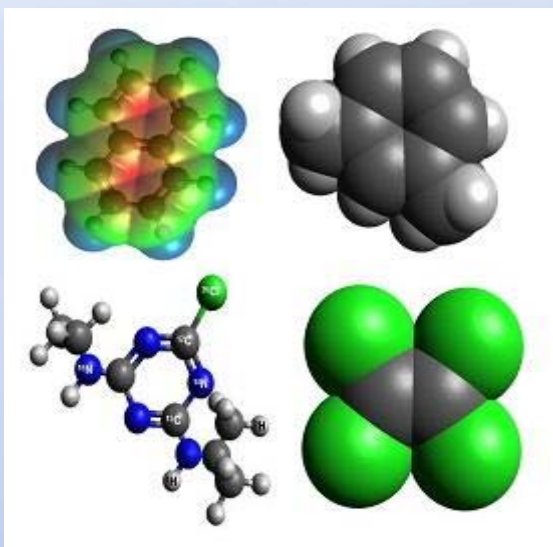


Organic contaminants and isotopes



WATER

GEOTHERMAL ENERGY

TRACER TESTS

POLLUTANTS

FILTER TECHNIQUES

FOOD

RENEWABLE REOURCES

ISOTOPES

GASES

SOLIDS

ANALYSIS

HYDROISOTOP GMBH
Woelkestraße 9
85301 Schweitenkirchen
Germany

Tel. +49 (0)8444 / 92890
Fax +49 (0)8444-928929
eMail info@hydroisotop.de
Web: www.hydroisotop.de

accredited according to DIN EN ISO/IEC 17025:2005

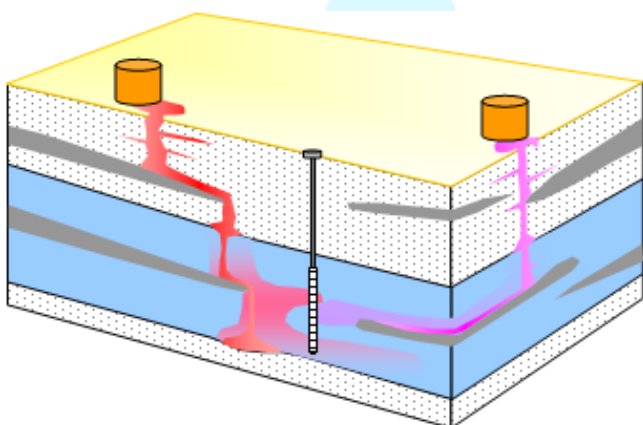
Isotopy & Chemistry in Environmental Hydrology & Food



ORGANIC CONTAMINANTS AND ISOTOPES

Background

Many of the most common pollutants in groundwater are suspected to cause health damages. Therefore, cases of contamination with organic pollutants impose considerable costs on the private and public sector. Isotope methods help to make conclusions concerning remedial actions, even in complex contamination situations.



Range of use of isotope methods

In industrialised areas contaminant plumes often consist of contaminants from different sources. When multiple polluters are involved in a contamination, classical chemical analysis do not help to specify the responsible polluter. This, however, can be done by using isotopes.

As classical pump-and-treat methods can be inefficient, natural biodegradation of pollutants in groundwater gains increasingly in importance. By using isotope methods potential degradation processes and their efficiency can be determined.

Which questions can be answered?

Source of pollution/distinction of multiple pollutions

Is there only one source of pollution or are there more?

Who is responsible for the contamination?

Natural Attenuation:

Is biological degradation taking place?

Are bioremediation measurements successful?

Age and degradation rate

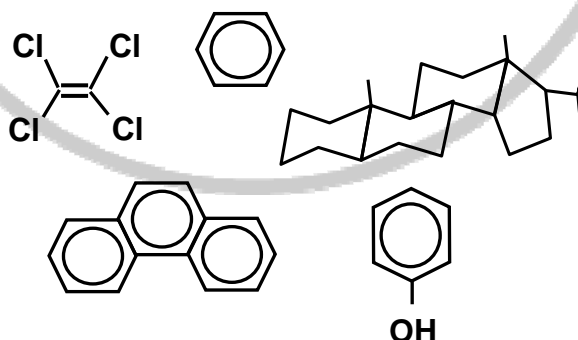
When did the input take place and how fast are contaminants being degraded?

User

Owners of contaminated land, engineering offices, insurance companies, public authorities, companies that are working with abandoned polluted areas...

Pollutants

- Chlorinated hydrocarbons (CHC)
- Aromatics (BTEX)
- Petroleum derived hydrocarbons (TPH)
- Polycyclic aromatic hydrocarbon (PAH)
- Phenols





ORGANIC CONTAMINANTS AND ISOTOPES

Which isotopes do we analyse?

Isotopes are atoms of one element that differ from others in mass and physical properties but not in chemical properties. For example, **carbon** has two stable isotopes with the masses 12 (^{12}C) and 13 (^{13}C). The determination of the $^{13}\text{C}/^{12}\text{C}$ ratio of organic pollutants is done by Purge and Trap and GC Combustion Isotope Ratio Mass Spectroscopy (P&T-GC-C-IRMS). **This method is accredited according to DIN EN ISO/IEC 17025:2005.**

The analysis can be supplemented by the isotope ratios of **hydrogen** ($^2\text{H}/^1\text{H}$) and/or **chlorine** ($^{37}\text{Cl}/^{35}\text{Cl}$).



Analytical requirements

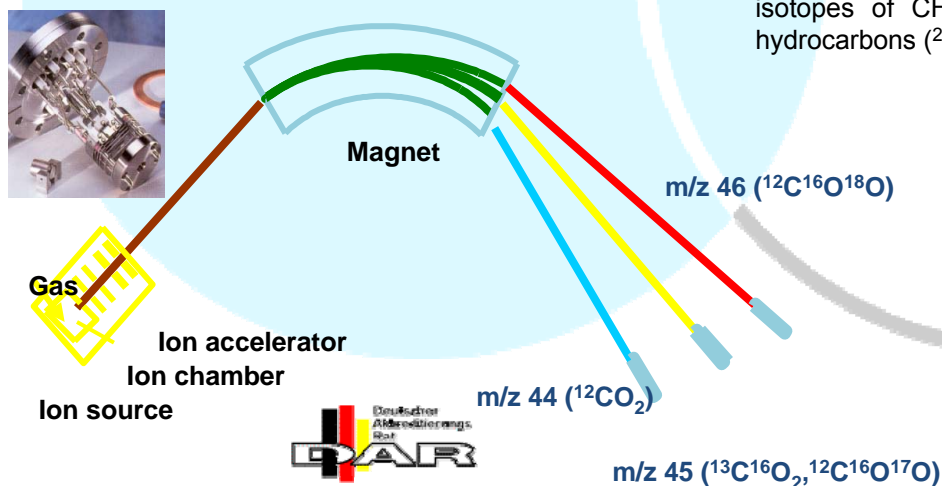


Sampling is usually done by the client. Sample containers including stabilisation chemicals for water samples are provided. The sample amounts required for analysis are listed in the following table according to pollutant class:

Minimum amount per single component

$^{13}\text{C}/^{12}\text{C}$	Water samples		Soil samples	
	($\mu\text{g}/\text{L}$)	(L)	(mg/kg)	(kg)
CHC	> 5	0.2	0.1	1 - 2
Aromatics	> 5	0.2	0.1	1 - 2
TPH	> 5	5	0.1	1 - 2

On request, we will inform you about the requirements for analysis of the stable chlorine isotopes of CHCs ($^{37}\text{Cl}/^{35}\text{Cl}$) and of hydrogen in hydrocarbons ($^2\text{H}/^1\text{H}$).



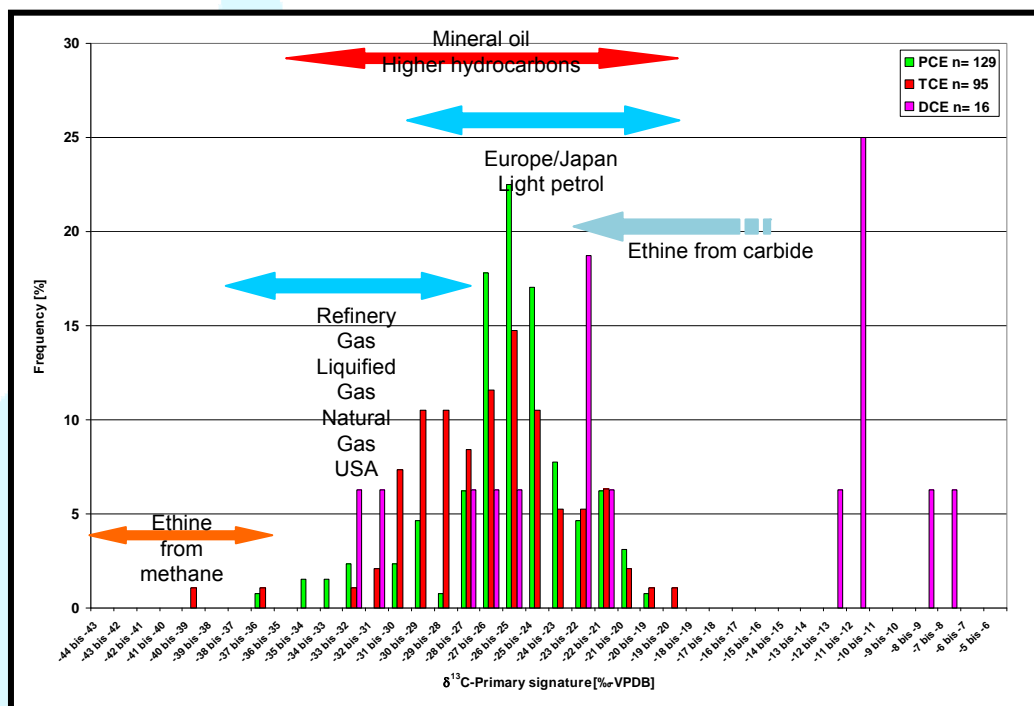
The method for analysing ^{13}C of CHCs is accredited according to DIN EN ISO/IEC 17025:2005



CAUSES OF CHC POLLUTIONS

CHCs are one of the main contaminants of groundwater. Most abundant are primary pollutants such as PCE, TCE and their degradation products cDCE and VC.

The isotope signatures of PCE and TCE emitted by different polluters are usually different. This can be seen in the following frequency distribution made from data of more than 250 case studies. The differences in isotope signatures can be used to associate contaminations with the polluter.



Why are there differences?

The isotope signatures of CHCs differ depending on the production path. The CHCs obtain their specific isotopic fingerprint because they were made from different substances with different isotope signatures.

Production method

until 1980

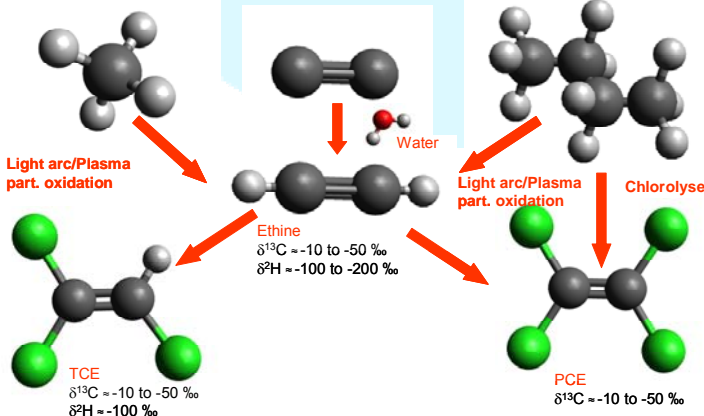
Methane
 $\delta^{13}\text{C} \approx -30$ to -50 ‰
 $\delta^2\text{H} \approx -60$ to -200 ‰

until 1940

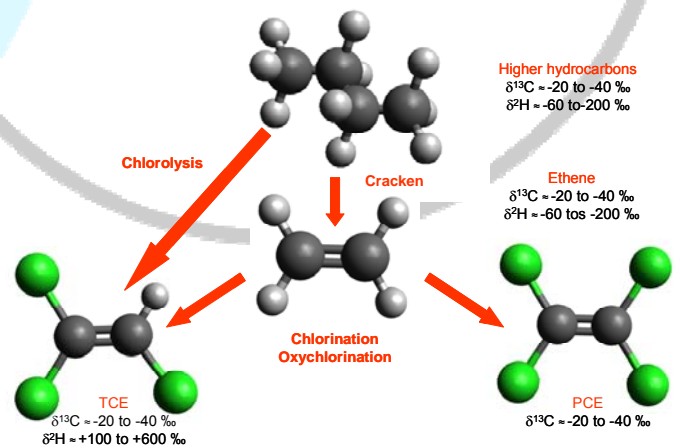
Carbide
 $\delta^{13}\text{C} \approx -10$ to -25 ‰

until 1980

Higher hydrocarbons
 $\delta^{13}\text{C} \approx -20$ to -40 ‰
 $\delta^2\text{H} \approx -60$ to -200 ‰



Today's production method since 1980



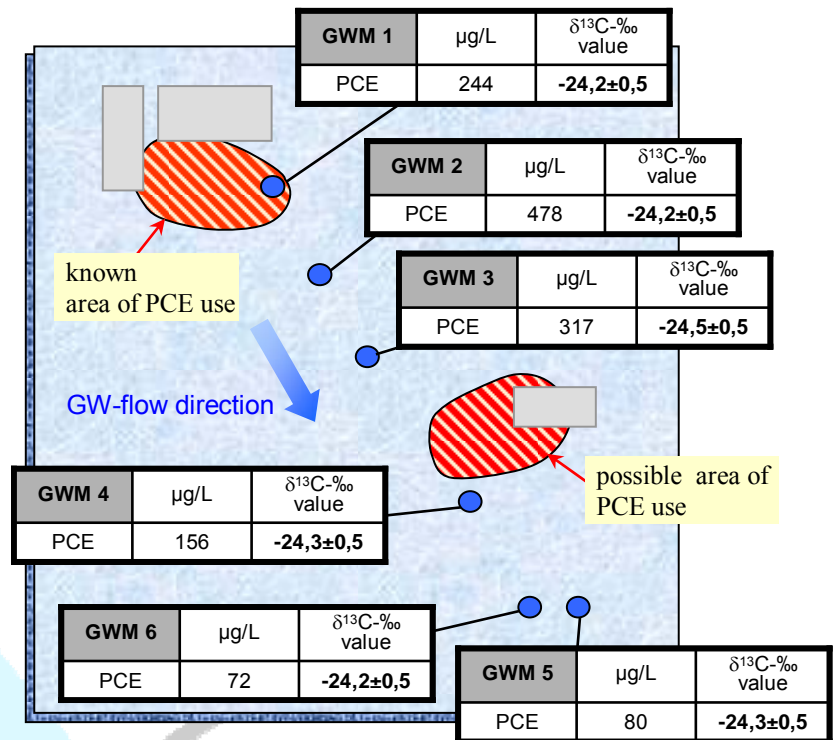


CAUSES OF CHC POLLUTIONS

Example A-1: Allocation of contaminants to a source

Question: Is there only one contamination plume coming from the area around GWM 1 or is there another source of PCE around GWM 4?

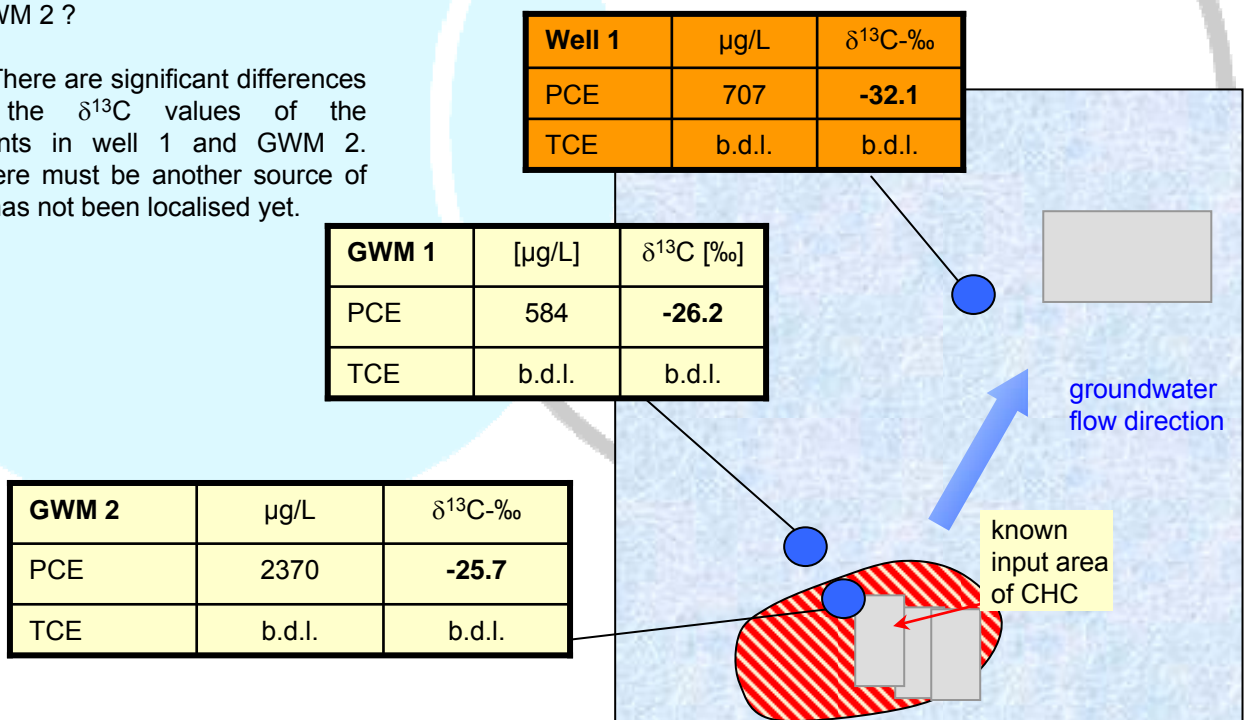
Answer: The $\delta^{13}\text{C}$ values in the groundwater are equal. Hence, only one contaminant plume comes from the area of GWM 1 and there is no other source of contaminant.



Example A-2: Differentiation between sources of contaminants

Question: Do the CHCs in well 1 originate from the contamination in the area of GWM 2?

Answer: There are significant differences between the $\delta^{13}\text{C}$ values of the contaminants in well 1 and GWM 2. Hence, there must be another source of PCE that has not been localised yet.



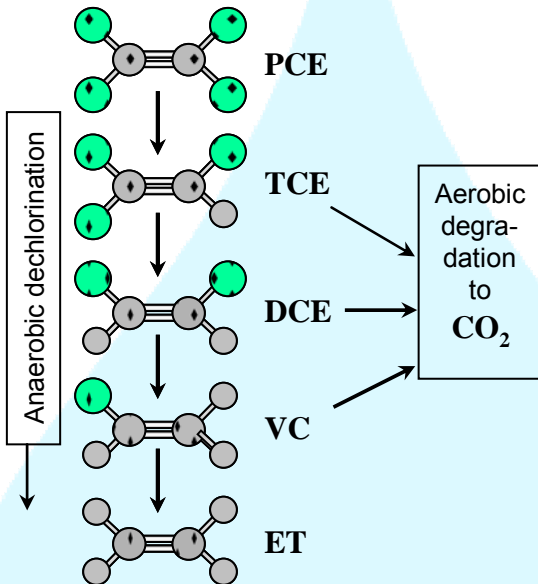
All examples are based on real cases that have been simplified and anonymised for reasons of data protection.



DETECTION OF CHC DEGRADATION (NATURAL ATTENUATION)

Microbial degradation

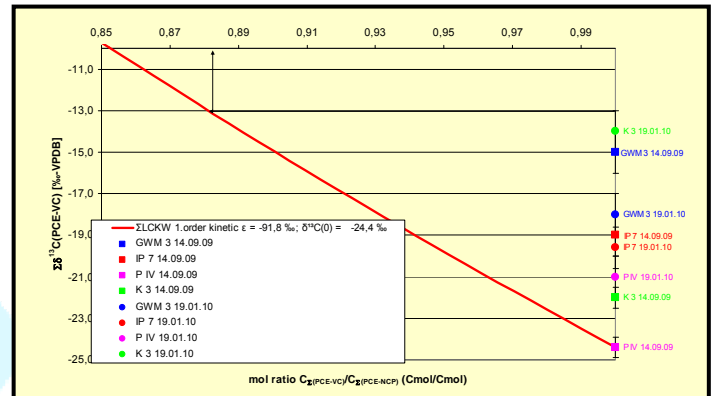
Natural biodegradation („Natural Attenuation“) is gaining importance as an alternative to other methods of remediation. It is effective because degradation of TCE and PCE takes place under oxidising as well as reducing conditions.



How is data evaluated?

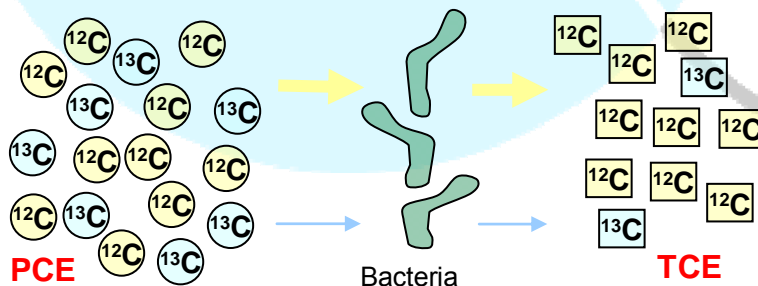
In most cases, isotope fractionation can be described by a model based on Rayleigh equation or first order kinetics. By comparing the measured value with the model result, conclusions on the degradation of CHCs can be drawn.

The sum signature model provides information on the complete degradation of CHCs or pollutants, respectively.



What is isotope fractionation?

Microorganisms cause a modification of the natural isotope ratio (e.g. ¹³C/¹²C) of a substrate by degrading the pollutants. Preferably, the microorganisms degrade pollutants, which are built by the "light" isotopomers. Thus, the "heavy" isotopomers will be enriched in the residual pollutant fraction.



- NCP – non-chlorinated products ⇒ NA
- Initial Isotope signature: can be derived from a sample (soil, water) from the source of pollution
- fractioning factors: published values

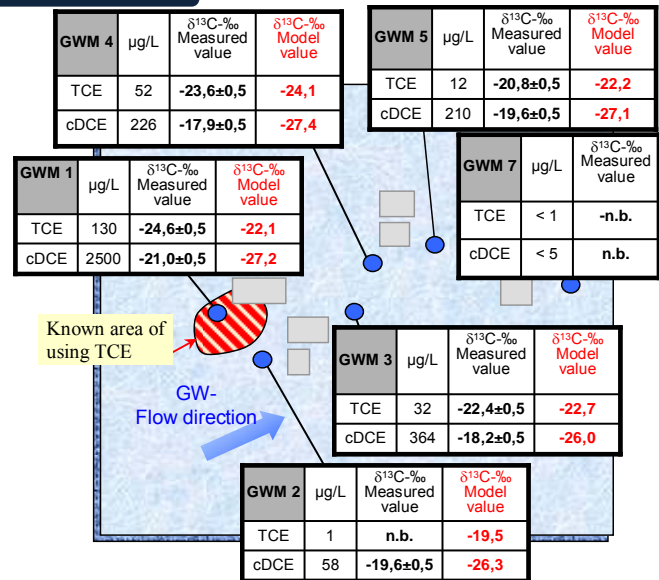


DETECTION OF CHC DEGRADATION (NATURAL ATTENUATION)

Example B-1: Natural Attenuation

Question: Is the reduced size of the contaminant plume due to degradation of TCE beyond cDCE?

Answer: The differences between the measured values of ^{13}C isotope signature and the model results, especially for the intermediate cDCE, show that oxidative degradation of cDCE to non-chlorinated products is at an advanced stage. Natural attenuation processes account for the reduced size of the contaminant plume.



Measured value = Model result:
All single components are degradation products of the identified primary contaminant

Measured value (degradation products) > Model result
Possibly, further degradation to non-chlorinated non-toxic products such as ethene or CO_2 is taking place.

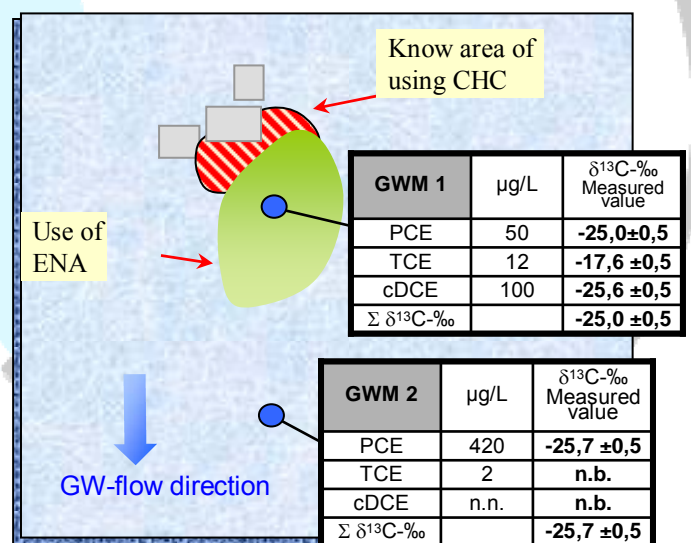
All other cases:
Differences in $\delta^{13}\text{C}$ values are not (only) due to degradation. In many cases there are different sources of contaminants.

Example B-2: Enhanced Natural Attenuation

Another method of evaluation is the calculation of the sum signature of $\delta^{13}\text{C}$ values. If the ^{13}C primary signature is known and there is no further input or output of carbon, allocation to a primary contamination and evaluation of the degree of degradation is possible.

Question: Is a complete reductive degradation of PCE to non-chlorinated compounds attained by using enhanced natural attenuation (ENA)?

Answer: The composition and isotope signature of the sample from GWM2 is not influenced by HRC. The $\Sigma \delta^{13}\text{C}$ -value of -25 ‰ at GWM 1 shows, that stimulated degradation is **only going down** to cDCE. There is only little degradation to non-chlorinated products.



All examples are based on real cases that have been simplified and anonymised for reasons of data protection.



CHARACTERIZATION OF TPH DAMAGES

Pollution caused by total petroleum derived hydrocarbons (TPH)

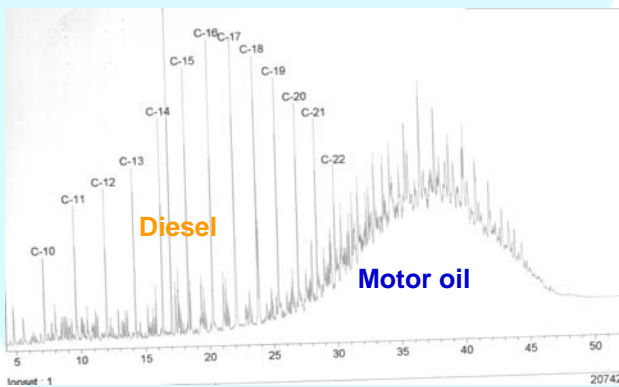
When pollution is caused by TPH, it is composed of a mixture of different hydrocarbons that originate mainly from refineries.

Composition and isotope signature are specific for the substances causing the damage and is therefore called fingerprint.

Possible components:

- petrol
- crude oil/kerosene
- fuel oil/diesel
- spindle oil
- motor oil

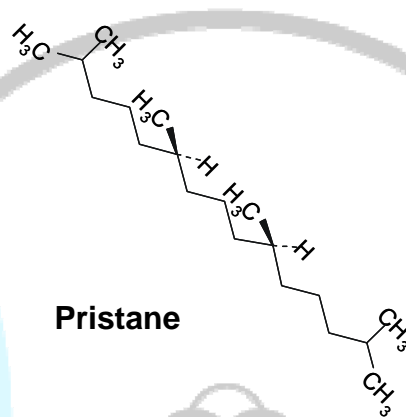
The following GC spectrum shows the differentiation between a contamination with **fuel oil/diesel** and one with **motor oil**.



What are biomarkers?

Biomarkers are organic molecules, which stay nearly unchanged by genesis of crude oil. Because they are not degraded easily, they can give important evidence concerning source and age of petroleum hydrocarbons. Common biomarkers are:

- PAH
- diasteranes
- triterpenes
- pristane
- phytane





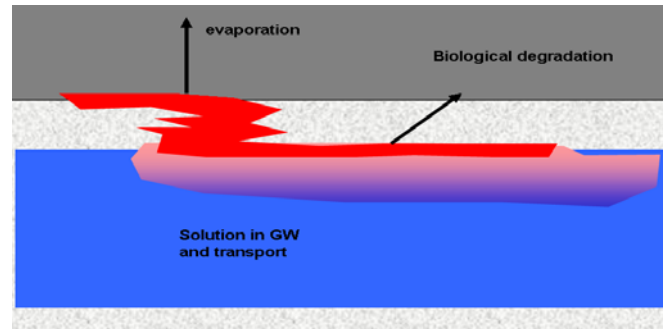
ESTIMATING THE AGE OF TPH POLLUTIONS

Aging processes

From the point of their release into environment, TPH are exposed to various influences. Hereby, the different components of the TPH have different speeds of aging.

Moreover, these processes differ locally and are dependent on environmental factors such as:

- Composition of the initial products
- Hydrogeology
- Geology
- Temperature
- Oxygen content
- Water content



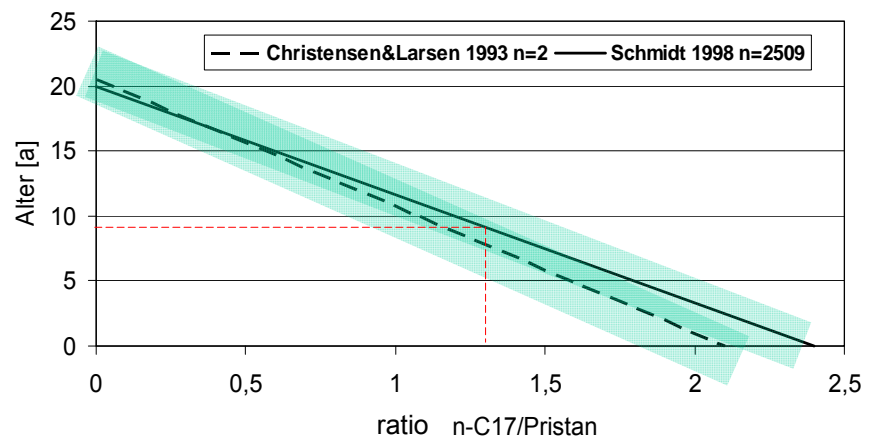
Grade of degradation and age of the pollution

The table on the right shows the process of microbial degradation of petroleum hydrocarbons. Characteristic changes in composition of a mineral oil product can be used as a measure for estimating the age of the pollution.

1	n-Alkanes unchanged	Enrichment of biodegradation
2	volatile alkanes removed	
3	Alkanes of middle range, Olefine, Benzene und Toluene removed	
4	More than 90% of n-alkanes removed	
5	Alkylcyclohexanes and Alkylbenzene removed; Isoprenoides und Naphthalene partial removed	
6	Isoprenoides, C ₁ -Naphthalines, Benzothiophene and Alkylbenzothiophenes removed ; C ₁ -Naphthalines selective partial removed	
7	Dibenzothiophene, Phenanthren and other PAH selective partial removed	
8	Tricyclische Terpanes enriched; special regular Steranes removed; C ₃₁ -C ₃₅ Homohopanes partial removed	
9	Tricyclische Terpanes, Diasteranes and aromatic Steranes enriched	

Quantifying the age of pollution by middle destilates

For age determination of pollutions by middle destilates (e.g. Diesel, fuel oil), the ratio between n-C17 and pristane can be used. For middle distillates in soil, this ratio is decreasing down to zero within 18-25 years under optimal degradation conditions.





ESTIMATING THE AGE OF TPH POLLUTIONS

Example C-1: Using age determination to identify the source of pollution

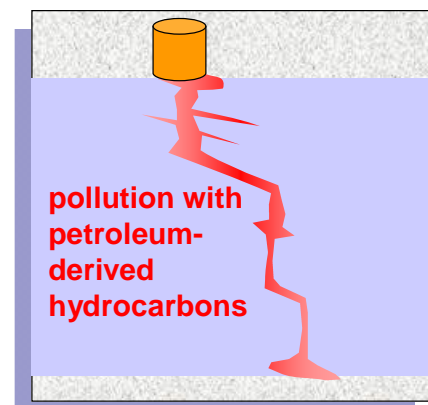
Question: Who of the two tenants has caused the TPH-pollution?

Answer: By approximating the input date of the pollution from the n-C17/pristane values, an age 15-17 years can be derived. Further analytical results (absence of highly volatile alkanes and the majority of n-alkanes) support this date. Using the table above, the pollution can be assigned to a grade of degradation of step 4.

Hence, the contamination must have taken place at early 1990ies and thus, has been caused by tenant Heinz.

tenant Heinz
before 1999

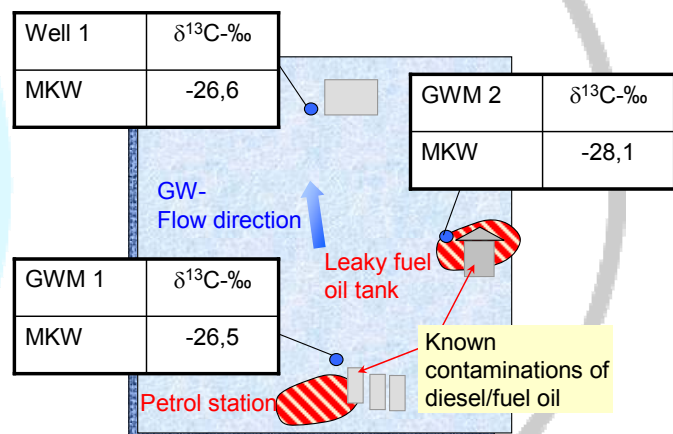
tenant Jürgen
after 1999



Example C-2: Using isotope signatures to identify the source of pollution

Question: Is the contamination with diesel in Well 1 caused by the petrol station or by the leaking fuel oil tank close to GWM 2?

Answer: The isotope signatures of well 1 and GWM 1 are identical in terms of measurement accuracy while the one of GWM 2 is significantly different. So the pollution around well 1 must have been caused by a contamination around GWM 1.



All examples are based on real cases that have been simplified and anonymised for reasons of data protection.