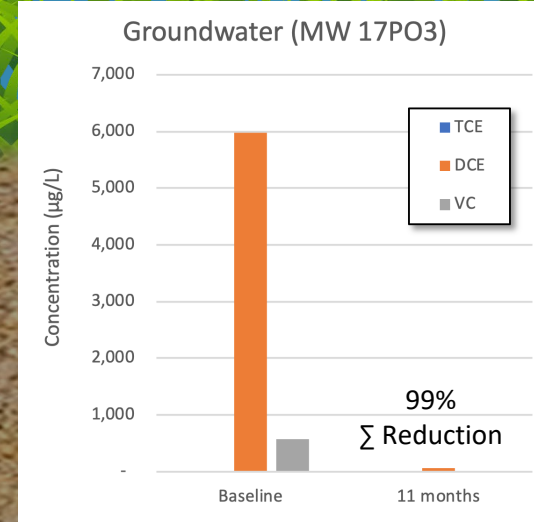
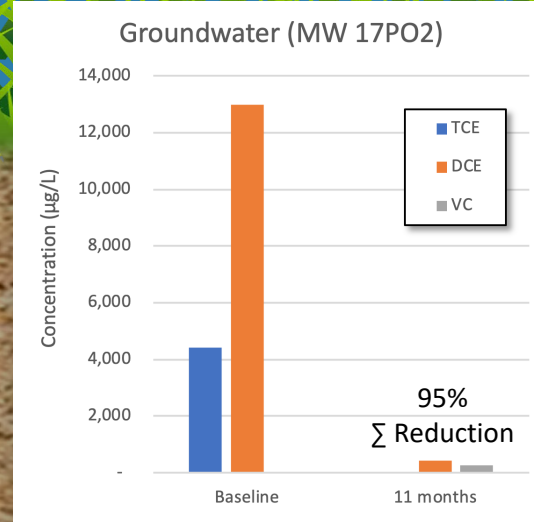
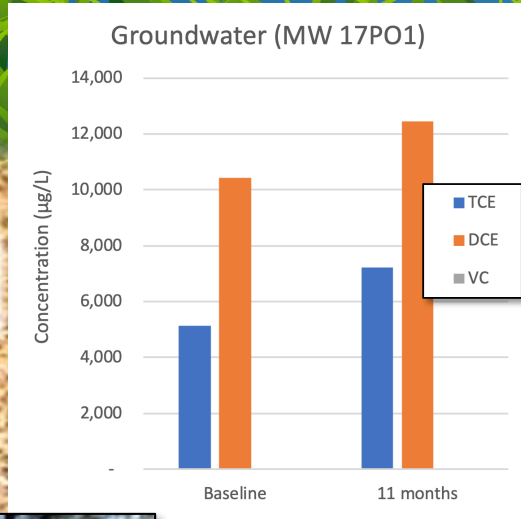
$f_{oc} = 0.001$   
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LAC™ Emplaceable Range:  
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# Contaminant Destruction (11 months)

Water →



Treatment Zone

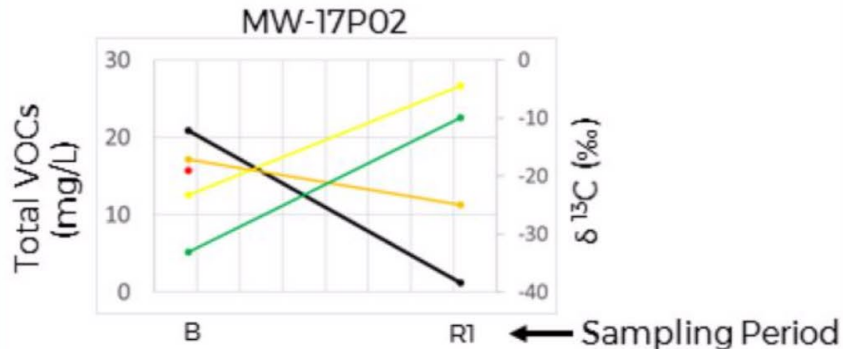




Sam Rosolina

# Results - CSIA

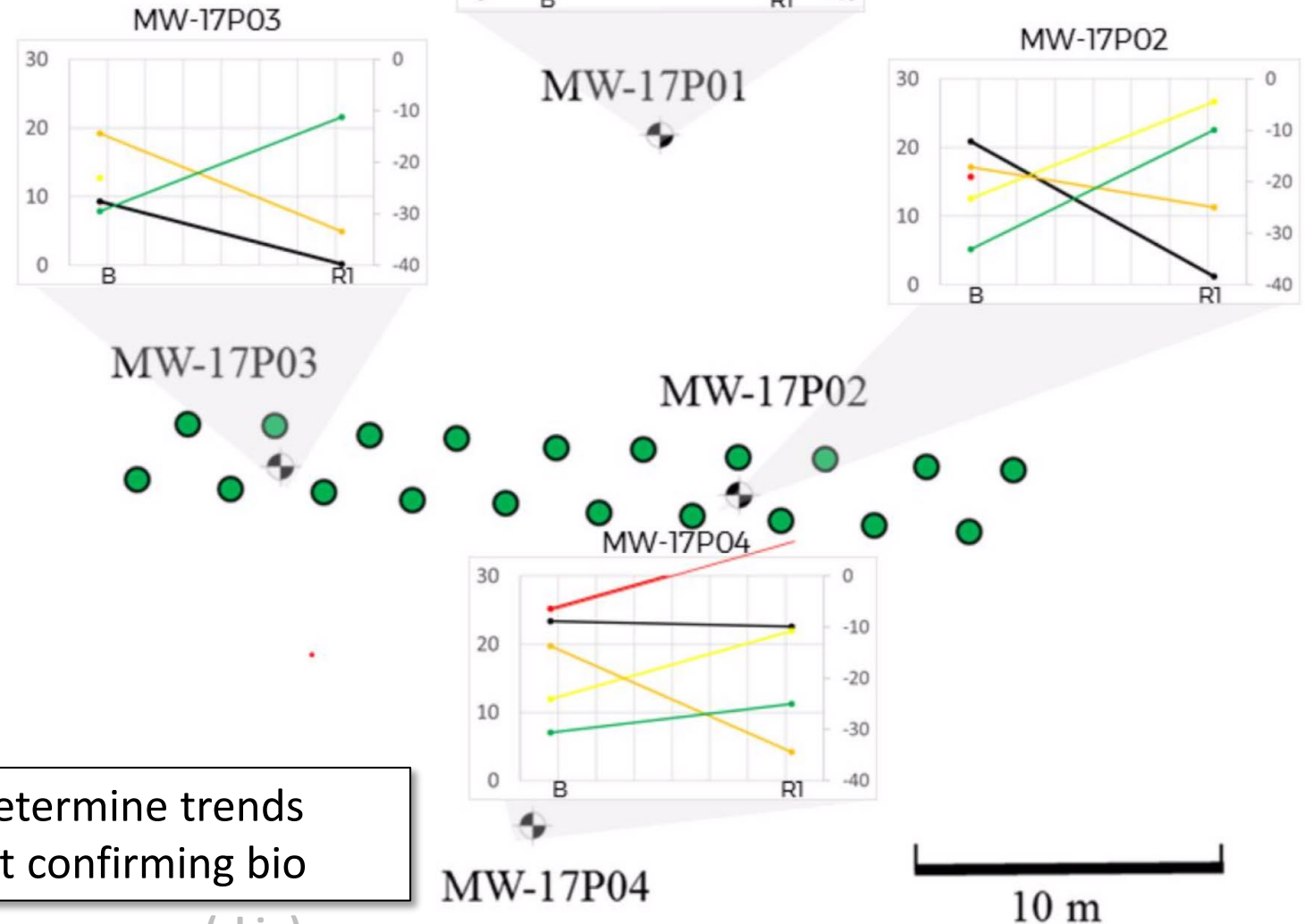
## Legend



← Sampling Period  
 B = 10/17  
 R1 = 9/18

- Total VOCs
- TCE  $\delta^{13}\text{C}$
- cis-DCE  $\delta^{13}\text{C}$
- 1,1-DCE  $\delta^{13}\text{C}$
- Vinyl Chloride
- Pilot Test Monitoring Well
- Injection Point

- GW TCE reduced to n/d – nothing left to determine trends
- cis-DCE and VC show clear  $\delta^{13}\text{C}$  enrichment confirming bio



(skip)

# Estimation of Destruction Rate

- Trendlines cannot be established from only two data points
  - But minimum rates can
  - This is sufficient to validate design assumptions
  - There is design compliance if the rate is greater than the design minimum

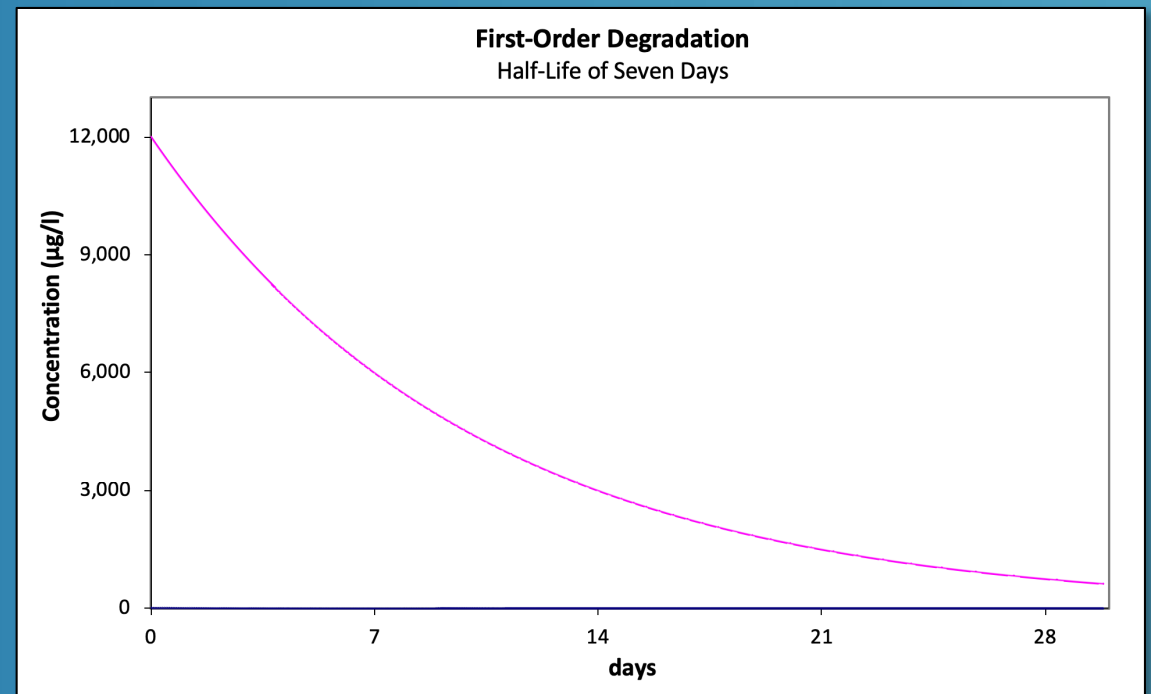


# Estimation of Destruction Rate

- Simple exponential (first-order) fits
- These may be also expressed as half-lives

$$k = -\frac{\ln\left(\frac{C_1}{C_0}\right)}{t}$$

$$t_{1/2} = \frac{-\ln(0.5)}{k}$$

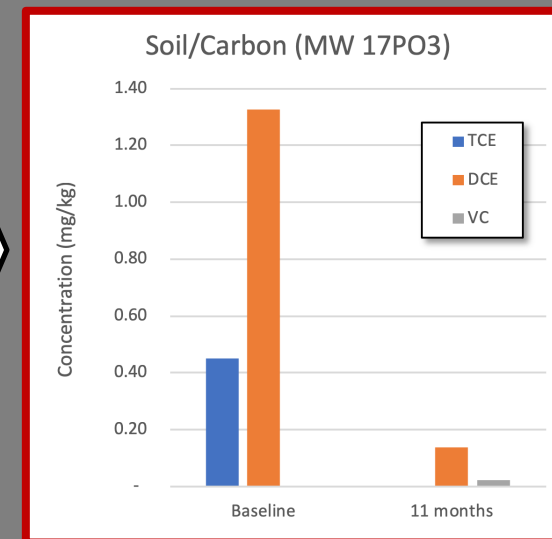
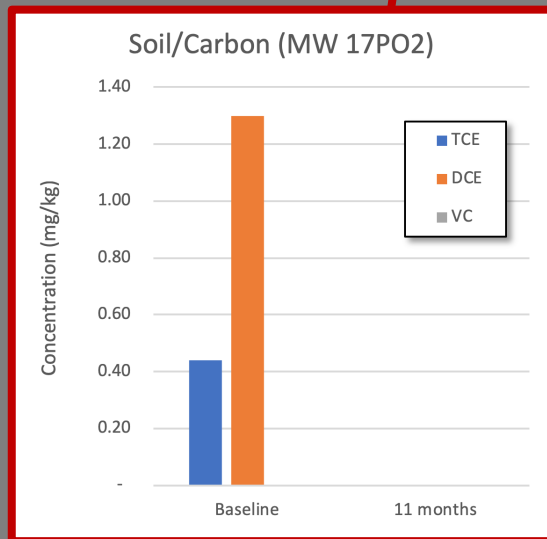


# Estimation of Destruction Rate (bookending the minima)

TCE $t_{1/2}$ (days)	MW17P02	MW17P03
Soil / Carbon	<b>38.1</b>	37.6

DCE $t_{1/2}$ (days)	MW17P02	MW17P03
Soil / Carbon	24.5	<b>154</b>

Balance of loss and formation – very conservative as loss rate.



# Estimation of Destruction Rate

- Daughter loss rates can be refined using model-fits
  - Simple models are sufficient
  - The minimum is independently assignable rates and a parent-daughter molar cascade
- Model-unwrapped minimum half-lives from ISM data:
  - TCE = 38 days
  - DCE = 141 days
  - VC = 3 days

These can now be used in our design model for calibration



# Design Model - Quebec Rail Yard

(i.e. Post LAC™ Application)

## Design

Deg. Rates  $k$  (as  $t_{1/2}$ )

100 days (TCE, DCE)

30 days (VC, ethene)

## Calibrated

Deg. Rates  $k$  (as  $t_{1/2}$ )

38 days (TCE)

141 days (DCE)

3 days (VC)

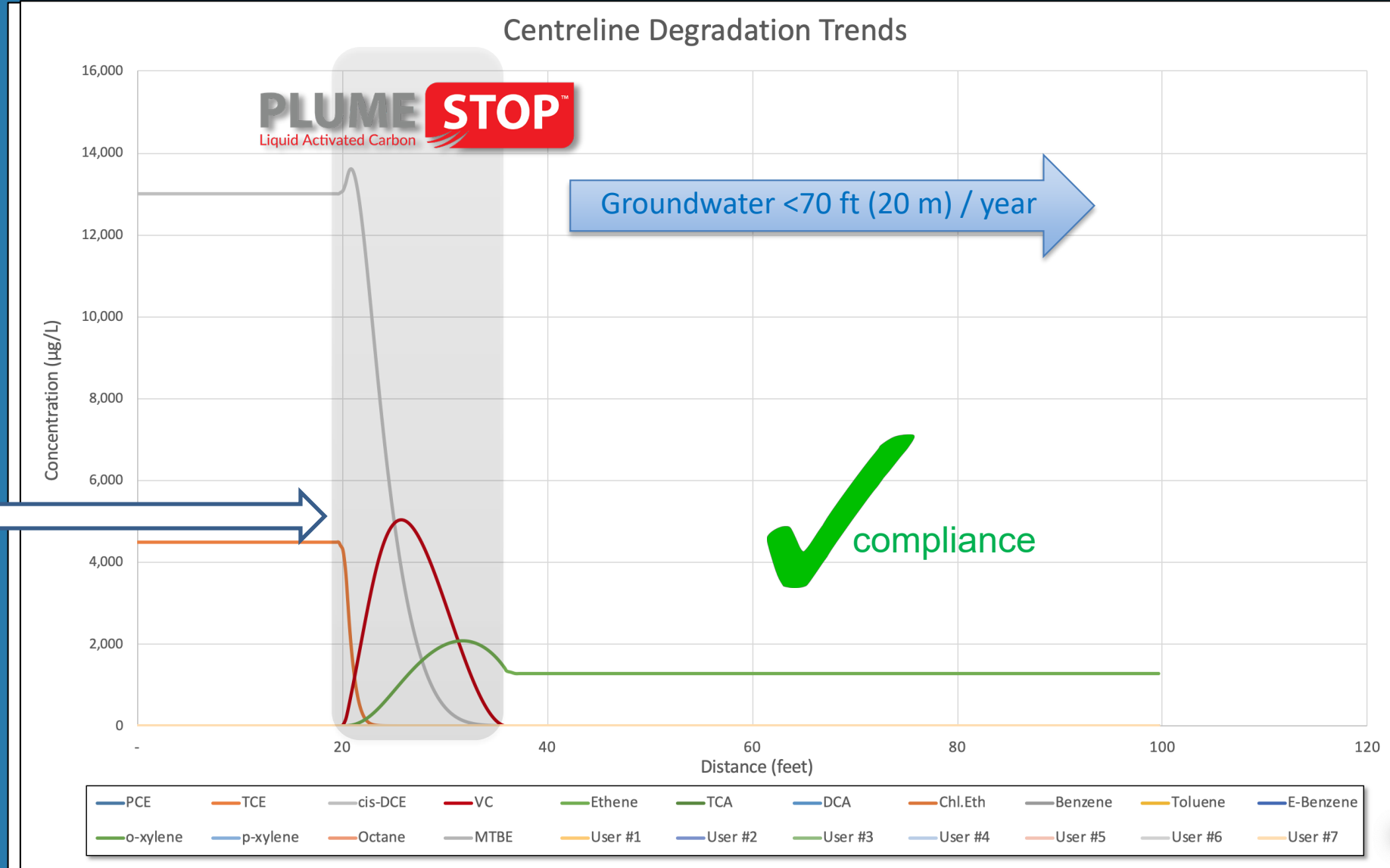
(3 days ethene)

$f_{oc} = 0.001$

$f_{PlumeStop} = 0.0003$

LAC™ Emplaceable Range:

~0.0001 - 0.02 (:0.0003 ≈ 1.5%)



(close)

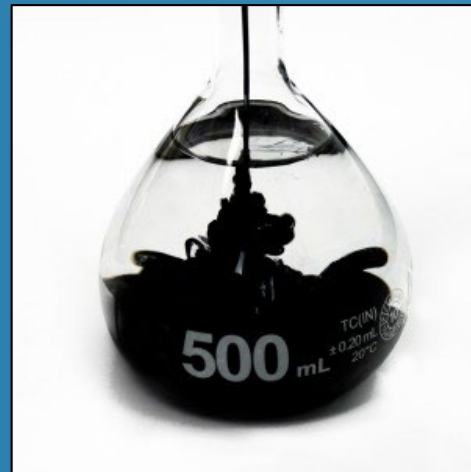


- Summary & Conclusions -

# Summary and Conclusions

- **Injectable carbon – combined retardation and biodegradation**
  - More destruction in a shorter distance
  - Contained treatment without O&M costs

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# Summary and Conclusions

- ISMs – a management tool for engineers
  - Validation of design assumptions
  - Longevity compliance prediction / early intervention alert
  - Ensure performance remains within design boundaries



A developing art!

# Taking this forward

- Method refinements for established barriers
  - Identifying and quantifying new bias
    - E.g. acclimated barriers vs. non-acclimated ISMs
- Expanded use of microbial diagnostic tools
  - Attached community QuantArrays (ISMs  $\approx$  BioTraps<sup>®</sup>)
  - Stable Isotope Probing (SIP) (aerobically degradable contaminants only)
- Combine with *in situ* retardation quantification
  - Full model calibration capability
  - Comprehensive management tool-kit for engineers





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**Thank You**