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Enhanced Bioremediation Using Sulfate and/or Nitrate

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Environmental Technology

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Overview

- Why add sulfate (and/or nitrate)?
- **What kinds of contaminants can be addressed?**
- Why bother if anaerobic rates are slower than aerobic rates?
- What about Hydrogen Sulfide?
- Application Guidance

Hydrocarbon Biodegradation

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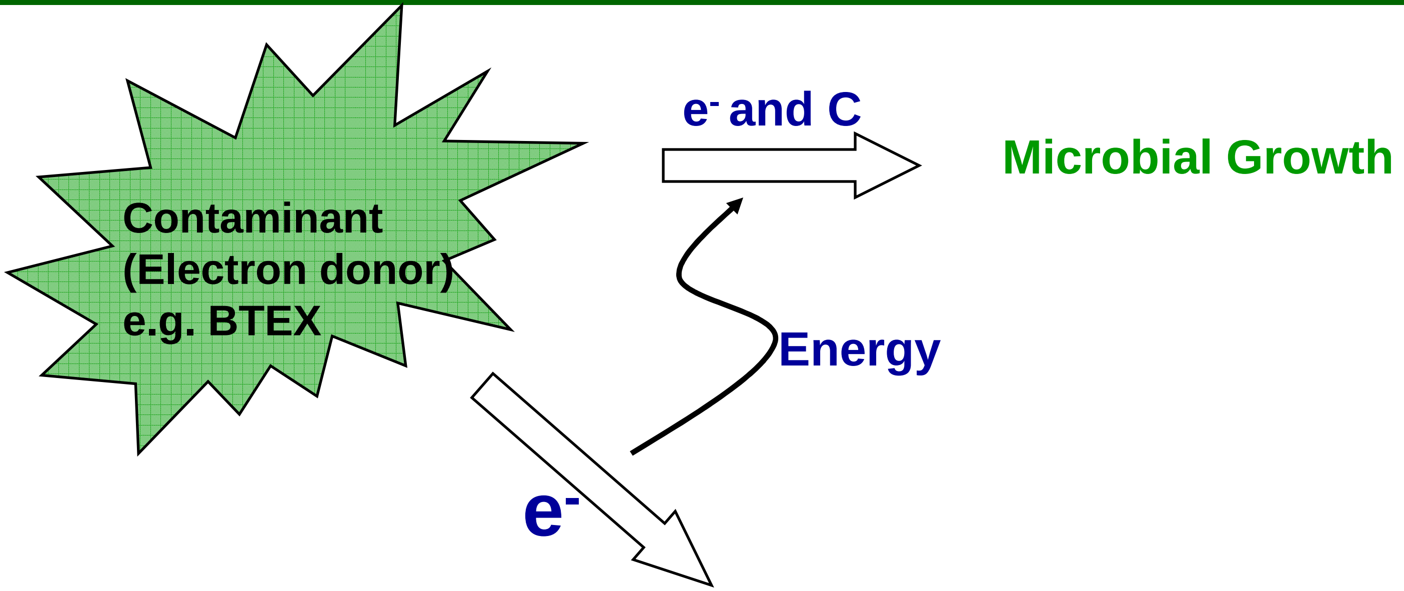


Contaminant (Electron donor) e.g. BTEX

e^- and C

Microbial Growth

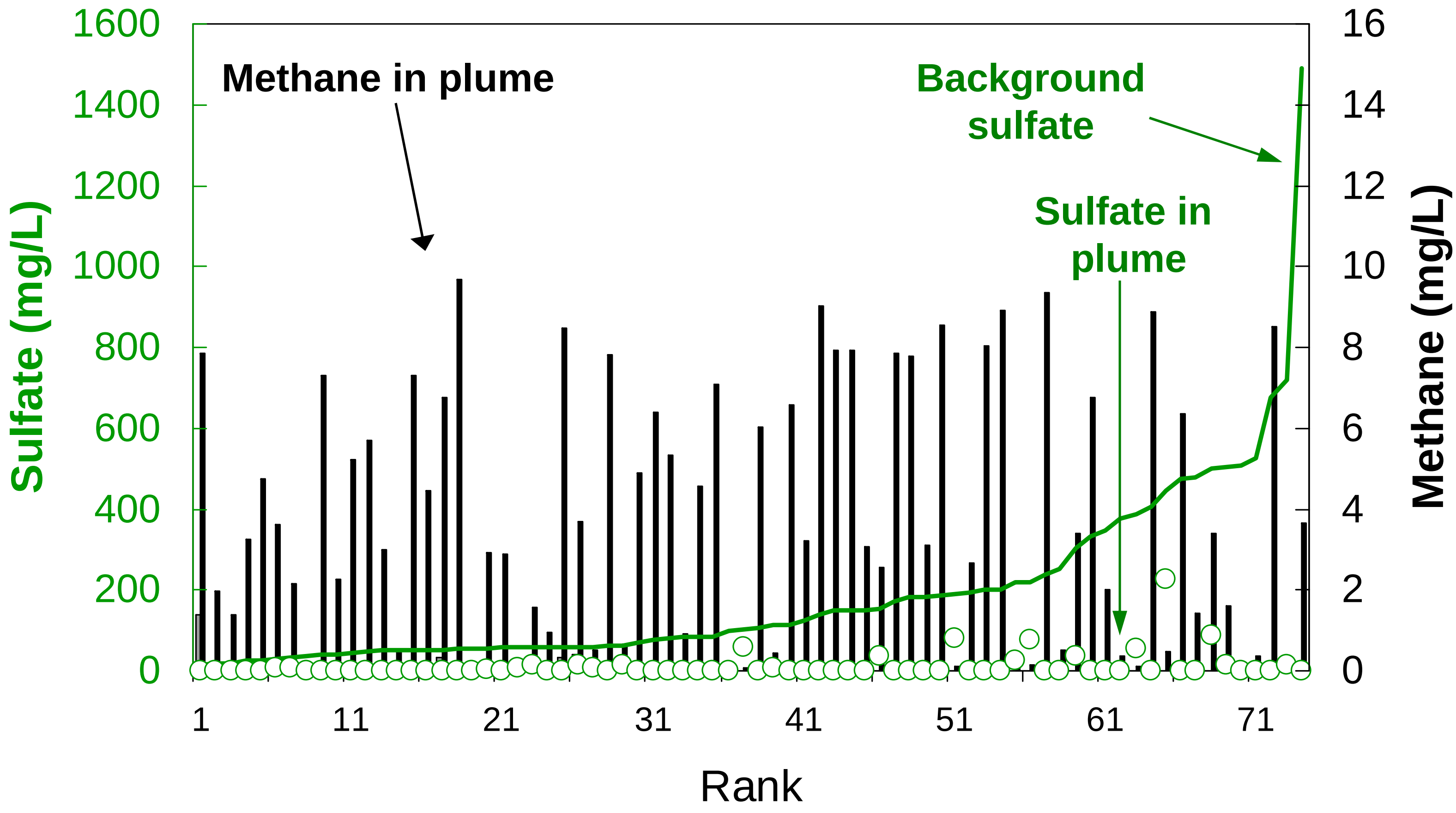
Energy

e^-

	Electron Acceptors		**Products**
1.	Oxygen	>>>	Water, CO_2
2.	Nitrate	>>>	Nitrogen, CO_2
3.	Fe(III)	>>>	Fe(II), CO_2
4.	Mn(IV)	>>>	Mn(II), CO_2
5.	Sulfate	>>>	Sulfide, CO_2
6.	None (fermentation)	>>>	Methane, CO_2

Energy Yield	Kinetics in lab experiments
High	Fast
Low	Slow

Sulfate in Ground Water at Retail Sites(BP-EPA Study)

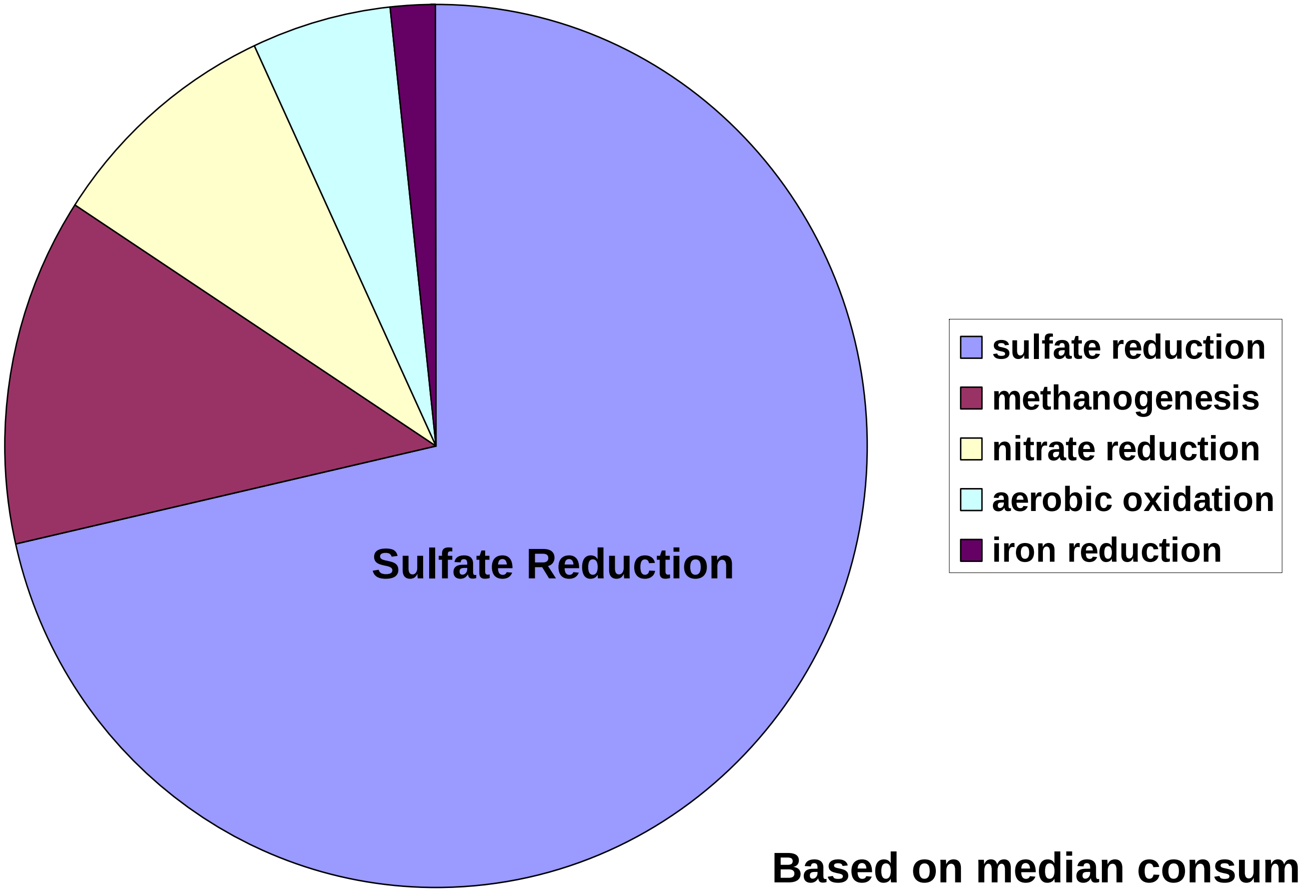


Sulfate is absent in most of the plumes

Why Sulfate?

Electron Acceptor (EA)	Maximum Concentration (mg/L)	Mass of benzene degraded per unit mass of EA	Potential Benzene Degraded (mg/L)	Issues
Oxygen (in air)	9 - 10	0.33	3.0 – 3.3	•Limited solubility •Numerous oxygen sinks •Potential aquifer clogging •Biofouling near injection point
Pure Oxygen	60 - 70	0.33	19.8 – 23.1	
Sulfate	100 – 250*	0.22	22.0 – 55.0	•Hydrogen sulfide; never documented as an issue in the field •Secondary MCL for sulfate – 250 mg/L*
Nitrate	80 - 100	0.21	16.8 – 21.0	•DW concern •Primary MCL – 10 mg/L NO_3-N (45 mg/L NO_3)
Iron (III)	0 - 1	0.024	0 – 0.024	•Very low solubility •Aquifer clogging

Sulfate Does the Heavy Lifting!



Based on median consumptions of electron acceptors at 74 sites

BP-EPA study

Gasoline Release Sites

Field Data - Conclusions

- Most hydrocarbon plumes are anaerobic and depleted of sulfate
- Sulfate reduction is important in ground water

⇒ Adding sulfate to ground water will likely stimulate BTEX degradation

- ➢ **No solubility constraints (unlike oxygen)**
- ➢ **No chemical sinks (unlike oxygen)**
- ➢ **Can address "non-target" electron acceptor demand enabling contaminants of concern (e.g. benzene) to "see" oxygen**

Is Anaerobic Biodegradation Slower?

- **Laboratory Experiments**
  - Electron acceptor supply (DO, nitrate,..) >> Electron Donor (BTEX) demand
  - Rate dictated by biodegradation

    A > NR > IR > SR > M (rates follow same order)

- **Natural Field Setting**
  - Electron donor demand (BTEX) >> Electron acceptor supply (DO, nitrate,..)
  - Rate dictated by transport of electron acceptors

    A ~ NR ~ IR ~ SR (rates are similar)

    M (rate dictated by biodegradation)

No, rates are comparable in the field

Data from Push-pull Tests

Environment	Method	First order rate constant (day^{-1})	Reference
Sulfate Reduction			
Petroleum Impacted Aquifer (PIA)	Flow path	0.02 to 0.08	Chappelle, 1996
PIA	Augmented flow path	0.1	Cunningham et al. 2000
Petroleum and CHC impacted aquifer	Push-pull tests	4.32 to 6.48	McGuire et al., 2002
Nitrate Reduction			
PIA	Push-pull tests	5.28	Schroth et al., 1998
PIA	Augmented flow path	0.1 to 0.6	Cunningham et al. 2000
Petroleum and CHC impacted aquifer	Push-pull tests	5.04 to 7.44	McGuire et al., 2002

McGuire et al., Enviro. Sci. Technol., 36, 2693-2700, 2002

Normal Alkanes

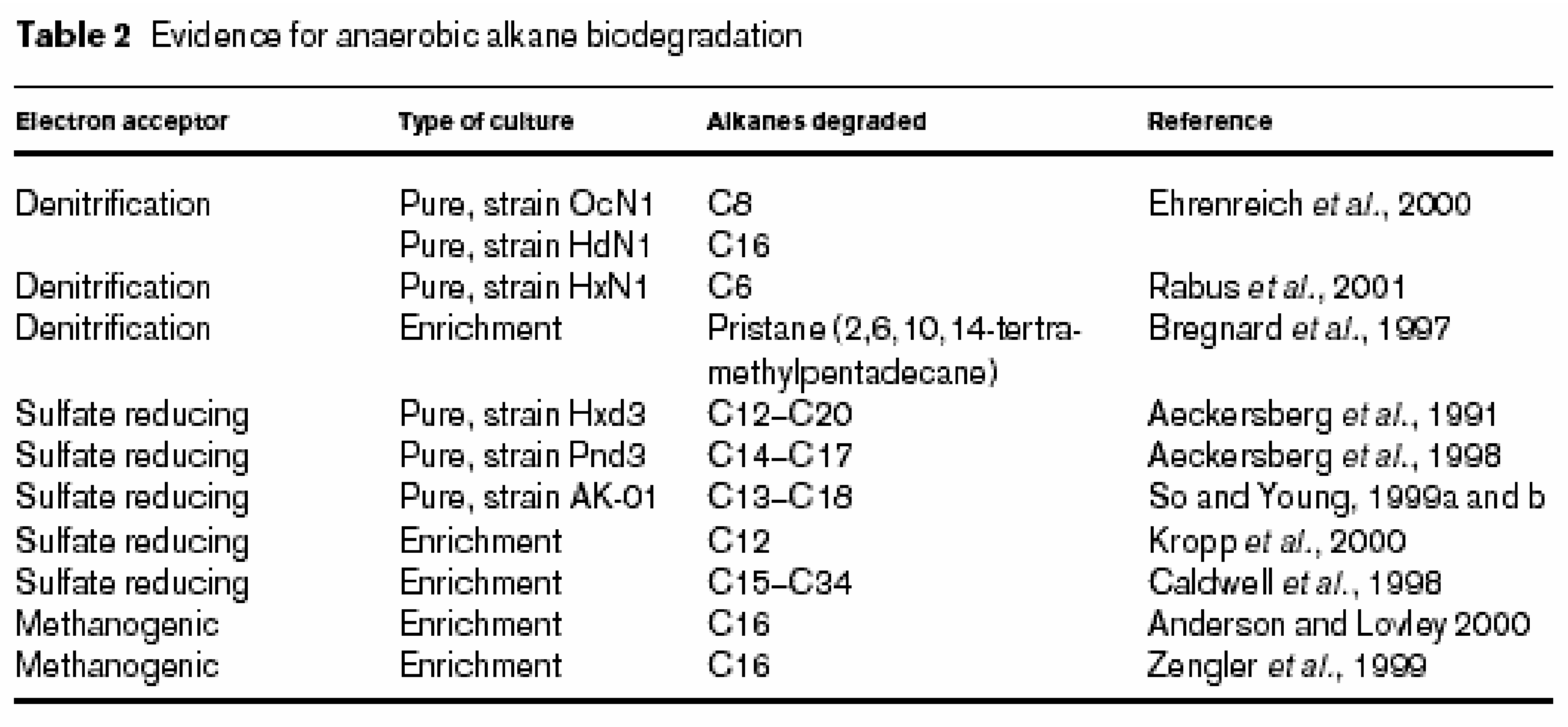


Table 2 Evidence for anaerobic alkane biodegradation

Electron acceptor	**Type of culture**	**Alkanes degraded**	**Reference**
Denitrification	Pure, strain OcN1	C8	Ehrenreich *et al.*, 2000
	Pure, strain HdN1	C16	
Denitrification	Pure, strain HxN1	C6	Rabus *et al.*, 2001
Denitrification	Enrichment	Pristane (2,6,10,14-tertra-methylpentadecane)	Bregnard *et al.*, 1997
Sulfate reducing	Pure, strain Hxd3	C12–C20	Aeckersberg *et al.*, 1991
Sulfate reducing	Pure, strain Pnd3	C14–C17	Aeckersberg *et al.*, 1998
Sulfate reducing	Pure, strain AK-01	C13–C18	So and Young, 1999a and b
Sulfate reducing	Enrichment	C12	Kropp *et al.*, 2000
Sulfate reducing	Enrichment	C15–C34	Caldwell *et al.*, 1998
Methanogenic	Enrichment	C16	Anderson and Lovley 2000
Methanogenic	Enrichment	C16	Zengler *et al.*, 1999

McGuire et al., Enviro. Sci. Technol., 36, 2693-2700, 2002?????

Normal Alkanes

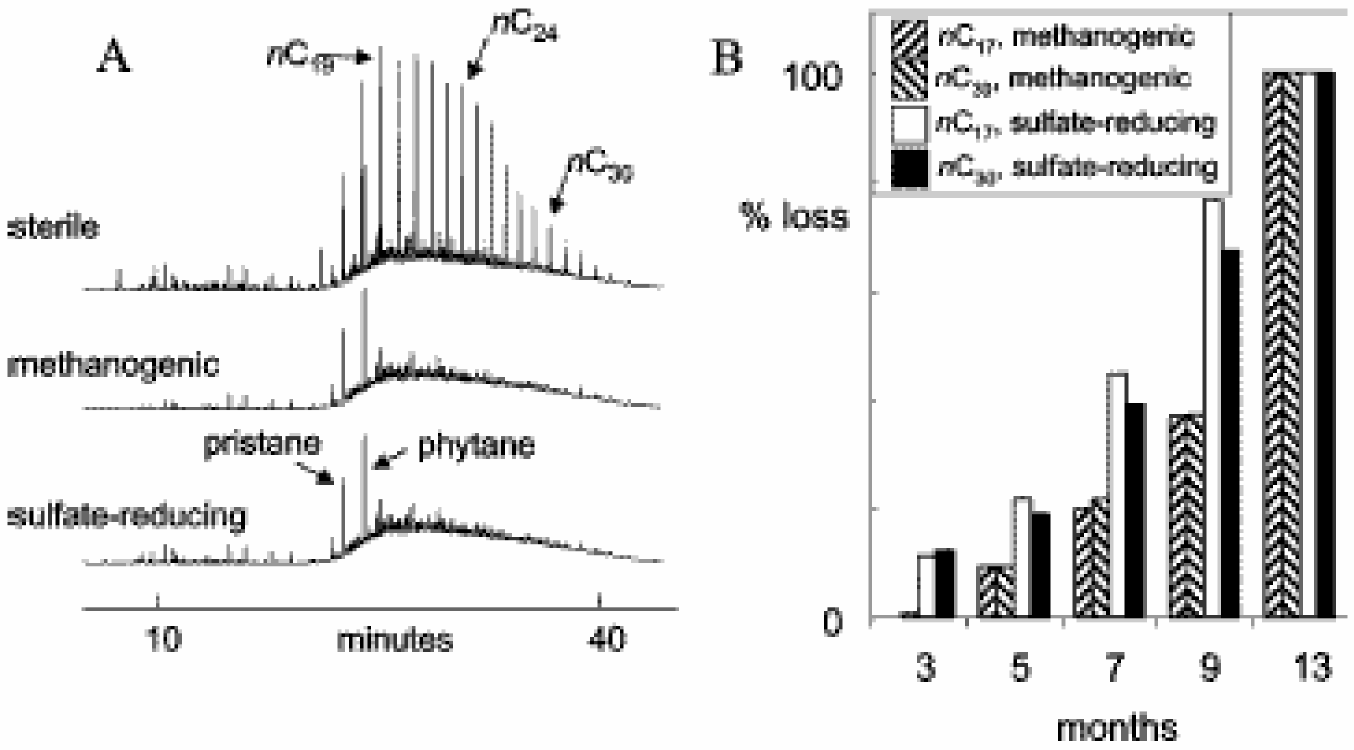


FIGURE 3. *n*-Alkane biodegradation in artificially weathered Alaska North Slope crude oil. (A) Chromatograms of residual oil after 13 months of incubation. (B) Time course of biodegradation of two *n*-alkanes. The incubations initially contained 3.62 mg of heptadecane and 1.13 mg of triacontane.

Townsend et al., Enviro. Sci. Technol., 37, 5213-5218, 2003

PAH

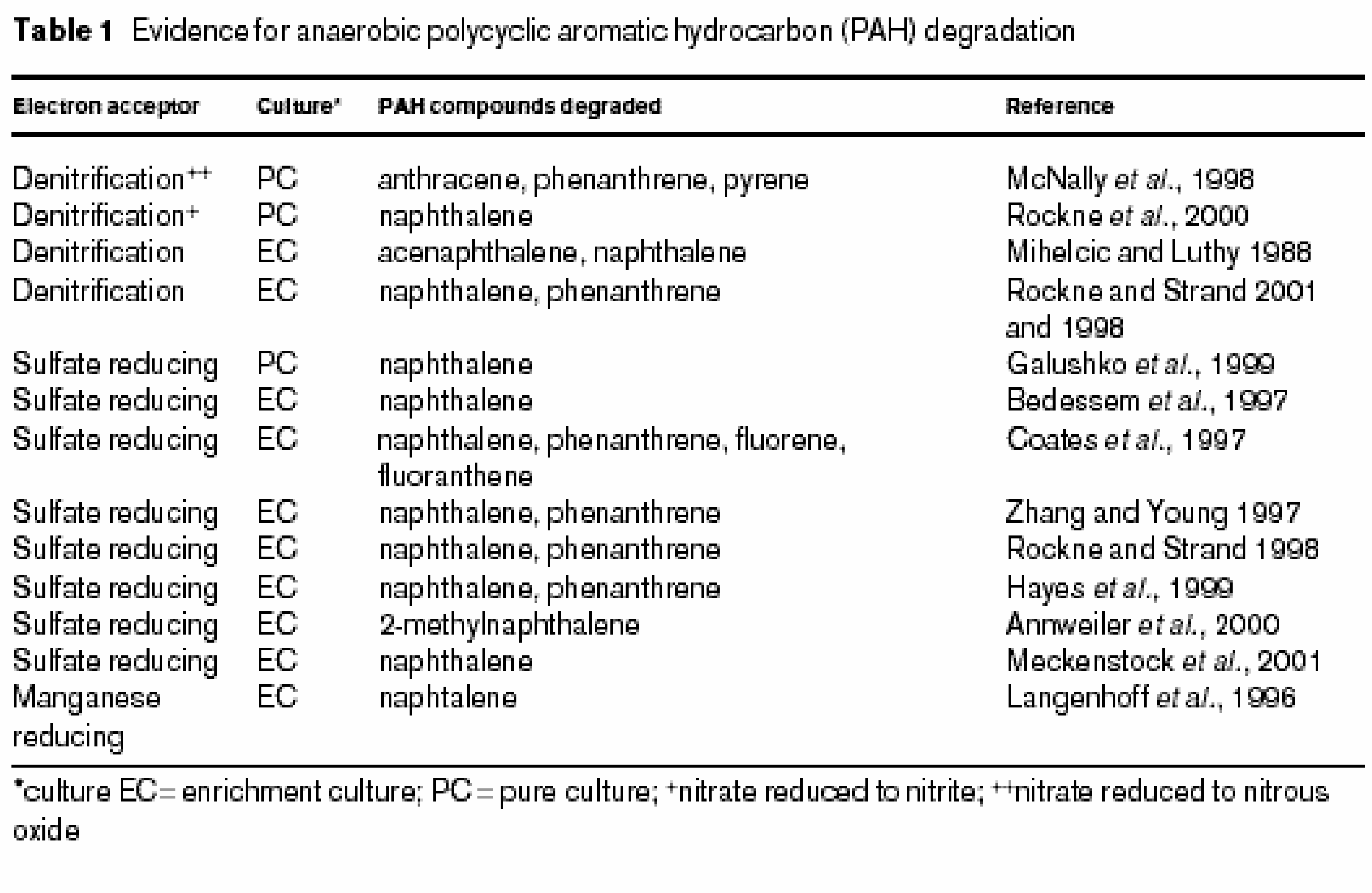


Table 1 Evidence for anaerobic polycyclic aromatic hydrocarbon (PAH) degradation

Electron acceptor	Culture*	PAH compounds degraded	Reference
Denitrification^{++}	PC	anthracene, phenanthrene, pyrene	McNally *et al.*, 1998
Denitrification^{+}	PC	naphthalene	Rockne *et al.*, 2000
Denitrification	EC	acenaphthalene, naphthalene	Mihelcic and Luthy 1988
Denitrification	EC	naphthalene, phenanthrene	Rockne and Strand 2001 and 1998
Sulfate reducing	PC	naphthalene	Galushko *et al.*, 1999
Sulfate reducing	EC	naphthalene	Bedessem *et al.*, 1997
Sulfate reducing	EC	naphthalene, phenanthrene, fluorene, fluoranthene	Coates *et al.*, 1997
Sulfate reducing	EC	naphthalene, phenanthrene	Zhang and Young 1997
Sulfate reducing	EC	naphthalene, phenanthrene	Rockne and Strand 1998
Sulfate reducing	EC	naphthalene, phenanthrene	Hayes *et al.*, 1999
Sulfate reducing	EC	2-methylnaphthalene	Annweiler *et al.*, 2000
Sulfate reducing	EC	naphthalene	Meckenstock *et al.*, 2001
Manganese reducing	EC	naphtalene	Langenhoff *et al.*, 1996

*culture EC = enrichment culture; PC = pure culture; $^{+}$nitrate reduced to nitrite; $^{++}$nitrate reduced to nitrous oxide

PAH

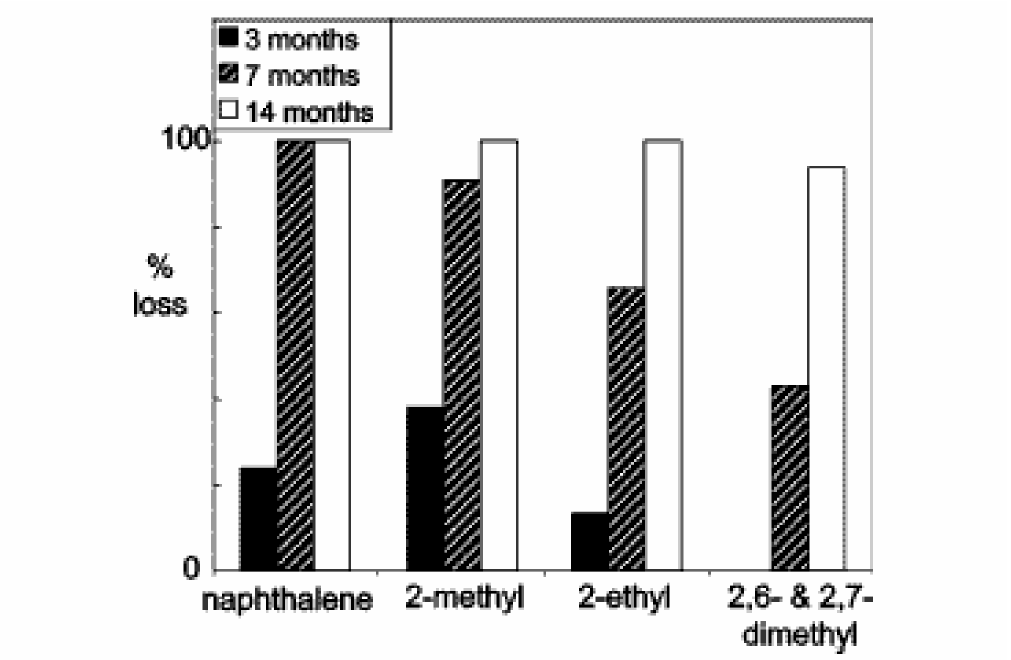


FIGURE 6. Time course of naphthalene homologue biodegradation in Alba crude oil.

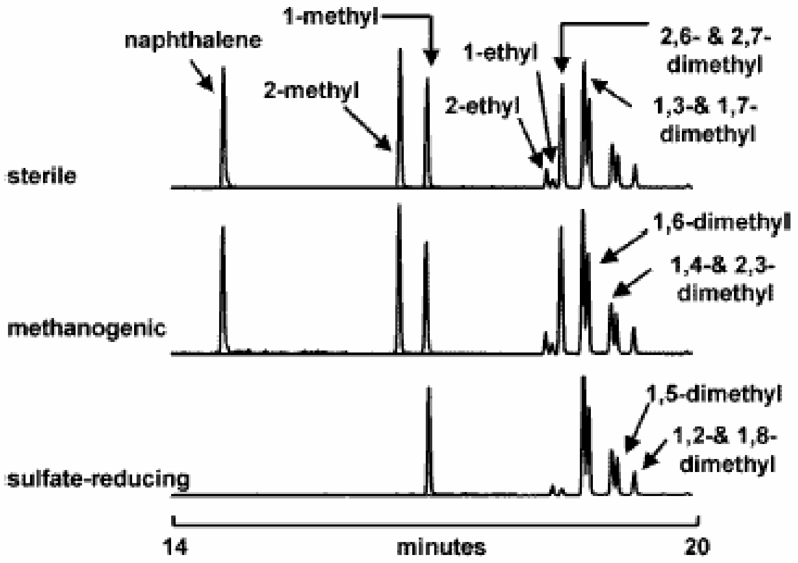


FIGURE 5. Selective biodegradation of naphthalene, 2-methylnaphthalene, 2-ethylnaphthalene, and the coeluting 2,6- and 2,7-dimethylnaphthalenes in Alba crude oil-amended incubations held under sulfate reducing conditions after 14 months. The *m/z* 128, 142, and 156 chromatograms are overlain.

Townsend et al., Enviro. Sci. Technol., 37, 5213-5218, 2003

PAH in Sediments

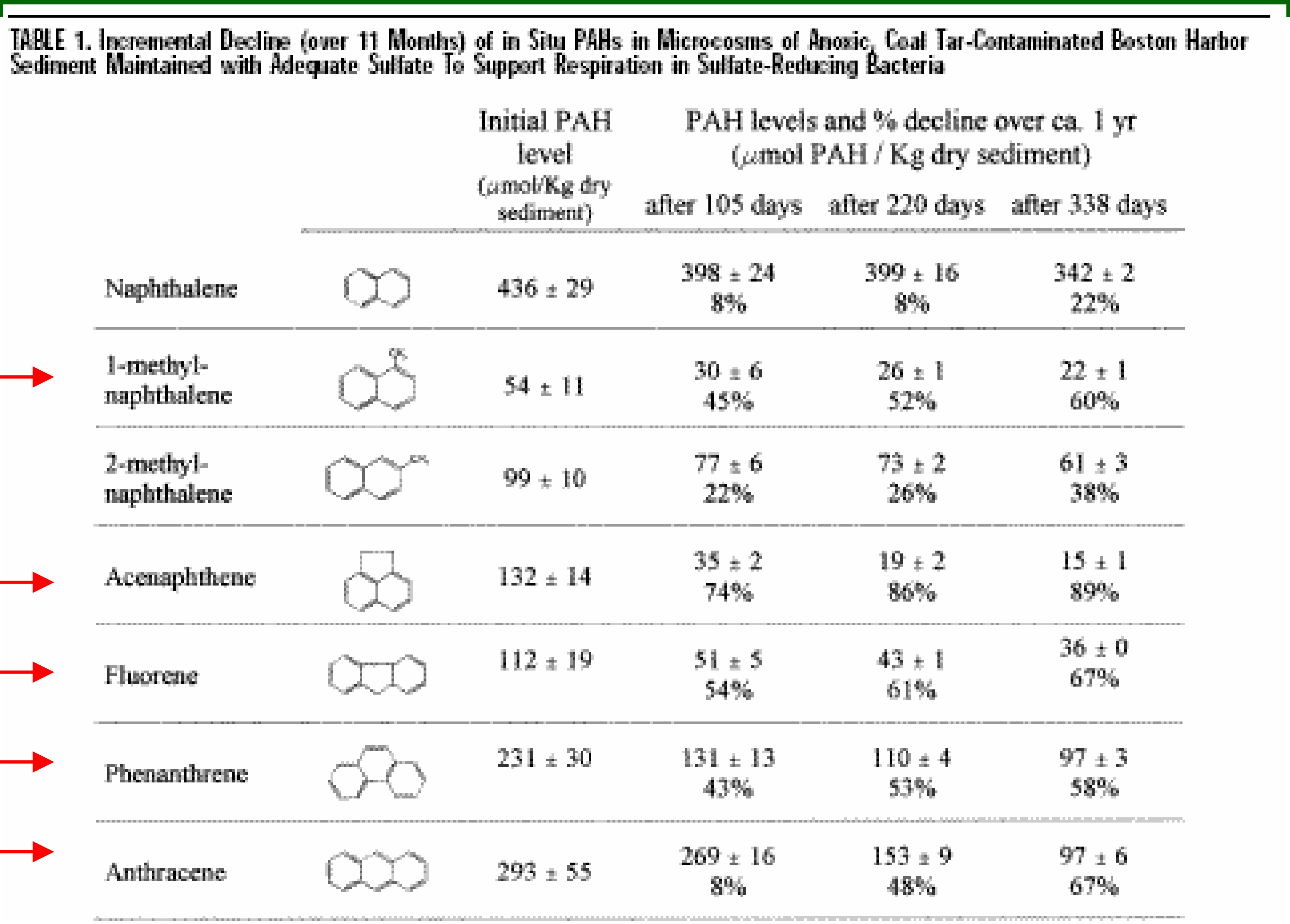


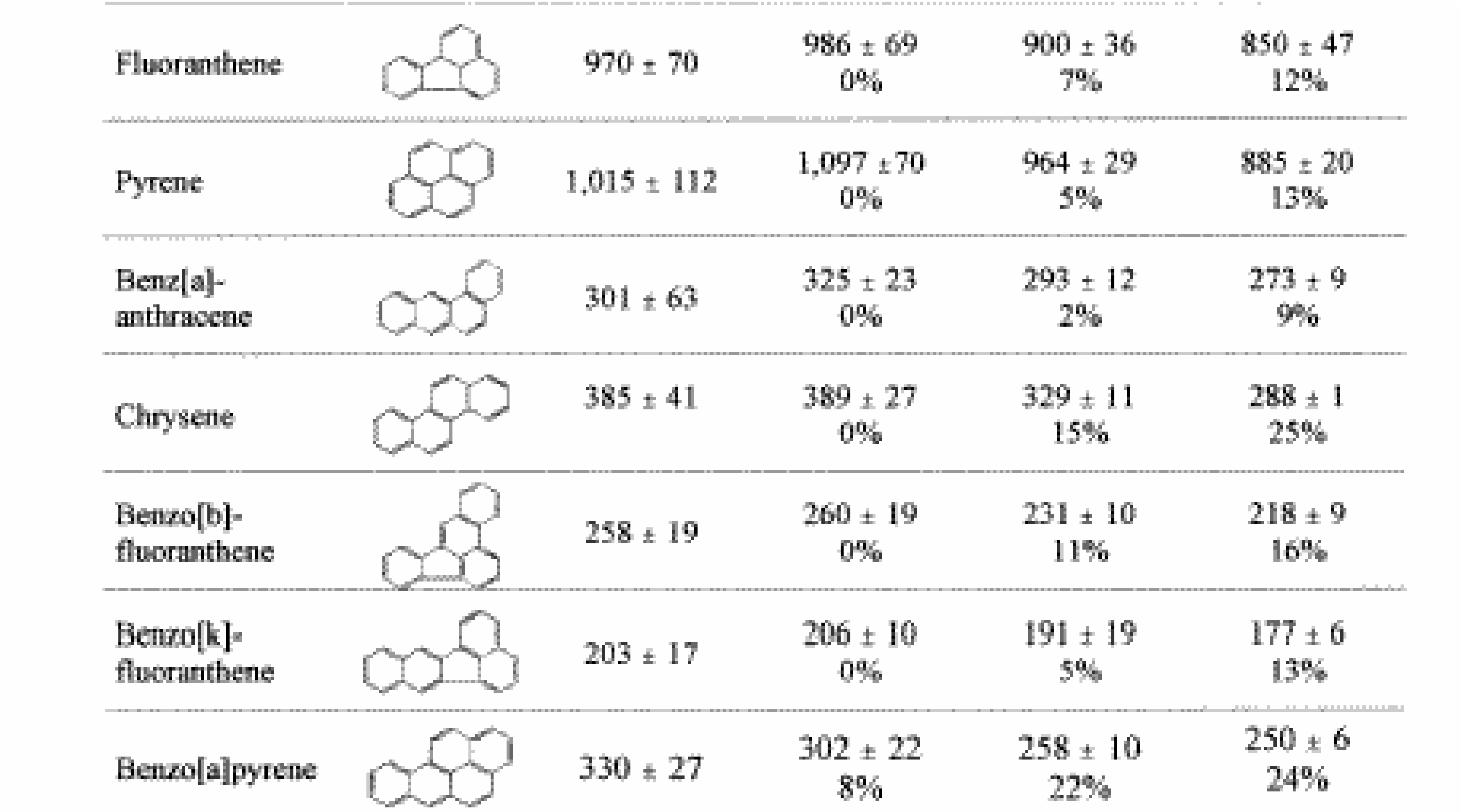
TABLE 1. Incremental Decline (over 11 Months) of in Situ PAHs in Microcosms of Anoxic, Coal Tar-Contaminated Boston Harbor Sediment Maintained with Adequate Sulfate To Support Respiration in Sulfate-Reducing Bacteria

		Initial PAH level (μmol/Kg dry sediment)	PAH levels and % decline over ca. 1 yr (μmol PAH / Kg dry sediment)		
			after 105 days	after 220 days	after 338 days
Naphthalene		436 ± 29	398 ± 24 8%	399 ± 16 8%	342 ± 2 22%
1-methyl-naphthalene		54 ± 11	30 ± 6 45%	26 ± 1 52%	22 ± 1 60%
2-methyl-naphthalene		99 ± 10	77 ± 6 22%	73 ± 2 26%	61 ± 3 38%
Acenaphthene		132 ± 14	35 ± 2 74%	19 ± 2 86%	15 ± 1 89%
Fluorene		112 ± 19	51 ± 5 54%	43 ± 1 61%	36 ± 0 67%
Phenanthrene		231 ± 30	131 ± 13 43%	110 ± 4 53%	97 ± 3 58%
Anthracene		293 ± 55	269 ± 16 8%	153 ± 9 48%	97 ± 6 67%

Rothermich et al., Enviro. Sci. Technol., 36, 4811-4817, 2002

PAH in Sediments

More complex PAH relatively difficult to degrade



Fluoranthene		970 ± 70	986 ± 69 0%	900 ± 36 7%	850 ± 47 12%
Pyrene		1,015 ± 112	1,097 ±70 0%	964 ± 29 5%	885 ± 20 13%
Benz[a]-anthracene		301 ± 63	325 ± 23 0%	293 ± 12 2%	273 ± 9 9%
Chrysene		385 ± 41	389 ± 27 0%	329 ± 11 15%	288 ± 1 25%
Benzo[b]-fluoranthene		258 ± 19	260 ± 19 0%	231 ± 10 11%	218 ± 9 16%
Benzo[k]-fluoranthene		203 ± 17	206 ± 10 0%	191 ± 19 5%	177 ± 6 13%
Benzo[a]pyrene		330 ± 27	302 ± 22 8%	258 ± 10 22%	250 ± 6 24%

Rothermich et al., Enviro. Sci. Technol., 36, 4811-4817, 2002

PAH in Sediments

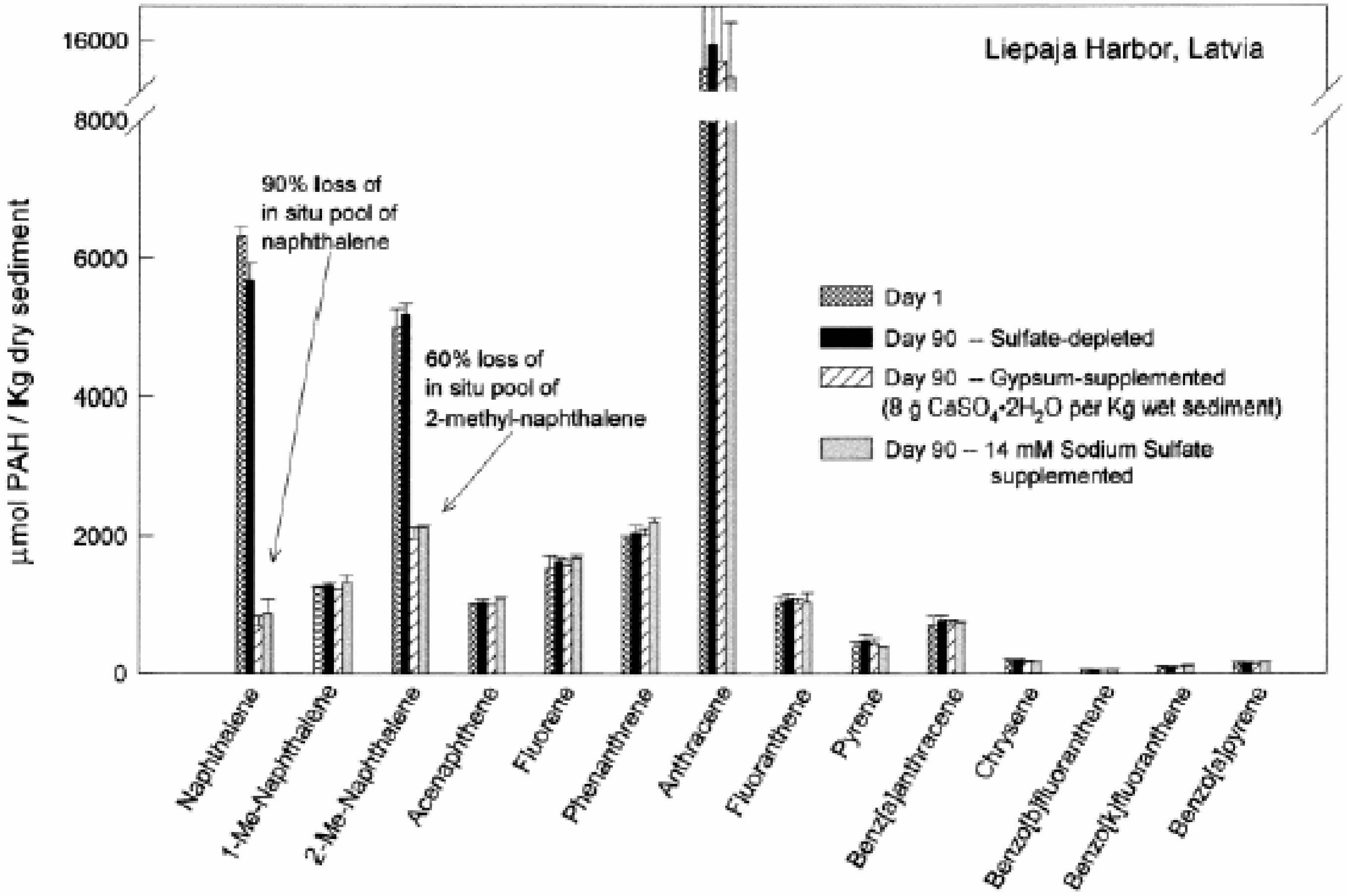


FIGURE 3. In situ contaminant PAHs in sediment approximately 3 weeks after collection from Liepaja Harbor, Latvia and after 90 days of incubation under in situ-like conditions. The sediment was sulfate-depleted upon arrival in the laboratory. Gypsum-supplemented and sodium sulfate-supplemented samples were amended after sediment was placed in incubation bottles. The results are the means of duplicate sample bottles. Each bottle value was determined from triplicate extractions.

Rothermich et al., Enviro. Sci. Technol., 36, 4811-4817, 2002

Anaerobic Benzene Biodegradation

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Table 2. Summary of anaerobic benzene degradation that was published with different TEAP.

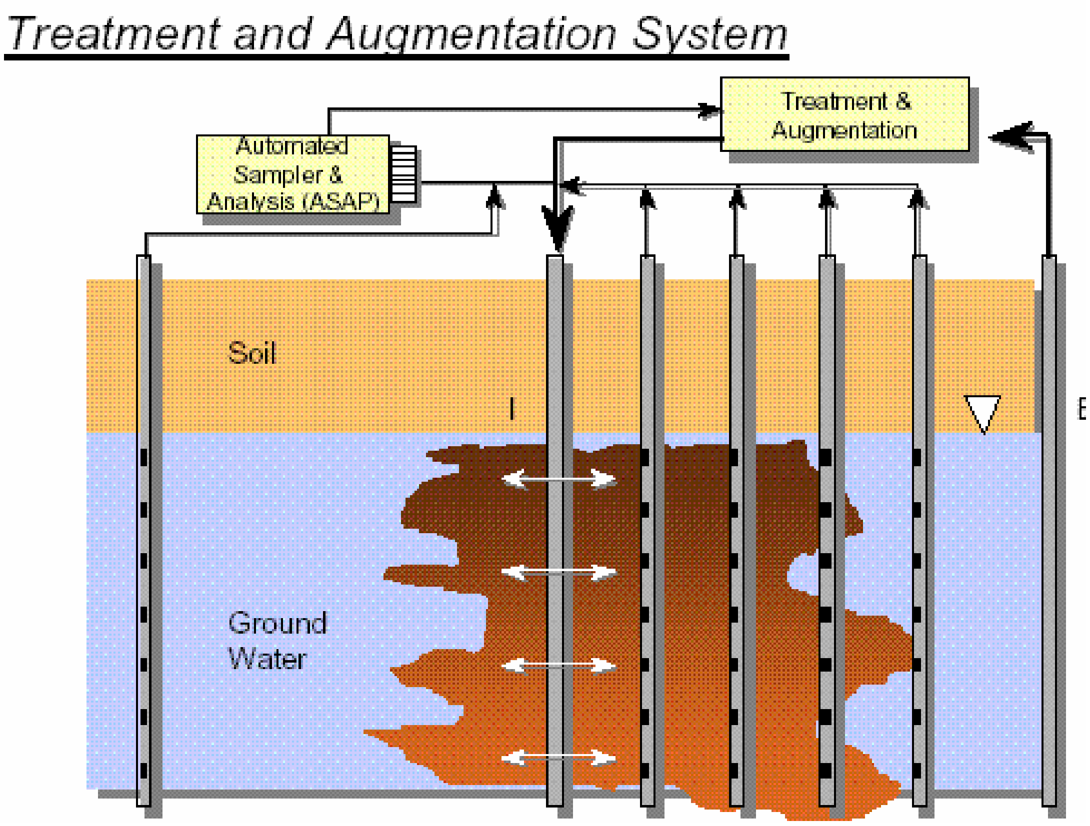
TEAP conditions	Percentage degraded	Concentration (mM)	Originated from	Lag phase (d)	Reference
CH_4/CO_2	6[1] (50[2])	1.5 - 30	Ferulic acid degrading sludge	16	(10)
CH_4/CO_2	82[1]	0.05	aquifer sediment, MI	420	(12)
CH_4/CO_2	73[2]	0.675	aquifer sediment, MI	360	(12)
CH_4/CO_2	53[1]	???	aquifer Ponca City, OK	0	(28)
SO_4^{2-}/H_2S	90[1]	0.20	Seal Beach, CA	70-100	(9)
SO_4^{2-}/H_2S	92[1]	1.7	San Diego Bay, CA	55	(14)
SO_4^{2-}/H_2S	92[3]	0.125	Guaymas Basin, Mexico	84	(18)
SO_4^{2-}/H_2S	78[1]	0.050	aquifer sediment, MI	400	(12)
SO_4^{2-}/H_2S	76[1]	0.057	Seal Beach, CA	120	(12)
SO_4^{2-}/H_2S	85[2]	0.125	NY/NJ Harbor sediment	60	(12)
SO_4^{2-}/H_2S	101[2]	0.100	Sleeping Bear Dunes National Lakeshore, Empire, MI	100	(20)
NO_3^-/N_2	95[4]	0.038	Canada Force Base Borden, Ontario	-	(17)
NO_3^-/NO_2^-	92-95[1]	0.150	Toronto, Ontario	30	(3)
NO_3^-/NO_2^-	92-95[1]	0.150	Fresh water swamp, Perth, Ontario	30	(3)
NO_3^-/N_2	47[1]	0.163	Strain JJ and RCB	0	(7)
Fe^{3+}/Fe^{2+}	86[1] 97[2]	0.608	Sediment Defense Fuel Center, Hanahan, SC	87-122	(16)
Fe^{3+}/Fe^{2+}	95[5]	0.010	Sediment Defense Fuel Center, Hanahan, SC	25	(15)
Fe^{3+}/Fe^{2+}	46[4]	0.125	NY/NJ Harbor sediment	100	(12)
Fe^{3+}/Fe^{2+}	100[4]	0.003	Potomac River, Maryland	50	(12)
Fe^{3+}/Fe^{2+}	50[1]	???	USGS Groundwater Toxic site, Bemidji, MN	0	(1)
Fe^{3+}/Fe^{2+}	90[1]	0.050	aquifer Ponca City, OK	???	(5)

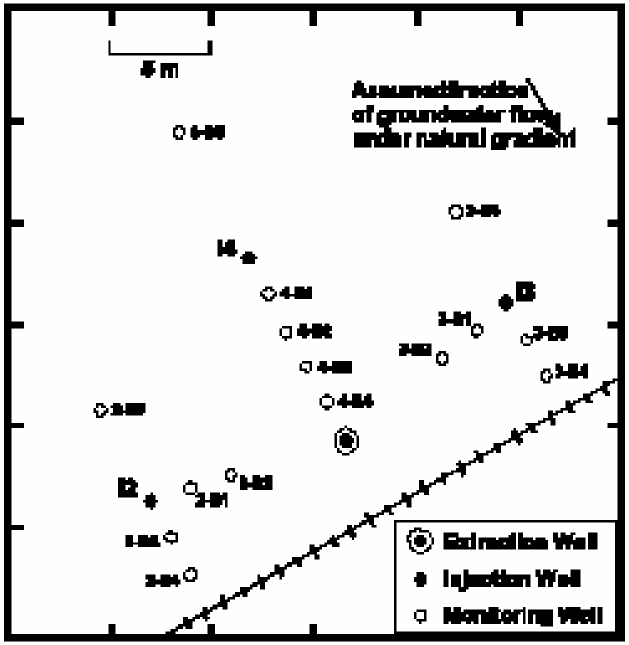
Naval Weapons Station, Seal Beach, CA

- Pilot study – Stanford University and NFESC
- “Injection-extraction” cells to create 3 remediation zones
  - With sulfate
  - With sulfate and nitrate
  - No amendment (naturally methanogenic)
- Sulfate and nitrate were quickly consumed ➔ supply of electron acceptors was limiting under natural conditions
  - Nitrate (0.1 to 0.6 d^{-1}) and sulfate (0.1 d^{-1}) were consumed at similar rates
  - Nitrate effective at oxidizing sulfide back to sulfate
- BTEX removal:
  - Toluene preferentially degraded naturally over B, EB and X
  - Sulfate preferentially stimulated removal of o-X, but not B, EB and m+p-X
  - Nitrate stimulated removal of EB and m+p-X
  - Benzene biodegradation was the slowest in all conditions, if at all

ESTCP Cost & Performance Report, December 1999
http://www.estcp.org/documents/techdocs/199522.pdf

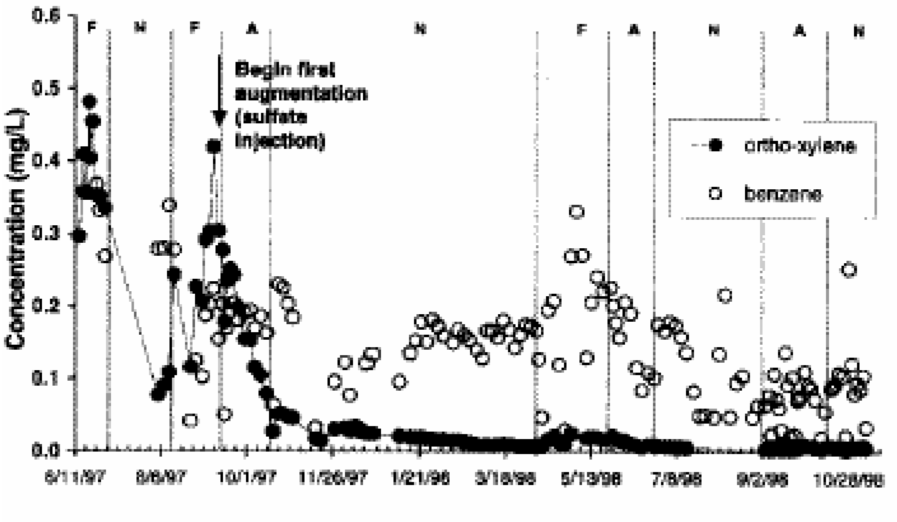
Application





ESTCP Cost & Performance Report, December 1999
http://www.estcp.org/documents/techdocs/199522.pdf

BTEX Removal with Sulfate and Nitrate



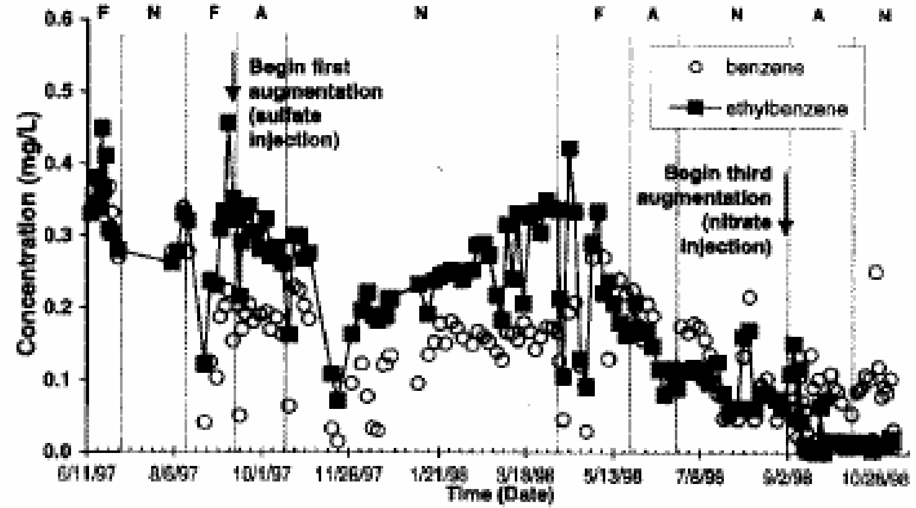


Figure 11. Concentration histories of benzene, *o*-xylene, and ethylbenzene at well 2-B1-4. Upper graph: augmentation with sulfate preferentially stimulates removal of *o*-xylene. Lower graph: ethylbenzene is recalcitrant under sulfate-reducing conditions, but is readily removed under nitrate-reducing conditions.

ESTCP Cost & Performance Report, December 1999
http://www.estcp.org/documents/techdocs/199522.pdf

MTBE – Surface Water Sediments

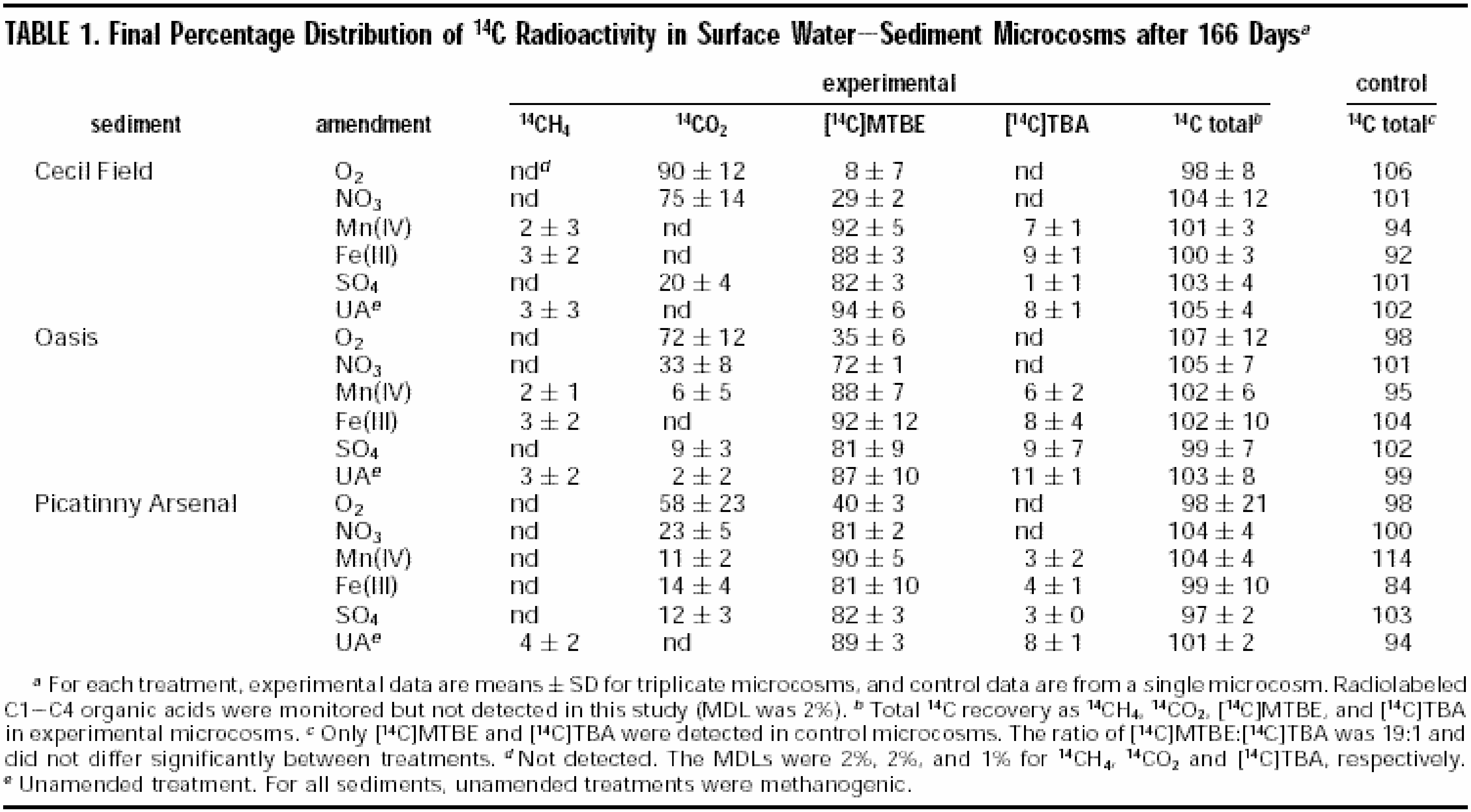


TABLE 1. Final Percentage Distribution of ^{14}C Radioactivity in Surface Water–Sediment Microcosms after 166 Days[a]

sediment	amendment	experimental					control
		$^{14}CH_4$	$^{14}CO_2$	$[^{14}C]MTBE$	$[^{14}C]TBA$	^{14}C total[b]	^{14}C total[c]
Cecil Field	O_2	nd[d]	90 ± 12	8 ± 7	nd	98 ± 8	106
	NO_3	nd	75 ± 14	29 ± 2	nd	104 ± 12	101
	Mn(IV)	2 ± 3	nd	92 ± 5	7 ± 1	101 ± 3	94
	Fe(III)	3 ± 2	nd	88 ± 3	9 ± 1	100 ± 3	92
	SO_4	nd	20 ± 4	82 ± 3	1 ± 1	103 ± 4	101
	UA[e]	3 ± 3	nd	94 ± 6	8 ± 1	105 ± 4	102
Oasis	O_2	nd	72 ± 12	35 ± 6	nd	107 ± 12	98
	NO_3	nd	33 ± 8	72 ± 1	nd	105 ± 7	101
	Mn(IV)	2 ± 1	6 ± 5	88 ± 7	6 ± 2	102 ± 6	95
	Fe(III)	3 ± 2	nd	92 ± 12	8 ± 4	102 ± 10	104
	SO_4	nd	9 ± 3	81 ± 9	9 ± 7	99 ± 7	102
	UA[e]	3 ± 2	2 ± 2	87 ± 10	11 ± 1	103 ± 8	99
Picatinny Arsenal	O_2	nd	58 ± 23	40 ± 3	nd	98 ± 21	98
	NO_3	nd	23 ± 5	81 ± 2	nd	104 ± 4	100
	Mn(IV)	nd	11 ± 2	90 ± 5	3 ± 2	104 ± 4	114
	Fe(III)	nd	14 ± 4	81 ± 10	4 ± 1	99 ± 10	84
	SO_4	nd	12 ± 3	82 ± 3	3 ± 0	97 ± 2	103
	UA[e]	4 ± 2	nd	89 ± 3	8 ± 1	101 ± 2	94

[a] For each treatment, experimental data are means ± SD for triplicate microcosms, and control data are from a single microcosm. Radiolabeled C1–C4 organic acids were monitored but not detected in this study (MDL was 2%). [b] Total ^{14}C recovery as $^{14}CH_4$, $^{14}CO_2$, $[^{14}C]MTBE$, and $[^{14}C]TBA$ in experimental microcosms. [c] Only $[^{14}C]MTBE$ and $[^{14}C]TBA$ were detected in control microcosms. The ratio of $[^{14}C]MTBE$:$[^{14}C]TBA$ was 19:1 and did not differ significantly between treatments. [d] Not detected. The MDLs were 2%, 2%, and 1% for $^{14}CH_4$, $^{14}CO_2$ and $[^{14}C]TBA$, respectively. [e] Unamended treatment. For all sediments, unamended treatments were methanogenic.

TBA accumulation tendency increased with more anaerobic conditions

Bradley, P. et al., Enviro. Sci. Technol., 35(23), 4643-4647, 2001

MTBE – Marine Sediment Enrichments with Sulfate

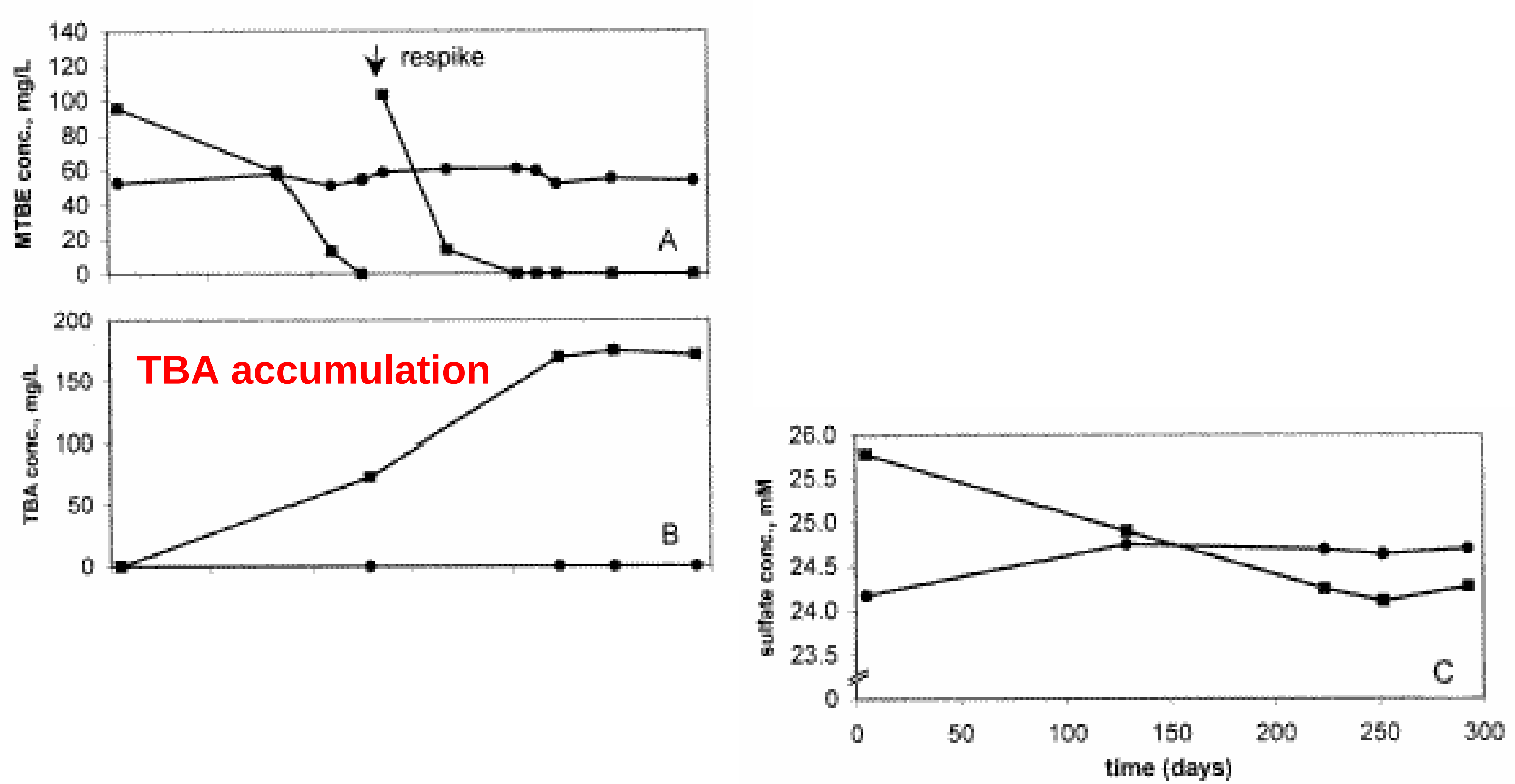


Fig. 2. Anaerobic biotransformation of MTBE by MTBE-enriched sulfidogenic cultures (■) upon transfer into fresh sulfidogenic medium, compared to those of sterile control (●). MTBE biotransformation (A), TBA formation (B), sulfate reduction(C).

Somsamak, P. et al., FEMS Microbiol. Ecology., 37, 259-264, 2001

TBA – Surface Water Sediments

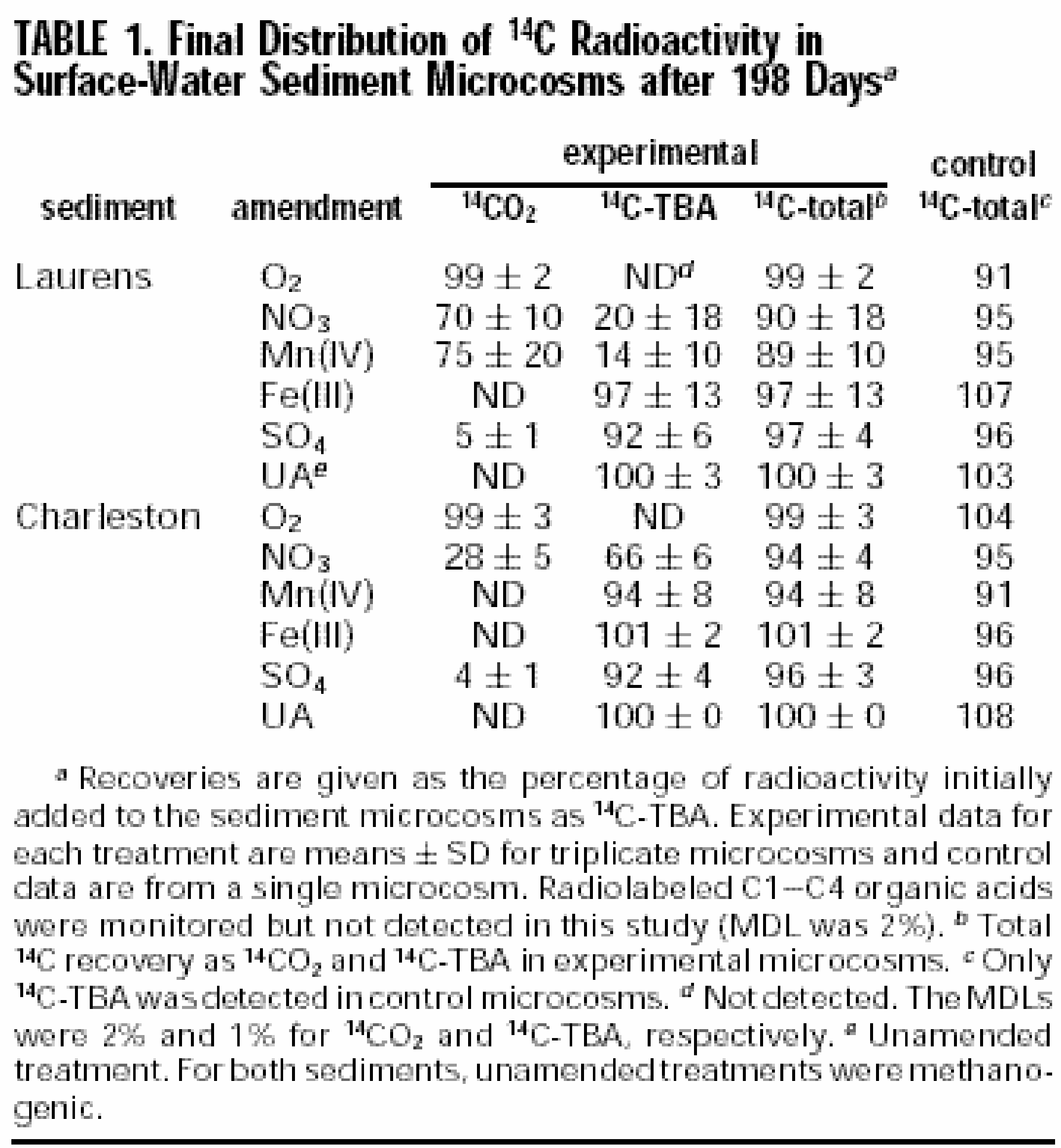


TABLE 1. Final Distribution of ^{14}C Radioactivity in Surface-Water Sediment Microcosms after 198 Days[a]

sediment	amendment	experimental $^{14}CO_2$	experimental ^{14}C-TBA	experimental ^{14}C-total[b]	control ^{14}C-total[c]
Laurens	O_2	99 ± 2	ND[d]	99 ± 2	91
	NO_3	70 ± 10	20 ± 18	90 ± 18	95
	Mn(IV)	75 ± 20	14 ± 10	89 ± 10	95
	Fe(III)	ND	97 ± 13	97 ± 13	107
	SO_4	5 ± 1	92 ± 6	97 ± 4	96
	UA[e]	ND	100 ± 3	100 ± 3	103
Charleston	O_2	99 ± 3	ND	99 ± 3	104
	NO_3	28 ± 5	66 ± 6	94 ± 4	95
	Mn(IV)	ND	94 ± 8	94 ± 8	91
	Fe(III)	ND	101 ± 2	101 ± 2	96
	SO_4	4 ± 1	92 ± 4	96 ± 3	96
	UA	ND	100 ± 0	100 ± 0	108

[a] Recoveries are given as the percentage of radioactivity initially added to the sediment microcosms as ^{14}C-TBA. Experimental data for each treatment are means ± SD for triplicate microcosms and control data are from a single microcosm. Radiolabeled C1–C4 organic acids were monitored but not detected in this study (MDL was 2%). [b] Total ^{14}C recovery as $^{14}CO_2$ and ^{14}C-TBA in experimental microcosms. [c] Only ^{14}C-TBA was detected in control microcosms. [d] Not detected. The MDLs were 2% and 1% for $^{14}CO_2$ and ^{14}C-TBA, respectively. [e] Unamended treatment. For both sediments, unamended treatments were methanogenic.

Bradley, P. et al., Enviro. Sci. Technol., 36(19), 4087-4090, 2002

What About Hydrogen Sulfide?

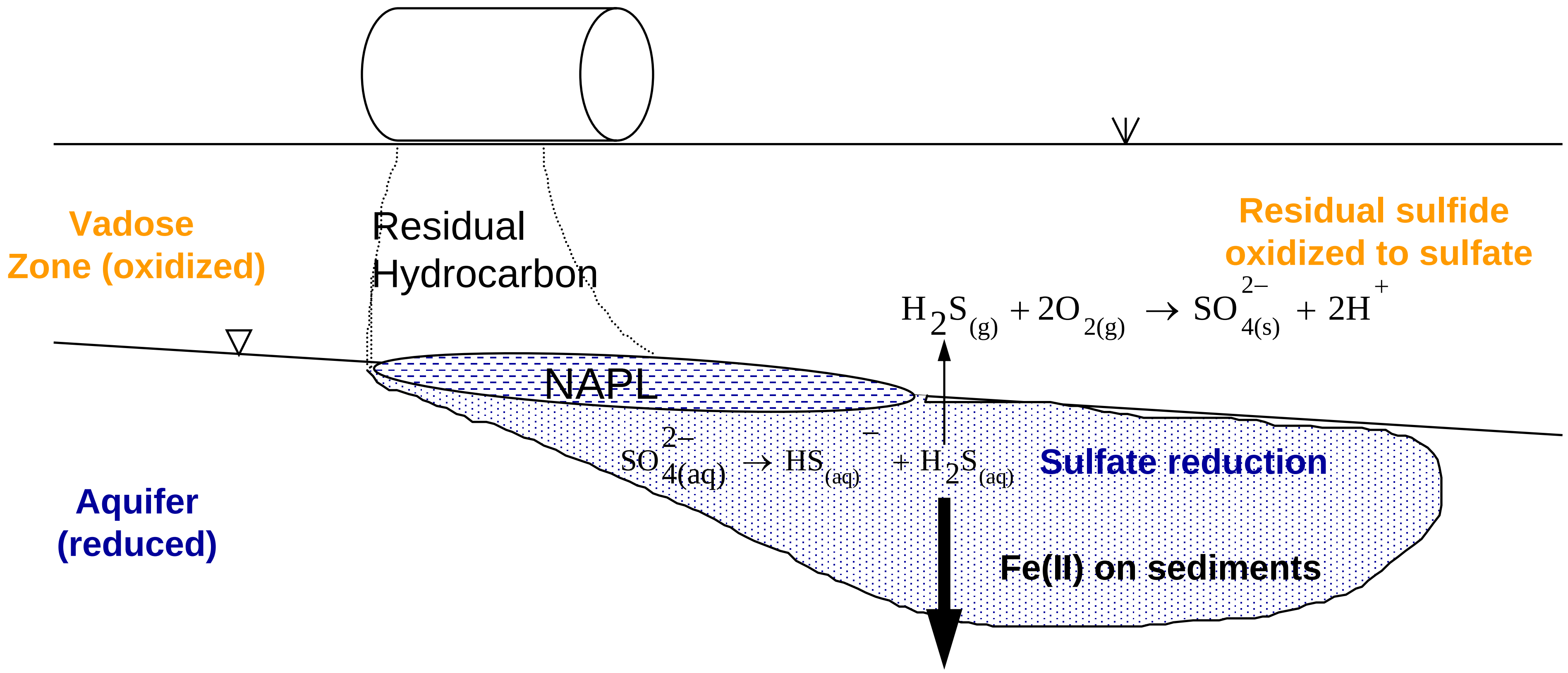
- Colorless gas with a strong odor of rotten eggs

- Exposure limits
  - NIOSH: 10 ppmv (10 minutes)
  - OSHA: 20 ppmv
  - IDLH: 100 ppmv

- Health Hazards
  - Inhalation: irritation to eyes, conjunctivitis, affects CNS
  - Ingestion: excitement, colored urine
  - Contact: nausea, dizziness, suffocation, rapid breath

- Explosive limits: 4% to 44%

Most of Sulfide is Bound to Soil



Vadose Zone (oxidized)

Residual Hydrocarbon

Residual sulfide oxidized to sulfate

$$H_2S_{(g)} + 2O_{2(g)} \rightarrow SO_{4(s)}^{2-} + 2H^{+}$$

NAPL

$$SO_{4(aq)}^{2-} \rightarrow HS_{(aq)}^{-} + H_2S_{(aq)}$$

Sulfate reduction

Aquifer (reduced)

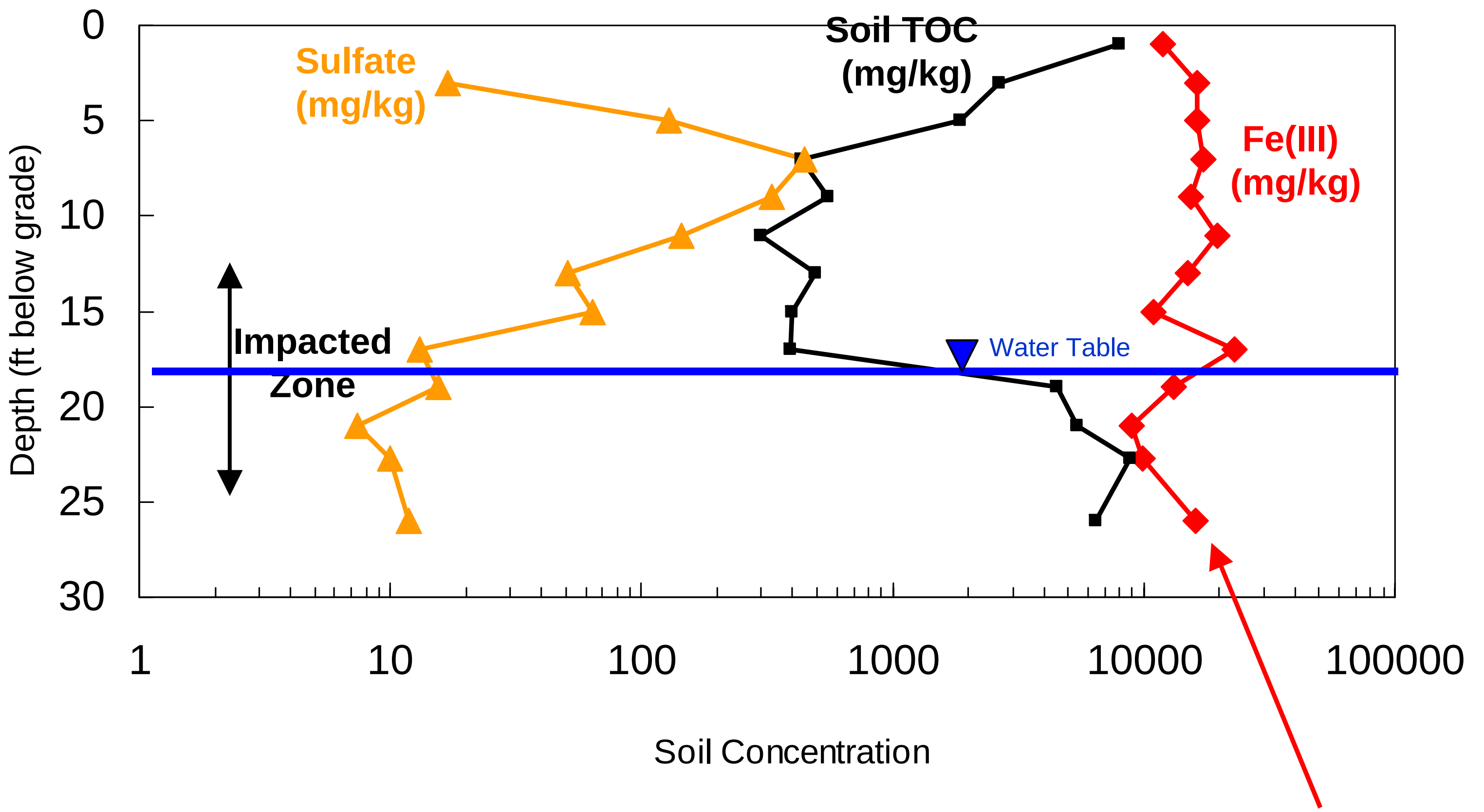
Fe(II) on sediments

$$H_2S_{(aq)} + Fe(II)_{(s)} \rightarrow FeS_{(s)} + 2H_{(aq)}^{+}$$

Sulfide sequestered as iron sulfides

$$FeS + S^{0} \rightarrow Fe_2S$$

Soil Profile at Neodesha (SOW-9)



Plenty of iron to Bind sulfide

Refinery Site in Oklahoma

- Operating refinery with an old benzene plume (max. 7.8 mg/L)
- Hydrogeology:
  - Coarse sand (GW seepage velocity 2500 ft/y)
  - DTW: 9-12 ft bgs
- Sodium sulfate injection
  - 40 one-inch wells in 2 rows
  - Sulfate injected: 770 mg/L @ 0.14 gpm (total flow)
  - Maximum sulfate detected in GW: 58 mg/L
  - Sulfide not detected in GW
- **Benzene concentrations were reduced between 73% to 93% in 165 days (half life ~ 2 months)**

Anderson and Loveley, Enviro. Sci. Technol., 34, 2261-2266, 2000

Benzene Reduction Following Sulfate Addition

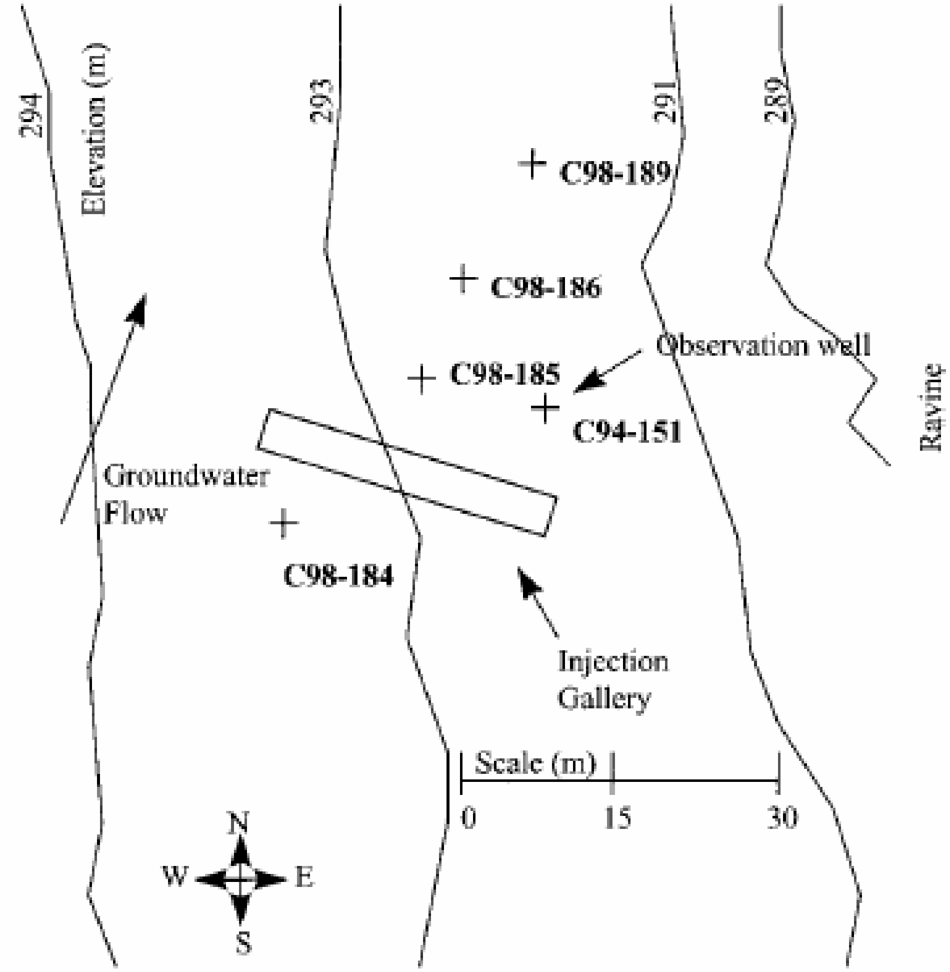


FIGURE 1. Plan view of the injection gallery and positions of the observation wells.

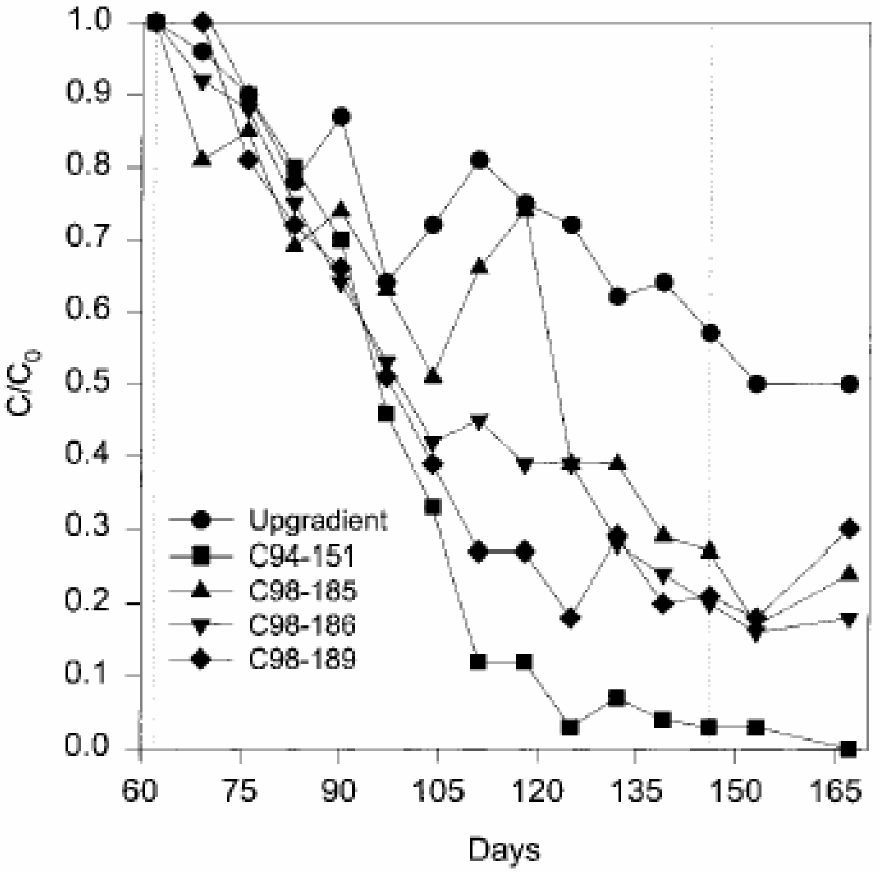


FIGURE 5. Relative decreases in benzene concentrations at the observation wells. All concentrations are normalized to observed benzene concentrations measured just prior to the start of the injection period. Dashed lines indicate the period of sulfate injection.

Anderson and Loveley, Enviro. Sci. Technol., 34, 2261-2266, 2000

Nitrate for Enhanced Bioremediation

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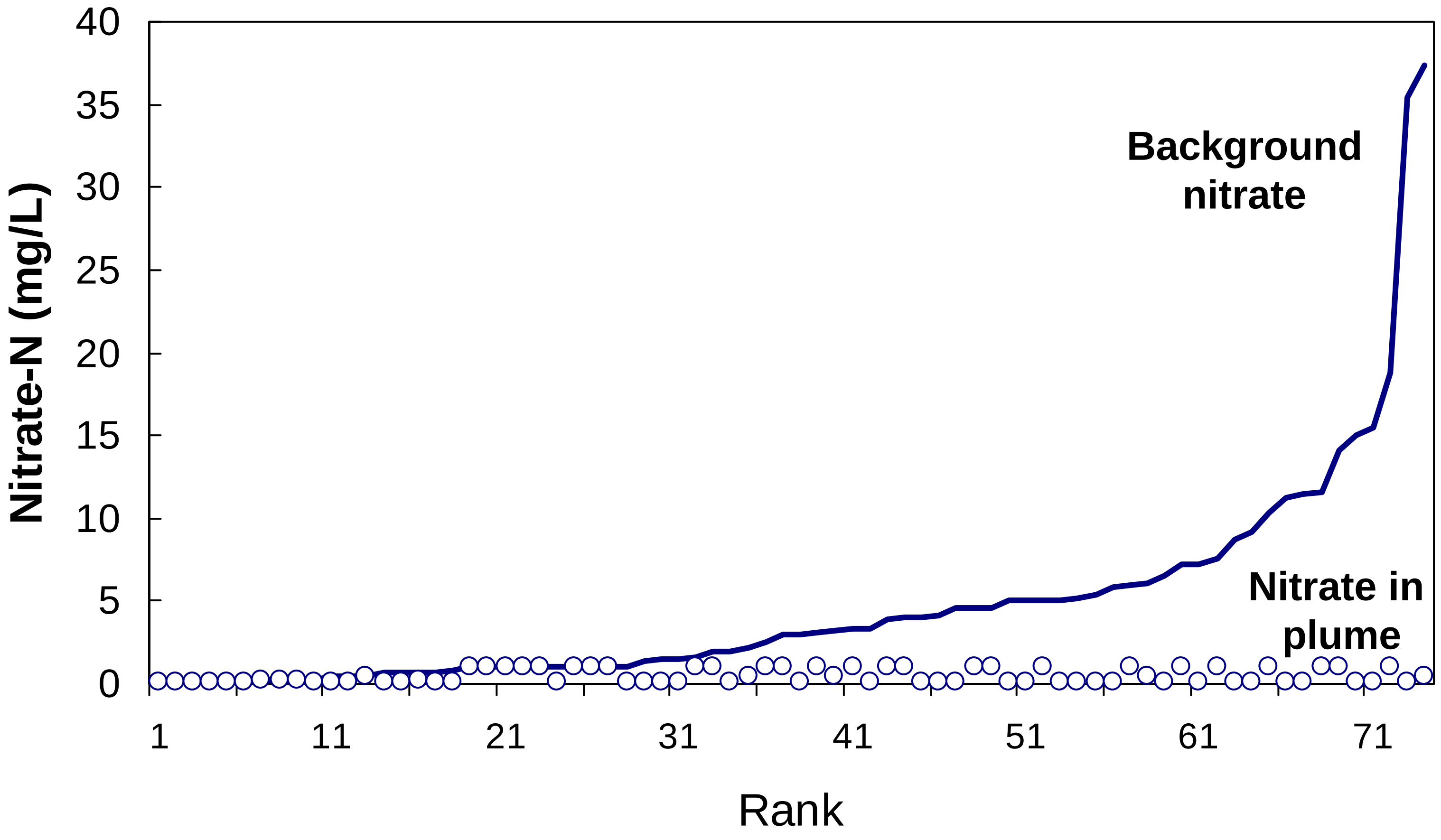

Background nitrate concentrations are generally lower and nitrate is depleted in plumes

Nitrate for Enhanced Bioremediation

Facts

- Background levels are generally low
- **Primary MCL of 45 mg/L nitrate**
- Like oxygen, nitrate is utilized to oxidize reduced species (e.g. iron sulfides), as well as other organic carbon

Observations from Field Studies in Literature

⇒ Most pilots and field applications have employed extraction-injection pairs (“recirculation cell”)

⇒ Injection concentrations – 50 – 200 mg/L nitrate

⇒ Monitoring periods from 2 to 5 months

⇒ Required 10 to 100 times more nitrate over that required for BTEX biodegradation. **Nitrate known to oxidize sulfide back to sulfate.**

⇒ TEX compounds degraded, but Benzene generally remained persistent (total duration too short?). **Recent evidence of benzene biodegradation with nitrate.**

⇒ **Consider nitrate together with sulfate to increase the electron acceptor pool**

⇒ Naval weapons site, Seal Beach, CA data recommend the same

Benzene and Nitrate Reduction

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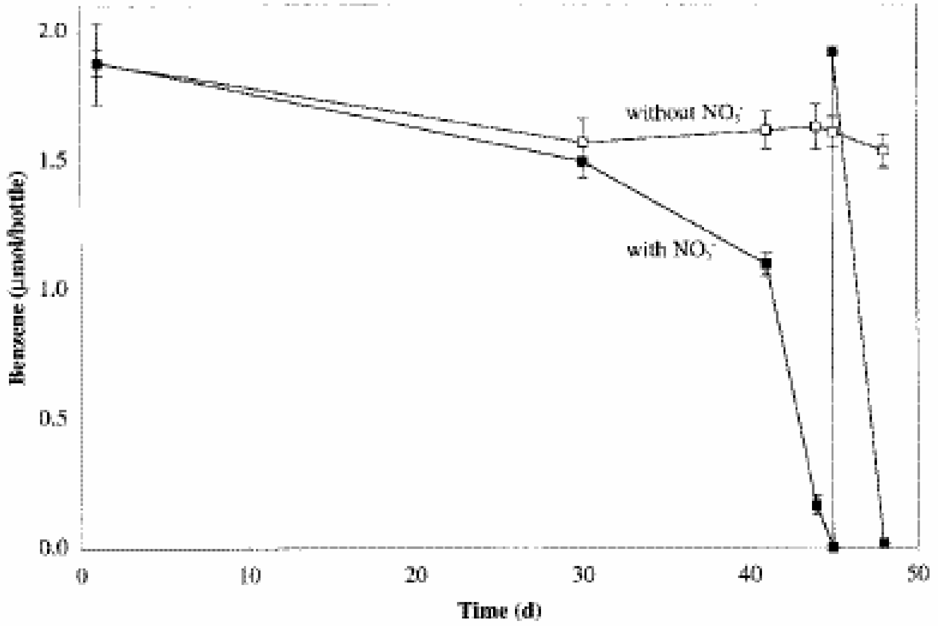


FIG. 2. Plot of benzene concentration versus time for transfer cult in the presence of nitrate (■) and in the absence of nitrate (□). Tl means ± standard deviations from triplicate cultures (without ni means ± ranges from duplicate cultures (with nitrate). d, days.

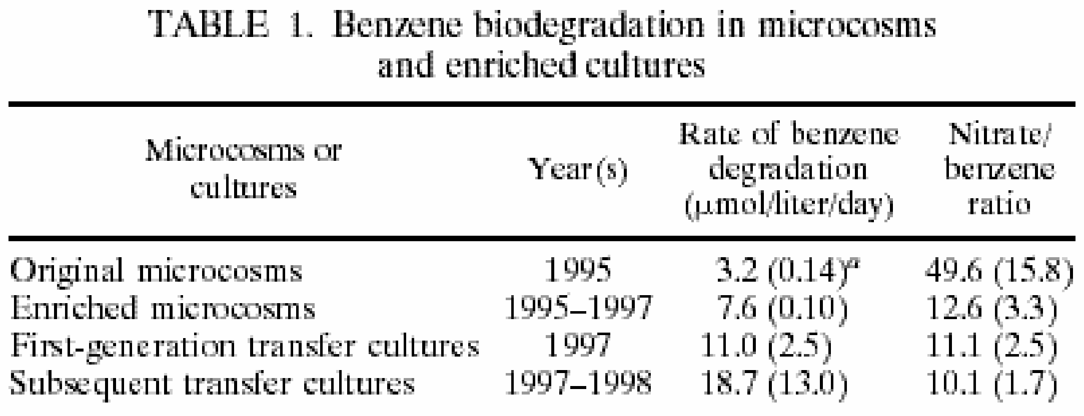


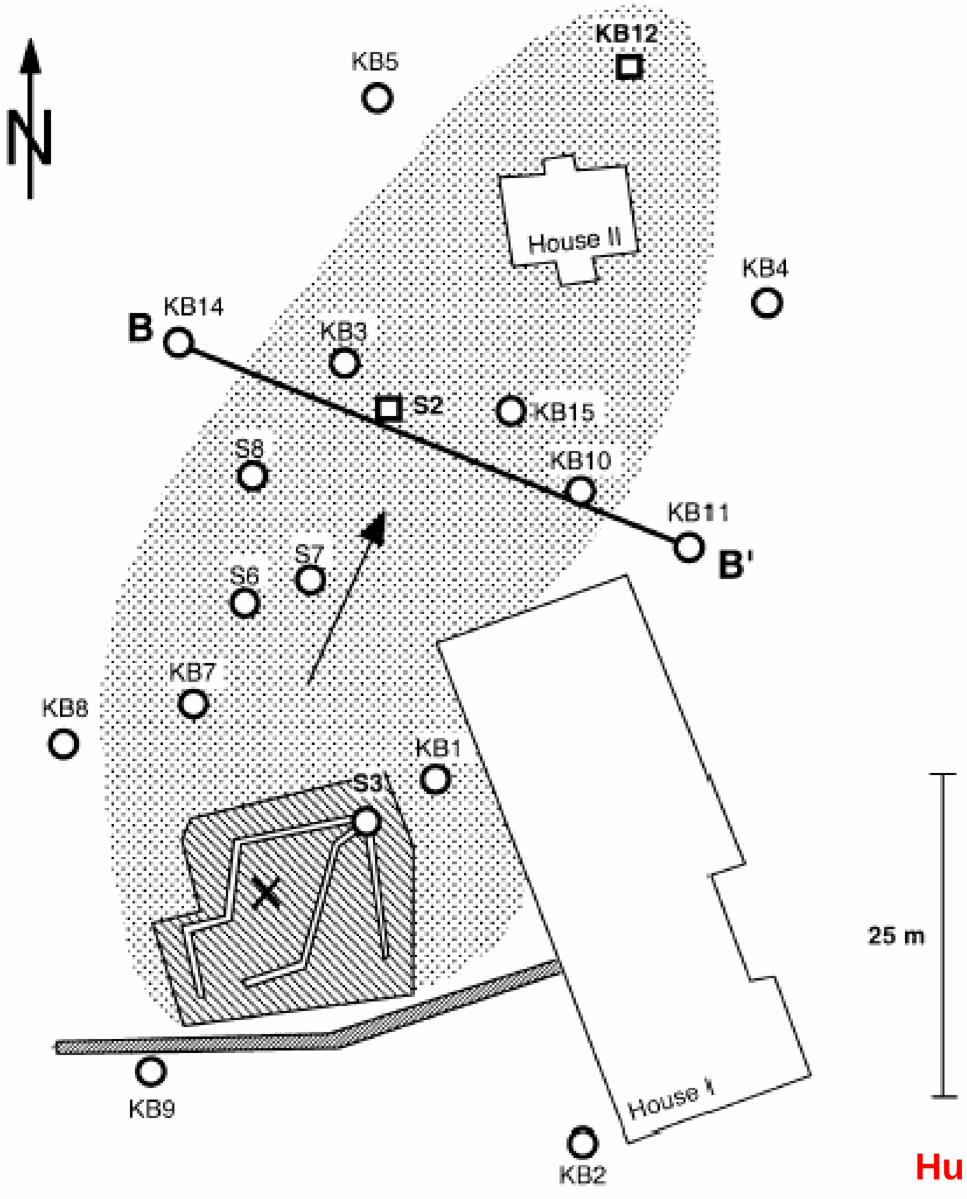
TABLE 1. Benzene biodegradation in microcosms and enriched cultures

Microcosms or cultures	Year(s)	Rate of benzene degradation (µmol/liter/day)	Nitrate/benzene ratio
Original microcosms	1995	3.2 (0.14)[a]	49.6 (15.8)
Enriched microcosms	1995–1997	7.6 (0.10)	12.6 (3.3)
First-generation transfer cultures	1997	11.0 (2.5)	11.1 (2.5)
Subsequent transfer cultures	1997–1998	18.7 (13.0)	10.1 (1.7)

[a] Values are means (standard deviations).

Rothermich et al., Enviro. Sci. Technol., 36, 4811-4817, 2002

Engineered Bioremediation of a Diesel-impacted Aquifer



- Menziken, Switzerland
- 4.5 years
- GW pumped from S2 or KB12
- Water aerated and amended with KNO3 (84 mg/L nitrate) and ammonium phosphate
- Re-injected in S3 connected to infiltration gallery

Hunkeler et al., J. Contam. Hydro., 59, 231-245, 2002

Natural Diesel Biodegradation Following Engineered Bioremediation

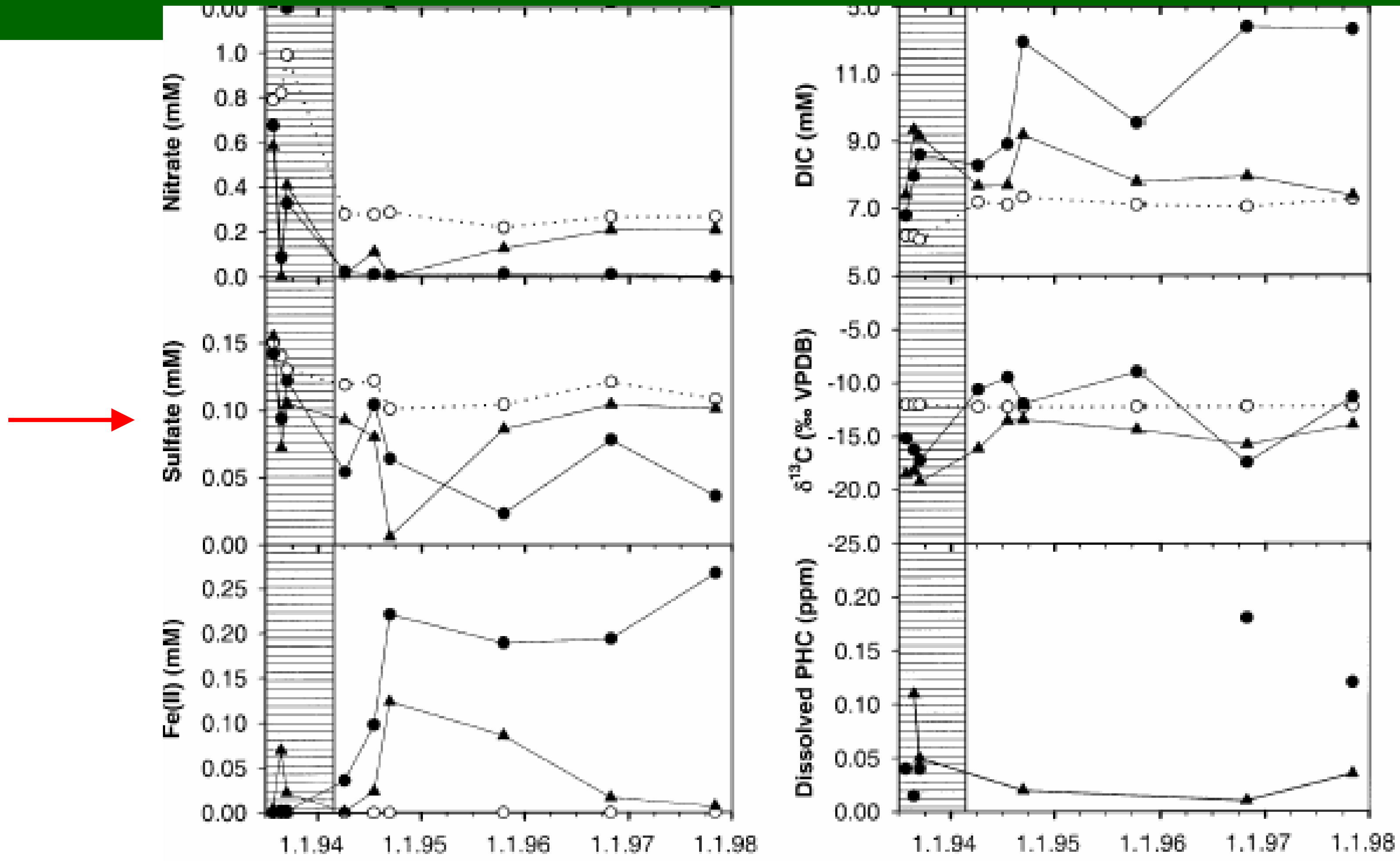


Fig. 3. Values of selected parameters for monitoring wells S6 (●) and KB15 (▲) during and after engineered in situ bioremediation. Expected values at S6 if the species entering the contaminated zone had behaved like a non-reactive tracer (○). The expected values were calculated according to Eq. (3). Shaded area: engineered in situ bioremediation in operation.

Hunkeler et al., J. Contam. Hydro., 59, 231-245, 2002

Applications

- Dissolved Plume
  - Addition of solution of sulfate salts (e.g. epsom, sodium sulfate)
  - Design sulfate addition (concentration and flow rate) based on sulfate demand for the mass flux of dissolved BTEX
    - Continuous addition, Periodic slug addition
    - Row of addition wells, infiltration gallery
    - Gypsum socks in transect of wells
    - Extract down-gradient, amend sulfate-nitrate and re-infiltrate up-gradient
- Source Area (or hotspots)
  - Agricultural gypsum amendment (up to 1% w/w) to source area excavation backfill material as a long term source of sulfate
  - Cost effective: ag gypsum ~ $ 19 to 150/t vs $16530/ton for ORC
  - Site selection criteria and application procedure (Gypsum FAQs)

Site Selection Criteria (Sulfate)

- Site with residual impact (“sheen” or high dissolved), but not with “gross” free product impacts
- Shallowest water table > 5 ft below grade
- Distance to residence, surface water or private well > 100 ft
- Distance to municipal DW well (100s of gpm) > 1250 ft
- Analyze GW samples from “clean” and “impacted” wells for BTEX, sulfate, sulfide, Fe(II), pH, Total Inorganic Carbon (or total alkalinity). Site suitable if
    1. Sulfate in clean wells > 15 mg/L and
    2. Sulfate depleted in impacted wells
    3. Elevated Fe(II) in impacted wells

Remedial Design Guidance

Data Input (in yellow highlighted cells)

Comments/Basis

Site Name			
Hydraulic Conductivity Estimate (K)	200	ft/d	Preferablly based on slug test or pump test data
Thickness of impacted saturated zone	10	ft	Estimate as length of screened interval of most impacted well
Hydraulic gradient	0.003	ft/ft	
Width of GW plume being addressed	10	ft	Lateral extent of proposed treatment (e.g. row of wells)
Maximum BTEX concentration	3.50	mg/L	
Safety Factor for sulfate demand (over stoichiometric)	2		Assume 2 to 4
Injection Sulfate Concentration	500	mg/L	Higher of sulfate in un-impacted water or 250 mg/L
Number of injection wells	2		Design choice

Calculations

Total groundwater volumetric flux (Q = KiA)	60	ft3/d	
Mass flux of BTEX Through Treatment Zone	5945	mg BTEX/d	
BTEX degraded/mass of sulfate	0.22	(mg/mg)	Based on stoichiometry for benzene and sulfate
Stoichiometric Sulfate Demand	27025	mg sulfate/d	
Total sulfate injection volume (w/ safety factor)	29	gal/d	

Design Choices for Liquid Sulfate Addition

Option 1: Continuous Addition			
Solution Flow/well	0.010	gpm/well	Adjust sulfate concentration to get reasonable flow
Option 2: Addition in Slugs			
Slug Addition Frequency	2	times/week	
Required Slug Addition Rate	200	gal/week	
Slug volume/well/event	50	gal	

Chemical Requirements

Salt Used	MW (gm)	Quantity Required (gm/d)	Unit Cost ($/lb)	Chemical Cost ($/year)
Epsom salt ($MgSO_4.7H_2O$)	120.37	**68**	0.75	**41**
anhydrous Sodium Sulfate	142	**80**	1.76	**113**

Summary

- Most plumes are anaerobic and depleted of soluble electron acceptors (nitrate and sulfate)
- Sulfate
  - Sulfate is more efficient and stimulates existing anaerobic conditions
  - Suitable for a variety of hydrocarbons – gasoline, gas condensate, alkanes, PAH, diesel…
  - Sulfide not been an issue in studies (OK refinery, Seal Beach site, other literature, closed BP refinery site)
  - Expect some lag time after sulfate shows up at the wells (3 – 6 months)!
- Nitrate
  - Useful to oxidize iron sulfides to sulfate
  - Useful to boost the total electron acceptor pool

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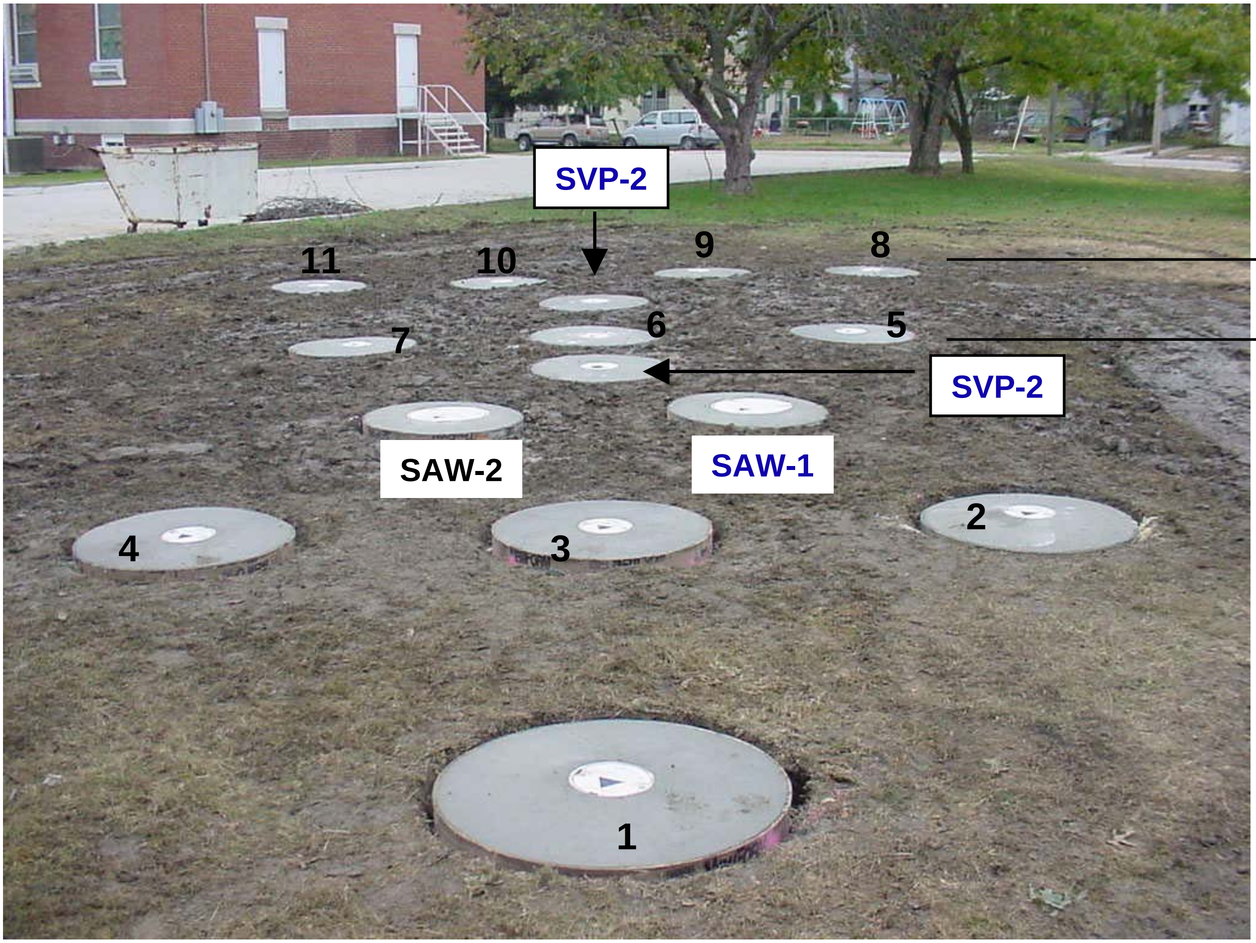
Pilot Layout

35 gal of 500 mg/L sulfate, 100 mg/L bromide twice a week/well



GW Flow

20 ft

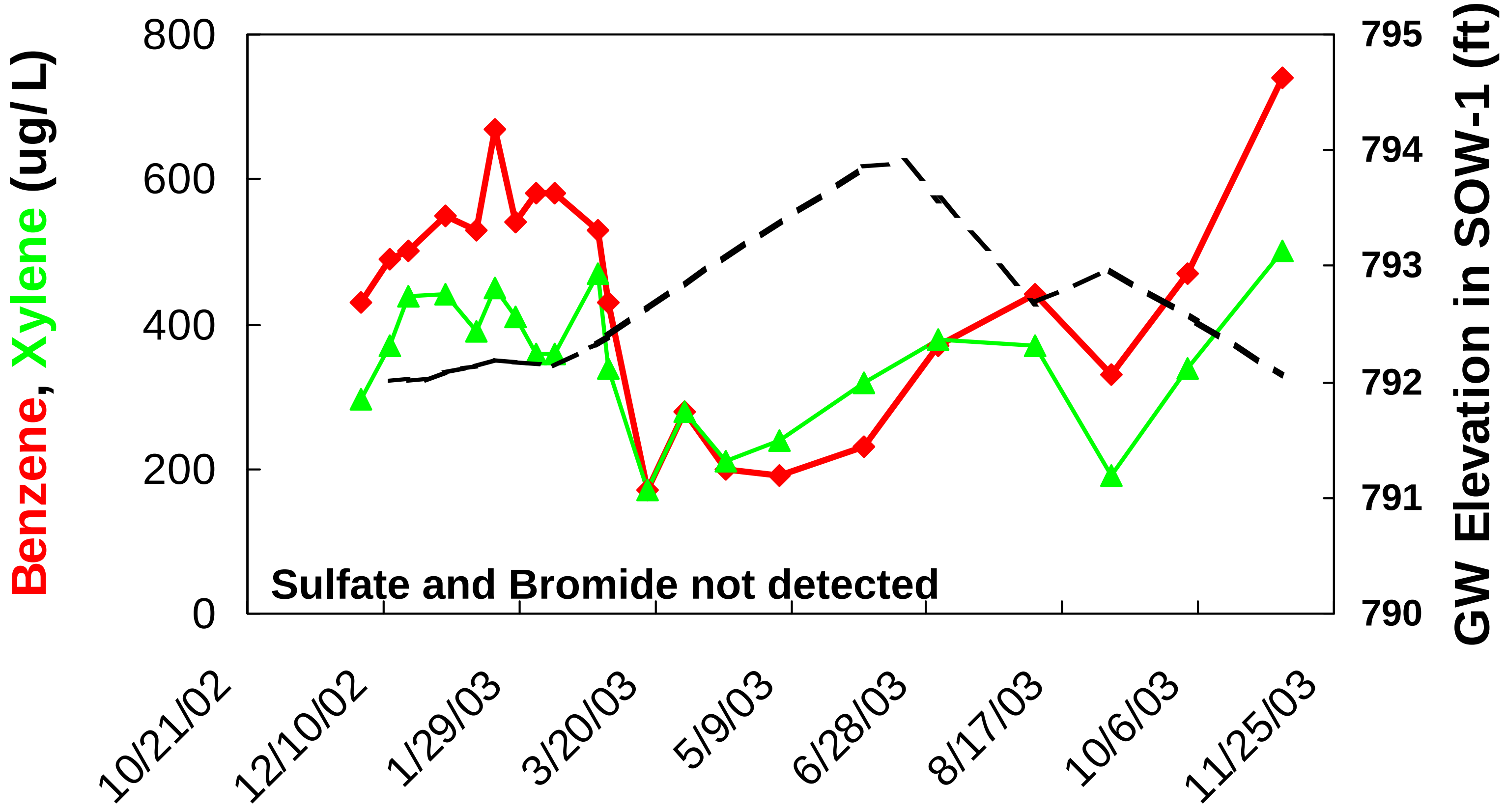
8 ft

Addition well

- 8 ft

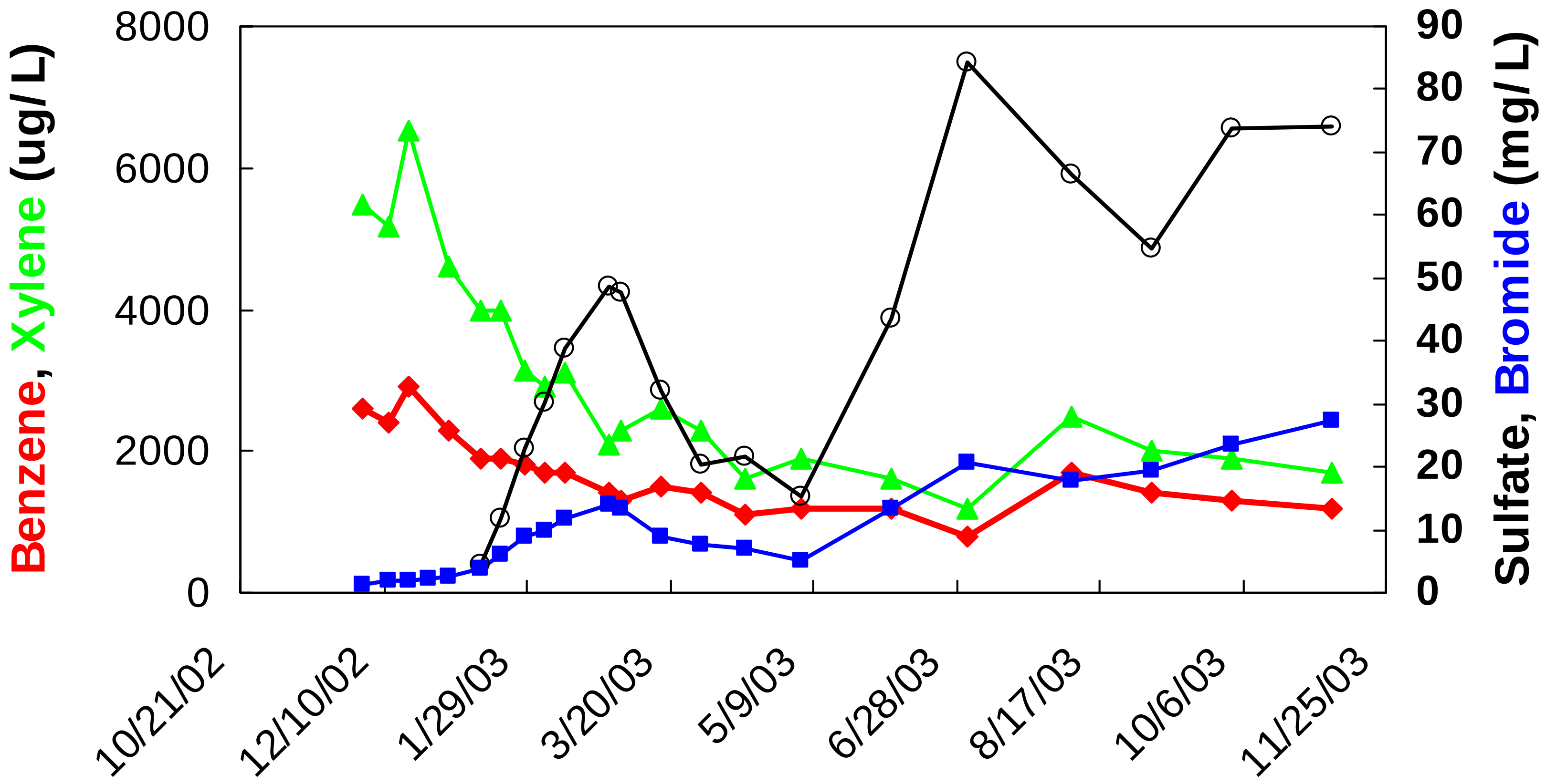
- 20 ft

Up-gradient Well (SOW-1)



Variations in B and X related to groundwater fluctuations

20 ft Downgradient Well (SOW-10)



Significant decrease in B and X in presence of sulfate

20 ft Downgradient Well (SOW-11)

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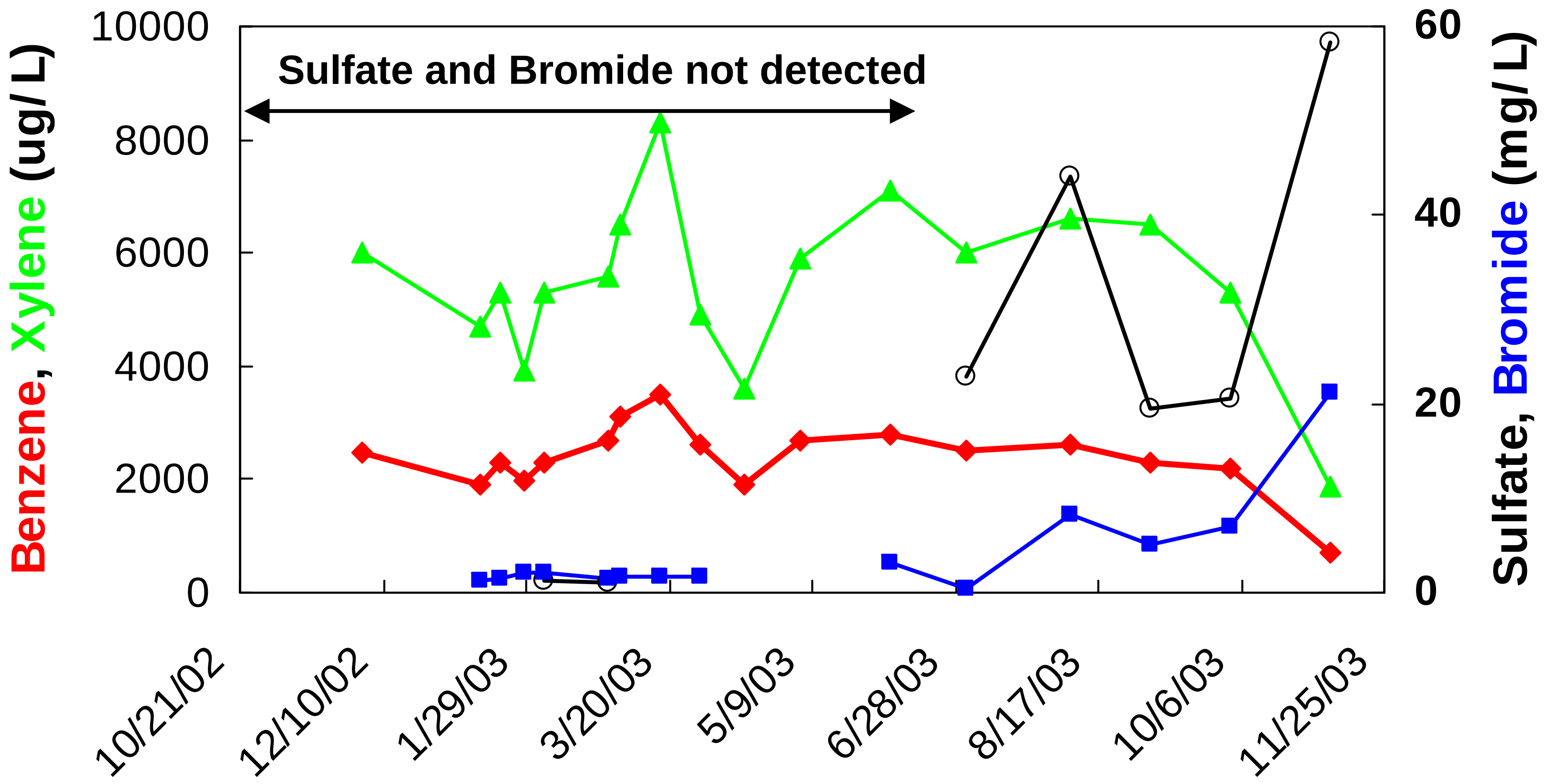

Decrease in B and X following arrival of sulfate

Terminal in Minnesota
Ag gypsum in Excavation

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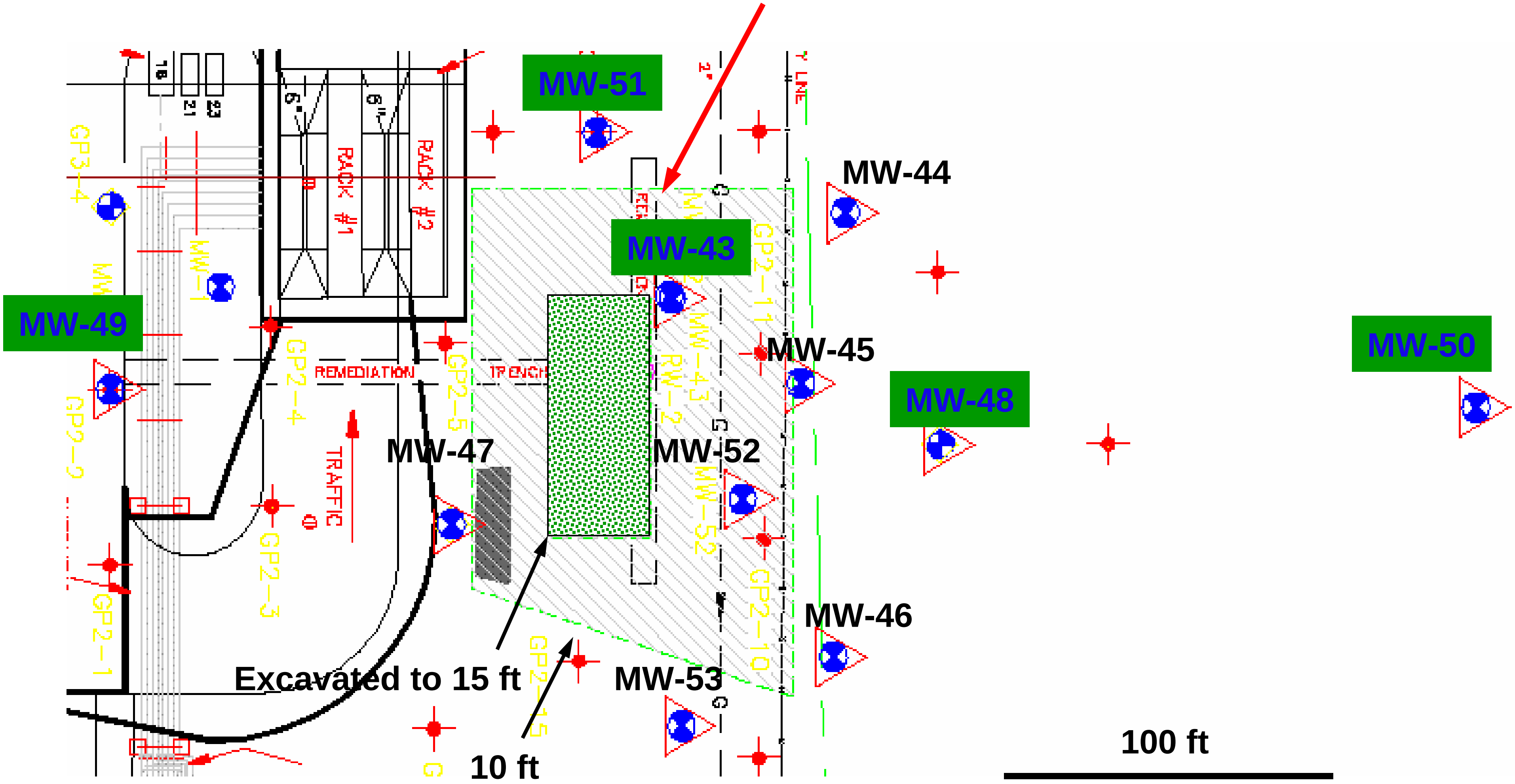


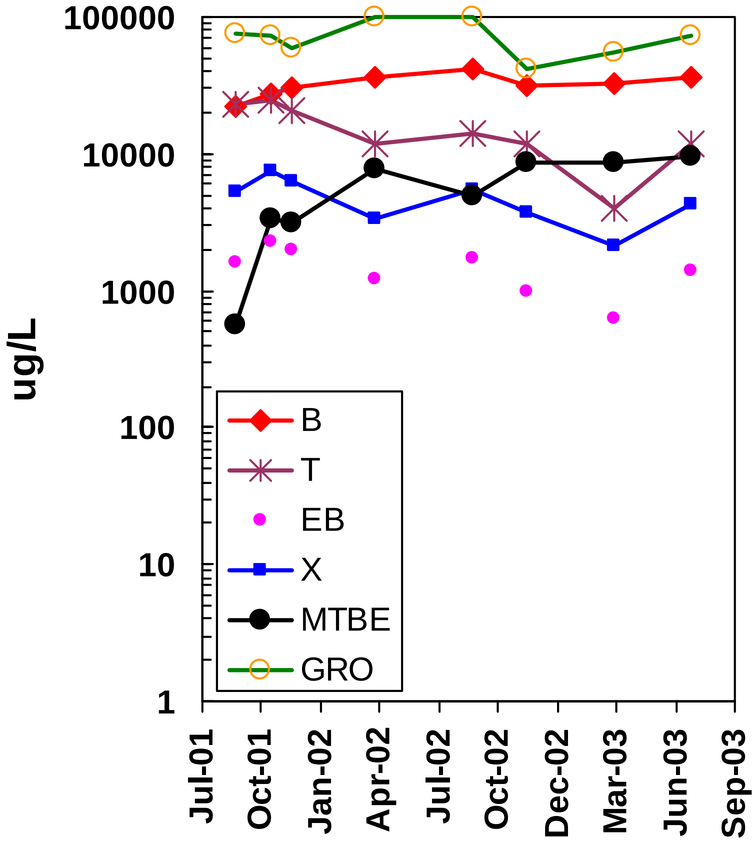
0.5% w/w ag gypsum in backfill

Excavated to 15 ft

10 ft

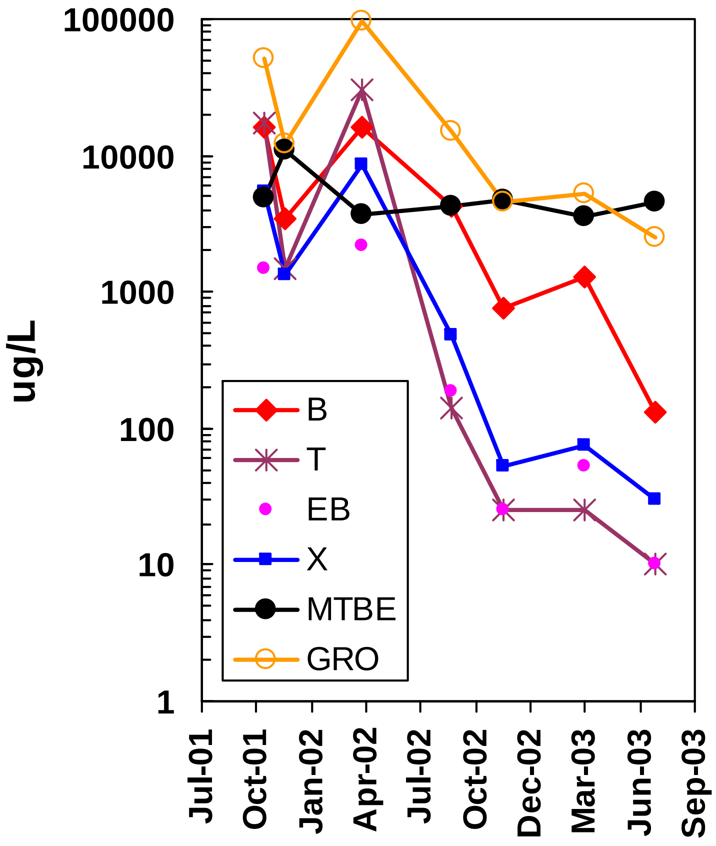
Effect of Sulfate on BTEX and TPH

MW-49 Up-gradient of excavation



- Sulfate not present
- Groundwater impact stays

MW-45 Down-gradient of excavation



- Sulfate upto 290 mg/L
- Groundwater cleans up!