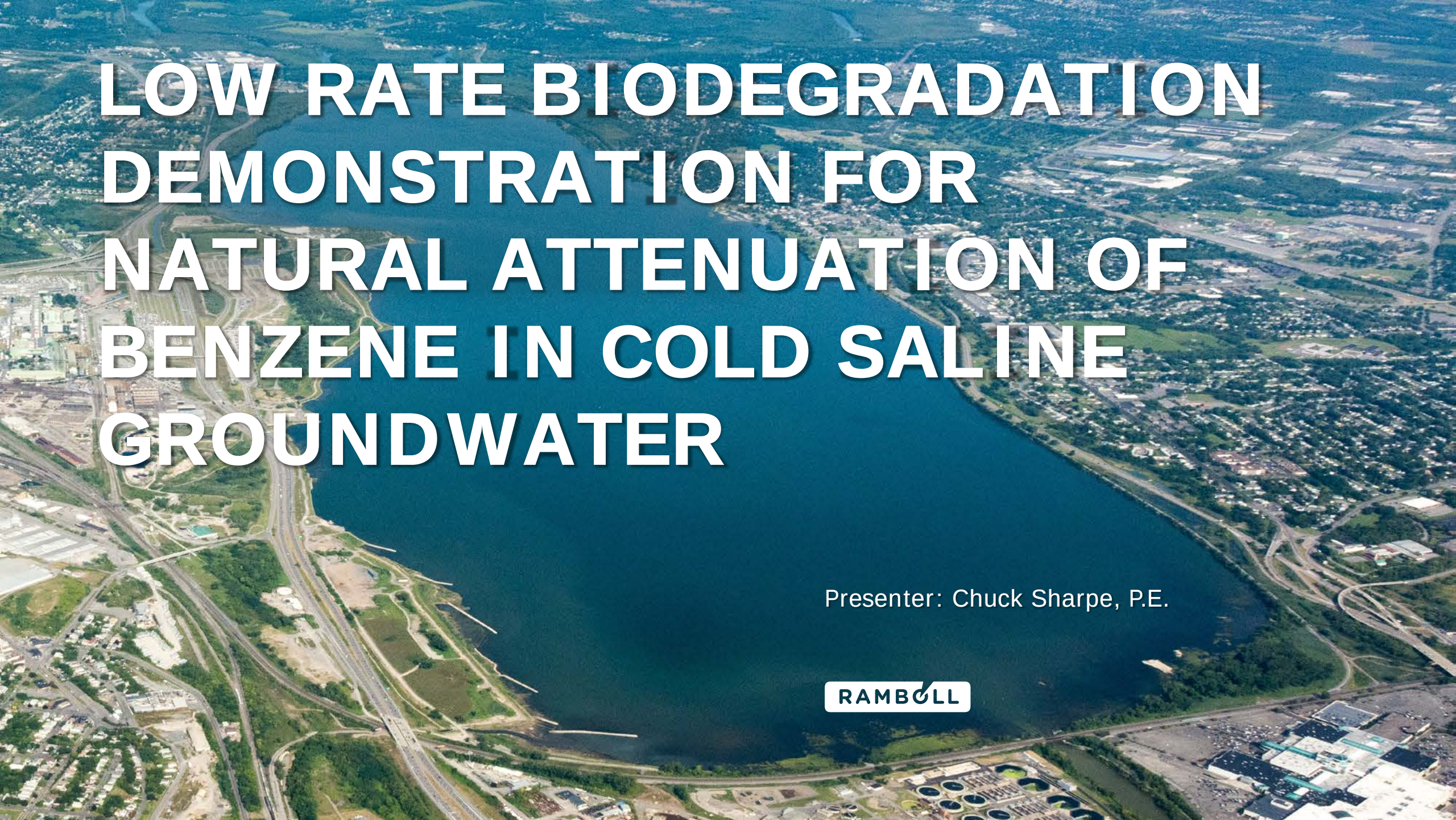

LOW RATE BIODEGRADATION DEMONSTRATION FOR NATURAL ATTENUATION OF BENZENE IN COLD SALINE GROUNDWATER

Presenter: Chuck Sharpe, P.E.

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ONONDAGA LAKE SHORELINE SITES

- Wastebeds 1-8
- Semet Residue Ponds
- Willis Avenue
- Wastebed B/Harbor Brook
- Ballfield

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Site History

Halite brine pool formed under the lake and beyond

An estimated 11,000,000 tons of salt produced between 1797 and 1917 with wells pumped until 1926

Solvay industry began operations in 1888 with Solvay waste materials placed in lakeshore wastebeds through 1944

Impacts to Deep Groundwater

Vertical gradients associated with the wastebeds and historical brine well pumping led to migration of Solvay leachate within the deep groundwater

Historical comingling of waste materials resulted in impacts to deep groundwater

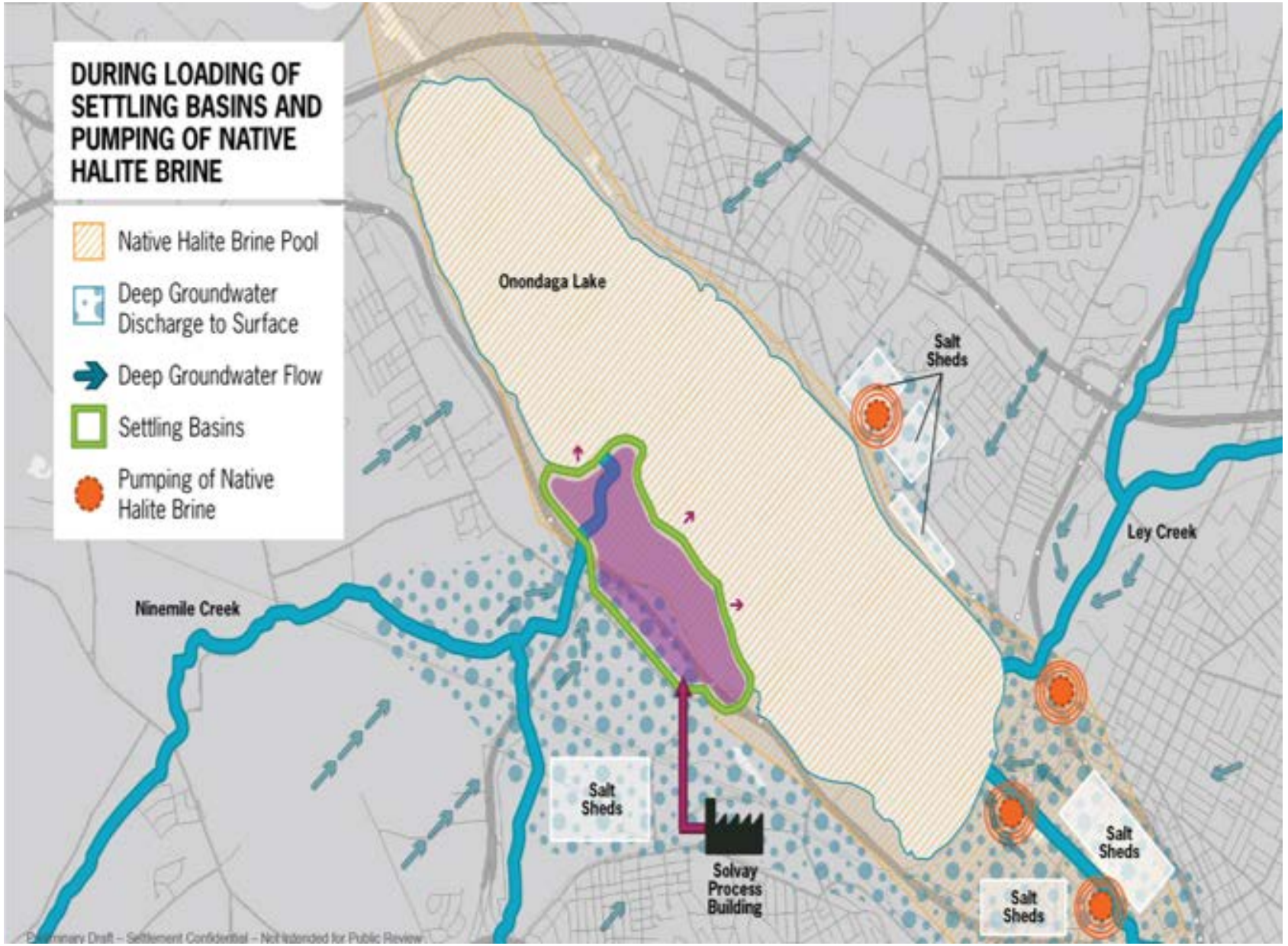
Portions of the plume farther offshore migrate very slowly upward through low-permeability sediments separating the deep groundwater zone from the lake

PROBLEM STATEMENT

Deep groundwater beneath Onondaga Lake impacted by the regional halite brine from salt beds and Solvay waste leachate

Benzene in deep groundwater could migrate upwards through confining sediment to the lake

Conventional evidence for natural attenuation was of limited value

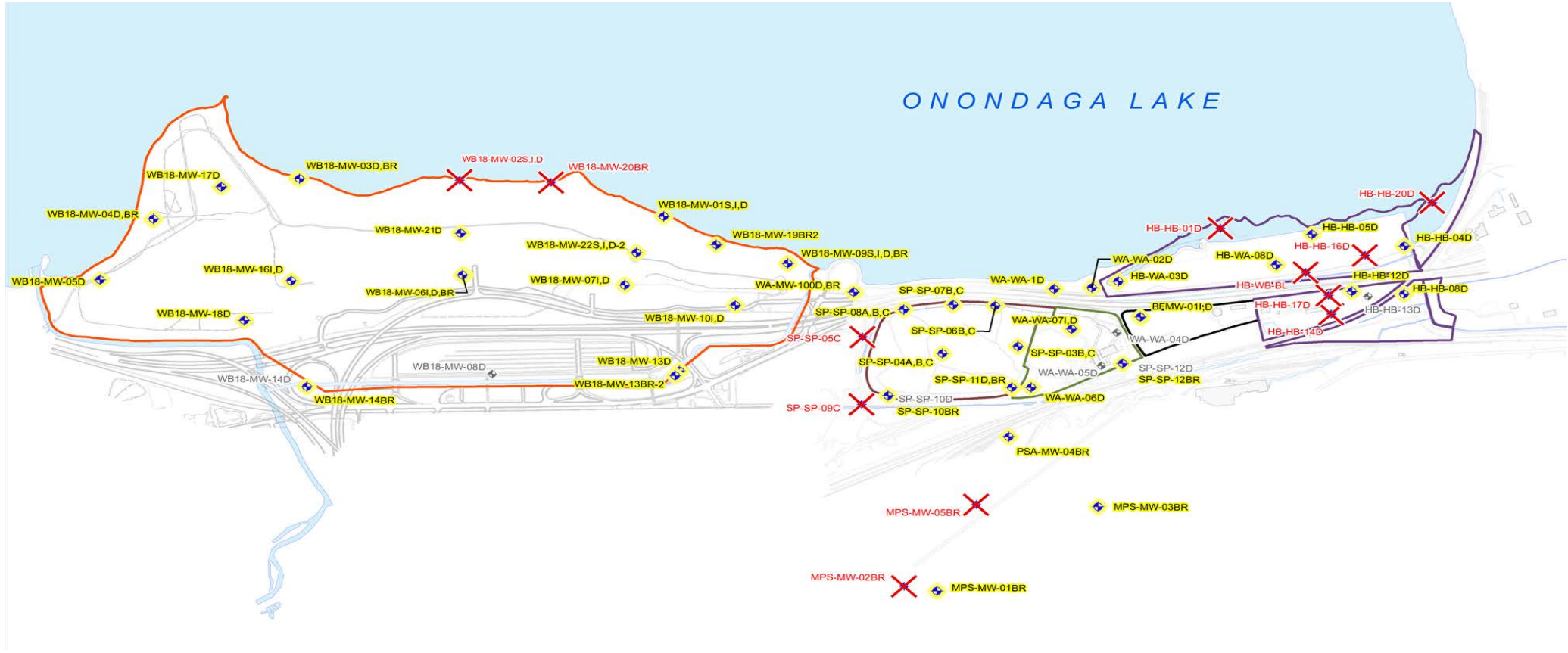


LINES OF EVIDENCE

Field Investigation	Geochemical Data Review	Compound-Specific Isotope Analysis (CSIA) Evaluation	Groundwater Flow Modeling

FIELD INVESTIGATION

Groundwater collected from 14 bedrock wells, 31 deep wells, 14 intermediate wells, and 5 shallow wells



FIELD INVESTIGATION

Laboratory and Field Analyses

Analyzed for VOCs, SVOCs, dissolved gases, cations/anions, alkalinity, sulfide, TDS, TOC, and CSIA (C and H for benzene, toluene, and chlorobenzene)

Field measurements for ferrous iron, pH, DO, temperature, specific conductance, ORP, and turbidity

GEOCHEMICAL DATA SUMMARY

Results indicate an anaerobic, reducing environment in the deep groundwater.	
pH generally between 6 to 8	Ideal for biotic activity
DO general < 0.2	Anaerobic conditions
ORP < 100 mV (some data < 200 mV)	Fe-reducing conditions (SO_4-reducing; CO_2-reducing)
Nitrate & Ferrous Iron: Little to non-detect values	Fe-reducing conditions
Sulfate presence	Due to natural halite brine source
Sulfide detected (some wells)	SO_4-reducing
Methane detected (some wells)	Methanogenic conditions

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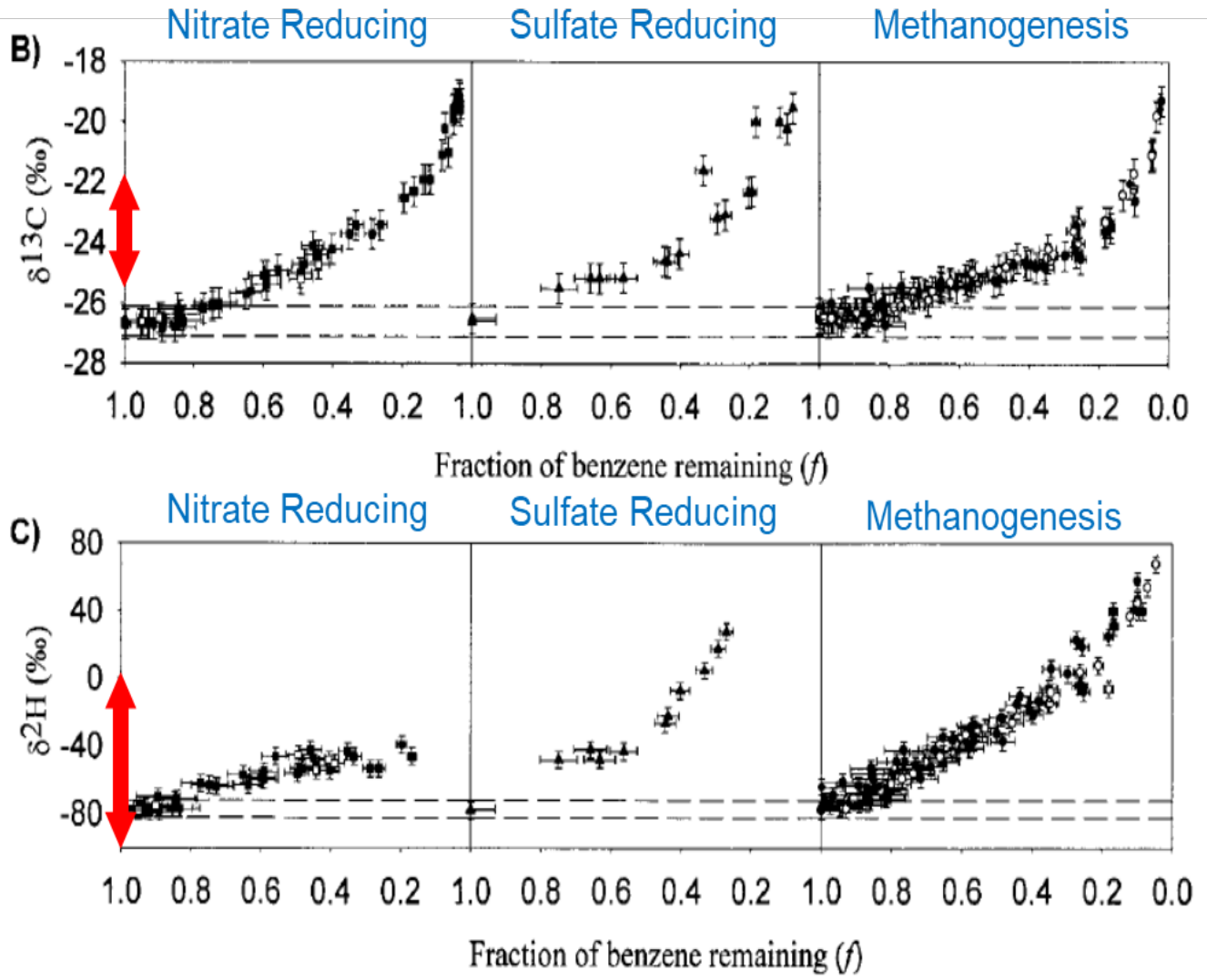
CSIA EVALUATION – ANALYTICAL RESULT

- $\delta^{13}C$ ‰ and $\delta^{2}H$ ‰ value ranges exceed analytical precision

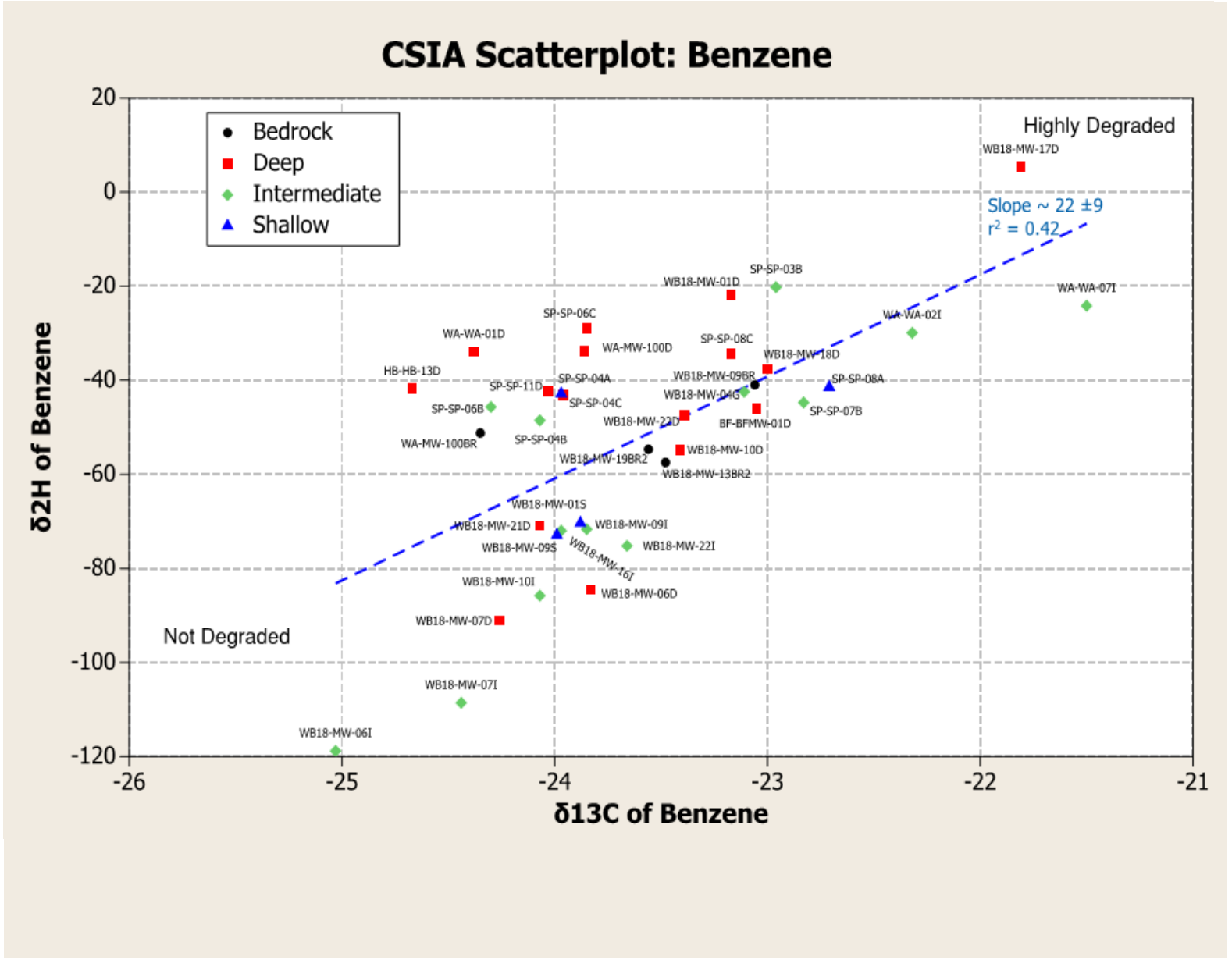
- Comparison of site data (red arrows) to literature (Mancini et *al*, 2003)



CSIA EVALUATION – BENZENE 2D PLOT

- Slope statistically significant at 95% confidence level

- Slope r^2 = 0.42



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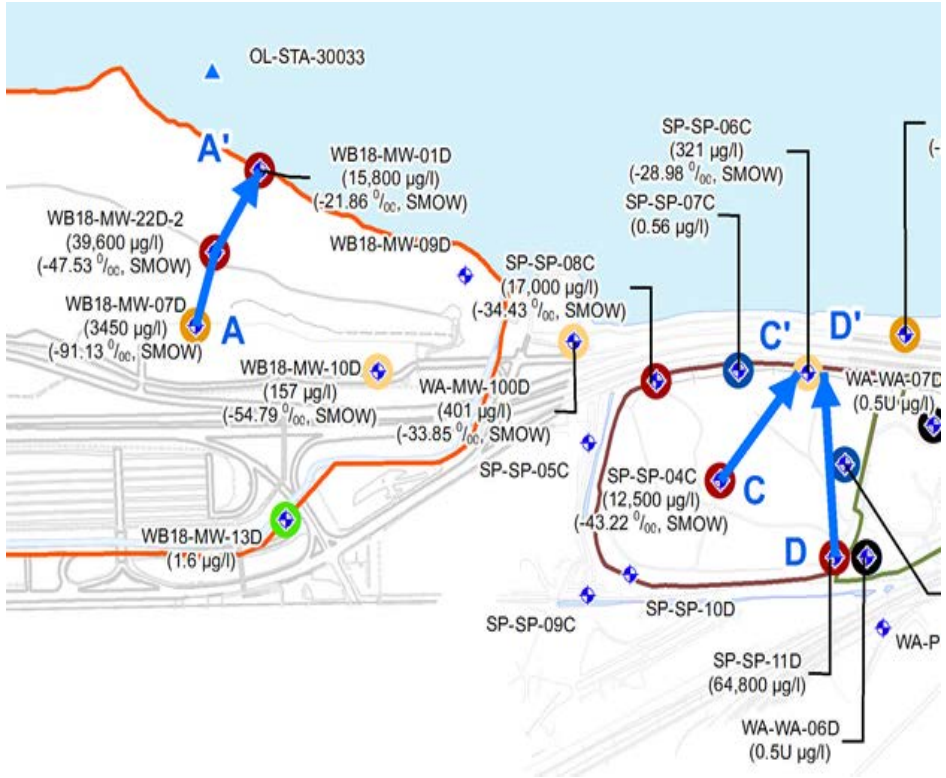
CSIA EVALUATION – FLOW PATHS

Flow path analysis shows benzene degradation



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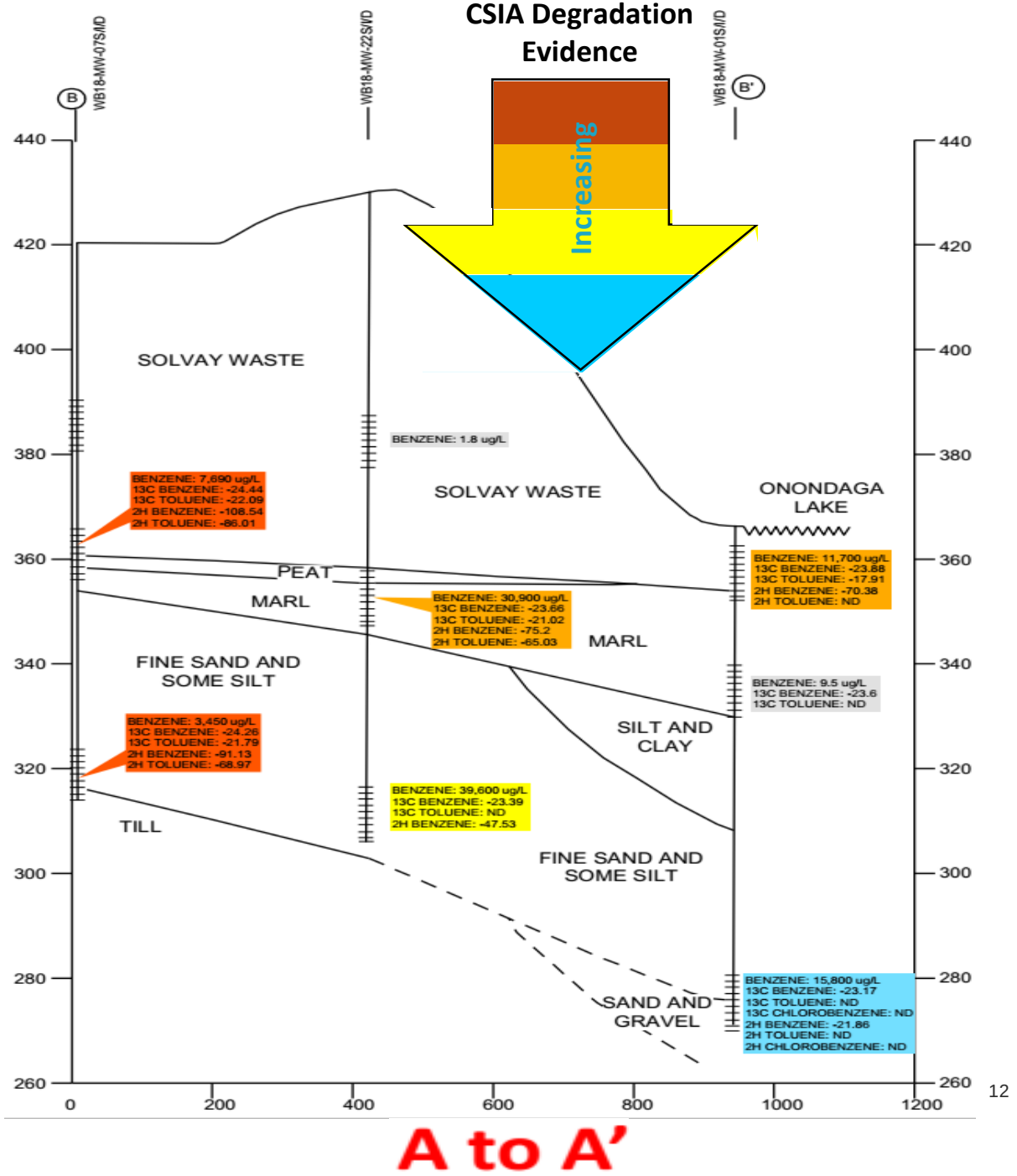
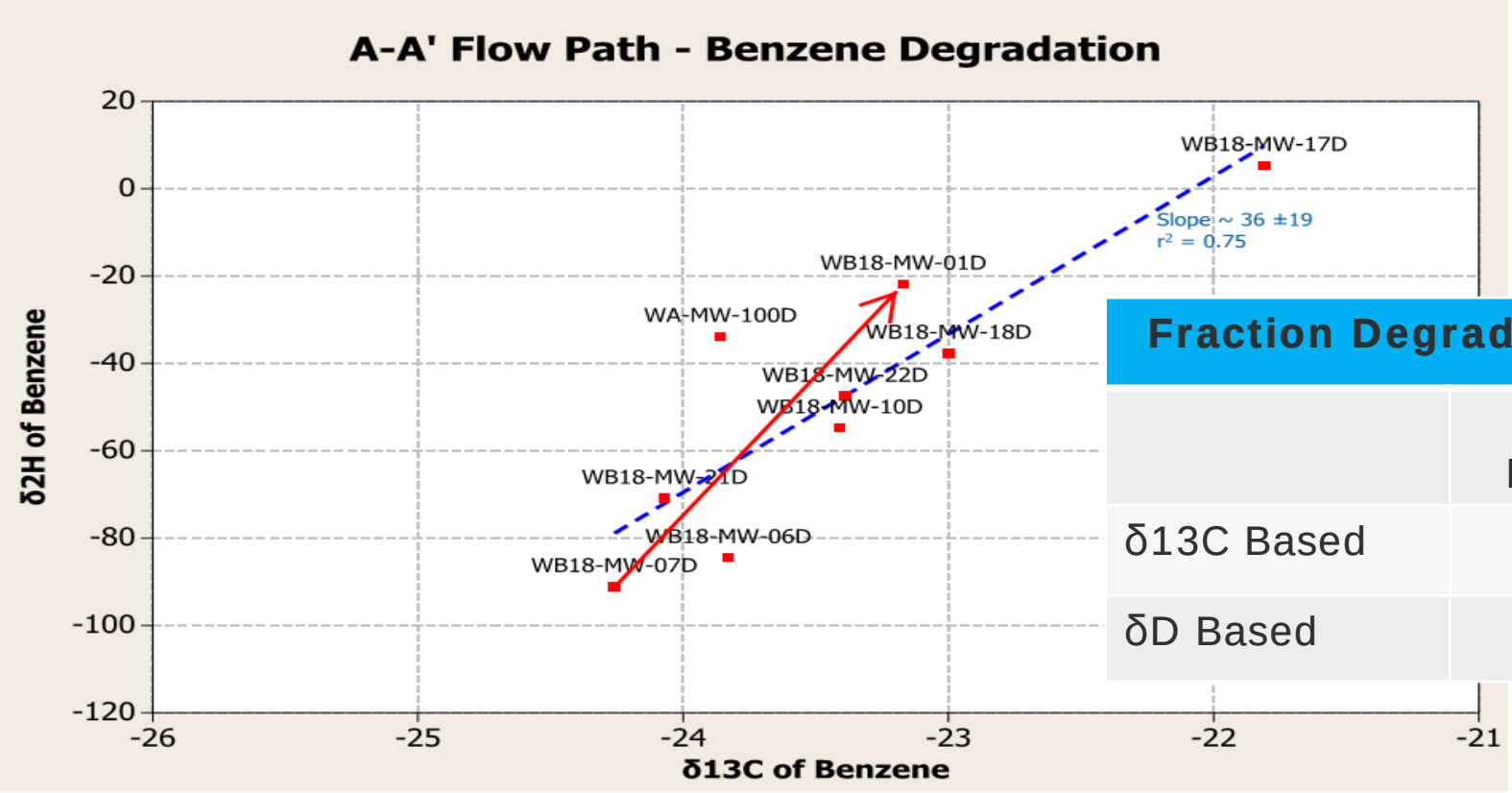


A to A'

CSIA EVALUATION – FRACTION DEGRADED & HALF-LIFE



Fraction Degraded and Rate Estimates: A to A'

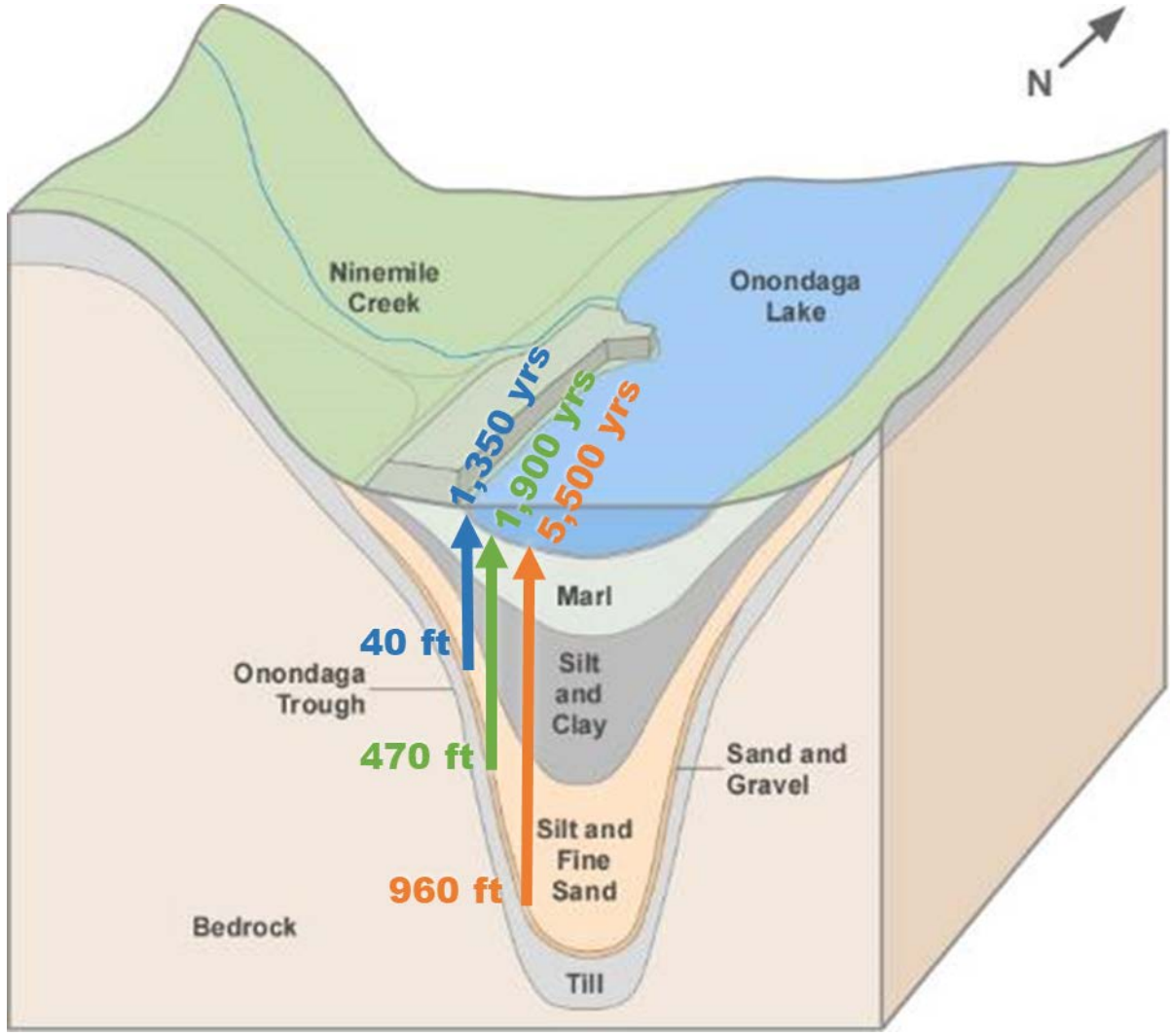
	Fraction Degraded	Calculated ½-life
δ13C Based	60%	~62 to ~120 years
δD Based	27%	~24 to ~48 years

CSIA EVALUATION - SUMMARY

Data provide unequivocal evidence of benzene degradation occurring as deep groundwater migrates toward the lake

δ^2H half-life considered more reliable and is slow for benzene but likely due to unique brine conditions and temperature

GROUNDWATER FLOW MODELING



Groundwater model-calculated vertical travel times from deep Sand and Gravel unit to Onondaga Lake.

ESTIMATED TRAVEL TIMES

- 40 ft offshore = **1,350 years**
- 470 ft offshore = **1,900 years**
- 960 ft offshore = **5,500 years**

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TRAVEL TIMES VS. HALF-LIFE CONCENTRATION CALCULATION

Half-Lives	Travel Time		
	1,350 years	**1,900 years**	**5,500 years**
24 years	$2.4x10^{-13}$ µg/L	$2.0x10^{-20}$ µg/L	$2.1x10^{-65}$ µg/L
48 years	0.00007 µg/L	$2.6x10^{-8}$ µg/L	$6.8x10^{-31}$ µg/L

Calculations based on initial (historic maximum at lakeshore) benzene concentration of 20,000 µg/L

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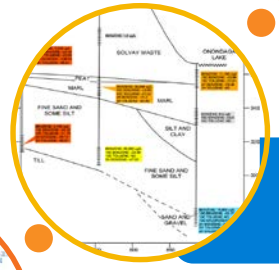
COMBINED OBSERVATIONS FROM THE MULTIPLE LINES OF EVIDENCE

- Geochemical data demonstrates anaerobic, reducing conditions
- CSIA data show “unequivocal evidence” of degradation
- Calculated half-life of 24 to 48 years
- Model-predicted travel times are 1,350 to 5,500 years
- Flow and degradation rates indicate biodegradation reduces benzene before reaching Onondaga Lake

Benzene Reduced Before Migrating to Lake

Migration Modeled



Half-life Calculated

Attenuation and Degradation are Occurring

Deep Groundwater Data Collected

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THANK YOU

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