



# Stable Isotope Analyses

## Demonstrate Natural Attenuation (NA)

Natural attenuation and/or stimulated bioremediation can be assessed via compound specific stable isotope analyses (CSIA). This is a new method that is used to measure and demonstrate the biodegradation of a specific compound. This is done by measuring the shift in isotope ratio (e.g. the  $^{13}\text{C}/^{12}\text{C}$  ratio or  $\delta^{13}\text{C}$ ) of the residual compound compared to its original value.

This method can be used to support the occurrence of biodegradation of a specific compound.

Traditionally, three lines of evidence (documented loss of mass, geochemical evidence, and the presence of active bacteria) are used for this. CSIA is an additional technique to predict and quantify the degradation of a specific compound in the field, as the  $^{12}\text{C}$  is preferentially degraded. This results in a shift in the  $^{13}\text{C}/^{12}\text{C}$  ratio of a compound (Figure 1).

This relatively fast method gives information if

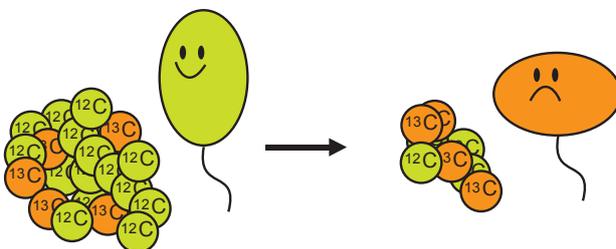


Figure 1. Principle of isotope fractionation

natural attenuation (NA) is possible or an active bioremediation is needed (cost-effective).

CSIA can be used for compounds such as BTEX, PAH,  $\text{CO}_2$ , n-alkanes ( $\text{C}_{10}$ - $\text{C}_{30}$ ), chlorinated ethenes (PCE, TCE, DCE, VC), MTBE, TBA, TBF, and phospholipid fatty acids (PLFA).

### Prerequisites for the use of CSIA to assess natural attenuation and biodegradation

- The concentrations of the target compounds in the groundwater are above the detection limit, appr. 10 mg/l for  $^{13}\text{C}$  and 50 mg/l for  $^2\text{H}$ .
- The compounds of interest fractionate under the present conditions (few exceptions exist).
- Groundwater samples are available in time or space (e.g. a flowpath).
- The measured fractionation is significant ( $> 0,5\text{‰}$  for  $\delta^{13}\text{C}$  and  $>5\text{‰}$  for  $\delta^2\text{H}$ ).

Our biological and geochemical knowledge will further help to develop an optimal strategy.

### Advantages

- This technique gives information about the degradation of a specific compound in a mixture with other pollutants.
- This technique is independent of concentration measurements.
- Distinguishing between different sources is possible.
- Fractionation is more pronounced at the end of the degradation.

### Disadvantages

- The detection limit varies per isotope of interest. Luckily, the method is continuously under development (e.g. at Deltares) and the detection limit concentrations are still decreasing.



- Not every degradation process is suitable for this method. Knowledge about biological degradation processes and fractionation are continuously under development.

## Examples

### Field study 1

The carbon isotope fractionation of benzene was measured in a field study. The wells are located in the direction of the groundwater flow, and the increase in  $\delta^{13}\text{C}$  in the flow path indicates degradation of benzene (Figure 2).

### Field study 2

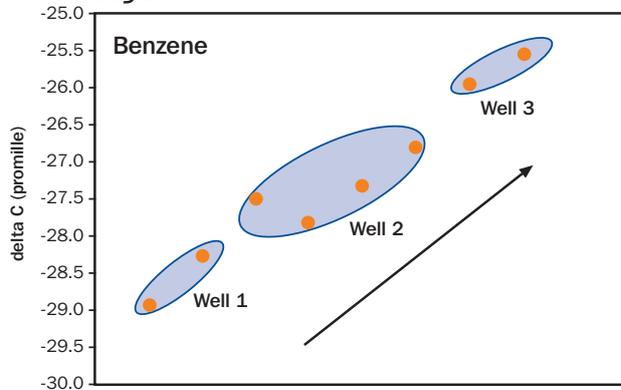


Figure 2. Fractionation of isotope in groundwater samples of a site in a flow path.

The fractionation of the carbon ( $\delta^{13}\text{C}$ ) and hydrogen isotope ( $\delta^2\text{H}$ ) of benzene was measured in a field study performed by Deltares at a contaminated site. The data show a significant isotope fractionation of benzene and plotting the  $\delta^2\text{H}$  over the  $\delta^{13}\text{C}$  values in a two-dimensional plot, indicates anaerobic degradation of benzene (Figure 3).

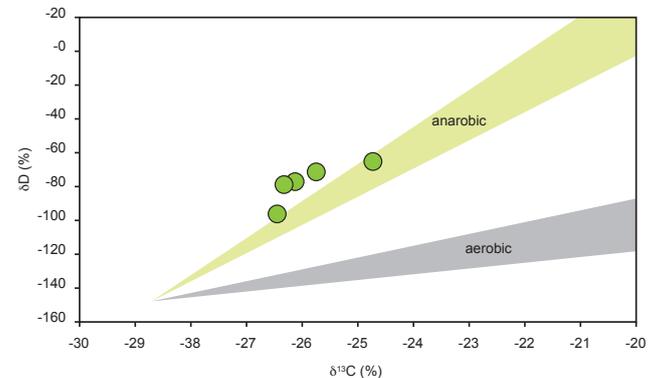


Figure 3. Two-dimensional plot ( $\delta^2\text{H}$  vs  $\delta^{13}\text{C}$ ) of benzene

## Conclusion

Compound specific stable isotope analysis is applicable to demonstrate biodegradation. The extent of fractionation depends on the compound of interest, redox condition and measured isotope (C, H, or Cl). CSIA is a useful tool to demonstrate natural attenuation in the field.

## For more information

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