Isotope Hydrogeology

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17.1 Introduction

The application of naturally occurring stable isotopes in hydrology dates back to 1935, when oxygen isotopic composition of water from Lake Michigan was determined by Dole (1935) (after Edmunds 2007). However, the beginning of modern stable isotope geochemistry is commonly connected with the landmark paper of Harold Urey published in 1947, where the basis of isotope fractionation was discovered, which subsequently opened up huge possibilities for stable isotope application in a variety of environmental studies. Several very well-written up-to-date reviews on the subject of application of environmental isotopes in hydrogeology and hydrology have been published, for example, Fritz and Fontes (1980, 1986), Clark and Fritz (1997), Criss (1999), Cook and Herczeg (2000), or Leibundgut et al. (2009).

The application of isotopic methods and isotopic data in hydrogeological studies noted a fast increase in the last decades. Scientists, hydrogeologists, and environmental engineers have understood that isotopic data give unique information and knowledge complementary to that obtained by classical geochemistry and classical hydrogeology and hydraulics.

Isotopes are atoms of a single element whose nuclei contain the same number of protons but a different number of neutrons. All isotopes can be divided into three fundamental kinds, namely, radioactive, radiogenic, and stable (e.g., Drever, 1997).

In hydrogeology and hydrology, the most widely used are stable or radioactive isotopes called environmental isotopes, that is, the naturally occurring isotopes of principal elements found in abundance in Earth’s environment like H, O, N, C, and S. The relative mass differences between isotopes of these elements are large and show measurable fractionation during physical, chemical, or biological reactions encountered in our environment. That is why the isotopic composition of different compounds of these elements can be used for tracing the water in hydrological cycle, as well as tracing the cycle of nutrients, carbon, nitrogen, and sulfur.

Environmental isotopes are used not only for tracing the isotopic signature of different compounds or groundwater origin but also for tracing and explaining various biogeochemical processes encountered in our environment and their rates. Isotopic methods are significant tool for studying recharge processes, soil–water–atmosphere interactions, and contaminant transport and sink.

Watershed characterization and catchment studies concerning basin budget (i.e., assessment of groundwater recharge, storage, and discharge) are also the most important fields where isotopic methods are successfully applied.

This chapter discusses the basic issues of the isotopes in environmental studies and summarizes their most useful applications.
17.2 Basis of Isotopes in Environmental Studies: Definitions, Abundances, and Measurements

Isotopes are atoms (i.e., nuclides) of a single element whose nuclei contain the same number of protons but a different number of neutrons. The number of protons uniquely defines the element, whereas the number of neutrons defines the isotope of that element. It means that isotopes of a particular element occupy the same position in the periodic table: they have the same atomic number but different atomic weights.

Normally simplified form of isotope identification is used: \( \text{XX} \), for example, \(^{18}\text{O},^{2}\text{H}\).

Isotopes can be divided into three fundamental kinds, namely, radioactive, radiogenic, and stable. The characteristic feature of radioactive isotopes is their decay into different forms called “daughter” atoms, at statistically predictable rates (Criss, 1999). Such decay is accompanied by the emission of radiation such as \( \alpha \)-particles (‘He’), \( \beta \)-particles (i.e., electrons or positrons), or \( \gamma \)-rays (i.e., electromagnetic radiation). On the other hand, stable isotopes do not decay. However, the term “stable” is relative, and it is possible that some nuclides have half-lives so long that their radioactivity has not been detected. The radiogenic isotopes are continuously formed by the decay of radioactive parent nuclides, and they may be stable or radioactive. Their abundance in the environment depends on the time period, the amount of parent nuclides present, as well as diffusion processes. Nonradiogenic stable isotopes (e.g., \(^{18}\text{O},^{13}\text{C},^{34}\text{S}\)) are those whose overall abundance is not a function of time, and variations in their abundance are caused by certain physicochemical processes. That is why they are of primary importance in various hydrological, hydrogeological, and geochemical applications. For example, they are used to understand the origin of water or processes that have affected water since it was formed (i.e., entered the particular aquifer). Radioactive isotopes in water studies are used primarily to measure age or water residence time. Up to date about 270 stable nuclides and over 1700 radioactive nuclides have been identified (Clark and Fritz, 1997). Only 21 elements are pure elements, in the sense that they have only one stable isotope (Hoefs, 1997). All other elements are mixtures of at least two isotopes. It means that the atomic weight of any particular element represents the weighted average of the atomic weights of constituent isotopes (Criss, 1999):

\[
A_w = \sum_i B_i^X W_i
\]  

(17.1)

where

- \( A_w \) is the atomic weight of the element
- \( B_i \) is the relative abundance
- \( W_i \) is the intrinsic weight of the \( i \)th nuclide

Such isotopically controlled variations of atomic weights of the elements have important consequences for physicochemical properties of elements and molecules.

17.2.1 Isotope Effects and Fractionations

The chemical properties of an element are generally determined by atomic number. It means that the chemical behavior of different isotopes of the same element is almost identical. However, the replacement of any atom in a molecule by one of its isotopes produces some variations in atomic mass and, in consequence, differences in thermodynamic properties of the element and the molecules of which they may be composed. Such differences in physicochemical properties arising from variations in atomic mass of the elements are usually called isotope effects, which source arises as a result of quantum mechanical effects. More detailed description of this subject can be found, for example, in Bigeleisen (1965),...
Kyser (1987), O’Neil (1987a), and Criss (1999). To demonstrate such isotopic effects, a good example is the properties of water composed of different stable isotopes of oxygen and hydrogen (Table 17.1).

The relative mass differences are significant only among isotopes of the lighter elements, in which the difference in mass is a large fraction of the total mass of the atom. For example, deuterium (\(^{2}\text{H}\)) has 100\% larger mass than its isotope protium (\(^{1}\text{H}\)); mass difference between \(^{18}\text{O}\) and \(^{16}\text{O}\) is 12.5\%, whereas between \(^{81}\text{Br}\) and \(^{79}\text{Br}\) is only 2.5\%; heavy water, \(^{2}\text{H}_{2}{^{16}}\text{O}\), has a mass of 20 compared to normal water, \(^{1}\text{H}_{2}{^{16}}\text{O}\), which has a mass of 18.

The most important here is the fact that molecules with differences in mass have different reaction rates, which leads to isotope fractionation—that is, unequal distribution of isotopes between two coexisting substances or two phases of the same substance. Therefore, isotope fractionation occurs in any thermodynamic reaction that causes isotopic ratios in particular phases to differ from one another. It is expressed by the fractionation factor \(\alpha\), which is defined as the ratio of the isotope ratios for the reactant and product (Clark and Fritz, 1997):

\[
\alpha = \frac{R_{\text{reactant}}}{R_{\text{product}}}
\]  

(17.2)

for example,

\[
\alpha^{2}\text{H}_{\text{water-vapor}} = \frac{{^{2}}\text{H}/^{1}\text{H}}_\text{water} \quad \left(\frac{{^{2}}\text{H}/^{1}\text{H}}_\text{vapor}\right)
\]  

(17.3)

where \(R\) is the ratio of the heavy (usually rare) isotope to the light (usually common) stable isotope in reactant and product.

Isotopic fractionation effects are small, and \(\alpha\)-values in most systems are close to unity, for example,

\[
\alpha^{18}\text{O}_{\text{water-vapor}} = 1.0094 \text{ at } 25^\circ\text{C}
\]

\[
\alpha^{2}\text{H}_{\text{water-vapor}} = 1.079 \text{ at } 25^\circ\text{C}
\]

However, hydrogen exhibits the largest fractionations observed in nature mostly due to two times difference in mass between \(^{1}\text{H}\) and \(^{2}\text{H}\). In the artificial system in which hydrogen gas is equilibrated with water using a platinum catalyst in room temperature fractionation, factor \(\alpha\) is equal to 3.7—which is not close to unity (Criss, 1999).
Isotope fractionation is generally considered for equilibrium conditions for which reliable fractionation factors can be calculated or experimentally measured (Clark and Fritz, 1997). In case, when isotopes are randomly distributed over all the positions in substrates and products, $\alpha$ is related to the equilibrium constant, $K$, for isotope exchange reactions (Kyser, 1987):

$$\alpha = K^n$$ (17.4)

where $n$ is the number of atoms exchanged (usually $n = 1$ and $\alpha = K$).

All thermodynamic processes producing isotope fractionation can be divided in two main groups (Kyser, 1987; O’Neil, 1987a; Hoefs, 1997; Criss, 1999):

1. Isotope exchange reactions
2. Kinetic processes

Isotope exchange reactions are equilibrium reactions in which the isotopes of a single element are exchanged between two substances (O’Neil, 1987a,b).

They can be simple physical changes of state,

$$\text{H}_2\text{O}_{\text{water}} \leftrightarrow \text{H}_2\text{O}_{\text{vapor}}, \alpha^{18}\text{O}_{\text{water}} - \text{vapor} = \frac{^{18}\text{O}/^{16}\text{O}}{^{18}\text{O}/^{16}\text{O}}_{\text{vapor}}$$ (17.5)

or chemical transformation,

$$\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3, \alpha^{13}\text{C}_{\text{CO}_2} - \text{H}_2\text{CO}_3 = \frac{^{13}\text{C}/^{12}\text{C}}{^{13}\text{C}/^{12}\text{C}}_{\text{H}_2\text{CO}_3}$$ (17.6)

or other aqueous, mineral–solution, and gas solution reactions.

The basis of such physicochemical isotopic fractionation is the difference in the strength of bonds formed by the light or the heavy isotopes of a given element, which, in consequence, provide differences in their reaction rates.

Kinetic isotope effects are also common in nature. They are usually associated with fast, incomplete, or unidirectional processes like evaporation, diffusion, dissociation, or metabolic processes (i.e., especially bacterially mediated irreversible reactions, e.g., sulfate reduction, methanogenesis). In case of diffusion or evaporation, such kinetic effects are explained by the different translation velocities of isotopic molecules moving through a phase or across a phase boundary, which arise from mass differences between isotopes. Whereas in case of dissociation reactions, the strength of bonds in molecules containing the heavy or light isotope plays the key role, molecules containing the heavy isotope are more stable and characterize higher dissociation energies (O’Neil, 1987a).

Mass differences that influence on the bond strengths between heavy and light isotopes as well as on the translation velocities and reaction rates cause the heavy isotopes to preferentially fractionate into more condense phase, that is, into the solid phase in mineral–solution reactions, or into the aqueous phase in gas (or vapor)–liquid reactions. The most important and useful fact is that the isotopic fractionation is strongly dependent on the temperature and not on any other variable of state (Criss, 1999). The fractionation factor $\alpha$ is very close to 1 at high temperature (i.e., if $\alpha = 1.000$, no fractionation occurs; system is well mixed); with decreasing temperature, $\alpha$ departs from unity and isotopic fractionation between substrates and products occurs. Equilibrium fractionation factors can be determined at different temperatures experimentally and can be also calculated from the partitioning functions.
17.2.2 Isotopic Ratios, Delta (δ) Notation, and Standards

In geochemical and environmental applications, the stable isotopes are measured as the ratio of the two most abundant isotopes of a given element. However, an absolute isotope ratio $R$ is not used to report stable isotope measurements or to report isotopic composition of a given element. It is common practice to report the measured difference in the isotopic composition of the sample and of the standard (i.e., known reference) in terms of δ-values according to the formula

$$\delta_S = \left( \frac{R_S}{R_{ST}} - 1 \right) \times 1000$$  \hspace{1cm} (17.7)

where $R$ refers to the isotope ratio in the sample $S$ and in the internationally accepted reference (standard) $ST$; the coefficient 1000 converts the δ-values to per mil (‰), as the fractionation processes do not cause huge variation in isotopic composition. Isotopic international standards are assigned to the value of zero per mil on the δ-scale of interest. The appropriate reference standards for the main stable environmental isotopes are listed in Table 17.2.

Fractionation factor $\alpha$ between two substances $A$ and $B$ in terms of δ-values is expressed by the equation (O’Neil, 1987b)

$$\alpha_{A-B} = \frac{1 + \frac{\delta_A}{1000}}{1 + \frac{\delta_B}{1000}} = \frac{1000 + \delta_A}{1000 + \delta_B}$$  \hspace{1cm} (17.8)

$$\delta_A - \delta_B \approx 1000 \ln \alpha = \Delta_{A-B}$$  \hspace{1cm} (17.9)

The value of $\Delta_{A-B}$ represents the difference in isotopic composition between substance $A$ and $B$. This difference is also an approximation of the term $1000\ln \alpha$, which is the widely used and convenient

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Ratio (Abundance Ratio)</th>
<th>International Reference Standard</th>
<th>Material</th>
<th>Name of Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^2$H</td>
<td>$^2$H/$^1$H</td>
<td>VSMOW (1.5575*10$^{-4}$)</td>
<td>Water</td>
<td>VSMOW2</td>
</tr>
<tr>
<td>$^{18}$O</td>
<td>$^{18}$O/$^{16}$O</td>
<td>VSMOW2 (2.0051*10$^{-3}$)</td>
<td>Water</td>
<td>VSMOW2</td>
</tr>
<tr>
<td>$^{18}$O</td>
<td>$^{18}$O/$^{16}$O</td>
<td>VPDB (2.0672*10$^{-3}$)</td>
<td>Calcite</td>
<td>VPDB</td>
</tr>
<tr>
<td>$^{13}$C</td>
<td>$^{13}$C/$^{12}$C</td>
<td>VPDB (1.1237*10$^{-2}$)</td>
<td>Calcite</td>
<td>VPDB</td>
</tr>
<tr>
<td>$^{15}$N</td>
<td>$^{15}$N/$^{14}$N</td>
<td>AIR N$_2$ (3.677*10$^{-4}$)</td>
<td>Gas</td>
<td>Air nitrogen</td>
</tr>
<tr>
<td>$^{34}$S</td>
<td>$^{34}$S/$^{32}$S</td>
<td>VCDT (4.5005*10$^{-2}$)</td>
<td>Troilite</td>
<td>VCDT</td>
</tr>
</tbody>
</table>

expression of fractionation factor $\alpha$ in per mil convention of $\delta$-values. This expression arises from the correlation between $\alpha$ and absolute temperature:

$$\ln \alpha_{A-B} = aT^{-2} + bT^{-1} + c$$  \hspace{1cm} (17.10)

where

$A$ and $B$ are reacting substances
$a$, $b$, $c$ are correlation coefficients
$T$ is the temperature in K

This relation is linear when plotting $\ln \alpha$ against the inverse of absolute temperature.

The most useful standard for oxygen and hydrogen isotopes is standard mean ocean water (SMOW), defined by Craig (1961a). For example, notation $\delta^{18}O_S = -3.5\%$ vs. SMOW means that our sample $S$ is 3.5‰ depleted in oxygen-18 isotope in relation to SMOW. To be more specific, isotopic ratio $^{18}O/^{16}O$ in sample $S$ reveals depletion in concentration of oxygen-18 in relation to $^{18}O/^{16}O$ ratio in SMOW. When absolute isotopic ratios of reference materials are known, it is easy to calculate absolute isotope concentration ratio of a given sample of interest. However, $\delta$-values are used in stable isotope geochemistry to report isotopic composition and compare the results of isotopic measurements.

Over the past few decades, appropriate materials have been established as internationally accepted reference standards, the so-called certified reference materials, due to the fact that stocks of international standards have been already exhausted, that is, Vienna Canyon Diablo Troilite (VCDT) or Vienna Pee Dee Belemnite (VPDB) is no longer available. The International Atomic Energy Agency (IAEA) has taken steps to produce replacements (e.g., certified reference materials or reference materials) that are almost the same in isotopic composition (e.g., Vienna standard mean ocean water (VSMOW2)) or very close and carefully calibrated according to international standards. These references, however, are also limited in quantities and cannot be used by laboratory on an each day basis. Therefore, it is important that each laboratory has its own internal “working standards” calibrated according to internationally accepted reference materials and standards. Two organizations collaborate on the calibration, cataloguing, and distribution of international reference materials: (1) the IAEA and (2) the National Institute of Standard and Technology (NIST, formerly the National Bureau of Standards (NBS)). Reference materials and further information are available through both of these organizations. The useful websites are as follows:

IAEA: www.iaea.org; for reference materials, see page http://nucleus.iaea.org/rpst/index.htm
NIST: www.nist.gov; for reference materials, see page http://www.nist.gov/srm/

17.3 Environmental Isotopes in Hydrogeological Applications

17.3.1 Stable Isotopes of Oxygen and Hydrogen in Hydrological Cycle

Hydrological cycle is a process of continuous movement (cycling) of water masses between the Earth’s lithosphere, atmosphere, hydrosphere, and biosphere. It moves from one reservoir to another by way of processes like evaporation, condensation, precipitation, deposition, runoff, infiltration, sublimation, transpiration, melting, and groundwater flow. During its movement the water changes state among liquid, vapor, and ice. Each step of this cycle and phase transformation causes specific fractionation of oxygen and hydrogen isotopes in water molecules. In consequence, the oxygen and hydrogen isotopic ratios provide conservative tracers that elucidate origin, phase transitions, and transport of water during hydrological cycle.

17.3.1.1 Precipitation and Global Meteoric Waterline

The first step of hydrological cycle, the formation of atmospheric water vapor by evaporation from oceans, is a nonequilibrium process due to the effects of low humidity and mixing of different vapor masses (Gonfiantini, 1986; Clark and Fritz, 1997).
The reverse process—condensation of atmospheric water vapor and formation of precipitation and meteoric waters—takes place in equilibrium maintained between vapor and condensed water in particular air temperature. This process is the most important for hydrological studies because it produces atmospheric precipitation and meteoric waters—that is, all waters that originate from atmospheric precipitation. To produce rain, the vapor masses evaporated over the ocean have to be cooled down. Cooling occurs by adiabatic expansion (i.e., no loss of enthalpy) as warm air rises to lower pressures or by radiative heat loss (Clark and Fritz, 1997). When the dew point is passed (i.e., the temperature at which humidity is 100%), water vapor condenses to maintain thermodynamic equilibrium, and it will rain (or snow). The evaporative flux of ocean water to the atmosphere is mainly controlled by temperature, and more than 70% of water vapor is produced from evaporation over oceans in warm, subtropical regions. That is why the air masses with water vapor normally move from its vapor source area to higher latitudes, and over continents, it cools and loses water vapor along this way as precipitation. Within the cloud, equilibrium fractionation between vapor and the condensing water preferentially fractionates $^{18}$O and $^2$H into the rain or snow. Such process of vapor mass evolution toward colder regions and toward isotopically depleted precipitation is called as rainout. The process of condensation and rainout causes large variation in the isotopic composition of meteoric water. The total range of $\delta^{18}$O values in natural precipitation is about +4‰ to −62‰, while that of $\delta^2$H values is about +40‰ to −500‰ (Criss, 1999), (See Table 17.3).

However, analyses of isotopic composition of meteoric water from different parts of the world revealed that their $^{18}$O and $^2$H isotopes vary in characteristic, predictable manner and undergo linear correlation defined by the equation

$$\delta^2H = 8\delta^{18}O + 10$$  \hspace{1cm} (17.11)

The previous equation became known as the "global meteoric waterline (GMWL).” This relationship, derived first by Craig (1961b), traces the isotopic compositions of all natural waters originating from atmospheric precipitation and not subjected to surface evaporation (Figure 17.1).

Nowadays, based on the isotopic composition of precipitation provided by the Global Network of Isotopes in Precipitation (GNIP)—a worldwide network of meteorological stations that monitor isotopic composition of precipitation coordinated by the IAEA since 1961—from 1961 to 2000, the GMWL is defined more precisely by the equation (Gourcy et al., 2007)

$$\delta^2H = 8.14 (\pm 0.02) \delta^{18}O + 10.9 (\pm 0.2), \text{ } R^2 = 0.98$$  \hspace{1cm} (17.12)
The slope of the GMWL is close to eight due to the in-cloud ratio of the water–vapor equilibrium fractionalization factors for $^2$H and $^{18}$O:

$$s = \frac{1000\ln\alpha^2H_{water-vapor}}{1000\ln\alpha^{18}O_{water-vapor}} = 8.2 \text{ at } 25^\circ\text{C}$$  \hspace{1cm} (17.13)

Deuterium excess factor $d$, proposed by Dansgaard (1964), is defined as

$$d = \delta^2H - 8\delta^{18}O$$  \hspace{1cm} (17.14)

and characterizes the deuterium excess in global precipitation for which the average value of $d$ is about 10‰. The deuterium excess factor explains, for example, the displacement of GMWL from the position of ocean water, that is, VSMOW (Figure 17.1).

On a regional scale, minor deviations from GMWL are observed as a result of local meteorological conditions. It means that any location on the globe will have its own local meteoric waterline (LMWL) with particular slope $s$ and $d$ factor (Figure 17.2).

The largest deuterium excesses in precipitation are found in the Eastern Mediterranean region (Criss, 1999). For example, the eastern meteoric waterline (EMWL) introduced by Gat and Carmi (1970) is described by the following equation:

$$\delta^2H = 8\delta^{18}O + 22$$  \hspace{1cm} (17.15)

This fact clearly shows that for detailed stable isotope studies within a particular geographical region, the LMWL should be established to compare surface and groundwater data and to avoid interpretation errors. Generally, the strong correlation between temperature and $^{18}$O and $^2$H determines the position of precipitation on the MWLs. The $T$-$\delta$ (i.e., temperature-isotope) correlation
and evolution of isotopic composition during rainout can be described and modeled according to the Rayleigh distillation equation:

$$R = R_0 f^{(\alpha - 1)}$$

(17.16)

where

- $R_0$ is the initial isotope ratio of the vapor
- $R$ is the isotope ratio of the vapor when given fraction $f$ of the vapor had reacted (i.e., rained out)
- $f$ is the residual fraction of the vapor in the cloud
- $\alpha$ is the fractionation factor for equilibrium water–vapor isotopic exchange at ambient in-cloud temperature

For $T$–$\delta$ correlation it is possible to derive isotope effects due to seasons, altitude, latitude, continentality, and paleoclimates. The linear relationships between surface air temperatures and $^{18}$O and $^2$H of mean annual precipitation on a global scale were derived by Dansgaard (1964):

$$\delta^{18}O = 0.695T - 3.6\%$$

$$\delta^2H = 5.6T - 100\%$$

where $T$ refers to annual surface air temperature in °C.

Departures from these relationships can occur on local and regional scale and when monitoring data are too short or when event scale is investigated (i.e., individual storm).

From this correlation however, it can be deduced that precipitation at higher latitudes tends to have more negative $\delta^{18}$O and $\delta^2$H values (the so-called latitude effect: $\delta^{18}$O and $\delta^2$H contents decrease with rainout of air masses); it is important to notice that polar regions are situated at the end of the Rayleigh
distillation process (Clark and Fritz, 1997). Land masses and continents induce the rainout from vapor masses and more rapid evolution of isotopic composition of precipitation (continental effect), mostly due to influence of topography and temperature extremes that occur over the continents. Altitude effects (due to diversify relief of lands, $^{18}$O and $^2$H contents decrease with increasing altitude) and seasonal effects (i.e., winter precipitation is usually depleted in $^{18}$O and $^2$H relative to summer precipitation) are characteristic for particular local settings and meteorological conditions.

17.3.1.2 Identification of Groundwater Origin

All groundwater encountered in the Earth’s crust can be classified into three categories depending on the origin (Gat, 1981): (1) meteoric waters, (2) paleowaters, and (3) formation waters.

17.3.1.2.1 Meteoric Waters

Meteoric waters can be defined as waters that originate from atmospheric precipitation (e.g., rain, snow, rivers, lakes, most of shallow groundwater of low-temperature environment) and actively take part in the modern hydrological cycle. These types of waters constitute the vast majority of fresh and potable water reservoirs. From the origin point of view, any type of water found in geological environment where $\delta^{18}$O and $\delta^2$H isotopic values cause its location along the GMWL or LMWL should be considered as meteoric in origin. The shallow groundwaters usually belong to meteoric waters and lie along or close to LMWL or GMWL. It means that their isotopic composition is equal to the mean weighted annual composition of precipitation. However, in some cases, the important deviations from isotopic composition of MWL are found in groundwaters, which may complicate proper interpretation of their origin. Such deviations are most likely where depth to the groundwater table is small, reflecting isotopic variability in rainstorms or recharge. There are three main reasons of such deviations: (1) propagation of seasonal variations from precipitation, (2) seasonal or local biases in recharge, and (3) evaporation processes.

In the unsaturated zone, between surface and groundwater level of saturation zone, infiltration waters reveal seasonal variation of the isotopic composition. However, these variations usually are attenuated with depth by the geological environment. The attenuation scheme is presented in Figure 17.3.

This attenuation arises from hydrodynamic dispersion within the soil, where the infiltration travels at different velocities through pores of different sizes and in some cases also through cracks, fissures, or

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**FIGURE 17.3** Scheme of the attenuation of seasonal variation of $^{18}$O and $^2$H isotopic composition of precipitation during infiltration through the unsaturated zone and filtration within saturated zone up to a critical depth below which isotopic variability is less than the analytical precision. (From Clark, I. and Fritz, P., *Environmental Isotopes in Hydrogeology*, Lewis Publishers, New York, 328pp, 1997.)
macropores (Leibundgut et al., 2009). In fine-grained soils, the depth at which the seasonal variations are damped out is less than in coarse-grained soils. In fractured or karstified rocks, attenuation is expected to be slow and depth of full attenuation relatively large. If the infiltration water reaches the water table of saturated zone before the seasonal signal has been fully attenuated (i.e., in case where thickness of unsaturated zone is less than depth of attenuation), this fluctuations will also be found in the groundwaters.

Seasonal or local biases in recharge can also be responsible for deviation between weighted average annual precipitation and groundwater. It regards the situation when recharge rates at one season of the year are greater than at other times of the year. For example, the recharge from snowmelt may be responsible for observed slight depletion in $^{18}$O and $^2$H of shallow groundwater. Moreover, in arid climates only the largest and longest-lived storm events recharge the groundwater systems, and the $^{18}$O and $^2$H values of those storms may differ from average values of MWL in arid regions.

Subaerial evaporation from water body results in a deviation from the MWL along a line with a lower slope, which depends mostly on the relative humidity (Figure 17.4) (Gonfiantini, 1986).

The same process of evaporation can remove moisture from soil of unsaturated zone, especially in arid and semiarid regions (see Figure 17.12).

Geyh and Ploethner (1997) proposed useful correction of $^{18}$O for evaporative enrichment:

$$\delta^{18}O_{corrected} = \delta^{2}H_{measured} - \epsilon \delta^{18}O_{measured} - d \quad (\text{Leibundgut et al., 2009}) \quad (17.17)$$

where

- $\epsilon$ corresponds to the slope of the evaporation line determined
- $d$ is the deuterium excess factor for global precipitation

Corrected values indicate the isotopic composition of water without evaporative enrichment. Once the $^{18}$O has been corrected, the corresponding $^{2}H$ value can be obtained by solving the equation for GMWL, as the evaporation line intersects the GMWL in the point of corrected $^{18}$O.

### 17.3.1.2 Paleowaters

Paleowaters (or more adequately—paleogroundwaters) are also meteoric in origin but were recharged in the geological past under similar or different climatic conditions. In many regional flow systems,
groundwaters qualified as paleogroundwaters may be old due to their very low filtration velocities and long flow paths, but they may actually receive modern inputs in the recharge areas (Clark and Fritz, 1997) (Figure 17.5B). Paleogroundwaters may also form isolated reservoirs that are not in contact with modern hydrological cycle; their resources are then finite (e.g., Figures 17.6 and 17.7). Majority of paleogroundwaters are not part of active flow systems.

The basis of climate change is the change in air temperature and precipitation patterns. Taking into account the existence of clear correlation between isotopic composition of precipitation and groundwater of meteoric origin, we can expect that also paleogroundwaters reveal this correlation and their isotopic composition records past changes in climatic conditions under which the water has entered geological environment. Thus, the “paleoclimatic effect” is one of the most important tools in identifying paleogroundwaters (Clark and Fritz, 1997).

In temperate latitudes the dominant paleoclimatic effect is connected with Pleistocene glaciation and recharge in much colder climatic conditions. Late Pleistocene paleogroundwaters are isotopically depleted with respect to modern meteoric groundwaters and shifted along GMWL toward negative values (Figure 17.5A).

A very good illustration of Holocene- vs. Pleistocene-recharged groundwaters is the confined quaternary aquifer of the Great Hungarian Plain (Figure 17.5B). Groundwaters recharged during Pleistocene
FIGURE 17.6 Examples of paleogroundwaters from the Middle East and North Africa. (From Clark, I. and Fritz, P., *Environmental Isotopes in Hydrogeology*, Lewis Publishers, New York, 328pp, 1997.) Data compiled from many authors.

FIGURE 17.7 Example of paleogroundwaters (mine drainage waters) from Permian sediments of Foresudetic Monocline, Poland (Porowski, unpublished).
times in this region have δ¹⁸O values more negative than −10‰. Moreover, content of ¹⁴C of groundwater decreases along flow lines and reaches values less than 10 pmC (i.e., more than 20 ka BP) for water recharged in Pleistocene times (Deak and Coplen, 1996).

On the other hand, in arid regions, like the Eastern Mediterranean and North Africa, the paleoclimatic effect connected with the Late Pleistocene—Early Holocene is manifested by a displacement of the MWL. This is because the humid climates have characterized these regions in the past. The groundwater recharged during pluvial climatic conditions in the Late Pleistocene or Early Holocene have isotopic composition, which locates them on or even below the modern GMWL (d = 10‰), whereas modern meteoric waters in these regions are located along MWL with deuterium excess factors of 15‰–30‰ (Figure 17.6).

In geological environment of temperate latitudes, it is also possible to find paleogroundwaters recharged in much warmer climatic conditions than nowadays in a particular geographical region (Figure 17.7).

Such waters are isotopically enriched with respect to modern waters and shifted toward positive δ¹⁸O and δ²H values along GMWL. They are much older than Pleistocene ones, presumably remained in pores of sediments since recharge in geological past and were disconnected completely from the modern hydrological cycle.

17.3.1.2.3 Formation Waters

Formation waters are those found in interstices and pores of crystalline and sedimentary rocks at greater depths. They are usually very slow moving or even stagnant, with heightened salinity, and their specific ¹⁸O and ²H isotopic composition is a result of water–rock interactions over a long time scale usually in elevated temperatures (Gat, 1981; Sheppard, 1986; Welhan, 1987). The term “formation water” is wide and has no implication on the origin or age of the water. Nevertheless, some waters formed in particular geochemical process can be identified as separate types with specific isotopic composition, for example, metamorphic waters and magmatic waters (Figure 17.8).

The majority of formation waters presented in Figure 17.8A and B come from depths between 500 and 3700 m; most of the reservoir rocks in sedimentary basins are of marine origin, within the Canadian Shield—crystalline rocks; presented waters are saline or brines (Sheppard, 1986). Waters plotted on or near MWL are the least saline and reveal meteoric origin. The trends of increasing salinity with enrichment in ¹⁸O and/or ²H are observed. As can be seen (Figure 17.8), unlike most modern meteoric waters and paleogroundwaters, in which stable isotopes of H and O behave conservatively, formation waters have been considerably affected by isotopic exchange with rock-forming minerals, usually in elevated temperatures, and presumably also by secondary mixing processes.

The characteristic ¹⁸O-shift to the right of the MWL (Figure 17.8A) is predominantly due to isotopic exchange with ¹⁸O-rich rock-forming minerals and particularly carbonates; the ⁶D variations are less understood, and few possibilities are usually considered during interpretation, for example mixing of different waters (e.g., meteoric and metamorphic), exchange with H₂S (which is depleted in ²H relative to water), fractionation during membrane filtration, or exchange with hydrous minerals. Some rare formation waters like those observed in oceanic crust and Canadian Shield can reveal enrichment in ²H, which shifts them to the left of the MWL (Figure 17.8B). Fritz and Reardon (1979) attributed enrichment in ²H to water participation in the process of hydration of primary silicates under closed-system conditions or low-temperature exchange with feldspars. The observed trend between some allochthonous end member (i.e., the most ²H-enriched water) and meteoric water suggests mixing line rather than line of evolution of ¹⁸O and ²H composition (Clark and Fritz, 1997). Pore waters in oceanic sediments at depths of 100 m or more (Figure 17.8B) are often depleted in ¹⁸O and ²H in relation to modern ocean water. Such changes in isotopic composition of pore waters are related to the low-temperature alteration of basalts or of volcanic ash in the sediments (Muehlenbachs and Clayton, 1971).
FIGURE 17.8 Isotopic composition and fields of formation waters in sedimentary basins, crystalline rocks, and other types of specific groundwaters encountered in deep geological environment. The field for common sedimentary rocks, kaolinite weathering line, and MWL is plotted for reference. Trends for the $^{18}O$-shift due to water-rock interaction in hydrothermal systems for thermal waters of meteoric (A and B) and seawater origin (dashed arrows) were also shown. Plots after Sheppard (1986); data after many authors cited in Sheppard (1986). See text for additional explanation.
Other specific types of waters indicated on the plots (Figure 17.8) are usually connected with particular geochemical processes of their formation. Sheppard (1986) provides comprehensive description of these type of waters:

- **Metamorphic waters**—are defined as waters that equilibrated with or were released from metamorphic rocks undergoing dehydration.
- **Magmatic waters**—waters that were equilibrated with magma, regardless of their ultimate origin; it refers to separate aqueous phase and not to all types of water of any speciation that are physically dissolved in the magma.
- **Juvenile waters**—waters that originate from the Earth’s mantle or core and that have never been involved in the hydrosphere; hypothetical waters that have never been convincingly recognized.
- **Organic waters**—those whose $^{2}\text{H}/^{1}\text{H}$ ratios are derived from the direct or indirect transformation of organic matter, bitumen, coal, kerogen, petroleum, organic gases, etc., by processes such as dehydration, dehydrogenation, oxidation, and/or exchange; the H isotope composition of organic water is related to that of their organic source material by the appropriate isotopic fractionation.

As can be seen on the plot (Figure 17.8), the fields for $\delta^{18}\text{O}$ and $\delta^{2}\text{H}$ of different waters may partly overlap each other, which may cause problems with proper interpretation and unambiguous water identification.

Figure 17.9 presents a general scheme that summarizes the interpretation of the observed trends in isotopic composition of waters, which deviate considerably from MWL.

The idea of differential fractionation of O and H during water reactions with rocks as well as mixing of waters of different origins is discussed in the next chapters.

17.3.1.3 Water–Rock Interaction and Hydrothermal Systems

The processes of water–rock interactions are of primary importance in modification and formation of specific isotopic composition of groundwater in deep parts of the geological environment, in high-temperature conditions, and over a geological time scale. Some evidence of water–rock interaction in low
temperatures in shallow groundwater flow systems is also known. The alteration of the $^{18}$O and $^2$H composition of groundwater gives the insight into its origin, subsurface history, and geochemical reactions.

The isotopic exchange between water molecules and minerals is restricted to $^{18}$O and $^2$H. Isotope exchange is achieved by dissolution and reprecipitation (i.e., during chemical reactions) or by direct exchange of isotopes between water and the mineral crystal lattice (Clark and Fritz, 1997).

The ratios of $^2$H/$^1$H and $^{18}$O/$^{16}$O in composition of waters provide two independent “labels” or traces of their origin. The water-to-rock ratio, that is, the amount of exchangeable oxygen and hydrogen atoms in water and in the rock, determines the differential fractionation of O and H isotopes between reacting phases. In ordinary rocks oxygen is the most abundant element, making up about 50% by weight. In contrast, hydrogen is usually a trace element in a rock with concentration less than 2000 ppm (e.g., a rock with 1% of water by weight contains only 0.11% of hydrogen) (Sheppard, 1986). During water–rock interaction, both H and O isotope exchange may occur among the phases. In systems where the water is of external origin, this water is generally the dominant hydrogen reservoir, and it will therefore control the $^2$H/$^1$H ratio of the system. The $^{18}$O/$^{16}$O ratio of the water, however, may be determined by that of the exchangeable mineral oxygen and the temperature of exchange unless water-to-rock ratios are very large or the exchange reaction is ineffective for kinetic or other reasons.

The characteristic $^{18}$O-shift, generally to more positive $\delta^{18}$O values (Figure 17.9), is a result of the water trying to attain O isotope equilibrium with the $^{18}$O-rich silicates and carbonates. The size of the shift is related to (1) the ratio of the quantity of oxygen in the exchangeable minerals to that in the water, (2) the temperature of exchange, and (3) the initial isotopic composition of the phases (Sheppard, 1986). Thus, the $\delta^{18}$O of the water may not retain its “label” or memory of its source. For these reasons, the $\delta^2$H of the water is often a better parameter to determine the source of the water. This is a crucial point in interpreting the origin of thermal waters (Figure 17.10).

![Figure 17.10](image-url)

**FIGURE 17.10** Isotopic composition of thermal waters and steam from various regions derived from meteoric water (open symbols) and of meteoric water local to each system (closed symbols). Thermal water demonstrates the strong $^{18}$O-shift due to isotopic exchange with rocks. (From Truesdell, A.H. and Hulston, J.R., Isotopic evidence on environments of geothermal systems, Chapter 5, in Fritz, P. and Fontes, J.Ch. (eds.), *Handbook of Environmental Isotope Geochemistry, Volume 1, The Terrestrial Environment*, A. Elsevier, Amsterdam, the Netherlands, 179pp, 1980.) Modified by the author.
Craig (1963) showed that high-temperature geothermal systems have waters with the same $\delta^2$H values as local precipitation but have variable enrichment in $^{18}$O. Such $^{18}$O-shift is attributed to exchange of oxygen in water with oxygen in silicate and carbonate minerals. Groundwaters of meteoric origin are generally far from isotopic equilibrium with minerals of the host rocks. Observed $^{18}$O-shift in thermal waters reflects isotopic evolution toward mineral–water equilibrium (Clark and Fritz, 1997). The initial isotopic difference between the rocks and the recharge water, and the water-to-rock ratio, is also important: The $^{18}$O contents of crystalline and carbonate rocks are much higher than in most meteoric waters; in case of low water–rock ratio, even a minor exchange will impart a measurable shift to the water. Thermal waters in systems with high water–rock ratios will have a diminished shift.

In low-temperature environments, another shift may be observed: fractionation between water and minerals may result in $^2$H-enriched and $^{18}$O-depleted waters located to the left of the MWL. Two dominant exchange reactions are usually considered in such case: (1) retrograde exchange between water and primary silicate minerals and (2) hydration of primary silicates (Clark and Fritz, 1997). To observe significant water enrichment in $^2$H, very low water–rock ratios are required together with the geological time scale, because rates of exchange and hydration are very slow at low temperatures.

### 17.3.1.4 Groundwater Mixing

Mixing processes between different types of groundwaters occur at various scales in various hydrogeological conditions. The process of attenuation of seasonal variations in groundwater, described previously, can be an example of microscale mixing. Nevertheless, the isotopic methods can be used to quantify groundwater mixing at the local and regional scales, where mixing between groundwaters of different recharge origins, from different aquifers, and different flow systems can occur.

Mixing between two different groundwaters $A$ and $B$ (i.e., two-component mixing) can be quantified by a simple linear equation using $\delta^2$H and/or $\delta^{18}$O:

$$\delta_{AB} = f \delta_A + (1 - f) \delta_B$$

(17.18)

where

- $\delta_A$ and $\delta_B$ refer to $\delta^2$H or $\delta^{18}$O in water $A$ and $B$, respectively
- $\delta_{AB}$ refers to $\delta^2$H or $\delta^{18}$O in mixture of two waters
- $f$ refers to the fraction of water $A$ in mixture $AB$

To solve the equation, all $\delta$-values should be known. A graphical presentation of the two-component mixing is shown in Figure 17.11.

**FIGURE 17.11** Two-component mixing quantified on the basis of isotopic compositions of groundwater $A$ and $B$. The mixing line shows fraction of water $A$ in $AB$ mixture. (From Clark, I. and Fritz, P., *Environmental Isotopes in Hydrogeology*, Lewis Publishers, New York, 328pp, 1997.)
Unlike most geochemical tracers, the $^{18}$O and $^2$H isotopes reveal a conservative behavior in mixing relationships and preserve the mixing ratio. That is why the mixing lines can be observed in various types of formation waters in sedimentary basins, which strongly suggest the admixture of water of meteoric origin even in greater depths (Figure 17.8).

Mixing process of two components can be observed in unsaturated zone between rain that infiltrates into the soil and evaporated soil moisture when low recharge rates occur (Allison et al., 1984). In such case, isotopic composition of infiltrating groundwater follows a line parallel to MWL but displaced to the right.

Catchment study concerning groundwater recharge, storage, and discharge is also one the most important fields where $^{18}$O and $^2$H isotopes are used to separate between mixing waters constituting, for example, baseflow and surface runoff. In the case of basing budget studies, the key issue is to assess the proportion of water resulting from storm events, which recharges groundwater and which is lost by surface runoff. Such isotopic method of the stream hydrograph separation into baseflow component and surface runoff component is based on different isotopic compositions of the groundwater in the basin and that of a given storm (Figure 17.12).

The groundwater should have an isotopic composition that reflects long-term average input value for the whole basin, whereas the isotopic composition of storm water will reflect actual conditions of falling in particular time and space.

In regional flow systems, sometimes three-component mixing can be identified. A well-known example comes from the northern Canadian Shield and was identified by Douglas et al. (2000) (Figure 17.13). In this example, mixing between shield brines and meteoric waters was demonstrated by the decrease in salinity over time and curtained sampling sites. Additionally, a third type of groundwaters of depleted isotopic composition and intermediate salinity was identified, which deviated from the simple two-component mixing line.

Such regional scale mixing processes can be observed in deep groundwaters within basins as well as in shallow but confined systems with long subsurface flow paths (Clark and Fritz, 1997).

### 17.3.2 Groundwater Quality and Origin of Dissolved Compounds

The dissolved compounds in groundwater and their chemical types and amounts (i.e., salinity) are components of water quality. Application of stable isotope techniques in many cases allows tracing the origin of dissolved compounds, their formation, transformation, and sinks during different geochemical processes in the hydrosphere. This chapter is focused on the isotopic composition of dissolved sulfates.

**FIGURE 17.12** Example of $^{18}$O isotope stream hydrograph separation for a two-component water system: storm event and groundwater. (From Clark, I. and Fritz, P., *Environmental Isotopes in Hydrogeology*, Lewis Publishers, New York, 328pp, 1997.)
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(i.e., $\delta^{34}S$ and $\delta^{18}O$ of $SO_4^{2-}$) and nitrates (i.e., $\delta^{15}N$ and $\delta^{18}O$ of $NO_3^-$) as they are common and important constituents of surface water and groundwater. Identifying their sources and biogeochemical processes that govern their occurrence and transformation in aquatic environment is very important knowledge for water resources and water quality management.

17.3.2.1 Isotopic Composition and Sources of Dissolved Sulfates

Main forms of sulfur in geological environment include sulfate and sulfide minerals, sulfate ($SO_4^{2-}$) and sulfide ($HS^-$) dissolved in water, and hydrogen sulfide gas ($H_2S$). Under oxidizing conditions in water, sulfate is the dominant sulfur species, while under reducing conditions, sulfides prevail. Organic sulfur is a component of organic compounds such as humic substances, kerogen, and hydrocarbons. Atmospheric sulfur sources include natural and industrial $SO_2$, particulate sulfur, and aerosols of marine sulfate. Sulfur compounds from these various sources participate in the geochemical evolution of groundwater.

Sulfur has four stable isotopes, $^{32}S$, $^{33}S$, $^{34}S$, and $^{36}S$, occurring naturally with respective absolute abundances of about 95.02%, 0.75%, 4.21%, and 0.02% (MacNamara and Thode, 1950). Normally $^{34}S/^{32}S$ and $^{18}O/^{16}O$ are measured to obtain isotopic composition of sulfates. On a $\delta$-scale isotopic composition of sulfate is defined as follows:

$$
\delta^{34}S = \left( \frac{^{34}S_{sample}}{^{32}S_{SVCDT}} - 1 \right) \times 1000 \tag{17.19}
$$

$$
\delta^{18}O = \left( \frac{^{18}O/^{16}O_{sample}}{^{18}O/^{16}O_{VSMOW}} - 1 \right) \times 1000 \tag{17.20}
$$

Typical ranges of $\delta^{34}S$ and $\delta^{18}O$ for main sulfate sources are presented in Figure 17.14.

FIGURE 17.13 Three-component mixing for groundwaters from crystalline rocks of the Canadian Shield. The glacial meltwater end member was identified based on the depleted isotopic composition, its $\delta^{18}O$–$Cl^-$ relationship, and ‘H-free. (From Douglas, M. et al., *J. Hydrol.*, 235, 88, 2000.)
The first input of sulfates to surface water and groundwater is connected with atmospheric inputs, although this contribution is usually minor in comparison to the amount of sulfates, which can be gained in subsurface environment. The $^{34}$S isotopic composition of atmospheric sulfates is controlled mainly by emissions from fossil fuel combustion and by sulfate from sea spray—at least in the coastal areas. The $\delta^{34}S$ values of sulfur from combustion of both petroleum and coal typically range from slightly negative to +10‰ vs. VCDT (usually from −3‰ to +9‰) and exceptionally can reach values as high as +16‰ from the combustion of Paleozoic crude oils in North America (Clark and Fritz, 1997). The $^{18}$O isotopic composition of atmospheric sulfates is dependent on the oxidation conditions in the atmosphere and the $^{18}$O composition of the moisture involved in the oxidation of atmospheric SO$_2$. In temperate regions $\delta^{18}O$ values of sulfate in atmospheric deposits range between +5‰ and +17‰ vs. VSMOW (Cortecci and Longinelli, 1970).

Major sources of sulfates in groundwater are connected with geological sources of sulfur compounds (minerals) in igneous, metamorphic, and sedimentary rocks. Especially, the sedimentary rocks are the most important source of groundwater sulfates as they may contain large amounts of oxidized and/or reduced sulfur minerals. Gypsum and anhydrite are principal constituents of marine evaporites in the sedimentary strata; they are very well soluble in water and are usually major contributors to groundwater sulfates. Gypsum also accumulates in the soil of arid regions and usually occurs together with limestone and dolomite sequences. The dissolution of gypsum and anhydrite occurs without measurable isotope fractionation. This allows to use directly the isotopic composition of SO$_4^{2-}$ as tracer for sulfate origin as well as the origin of sulfate salinity. On the other hand, crystallization of sulfate minerals only slightly favors the heavier isotopes in the precipitates, for example, for gypsum, the $\delta^{34}S$ and $\delta^{18}O$ values have been measured to be 1.7‰ and 3.6‰ higher than for dissolved sulfate, from which they form (Szaran et al., 1998). The isotopic composition of SO$_4^{2-}$ of modern ocean water has a well-defined value of $\delta^{34}S_{SO_4} = 21$‰ VCDT and $\delta^{18}O_{SO_4} = 9.5$‰ VSMOW. However, this composition was not constant in the past. Based on marine evaporite deposits, the measured $\delta^{34}S$ values varied over long-term trends with a maximum near +35‰ in the Cambrian and minimum of less than +10‰ in the Permian; the respective $\delta^{18}O$ varied between +20‰ and +7‰ (Claypool et al., 1980). Comparison of the isotopic composition of sulfate in groundwaters with the appropriate geological period (i.e., with determined isotopic composition of sulfate evaporates) allows to distinguish geogenic sources from other sources of sulfate salinity.

**FIGURE 17.14** Isotopic composition of main sources of sulfates: evaporite, modern marine, terrestrial, and atmospheric. (From Clark, I. and Fritz, P., *Environmental Isotopes in Hydrogeology*, Lewis Publishers, New York, 328pp, 1997.) For additional explanation, see the text.
Another important source of sulfate in groundwater is oxidation of aqueous sulfide in surface or near-surface environment and oxidation of sulfide minerals as pyrite and others. Especially oxidation of sulfide minerals can contribute considerable amounts of sulfates to surface and groundwater (plus metals and acidity) and can produce gypsum crusts in arid regions. When dissolved sulfides are oxidized chemically by O_2, about 5‰ depletion is observed in δ^{34}S of accumulating sulfate phase; when oxidation process is mediated biologically involving aerobic bacteria (e.g., *Thiobacillus concretivorus*), sulfate may be depleted by up to 20‰ from the sulfide (Kaplan and Rittenberg, 1964; Fry et al., 1988). The ¹⁸O content of sulfate from oxidation of dissolved sulfides is dependent on the reaction pathway and is similar to sulfate from sulfide minerals (Clark and Fritz, 1997). The δ^{34}S values of sulfate originating from biologically mediated oxidation of base-metal sulfides are depleted by 2‰–5.5‰ (Toran and Harris, 1989).

All the sulfates that form in this way in the hydrosphere contribute to the “terrestrial sulfates” field distinguished in Figure 17.14. In some cases, a plot of δ^{34}S−δ¹⁸O values may reveal the mixing of sulfates from two sources. However, simultaneous monitoring of spatial or temporal trends in concentrations and isotopic compositions of sulfate in groundwater and surface water is a much more effective approach for revealing addition of sulfates from various sources and for identifying sulfate transformation processes (Figure 17.15).

One of the most important processes that modify the sulfate isotopic composition and concentration in aquifers is bacterial (dissimilatory) sulfate reduction. This biologically mediated process causes the decrease of sulfate concentration and preferential enrichment in ³⁴S and ¹⁸O in the residual sulfate (e.g., Mizutani and Rafter, 1969). The typical trend of δ^{34}S and δ¹⁸O of the remaining dissolved sulfates resulting from bacterial sulfate reduction is shown in Figure 17.16.

### 17.3.2.2 Isotopic Composition and Sources of Dissolved Nitrates

In the aqueous environment, nitrogen occurs usually as NO₃⁻, NO₂⁻, NH₄⁺, dissolved N₂ gas, and amino acids. The most stable form of nitrogen in most surface waters and groundwaters is dissolved N₂ gas and nitrates (NO₃⁻). The latter is the most abundant nitrogen species in aqueous environment, and ammonia is noticeable only in reducing environments such as peat bogs and sewers (Letolle, 1980; Clark and Fritz, 1997).

Nitrogen has two stable isotopes, ¹⁴N and ¹⁵N, occurring naturally with respective abundances of 99.6337% and 0.3663%. Isotopic composition of nitrates on a δ-scale isotopic is expressed as follows:

\[
\delta^{15}N = \left( \frac{^{15}N/^{14}N_{\text{sample}}}{^{15}N/^{14}N_{\text{AIR}}} - 1 \right) \times 1000
\]

(17.21)

\[
\delta^{18}O = \left( \frac{^{18}O/^{16}O_{\text{sample}}}{^{18}O/^{16}O_{\text{VSMOW}}} - 1 \right) \times 1000
\]

(17.22)

Typical ranges of δ^{15}N and δ¹⁸O for main nitrate sources are presented in Figure 17.17.

Nitrogen is a biologically active element and participates in a number of reactions that are important to life but also affect water quality. Decay of biomass releases organic nitrogen, which oxidizes to NO₃⁻, which, in turn, is a contaminant in drinking water. The sources of nitrate in groundwater can be classified as diffusive (synthetic and organic fertilizers) and point sources (septic tanks, sewerge lagoons, manure piles) and are mainly associated with agricultural activities (Kendall and Aravena, 2000). Identification of the nitrate sources and biogeochemical processes that affect its formation, transport, evolution, and attenuation in geological environment is the main task of the application of isotopic studies.

Two factors control the δ^{15}N values of any N-bearing compound in the subsurface: (1) variations in the δ^{15}N values of inputs (i.e., sources) and outputs (i.e., sinks) of the compound in the subsurface and
chemical, physical, and biological transformations of materials within the soil and groundwater that produce or remove the compound (Kendall and Aravena, 2000).

Atmospheric input is a minor source of \( \text{NO}_3^- \) to groundwater systems. Moreover, \( \delta^{15}\text{N} \) and \( \delta^{18}\text{O} \) values of atmospheric nitrate reveal a large range of variation due to many different chemical reactions and compound involved, seasonality, meteorological conditions, ratio of \( \text{NH}_4 \) to \( \text{NO}_3 \) in precipitation, types of anthropogenic inputs, proximity to pollution sources, etc. (Hubner, 1986). Usually \( \delta^{15}\text{N} \) values of atmospheric \( \text{NO}_3 \) and \( \text{NH}_4 \) are in the range of \(-15\%_o\) to \(+15\%_o\); \( \delta^{18}\text{O} \) values reveal larger variability.

from +18‰ to +70‰ as was observed in rainwater, snow, and snowmelt from forested watersheds in the United States (Kendall and Aravena, 2000).

High concentration of NO\textsubscript{3} in surface waters and groundwaters in agricultural areas is connected with input from fertilizers. Synthetic fertilizers have $\delta^{15}$N in the range of −4‰ to +4‰ and $\delta^{18}$O values between +18‰ and +22‰ (Hubner, 1986; Amberger and Schmidt, 1987). Organic fertilizers reveal
higher δ¹⁵N values and a wider range of compositions, generally from −2‰ to +30‰; their δ¹⁸O values range between +38‰ and +50‰ (Hubner, 1986; Bohlke et al., 1997; Kendall and Aravena, 2000).

Nitrate derived from manure or sewage is usually characterized by δ¹⁵N values between +10‰ and +20‰ and δ¹⁸O values usually less than +15‰ (Aravena et al., 1993).

Tracing the isotopic composition of nitrate and nitrogen-containing compounds in subsurface environment (i.e., water unsaturated and saturated zones) is not straightforward since numerous transformation processes in the nitrogen cycle are associated with significant both kinetic and thermodynamic fractionation effects. Moreover, large variations in isotopic composition of nitrates and overlapping of similar δ¹⁵N and δ¹⁸O values from different processes make interpretation sometimes very difficult.

The main biologically mediated reactions that control nitrogen dynamics in the soil and groundwater are (1) assimilation, (2) nitrification, and (3) denitrification (Kendall and Aravena, 2000). The most important are the two latter processes.

Nitrification is a multistep process of organic N-compound oxidation by several different autotrophic organisms for the purpose of deriving metabolic energy; the process produces acidity and NO₃⁻ together with other intermediate species like NH₄⁺, NO₂⁻, NO, and N₂O (Kendall and Aravena, 2000):

\[
\text{Organic } - \text{N} \rightarrow \text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^-(17.23)
\]

Nitrification in the unsaturated zone can increase the concentration of NO₃⁻ significantly in groundwater. The source of N can be soil organic N-compounds, organic and inorganic fertilizer, and N-compounds from septic systems and sewerage lagoons.

On the other hand, the denitrification is one of the most important processes of nitrate attenuation in groundwater. This is a multistep process involving various nitrogen oxides (e.g., N₂O, NO) as intermediate compounds resulting from a biological-mediated reduction of NO₃⁻ to N₂. Denitrification occurs in anaerobic conditions and causes the δ¹⁵N and δ¹⁸O of the residual nitrate to increase exponentially as nitrate concentrations decrease (Hubner, 1986; Kendall and Aravena, 2000) (Figure 17.18).

The changes in δ¹⁵N value of the residual nitrate during denitrification can be expressed using the Rayleigh distillation equation (similar like during sulfate reduction process). Since mixing and denitrification curves can be similar, it is often difficult to distinguish whether mixing or denitrification has

![Figure 17.18](image_url)
occurred. In such case, data should be additionally considered by plotting $\delta^{15}N$ vs. $1/[\text{NO}_3^-]$, which will yield a straight line for mixtures of two sources. The plot $\delta^{15}N$ vs. $\ln[\text{NO}_3^-]$ will yield a straight line for any process like denitrification, which can be described using the Rayleigh equation, that is, any exponential relation (Mariotti et al., 1988; Kendall and Aravena, 2000).

### 17.3.3 Modern Groundwater Dating with Tritium

The dating of groundwater and determination of the time of its residence in the geological environment have important implication for water resource management, contaminant transport, determination of groundwater flow parameters, hydraulic conductivity, porosity, water velocity, etc. A number of methods based on the decay of radionuclides are used to date groundwaters. Radioactive isotopes with a long half-life are used to date paleogroundwaters, for example, $^{14}C$, $^{36}Cl$, and $^{39}Ar$. Short-lived radioisotopes are used to date modern groundwaters, for example, $^3H$, $^{14}C$, $^{32}Si$, $^{37}Ar$, and $^{85}Kr$. Modern groundwaters are those that take active part in modern hydrological cycle and that presumably were recharged in the past few decades.

Tritium ($^3H$) is probably the most commonly employed radioisotope used to date the modern groundwater and to identify the occurrence of modern recharge. A half-life of tritium is equal only to 12.43 years. Natural tritium is produced by cosmic radiation in the upper atmosphere (Clark and Fritz, 1997):

$$ ^{14}N + \frac{1}{n}n \rightarrow ^{12}C + ^3H $$

Concentrations of $^3H$ are expressed in tritium units (TU):

1. TU = 0.118 Bq/kg water = 3.19 pCi/kg water = 1.3H per $10^{18}$ hydrogen atoms

Atmospheric testing of thermonuclear bombs between 1951 and 1980 released a huge amount of the so-called anthropogenic tritium and provided the tritium input signal that defines modern water. This substantial input created a tritium reservoir in the stratosphere, which contaminated global precipitation systems for over four decades. By about 1990 most of this bomb tritium had been washed from the atmosphere and tritium concentration tends to reach natural values, that is, about 3–6 TU (Kaufman and Libby, 1954; Clark and Fritz, 1997).

It should be stressed that tritium as a part of the water molecule can really date the water in the sense of determining its age. All other dating methods rely on dissolved constituents in water; therefore, their abundance is controlled by physicochemical and biological processes. However, only in well-defined and usually regional artesian aquifers, age gradient of the water will be preserved along the flow path. Thus, it is much safer to use the term “mean residence time” than “age” in relation to water dating.

As a component of water molecules, $^3H$ can be used as natural tracer of water in different stages of the hydrological cycle. In addition to conventional hydrological methods, it may be applied to determine the origin of water and mixing processes, the storage properties of the catchment, groundwater dynamics, and interactions between surface water and groundwater. The quantitative evaluation of these data is most often based on application of lumped parameter models. The advantage of these models is their relative conceptual simplicity, because they require only the knowledge of the tracer concentration in the recharge area (i.e., input function, $C_{in}(t)$) and some records of the tracer data at the observation site (i.e., output function, $C_{out}(t)$) (Figure 17.20). The lumped parameter models were described in detail by Maloszewski and Zuber (1982, 1996), Zuber and Maloszewski (2001), and Maloszewski et al. (2004). Generally, in lumped parameter approach, the groundwater system is assumed to be closed, sufficiently homogeneous, being in a steady state, and having a defined input (i.e., recharge or infiltration area) and output (pumping wells, springs, or streams draining the system) (Figure 17.19).
Each lumped parameter model has its own function that describes transit time distribution in the system $g(\tau)$, sometimes called residence time distribution (RTD) function (Figure 17.20).

The function $g(\tau)$ has to be known or assumed for particular studied system based on the hydrogeological information about this system. In most cases the $g(\tau)$ function has one or two unknown (fitting) parameters, in which values should be determined by calibrating the model to the experimental data observed in the output from the system. The main parameter of all models in monoporous media is the mean transit time of water $T_m$. It refers to the free, mobile water in the system and relates to its volume $V_m$ and flow rate $Q$:

$$V_m = QT$$

(17.25)
To determine the $T$ value, the temporal variation of the measured tritium input concentration, $C_{\text{in}}(t)$, is used to calculate the tritium output concentration, $C_{\text{out}}(t)$, which is then compared with real concentrations measured in the output from the system (Maloszewski and Zuber, 1982; Zuber, 2007). The input concentration of the tracer (i.e., tritium) is directly measured or has to be calculated from known hydrological and isotope data as it was shown by Maloszewski and Zuber (1982, 1996) and Grabczak et al. (1984).

The relationship between $C_{\text{in}}(t)$ and $C_{\text{out}}(t)$ is described by the following convolution integral:

$$C_{\text{out}}(t) = \int_{0}^{\infty} C_{\text{in}}(t - \tau) g(\tau) \exp(-\lambda \tau) \, d\tau$$

where

- $C_{\text{out}}(t)$ is the output $^3\text{H}$ concentration (i.e., measured based on sampling)
- $C_{\text{in}}(t)$ is the input $^3\text{H}$ concentration
- $t$ is the calendar time
- $\tau$ is the transit time of individual streamlines
- $t - \tau$ is the input time of individual streamlines
- $g(\tau)$ is the RTD function (i.e., function showing response of the system for fitted parameters)
- $\lambda$ is the decay constant; for $^3\text{H}$, $\lambda = \frac{\ln 2}{T_{1/2}} = 0.0558$

The integral over the $g(\tau)$ for all possible transit times $\tau$, that is, from zero to infinity, has to be equal to one. For most frequently applied models used for the interpretation of isotope data in the so-called monoporous media (i.e., no stagnant water in the system, no diffusion of tracer), the mean value of $\tau$ has to be equal to the mean transit time of water $T$.

The most common types of the transit time distribution function $g(\tau)$ used for monoporous media are as follows:

a. Piston flow model (PFM)

$$g(\tau) = \delta(\tau - T)$$

b. Exponential model (EM)

$$g(\tau) = \left(\frac{1}{T}\right) \exp\left(-\frac{\tau}{T}\right)$$

c. Dispersion model (DM)

$$g(\tau) = \left(\frac{1}{T}\right) \left[\frac{4\pi P_{D}}{(\tau/T)^3}\right]^{\frac{1}{2}} \exp\left[-\left(\frac{1 - \tau}{T}\right)^2\right] \left\{\left(\frac{\tau}{T}\right)^2 - \frac{P_{D} \tau}{T}\right\}$$

where

- $P_{D}$ is the dispersion parameter (i.e., fitted parameter; see Figure 17.20)

The selection of the proper model depends on the hydrogeological conditions. Some examples of popular hydrogeological situation are presented in Figure 17.21.

Generally, the dispersion and PFMs are applicable for confined or partly confined aquifers (Figure 17.21A through C). EM can be used only for unconfined aquifers, where the unsaturated zone is small and can be neglected (Figure 17.21B).
When we have a confined aquifer with a narrow recharge zone and sampling point located far away from the recharge (Figure 17.21A), the DM can be applied assuming that the confined part is impermeable with a negligible portion of stagnant water. If the flow distance is very long (which permits to assume $P_D = 0$), then the PFM can be applied.

In case of unconfined porous aquifer (Figure 17.21B), where the unsaturated zone is small, then the EM can be applied for the sampling points a, b, and d. Otherwise, when the unsaturated zone has to be taken into account, the combined exponential-PFM should be applied (not mentioned in this chapter; please refer, e.g., to Maloszewski and Zuber, 1996). In case of partly confined porous aquifer (Figure 17.21C), the DM will be most applicable.

### 17.4 Summary and Conclusions

The most important isotopes for hydrological and hydrogeological applications are those usually called as environmental. They are naturally occurring isotopes of elements found in abundance in our environment such as C, O, H, S, and N, that is, principal elements of hydrogeological, geological, and biological systems. The principal application of stable environmental isotopes is tracing of water, carbon, nutrient, and solute cycling, as well as understanding fundamental physicochemical processes governing isotope transport and fractionation. Especially isotopes of water (i.e., H and O) and their conservative nature in low-temperature environment constitute a powerful tool for tracing the origin, formation, movement, mixing, and geochemical evolution of various types of waters encountered in the Earth’s hydrosphere. Isotopic studies of dissolved biologically active compounds in aquatic environment give tremendous possibilities for tracing water quality and identification of contaminant formation, transport, and sink. On the other hand, radioactive environmental isotopes, for example, $^3$H or $^{14}$C, are used mostly for
determining the age of groundwaters. This allows groundwater recharge rates and flow velocities to be determined, often more accurately than with traditional hydraulic methods, and is very helpful in the management of groundwater reservoirs.

References


