Natural and Enhanced Bioremediation

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Our warning from past efforts

We can’t

- understand,
- take advantage of, or
- manipulate

processes we don’t realize are important or possible

Our focus in this talk: Groundwater contamination from fuels

- Gasoline
- Oxgenated gasoline
- Gasohol
- Future bio-fuels

Gasoline

- A multi-component organic liquid composed of 100s of components ("petroleum hydrocarbons")

- With regard to groundwater contamination, the main regulatory concerns in the past have been:
  - **BTEX species**:
    - B: benzene
    - T: toluene
    - E: ethylbenzene
    - X: xylene isomers
      - (o-X, m-X, p-X)

BTEX migration is often limited by "natural attenuation"

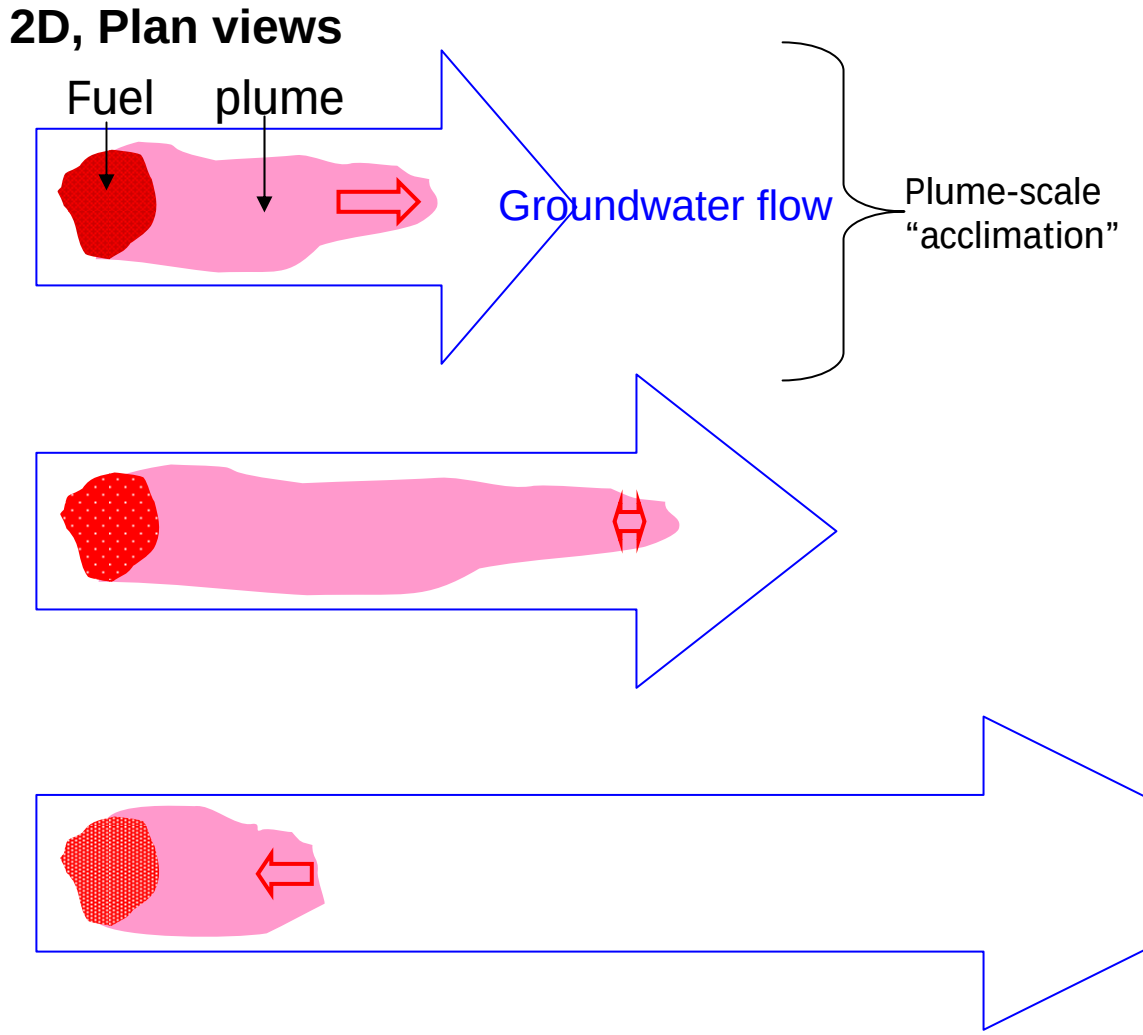
- BTEX species in groundwater are often efficiently degraded by native microbial communities using naturally available dissolved or solid "electron acceptors"

	Electron acceptor	Redox condition	Relative rate
Diss	Oxygen (O_2)	AEROBIC	Fastest
Diss	Nitrate (NO_3^-)	NITRATE REDUCING	↓
Diss	Sulfate (SO_4^{2-})	SULFATE REDUCING	
Solid	Manganese (Mn^{4+})	MANGANESE REDUCING	
Solid	Iron (Fe^{3+})	IRON REDUCING	
Diss	Carbon Dioxide (CO_2), etc.	METHANOGENIC	Slowest

Qs: What is total biodegradation capacity for available electron acceptors?
How "bioavailable" are e-acceptors from solid phases?

Conventional wisdom: BTEX natural attenuation

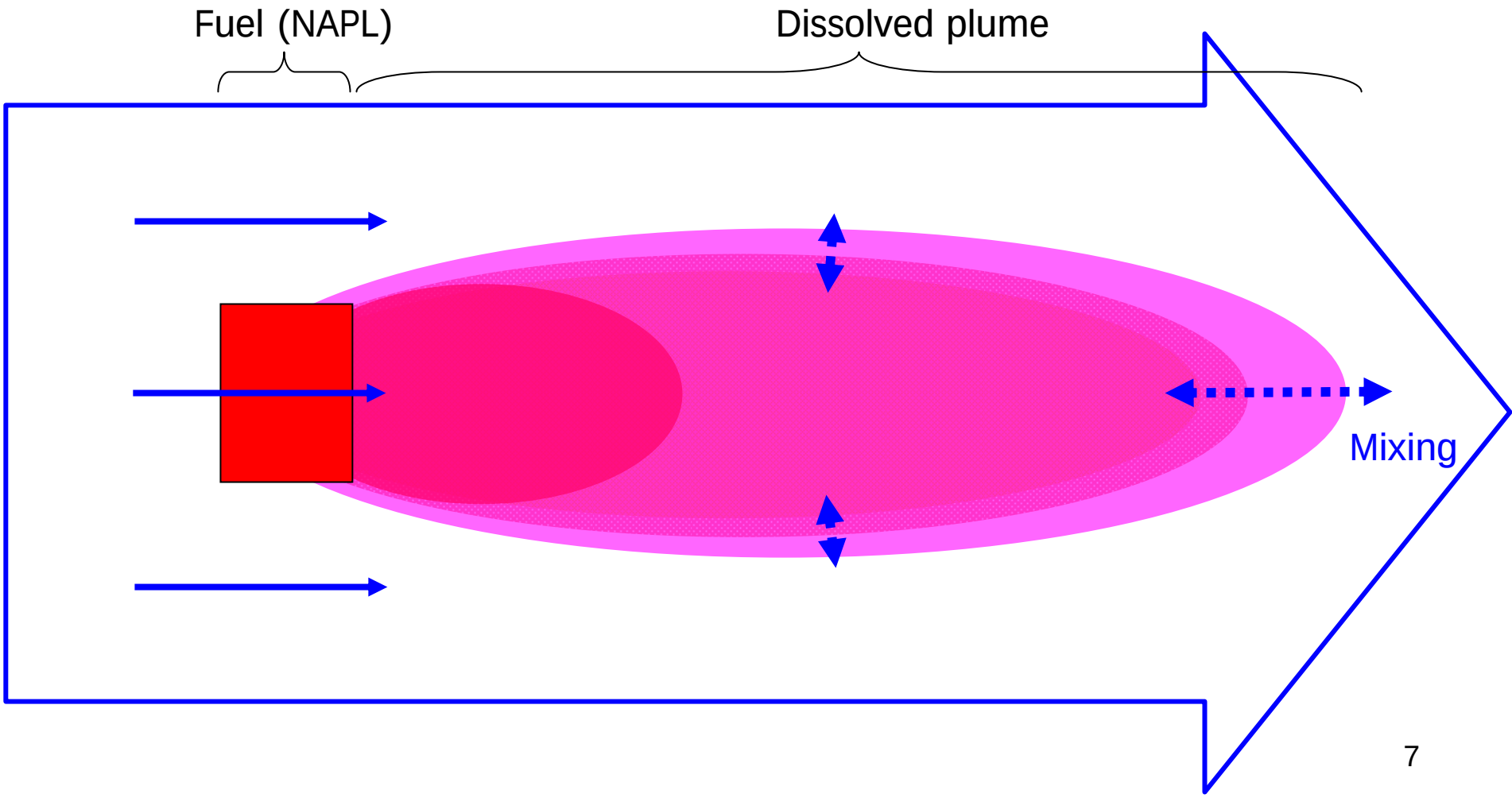
- EARLY: Initial plume growth from large source
- MID-TERM: Plume at maximum length, controlled by increasing rate of biodegradation and/or decreasing source release
- LATER: Plume shrinkage as biodegradation rate reaches maximum rate and source release stabilizes or decreases



Qs: Where in this sequence is any particular site at the time of interest?
Why not leave fuel residuals in place as long as plume stays short?

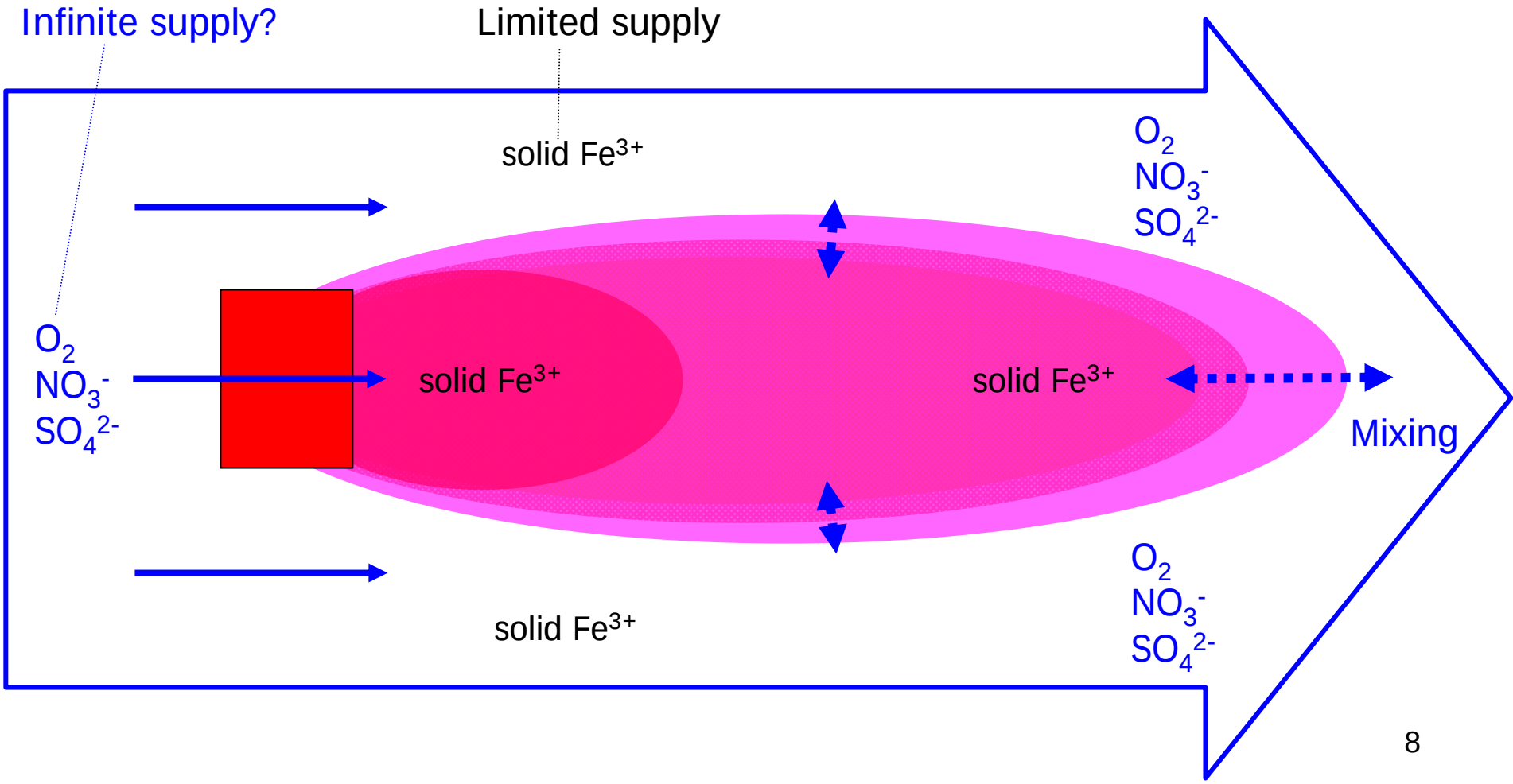
Expected flow and mixing

2D, Plan view



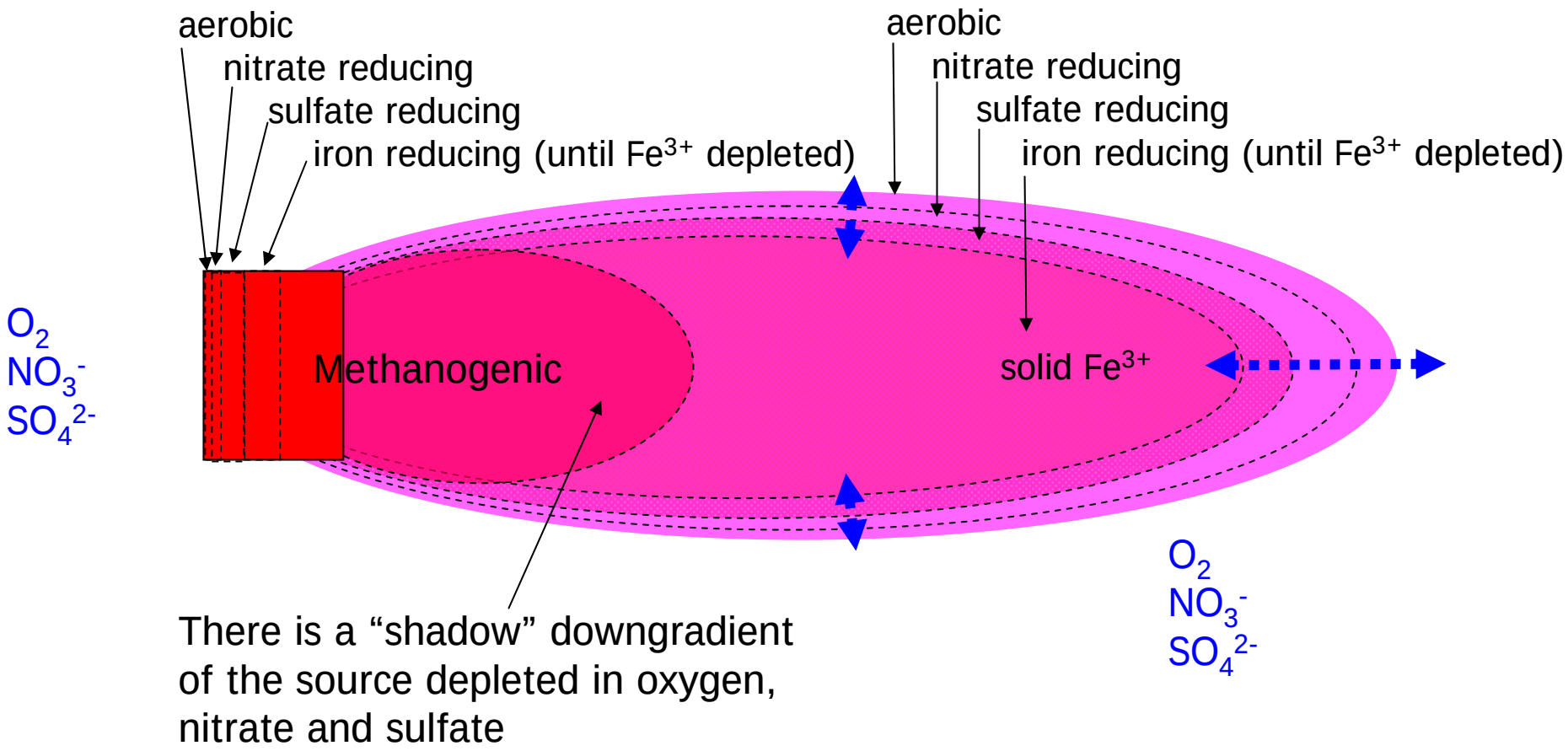
Available electron acceptors

Assume no bioavailable Mn^{4+}, NO_3^-, or SO_4^{2-} in solid phase
Assume flow is perfectly horizontal for the <u>plan view</u> shown below (no infiltration)

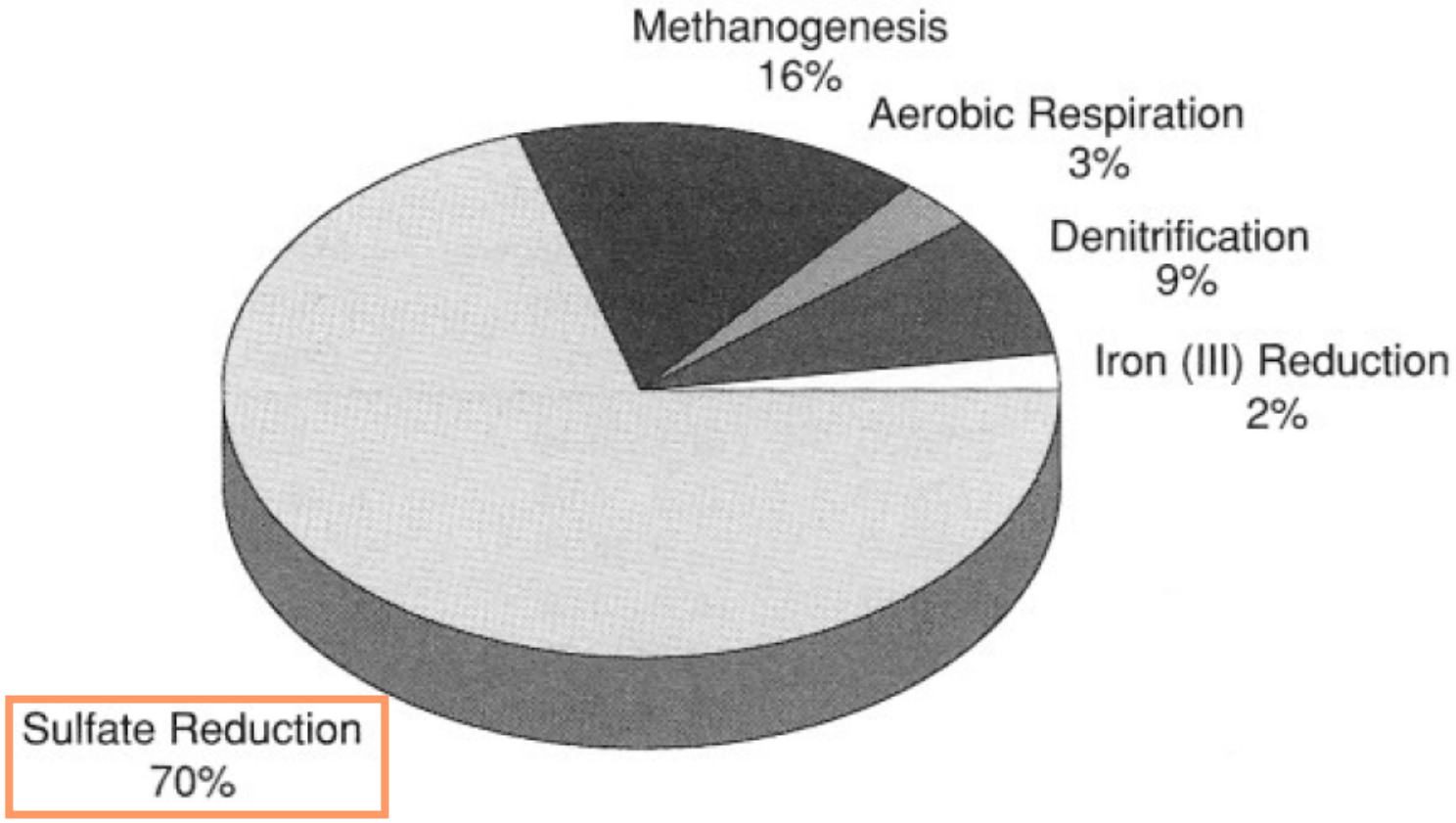


Expected locations of redox reactions

Assume no bioavailable Mn^{4+}, NO_3^-, or SO_4^{2-} in solid phase
Assume flow is perfectly horizontal for the <u>plan view</u> shown below (no infiltration)



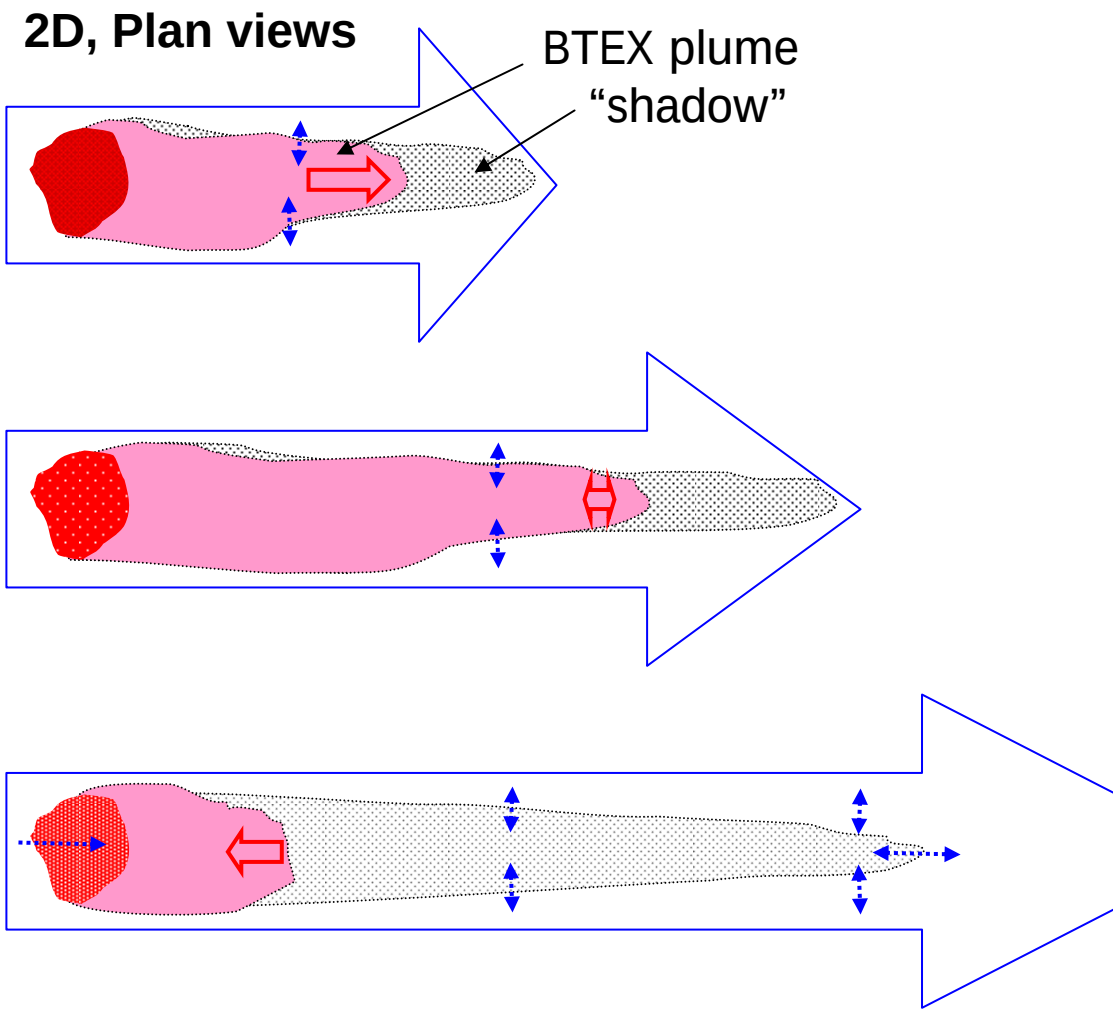
In U.S., biodegradation of fuel contaminants in groundwater is accomplished mostly by sulfate-utilizing microbes



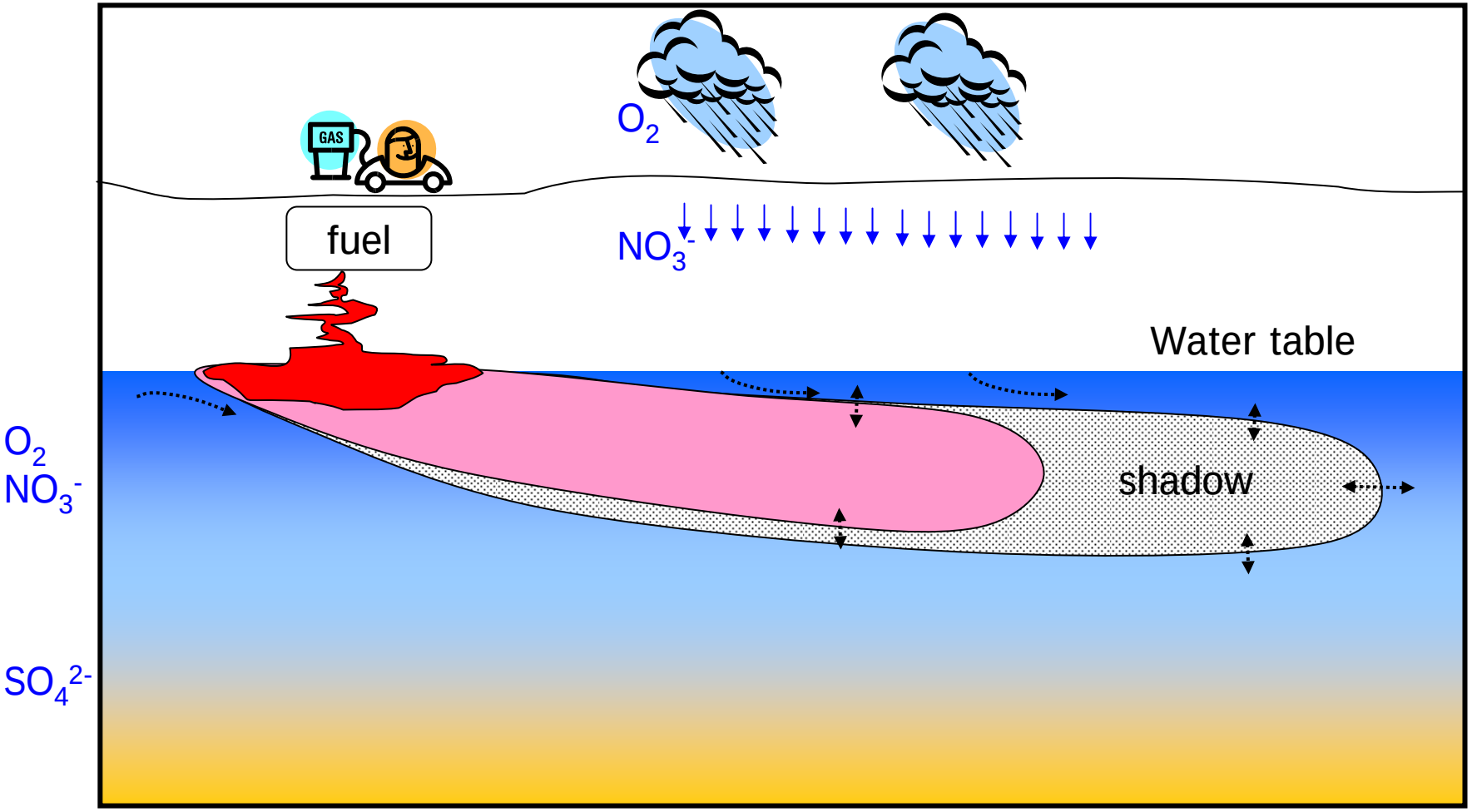
Wiedemeier et al., 1999

Refined 2D cartoon: BTEX natural attenuation

- EARLY: Initial plume growth from large source; zone of depleted electron acceptors (“shadow”) migrates faster than BTEX
- MID-TERM: BTEX at maximum length, anaerobic shadow still growing
- LATER: BTEX plume shrinkage; anaerobic shadow may stabilize as electron acceptors are mixed in at edges or end



These are 3D problems! Simple case:



Implication: expect vertical variations in available electron donors

How can we use this understanding?

- Let's consider a fuel spill case from Thailand, slides courtesy of Tim Buscheck of Chevron Technology Company
  - Buscheck, Harding, Hoelen, Mackay and Sublette. Application of molecular biological tools for benzene biodegradation in Southeast Asia. Battelle Sixth International Conference on Remediation of Chlorinated and Recalcitrant Compounds. Poster to be presented May 19, 2008; Monterey, CA.

Chonburi, Thailand Site

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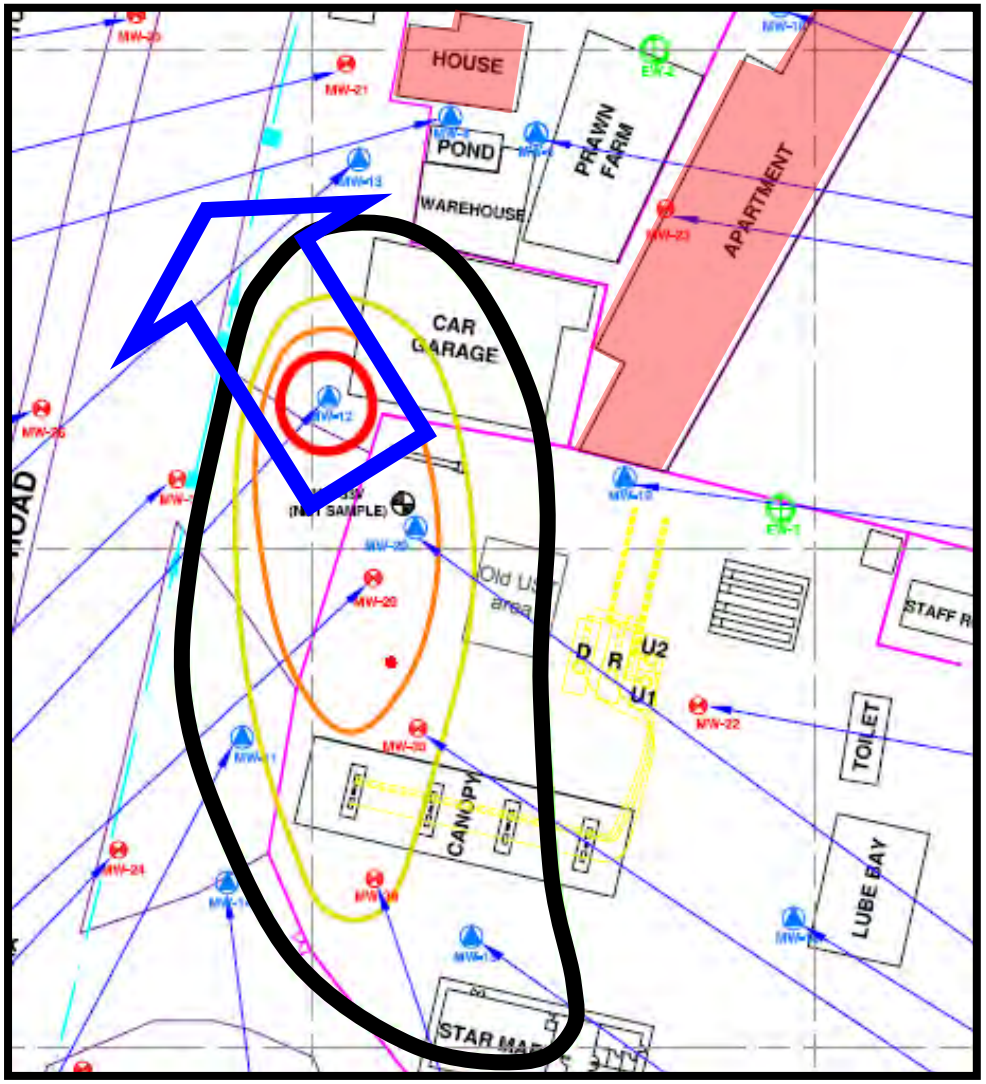
- Kerry Sublette, U. Tulsa

Adapted from Tim Buscheck, Chevron Energy Technology Company, 2007, with permission

Groundwater flow and benzene contamination



Houses and apartments immediately next to site, so “natural attenuation” not protective enough

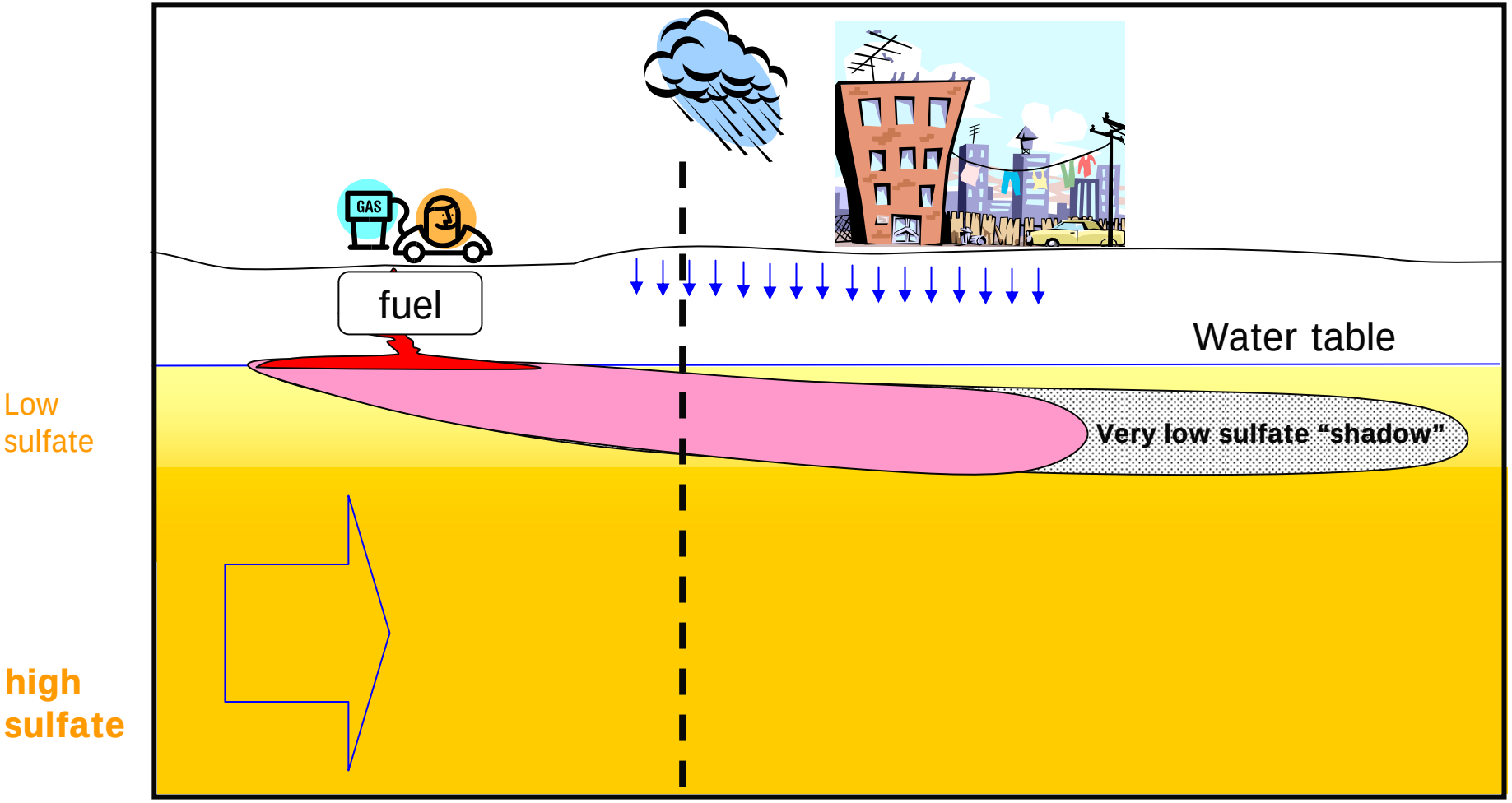
Note: groundwater flow direction is variable; blue arrow denotes approximate average flow direction

Adapted from Tim Buscheck, Chevron Energy Technology Company, 2007, with permission

Findings to date: Chonburi

- Sulfate is the predominant electron acceptor
- Sulfate lower where fuel contamination is present
- Benzene is biodegrading under sulfate reducing conditions
  - CSIA (compound specific isotope analysis)
  - Biotraps (showing incorporation of ^{13}C in biomass)
- Current benzene biodegradation apparently too slow to prevent off-site migration
- Remediation options being considered
- Sulfate is high <u>under</u> the plume

Conceptual model for Chonburi



Option based on understanding of site:
Mixing to access more "free" electron acceptor

Vertical recirculation

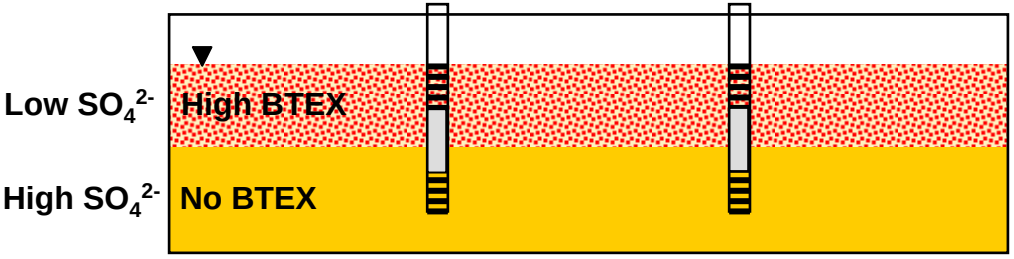
Such an approach assumes:

1) BTEX degradation rate would increase if sulfate concentrations were increased

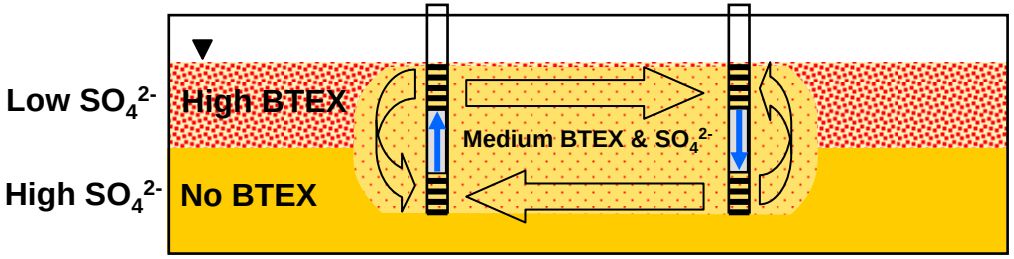
2) Vertical recirculation would induce mixing which should bring more sulfate in contact with BTEX and thus possibly raise degradation rate

Vertical section
(regional flow into page)

Before recirculation



During recirculation



At many fuel release sites

- There is enough distance along flowpath for BTEX plume to naturally degrade to below levels of concern

- These sites are often managed by an approach called "Monitored Natural Attenuation" (MNA)
  - Periodic monitoring to confirm that natural biodegradation is still working to keep plume from presenting risks

MNA use at fuel release sites in California

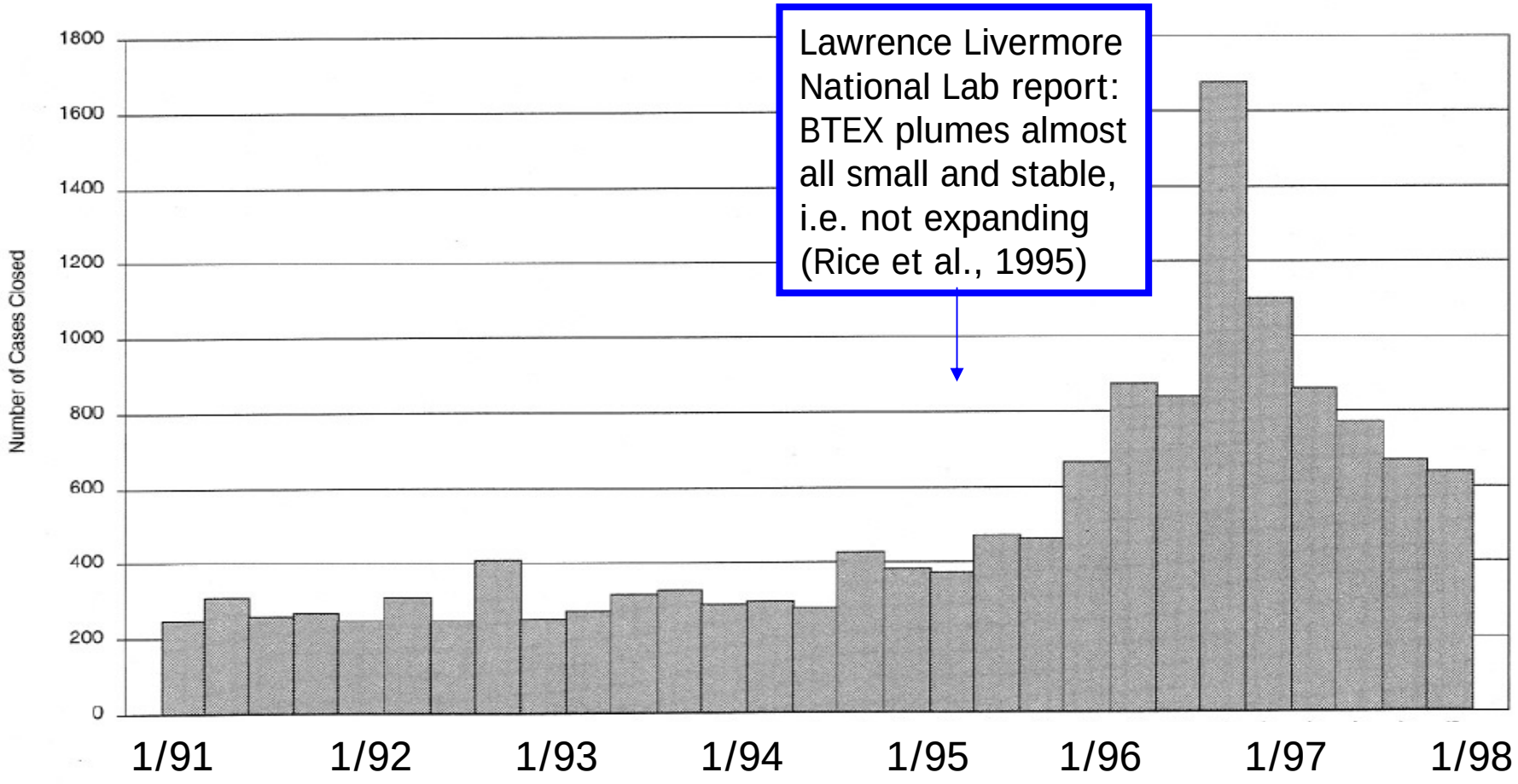
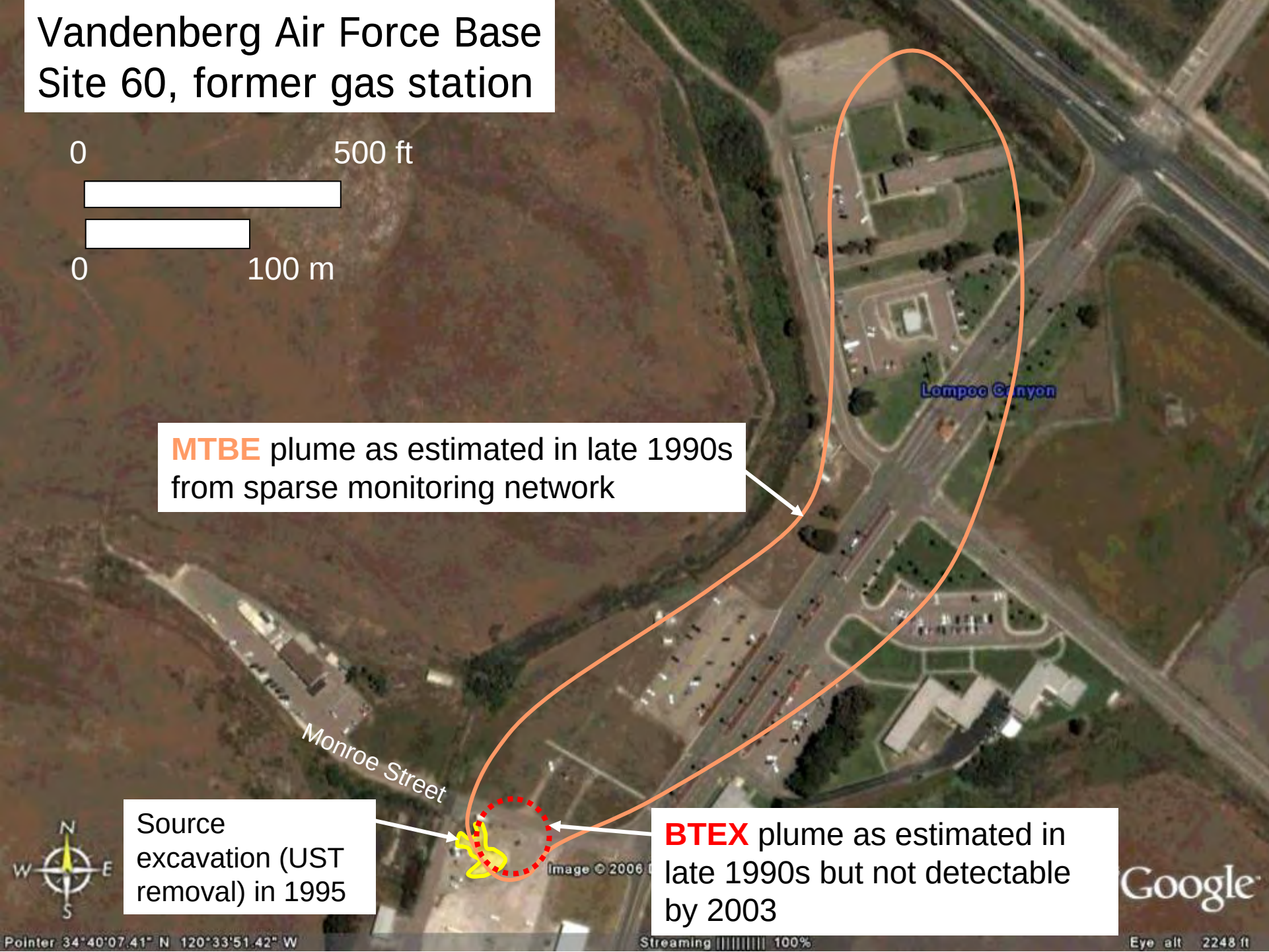


FIGURE 1-4 Closure of leaking underground storage tank cleanup projects in the state of California, January 1, 1991, through January 1, 1998. SOURCE: James Giannopoulos, California Water Resources Control Board, Sacramento, California.

National Research Council, 2000


Vandenberg Air Force Base
Site 60, former gas station
0
500 ft
0
100 m
MTBE plume as estimated in late 1990s from sparse monitoring network
Lompoc Canyon
Monroe Street
Source excavation (UST removal) in 1995
BTEX plume as estimated in late 1990s but not detectable by 2003
Image © 2006
Google
N
W
E
S
Pointer 34°40'07.41" N 120°33'51.42" W
Streaming 100%
Eye alt 2248 ft

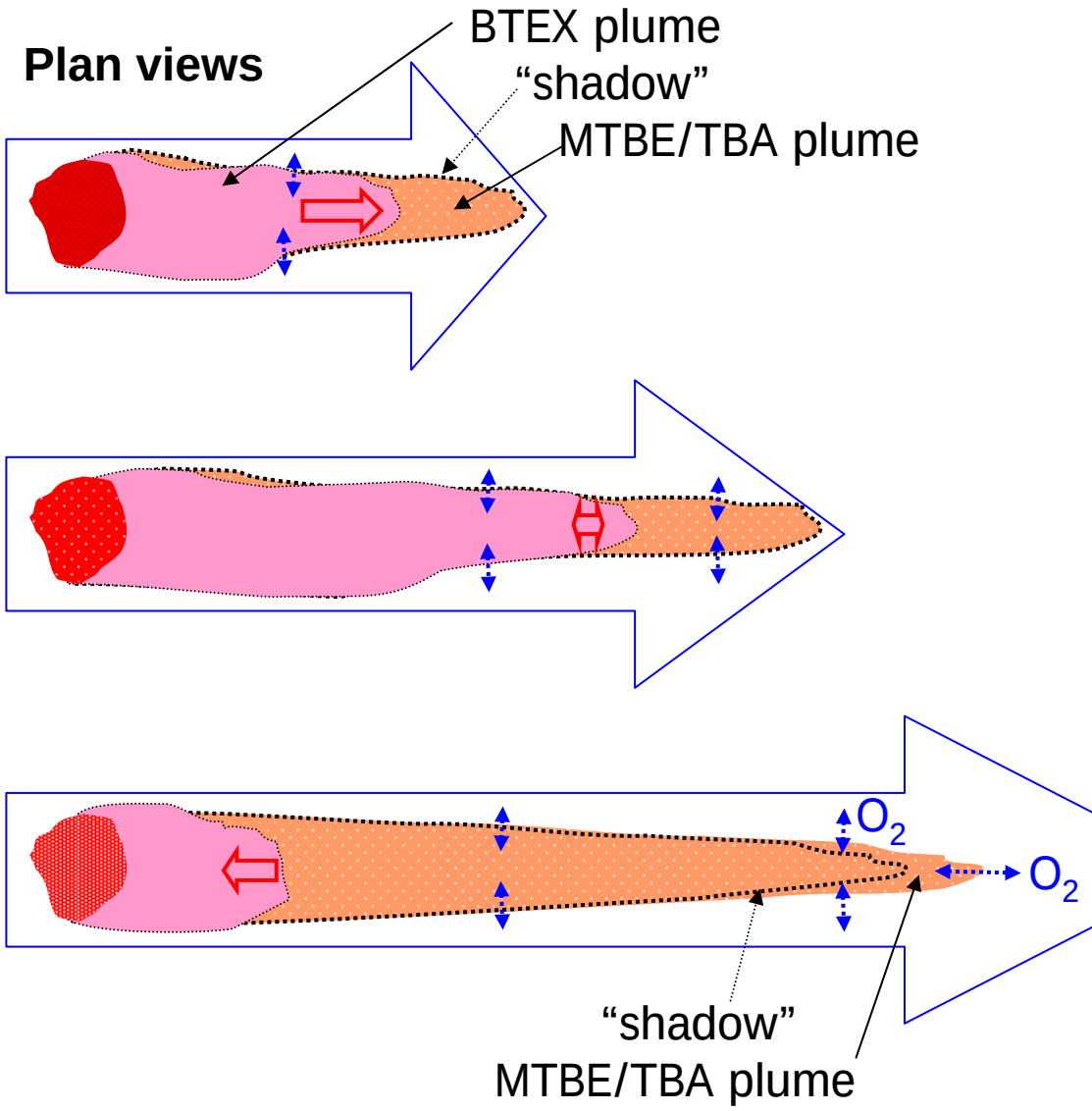
Oxygenated gasoline

- Oxygenates of most concern to date:
  - MTBE: methyl tert-butyl ether
  - TBA: tert-butyl alcohol

- <u>From years of research we now know</u>:
  - Under anaerobic conditions:
    - MTBE biotransformation to TBA can occur, if strongly reducing (i.e. methanogenic)
    - Some MTBE may escape the methanogenic zone
    - So a mixed MTBE/TBA plume can emerge from the methanogenic zone and migrate down the “shadow” where electron acceptors are depleted
    - Neither MTBE nor TBA degrade very rapidly (if at all) under less strongly reducing (anaerobic) conditions, so even if sulfate and nitrate mix into the shadow, no significant effect on MTBE/TBA is anticipate
  - Under aerobic conditions, both MTBE and TBA are degradable
    - But aerobic conditions are rare at gasoline-contaminated sites

Refined cartoon: BTEX/MTBE/TBA natural attenuation

- EARLY: Initial plume growth from large source; MTBE faster than BTEX moving within shadow
- MID-TERM: BTEX at maximum length, MTBE still growing along shadow
- LATER: BTEX plume shrinkage; MTBE plume persists along shadow, but may degrade at edges or end if there is oxygenated groundwater which is mixed in



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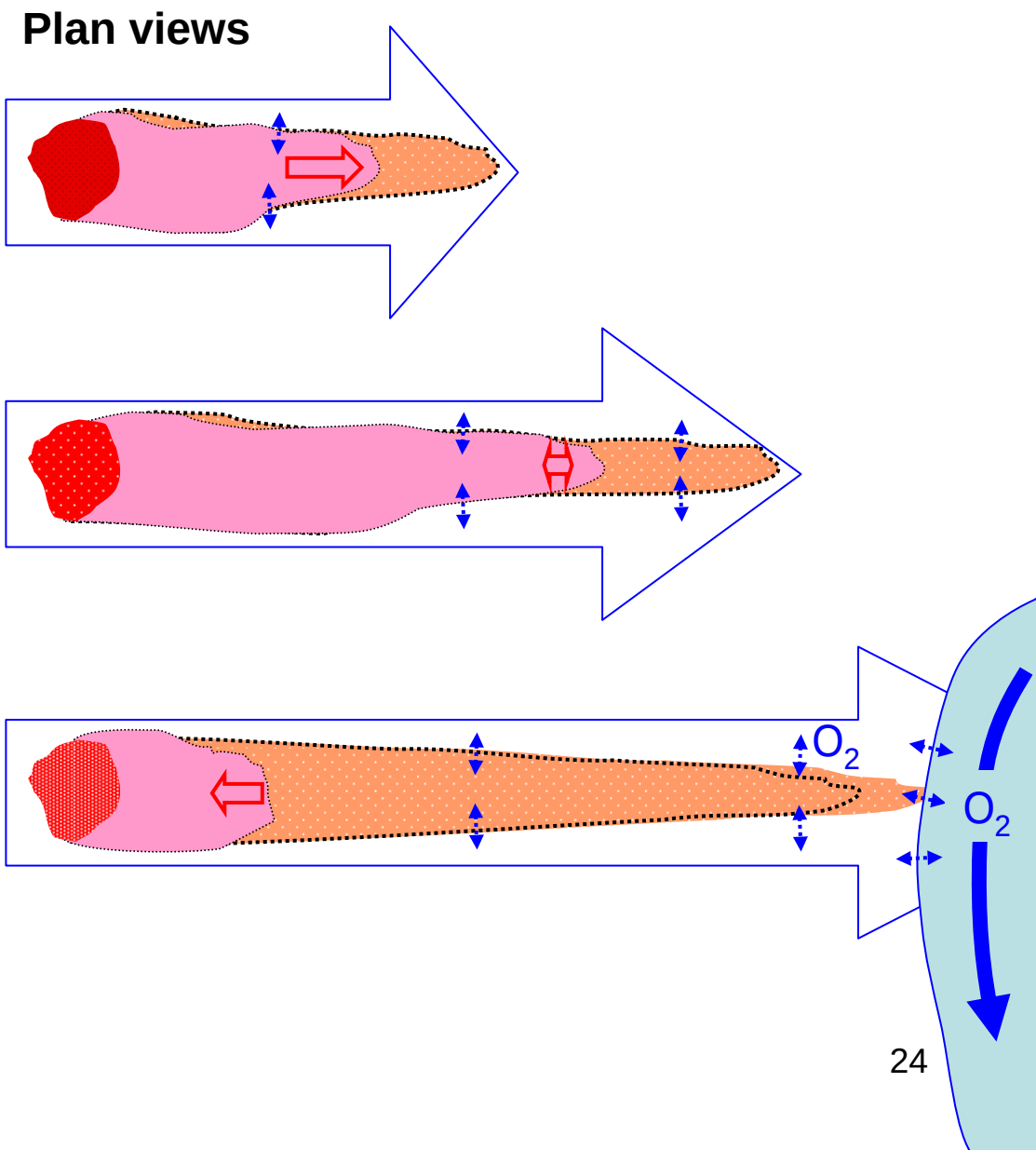
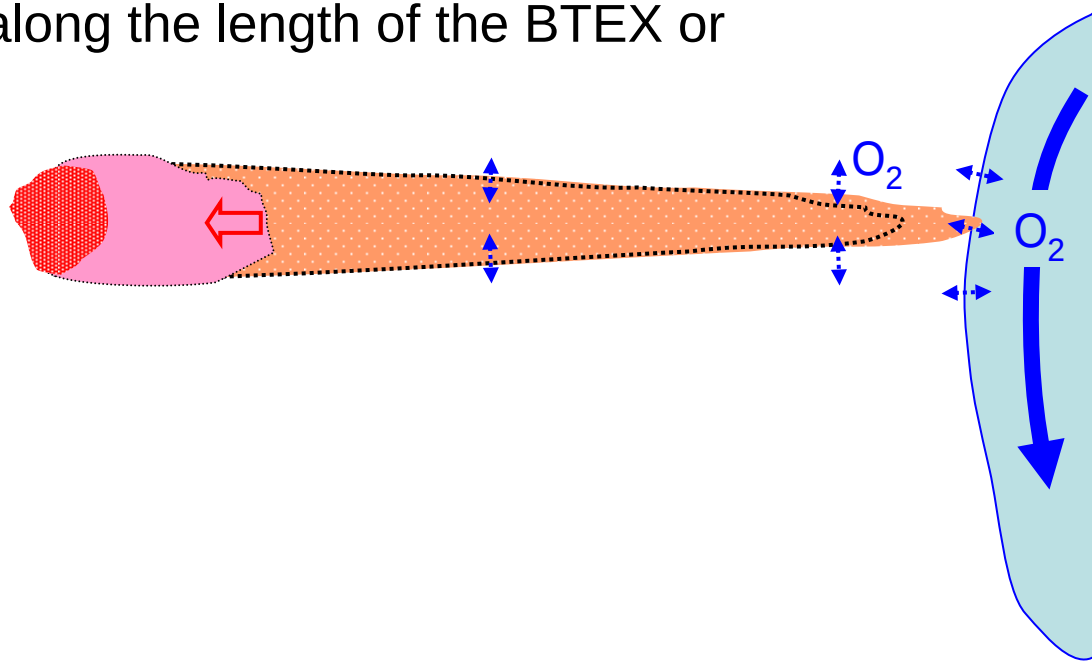


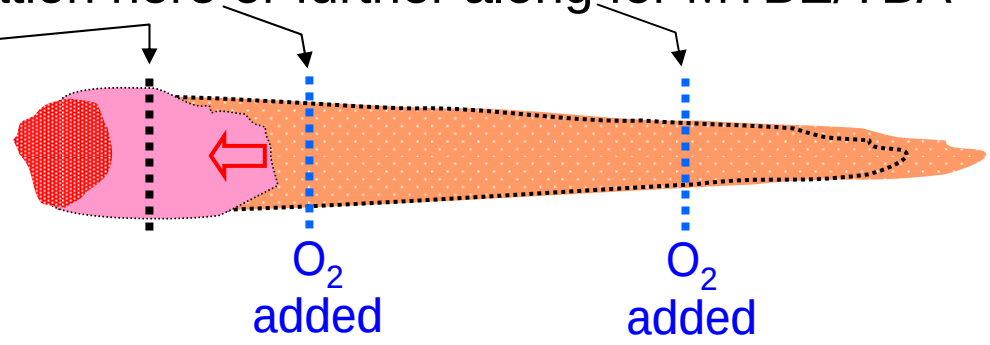
How can we use this understanding?

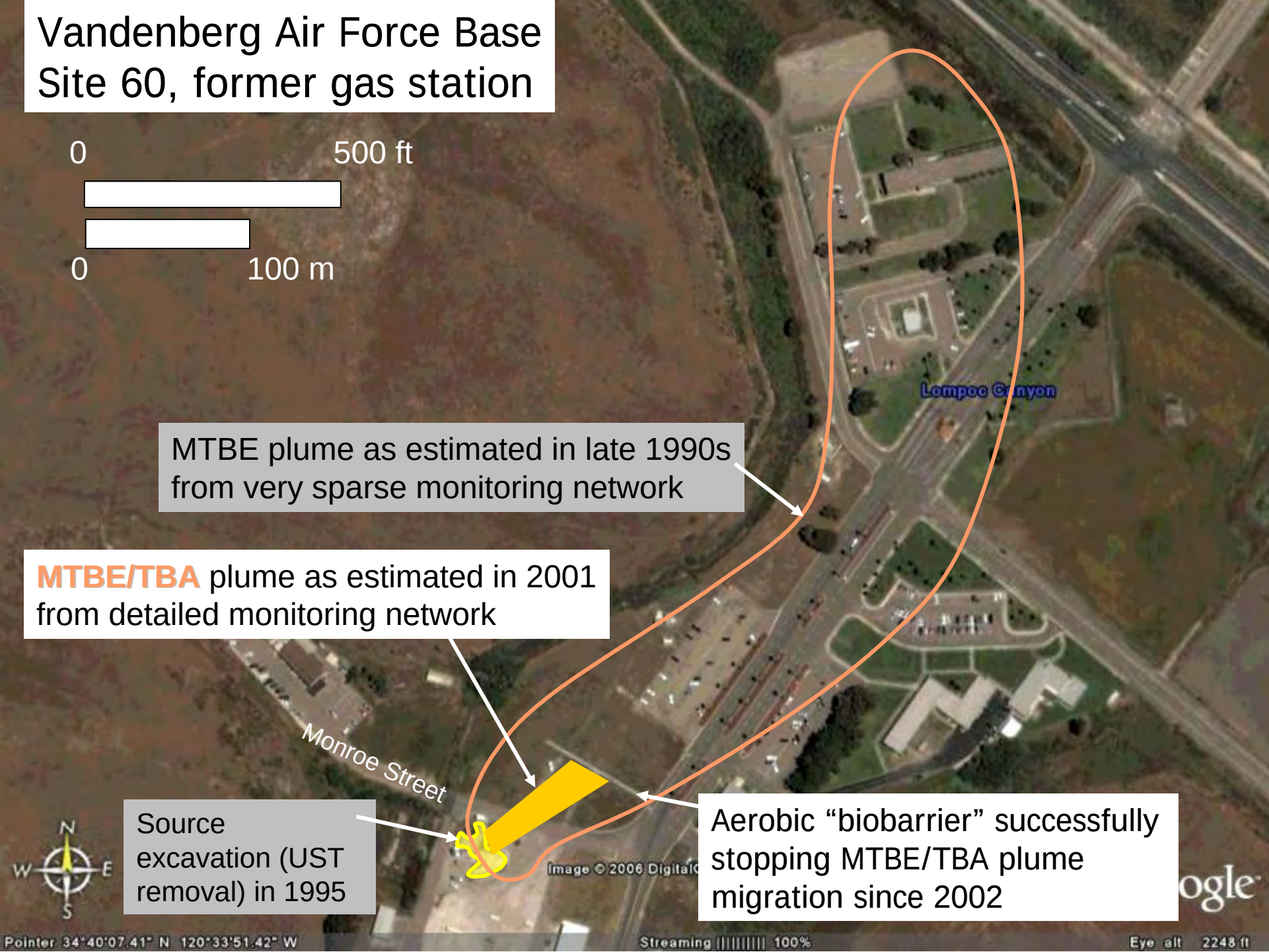
- Use MNA approach <u>IF</u>
  - Source area is naturally degrading and presents no risk
  - MTBE/TBA plume is degraded enough to stabilize and stop growing
  - There is no risk posed along the length of the BTEX or MTBE/TBA plume



How can we use this understanding?

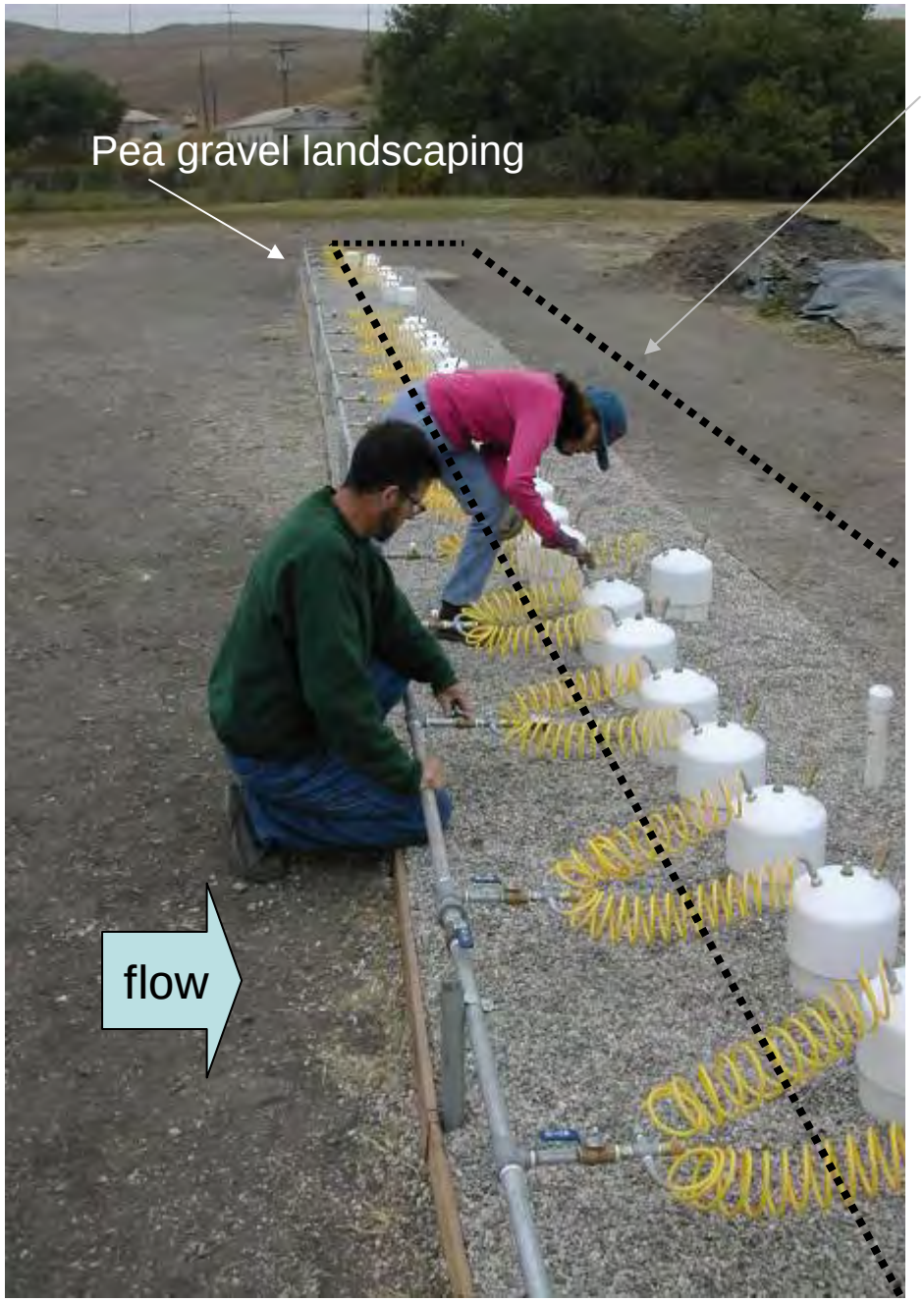
- Remediate for plume migration control IF
  - Source area is naturally degrading and presents no risk
- However, avoid disturbing the natural strongly anaerobic degradation zone which is treating BTEX
  - Use aerobic bioremediation here or further along for MTBE/TBA
  - But not here




Vandenberg Air Force Base
Site 60, former gas station
0
500 ft
0
100 m
MTBE plume as estimated in late 1990s from very sparse monitoring network
MTBE/TBA plume as estimated in 2001 from detailed monitoring network
Monroe Street
Source excavation (UST removal) in 1995
Aerobic "biobarrier" successfully stopping MTBE/TBA plume migration since 2002
Lompoc Canyon
N
W
E
S
Image © 2006 DigitalG
Pointer 34°40'07.41" N 120°33'51.42" W
Streaming 100%
Eye alt 2248 ft

Aerobic permeable biobarrier at Vandenberg AFB installed by IT/Shaw in 2002

Oxygen release wells were installed in a ~12' deep trench backfilled with pea gravel in saturated zone and covered with native media



Approximate area of trench backfilled with pea gravel

"Waterloo emitter"
www.solinst.com

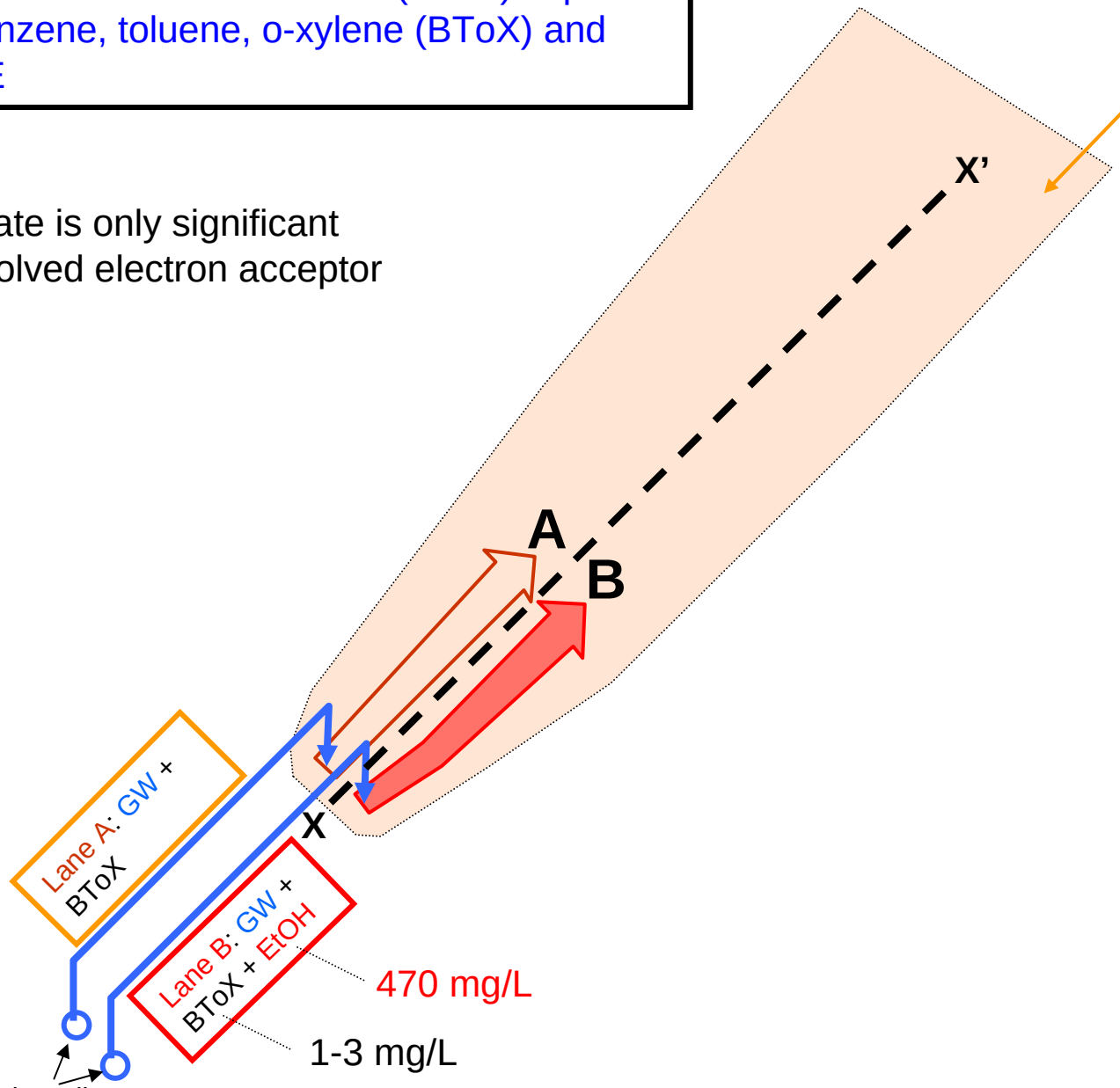
Gasohol

- Gasohol (gasoline containing ethanol) use is rising despite controversy

- Spills of gasohol have already occurred and will continue
  - High ethanol (EtOH) concentrations in groundwater are expected
  - Ethanol is more readily degradable than other gasoline components
  - Rapid, preferential degradation of ethanol *in situ* will
    - Consume most or all available dissolved electron acceptors
    - Create a more extensive or active methanogenic zone
    - Slow natural biodegradation of BTEX
    - Cause longer BTEX plumes, presenting more risk
    - Accelerate transformation of old MTBE spills to TBA

2004-2005 research: Ethanol (EtOH) impact on benzene, toluene, o-xylene (BToX) and MTBE

Sulfate is only significant dissolved electron acceptor



MTBE plume already present from original spill in 1990s

No significant BTEX remaining by 2003

Goals: 9 month injection:

Lane A

1) BToX degradation rate under sulfate-reducing conditions

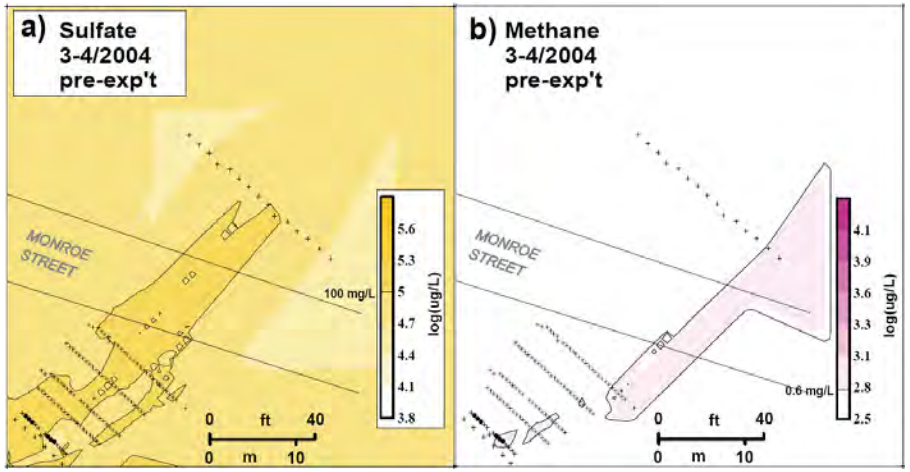
Lane B

1) BToX degradation rate when impacted by ethanol
2) MTBE transformation rate when impacted by ethanol

Mackay et al., Environmental Science & Technology, 40:19, 6123; 2006

Significant geochemical impacts

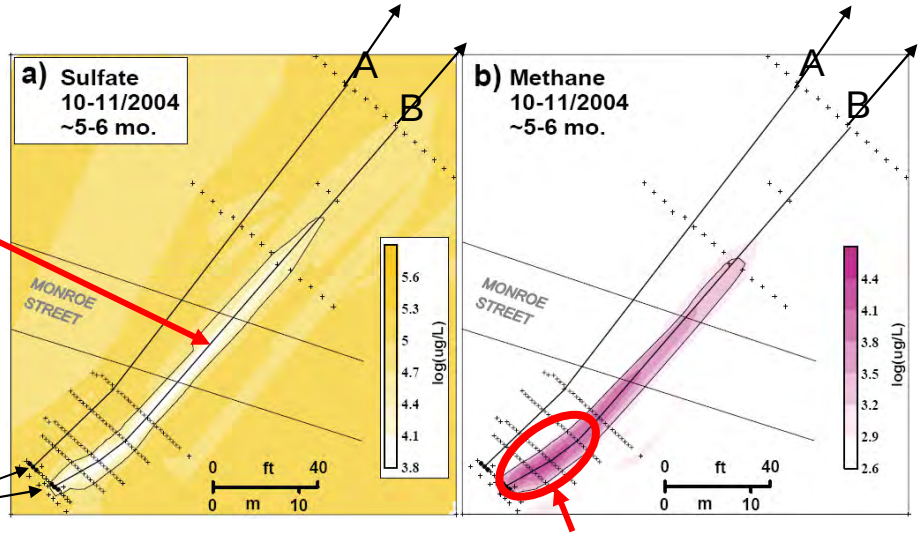
Sulfate **Methane**



Before expt

Sulfate ~100 ppm throughout,

Methane < 1 ppm, and only on east side



Sulfate-depleted "shadow"

Lane A: GW + BToX

Lane B: GW + BToX + EtOH

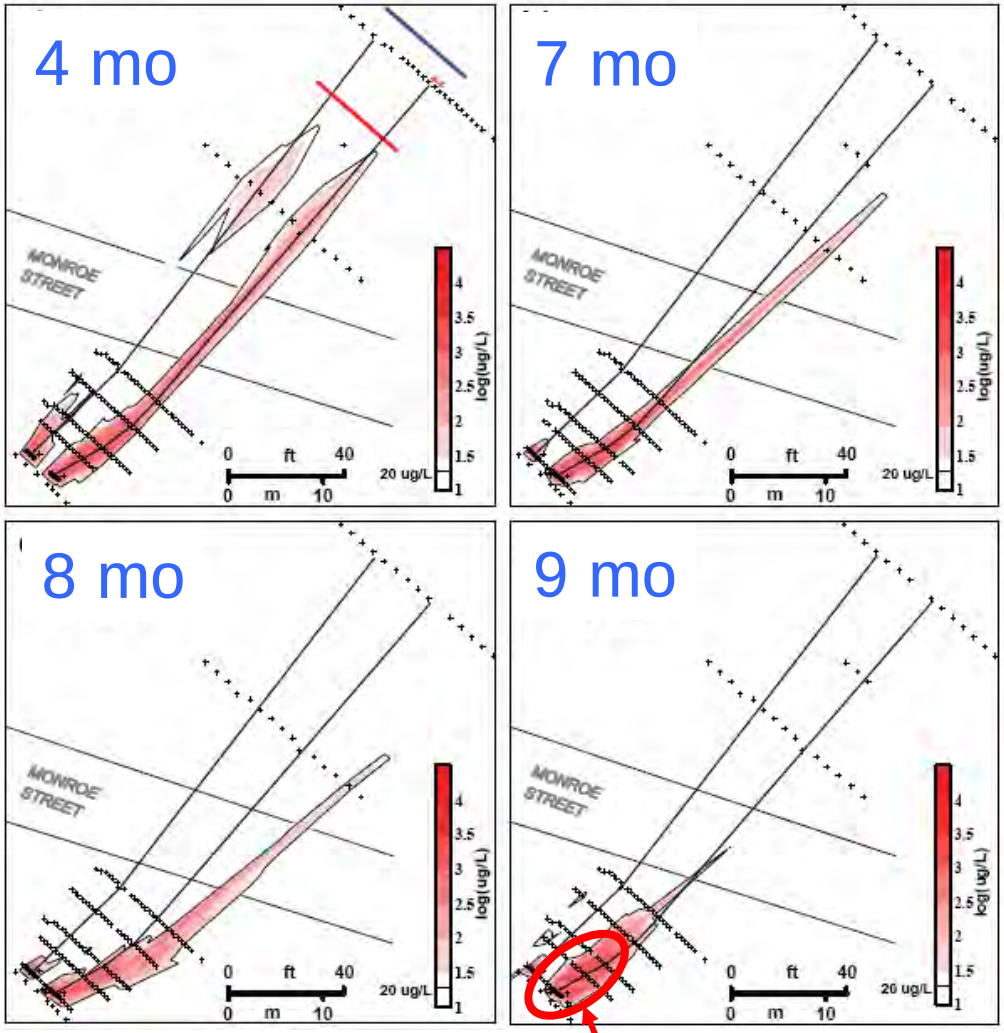
Methanogenic zone

During expt

Ethanol degraded immediately, consumed sulfate and generated a methane plume <u>and probably methane loss to unsaturated zone</u>

No sulfate depletion or methane generation in Lane A

Benzene fate impacted by ethanol



Methanogenic zone

Ethanol impacts:

- slower benzene degradation within sulfate-free shadow
- slower approach to steady state
- longer plume at steady state

Similar impacts on toluene and *o*-xylene

B, T, and oX results in a nutshell:

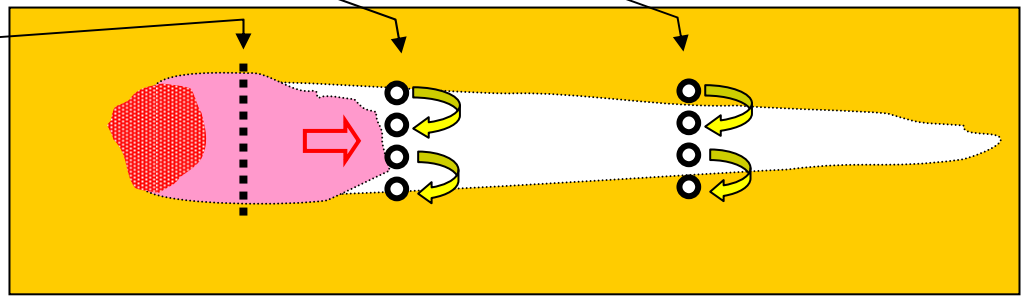
- degraded very fast along paths unaffected by ethanol since plenty of sulfate to support degradation

- degraded more slowly along paths impacted by ethanol, i.e. within the sulfate-depleted shadow
  - sulfate available only by mixing at edges
  - degradation rates slower within methanogenic zone

- disappeared rapidly after we stopped injecting ethanol (no more shadow!)
  - i.e. <u>no lasting impact of prior ethanol release on BToX natural biodegradation</u>

How can we use this understanding?

- At sites using/dispensing gasohol
  - Monitor for increase in methane generation or decrease in electron acceptors as early warning of gasohol leaks
- Reduce or eliminate elongating BTEX plumes by inducing mixing to take advantage of “free” electron acceptors (i.e. those outside ethanol impacted pathway)
- However, avoid disturbing the strongly anaerobic degradation zone treating BTEX
  - Use lateral or vertical mixing here and/or further along for BTEX
  - But <u>not</u> here



Many remaining questions about gasohols and other biofuels

- Gasohol impacts on groundwater appear very different from those of gasoline
  - longer BTEX plumes, increasing risk
  - significant release of methane into soil zone and groundwater
- Other biofuels may have similar impacts, but perhaps to very different degrees
- Biofuel <u>additives</u> need to be studied
- Additional field research will be needed to build base of understanding we will rely on in future

Our proposal: A biofuels test site

- Vandenberg AFB Site 60 appears ideal
  - Shallow groundwater; easy and cheap to instrument
  - Relatively steady groundwater flow direction
  - Relatively steady and rapid groundwater flow rate
  - Typical geochemistry (sulfate-dominated)
  - Detailed understanding of site via prior research

- A <u>biofuels test site</u> would allow
  - rapid research
  - comparisons among biofuels and release scenarios
  - evaluation of monitoring and remediation approaches

Overall goals of a biofuels test site

- Understand natural attenuation processes, particularly biodegradation, for these new challenges

- For each type of biofuel now or soon in use
  - Define scenarios for which MNA may work
  - Define scenarios for which MNA may <u>not</u> work
  - Evaluate alternative remediation strategies that capitalize on new understanding

- For biofuels under development
  - Provide ability for rapid field screening of environmental behavior

Acknowledgments: 2004-2005 field experiments

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