Assessment and Application of Monitored Natural Attenuation for the Management of Contaminated Groundwater

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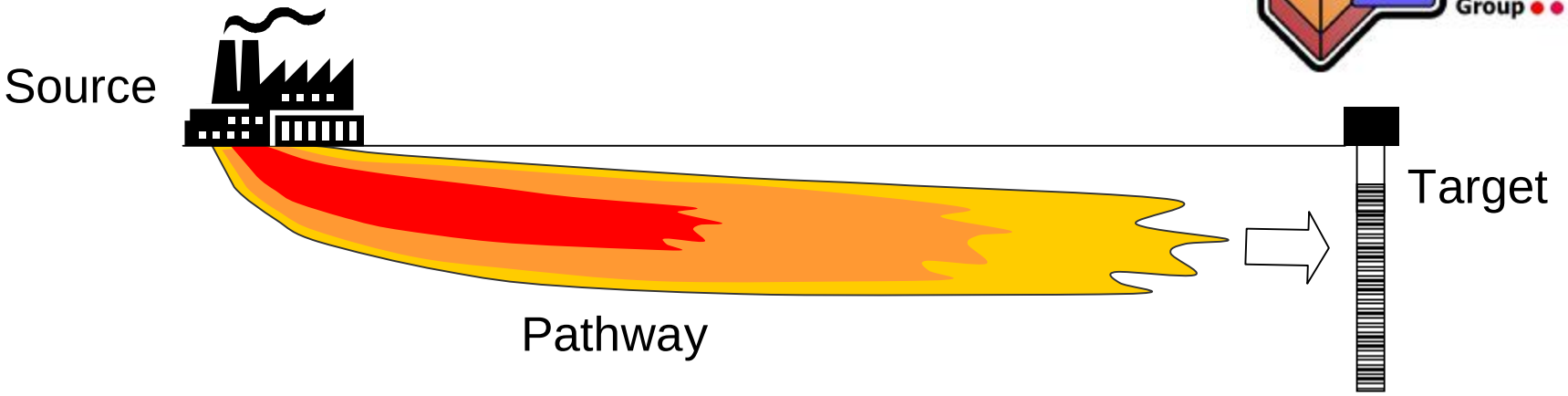
- Industrial collaborators
  - Total UK, Entec UK, CL:AIRE
- Sponsors
  - EPSRC, Environment Agency, Total UK

Outline

- Concepts and definitions
- Case study
  - Site characterisation approach
  - Assessment using MNA guidance
    - BTEX
    - MTBE
  - Controls on plume development and NA
  - Final assessment
- What did we learn ?

Concepts and definitions

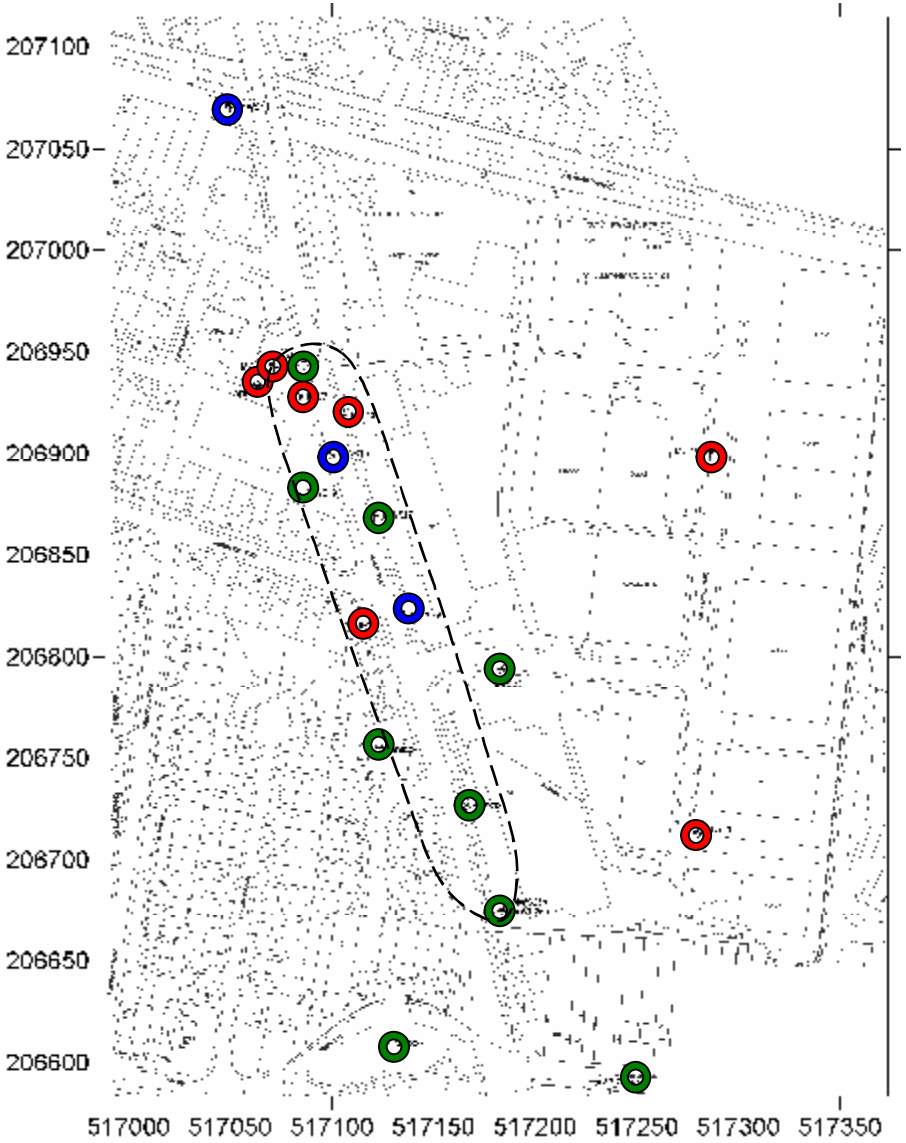


- Risk-based restoration
  - Intervene only if significant harm to target
- Predicting target impact
  - Characterise source
  - Quantify pathway effects
- Pathway effects
  - If predictable & sufficient – MNA acceptable

- Natural attenuation (R&D 95)
  - "Naturally occurring physical, chemical & biological processes acting to reduce load, conc., flux or toxicity of pollutant in groundwater…& limit plume expansion."

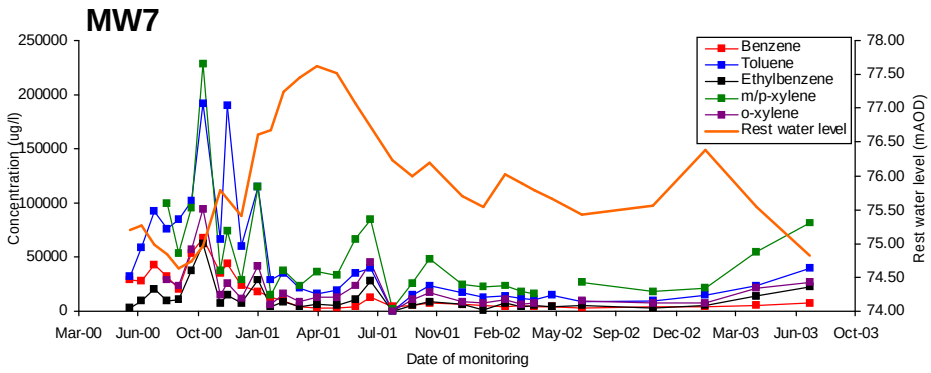
- *Monitored* natural attenuation
  - "Monitoring of groundwater to confirm NA processes act at sufficient rate to ensure wider environment unaffected & remedial objectives achieved within reasonable timescale (< 30 yrs)."

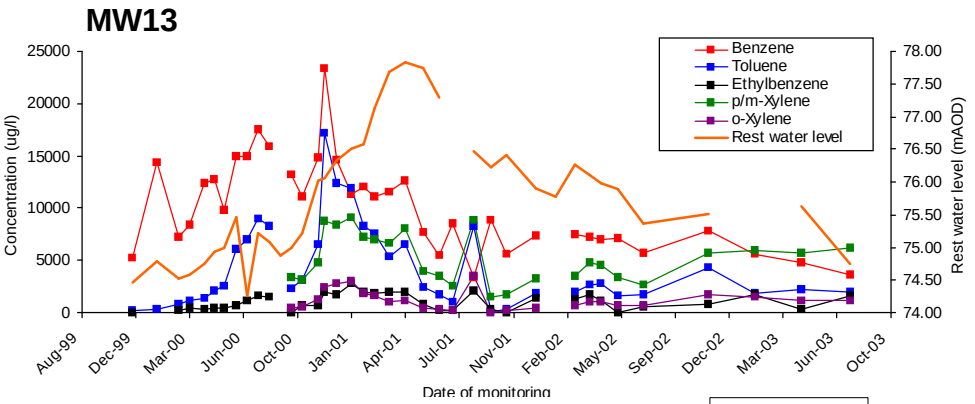
Monitoring well network

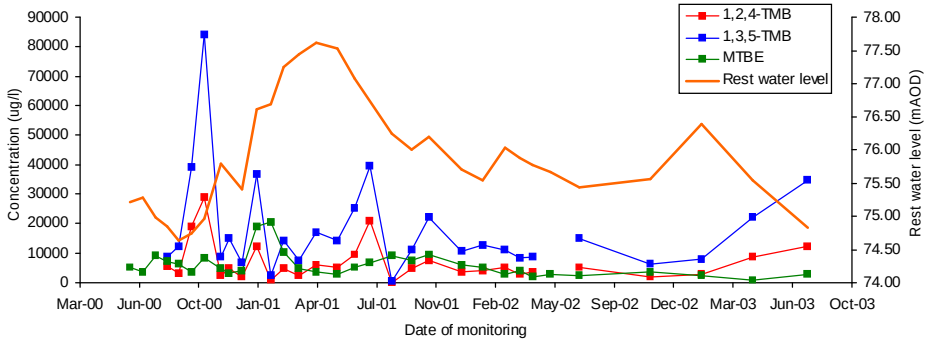


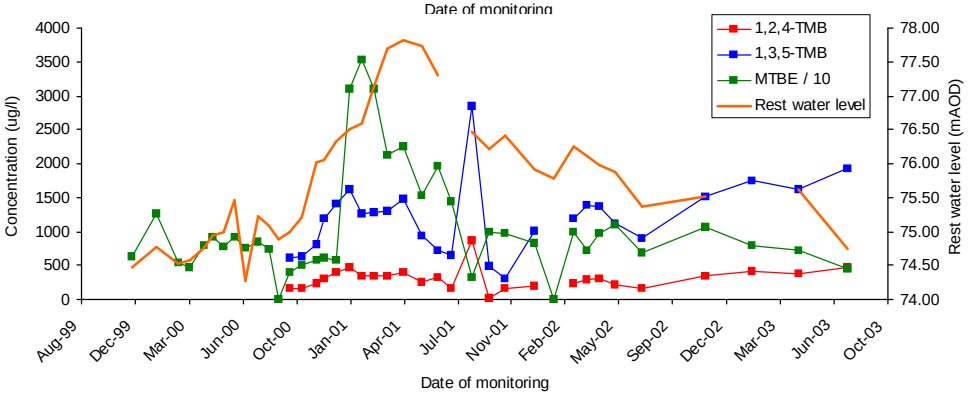
- Staged development of MW network
  - Phase 1 : 1999-2000
  - Phase 2 : 2000-2001
  - Phase 3 : 2001-2004
- Varied MW design
  - Phase 1 : single screen
  - Phase 2 : MLS
  - Phase 3 : MLS / single screen

Controls on plume development
Contaminant flux









- Spatial / temporal variation in contaminant release
- Changing source term over plume history
- Important for assessing NA potential and risk
- MW network must capture source composition heterogeneity

Site characterisation approach

Integrated methodology

Site characterisation flow chart

1 Open drilling to water table

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2 Rotary cored drilling to final depth

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3 ATV/OPTV/caliper/resistivity geophysical logs

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4 Hydraulic testing

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5 Fracture logs

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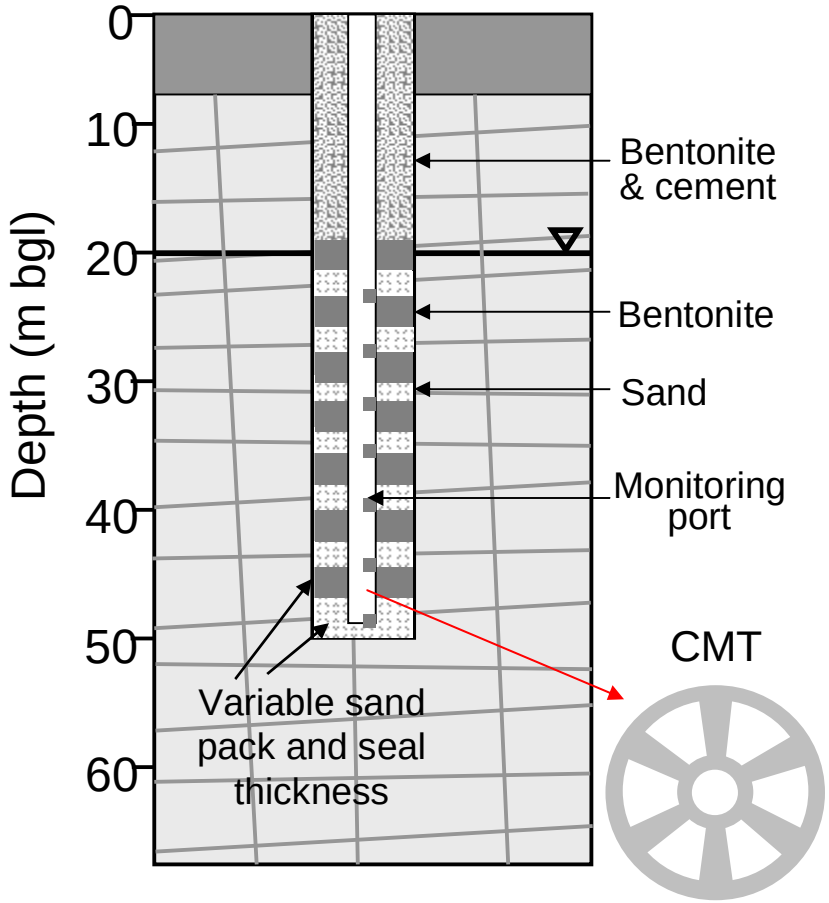
6 Install CMT



CMT = Continuous Multi-channel Tubing

Assessment using MNA guidance

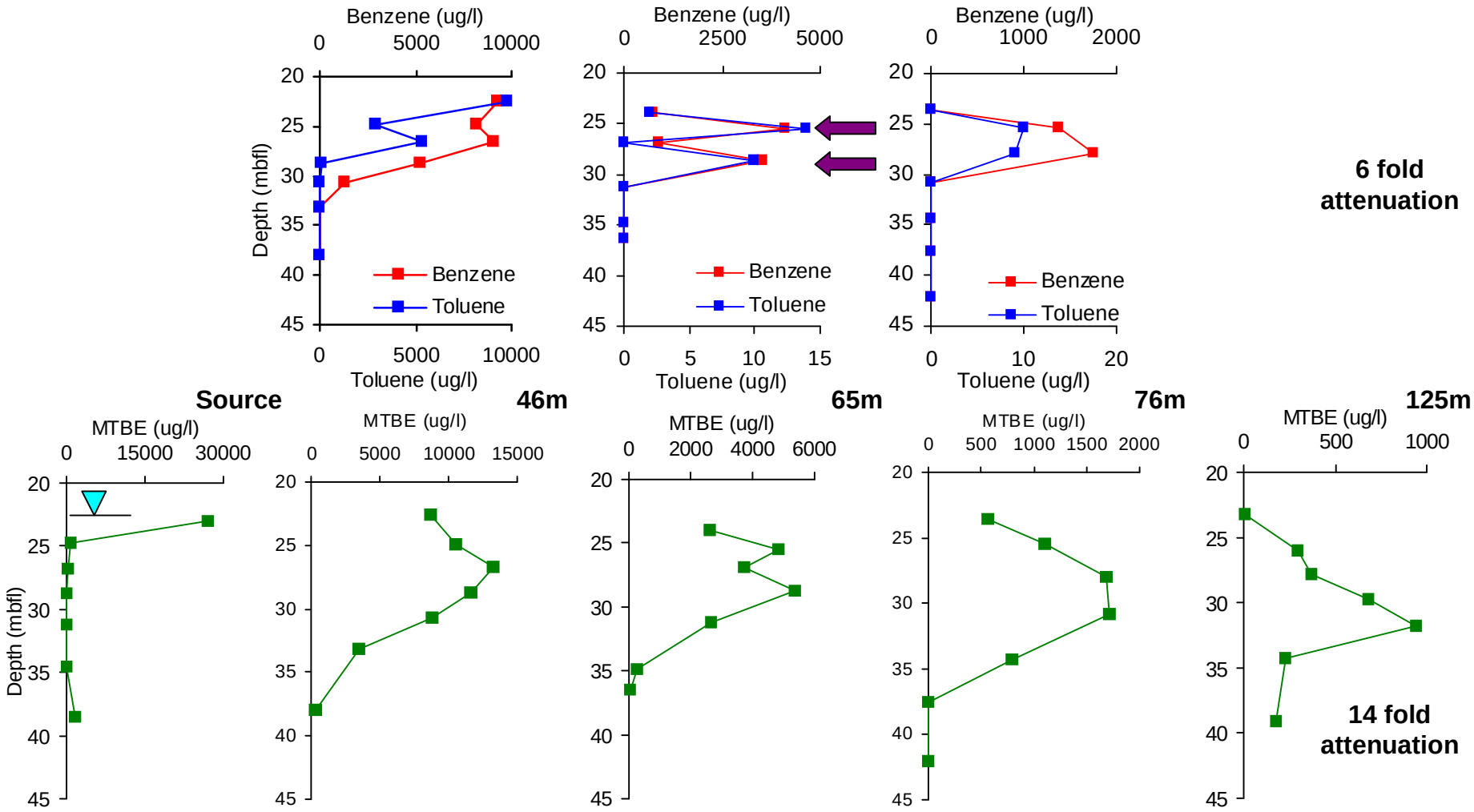
- Evidence of concentration reduction in field
  - Stable / decreasing concentrations over time
  - Concentration vs distance / time analysis along flow path

- Evidence of contaminant biodegradation
  - O_2 **ê** NO_3 **ê** SO_4 **ê** Mn^{2+} **é** Fe^{2+} **é** CO_2 **é** CH_4 **é** S^- **é** organic contaminant **ê** metabolites **é**
  - Distribution in plume vs background groundwater

- Evidence from supporting studies
  - Matrix pore water chemistry vs fracture water chemistry
  - Microcosm studies – processes, rates, controls for BTEX, MTBE

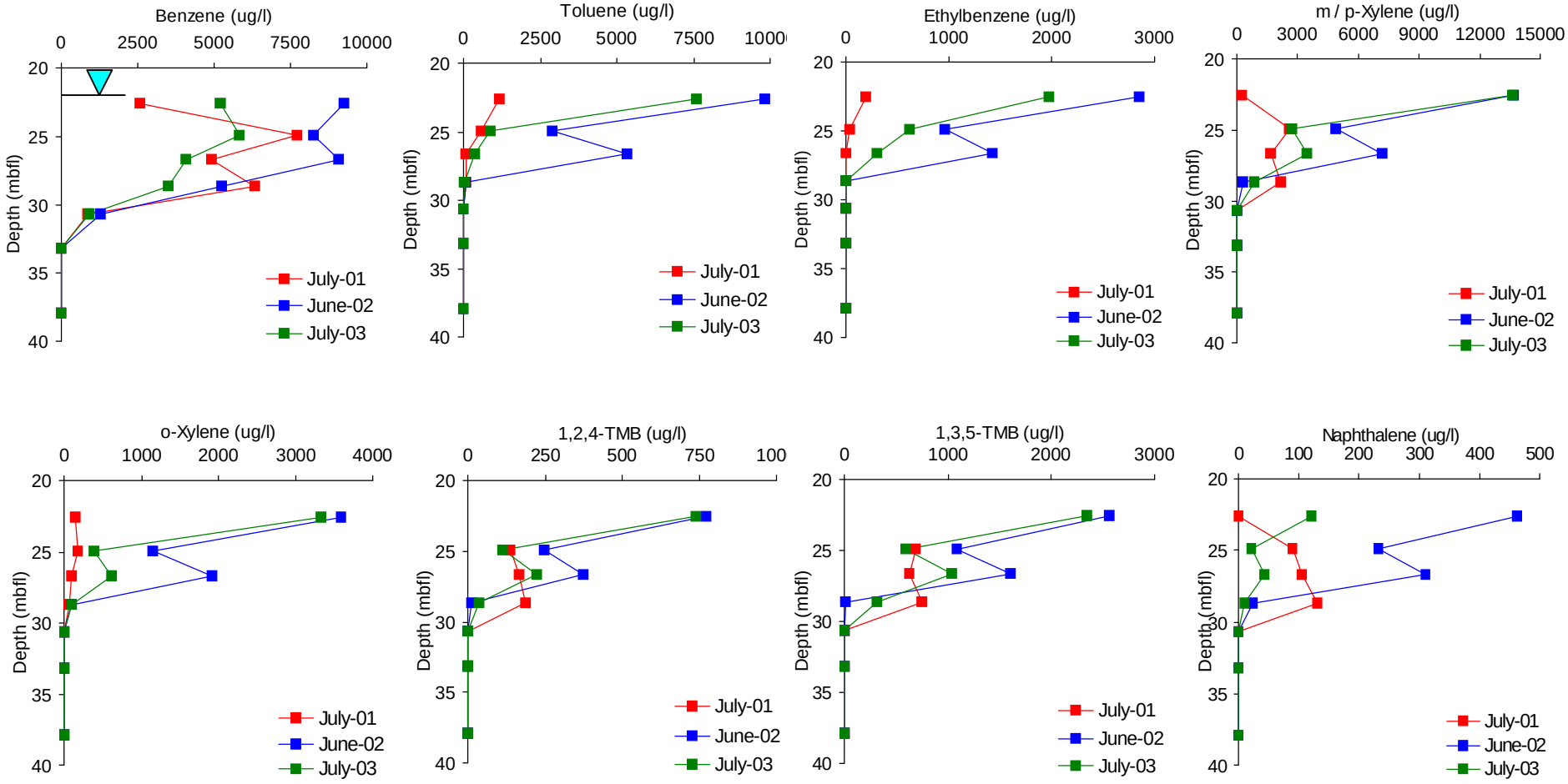
Assessment using MNA guidance

Contaminant conc vs distance



Assessment using MNA guidance

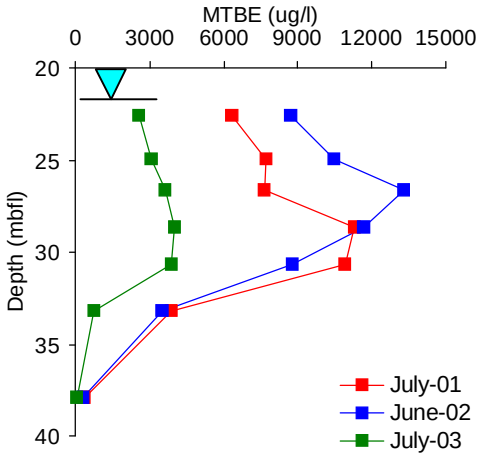
BTEX conc vs time @ 46m

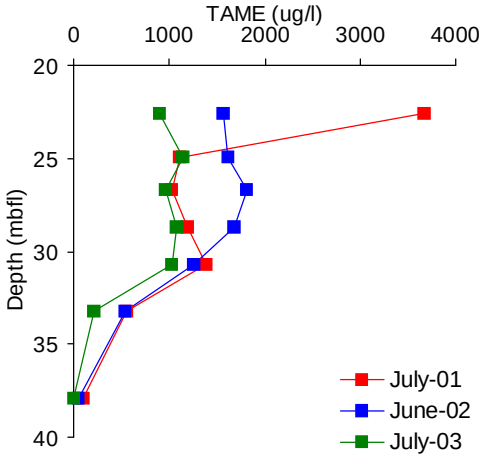


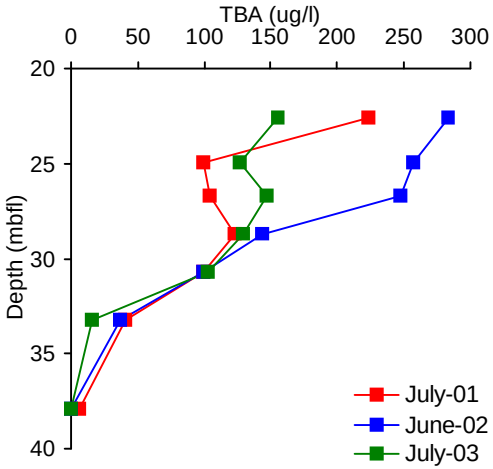
Assessment using MNA guidance

MTBE, TAME & TBA conc vs time

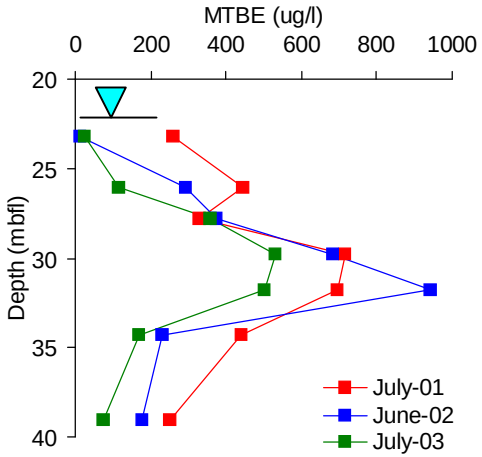
46m

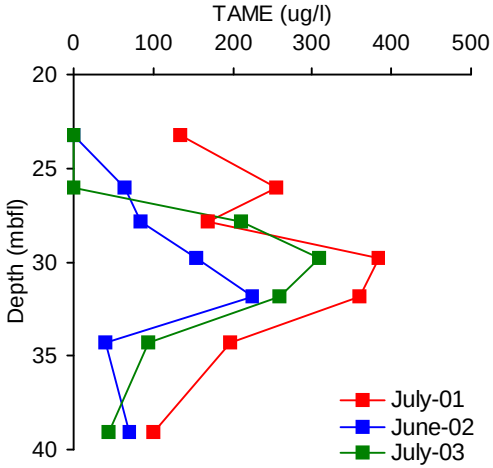


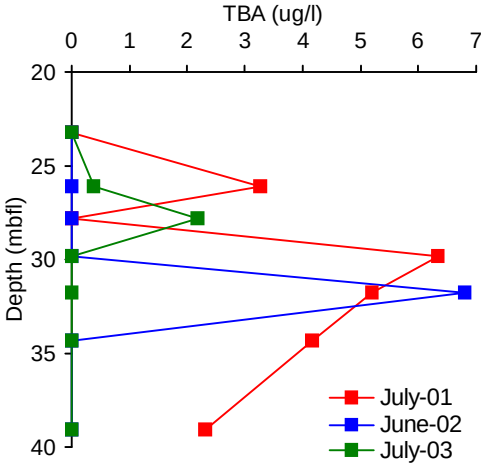




125m







Assessment using MNA guidance

- Evidence of concentration reduction in field ?
  - Stable / decreasing concentrations over time
  - Concentration vs distance / time analysis along flow path

- Yes - directly from observation wells
- Lower BTEX, MTBE, TAME concs downgradient
- Preferential flow paths exist – focused monitoring
- Fluctuating concs over monitoring period but apparent stability
- Preferential attenuation of BTEX components
- Greater mobility / migration of MTBE, TAME, TBA

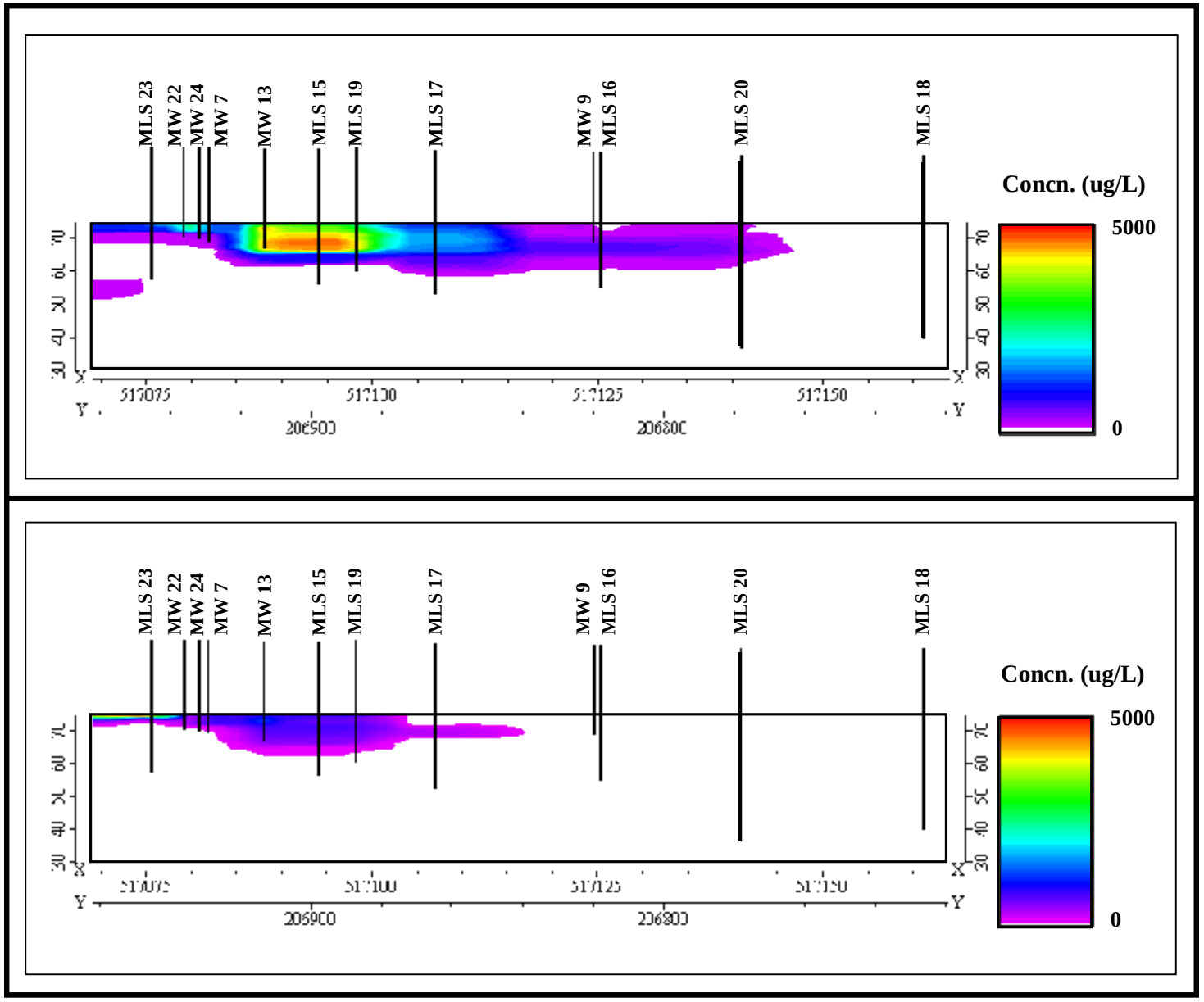
Assessment using MNA guidance

- Evidence of contaminant biodegradation
  - O_2 ê NO_3 ê Mn^{2+} é Fe^{2+} é CO_2 é SO_4 ê S^- é CH_4 é organic contaminant ê metabolites é
  - Distribution in plume vs background groundwater

Toluene		Oxidant				Reduced species		Metabolites			Process
C_7H_8	+	$9O_2$			⇒			$7CO_2$	+	$4H_2O$	Aerobic respiration
C_7H_8	+	$7.2NO_3$	+	$7.2H^+$	⇒	$3.6N_2$	+	$7CO_2$	+	$7.6H_2O$	Denitrification
C_7H_8	+	$4.5SO_4$			⇒	$4.5S^{2-}$	+	$7CO_2$	+	$4H_2O$	SO_4-reduction
C_7H_8	+	$18MnO_2$	+	$36H^+$	⇒	$18Mn^{2+}$	+	$7CO_2$	+	$22H_2O$	Mn-reduction
C_7H_8	+	$36Fe(OH)_3$	+	$72H^+$	⇒	$36Fe^{2+}$	+	$7CO_2$	+	$94H_2O$	Fe-reduction
C_7H_8	+	$5H_2O$			⇒			$4.5CH_4 + 2.5CO_2$			Methanogenesis

Assessment using MNA guidance

MTBE and TBA distribution



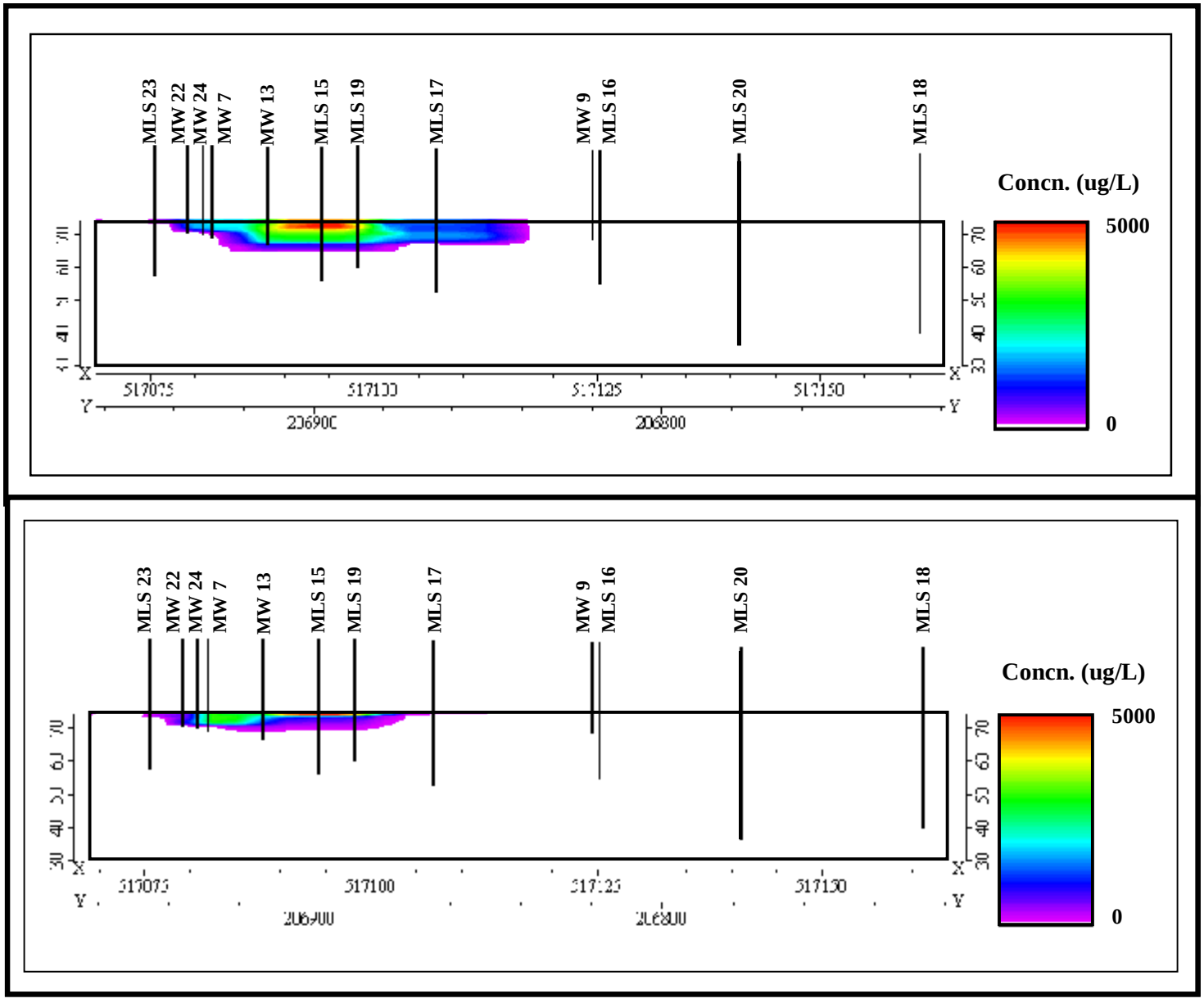
- MTBE
- 100 µg/L contour

- Greater migration
- Confounding evidence of TBA distribution

- TBA
- 10 µg/L contour

Assessment using MNA guidance

Benzene and toluene distribution



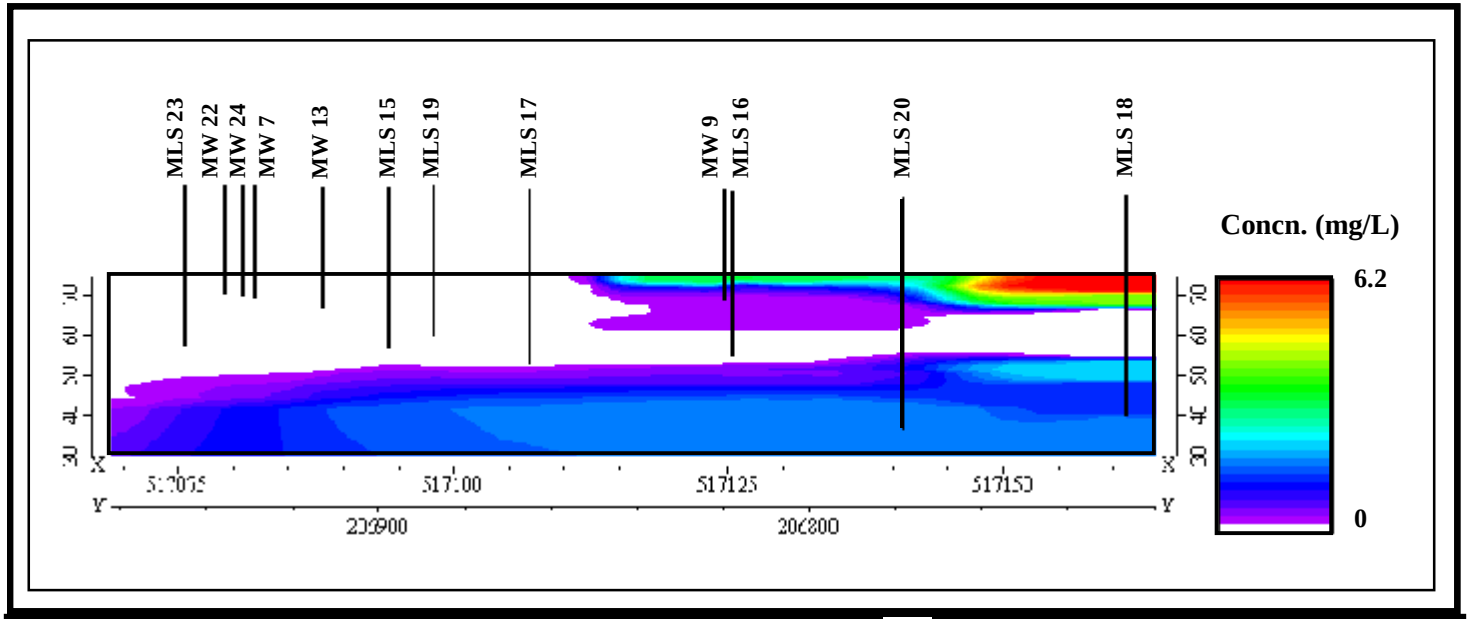
- Benzene
- 100 µg/L contour

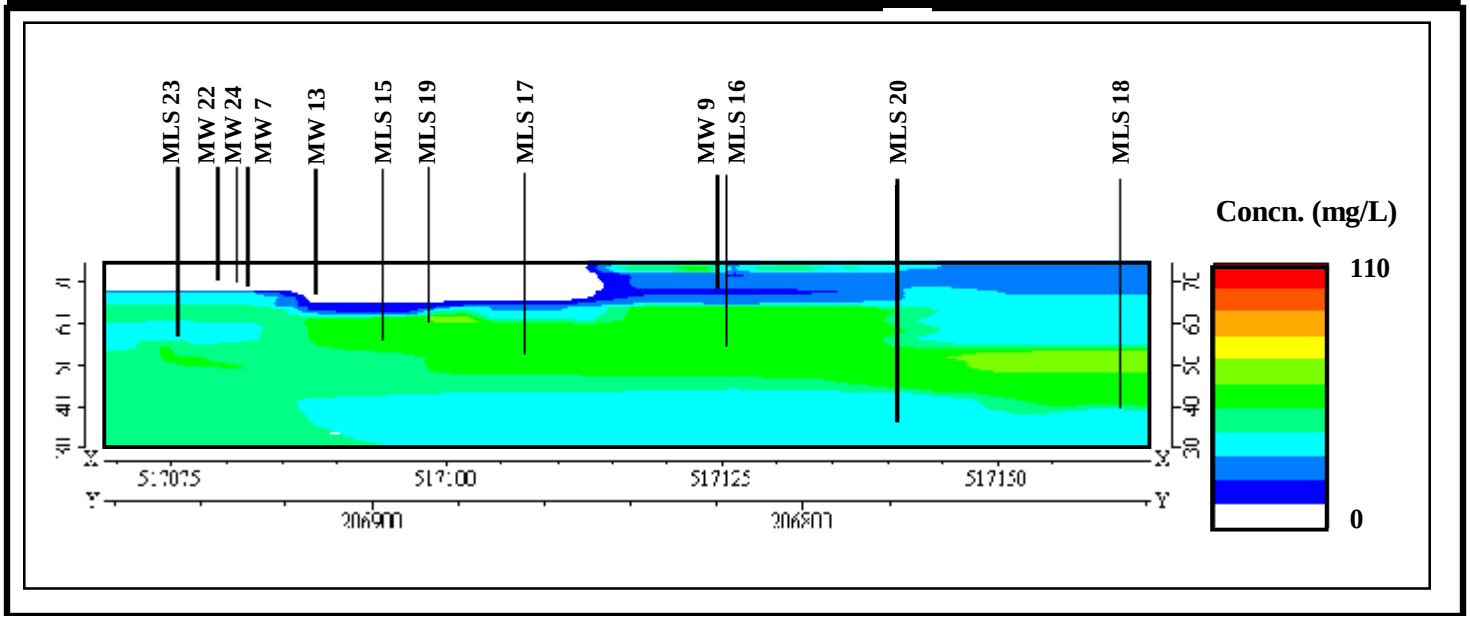
- Restricted migration
- Preferential attenuation

- Toluene
- 100 µg/L contour

Assessment using MNA guidance

O_2 and NO_3 distribution





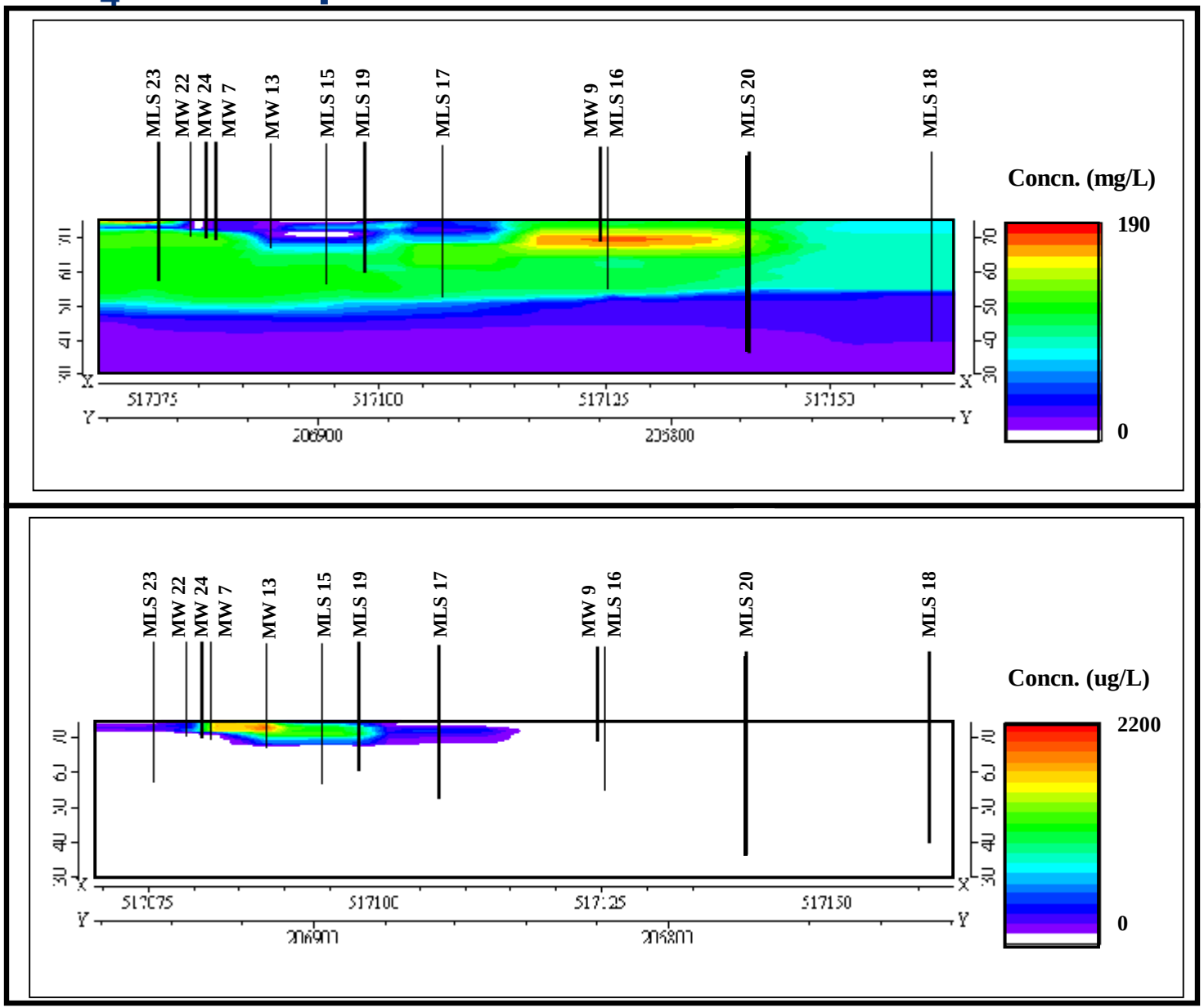
- O_2
- 0.2 mg/L contour

- Depletion within BTEX zone

- NO_3
- 0.2 mg/L contour

Assessment using MNA guidance

SO_4 and sulphide distribution



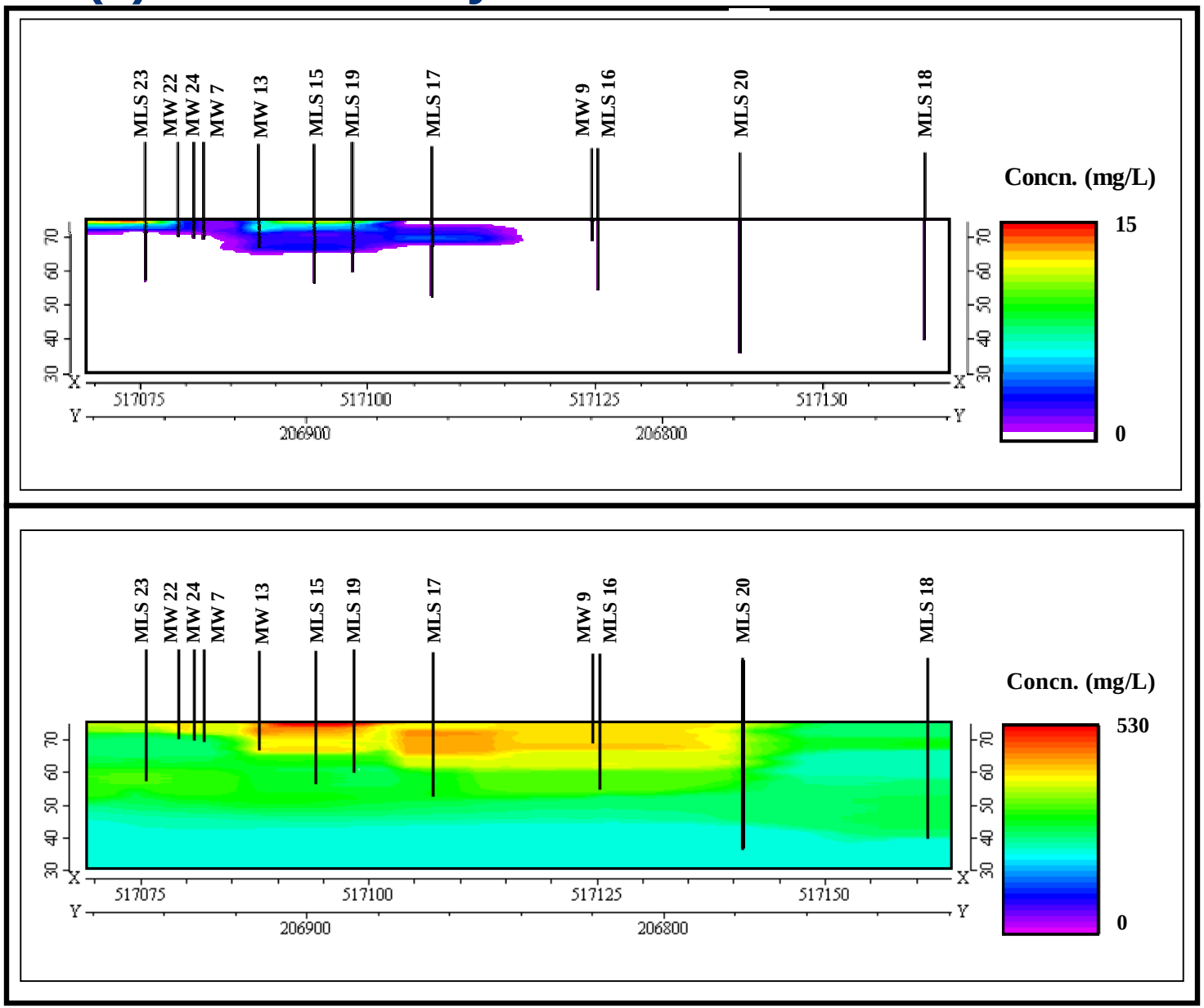
- SO_4
- 0.2 mg/L contour

- SO_4 depletion & HS^- production within BTEX zone

- Sulphide
- 100 µg/L contour

Assessment using MNA guidance

Fe(II) and alkalinity distribution



- Fe(II)
- 0.2 mg/L contour
- Production within BTEX zone
- Alkalinity

Assessment using MNA guidance

- Evidence of contaminant biodegradation
  - O_2 ê NO_3 ê Mn^{2+} é Fe^{2+} é CO_2 é SO_4 ê S^- é CH_4 é organic contaminant ê metabolites é
  - Distribution in plume vs background groundwater

- Wide range of degradation processes from biogeochemical indicator species
- Distribution with BTEX confirms mass loss for hydrocarbons
- But……primary and secondary lines of evidence inconclusive for MTBE
- Further assessment appropriate – tertiary lines of evidence

Assessment using MNA guidance

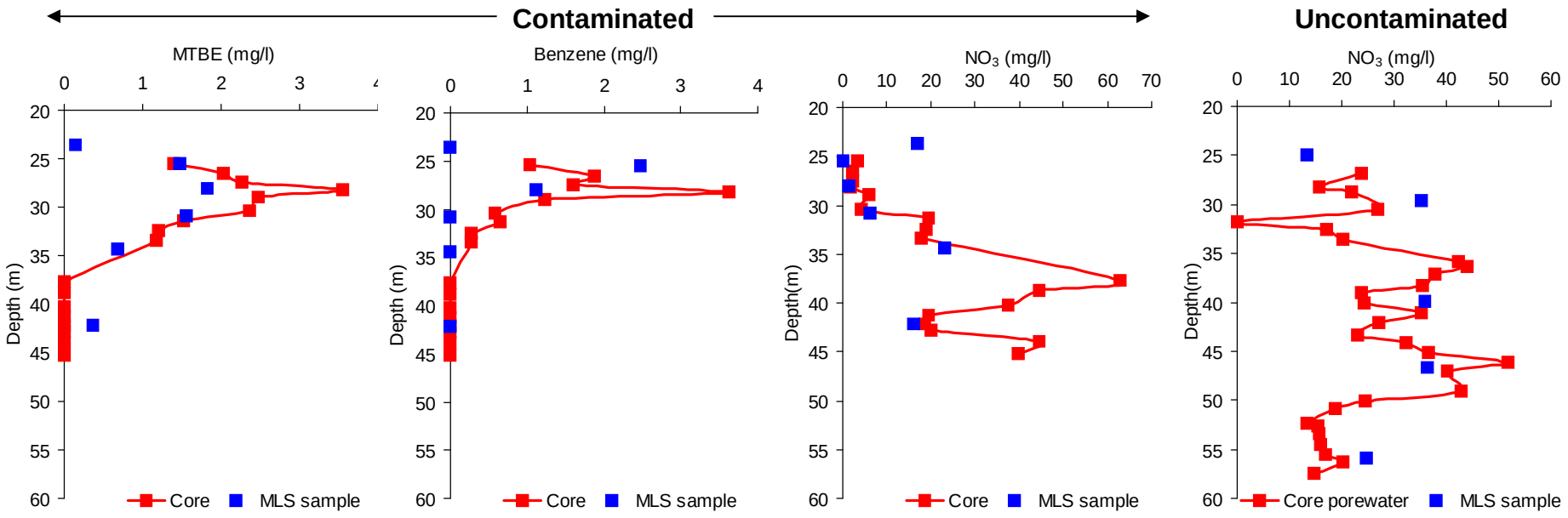
- Evidence from supporting studies
  - Matrix pore water chemistry vs fracture water chemistry
  - Microcosm studies – processes, rates, controls for BTEX, MTBE

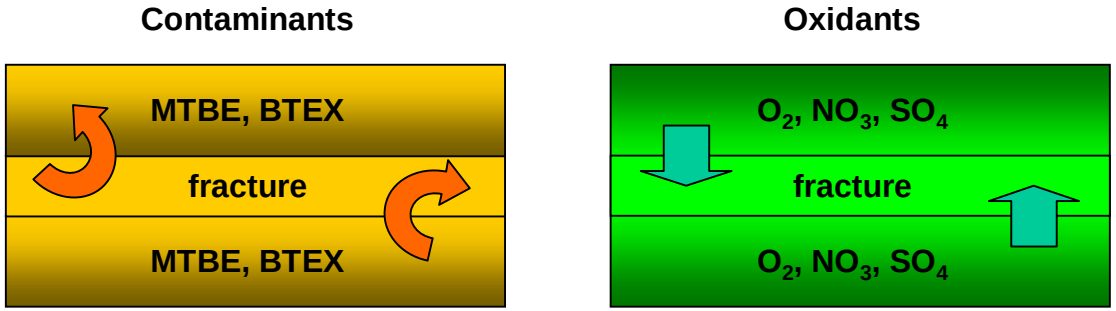
- Key issues / activities
  - Mass balances
  - Estimate degradation rates
  - Identify limitations / controls on degradation
  - Contribution of different processes in attenuation

} Performance assessment for MNA

Assessment using MNA guidance

Matrix porewater vs fracture water chemistry





- Diffusion is important for attenuation
- Matrix has different roles for contaminants & oxidants

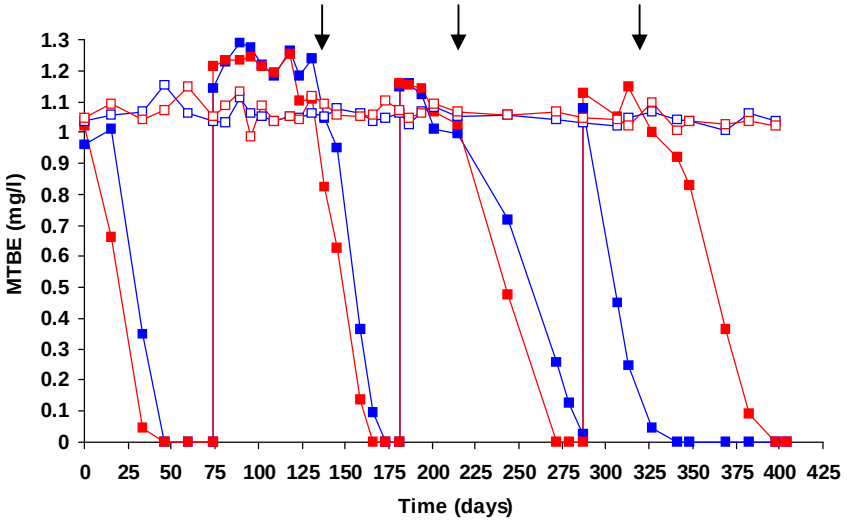
Assessment using MNA guidance
Electron acceptor consumption (kg)

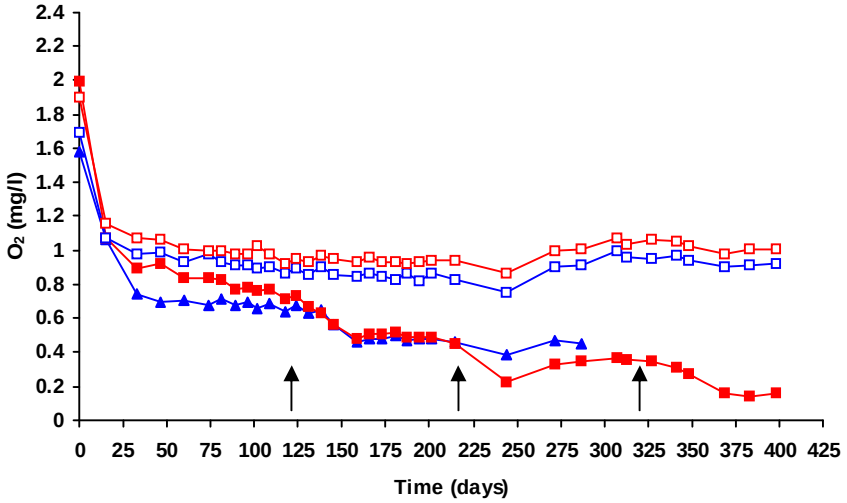
Process descriptor	Advection ($M_{advected\ EA}$)	Matrix diffusion ($M_{diffusion\ EA}$)	Plume residual ($M_{residual\ EA}$)	Total EA consumption	Equivalent BTEX degraded ($M_{SZ\ degraded}$)
O_2	137	29		166	53.1
NO_3	1,584	1,223		2,807	561.4
SO_4	3,311	1,720	814	4,217	886
Mn			10.6	10.6	0.97
Fe			46.2	46.2	2.1
CH_4			0.92	0.92	1.2
Total	**5,032**	**2,972**	**872**	**7,248**	**1,504**

- Dissolved electron acceptors dominant oxidant consumption (SO_4 = 60%)
- Mineral-based electron acceptors (oxides) unimportant
- Diffusion provides significant electron acceptors for degradation
- Total electron acceptor consumption = 1.5 tonnes BTEX; $T_{0.5}$ = ~2 yrs
- NO_3 & SO_4 most important (96%) for BTEX degradation

Controls on MTBE degradation

Microcosm studies





- Uncontaminated g/w & core from MW27, contaminated g/w from MW18, g/w temp
- Rapid and repeated degradation of MTBE
- Aerobic MTBE degradation demonstrated for plume concentrations & background O_2 content
- Other experiments show degradation potential in uncontaminated aquifer systems
- Expect MTBE degradation where O_2 available and other hydrocarbons absent
- Can qualify risk associated with MTBE, revise NA assessment

Final assessment - BTEX

Stage 1: Screening	**Is MNA a viable option?**	**Yes**
Stage 2: Demonstration	**Is there evidence that NA is occurring now?**	**Yes**
Stage 3: Assessment	**Will MNA meet risk management objectives in the future?**	**Yes, plume apparently stable**
Stage 4: Implementation	**Does MNA continue to meet objectives in practice ?**	**Design appropriate long-term monitoring programme**

Final assessment - MTBE

Stage 1: Screening	**Is MNA a viable option?**	**Yes**
Stage 2: Demonstration	**Is there evidence that NA is occurring now?**	**Yes, field & lab**
Stage 3: Assessment	**Will MNA meet risk management objectives in the future?**	**Increased confidence, supported by lab studies**
Stage 4: Implementation	**Does MNA continue to meet objectives in practice ?**	**Further monitoring required to verify performance**

What did we learn ?

- MNA performance assessment – Chalk aquifer, fuel spills
  - Integrated S.I. / data required for design of monitoring network
  - Consider MLS with “conventional” single screen MW
  - Consider temporal variability in interpretation – source, plume, processes etc
  - NA of MTBE may be difficult to detect from field data (monitoring, fuel composition issues)

- Case study plume
  - Demonstrated effective NA of BTEX
  - Likely effective NA of MTBE
  - Various NA processes important, different role for BTEX vs MTBE
  - Required all lines of evidence for analysis

Case study references

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