Fig. 7-1 Variations of δ¹⁸O in Weimakiriri River compared to the sinusoidal input from precipitation. Discharge for the well mixed catchment of 0.5, 1 and 5 years are shown (from Burgman et al., 1987).
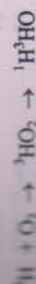
Tritium in Precipitation

Tritium (³H or T) is probably the most commonly employed radioisotope used to identify the presence of modern recharge. It is a short-lived isotope of hydrogen with a half-life of 12.43 years (Unterweger et al., 1980). It is directly incorporated into the water molecule ($^1H^3HO$ or ^1HTO) and so is the only radioisotope that actually dates groundwater. Tritium is produced naturally by cosmic radiation, although much greater production accompanied the atmospheric testing of thermonuclear bombs between 1951 and 1980. By ~1990 most of this "bomb" tritium had been washed from the atmosphere, and tritium levels in global precipitation are now close to natural levels. Small releases from nuclear power plants and weapons plants may preclude reaching the natural levels measured in pre-1951 water. Over the past three decades, the presence of thermonuclear tritium in groundwater was used as clear evidence for active recharge. While thermonuclear tritium can still be found in some slowly moving groundwaters, the largely natural ³H signal is now relied upon for dating modern groundwaters.
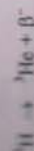
Cosmogenic tritium

Natural tritium is formed in the upper atmosphere from the bombardment of nitrogen by the flux of neutrons in cosmic radiation, following the reaction:

$$^{14}_{7}N + ^{1}_{0}n \rightarrow ^{12}_{6}C + ^{3}_{1}H$$

The tritium thus formed combines with stratospheric oxygen to form water:

$$^{3}_{1}H + O_2 \rightarrow ^{3}HO_2 \rightarrow ^{1}H^{3}HO$$

Tritium decays to ³He by beta release:

$$^{3}_{1}H \rightarrow ^{3}He + \beta^{-}$$

Tritium concentrations are expressed as tritium units (TU) where:

$$1\ TU = 1\ ^3H\ per\ 10^{18}\ hydrogen\ atoms$$

and $1\ TU = 0.118\ Bq \cdot kg^{-1}$ ($3.19\ pCi \cdot kg^{-1}$) in water   (IAEA 1983)

Natural tritium levels in precipitation are very low and represent a secular equilibrium between natural production and the combination of decay in the atmosphere plus loss to the hydrosphere and oceans. Production rates and concentrations in precipitation are a function of geomagnetic latitude, with greater production at higher latitudes. Very few measurements exist of natural, pre-bomb tritium in precipitation. Precipitation near Ottawa had about 15 TU, as measured in laboratory reagents mixed with Ottawa River water before 1951 (Brown, 1961). Kaufman and Libby (1954) used vintage wines to determined pre-bomb ³H concentrations of 3.4 to 6.6 TU for precipitation at the lower latitudes of the Naples NY, Bordeaux and Rhône regions. In Fig. 7-2 we see the concentrations of cosmogenic tritium measured in meteoric water prior to 1951, and the increases observed during the early tests of hydrogen-fusion devices.
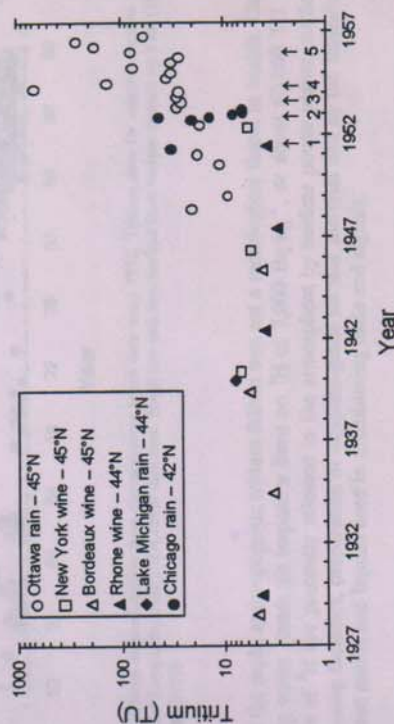
Fig. 7-2 Tritium levels in precipitation prior to and during the earliest atmospheric tests of thermonuclear devices. Ottawa rain — Brown, 1961; wines — Kaufman and Libby, 1954; Chicago rain, Lake Michigan — Kaufman and Libby, 1954). Atmospheric tests: 1 — George, 75 kilotons, U.S.A.; 2 — Ivy-Mike, 10 megatons, U.S.A.; 3 — RDS-6s, 400 kilotons, U.S.S.R.; 4 — Castle series, total 47 megatons, U.S.A.; 5 — second Soviet thermonuclear test, 2 megatons.

Thermonuclear (bomb) tritium

On May 9, 1951, the world's first thermonuclear flame was ignited by a ^2H-^3H-^{235}U device code-named George[1]. The Hagiwara-Fermi-Teller concept of hydrogen fusion had been successfully tested. On the first day of November, 1952, The Ivy-Mike shot demonstrated that megaton energy releases could be achieved by hydrogen fusion and the thermonuclear superbomb was born. The atmospheric detonation of these devices began a period of anthropogenic ³H production which raised concentrations in the stratosphere by several orders of magnitude.

[1] Physics Today, November 1996 <http://www.aip.org/pt/>.

Early configurations of the hydrogen bomb used the radiation of ^{235}U-fission to compress the deuterium-tritium fuel to initiate fusion. Subsequent designs use the high neutron production of ^{235}U-fission to split lithium deuteride, and the heat of fission to then ignite the deuterium and tritium products:

$$^{235}\text{U} \xrightarrow{\text{fission}} \text{Kr} + \text{Ba} + 2n$$

$$^{6}\text{Li}\,^{2}\text{H} \xrightarrow{\text{fission of }^{6}\text{Li}} {}^{3}\text{H} + {}^{2}\text{H} + {}^{4}\text{He} + \text{heat of U-fission}$$

$$\downarrow \quad \downarrow$$
$$\text{Fusion}$$
$$\downarrow \quad \downarrow$$
$$^{5}\text{He} + \text{energy}$$
$$\downarrow$$
$$^{4}\text{He} + n$$
$$^{14}\text{N} \rightarrow {}^{12}\text{C} + {}^{3}\text{H}$$

^{5}He is not very stable ($t_{\frac{1}{2}} = 6.7 \cdot 10^{-22}$ s) and decays by neutron emission to stable ^{4}He. The tremendous neutron flux at the end of this reaction chain activates atmospheric nitrogen, producing ^{3}H. Although fission from detonation of uranium and plutonium bombs began on July 16, 1945, the neutron flux from these comparatively small and low-level fission tests, had no impact on meteoric ^{3}H.

Table 7-1 Tritium released in the atmosphere by major thermonuclear tests (Gonfiantini, 1996; Rath, 1988)

Year	Country	Fusion Energy Megatons of TNT	Tritium released TBq*
1951	USA	0.075	0.1
1952	USA	6.0	4.4
1953	USSR	-0.2	-0.1
1954	USA	17.5	13
1955	USSR	1.5	1.1
1956	USA, USSR	15.3	11.3
1957	UK, USSR	10.0	7.4
1958	UK, USA, USSR	31.1	23
1958	USSR	96.9	72
1961	USA, USSR	140.8	104
1962	USA, USSR	0.21	0.15
Limited Test Ban Treaty			
1967	China	1.3	1
1968	China, France	2.6	1.9
1969	China	1.0	0.7
1970	China, France	1.2	0.9
1973	China	0.9	0.7
1974	China	0.15	0.1
1976	China	1.75	1.3

* Tera-becquerels (10^{12} Bq)

Atmospheric testing of nuclear devices between 1952 and 1962 (Table 7-1) generated a tremendous quantity of atmospheric tritium (Fig. 7-3). This substantial input created a tritium reservoir in the stratosphere which contaminated global precipitation systems for over four decades. A 1963 Soviet-American treaty banned the atmospheric testing of thermonuclear devices, although minor Chinese and French tests continued until 1980. The final year of megaton tests (1962) generated a huge peak, which appeared in precipitation in the spring of 1963. This 1963 peak became a marker used in many hydrological studies. Concentrations of ^{3}H in precipitation are now largely back to natural, cosmogenic levels.

Fig. 7-3 Tritium in precipitation from thermonuclear bomb tests. Tritium data for selected stations in North America and Europe, from the IAEA GNIP data base. Bomb test data summarized from various sources by Rath (1988) and Gonfiantini (1996).

Even at the peak, anthropogenic tritium fallout was not a radiological threat to health. Canadian drinking water standards impose a limit on ^{3}H of 7,000 Bq·kg^{-1}, or about 60,000 TU. Minor amounts of ^{3}H are presently released to the atmosphere by nuclear power plants, nuclear fuel reprocessing facilities, preparation of weapons-grade nuclear material and by the manufacture of tritiated paints and liquids used in illuminating dials and signals.

The longest record of atmospheric tritium concentrations was initiated by R.M. Brown for precipitation at Ottawa, Canada, and begins in 1953 (Fig. 7-4). The IAEA has established several long-term records from its monitoring stations throughout the world. Numerous short-term records at American stations were generated during the peak input years between 1960 and 1980. All data are available at <www.iaea.or.at:80/programs/ri/gnip/gnipmain.htm>.

Two features should be observed in this figure; the consistent annual fluctuation in ^{3}H, and the rapid decline from the 1963 peak. The greatest transfer of tritium from the stratosphere to the troposphere occurs during the spring in mid-latitude zones. This is due to seasonal disturbances in this boundary by displacement of the jet stream as upper level air circulation reorganizes in the spring. This "spring leak" annually recharges the hydrosphere (Fig. 7-4). The decline of tritium in precipitation is not due only to decay, which decreases tritium levels by only 5.5% per year (shown below in Fig. 7-8). A major factor is attenuation by the oceans and groundwater, which have since become major reservoirs of thermonuclear ^{3}H.

There are also strong variations in the global distribution of tritium. Circulation in the stratosphere is latitudinally constrained, resulting in a latitudinal banding of tritium in rainfall,

(Eriksson, 1966). Fig. 7-5 shows the strong variation in ^{3}H monitored at Ottawa, Cape Hatteras in North Carolina, and in the tropics at Barbados. Note the highest levels found at the most northerly station. As virtually all atmospheric testing was conducted in the northern hemisphere (with the exception of the French tests in the South Pacific), there is also a several year lag during mixing across the equator.
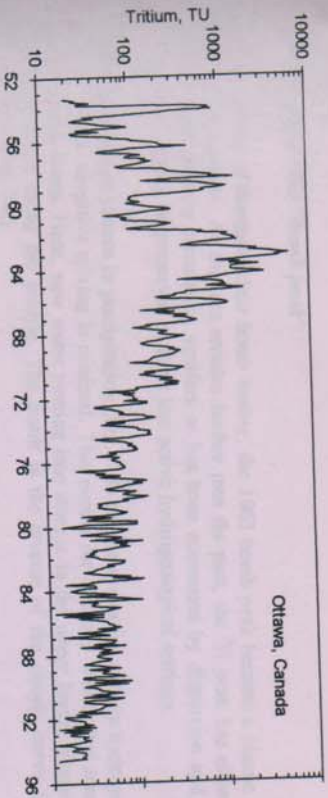
Tritium, TU

10000 — 1000 — 100 — 10

52 56 60 64 68 72 76 80 84 88 92 96

Ottawa, Canada

Fig. 7-4 Tritium in precipitation at Ottawa as measured in composite monthly samples (monitoring record established by R.M. Brown, AECL, Canada). Decreases from the peak in 1963 is due to attenuation in the oceans. The flattening of the decline after about 1980 and the sharp decline in 1990 likely reflect local activities in southern Ontario.

Tritium, T

10000 — 1000 — 100 — 10 — 1

52 56 60 64 68 72 76 80 84 88 92

Year

Ottawa – 45°N
Hatteras – 35°N
Barbados – 13°N
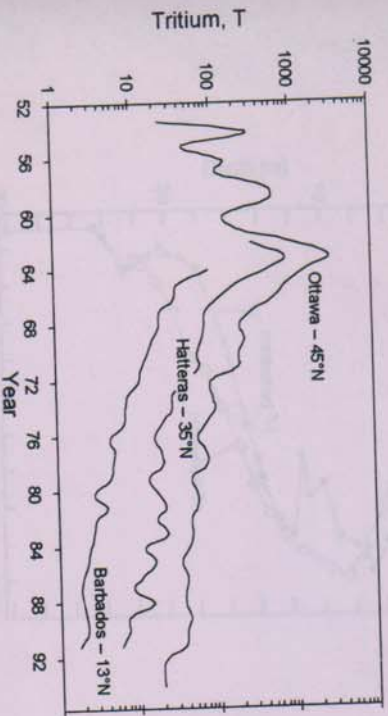
Fig. 7-5 Annually averaged tritium concentration in precipitation at three sites in North America showing the strong latitudinal variation.

Nuclear reactor tritium

Considering the high neutron fluxes in nuclear reactor cores, it is not surprising that tritium is also produced in such settings by neutron activation of nitrogen. Pathways into the environment occur through steam and water releases from power plants. Although these are only point sources from a global perspective, emissions can be locally high, and result in high-^{3}H halos in surface waters, groundwaters and plant cellulose. For example, 1000-MW boiling water reactors

discharge on the order of 10^{10} Bq/year (20 to 30 Ci/yr), which is in the range of some of the smaller nuclear bomb tests. Fast breeder reactors (reactors that create more fissionable daughter nuclides than parents consumed) can leak up to five times as much.

Geogenic production of ^{3}H

A neutron flux is then present not only from cosmic radiation, but also in the subsurface, due to spontaneous fission of U and Th. In rocks with appreciable amounts of lithium, this results in ^{3}H production through the fission of ^{6}Li according to:

$$^6Li + n \rightarrow\ ^3H + \alpha$$

Geogenic tritium is then incorporated directly into groundwater, where concentrations depend on the Li content of the host rock, and porosity (Gascoyne and Kotzer, 1995). The short half-life and low production rate generally preclude significant accumulation of geogenic ^{3}H, although some rocks can have measurable quantities. Andrews et al. (1989) calculate that levels up to 0.7 TU should exist for groundwaters in the Stripa granite, which may account for the low levels measured in the deeper samples. In most aquifers, geogenic ^{3}H is close to or less than the low-level analytical detection limit of 0.1 TU.

In contrast, the high neutron fluxes found in zones of uranium mineralization can generate levels higher than cosmogenic ^{3}H. In the ore zone at Cigar Lake, a UO_2 deposit at the base of Proterozoic sandstones in Saskatchewan, groundwaters have geogenic ^{3}H concentrations exceeding 250 TU (Fabryka-Martin et al., 1994). The Oklo natural reactors of Gabon also have elevated tritium in groundwaters due to subsurface production.

Dating Groundwaters with Tritium

Kaufman and Libby (1954) first recognized the potential for dating groundwater with cosmogenic tritium. As geogenic ^{3}H in most groundwaters is negligible, measurable ^{3}H in groundwaters virtually always signifies modern recharge. When levels are high (>~30 TU), thermonuclear bomb ^{3}H is implicated, indicating recharge during the 1960s. Groundwaters containing levels of tritium that are close to detection (~1 TU) are most often submodern or paleogroundwaters that have mixed with shallow modern groundwaters in the discharge zone (e.g. springs) or within boreholes. Both qualitative and quantitative approaches to dating groundwaters with ^{3}H are possible:

1. *Velocity of the 1963 ^{3}H peak* — identification of the bomb-spike preserved in groundwaters clearly identifies their age.

2. *Radioactive decay* — calculating the time for decay from a known input level to the measured level.

3. *Exponential model for input function* — determining the "recharge attenuated" decay tritium levels for a given groundwater flow system, and applying the decay equation.

4. *Time series analysis* — repeat sampling from specific points over several years allows monitoring of the bomb spike as it passes through the aquifer, giving an indication of mean residence time.

5. *Qualitative interpretation* — measurable $^3H \equiv$ component of modern recharge.

Velocity of the 1963 "bomb peak"

During the era of thermonuclear bomb testing, the 1963 bomb peak became a classic "marker horizon" in aquifers. As this era recedes further into the past, the ^3H peak has either moved through most actively circulating aquifers or has been attenuated by dispersion and mixing. Nonetheless, it may be preserved in some less active hydrogeological settings.

The tritium fallout pattern in precipitation (Fig. 7-4) can be preserved only in hydrogeological systems where advective mixing is minimal. This occurs for recharge waters that transit thick non-saturated zones. Here, new water moving into storage in the upper layers displaces older water downward along the profile. The result is the reverse of the classic curve for ^3H in precipitation (Fig. 7-6).
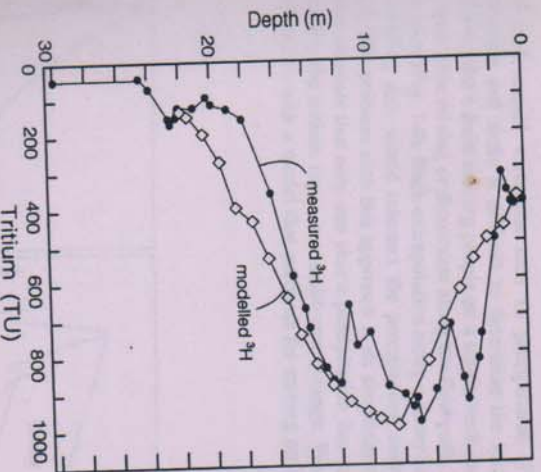
Fig. 7-6 Tritium in soil moisture in a sand aquifer, Denmark. The measured ^3H profile is shown with the profile generated with a piston flow model incorporating dispersion (modified from Andersen and Sevel, 1974).

If a specific year can be identified at a given depth in a recharge profile, then the soil moisture content above this level compared to total precipitation since that year represents the percent infiltration. Dincer et al. (1974) use this approach and show that net recharge through dune sands in Saudi Arabia was as high or higher than 30%. Unfortunately, the thermonuclear bomb peak has long since moved through the non-saturated zone in most aquifers. Only examples with either low infiltration rates or thick non-saturated zones may still preserve the ^3H profile.

Hydrodynamic dispersion and mixing below the water table tend to attenuate variations in the ^3H input function. Nonetheless, some groundwaters have preserved the 1963 tritium bomb peak below the water table sufficiently well that its position can be used to determine groundwater flow rates below the water table. This method provides estimates of flow velocities and mean circulation times, which can be compared to hydrodynamic velocities. Michel et al. (1984) used the 1963 tritium peak to determine the velocity of groundwater moving into a confined sandy aquifer from a special waste disposal site in Gloucester, Ontario. Tritium values in 1982 (Fig. 7-7) show that three tritium peaks are preserved in the aquifer; immediately below the special waste compound, at 250 m along the flow path through the aquifer, and further down-gradient in the sand. The close peak is due to tritium-labeled organic compounds in the waste sorbing on the sand. The most distal peak at 250-m peak is 1963 recharge, which gives a flow velocity of 4.4 cm/day. The 250-m peak represents rapid flow through coarse basal sediments overlying bedrock.
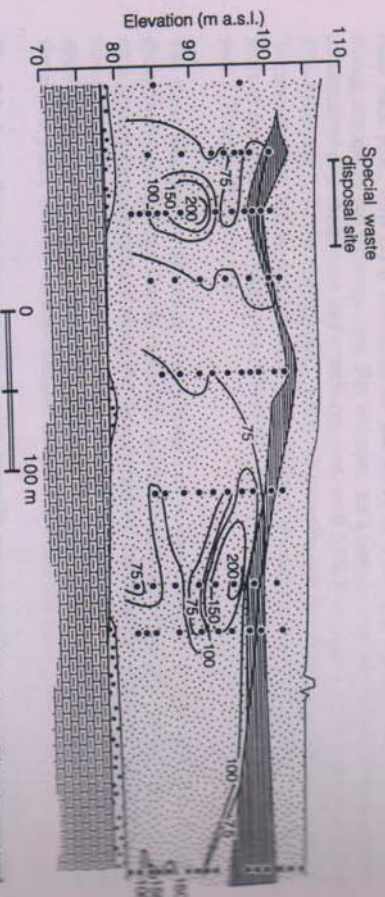
Fig. 7-7 Distribution of tritium in groundwaters in a confined sandy aquifer down-gradient of a special waste compound (Michel et al., 1984). Aquifer is confined by clay silts at about 5 m depth.

A much better definition of the tritium fallout peak in recharge environments can be obtained if it is possible to analyze for ^3He — the decay product of tritium, as well as ^3H. Several studies have been undertaken to document the usefulness of this approach especially since only 40 cm³ of water collected in absolutely airtight Cu-tubes is required for these measurements (Ekwurzel et al., 1994). The $^3H/^3He$ dating technique is discussed in more detail below.

Radioactive decay

Dating of groundwater by decay of tritium is based on the assumption that the tritium input into a groundwater is known and that the "residual" tritium measured in a groundwater is the result of decay alone, according to the decay equation:

$$a_t{}^3H = a_o{}^3H \, e^{-\lambda t}$$

Here, $a_o{}^3H$ is the initial tritium activity or concentration (expressed in TU) and $a_t{}^3H$ is the residual activity (measured in a sample) remaining after decay over time t. The decay term λ is equal to ln2 divided by the half-life $t_{1/2}$. Using tritium's half-life, $t_{1/2}$ = 12.43 years, this equation can be rewritten:

$$t = -17.93 \ln \frac{a_t {}^3H}{a_o {}^3H}$$

For the example of $a_o {}^3H = 10$ TU, this gives the decay series:

years:	0	10	20	30	40	50	60
TU:	10	5.7	3.3	1.9	1.1	0.6	0.4

Thus, the useful range for dating with ^3H is less than about 50 years when analyses are performed by the enriched method (limit of detection = 0.8 TU). Pre-bomb tritium could be measured if low-level measurement techniques such as propane synthesis or ^3He ingrowth (± 0.1 TU) are used. Rarely do we find groundwaters that are uncontaminated by mixing with modern waters, or *in situ* production of ^3H are to be measured. Tritium levels in modern precipitation dating by ^3H decay. High-precision analyses are important where minor mixing with modern are now close to stable, natural levels, and the possibility of using the decay equation for young groundwaters becomes more straightforward.

The strong seasonal and annual variations seen in precipitation (Fig. 7-4) represent a complicated input function and make it difficult to determine the initial ^3H at the time of recharge. For piston flow (like a train moving people on a single track compared with cars on a multi-lane freeway), with little mixing or dispersion along the flow path, a recharge date can be estimated from decay lines (Fig. 7-8). Back-extrapolation along a decay line from a measured ^3H value for a given sampling date would intersect the precipitation curve at the year(s) when infiltration took place. The problem with this approach is its simplicity (not a characteristic of natural systems) which assumes that only one year's precipitation has contributed to the water sample. More commonly, the tritium input function is a multi-year average. We need to calculate this more realistic input function with a model that accounts for mixing and decay in the recharge environment.
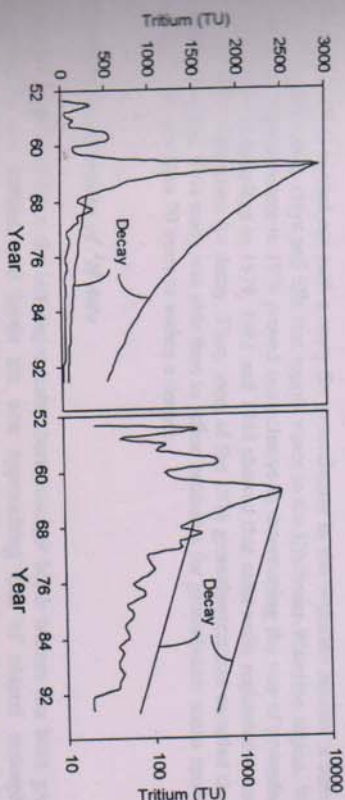
Fig. 7-8 Decay of tritium from given inputs from precipitation (on normal and semi-log plots). The input function is more complicated than this simple decay function would imply, due to mixing and decay in the recharge area. The decline of tritium is far greater than accounted for by decay alone, due to mixing with oceans and groundwater.

Input function for ^3H in groundwater

Consider a parcel of groundwater in a regional aquifer. In most cases it is a composite of several years' precipitation which have contributed to this water through mixing within the unsaturated zone, and by flow through the recharge area where additions to the water table continually contribute to the groundwater. Once this groundwater has moved into a confined zone, or to depths where it no longer receives additions from the surface, its ^3H content will decrease by decay. The ^3H concentration in this groundwater parcel will be a function of its residence time in the recharge environment.

The multi-year ^3H input function can be determined from: (1) the weighted contribution of ^3H from each year, with (2) a correction for the decay of each year's precipitation contribution during storage in the recharge area. For example, let's assume that our parcel of groundwater accumulated over three years in the recharge area, with 25% from year 1, 50% from year 2 and 25% from year 3. At the end of year 3, when our groundwater moves past the recharge zone, its ^3H concentration will be equal to 25% of the ^3H level in year 1 precipitation times 25%, with 3 years of decay (5.5% per year) plus 50% of the ^3H in year 2, decayed over 2 years, plus 25% of year 3 ^3H decayed over 1 year.

The input function for tritium in precipitation can be approximated by this approach, using a decay model of recharge that is essentially a smoothing calculation. The model assumes that each groundwater component along the flow system has received the same weighing of multi-year contributions from precipitation in the recharge environment. The weighing of each year is approximated by a normal distribution that puts the greatest weight on the precipitation from the central years, with lowest contributions from the first and last years.

Fig. 7-9 shows three recharge models for the annually averaged tritium curve for Ottawa. The recharge curves are plotted for the year when the groundwater becomes shut off from additional recharge. Increasing the number of recharge years in the model attenuates the peak fallout level, and increases inputs in post 1962 recharge relative to the input curve (1 year MRT).
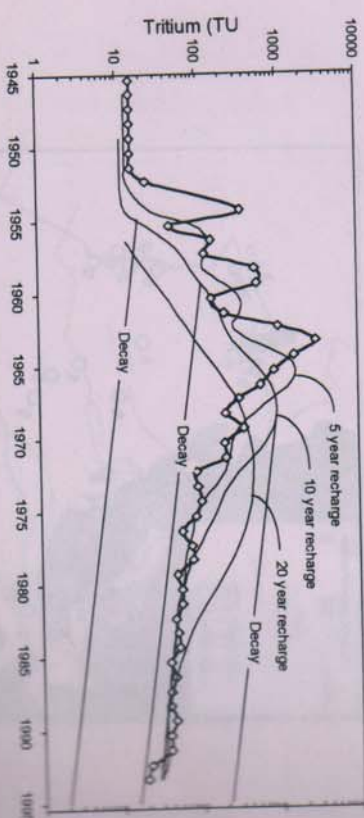

Fig. 7-9 Tritium fallout (weighted annual average) in precipitation collected at Ottawa (heavy line), with decay models for initial tritium in groundwater. Models assume that recharge to a given parcel of groundwater takes place over 3, 10 and 30 year periods and are plotted for the year that the groundwater becomes closed to further contributions from precipitation. The decay lines are valid for "closed system conditions" following the movement of the groundwater beyond the recharge area.

Extrapolation from a measured value for groundwater sampled at a given date to the most appropriate recharge input curve provides an estimate of groundwater residence time beyond the recharge environment. For example, lets assume that in 1995 we measured 2 TU in groundwater from an aquifer with an estimated 10 year period of accumulation in the recharge area. Back extrapolation along the bottom decay curve in Fig. 7-9 intersects the 10 year recharge curve at the end of 1954. Total mean subsurface residence time would then be about 40 years plus the mean residence time in the recharge area (about 5 years).

The MRT selected for the model depends on the hydrogeological setting in the recharge environment. Systems with thick unsaturated zones and large, unconfined recharge areas may mix recharge over 5 to 10 years or more before a given groundwater parcel becomes closed to further inputs. In contrast, systems with recharge regions of limited areal extent may have little mixing in the recharge area. In this case, the recharge period may be less than 5 years.

Time series analysis

Sequential sampling of groundwater for tritium analysis can be used to identify the bomb-spike and provide a good indication of mean residence time. Using a smoothed atmospheric ³H input function, the ratio of two samples from the same piezometer or well (corrected for decay) will indicate the relative location of the 1963 peak. This can be expressed as a ratio of the tritium level at the early sampling, corrected for losses due to radioactive decay between sampling times, to the level in the later sampling:

$$\frac{^3H_{early} \cdot e^{\lambda t}}{^3H_{later}}$$

where t is the time between samplings in years (t = t_{later} − t_{early}), and λ is the decay constant (λ = ln 2/$t_{1/2}$) which for tritium is 0.05576. A ratio greater than 1 would suggest that the peak has passed the observation point, whereas if this ratio is less than 1, then the observation point is sampling the leading edge of the spike. Sequential sampling with a frequency as low as every 5 to 10 years would then be useful.

Fritz et al. (1991) carried out such a study for groundwater in the Waterloo aquifer, a complex of glaciofluvial sands, clays and tills that supply water to the Kitchener-Waterloo region. While a sampling of piezometers in 1976 proved inconclusive in determining the rate of groundwater flow, subsequent sampling in 1979, 1981 and 1988 showed that most wells registered a drop in ³H levels, after correction for decay. Thus, most of the 1976 groundwaters had sampled the tail of the bomb spike. This study was able then to refine estimates for groundwater mean residence time from younger than 30 years to within a decade.

Qualitative interpretation of ³H data

In the three decades since the last major tests, thermonuclear bomb tritium has been greatly attenuated by the oceans, and levels are now approaching that of natural atmospheric production. This evolution of the input function plus mixing in some aquifers with pre-bomb groundwater conspire against refined interpretations of groundwater ages. A quantitative interpretation of groundwater mean residence times may not be possible, and only qualitative interpretations can be made:

For continental regions:

<0.8 TU	Submodern — recharged prior to 1952
0.8 to ~4 TU	Mixture between submodern and recent recharge
5 to 15 TU	Modern (<5 to 10 yr)
15 to 30 TU	Some "bomb" ³H present
>30 TU	Considerable component of recharge from 1960s or 1970s
>50 TU	Dominantly the 1960s recharge

For coastal and low latitude regions:

<0.8 TU	Submodern — recharged prior to 1952
0.8 to ~2 TU	Mixture between submodern and recent recharge
2 to 8	Modern (<5 to 10 yr)
10 to 20	Residual "bomb" ³H present
>20 TU	Considerable component of recharge from 1960s or 1970s

Tritium in alluvial groundwaters — an example from Oman

Shallow alluvial groundwaters in Oman are recharged primarily by infiltration of flash flood events, whereas interchannel areas receive direct infiltration and subsurface flow. Recharge is sporadic, and shallow groundwater can have a wide range of ages. Tritium becomes an excellent indicator of the occurrence of modern inputs.

Fig. 7-10 shows the tritium concentrations in groundwater in the alluvial fans flanking the Northern Oman Mountains. In this case, recharge is dominantly from infrequent convective rainfall occurring in the mountains. Tritium levels in these groundwaters decline with increased distance along the principal wadi courses. In the most up-gradient areas, ³H contents are in the range found for modern precipitation at nearby Bahrain. However, they are below detection in the thick alluvial sediments found towards the *serir* (interior plain).
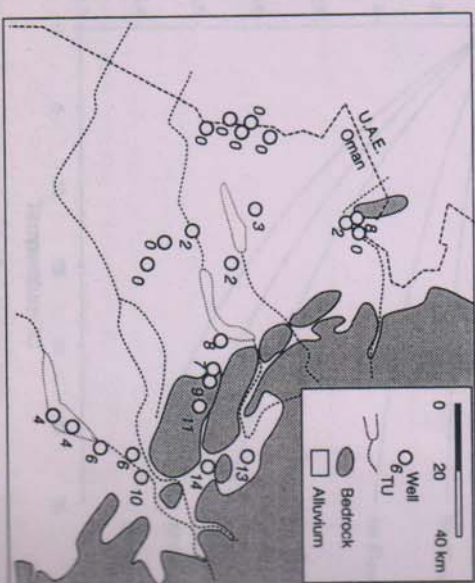

Fig. 7-10 Tritium contents in groundwaters from shallow alluvial aquifers of the interior drainage system in northern Oman

If groundwater ages increased rather uniformly down-gradient, one would expect an *increase* in ³H down-gradient, despite decay, because the thermonuclear ³H input function is decreasing faster than natural decay (Fig. 7-8). If this were the case, plug flow would dominate. So what do these tritium levels tell us? Groundwater in the upper reaches of the alluvial aquifers comprises mixtures of recharge from the past few years only (<~5 year mean residence time). Groundwater in the interfluvial regions (fossil alluvial channels) are sub-modern in age, which demonstrates that direct infiltration of rainfall is not an efficient recharge mechanism in such regions.

Deep groundwaters - mixing in fractured rock

Groundwater found at depth in crystalline or sedimentary basin settings have high salinities developed through water-rock interaction over long (perhaps geologic) time scales. When measurable ³H above 1 TU is found in these brines this signifies a hydraulic connection with the surface. Although leakage through shafts, adits and boreholes can be implicated, connected fractures and faults are often responsible. This has important implications for contaminant transport, and in particular for the security of potential radioactive waste repositories. Monitoring tritium in deep mine settings demonstrates that such short-circuits can be established over short time periods.

Tritium levels (and ¹⁴C) increase over time in some mine inflows (Moser et al., 1989; Douglas, 1997), indicating that near-surface groundwaters are mixing at increasingly greater depths. Frape and Fritz (1987) show ³H increasing from less than detection to near modern levels (37 TU in the Con mine in Yellowknife, and 70 TU in Sudbury) over several years of active discharge. Douglas (1997) shows a decrease at the Con mine by 1996, signifying the passage of the 1964 peak.

However, measurements at the Stripa site, a closed iron mine in central Sweden which was under study as an analogue for a radioactive waste repository, show small amounts of tritium in some groundwaters up to 1000 m deep. For this situation, Andrews et al. (1989) show that a minor component of ³H may be due to subsurface production. This can occur in rocks with high U, Th and K levels (granites, shales) due to neutron activation of N. The short half-life will maintain concentrations generally very close to detection and at Stripa below 0.7 TU, the maximum level of production. Such occurrences of tritium in the deep groundwater has important implications with respect to the degree of isolation provided at this depth. Similar observations and calculations were made for the saline waters of the KTB deep drillhole in Germany where fluids had 0.35 TU. This can be attributed to *in situ* production.

Groundwater Dating with ³H - ³He

The earlier discussion leaves us with the impression that our ability to produce quantitative tritium ages for groundwaters is fading as fast as the thermonuclear bomb peak. However, by measuring ³H together with its daughter ³He, true ages can be determined through calculations that do not rely on the complicated tritium input function. The drawback to this approach is that ³He is not a routinely sampled nor measured isotope (Clarke et al., 1976). The method was first introduced to the field of hydrogeology in 1979 (Torgersen et al., 1979). Schlosser et al. (1988) provide an excellent review and application and Ekwurzel et al. (1994) compare this technique with dating based on chlorofluorocarbons (CFCs) and ⁸⁵Kr.

Helium-tritium systematics

The decay of tritium from an initial concentration $^3H_0$ after some time t is predicted by:

$$^3H_t = {}^3H_0\, e^{-\lambda t}$$

However, determining t requires that we know $^3H_0$. The decay of tritium leads to an ingrowth of ^3He, which would then be:

$$^3He_t = {}^3H_0(1 - e^{-\lambda t})$$

By combining both equations, we can cancel the dependency on the input concentration of tritium $^3H_0$:

$$^3He_t = {}^3H_t(e^{\lambda t} - 1)$$

The helium concentration at time t, ^3He_t, is expressed in TU (1 ^3He per 10^{18} H). The measured ^3He must be corrected for atmospheric ^3He that is dissolved at the time of recharge. Note that atmospheric He is dominantly ^4He. This input is assumed to be at equilibrium with the atmosphere, and considers the following points:

- Atmospheric ^4He concentration is 5.24 ppmv (Glueckauf, 1946)
- Atmospheric $^3He/^4He$ ratio is $1.3 \cdot 10^{-6}$ (Coon, 1949, cited in Andrews, 1987)
- The solubility of atmospheric helium is temperature dependent, and for 10°C is $4.75 \cdot 10^{-8}$ cm³ STP/cm³ H₂O (Fig. 7-11).
- ^4He is slightly more soluble in water, with a fractionation factor, $\alpha_{w-air} \sim 0.983$ (Benson and Krause, 1976)
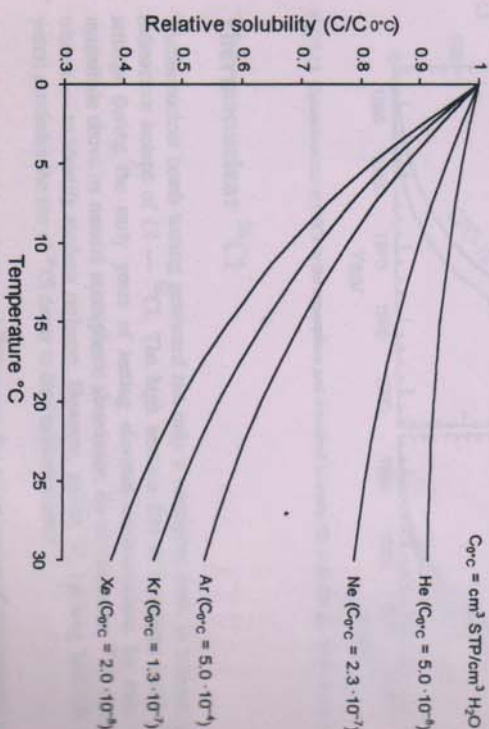

Fig. 7-11 Solubility of noble gases in water (modified from Andrews, 1992).

The measured value of ^3He, corrected for atmospheric ^3He, represents ^3He ingrown from ^3H decay, and is then used in the dating equation:

$$t = 12.43/\ln 2 \cdot \ln(1 + [^3He_t]/[^3H_t])$$

where $[^3He_t]/[^3H_t]$ is the concentration ratio of these two isotopes expressed in tritium units.

Applications of the ^3H-^3He method

Schlosser et al. (1988) apply this method to groundwater in shallow alluvial aquifers in Germany, using the bomb peak for verification (Fig. 7-12). In this example, the ingrown ^3He signal clearly follows the bomb ^3H peak. They find that 77 to 85% of the tritogenic ^3He remained in the groundwater, the rest presumably lost by diffusion. Comparing their calculated $^3He/^3H$ age for the 1963 bomb peak in the groundwaters, they find only a 3 year (15%) discrepancy, which is not bad precision in groundwater dating.
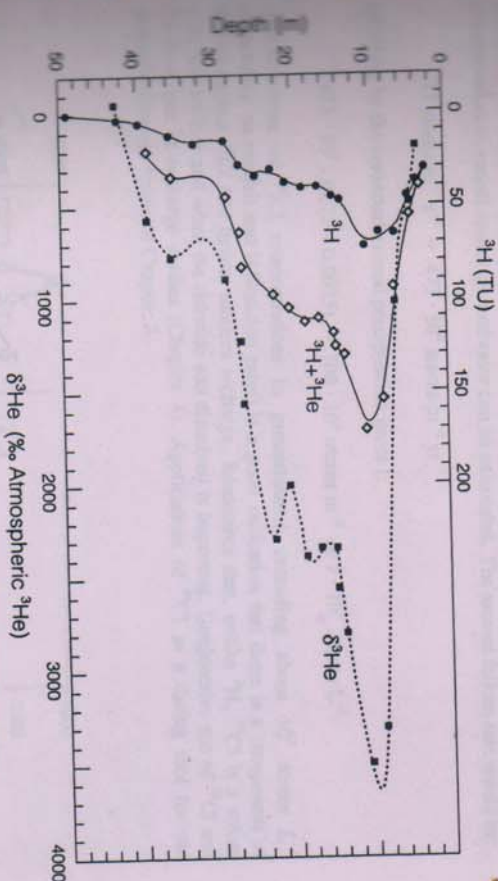
Fig. 7-12 Tritium and ^3He profiles from multi-level wells in Germany (modified from Schlosser et al., 1988).

Very similar observations on the retention of ^3He in the groundwater are made by Eckwurzel et al. (1994) and by Szabo et al. (1996) investigating shallow groundwaters in New Jersey. Because of rapid vertical flow (~1 m/yr), confinement of ^3He was very high — a prerequisite for the technique. The study demonstrates the value of the $^3H/^3He$ dating technique and compared it with a complementary dating tool — chlorofluorocarbons or CFCs.

Chlorofluorocarbons (CFCs)

Like tritium, hydrogeologists have managed to find a use for CFCs, an otherwise unwanted contaminant in our atmosphere. These compounds are resistant to degradation, making them a useful marker for modern groundwater. Atmospheric CFC concentrations have been increasing

since the 1940s (Fig. 7-13), providing a characteristic input function. CFCs have been extensively used to trace oceanic circulation patterns over the past decade. Thompson and Hayes (1979) and subsequent studies have documented their usefulness for dating young groundwaters.

Szabo et al. (1996) note that apparent groundwater ages based on the ^3H-^3He dating technique were identical to CFC ages, within the margin of error of the methods. However, the CFC technique may require local adjustments to the input function inasmuch as local urban emissions of CFCs cause variations in its atmospheric concentration. The solubility of CFC compounds are also highly sensitive to temperature, and must be calculated for groundwater temperatures in the recharge environment according to the Henry's law constants (Warner and Weiss, 1985).

Measurements are carried out by analytical methods for measuring trace organic compounds. Compounds are stripped from solution with He, separated by gas chromatography and detected by electron capture. The analysis of CFC compounds is less complicated than for ^3H, although potential contamination by exposure to the atmosphere during sampling is a risk. Furthermore, retention in aquifers with a high organic fraction, and subsurface degradation can affect transport. CFC-12 appears to exhibit the most conservative behaviour (Cook et al., 1995).
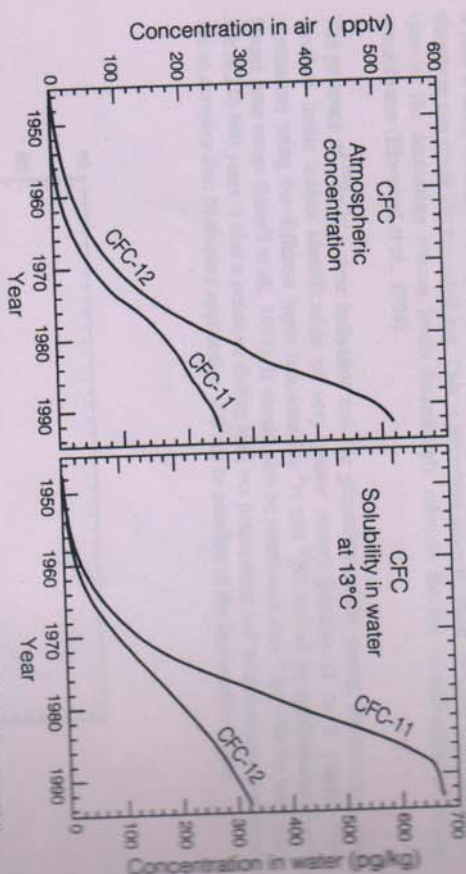
Fig. 7-13 Concentrations of CFCs in the atmosphere and dissolved in water (Ekwurzel et al., 1994; Szabo et al., 1996)

Thermonuclear ^{36}Cl

Thermonuclear bomb testing generated not only a whopping peak in tritium, but also in the radioactive isotope of Cl — ^{36}Cl. The high neutron flux of hydrogen bomb tests in marine settings during the early years of testing elevated concentrations by over two orders of magnitude above its natural abundance. By consequence, ^{36}Cl can be used — like tritium — to identify modern recharge. However, unlike ^3H, its long half-life ($t_{1/2}$ = 300,000 years) precludes the use of ^{36}Cl decay to date modern waters.

Natural atmospheric production of ^{36}Cl occurs due to activation of atmospheric argon by cosmic radiation and arrives at the earth's surface as a dry fallout or in precipitation. Natural production