



TBA – Occurrence and Sources

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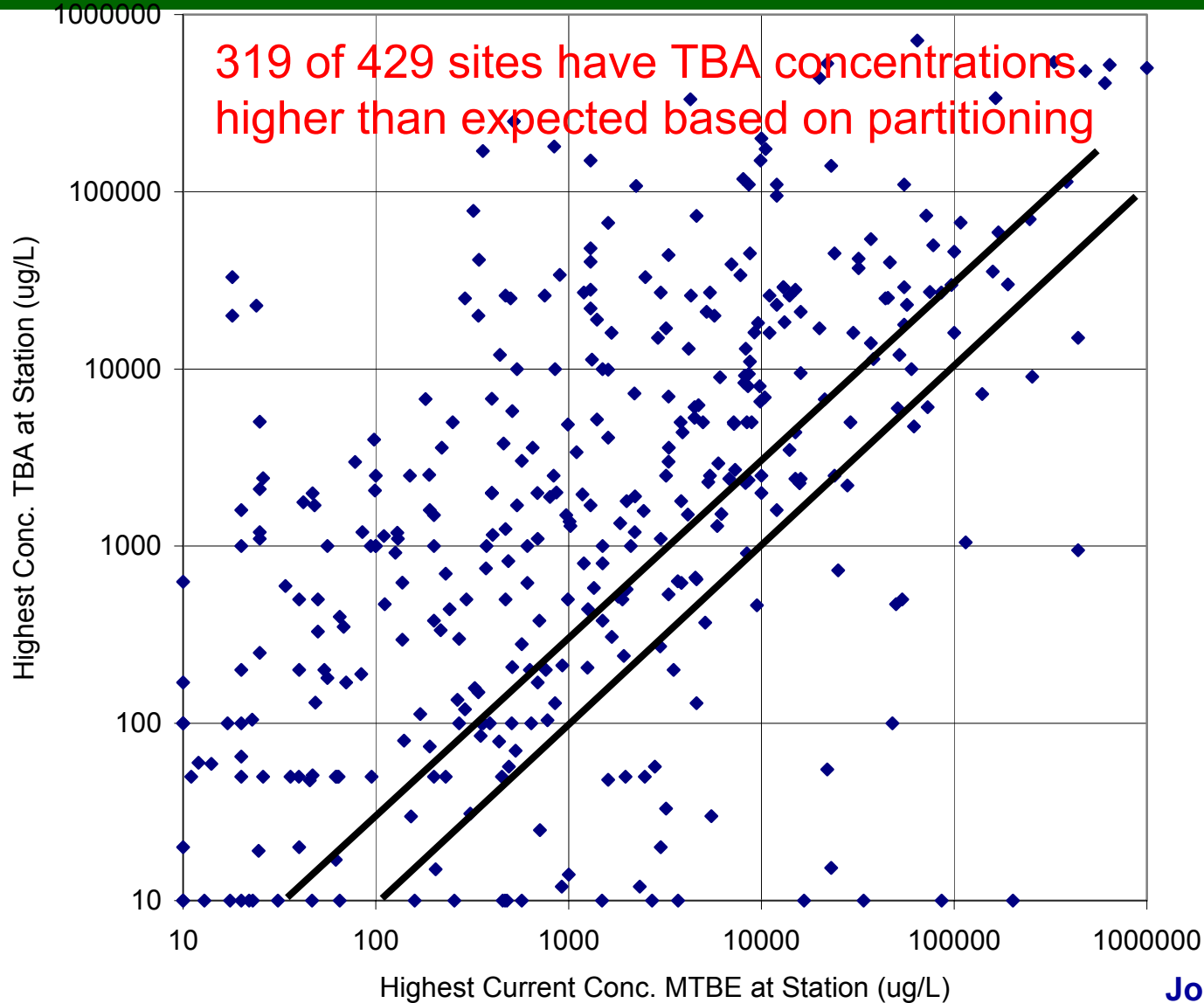
GEM, A BP Affiliated Company

Oxygenates Workshop

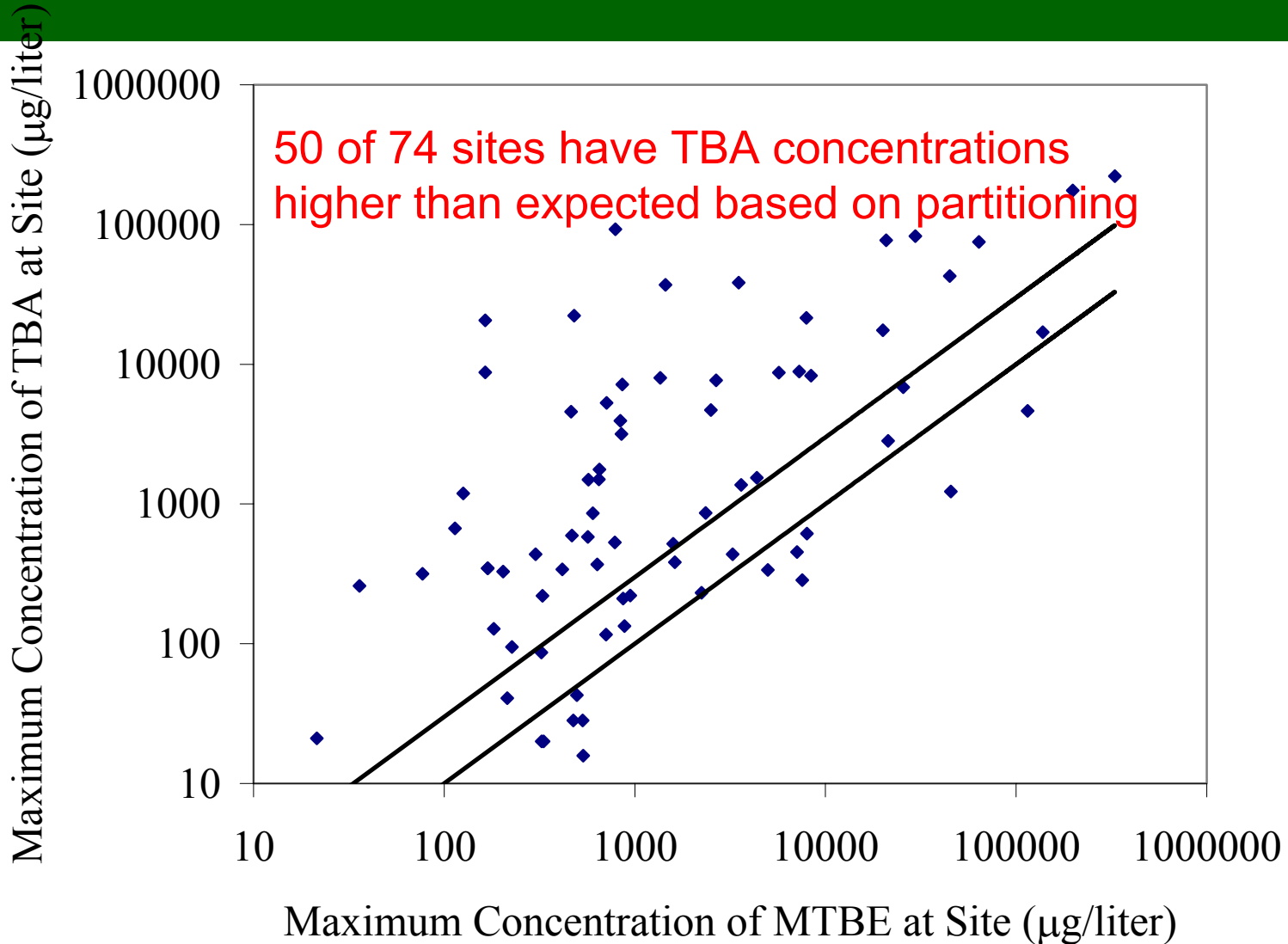
Costa Mesa

August 19, 2003

Orange County Sites



Sites in Eastern United States

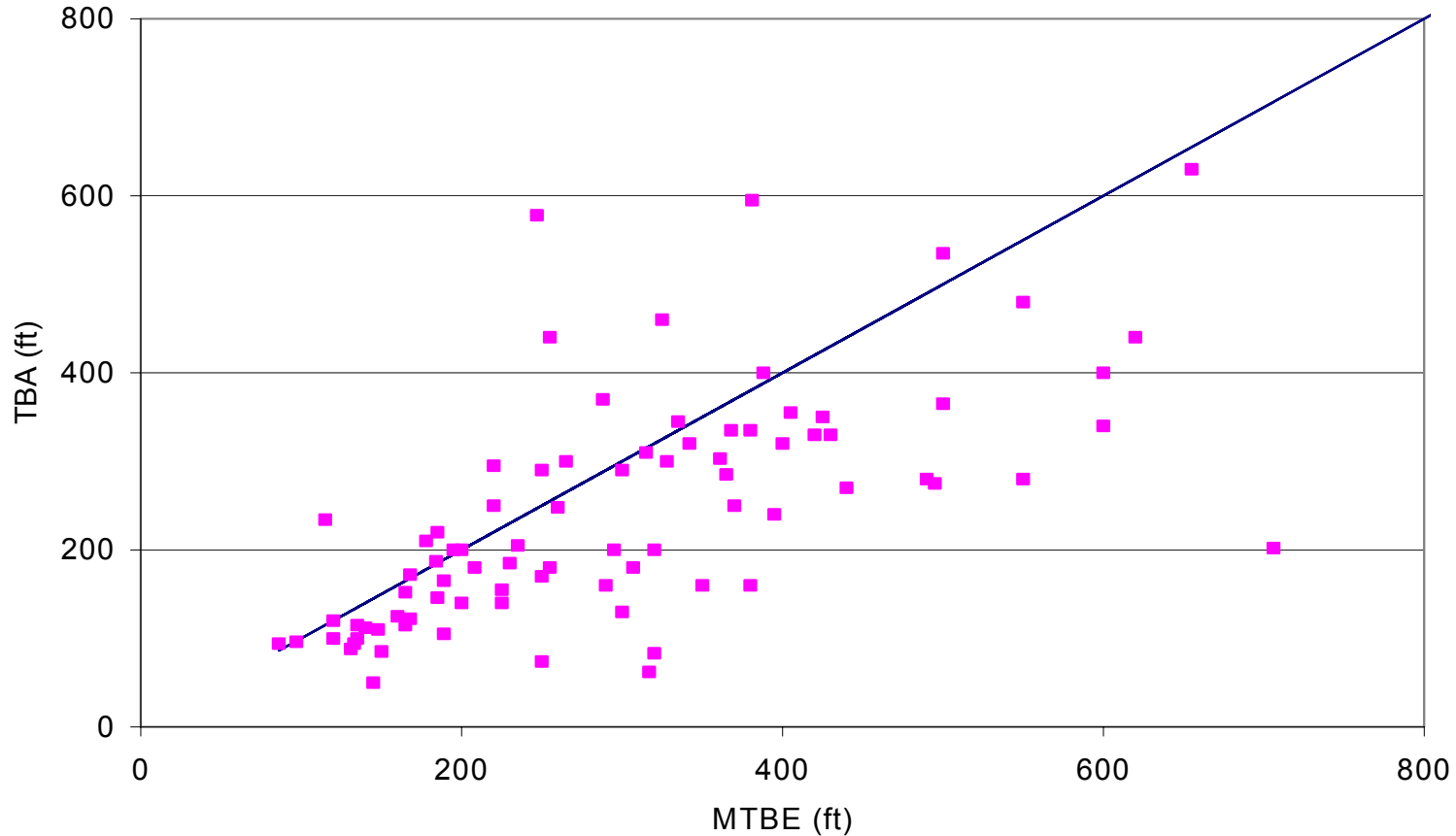


Data from Kolhatkar et al. (2000)

Plume Lengths



TBA shorter than MTBE plumes at 75% of the sites



Shih et al. (2003)

TBA – Occurrence



- TBA co-occurs with MTBE in ground water
- TBA concentrations can be much higher than MTBE
- TBA plumes appear to be shorter than MTBE

TBA – Potential Sources



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

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)

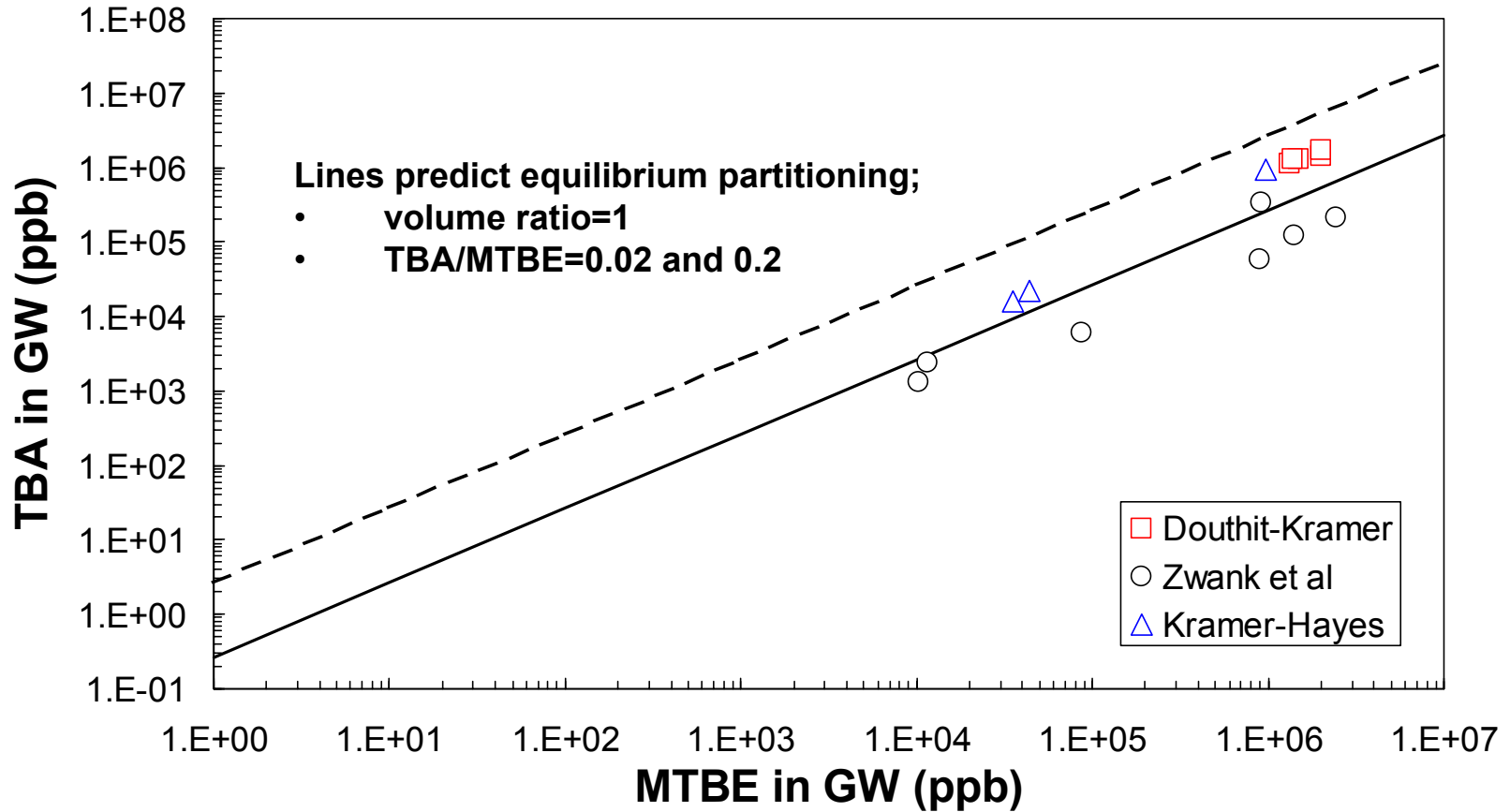
Analysis of Partitioning Studies



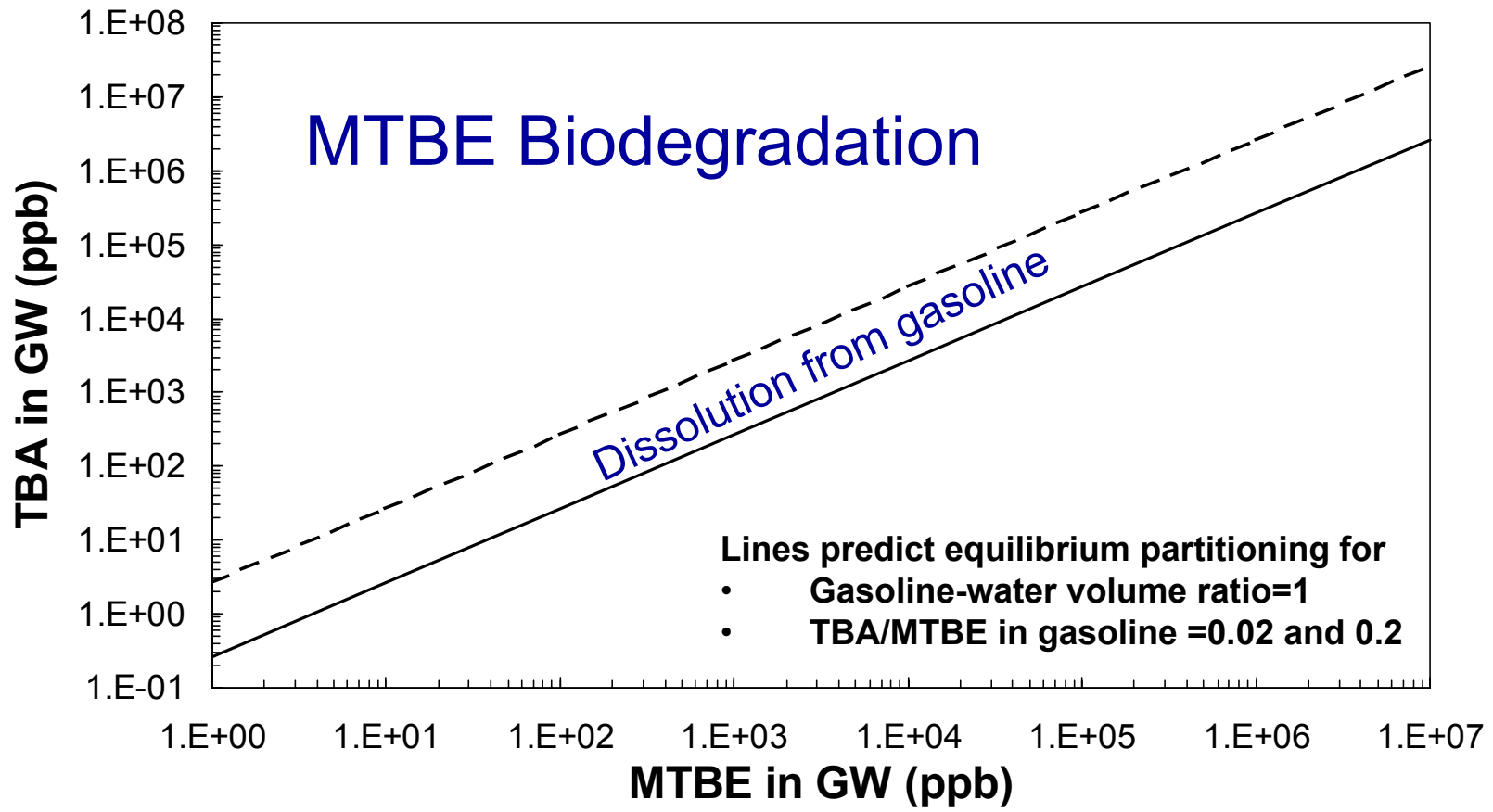
Measured MTBE (aq) (ppb)	Measured TBA (aq) (ppb)	Estimated TBA/MTBE in original gasoline		Estimated %v/v in gasoline	
		%w/w	%v/v	MTBE	TBA
Kramer-Douthit Data (2000 expts)					
1330000	1120000	18.3%	17.2%	3.5%	0.6%
1990000	1430000	15.6%	14.7%	5.2%	0.8%
1480000	1270000	18.7%	17.5%	3.9%	0.7%
2000000	1690000	18.4%	17.2%	5.3%	1.0%
1390000	1270000	19.9%	18.6%	3.7%	0.7%
Zwank et al. 2002 data (personal communication with Dr. Schmidt)					
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%
Kramer and Hayes (1987)					
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

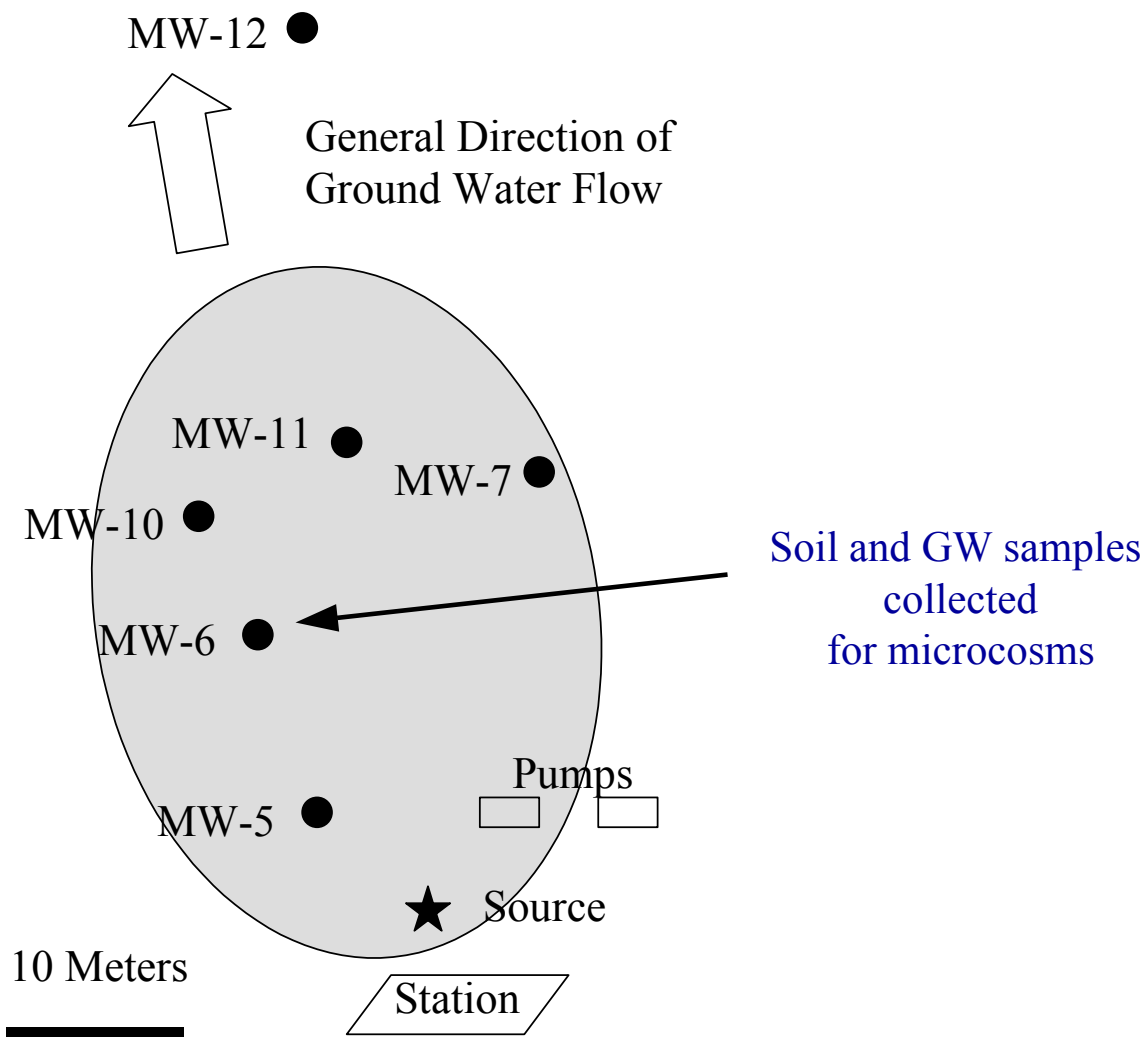
TBA from Dissolution of Gasoline



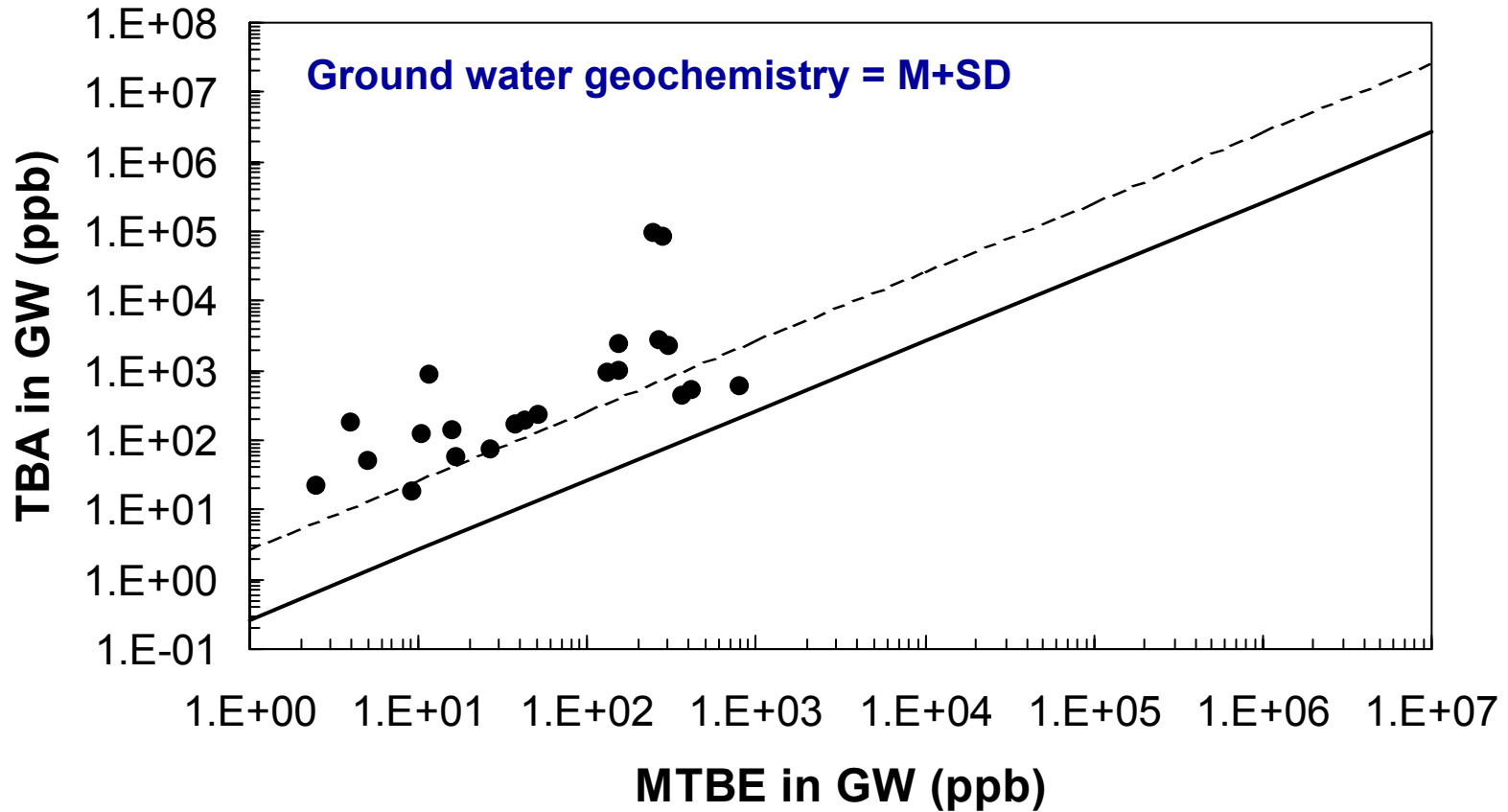
Screening Tool to Evaluate Importance of MTBE Biodegradation



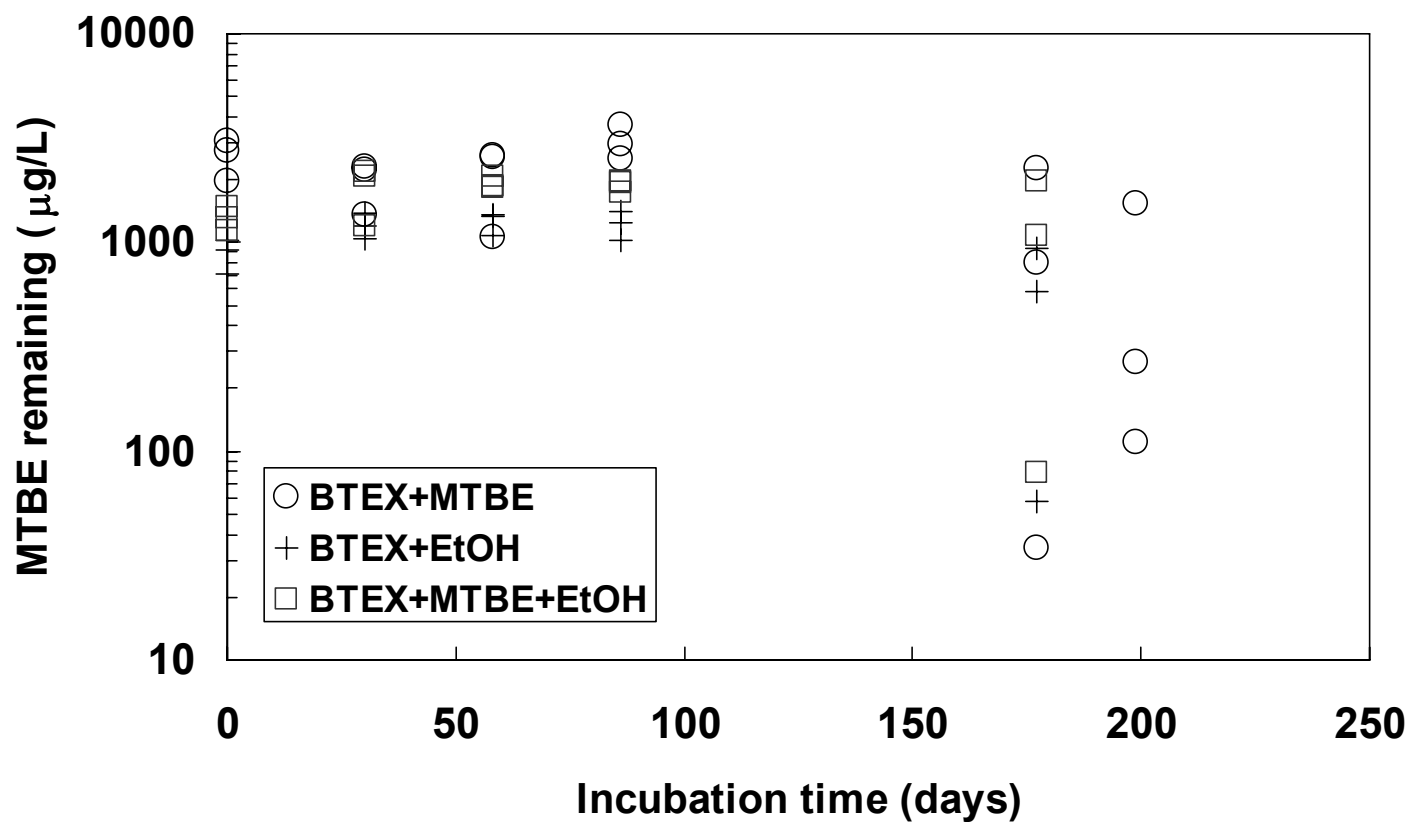
Anaerobic Biodegradation of MTBE – Site in NJ



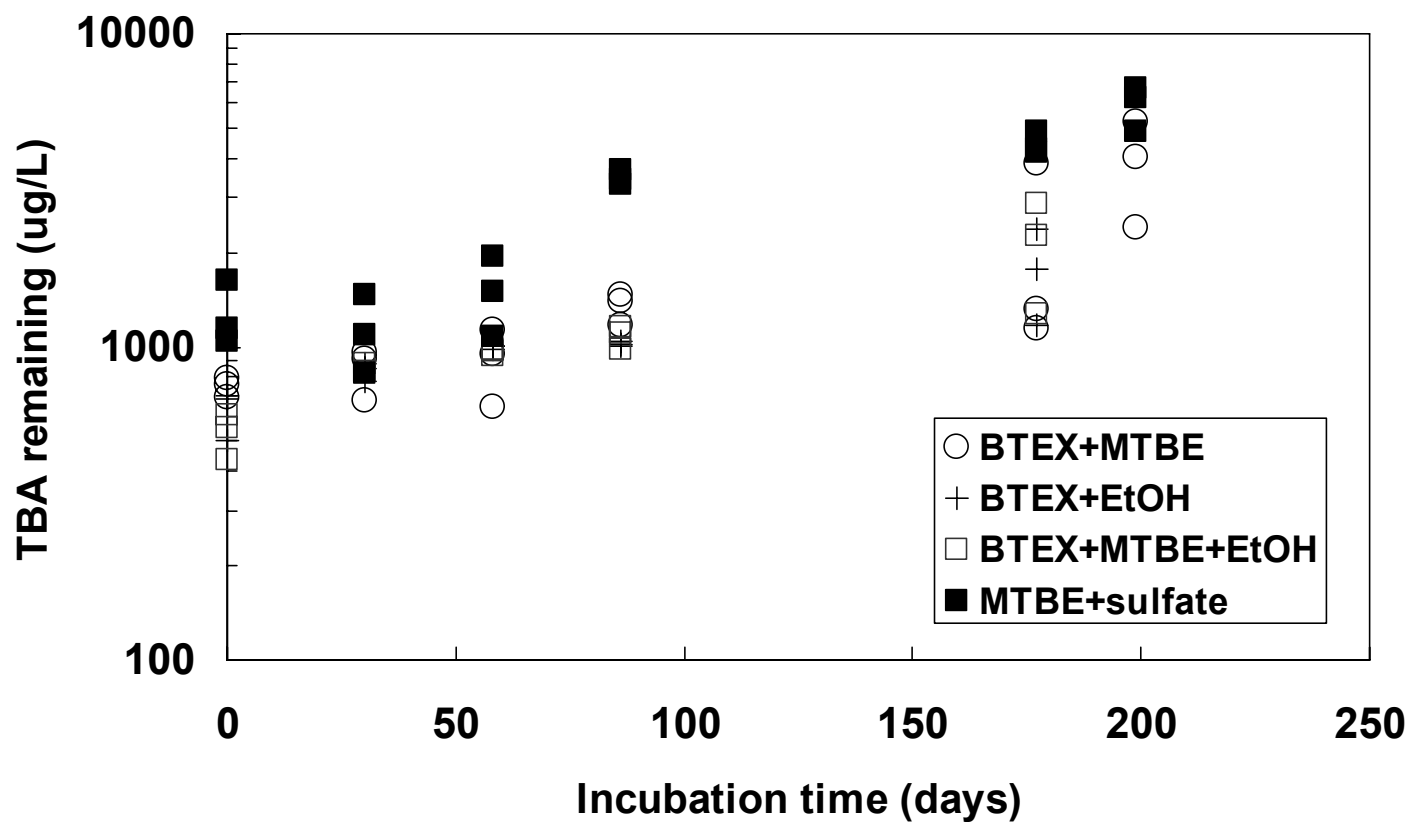
TBA in GW at NJ Site BP-EPA Study



Anaerobic MTBE Biodegradation in Laboratory



Corresponding TBA Accumulation



Stable Carbon Isotopic Ratios (SCIR) of MTBE



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

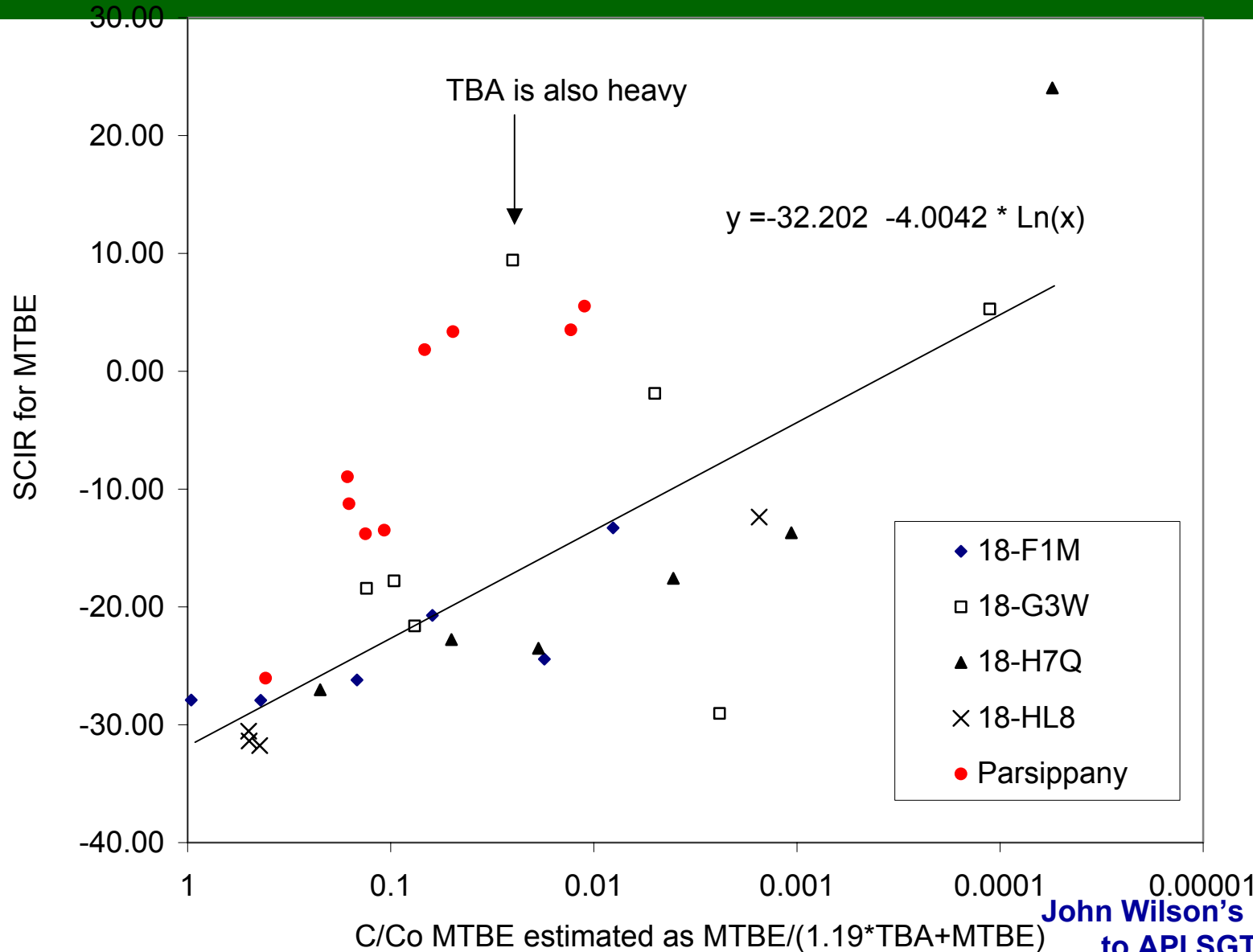
Basis

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

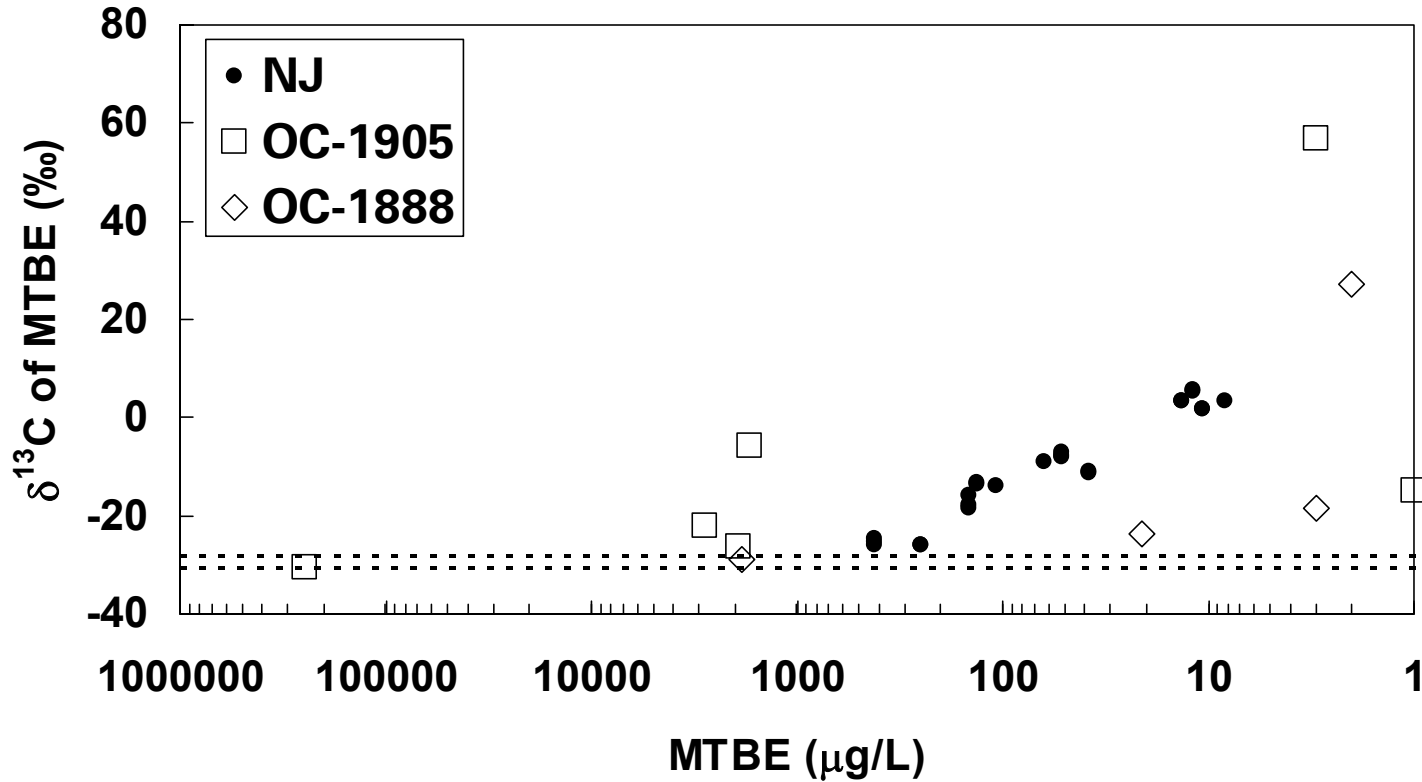
Expectation

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

TBA from MTBE Biodegradation

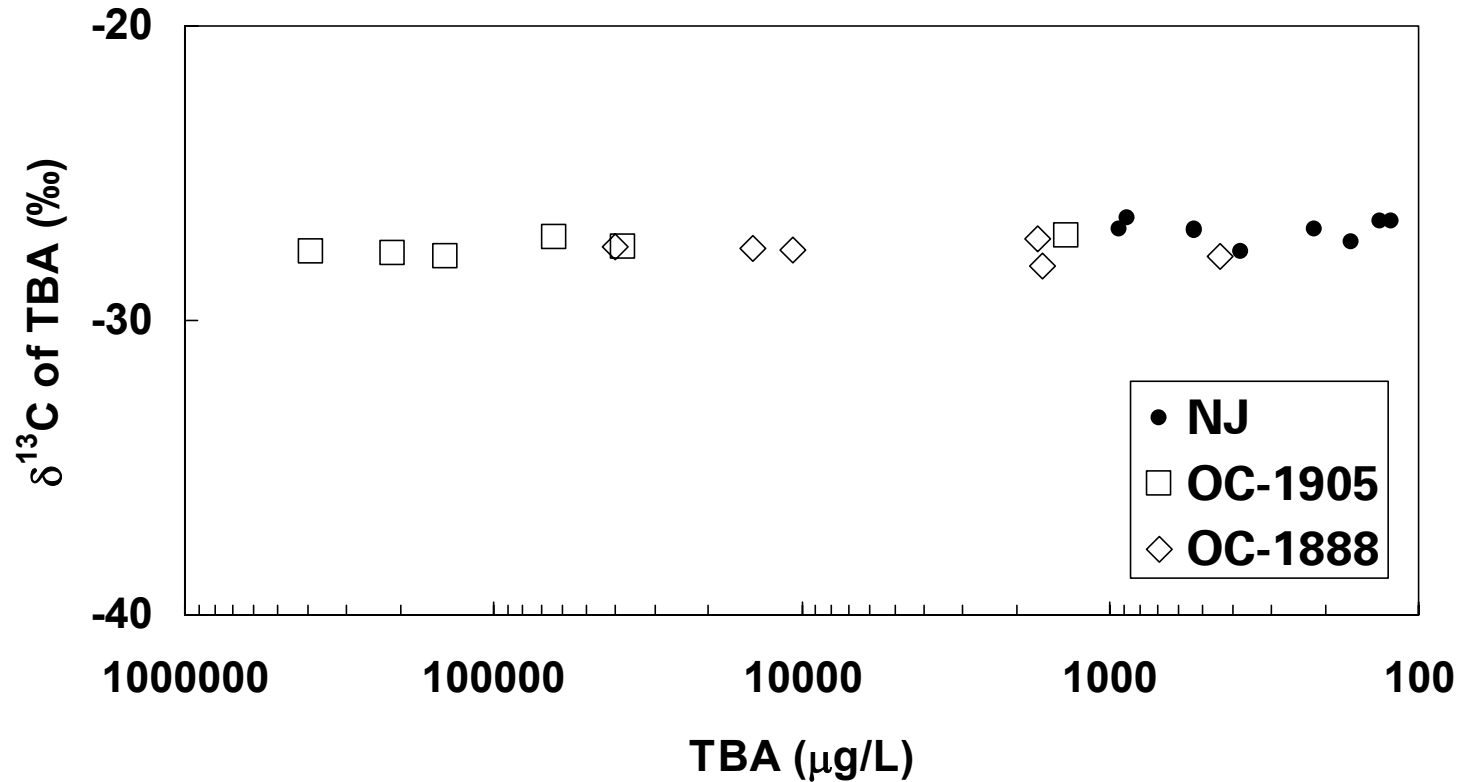


MTBE SCIR Data – Orange County Sites



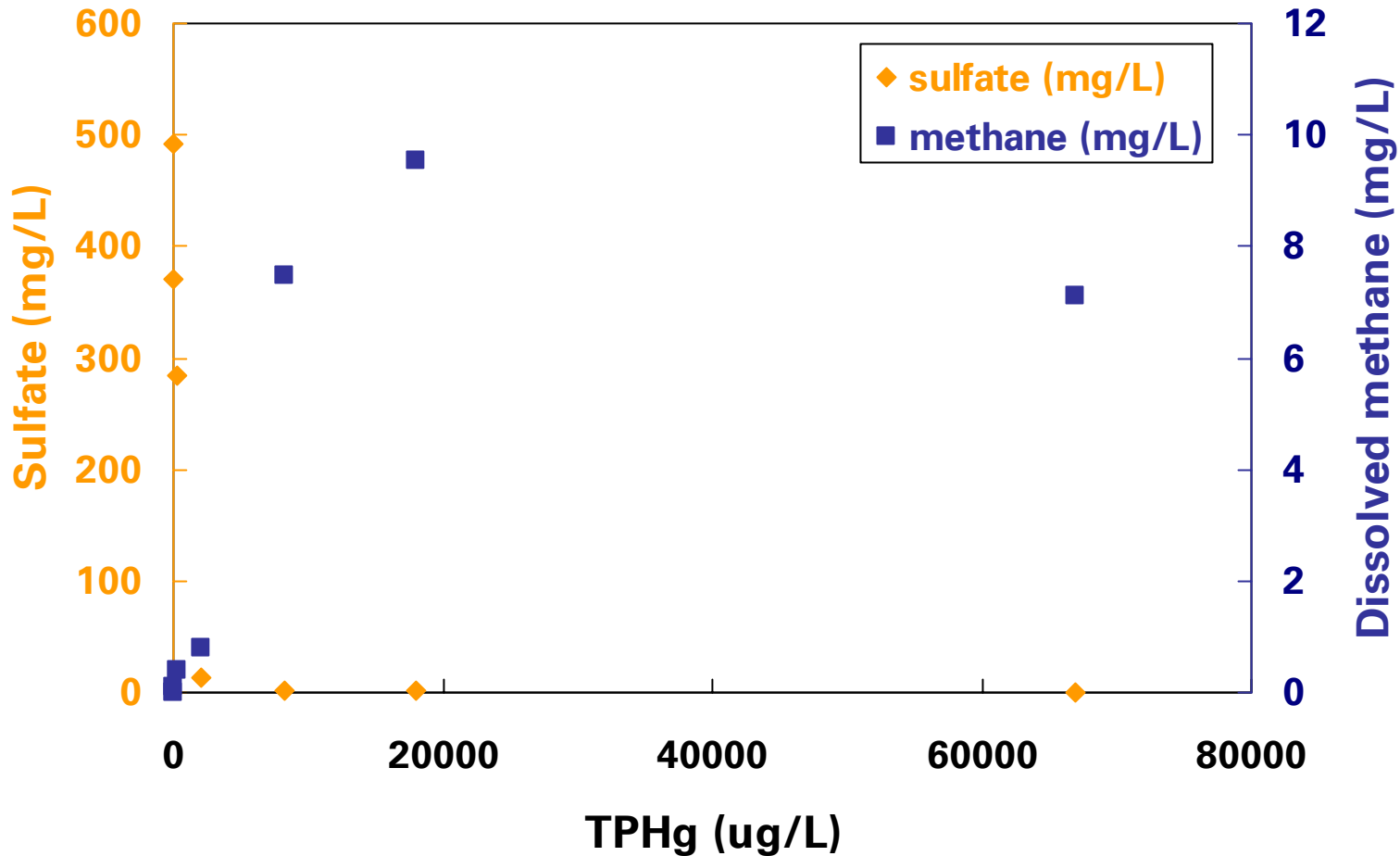
SCIR data indicate MTBE Biodegradation to TBA

TBA SCIR Data – Orange County Sites



Little Evidence of TBA Degradation in SCIR Data

Anaerobic GW at OC-1905



TBA Biodegradation - Summary



Aerobic

- Salanitro et al., (2000)
- Bob Borden and others, (Battelle 1999 poster)
- USGS papers (ES&T 2000, 2001)
- John Novak and others, (early 1990s)
- BioGAC is being looked as potential technology for ex-situ treatment
- Ongoing API study

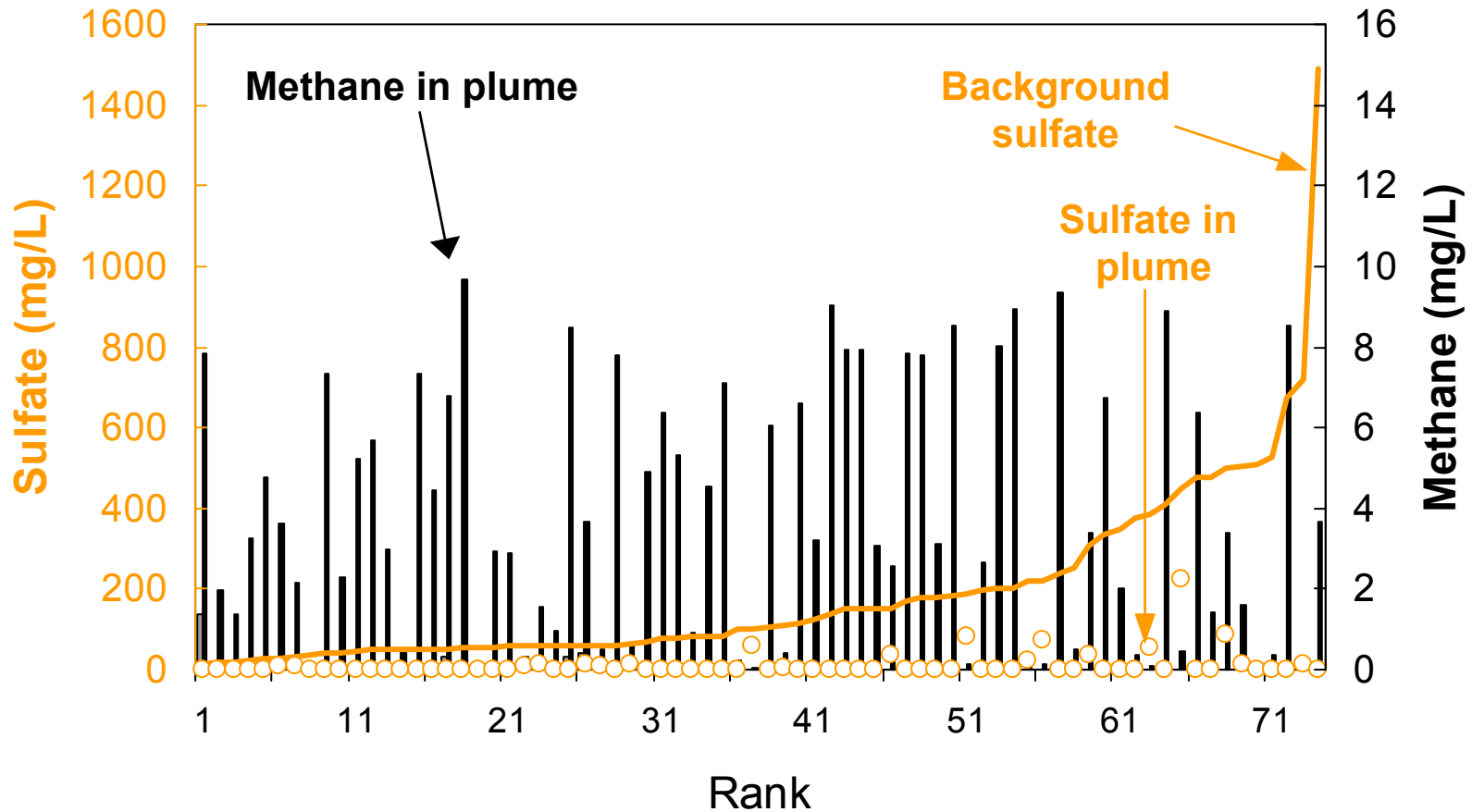
⇒ **Readily biodegradable (in-situ oxygen enhancements)**

Anaerobic

- Mike Day, 2001 (MNA of TBA in TX)
- BP-EPA field data from 1999-2000 survey
- Kevin Finneran, ES&T 2001 [Fe(III)]
- USGS paper in ES&T 2002 (biodegrades with **nitrate**, Mn(IV), and sulfate)

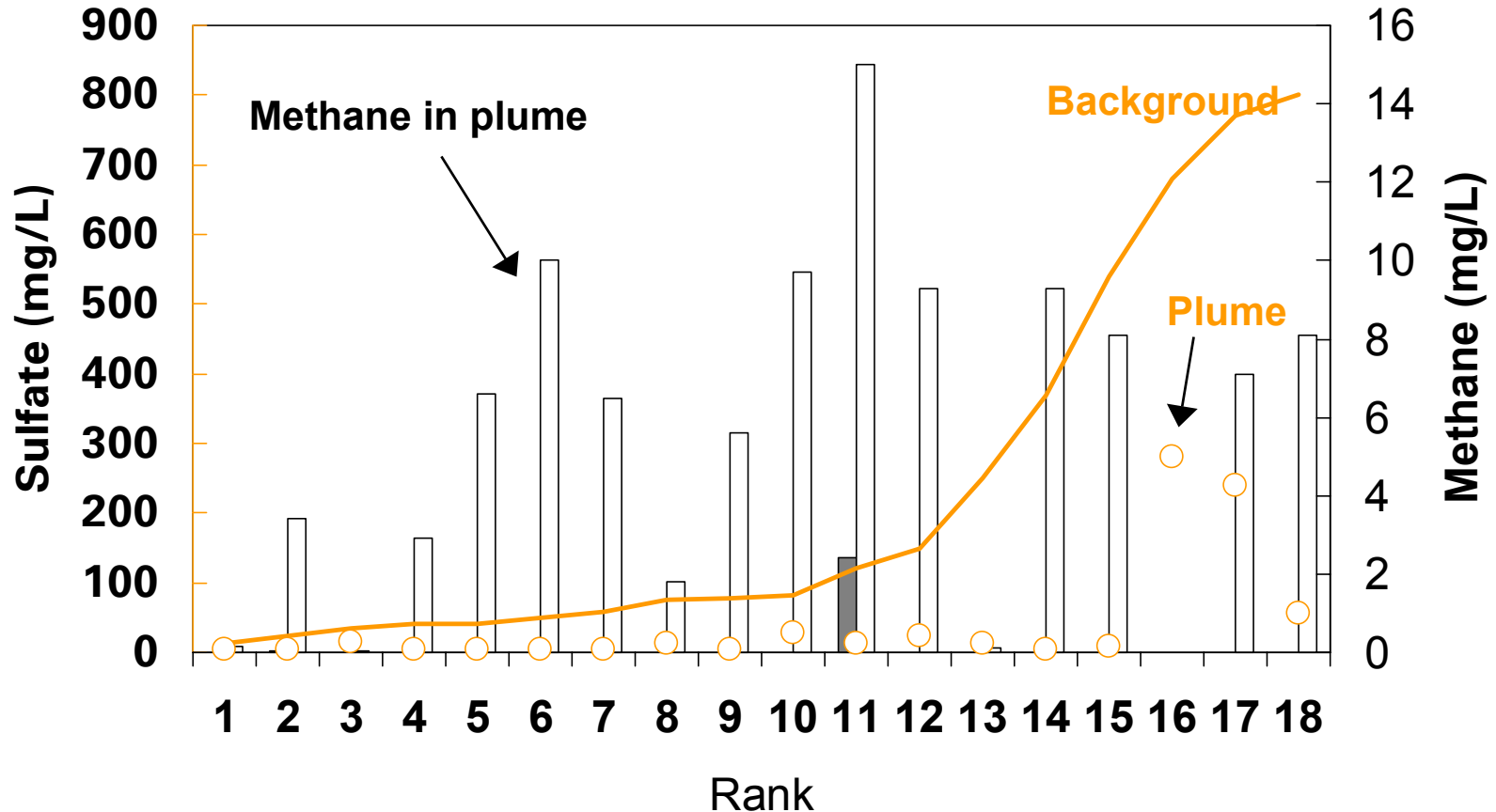
⇒ **More persistent under more reduced conditions**

GW Plumes in Eastern US (BP-EPA MTBE MNA Study)



Majority of plumes are anaerobic (M+SD)

GW Plumes in CA (API MTBE MNA Study)



Majority of plumes are anaerobic (M+SD)

- **Partitioning from fuel and MTBE transformation are potential sources of TBA**
 - Trace concentrations of TBA in gasoline can produce high TBA concentrations in water
- **Biodegradation of MTBE can result in TBA concentrations much higher than MTBE**
- **TBA Plumes typically shorter than MTBE plumes**
- **Ongoing API Studies on TBA**
 - plume study with LLNL – Will evaluate available GEOTRACKER data
 - Stable Isotopic Analyses (carbon and hydrogen)

References



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