

## What can stable isotopes tell us about biodegradation in groundwaters?

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## In-situ Biodegradation

Biodegradation is the key process underpinning natural attenuation of organic groundwater contaminants.

Unlike other attenuation mechanisms, in-situ biodegradation results in a reduction in contaminant mass.

## Why are isotopes useful for assessing biodegradation?

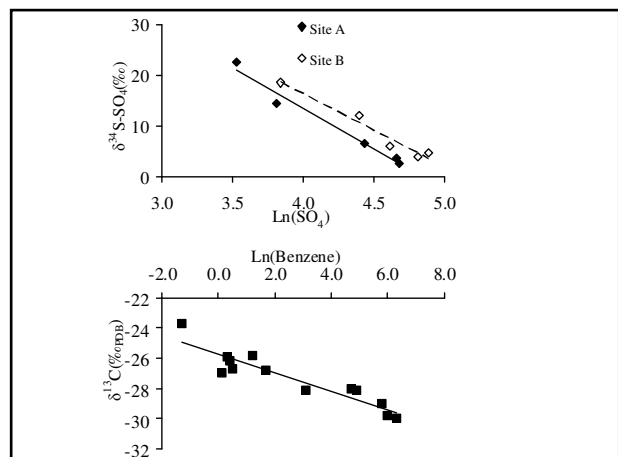
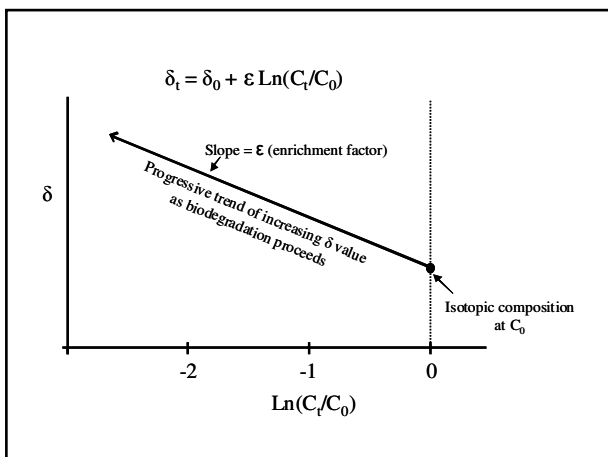
Reduction in contaminant concentration can result from a wide variety of processes: e.g. dilution, sorption.

In general these physical processes do not change isotope compositions

Isotopes fractionate during biodegradation  
- therefore they may act as a "fingerprint"

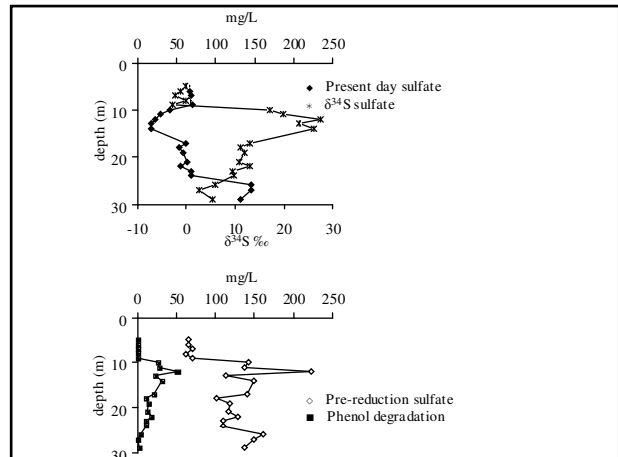
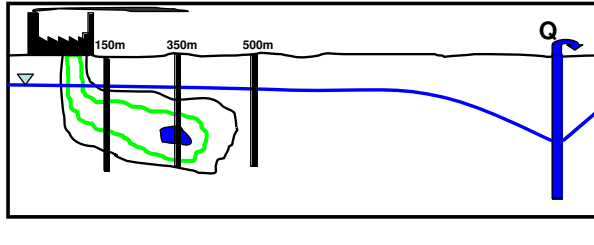
## How do we apply isotopes to study biodegradation?

Isotopes fractionate during biodegradation  
- light isotopes form weaker bonds and react faster  
This can be applied in two ways:  
1) changes in isotope composition of contaminants themselves (particularly C in organics);  
2) Changes in isotope composition of electron acceptors used during biodegradation (e.g. N in nitrate and S in sulfate).



**Former coal coking plant**  
 – plume dominated by phenols.

**-Sherwood Sandstone**, covered by thin alluvial sand and gravel



Isotope fractionation during biodegradation – approach

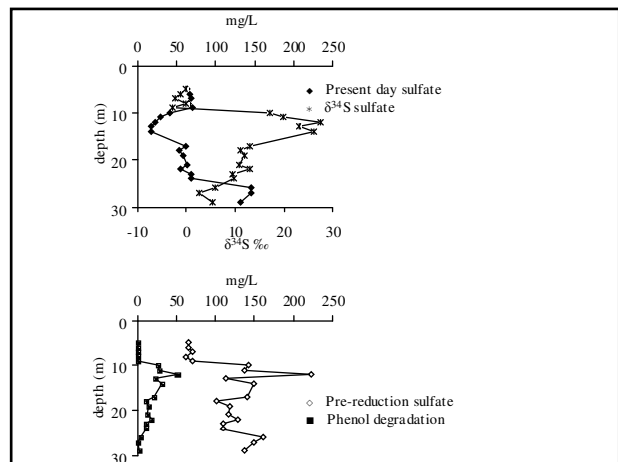
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First – establish  $\epsilon$ -value for sulfate reduction in this system.

Use observed enrichments in  $^{34}\text{S}$  to calculate amount of sulfate reduced:

→ back calculate original sulfate concentration profile

→ calculate corresponding amount of phenol biodegraded



Isotope fractionation during biodegradation – case study

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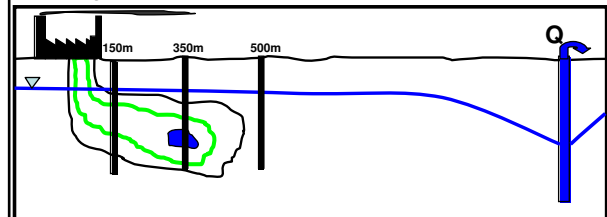
Total carbon processed by sulfate reduction is <5% of contaminant mass in this profile (in ~50 years).

Sulfate reduction is not limited by sulfate availability  
 - high sulfate concentrations persist in core of plume  
 Plume fringe, phenol <1200 mgL<sup>-1</sup> → extensive sulfate redn  
 Transition, phenol 1,200 to 1,800 mgL<sup>-1</sup> → limited sulfate redn  
 Plume core, phenol >1,800 mgL<sup>-1</sup> → no sulfate redn

**Phenol toxicity** is a key factor in limiting biodegradation in this plume.

**Former coal coking plant.**

**-Sherwood Sandstone**, covered by thin alluvial sand and gravel



-Overall less than 10% contaminant mass has degraded  
 -Much of that is in unsat. zone and upstream plume fringe  
 -Concentrated plume core detached and not degrading

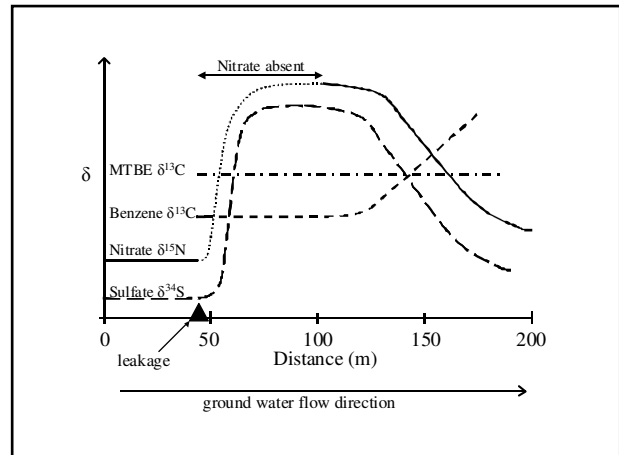
## Application of multiple isotope tracers



Using multiple isotope tracers for different processes it is possible to build a picture of the spatial pattern of biodegradation.

e.g. S isotopes – traces sulfate reduction  
 N isotopes – traces nitrate reduction  
 C isotopes – to trace degradation of specific contaminants

Example – unleaded fuel spill in Chalk



## Isotope fractionation during biodegradation – case study



Near contaminant spill:

→ nitrate is completely removed by nitrate reduction and sulfate has elevated  $\delta^{34}\text{S}$  as a result of sulfate reduction.

→  $\delta^{13}\text{C}$  of both benzene and MTBE are constant indicating that neither is undergoing biodegradation.

Further down-gradient:

→ nitrate re-enters the plume as a result of dispersive mixing.

→ nitrate  $\delta^{15}\text{N}$  is elevated, indicating active nitrate reduction.

→ benzene  $\delta^{13}\text{C}$  shows a marked increase.

→ biodegradation of benzene occurs via nitrate reduction.

## What limits the applicability of this technique?



### The major factor is uncertainty in the isotope enrichment factor:

- 1) The slope derived from field data is an “apparent” fractionation factor – biodegradation may not be the only process causing contaminant concentration to fall.
  - What is the relation between field data and “true”  $\epsilon$  value from experiments?
- 2) How variable are  $\epsilon$  values in the environment?
  - How do we select a realistic value?

## Conclusions



Isotope fractionation can be a useful tool for studying biodegradation

- at a qualitative level useful information can be gained on:

which biodegradation mechanisms are active

spatial patterns of these processes

factors limiting biodegradation

## Conclusions



Isotope fractionation can be a useful tool for studying biodegradation

- quantitative estimation of amount or rate of biodegradation is possible

- limited by uncertainty in isotope enrichment factors

## Thanks to:



Rob Newton – running the Leeds stable isotope lab.  
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## References



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Spence, M.J., **Bottrell, S.H.**, Thornton, S.F. and Lerner, D.N. Isotopic modelling of the significance of sulphate reduction for phenol attenuation in a polluted aquifer. **Journal of Contaminant Hydrology** 53: 285-304, 2001.