NATURAL ATTENUATION OF MTBE IN A GASOLINE PLUME

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Study Outline

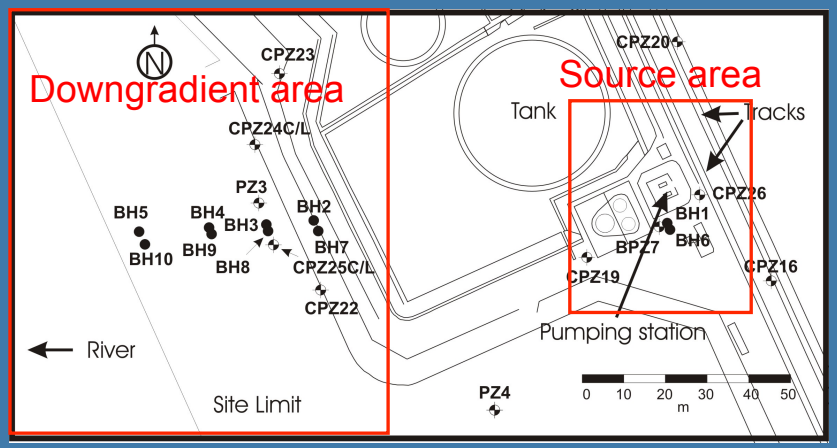
- Review of previous site studies
- Development of conceptual model
- Field work
  - Geology
  - Hydrogeology
- Laboratory analysis
  - Groundwater
  - Soil
  - Microcosm studies
  - Isotope analysis
- Refinement of conceptual model
- Numerical modeling
- Conclusions

Site and Release History

- Industrial site used as storage and distribution centre for heating oil, diesel, and gasoline
- Gasoline contains ether oxygenates ETBE and MTBE (max. 15% by volume)
- Gasoline release may impact river 800 m away
- Gasoline release occurred in second half of 1990s; volume estimated at 5 000 L; release occurred in the vicinity of pumping station near or at ground surface

Source Area

Past Characterization Work

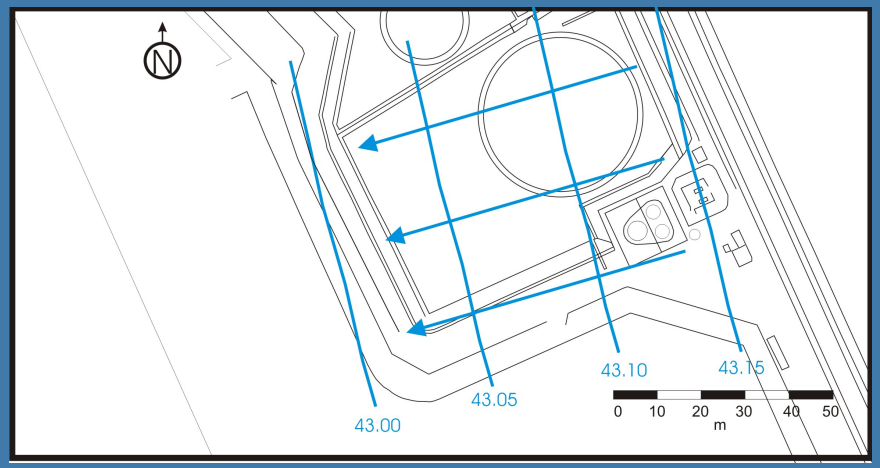


Site plan

Downgradient area

- Fourteen monitoring wells installed in southern half of site; most screened at water table
- Additional boreholes sampled in June 2004 to characterize vertical profile of plumes and to detect contamination further downgradient
- Approximate location of source identified with soil sampling in 2003
- Groundwater sampled and analyzed on a bi-quarterly basis for TPH, BTEX, ETBE, and MTBE

Groundwater Flow



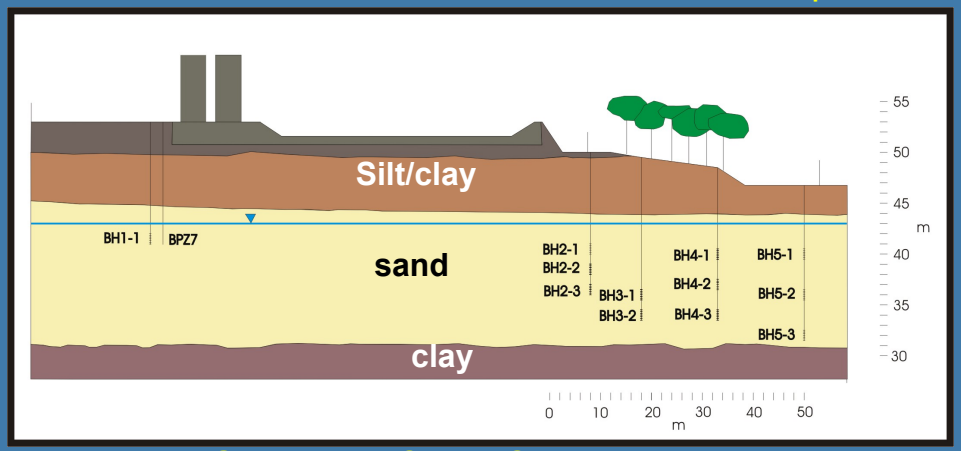
Piezometric Water Table Contours (February 2004)

Aerial View of Study Site

Geologic Characterization

- Water-bearing unit is carbonaceous sand rich in iron
- Aquifer underlain by thick clay and overlain by heterogeneous clayey and siltey alluvial deposit
- Unconfined aquifer – recharge passes through silt/clay layer

Soil Samples from Saturated Zone



Geological Cross-Section

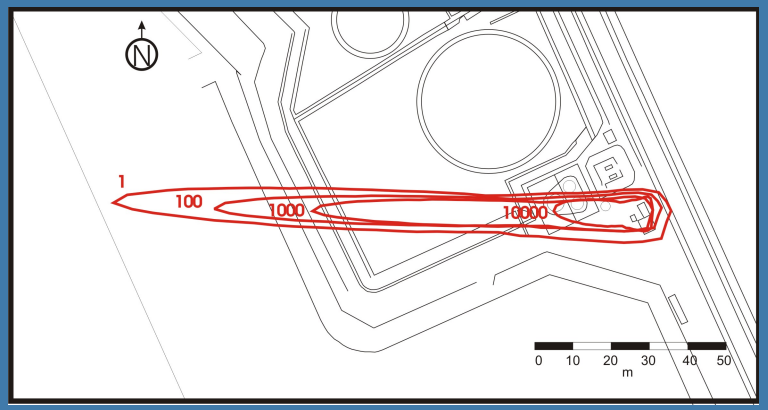
Source Characterization

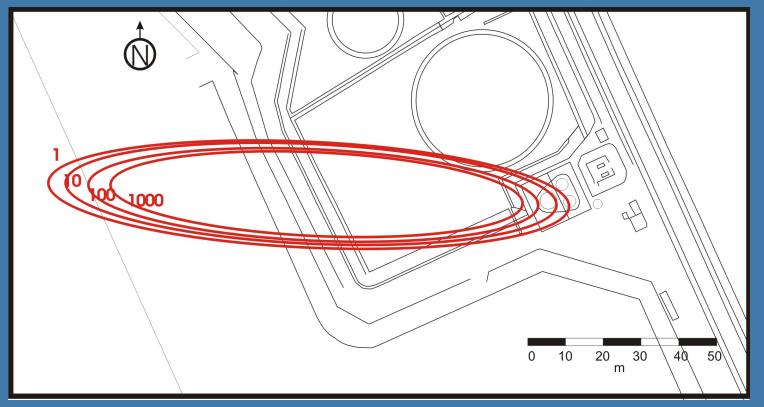
- Point-source consists of gasoline contamination in the unsaturated zone and smear zone; diesel contamination close to surface
- Gasoline LNAPL detected at water table at well BPZ7 (photo)
- Aqueous concentrations (June 2004) at source:
  - Benzene: ~10 000 ug/L
  - TEX: ~ 40 000 ug/L
  - MTBE: < 1 ug/L
  - ETBE: 192 ug/L
- Soil analysis show diesel and gasoline contamination in the unsaturated zone

Groundwater and Soil Sampling at Source

Plume Characterization

Benzene ppb

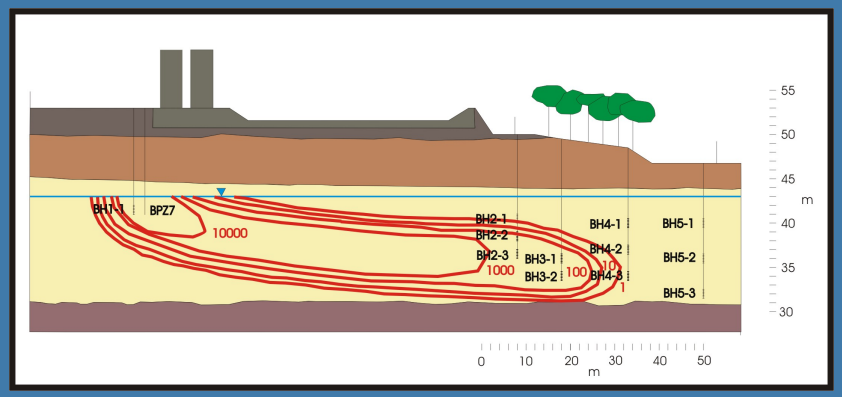




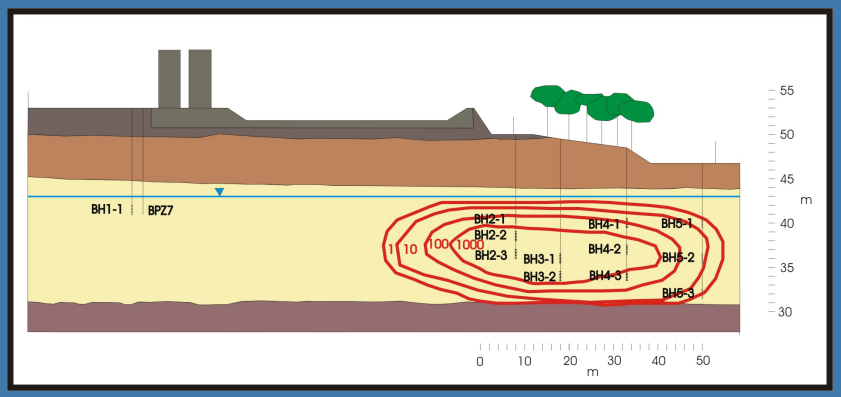
MTBE ppb

- In downgradient area, max. concentrations in 2004 are 780, 47, 33 and 4700 µg/L for benzene, TEX, ETBE, and MTBE respectively
- BTEX plumes narrow, attached to source, and located on-site
- MTBE plume wider, flushed from source, and migrating off-site

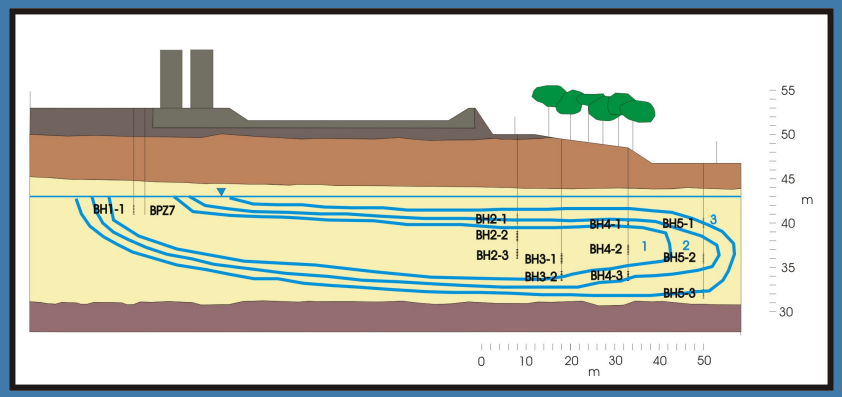
Plume Characterization



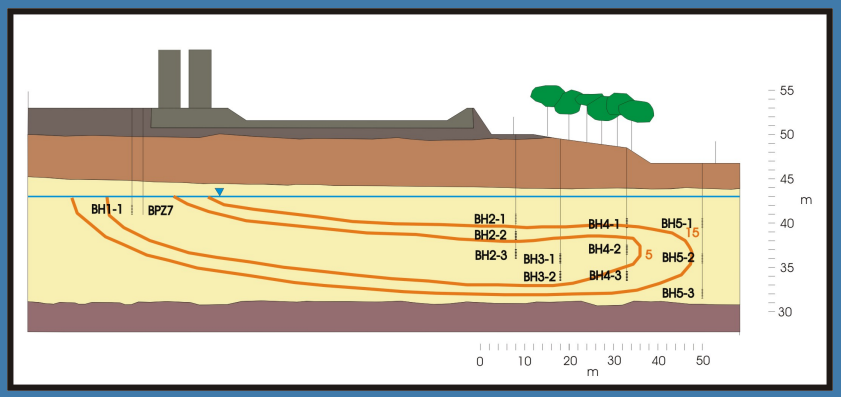
Benzene ppb



MTBE ppb



Dissolved oxygen ppm



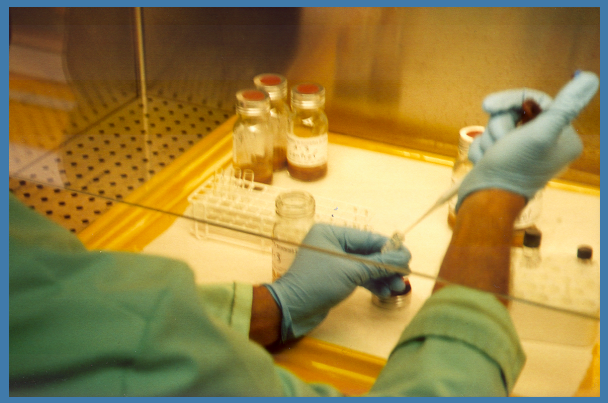
Nitrate ppm

Field Indicators of Attenuation

- In-situ indicators of biodegradation
  - Groundwater is more acidic within the gasoline plume: may be due to CO_2 generation from biodegradation of certain gasoline compounds
  - DO- and nitrate depletion within the gasoline plume
  - Persistence of MTBE in lateral wells; disappearance of BTEX in lateral wells: MTBE more resistant to biodegradation
- These observations suggest that biodegradation is active but is not necessarily caused by presence of MTBE; however, absence of MTBE and ETBE transformation product TBA indicates that the ether oxygenates may be resistant to biodegradation

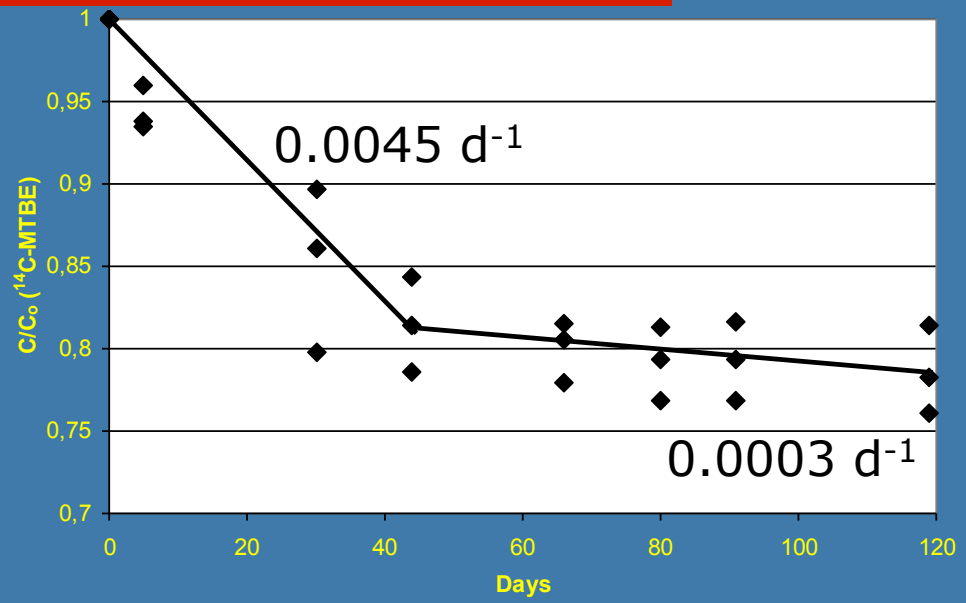
Microcosm Studies

- Microcosms prepared at Total Reseach Centre (Lacq, France)
- Study monitored ^{14}C-MTBE converting to ^{14}C-CO_2 in aquifer soil and water mixtures
- Active and control microcosms prepared in triplicate, and under aerobic conditions



Preparation of microcosms

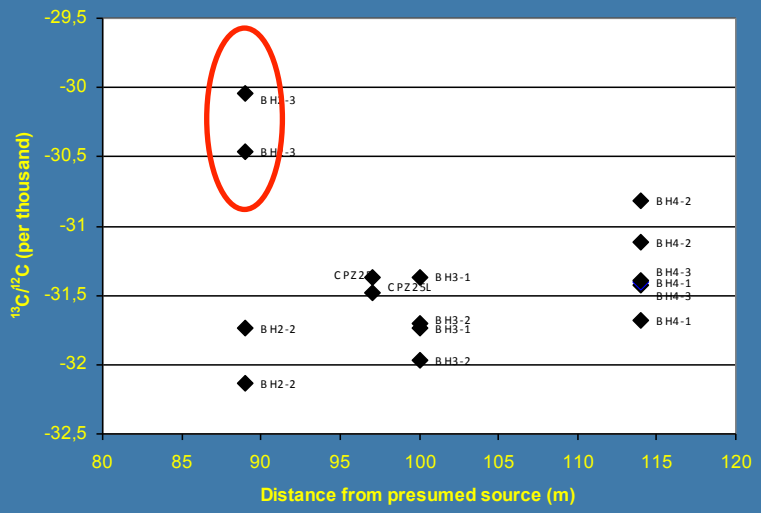
Microcosm Studies

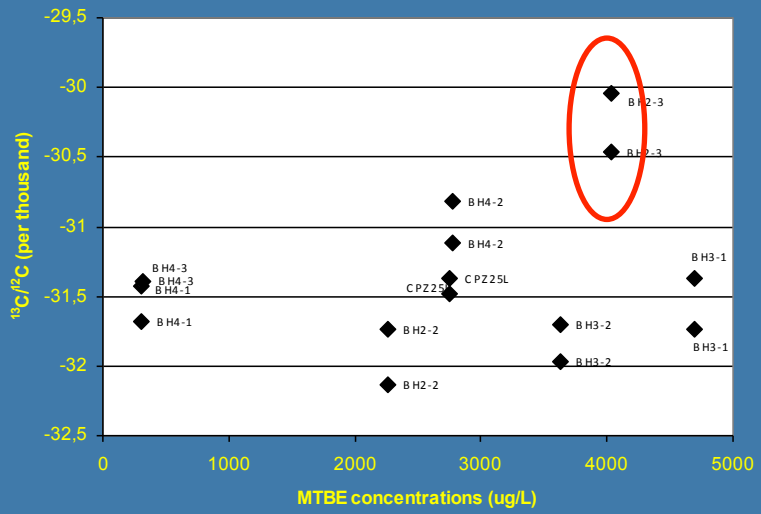


MTBE/aerobic

- ~20% MTBE removal after 120 days in MTBE/aerobic microcosms
- Maximum rate in first 40 days

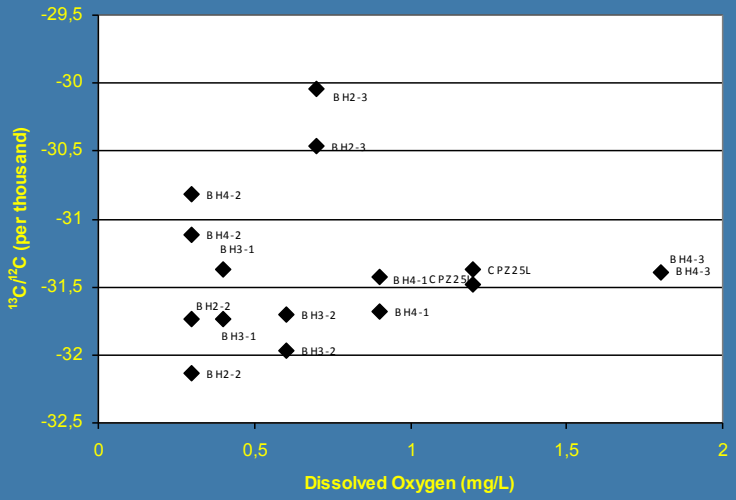
Isotope Studies

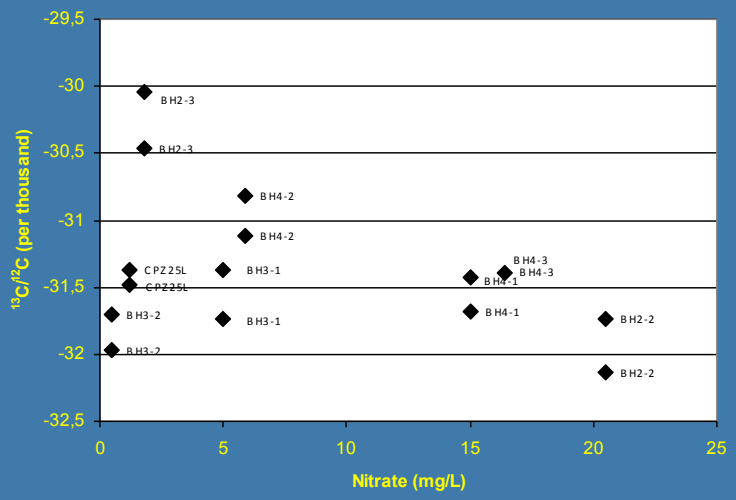




- Groundwater analyzed for MTBE-specific $^{13}C/^{12}C$ ($\delta^{13}C$)
- $\delta^{13}C$ enrichment weak with increasing distance
- $\delta^{13}C$ stable regardless of MTBE concentration
- Outlying $\delta^{13}C$ (circled) may originate from different MTBE

Isotope Studies



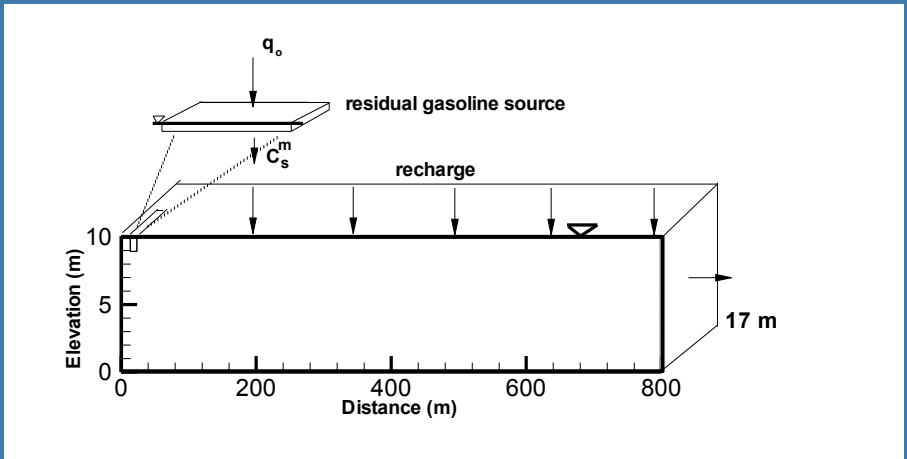


- $\delta^{13}C$ stable in both aerobic and nitrate-reducing environments
- Based on isotope data, MTBE appears resistant to biodegradation in the studied aquifer

Numerical Modeling of BTEX and MTBE

- **Objective**: analyze behaviour and extent of BTEX and MTBE plumes; study impact of attenuation processes on plumes; predict impact of contaminants on potential receptor (river located 800 m downgradient of source)
- Numerical model selected: BIONAPL developed by John Molson (Polytechnique de Montréal, Quebec, Canada)
- BIONAPL simulates 3D advective-dispersive reactive transport within a porous medium in the saturated zone. The model considers multiple components dissolving from a NAPL source, and electron acceptor biodegradation.
- Two approaches are considered for biodegradation: 1) simplified Monod approach neglecting microbial growth and 2) first order degradation

Conceptual Model of System

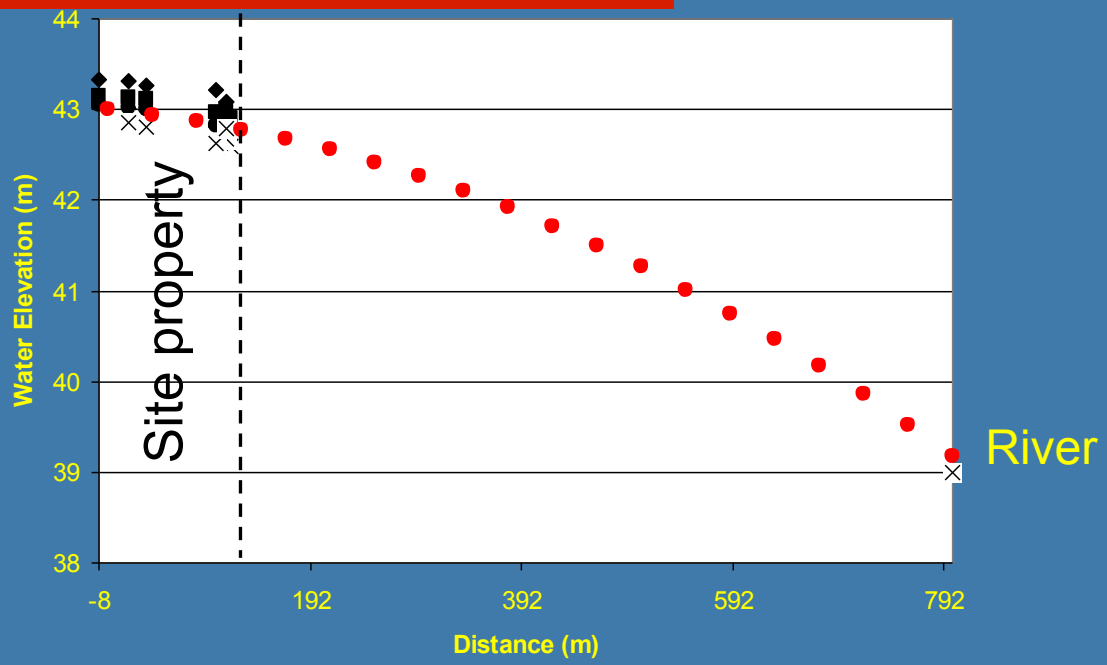


- Background DO: 3 mg/L
- Background nitrate: 12 mg/L
- Initial volume NAPL: 5 000 L
- NAPL components: benzene, TEX, MTBE, remaining components (inert)

Base Scenario

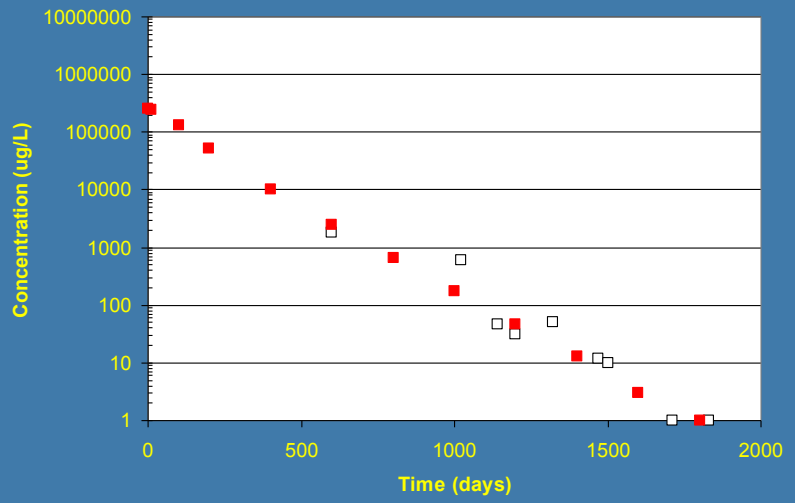
- Source dimensions: 8 x 8 x 1 m
- Domain: 800 x 17 x 10 m
- Low-k layer: 4 x 10^{-5} m/s; high-k layer: 9 x 10^{-5} m/s
- Gradient: 0.005
- Effective porosity: 0.15
- Flow Velocity: 95 m/d
- Recharge: 230 mm/year
- Dispersivity long: 2.0
- Dispersivity trans hor: 0.02
- Dispersivity trans ver: 0.01
- Organic carbon fraction: 0.0011

Groundwater Flow Calibration

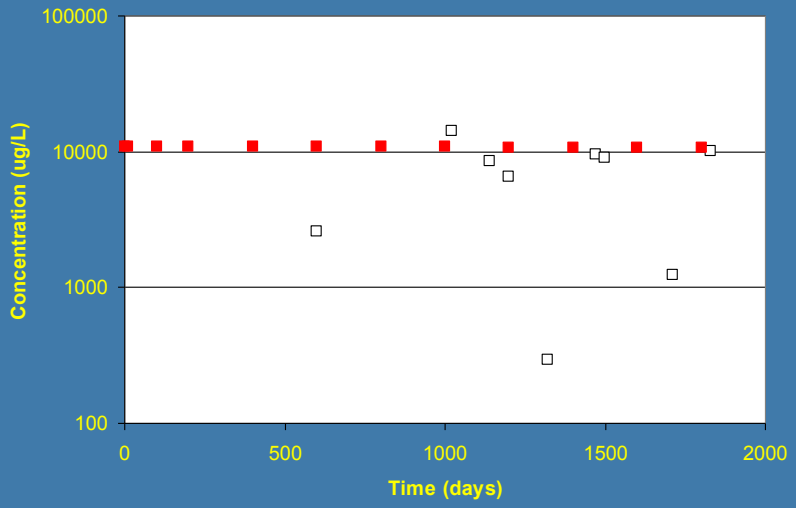


- Water elevations taken from on-site wells during five monitoring rounds (2003-2004)
- Flux and recharge were calibrated until simulated gradient matched observed gradient

Source Calibration



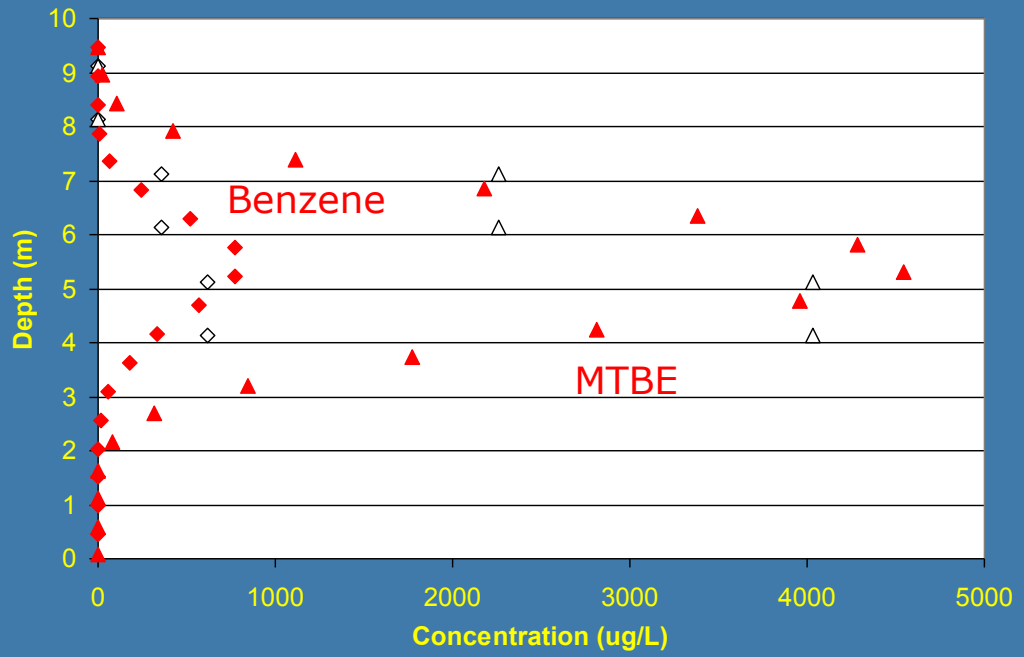
MTBE



Benzene

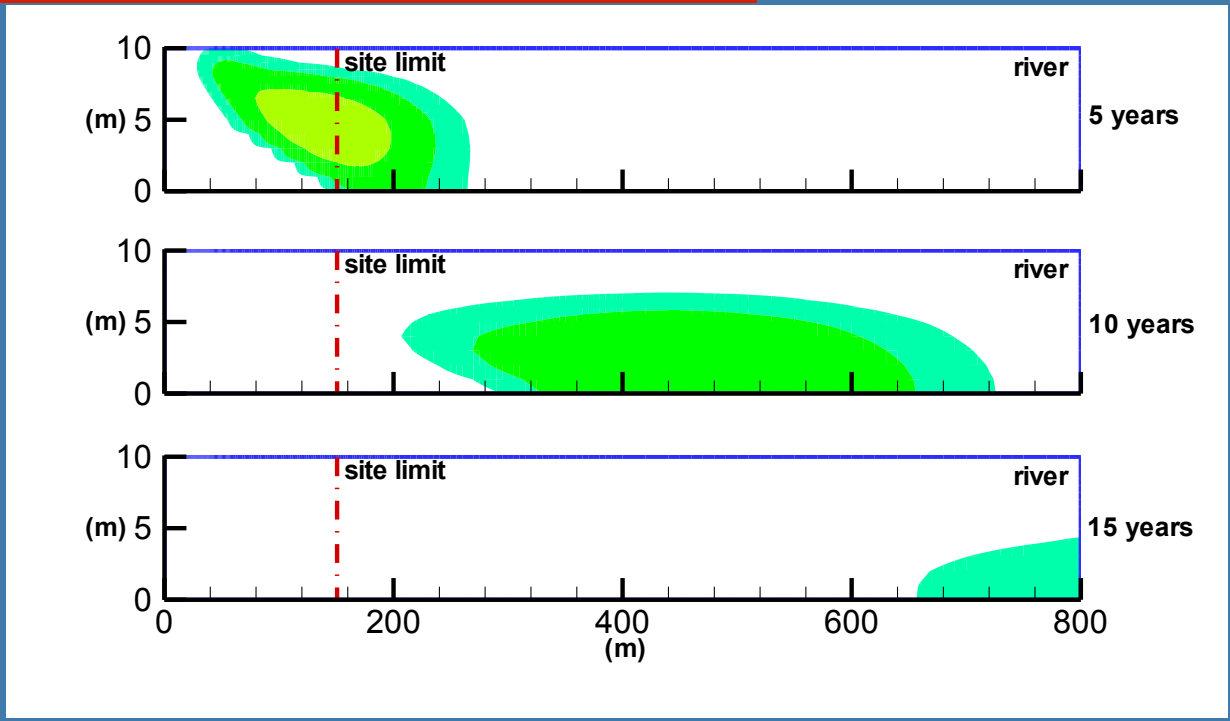
- Simulated aqueous concentrations (red pts) fitted with concentrations (white pts)
- Benzene persists at high concentrations at source, but MTBE is rapidly flushed from source

Flow/Plume Calibration



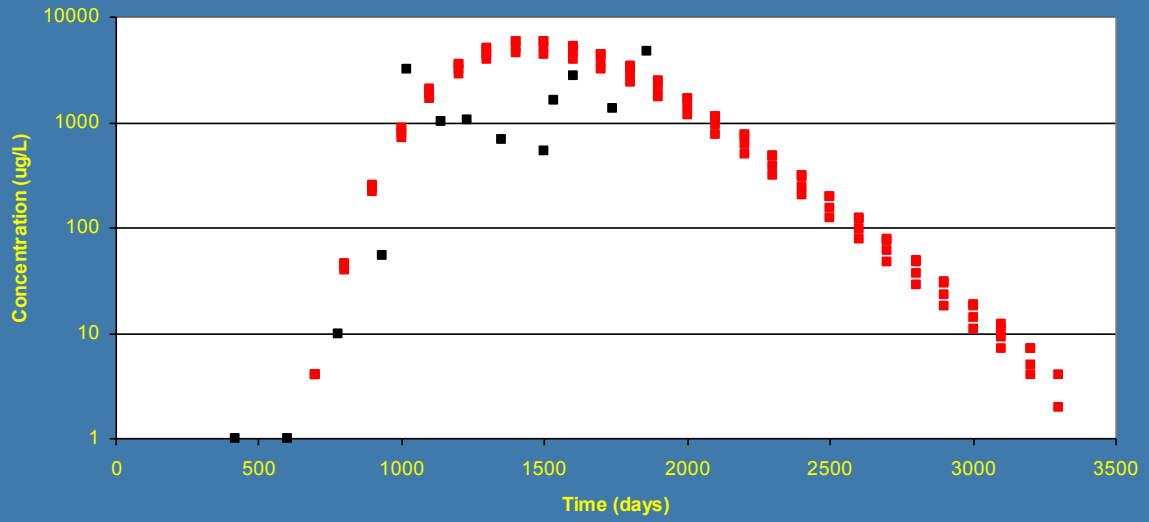
- Fitted vertical position of observed plume with simulated plume
- Placement of plume took into account trans. vert. dispersivity, aqueous concentration, and magnitude of fluxes into system

Transport Calibration (MTBE)



- MTBE plume calibrated with first-order rate (λ=1 x 10^{-4} d^{-1}).
- Decay rate is weaker than that of benzene
- MTBE plume reaches river with max. conc. of ~500 ug/L

Sensitivity Analysis (MTBE)



- Sensitivity analysis of decay rate:
  - $\lambda = 9 \times 10^{-5}\ d^{-1}$: max conc. 5896 µg/L
  - $\lambda = 1 \times 10^{-4}\ d^{-1}$: max conc. 5819 µg/L
  - $\lambda = 2 \times 10^{-4}\ d^{-1}$: max conc. 5101 µg/L
  - $\lambda = 3 \times 10^{-4}\ d^{-1}$: max conc. 4508 µg/L
  - Max. observed: 4700 µg/L

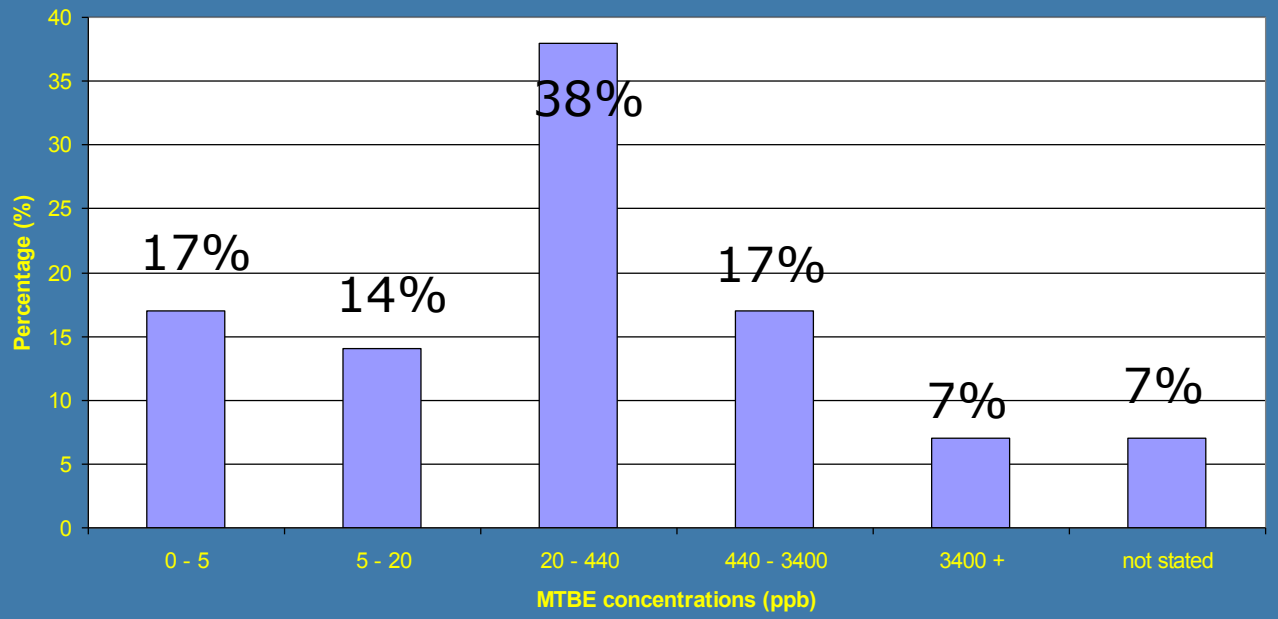
Conclusions

- Simulations show that MTBE represents a very small fraction of the gasoline release (0.1 molar %); total mass of MTBE is small: 1.5 kg
- Gasoline release occurred in mid-1998
- MTBE is attenuated to around 500 µg/L at the river 13 years after gasoline release
- MTBE concentrations reaching potential receptor is well below Canadian water quality guideline for protection of aquatic life (10 mg/L)
- In the aquifer system, MTBE is attenuating by dispersion and likely by aerobic biodegradation in the MTBE-only plume
- However, MTBE degrades at slower rate than benzene
- Unlike MTBE, benzene remains attached to source and stabilises within site limit; plume behaviour for both benzene and MTBE was successfully replicated in the simulations

MTBE in Canada

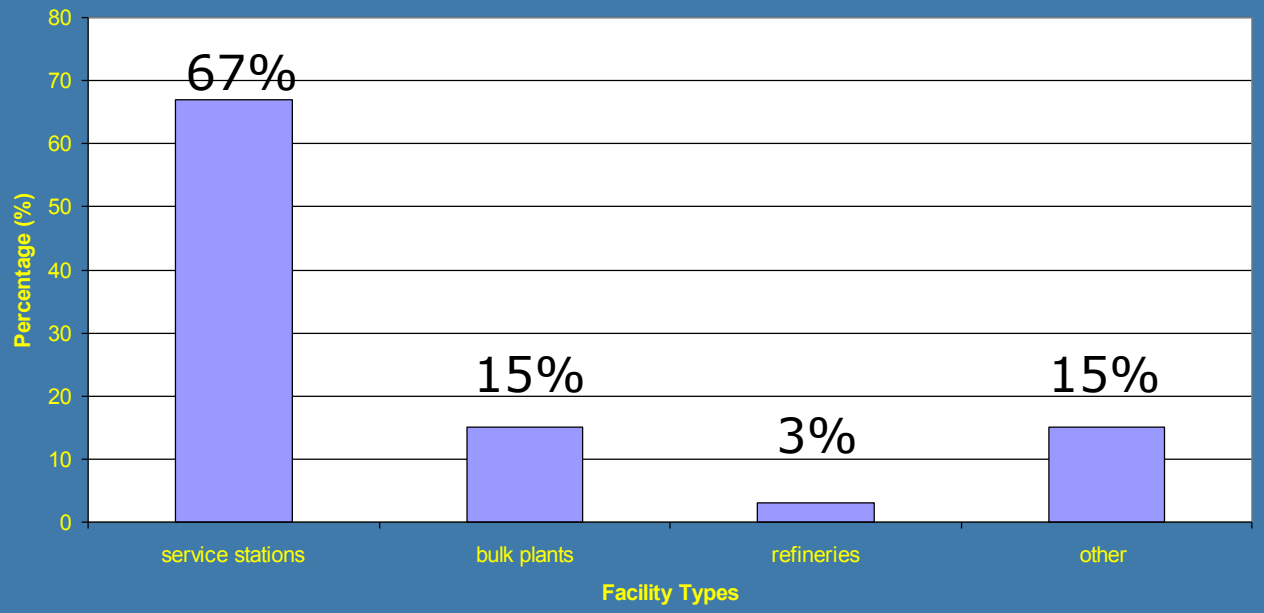
- Overall, use of MTBE in Canada is minimal
- Unlike some US states, Canada has not banned or phased-out MTBE
- 1998: gasoline containing MTBE accounted for 10% of gasoline pool in Canada; 2001: fraction decreased to less than 1%
- Canadian companies ceased adding MTBE to gasoline by the end of 2001; most gasoline with MTBE was being exported to the U.S.
- Small number of contaminated sites (250) across the country according to Environment Canada
- 6 out of 250 were sites where groundwater used as drinking water; however, all samples were below the USEPA consumer advisory level of 20 to 40 ppb
- Some provinces have water quality guidelines for MTBE: levels vary from 15 ppb (aesthetic) to 3400 ppb (aquatic life)

MTBE in Canada



- Concentration distribution based on 250 recorded cases of groundwater contamination in Canada

MTBE in Canada



- Majority of MTBE contamination occurs at service stations
- Category « other » includes terminals, MTBE transport, and MTBE production

MTBE Studies at Waterloo

- **Hubbard et al. (1994)** measured the mass of MTBE in the Borden aquifer as part of a tracer test: BTEX mass was removed but MTBE showed only small decrease in mass
- **Schirmer and Barker (1998)** compared simulation results with field observations of the same aquifer, concluding only 3% of MTBE remained in the system and that biodegradation was the cause
- **Schirmer et al. (2003)** conducted microcosm tests with Borden aquifer material; observed that some microcosms degraded MTBE to below detection levels
- **Hunkeler et al. (2001)** demonstrated in laboratory studies that carbon isotope fractionation of MTBE was significant for the biodegradation process compared to physical processes