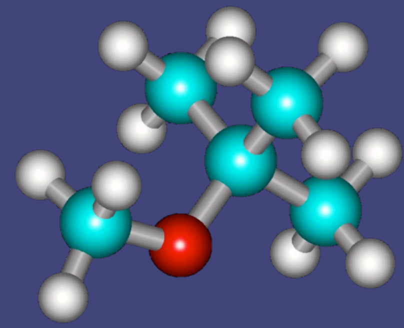

Technologies pour la réhabilitation des eaux souterraines polluées par le MTBE : Tendances et perspectives

Remediation technologies for MTBE-contaminated groundwater: Trends and new insights

intersol' 2007

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Environmental Resources Management - ERM

Villeurbanne, 30 Mars 2006

Outline of this Presentation

1. Fuel oxygenates & their characteristics
2. The MTBE problem
3. The regulatory framework
4. Remedial technologies
5. Trends & perspectives
6. Questions & answers

1. Fuel oxygenates & their characteristics

- **Additives for unleaded gasoline (post 1980s)**
  - Ethers and alcohols
  - Oxygenate: raise O_2 content of gasoline
  - Prevent “knocking”
  - Makes fuel burn cleaner
    - In winter when CO is a problem (in the US also called the winter oxy fuels)
    - “reformulated gasoline” in smoggy cities
  - Replaced the alkyl lead additives

Figure 2-1. Molecular Structures of Common Fuel Oxygenates

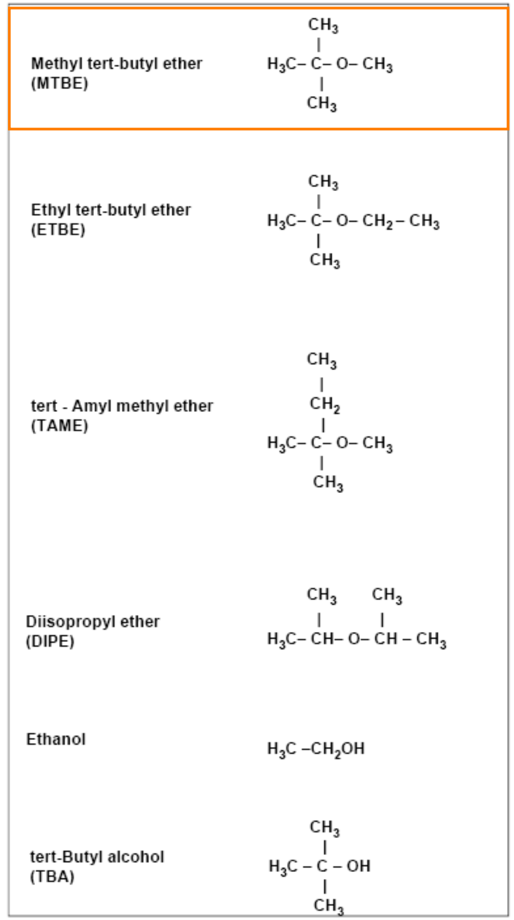


Figure 2-2. Physical Properties of Fuel Oxygenates Relative to Benzene

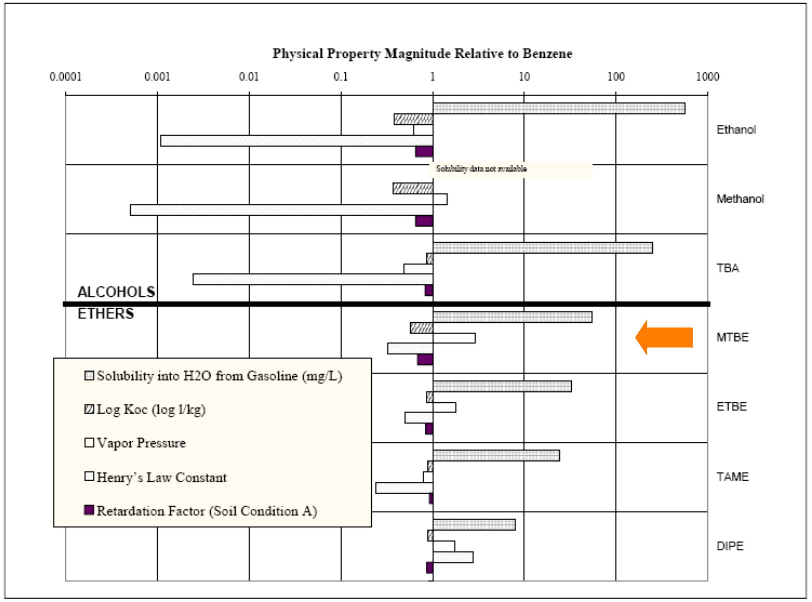
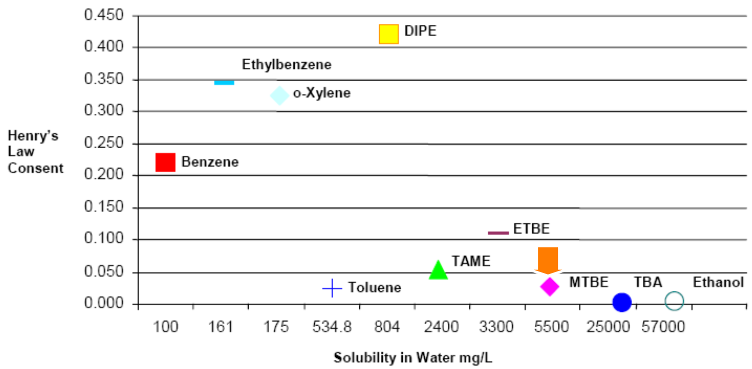


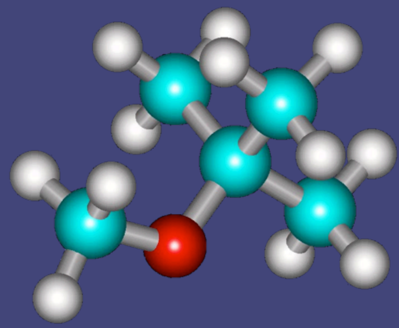
Figure 2-3. Relative Solubility and Henry's Law Constants for Selected Fuel Oxygenates (Henry's Law data for MtBE, TBA, and Benzene based on Zogorski et. al., 1997)

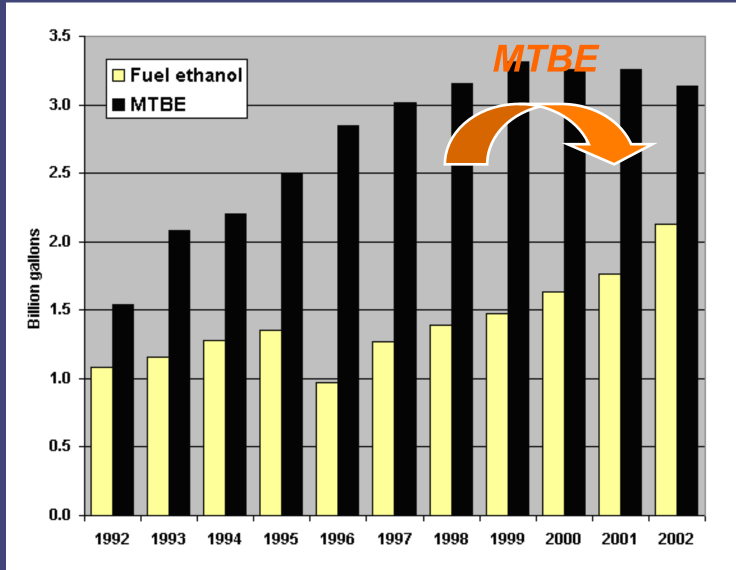


- MTBE is more soluble and volatile, the low Henry's constant makes stripping more difficult
- Lower K_{oc} makes adsorption on GAC more difficult
- MTBE has a low soil retardation, MTBE plumes can be larger than the traditional service station BTEX/oil plumes
- ***The oxygenate's properties do not only drive the risk assessment, they also steer the possible remedial design and strategies***

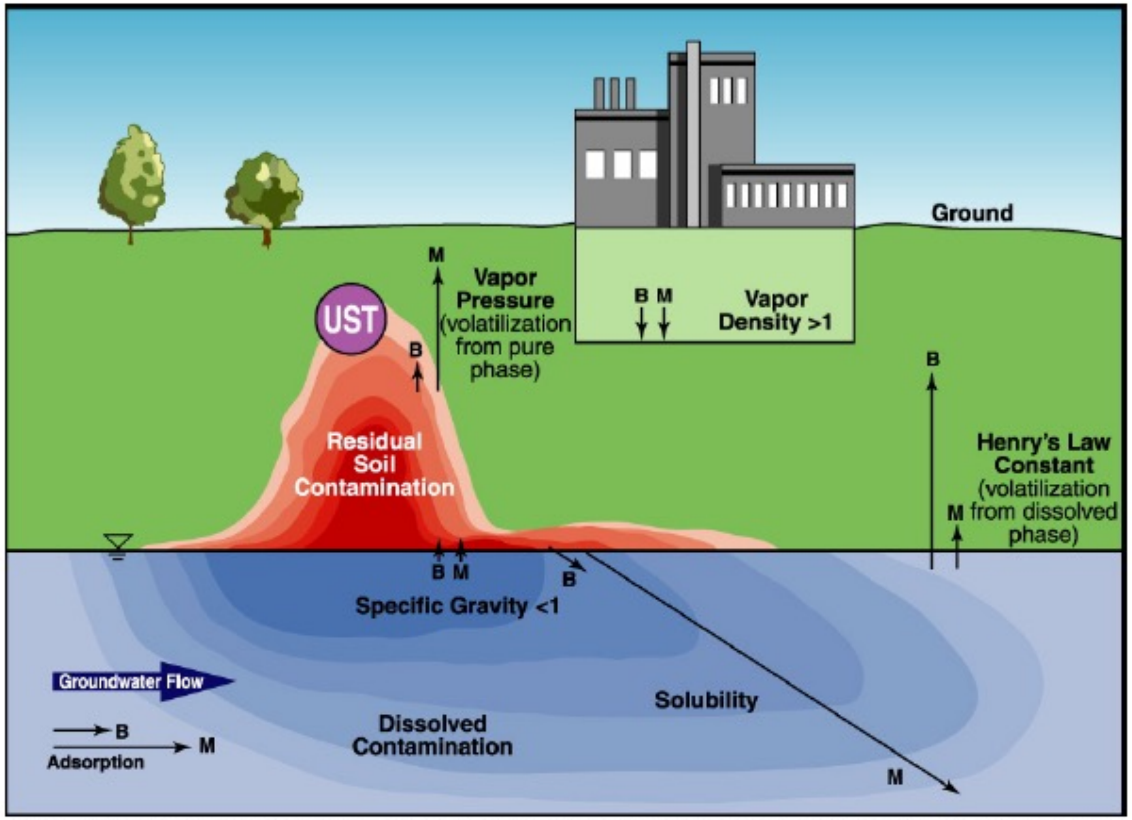
Methyl-Tertiary-Butyl-Ether (MTBE)

- MTBE is the most commonly used oxygenate, it is present in 80% of the oxygenated fuels
- MTBE has been used also in heating fuel and diesel fuel
- The use of ethanol as oxygenate is increasing
- Average MTBE content in gasoline 2,1% (1999)
- Flammable liquid with a distinctive, disagreeable odor (turpentine), the odor drives the low drinking water/remedial target levels





Methyl-Tertiary-Butyl-Ether (MTBE) : Fate & Transport



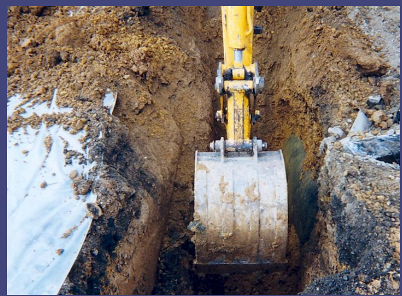
M = MTBE, B = benzene; length of arrow indicates relative significance of process; from Moyer and Kostecki (2003)

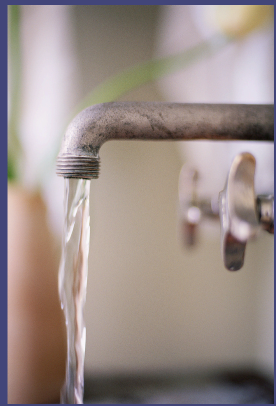
Figure 2-3. Relative fate and transport processes for MTBE and benzene.

Significant differences between benzene & MTBE

Possible exposure/risks to fuel oxygenates/MTBE

- Increased MTBE levels give the drinking water a bad taste/odor
- Touching the skin or breathing contaminated air while pumping gasoline
- Breathing exhaust fumes while driving a car
- Breathing air near highways or in cities
- Drinking, swimming, or showering in water that has been contaminated with MTBE
- No adverse human health effects





2. The MTBE problem

- **2,5 Million Tonnes of MTBE consumed in Europe (2003)**
- **Significant MTBE concentration variations within the EU countries gasolines**
- **Diffuse sources:**
  - US: 1.15 ton MTBE km²/ yr (Effenberger 2000)
  - Compare: Germany (1.13), Netherlands (2.4), Belgium (3.3)
- **Point sources:**
  - Industrial sites: Ranges from 0 – more than 7000 mg/L in groundwater
  - Gas stations: 30% exceeds remedial threshold (300 µg/L), 75% has an MTBE impact

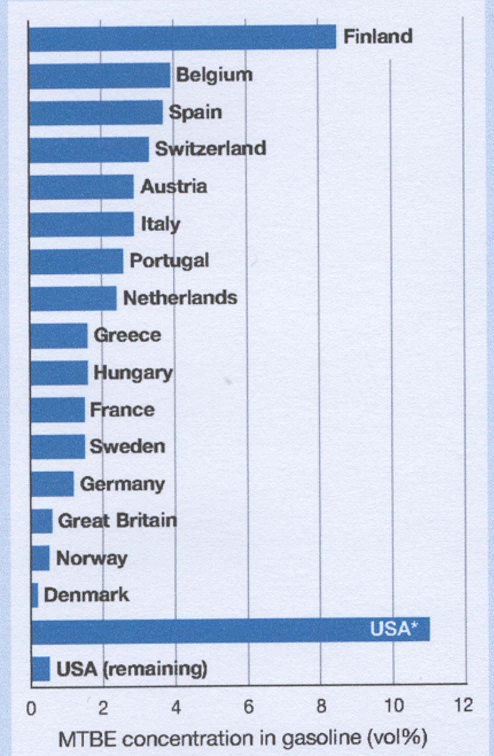


Fig. 1: MTBE is used as an antiknock agent in gasoline. The MTBE content of gasoline, indicated here are mean values from 1996/97, differs substantially among European countries. Furthermore, variations within each country may be of equal magnitude.
* = Regions in the US where a minimum content of oxygen in gasoline is required to curb traffic emissions.

3. The regulatory framework

- The regulatory framework for the fuel oxygenates is being implemented in Europe
- Significant variations within the ‘generic/accepted’ remediation norms for soil and groundwater within the EU member states (*see table*)
- US situation similar (*see figure*)
- Drinking water levels range from 5 to 300 µg/L MTBE

European MTBE norms or guidance values

Country	Soil (mg/kg dm)	Groundwater (µg/L)
Flanders (Belgium)	9 (residential) 140 (industrial)	300
Brussels (Belgium)	2 (residential) 30 (industrial)	300
The Netherlands	100	9,200
France	*Risk-based*	*Risk-based*
Germany	-	5-50 (not fixed)
UK	*Risk-based*	*Risk-based*
Spain	*Risk-based*	*Risk-based*
Italy	10 (residential) 250 (industrial)	10

The US situation

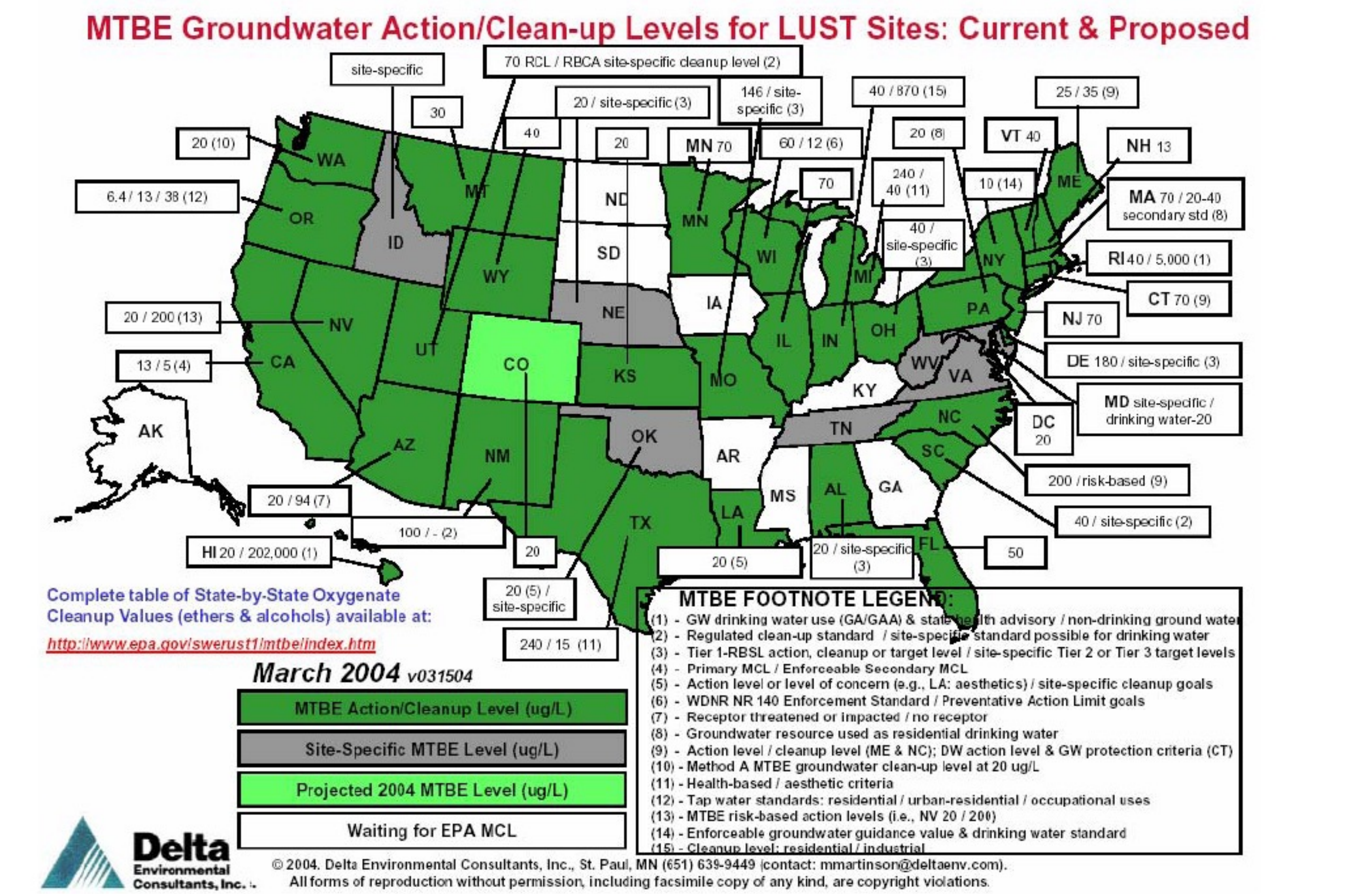
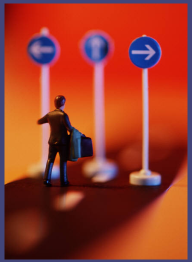


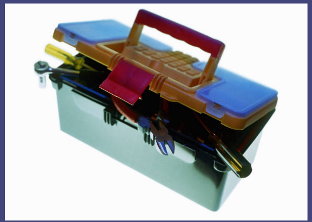
Figure 3-9. State groundwater action/cleanup levels for MTBE.
Reproduced with permission.

4. Remedial technologies for MTBE remediation



- Air sparging (AS)
- Soil vapor extraction (SVE)
- Multiphase extraction (MPE)

- Pump & Treat (P&T)
- In-situ chemical oxidation (ISCO)



- Bioremediation
- Monitored Natural Attenuation (MNA)

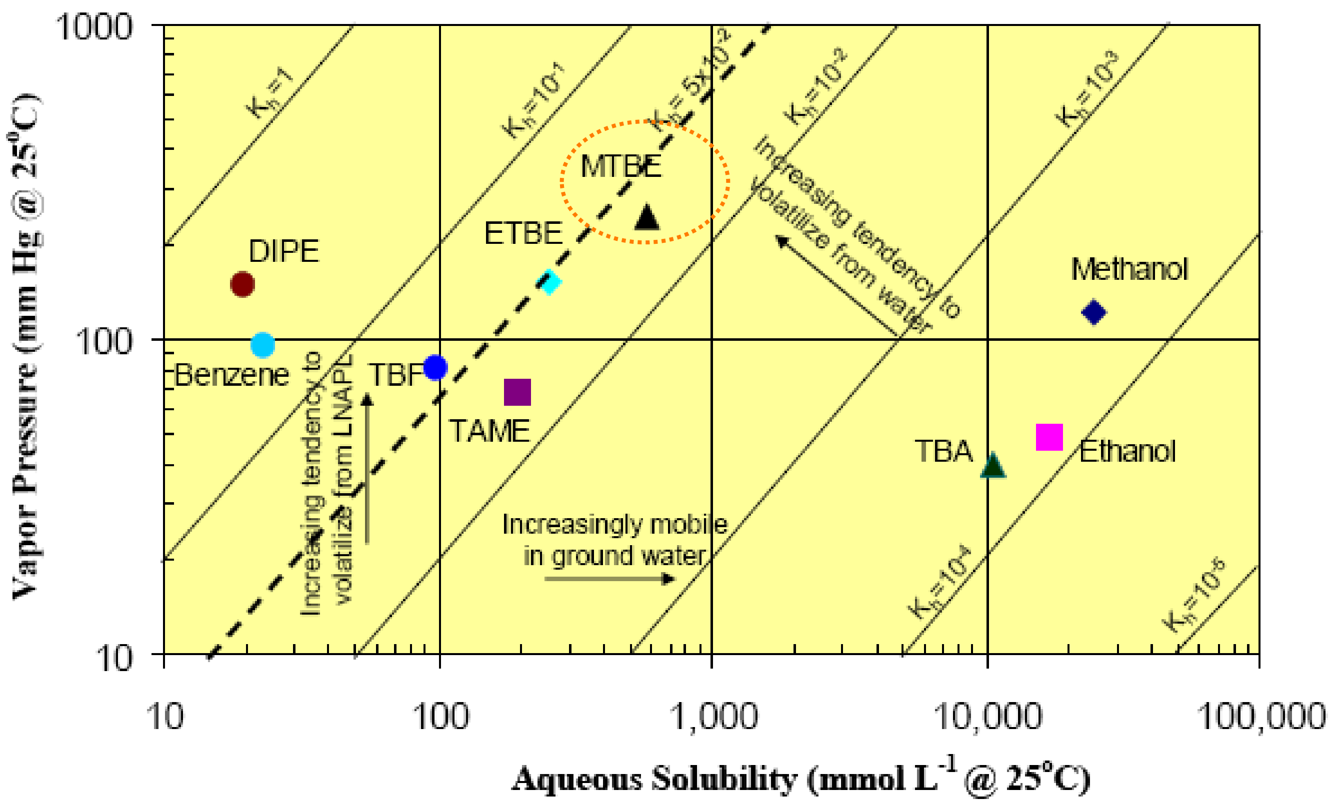
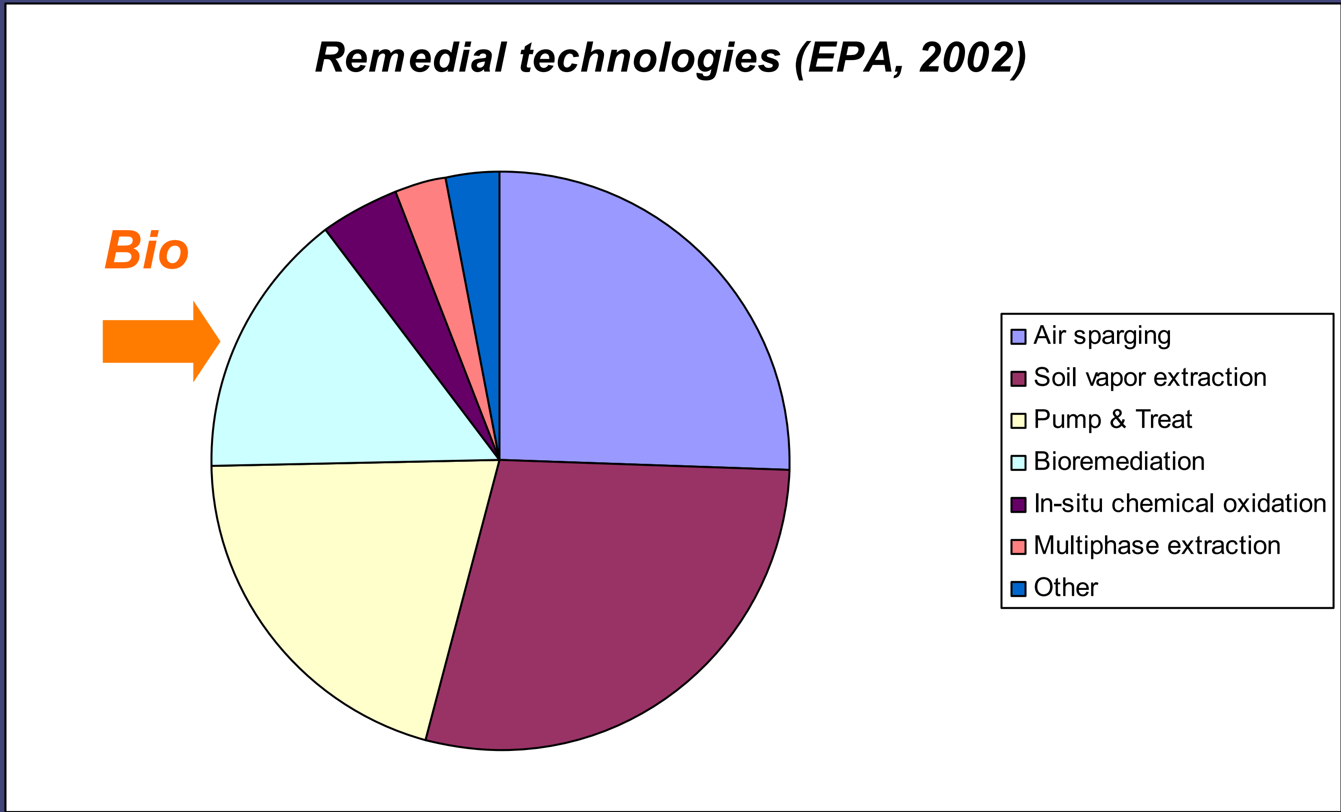


Figure 2-1. Plot of vapor pressure, aqueous solubility, and volatility as expressed in Henry's law.



***Observation** : the selected MTBE treatment technologies are closely linked to the oil/BTEX applied technologies, MNA as stand-alone approach not listed*

Table 3-4. Total Project Cost[1] Data for MtBE Remediation Technology Applications (127 Applications Providing Data)

Technology	# of Projects with Cost Data	Total Project Costs Reported ($)		
		Minimum	Median	Maximum
In situ Chemical Oxidation	2	$60,000	$103,000	$146,000
Bioremediation	30	$4,000	$137,000	$5,200,000
Soil Vapor Extraction	24	$14,700	$206,000	$4,600,000
Air Sparging	39	$13,700	$247,000	$1,050,000
Multi-Phase Extraction	2	$130,000	$257,000	$383,000
Pump-and-Treat	43	$65,000	$327,000	$4,000,000

Note:

1 For projects where more than one technology was used, cost information is presented under each of the technologies used for the project. Table includes total costs for completed projects, and costs to date for ongoing projects. Projects were of varying sizes, concentrations, and other site conditions. A summary of project-specific data for these technologies is provided in Appendix A.

2 Total project cost included more than just the treatment cost, such as cost for ancillary treatment processes, monitoring costs, or source removal costs. The costs summarized in this table have not been normalized to account for the types of cost components included, locations of the projects, or the time when the costs were incurred (inflation factors, see EPA 2001c). For a majority of the applications, reported costs were based on actual incurred costs. However, for some applications, costs were estimated as projected full-scale costs based on a scale up of pilot- or bench-scale projects.

Source: EPA, 2002a

***Observation* : Bioremediation and ISCO are generally cheaper alternatives**

Table 4-7. Relative costs and durations of remedial technologies for MTBE and TBA in groundwater

Technology	Character-ization	Capital cost (equipment and construction)	Operation and mainte-nance	Monitoring and reporting	Time-frame	Ability to control process	Primary limitations
Pump and treat	\$\$	\$\$–\$\$\$	\$\$–\$\$\$	\$\$	Months–years	High	Sensitive to discharge requirements
Air sparging	\$–\$\$	\$–\$\$	\$–\$\$	\$	Months–years	Moderate	Fine grain material; fugitive emissions
In situ bioremedia-tion	\$\$\$	\$	\$	\$\$–\$\$\$	Months–years	Low–moderate	Accurate delivery; mixing
In situ chemical oxidation	\$\$–\$\$\$	\$\$–\$\$\$	\$	\$\$	Days–months	Low–moderate	Accurate delivery; mixing
Phytoremedia-tion	\$\$	\$\$	\$–\$\$	\$\$–\$\$\$	Years	Low	Root depth and residence time; seasonality
Monitored natural attenuation	\$\$\$	\$	\$	\$\$\$	Years–decades	Low	Timeframe; going to completion (e.g., meeting cleanup goals)

Note: Table applies to dissolved-phase (plume) remediation and is not specific to source zones.

***Observation* : Site, project & regulatory specific constraints are key**

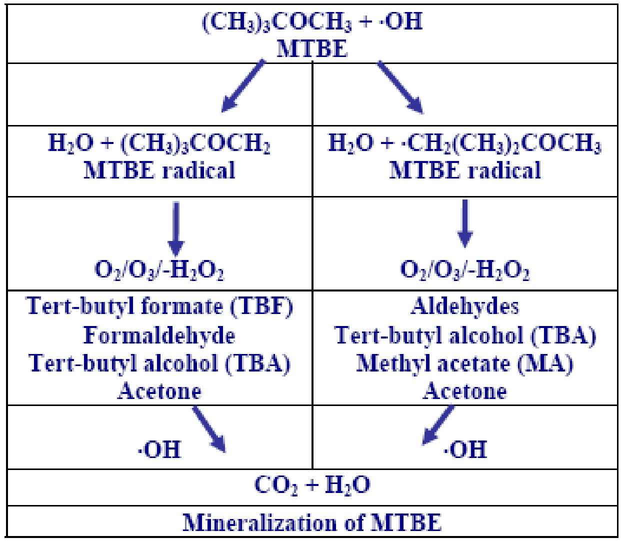


Figure 4-6. Example chemical oxidation products of MTBE.

ISCO works fast

Table 4-6. Summary of oxidants and their properties

Compound	Oxidation potential (volts)	Relative oxidizing power (Cl_2 = 1.0)	Effectiveness on MTBE and BTEX	Potential limitations
Hydroxyl radical[a] (Fenton's reagent)	2.8	2.1	Yes	pH, k-lower, temp
Sulfate radical[b]	2.6	1.9	Yes	Not widely used, catalysts not fully developed
Ozone	2.1	1.5	Yes	Capital equipment
Persulfate	2.0	1.4	Yes	Not widely used
Hydrogen peroxide	1.8	1.3	Yes	pH, k-lower, temp
Permanganate	1.7	1.2	No	k-lower, slower reaction

[a] Formed during Fenton's reagent process and as product of ozone application.
[b] Formed by activating persulfate with a catalyst.
Sources: Leethem 2002, McGrath and O'Reilly 2003, Cookson and Sperry 2002.

- **Remedial design**
  - Sequential or simultaneous approach for both the oil/ BTEX and the MTBE impacts
- **Remedial strategies:**
  - Source control and/or reduction
  - Receptor protection
  - Exit using MNA
  - Fast intervention needed in case of incidental release (fe. Zürich 1994 train incident, Switzerland)
- **Regulatory framework & stakeholders acceptance**

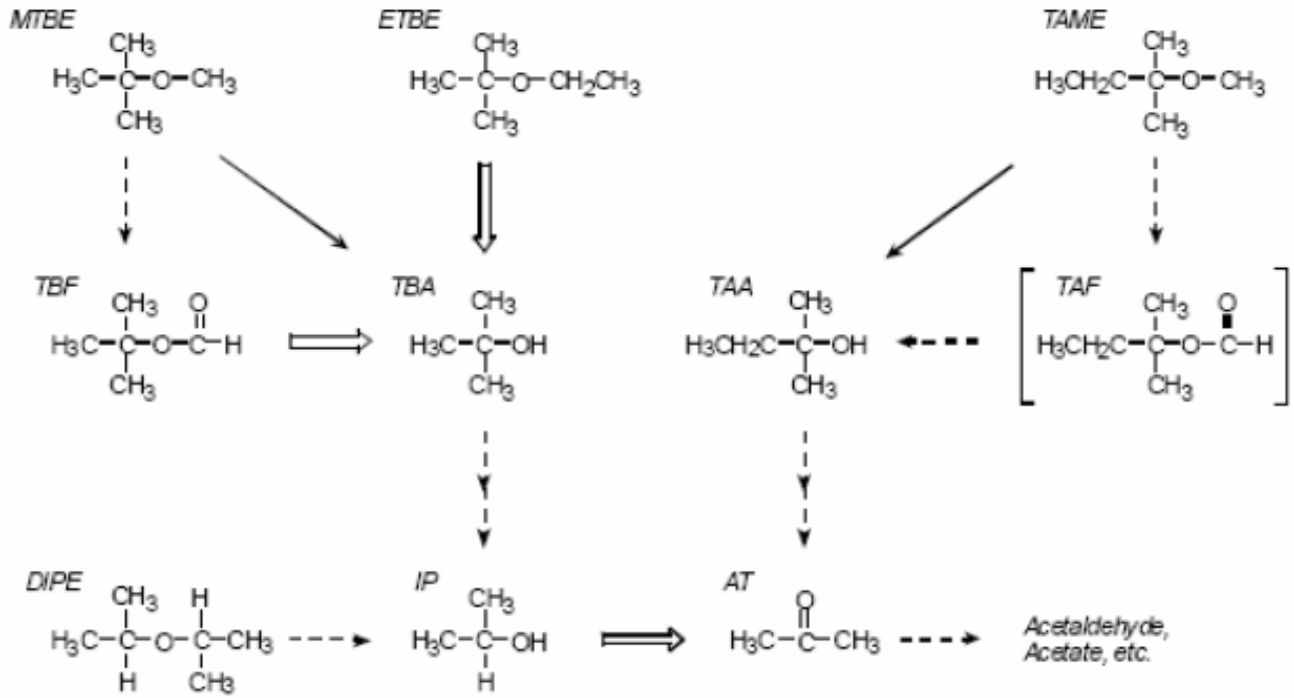
- Successful remediation is only possible after complete delineation given the mobility and recalcitrance of MTBE, and if needed, followed by feasibility testing
- The WWTU design for a P&T system is strongly driven by MTBE loading, pump rate and remedial target levels, GAC should be combined with strippers, bioreactors/filters and peroxide/UV are becoming BAT alternatives

5. Trends & perspectives

- **Risk based remediation & exit strategies**
- **Bioremediation is gaining terrain fast**
  - More positive Lab/Field pilot test data occurring
  - Successful project closures obtained within a relatively fast time span
- **Acceptance of MNA application is increasing**

MTBE degradation

Figure 4.4-1. Proposed Degradation Pathway of MtBE and Other Oxygenates (Church and Tratnyek, 2000)



6. Questions & answers

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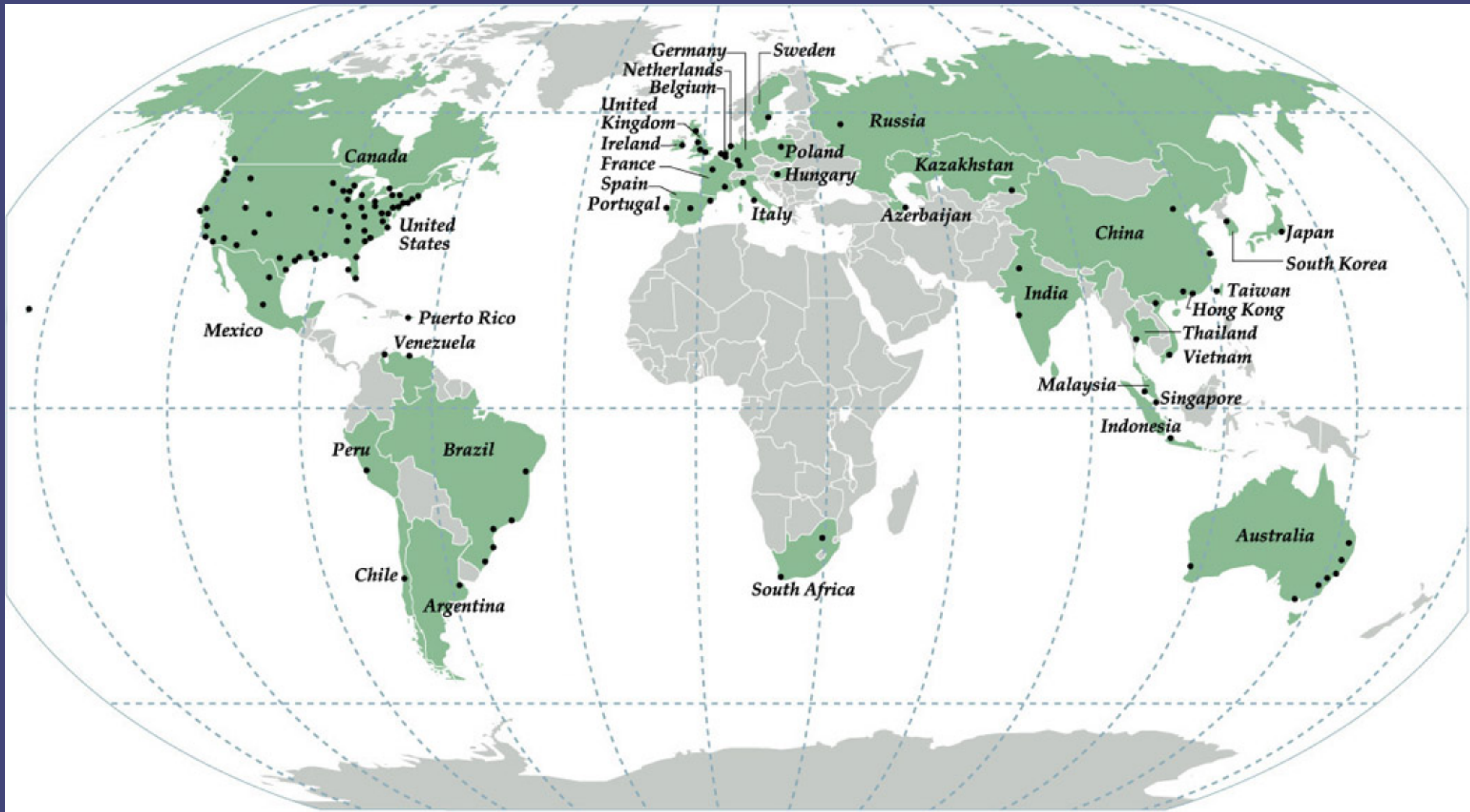
ERM Services Portfolio

Strategic Advice	Development Impacts & Planning	Managing Liabilities & Risks	Managing Contaminated Sites	Permitting & Technical Work
Social & environmental performance Climate change, biodiversity, natural resources Policies for sustainable development Strategies to manage risks, liabilities and EHS costs	Strategic and economic assessments Environmental planning and environmental impact assessments Environmental mitigation actions Social impact assessment & Management Plans	Evaluation of potential liabilities Quantification & Management of Risk Management Systems Compliance audit Environmental Management Information Systems	Site Investigation & Remediation Strategies for contaminated sites Construction management services Decontamination, decommissioning & demolition	Air Quality & Noise Water, Wastewater & Waste Management Health & Safety Risk Management Auditing & Verification

ERM's global reach & local implementation



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