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Natural Attenuation of an Anaerobic Naphthalene Plume: Field and Laboratory Evidence of Bioattenuation

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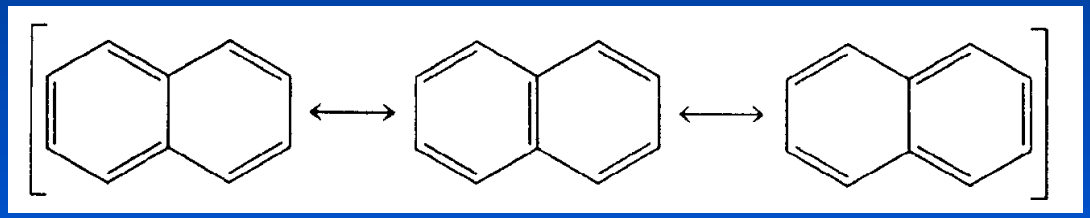
Introduction

- Naphthalene is the most simple polycyclic aromatic hydrocarbon (PAH)



- It is principally produced by petroleum refining and coal-tar distillation

- Contaminant widely found in groundwater at wood preserving facilities

Background

- Naphthalene is known to degrade aerobically (Ehrlich et al., 1982; Heitkamp and Cerniglia, 1989)

- However its biodegradation under anaerobic conditions is less certain

- Most old contaminated sites are under anaerobic (reductive) conditions

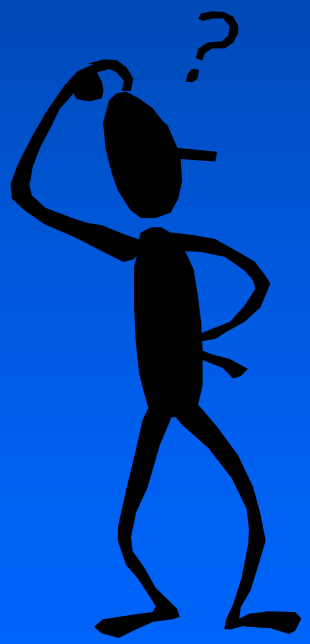
Background

- Naphthalene biodegrades anaerobically :)
  - Mihelcic and Luthy, 1988
  - Al-Bashir et al., 1990
  - Thierrin et al., 1995
  - Rockne and Strand, 1998

- Naphthalene does not biodegrade anaerobically :(
  - Goerlitz et al., 1985
  - Klecka et al., 1990
  - Genthner at al., 1997
  - Bjerg et al., 1999

Background

- Field evidence --- Support biodegradation
- Lab work --- Do not support biodegradation
  - Godsy et al., 1992
  - King et al., 1999



Present Study

The problem at the study site:

- Wood preserving site
- Contaminant plume composed mainly naphthalene
- Discharging into a tidally influenced river
- Anaerobic conditions
- Apparent steady plume
- Apparent mass loss of naphthalene by biodegradation
- Previous laboratory microcosm experiments showed no anaerobic biodegradation

Objectives and Activities

OBJECTIVE: to determine if anaerobic biodegradation of naphthalene is occurring at the site

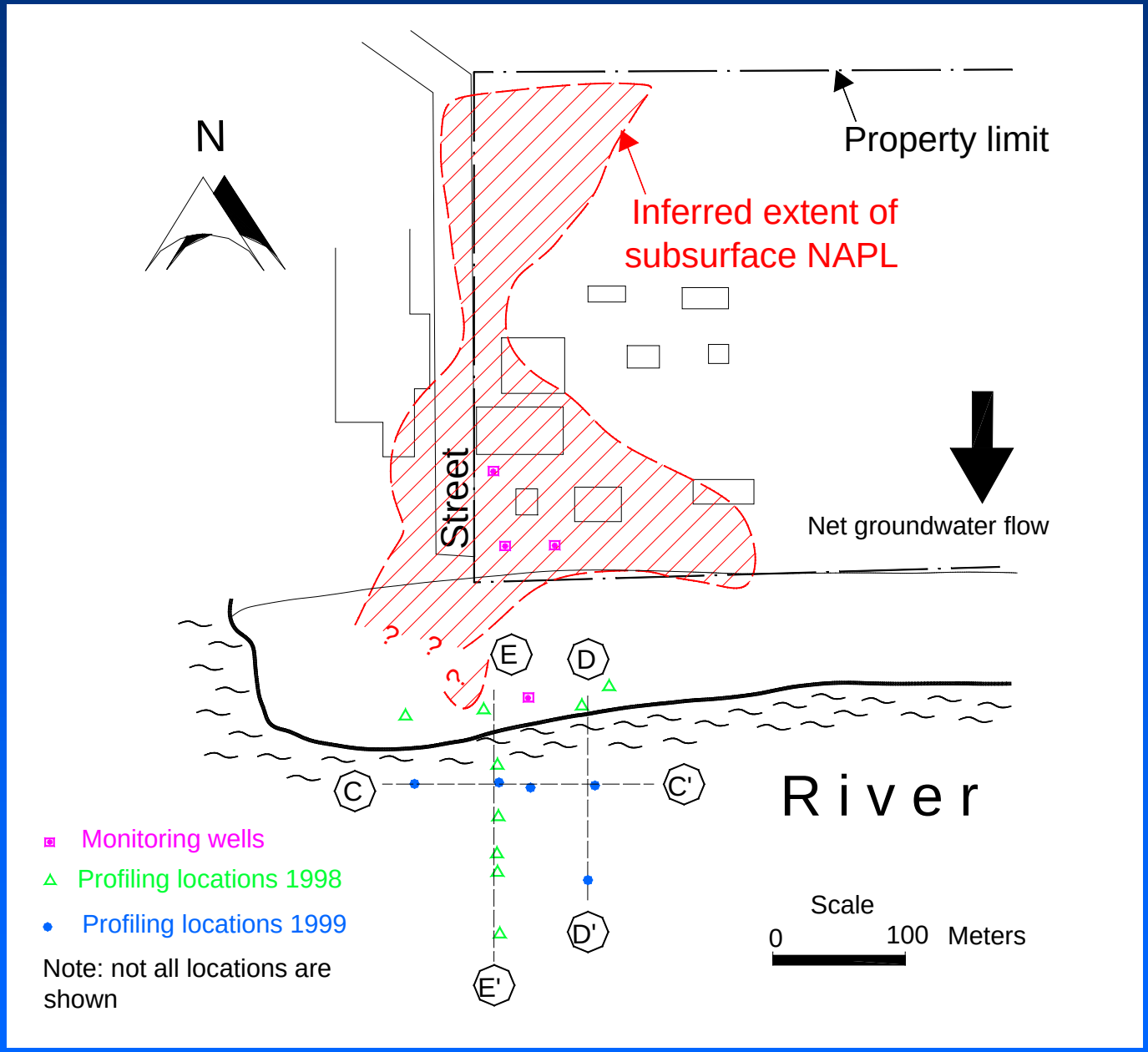
- Re-asses the contaminant plume (Field Work with UBC)

- Laboratory microcosm experiments with sediments from underneath the river

- Determine the stable carbon isotope ratio ($\delta^{13}C$) of naphthalene

- A tracer test using radiolabelled (^{14}C) naphthalene (UBC)

Field Work

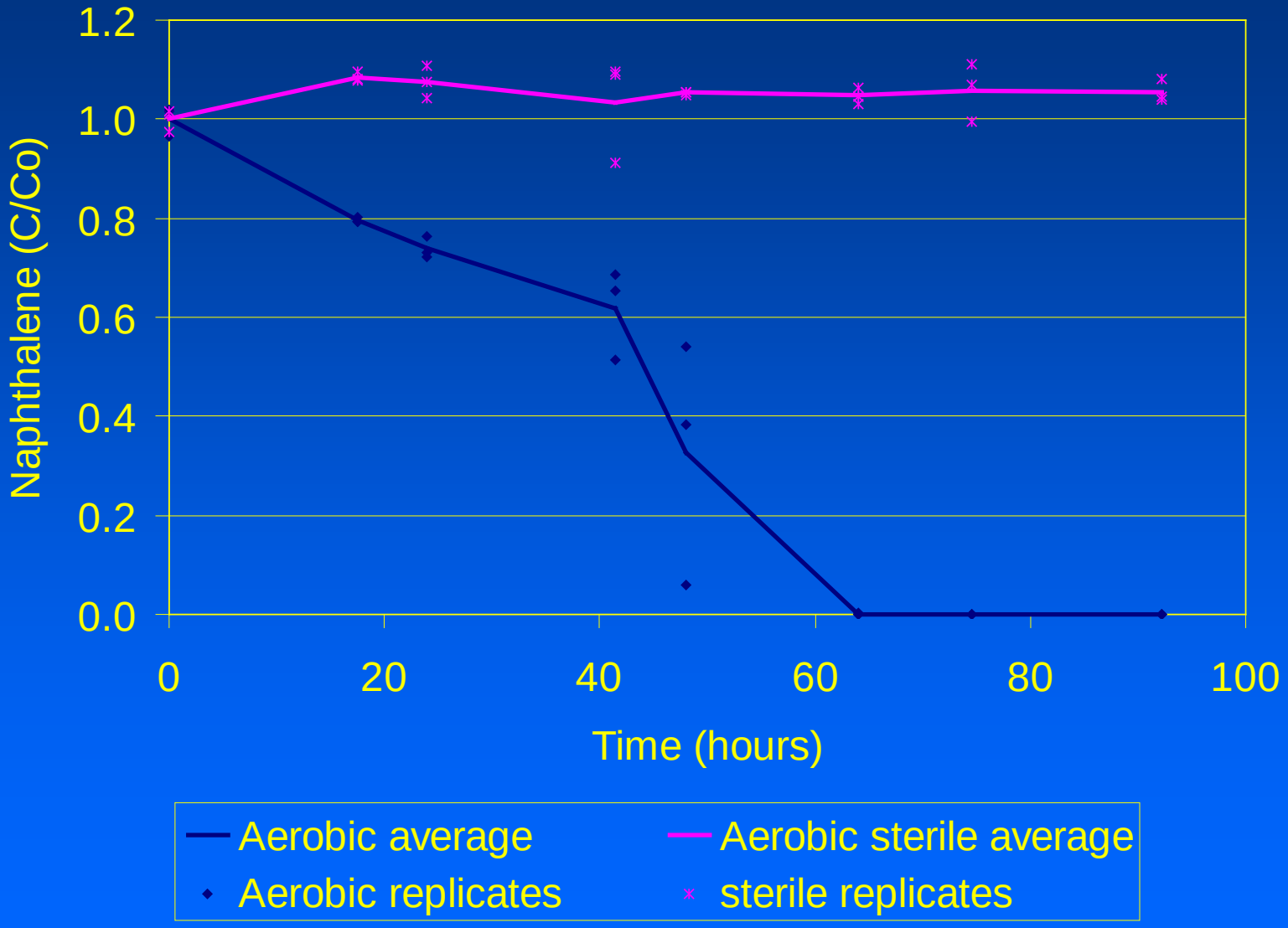

N
Property limit
Inferred extent of subsurface NAPL
Net groundwater flow
Street
River
E
D
C
C'
D'
E'
? ? ?
Monitoring wells
Profiling locations 1998
Profiling locations 1999
Note: not all locations are shown
Scale
0
100 Meters

Lab Work

1) Microcosm experiments

- Aerobic
- Anerobic unamended
- Anerobic NO_3^--amended
- Anerobic $SO_4^=$-amended

Results - Microcosms



Results - Microcosms

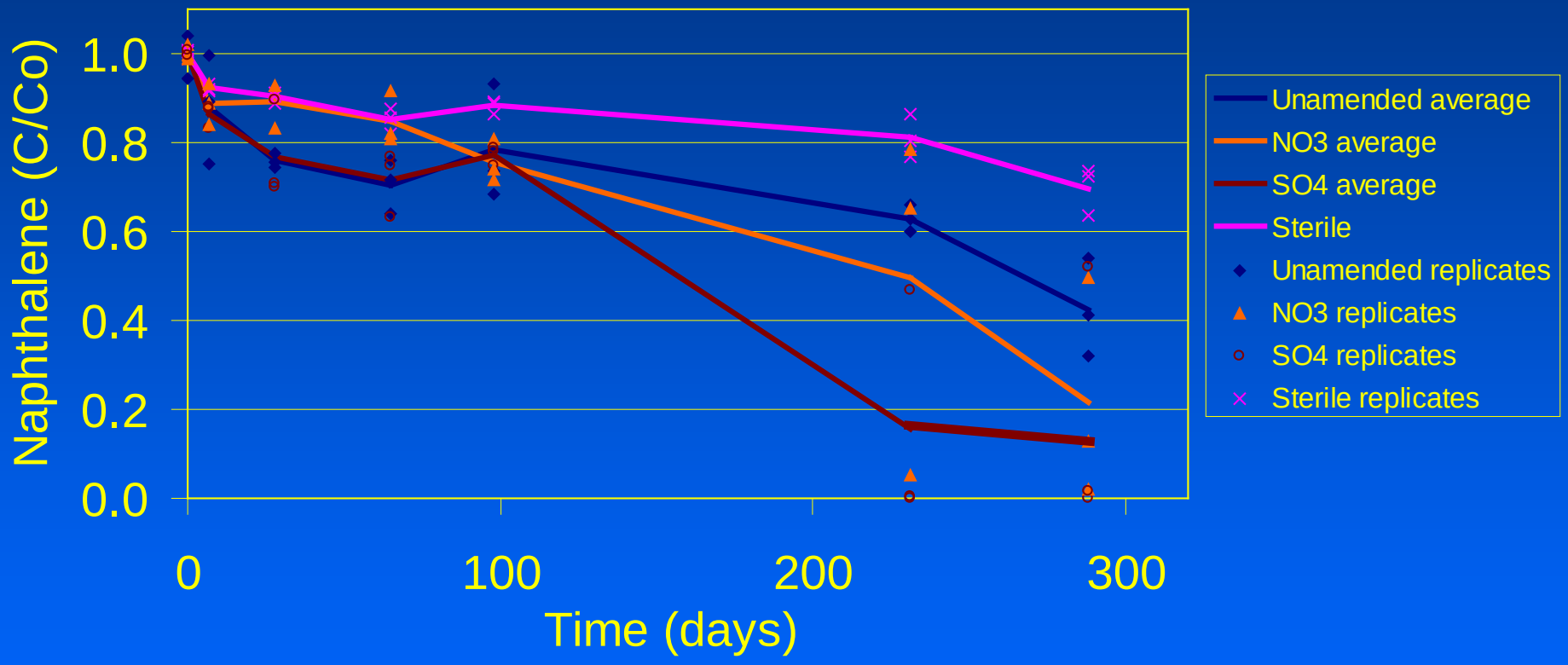
- Aerobic microcosms biodegraded all naphthalene after 60 hours

- This may apply at discharge end of plume

Results - Microcosms

- Anaerobic microcosms biodegraded 30 to 60% of naphthalene after 288 days
- Slow rate!!
- Also sporatic - degrades in some, but not much in other replicates

Results - Microcosms



Lab Work

2) Analyses of $\delta^{13}C$ on naphthalene

- Carbon has 2 stable isotopes: ^{13}C (abundance 1.11%) and ^{12}C, and one radioactive isotope: ^{14}C ($T_{1/2}$= 5,730 years)

- Preference of microorganisms to break ^{12}C-^{12}C bonds rather than ^{13}C-^{12}C bonds during biodegradation, hence should expect the residual C to be enriched in ^{13}C

Lab Work

- Therefore the $^{13}C/^{12}C$ ratio of the reactant could increase when biodegradation occurs

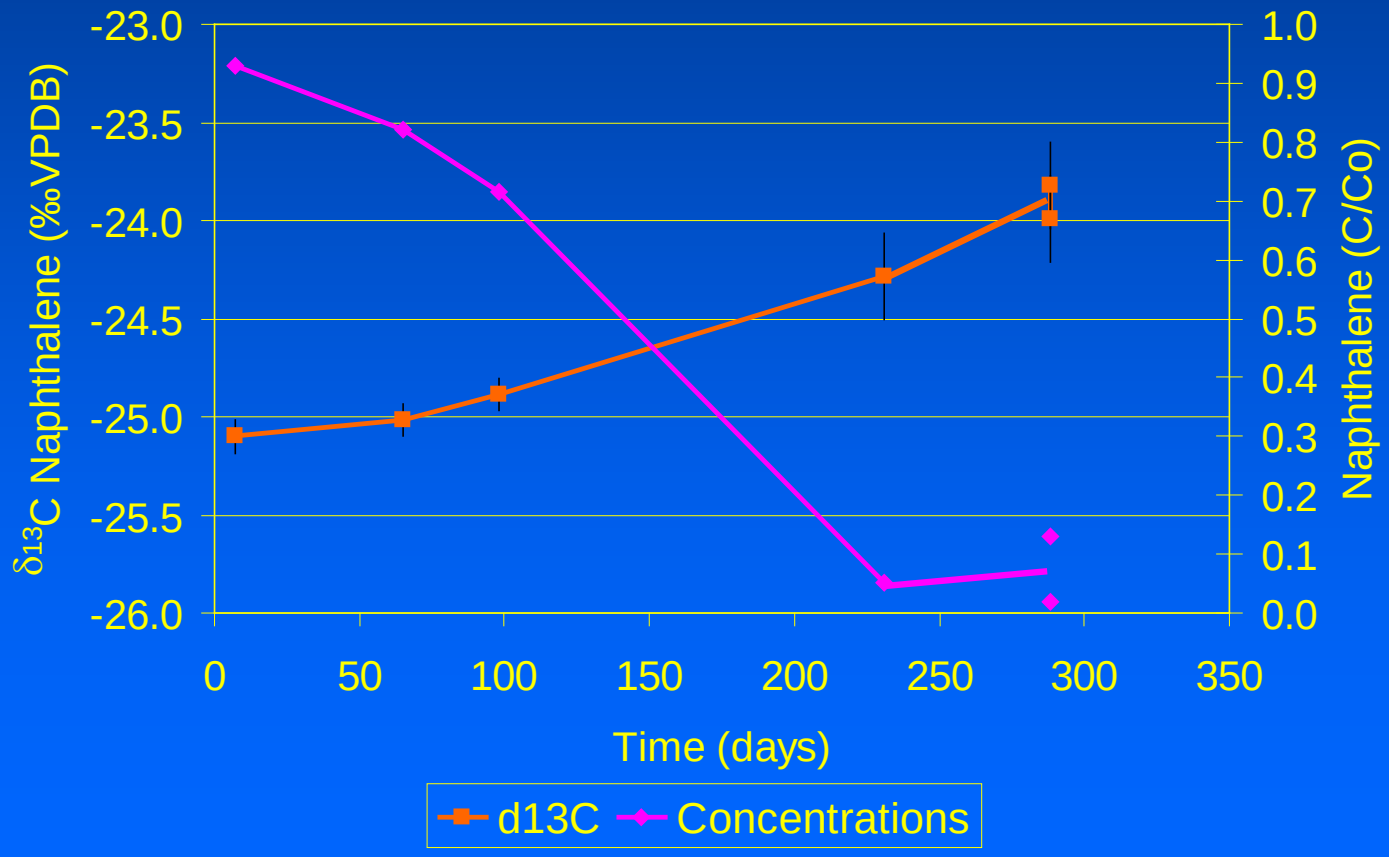
$$\delta^{13}C = \frac{\left(^{13}C/_{12}C\right)_{Sample} - \left(^{13}C/_{12}C\right)_{VPDB}}{\left(^{13}C/_{12}C\right)_{VPDB}} x1000‰$$

- A change in $\delta^{13}C$ has succesfully been demonstrated during biodegradation of chlorinated solvents

- Hunkeler et al., 1999; Bloom et al., 2000; Sherwood Lollar et al., 1999 (large fractionation)

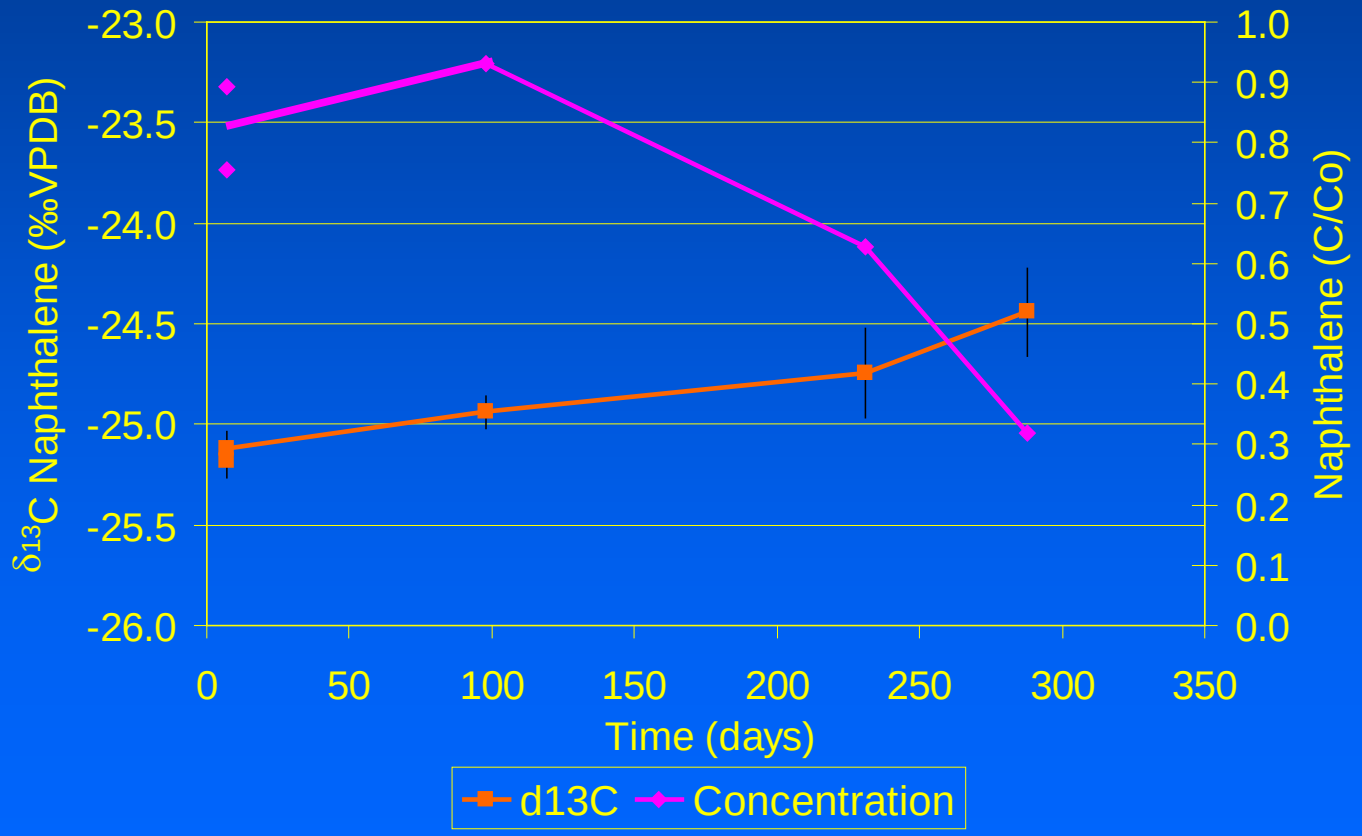
Results - δ^{13} on microcosms

- Slight $\delta^{13}C$ enrichment on naphthalene (1.3±0.3‰) in the denitrifiying microcosms



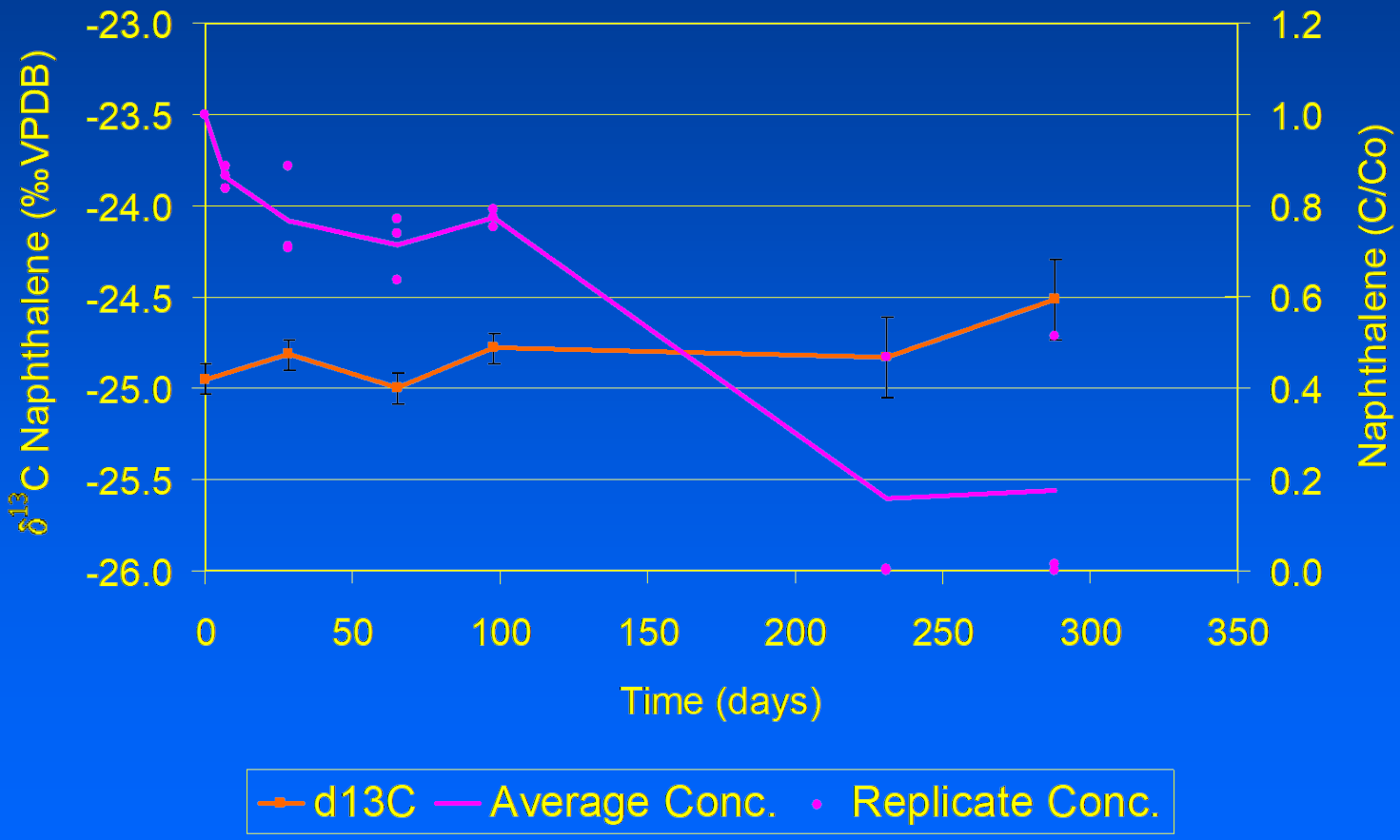
Results - δ^{13} on microcosms

- Slight δ^{13}C enrichment on naphthalene (0.7±0.3‰) in the unamended microcosms



Results - δ^{13} on microcosms

- No δ^{13}C change in sulphate-reducing microcosms



Summary - Results microcosms

- Potential for anaerobic biodegradation of naphthalene

- $\delta^{13}C$ fractionation of 0.7 to1.3±0.3‰ during anaerobic biodegradation of naphthalene (smaller during aerobic biodegradation)

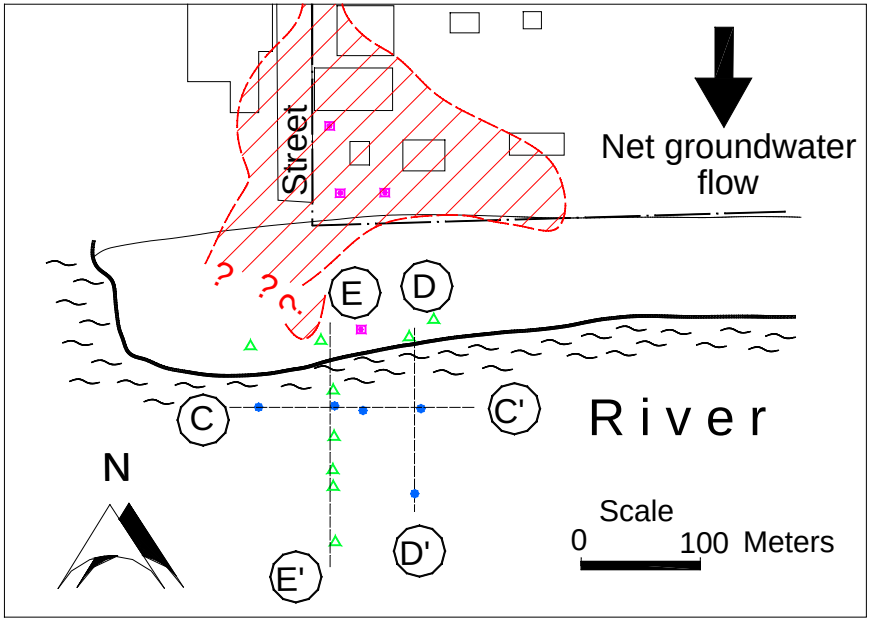
- Apparent biodegradation rates (anaerobic)

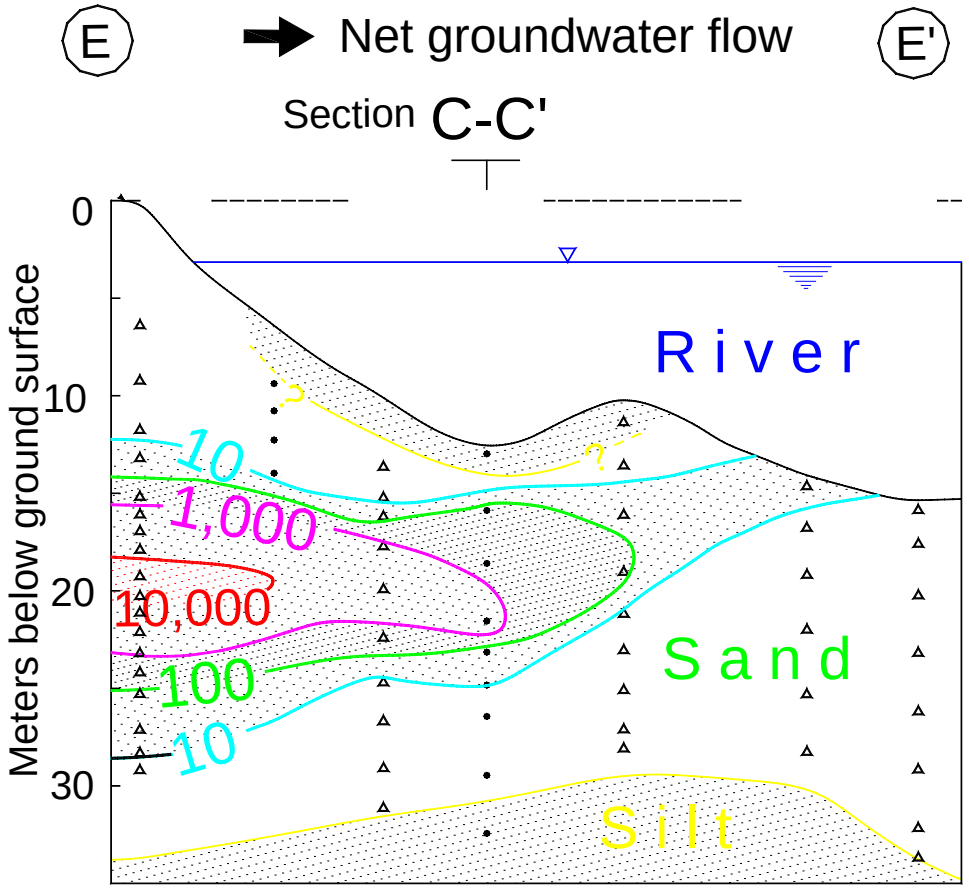
  0.3 to 2.2 yr^{-1}

Results - Site Profiling

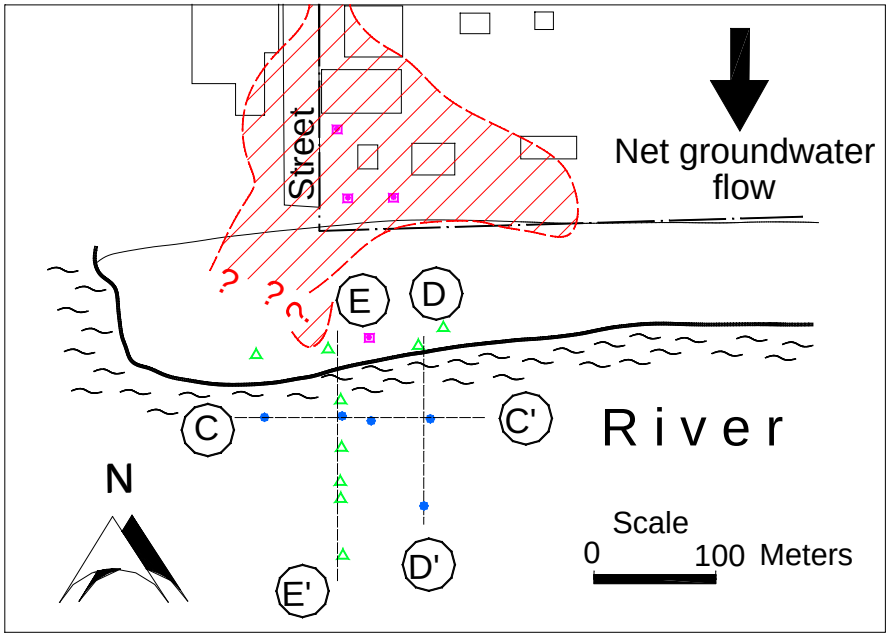
- Site groundwater is reductive (anaerobic)
- The plume is composed mainly of naphthalene
- Apparent steady plume

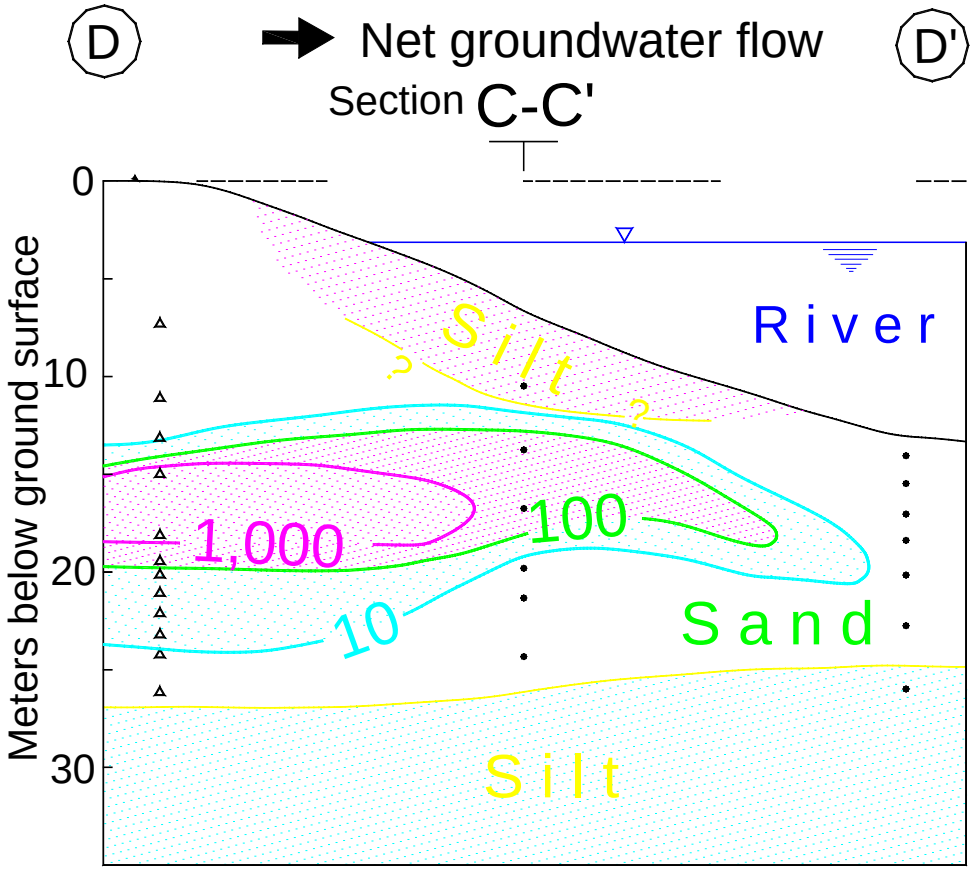
Results - Site Profiling



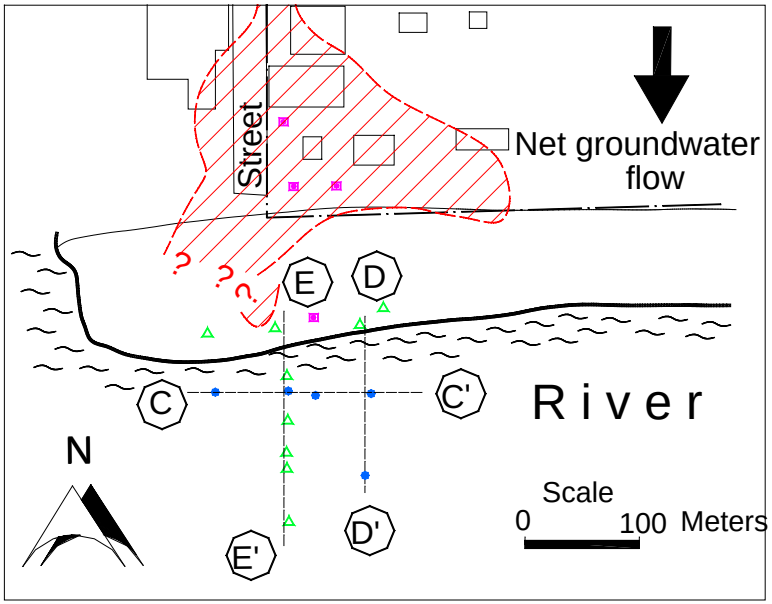


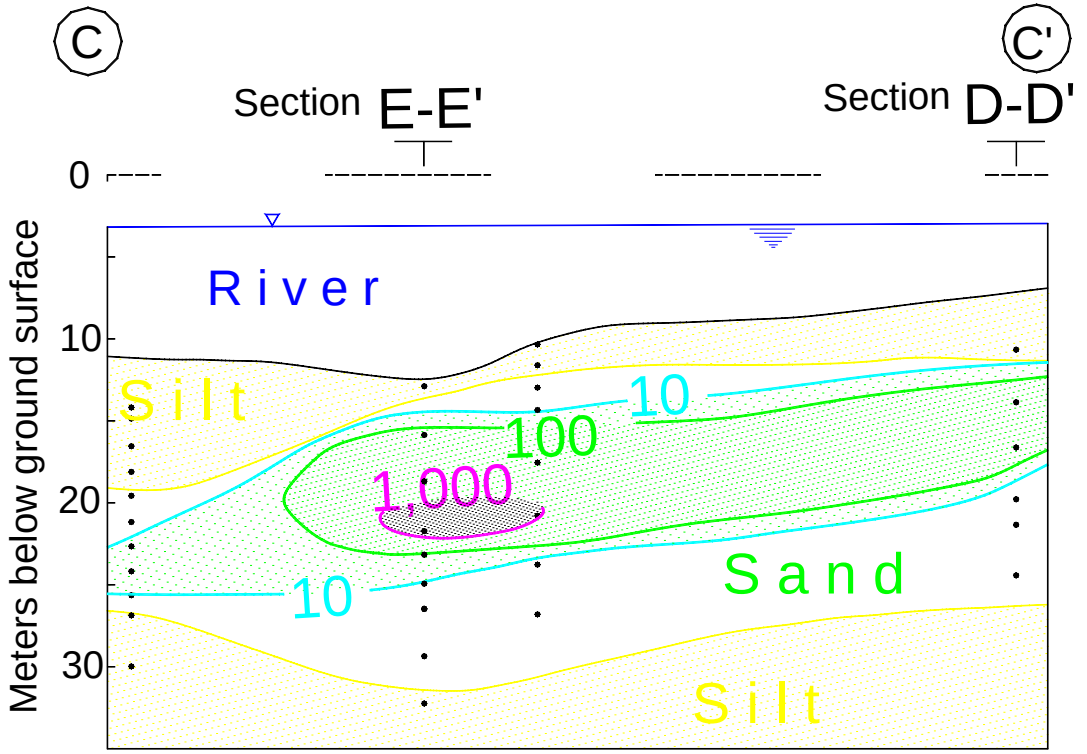
Results - Site Profiling





Results - Site Profiling





Results - Site modeling

- Transport model (Domenico's Equation in 3D) requires the use of biodegradation

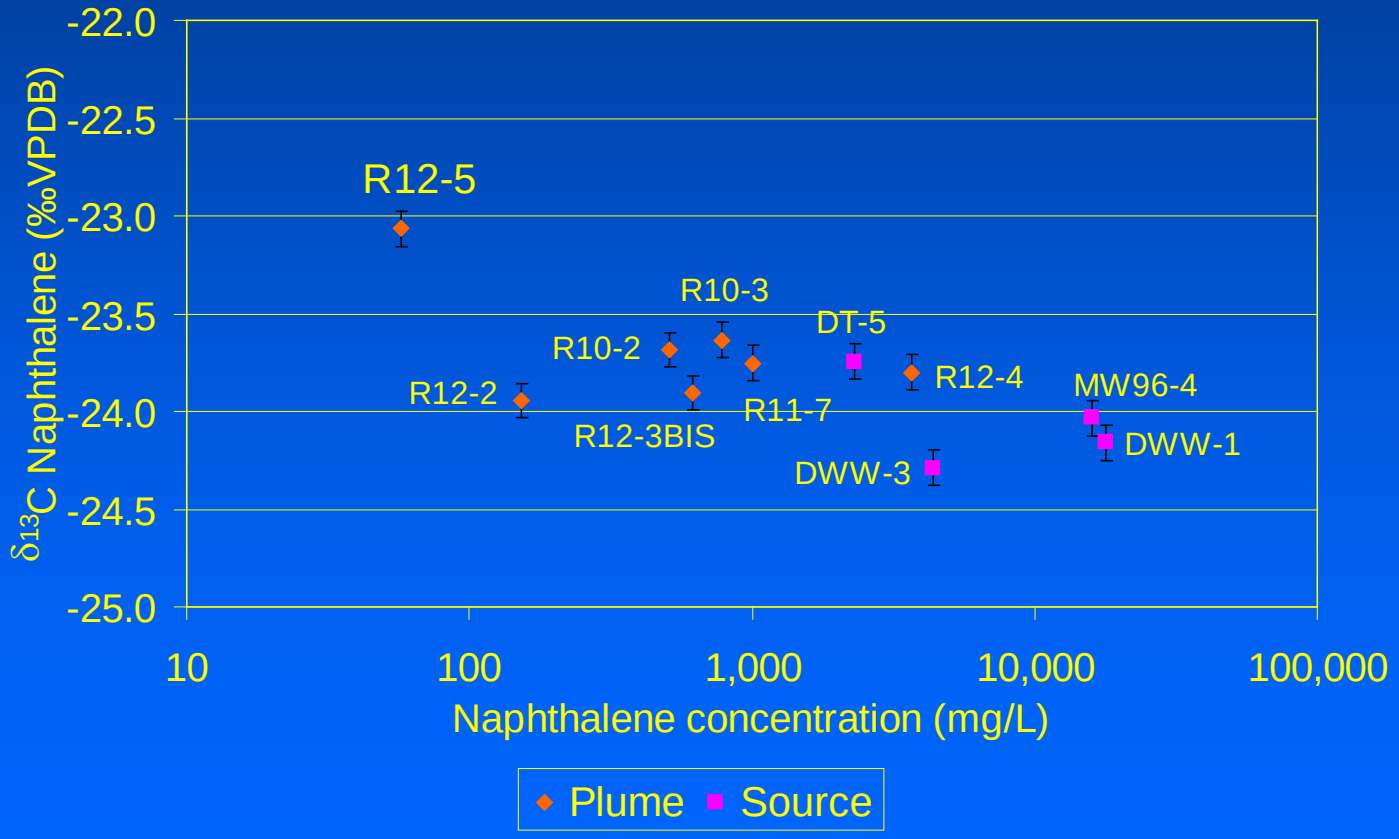
- Apparent biodegradation rates from transport model

  0.05 to 1.0 yr^{-1}

Results - Site $\delta^{13}C$

Results - Site $\delta^{13}C$

- Single point more enriched by 1.2±0.08‰



^{14}C-naphthalene tracer test

- Rationale:
  - Analyse for $^{14}CO_2$ as a possible by product of ^{14}C-naphthalene biodegradation
- Anaerobic conditions mantained
- Field work by UBC

^{14}C-naphthalene tracer test - Lab Work

Radioactivity analyses UW:

- Total ^{14}C activity
- ^{14}C-naphthalene
- $^{14}CO_2$ as a possible end product of biodegradation

^{14}C-naphthalene tracer test - Results

- Few samples contained small but measurable quantities of $^{14}CO_2$ (15 to 71 DPM/5ml ±4.4%)

- Bianchin (M.Sc., UBC) considered the significance of this low-concentration of $^{14}CO_2$

- Demonstrates mineralization of ^{14}C-naphthalene

Summary

- Laboratory microcosm experiments show potential for anaerobic biodegradation of naphthalene

($\delta^{13}C$ fractionation of 0.7 to 1.3±0.3‰,
and apparent biodegradation rates of 0.3 to 2.2 yr^{-1})

- Apparent biodegradation rates from transport model of the site: 0.05 to 1.0 yr^{-1}

- $\delta^{13}C$ fractionation from the field 1.2±0.08‰ (only one sample)

- Small amounts of $^{14}CO_2$ detected from tracer test.

Tentative Conclusion

- Anaerobic biodegradation of naphthalene is taking place, and is, in part, controlling the fate of naphthalene at the site.