



# **An Approach to Differentiate Gasoline and Non-Gasoline Sources of TBA in Groundwater**

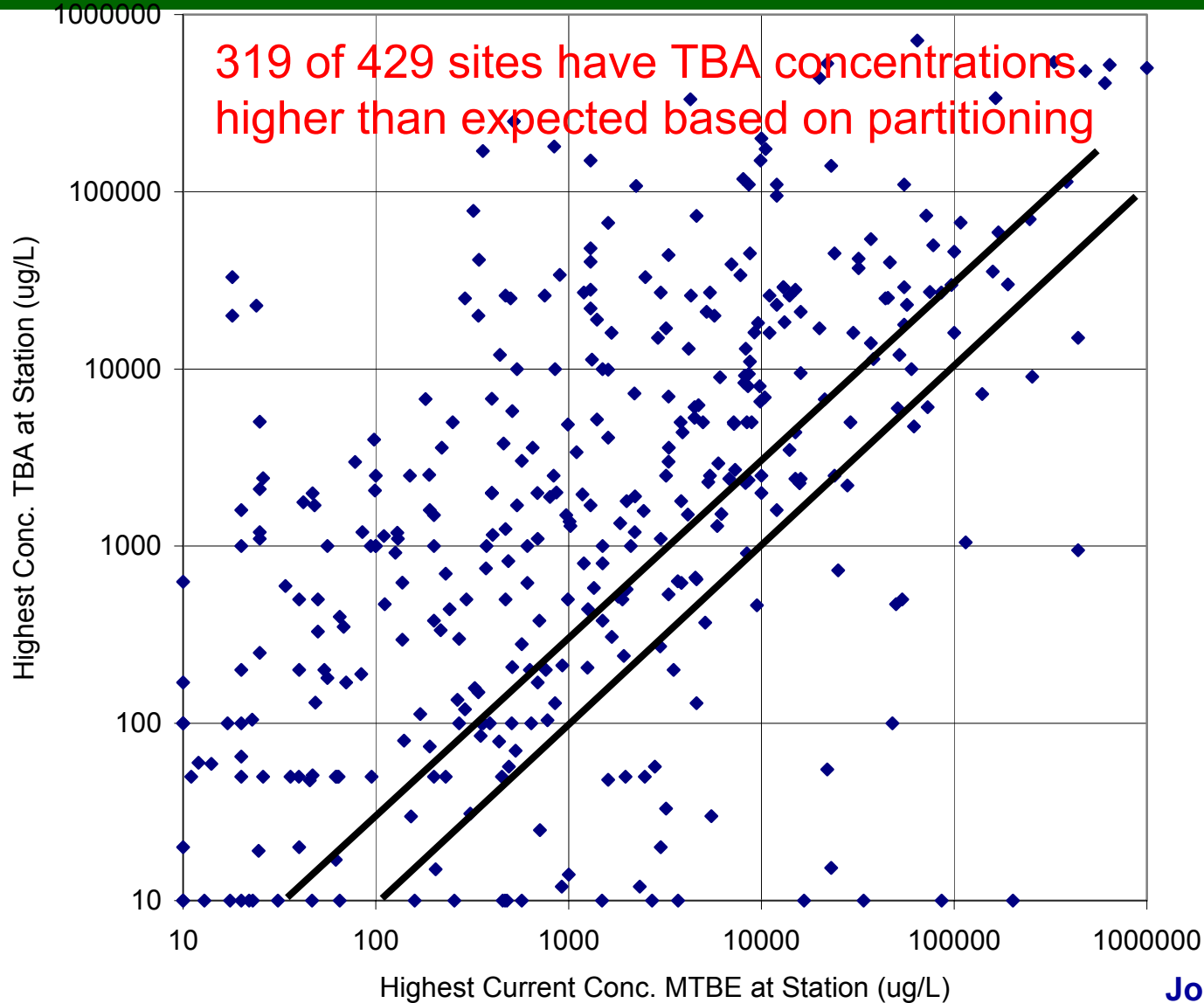
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**NGWA Conference**

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# TBA in GW at Orange County Sites



# TBA – Potential Sources



- Dissolution from gasoline - TBA in fuel grade MTBE
- Product of MTBE Transformation

Can we differentiate?

# Gasoline-Water Equilibrium Partitioning



$$C_{TBA}^{water} = C_{MTBE}^{water} * \left( \frac{TBA}{MTBE} \right)_{gasoline} * \left( \frac{K_{fw}^{MTBE} + \frac{V_{wat}}{V_{gas}}}{K_{fw}^{TBA} + \frac{V_{wat}}{V_{gas}}} \right)$$

- Where,  $K_{fw}$  are fuel-water partitioning coefficients (mg/L in fuel/mg/L in water at equilibrium)
  - $K_{fw}^{MTBE} = 15.5$  (Cline et al., 1991)
  - $K_{fw}^{TBA} = 0.24$ , average of 0.15 and 0.33 (Zwank et al., 2002)
- Kramer-Douthit, 2000. (volume ratio = 4)
- Zwank et al., 2002. (volume ratio = 1)
- Kramer and Hayes, 1987. (volume ratio = 1)

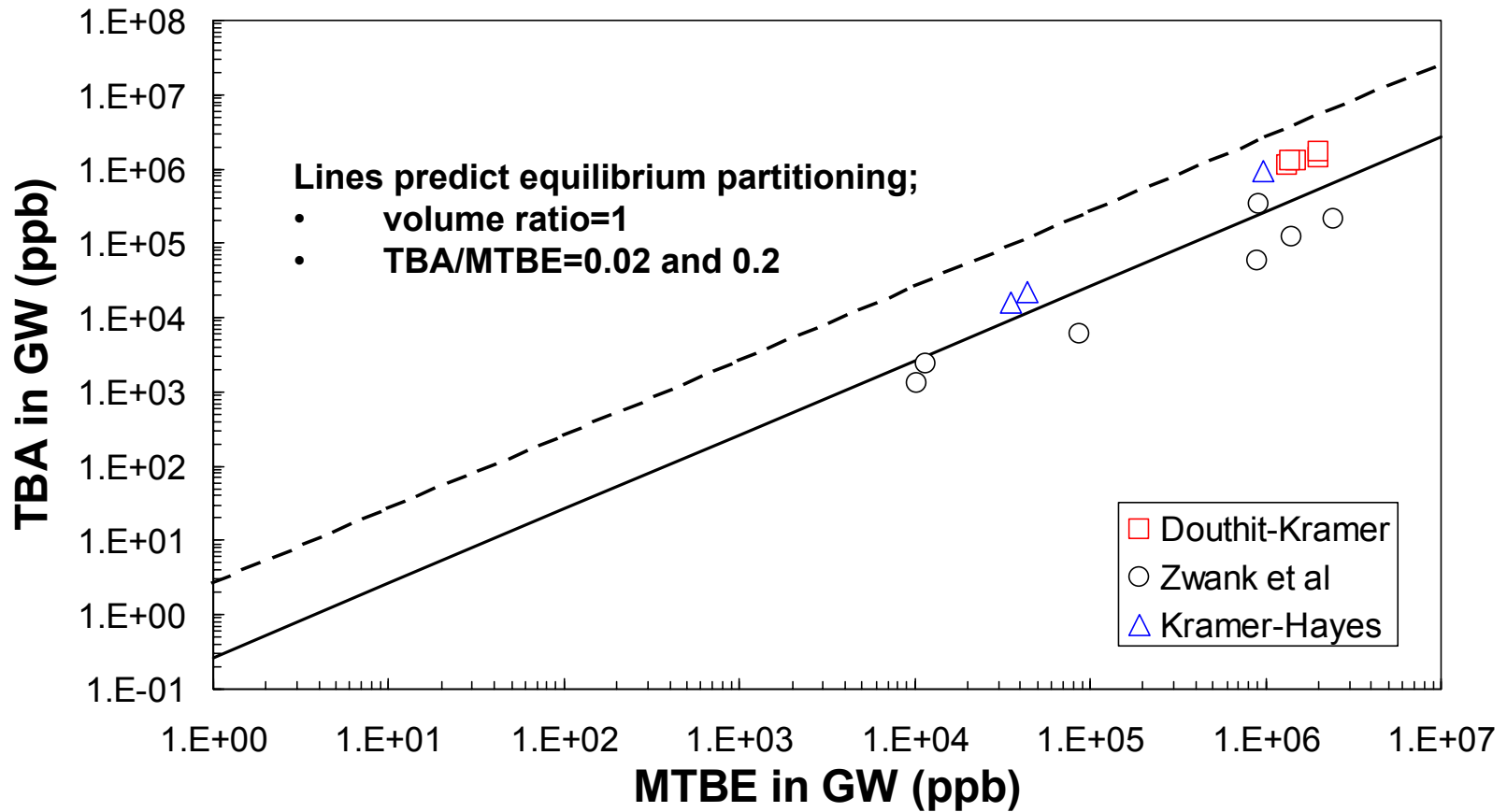
# Analysis of Partitioning Studies



Measured MTBE (aq) (ppb)	Measured TBA (aq) (ppb)	Estimated TBA/MTBE in original gasoline		Estimated %v/v in gasoline	
		%w/w	%v/v	MTBE	TBA
<b>Kramer-Douthit Data (2000 expts)</b>					
1330000	1120000	18.3%	17.2%	3.5%	0.6%
1990000	1430000	15.6%	14.7%	5.2%	0.8%
1480000	1270000	18.7%	17.5%	3.9%	0.7%
2000000	1690000	18.4%	17.2%	5.3%	1.0%
1390000	1270000	19.9%	18.6%	3.7%	0.7%
<b>Zwank et al. 2002 data (personal communication with Dr. Schmidt)</b>					
917638.4	341462.4	2.80%	2.62%	2.046%	0.057%
11523.2	2415.1	1.58%	1.48%	0.026%	0.000%
10187.5	1318.0	0.97%	0.91%	0.023%	0.000%
1397587.6	121435.5	0.65%	0.61%	3.116%	0.020%
2455632.0	212639.4	0.65%	0.61%	5.475%	0.036%
87723.4	6067.4	0.52%	0.49%	0.196%	0.001%
888152.2	59060.4	0.50%	0.47%	1.980%	0.010%
<b>Kramer and Hayes (1987)</b>					
43700	22300	3.83%	3.60%	0.097%	0.004%
35100	15900	3.40%	3.19%	0.078%	0.003%
966000	933000	7.26%	6.81%	2.154%	0.156%

Trace Levels of TBA in Gasoline Can Yield High Concentrations in Water

# TBA from Dissolution of Gasoline

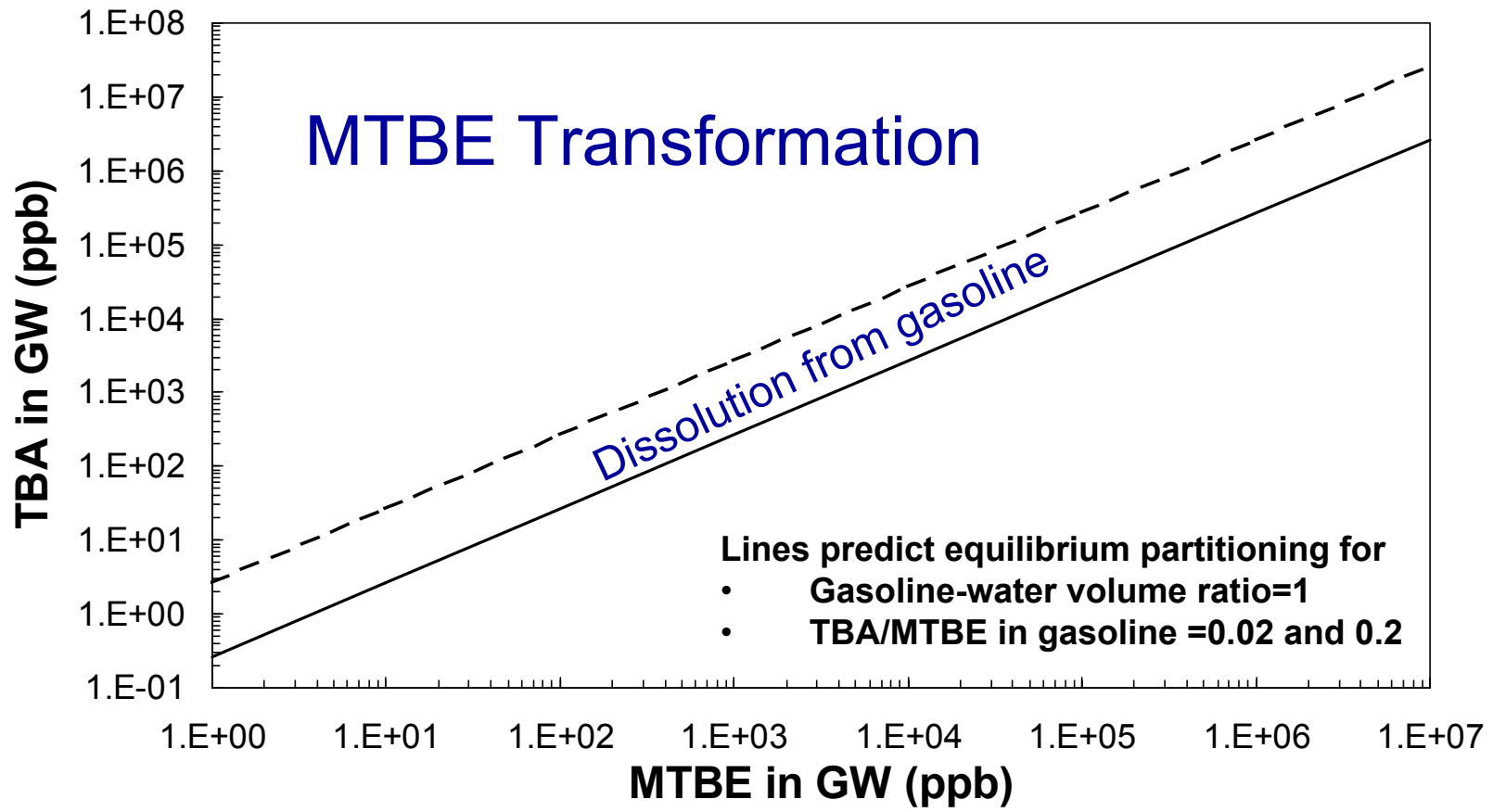


# Gasoline-Water Equilibrium Partitioning

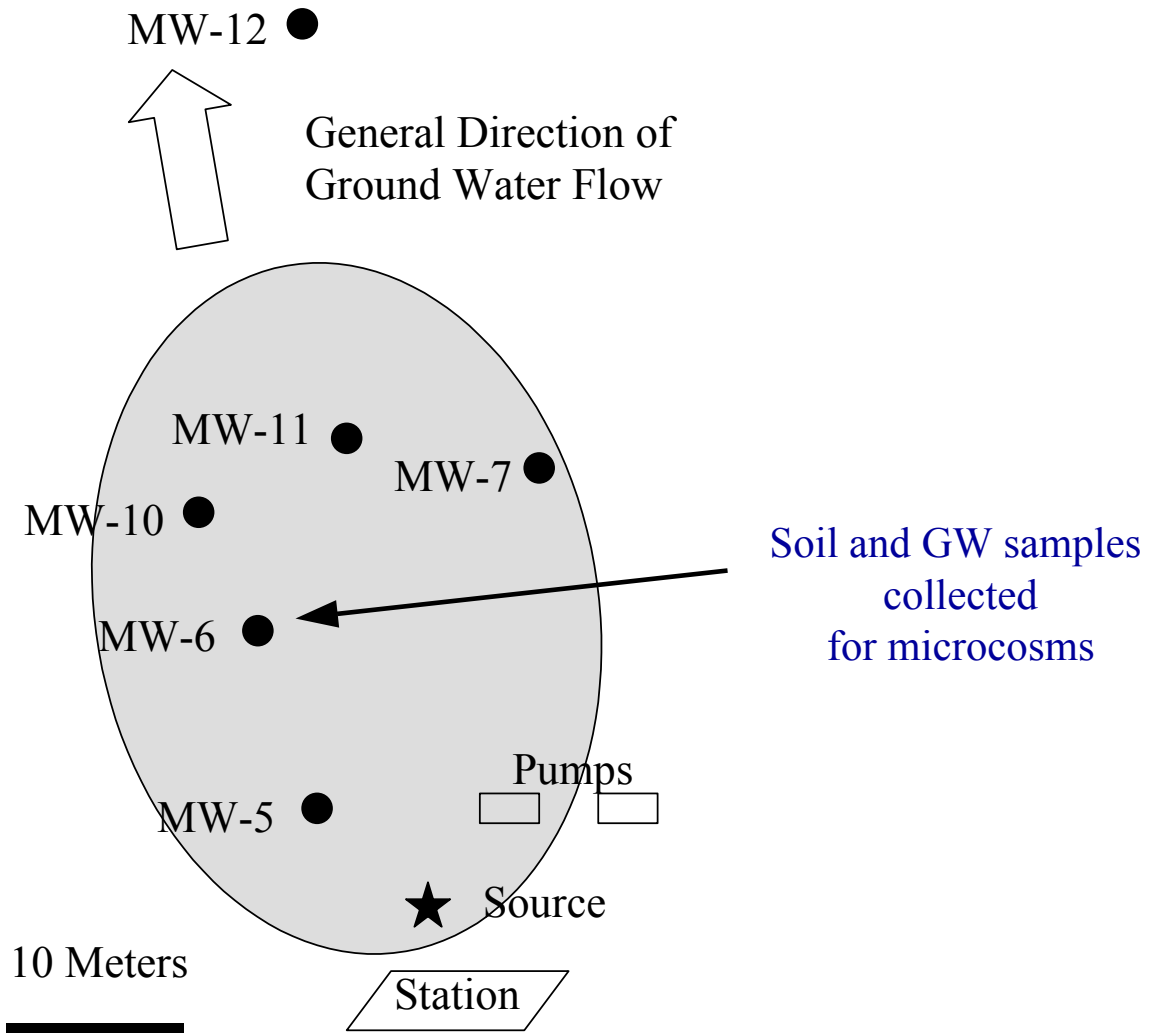


- The assumptions are very conservative. If the total porosity of sediment is 0.3, a volume ratio of 4 to 1 (water to fuel) is equivalent to 25,000 mg/kg TPH. A volume ratio of 1 is equivalent to 63,000 mg/kg TPH.

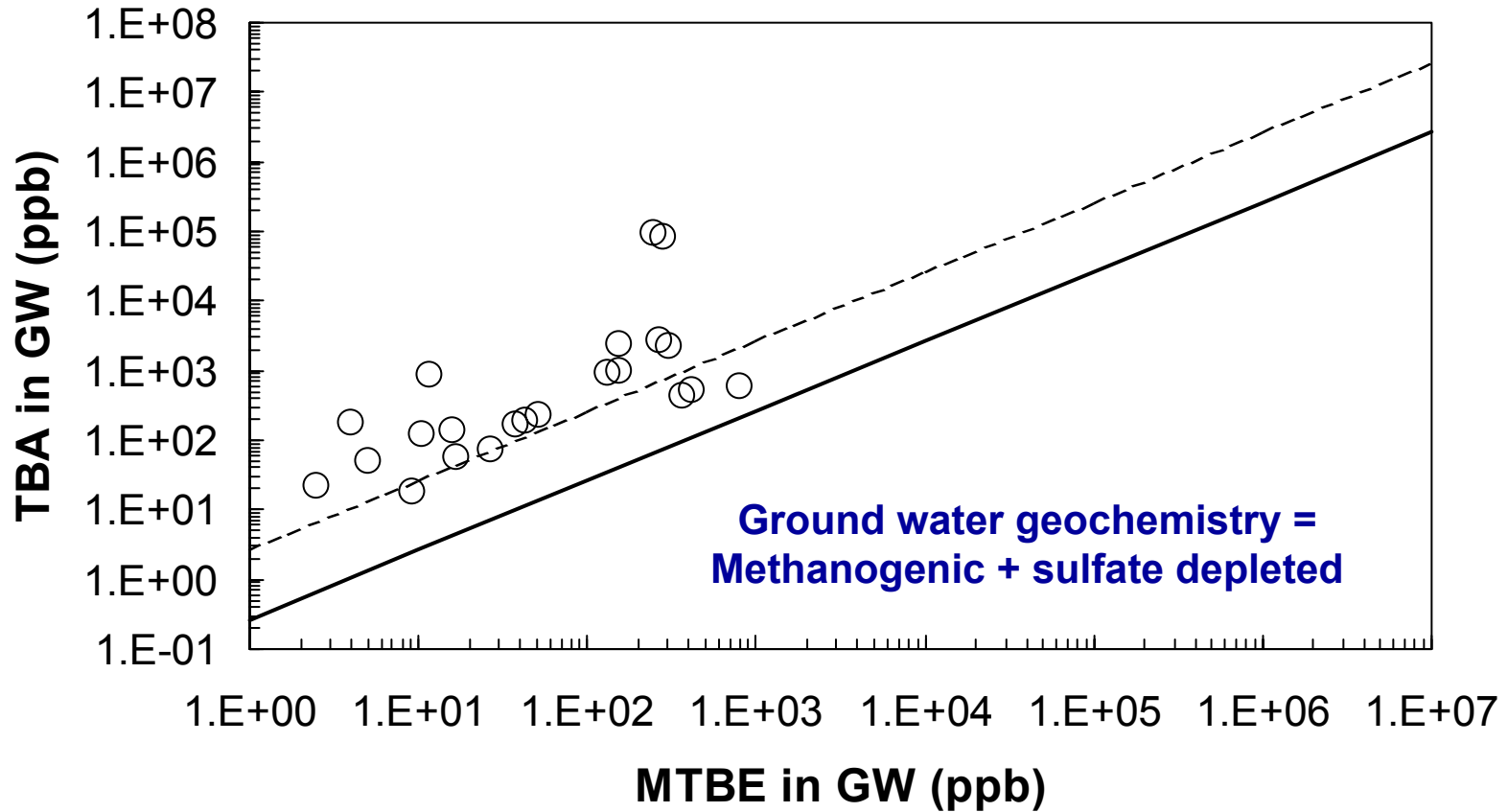
# Screening Tool to Evaluate Importance of MTBE Transformation



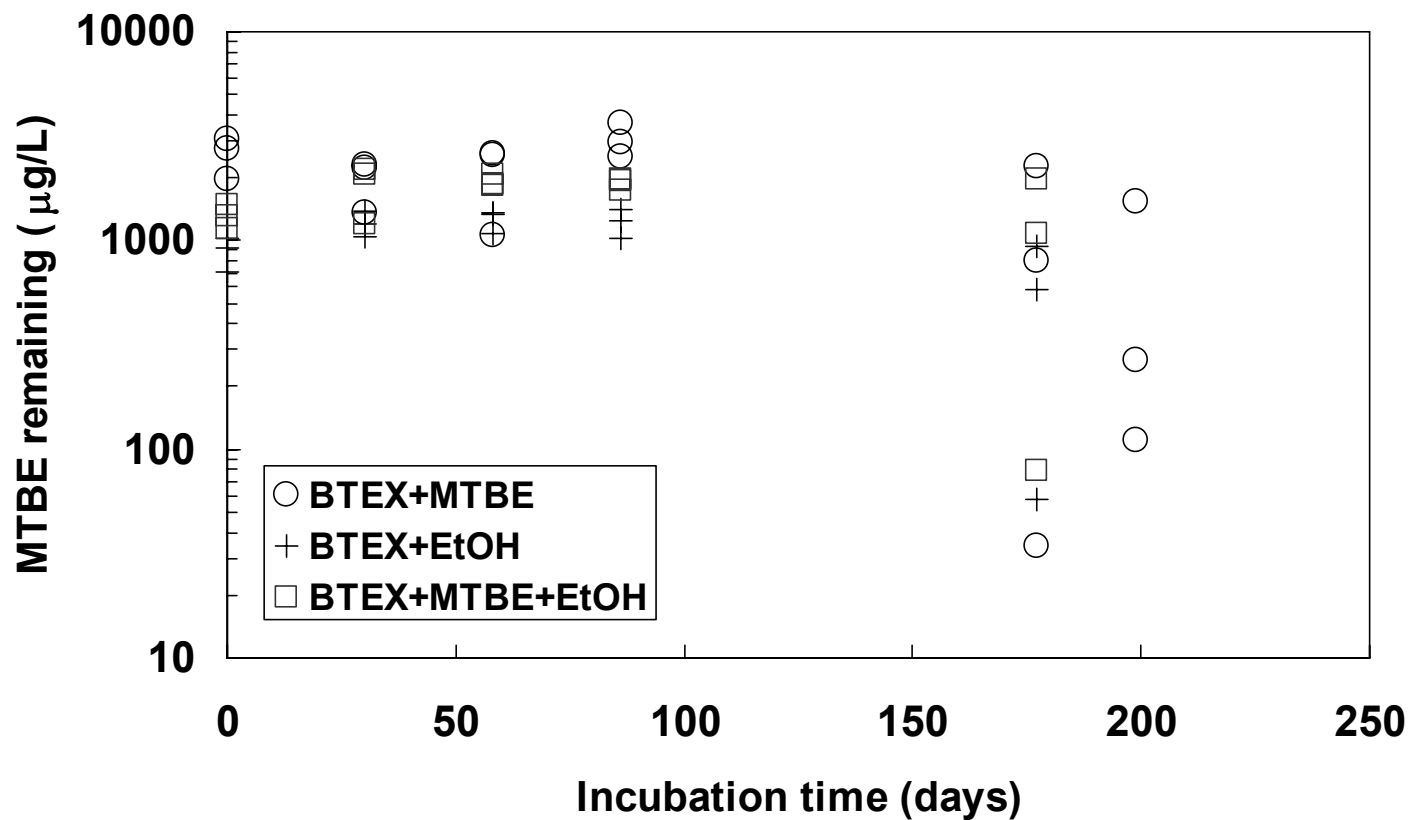
# Anaerobic Biodegradation of MTBE – Site in NJ



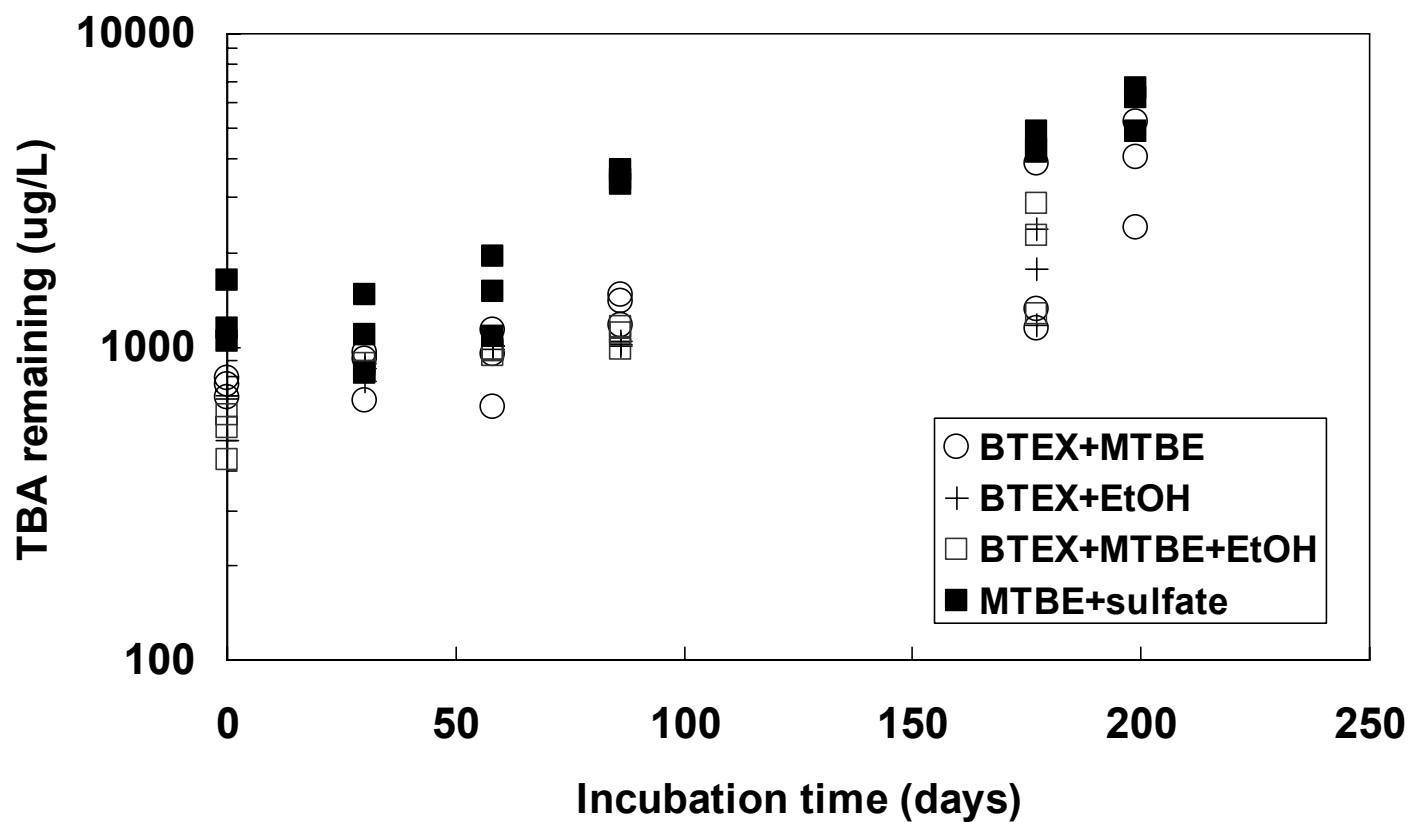
# TBA in GW at NJ Site BP-EPA Study



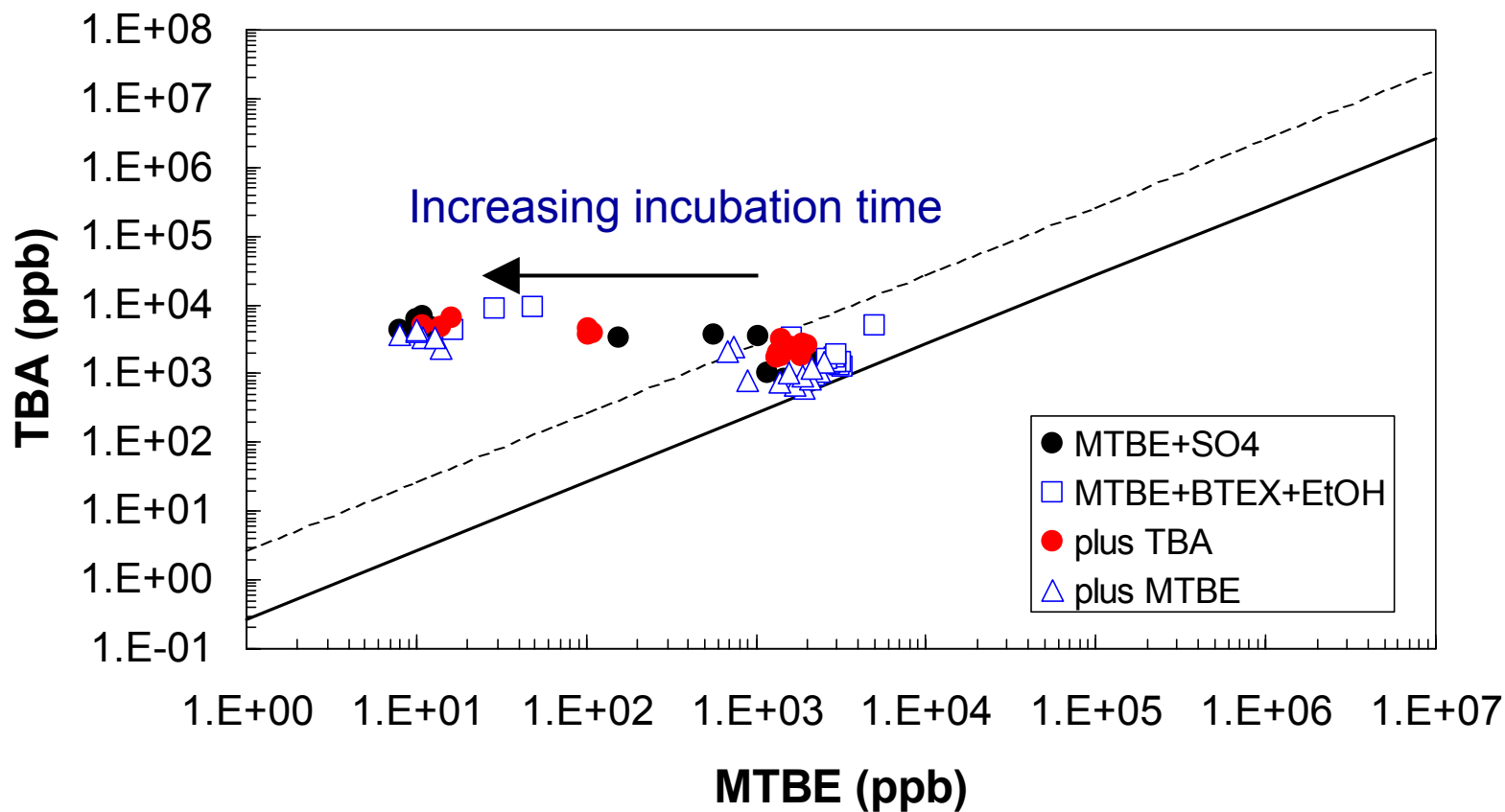
# Anaerobic MTBE Biodegradation in Laboratory Microcosms



# Corresponding TBA Accumulation



# TBA in Anaerobic Microcosms (NJ Site) BP-EPA Study



# Stable Carbon Isotopic Ratios (SCIR) of MTBE



$$\delta^{13}C(\text{permil}) = \frac{\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{sample}} - \left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{std}}}{\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{std}}} * 1000$$

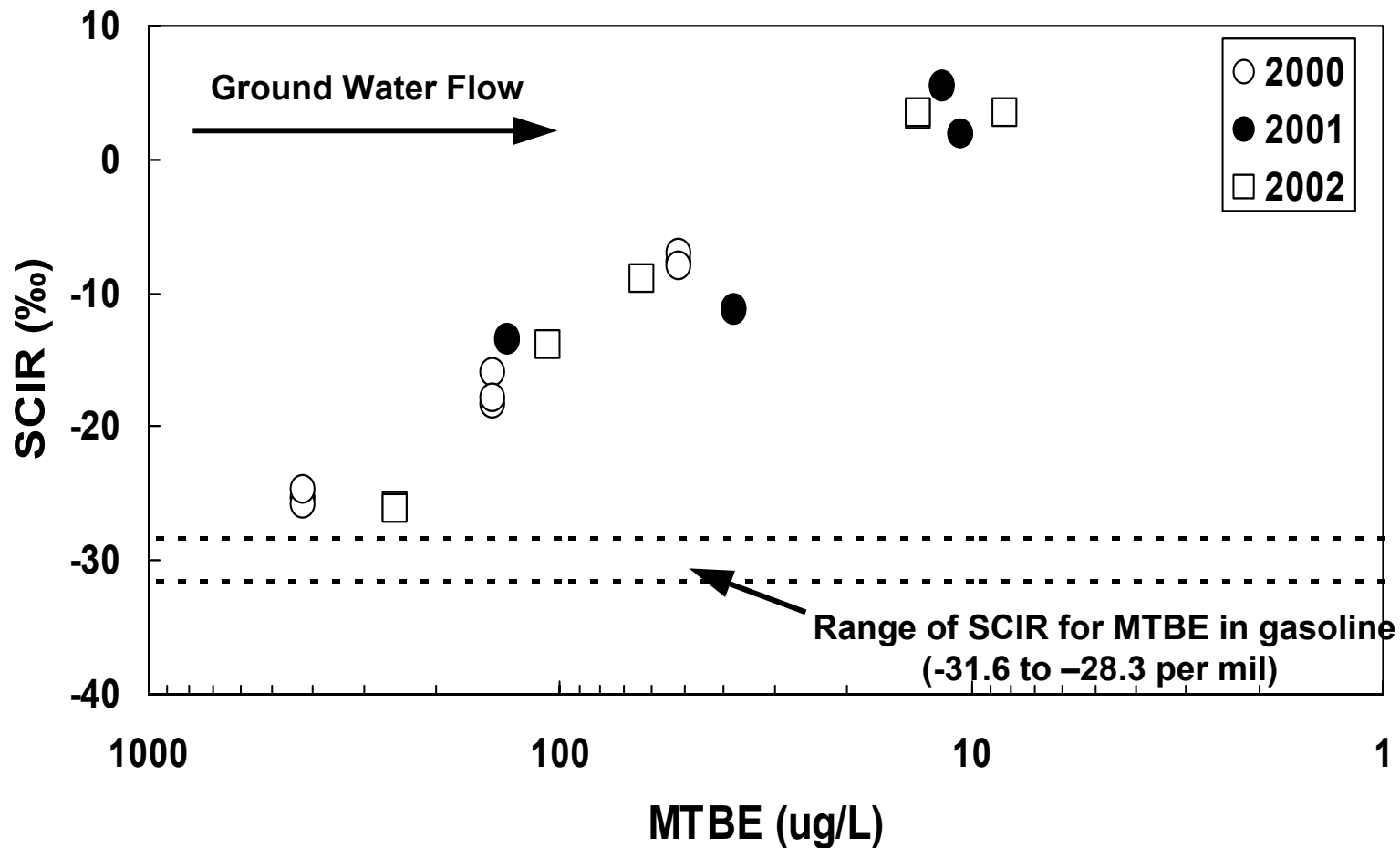
## Basis

- Micro-organisms preferentially use  $^{12}\text{C}$  isotope over  $^{13}\text{C}$
- Abiotic processes such as dilution or volatilization do not cause significant isotopic fractionation of MTBE

## Expectation

- MTBE will get enriched in  $^{13}\text{C}$  during biodegradation
- SCIR of MTBE will increase with distance along a flow-path if MTBE is being naturally biodegraded

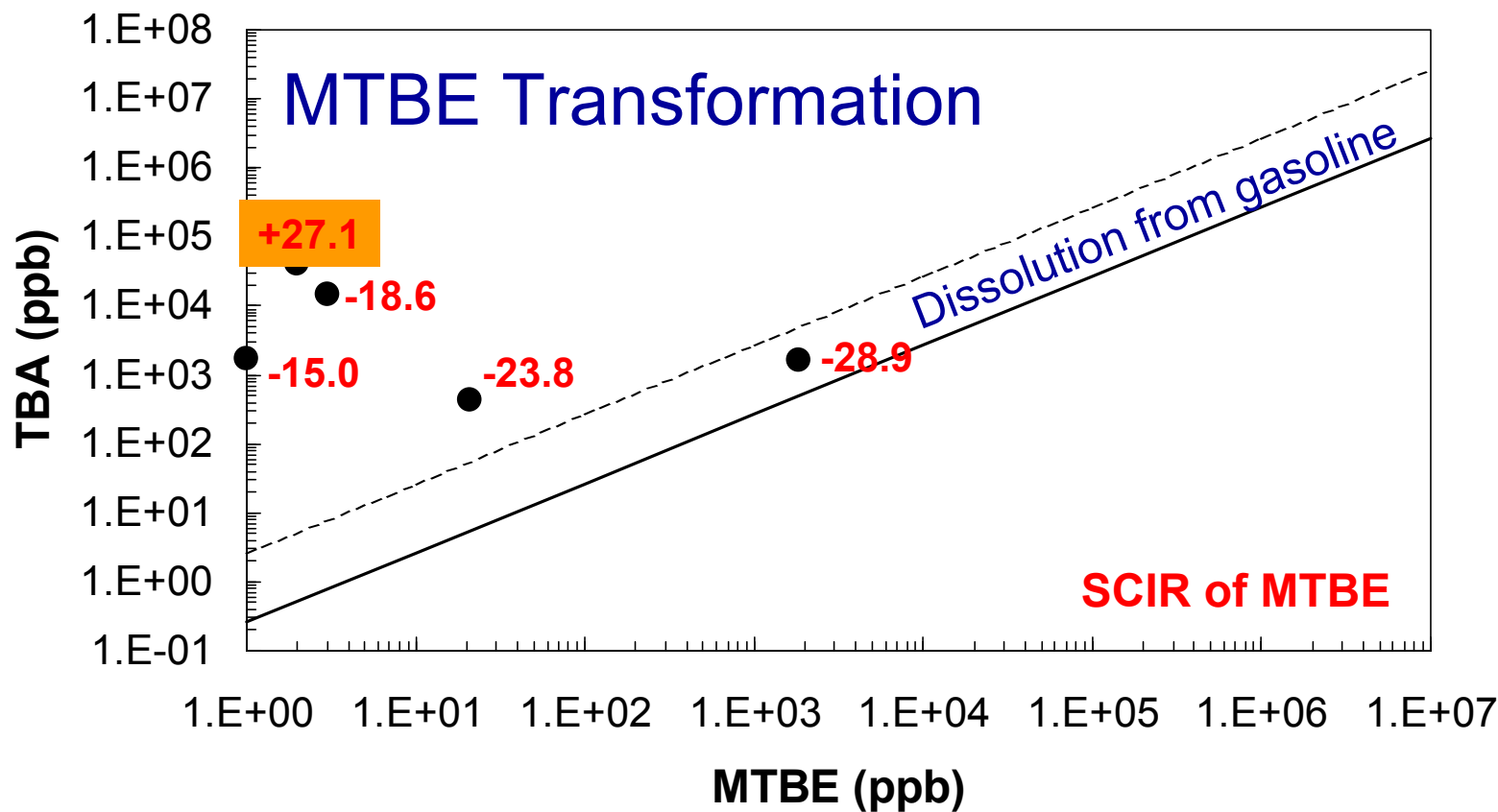
# MTBE SCIR as Indicator of MTBE Biodegradation – Field Data



**SCIR of MTBE increased with distance**

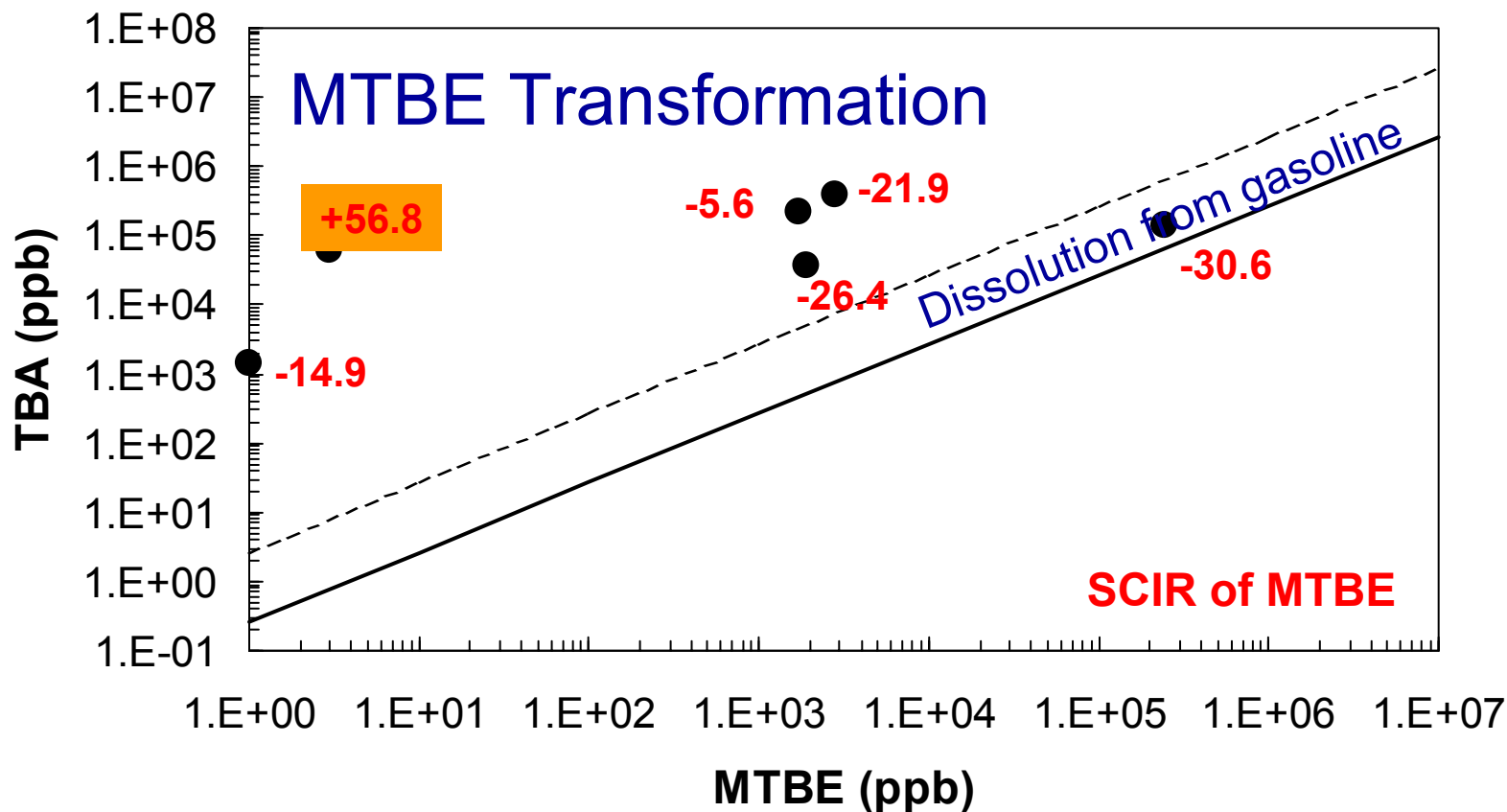
**SCIR > -28.3 per mil indicate MTBE Transformation to TBA**

# Orange County Site 1888

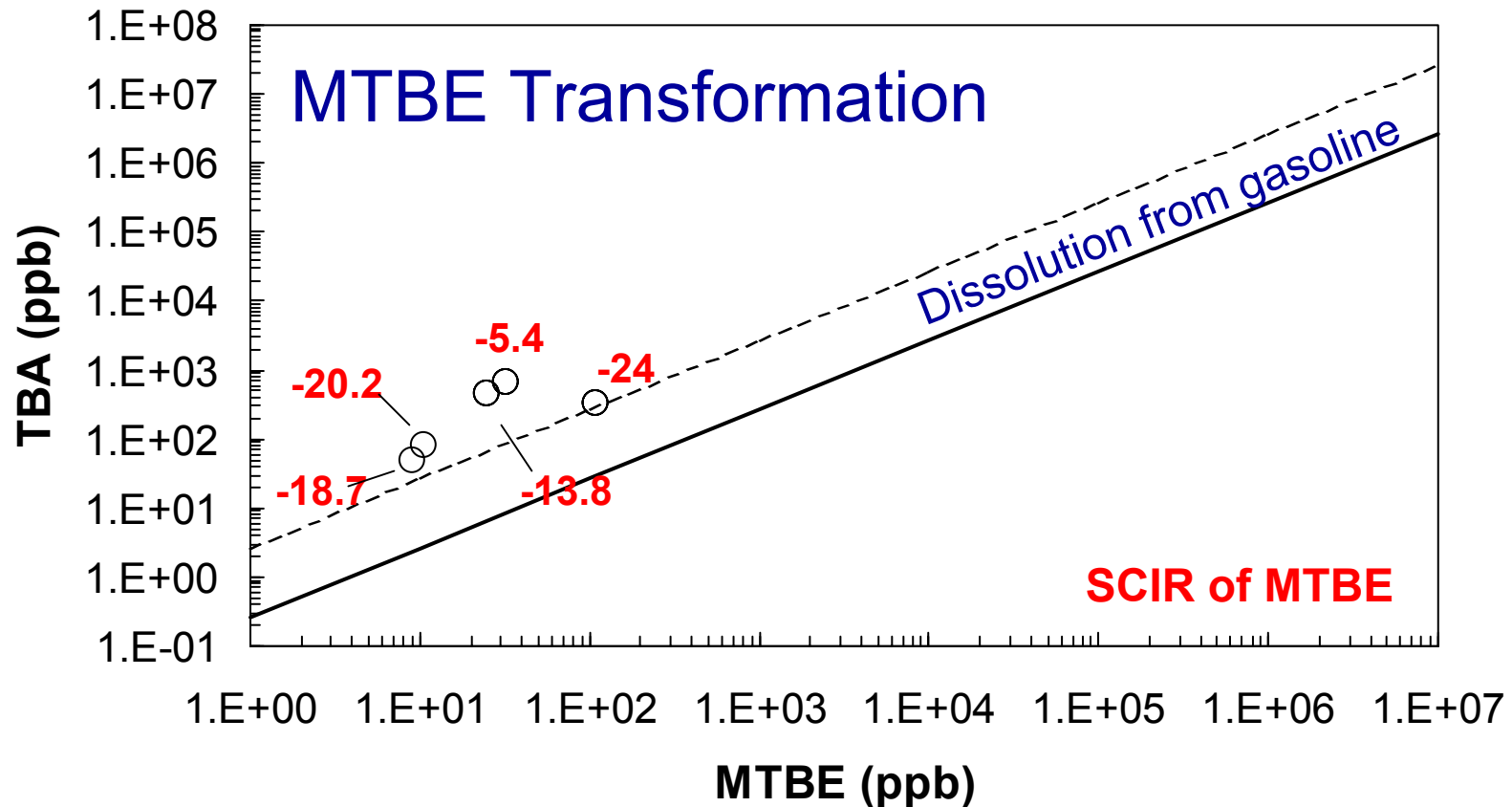


**Isotopic Data Validates Screening Tool**

# Orange County Site 1905



**Isotopic Data Validates Screening Tool**



**Isotopic Data Validates Screening Tool**

# Summary



- Cross-plot of TBA vs MTBE concentrations in GW reveals unexpectedly high concentrations of TBA in monitoring wells at some locations.
- TBA concentrations greater than those expected by partitioning suggest MTBE transformation as a source of TBA
- Stable isotope data validates the screening approach

# References



1. Wilson, J. T., Presentation to API Soil and Groundwater Technical Task Force, February 2003.
2. Kramer, W. H. and Douthit, T. L., 2000. " Water Soluble Phase Oxygenates in Gasoline from Five New Jersey Service Stations", In Proceedings of the 2000 API/NGWA Conference: Petroleum Hydrocarbons and Organic Chemicals in Groundwater, National Ground Water Association, Westerville, Ohio.
3. Zwank, L., Schmidt, T. C., Handlerlein, S. B., Berg, M., 2002. "Simultaneous Determination of Fuel Oxygenates and BTEX Using Direct Aqueous Injection Gas Chromatography Mass Spectrometry (DAI-GC/MS), *Environ. Sci. Technol.*, **36**, 2054-2059.
4. Kolhatkar, R., Kuder, T., Philp, P., Allen, J., Wilson, J., 2002. "Use of Compound-specific Stable Carbon Isotope Analyses to Demonstrate Anaerobic Biodegradation of MTBE in Groundwater at a Gasoline Release Site", *Environmental Science & Technology*. 36(24):5139-5146.
5. Somsamak, P., Cowan, R. M. and Haggblom, M. M., 2001. Anaerobic Biotransformation of Fuel Oxygenates Under Sulfate-reducing Conditions, *FEMS Microbiology Ecology*, 37, 259-264.
6. Bradley, P.M., F.H. Chapelle, and J.E. Landmeyer. 2001. Effect of Redox Conditions on MTBE Biodegradation in Surface Water Sediments. *Environmental Science & Technology*. **35(23)**:4643-4647.
7. Bradley, P. M., Landmeyer, J. and Chapelle, F. H., 2002. TBA Biodegradation in Surface-water Sediments Under Aerobic and Anaerobic Conditions, *Environmental Science & Technology*, **36(19)**: 4087-4090.

# Orange County SCIR Data

