



Earth Sciences Department

Evidence for Naphthalene Bioattenuation in a Groundwater Contaminant Plume Under a River

Luis E. Lesser

Now at:

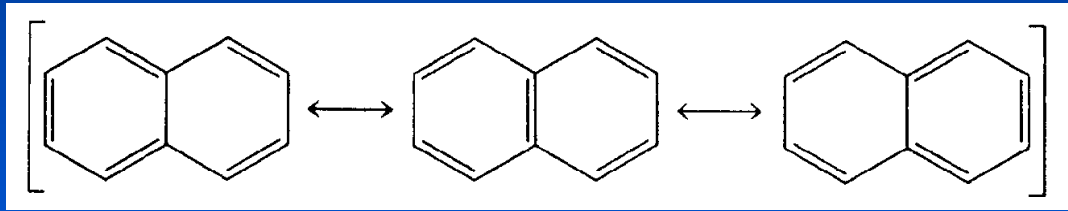
Department of Civil and Environmental Engineering



- Background
- Objectives
- Activities
 - Field work
 - Lab work
- Results and conclusions

Introduction

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



- It is principally produced by petroleum refining and coal-tar distillation
- Contaminant widely found at wood preserving facilities

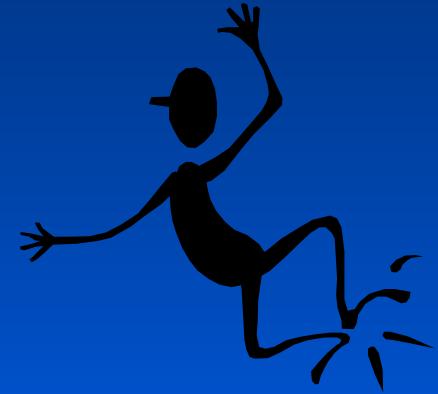
Background

- 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 et al., 1997
- Bjerg et al., 1999



Background

- Field evidence --- YES!
- Lab work --- NO!
 - Godsy et al., 1992
 - King et al., 1999



Present Study

The problem at the study site:

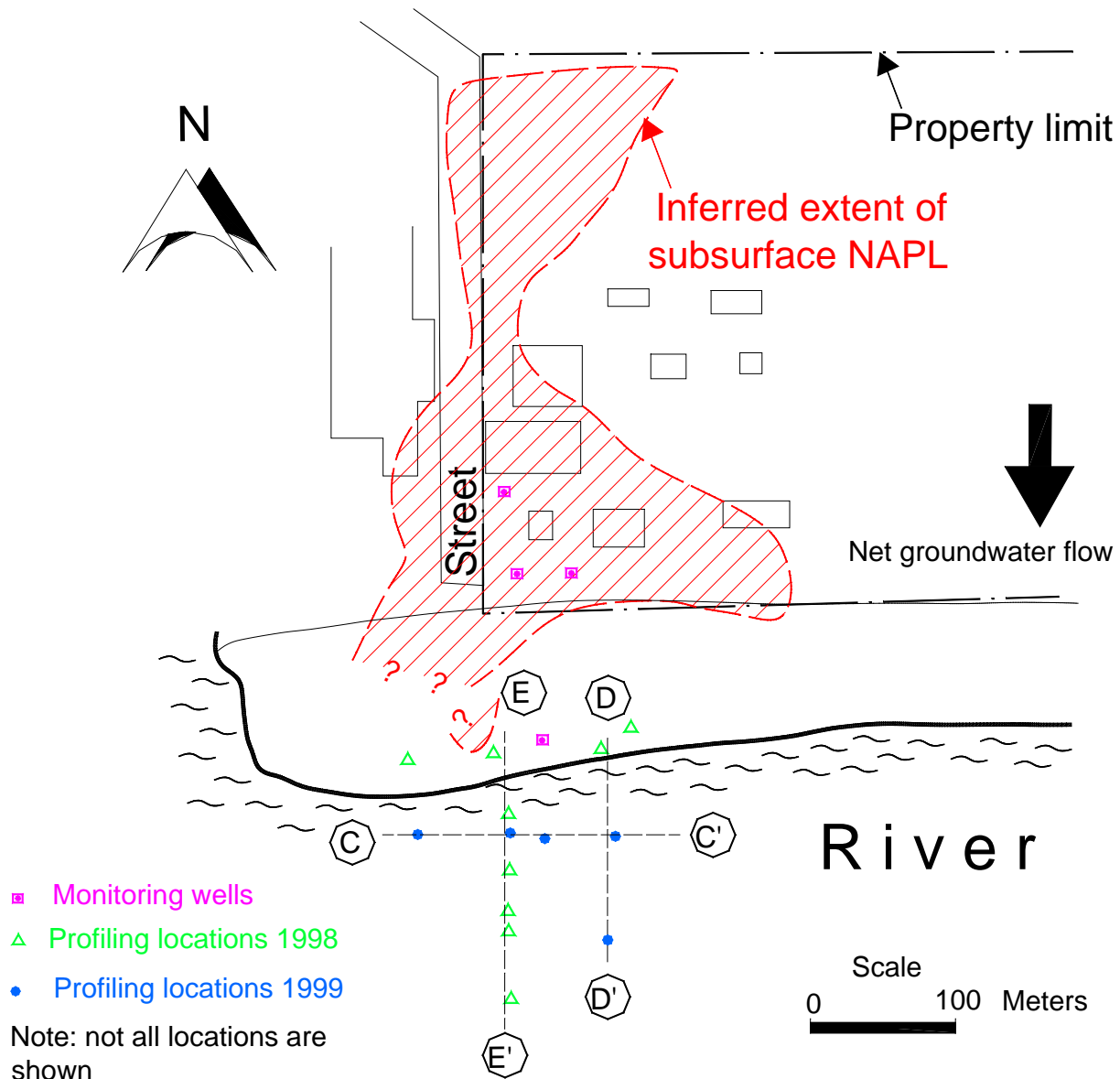
- Wood preserving site
- Contaminant plume composed mainly naphthalene
- Discharging into a tidally influenced river
- Anaerobic conditions
- Apparent steady plume
- Apparent mass loss of naphthalene by biodegradation
- Previous laboratory microcosm experiments showed no anaerobic biodegradation

Objectives and Activities

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

- Re-asses the contaminant plume (Field Work)
- Laboratory microcosm experiments with different sediments
- Determine the stable carbon isotope ratio ($\delta^{13}\text{C}$) of naphthalene
- A tracer test using radiolabelled (^{14}C) naphthalene

Field Work



Field Work



Field Work



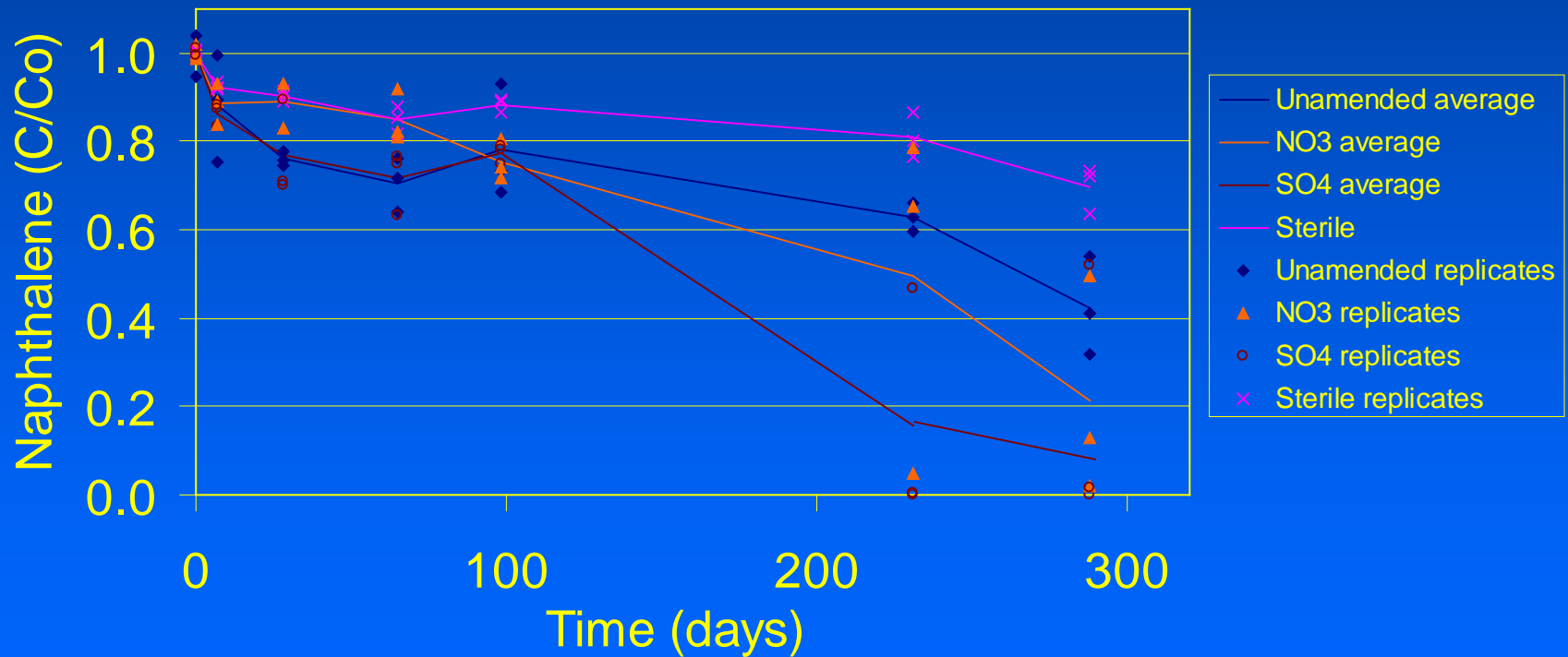
Lab Work

1) Microcosm experiments

- Anerobic unamended
- Anerobic NO_3^- -amended
- Anerobic $\text{SO}_4^{=}$ -amended

Results - Microcosms

- Anaerobic microcosms biodegraded 30 to 60% of naphthalene after 288 days. Slow rate!!



Lab Work

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

Lab Work

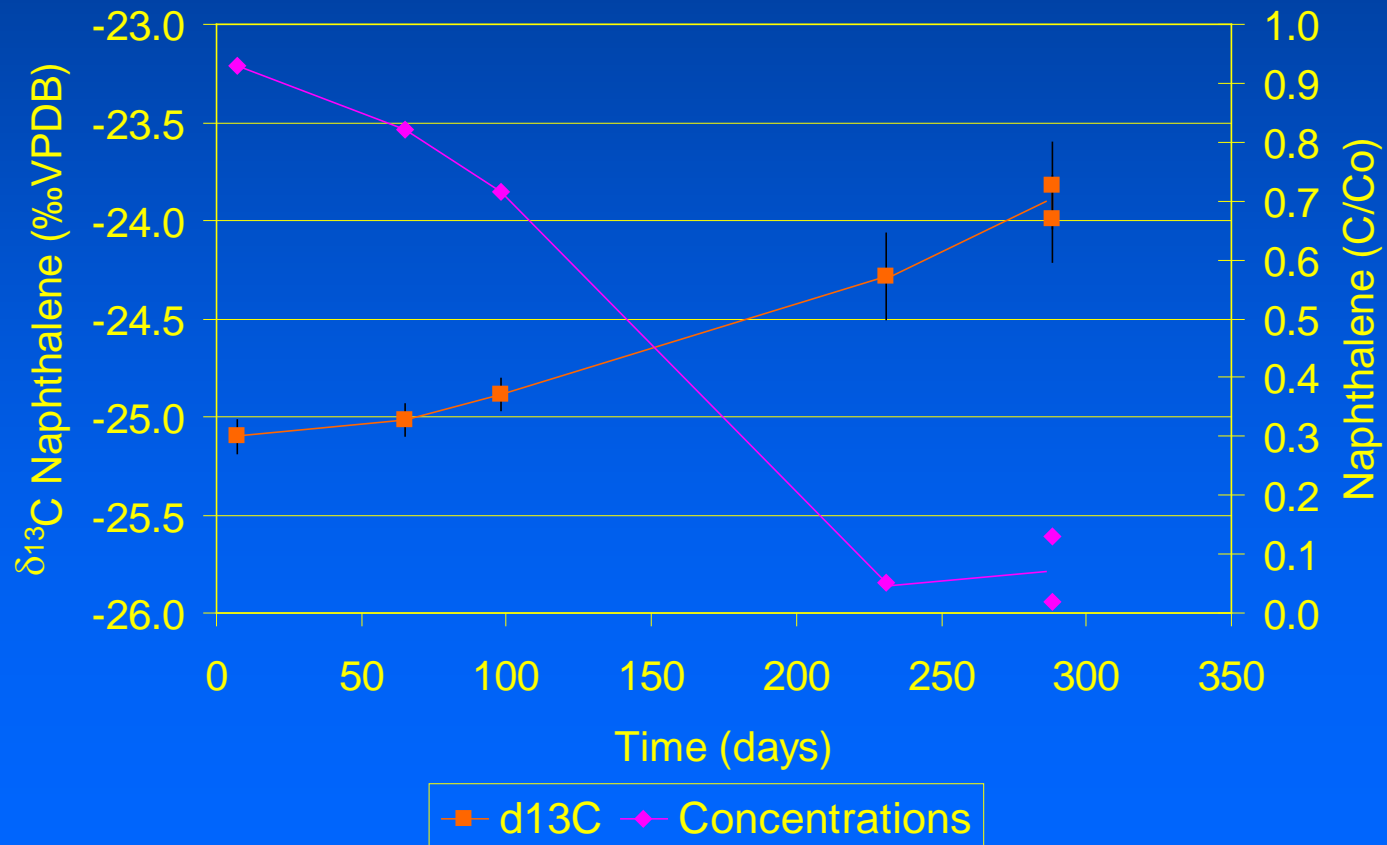
- Therefore the $^{13}\text{C}/^{12}\text{C}$ ratio of the reactant could increase when biodegradation occurs

$$\delta^{13}\text{C} = \frac{\left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{Sample}} - \left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{VPDB}}}{\left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{VPDB}}} \times 1000\text{‰}$$

- $\delta^{13}\text{C}$ has successfully demonstrated biodegradation of chlorinated solvents
- Hunkeler et al., 1999; Bloom et al., 2000; Sherwood Lollar et al., 1999 (large fractionation)

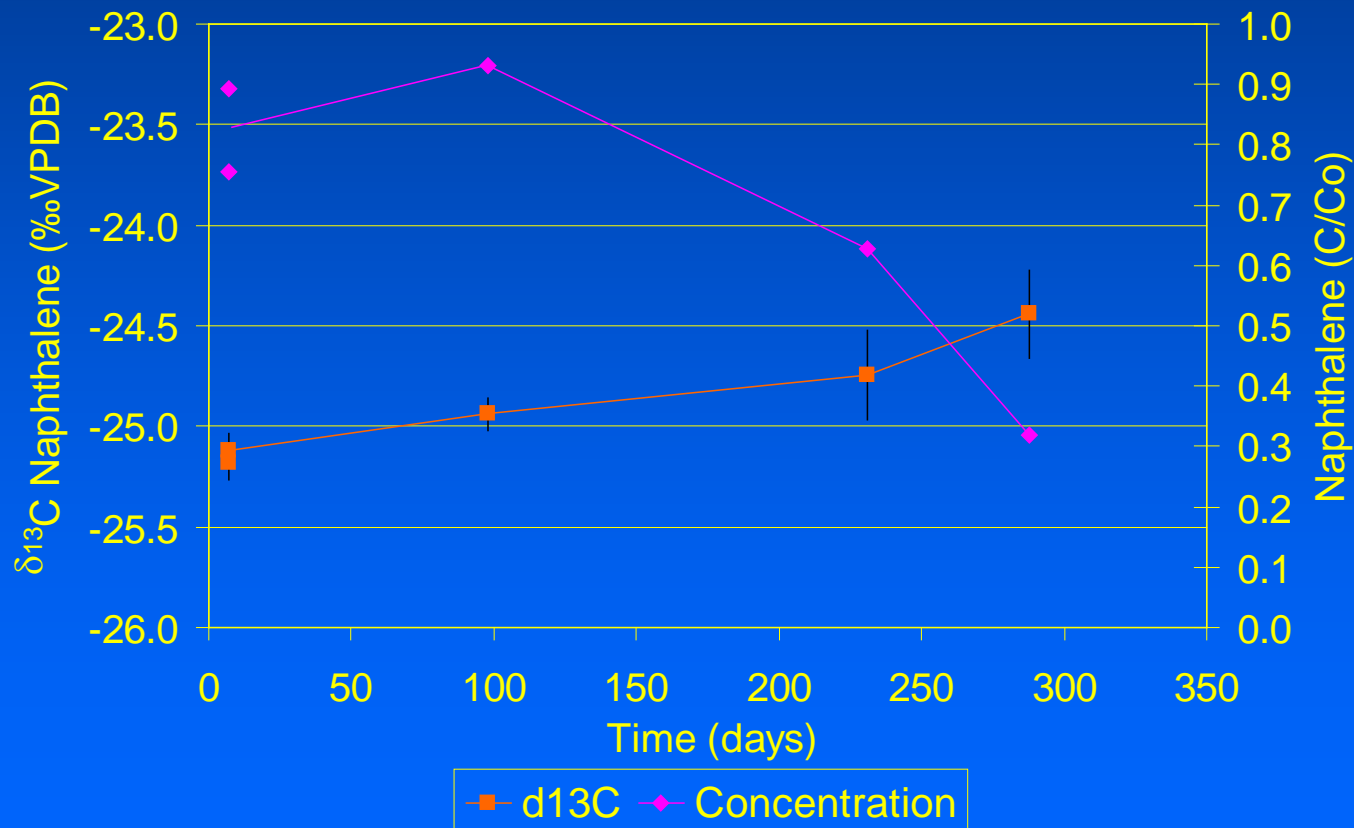
Results - $\delta^{13}\text{C}$ on microcosms

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



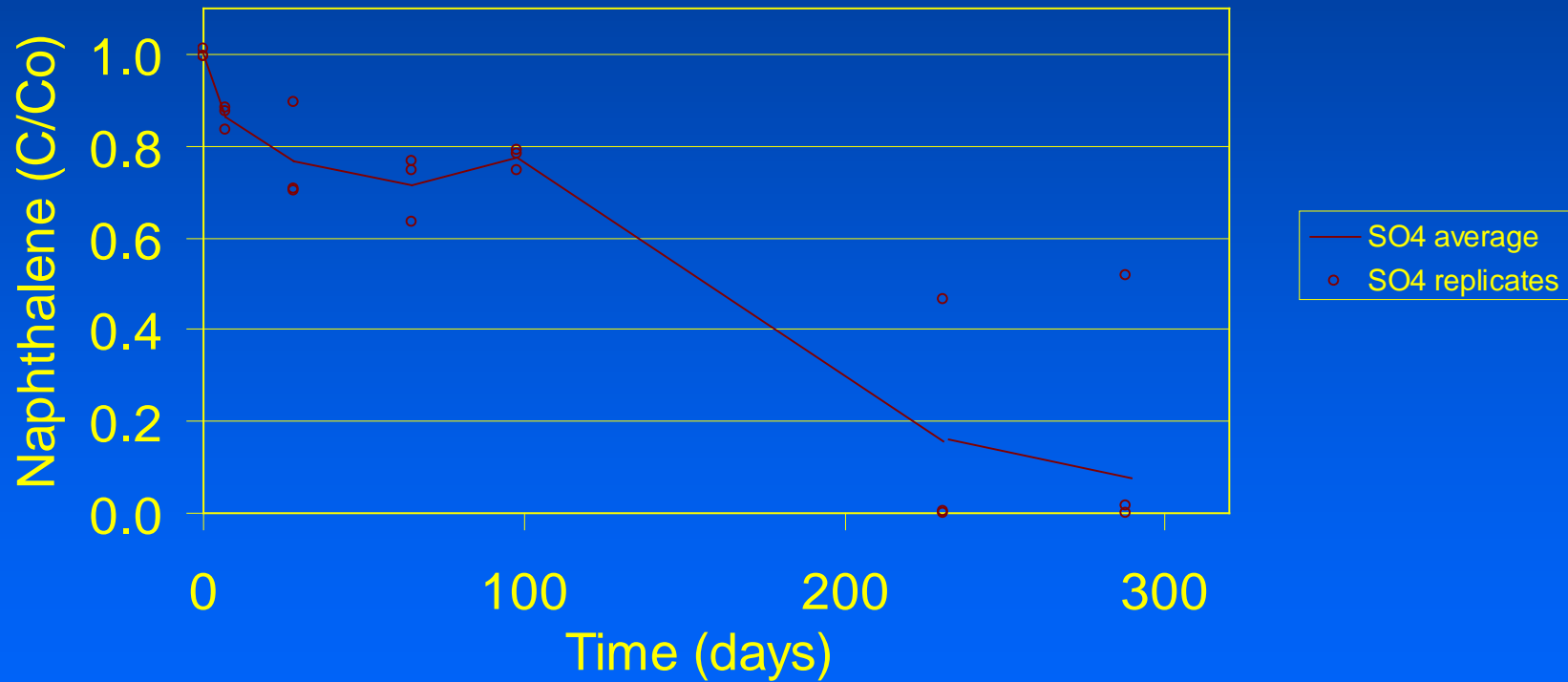
Results - $\delta^{13}\text{C}$ on microcosms

- Slight $\delta^{13}\text{C}$ enrichment on naphthalene ($0.7 \pm 0.3\text{‰}$) in the unamended microcosms



Results - $\delta^{13}\text{C}$ on microcosms

- No $\delta^{13}\text{C}$ change in sulphate-reducing microcosms



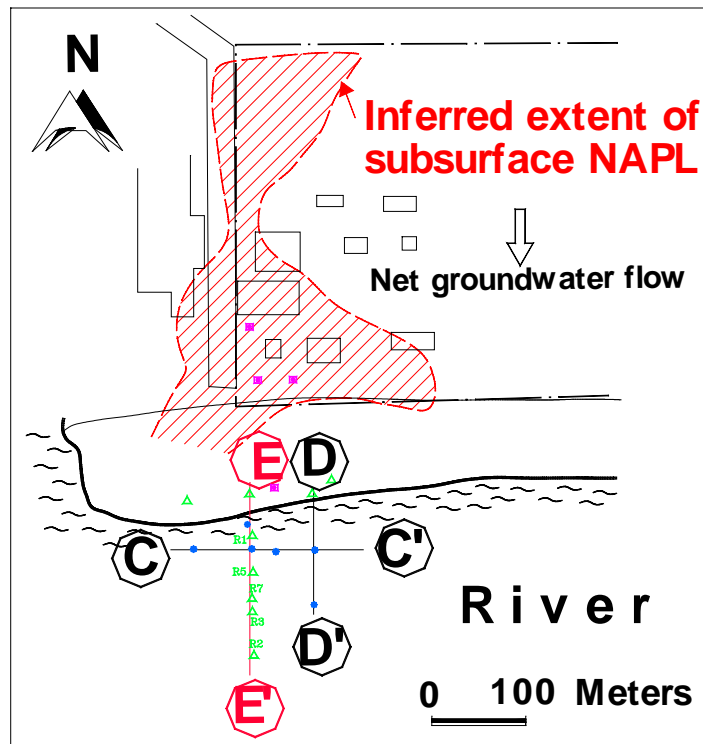
Summary - Results microcosms

- Potential for anaerobic biodegradation of naphthalene
- $\delta^{13}\text{C}$ fractionation of 0.7 to $1.3 \pm 0.3\text{‰}$ during anaerobic biodegradation of naphthalene (smaller during aerobic biodegradation)
- Apparent biodegradation rates (anaerobic)
0.3 to 2.2 yr^{-1}
- Also sporadic - degrades in some, but not much in other replicates

Results - Site Profiling

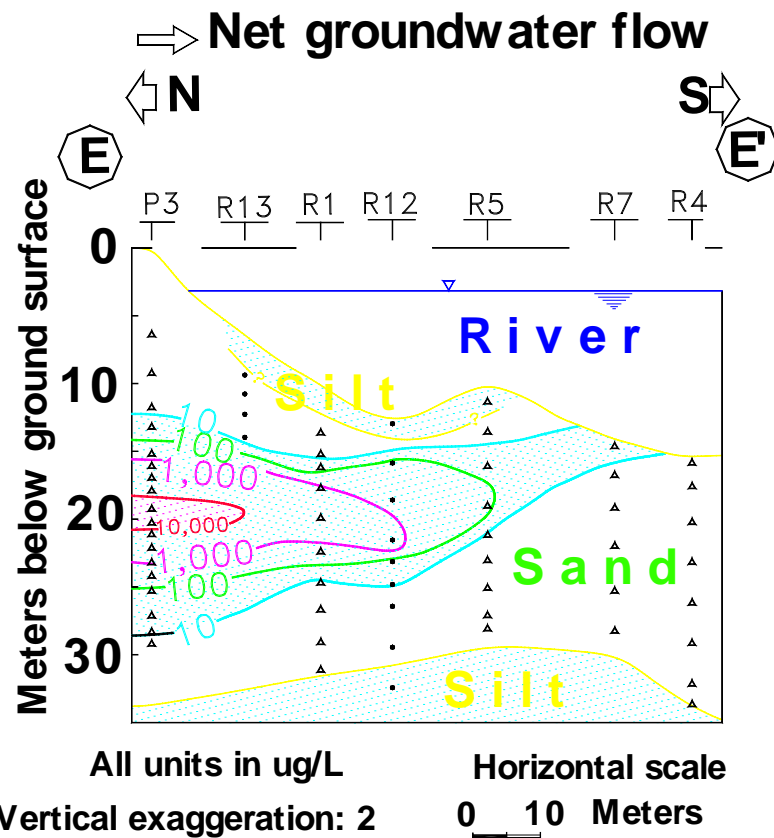
- Site groundwater is reductive (anaerobic)
- The plume is composed mainly of naphthalene
- The plume has reached a steady state

Results - Site Profiling



■ Monitoring wells
 ▲ From Anthony, 1997

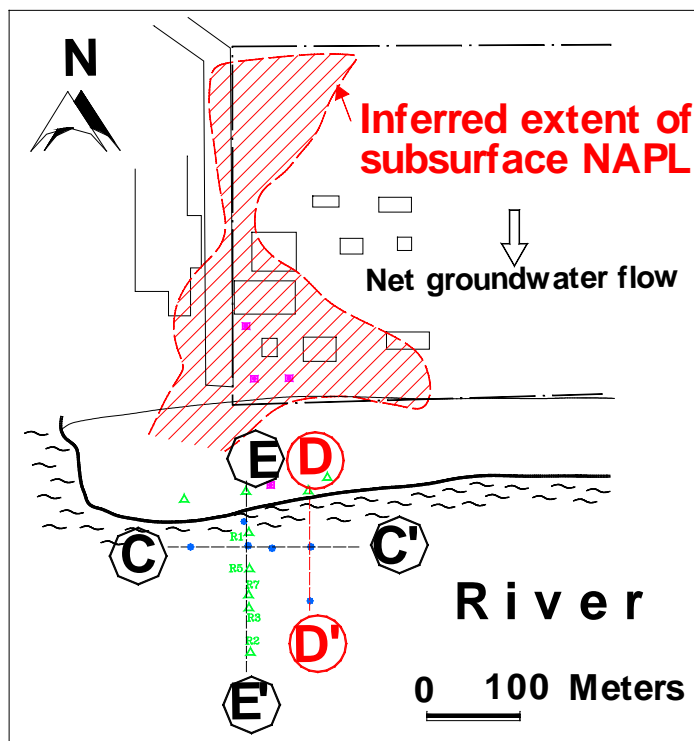
• Lesser and Bianchin, 1999



All units in ug/L
 Vertical exaggeration: 2

Horizontal scale
 0 10 Meters

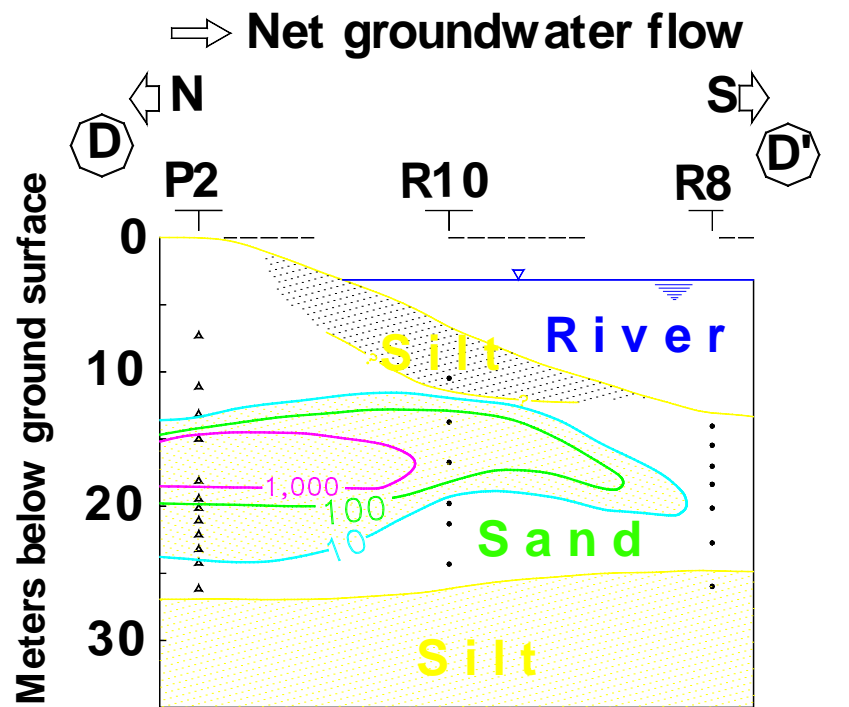
Results - Site Profiling



■ Monitoring wells

△ From Anthony, 1997

• Lesser and Bianchin, 1999



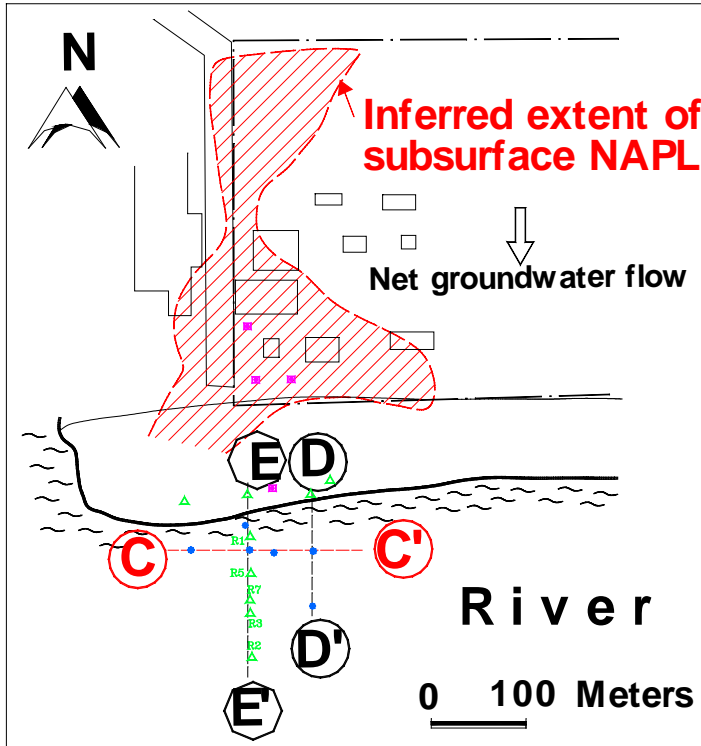
All units in ug/L

Vertical exaggeration: 2

Horizontal scale

0 10 Meters

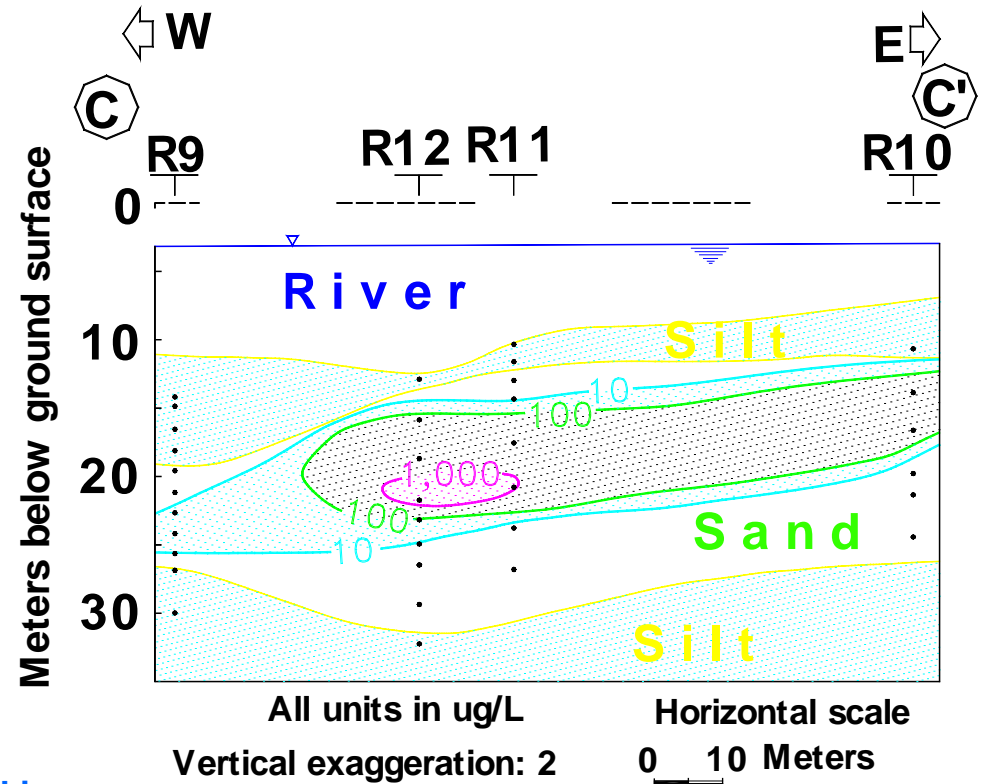
Results - Site Profiling



■ Monitoring wells

• Lesser and Bianchin, 1999

△ From Anthony, 1997

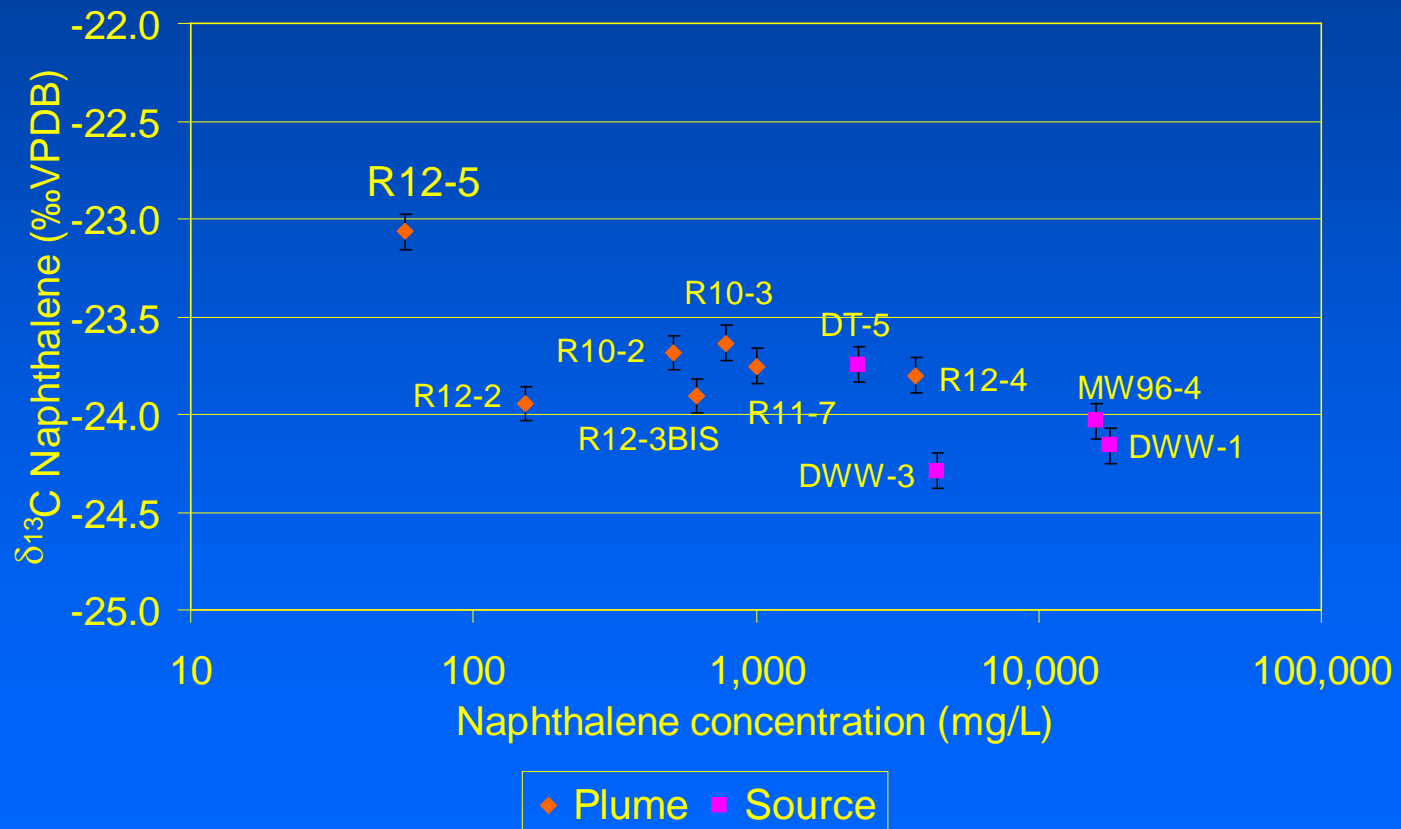


Results - Site modeling

- 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 $\delta^{13}\text{C}$

- Single point more enriched by $1.2 \pm 0.08\text{‰}$



^{14}C -naphthalene tracer test

- Rationale:

- Analyse for $^{14}\text{CO}_2$ as a possible by product of ^{14}C -naphthalene biodegradation

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

Field work by UBC:

- Installed a temporary drive-point piezometer
- Extracted 5m^3 of groundwater under a N_2 headspace
- Spiked with ^{14}C -naphthalene and bromide
- Re-injected into the aquifer
- The plume was sampled 48, 78 and 115 days after injection, using the Waterloo Profiler

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

Radioactivity analyses UW:

- Total ^{14}C activity
- ^{14}C -naphthalene
- $^{14}\text{CO}_2$ as a possible end product of biodegradation

^{14}C -naphthalene tracer test - Results

- Few samples contained small but measurable quantities of $^{14}\text{CO}_2$ (15 to 71 DPM/5ml $\pm 4.4\%$)
- Demonstrates mineralization of ^{14}C -naphthalene

Summary

- Laboratory microcosm experiments show potential for anaerobic biodegradation of naphthalene
($\delta^{13}\text{C}$ fractionation of 0.7 to $1.3 \pm 0.3\text{‰}$,
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}
- $\delta^{13}\text{C}$ fractionation from the field $1.2 \pm 0.08\text{‰}$
(only one sample)
- Small amounts of $^{14}\text{CO}_2$ detected from tracer test.

Conclusion

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