

1 BASIC CONCEPTS AND MODELS

1.1 INTRODUCTION

This Volume III in the series of textbooks is focused on applications of environmental isotopes in surface water hydrology. The term *environmental* means that the scope of this series and the Volume III is essentially limited to isotopes, both stable and radioactive, that are present in the natural environment, either as a result of natural processes or introduced by anthropogenic activities. Artificial isotopes and/or chemical substances, that are intentionally released in order to obtain information about a studied system, will be mentioned only marginally.

Generally, isotopes are applied in hydrology either as *tracers* or as *age indicators*. An ideal tracer is defined as *a substance that behaves in the studied system exactly as the material to be traced as far as the sought parameters are concerned, but that has at least one property that distinguishes it from the traced material* (Zuber, 1986).

Using stable isotopes as tracers, this property is the molecular mass difference between the substance and its tracer. The radioactive decay of radioisotopes also offers the possibility to determine the residence time of water in a system, which, under given conditions, is called the age or transit time (see also Sect.1.4).

In Volume I the characteristics and natural occurrence of the environmental isotopes is discussed in detail. Here we present a brief summary.

In nature, there exist two stable isotopes of hydrogen (^1H - protium and ^2H - deuterium) and three stable isotopes of oxygen (^{16}O , ^{17}O , ^{18}O). Out of nine isotopically different water molecules, only three occur in nature in easily detectable concentrations: H_2^{16}O , H_2^{18}O and $^1\text{H}^2\text{H}^{16}\text{O}$. The isotopic concentration or abundance ratios are generally referred to those of a specifically chosen standard. The internationally accepted standard for reporting the hydrogen and oxygen isotopic ratios of water is Vienna Standard Mean Ocean Water, V-SMOW (Coplen, 1996). The absolute isotopic ratios $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ of V-SMOW were found to be equal to

$$^2\text{H}/^1\text{H} = (155.95 \pm 0.08) \times 10^{-6} \text{ (De Wit et al., 1980)}$$

$$^{18}\text{O}/^{16}\text{O} = (2005.20 \pm 0.45) \times 10^{-6} \text{ (Baertschi, 1976)}$$

These values are close to the average isotopic composition of ocean water given by Craig (1961a; b). Since the ocean represents about 97% of the total water inventory on the earth's

surface and the observed variations of $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ within the water cycle are relatively small, the heavy isotope content of water samples is usually expressed in delta (δ) values defined as the relative deviation from the adopted standard representing mean isotopic composition of the global ocean:

$$\delta_{S/R} = \frac{R_{\text{Sample}}}{R_{\text{Reference}}} - 1 \quad (1.1)$$

where R_{Sample} and $R_{\text{Reference}}$ stands for the isotope ratio ($^2R = ^2\text{H}/^1\text{H}$ and $^{18}R = ^{18}\text{O}/^{16}\text{O}$) in the sample and the reference material (standard), respectively.

We will use the following symbols, applying the superscripts as in ^2H , ^{18}O and ^{13}C :

$$^2\delta (\equiv \delta^2\text{H} \equiv \delta\text{D}) = ^2R_S / ^2R_R - 1$$

$$^{18}\delta (\equiv \delta^{18}\text{O}) = ^{18}R_S / ^{18}R_R - 1$$

$$^{13}\delta (\equiv \delta^{13}\text{C}) = ^{13}R_S / ^{13}R_R - 1$$

As the thus defined δ values are small numbers, they are expressed in ‰ (per mill). It should be emphasised, however, that also then the δ values remain small numbers, because ‰ stands for $\times 10^{-3}$.

^2H and ^{18}O isotopic compositions of meteoric waters (precipitation, atmospheric water vapour) are strongly correlated. If $^2\delta$ is plotted versus $^{18}\delta$, the data cluster along a straight line:

$$^2\delta = 8 \cdot ^{18}\delta + 10\text{‰}$$

This line is referred to as the *Global Meteoric Water Line* (Craig, 1961b).

The observed variations of ^2H and ^{18}O content in natural waters are closely related to the isotope fractionation occurring during evaporation and condensation (freezing) of water, where the heavy water molecules, H_2^{18}O and $^1\text{H}^2\text{H}^{16}\text{O}$, preferentially remain in or pass into the liquid (solid) phase, respectively. This isotopic differentiation is commonly described by the fractionation factor α , which can be defined as the ratio of the two isotope ratios:

$$\alpha_{B/A} = \frac{R_B}{R_A} \quad (1.2)$$

expresses the isotope ratio in phase B relative to that in phase A. If B refers to liquid water and A to water vapour in thermodynamic equilibrium, the fractionation factor α_e corresponds to the ratio of the saturation vapour pressure of normal water (H_2O) to that of "heavy" water ($^1\text{H}^2\text{HO}$ or H_2^{18}O).

Since in general isotope effects are small ($\alpha \approx 1$), the deviation of α from 1 is often used rather than α . This quantity is called isotope fractionation and defined by:

$$\varepsilon_{B/A} = \alpha_{B/A} - 1 = \frac{R_B}{R_A} - 1 \quad (1.3)$$

ε is referred to as an enrichment if $\varepsilon > 0$ ($\alpha > 1$), and as a depletion if $\varepsilon < 0$ ($\alpha < 1$); generally ε values are reported in ‰, being small numbers.

Also for α and ε we apply the same superscripts:

$${}^2\alpha_{B/A} = {}^2R_B/{}^2R_A = {}^2\varepsilon + 1 \text{ and } {}^{18}\alpha_{B/A} = {}^{18}R_B/{}^{18}R_A = {}^{18}\varepsilon + 1.$$

1.2 ISOTOPE EFFECTS BY EVAPORATION

Under natural conditions, thermodynamic equilibrium between liquid and vapour phase is not always established, for instance during evaporation of an open water body into an unsaturated atmosphere. In this case, slight differences in transfer of light and heavy water molecules through a viscous boundary layer at the water-air interface result in additional isotopic fractionation denoted by the so-called *kinetic fractionation factor*, α_k . This kinetic fractionation factor is controlled by molecular diffusion of the isotopically different water molecules through air, the moisture deficit ($1 - h$) over the evaporating surface and, to a lesser extent, by the status of the evaporating surface (Merlivat and Coantic, 1975; Merlivat and Jouzel, 1979).

The model generally adopted to describe isotope effects accompanying evaporation into an open (unsaturated) atmosphere was formulated by Craig and Gordon (1965). Its schematic description is presented in Fig.1.1. In the framework of this conceptual model, the isotopic composition of the net evaporation flux can be derived as a function of environmental parameters controlling the evaporation process (see Volume II for detailed discussion):

$$\delta_E = \frac{\alpha_{V/L} \delta_L - h_N \delta_A + \varepsilon_{V/L} + \varepsilon_{\text{diff}}}{1 - h_N - \varepsilon_{\text{diff}}} \quad (1.4)$$

where:

δ_L isotopic composition of the lake water

h_N relative humidity of the atmosphere over the lake, normalised to the temperature of the lake surface

δ_A isotopic composition of the free-atmosphere water vapour over the lake

$\alpha_{V/L}$ equilibrium isotope fractionation factor between water vapour (V) and liquid water (L), at the temperature of the lake surface

$\varepsilon_{V/L} = \alpha_{V/L} - 1 (< 0)$

$\varepsilon_{\text{diff}}$ transport (kinetic) or diffusion fractionation = $n \Theta (1 - h) \Delta_{\text{diff}}$ (see Volume II).

The overall fractionation by evaporation is now: $\varepsilon_{\text{tot}} = \varepsilon_{V/L} + \varepsilon_{\text{diff}}$. All ε values are negative, as the fractionation processes cause an ^{18}O depletion of the escaping water vapour.

The α values for kinetic or transport isotope processes are defined as the "new" isotopic ratio relative to (= divided by) the "old": $\alpha_{\text{after/before}} = R_{\text{after}}/R_{\text{before}}$. For the diffusion process this means that the (kinetic) fractionation factor $\alpha_{\text{after/before diffusion}} < 1$, as the isotopically heavy gas diffuses more slowly. The kinetic fractionation $\epsilon = \alpha - 1$ is then negative.

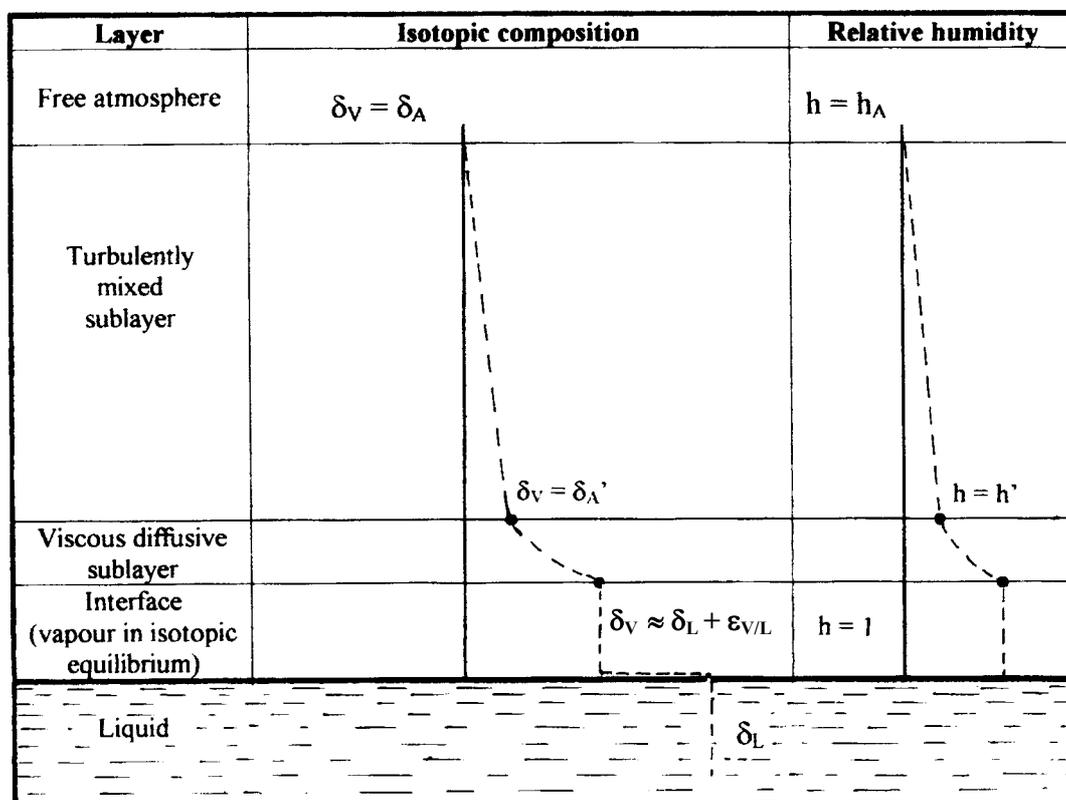


Fig.1.1 The Craig-Gordon model for isotopic fractionation during evaporation of open water body into the free atmosphere (Craig and Gordon, 1965). The boundary region between evaporating surface and free atmosphere is subdivided into several layers: (i) the interface located immediately above the evaporating surface, where isotope equilibrium is maintained between liquid and vapour phase, (ii) the viscous diffusive sublayer where molecular transport is dominating, introducing additional kinetic fractionation among various isotopic species of water vapour, and (iii) the turbulently mixed sublayer where no further isotope differentiation occurs. Schematic profiles of relative humidity and isotopic composition of water vapour across the boundary region are shown (modified from Gat, 1966).

Summarising, in the total (overall) process the first stage –the formation of water vapour in isotopic equilibrium with the water –causes isotopic depletion of the vapour with respect to the water by a fractionation $\epsilon_{V/L}$ being negative. Also the second stage –the (partial) diffusion of vapour out of the diffusive sub-layer to the free atmosphere– causes the escaping vapour to become depleted in ^2H and ^{18}O by $\Delta\epsilon$ also being negative.

ϵ_{diff} represents the kinetic, i.e. the diffusion part of the overall fractionation process and has the following general expression in the framework of the Craig-Gordon model (see Volume II):

$$\epsilon_{\text{diff}} = n \Theta (1 - h) (1 - D_m/D_{mi}) = n \Theta (1 - h) \Delta_{\text{diff}} \quad (1.5)$$

where Δ_{diff} presents the maximum diffusion isotope depletion of ^2H and ^{18}O in the case of a fully developed diffusive sub-layer ($h = 0$, $\Theta = 1$, $n = 1$), which values are equal -25.1‰ for ^2H and -28.5‰ for ^{18}O (Merlivat, 1978), while the factor n varies: $0.5 \leq n \leq 1$. The weighting factor Θ can be assumed to be equal 1 for small water bodies whose evaporation flux does not significantly perturb the ambient moisture (cf. Volume II and Sect.3.2.1.3.4 of this volume for further discussion). For an open water body, a value of $n = 0.5$ seems to be most appropriate. This has been confirmed by wind-tunnel experiments (Vogt, 1978), where the following ϵ_{diff} values were obtained:

$$\text{For } ^2\text{H:} \quad \epsilon_{\text{diff}} = -12.5^6(1 - h_N) \text{‰}$$

$$\text{For } ^{18}\text{O:} \quad \epsilon_{\text{diff}} = -14.2^4(1 - h_N) \text{‰}$$

The temperature dependence of the equilibrium fractionation factors α for ^2H and ^{18}O of liquid water with respect to water vapour has been well established experimentally and can be calculated from (Majoube, 1971):

For ^{18}O :

$$\ln^{18}\alpha_{\text{V/L}} = -\ln^{18}\alpha_{\text{L/V}} = 2.0667 \cdot 10^{-3} + \frac{0.4156}{T} - \frac{1.137 \cdot 10^3}{T^2} \quad (1.6)$$

For ^2H :

$$\ln^2\alpha_{\text{V/L}} = -\ln^2\alpha_{\text{L/V}} = -52.612 \cdot 10^{-3} + \frac{76.248}{T} - \frac{24.844 \cdot 10^3}{T^2} \quad (1.7)$$

where T stands for the absolute water temperature in [K]. The above equations are valid for the temperature range 273.15 to 373.15 K ($0^\circ\text{C} - 100^\circ\text{C}$). More recent determinations of equilibrium fractionation factors between water and water vapour (Horita and Wesolowski, 1994) essentially confirm the validity of Eqs.1.6 and 1.7 for the above-mentioned temperature range. Table 1.1 contains numerical values of the equilibrium fractionation factors calculated according to Eqs.1.6 and 1.7 for the temperature range of 0 to 30°C .

The relative humidity above the lake is usually reported with respect to air temperature. To normalise this quantity to the temperature of the lake surface the following equation can be used:

$$h_N = h \frac{P_{\text{SAT(air)}}}{P_{\text{SAT(water)}}} \quad (1.8)$$

where $p_{\text{SAT(air)}}$ and $p_{\text{SAT(water)}}$ indicate saturation vapour pressure with respect to air and water temperature, respectively, h and h_N are the measured in ambient air and normalised relative humidity, respectively.

The saturation vapour pressure can be calculated from the empirical equation (e.g. Ward and Elliot, 1995):

$$p_{\text{SAT}} = \exp\left(\frac{16.78T - 116.9}{T + 237.3}\right) \text{ [kPa]} \quad (1.9)$$

where T is the air temperature expressed in degrees Celsius. Eq.1.9 is valid for temperatures ranging from 0 to 50°C.

Table 1.1 Equilibrium fractionation factors $\alpha_{L/V}$ of liquid water relative to water vapour (Majoube, 1971), and the saturation vapour pressure p_{SAT} over liquid water (Ward and Elliot, 1995), as a function of the water temperature.

t (°C)	$^{18}\alpha_{L/V}$	$^2\alpha_{L/V}$	p_{SAT} (hPa)	t (°C)	$^{18}\alpha_{L/V}$	$^2\alpha_{L/V}$	p_{SAT} (hPa)
0	1.01173	1.11255	6.110	16	1.01015	1.09006	18.192
1	1.01162	1.11099	6.570	17	1.01007	1.08882	19.388
2	1.01152	1.10944	7.059	18	1.00998	1.08760	20.651
3	1.01141	1.10792	7.581	19	1.00989	1.08639	21.986
4	1.01131	1.10642	8.136	20	1.00980	1.08520	23.396
5	1.01121	1.10495	8.727	21	1.00972	1.08403	24.884
6	1.01111	1.10349	9.355	22	1.00963	1.08288	26.455
7	1.01101	1.10206	10.023	23	1.00955	1.08174	28.111
8	1.01091	1.10065	10.732	24	1.00946	1.08061	29.857
9	1.01081	1.09926	11.486	25	1.00938	1.07951	31.697
10	1.01071	1.09788	12.285	26	1.00930	1.07841	33.635
11	1.01062	1.09653	13.133	27	1.00922	1.07734	35.676
12	1.01052	1.09520	14.032	28	1.00914	1.07627	37.823
13	1.01043	1.09389	14.985	29	1.00906	1.07523	40.083
14	1.01034	1.09259	15.994	30	1.00898	1.07419	42.458
15	1.01025	1.09132	17.062				

The isotopic composition of atmospheric moisture over a lake, δ_A , can be directly measured in samples of atmospheric moisture collected over the studied lake system, estimated from the available isotope data for local precipitation or derived from evaporation-pan data. The approach based on the isotopic composition of local precipitation was shown to provide reasonable results for relatively small lake systems that do not significantly influence the

moisture content in the local atmosphere above the lake (cf. Sect.3.2.1.3.3). In the majority of situations, the isotopic composition of monthly rainfall appears to be in isotopic equilibrium with atmospheric moisture at the ground-level temperature (Schoch-Fischer et al., 1984; Jacob and Sonntag, 1991). Thus, having information about the isotopic composition of local precipitation close to the lake, one can back-calculate the isotopic composition of atmospheric moisture:

$$\delta_A = \alpha_{V/L}\delta_P + \varepsilon_{V/L} \approx \delta_P + \varepsilon_{V/L} \quad (1.10)$$

where δ_P is the mean isotopic composition of local precipitation and $\alpha_{V/L}$ is the equilibrium fractionation factor between water vapour and liquid (the first with respect to the second) calculated from Eqs.1.6 or 1.7 for the corresponding mean local ground-level temperature.

As the evaporation process continues, the isotopic composition of an evaporating water body (δ_L) and the net evaporation flux (δ_E) define a ($^2\delta, ^{18}\delta$) relation, that is called *evaporation line*. The slope S of this line is given by the following equation:

$$S = \frac{h_N(^2\delta_A - ^2\delta_L) - ^2\varepsilon_{tot}}{h_N(^{18}\delta_A - ^{18}\delta_L) - ^{18}\varepsilon_{tot}} \quad (1.11)$$

where $\varepsilon_{tot} = \varepsilon_{V/L} + \varepsilon_{diff}$ and the superscripts refer to ^2H and ^{18}O , respectively.

The initial isotopic composition of the water, the evaporated moisture, and the residual water must all plot on the same straight line because of mass balance considerations (cf. Fig.3.2b). The slope of the evaporation line is determined by the air humidity and the equilibrium and kinetic fractionations, both depending on temperature and boundary conditions.

1.3 ISOTOPE INPUT TO SURFACE WATER SYSTEMS

The observed spatial and temporal variability of the isotopic composition of precipitation stems from physical processes operating on both micro- and macro-scales. Whereas the equilibrium and kinetic isotope fractionation effects play a decisive role during phase transitions and diffusion-controlled transport, respectively, the Rayleigh mechanism contributes to the observed isotope variability during transport in macro-scale (see Vol. II).

The relationship between the isotopic composition of precipitation (input) and newly formed groundwater and surface runoff (output) is build upon processes that differentiate between rain events on a meteorological or seasonal basis, and processes that fractionate between the different isotopic water species, primarily evaporation (Gat and Tzur, 1967). These processes having the collective name of *catchment isotope effect* may encompass a wide range of temporal and spatial scales. Some occur during or immediately after the rain event on or above the ground surface. Others involve soil moisture or shallow water reservoirs. It is worth

to note that the catchment effect for any given area may vary in time due to both natural (climate) and man-induced changes (Gat and Lister, 1995).

Fig.1.2 shows schematically the compartments and flow pattern across the atmosphere - land surface - soil zone interface, contributing to formation of the isotopic composition of input to surface water and groundwater systems. The residence time of water in the surface reservoirs depicted schematically in Fig.1.2 varies between minutes (the canopy) to many years in case of large lakes.

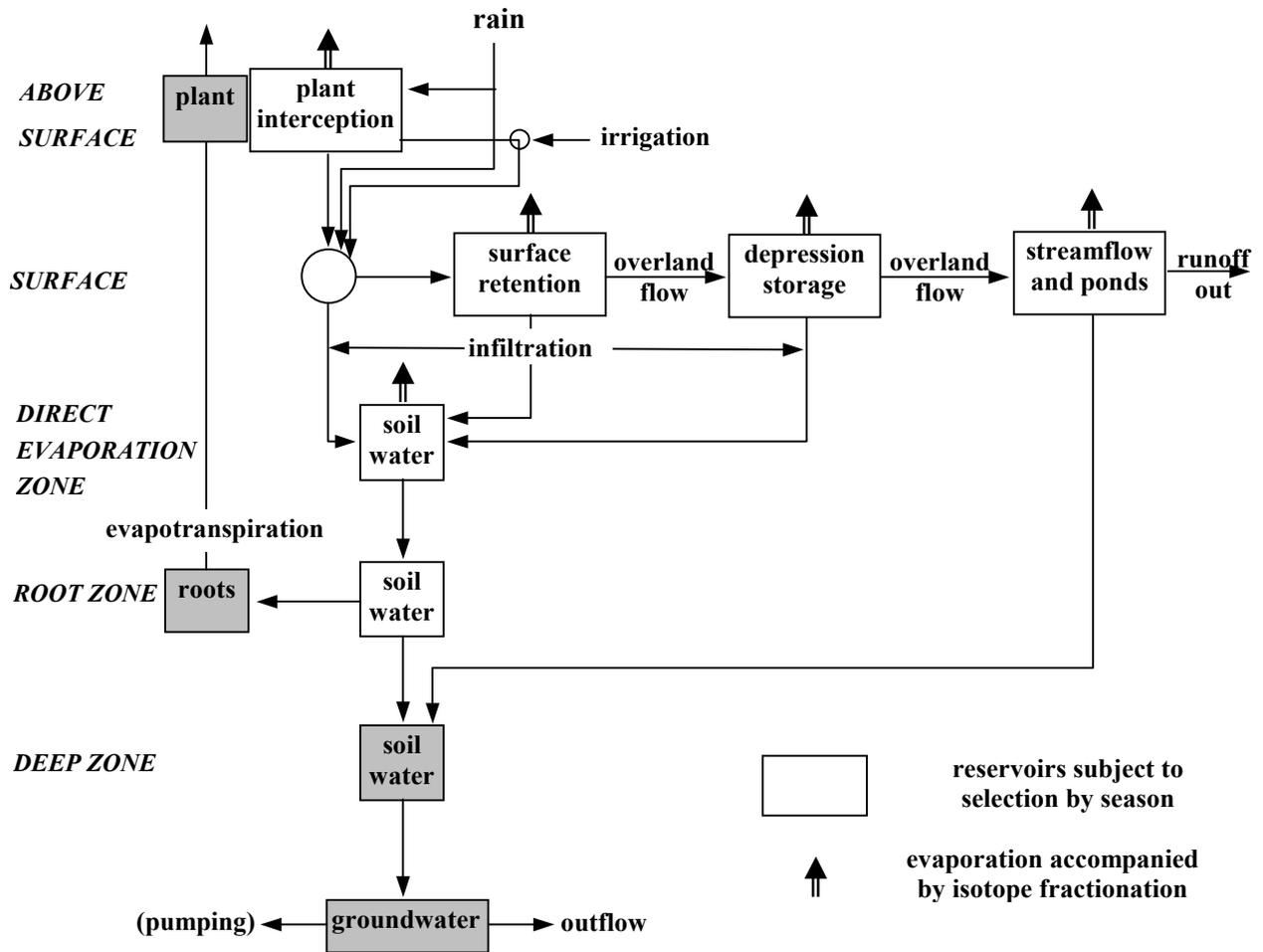


Fig.1.2 Flow patterns and processes accompanying transformation of precipitation to runoff and newly formed groundwater. Reservoirs subject to selection by season are shown as rectangular boxes. Double arrows indicate fluxes subject to isotope fractionation (cf. Volume II).

1.4 MEAN TRANSIT TIME, MIXING RELATIONSHIPS

When studying the dynamics of water flow in catchments or in surface reservoirs and lakes one often uses the term *mean transit time* or *turnover time* to describe how much time the water molecules spent in the given system before leaving it via outflow or evaporation flux. The turnover time is defined for a hydrological system which is in a steady state (e.g. Nir and Lewis, 1975; Zuber, 1986):

$$T = V_m/Q \tag{1.12}$$

where Q is the volumetric flow rate through the system and V_m is the volume of mobile water in the system. The assumption of steady state requires that $V_m = \text{const.}$

When a tracer is applied to obtain information about a given system, careful analysis has to be carried out with respect to the relation between the mean transit time of a tracer and that of water in the studied system, depending on the injection-detection mode and the behaviour of the tracer in the system (cf. Volume VI, see also Zuber, 1986).

In problems related to interaction of river or lake water with groundwater, or in problems related to hydrograph separation, one often deals with a mixture of two (or more) waters having different isotopic signatures. For instance, evaporated lake water mixing with local infiltration water in the adjacent groundwater system. From the mass balance considerations, the isotopic composition of the mixture can be easily derived if the end-members are fully characterised:

$$\delta_{\text{MIX}} = \frac{M_1}{M} \cdot \delta_1 + \frac{M_2}{M} \cdot \delta_2 + \dots \dots \dots \frac{M_N}{M} \cdot \delta_N \tag{1.13}$$

where $M_1 \dots M_N$ are the contributions of the individual end-members to the total mass (flux) M of the system, whereas $\delta_1 \dots \delta_N$ are their respective isotopic compositions.

If plotted as $^{2}\delta$ versus $^{18}\delta$, the two-component mixtures will fall on a straight line connecting the isotopic signatures of the end-members. However, it has to be noted that mixtures of two components that have different isotope ratios (e.g. $^{13}\text{C}/^{12}\text{C}$ or $^{15}\text{N}/^{14}\text{N}$) and different concentrations of the element in question (e.g. C or N) do not form straight lines if plotted in diagrams with co-ordinates of isotope ratios (δ values) versus concentration (see, for instance, Sect.3.2.2). In such cases, linear relations could be obtained if plotting the isotope content versus the inverse of the respective concentration, e.g. $^{15}\delta$ versus $1 / (\text{nitrate concentration})$, where

$$^{15}\delta = \frac{(^{15}\text{N} / ^{14}\text{N})_{\text{nitrate}}}{(^{15}\text{N} / ^{14}\text{N})_{\text{air standard}}} - 1$$

