Chapter 6
Isotopic Composition of Water in the Unsaturated and Saturated Zones

On the basis of experimental data, it has been pointed out that the isotopic composition of shallow groundwaters, which are replenished by infiltration of atmospheric precipitation through the unsaturated zone, is characterized on average by the heavy isotopes of typical precipitation of a given region. Under certain conditions, there are some differences in isotopic ratios for the two types of water mentioned above. This is explained by the fact that precipitation in the spring–summer season is partially and often completely re-evaporated from the Earth's surface and from the unsaturated zone both directly and due to transpiration of moisture by plants.

As Zimmermann et al. (1967) have shown, the water which infiltrates from the Earth's surface into the unsaturated zone is already enriched with the heavy isotopes compared with precipitation due to the evaporation process. Under identical soil conditions, water enriched in places which are covered with plants is, on average, 10‰ greater than in those areas which have plant cover. The above mentioned values, as Zimmermann et al. (1967) noted, are characteristic for Central Europe where the average relative deuterium (D) concentration is about −70‰. The above authors have also shown that variations in the isotopic composition of the soil moisture remain unaffected by the observed ratio between moisture movement velocity in the unsaturated zone, the rate of evaporation of moisture from the surface, and the process of diffusion and exchange through transpiration by plants. At the same time, Gonfiantini et al. (1965) reported that the process of water evaporation by leaves results in its isotopic fractionation. It should also be noted that precipitation water in the spring–summer season is enriched with heavy isotopes compared to groundwaters. The autumn–winter precipitation is more depleted in δD and $\delta^{18}O$ and also undergoes enrichment due to evaporation from the surface. Finally, this results in isotopic balance between the atmospheric precipitation and shallow groundwater.

Analogous investigations regarding formation of the isotopic composition in near-surface ground waters of the arid zone of the south–east Mediterranean coastal region were carried out by Gat and Tzur (1967). They found that groundwaters which are fed by local precipitation are enriched with oxygen-18 (^{18}O) by 1–3‰ relative to standard of the ocean water (SMOW). Studies carried out using lysimeter have shown that under experimental conditions, an excess of ^{18}O of up to 2‰ has also been observed in the infiltrating moisture due to surface evaporation. In general,

DOI 10.1007/978-94-007-2856-1_6,

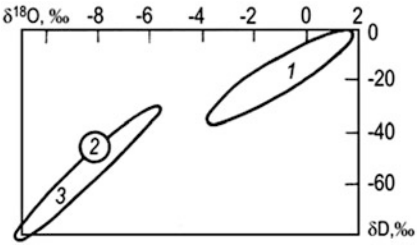

Fig. 6.1 δD–δ^{18}O relationship in waters of south–central Turkey: *1* lakes; *2* costal springs; *3* precipitation. (After Dinçer and Halevy 1968)

surface evaporation results in the visible enrichment of ground waters in D and ^{18}O in arid and semi-arid regions (Gat and Tzur 1967; Gonfiantini et al. 1974; Dinçer et al. 1974; Gonfiantini et al. 1976).

The knowledge of the formation of groundwater isotopic composition in active water exchange zones helps to solve a number of practical problems. Some characteristic examples of solutions to such problems are given below.

6.1 Relationship Between Surface and Ground Water

This problem is rather widespread in hydrological and hydrogeological investigations. When solving it on the basis of D and ^{18}O content of the waters being investigated, the following effects are used. Enrichment with heavy isotopes occurs during evaporation of the reservoir water. Direct recharge to the reservoirs by precipitation does not result in enrichment of water with D and ^{18}O. Thus, the existence or absence of the relationship between surface and groundwaters can be established by plotting and analyzing δD–δ^{18}O diagrams (see Fig. 6.3). In this diagram, for precipitation which has not undergone evaporation, the relationship $\delta D = 8\delta^{18}O + 10$ (or a similar characteristic for a given region) holds. While evaporation of the reservoir water—which is being fed by precipitation—takes place, the slope of the line in the diagram δD–δ^{18}O decreases to values between 3 and 6.

In a study in south–western Turkey with the method outlined above, it was possible to reject the hypothesis of interconnection of two large lakes, where the water is lost through fractured limestone formations with some large limestone springs (Fig. 6.1). In another case, a similar conclusion was reached regarding the connection of Lake Chala in Africa and some springs in the same region (Dinçer and Halevy 1968).

By means of isotopic and hydrochemical methods, Mazor (1976) checked the ancient groundwater tracing experiment. They say, 2,000 years ago, the ruler Philip established by his belief that Ram Lake is the feeder of the Banias spring, located 6 km to the west of the slopes of Mount Hermon. Philip's experiment consisted of throwing chaff into Ram Lake and observing it in the Banias spring. The modern studies do not prove the above version. The crater is surrounded by tuff, the highest point of which has an altitude of 1,000 m, whereas the altitude of the water table of the lake is about 940 m and its D and ^{18}O contents are close to the sea water. This

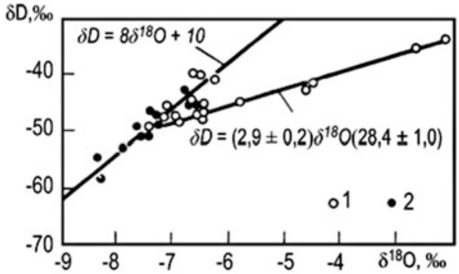

Fig. 6.2 δD–δ^{18}O relationship in groundwaters of salt plane Chott-el-Hodna, Algiers. Ground waters: *1 shallow*; *2 deep*. (After Gonfiantini et al. 1974)

enrichment with the heavy isotopes is a result of intensive evaporation because of the arid climate. In spring Banias, which is 600 m lower than the lake, $\delta D \approx -40‰$ and $\delta^{18}O \approx -8‰$. The D, ^{18}O, and Cl^- values in the well Masada, 500 m south–west of the lake, show that its water is a mixture of the regional groundwater with water infiltrated from the lake.

Enrichment of heavy isotopes in shallow waters due to evaporation with respect to the deep groundwaters was used for identification of local recharge areas in the salt plane of the Chott-el-Hodna, Algiers (Gonfiantini et al. 1974). The shallow groundwater was reported to be recharged by deep groundwater. Stable isotopes demonstrate that this does not occur. Some local low salinity shallow groundwater and the shape of the watertable were found to be recharged from wadis (dry river beds); however, the shallow waters in the alluvial Quaternary and continental Cretaceous formations have different origin. According to the isotope data, to the south of the Chott, the groundwaters evaporated more intensively compared to the deep waters (Fig. 6.2). This can be explained by discharge of the deep waters to the shallow horizons and intensive evaporation from the surface of the groundwater which locate close to land surface (less than 1 m). This assumption is also proved by the increase in water mineralization (100 g/l) and δ^{18}O content from $-7‰$ to $-2‰$.

In the areas north and east of the Chott-el-Hodna, the recharge of the deep aquifer appears to be limited. Isotope data demonstrate more active infiltration of atmospheric water from wadis. The experimental points of δD and δ^{18}O here lie along straight line $\delta D = 8\delta^{18}O + 10$ characteristic for atmospheric precipitation.

In another study (Dinçer 1968; Dinçer and Payne 1971), the hydraulic relationship of a group of karstic lakes was studied. The lakes are situated on the northern slope of the Taurus Mountains, at a distance of 100–150 km from the coast of the Mediterranean Sea, with several rivers and springs which start their course in the same region. The area of investigation was a typical karstic region of Mesozoic and Eocenic limestones. Based on results of isotopic measurements for water and precipitation at various points over the region and of the lake water, it was found that the conditions and sources of river recharge during different seasons of the year are in response to surface runoff and supply from the lakes through the karst-like rocks. Data on other environmental isotopes (tritium, carbon-13, carbon-14 contents) in precipitation, in surface reservoirs, and in groundwater were used in most studies to estimate the hydraulic relationship and the parameters of water exchange time.

6.2 Groundwater Recharge at Present Time

The seasonal variations of isotopes in precipitation, the feeding groundwater may be used for identification of the season of groundwater recharge (Winograd et al. 1998). As a rule, D and ^{18}O content in groundwater corresponds to the mean-weighted content of the isotopes in the inflow water for a large period of time. Thus, short periodic variations in D and ^{18}O content can be identified in a high-dynamic groundwater like, for example, in karstic regions.

Bowen and Williams (1973), while investigating groundwaters in the western region of Ireland, found that ^{18}O content in karstic waters of the Gort plateau was lower ($\delta^{18}O \leq -7.2‰$) than the average one in precipitation ($\delta^{18}O = -5.4‰$). The authors concluded that the seasonal water supply of this region is the result of depleted winter precipitation. The spring–summer precipitation enriched with heavy isotopes is lost by evapotranspiration.

Groundwater aquifers in the Sahara (Conrad and Fontes 1970) and the Kalahari Desert (Mazer et al. 1974a) were found to be depleted in heavy isotopes compared with the average δD and $\delta^{18}O$ values detected in precipitation. This evidence, combined with the tritium and radiocarbon studies, allowed the authors to determine that they are supplied with water of shower precipitation. With the help of known data about the duration of showers, the authors estimated the conditions of formation of the groundwater storage in this region.

6.3 Groundwater Recharge in the Past

The mean yearly values of temperature for all the Earth's regions in the last Pleistocene glacial epoch were lower than the modern (Emiliani 1970). Climatic conditions of the many arid regions were also different from the present days with respect to mean yearly temperature and humidity. Shower precipitation was found in the northern parts of the desert belts in glacial epochs (Bowen). It was formed because the western winds' belt in the Northern hemisphere was deviated to the south due to very wide glacial areas. Climatic changes in the northern latitudes of the modern arid regions were characterized by decreased concentration of D and ^{18}O in the covering glacial due to precipitation during the pluvial periods.

By the data of Emiliani (1970) and Epstein et al. (1970), the end of the Pleistocene glacial period (the Pleistocene–Holocene border) happened about 10,000 years ago. The influence of the pluvial epochs on groundwater in the arid regions' recharge is fixed by isotope data for the modern deserts in Africa, Arabian Peninsula, and Middle Asia. Vogel and Ehhalt (1963) have determined the age by radiocarbon method for fresh groundwater in western desert of Egypt which appeared to be 20,000–30,000 years, that is main part of the groundwater resources was recharged during the pluvial period of Pleistocene. This conclusion is well agreed with the groundwater data of D and ^{18}O, which are even lower than the modern precipitation for this region and even in modern precipitation of the Central Europe. Analogous data were obtained during groundwater study in Sahara (Conrad and Fontes 1970; Gonfiantini et al. 1974; Sonntag et al. 1979), Sinai Peninsula (Issar et al. 1972), Saudi Arabia (Champine et al. 1979; Yurtsever and Payne 1979), Potiguar Basin, Northern Brazil (Salati et al. 1974), and other regions.

6.4 Identification of Area of Groundwater Recharge

The solution of the problem of identification of recharge areas in mountain regions is based on the observed orographic effect on the distribution of the stable oxygen and hydrogen isotopes (see Eqs. 4.10 and 4.11).

Arnason and Sigurgeirsson (1967) were the first who attempted to identify drainage basins for a number of hot and cold springs in the eastern part of Iceland. Systematic sampling was carried out monthly (for 2–8 years) and the D content was measured in precipitation, springs, and ground waters. A map of δD distribution in precipitation and groundwater was plotted (Fig. 6.3). Later on a map like this (Arnason 1977b) was plotted for all the Iceland territory.

It is seen from the figure that the D content in precipitation decreases toward the northeast direction depending on the distance from the southern coastal area. This distribution is controlled by the southern winds which determine the air moisture transfer over the island. In average, D content decreases by 2‰ per km from the coast. This regularity is superimposed by the altitude effect and while the absolute marks of the land are dropped, the D concentration decreases. For example, maximum values of $\delta D = -50‰$ were registered in the southern coastal area and the lower were $\delta D = -94‰$ near glacier Hofsjökull on the northeast of the studied area. A large cold spring Keldur emerging from an extensive lava field produced by the volcano Hekla has local value of $\delta D = -58‰$, but the spring has $\delta D = -67‰$.

In the city of Reykjavik, there is a rich geothermal area where many boreholes have been drilled down to 700–800 m and one to a depth of 2,000 m. The base temperature is 140°C. The water in all these boreholes has δD from $-65‰$ to $-66‰$. This water could come from Lake Thingvallavatn, but a more likely recharge area would be a group of mountains north of the lake some 40–50 km away. At the same time in Krisuvik—a geothermal area on the Reykjanes peninsula, 25 km southwest from Reykjavik, 140 m above sea level—the water with a base temperature of 230°C was observed. The value of δD for this water is $-51‰$ (taking into account the evaporation effect on the way up through the borehole) which, in the author's opinion, says about the local recharge of the geothermal system located on the peninsula or little farther to the northeast where δD values are lower. In this case, say the authors, we can assume that δD values are increased while the water moves along the aquifer. Theodorsson (1967) continued the study in the same region, applying tritium indicator, and improved the results and conclusions.

Payne and Yurtsever (1974), while studying distribution of D and ^{18}O, determined relative importance of local atmospheric precipitation and mountain slope drainage in recharge of groundwater for the Chinandega Plain, the area of about 1,100 km^2

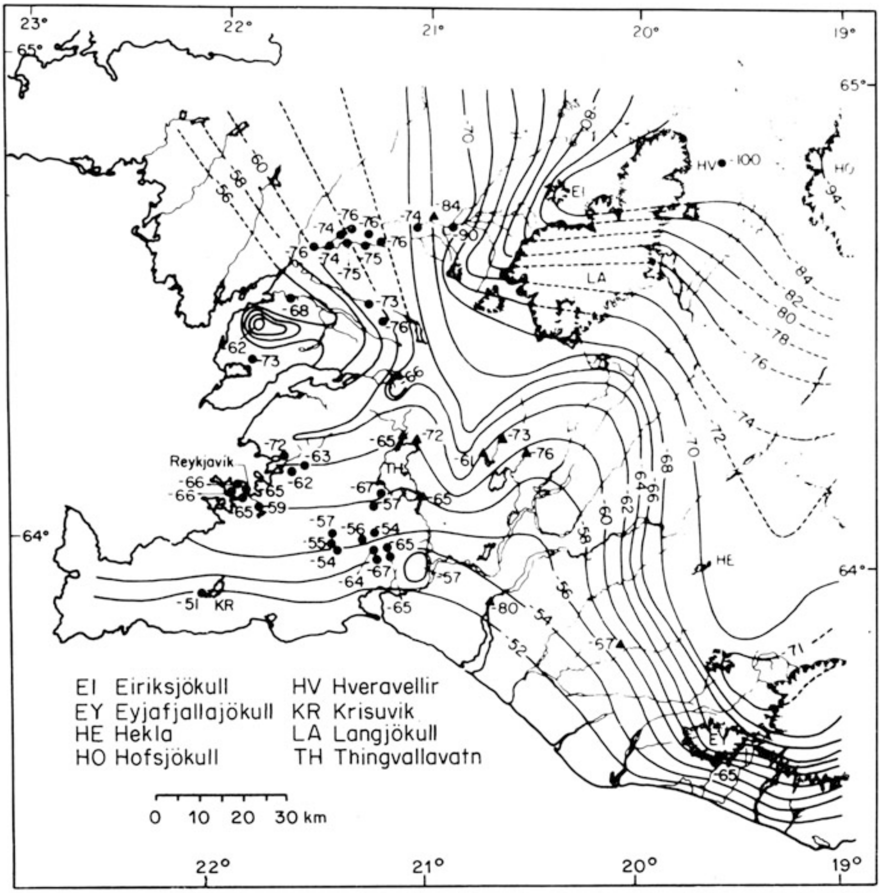

Fig. 6.3 Map of contours of δD values in precipitation and in geothermal springs (points) and in cold springs (three angles) of south-west Iceland. (After Arnason and Sigurgeirsson 1967)

located between the Pacific Ocean coast and the Cordillera de Marrabios in Nicaragua. It was found that $\delta^{18}O$ value of the direct plane precipitation partly recharged groundwater is equal to −5.9‰. On the basis of water and isotopic balance, the calculations show that ^{18}O in precipitation along the slope of Cordillera is decreased by equation $\delta^{18}O = -5.653 - 0.0026\,H$ (here H is the height of the sampling place above sea level, m). It is evident from the equation that the slope of the straight line is −0.26‰ per 100 m. In the borehole on the plane at an altitude of 280 m above sea level, the water has $\delta^{18}O = -7.18$‰, which means that the recharge area of this water is higher than the 600 m above-sea level.

Analogous investigation was done by Stahl et al. (1974) in Greece. It was found by use of the height gradients in the area of study ($\Delta\delta D = -1.2$‰/100 m, $\Delta\delta^{18}O = -0.16$‰/100 m) and the D concentrations that the potential areas of recharge for the artesian waters situate on different hypsometric levels differed more than 1,000 m. The same situation was found to be for the recharge areas of thermal waters.

The natural isotope tracing in precipitation depending on temperature of their condensation was used for identification of water recharge to mountain tunnels.

Rauert and Stichler (1974) applied isotope techniques to study seepage water in a 7-km-long tunnel in the Austrian Central Alps. It was found that the water comes to the tunnel from the top of the fractured rocks. The conclusion was made on the basis that the D content in recharge water along the tunnel practically reflected its high-level location ($\Delta\delta D = -3‰/100$ m) for the given region. It was found using tritium that the minimum velocity of the infiltrated water was equal to about 20 m per year.

Fontes et al. (1979) have undertaken investigations close to above in Mont Blanc tunnel (11.6-km-long). The study allowed not only localizing the recharge area and determine the velocity of vertical movement of water but also to contribute to the study of hydrogeological and hydrochemical processes in the massif of Mont Blanc. In particular, it was found that the residence time of water in the massif does not exceed a number of years and the infiltration of the surface water through the fractured granite rocks is accompanied by its significant evaporation. Concentration of chlorides in the water having contact from the French side of the tunnel with the crystal slates has increased. The data on hydrothermal water obtained in a number of points along the tunnel have not solved the problem about the source of water recharge because the water temperature seems to be determined mainly by its vertical movement velocity.

After studying the distribution of hydrogen and oxygen isotopes in the possible sources of water recharge, Rodriges (1979) localized the area of water flow into large tunnel Palacio, which was constructed for water supply of Bogota (Columbia) in Andean Cordillera. After the main part of the tunnel was constructed, the works were cut off because of catastrophic water recharge (4 m^3/min) to the face. A number of versions were assumed based on general geological and hydrodynamic date. In particular, it was assumed that the water enters from a local lake. The isotopic and chemical content of water from the lake and also from water of the modern, paleogene, and cretaceous sediments, situated around the tunnel, were measured. The mean value of hydrogen $\delta D = -76‰$ was found to be close to that of water from the fractured carbonate rocks of the upper Guadalupe formation (K_2). The waters from lake and some other possible sources were enriched with heavy hydrogen (δD from -49 to $-71.1‰$) compared with water from the carbonate massif. The macrocomponent contents of groundwater from the Guadalupe sediments and from the tunnel were found to be close. Those data allowed the author to conclude that the tunnel water recharge comes mainly from the groundwater of the carbonate rocks massif.

The author of the same work reports about study on groundwater migration in a large landslide Quebradablanca composed by alluvial sediments be deposited on the slope of a massif on metamorphic rocks. Earlier, on the basis of traditional observation and hydrogeological calculation, it was concluded that a cause of the landslide motion is the infiltrating atmospheric precipitation of local origin. The water from

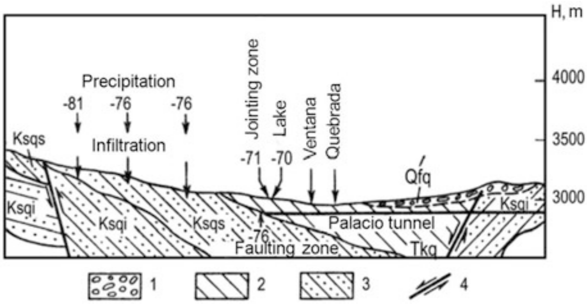

Fig. 6.4 Hydrogeological situation in construction of tunnel Palacio: *1* fluvial-glacial sediments; *2* Tertiary clays; *3* Cretaceous sandstones; *4* fractures. Figures show values of δD, ‰. (After Rodriges 1979)

the metamorphic rocks was not taken into account. In order to cut the infiltrating precipitation water access, a special drainage system was constructed which has not solved the problem. It was found by isotopic composition of hydrogen and ^{18}O that the groundwater of the alluvial deposits (δD from −57 to −58‰; δ^{18}O from −8.2 to −8.5‰) differ from those in drainage system (δD = −54‰). This water was formed by mixing water from the metamorphic rocks (δD = −64‰) and the infiltrating atmospheric precipitation. The water from the metamorphic rocks with lighter isotopic content (δD = −64.5‰; δ^{18}O = −9.37‰) have a higher located recharge area. In principle, the new hydrogeologic conclusions related to the dynamics of groundwater in the landslide were made. A schematic picture of the isotope application for solution of hydrogeologic problems in Columbia is given in Figs. 6.4 and 6.5.

In the above considered examples, the localization of areas of groundwater recharge is based on isotope data where difference in isotopic composition of precipitation depends mainly on the process of condensation of the atmospheric moisture. At the same time, the kinetic factors of marine water evaporation in the regions with different climatic conditions change the general correlation dependence δD–δ^{18}O‰. For instance, this dependence for the East Mediterranean has the form $\delta D = 8\delta^{18}O + 22$

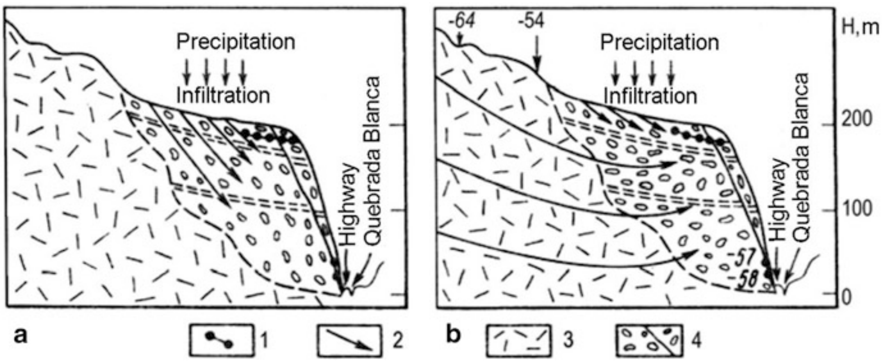

Fig. 6.5 Hydrogeological conditions of landslide Quebradablanca: (**a**) before studies; (**b**) after studies; *1* drainage row; *2* direction of flow; *3* hard rocks; *4* landslide cone. Figures show values of δD, ‰. (After Rodriges 1979)

(Gat and Tzur 1967) which differs from the Craig's correlation $\delta D = 8\delta^{18}O + 10$ for the regions obtaining the Atlantic Ocean's moisture.

Sentürk et al. (1970) carried out studies in central Anatolia for the semi-arid region of the Konya valley in the south–western part of the Mediterranean coast of Turkey. The Konya plain is surrounded by mountains and is situated in the semi-arid zone of the central part of the Anatolian Peninsula. In order to widen the usage of groundwater for irrigation, the investigations of their resources were undertaken. The isotopic composition of groundwater and local precipitation has been examined to identify the sources and recharge conditions of the two most important aquifers. It was found that in the first shallow aquifer, the isotopic ratios of water plot on a line is defined by the equation $\delta D = 8\delta^{18}O + 22$. This equation, relating the D and ^{18}O contents, is characteristic for atmospheric precipitation in the eastern part of the Mediterranean basin. This led to the conclusion that the shallow aquifer is recharged by precipitation of Mediterranean origin. The isotopic ratios of the deep aquifer fell on the lower line defined by the equation $\delta D = 8\delta^{18}O + 10$. The latter is a feature of precipitation originating in the northern continental regions. Thus, conclusions regarding the feeding of the deep aquifer by precipitation could be drawn. The isotopic analyses were also supported by conclusions which were made on the basis of geological and hydrogeological data concerning the principal direction of motion of groundwater in the region.

6.5 Relationship Between Aquifers

The study of water percolation from one aquifer into another through weakly permeable rocks is an important problem of groundwater dynamics. Isotope composition of the two aquifers is a good indicator of their degree of connection and in same cases the only method in solving the problem.

Deak (1974, 1979) has been solving this problem in Hungary using isotope techniques. He has measured the D content in two aquifers in order to find out if the storage of groundwater is replenished from the Upper Pleistocene artesian aquifer. It has been found that the difference in average δD values for ground ($-63‰$) and artesian pressure water ($-86‰$) is too great to play any significant role in groundwater supply due to percolation of the Pleistocene waters. Later on, this conclusion was proved by radiocarbon measurements of both aquifer waters (Deak 1979).

In the earlier cited work of Gonfiantini (1974) on distribution of hydrogen and oxygen isotopes in the salted area Shott-el-Hodna (Algiers), the conclusion was made about discharge of the pressurized deep groundwater into shallow horizon. In zones to the north and east from this area, a percolation of water from the shallow to the deep horizon is observed. This phenomenon takes place in a narrow zone inside the area but outside of the artesian basin. Within the northern part of the area $\delta^{18}O$ values are decreased with the depth from $-6.6‰$ to $-8.4‰$. It is found by radiocarbon dating that if ^{18}O values are increased then the age of the groundwater is increased. The author interprets this result as a proof of the fact that deep water here are recharged by the shallow one.

Dinçer et al. (1974) investigated the problem of replenishing of shallow and artesian groundwater in Saudi Arabia. The Neogene, Eocene, and Paleocene aquifers were studied by distribution of ^{18}O and chemical contents and the conclusions were made about interconnection of water horizons and the conditions of their recharge. The criteria for the conclusions are as follows.

The groundwaters with values of stable isotopes identical to the modern precipitation (^{18}O values for the studied region varied from $-2.5‰$ to $-3.5‰$) and mineralization (dry residue) less than 1 g/l are recharged mainly by means of infiltration from irrigation channels and vadis (dry river beds). The groundwaters with the moderate isotope enrichment (from about 1–2‰ in ^{18}O) compared with the modern precipitation and moderate mineralization (from 1–3 g/l) are possibly recharged from the irrigated channel and vadis. The groundwaters of such isotopic and chemistry content are observed in the irrigated areas. The groundwaters with considerable enrichment of heavy isotopes (especially ^{18}O) and relatively low mineralization have additional feeding from precipitation within the areas of sandy dunes. The groundwaters with considerable enrichment of heavy isotopes and high salinity in their origin have relation to marine intrusion of intensive evaporation in the zone of salt areas. In this case, the ratios of D and ^{18}O contents may indicate the source high mineralization. Concentration of D and ^{18}O lower than in the modern precipitation (^{18}O less than $-3.5‰$) indicates that groundwater recharged in colder epochs. Mineralization of such waters on Arabian Peninsula varies between 1–10 g/l. Based on the above criteria, Dinçer et al. (1974) presented their study of groundwater recharge in Saudi Arabia.

Three identified aquifers, in the northeast coast of New Zealand's south Island on the Kaikoura Plain, were investigated with the help of isotopic and hydrogeologic methods by Brown and Taylor (1974). Distribution of hydrogen and oxygen isotopes in precipitation was obtained. Concentration of ^{18}O values in groundwater water in different parts of island varies from -5.9 to $-8.5‰$. These data point out on a complicated character of the groundwater recharge which originate directly by infiltration of the atmospheric precipitation ($^{18}O = -5.9‰$ and $-6.4‰$), by surface run-off from the Mount Fyffe ($^{18}O = -8.0‰$), and also by near-shore filtration from the Kowhai River ($^{18}O = -8.5‰$). Water of the pressurized horizon is characterized by $^{18}O = -9.4‰$ and in weakly pressurized water $^{18}O = -8.9‰$. The tritium content in the weakly pressurized horizon is close to the tritium content in the river. The tritium content in the pressurized horizon is very low. It follows from those data that there is no close hydraulic relationship despite they both are recharged from the Kowhai River. The authors explain the lower content of ^{18}O in both horizons and in the Kowhai River at present by possible change in climatic conditions observed in the last decade and also by disappearance of vegetation on the higher landmarks. All the above effects together led increase in the surface run-off to the river from the lower landmarks.

Analogous investigations on study of relationship between aquifers carried out in Algeria, Tunis, and Brazil (Gonfiantini et al. 1974; Klitsch et al. 1976; Salaty et al. 1974), on the Siberian polygon for nuclear wastes disposal (Polyakov et al. 2008; Tokarev et al. 2009), and in the Asov-Kuban artesian basin (Sokolovsky et al. 2007).

6.6 Mixing Proportions of Groundwater of Different Genesis

The solution of this problem is based on the assumption that waters of different genesis differ in their isotopic composition. Note that one does not succeed to obtain two independent equations based on the data of D and ^{18}O value because, as a rule, for atmospheric precipitation there is close correlation between the two isotopes. The only possible case of the above isotope data use when one of the mixing components was subjected, for example, to evaporation and changed its isotope values (Dinçer and Halevy 1968). In general, the process of mixing can be written by two mass and tracer conservation equations:

$$Q_{mix} = \sum Q_i,$$
$$Q_{mix}\delta_{cmix} = \sum Q_i\delta_i,$$

where Q_{mix} and Q_i are quantitative mass values of mixture components; δ_{mix} and δ_i isotope values of the mixture components.

Evidently, for a multi-component mixture, the equation $n+1$ can be written using the results of measurement of n for independent isotopes, for instance, D, tritium, carbon-14 and so on. It was pointed out that using the data of D and ^{18}O values, it is possible to separate binary systems even if the chemical contents are identical. In the work of Vinograd and Friedman (1972), using the equation of mass balance, the proportions of waters from different regions feeding one group of springs was calculated. Earlier this problem, when solved by classical hydrogeological methods, has not found single-valid interpretation. The mean value of D content in the first discharging area was $\delta\text{D} = -113‰$, in the second are $\delta\text{D} = -103‰$, in the recharged area $\delta\text{D} = -106‰$, the mean value of the water recharge was 57,500 m^3/day. By solving these two equations, it is not difficult to find that from the first discharging area, about 20,000 m^3 per day or 35% of the total discharging water flow out. The authors pointed out that this method can be used if the following conditions are satisfied: the statistic values of D and ^{18}O should be significantly different differed in both components of the mixture; the isotope content should be constant in time; the isotopic contents of water should not be affected due to interaction with water-bearing rocks; and the other components of mixing waters should be ignored.

Payne and Schotterer (1979) have studied the process of water infiltration from the Chimbo River in Equador to groundwater. It was found that isotopic composition of the Chimbo River, which leaves in the Andes Mountains, does not vary too much during the year. Mean values of isotopic composition in the river water and accounted for $\delta\text{D} = -47.0 \pm 0.7‰$, $\delta^{18}\text{O} = -7.34 \pm 0.09‰$. Mean local precipitation on the plane during 7 months in the year ($\sim$2000 m) were determined as regular observation and characterized by $\delta\text{D} = -24.1 \pm 0.8‰$, $\delta^{18}\text{O} = -4.43 \pm 0.07‰$. The groundwater infiltrated from the river has mean values of $\delta\text{D} = -30‰$ and $\delta^{18}\text{O} = -4‰$. Based on the above data, the authors calculated the recharged portion to the groundwater from the local precipitation, the minimum limit of which appeared to be $73 \pm 5\%$. It was discovered that the deeper aquifers are also recharged from the river bed. Distribution of D in the depth of the aquifer is also studied: at 10 m depth $\delta D = -31.9$, at 40 m it is -39.2, and at 80 m it is -46.6‰. The calculated parts of water from precipitation in the studied aquifer were 66% at the depth 10 m, 23% at 40 m, and about 1% at 80 m.

Analogous investigations regarding the study of mixing proportions of water of different genesis and in mining recharge were done by Verhagen et al. (1979), Zuber et al. (1979) and Karasev et al. (1981b).

6.7 Groundwater Residence Time in an Aquifer

Radioactive isotopes, like tritium and radiocarbon, are often used for solution of this problem, but in several cases the time-dependent characteristics can be successfully obtained by analysis of the stable isotope content. The seasonal δD and $\delta^{18}O$ variations at the input of the hydrological system, and the regularity of their deviation with time in the water-bearing complex, may provide basis for solving this problem. In general case, the residence time τ of water and any dynamical hydrogeological system can be determined as $\tau = V/q$, where V is the system's volume and q is the water discharge.

Eichler (1965) has measured D contents in precipitation and the soil moisture along profile of the unsaturated zone. He found that δD values in the moisture profile are the repeated seasonal variation of D in precipitation, but these variations are equalized with the increase in infiltration time. On the basis of these measurements, Eichler proposed a model for determination of the residence time of precipitation water in the unsaturated zone and also in groundwater.

The method was used by Kusakabe et al. (1970) to study the residence time of thermal waters in the volcanic region of Nasudake (Japan). Isotope balance for a system can be described by a simple equation:

$$d\,(VR_v)/dt = q_i R_i - q_o R_o,$$

where V is the volume of a mixing reservoir; q_i, q_o are velocities of the recharge to and discharge from the system; R_v, R_i, R_o are the ratios of the isotopes and their corresponding components in the system.

In the δ values, for example for $\delta^{18}O$, the equation obtains the form

$$d[V(1 + \delta^{18}O \times 10^{-3})]/dt = q_i(1 + \delta^{18}O \times 10^{-3}) - q_0(1 + \delta^{18}O \times 10^{-3}).$$

At the stationary state, $V_i = \Phi$ and the volume of the reservoir does not depend on time. Seasonal variations of the oxygen isotopic content in precipitation can be presented in the form of equation of harmonic oscillations $\delta_i^{18}O = \overline{\delta^{18}O} + A\cos 2\pi t$, where $\delta_i^{18}O$ is the ^{18}O content at the system enter; $\overline{\delta^{18}O}$ is the mean value of ^{18}O in precipitation; A is the amplitude of the ^{18}O in precipitation relative to its mean value. Taking into account that $\tau = V/q$, the equation can be used for obtaining solution describing change of the ^{18}O ($\delta_v{}^{18}O$) at the exit of the system,

$$\delta_v{}^{18}O = \overline{\delta^{18}O} + [A(1 + 4\pi^2\tau^2)](2\pi\tau\sin 2\pi t + 2\cos 2\pi t)$$
$$+ \delta_{vo}{}^{18}O - \overline{\delta^{18}O} - [A/(1 + 4\pi^2\tau^2)]\exp(-t/\tau),$$

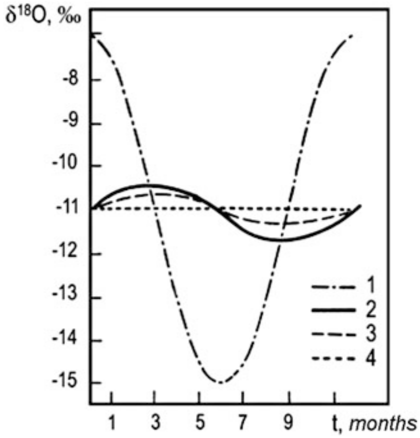

Fig. 6.6 Variation of δ^{18}O values in time τ versus residence time in the system: *1* entering function; *2* $\tau = 1$ year; 3–5 years; 4–10 years. (After Kusakabe et al. 1970)

where $\delta_v{}^{18}$O and $\delta_{v_0}{}^{18}$O are the ^{18}O content of water in the system's outflow at time t and t_o accordingly. Figure 6.6 shows variation of $\delta_v{}^{18}$O values in time (during 1 year) for values $\overline{\delta^{18}\mathrm{O}} = -11‰, A = 4‰$ and $\delta_{v_0}{}^{18}\mathrm{O} = -11‰$ characteristic for the studied region. One can see that the system practically equalizes the entering oscillations at outflow for $\tau = 10$ years.

Analysis of the above equation for the thermal waters of the volcanic region Nasudake based on variation of ^{18}O in hot springs in time says that the residence time of thermal waters is accounted by several years or longer periods.

Analogous studies have been carried out by Dubinchuk et al. (1974) using the hydrogen and oxygen isotope variation in precipitation and mines.

6.8 Relationship of Waters in Conjugate Hydrologic Basins

The determination of the portion of groundwater in surface flow recharge is based on the analysis of seasonal variations of stable isotope concentration in surface and subsurface waters. An example of the solution of this problem is the investigation undertaken in the Alpine region for the Dishma basin, Switzerland, in the range 1668–3146 (Martinec et al. 1974). The experimental data on the ^{18}O content in precipitation, snowpack, and river water of the basin during the period 1969–1972 are shown in Fig. 6.7. One can see that variation in δ^{18}O in summer and winter precipitation range considerably (from $-3‰$ in summer to $-25‰$ in winter). The δ^{18}O values in snow cover were found to be close to those in winter precipitation. At the same time, seasonal variation of ^{18}O content in waters discharged from the basin was gradually diminishing. Martinec et al. (1974) explained this in terms of the main contribution to the surface run-off being derived from water flowing out of subsurface reserves. Simultaneous investigations with tritium as a tracer have shown that the average age (the residence time) of groundwater in the basin is about 4.5–4.8 years.

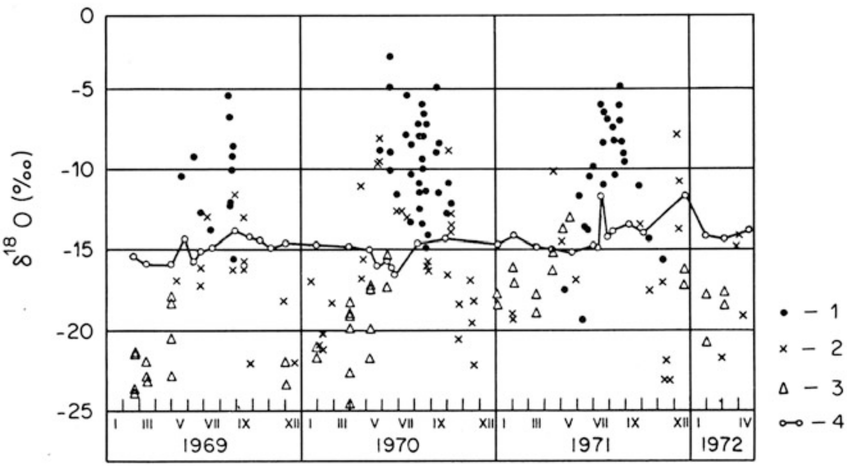

Fig. 6.7 ^{18}O content in *1* precipitation, *2* snow precipitation, *3* snow cover, and *4* discharge water of Dishma basin, Switzerland. (After Martinec et al. 1974)

Thus, in general, as it is seen from Fig. 6.7, isotopic composition of discharged water is close to its mean value in precipitation if the residence time of groundwater is equal to several years.

The other works on solution of the balance problems for the river basins, lakes, and reservoirs are presented by many authors (Brown 1970; Payne 1970; Dinçer et al. 1970; Merlivat 1970; Gat 1970; Behrens et al. 1979; Baonza et al. 1979; Brezgunov and Nechaev 1981).

In conclusion it is noteworthy that in addition to the above described problems, based on the use of natural concentration of D and ^{18}O, there are other hydrological problems that can be solved, which are: seasonal recharge of groundwater by precipitation and portion of recharge by precipitation in different seasons in karstic regions (Dinçer and Payne 1971); study of groundwater dynamics around boreholes and reservoirs for municipal water supply (Fritz et al. 1974); recharge of modern and ancient marine water to the fresh water aquifers (Salati et al. 1974; Cotecchia et al. 1974; Yurtsever and Payne 1979). Combination of different stable and radioactive isotopes with conventional hydrological and hydrochemical data gives more reliable results (IAEA 1976).