

Use of Deuterium and Oxygen-18 as natural environmental isotopes and as artificial tracer



WATER

GEOTHERMAL ENERGY

TRACER TESTS

POLLUTANTS

FILTER TECHNIQUES

FOOD

RENEWABLE RESOURCES

ISOTOPES

GASES

SOLIDS

ANALYSIS

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Isotopy & Chemistry in Environmental Hydrology & Food



Basics

All chemical elements have isotopes. Hydrogen, for example, has two stable isotopes: Protium (^1H) has a mass number of one and is the major isotope with an abundance of 99.985 %, whereas Deuterium (^2H) with mass number of two is abundant just up to approximately 0.015 %. In addition, there is also a radioactive isotope of hydrogen, the so called Tritium (^3H). Tritium is of significant relevance in the field of age determination of groundwater.

Also oxygen has two further stable isotopes beneath its major isotope ^{16}O : ^{17}O and ^{18}O , whereupon just ^{18}O is of practical relevance.

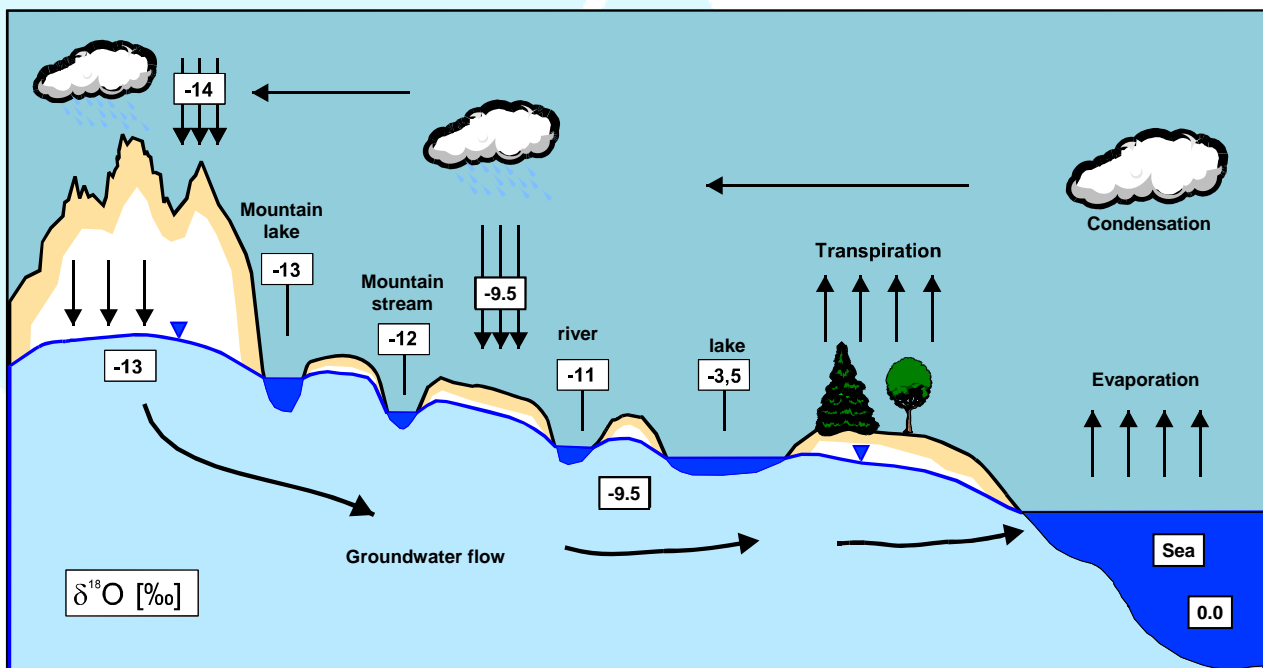
In natural waters with „normal“ composition, on 10^6 water molecules of $^1\text{H}_2^{16}\text{O}$, about 2000 molecules $^1\text{H}_2^{18}\text{O}$ with heavy oxygen isotope ^{18}O exist, and 160 molecules, in which one of both hydrogen atoms are replaced by ^2H (Deuterium).

However, in natural waters, the ratio of isotopes is not constant.

Due to physical, chemical and biological processes, the isotope ratios can be changed (isotope effects). Systematical investigations in the entire global hydrological cycle revealed that among 10^6 water molecules the portion of $^1\text{H}_2^{18}\text{O}$ vary between 1880 to 2010 molecules and the portion of $^2\text{H}^1\text{H}^{16}\text{O}$ vary between 90 to 170 molecules, respectively.

The hydrological application of measurements of the content of stable isotopes of ^2H and ^{18}O from water molecules bases essentially on these natural variations.

Different isotope effects cause a local and temporary characteristic marking of precipitation. Hence, also the different water bodies are characteristically marked locally and temporarily (see scheme below).





General basics

Measurement and instrumentation

In contrast to the analysis of the chemical contents, the analysis of deuterium and oxygen-18 targets usually not the absolute isotope contents.

Thus, stable isotopes are measured in isotopic abundance ratios ($^{18}\text{O}/^{16}\text{O}$ or $^2\text{H}/^1\text{H}$, respectively), which are compared to an international standard.

The divergence of the isotopic abundance ratio of a sample in relation to the standard is specified with a delta(δ)-value, given in per mille (‰).

$\delta^2\text{H}$ and $\delta^{18}\text{O}$ values refer to the international standard **V-SMOW** (Vienna **S**tandard **M**ean **O**cean **W**ater).

As most natural waters contain less 'heavy' isotopes than the standard, the δ -values are negative in most cases.

To determine the stable isotopes deuterium and oxygen-18 from water, only small sample volumes (a few milliliters) are required.

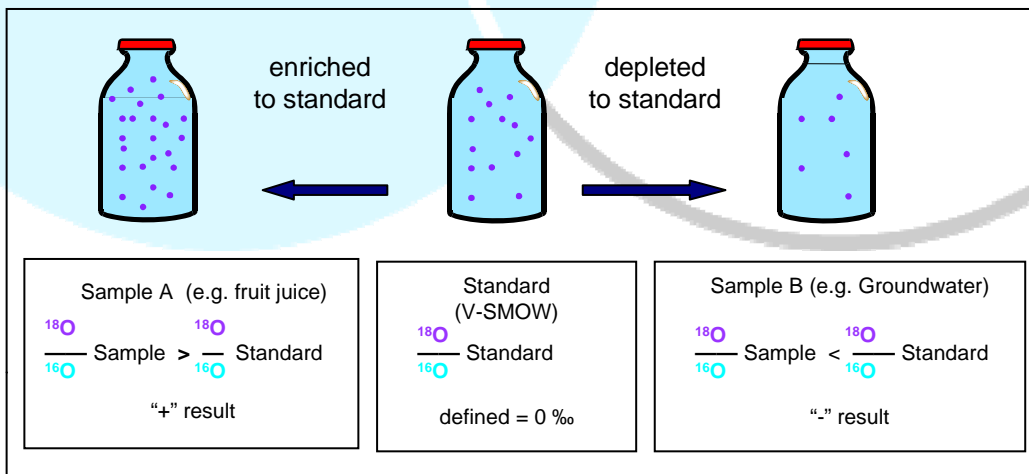
After preparation of the sample, in which the sample is transferred to a suitable sample gas, the isotope abundances are analyzed in a mass spectrometer (Fig. 1)

Preparation of samples

Transfer into sample gas (CO_2)



Analysis in mass spectrometer





Evaluation of the origin of waters

The variations of the ^2H and ^{18}O compositions are caused by isotope effects in the hydrological cycle due to isotope fractionation at all kind of phase transformation: evaporation, condensation and others.

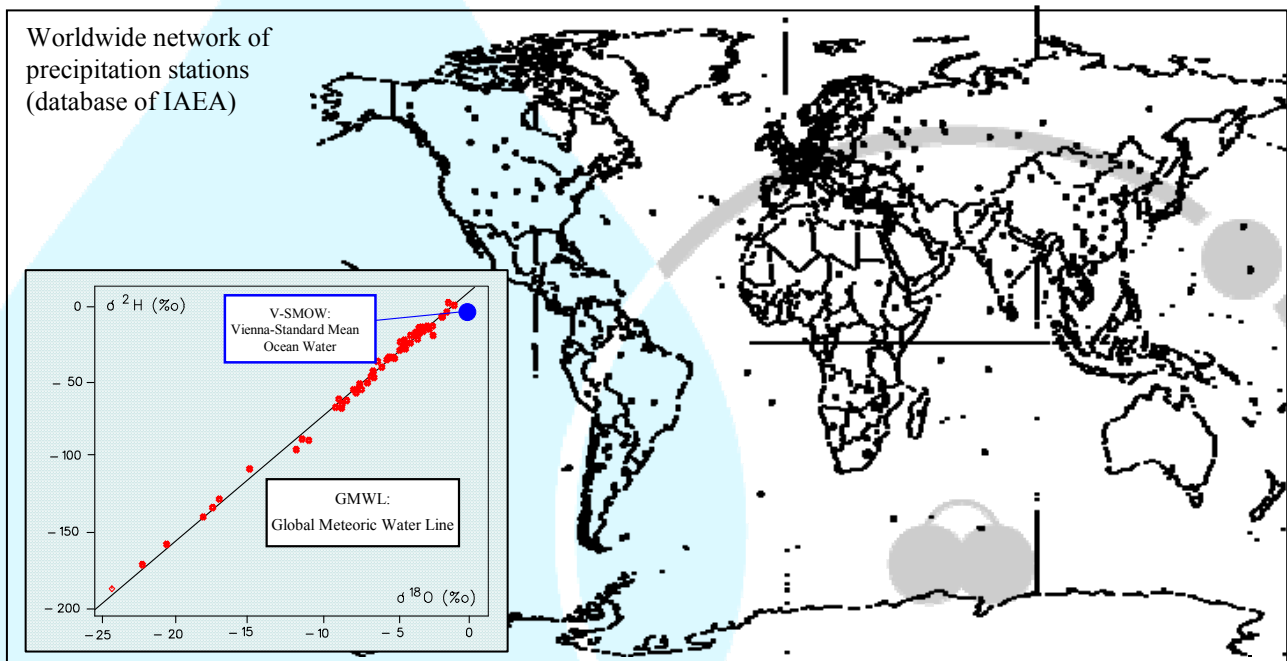
Basically, the isotope fractionation is dependent of temperature.

Therefore, by the results of the determination of oxygen-18 and deuterium from groundwater samples, conclusions can be drawn to the climatic conditions during groundwater recharge.

The Precipitation Line (Global Meteoric Water Line)

The ratio of the ^2H content to the ^{18}O content in precipitation is influenced by thermo-dynamical processes at phase transformations.

In principle, a linear correlation of ^2H to ^{18}O contents is observed in precipitation. Following figure shows the weighted mean values of $\delta^2\text{H}$ - and $\delta^{18}\text{O}$ values from 74 IAEA precipitation stations in a $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ diagram, which illustrates the linear correlation.



For precipitation in Central Europe, the linear correlation (so called mean precipitation line) can be expressed by

$$\delta^2\text{H} = 8 \times \delta^{18}\text{O} + 10$$



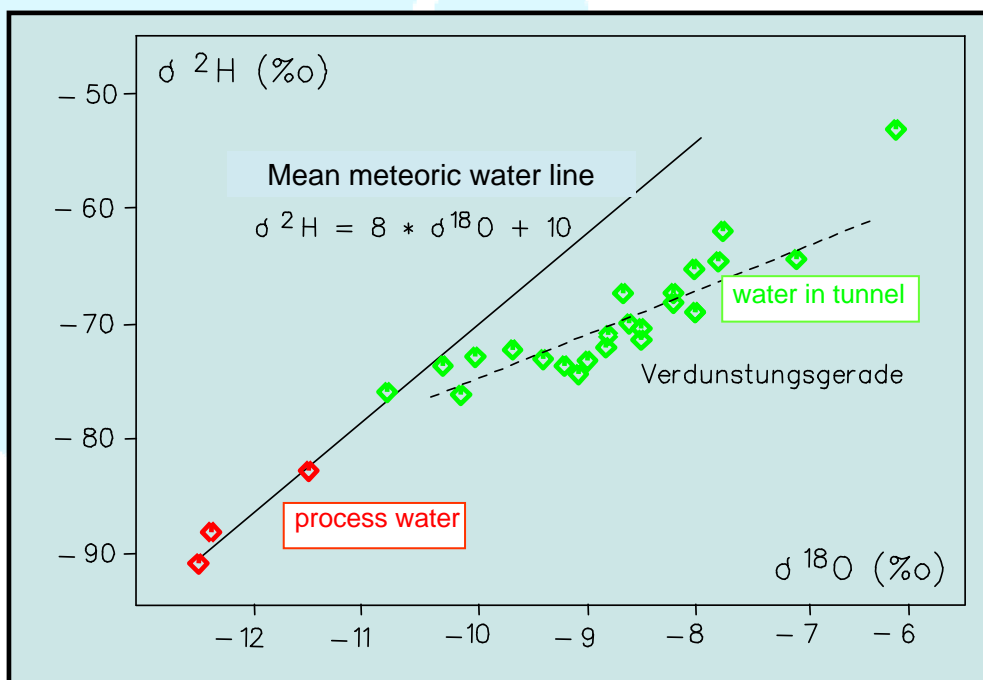
Evaluation of the origin of waters

If the $\delta^2\text{H}/\delta^{18}\text{O}$ pair of values determined from groundwater samples plot in the range of the meteoric water line, it can be concluded that this groundwater was recharged by local precipitations and, hence, originate from meteoric water.

In case of evaporation processes during groundwater recharge (e.g. infiltration of lake water), or in case of oxygen isotope-exchange with rock material (e.g. in high-temperature thermal waters), the $\delta^2\text{H}/\delta^{18}\text{O}$ pair of values plot characteristically apart from the meteoric water line.

In the following example given from a tunnel construction site, the aim was to determine the origin of water from the tunnels bottom. It had to be figured out, if the water originated from the service water (leakage from supply pipes), or if the water originated from influxes of autochthonic mountain water.

From the analytical results, it was possible to exclude the service water as the origin of the water from the tunnels bottom. This conclusion has been verified by other parameters (e.g. tritium).





Evaluation of the origin of waters

Altitude effect

With increasing orographic altitude, a depletion of the heavy isotopes in precipitation and groundwater can be observed. This is basically caused by the decreasing temperature with increasing altitude. Hence, in highly morphological regions, the mean altitude of the recharge area of groundwaters can be approximated by ^2H - and ^{18}O -measurements.

The following example shows the application of this method in the region of the Northern Tyrolean limestone alps (Upper Austria).

From a 60 m deep, newly constructed exploratory well ("Brunnen TB1"), the groundwater catchment area had to be evaluated to determine the protective area for the planned usage of the water as drinking water.

The exploratory well taps the deep groundwater of a large-scale talus cone.

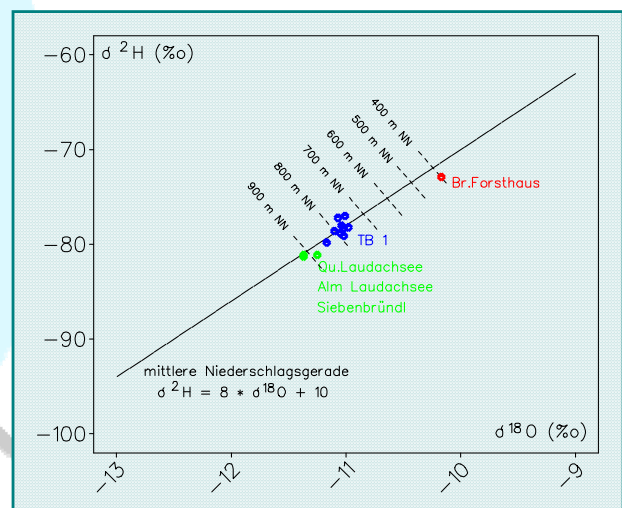
The aim of the study was to clarify, if the groundwater is recharged in the region of the talus material, or if the tapped groundwater originates from higher altitudes of the catchment in the region of the adjacent mountain range ("Traunstein-Katzenstein").

- Sampling well "Br. Forsthaus" represents the shallow groundwater of the talus cone. The groundwater is recharged in the close-range, which corresponds to a catchment altitude of about 420 m AMSL.

- Sampling wells "Quelle Laudachsee", "Alm Laudachsee" and "Siebenbründl" represent groundwater, which is recharged in the region of the mountain range of "Traunstein-Katzstein". For these wells, the catchment altitude is estimated to about 900-1200 m AMSL.

- From the results of these wells, an altitude-depending depletion of the ^{18}O -content of about 0.2 ‰ per 100 m was determined. This is in the typical range of the altitude effect.

- The by the exploratory well tapped groundwater shows δ -values in between the results from the low altitude and high altitude wells. From the situation of the pairs of values in the $\delta^2\text{H}$ - $\delta^{18}\text{O}$ -diagram, the mean altitude of the recharge area of "Brunnen TB1" was determined to about 700-800 m AMSL.



Consequence for determination of the protective area:

A considerable fraction of the groundwater, which is tapped by the well „Brunnen TB1“, is recharged in the region of higher altitudes.

Therefore, this region has to be included into the determination of the protective area.



Dating of young groundwaters

Groundwater age and mean residence time

In hydrology, the age of groundwater corresponds to the time period, which the groundwater stays in the underground since it percolated from precipitation. As in groundwater usually a mixture of several years of precipitation is present, it is not possible to give an exact age of the groundwater. Rather, the age is expressed as the “mean residence time” of the groundwater.

The mean residence time of a groundwater can be used as an indication for the guardedness of the groundwater body.

In shallow groundwater bodies, in which short mean residence times in the range of a few years can be assumed, the oxygen-18-method is, beside the tritium and krypton-85-method, an ideal tool to determine the groundwater age.

But, to yield detailed information on the groundwater age structure, time-series of the ^{18}O -content in precipitation and in groundwater of the length of at least one hydrological year are necessary.

The oxygen-18-method to date young groundwaters

Caused by the temperature-dependency of isotope fractionation, the isotope contents in precipitation have a maximum in summer and a minimum in winter, which results in a characteristic developing of the $\delta^{18}\text{O}$ -values of precipitation. This general trend is interfered by short-term variations of the isotope contents (see figure below).

Groundwater age dating with ^{18}O is based on this quasi-periodical, seasonal variation of the isotope content in precipitation and thereby, also in recently recharged groundwater.

As long as these variations are detectable in groundwater, groundwater residence times between a few months and a few years can be estimated. The estimation of the residence time is dependent on the chosen fitting model.

The example in the following shows the determination of the mean residence time of a shallow pore aquifer in Southern Germany. The data is fitted (best-fit-method) by using the “dispersion model”.



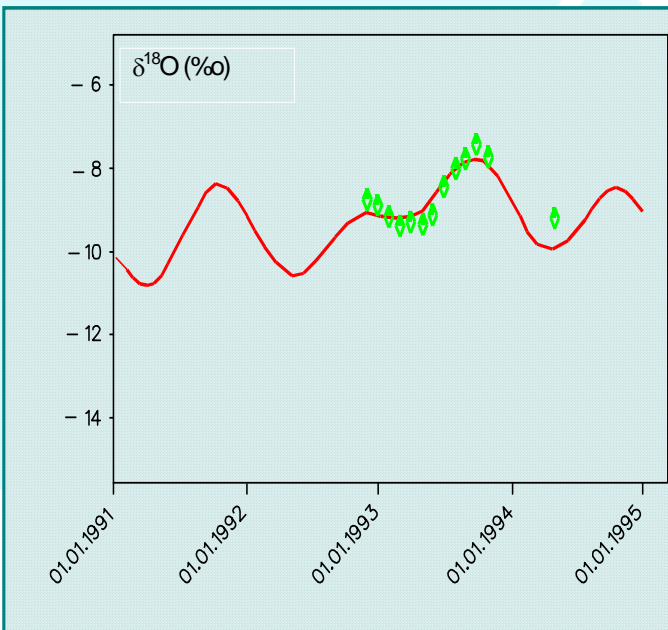
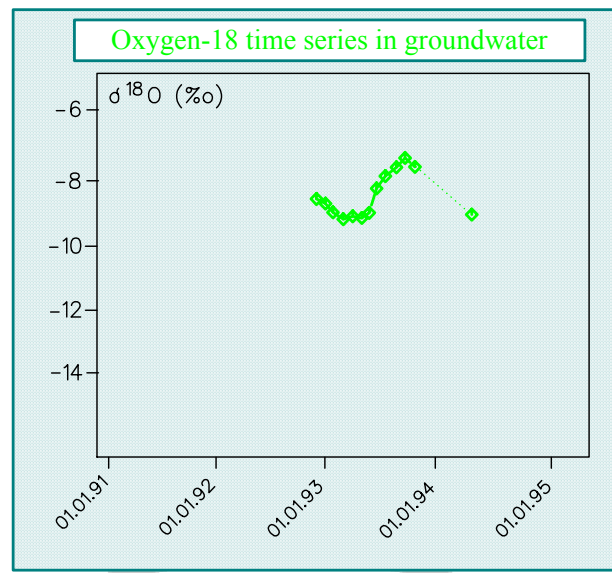
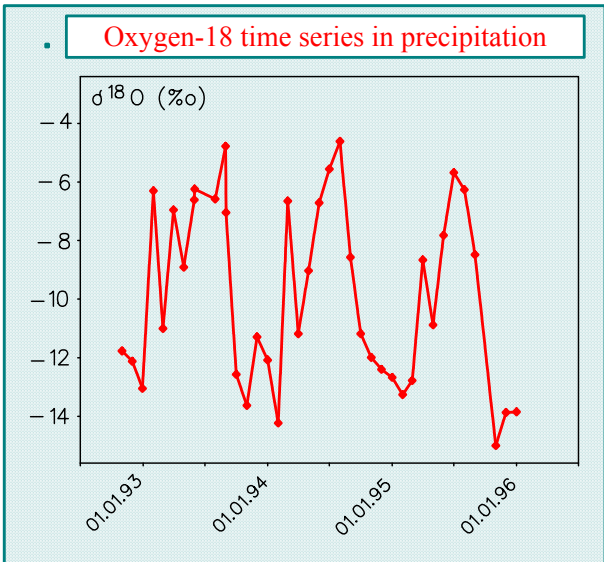
Sampling of precipitation:
weekly or monthly collective sample
with record of depth of precipitation



Sampling of groundwater:
Weekly or biweekly sampling



Dating of young groundwaters



**Result of modelling
aquifer model:
Dispersion model
mean residence time
ca. 4 years**



Dating of young groundwaters

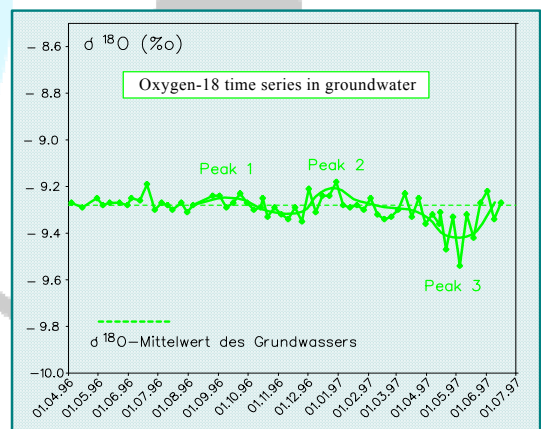
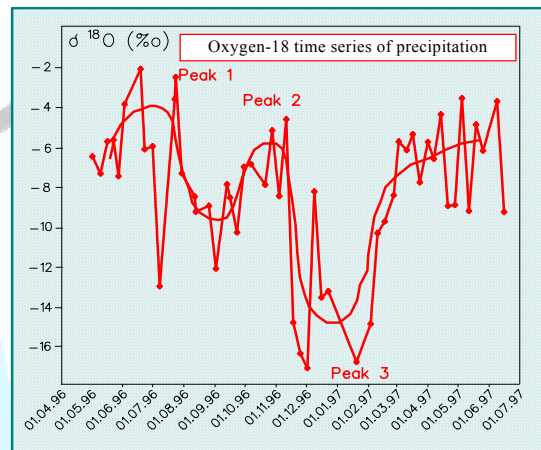
Specification of recharge conditions

If time series of ^{18}O values from precipitation and groundwater are available in high temporal resolution (at least weekly sampling), portions and residence times of rapid runoff components of the precipitation can be conceived.

In the shown example of a well tapping groundwater from shell limestone in Franconia, Germany, the age distribution of the groundwater was characterized. The amplitude of the ^{18}O input function of the precipitation was found strongly damped in the groundwater, which argues for a mean residence time of the groundwater of several years.

However, the direct comparison of the ^{18}O data series of precipitation and groundwater results in a portion of 5-10 % of a very young groundwater component (residence time of a few months).

In addition, from this example it can be seen that precipitation fallen in autumn and winter mark the groundwater more distinct than summer rains do. Hence, from appropriate long-term observations of the ^{18}O data, the groundwater recharge period in the catchment of a groundwater body can be determined.



Results of data comparison

Mean residence time (from damping):	ca. 4-5 years
Portion of very young component:	ca. 5-10 %
Residence time of very young component:	ca. 2-3 months



Detection of groundwater-recharge during the ice-ages

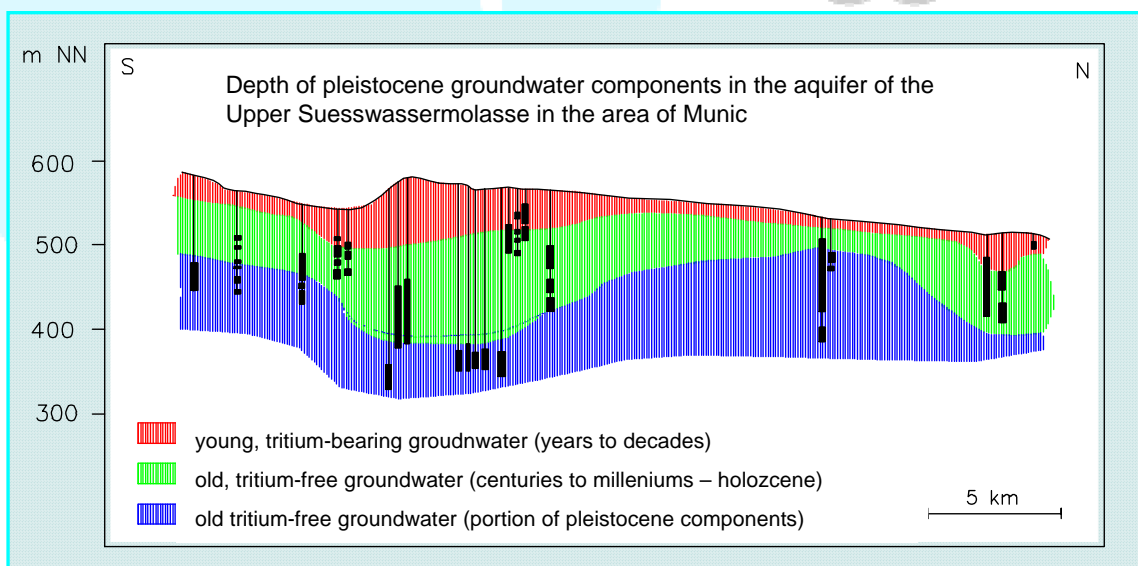


Groundwater that was recharged in cold periods of the Pleistocene have smaller contents of ^2H and ^{18}O because of the cooler climate at that time. The relationship between the ^{18}O -content in precipitation and the global climate history is documented impressively in drilling cores drawn from the Greenland ice-shield.

Groundwater with low contents of ^2H and ^{18}O , which in addition can be announced as "very old" from their age distribution (e.g. low content of carbon-14), holds at least portions of a groundwater component recharged in the Pleistocene (> 10,000 years).

By determining the stable isotopes ^2H and ^{18}O of multiple large-scale groundwater systems in conjunction with other hydro-isotopic investigations, the depth of the Pleistocene groundwater component was identified. Herefrom, conclusions on the groundwater recharge-rate was drawn.

In general, a groundwater system with a great groundwater age implies a large grade of guardedness. This idea already found its way into the advertisements of several mineral water producers.



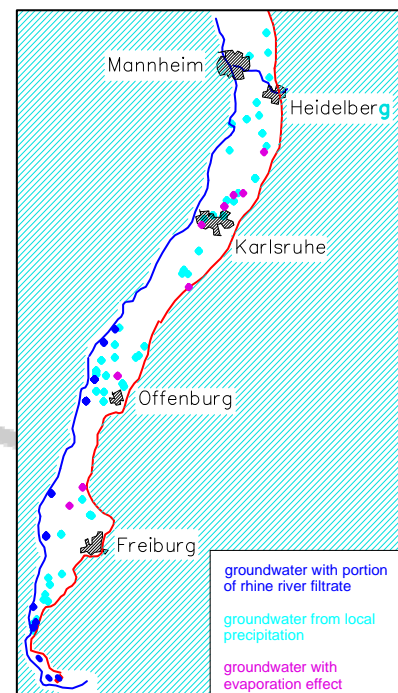
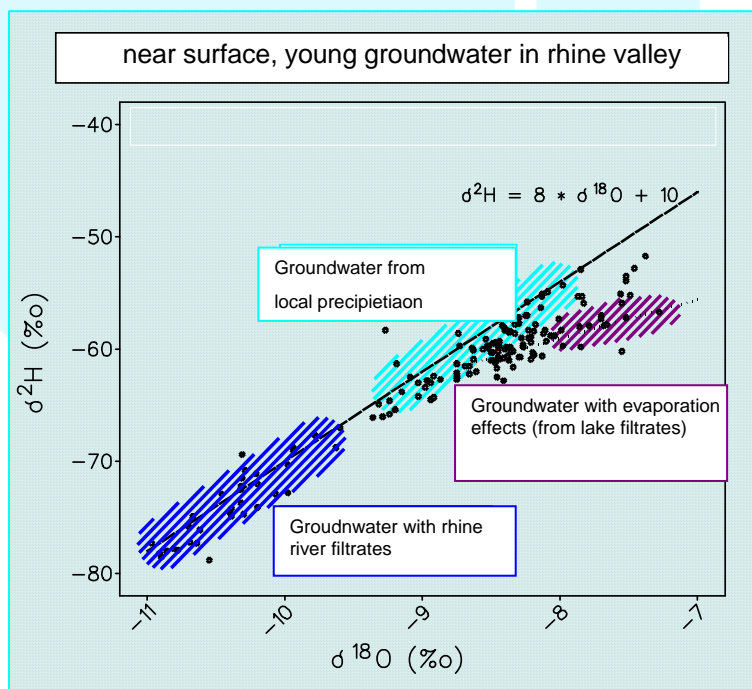
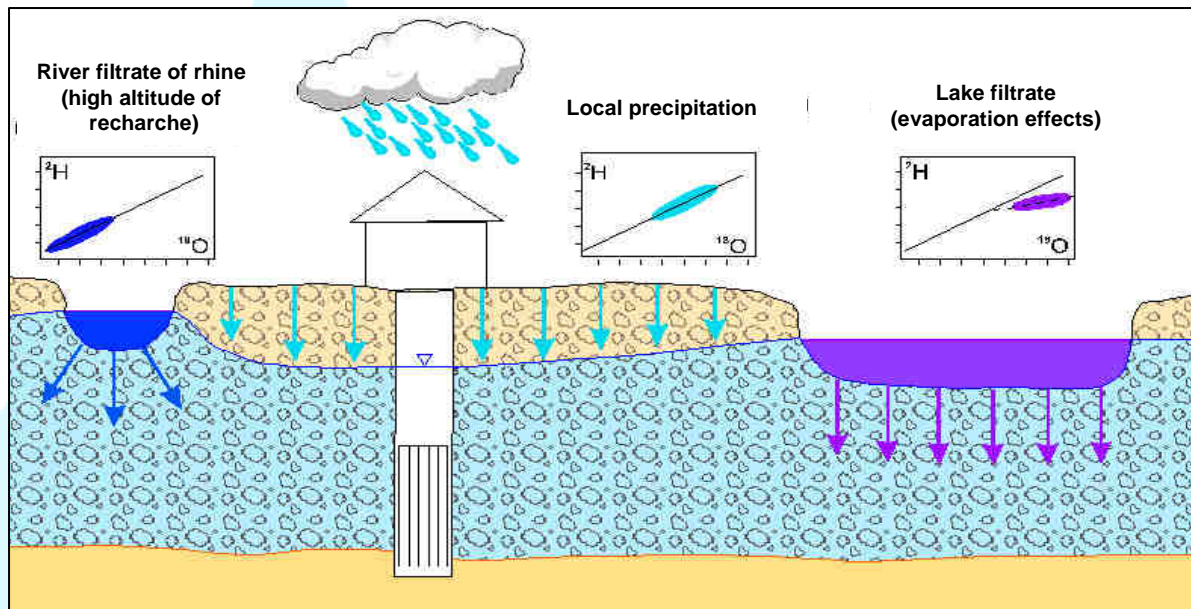


River water infiltration

As rivers are mostly recharged in catchments of high altitude, the river water in general has lower contents of ^2H and ^{18}O than the locally recharged groundwater adjacent to the rivers in the lowlands. Hence, infiltrating river water can be distinctly identified in the near-river groundwater body by the determination of the ^2H and ^{18}O contents.

Identification of infiltration areas

In an example from the Upper Rhine Valley it is shown, how regions with infiltration of river water into the groundwater were identified by determining the ^2H and ^{18}O signatures of the adjacent shallow groundwater bodies.





River water infiltration

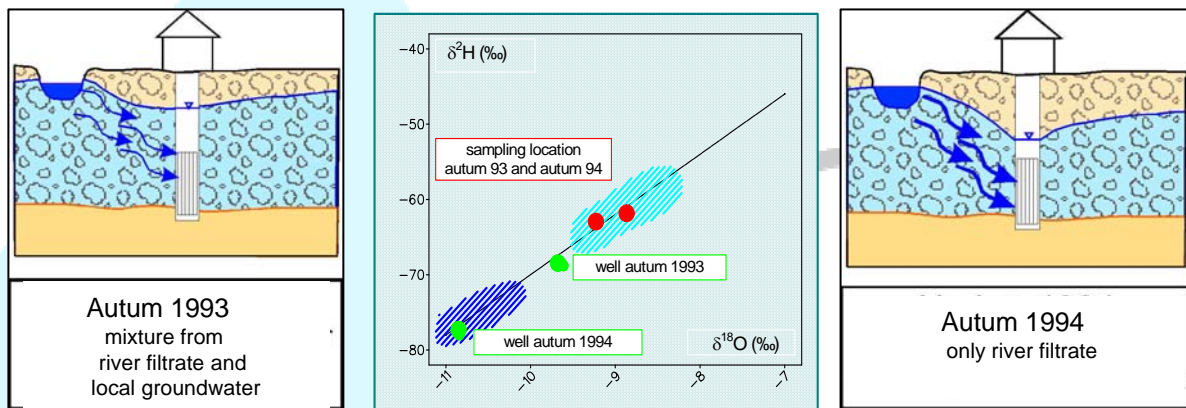
Quantifying the portion of bank filtrate

If the isotope signatures (^2H , ^{18}O) of the river water and of the adjacent groundwater are known, the portion of river water in the near-river groundwater can be quantified by a simple mixing model.

In some study regions in the Upper Rhine Area, the relation of the bank filtrate portion in groundwater to the extraction rate of river-near pumping wells was identified by only a few individual measurements of ^2H and ^{18}O .

This is exemplarily shown for a drinking water well in the city of Freiburg area in the following figure.

A few 100 m upstream of the drinking water well, an observation well with no detected portion of river water is located. In contrast, in the drinking water well, seasonal variable portions of infiltrating river water were detected. This argues for localized triggered bank filtration caused by pumping-induced groundwater depletion in the direct proximity of the drinking water well.





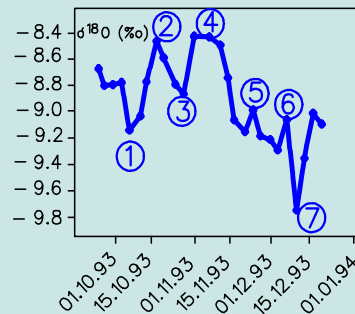
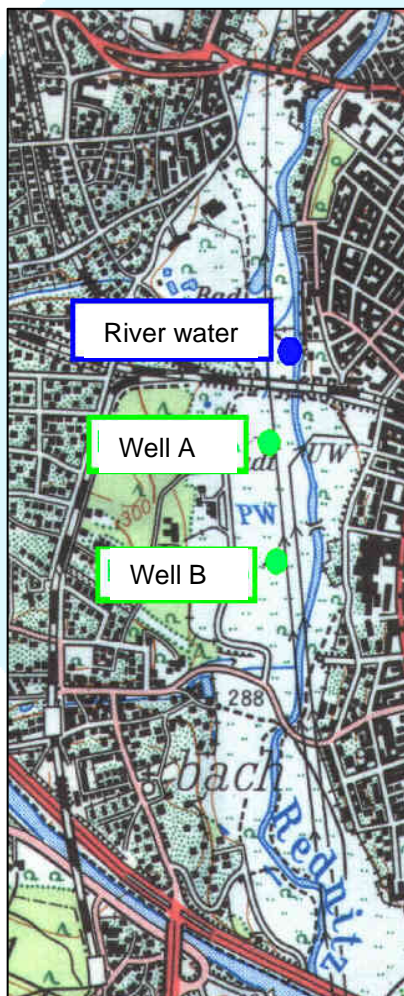
River water infiltration

Determining the travel time of infiltrating river water

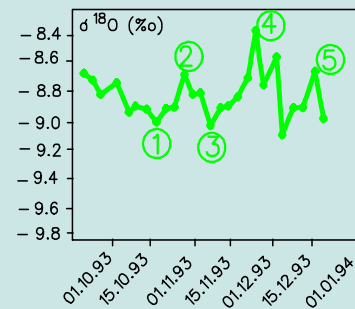
In general, rainfall events mark the river water relatively fast, as well in runoff as also in the hydro-chemical and isotopical composition. Therefore, the seasonal run of the ^2H and ^{18}O contents in precipitation is observable in damped manner in the river water, too. By comparing data series of river water ^2H and ^{18}O contents with data series of ^2H and ^{18}O -contents from groundwater, valuable insights into the river-groundwater interaction can be acquired and travel times of the bank filtrate into the groundwater body can be determined.

An important advantage of using the oxygen-18-method to determine bank filtration is that the ^{18}O content of the infiltrating river water, as being part of the water molecule, is not changed by any chemical and biological process as most other hydro-chemical parameters (e.g. nitrate).

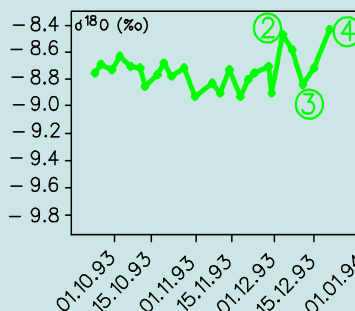
In the shown example, the ^{18}O contents of river water and of two drinking water wells (municipal water production in the city of Nurnberg area) were monitored over a period of 3 months. The drinking water wells are about 100 m apart from the river. By comparing the data series, the travel times of the infiltrating river water from the river to the both wells were determined.



Oxygen-18 series
river water
distinctive peak
sequence



Oxygen-18 series
well A
from series comparison:
flow time river-well
ca. 15 to 25 days



Oxygen-18 series
well B
From series comparison:
flow time river-well
ca. 35 to 50 days

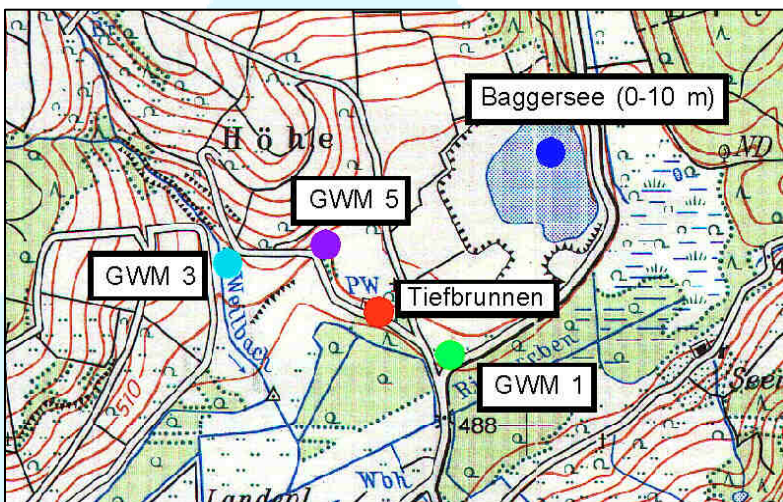


Lake water infiltration

During evaporation (e.g. from lake surfaces), the heavy isotopes get enriched in the remaining liquid phase. In such phase transformations ^{18}O gets more enriched than ^2H . Therefore, the ratios of the $\delta^2\text{H}$ - to the $\delta^{18}\text{O}$ values are shifted apart from the general relation given by $\delta^2\text{H} = 8 \times \delta^{18}\text{O} + 10$ (so called mean water line). The shift causes the $\delta^2\text{H}$ to the $\delta^{18}\text{O}$ ratio values to plot along a line with lower slope (so called evaporation line).

Therefore, the determination of ^2H and ^{18}O contents is suitable to qualitatively and quantitatively identify the portions of infiltrating lake water in the groundwater body.

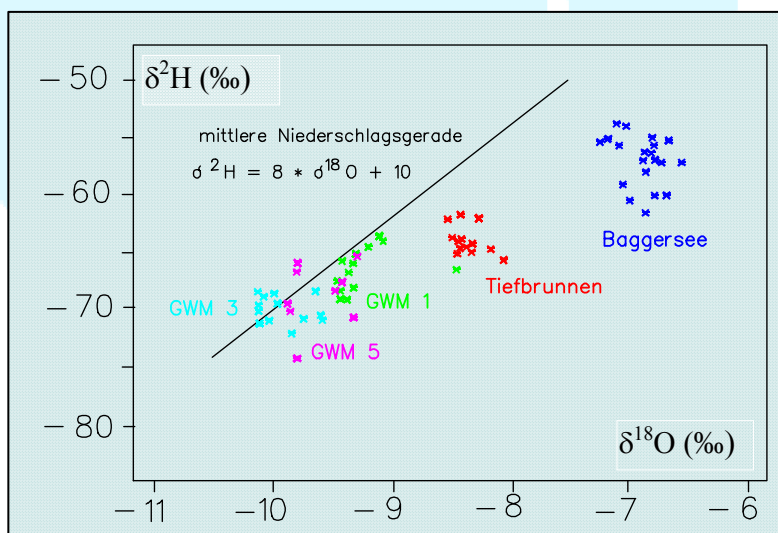
In the figure below, a water-filled gravel mining pit ("Baggersee") is situated upstream of a drinking water production well ("Tiefbrunnen"). The determination of ^2H and ^{18}O contents in the area of the Baggersee gave detailed insights to the influence of lake water portions to the groundwater, and hence, to the water of the drinking water production well.



Review of influence of the production well („Tiefbrunnen“) by filtrate of the Baggersee:

Monitoring: Time series of ^{18}O and ^2H in biweekly samples:

- Tiefbrunnen
- Baggersee (3 depths)
- Sampling locations (GWM)



- Water from Baggersee is significantly enriched to the groundwater (evaporation effect)
- Results of sampling locations without lake filtrate vary around the MWL
- The Tiefbrunnen and other sampling locations contain portions of lake filtrate. Results are on a mixture line between groundwater and isotopic enriched lake water



Deuterium as artificial tracer

All isotope hydrological methods described above base on the characteristic natural distribution of oxygen-18 and deuterium in the global water cycle (as environmental tracers).

In contrast, tracer studies in groundwater often base on the injection of artificial tracers (e.g. dye tracer). The distribution of these tracers in the water bodies is then monitored qualitatively and quantitatively.

In most hydrological questions, fluorescent dye tracers are used (uranin, eosin, pyranin, sulphorhodamin etc.). In addition to the dye tracers, also isotopically (stable and radioactive) marked substances can be used. In practice, especially deuterium-enriched water is used to mark the studied water bodies.

Deuterium-enriched water consists to about 96 % of heavy water molecules ($^2\text{H}_2\text{O}$, D_2O , "heavy water"). Analogously, also the use of oxygen-18-enriched water is possible. But because of its immense costs, tracing with oxygen-18-enriched water is not feasibly.

In the following, the pros and contras of using D_2O as tracer in hydrology are mentioned in short.

Advantages of deuterium as tracer

- D_2O can be seen as an ideal tracer as the water molecule itself is marked. Hence, $^1\text{H}_2\text{O}$ and D_2O are chemically equal. Therefore, the injected tracer is not affected by changes due to physical, chemical and biological processes (e.g. adsorption, microbial degradation, etc.).
- In general, the use of D_2O does not need to be authorized by an authority.
- D_2O is non-hazardous to human toxicology. By marking groundwater with D_2O , the natural deuterium content is increased by about 10-100 %. Hence, the deuterium contents in groundwater induced by the injection of D_2O are in the range of natural occurring waters (e.g. $\delta^2\text{H}$ of ocean water: ca. 0 ‰, fruit juices: ca. +10 ‰).

- D_2O leads to no perceivable variation of water, which in most tracer studies is of primary importance (e.g. tracing groundwater in direct proximity of mineral water production wells). In contrast, in the application of fluorescent dye tracers it cannot be excluded that the tracer reaches concentrations above the visibility limit in the extraction wells.

Disadvantages of deuterium as tracer

- Comparatively high cost, both, for the tracer substance itself as well as for its analysis. In particular, the high cost of D_2O reduces its application to small groundwater bodies or short flow distances, respectively. As a rule of thumb, to mark 500 to 1000 cubic meter of water, the volume of 1 L D_2O is needed.
- In contrast to fluorescent dye tracers, the sample throughput of deuterium samples in the laboratory is smaller due to the more sophisticated laboratory analytics (about 40 samples per week). To measure deuterium online in the field is not feasible. However, in some studies, a fast analysis of the tracer is needed to adapt the sampling interval. Such feedback between analytics and sampling interval is not possible in the application of D_2O as tracer.
- Native deuterium contents of groundwater may have natural variations. Therefore, in the application of D_2O as tracer, a tracer-unaffected reference well in the study area should be also sampled to monitor these natural variations. This is the only way to attribute variations in the measured breakthrough curves of the deuterium content to the injected deuterium.