# Chapter 13
# Tritium in Natural Waters

Among the environmental radioisotopes, tritium is the most attractive to those researchers who are studying the principles of water circulation in nature. It is a constituent of water molecules and, therefore, is a perfect water tracer. The interest in application of tritium for hydrological and meteorological purposes was increased greatly during the period of thermonuclear tests in 1953–1962, and also subsequently when a large amount of this artificially produced isotope had been injected into the atmosphere. The bomb-tritium, injected into the atmosphere by installments after each nuclear test, is a kind of fixed time mark of water involved in water cycling.

## 13.1 Properties of Tritium and Sources of Its Occurrence

Tritium is produced in the atmosphere by the interaction between secondary nuclear particles of cosmogenic origin, mainly neutrons and protons, and nitrogen and oxygen nuclei. Neutrons produced by cosmic radiation originally have energies of about several dozens of MeV. Then, due to inelastic scattering on nitrogen and oxygen nuclei, they are slowed down. At energies greater than 1 MeV the prevailing nuclear reaction is

$$^{14}\mathrm{N} + n + {}^{12}\mathrm{C} + {}^{3}\mathrm{H}.$$

The cross-section of this reaction is about 0.01 barn. Only 3–5% of all the neutrons generated by cosmic rays in the Earth's atmosphere take part in the production of tritium (Table 13.1).

Besides the above reaction, tritium may produced to other reactions, the main ones of which are presented in Table 13.2.

It follows from Table 13.2 that the first two reactions of interactions of $^{14}$N with medium energy neutrons, fission of $^{14}$N and $^{16}$O nuclei by protons at energy higher than 100 MeV have the highest cross-section. The production rate of tritium by protons with energies ranging from 10 to 100 MeV has been estimated to be 0.01 atom/cm$^2$ s because of an absence of reliable experimental data. The contribution of tritium production by the other components of cosmic radiation is 0.1–0.2

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**Table 13.1** Main reactions with neutrons in the atmosphere

| Reaction | Absolute rate, (neutron/cm$^2$ s) | Relative rate |
|---|---|---|
| Radiocarbon production | 4.0 | 0.56 |
| Tritium production | 0.13 | 0.02 |
| Other reactions | 2.2 | 0.31 |
| Loss | 0.8 | 0.11 |
| Total | 7.13 | 1.0 |

**Table 13.2** Reactions of cosmic ray production of tritium in the atmosphere

| Reaction | Energy of particles (MeV) | Cross-section of reaction (mbarn) | Production rate (atom/cm$^2$ s) |
|---|---|---|---|
| $^{14}$N($n$, $^3$H) $^{12}$C | >4.4 | 11 ± 2 | 0.1–0.2 |
| $^{16}$O($p$, $^3$H) $^{14}$O | >100 | 25 | 0.08 |
| $^{14}$N($p$, $^3$H) $^{12}$N | – | – | – |
| $^{16}$O($p$, $^3$H) $^{14}$O | 10–100 | – | 0.01 |
| $^{14}$N($p$, $^3$H) $^{12}$N | – | – | – |
| $^{14}$N($p$, $^3$H) $^{12}$N | <10 | – | 0.05 |
| N, O($\gamma$, $^3$H) | – | – | $10^{-5}$ |

atom/cm$^2$ s. This value is less than that actually observed, which is 0.3 atom/cm$^2$ s. An additional tritium input to the atmosphere may take place during intense solar flares. It is most probably formed in the course of the reaction $^4$He ($p$, 2$p$)$^3$H in the chromosphere of the Sun.

The steady-state amount of tritium on the Earth, formed by cosmic radiation, varies from 3 to 10 kg. The major part of tritium (~93%) stays in the hydrosphere and only about 7% is in the atmosphere (see Table 12.4). Due to insignificant amounts in natural objects, tritium is commonly expressed in tritium units (TU). A TU corresponds to 1 atom of tritium per $10^{18}$ atoms of protium, which is equivalent to 7.2 disintegrations per minute per liter of water, or 0.119 Bq/kg. Tritium is a soft $\beta$-emitter, characterized by a maximum energy of $\beta$-particles equal to 18 keV and half-life of 12.43 years. The final product of tritium decay is the stable isotope of $^3$He.

Shortly after production tritium is oxidized and forms molecules of water HTO. Since the masses of tritium and protium differ, fractionation occurs during phase transitions of water from gases to solid states and vice verse (Fig. 13.1).

It is for this reason that inhomogeneity is observed in tritium distribution between hydrogen-bearing systems in the tritium–protium exchange reactions. Experiments involving different types of clays (kaolinite, montmorillonite, and silty clays) have shown that in the course of their interaction with water labeled by tritium a marked exchange reaction between tritium and protium is observed. The protium constitutes the clay minerals and hydroxides (Stewart 1965). This effect may be considered as significant in groundwater dating and the large time-scale involved in the investigation of water motion in rocks based on tritium labeling.

Before the first thermonuclear tests in the atmosphere (1952), the majority of the tritium in nature resulted from cosmic ray production. At that time only a few

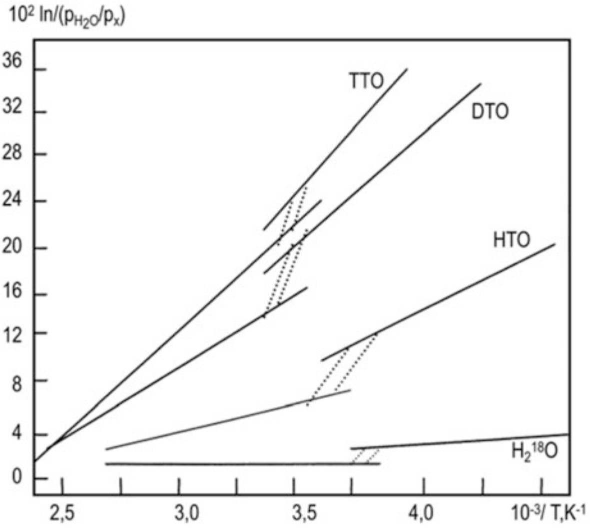


**Fig. 13.1** Experimental relationship from vapor pressure of heavy and light water molecules and temperature. (After Van Hook 1968)

measurements of natural tritium on the Earth had been carried out. According to the data of Libby (Kaufmann and Libby 1954), who was the first to study its applicability in hydrology and carried out measurements in Chicago, the average content of environmental tritium in precipitation was about 8 TU. Brown (1961) measured tritium concentrations in the Ottawa Valley (Canada) and found that the mean level of tritium is 15 TU. According to the calculations of Lal and Peters (1962), this value corresponds to 6 TU. Later on, when some principles of distribution and fallout of corresponding amounts of tritium on the Earth were established, it become clear that it's content varies within a large range both in space and time. This range may be estimated as being equal to 0.1–10 TU for both hemispheres at a constant rate of tritium production of about 30 atoms/cm$^2$ min relative to the terrestrial surface (Suess 1969).

Using data obtained by different authors, Burger (1979) has reported the data of tritium distribution in individual geospheres given in Table 13.3. Estimations were made of tritium fallout on the Earth with the cosmic dust and micrometeorites

**Table 13.3** Distribution of tritium in the geospheres. (From Burger 1979. © IAEA, reproduced with permission of IAEA)

| Geosphere | HTO | | HT | | $CH_3T$ | |
|---|---|---|---|---|---|---|
| | Ci | TE | Ci | TE | Ci | TE |
| Ocean, top 100 m | $9 \times 10^8$ | 10–20 | (1–10) $\times 10^3$ | ? | – | – |
| Troposphere, (3.8 $\times 10^{18}$ kg air) | (2–8) $\times 10^6$ | – | (8–18) $\times 10^6$ | (3–7) $\times 10^6$ | (6–20) $\times 10^6$ | ~5 $\times 10^4$ |
| Stratosphere, (1.3 $\times 10^{18}$ kg air) | (0.6–5) $\times 10^8$ | (2–8) $\times 10^7$ | (1–4) $\times 10^4$ | – | $<10^5$ | ~5 $\times 10^4$ |

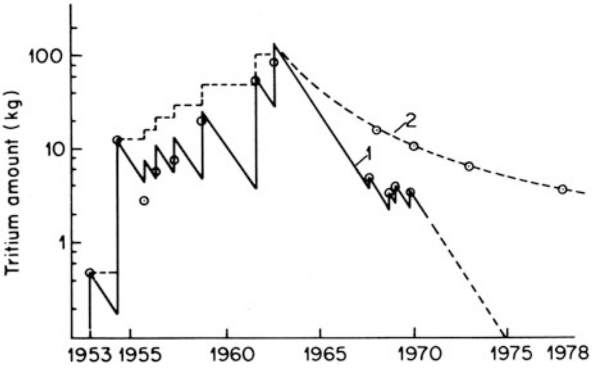


**Fig. 13.2** Growth of thermonuclear amounts in the atmosphere taking into account its fallout (*1*) and the stratosphere taking into account its natural decay (*2*). (After Ferronsky et al. 1975. © IAEA, reproduced with permission of IAEA)

(Fireman 1962, 1967). It was shown that in stone meteorites, the tritium activity equals to 200–400 disintegrn/kg min and for iron meteorites this value was 40–90 disintegrn/kg min. Thus, the tritium component contained in meteorites falling down on the terrestrial surface is insignificant and is less than $10^{-5}$ atoms/cm$^2$ s.

The results of measurements of tritium concentrations in lunar rocks, carried by spacecrafts Apollo-11 and Apollo-12, gave 270–300 disintegrn/kg min (Bochaler et al. 1971) and appeared to be similar to those in meteorites. The production of tritium in lunar rocks and meteorites occurs due to spallation reactions between cosmic high-energy protons and nuclei or rock-forming elements, such as Fe, Si, Al, etc.

Thermonuclear tests in the atmosphere, carried out since 1952, represent another source of atmospheric tritium. The output of tritium released during a thermonuclear explosion averaged from 0.7 to 5 kg/mt of thermonuclear fission and 0.07 kg/mt of nuclear fission (Miskel 1973). A diagram of tritium injection to the atmosphere from thermonuclear explosions since their beginning is shown in Fig. 13.2 plotted on the basis of data obtained by Eriksson (Schell and Sauzay 1970). Curve 1 accounts for the residence time of tritium in the stratosphere, the main reservoir of accumulation. According to the data obtained for precipitation, this residence time is about 1 year. The residence time in the reservoir is the time required for one half of the tritium present at the beginning to remain in the reservoir. Curve 2 shows the annual variations of the total amount of tritium in the stratosphere.

Up to 1957, the energy of thermonuclear explosions of megaton energy was carried out by the USA in August 1958 at an altitude of 4–7.5 km. In 1957–1958, at a lower altitude, there were 8 mt tests carried out by the UK. Some portion of tritium produced during these explosions has moved in the stratosphere. The most powerful megaton explosions were made in 1961–1962 by the USA and the former USSR in various places of the globe and at high altitudes. As a result, a large amount of tritium (up to 400 kg) has been stored in the stratosphere (Ostlund and Fine 1979), and its concentration in individual places on the Earth (e.g., White Horse, Canada) in the spring–summer months reached 10,000 TE (Thatcher and Payne 1965). It was found later on, after the interdiction of nuclear tests in the three spheres that estimation of the residence time of tritium in the stratosphere, which was accepted to be about 1 year, appeared to be imprecise. Its concentration in precipitation has decreased up to the present time but far more slowly than was assumed theoretically. Thus, the tritium concentrations in precipitation should have reached the natural level by 1970. However, in Western Europe in the summer months of 1968–1970 the levels were still fixed as they had been at the end of 1960, amounting to about 30 TU.

During the last few years up to 1970, some increases in tritium content of the atmosphere were observed due to thermonuclear explosions carried out by France and China. However, the values of these tritium injections are insignificant compared with the previous ones (see in Fig. 13.4 the maxima corresponding to 1967–1970).

Atomic industries (power and research reactors, plants of nuclear fuel reprocessing, etc.) are also sources of environmental tritium. The output of tritium during uranium fission in different types of reactors depends on the choice of fuel, energy spectrum of neutron flux, and a number of technological factors. Depending on the type of reactor tritium is produced in the course of the activation of boron, lithium, and deuterium atoms by neutrons. In the controlled thermonuclear reactor, which is now under construction, tritium will be the main radionuclide. In this case, the major portion of tritium will be ejected from nuclear plants into the environment in the gaseous state (HT, DT, $T_2$), and partly in the liquid phase in the form of HTO. The gaseous tritium ejected into the atmosphere oxidized quickly and forms water molecules.

According to data obtained by Sehgal and Remport (1971), in the course of uranium and plutonium fission 0.8 atom of tritium is formed per $10^4$ acts of $^{235}$U fission, 0.9 atom of tritium for that of $^{238}$U, and 1.8 atom of tritium for that of $^{239}$Pu. Fluss and Dudey (1971) have studied the dependency of tritium production on the energy of neutrons for $^{235}$U. According to them, when the energy of neutrons changes from 175 to 630 keV the yield of tritium increases from 2 to 3.4 atom per $10^4$ acts of uranium nuclei fission.

In the slow-neutron reactors during $^{235}$U fission, the yield of tritium amounts to $8.7 \times 10^{-3}\%$ (Taylor and Peters 1972) and in the fast-neutron reactors it corresponds to $2.2 \times 10^{-2}\%$ (Dudey et al. 1972). This efficiency of yield corresponds to the VVER and RBMK reactor which provides $1.1 \times 10^{-2}$ Ci/day Mw (t) and for the fast-neutron reactors $-2.8 \times 10^{-2}$ Ci/day Mw (t).

During reactions proceeding in the control rods of the reactors, tritium is ejected in accord with the reactions $^{10}\mathrm{B}(\alpha, 2\alpha)^3\mathrm{H}$; $^{11}\mathrm{B}(\mathrm{n}, {}^3\mathrm{H})^9\mathrm{B}$; $^{10}\mathrm{B}(\mathrm{n}, \alpha)^7\mathrm{Li}$; $^7\mathrm{Li}(\mathrm{n}, \mathrm{n}\alpha)^3\mathrm{H}$. The cross-section of these reactions increases with the energy of neutrons. Therefore, the yield of tritium in fast-neutron reactors is considerably higher than in reactors of the other type. Lokante (1971) has reported that the tritium yield corresponding to fission reactions amounts to 11,000 Ci and for boron reactions is about 1,380 Ci in the 3,500 Mw boiling water reactor. In the 300 Mw breeder reactor, the tritium yield is 1,670 Ci for the fission reaction and 3,980 Ci for the boron reaction. The tritium output from the heat-generating elements to the heat carrier depends on the material of the shell. Stainless steel passes up to 60–80% of the produced tritium and zirconium only 0.1% (Lokante 1971).

**Table 13.4** Tritium production in various types of reactors. (Bonka 1979. © IAEA, reproduced with permission of IAEA)

| Nuclear reaction | Tritium production in Ci/Mw(e) per year | | | | | |
|---|---|---|---|---|---|---|
| | BWR[a] | PWR[b] | HWR[c] | AGR[d] | HTR[e] | FBR[f] |
| Efficiency | 0.33 | 0.33 | 0.32 | 0.41 | 0.41 | 0.41 |
| *Fuel element* | | | | | | |
| Fission | 18 | 18 | 20 | 15 | 12 | 30 |
| $^6$Li in fuel (0.05 ppm) | 0.3 | 0.3 | 0.8 | 1 | 0.2 | 0.1 |
| $^{10}$B in fuel (0.05 ppm) | $4 \times 10^{-5}$ | $4 \times 10^{-5}$ | $3 \times 10^{-5}$ | $5 \times 10^{-5}$ | $1 \times 10^{-5}$ | $2 \times 10^{-5}$ |
| $^6$Li in graphite | – | – | – | – | 0.5 | – |
| $^9$Be in graphite | – | – | – | – | $1 \times 10^{-4}$ | – |
| $^{10}$B in graphite | – | – | – | – | $3.5 \times 10^{-3}$ | – |
| *Coolant* | | | | | | |
| $^1$H in water | $8 \times 10^{-3}$ | $8 \times 10^{-3}$ | – | – | – | – |
| $^2$H in water | $4 \times 10^{-3}$ | $4 \times 10^{-3}$ | 150 | – | – | – |
| $^{10}$B in water | – | 0.8 | – | – | – | – |
| $^3$He in helium | – | – | – | – | 1 | – |
| $^6$Li in sodium | – | – | – | – | – | 2 |
| $^9$Be in sodium | – | – | – | – | – | 0,01 |
| $^{10}$B in sodium | – | – | – | – | – | 0,01 |

[a] BWR is boiling-water reactor
[b] PWR is pressurized water reactor
[c] HWR is heavy-water reactor
[d] AGR is advanced gas-cooled reactor
[e] HTR is high-temperature reactor
[f] FBR is sodium-cooled fast breeder reactor

According to Golubev et al. (1979) and Broder et al. (1979), the tritium exhausts from typical VVER-440, VVER-1000, and RBKM-1000 reactors are equal to 0.6, 1.6, and 2.28 Ci/day, respectively. At the Novovoronezhskaya nuclear power station, for example, about 55% of the total amount of tritium is ejected into the atmosphere, 27% into surface waters, and 13% into groundwaters. According to the data for yearly observations, the tritium concentrations at 1 km downstream of the river are higher by one order of magnitude than in water upstream of the river.

As pointed out above, tritium is produced at nuclear power stations (reactors) both due to the process of uranium fission and due to interactions of neutrons of various energies with the constructional materials and coolants. The following substances are some of those used as coolants: light and heavy water, noble gases, melted metallic sodium. The main nuclear reactions, in the course of which tritium is formed, are the reaction of fission of enriched uranium (X) leading to the formation of the fission products $X(n,f)^3H$; $X(n,f)^6He \rightarrow {}^6Li(n,\alpha)\,{}^3H$; ${}^{10}B(n,2\alpha)\,{}^3H$; ${}^2H(n,\gamma)\,{}^3H$; ${}^9Be(n,2\alpha)\,{}^3H$ and so on.

In Table 13.4 data on the tritium yield in different types of reactors due to the above-mentioned reactions are given. In Table 13.5, data on tritium input into the atmosphere

**Table 13.5** Tritium emission rates from nuclear power reactors under normal operation and reprocessing plants without tritium retention. (Bonka 1979. © IAEA, reproduced with permission of IAEA)

| Nuclear facility | | Emission rate (Ci/year) | |
|---|---|---|---|
| | | Atmosphere | Surface water |
| Reactor (1,000 Mw(e)) | BWR | 30 | 150 |
| | PWR | 20 | 900 |
| | HTR | 10 | 900 |
| | FBR | 100 | 200 |
| Reprocessing plant (40,000 Mw(e) full load) | BWR and PWR | $7 \times 10^{-5}$ | 1,000 |
| | PWR | $7 \times 10^{-5}$ | 1,000 |
| | HTR | $6 \times 10^{-5}$ | 1,000 |
| | FBR | $6 \times 10^{-5}$ | 1,000 |

and surface waters for various nuclear reactors and nuclear fuel processing plants are presented.

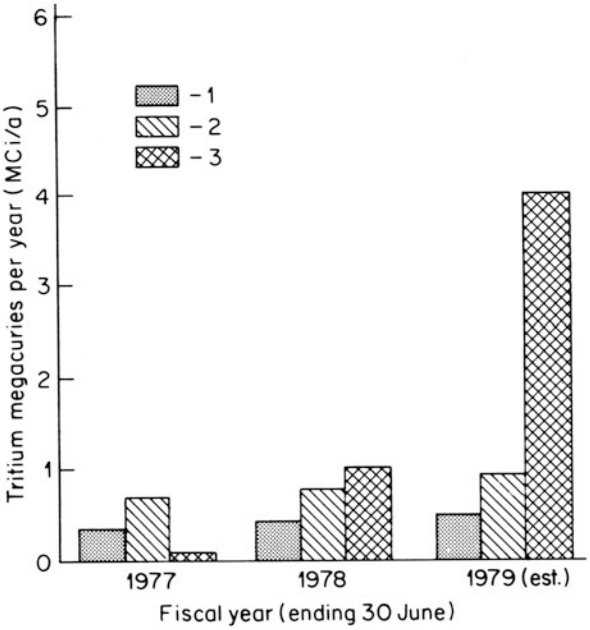
In the report made by the National Council on Radiation Protection and measurements of the USA (Eisenbund et al. 1979) the following data on the tritium yield due to diverse sources are given. The global amount of tritium produced by cosmic radiation equals to 70 MCi (1 kg of tritium is equivalent to about 10 MCi), that is, its production rate is about 4 MCi/year. In 1963, an amount of tritium, estimated at 3,100 MCi, was injected into the atmosphere and hydrosphere as a direct result of nuclear and thermonuclear tests. Thus, the natural level of tritium (70 MCi) may be attained as a result of a decay process up to 2030. The production of tritium in nuclear reactors of the PWR type due to fission reactions ranges from 12 to 20 Ci/day per Mw of the thermal power. The activation of the light elements gives an additional yield of tritium which averages from 600 to 800 Ci/year per Mw of electrical power. These values are equal to 63 Ci/year for the reactors of the BWR and PWR types with light-water cooling. The average residence time of the tritiated water vapor in the troposphere ranges from 21 to 40 days.

The main residence time of HTO molecules in the mixing ocean layer (50–100 m thickness and equal to 75 m on average) is approximately 22 years.

The average time of half-removal of tritium from the human body depends upon individual biological features and is equal to hundreds of days. For two arbitrarily chosen and absolutely healthy men of middle age, the time of half-removal was found to be 340 and 630 days.

Some portion of tritium is injected into the environment from research centers, medical institutions, and industrial plants dealing with works involving the application of artificial tritium. According to the data reported by König (1979), tritium activities of $(1.2–2.1) \times 10^3$ Ci/year have been released into the atmosphere from the Nuclear Research Centre in Karlsruhe (Germany) since 1969. Krejči and Zeller (1979) have reported that a large amount of tritium is ejected into atmosphere from the luminous compound industry, producing tritium, gas-filled light sources and tritium luminous compounds. The urine of the operators working on one of the plants

**Fig. 13.3** Quantities of tritium produced annually in the USA for digital watch lighting (*1*), by power reactors (*2*), and for other commercial products (*3*). (After Combs and Doda 1979. © IAEA, reproduced with permission of IAEA)



producing luminophor contains about 25 Ci/l of tritium (1 TU = 3.2 pCi/l). In the waste water within the plant area, the concentration of tritium is about 0.3 Ci/l and in water at the exit from the cleaning installations the concentration is 0.004 Ci/l. In precipitation at a distance of 50 m from the ventilation system of the tritium department, the concentration of tritium is 0.1 Ci/l, at a distance of 200 m it amounts to 0.02 Ci/l, and at 2,000 m it is equal to 0.001 Ci/l. A large amount of tritium is now used for the production of liquid crystal displays for digital electronic readouts. The annual production of tritium by different industries in the USA is shown in Fig. 13.3 reported by Combs and Doda (1979). According to their estimations, the amount of tritium used for the production of backlighted digital watches will reach (and it has reached) 4 MCi in 1979.

A considerable amount of tritium in the environment originates from the nuclear fuel reprocessing industry. Daly et al. (1968) have shown that the nuclear fuel reprocessing plant situated in New York State ejects about 200 Ci of tritium per day, 25% of which is released into atmosphere, 65% is contributed in liquid form to the river, and 10% goes into the soil.

Taking into account the modern trend of development of nuclear power stations in most countries of the world, it is easy to estimate that by the beginning of new twenty-first century the production of technogenic tritium, which will be continuously ejected into the environment, will overcome the amount of cosmogenic tritium produced in the atmosphere.

In fact, the tritium production rate from all the nuclear plants (power reactors and nuclear fuel reprocessing plants) of the world at 2000 is overcome by four times the rate of its natural production by cosmic radiation. However, the release of tritium into the environment is negligible since its major portion is collected and buried as radioactive waste. Besides, the tritium produced by nuclear plants cannot reach the stratosphere, where it would be subjected to global redistribution. Therefore, its ejection into the precipitation, surface, and groundwaters is of a local character, related to the neighborhood of the organization of studies of surface and groundwaters involving tritium measurements.

According to Katrich (1990), some amount of tritium was injected into the environment as the result of Chernobyl accident. Concentration of tritium over the European part of Russia in May 1986 increased by 2–5 times compared with May 1985, however, in June–July, the level of contamination was dropped to the normal because the tritium was reached only troposphere.

At least some portion of tritium will be released into the atmosphere due to nuclear explosions used for peaceful purposes (such as the performance of underground oil, gas, and water capacities, excavation of rocks in the course of construction works, etc.). However, the major portion of tritium precipitating in the hydrological cycle in the near future will be, as previously, the bomb-tritium released in the period from 1952 to 1962.

## 13.2 Global Circulation of Tritium Water

At present the total amount of tritium on the Earth exceeds its prebomb level only by 1.5–2 times. This situation is explained by continuous decay of tritium and the isotopic exchange with the ocean's waters.

Figure 13.4 demonstrates general scheme of the global circulation of tritium water in nature. From the atmosphere, which is the only source of the natural and thermonuclear tritium, the tritium water molecules together with the air flows enter the troposphere where they form isotopic composition of the tropospheric moisture. The other effects which determine tritium content of the tropospheric moisture is the evaporation from the ocean surface and the molecular exchange between the surface ocean layer and the atmospheric moisture. The continental atmospheric precipitation of high tritium content forms river run-off, lake and groundwaters, and also glaciers. Some part of precipitation is evaporated. Concentration of tritium in the river water is close to that in precipitation and in the lakes it depends on residence time of water: the longer residence time, the less content of tritium because of its decay. The same relates to the groundwater basins. In glaciers, especially in polar latitudes (Greenland, Antarctic), water looks like conserved and in the deep layers tritium is completely decayed. The nondecayed part of the HTO molecules from the rivers, lakes and groundwater comes to the oceans together with the surface and underground run-off.

The oceans' waters are divided in two layers: (1) the upper, well mixed with depth of several hundred meters and (2) lower, divided from the upper by the thermocline,

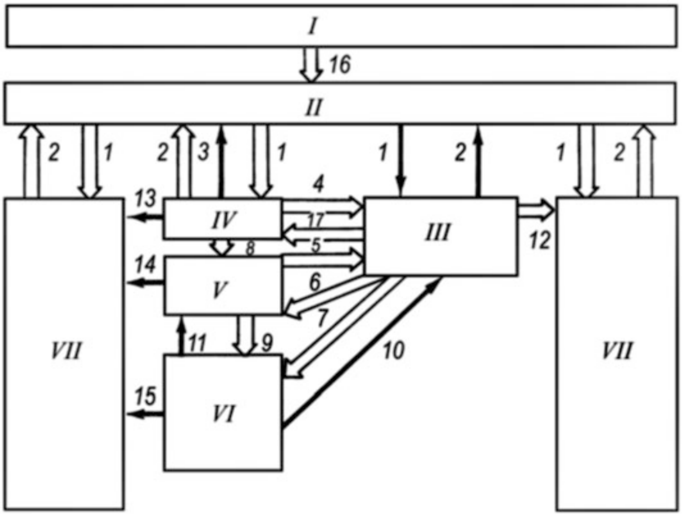


**Fig. 13.4** Scheme of tritium cycling in hydrosphere's reservoirs: (*I*) stratosphere; (*II*) troposphere moisture; (*III*) continental surface water; (*IV*) soil moisture; (*V*) shallow groundwater; (*VI*) deep groundwater; (*VII*) ocean water; (*1*) atmospheric precipitation; (*2*) evaporation and molecular exchange; (*3*) transpiration; (*4*) soil run-off discharge; (*5*) underground run-off discharge; (*6*), (*7*) surface run-off discharge; (*8*) infiltration of soil water; (*9*) infiltration of groundwater; (*10*) discharge of deep groundwater to surface water; (*11*) discharge of deep groundwater to groundwater; (*12*) surface run-off to the oceans; (*13*) soil water run-off to the oceans; (*14*), (*15*) submarine discharge to groundwater (*16*) output of tritium from stratosphere; (*17*) discharge of surface water to the soil layer

with water exchange time of several hundreds and even thousand years. The thermocline may absent in the Polar regions and in this case the most favorable conditions for vertical water mixing appear. In the upper layer, maximum concentrations of tritium in waters are observed, which at immersion to the depth and mixture long time lose tritium at its decay.

Thus, the stratosphere is the source of tritium in the hydrologic cycle and the deep ocean waters and glaciers and the deep groundwaters are the reservoir of tritium run-off where it decays. It follows from here that the definite regularities should be expected in distribution of tritium in all chains of the hydrosphere.

### 13.2.1 Tritium in Atmospheric Hydrogen and Methane

Except the water, which is the main object for the study of tritium distribution on the Earth, there are two other hydrogen-bearing compounds: (1) The molecular hydrogen ($H_2$) and (2) Methane ($CH_4$). The study of their behavior is important for the understanding of geophysical and physical–chemical processes in the atmosphere. Of a special interest are $H_2O$, $H_2$, and $CH_4$ cycles, which have close relationship in the atmosphere. Their passage from one form to another may be used as the tracer for determining the residence time of hydrogen stay in its compounds, for estimation of the exchange rate between the hemispheres, for study of the air exchange between the troposphere and stratosphere, and for understanding the nature of the compounds origin.

At present the concentration of $H_2$ in the nonindustrial regions amounts to 0.575 ppmv in the northern hemisphere and 0.550 ppmv in the southern hemisphere (Schmidt 1974). On a global scale, 50% of the $H_2$ is of anthropogenic origin. The most significant natural source of $H_2$ in the biochemical process occurring in the ocean, where waters are enriched with hydrogen by a factor of three. The process of water molecule dissociation and hydrogen photosynthesis occurring in the atmosphere (Romanov and Kikichev 1979) also contribute significantly to $H_2$ concentration.

The majority of tritium in atmospheric hydrogen is of cosmogenic origin. The principal reaction leading to the production of HT molecules, according to the estimations made by Harteck (1954) for tritium generated by cosmic rays, is the recurrent photodissociation of $TO_2$ and the subsequent exchange reaction of the form

$$T + H_2 \rightarrow HT + H.$$

Only 0.1% of the tritium produced by cosmic rays exists in the form of the HT molecules and 99.9% is in the form of the HTO molecules. The bulk of the HT molecules are formed at altitudes ranging from 10 to 40 km. The total mass of the HT molecules of cosmogenic origin in the atmosphere is about 5 g (Rowland 1969).

Besides the release of tritium from the device itself during thermonuclear explosions, tritium is produced according to the following main reaction:

$$D + D \rightarrow T + H + 4\text{MeV}.$$

It is considered that approximately the same relative content of the bomb-tritium is contained both in the molecules of $H_2O$ and $H_2$, which is the result of isotopic exchange between $H_2O$ and $H_2$ in the expanding and cooling thermonuclear sphere. In this case, the main reactions are:

$$T + O_2 \rightarrow TO_2,$$

$$TO_2 + O \rightarrow TO + O_2 + 61\text{kcal},$$

$$TO + H_2 \rightarrow HTO + H + 17\text{kcal},$$

$$HTO + H_2 \leftrightarrow H_2O + HT.$$

In the course of underground thermonuclear tests, the increase of tritium content in atmospheric hydrogen has not been accompanied by an increase of tritium content in the atmospheric moisture. This is likely to be due to the lack of conditions necessary for oxidizing reactions in the medium where explosion takes place.

The main sources of technogenic tritium, as pointed out earlier, are nuclear power plants, which release a considerable amount of tritium in the form of HT molecules.

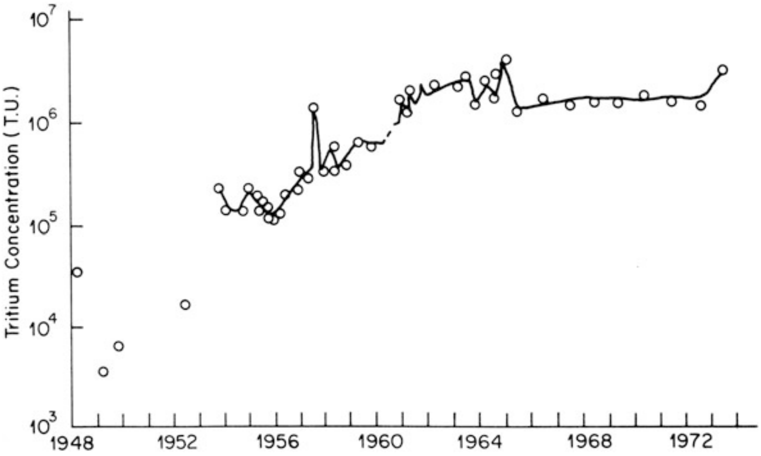


**Fig. 13.5** Tritium concentration increase in atmospheric hydrogen from 1948 to 1973 over continents. (After Ehhalt 1966; Martin and Harteck 1974; Östlund and Mason 1974)

Tritium was first measured in atmospheric hydrogen in 1948 near Hamburg, where its concentration was found to be equal to 4 × $10^3$ TU (Faltings and Harteck 1950). Later on, due to thermonuclear tests, the concentration of tritium in atmospheric hydrogen sharply increased (Fig. 13.5). It can be seen from the figure that the concentration of tritium increased from 4 × $10^3$ to 4 × $10^6$ TU from 1948 to 1973 (Ehhalt 1966; Martin and Harteck 1974; Östlund and Mason 1974). In the tropospheric HT, its concentration reached maximum values with a delay of about 2–2.5 years. Ehhalt (1966) has assumed this to be the effect of removal of HT molecules from the stratosphere, which is the main reservoir of tritium accumulation during thermonuclear explosions, into the troposphere after a certain long time, corresponding to that which was observed.

After thermonuclear tests were stopped in the three media, tritium content in the $H_2$ remained approximately unchanged from 1963 to 1973 at the level of (2–4) × $10^6$ TE. The constancy of the HT concentration in the atmosphere can only be explained by ejection of tritium into the atmosphere from some sources in order to maintain the corresponding partial pressures of the HT molecules and compensate the natural losses caused by radioactive decay and other processes of removal.

According to existing estimations (Martin and Hackett 1974), the total anthropogenic release of tritium into the atmosphere should amount to 1.2 × $10^6$ Ci/year in order to maintain the average concentrations of tritium in atmospheric hydrogen at the level of about 80 atom/mg of air. These sources of anthropogenic tritium release are likely to be atomic industrial plants and underground tests.

In contrast to the distribution of the HTO, the spatial distribution of tritium in atmospheric $H_2$ is characterized by a high homogeneity in the whole atmosphere. According to the data of Östlund and Mason (1974), the concentration of tritium was about 50 atom/mg of air in 1971–1972. Only at high latitudes (60°N and higher)

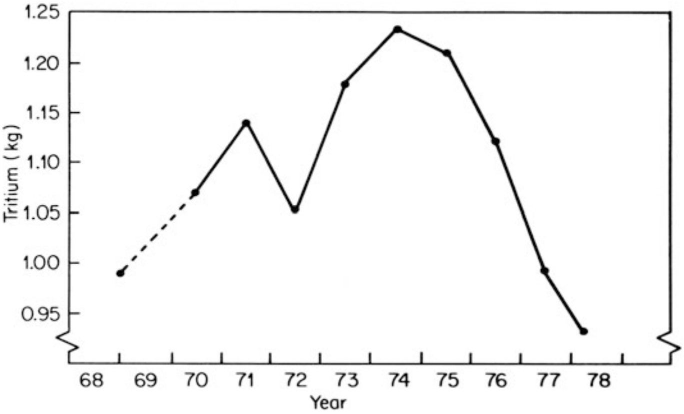


**Fig. 13.6** Inventory of the global atmospheric HT for 1968–1978. (After Mason and Östlund 1979. © IAEA, reproduced with permission of IAEA)

does the concentration of tritium increase up to 80 atom/mg of air. According to the limiting data, tritium concentration in the stratosphere decreases with altitude following the barometric law. Thus, in North Alaska at 70–75°N the tritium content in the lower stratosphere varies with altitude from 80 to 30 atom/mg of air (Östlund and Mason 1974). The exceptions to these principles are the regions of anomalous release of $H_2$ of industrial origin with zero concentration of tritium, and also the regions where nuclear industries are located, characterized by raised tritium content. The global content of HT molecules in the atmosphere during the period 1968–1978 is shown in Fig. 13.6 (Mason and Östlund 1979).

According to the data of Ehhalt (1974), the $CH_4$ early production is accounted by $(5.4–10.6) \times 10^{14}$ g, from which 80% have biogenic origin. Tritium concentration there is more than $10^4$ TU (Ehhalt 1974). Creation of $CH_3T$ molecules in the atmosphere occurs as a result of nuclear and exchange reactions between HT and $CH_4$. However, as investigations show, these reactions have small efficiency (Begemann and Friedman 1968). It is assumed that the main sources of tritium in $CH_4$ are research laboratories and institutions of atomic industry, technology of which relates to tritium (Burger 1979).

Molecules $CH_3T$ of biochemical reactions have the same T/H ratio as the environmental water. It is obvious that atmospheric HT takes part in biogenic $CH_4$. As a result of this process, tritium content in the $CH_4$ is correspondingly increases. The exchange time of $CH_4$ in the atmosphere is to about 4–7 years.

### *13.2.2 Tritium in Atmospheric Water Vapor*

As pointed out above, the upper layer of the atmosphere, its stratosphere (15–17 km), is the reservoir where the bulk of natural tritium is accumulated. Despite the small amount of stratospheric moisture is the main source of the tropospheric tritiated water falling to the Earth's surface as precipitation. It will be shown that the stratosphere is also a reservoir accumulating thermonuclear tritium.

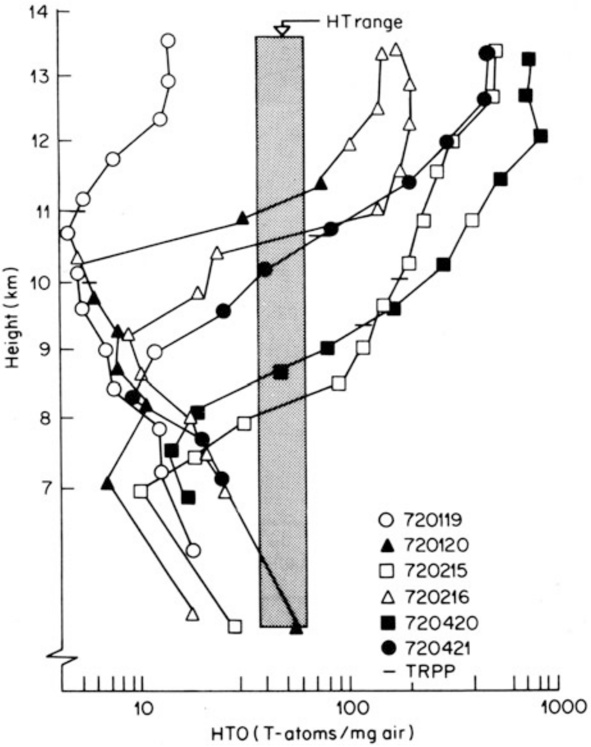
Martell (1963), using a supposed production rate of natural tritium of 0.3 atom/cm$^2$ s, obtained a value of tritium concentration of about $10^6$ TU. The first measurements of stratospheric tritium in the air above Minneapolis in 1955–1958 at an altitude of 14–28 km carried out by Hagemann et al. (1959), had shown that the tritium content was equal to $1.1 \times 10^6$–$1.52 \times 10^7$ atom/g of air. On the basis of these measurements and on the ratio of $T/C^{14}$, it was found that the amount of tritium in the stratosphere is equal to $6 \times 10^{23}$ atoms (6 kg). Later, Scholz et al. (1970) obtained a tritium concentration of $2.2 \times 10^6$–$8 \times 10^7$ TU using their own experimental data.

The most complete studies of tritium distribution in the troposphere were carried out by Ehhalt (1971). Measurements were conducted from November 1965 to January 1967 at continental (Scottsbluff, Nebraska) and oceanic (near California) stations up to an altitude of 9.2 km. The results of Ehhalt's measurements have shown that concentrations in water vapor increase with altitude. The lowest concentrations were found at an altitude of 2,300 m above the sea level in the spring–summer seasons (1,200 TU) and maximum values at an altitude of 9 km (26,000 TU). It has been found that the altitude of the seasonal variations at amplitude of 7.5–9 km is greater by a factor of 10 than the variation of tritium concentrations at the Earth's surface.

Detailed data concerning the distribution of HTO molecules with height were reported by Mason and Östlund (1979). Water and hydrogen samples were taken with the help of a molecular trap, placed on a special aircraft, up to a height of 13 km. The distribution of HTO in the troposphere and stratosphere during the flights over Boulder, Colorado, is presented in Fig. 13.7. Figure 13.8 shows the distribution of the HTO in the stratosphere below 19.2 km (T-atoms/mg air), discovered during flights in August 1976 and July 1977. Differences in the HTO distribution both with altitude and latitude were observed between 1976 and 1977, caused by an atmospheric thermonuclear test conducted by the People's Republic of China on 17 November 1976, which resulted in the release of a large amount of tritium into the stratosphere. According to the estimations of Mason and Östlund, the inventories of atmospheric tritium were about 1 kg of the HT molecules and 5.3 kg of the HTO at the end of 1977. The major portion of the HTO (about 5.1 kg) has been stored in the stratosphere and 0.2 kg has been in transit to the ocean surface through the troposphere.

Bradley and Stout (1970) carried out individual measurements in order to obtain tritium distribution profiles in atmospheric moisture in Illinois State (USA) up to the amplitude of 5 km. They obtained three different types of distribution of tritium with altitude. The first type is characterized by an increase of tritium concentration with altitude, the second type by a constancy of tritium concentration, and the third type by a decrease of tritium concentration with altitude up to 2.5 km and then by a subsequent increase in concentration. These tritium distributions were explained by Bradley and Stout as the result of different conditions of formation and mixing of atmospheric moisture in the lower troposphere and also in terms of different sources of tritium.

**Fig. 13.7** Vertical HTO/HT mixing ratio profiles over Boulder, Colorado, 1972. (After Mason and Östlund 1979. © IAEA, reproduced with permission of IAEA)



In mountainous region, the vertical distribution of tritium in the atmosphere can be estimated using the data of precipitation measurements at different altitudes. These studies have been carried out by Romanov (1978) in the Caucasus near the Aragats Mountain (Table 13.6). It was found that the average annual concentrations of tritium in precipitation, sampled at an altitude of 850–3,500 m in 1971 and 1972 increased by factor three. Assuming the equilibrium conditions of condensation of atmospheric precipitation, it may be assumed that such relationships reflect the actual vertical distribution of tritium in water vapor.

The obtained data by the same author on tritium concentration in the annual layers of the Pamir glacier at an altitude of 4,500 m (Table 13.6) found to be lower. This was explained by difference in the origin of the atmospheric moisture (Indian Ocean), which forms the sampled precipitation.

### 13.2.3 Tritium in Precipitation

The applicability of environmental tritium as a tracer of air mass circulation in the atmosphere and the formation of precipitation and discharge on the continental surface and in groundwaters, is based upon the experimental data of tritium content in

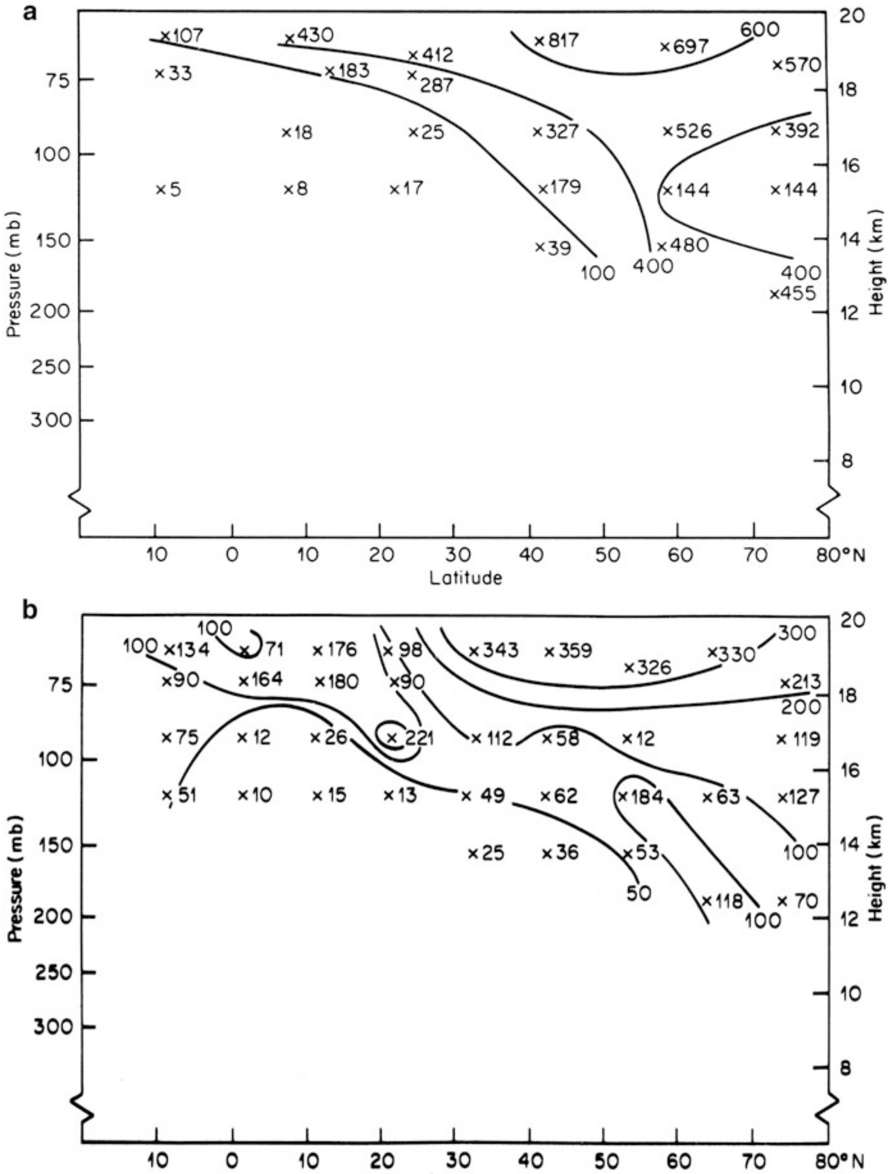


**Fig. 13.8** Stratospheric HTO mixing ratios, T-atoms/mg air for May–June, 1976 (**a**) and for August 1976 (**b**). (After Mason and Östlund 1979. © IAEA, reproduced with permission of IAEA)

**Table 13.6** Relationships of tritium concentrations from altitude in Aragats Mountain (Caucasus)

| Sampling place | Altitude (m) | Mean annual concentration in precipitation (TE) | |
|---|---|---|---|
| | | 1971 | 1972 |
| Oktemberian | 850 | 37 | 82 |
| Garnovit | 1,100 | 114 | 162 |
| Aragatz | 3,238 | 143 | 201 |
| Pamir (Abramov glaciar) | 4,500 | 65 | 72 |

precipitation on a global scale. This work was initiated in 1961 by the IAEA and the WMO jointly. In order to detect the tritium, deuterium, and oxygen-18 ($^{18}$O) content in precipitation, more than 100 meteorological stations linked to the WMO, located in different countries, were involved (see Fig. 4.5). The ocean samples were collected on islands and weather ships. Thus, the network of stations included the most characteristic points of the globe both on the continents and oceans in both the northern and southern hemisphere.

In 1965, in connection with the International Hydrological Decade program (1965–1974), the network of stations included additional stations for water sampling from rivers. However, the majority of rivers fell out of this network of stations and therefore, a representative river network was not established. Up to present, the network includes more than 100 stations plus many national points of observation at which the tritium content is measured and measurements of tritium content in precipitation continue.

Sampling and analysis has been performed according to the techniques developed by the IAEA. Samples of atmospheric waters, taking every month, corresponds the monthly average tritium content in precipitation. Tritium content in water samples was measured in low-level counting laboratories in the IAEA and in Canada, Denmark, India, Israel, New Zealand, Germany, Sweden, USA, USSR, and other countries.

All these data are being collected by the IAEA and after processing together with the results of analysis of the stable isotopes (deuterium and $^{18}$O) content, measured in the same samples, and also together with meteorological data, are published in special issues of Environmental Isotope Data (IAEA 1969–1994).

The tritium concentrations in precipitation may have substantial difference in individual fallouts, depending on their origin and trajectory of motion. However, in principle, distribution of the fallouts depends on mechanism of circulation of the atmosphere. The seasonal and annual variations are observed. Seasonal variations are related to the strengthening of the air masses exchange between spring and summer stratosphere and the troposphere. The effect leads to occurrence of the so-called spring–summer maximum in the annual tritium distribution. Weakening of this process in the winter and autumn leads to occurrence of the autumn–winter minimum.

The long-term variation of tritium concentration of the natural origin can be related to phases of the solar activity. This is because it occurs at antiphase with intensity of the galactic cosmic rays, which are accepted as a source of tritium.

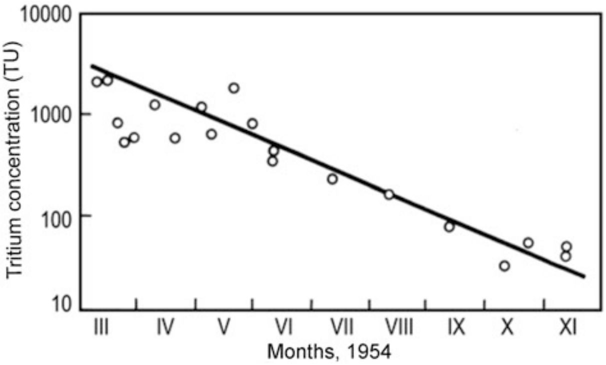


**Fig. 13.9** Changes of tritium concentration atmospheric precipitation over Ottawa (Canada) after thermonuclear test in 1 March 1954. (After Brown 1961)

Some researchers tried to study correlation between the long-term tritium variations, which were observed in Greenland glaciers formed before 1952, with solar activity. However, single-valued result was not found, for example, Begemann (1959) in the Greenland glaciers discovered negative correlation between the tritium concentration and solar maximum activity. Ravoire et al. (1970) in Antarctic snow (1950–1957), found this correlation is positive and Aegerter et al. (1967) discovered both types of correlation.

During atmospheric thermonuclear tests tritium in the form of HTO occurs both in the stratosphere and in the troposphere. Proportion of its amount depends on the height and power of the explosion. Tropospheric component of HTO must have the residence time compared with that of the tropospheric moisture, i.e., equal to several weeks. Experimental data proved this conclusion (Buttlar and Libby 1955). Figure 13.9 demonstrates changes of tritium concentration over Ottawa, Canada after thermonuclear test in 1 March 1954 (Brown 1961). Period of removal of half of the tritium from the troposphere here was 45 days. The close figure to this value was obtained by Buttlar and Libby by measurements of tritium in precipitation in Chicago.

The stratospheric tritium part is removed substantially lower. A velocity of this process corresponds with the velocity of exchange between the tropospheric and stratospheric air and have seasonal cyclic character. The annual tritium concentration changes in the Ottawa River water are shown in Fig. 13.10 (Brown 1970). Figure 13.11 demonstrates the annual means of tritium concentration changes over Moscow and in Moscow River (Russia) during the period of 1953–1969, obtained by the authors.

It follows from Figs. 13.10 and 13.11 that the entering of tritium into the atmosphere occurs during the 1954, 1956, 1958 tests. In the period of the moratorium from 1959 up to its interruption in September 1961, the tritium concentration within Moscow region has dropped from 760 to 200 TU. The period of removal of half tritium value for this time interval was equal to about 1 year. In September 1961, the thermonuclear tests were renewed and continued up to December 1962. In that

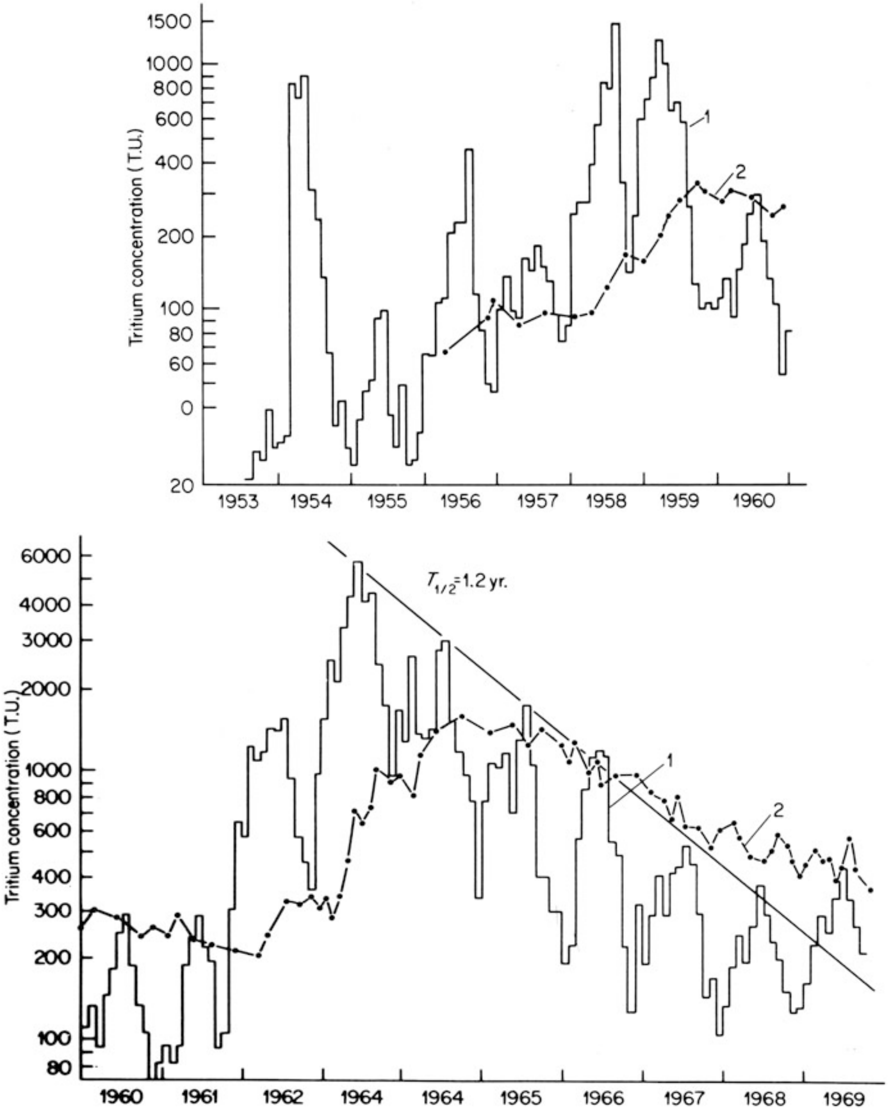


**Fig. 13.10** Tritium concentration change during 1953–1969 in precipitation (*1*) and in Ottawa River water (*2*). (After Brown 1970. © IAEA, reproduced with permission of IAEA).

period, the main part of bomb-tritium has accumulated in the stratosphere, which is observed up to now.

The maximum yearly means of tritium concentrations over Moscow region were reached 3,900 TU (see Fig. 13.11). After the thermonuclear test ban treaty in the three spheres had come into force, the stratospheric tritium reserve started to decrease with the period of 1.2 years up to 1967–1968, after that the decrease was slowing

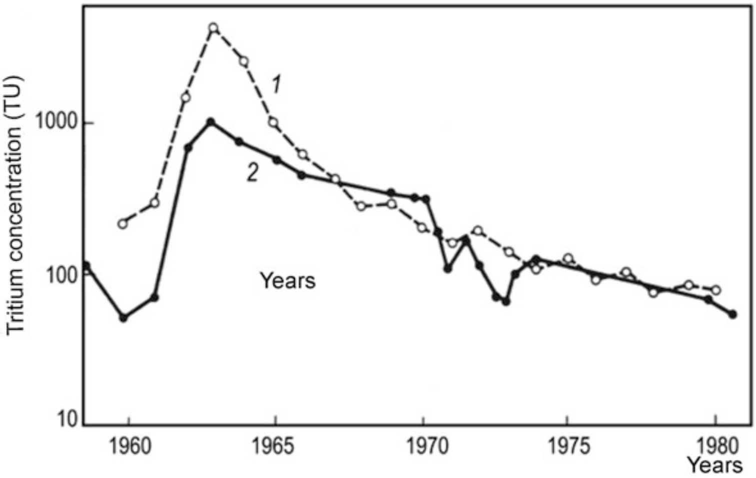
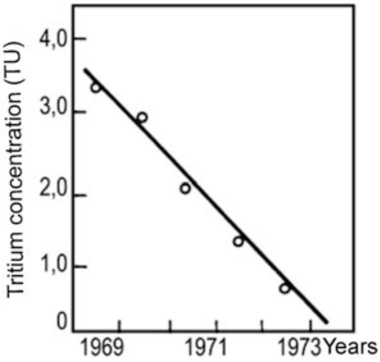


**Fig. 13.11** Mean annual distribution of tritium concentration in atmospheric precipitation over Moscow region (*1*) and in Moscow River water (*2*) 1958–1981

**Fig. 13.12** Changes of mean annual tritium concentration by the data of 18 stations over the USSR area



down. During 1969–1974 that period becomes equal about 3 years (see the graph on Fig. 13.12). This value was obtained by the authors on the basis of data over vast territories and, therefore, may be considered adequately authentic. One more explanation of the above phenomenon can be redistribution of tritium in stratosphere between the northern and southern hemispheres. During recent years this transfer was decreased due to approaching the quasiequilibrium state.

It was shown in the work of Weiss et al. (1979) that, starting from 1970, over the Central and Western Europe, technogenic tritium plays a notable role in the formation of its occurrence in precipitation. From here it follows that the sampling stations should be placed in appropriate distance from the industrial plants and institutions.

Variations of tritium concentrations in precipitation during spring and summer are determined by specific conditions of the mass air exchange between the stratosphere and the troposphere, resulting from their easier connection (see Fig. 13.9).

**Table 13.7** Seasonal distribution of tritium concentrations in precipitation for stations of the North hemisphere

| Month | Yearly means of concentration in precipitation (TU) | | | | | |
|---|---|---|---|---|---|---|
| | 1964 | 1965 | 1967 | 1968 | 1969 | Mean value |
| *0–20°N* | | | | | | |
| January | 1.09 | 1.13 | 1.26 | 0.94 | 0.99 | 1.07 |
| February | 1.17 | 1.29 | 1.18 | 1.06 | 1.04 | 1.12 |
| March | 1.17 | 1.28 | 1.20 | 1.24 | 1.23 | 1.19 |
| April | 1.30 | 1.07 | 1.27 | 1.09 | 1.03 | 1.13 |
| May | 1.31 | 1.23 | 1.07 | 1.16 | 1.04 | 1.13 |
| June | 1.34 | 1.40 | 1.30 | 1.10 | 1.09 | 1.22 |
| July | 1.44 | 1.24 | 1.13 | 1.27 | 1.34 | 1.35 |
| August | 0.96 | 0.84 | 0.92 | 1.09 | 1.24 | 0.99 |
| September | 0.71 | 0.66 | 0.83 | 0.88 | 0.92 | 0.78 |
| October | 0.51 | 0.62 | 0.66 | 0.72 | 0.77 | 0.64 |
| November | 0.51 | 0.62 | 0.68 | 0.75 | 0.66 | 0.63 |
| December | 0.49 | 0.62 | 0.51 | 0.70 | 0.64 | 0.58 |
| *20–90°N* | | | | | | |
| January | 0.89 | 0.63 | 0.73 | 0.46 | 0.63 | 0.70 |
| February | 1.09 | 0.98 | 0.90 | 0.80 | 0.76 | 0.89 |
| March | 1.18 | 1.20 | 1.09 | 1.04 | 1.04 | 1.08 |
| April | 1.46 | 1.46 | 1.22 | 1.19 | 1.11 | 1.29 |
| May | 1.67 | 1.54 | 1.60 | 1.42 | 1.49 | 1.57 |
| June | 1.70 | 1.73 | 1.58 | 1.59 | 1.62 | 1.64 |
| July | 1.41 | 1.51 | 1.36 | 1.44 | 1.47 | 1.45 |
| August | 0.99 | 1.10 | 1.17 | 1.28 | 1.29 | 1.18 |
| September | 0.56 | 0.60 | 0.88 | 0.86 | 0.80 | 0.74 |
| October | 0.43 | 0.43 | 0.54 | 0.60 | 0.63 | 0.53 |
| November | 0.31 | 0.35 | 0.48 | 0.54 | 0.50 | 0.44 |
| December | 0.32 | 0.36 | 0.46 | 0.77 | 0.64 | 0.50 |

The peak of the tritium concentrations in precipitation for the northern hemisphere is observed, as a rule, in June, and in the southern hemisphere in September. However, deviations from this rule are happened very often due to the meteorological peculiarities of differed years. This peak is occurred in a pure sight very seldom. In this connection, it is more correct to obtain average data for a number of regions with more or less identical physical-geographical characteristics at the same time interval. Tables 13.7 and 13.8 are an example of such an average. The tables were prepared on the basis of the data published by the IAEA (1969–1994) using more than 250 stations of the Earth's globe. For the former USSR area the author's own data were used.

Figure 13.13a shows the normalized seasonal variations of tritium in continental precipitation of the northern hemisphere. In Fig. 13.13b, the analogous data are shown for the latitudinal belt 20–90°S and in Fig. 13.14 the same for area of the former USSR. It is seen from the figures that in the equatorial belt between 20°S–0°–20°N the picture of tritium variation does not observed. There are a number of maximum peaks. However, values with minimum concentrations have less dispersion. In the northern hemisphere, those occur in November and in the southern are in May.

**Table 13.8** Seasonal distribution of tritium concentration in precipitation for stations of southern hemisphere

| Month | Yearly means of concentration in precipitation (TU) | | | | | |
|---|---|---|---|---|---|---|
| | 1965 | 1966 | 1967 | 1968 | 1969 | Mean value |
| *0–20°S* | | | | | | |
| January | 1.26 | 1.01 | 0.94 | 1.22 | 1.15 | 1.15 |
| March | 0.96 | 1.10 | 0.89 | 0.88 | 0.91 | 0.95 |
| April | 0.70 | 1.20 | 0.86 | 0.82 | 0.86 | 0.93 |
| May | 0.75 | 0.89 | 0.71 | 0.74 | 0.76 | 0.77 |
| June | 0.94 | 0.76 | 0.73 | 0.88 | 0.93 | 0.85 |
| July | 0.93 | 0.98 | 1.22 | 1.04 | 0.93 | 1.02 |
| August | 1.03 | 1.06 | 1.03 | 0.98 | 1.11 | 1.04 |
| September | 1.16 | 0.69 | 0.94 | 1.21 | 1.12 | 1.02 |
| October | 1.03 | 0.71 | 1.30 | 0.99 | 0.99 | 1.02 |
| November | 0.94 | 1.28 | 1.06 | 0.91 | 0.87 | 1.01 |
| December | 1.00 | 1.14 | 1.17 | 0.98 | 1.10 | 1.08 |
| *0–20°N* | | | | | | |
| January | 1.06 | 0.94 | 1.02 | 1.00 | 1.05 | 1.01 |
| February | 1.01 | 0.87 | 0.79 | 1.29 | 0.89 | 0.97 |
| March | 0.67 | 0.90 | 0.78 | 0.67 | 0.67 | 0.74 |
| April | 0.77 | 0.64 | 0.86 | 0.70 | 0.70 | 0.73 |
| May | 0.63 | 0.73 | 0.79 | 0.71 | 0.73 | 0.86 |
| June | 0.72 | 0.59 | 0.70 | 0.71 | 0.75 | 0.69 |
| July | 0.82 | 0.88 | 0.98 | 0.86 | 0.84 | 0.88 |
| August | 1.43 | 1.18 | 1.27 | 1.38 | 1.43 | 1.34 |
| September | 1.56 | 1.66 | 1.35 | 1.54 | 1.60 | 1.54 |
| October | 1.29 | 1.43 | 1.16 | 1.22 | 1.27 | 1.27 |
| November | 0.97 | 1.06 | 1,02 | 1.00 | 1.,06 | 1.02 |
| December | 1.06 | 1.10 | 1.28 | 0.93 | 0.90 | 1.06 |

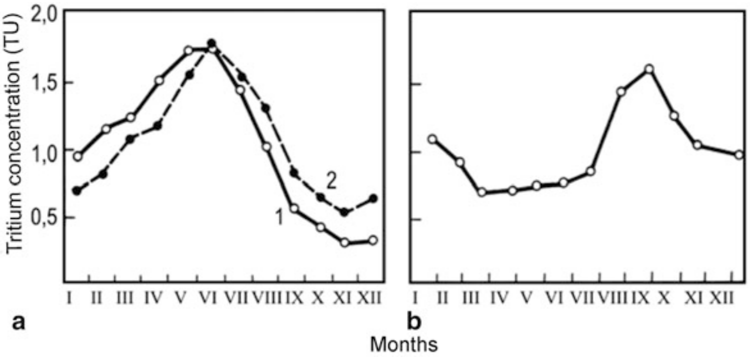


**Fig. 13.13** Seasonal change of ratio between mean monthly and yearly means of tritium concentration in precipitation: (**a**) over the continents of the northern hemisphere in 1964 (*1*) and in 1969 (*2*); (**b**) over the southern hemisphere in 1969

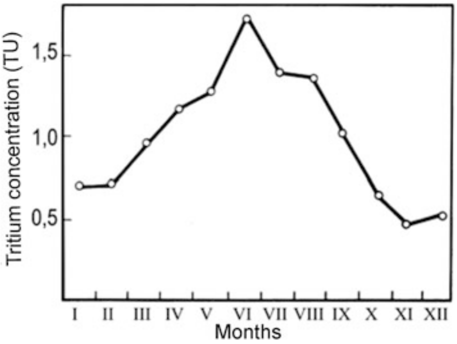


**Fig. 13.14** Seasonal change of ratio between mean monthly and mean yearly tritium concentrations for 19 stations of the former USSR area in 1969–1974

Sometimes a substantial deviation in mean monthly tritium values from these for seasonal variations is observed. In this connection, it is interesting to draw attention on the situation observed in a number of stations located in East European and South-Asian regions in December 1969. The tritium concentration in precipitation here was accounted by 0.64 compared to its seasonal mean value (Table 13.9). It seems, this was caused by the air intrude with high tritium content from the upper troposphere into narrow meridian direction on Moscow–Tbilisi–Teheran.

## *13.2.4 Global Distribution of Tritium*

A general picture of global tritium distribution over time (Fig. 13.15) shows that although the degree of decrease of tritium content depends upon the site of a given place, the general features of its distribution remains unchanged. The observed constancy in the character of tritium content variations in precipitation with time indicates the global principle of increases of tritium concentration with latitude, both for oceanic and continental regions. This may be observed while plotting general pictures of global tritium distribution in time. Figure 13.15 gives such pictures for 1964, 1969, and 1975 prepared by the authors. The figure gives general idea

**Table 13.9** Tritium concentrations in precipitation for some European and Asian stations in December 1969

| Station | Tritium concentration (TE) | | Norm for December 1969 | Ratio of the norm in December 1969 to the yearly means |
|---|---|---|---|---|
| | December 1969 | Yearly means | | |
| Arhangelsk | 133 | 194 | 0.69 | 1.07 |
| Odessa | 134 | 207 | 0.68 | 1.01 |
| Vien | 119 | 210 | 0.57 | 0.88 |
| Ankara | 54 | 217 | 0.25 | 0.39 |
| Teheran | 265 | 133 | 1.99 | 3.11 |
| Moscow | 500 | 233 | 2.24 | 3.50 |
| Tbilisi | 720 | 218 | 3.30 | 5.16 |

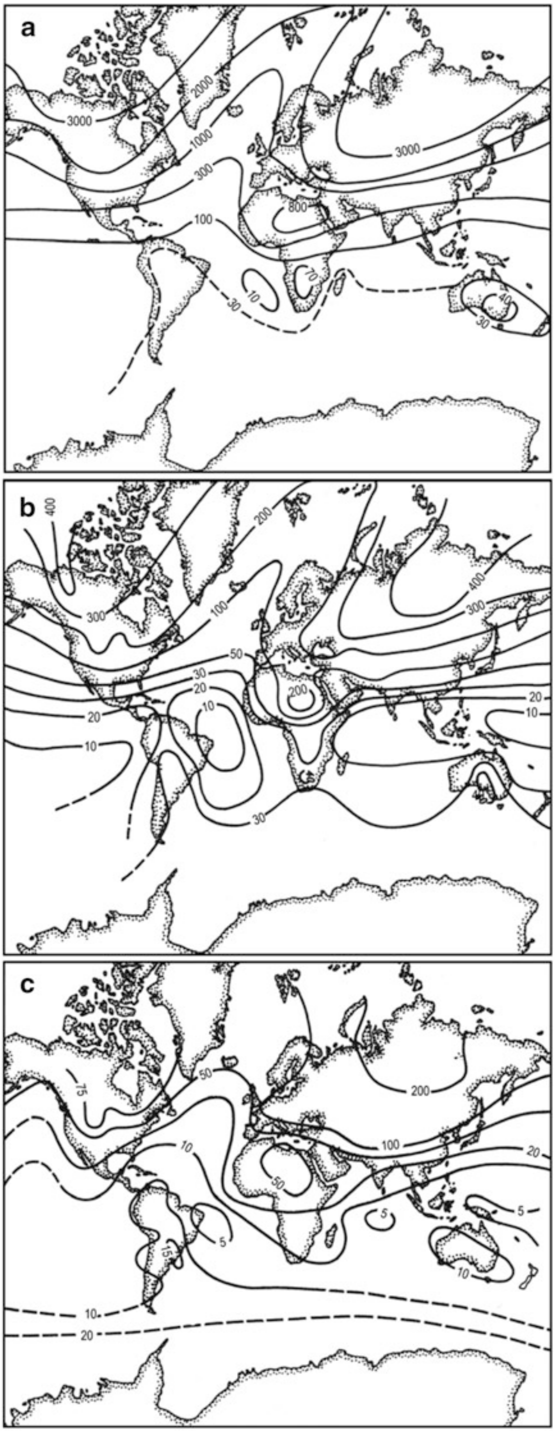


**Fig. 13.15** Isolines of yearly weighted tritium means in precipitation of the Earth's globe in 1964 (**a**), 1969 (**b**), and 1975 (**c**). (After Romanov 1978)

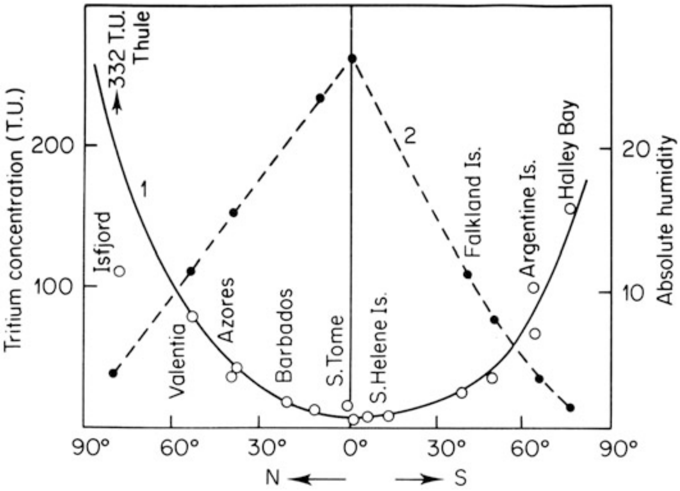


**Fig. 13.16** Tritium concentration profile in precipitation (*1*) and atmospheric moisture (*2*) for Atlantic Ocean island stations; average over 1969. (Romanov 1978)

about global tritium distribution in precipitation and changes in time of the distribution due to tritium transfer into the oceans and interhemispheric redistribution in the stratosphere. The similarity of the isolines of the tritium concentrations during 1964–1975 is the evidence of constancy and regular character of its distribution in precipitation.

The latitude effect of the meridional distribution of tritium is its second main regularity, which means decrease of the tritium concentration with latitude both for the oceans and the continents. Figure 13.16 demonstrates this effect for precipitation over the Atlantic Ocean. The mean values of the absolute air humidity are although shown on the graph. Analogous picture for the Pacific Ocean island stations in Fig. 13.17 is presented.

Continental area has a considerable effect on global tritium distribution in precipitation. The total continental area of the northern hemisphere is greater than that of the southern hemisphere. Figure 13.17 also represents the effect of tritium redistribution between the northern and southern hemispheres, which resulted in the relative equality of the tritium content in both of the hemispheres in 1969.

The next characteristic peculiarity, observed in the general picture of tritium fallout, is the influence of continents upon its distribution. At the same latitude, raised tritium concentration is observed above the continents where active enrichment of atmospheric moisture with tritium in the air masses exchange between the troposphere and stratosphere takes place. The continental effect and effect of the relief heights is demonstrated in Fig. 13.18.

Here from 35 to 40°N a number of huge mountain ridges up to 7,000 m in height stretch latitudinally (the Himalayas, Hindu Kush, Tien Shan, and Pamirs). These mountainous ridges stop the motion of atmospheric moisture enriched with tritium over the European–Asiatic continent to the Indian Ocean. At the same time, the same

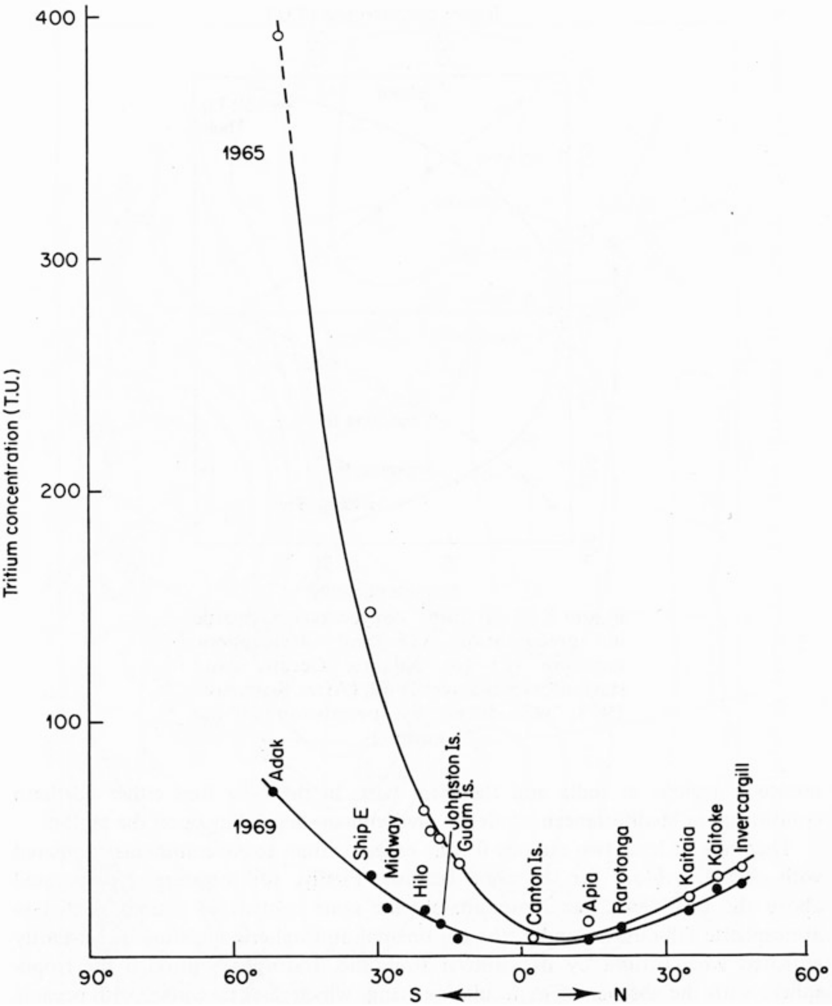


**Fig. 13.17** Tritium concentration profile in precipitation for Pacific Ocean island stations; average over 1965 (*1*) and over 1969 (*2*). (After Romanov 1978)

mountainous system prevents the transfer of atmospheric moisture depleted in tritium from the Indian Ocean and Persian Gulf to Siberia and Middle Asia. These factors cause a large gradient of tritium concentration in precipitation over this mountainous region. In the Asian plain, in the region located above 45°N the tritium content in precipitation is governed by the latitude effect.

Figure 13.19 shows the curve of the average tritium content in precipitation for the latitudinal belt 45–60°N, plotted on the basis of data obtained during the second half of 1969 (Ferronsky et al. 1975) and demonstrated also the continental effect.

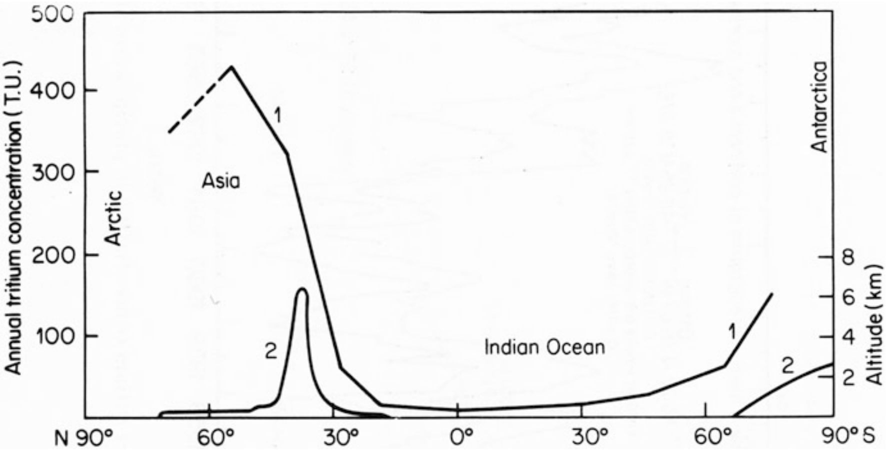


**Fig. 13.18** Latitudinal variation of tritium concentration in precipitation at 80–90°E (*1*) relative to relief heights (*2*); average over 1969. (After Romanov 1978)

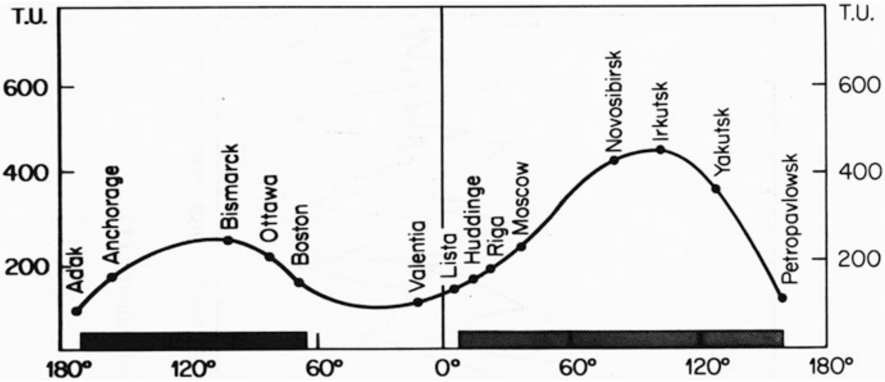


**Fig. 13.19** Variation of tritium concentration in precipitation for stations at latitudes 45–60°N; average over July–December, 1969. (After Ferronsky et al. 1975)

One can see the enrichment of atmospheric moisture with tritium in the course of its motion across the European–Asiatic and North American continents, and decreases of the tritium content during the formation of atmospheric moisture above the Atlantic and Pacific Oceans.

## 13.3 Regional Distribution of Tritium in Precipitation

It follows from the global distribution of tritium in precipitation, presented in Fig. 13.15 that, beside some general features, there are some regional effects. These effects were analyzed by Thatcher and Payne (1965) and Romanov (1978), from whom the following information has been gathered.

### *13.3.1 The North American Continent*

There are more than 30 stations located in this continent, aimed at systematic measurements of the tritium content in precipitation. At the station located near Ottawa (Canada), systematic measurements were made from 1954 (see Fig. 13.10). Tritium variations with time found at this station are typical for the whole continent. Maximum tritium content occurs in the central part of Canada (Edmonton, Fort Smith), where, in April 1963, the concentration of tritium reached 10,000 TU.

Precipitation falling out above the North American continent is formed mainly over the Atlantic Ocean and the Gulf of Mexico (see Fig. 13.15). The mountain chain of the Western Cordilleras and the warm Golf Stream current prevents the movement of Pacific air masses. The great gradient of the tritium concentrations at the west coast is evidence of this mountain effect. However, the contribution of Pacific Ocean moisture coming from Alaska results in a deep bend of concentration isolines toward the continent (Fig. 13.15). Both the continental and latitudinal effects are evident in this region.

### *13.3.2 The European–Asiatic Continent*

There are about 60 observation stations in the Scandinavian countries and Western and Central Europe, 18 stations in European and 19 in Asian part in the former USSR, 10 stations in Near East countries, and about 10 stations in South-East Asia and the Far East.

The Atlantic Ocean is the main source of precipitation over the major part of the European–Asiatic continent. Here, the preferred direction of air mass movement is from west to east. Thus, moisture depleted in tritium while passing over the Atlantic coast of Europe gradually becomes enriched in the course of inland movement. Valentia (Ireland) and Vienna (Austria) (Fig. 13.20) are typical points, corresponding to the Atlantic coast and continental West Europe, with a time-dependent distribution of tritium in precipitation.

The distribution of tritium in the southern part of Europe is affected markedly by moisture coming from the Mediterranean Sea. In addition to continental effect, industrial injections of tritium are significantly increased tritium concentrations over the continental Europe. The studies of Weiss et al. (1979) demonstrate this conclusion (Fig. 13.21).

The long-term picture of tritium distribution in precipitation in principle looks like the Central European picture (see Fig. 13.11). A total yearly means of tritium concentrations decrease over the USSR territory to the end of 1980s of the last

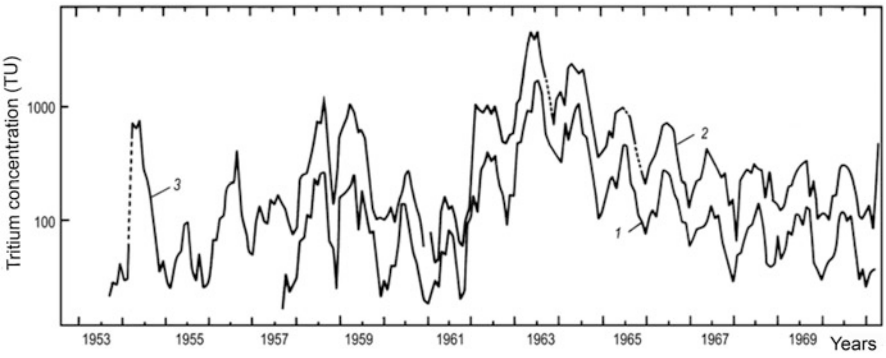


**Fig. 13.20** Variation of tritium concentration in precipitation at Valentia (*1*), Vienna (*2*) and Ottawa (*3*) in 1953–1971. Correlation between Vienna and Ottawa is 17%

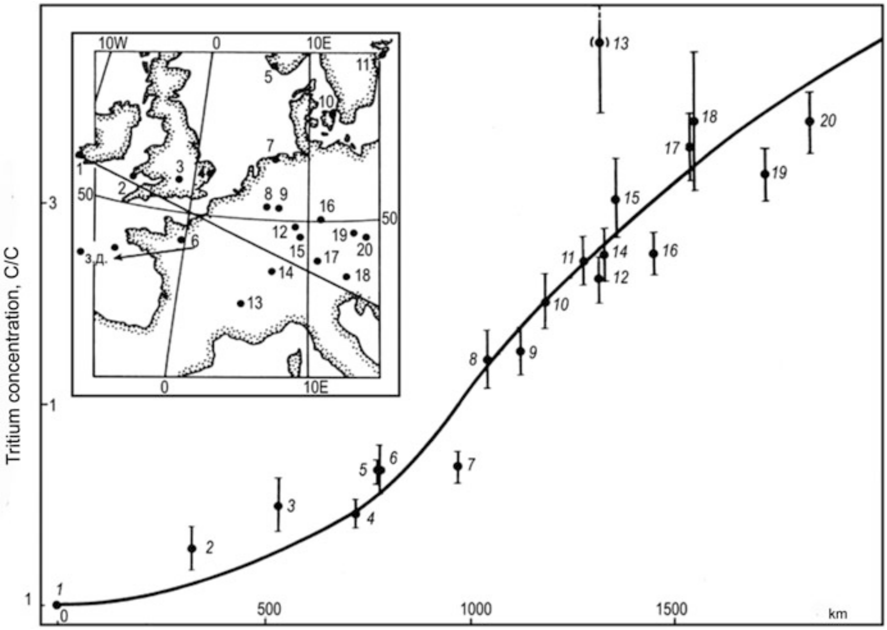


**Fig. 13.21** Continental effect of tritium content in precipitation over Western and Central Europe relative to those at the reference station Valentia, taken from observations up to 1970. (After Weiss et al. 1979. © IAEA, reproduced with permission of IAEA)

century, without taking into account the 1975 and 1978 maximums, is described by the equation:

$$C = 2.26\exp(-0.096t),$$

where $C$ is the ratio of tritium concentration for a particular year to the concentration in 1979.

**Table 13.10** Normalized monthly means of tritium concentrations in precipitation over the former USSR for 1972–1979

| Month | Normalized monthly means of concentrations | | | | |
|---|---|---|---|---|---|
| | 1972 | 1975 | 1976 | 1978 | 1979 |
| January | 0.91 | 0.62 | 0.74 | 0.54 | 0.79 |
| February | 0.72 | 0.82 | 0.77 | 0.89 | 0.82 |
| March | 0.95 | 1.08 | 0.88 | 1.03 | 1.01 |
| April | 1.18 | 1.55 | 0.84 | 1.07 | 1.11 |
| May | 1.20 | 1.68 | 1.22 | 1.37 | 1.30 |
| June | 1.63 | 1.31 | 1.46 | 1.47 | 1.41 |
| July | 1.49 | 1.23 | 1.55 | 1.39 | 1.35 |
| August | 1.12 | 1.05 | 1.41 | 1.28 | 1.12 |
| September | 0.86 | 0.92 | 1.06 | 0.98 | 0.94 |
| October | 0.71 | 0.63 | 0.86 | 0.65 | 0.82 |
| November | 0.62 | 0.53 | 0.64 | 0.75 | 0.65 |
| December | 0.60 | 0.58 | 0.57 | 0.57 | 0.68 |

The correlation coefficient of this equation is equal to 0.96. Seasonal effects of tritium distribution in time are very clearly expressed (see Fig. 13.14). The monthly means of tritium concentrations for 1972–1979 are given in Table 13.10.

The peculiarity of the European–Asiatic region of the former USSR is the result of high mountainous chains in the south, preventing the arrival of atmospheric moisture from the Indian Ocean. The preferred direction of moisture movement over this territory is toward the east. This effect is manifested particularly in the autumn–winter period. In the summer, when the cyclonic activity becomes stronger, air masses from the South China Sea break through East Siberian and reach Central Asia up to Irkutsk. Pacific air masses depleted in tritium also reach Irkutsk. Thus, it was found that at the Far East stations of Skovorodino, Khabarovsk, and Holmsk the range of tritium variation from month to month may be rather great, depending on the source of moisture coming either from the Atlantic Ocean or the Pacific Ocean (Figs. 13.22 and 13.23).

The Baltic, Black, and partly Mediterranean Seas make substantial influence on the European yearly means of tritium concentrations. This conclusion is proved by the isoconcentration lines of the near Baltic, Black Sea, and Caucasus regions where tritium values are lower compared to the neighboring areas.

Being averaged during the 6 years of observation, the data of Fig. 13.22 are representative and indicate features of the annual mean water transference in the atmosphere over the USSR area. The highest mean annual tritium concentrations in precipitation were detected near Irkutsk. In 1979 (Fig. 13.23), the shape of isolines extends along meridian plane direction and the maximum gradient of concentrations is observed in the domain of 130–145°E. It is obvious, that such a configuration determined the border of influence of the air masses which transfer moisture from the Pacific. The bend of the isolines to the continental depth here along meridian of to 90°E can be considered as a consequence of the Atlantic air masses intervention in this region with farther transfer to the south–east direction. To the contrary of the Atlantic air masses, those from the Pacific move in wide front without a direction privilege. Analyses of tritium distribution in precipitation on the European–Asiatic

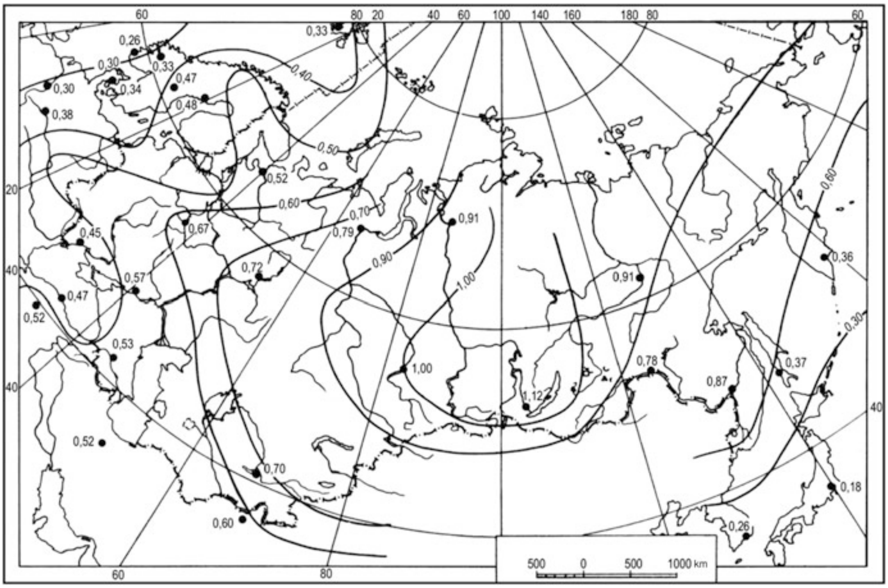


**Fig. 13.22** Distribution of tritium concentration in precipitation for the former USSR, normalized relative to 200 TU, and averaged over 1969–1974

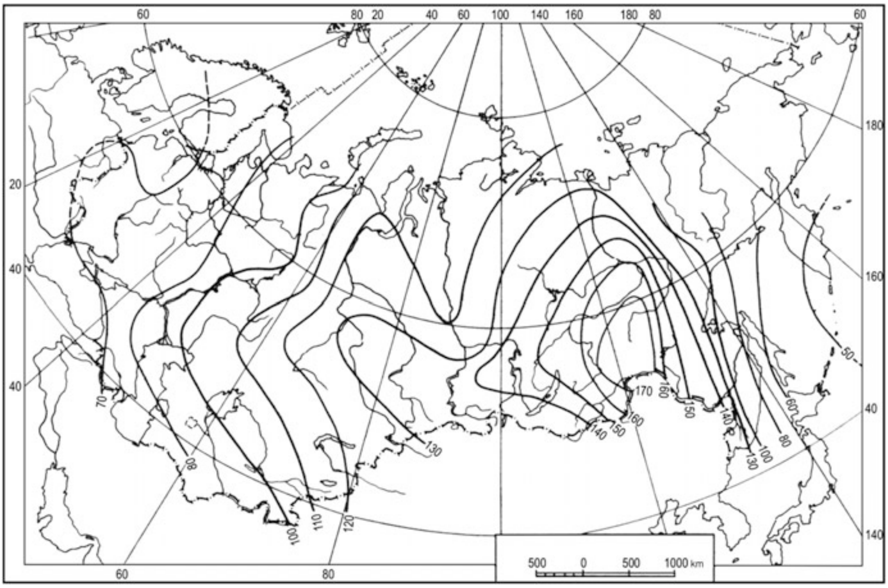


**Fig. 13.23** Distribution of yearly (1979) means of tritium concentration in precipitation for the USSR area

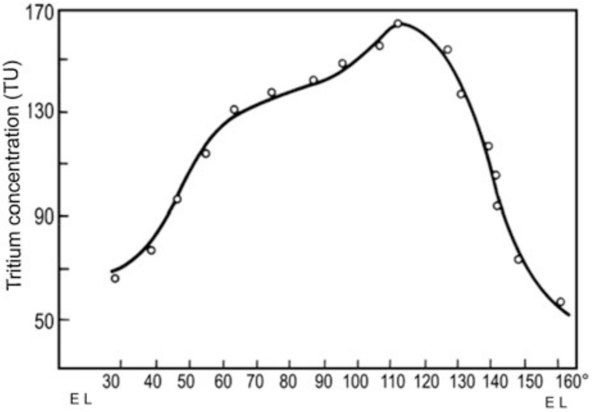


**Fig. 13.24** Annual longitudinal means of tritium concentrations in precipitation along 55°N over the former USSR territory in 1979

continent have shown that tritium fallout is very sensitive instrument to dynamics of the atmospheric moisture.

The continental effect over the former USSR territory is developed very clear (Fig. 13.24).

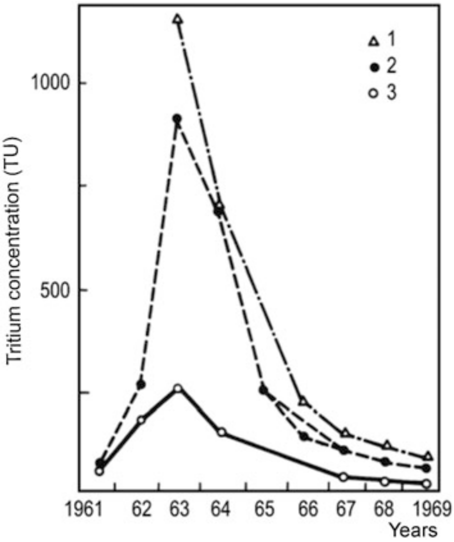
South-East Asia and the Far East may be considered as independent regions from the viewpoint of general principles of tritium distribution in precipitation. The former is a region of monsoon activity with downpours of rain occurring from June to September. During this period the tritium content in precipitation arriving from the Indian Ocean declines sharply. The region is presented by the stations Bahrain, Karachi, New Delhi, Mumbai, and Singapore.

In the Far East region the Pacific moisture plays an important role in the formation of precipitation. When the Pacific moisture is with the continental moisture, the tritium concentration in precipitation decreases. As a result, the tritium concentration in the spring–summer season never reaches maximum value. The region is presented by the stations Hong Kong, Pohang, Tokyo, Habarovsk, and Holmsk. Figure 13.25 shows the yearly (1979) means of tritium concentrations of this region with its distribution effects.

### 13.3.3 The African Continent

The conditions of the formation of tritium are different in the northern and southern parts of this continent, relative to the equator, because of differences in the formation of atmospheric circulation. This effect was particularly evident during the period of thermonuclear tests (see Fig. 13.15). The annual mean concentration of tritium in precipitation was 125 TU in 1963 in Entebbe (0° 05′ N). At the same time in Dar-es-Salaam (6° 52′ S) it was only 17 TU, which reflects the restricted connection between the hemispheres relative to air mass circulation. Up to 1968 the tritium content in precipitation measured in the northern and southern parts of the continent

**Fig. 13.25** Annual means of tritium concentrations in precipitation in 1979 for stations: Pohang (*1*), Tokyo (*2*), Hong Kong (*3*)



was approximately the same. However, at the same time, the gradient of tritium concentrations between the equator and the poles was great (Fig. 13.26), which is explained by the continental effect and the hemispheres gravitational potential restriction.

The results of yearly measurements of tritium content in precipitation at four stations located in North Africa are presented in Fig. 13.27. As in the hemisphere as a whole, the maximum concentrations were observed in 1963, and the decrease

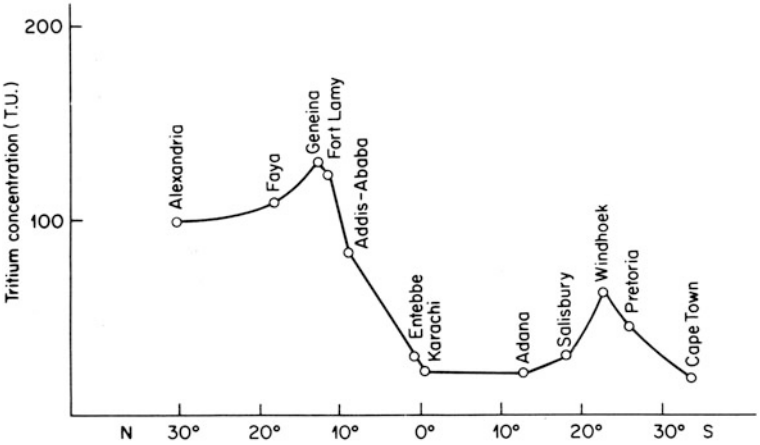


**Fig. 13.26** Meridional distribution of tritium concentration in precipitation over the African continent, averaged over 1968. (After Romanov 1978)

**Fig. 13.27** Variation of annual tritium concentration in precipitation over North Africa for Alexandria (30° 20′°N) (*1*), Khartoum (15° 60′°N) (*2*), Fort Lamy (12° 13′°N) (*3*), Entebbe (0° 05′°N) (*4*). (After Romanov 1978)

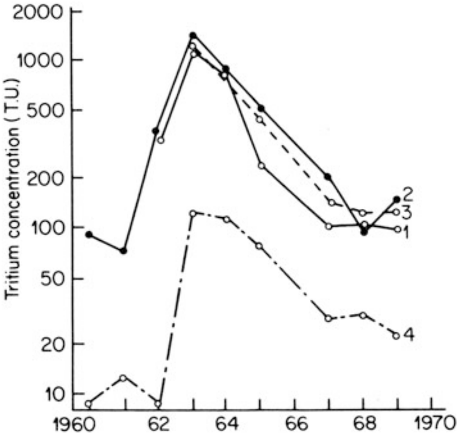
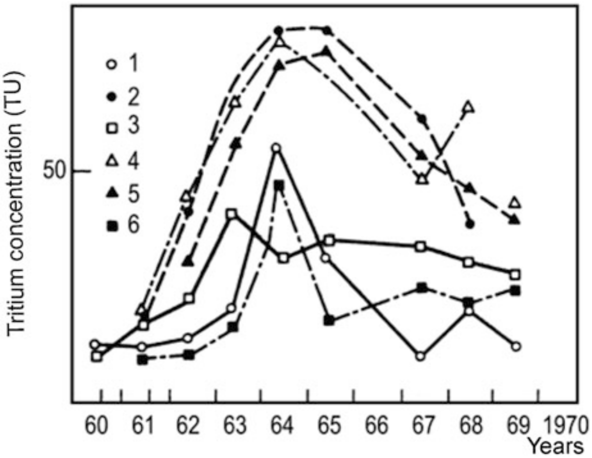


**Fig. 13.28** Variation of annual tritium concentration in precipitation over Equatorial Africa for Dar-es-Saalam (*1*), Kinshasa (*2*), Harare (*3*), Windhoek (*4*), Pretoria (*5*), Cape Town (*6*). (After Romanov 1978)



of concentrations with time slowed up to 1967. The half-removal period of tritium estimated for Alexandria region, locater in the north of the continent, was 1.1 years. For Khartoum and Fort Lamy (12–15°N) this period is equal to 1.5 years and for Entebbe (0° 05′°N) is 2.2 years.

The results of yearly measurements of tritium concentration in precipitation at equatorial African stations are shown in Fig. 13.28. The same effects as for southern stations are observed here.

Maximum tritium concentrations were observed in South Africa in 1964 and decrease in tritium content occurred slowly over the period of half-removal equal to 5–6 years. The seasonal variations of tritium concentrations correspond maximum to September and minimum to March. The latitudinal and continental effects are clearly evident.

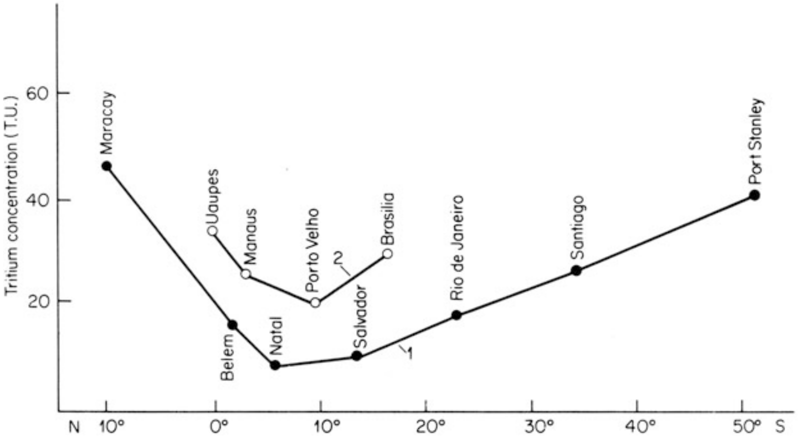


**Fig. 13.29** Variation of tritium concentration in precipitation over the South American continent for costal (*1*) and inland (*2*) stations, averaged over 1967. (After Romanov 1978)

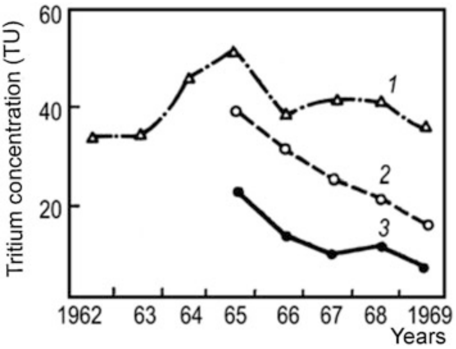


**Fig. 13.30** Annual means of tritium concentration in precipitation over the South America for stations: Stanley (*1*), Manaus (*2*), Salvador (*3*)

### *13.3.4 The South American Continent*

There are about 20 stations of IAEA/WMO. Figure 13.29 shows the meridional distribution of tritium concentration in precipitation during 1967 for the continental and costal stations.

The continent as a whole is characterized by relatively low values of tritium with a maximum observed near the Falkland Islands in 1965, according to yearly observations. The effect of the mixing of Atlantic and Pacific moisture is the bending of tritium isolines toward the continent to the north-west. The Amazon River basin in the northern part of the continent and the southern part of the Caribbean Sea basin represent an equatorial region with characteristic features. Minimal values for coastal and inland stations were observed in the region of 10°S with maximum values in 1965 (Fig. 13.30).

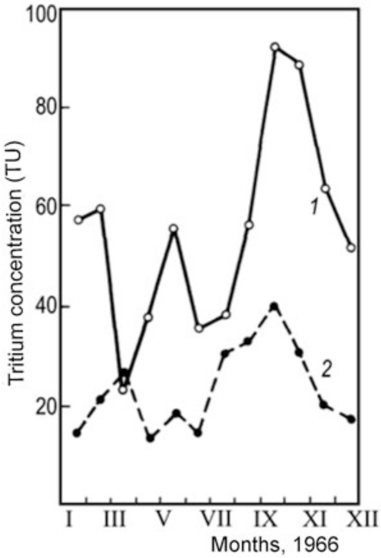


**Fig. 13.31** Variation of annual tritium concentrations in Melbourne (*1*) and Kaitaia (*2*) for 1962–1968. (After Romanov 1978)

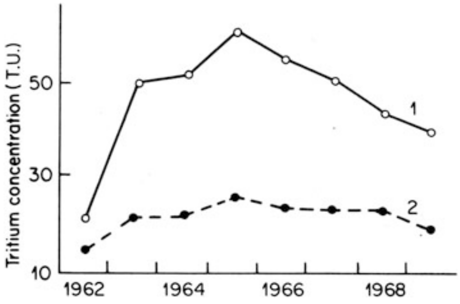


**Fig. 13.32** Seasonal variation of tritium concentration in precipitation over Australia (*1*) and New Zealand (*2*) for 1966. (After Romanov 1978)

## *13.3.5 Australia and New Zealand*

The continental effect of tritium distribution in precipitation can be clearly demonstrated in the small Australian continent and the New Zealand Islands. Figures 13.31 and 13.32 show data for annual and seasonal variation of tritium concentration in the stations Melbourne and Kaitaia. The maximum yearly concentration occurred in 1965, i.e., 2 years later than a similar maximum in the northern hemisphere. The seasonal variations of tritium concentrations are typical with maximum in September and minimum in March.

From the spatial picture of tritium distribution averaged during a number of years of systematic observations, presented in Fig. 13.33, it follows that the region of the maximum tritium concentrations lies in the south-eastern part of the continent (the Melbourne region). This indicates the preferential continuous transition of atmospheric moisture from the north-west to the south-east. This is also evidenced by tritium content in precipitation over the southern part of New Zealand. The tritium distribution picture permits the application of balancing equations for accounting

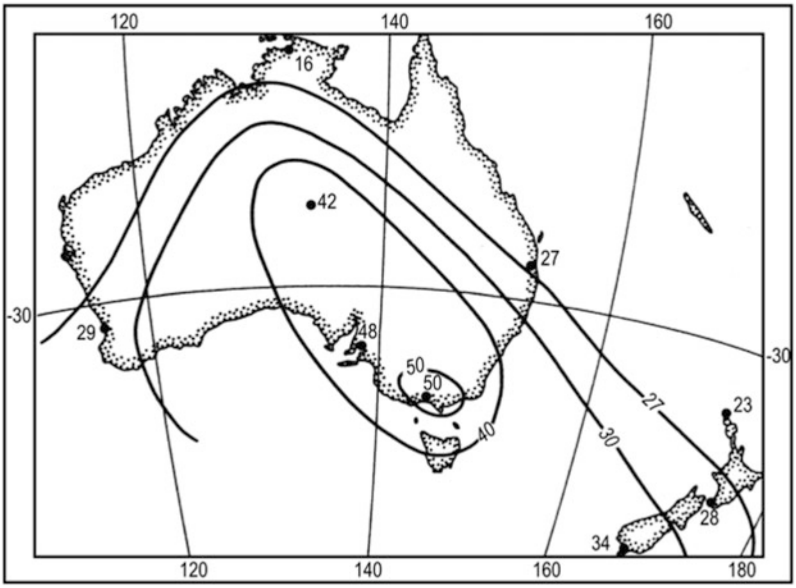


**Fig. 13.33** Spatial distribution of tritium concentrations over Australia and New Zealand, averaged over 1963–1969. (After Romanov 1978)

tritium and moisture transfer in order to estimate atmospheric moisture release over the continent.

### *13.3.6 Antarctic*

Jouzel et al. (1979) presented the most complete results on the tritium formation of snow precipitation over the Antarctic. In accordance with their data, which does not differ from other researchers, before the thermonuclear tests tritium concentration were not exceeded 34 TU. The thermonuclear tritium traces after 1952 USA tests were found in a snow layer dated by 1954. The following later on thermonuclear tests (1954–1958) were made tritium peaks delayed also with 2 years. However, the most powerful explosions in the northern hemisphere in 1961–1962 occurred in the southern hemisphere after 2–4 years. The thermonuclear tests done by France in southern hemisphere also accompanied with increase of tritium concentrations.

The only regional IAEA/WMO station on systematic sampling for isotope analysis was Halley Bay. The maximum of tritium concentration within long time observation was fixed in 1969 (Fig. 13.34). The seasonal peak is observed in August–September.

The above authors explained by winter exchange between the stratosphere and atmosphere in the polar region and by direct fallout of precipitation from the overcooled low stratosphere during arctic winter that the high level of tritium concentration is up to 1,800 TU per year.

The continental effect in Antarctic is markedly observed.

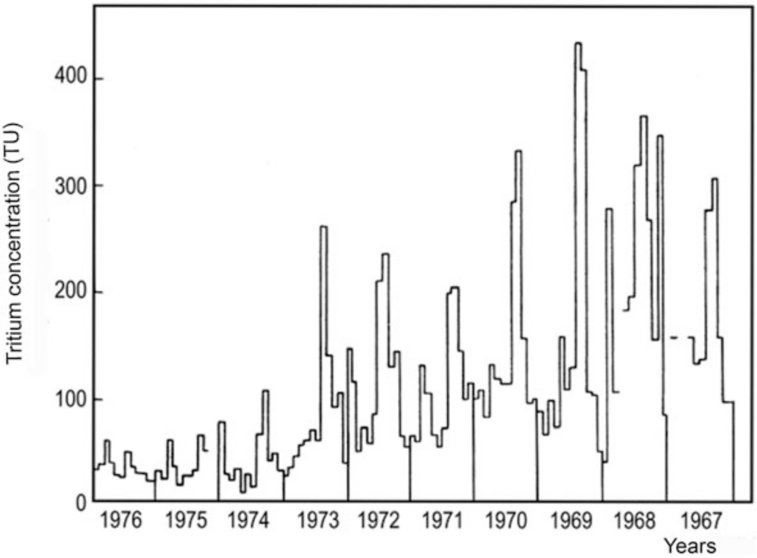


**Fig. 13.34** Variation of tritium concentration in precipitation for Halley Bay (Antarctic) during 1967–1976

### 13.3.7 Tritium in Precipitation over the Oceans

A general picture of the tritium distribution in precipitation over the oceans can be seen in Fig. 13.15. There are three regions characterized by minimal concentrations: (1) The Pacific Ocean (10°N–25°S; 160°E–100°W), (2) The Atlantic Ocean (5°N–20°S; 40°W–0°E), and (3) The Indian Ocean (15°N–25°S; 60°E–100°W).

Such a distribution of tritium in precipitation can be accounted for by intense water exchange between the atmosphere and the oceans, which results in the intense dilution of atmospheric tritium with moisture which is depleted in tritium. Tritium content in atmospheric precipitation gradually increases to the north and to the south of these regions, reflecting the main features of the moisture exchange between the atmosphere and the ocean. Relationship between the atmospheric moisture and the tritium concentration is shown in Fig. 13.16.

## 13.4 Formation of Tritium Concentrations in the Atmosphere

General principles observed from the picture of tritium concentration, related to latitudinal distribution and seasonal cycles, indicate the existence of a strict mechanism which governs the process of tritium distribution and concentration to precipitation.

In the period of intensive thermonuclear tests the release of tritium in the stratosphere occurred periodically from individual points where the explosions took place. At the same time, the average concentration of tritium fallout does not depend upon the place of injection but is related to latitude and time of the year. This fact has resulted in the conclusion that the upper layer of the atmosphere (its stratosphere) is the reservoir where the accumulation and latitudinal redistribution of tritium occurs on a global scale and from which seasonal tritium releases to the lower atmospheric layer (troposphere) take place. Precipitation is formed in the troposphere. Such a reservoir exists for each hemisphere independently and the relationship between them is rather restricted. The mechanism of formation of tritium concentrations is presented as follows. The oceanic water, evaporated from its surface and having low tritium concentration, moves by the rising up air flows with velocity of about by 3–5 m/s. In the case of unstable thermal atmospheric stratification the velocity may overreach 10 m/s. The created water vapor during the day and night is roused several kilometers in high. On the other hand, the process of mixing of the stratosphere and troposphere leads to interference to the last of enriched by tritium water vapor.

The vertical distribution of tritium shows that its interference into the upper layers of the troposphere begins in December and continues up to June–July. In winter time, the tritium transfer is made by the eddy flows and in spring and summer by high tropic cyclones. In Antarctic region, in winter time, a direct condensation of vapor from the overcooled lower stratosphere is possible (Jouzel et al. 1979). The process of the tritium moisture enrichment in the clouds is continued due to the molecular exchange.

The idea of the accumulation of radioactive products of thermonuclear tests in the stratosphere, with their subsequent redistribution and injection into the troposphere, where precipitation is formed, was first suggested by Libby in 1956 (Libby 1963). Later on, attempts were made to develop this idea and to construct the box model of interacting exchangeable reservoirs: the stratosphere, the troposphere, and the ocean. Investigations were mainly aimed at determining the residence time of a radioactive tracer in each of the exchangeable reservoirs. The final goal of these studies was to fix a relationship between the residence time of a tracer in the stratosphere and the motion of air masses in the stratosphere and troposphere.

In estimating the residence time of tritium in the stratosphere, it was assumed that the release of tritium into the troposphere is exponential. Thus, the residence time of tritium in the reservoir was taken, by the analogy with its half-life, to be the time required for one half of the amount to be discharged from the stratosphere.

On the basis of experimental data concerning tritium concentrations in precipitation measured after 1953 at the two stations of Vienna and Valentia (see Fig. 13.20), which represent typical continental and coastal regions in terms of fallout, it was found that the residence time of tritium in the stratosphere is equal to 1 year (Schell and Sauzay 1970). According to the data of Brown (1970) for the Ottawa River Valley it is equal to 1.2 years. As a result of the observed residence time of tritium in the stratosphere, its total storage (see Fig. 13.2), and the half-life removal, it can be estimated that by 1970 the tritium concentration in precipitation should already have been close to the natural concentration. At the same time, according to experimental data obtained for Western Europe (see Fig. 13.20) and North America (see Fig. 13.10) from the beginning of 1967, the tritium content in precipitation in the northern hemisphere remains constant at a level of 150–200 TU and, by Romanov's estimations (Romanov 1978), decreases with a half-life removal time of about 3 years. This tritium content is an order of magnitude greater than natural tritium concentrations in precipitation. Different causes of this phenomenon were considered, particularly those related to the injection of tritium from thermonuclear tests conducted in the atmosphere during the preceding years. However, in accordance with the measures carried out at a number of stations (e.g., in Tokyo), the increase in tritium concentration in fallout is insignificant because these explosions were not very powerful and provided only small concentrations of tritium to the stratosphere (see Fig. 13.2), where the maximum concentration occurred between 1967 and 1970. Another source of tritium contribution to the atmosphere may be the various installations of the atomic industry. This idea has been well demonstrated by Weiss et al. (1979). However, as pointed out earlier, the possible input of tritium into the stratosphere from this source should be negligible and this tritium should have only a local effect upon sampling stations located near to nuclear plants.

Therefore, the residence time of tritium in the stratosphere (1–3 years) does not remain constant and the distribution and mixing of tritium in the atmosphere is a more complicated process than that described by the model of exchangeable reservoirs.

The questions of interpretation of global tritium distribution in precipitation were studied by a number of researchers (Eriksson 1965a; Libby 1963; Smith 1966; Taylor 1968). In one of the works (Schell et al. 1970), an attempt was made to develop a general model of tracer release from the stratosphere into precipitation in which the injection, exchange, evaporation, and condensation of the water vapor would be related to the meteorological parameters of the troposphere.

The model is based on the following physical reasoning. The exchange of air masses between the stratosphere and troposphere occurs mainly due to powerful air streams being thrown down periodically into the troposphere as a kind of trough or trench. This process coincides with the observed spring maximum of radioactive falls in precipitation at mid-latitudes of the northern hemisphere. Therefore, in the general mechanism of air masses exchange between the two reservoirs, the process of stratospheric air transfer to the troposphere due to diffusion is a secondary factor. The periodic rushes of the dry stratospheric air into the troposphere which contains excessive concentrations of radioactive substances and have large potential velocities determine the mechanism of stratospheric–tropospheric exchange of air masses.

Another process responsible for the ejection of highly radioactive stratospheric air pertains to powerful convective storm fluxes rushing into the stratosphere. These air fluxes, containing a large amount of water vapor, are mixing with radioactive substances and return with a high radioactive content as subsequent precipitation.

It has been found that the greatest concentrations of various radioactive nuclei, e.g., $^{90}$Sr, $^{14}$C, and T, in precipitation always occur in the spring–summer period. However, the maximum T-values appear with a delay of 1 month compared with that of Strontium-90 ($^{90}$Sr) and 1–2 months earlier than the maximum $^{14}$C-values at the same latitude. The reason for this lies in the differences in their masses and physicochemical properties relative to those of the other atmospheric constituents. In the stratosphere, the behavior of tritium a constituent of water molecules HTO, is the same as that of $^{90}$Sr and $^{14}$C since gaseous T is usually transferred through the air by eddy diffusion.

It has been found that the T/$^{14}$C ratio in the lower stratosphere exceeds that in the humid air layers and is equal to 0.4. While approaching the humid layers of the troposphere, stratospheric HTO molecules may exchanged with water at the ocean surface, reevaporated, and transferred in groundwater by infiltration.

The water circulation process in nature is as follows. Water with some tritium evaporates from the ocean surface. The water vapor rises and reaches the temperature of condensation by cooling. Dry air from the lower stratospheric layers with a high tritium content exchanges tritium with the rising ocean water vapor, which contains low concentrations of tritium. The time of exchange appears to be an important factor, the longer the vapor stays in the atmosphere, the greater is the probability that it will become enriched in tritium. At some thermodynamic and meteorological conditions precipitation is formed which is a mixture of ocean and stratospheric water vapor.

The water balancing equation is based on the relationship between radioactive fallout and meteorological parameters for a given atmospheric volume. Near the Earth this equation is:

$$E - P - \Delta F = 0, \tag{13.1}$$

where $P$ is precipitation; $E$ is evaporation–transpiration; $\Delta F$ is the derivation of the water flux in the considered air volume.

In order to establish the relationship between the equation and the real conditions, it has been assumed that water transfer is caused by winds characterized by velocities which vary in space. The balancing equation at a concentration of the indicator $C$, and for a vertical column of air relative to the Earth's surface, is as follows (Schell et al. 1970):

$$\iint (EC_E - PC_P - Q_t C_t)\mathrm{dxdy} = \iiint \left[\frac{\partial(QC_v \cos\theta)}{\partial x} + \frac{\partial(QC_v \sin\theta)}{\partial y}\right]\mathrm{dxdydz}, \tag{13.2}$$

where $Q_t$ is an upward loss of moisture; $C_E$, $C_P$, $C_t$ and $C_v$ are the tritium concentration in evaporation, precipitation, and atmospheric moisture at the border of air volume accordingly; $Q$ is the flux of moisture; $\theta$ is the angle of wind direction.

The equation may be simplified for computation:

$$\langle \bar{E}\bar{C}_E \rangle - \langle \bar{P}C_P \rangle - \langle \bar{Q}_t \bar{C}_t \rangle = \frac{1}{L}\int\limits_z (Q_2 v_2 C_2 \cos Q_2 - Q_1 v_1 C_1 \cos Q_1) dz,$$

where $L$ is the distance between the observation stations, and indexes 1 and 2 for the parameters $Q$, $v$ and $C$ relate to those stations.

The above model has been applied for estimate the relationship between the content of $T$, $^{90}$Sr, and $^{14}$C in precipitation and meteorological parameters characteristic for a number of sites in Western Europe. Those calculations produce reasonable results.

In order to demonstrate the effects of the global distribution of tritium, Romanov (1978) made a number of assumptions in order to obtain a simpler expression describing the transfer of the atmospheric moisture. The balancing equation then becomes:

$$\frac{dW}{dt} = E - P, \tag{13.3}$$

where $W$ is the moisture content in the atmosphere; $E$ and $P$ are the amounts of moisture in evaporation and precipitation per unit of time.

The balancing equation of HTO in the atmospheric moisture above the ocean is

$$d(WC_A) = qdt - C_A Pdt + C_0 Edt - M(C_A - C_0)\,dt, \tag{13.4}$$

where $C_A$ is the concentration of tritium in the atmospheric moisture; $q$ is the rate of tritium release from the stratosphere; $t$ is the residence time of an air mass over the ocean; $C_0$ is the tritium concentration in the surface oceanic layer; $M$ is the rate of the eddy transfer of the atmospheric moisture to the surface oceanic layer. The fractionation of tritium during the phase transition is not accounted for.

The left hand side of the equation expresses the change in the tritium content of atmospheric moisture over the time period $dt$. In the right hand side, the first term defines the discharge of tritium from the stratosphere, the second term corresponds to the removal of tritium in precipitation, the third term to the release of tritium from the ocean surface layer by evaporation, the fourth term to the injection of tritium into the ocean due to molecular exchange. The last term in Eq. (13.4), according to experimental data obtained by Romanov, is proportional to the gradient of the tritium concentration in the system: atmospheric moisture–ocean surface layer together with the water vapor.

In writing Eq. (13.4) it has been assumed that the tritium content in precipitation is equal to its concentration in the whole of the upper atmospheric moisture layer and that the tritium concentrations in the ocean surface layer are little affected compared with concentrations in the atmospheric moisture and the rate of tritium injection from the stratosphere is constant during the whole time of air mass transfer.

Using (13.3), Eq. (13.4) can be rewritten in the form of

$$\frac{dC_A}{dt} + C_A \frac{E+M}{W} = q + C_0 \frac{E+M}{W}. \tag{13.5}$$

The solution of Eq. (13.5) is

$$C_A = C_0 + \frac{q}{E+M}\left\{1 - \exp\left[-\frac{E+M}{W}t\right]\right\}. \tag{13.6}$$

The integration constant can be defined from the initial conditions: $C_{\mathrm{A}} = C_0$ at $t = 0$.

It follows from Eq. (13.6) that the tritium concentration in the atmospheric moisture is greater when the moisture content $W$ is lower and when the interrelationship between the ocean and the atmosphere, expressed by parameters $E$ and $M$, is weaker. This principle can be observed in nature by analyzing the experimental data on global

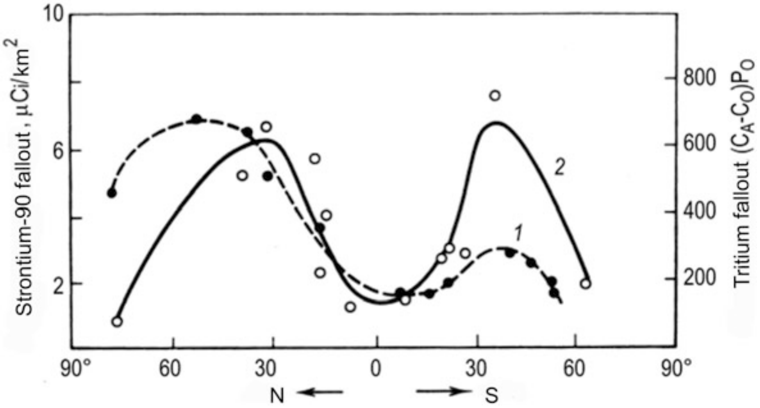


**Fig. 13.35** Latitudinal fallout of tritium (*1*) and $^{90}$Sr (*2*) from the stratosphere over Atlantic Ocean in 1969

tritium distribution in precipitation. The lower values of moisture content, evaporation, and molecular exchange in high latitudes result in the observed latitudinal effect of tritium concentration exchange in precipitation.

Taking into account that the rate of water evaporation is proportional to the humidity gradient ($p_0$–$p$), the rate of molecular exchange is proportional to atmospheric humidity $p$, and that both processes are identically related to wind velocity, Eq. (13.6) may be rewritten in the form:

$$C_A = C_0 + \frac{q}{kp_0}\left[1 - \exp\left(-\frac{tkp_0}{W}\right)\right], \tag{13.7}$$

where $p_0$ is the pressure of the saturated vapor at the ocean surface temperature $t$; $k$ is the parameter determined from the relationship $M = kp$.

If value $t$ is large enough, then

$$C_A = C_0 + \frac{q}{kp_0}. \tag{13.8}$$

From Eq. (13.8) the velocity $q$ of injection of tritium from the stratosphere can be obtained. The plot of dependence of the velocity from the latitude is presented in Fig. 13.35. The values of T and $^{90}$Sr content in the atmosphere are placed on the plot. It is seen that in both cases the maximum is located in the belt of 40–50°N, which evidences on the common nature of injection to the troposphere the bomb-tritium and $^{90}$Sr.

Let us determine the relationship between tritium concentration and the residence time of the air mass above the continent. The balancing equation in this case is:

$$d(WC_A) + qdt - C_APdt + C_EEdt, \tag{13.9}$$

where $C_E$ is the tritium concentration in the evaporating continental water.

Taking into account the insignificant difference between tritium concentrations in the surface continental water and in precipitation one can assume that $C_E \approx C_A$. In this case, using the balancing equation for the atmospheric moisture (13.3), a solution of (13.9) is obtained in the form:

$$C_A = \frac{q}{W} t + const. \tag{13.10}$$

The integration constant can be determined by the initial conditions $t = 0$ at which the tritium content in the atmospheric moisture is equal to its content in moisture transported from the ocean. Then

$$C_A = C_0 + \frac{q}{W} t. \tag{13.11}$$

The last equation accounts for the observed continental effect. In fact, the longer the air mass moves above the continent, the greater the concentration $C_A$ becomes and the better the function $C_A(t)$ may be approximated by a linear dependence, which is confirmed by experimental data obtained in many regions of the world.

Further development of the models establishing the relationship between tritium concentrations in precipitation and meteorological parameters requires a deeper understanding of the natural principles governing air mass circulation in the atmosphere. Experimental data already obtained on tritium falls and their analysis will, in turn, lead to better understanding of the natural principles and also to a more reliable and well-grounded hypothesis.

## 13.5 Tritium in Ocean Waters

The oceans are the main reservoir of the hydrosphere and the main source of atmospheric moisture on the Earth. From continental run-off, direct falls of precipitation and exchange with the atmosphere, the oceans receive the majority (about 90%) of natural and bomb-tritium. Therefore, the oceans are the main reservoir of the tritium accumulation on the Earth. The distribution of tritium in the surface and deep ocean layers is of interest while studying the principles of water circulation of the oceans together with atmospheric moisture and, in particular, of the ocean itself.

Before the thermonuclear tests the tritium concentrations in the ocean water, measured at different sites, had characteristic values from ~0.5 TU (Kaufmann and Libby 1954) to 1 TU (Begemann and Libby 1957; Brown and Grummit 1956). After the thermonuclear tests in March 1954 tritium concentrations increased at an average to 1.9 TE (Giletti et al. 1958). It was difficult to measure such a concentration by the existing that time techniques with an appropriate accuracy.

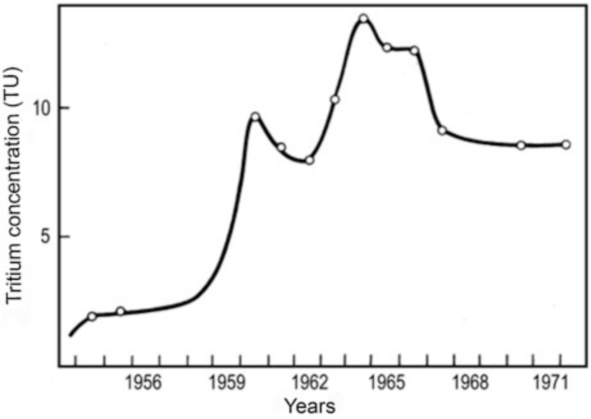
After 1980, the systematic measurements of tritium concentrations in the oceans were started. The obtained results allowed Östlund and Fine (1979) to calculate the approximate amounts of tritium in different ocean regions (Table 13.11).

Tritium content in the ocean waters is defined by the effect of interaction between the ocean surface and atmospheric moisture, which is developed in precipitation, by

**Table 13.11** Tritium inventory in the oceans. (From Östlund and Fine 1979)

| Ocean | Tritium (kg) |
|---|---|
| North Atlantic | 66 |
| South Atlantic | 7 |
| Arctic Basin | 6 |
| North Pacific | 59 |
| South Pacific | 14 |
| Antarctic | 6 |
| Indian Ocean | 6 |
| Total | 164 |

**Fig. 13.36** Latitudinal variation of tritium concentration along 30°N in Atlantic Ocean in 1954–1972



the evaporation and molecular exchange, by life time of the surface layer existence, depending on the mean time of vertical mixing of water, and by interaction of water masses having different origin and tritium concentrations.

The general character of tritium content variations in the surface waters of the ocean reflect the picture of tritium input into precipitation including the rise of tritium content during the period of thermonuclear tests and seasonal cycles in each year. At the same time, it follows from the data that the input to the surface layer is delayed and the amplitude of tritium concentration is decreased because of dilution in larger water volume. Figure 13.36 shows variation of tritium concentration in surface water layer along 30°N in Atlantic Ocean plotted by the data of a number of researchers (Dockins et al. 1967; Giletti et al. 1958; Münnich and Roether 1967; Östlund and Fine 1979; Rooth and Östlund 1972).

The corresponding changes in tritium content because of the series of thermonuclear tests in 1958 and 1961–1962 is obvious. However, the peaks are shifted on 2–3 years compared with concentrations in precipitation. The maximum of the amplitudes with higher tritium concentrations were observed in the middle and high latitudes (Östlund and Fine 1979) (Fig. 13.37). The effect is strongly smoothed in the equatorial latitudes.

Tritium content variations in the surface layer differ seasonally. In the summer time, surface concentrations are higher because of its high content in the atmospheric

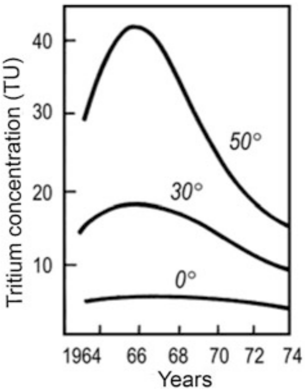


**Fig. 13.37** Maximum changes in tritium concentrations in surface layer of Pacific Ocean. (After Östlund and Fine 1979. © IAEA, reproduced with permission of IAEA)

moisture, higher velocity of the molecular exchange and lower dilution of surface layer by the deep low-active oceanic water due to the thermocline effect. Dockins et al. (1967) studied tritium concentrations in Pacific Ocean between 14°S and 52°N during 1959–1966. The highest concentrations correspond to the summer maximum in the northern part of the ocean which marked smoothed in the low latitudes. In the southern hemisphere, the tritium concentrations in the surface layer decline quickly, which is in agreement with the general picture of tritium falls in precipitation.

Münnich and Roether (1967) studied tritium variations in the surface and depth profiles of the Atlantic Ocean. As for the Pacific Ocean, the latitudinal distribution of tritium in the surface water has maximum concentration in the mid-latitudes of the northern hemisphere. The minimum concentrations of tritium were observed in the equatorial region (not more than 1–3 TU), being obviously close to the natural level observed before the bomb tests. The depth of the tritium mixing layer also increases with latitude from 100 m near the equator to several hundreds of meters in high latitudes. The absolute values of tritium concentrations in the Pacific Ocean are higher than those in the Atlantic Ocean due to the more intensive vertical mixing.

Rooth and Östlund (1972) studied the distribution of tritium in the North Atlantic surface waters during 1963–1968. They confirmed the latitudinal increase of tritium content there. Longitudinal variations in concentration are small. They proposed a model applicable for calculation of the vertical turbulent transfer through the ocean thermocline, including advection.

Bainbridge (1963), Michel and Suess (1975) and other researchers, using the ratio between tritium content in the surface ocean layer and in atmospheric moisture carried out assessment of residence time in that layer. For this purpose, they applied a box model where the ocean was divided on two reservoirs: first was the surface well-mixed layer, and second was deep layer with lower tritium concentration compared with the surface one. Thus, it was assumed that tritium input is provided only through the dividing border between the atmosphere and the ocean and the tritium loss results by the radioactive decay in the well-mixing layer. Horizontal advection is refused here because the horizontal tritium gradient in the open ocean is, as a rule, very small.

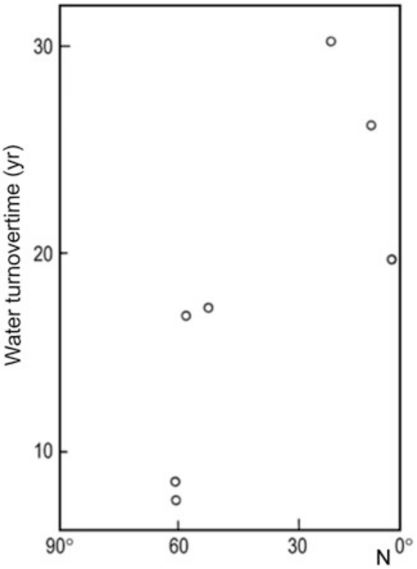


**Fig. 13.38** Relationship between water exchange time and latitude for surface layer of the Pacific Ocean

Applying the box model, Michel and Suess (1975) has found that water exchange time for 12 stations in the Pacific Ocean for the period of 1967–1973 is equal to 7.5–26 years. At the same time, they obtained maximum velocities in the subtropical latitudes and minimum in the equatorial zone (Fig. 13.38). Values close to the above, but calculated by a modified methodology, were obtained by Romanov (1982) for the Black and Caspian Seas (10–15 years) and for the margin seas of the Arctic Ocean.

The vertical tritium distribution in ocean water has its specific features related to its circulation on the globe. A typical picture of the vertical tritium distribution is shown in Fig. 13.39 (Östlund 1973). It is specified by presence of the density jump at the thermocline, which confined the surface layer with relatively high level of tritium content and the deep layer with almost zero tritium content. The two layers are divided by an intermediate thin layer where the vertical turbulent mixing of tritium takes place. Such conditions are characteristic for the equatorial and low latitudes.

Applying the tritium gradient of concentration, it is possible to calculate the coefficient of vertical turbulent diffusion $K_z$. Roether et al. (1970) used this method and for the northern part of Pacific Ocean obtained $K_z = 0.15\ \mathrm{cm}^2/\mathrm{s}$. Rooth and Östlund (1972) for the Sargasso Sea obtained the value of $K_z$ close to the calculated value. In order to obtain this parameter, the authors compile an equation which takes into account the processes of the turbulent diffusion and the vertical advection. In this case, the change of tritium concentration $C(x, y, z, t)$, as a conservative radioactive indicator, in time $t$ in any point can be written in the form:

$$\frac{dC}{dt} = \frac{K_z \partial^2 C}{\partial z^2} + K_H \left( \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} \right) - \bar{\mathrm{V}} \nabla \mathrm{C} - \lambda \mathrm{C}.$$

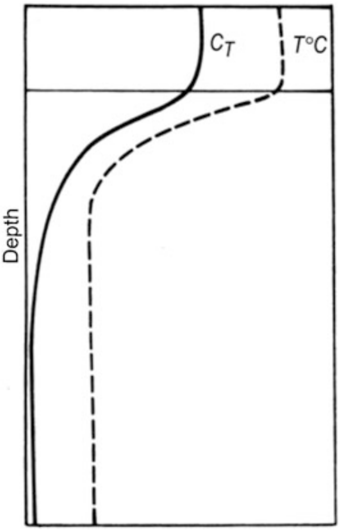


**Fig. 13.39** Typical vertical tritium distribution in oceanic waters

The coefficient of turbulent diffusion $K_H$ in the horizon plane (at $x$ and$y$) is taken the same. The vector of velocity of advective transfer $\bar{V}$ appears to be the vectors sum on all the three space coordinates.

Romanov (1982), in order to determine the coefficient of vertical diffusion for the Black Sea, applied a simplified equation in the form:

$$\frac{dC}{dt} = \frac{K_z \partial^2 C}{\partial z^2} - \lambda C.$$

Its solution for nonstationary conditions is

$$C = \frac{1}{2} C_n \left[ \exp\left( -\sqrt{\frac{\lambda}{K_z}} z \right) \left( 1 - erf \frac{z - 2\sqrt{K_z \lambda t}}{2\sqrt{K_z t}} \right) + \exp\left( \sqrt{\frac{\lambda}{K_z}} z \right) \left( 1 - erf \frac{z - 2\sqrt{K_z \lambda t}}{2\sqrt{K_z t}} \right) \right],$$

where $C_n$ is the tritium concentration in the surface layer of marine water.

As the tritium concentration $C_n$ in the surface layer does not expressed in analytical form due to the occasional character of thermonuclear tests, then a numerical solution with presentation of $C_n$ in a histogram form is used. After that the value of $C$ for each step is found. This way was used for the interpretation of Black Sea data, where the value of $K_z = 0.1$ cm$^2$/s was obtained.

In high latitudes, where the process of air masses vertical mixing is more powerful, vertical tritium distribution appears to be more complicated. The same picture of tritium distribution for the regional concentrations and divergence of ocean water is observed.

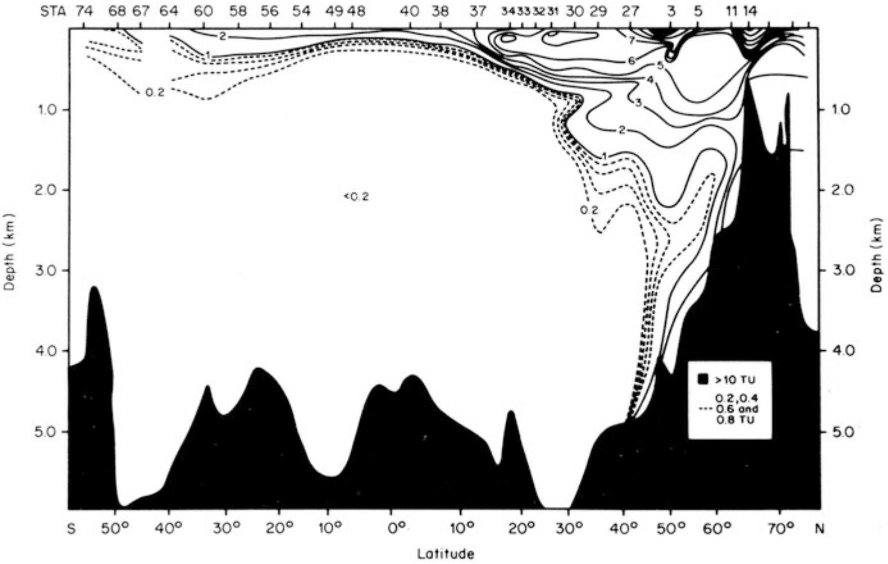


**Fig. 13.40** Meridional distribution of tritium concentrations in Western Atlantic according to GEOSECS studies in 1972. (After Östlund and Fine 1979. © IAEA, reproduced with permission of IAEA)

In 1972, tritium content studies at the deep water stations in the western Atlantic Ocean from 3 to 74°N were carried out as a part of the GEOSECS program (Östlund 1973; Östlund and Fine 1979; Östlund et al. 1974). The results obtained (Fig. 13.40) were mainly in agreement with those obtained by Münnich and Roether (1967) and supplemented their profiles to the north and south. In the north latitudes, the penetration of the bomb-tritium—with concentration more than 0.2 TU—was observed up to the depth of 3,500 m, whereas in the equatorial region a sharp decrease in content was observed at the depth of only 200 m.

Analogous profiles, obtained by the same authors for the Pacific Ocean (Fig. 13.41), shows that here bomb-tritium has not fell so deep as it was in Atlantics at the north, and most of it was in the upper layers which circulate in opposite sides in both hemispheres.

The northern and southern currents divide these systems. The deepest tritium penetration (up to 1,000 m) in the northern part of Pacific Ocean is observed. The most complete mixing, especially up to 500 m, in the region of 20–40°N is reached. The maximum tritium concentrations in the near-equatorial current (8–20°N) at the depth of 200 m and at the surface are observed. This is because being formed at higher latitudes and moving along constant density, oceanic water are dropped. Analogous results and conclusions were obtained in their earlier works by Michel and Suess (1975).

Asymmetric distribution of tritium concentrations in both oceans relative to equator is explained by prevailing fallout in the northern hemisphere.

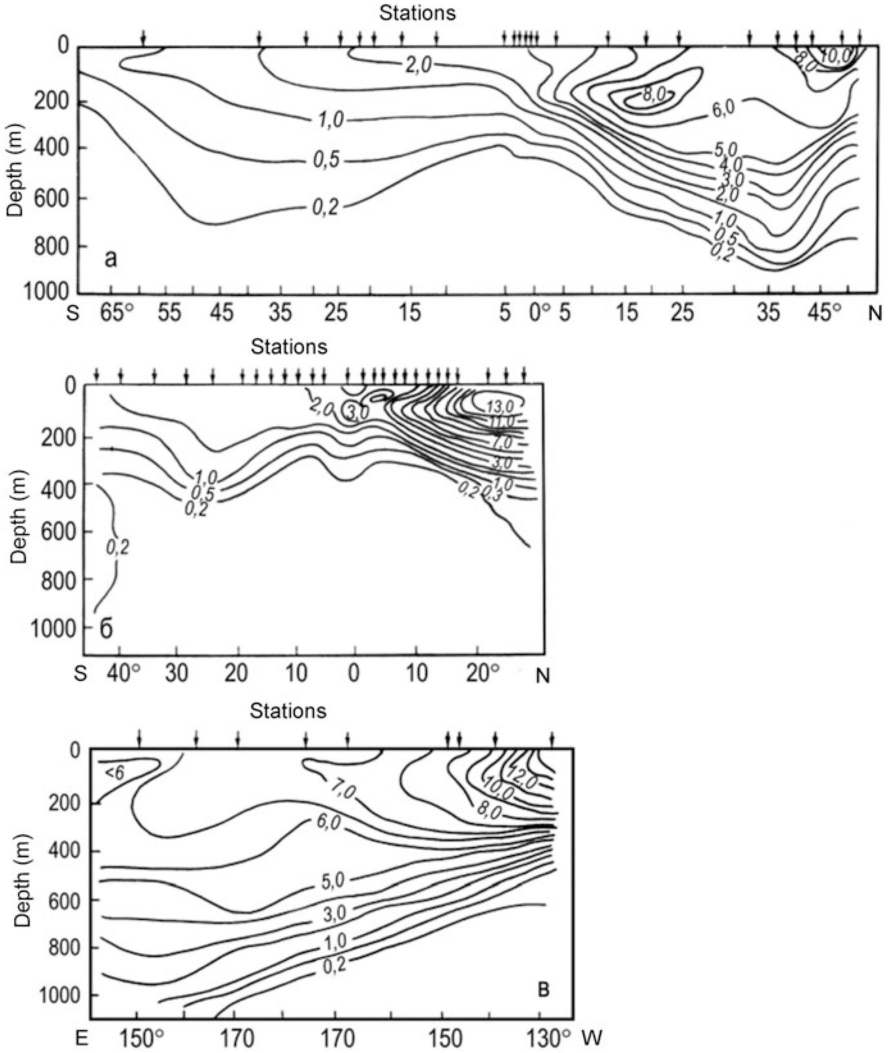


**Fig. 13.41** Distribution of tritium concentrations (TU) in waters of western (**a**), eastern (**b**) and northern (**c**) parts of Pacific Ocean for 1973–1974. (After Östlund and Fine 1979. © IAEA, reproduced with permission of IAEA)

Note that the marked influence on distribution of tritium in the surface oceanic layer in a near-shore and continental regions the river run-off effects. There is also a good correlation between the tritium concentrations and the salinity and temperature of the sea water.

## 13.6 Tritium in Continental Surface Waters

The continental surface waters, together with the precipitation, are an important transport chain of the global water circulation on the Earth. At evaporation they markedly affect on isotopic composition of atmospheric moisture. The surface continental waters are the main source for the groundwaters recharge and in significantly degree determine conditions of formation of isotopic composition and salinity of the marginal seas. A study of isotopic composition of the surface waters helps in obtaining valuable information about the parameters of water dynamics of the river and lakes basins. Thus, the study of regularities in tritium distribution of surface waters is an important scientific problem.

### *13.6.1 Tritium Content in River Water*

The factors which determine tritium content in the river waters are tritium concentrations in precipitation over area of the river catchment basin, residence time of the infiltrating precipitation water in the soil through which it discharged into the groundwater and the river.

Let us express the analytical relationship between the tritium concentration in river water and the water exchange velocity in a river basin. Assume that river water in a basin represents the surface run-off and groundwaters which are well mixed. The age spectral function of river water can be written as $a(t) = \varepsilon \exp(-\varepsilon t)$, where $a(t)$ is the relative portion of precipitation in river water with age $t$; $\varepsilon$ is the exchange velocity (the ratio of total annual recharge to the water volume of the catchment basin). Here value $1/\varepsilon$ has dimension of time (in years). Therefore,

$$\int_0^\infty a(t)dt = 1.$$

The tritium concentration in the river water $C_r$ can be expressed by the equation

$$C_r = \int_0^\infty C_p(t)\varepsilon e^{-\varepsilon t} e^{-\lambda t} dt,$$

or

$$C_r = \varepsilon \int_0^\infty C_p(t) e^{-(\varepsilon+\lambda)t} dt, \tag{13.12}$$

where $\lambda$ is the tritium decay constant; $C_p(t)$ is the tritium concentration in precipitation at the time moment $t$.

At $C_p(t) = \text{const} = C_p$ (e.g., during the prethermonuclear period) one obtains

$$C_r = \frac{\varepsilon C_p}{\varepsilon + \lambda}. \tag{13.13}$$

In order to obtain the solution of Eq. (13.12) when $C_p(t) \neq$ const. (after the beginning of the tests) the function $C_p(t)$ should be rewritten in the form of a histogram. Then

$$C_r = \frac{\varepsilon}{\varepsilon + \lambda}\left\{\sum_{i=1}^{n}[C_{p_{i=1}} - C_{p_i}]\exp[(\varepsilon + \lambda)(t_i - t_{i-1})]\right\} + \frac{\varepsilon}{\varepsilon + \lambda}C_{p_n}, \tag{13.14}$$

where $C_{p_n}$ is the concentration of tritium in precipitation for the time interval ($t_i$–$t_i$-$_1$); $n$ is the number of the time intervals in a period $t$.

Eriksson (1963) proposed another model for the interpretation of tritium data. It is based on the assumption that groundwaters, which are recharged by precipitation, move in parallel to the watershed. Then the precipitation waters, which fall at different distances from the watershed, do not become mixed. According to this model, $a(t) = \varepsilon$ for $t$ ranging from 0 to $1/\varepsilon$, equal to the residence time of infiltration water during its course from the watershed to the bed of the river. Then, the concentration of tritium in the river is as follows:

$$C_r = \varepsilon \int_0^{1/\varepsilon} C_p(t)e^{-\lambda t}dt. \tag{13.15}$$

At $C_p(t) = \text{const.} = C_p$ one has

$$C_r = \frac{C_p\varepsilon}{\lambda}(1 - e^{-\lambda/\varepsilon}). \tag{13.16}$$

Note that the ratio of the $C_p$-values, obtained from the expressions (13.13) and (13.16), is equal to 2.3.

Putting the expression for $C_p(t)$ written in the form of the histogram in (13.16), one obtains

$$C_r = \frac{\varepsilon}{\lambda}\left\{C_{p0}(e^{-\lambda t} - e^{-\lambda/\varepsilon}) + \sum_{i=1}^{n} C_{p_i}e^{-\lambda(t-t_i)}(1 - \exp[-\lambda(t_i - t_{i-1})])\right.$$
$$\left. + C_{p_n}(1 - e^{-\lambda t})\right\}. \tag{13.17}$$

Here the value of $t$ should be less than that of the maximum residence time $1/\varepsilon$.

However, a more reliable method for the estimation of water exchange rates in river basins is a balance method, proposed by Eriksson (1965b). In somewhat simplified form, it is as follows (Romanov 1978):

The spectral function of the water's age can be represented by a number of fixed values $a_0, a_1, \ldots, a_i$, where index $i$ corresponds to the portion of infiltration water characterized by the age $t_i$. Thus, the portion of precipitation falling in the year of observation is denoted by $a_0$, that in the previous year by $a_1$ and so on.

The balancing equation of water is

$$\sum_{i=0}^{\infty} a_i = 1. \tag{13.18}$$

An expression for tritium concentration in river run-off can be written as

$$C_r = \sum_{i=0}^{\infty} a_i C_{a_i} e^{-\lambda t}. \tag{13.19}$$

Before the thermonuclear tests, $n$ years ago, $C_a = \text{const.} = C$, then

$$C_r = \sum_{i=0}^{\infty} a_i C_{a_i} e^{-\lambda t} + C \sum_{i=0}^{\infty} a_i e^{-\lambda t}. \tag{13.20}$$

While studying river basin, the second term on the right-hand side of Eq. (13.20) can be neglected, so that

$$C_r = \sum_{i=0}^{\infty} a_i C_{a_i} e^{-\lambda t}. \tag{13.21}$$

One should write $n$ equations, such as (13.21), for the solution of the problem. In practice, the upper limit of summation can be bounded, for example, in the work of Soyfer et al. (1970) the value of $n = 1/\varepsilon$ has been determined beforehand from the conditions $i = 3$, i.e., for the coefficients $a_0$, $a_1$, $a_2$. The other coefficients were put equal to each other. Then

$$\begin{aligned}
C_{r_0} &= a_0 C_{a_0} + a_1 C_{a_1} e^{-\lambda} + a_2 C_{a_2} e^{-2\lambda} + [1 - (a_1 + a_2 + a_3)] \\
&\quad \exp\left\{-\frac{1}{2\varepsilon} + 1{,}5\right\} \frac{1}{1/\varepsilon - 2} \sum_{3}^{1/\varepsilon} C_{a_i} e^{-i\lambda}, \\
C_{r_2} &= a_0 C_{a_2} + a_1 C_{a_3} e^{-\lambda} + a_2 C_{a_4} e^{-2\lambda} + [1 - (a_1 + a_2 + a_3)] \\
&\quad \exp\left\{-\frac{1}{2\varepsilon} + 1{,}5\right\} \frac{1}{1/\varepsilon - 2} \sum_{3}^{1/\varepsilon} C_{a_{ii+2}} e^{-i\lambda}, \\
C_{r_i} &= a_0 C_{a_i} + a_1 C_{a_2} e^{-\lambda} + a_2 C_{a_3} e^{-2\lambda} + [1 - (a_1 + a_2 + a_3)] \\
&\quad \exp\left\{-\frac{1}{2\varepsilon} + 1{,}5\right\} \frac{1}{1/\varepsilon - 2} \sum_{3}^{1/\varepsilon} C_{a_{ii+1}} e^{-i\lambda}.
\end{aligned} \tag{13.22}$$

Treating the system of equations (13.22), one can obtain the values of $a_0$, $a_1$, $a_2$. In the similar way, any number of equations can be written and solved.

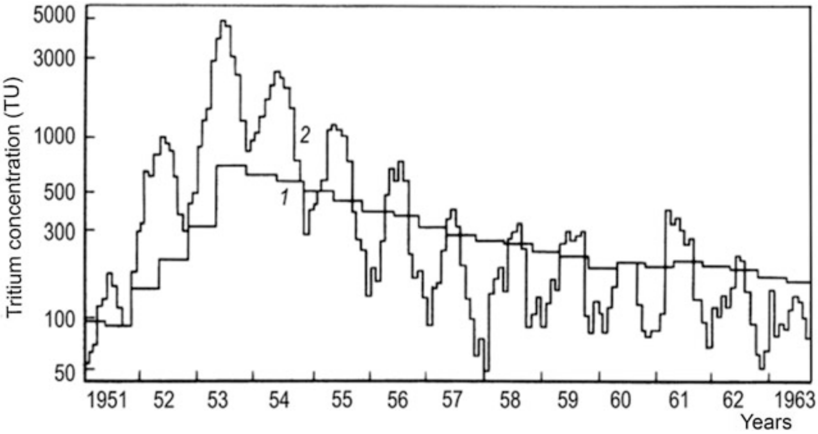


**Fig. 13.42** Variation of tritium concentrations in Rheins River (*1*) and in precipitation (*2*). (After Weiss and Roether 1975. © IAEA, reproduced with permission of IAEA)

Applying the balance method, Eriksson (1965b) has reestimated the partition function of the age of run-off in the Ottawa River. Using his solution and the box model, Romanov (1978) has reported that the value of $\varepsilon$ for the Moscow River in 1964–1965 is 0.195. This value coincides with the results obtained on the basis of the laminar flow model, following from Eq. (13.17). In this case, the values of the coefficients are $a_0 = 0.25$; $a_1 = 0.18$; $a_2 = 0.14$; $a_\mathrm{i} = 0.07$ at $i = 3–8$.

The tritium content in river water, as well as in the atmosphere, is varied in time and space. Long-term distribution of tritium concentrations is governed mainly by that of tritium content in precipitation. Figure 13.11 shows annual means of tritium content in precipitation over the central part of the former USSR territory and in the Moscow River water from 1958 to 1981 (Romanov 1982). The maximum tritium values in river water were observed in 1963 and are accounted by 0.25 part compared with precipitation. Decrease of HTO values in the river water was more smoothed than in precipitation. After 1971, the tritium level in river and precipitation were equalized.

Weiss and Roether (1975) were carried out analogous observations, starting in 1957, for Rheins River (Fig. 13.42). A study in the Ottawa River, as well as in precipitation, started in 1953 (see Fig. 13.10). Prethermonuclear concentrations were measured only in two tributaries of the Mississippi River near St Louis (Illinois, USA): in January 1952 it was 5.6 ± 0.6 TU, and in August 1952 it was 1.15 ± 0.08 TE (Stewart 1965).

Figure 13.43 shows variations of tritium content in the Colorado, News, Arkansas, and Potomac rivers during 1963–1964 according to USGS data (Stewart 1965). One can see in the figure that the tritium peak of 1963 is presented in precipitation (1) and in waters of all the rivers (2). The tritium peak in rivers appears with an average delay ranging from several days of even hours for the mountain regions (see Fig. 13.43a) to a year or even more for the plain regions (Fig. 13.43b), depending on the geological and

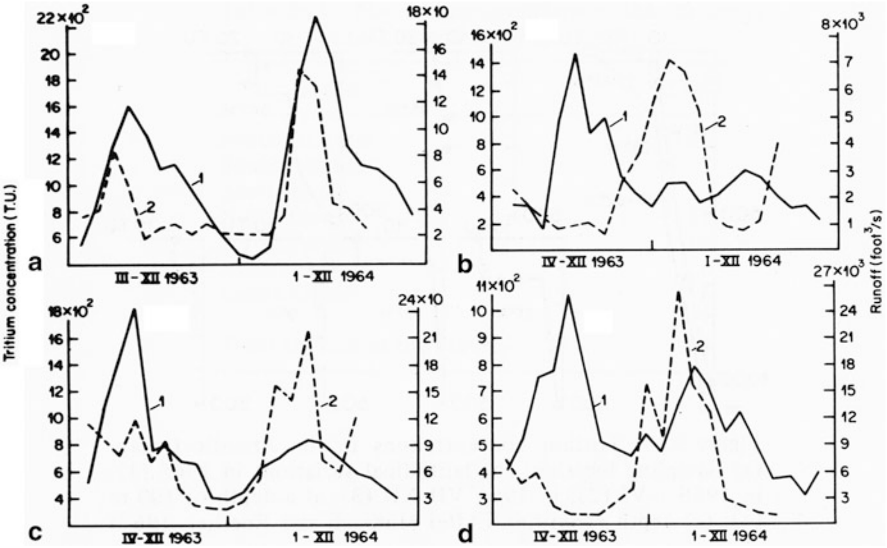
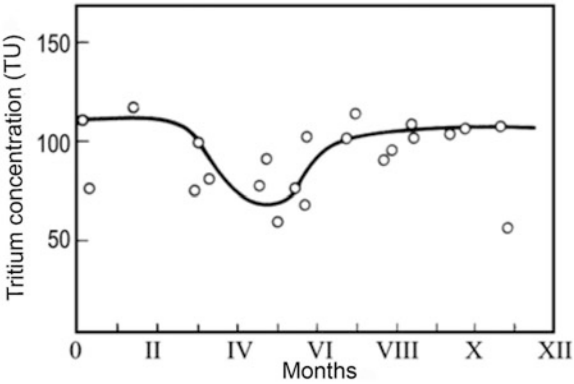


**Fig. 13.43** Variation of tritium concentrations in precipitation (*1*) and in river water (*2*) of Colorado (*a*), News (*b*), Arkansas (*c*) and Potomac (*d*). (After Stewart 1965. © IAEA, reproduced with permission of IAEA)

**Fig. 13.44** Seasonal means of tritium distribution in Pechora River 1976–1979



geographical conditions of their recharge. The travel time taken by a tracer to move from the catchment area to the river bed is an important parameter, characterizing drainage properties and the capacity of a basin. This parameter, and also the general character of tritium variations in the river water and precipitation over time, permits estimations of the residence time of tritium in the drainage can be gained.

The seasonal variations in tritium concentration are markedly lower than in precipitation. The inner annual maximum values of tritium content for the majority of rivers in the former USSR territory in the 1980s of the last century were shifted to the period of winter time. The seasonal distribution of tritium content for Pechora River during 1976–1979 is shown in Fig. 13.44. Analogous picture was received for Moscow River in 1973–1974.

The minimum tritium values are observed in the flood period, when the river recharge is mainly provided by melted winter snow, where tritium concentrations are by 1.5–2 times lower of the mean annual (Romanov 1982).

After flood pass, the rivers are recharged by the groundwaters of the catchment, where tritium accumulates by the previous fallouts in precipitation. Such a result was obtained in the Upper Angara River in autumn 1973, where after precipitation with about 250 TU of tritium content the river water activity contained about 350 TU (Romanov 1982).

The seasonal, annual, and long-term variations of tritium concentration were sucessfully used by many researchers for the calculation of hydrographs in different river basins, for the determination of residence time of water and water exchange time. For example, Brown (1970), using the box model, found for the Ottawa River (see Fig. 13.10) that about 75% of the river volume of water represents the surface run-off with mean residence time about 1 year and the volume rest of about 25% is the underground run-off which has residence time of about 6 years.

Weiss and Roether (1975) separated three components in the surface run-off on the basis of tritium concentrations in the Rheins River water and precipitation during 1961–1973 and by appropriate modeling. It was found that 25% of the run-off has the value of residence time less than 1 year, 35% have 5 years and 40% do not involve tritium at all. It seems that was old groundwater.

In addition to the time variation, there are space changes in tritium content of river water. Table 13.12 demonstrates tritium data obtainer in river waters and precipitation over a number of river basins in 1979, where also some hydrological characteristics of basins are shown (Romanov 1982).

The values of run-off coefficients of the tritiated water for the river basins were obtained by those data. The coefficients are equal to the ratio of tritium value discharged by the river to the sea and amount of that isotope fell out with precipitation over the catchment. The run-off coefficient is always equal to the run-off coefficient of the water, but some times it is rather different from it. An attempt was undertaken to compare the ratio of these values and also the ratio of the annual mean value of tritium concentration and the coefficient of the underground run-off. Figure 13.45 shows dependence of these values (relative to tritium concentration) on the underground run-off coefficient, which were taken from the work of Domanitsky et al. (1971).

Relationship between these values may be expressed by the regression equation in the form of $C_r/C_p = 1.4K_n + 1.65$, where $C_r$ and $C_p$ are the tritium concentration in the river water and precipitation over the catchment area of a corresponding river; $K_n$ is the coefficient of the underground water run-off of the river basin. The correlation coefficient of the regression equation is $r = -0.762$.

The geographical distribution of the relative tritium concentration in river water, for the European part of the former USSR territory, is characterized by a lower or close to unit value. At the same time, for the Siberian and the Far East regions that value is within 1.05–1.69 values and is increased toward east direction. This tendency is well expressed for the northern rivers (Fig. 13.46). The relative tritium concentrations in waters of the north rivers located between the North Dvina and

**Table 13.12** Tritium concentrations in river waters and precipitation and some hydrological characteristics of the basins for the former USSR territory in 1979

| River | Catchment area $\times 10^3$(km$^2$) | Run-off (km$^3$) | Precipitation (km$^3$) | Coefficient of surface run-off ($K_n$) | Concentration of tritium (TU) |  | Coefficient of surface tritium run-off, $K_T$ | $K_T/K_n$ | Coefficient of groundwater run-off |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | River | Precipn |  |  |  |
| Pechora | 322 | 130 | 229 | 0.57 | 98 | 105 | 0.53 | 0.93 | 0.19 |
| Northern Dvina | 357 | 110 | 255 | 0.43 | 83 | 90 | 0.40 | 0.92 | – |
| Onega | 57 | 16 | 41 | 0.39 | 86 | 79 | 0.42 | 1.09 | 0.32 |
| Neva | 281 | 80 | 212 | 0.38 | 141 | 72 | 0.74 | 1.96 | – |
| Svir | 66 | 19 | 52 | 0.38 | 143* | 67[a] | 0.81 | 2.13 | – |
| West Dvina | 88 | 21 | 68 | 0.31 | 67 | 68 | 0.30 | 0.99 | 0.35 |
| Dniester | 72 | 8.7 | 42 | 0.21 | 81 | 72 | 0.24 | 1.12 | 0.43 |
| Yuzhny Bug | 64 | 3.4 | 34 | 0.10 | 68 | 73 | 0.09 | 0.93 | 0.28 |
| Dnieper | 504 | 54 | 343 | 0.16 | 64 | 74 | 0.14 | 0.86 | – |
| Don | 422 | 30 | 240 | 0.12 | 65 | 80 | 0.10 | 0.81 | 0.56 |
| Volga | 1,360 | 243 | 900 | 0.27 | 90 | 90 | 0.27 | 1.00 | – |
| Oka | 188 | 29 | 212 | 0.24 | 51 | 78 | 0.16 | 0.65 | 0.62 |
| Moscow | 5 | 1 | 3.6 | 0.28 | 70[a] | 66[a] | 0.30 | 1.06 | 0.24 |
| Kama | 522 | 124 | 363 | 0.35 | 105 | 100 | 0.37 | 1.05 | 0.30 |
| Ural | 229 | 11.6 | 102 | 0.11 | 92 | 110 | 0.09 | 0.84 | 0.56 |
| Ob[b] | 2,450 | 390 | 1,650 | 0.24 | 126 | 125 | 0.24 | 1.01 | – |
| Yenisey | 2,620 | 623 | 1,360 | 0.46 | 142 | 120 | 0.54 | 1.18 | 0.30 |
| Angara | 1,045 | 138 | 455 | 0.30 | 55 | 140 | 0.12 | 0.39 | – |
| Upper Angara | 21.6 | 7.8 | 11.9 | 0.65 | 145* | 137[a] | 0.69 | 1.06 | 0.46 |
| Lower Tunguska | 483 | 116 | 251 | 0.46 | 182 | 130 | 0.64 | 1.40 | 0.29 |
| Lena | 2,490 | 508 | 1,145 | 0.44 | 199 | 155 | 0.56 | 1.28 | 0.21 |
| Indigirka | 360 | 57 | 117 | 0.49 | 220 | 130 | 0.83 | 1.69 | 0.09 |
| Kolyma | 665 | 129 | 270 | 0.45 | 116 | 70 | 0.75 | 1.66 | 0.18 |
| Amur | 1,855 | 343 | 1,113 | 0.31 | 207 | 155 | 0.41 | 1.34 | 0.15 |
| Sir-Darya | 219 | 14.5 | 100 | 0.14 | 111 | 105 | 0.15 | 1.06 | – |

[a] Data related to 1980

[b] Hydrological data do not valid for the mouth profiles

**Fig. 13.45** Dependence on tritium concentration in river water from coefficient of the underground water run-off for the rivers: Indigirka (*1*), Kolima (*2*), Amur (*3*), Lower Tunguzka (*4*), Lena (*5*), Enisey (*6*), Onega (*7*), Dnepr (*8*), Moscow (*9*), Kama (*10*), Upper Angara (*11*), Pechora (*12*), Southern Bug (*13*), Western Dvina (*14*), Ural (*15*), Don (*16*), Oka (*17*)

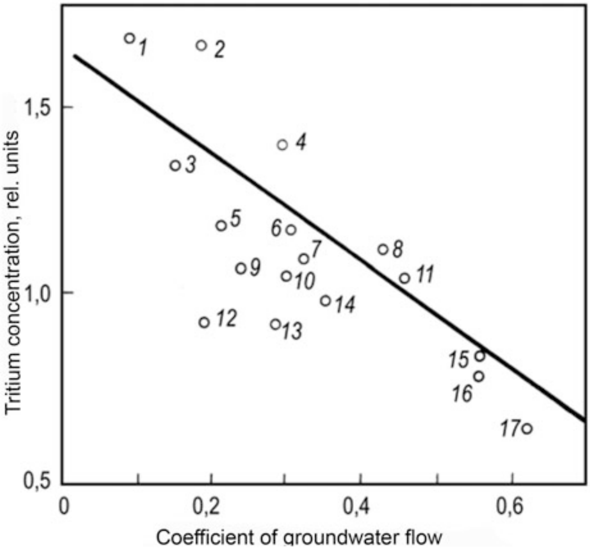
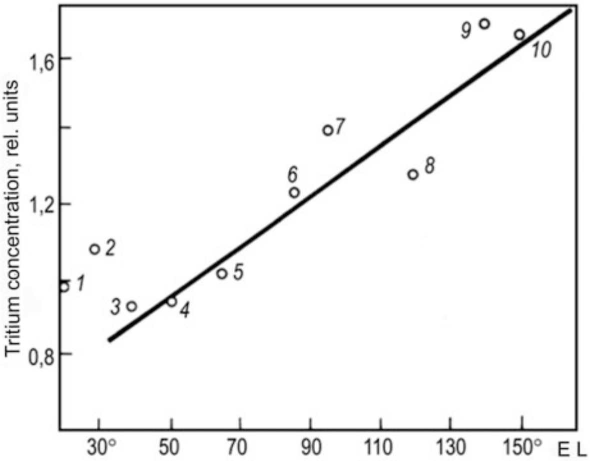


**Fig. 13.46** Variation of relative tritium concentration in river waters depending on their longitude: Western Dvina (*1*), Onega (*2*), North Dvina (*3*), Pechora (*4*), Ob (*5*), Evisey (*6*), Lower Tunguzka (*7*), Lena (*8*), Indigirka (*9*), Kolima (*10*)



Kolima are described by the regression equation like $C_r/C_p = 7.15 \times 10^{-3}\lambda + 0.56$ at the correlation coefficient $r = -0.95$ ($\lambda$ is the degree of the eastern longitude).

The space distribution of the relative tritium concentration in river waters can be explained by the groundwater discharge where its value is lower of unit. In the case when the relative concentration is higher of unit, then the modern precipitation water displaces the groundwater with lower tritium content.

There are experimental data which permit to assess tritium concentrations in groundwaters which take part in the river recharge by use of the equation of isotope balance like $C_r = C_p(1 - K_n) + C_nK_n$, where $C_n$ is the tritium concentration in groundwaters. Some results of the corresponding calculations are in Table 13.13.

**Table 13.13** Tritium concentrations in groundwaters taking part in river recharge

| River | Tritium concentration in Groundwater (TE) | $C_r/C_p$ |
|---|---|---|
| Pechora | 68 | 0.65 |
| Onega | 101 | 1.28 |
| Western Dvina | 65 | 0.96 |
| Dniester | 93 | 1.29 |
| Yuzhny Bug | 55 | 0.75 |
| Don | 53 | 0.66 |
| Oka | 34 | 0.44 |
| Moscow | 83 | 1.26 |
| Kama | 117 | 1.17 |
| Ural | 78 | 0.71 |
| Yenisey | 193 | 1.61 |
| Upper Angara | 154 | 1.12 |
| Lower Tunguska | 309 | 2.38 |
| Lena | 364 | 2.35 |
| Kolyma | 325 | 4.64 |
| Amur | 502 | 3.24 |

The calculated tritium concentrations in groundwaters are very high and correspond to its content in precipitation fallout 10–15 years ago. In this connection, it is interesting to note that the appropriate groundwater tritium measurements in Yakutia, carried out earlier, just showed high tritium concentrations like that (Afanasenko et al. 1973). At the same time, tritium content in groundwaters of the European part of the former USSR, by multiple studies, very seldom overtopped its value in precipitation (Romanov 1982).

The attempts in finding relationship between tritium content in river waters and some other hydrological parameters have failed.

From the general picture of space distribution in tritium concentration in river waters (see Table 13.12) the data for Svir, Neva, and Angara are of special interest. This is because water of the above rivers represents mainly run-off from the large lakes like Onega, Ladoga, and Baykal where formation of isotopic composition is defined by some other conditions.

Let us estimate the total amount of tritium fallout over the former USSR territory and compare it with the discharge by the rivers. It is seen from Table 13.14 that the run-off coefficient for tritiated water for all the investigated territory is higher of that for the river run-off (0.45 against 0.35). This is the evidence that the tritium has up to now washed out from the basins. In addition to this, about 65% of total tritium is washed out by the rivers to the North Arctic Ocean, about 24% to the North Pacific Ocean, and only about 11% to all other seas.

### 13.6.2 Tritium in Lakes and Reservoirs

While studying water exchange in lakes and water reservoirs with the help of the tritium tracer, a number of peculiarities should be taken into account which are affecting

**Table 13.14** Tritium fallout and run-off to the sea basins of the former USSR territory (data of 1979–1980)

| Basin | Catchment area $\times 10^3$(km$^2$) | Run-off (km$^3$/year) | Precipitation (km$^3$/year) | Coefficient of water run-off | Fallout over basin (Bq × $10^{15}$) | Run-off (Бκ × $10^{15}$) | Coefficient of tritium run-off | Annual tritium run-off (% from total) |
|---|---|---|---|---|---|---|---|---|
| Barents | 1,260 | 420 | 890 | 0,48 | 9,6 | 4,0 | 0,44 | 6,0 |
| Baltic | 661 | 171 | 510 | 0,34 | 4,6 | 2,1 | 0,46 | 3 |
| Black, Asov | 1,347 | 159 | 880 | 0,18 | 7,9 | 1,3 | 0,17 | 1,8 |
| Caspian | 2,927 | 300 | 1,430 | 0,21 | 17,2 | 3,3 | 0,19 | 4,5 |
| Kara | 6,630 | 1,331 | 3,700 | 0,36 | 58 | 21,6 | 0,38 | 29,4 |
| Laptev | 3,670 | 777 | 1,650 | 0,47 | 29,6 | 18,5 | 0,62 | 25,2 |
| East Siberian | 1,326 | 233 | 460 | 0,51 | 4,4 | 2,8 | 0,63 | 4 |
| Okhotsk | 2,561 | 626 | 1,600 | 0,39 | 24 | 17,5 | 0,73 | 24 |
| Central Asia (non recharged region) | 2,420 | 125 | 730 | 0,17 | 8,7 | 1,6 | 0,18 | 2,1 |
| Total | 22,802 | 4,142 | 11,850 | 0,36 | 164 | 72,9 | 0,45 | 100 |

tritium distribution patterns in them. Among them are the regime of the recharge, the ratio of the catchment area, and that of the reservoir itself, the existence or absence of run-off, the temperature regime, and many others. All these peculiarities determine whether a reservoir has steady state thermocline or a seasonal one, characterized by a complete mixing of water during cold times. Saline and some tropical reservoirs are of the first type. The majority of other lakes correspond to the second type. For the latter the balancing equations of water and tritium under a study regime can be written in the form:

$$\frac{dV}{dt} = \sum_{i=1}^{n} R_i + P - E \pm U - A, \tag{13.23}$$

where $dV$ is the lake volume change; $R_i$ is the river run-off; $P$ is the precipitation; $E$ is the evaporation;$U$ is the groundwater discharge; $A$ is the surface run-off from the lake.

At a steady state regime ($dV/dt = 0$), then equation of tritium balance is written as

$$\frac{d(CV)}{dt} = \sum_{i=1}^{n} C_i R_i + PC_p - EC_p - M(C - C) - \lambda CV - AC \pm UC_U. \tag{13.24}$$

Here $C$, $C_i$, and $C_p$ are the tritium concentrations in the lake water, river run-off and precipitation; $M$ is the rate of the turbulent exchange between the atmospheric moisture and the surface water of the lake (Östlund and Berry 1970); $C_U$ is tritium concentration in the groundwater discharge; $\lambda$ is the tritium decay constant.

Omitting the value $\pm U = 0$ due to small groundwater tritium discharge in Eqs. (13.23) and (13.24), one obtains

$$\frac{dC}{dt} = \bar{C}_i \bar{R}_i + PC_p - \bar{R}C + PC - M(C_p - C) - \lambda CV, \tag{13.25}$$

where

$$\bar{R} = \sum_{i=1}^{n} R_i;$$

$$\overline{C_i} = \sum_{i=1}^{n} C_i A_i.$$

Introducing the relative balance components $\bar{r} = \bar{R}/V$; $p = P/V$; $m = M/V$, we obtain the first-order differential equation:

$$\frac{dC}{dt} + C(\bar{r} - p - m - \lambda) = \bar{C}_i \bar{r} + C_p P. \tag{13.26}$$

**Table 13.15** Tritium concentrations and some of hydrological characteristics for the lakes of the former USSR territory (1979–1980)

| Lake, reservoir | Water volume (km$^3$) | Annual recharge (km$^3$/year) | Tritium concentration | | Water exchange time (year) | $C_i/C_p$ |
|---|---|---|---|---|---|---|
| | | | Lake $C_i$ (TU) | Precipitation $C_p$ (TU) | | |
| Ladoga | 908 | 79.8 | 122 | 66 | 11.4 | 1.85 |
| Onega | 295 | 13.6 | 138 | 67 | 21.6 | 2.06 |
| Sevan | 58.5 | 1.26 | 80 | 64 | 44 | 1.26 |
| Issyk-Kul | 1,730 | 5.25 | 35.5 | 115 | 330 | 0.31 |
| Baykal | 23,000 | 70.2 | 40 | 128 | 330 | 0.31 |
| Valday | 0.55 | 0.044 | 110 | 62 | 12.5 | 1.78 |
| Aral | 1,023 | 60.3 | 217 | 100 | 17 | 2.17 |
| Ribinsk Reservoir | 25.4 | 36 | 86 | 76 | 0.71 | 1.13 |

In the integral form the last equation becomes:

$$C = \exp\left[-\left(\bar{r} - p - m - \lambda\right) t\right] \int_0^t \left(\bar{C}_i \bar{r} + C_p p\right) \exp\left[-\left(\bar{r} - p - m - \lambda\right) t\right] dt + \text{const.} \tag{13.27}$$

The solution of Eq. (13.27) can be obtained by the summation of the integrand if the variables $\bar{C}_i \bar{r}$ and $C_p p$ are written in the form of a histogram.

The estimation of the water cycle time in the Baikal Lake, the largest in the world, carried out on the basis of the analysis of tritium patterns in the lake water, influents, and precipitation, has shown that this problem can be treated with the help of the box model. Using the balance method and corresponding experimental data on the tritium content in the water sources, it has been shown that complete water exchange in this lake lasts 330 years, whereas that in the river basins is 2–3 years (Romanov et al. 1979). These results are in good agreement with hydrological estimations (Afanasyev 1960).

Table 13.15 demonstrates the main hydrological characteristics and the data on tritium concentrations in lake waters of the former USSR territory. In order to exclude the influence of geographic differences on tritium content in precipitation over the lake and river catchment areas, the value of relative tritium concentration is used. This value is equal to the ratio of tritium concentration in water and that over the catchment are of the lake or river. This value is used for comparison with the value of time exchange of the lake or river water (see Table 13.15).

The results of tritium study of lakes on the former USSR territory are shown in Fig. 13.47. Here maximum relative tritium concentrations in reservoirs with the water exchange time about 17 years (the Aral Sea and Onega Lake) were found. It is interesting to note that the maximum fallout took place 17 years before the lake water was sampled.

The box model can be applied for the treatment of experimental data for open water reservoirs. The conditions for such treatment are as follows: (1) The equality of the

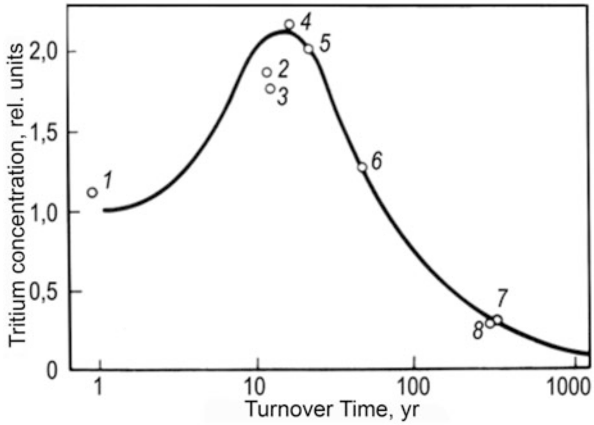


**Fig. 13.47** Dependence of relative tritium concentration on the water exchange time for: Ribinsk Reservoir (*1*); lakes Ladoga (*2*); Valday (*3*); Aral (*4*); Onega (*5*); Sevan (*6*); Issyk-Kul (*7*); Baykal (*8*)

mean value tritium concentration in the system itself and in the discharged water and (2) The constancy of volume of the reservoir in time. In fact, the reservoirs with the constant water level and with well-mixed water are satisfied to these conditions.

The box model was used in calculation of water exchange time for river basins, lakes, and reservoirs by many authors (Brown and Grummit 1956; Begemann and Libby 1957; Romanov and Soyfer 1968; Romanov 1978).

## 13.7 Tritium in Groundwaters

The main source of tritium in groundwaters is precipitation water. However, as pointed out by Andrews and Kay (1982), some amount of tritium is created by nuclear reaction ($n$, $\alpha$) on nuclei of $^6$Li just in the aquifers, especially those represented by acid rocks. The source of neutrons, in this case, is the spontaneous natural uranium and thorium decay. By Andrews and Kay calculations, the above reactions in the pure groundwaters produce tritium concentrations up to 2.5 TU, which can be reached in a granite massif.

The shortest transition time of precipitation and surface water into groundwaters is observed in the case of a direct hydraulic connection between them, which occurs in the regions of tectonic fractures, fissures, and karstic rocks and gravel–pebble sediments. The tritium half-life, equal to 12.43 years, is very often lesser than the groundwater exchange time. Therefore, the tritium radioactive decay is a significant factor which is decreasing its concentration. The intensive exploitation of groundwaters for economic purposes is accompanied with development of the depression funnels and washing of the rocks, intensifying the degree of relationship between the surface and groundwaters and affecting on their tritium content.

In the recent years, when the natural tritium content was disturbed by injection into the atmosphere of large amounts of bomb-tritium, the possibilities of the absolute dating of groundwater with the help of tritium were lost. At the same time, the wide-scale investigations of the tritium falls in precipitation on a global scale allow us to use the obtained data for studying the motion of groundwaters from a somewhat different viewpoint.

Tritium releases into the atmosphere during the decade of nuclear weapon tests occurred in the form of individual pulses, which correspond to a single powerful or a series of moderate explosions. The tritium falls during the test period, and the subsequent period of time, mirrored its injection into the atmosphere in the form of individual pulses differing in magnitude over the yearly cycle. The knowledge of atmospheric water patterns in the underground part of the hydrosphere together with tritium dating information provides the basis for the solution of different time-dependent problems while studying groundwater dynamics.

The study of problems dealing with the transition of tritium 'marks' in groundwaters over time is based on systematic measurements of tritium concentrations in the precipitation of a studied region. The occurrence of tritium in groundwaters depends on their recharge conditions.

The most typical case of recharge of the tritium from the surface aquifer is percolation of surface water through the unsaturated zone. Here, as a rule, the spring–summer component of the annual precipitation, containing the maximum tritium concentration, does not reach the aquifer. This portion of annual precipitation is lost mainly through evaporation–transpiration and partly by surface reservoir recharge. Some portion of the groundwater storage is similarly lost. During the autumn–winter period and in the early spring, when tritium content in precipitation is minimal, the evaporation and transpiration of precipitation water is also reduced. During this period groundwaters are replenished. Thus, in this case tritium concentrations in groundwaters are lower than the annual average concentration in precipitation.

The seasonal variations in tritium concentration were observed (Andersen and Sevel 1974). The delay time of the peak annual concentrations was ranged within about 1–3 months, and the peak itself compared with the tritium peak in precipitation was considerably smoothed. The tritium concentrations in the water of the unsaturated zone were changed in depth. Some times, the maximum concentration, which corresponds to the infiltrating precipitation of the peak fallout, on a definite depth was observed. This depth was depended on the filtration properties of the soil of that unsaturated zone (Andersen and Sevel 1974; Atakan et al. 1974; Morkovkina 1978). Such a tritium distribution was used for the determination of the infiltrated water velocity in that unsaturated zone.

According to the experimental data of Münnich et al. (1967) and Atakan et al. (1974), who carried out their studies on the alluvial plain of the Rhine River, bomb-tritium dating of shallow groundwaters can be used with a sufficient accuracy if the unsaturated soils and the aquifer itself are homogeneous in composition and properties. Tritium change in depth profiles over time, in an unsaturated zone composed of loess-loam soil and in an unconfined aquifer consisting of fine to medium-size and coarse sand were studied by the authors. According to the tritium dating techniques, the average recharge rate of groundwaters in the fine to coarse sand material

**Table 13.16** Tritium content in natural waters of Yakutia. (From Afanasenko et al. 1973)

| Object | Tritium concentration (TU) |
|---|---|
| Water from the spring of Upper Nekharan | 860 |
| Water from the spring of Yust Nekharan | 523 |
| Water from the river mouth Nekharan | 382 |
| Snow | 252 |
| Precipitation | 337 |

is 200 mm/year which is in good agreement with that measured on the basis of routine hydrologic techniques.

By the tritium distribution in time, the mean residence time of the water is determined in the aquifer. Taking into account that the aquifer water is drained by rivers then the portion of groundwater discharge to rivers can be calculated (Brown 1970) or if this value by some other method is obtained, then by balance relations the mean tritium concentrations discharged to rivers are obtained. The attempt was undertaken to obtain these values for the large northern river basins of the former USSR (Romanov et al. 1982). The results of these calculations, presented in the previous paragraph, show that tritium concentration in the groundwaters is increased from west to east of the basin location and also, for rivers, located to east behind the Ural, their concentration is higher than in modern precipitation. This is because of the continental maximum over the catchment area, and possible due to permafrost affect of the Siberian surface rocks which save tritium concentrations accumulated in the period of maximum fallout in 1962–1966. This idea is proved by the observational data of tritium in groundwaters, rivers and precipitation obtained in Yakutia (Table 13.16).

The aquifers of fractured and karstic rocks have intensive recharge from precipitation. In this case, there are good conditions for infiltration of water and restrictions for its evaporation. Here irregular distribution of tritium concentrations due to the existence of a number of hydrologic subsystems or different ways of water transit is observed.

Devis (1970) studied groundwaters in noncarbonate fractured rocks on volcanic island CheYu in South Korea; substantial variations in tritium content, discovered there. According to the author, the mean residence time of the water in the range of 1–8 years to be found, this is the normal “age” for groundwaters. A similar study was done in Aragatz Mountain in Armenia by Vlasova et al. (1978). The transit time for precipitation between the points of recharge and discharge in the summer time was found to be 2–3 months and in the cold period it was 7–8 months.

The tritium concentrations in such waters are, as a rule, high and close to precipitation, for example, high tritium concentrations in karstic waters with substantial seasonal variation were found in Southern Turkey (Dinçer and Payne 1971).

A number of researchers found good relationship between karstic and surface waters. The velocity of water movement in karstic rocks was found to be from several to hundreds of meters per hour (Fontes 1976).

The anthropogenic activity influence on the groundwater exchange rate is the problem of a special interest, for example, concentration of tritium in the water of the Middle Carboniferous rocks in the Moscow artesian basins, which groundwaters are intensively exploit, in 1978, was equal in average about 50 TU. At the same time, in marginal parts of the basin, which are closer to the recharge area, the values very seldom exceed 10 TU (Zlobina et al. 1980). This shows that anthropogenic activity may lead to substantial disturbance of the natural circulation of groundwaters.

Detailed studies of groundwater motion in saturated and unsaturated zones have been carried out by a number of researchers (Allison and Hughes 1974; Andersen and Sevil 1974; Atakan et al. 1974; Morkovkina 1979; Münnich et al. 1967; Verhagen et al. 1979).

## 13.8 Dating by Tritium

In view of the interpretation of isotope data and the solution of different problems elucidating groundwater dynamics, different models have become widely used. The mathematical ground for the construction of these models is the balancing equation of water masses and isotope tracers, together with the water dynamics in the system under investigation. Let us now consider some of the hydrological models.

One of the common problems in groundwater studies is the estimation of the residence (exchange) time of water in hydrological system, or, as a sometimes said, the age of the water. It has been suggested that several models applicable for the interpretation of experimental results involving tritium tracers for the determination of the age of groundwaters (Maloszewski and Zuber 1996; Nir 1964; Zuber 1994).

### *13.8.1 Piston Flow Model*

This model is based on the assumption that portions of water coming into the system follows each other along the flow and do not intermix. The model underestimates the residence time in hydrological systems since water mixing does occur in nature. However, it is useful for estimations of the minimal residence time in a system.

According to this model the concentration of radioactive isotope $C$ at a sampling point located at a distance $x_0$ from the recharge zone is defined as

$$C = C_0 \exp\left(-x_0 / vT\right) = C_0 \exp\left(-t / T\right), \tag{13.28}$$

where $C_0$ is the concentration of radioactive isotope in recharge water; $v$ is the rate of groundwater motion; $T$ is the lifetime of an isotope ($T = T_{1/2}/\ln 2$).

Introducing a dimensionless parameter $k = t/T$, one obtains:

$$C/C_0 = \exp(-k). \tag{13.29}$$

Thus, the residence time of water from the recharge region of a basin to the sampling point is determined by the ratio $C/C_0$. Equation (13.28) can be readily transformed into one which corresponds to the common exponential law of radioactive decay:

$$C = C_0\exp(-\lambda t), \tag{13.30}$$

where $t$ is the age of the water, $\lambda$ is the decay constant of an isotope $\lambda = 1/T = \ln 2/T_{1/2}$.

Therefore, the age of water at a sampling point for the piston flow model is

$$t = \frac{T_{1/2}}{\ln 2}\ln\frac{C_0}{C_t} = \frac{1}{\lambda}\ln\frac{C_0}{C}. \tag{13.31}$$

In the framework of this model, it has been admitted that $C_0$ is a constant and that intermixing of waters of different ages does not occur in the system.

### 13.8.2 Dispersive Model

According to this model, the hydrodynamic dispersion and intermixing of waters, entering the system at different time, results in a Gauss' distribution of transition times along the flow. As in the previous case, assuming the spatial distribution of isotope tracer being dependent on one coordinate $x$, one has

$$C(x_0, t) = \frac{C_0}{(4\pi Dt)^{1/2}}\exp\left[-\frac{(x_0 - vt)^2}{4Dt}\right]\mathrm{d}x, \tag{13.32}$$

or

$$C(x_0, x) = \frac{C_0}{(4\pi D_m x)^{1/2}}\exp\left[-\frac{(x_0 - x)^2}{4D_m x}\right]\mathrm{d}x, \tag{13.33}$$

where $D_m = D/v$ is the coefficient of hydrodynamic dispersion being characteristic for a given hydrogeological system.

Expression (13.33) represents the concentration of tracer $C(x_0, t)$ at a distance $x_0$ from the source of recharge. When the tracer passes the average distance $x = vt$, the amount of tracer remains unchanged in time and is equal to $C_0\mathrm{d}x$. The average lifetime of tracer is $T$ and the concentration at a point $x$ can be estimated from the equation

$$C(x_0, x) = \frac{C_0}{(4\pi D_m x)^{1/2}}\exp\left[-\frac{(x_0 - x)^2}{4D_m x} - \frac{x}{vT}\right]\mathrm{d}x. \tag{13.34}$$

If the concentration of tracer at the input of the hydrogeological system varies within time, which it does for natural isotopes, the variation of the concentration at the output will depend mostly on the input parameters of the tracer.

Let us consider a hydrological system of volume $V(t)$, having an inflow of water $a(t)$ and an outflow $q(t)$. In this case, the water age $t$ is

$$t = V(t)/q(t)\ .$$

For the steady hydrodynamic state, the input concentration of tracer in the discrete form can be given as follows (Martinec et al. 1974):

$$C(t) = \sum_{t=0}^{\infty} p(t)C_a(\theta - t)e^{-\lambda t}, \tag{13.35}$$

where $\theta$ is the year of sampling; $t$ is the age of the water; $\lambda$ is the constant of tritium (0.056 $\text{year}^{-1}$).

The distribution function of the water's age $p(t)$, in a hydrogeological system, is given in fractions of annual replenishment at the output of a system at the moment of sampling.

In the case of the dispersive model the distribution function of the water's age for a semiinfinite aquifer is as follows (Burkhardt and Fhöhlich 1970; Maloszewsky and Zuber 1996; Martinec et al. 1974):

$$p(t) = \frac{2}{\sqrt{\pi D t}} \exp\left[-\frac{(t - t_0)^2}{Dt}\right] - \frac{2\exp(4\pi t_0/D)}{D} erfc\left(\frac{t + t_0}{\sqrt{Dt}}\right). \tag{13.36}$$

The result of the above expression depends on two parameters, having dimensions of time: $t_0 = x_0/v$ ($t_0$ is not equal to the average residence time of water in the system) and $D = 4D_m/v^2$, ($x_0$ is the coordinate of a sampling point), where $D_m$ is the hydrodynamical dispersion. Using a radioactive isotope tracer, one should introduce in Eq. (13.36) a term to account for its decay to the moment of sampling.

Dispersive models have been used by a number of researchers for estimating the residence time of water in hydrological systems (Burkhardt and Fhöhlich 1970; Martinec et al. 1974; Maloszewsky and Zuber 1996; Zuber 1994; Zuber et al. 2001).

### *13.8.3 Complete Mixing Model*

According to this model water input at different times mixes quickly. It is not possible to account for water flow lines, as has been done in previous models, only to speak of water residence time in a system obeying exponential distribution. The model, as a rule, gives higher values of the residence time in a system if the distribution function of time is expressed by a continuous function.

In the interpretation of the observed results of tritium concentration changes in the Ottawa River basin, Brown (1961) used a box model which assumes complete mixing of the meteoric and groundwater in the bed flow. In this case, at the output of a hydrological system the relative fraction of water of a certain age is expressed as an exponential dependency of the form:

$$p\,(t) = (1/\tau)\exp\left(-t/\tau\right), \tag{13.37}$$

where $\tau$ is the average value of residence time of water in a system; $1/\tau = \varepsilon$ is the water exchange rate, i.e., the ratio of the total annual inflow of water to the volume of the basin.

Due to the function of water distribution (13.37), this model in literature is often called ‘the exponential model’.

The distribution of tritium concentration in water tritium distribution at the output of the system, in the discrete form and in accordance with Eq. (13.35), is

$$C(t) = \sum_{1953}^{\theta} \alpha C_a(\theta - t)p(t)e^{-\lambda t}. \tag{13.38}$$

where $\alpha$ is the statistical distribution of the input function, determined as a function of the seasonal precipitation, participating in the recharge of a system compared with the annual amount of precipitation.

During the prethermonuclear era when $C_a = \text{const.}$ we have expression (13.13) and when $C_a \neq \text{const.}$ we have expression (13.14).

In practice it is not always convenient to estimate $C(t)$ by a method of successive approximations. Expression (13.38) can be simplified by letting $\mathrm{e}^{-1/\tau} = k$. In this instance, at $1/\tau \ll 1$, expanding the function $k = \mathrm{e}^{-1/\tau}$ in a power series of $1/\tau$, one obtains

$$k = 1 - \frac{1}{\tau}, \tag{13.39}$$

or

$$\tau = 1 - \frac{1}{k}. \tag{13.40}$$

Substituting the last expression into the age function $p(t)$, coming into Eq. (13.38), one obtains

$$P(t) = (1 - k)k^t, (k < 1). \tag{13.41}$$

Then, taking $\alpha = 1$, Eq. (13.38) becomes (Dinçer and Payne 1971)

$$C(t) = \sum_{1953}^{t=n} C_t(\theta - t)(1 - k)k^t e^{-\lambda t}. \tag{13.42}$$

Here, as a rule, the summation is carried out over all the years since the beginning of thermonuclear tests, i.e., 1953, and $C_t(\theta - t)$ is accepted as an average tritium concentration in precipitation for a corresponding year. For practical purpose the values $C_t$ estimated at different values of $k$ (0.1, 0.2, 0.3, etc), are indicated in the plot together with the experimentally measured values of tritium in the aquifer. Then, comparing the theoretical and experimental curves, the most probable value of the averaged residence time of water in a basin is determined.

The complete mixing model has been used for estimating the residence time of groundwater in the karstic region of the Anatolian coast in Turkey (Dinçer and Payne 1971), for studying aquifers sited near Vladimir (Polyakov and Seletsky 1978) for studying the groundwater discharge characteristics of the Aragatz Mountain region (Vlasova et al. 1978) and for studying the water dynamics in Moscow artesian basin (Zlobina et al. 1980).

It should also be pointed out that the age distribution of water, described by Eq. (13.37), does not always imply the existence of an underground or surface reservoir with good mixing. This model is also advantageous for studying aquifers drained by the aquifer thickness.

### 13.8.4 Symmetrical Binominal Age Distribution Model

According to this model the probability of the appearance of water characterized by an age $t$ at the output of the hydrogeological system has the form (Martinec et al. 1974):

$$p(t) = \frac{1}{2N}\binom{N}{t}, \; t = 0, 1, 2, 3 \; \ldots, \tag{13.43}$$

The parameter $N$ in this case is dependent upon the mean residence time of water in the hydrogeological system and is given in the form: $N = 2\tau - 1$ or $\tau = (N + 1)/2$.

The numerical coefficient $N/t$ represents the binominal coefficient defined by the binominal theorem

$$(a+b)^N = \binom{N}{0}a^N + \binom{N}{1}a^{N-1}b + \binom{N}{2}a^{N-2}b^2 + \ldots + \binom{N}{N-1}ab^{N-1} + \binom{N}{N}b^N.$$

The following properties of this expansion are known: $N/0 = N/N = 1$, and the sum of all the binomial coefficients is equal to $2^N$. Therefore, it is evident from the discrete binomial distribution that in the case of the continuous variation of the parameter $t$ a normal distribution results with dispersion and average residence time depending upon the parameter $N$.

Figure 13.48 indicates some models of age distribution corresponding to the groundwater basin of the Dischma River (Switzerland).

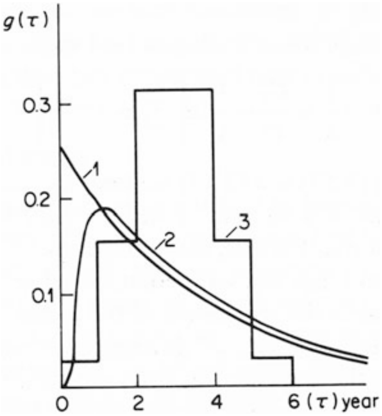


**Fig. 13.48** Models of age distribution for groundwater basin of the Dischma River: (*1*) experimental data, $\tau = 4$ years; (*2*) dispersive, $\tau = 4.8$ years; (*3*) binominal, $\tau = 3$ years. (After Martinec et al. 1974. © IAEA, reproduced with permission of IAEA)

### *13.8.5 Model of Mixing Waters of Different Ages*

This model accounts for the case when discrete differences in the distribution of residence times are observed, for example, young waters in an aquifer may mix with very old waters. If the volume of the whole system is $V$ and the volume of an individual constituent is $V_i$, then their relative contribution is

$$p_i = \frac{V_i}{V}, \tag{13.44}$$

where $V = \sum V_i$ and $\sum p_\mathrm{i} = 1$.

If the true age of an individual component is $t_i$, then the age of a mixture is

$$t_{\sum} = \sum p_i t_i = \bar{t}, \tag{13.45}$$

where $\bar{t}$ is the mean weighted age.

If the initial concentration of each constituent is $C_{0I}$, then at the moment of mixing its concentration is

$$C_i(t_i) = C_{0i} e^{-\lambda t}. \tag{13.46}$$

After mixing in a system its concentration becomes

$$C = \sum p_i C_i = \tau = \sum p_i C_{0i} e^{-\lambda t}.$$

While estimating the age of a water mixture, e.g., using the piston flow model, the formal application of expression (13.31) gives the age:

$$t' = \frac{1}{\lambda} \ln \frac{C_0}{C} = \frac{1}{\lambda} \ln \Big[ \sum p_i \exp\left(-\lambda t_i\right) \Big]^{-1}. \tag{13.47}$$

Comparing expressions (13.45) and (13.47) we find that actually $t \neq \bar{t}$. Therefore, it follows that the true age of a mixture of waters of different ages is equal to the average age of its components. Further, the isotope age of the water mixture does not normally equal to the true age and its theoretical value has nothing in common with that for a real system in the framework of the piston flow model. In principle, the problem of the mixing of waters of different ages can only be solved while taking into consideration the behavior of several radioisotopes and counting out the time from the moment the waters become mixed. In this way, the problem is reduced to the solution of the system of equations

$$C_k = \sum^{m} p_i C_{0ik} \exp(-\lambda kt), \sum^{m} p_i = 1, \tag{13.48}$$

where $C_{0ik}$ is the concentration of the $k$th isotope on the $i$th constituent of a mixture at $t=0$; $p_i$ is the contribution of the $i$th constituent; $\lambda_k$ is the decay constant of the $k$th isotope; $t$ is the time elapsed since the moment of mixing; $m$ is the number of constituents in a water mixture.

Using the stable isotopes only, i.e., those for $\lambda_k = \infty$, system (13.48) is reduced to that describing a simple mixing. For more details the reader is referred to Ferronsky et al. (1977).

### *13.8.6 Complicated Model*

Such a model is indicative of most natural systems. In this model, the output function of a system of one type becomes the input function of a system of another type, for example, the groundwater basin with a normal distribution of transition times is connected to a basin characterized by complete mixing, and so on. Studies of the complicated systems, involving a tritium and other tracer, require a detailed knowledge of the geology and hydrology of a basin.

Besides the above-mentioned models other combinations and varieties are used in hydrogeological studies.

A number of authors have carried out measurements of the tritium concentrations in groundwaters up to the depth of several hundreds of meters. These studies were carried out in various hydrogeological conditions: in the Vienna basin sited near the Alps, in the hydrothermal regions of New Zealand and Iceland, in the limestone and dolomitic formations of the Transvaal in South Africa and elsewhere. It has been found that tritium concentrations decrease sharply with depth. Seasonal variations of tritium in the depth of an aquifer are not observed, indicating the continuous replenishment of the aquifer during the year with a constant rate of recharge. Considerable variations of tritium content exist for various boreholes located within a basin at short distances from each other, indicating the various conditions of recharge and rates of inflow. While studying geothermal regions the applicability of the techniques for the estimation of the inflow rate of surface waters to the zone of heating, and their subsequent time of circulation, was demonstrated (Gonfiantini and Panichi 1982; Pinneker et al. 1978; Theodorsson 1967).

Tritium techniques are an effective instrument in investigation of pollution problems, especially the release of radio-nuclides into groundwater from nuclear power plants and atomic wastes. The last problem becomes actual in connection with active construction of the nuclear power plants. In the last decade, these studies are intensified (Polyakov and Golubkova 2007; Sokolovsky et al. 2007b; Tokarev et al. 2009).

In 1969, Tolstikhin and Kamensky (1969) proposed the helium–tritium method of groundwater age determination; by this method water age is calculated as

$$t = \frac{1}{\lambda} \ln \left( \frac{^3\mathrm{He}^*}{^3\mathrm{H}} + 1 \right),$$

where $^3\mathrm{He}^*$ is the helium-3 concentration in groundwaters which appears as a result of the tritium decay.

It is not necessary in determination of the input function $C_a(\theta - t)$ in Eq. (13.38). This method is used, first of all, for the study of "young" groundwater (Plumer 2005; Schlosser et al. 1988, 2000).