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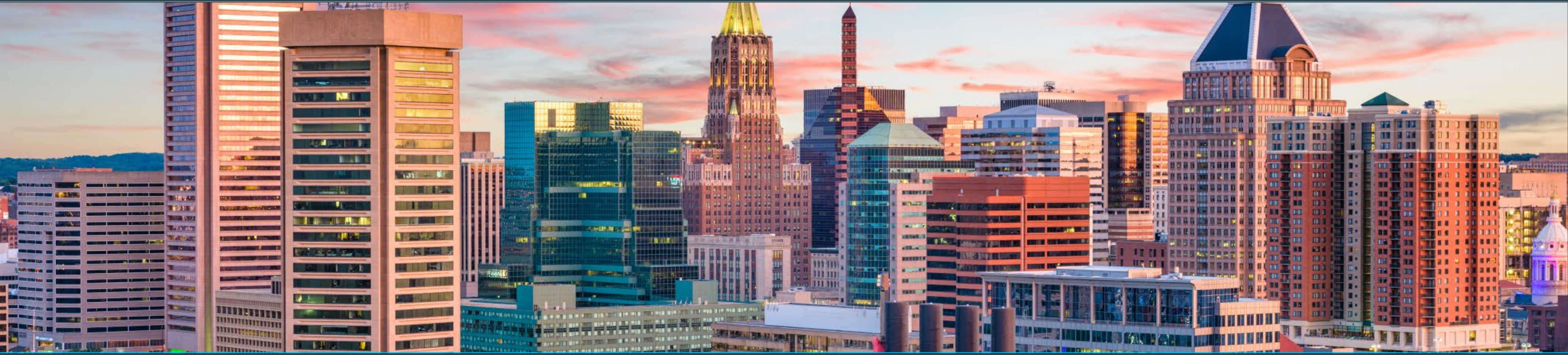

In situ Biodegradation Rates in Contaminated Sediments via a Novel High Resolution Isotopic Approach: A Field and Modeling Study

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April 17, 2019

Outline

– Site Conditions
– Problem Statement
– Approach
– Results and Discussion

01

Introduction

- Site Conditions
- Problem Statement

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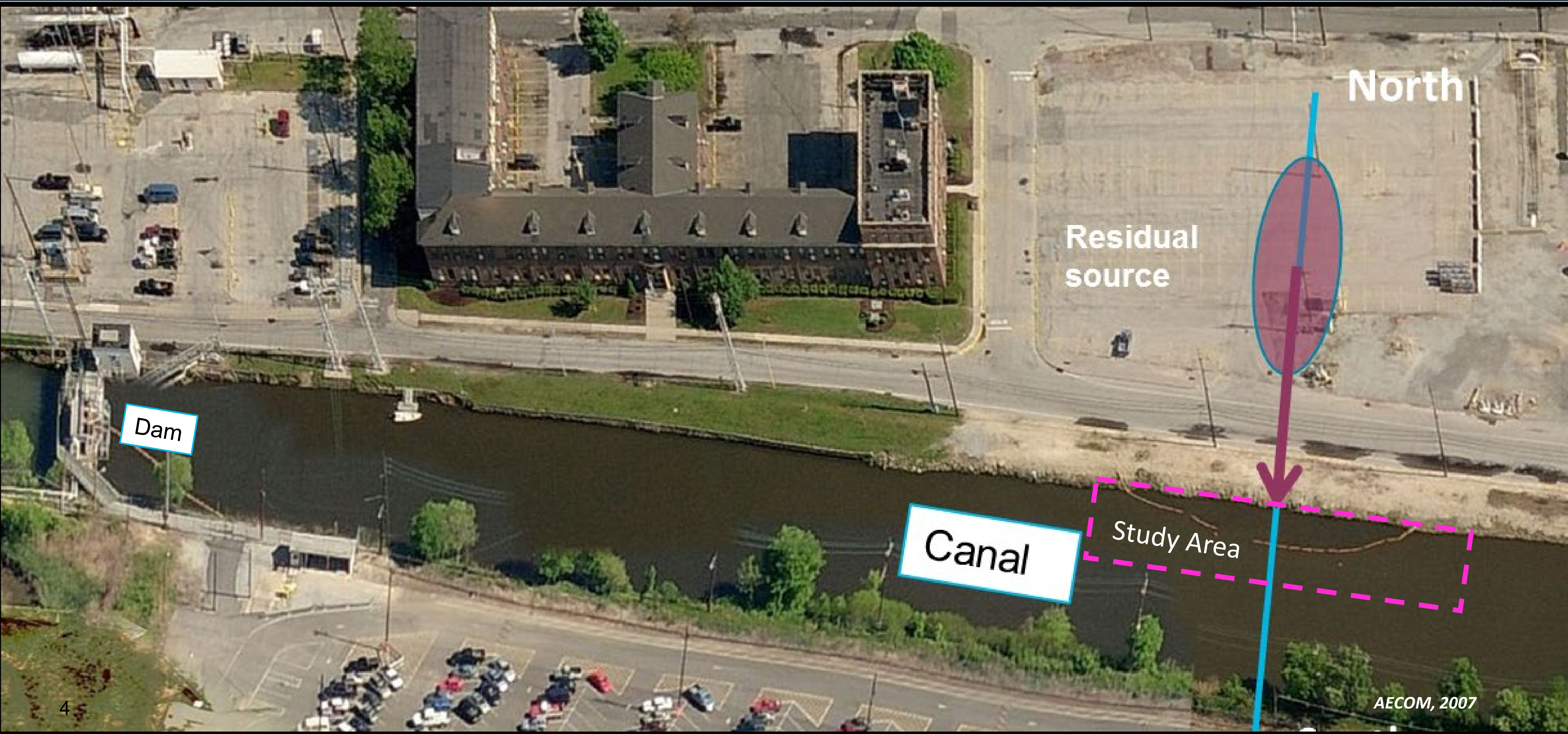
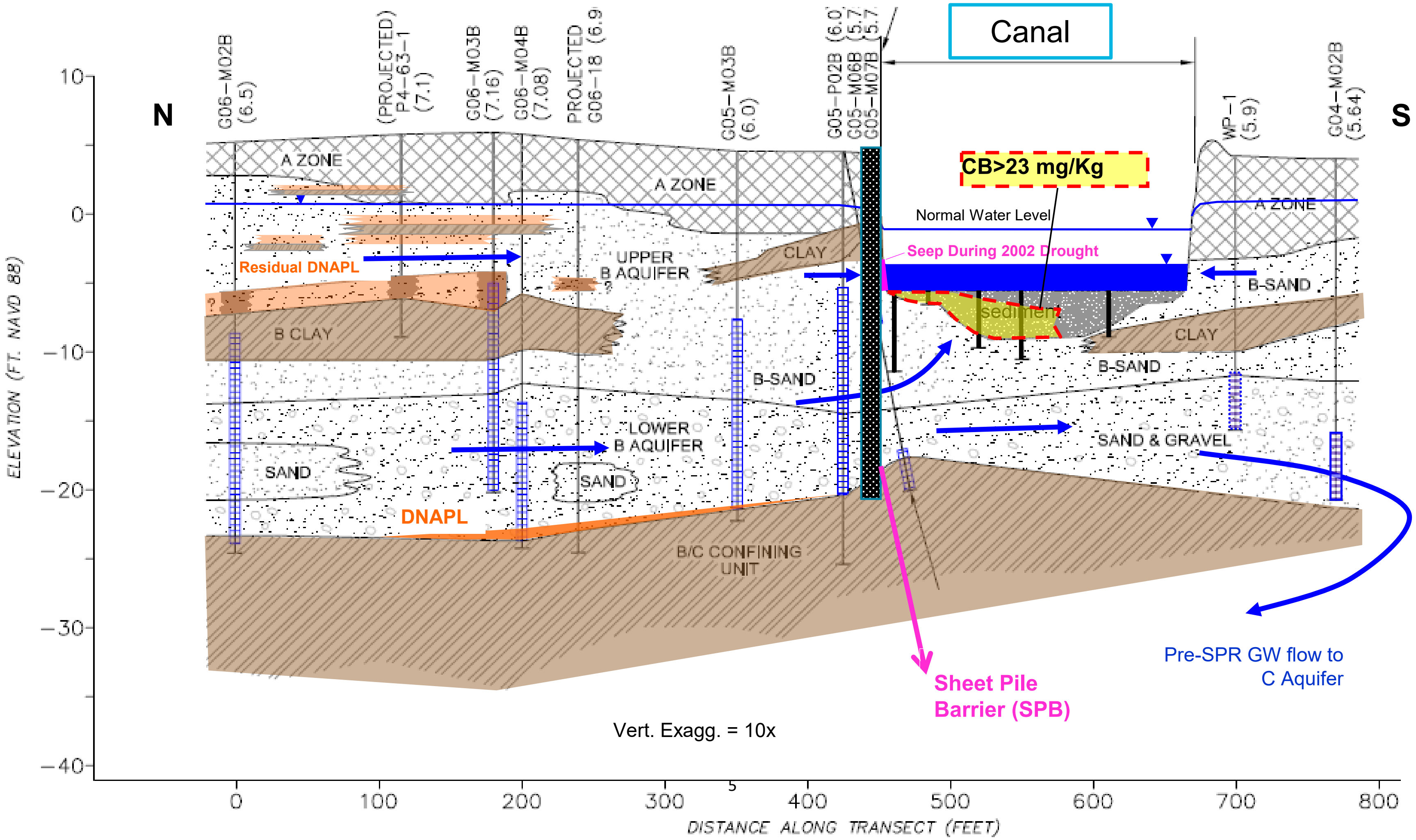
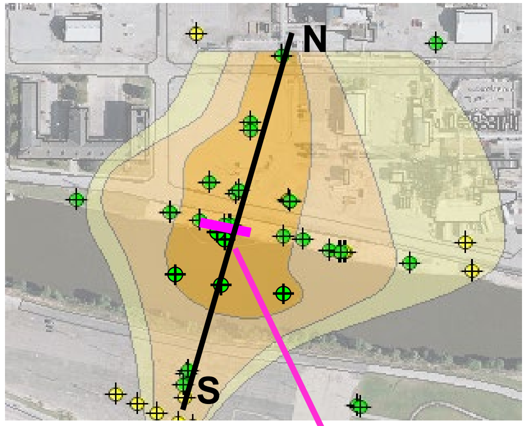
Site Map



Conceptual Site Model





Sheet Pile Barrier (SPB)

AECOM, 2007

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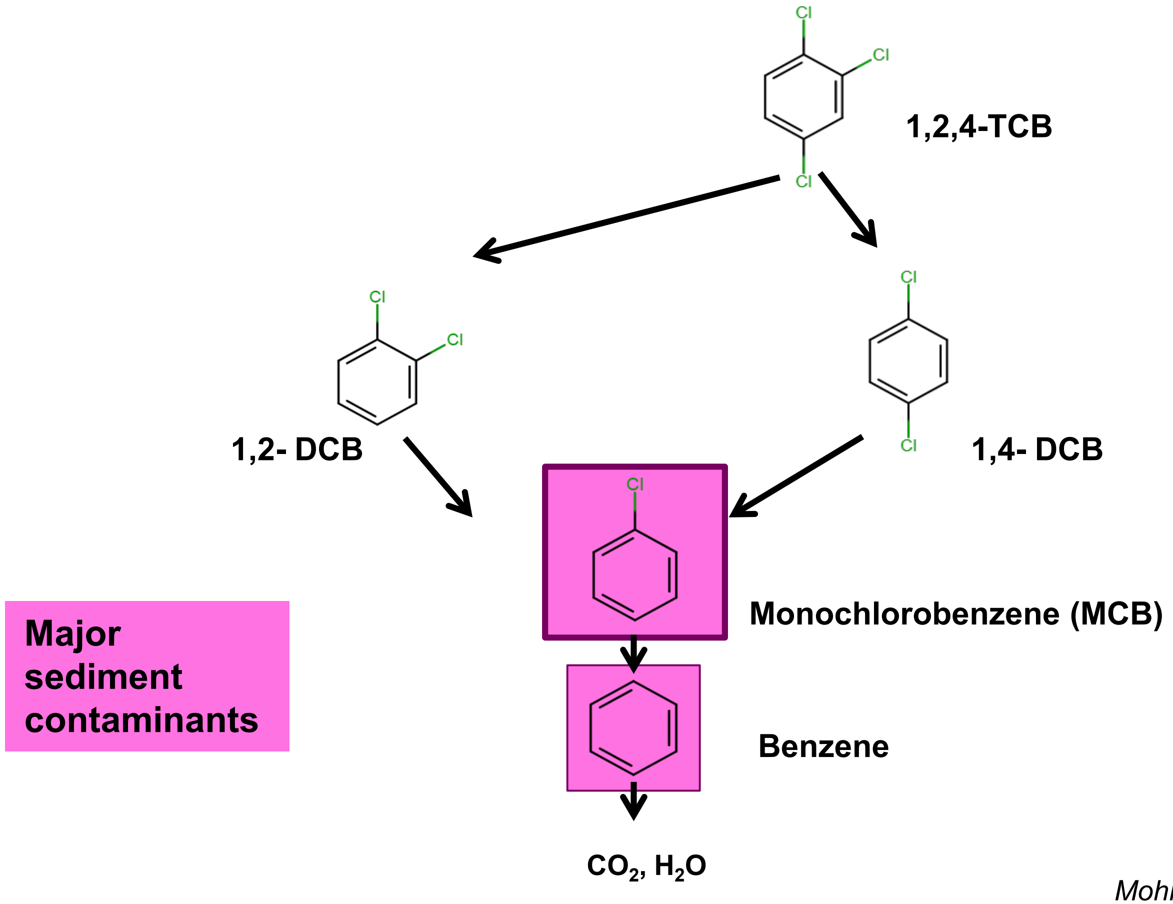
Compounds of Concern

Degradation pathway of chlorinated benzenes under anaerobic conditions



Mohn and Tiedje (1992), Edwards et al.(1992)

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Problem Statement

Monitored natural recovery (MNR) is desired remedial approach for sediment impacted by constituents of concern.

Regulator team requires evidence of:

1. Protective bioactive zone;
2. Demonstrative attenuation of site constituents in sediments;
3. Time to fall below sediment quality benchmarks throughout sediment column (i.e., biodegradation rates)

Challenges

- Provide evidence that biodegradation occurring at rate sufficiently protective to environment and human health
- Provide evidence that benzene degradation is faster than its production by MCB degradation (required to achieve reasonable risk assessment)
- Conventional methods based on concentration analysis alone is insufficient to differentiate between degradative and non-degradative attenuation processes (i.e., overestimation of degradation rates)

02

Approach

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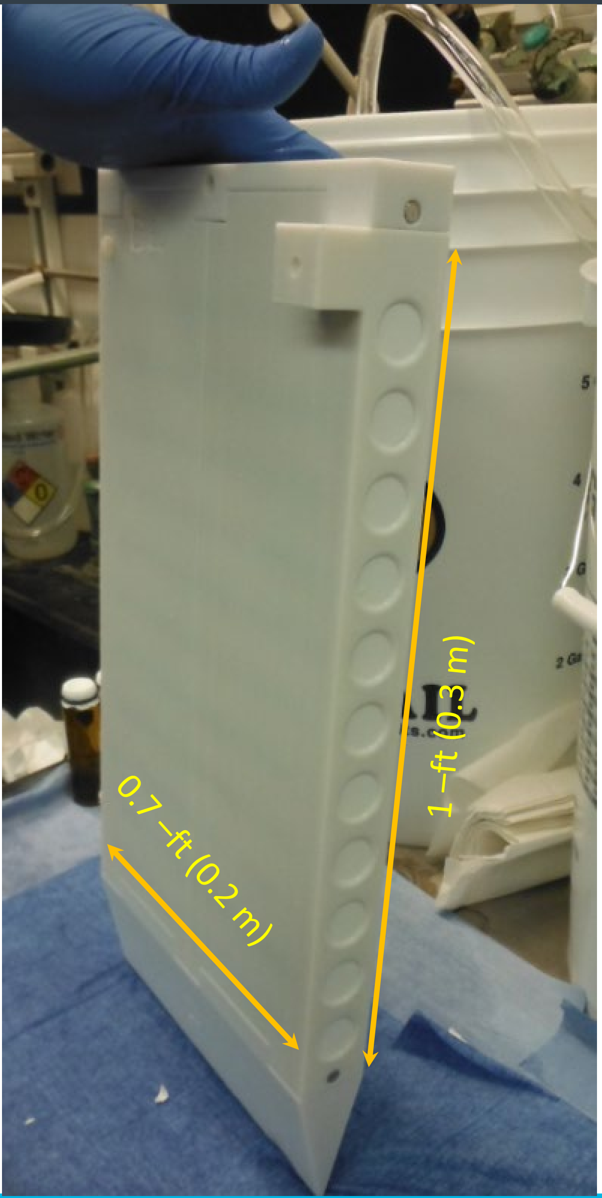
Novel Approach

– High resolution pore water sampling using modified passive diffusion samplers (peepers) across the sediment-water interface, coupled with measurements of concentrations and stable carbon isotope, in order to:

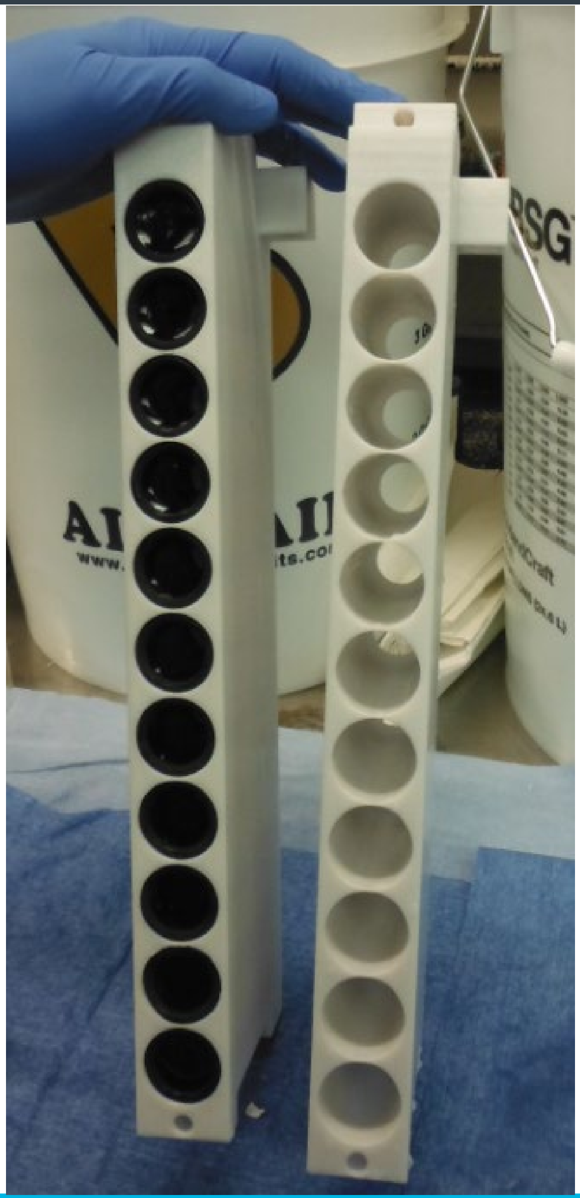
- Investigate MCB and benzene *In Situ* biodegradation
- Estimate biodegradation rates of MCB and Benzene
- Compare degradation rates derived from CSIA with those derived from concentration-based reactive transport modeling
- Apply the REV approach for CSIA to identify zones of maximum biodegradation potential

Modified Peeper

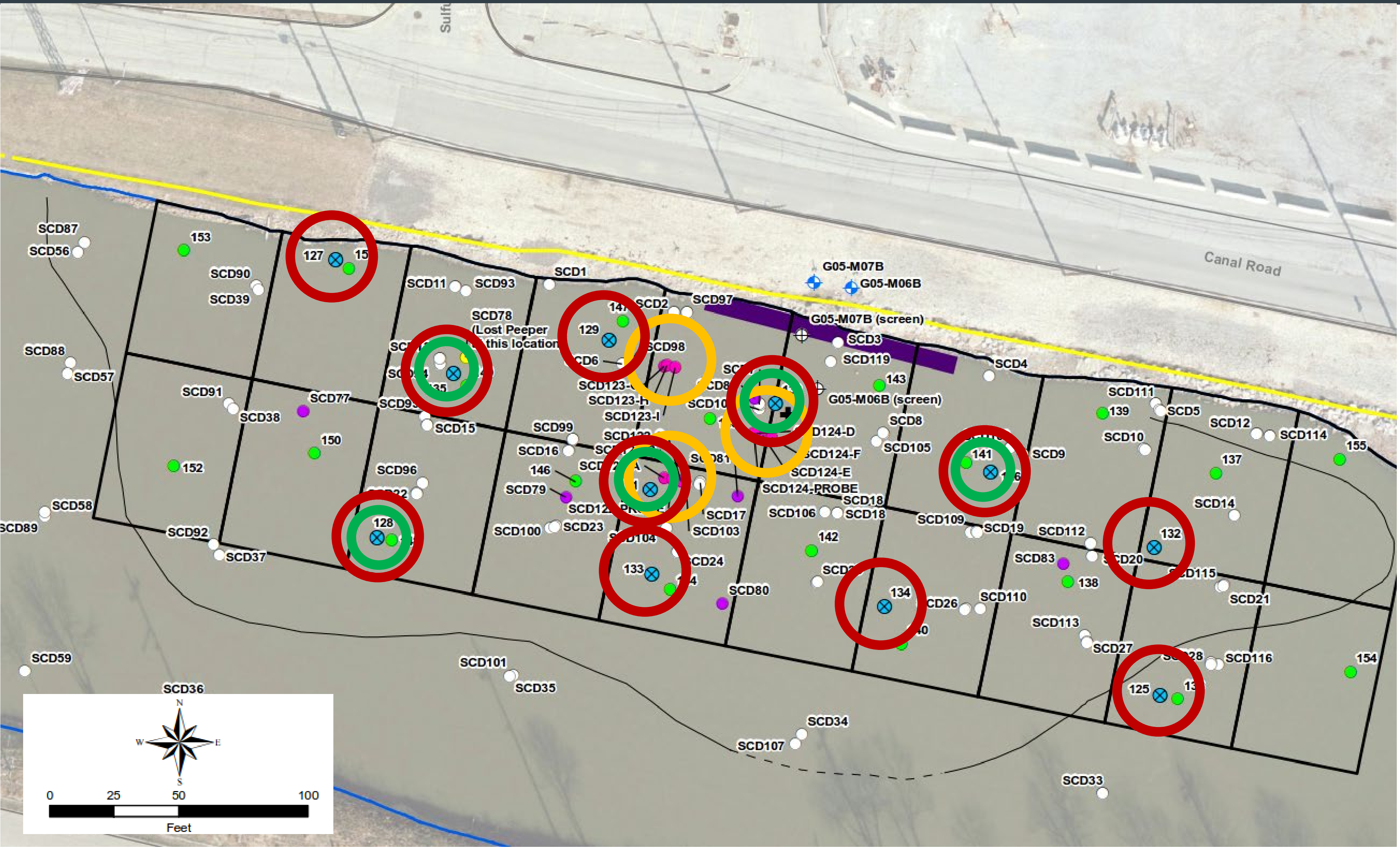


- Approximately 1-3 foot (0.3 m- 1 m) long
- Holds 22-40ml VOA vials
- Polysulfone membranes for CSIA sampling
- Hand driven insertion and removal
- At least 30-day soak time

E.Passeport et al./ Environ. Sci. Technol. 2014, 48,16, 9582-9590
E.Passeport et al./ Environ. Sci. Technol. 2016, 50, 12197-12204



Three Deployments



2011 CSIA Evaluation

2015 MNR Investigation
1-ft Peepers + Bulk Sediment + Surface Water + Sedimentation Rates

2016 MNR Investigation
7 1-ft peepers, **3 2-ft peepers, 1 3-ft peeper**

E.Passeport et al./ Environ. Sci. Technol. 2016, 50, 12197-12204

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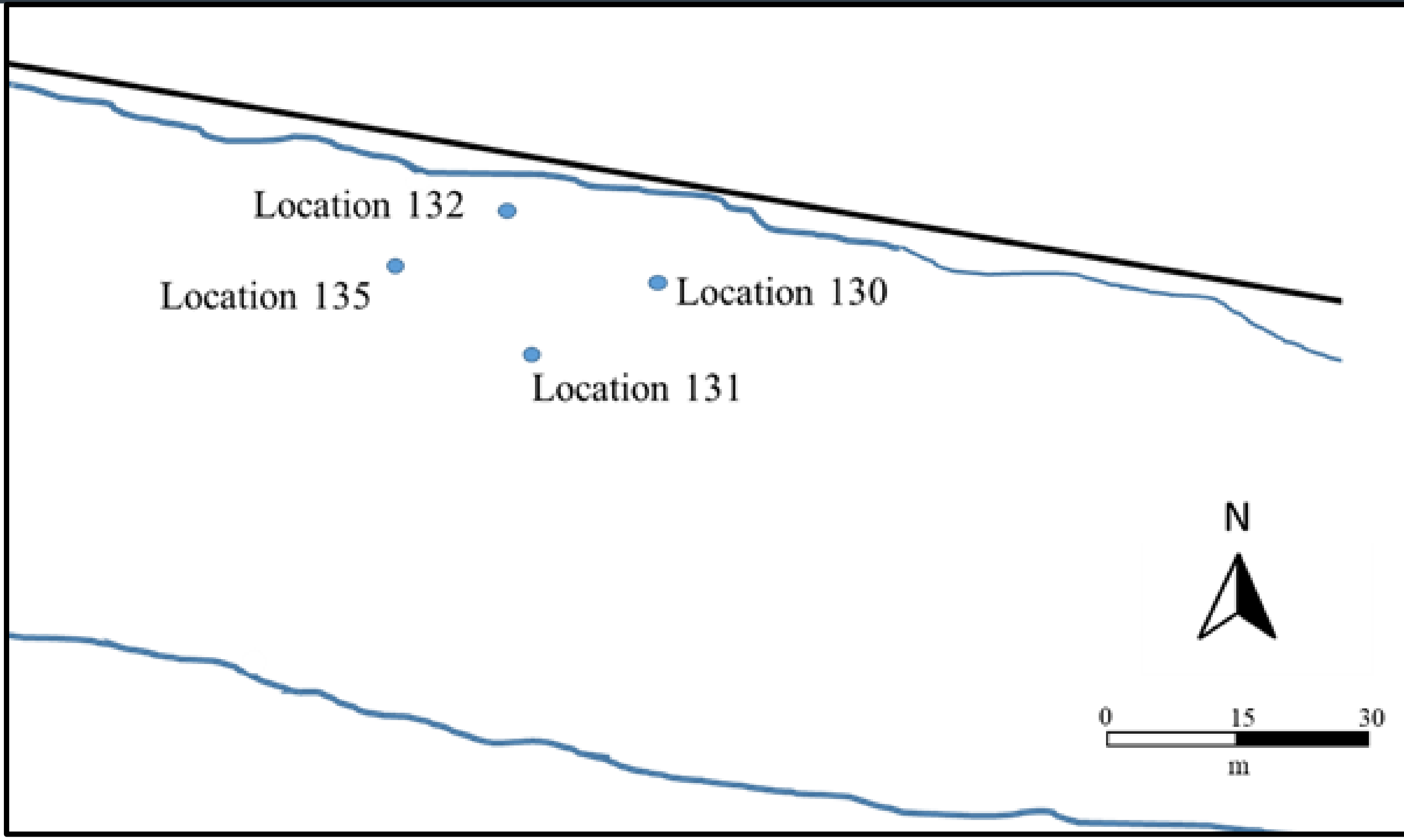
Deep Peepers

Field deployment

- Sampling July 2016
- 4 locations: 60 and 90 cm peepers

Analytical Measurement

- Redox species
- Chloride
- MCB and Benzene
- CSIA



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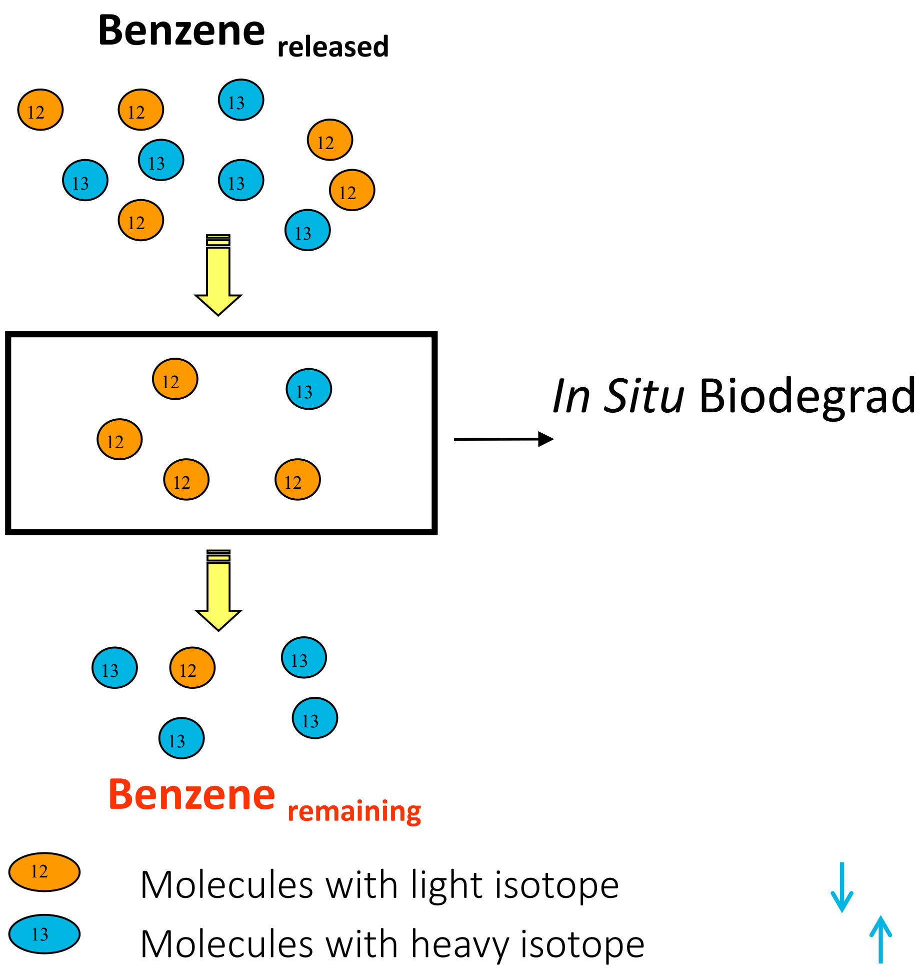
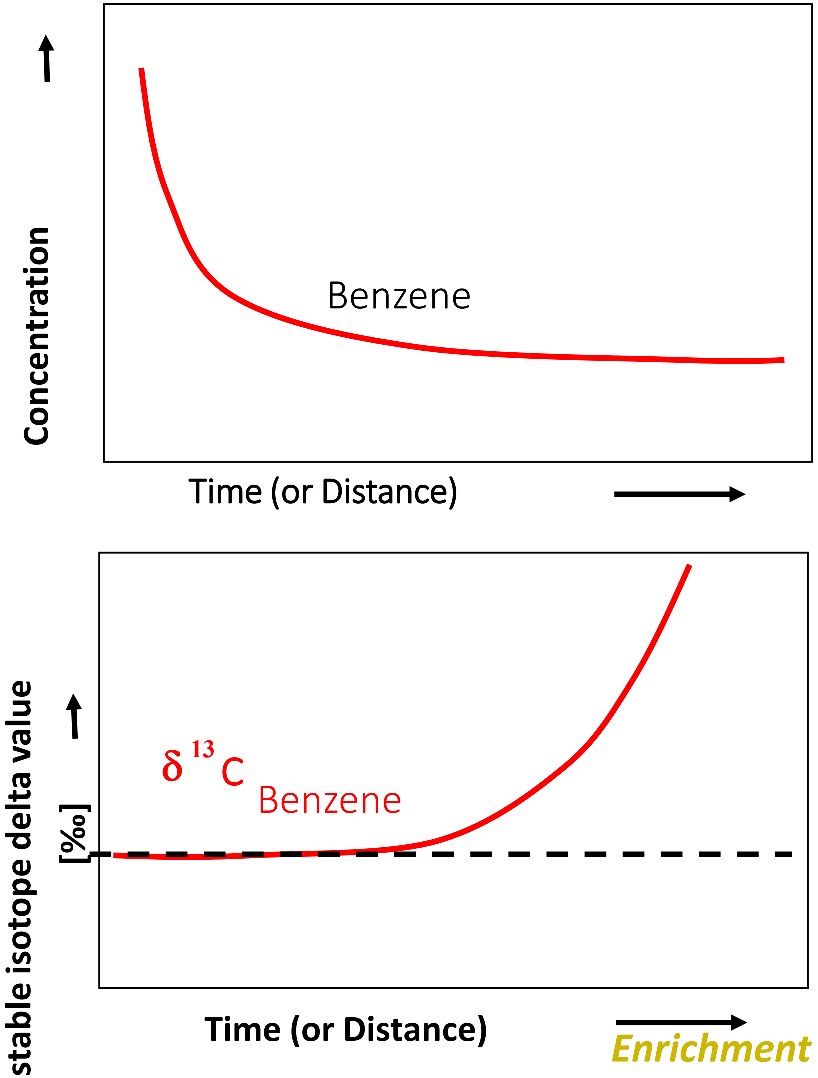
Compound Specific Isotopic Analysis (CSIA)



In Situ Biodegradation



Hunkeler et al., 2008

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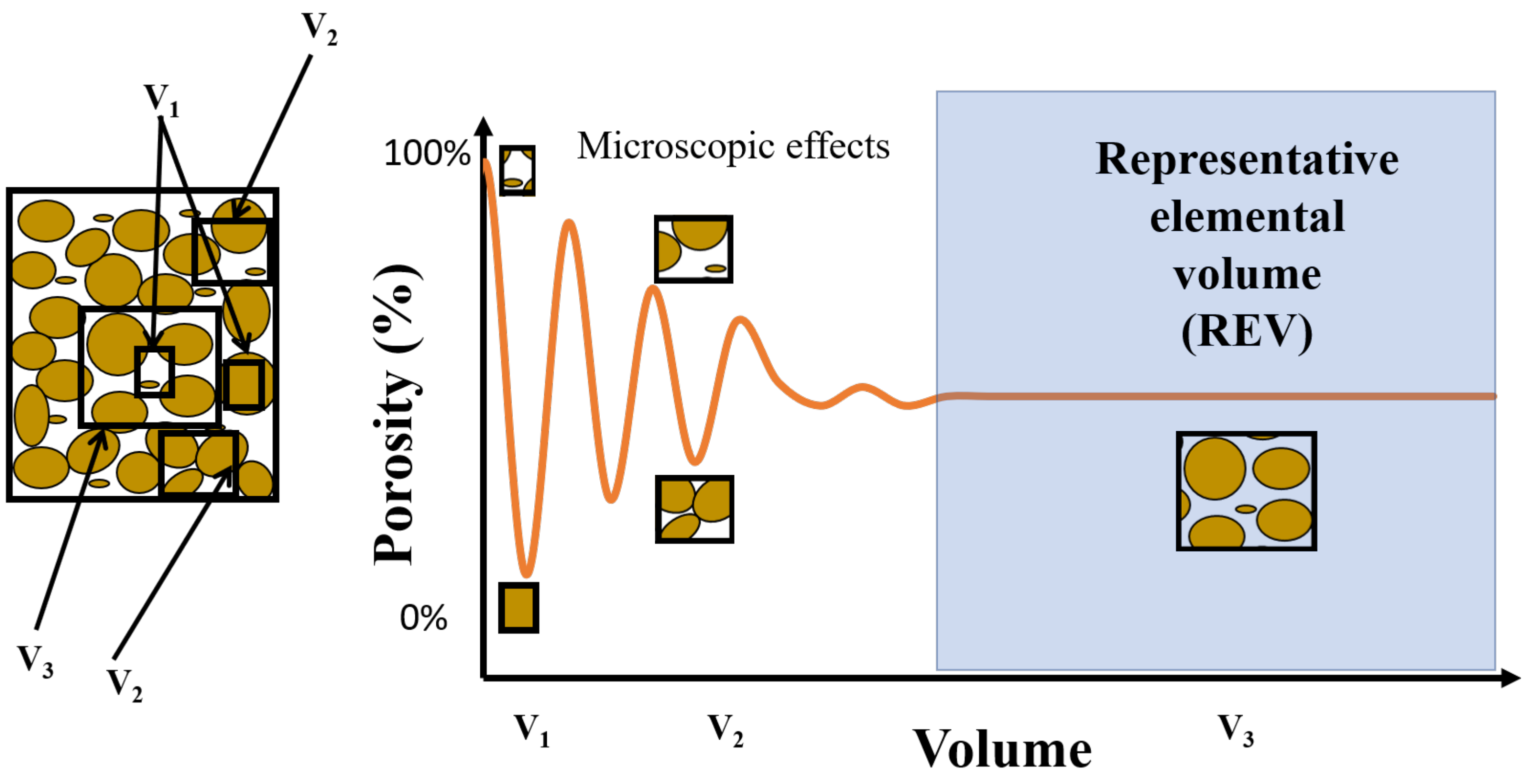
Representative Elemental Volume (REV)



Statistical evaluation of variations in carbon isotope signatures applying the concept of REV:

- Identify the most biologically active zones
- Allow better predictability of the time required for MNR

Representative elemental volume –appropriate scale of measurement at which a continuum is reached i.e. for which any given measurement is representative of the "whole".

Freeze & Cherry, 1979

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Application of REV Approach for CSIA

- The propagated error on the degradation rates accounted for $\delta^{13}C$ measurement reproducibility (0.3‰), the uncertainty in the reported enrichment factor (0.2‰) and uncertainty in calculated seepage velocity (7%).
- When difference between degradation rates calculated based on two successive points (3 cm apart) < propagated error: values considered to be representative of same REV zone
- REV zones identified and tested for significant differences by statistical analysis ($p < 0.05$, Kruskall Wallis Post hoc Dunn test).
- Degradation rates for each REV calculated by using isotope values of first and last points of each REV zone.

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Stable Isotope-derived Rate Calculations

Enrichment factor

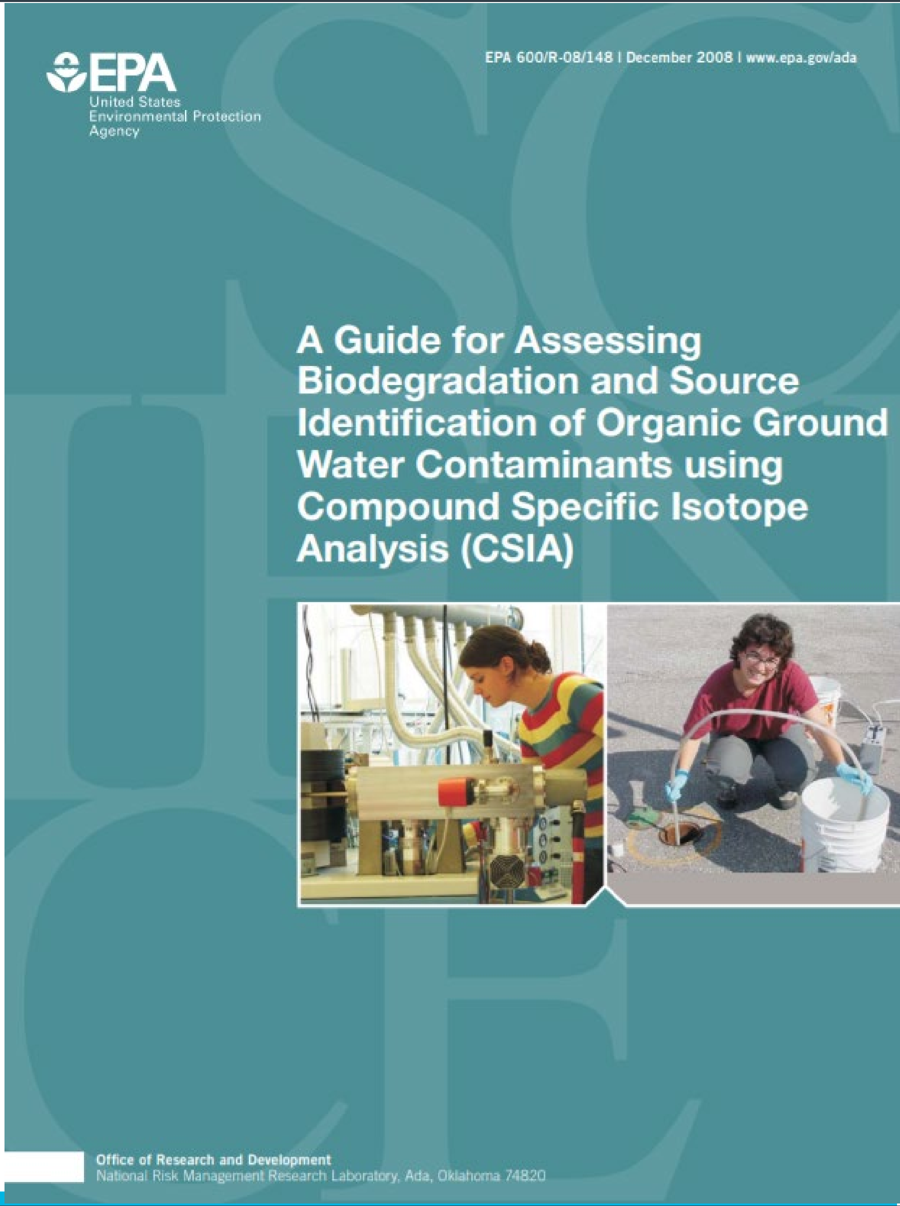
$$\lambda_{iso} = \frac{\frac{\varepsilon}{1} * ln \frac{\delta^{13}C_2 + 1}{\delta^{13}C_1 + 1}}{T}$$

Groundwater travel time

Isotope ratios

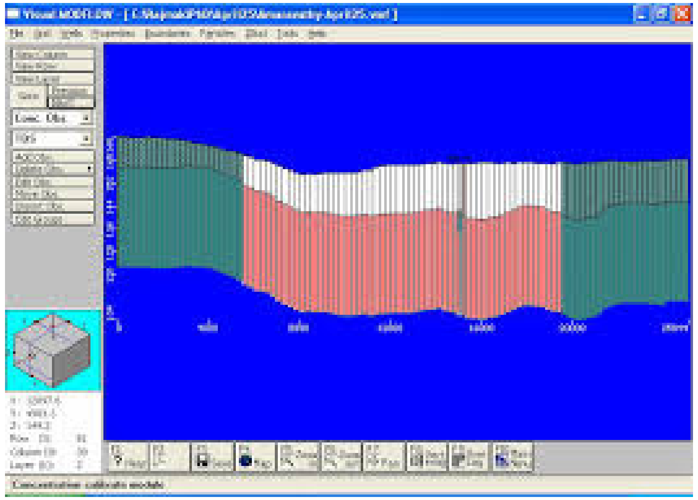
ε: MCB enrichment factor (known)
$\delta^{13}C_1$ and $\delta^{13}C_2$: isotope delta values at two different points along the vertical profile for each peeper location, and
T: average travel time (in years) calculated based on the seepage velocity and distance between the sampling ports

Hunkeler et al., 2008



Concentration-derived Rate Calculations

- 1-D reactive transport modelling using MODFLOW and MT3DMS/RT3D
- Non-degradative and degradative processes (i.e., advection, dispersion, diffusion, sorption, and sequential degradation of MCB and benzene)
- Model validity first verified by comparing numerical model outputs with Analytical Model (Lampert and Reible, 2009)
- Model parameters adopted from existing literature (Passeport et al., 2016)
- Chloride concentrations used to estimate seepage pore velocities
- First-order degradation rate constants derived from fitting model outputs to observed concentrations



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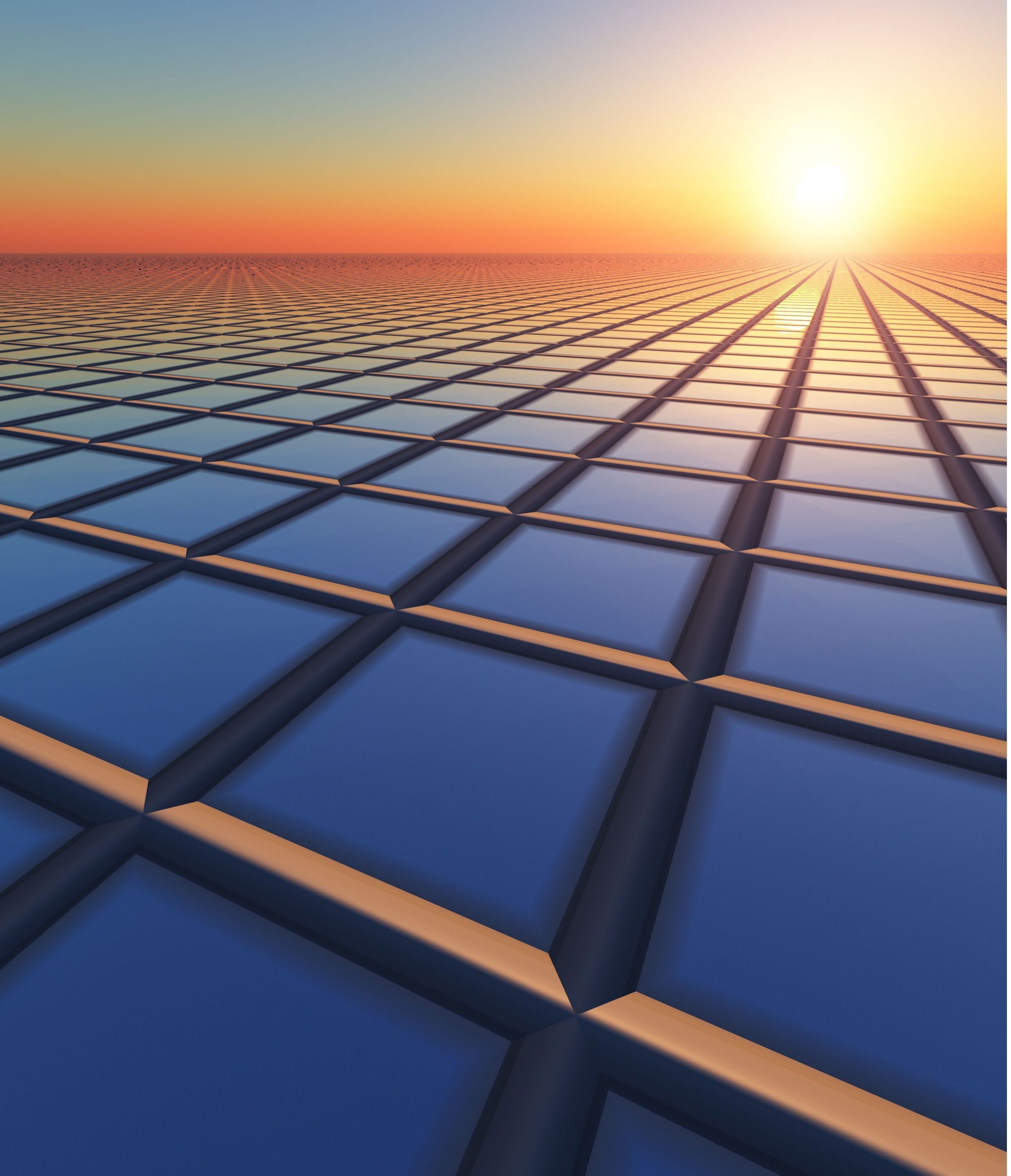
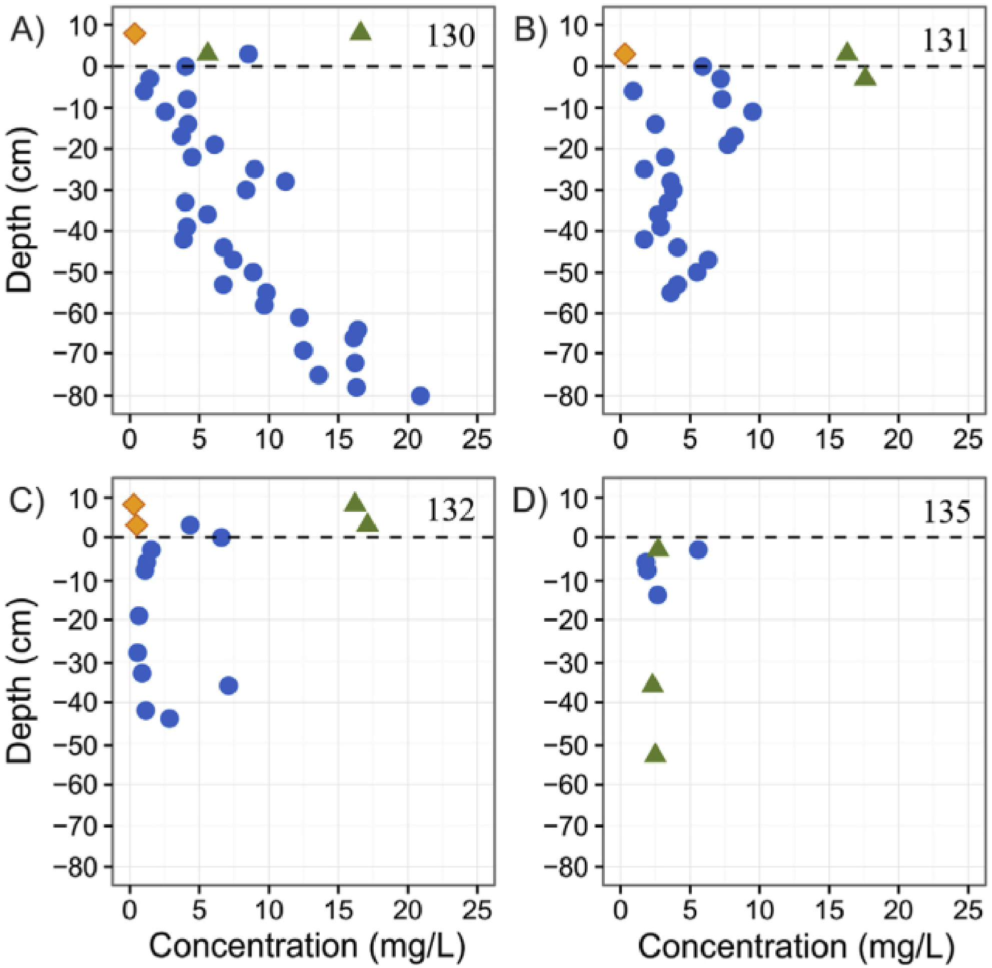


03

Results

Redox Condition



- Sulfate reducing/ methanogenic conditions at the sediment-water interface
- Iron reducing conditions across the sediment profile below 3 cm.
- Favorable for microbial degradation of both MCB and benzene via anaerobic pathways

Sulfate
Total dissolved iron
Nitrate

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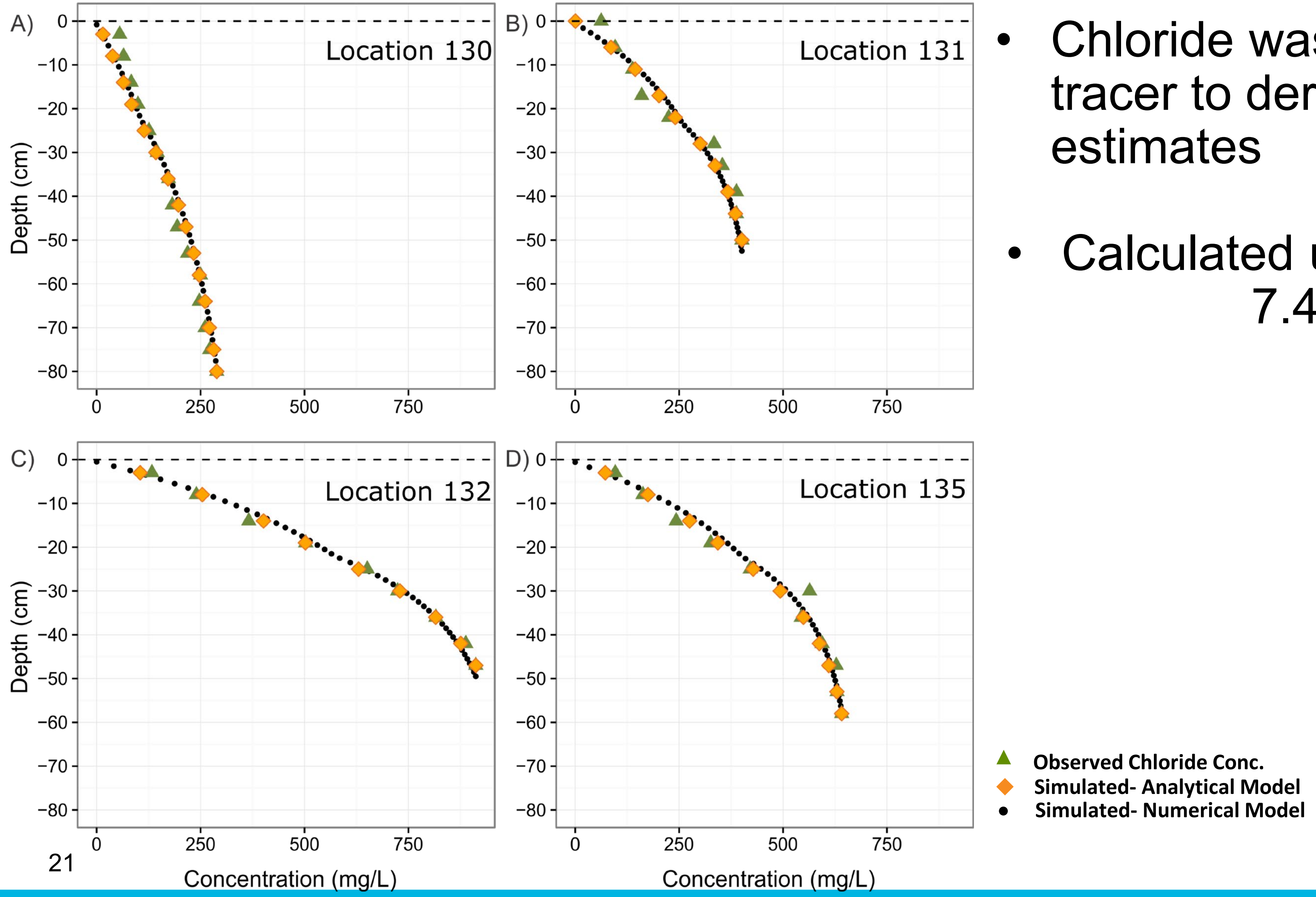
Quantification of Seepage Velocity via Chloride Profile Simulation



- Chloride was used as conservative tracer to derive seepage velocity estimates
- Calculated upward seepage velocities: 7.4 cm/yr- 20.6 cm/yr

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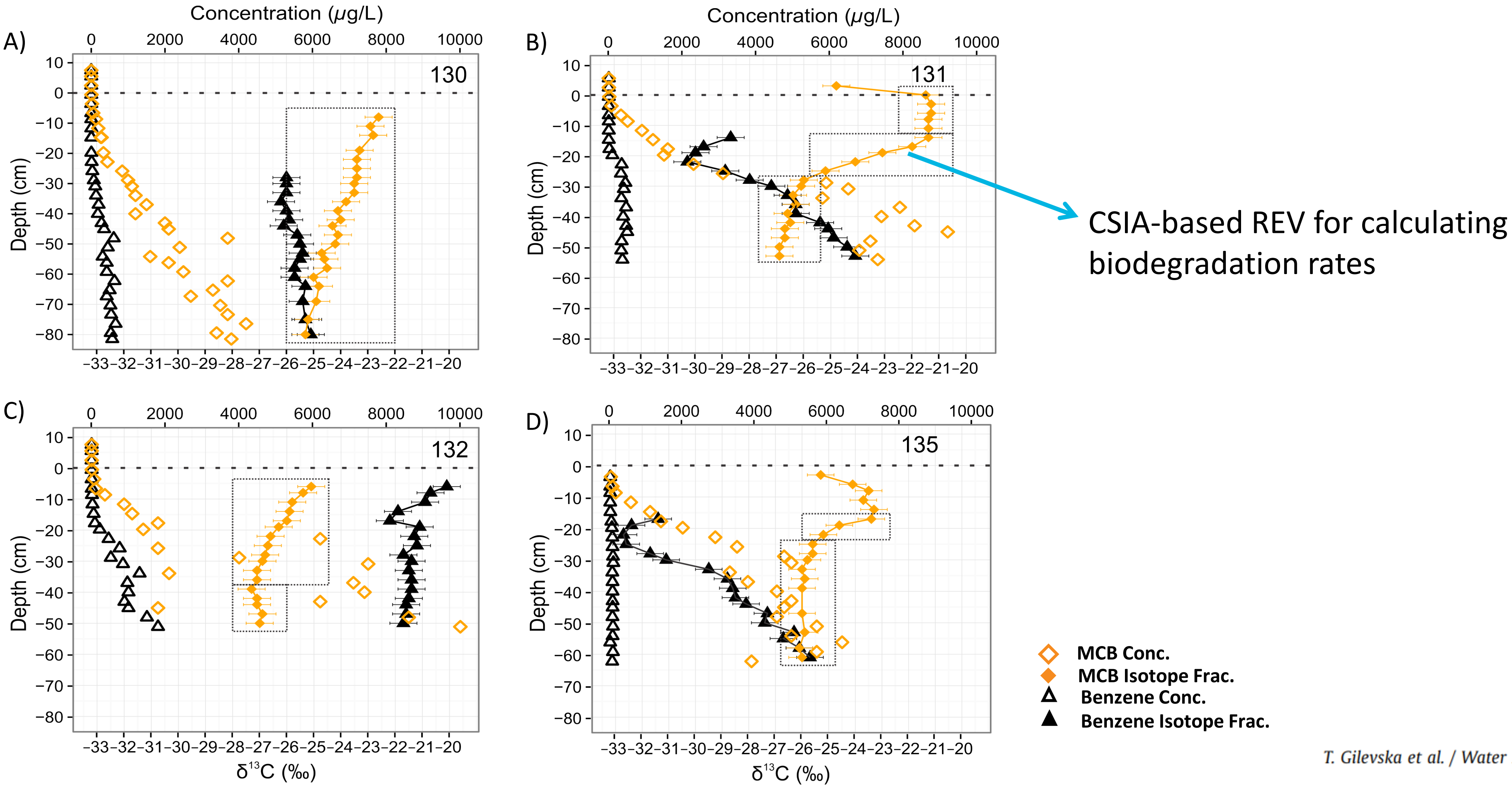
MCB and benzene concentration and isotope profiles



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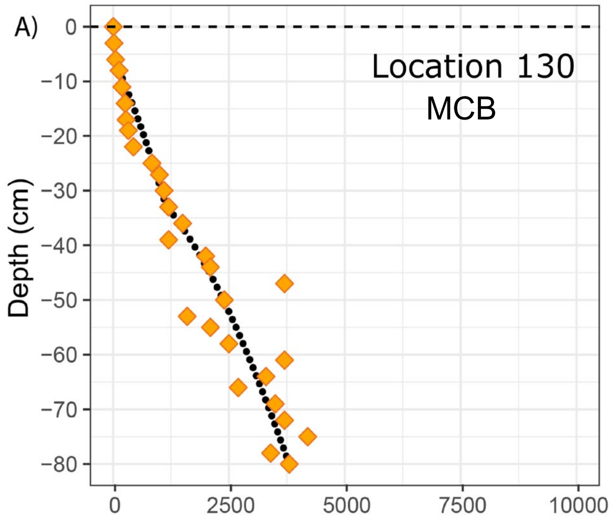
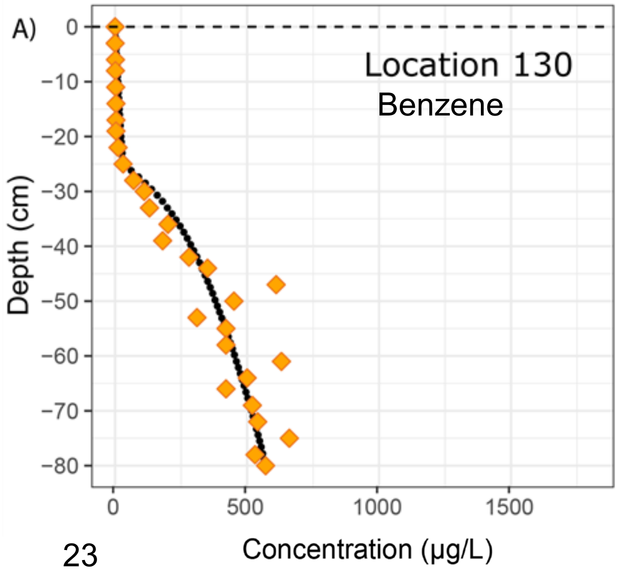
Quantitative Assessment of Biodegradation





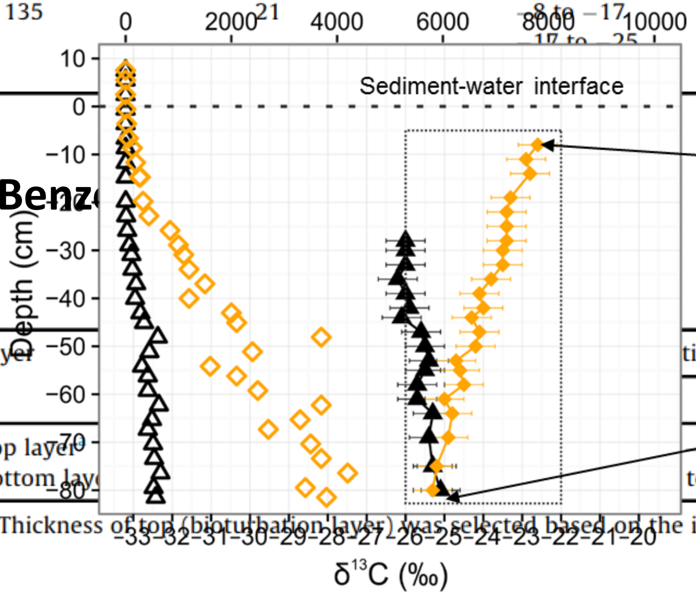
MCB

Location	v (cm/yr)	REV (cm)	MCB λ_c (yr^{-1})	MCB λ_{iso} (yr^{-1})	MCB B_c (%)	MCB B_{iso} (%)
130	7	−8 to −80	0.1	0.1	77	43
131	20	0 to −14	4.2	BDL	22	BDL
		−14 to −28	3.2	1.3	63	51
		−28 to −53	BDL	0.1	4	17
132	20	−6 to −39	1.1	0.3	71	36
		−39 to −50	1.1	BDL	24	BDL
135	21	−8 to −17	3.16	BDL	35	BDL
		−17 to −25	1.2	1.1	37	34
		[illegible]	0.1	0.1	20	BDL

Benzene

Layer	[illegible]	[illegible]	Location 131		Location 132		Location 135	
	[illegible]	[illegible]	[illegible]	λ_c (yr^{-1})	cm	λ_c (yr^{-1})	cm	λ_c (yr^{-1})
Top layer[a]	[illegible]	[illegible]	[illegible] 25	84	0 to −19	73	0 to −22	57
Bottom layer	[illegible]	[illegible]	[illegible] to −53	0	−19 to −50	5.7	−22 to −61	2.9

[a] Thickness of top (bioturbation layer) was selected based on the inflection point of chloride concentration profile (SI Table S1).



$$\lambda_{CSIA} = \frac{\frac{\varepsilon}{1000} * ln\frac{R_1}{R}}{T}$$

Groundwater travel time across zone

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04

Conclusions and Contributions

Summary

- Large isotopic enrichment trends in ^{13}C for MCB (1.9-5.7‰), with correlated isotopic depletion in ^{13}C for benzene (1.0-7.0‰) – expected isotope signatures for source & degradation by-product
- A pronounced ^{13}C enrichment trend up to 2.2‰ in uppermost sediments (most biologically active zone for benzene) demonstrated simultaneous benzene degradation & production
- Benzene degraded at faster rate (3.3- 84.0 yr^{-1}) than MCB (0.1-1.4 yr^{-1} and 0.2-3.2 yr^{-1}, respectively), i.e., MCB degradation did not lead to benzene accumulation & the uppermost sediment acted as a zone naturally protective of the surface environment
- CSIA-derived rates are more conservative & prevent “overestimation” based on conventional modelling of concentration profiles
- The range of degradation rates observed in each location likely due to heterogeneity of sediment structure, microbiological activity & sediment pore water redox chemistry

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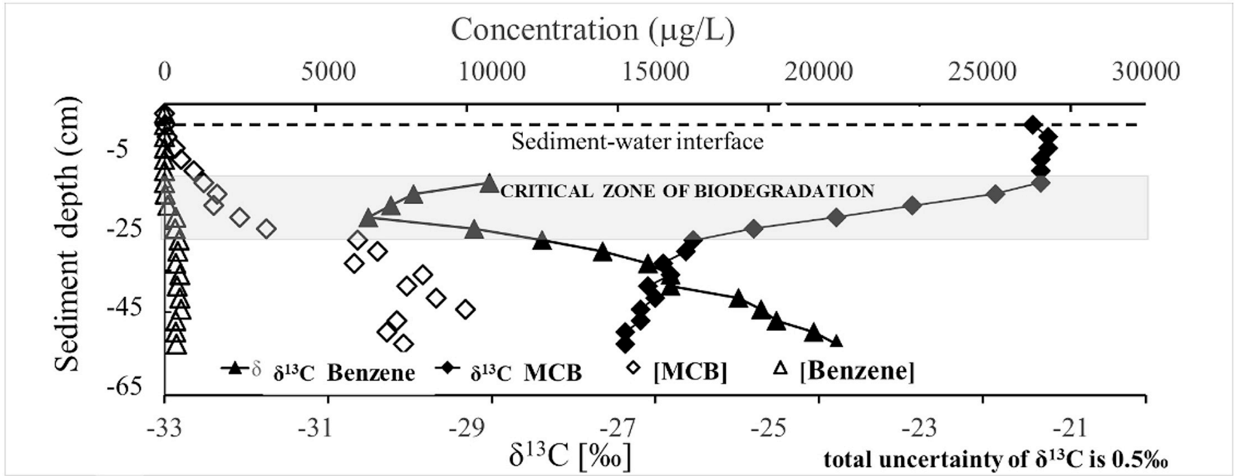
Field Implication

- Combining peeper sampling w/CSIA is a powerful approach to identify/quantify contaminant natural attenuation across sediment-water interface (SWI).
- ID of zones with maximum biodegradation rates, together w/assessment of non-degradative processes allow better predictability of time required for MNR & informs risk assessments at contaminated sites.
- High resolution data can provide a basis for selection & successful implementation of remediation actions such as biostimulation or bioaugmentation, if required
- Sediment acts as a natural protective zone of the surface environment, therefore dredging to remove such a zone is undesirable and costly



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Contributions

- High resolution passive sampling coupled w/CSIA to identify and quantify natural attenuation across SWI
- CSIA-based calculations combined w/numerical modeling as conservative approach to estimate *In Situ* biodegradation rate constants in sediments
- REV concept application to CSIA data to identify zones w/maximum biodegradation rates

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Determination of *in situ* biodegradation rates via a novel high resolution isotopic approach in contaminated sediments

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Environmental Science & Technology

Article

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Diffusion Sampler for Compound Specific Carbon Isotope Analysis of Dissolved Hydrocarbon Contaminants

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Environmental Science & Technology

Sediment Monitored Natural Recovery Evidenced by Compound Specific Isotope Analysis and High-Resolution Pore Water Sampling

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Supporting Information

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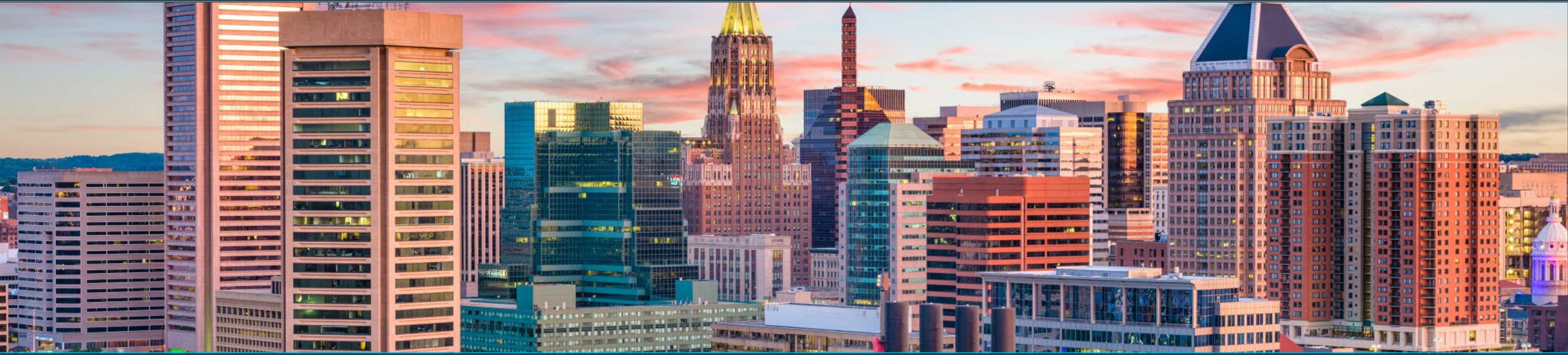

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