TBA – Occurrence and Sources

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Oxygenates Workshop

Costa Mesa

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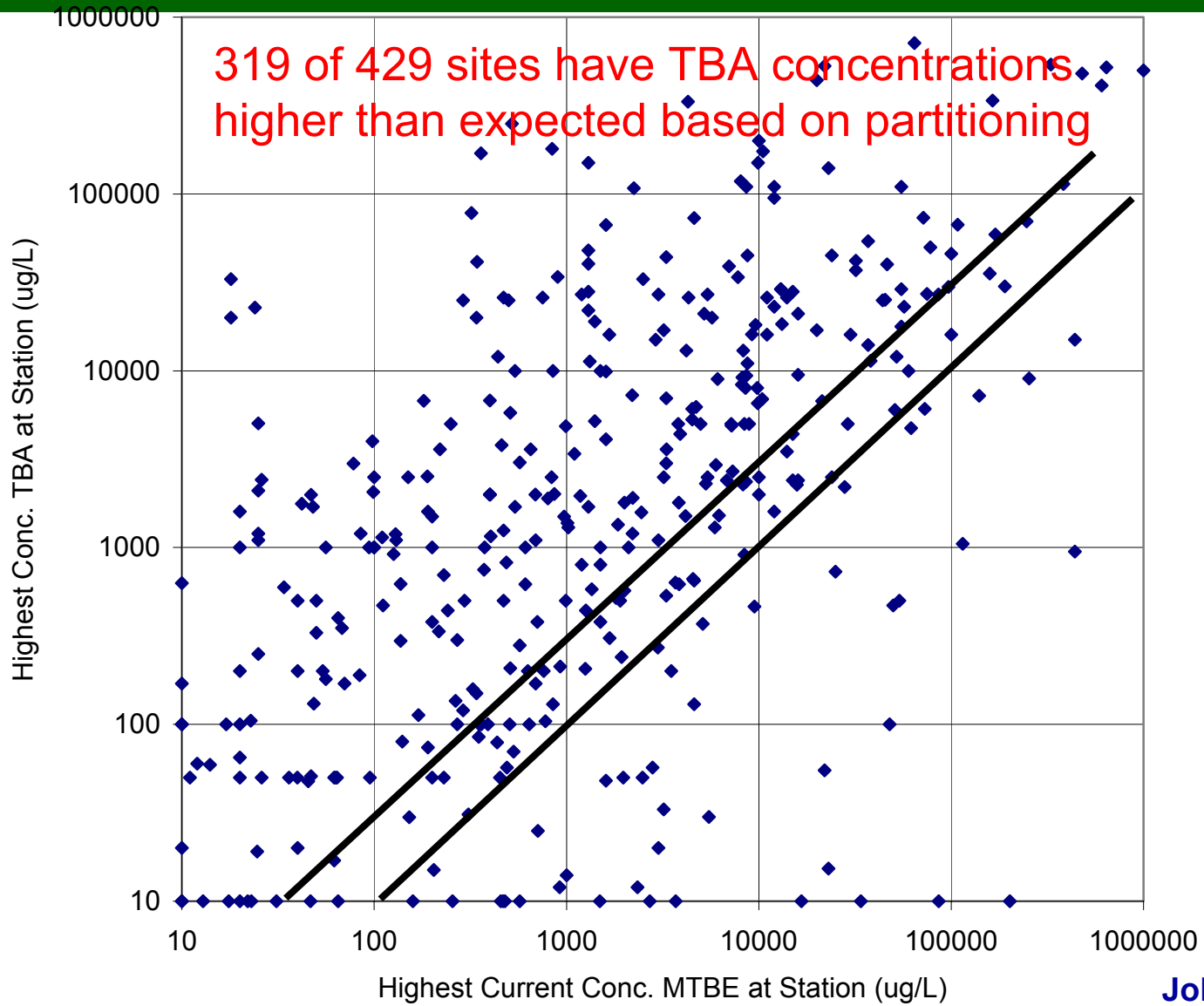
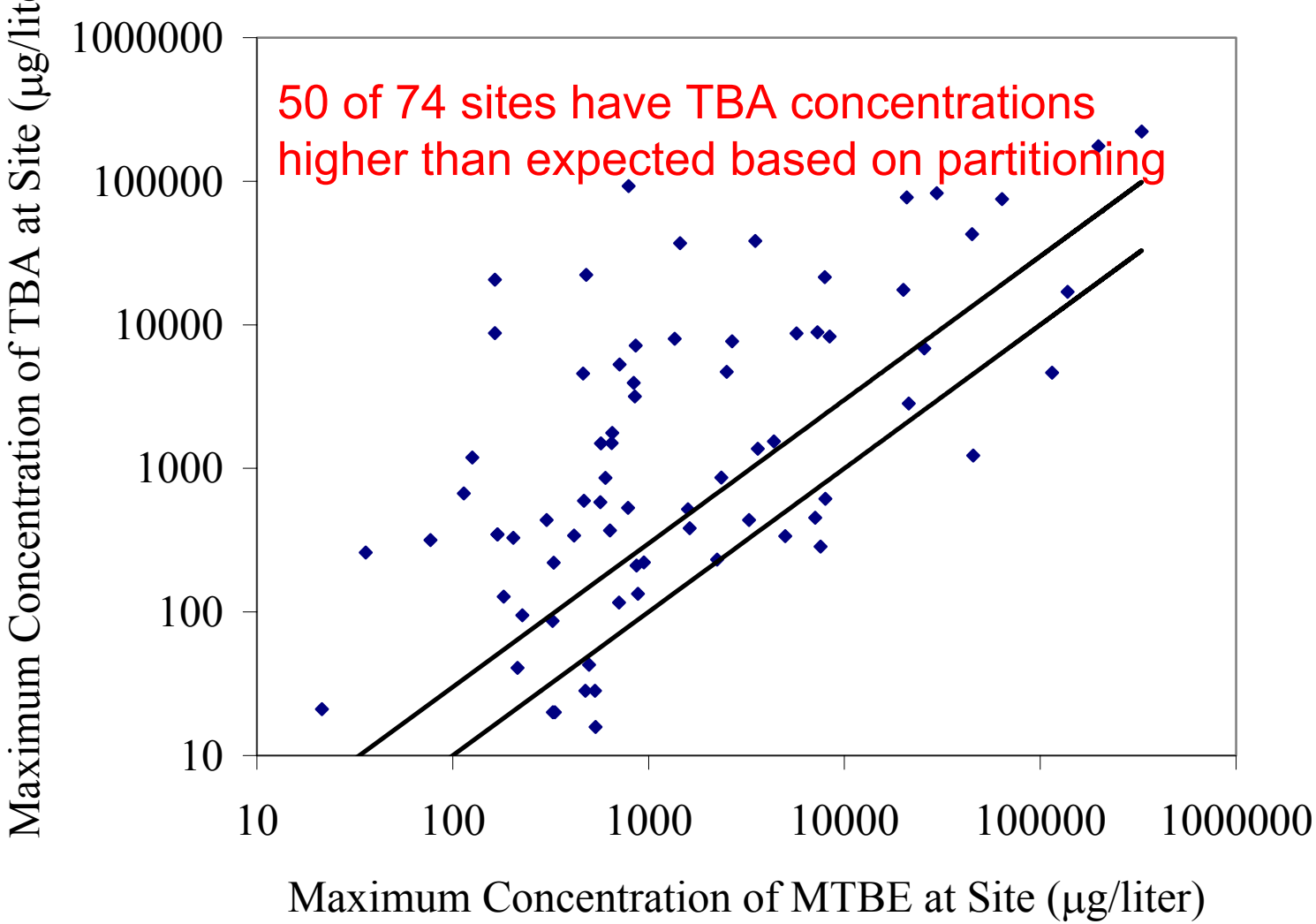
Orange County Sites



John Wilson (2003)[2]

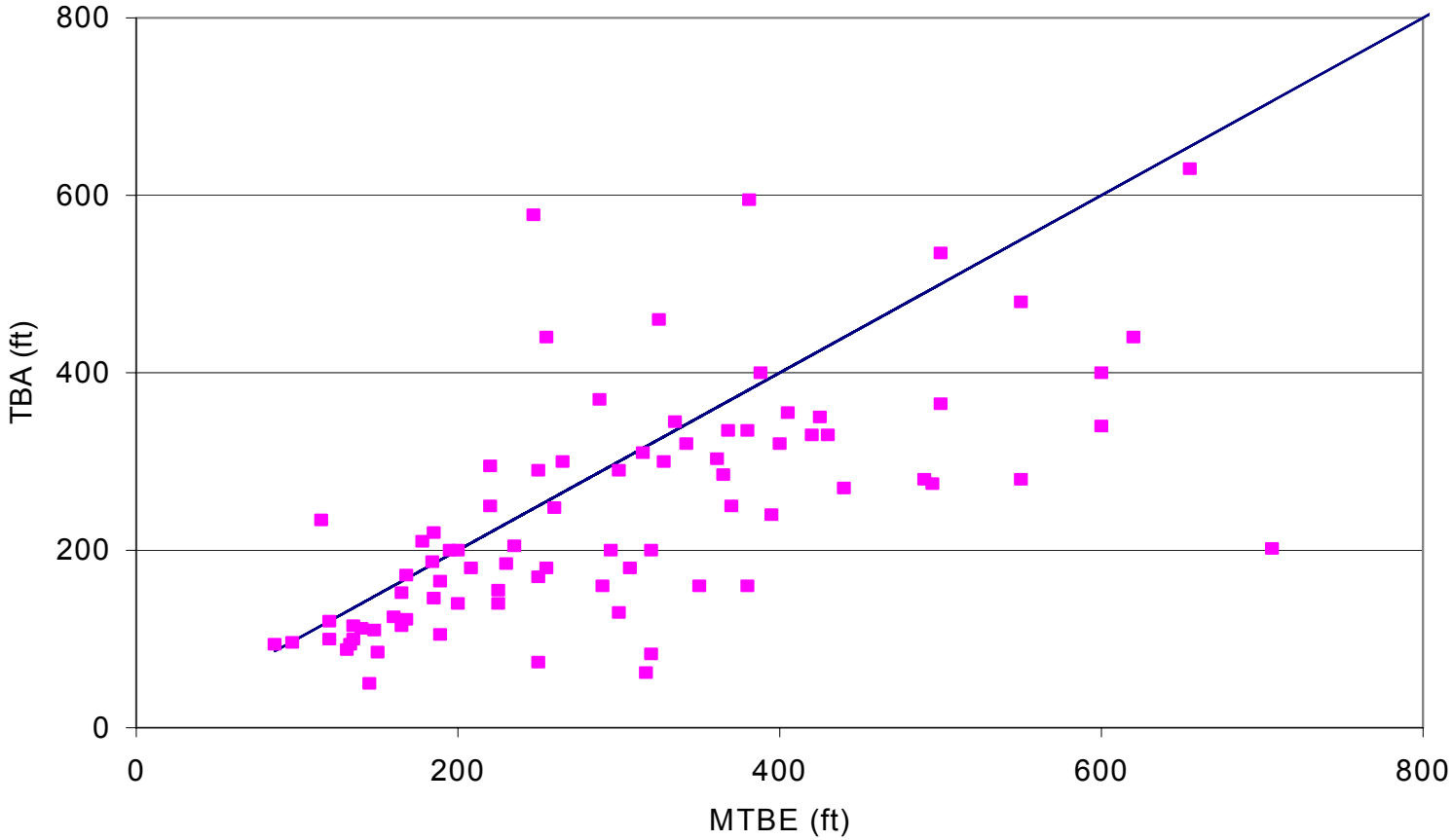
Sites in Eastern United States



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

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

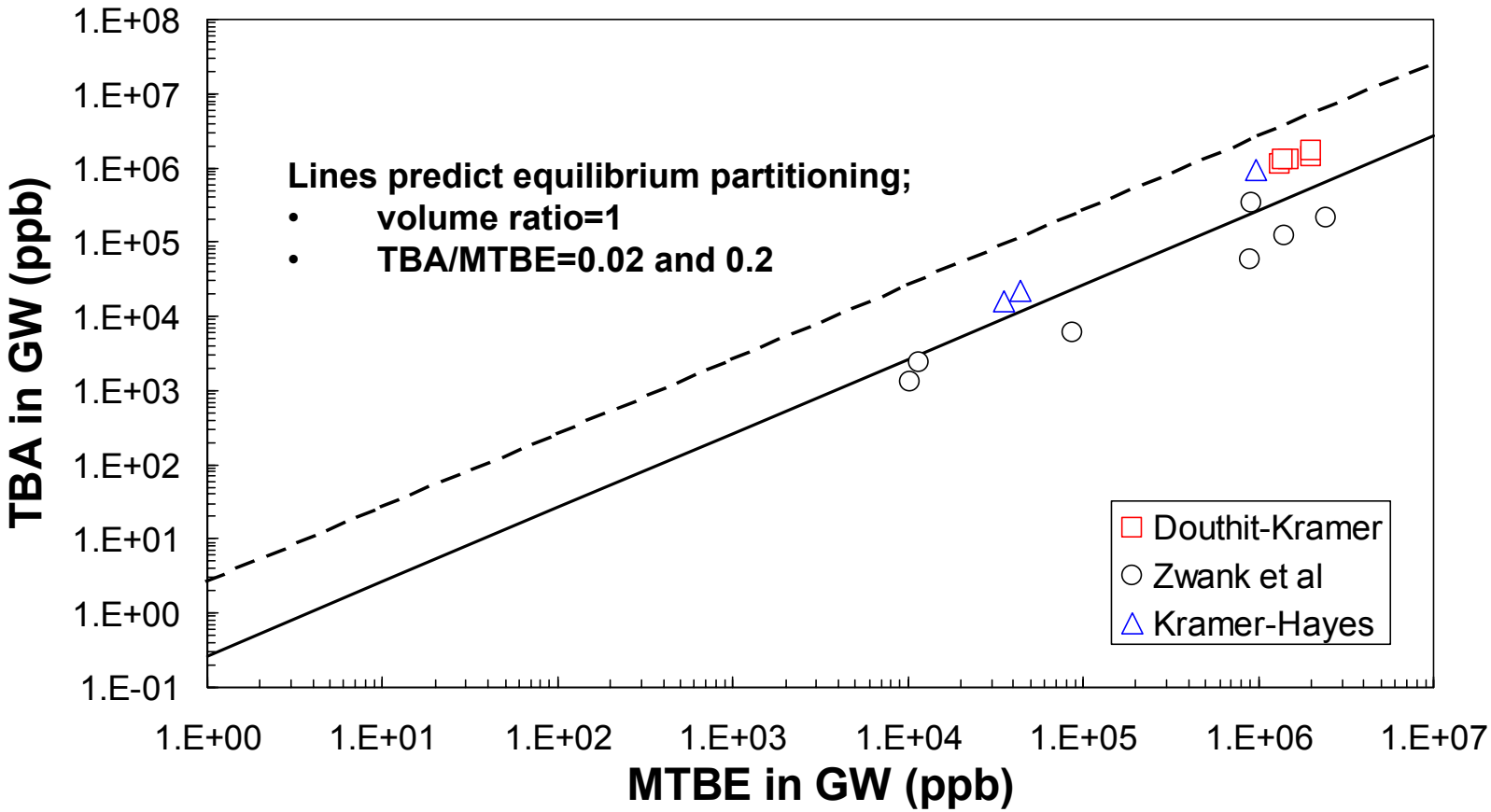
- Where, K_{fw} are fuel-water partitioning coefficients (mg/L in fuel/mg/L in water at equilibrium)
  - K_{fw}^{MTBE} = 15.5 (Cline et al., 1991)
  - K_{fw}^{TBA} = 0.24, average of 0.15 and 0.33 (Zwank et al., 2002)
- Kramer-Douthit, 2000. (volume ratio = 4)
- Zwank et al., 2002. (volume ratio = 1)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

Analysis of Partitioning Studies

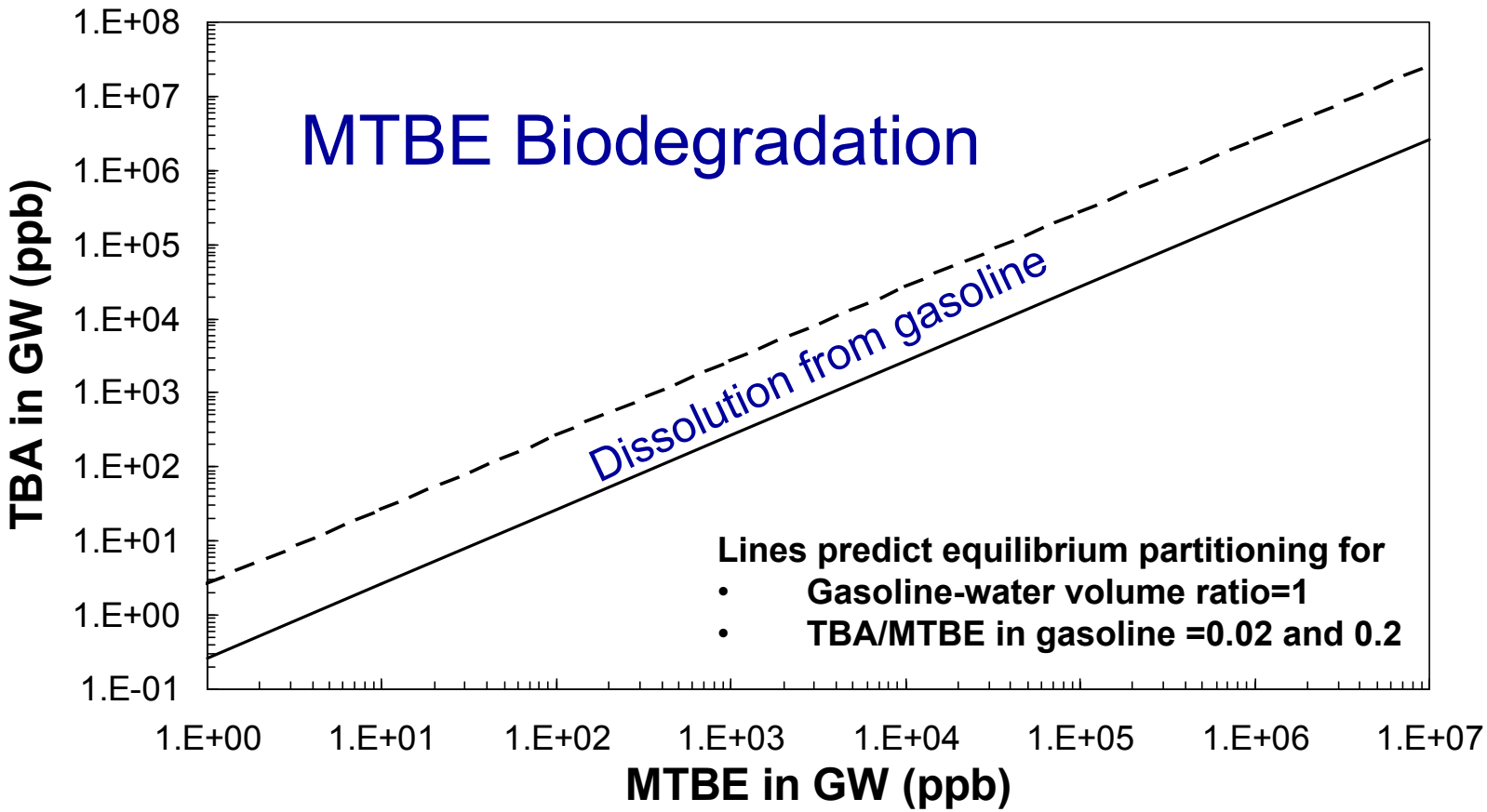
Measured MTBE (aq) (ppb)	Measured TBA (aq) (ppb)	Estimated TBA/MTBE in original gasoline %w/w	%v/v	Estimated %v/v in gasoline MTBE	TBA
Kramer-Douthit Data (2000 expts)					
1330000	1120000	**18.3%**	**17.2%**	3.5%	0.6%
1990000	1430000	**15.6%**	**14.7%**	5.2%	0.8%
1480000	1270000	**18.7%**	**17.5%**	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 (persoanl 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

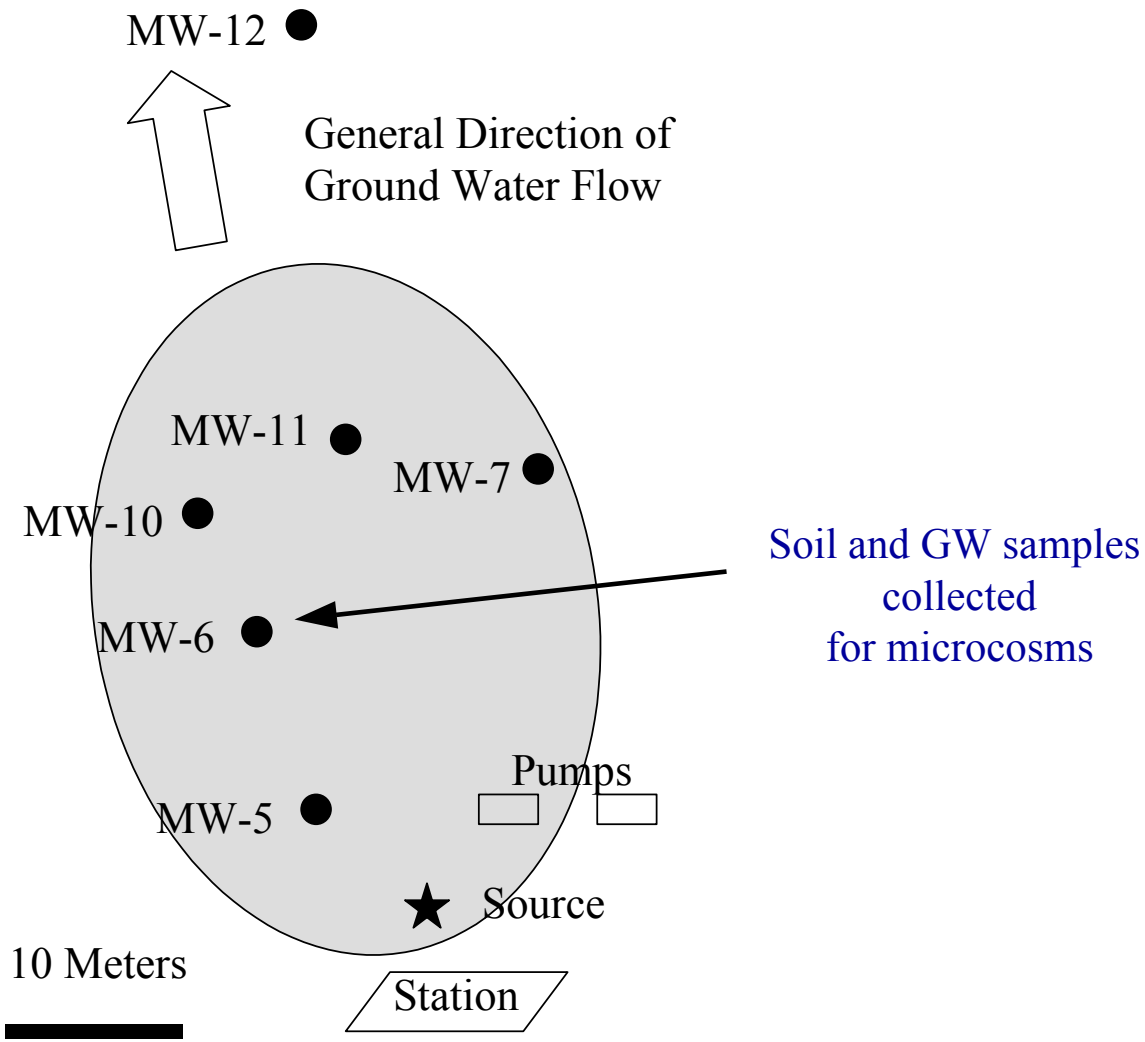
TBA from Dissolution of Gasoline



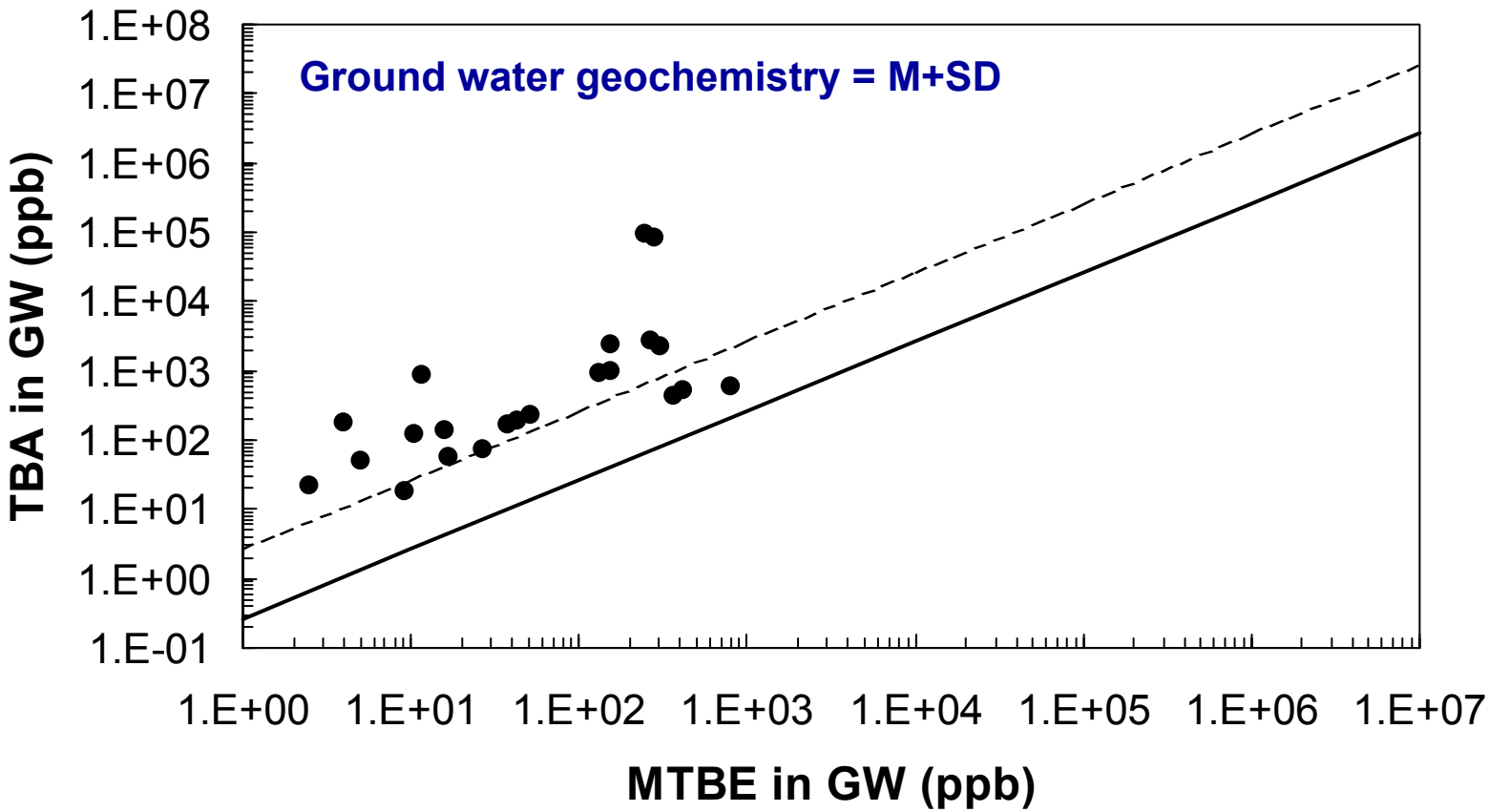
Screening Tool to Evaluate Importance of MTBE Biodegradation



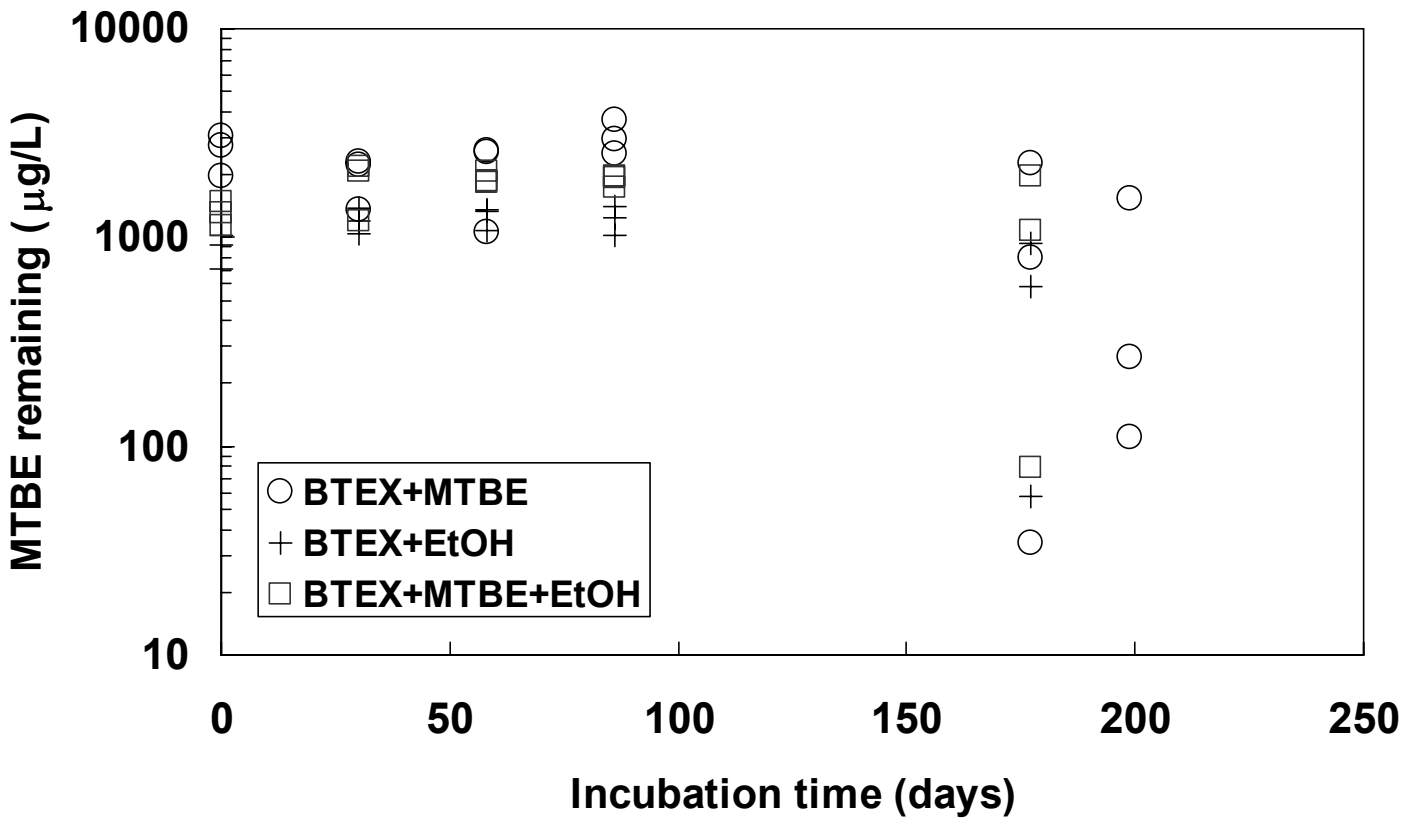
Anaerobic Biodegradation of MTBE – Site in NJ



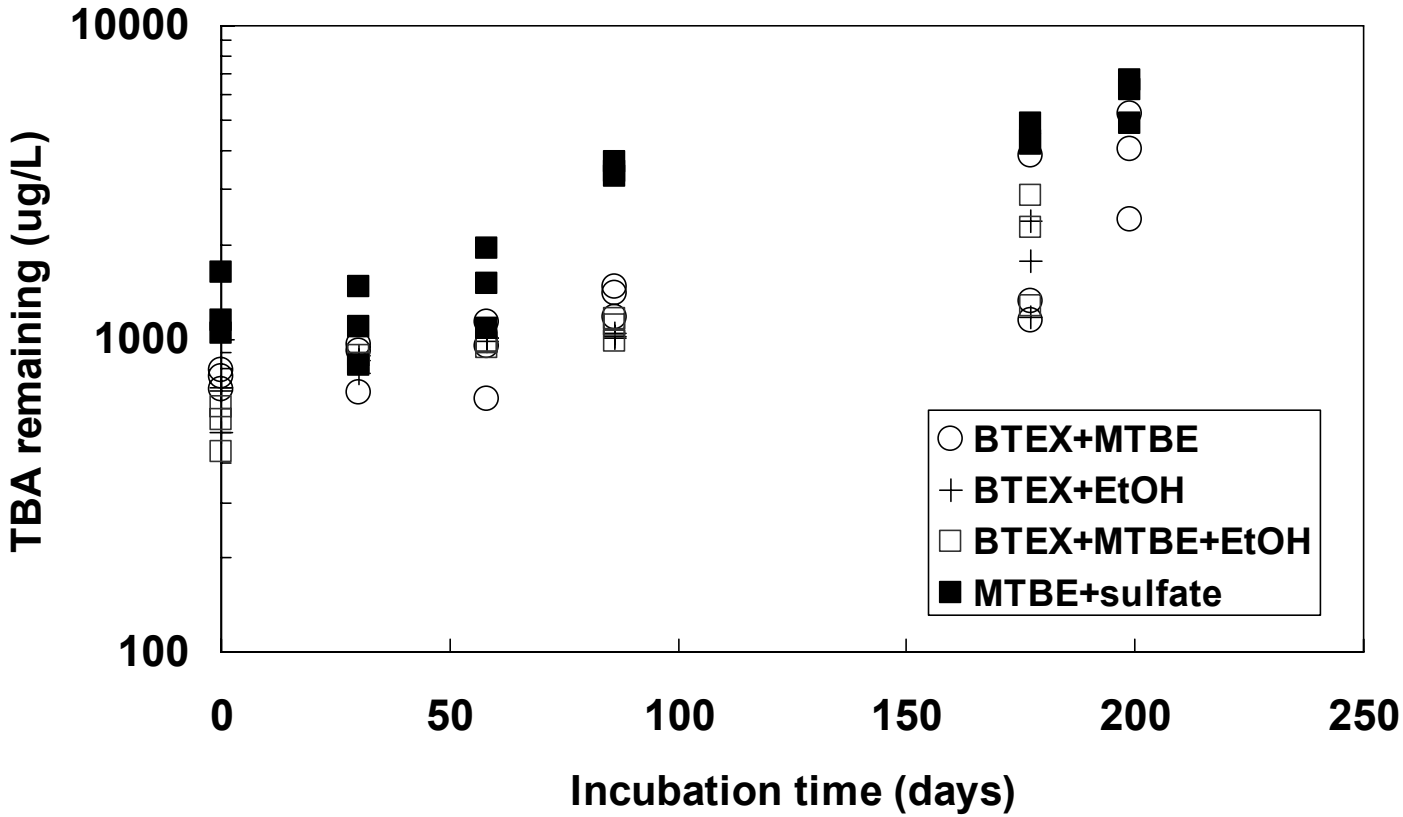
TBA in GW at NJ Site
BP-EPA Study



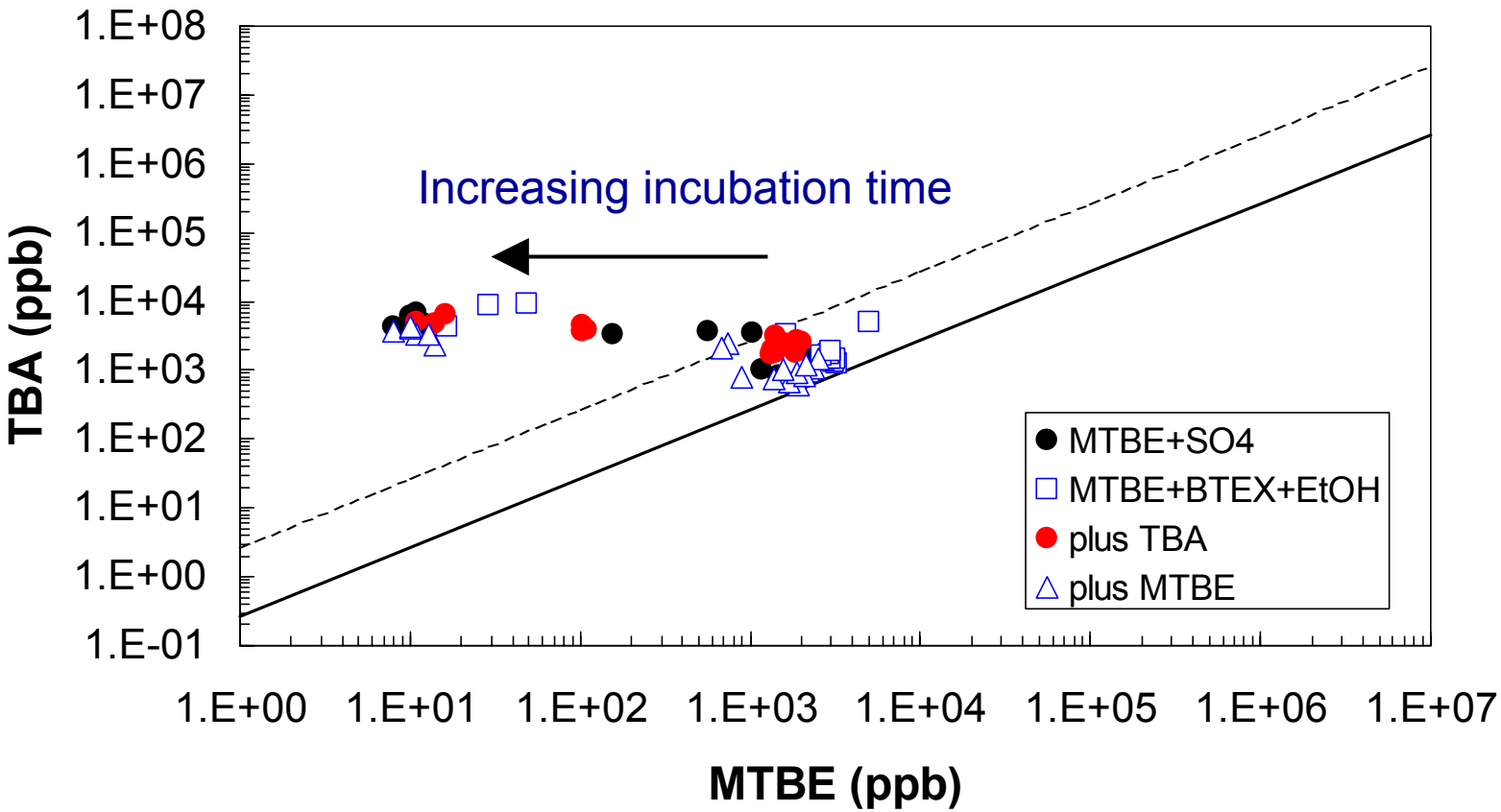
Anaerobic MTBE Biodegradation in Laboratory



Corresponding TBA Accumulation



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



Stable Carbon Isotopic Ratios (SCIR) of MTBE

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

Basis

–Micro-organisms preferentially use ^{12}C isotope over ^{13}C

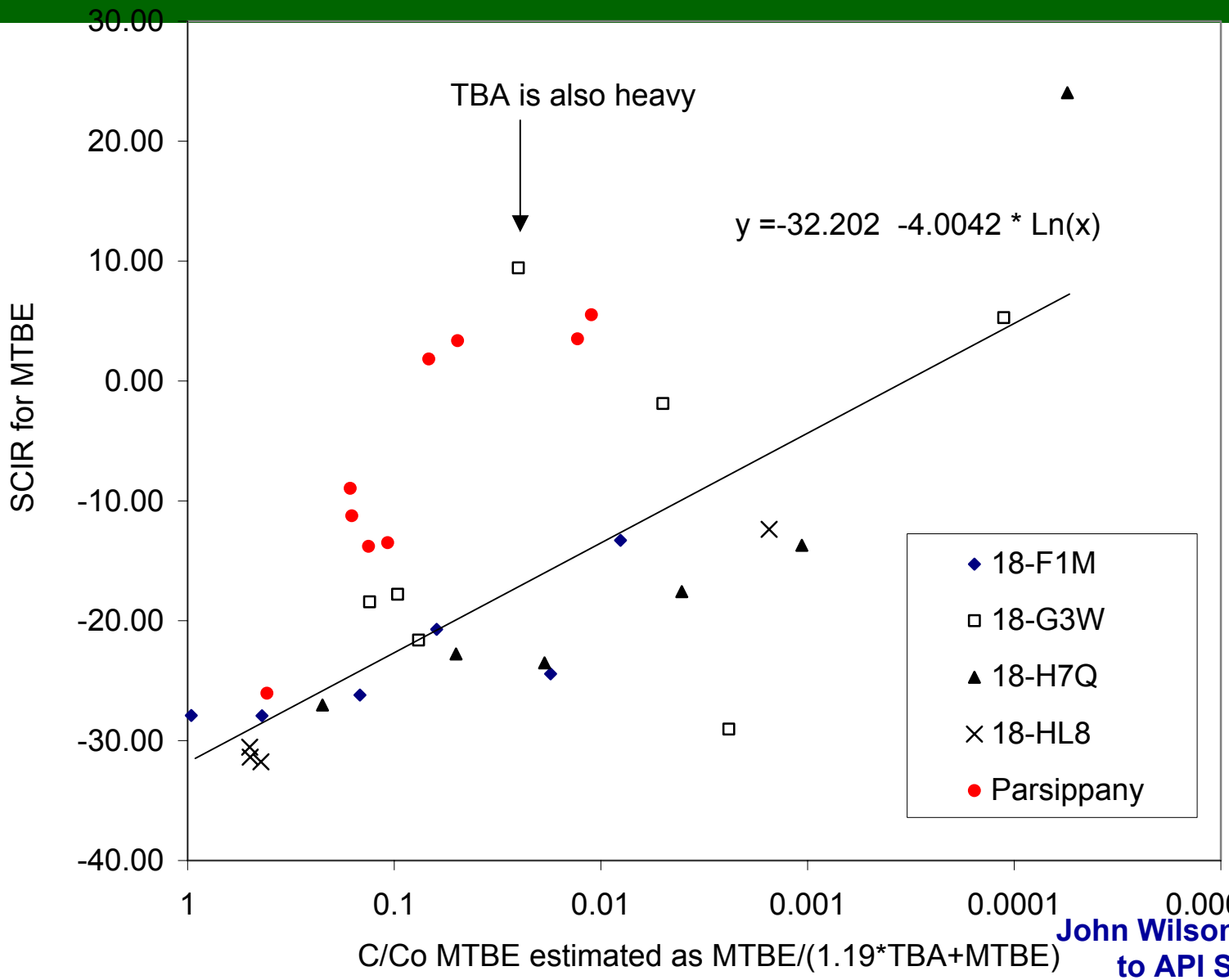
–Abiotic processes such as dilution or volatilization do not cause significant isotopic fractionation of MTBE

Expectation

–MTBE will get enriched in ^{13}C during biodegradation

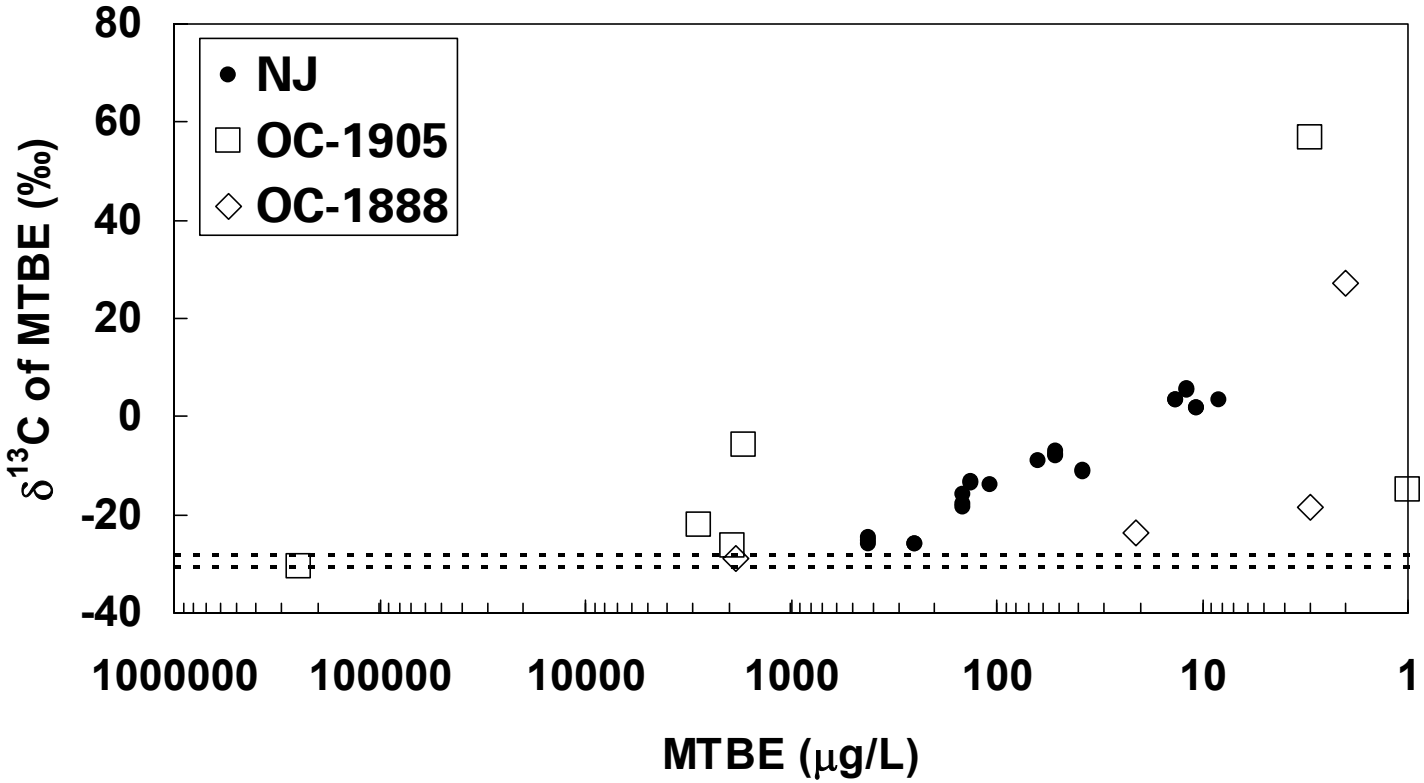
–SCIR of MTBE will increase with distance along a flow-path if MTBE is being naturally biodegraded

TBA from MTBE Biodegradation



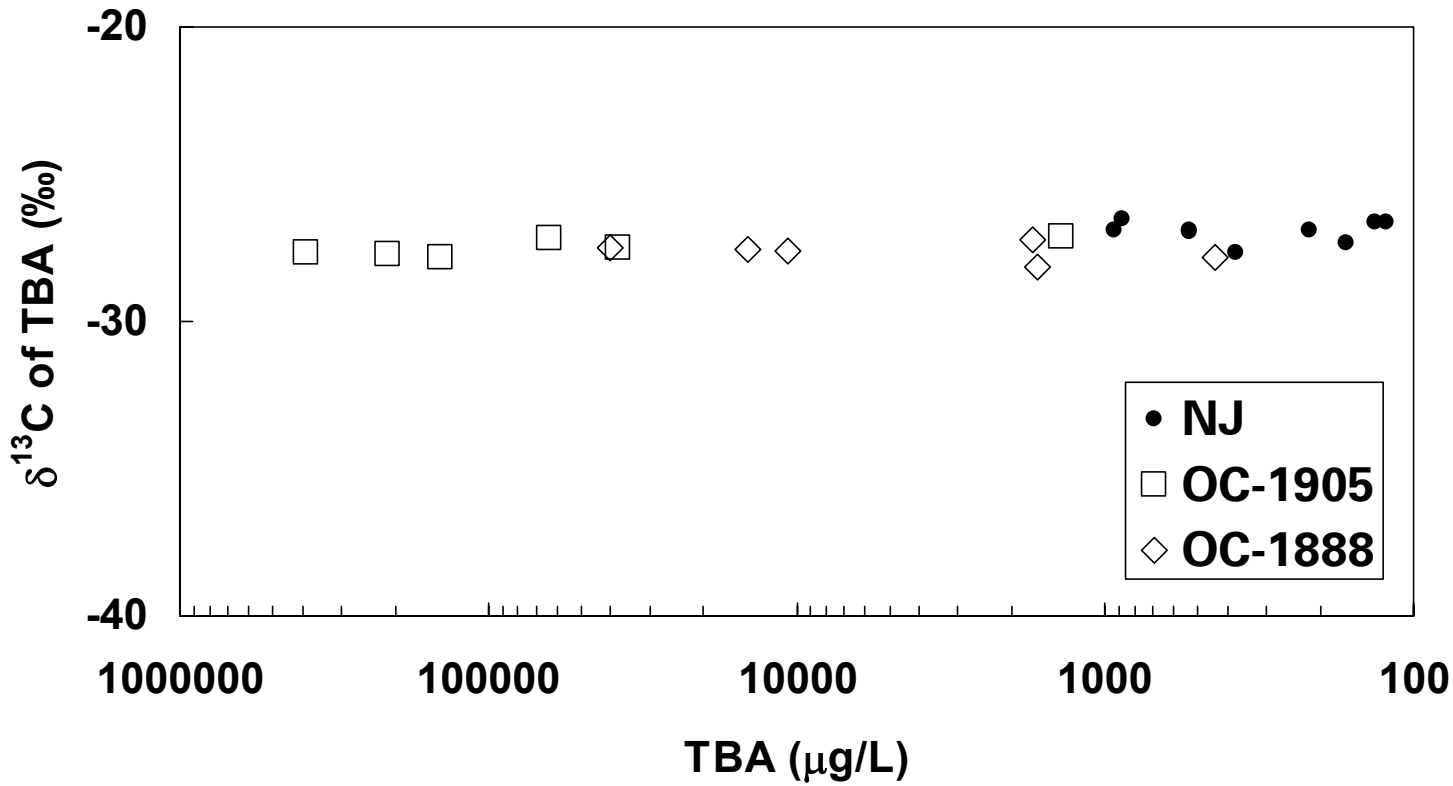
John Wilson's presentation to API SGTTF (2/03)

MTBE SCIR Data – Orange County Sites



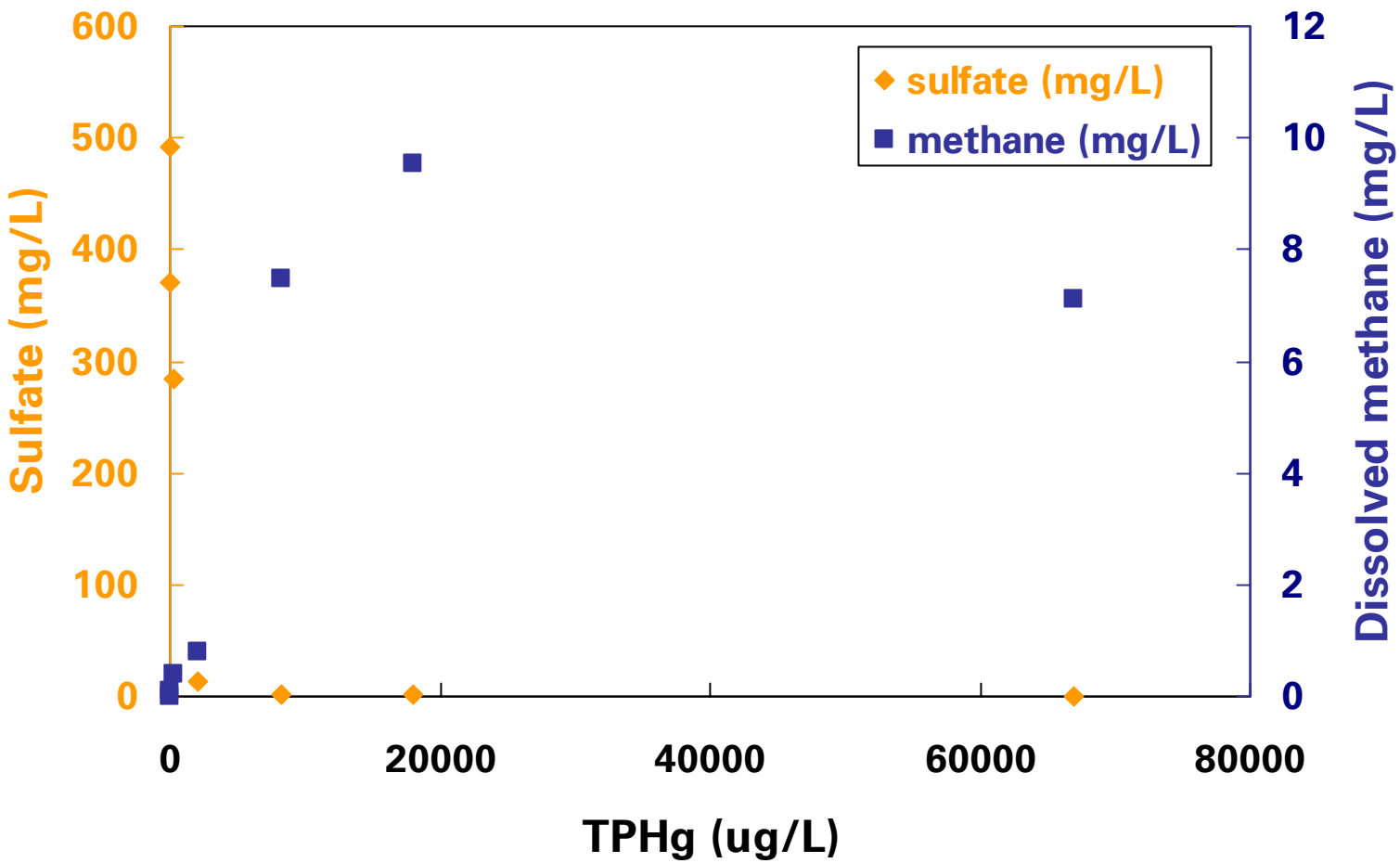
SCIR data indicate MTBE Biodegradation to TBA

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

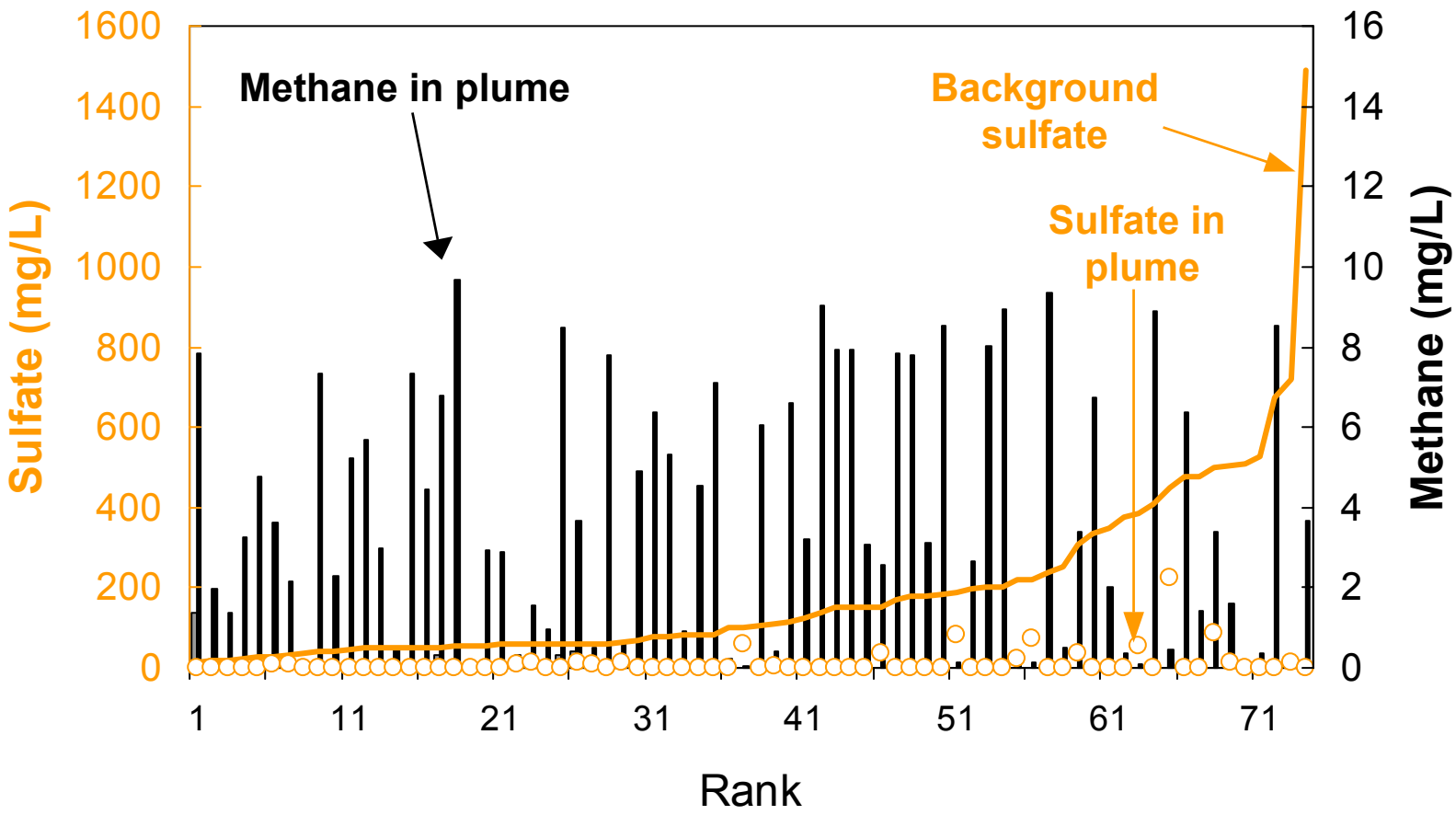
⇒ **Readily biodegradable (in-situ oxygen enhancements)**

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)

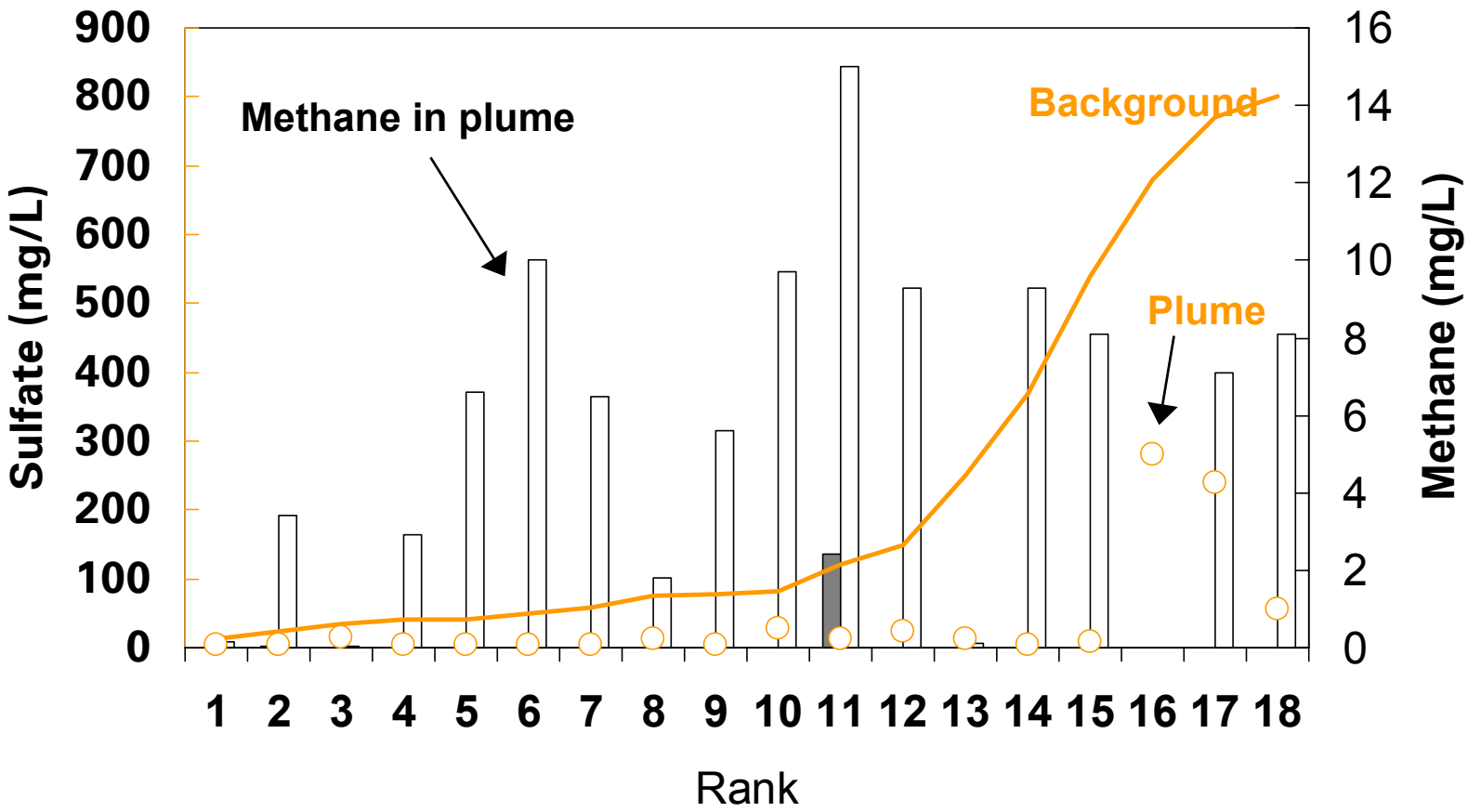
⇒ **More persistent under more reduced conditions**

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)

TBA – Occurrence and Sources

- **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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5. Zwank, L., Schmidt, T. C., Handerlein, 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.*
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