

Environmental isotopes in New Zealand hydrology

1 Introduction: The role of oxygen-18, deuterium, and tritium in hydrology

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Abstract The hydrological cycle of oxygen-18, deuterium, and tritium is discussed, with emphasis on the application of concentration variations in New Zealand waters. The stable isotopes (^{18}O and D) vary in concentration in non-oceanic waters because of temperature-dependent separation of the molecules H_2^{18}O , HDO, and H_2O during evaporation, condensation, and chemical exchange processes. Established relationships between ^{18}O and D concentrations allow these parameters to be applied as indicators of water sources, displacement, and mixing. The radioactive isotope tritium (half-life = 12.43 a) has found application because of the gradual release of thermonuclear HTO from the atmosphere since 1954. In the Southern Hemisphere, this enhanced HTO input is now essentially over, but HTO remains in varying concentration throughout environmental waters, revealing such features as presence or absence of recent recharge, water age, and mixing characteristics; the discussion concentrates on the input history of thermonuclear HTO to the New Zealand land surface and a general indication of the response of systems to this input. The paper is intended as an introductory survey preceding papers dealing with the isotope hydrology of particular regions and systems.

Keywords Stable isotopes; hydrology; oxygen-18; deuterium; tritium; hydrologic cycle; groundwater; surface waters; precipitation; runoff.

INTRODUCTION

Since 1960, isotope techniques have been increasingly applied in hydrological studies (e.g., see IAEA 1967, 1970, 1974, 1978; Fritz & Fontes 1980). Applications fall into two broad categories: those

involving environmental and artificial isotopes. The term environmental isotope refers here to those isotopes which are globally distributed in varying concentration in the environment. This paper is the first of a series which will be predominantly concerned with the environmental isotopes oxygen-18 (^{18}O), deuterium ($\text{D} = {}^2\text{H}$), and tritium ($\text{T} = {}^3\text{H}$). All three isotopes occur naturally, but tritium concentrations increased sharply following atmospheric testing of H-bombs during the 1950s and 1960s. Tritium is an example of a number of isotopes which are at least partly of man-made origin, but which are grouped as environmental isotopes because they are globally distributed. In our context, artificial isotopes are those produced by nuclear industry for purely localised application.

^{18}O , D, and T are unique water tracers because they are constituent atoms of water molecules (H^{18}O , HDO, HTO). In this paper we discuss their behaviour within the hydrological cycle, and establish a general picture of their variations and applications in the South Pacific-New Zealand environment. The second paper of the series discusses measurement scales and units, techniques, and sampling procedures. Later papers will describe individual hydrological studies.

Other environmental isotopes are constituent atoms of dissolved gases or ionic species, and have been widely applied overseas. For a variety of mainly practical reasons, we have not applied these isotopes to a great extent in New Zealand. Consequently, we shall refer to these only briefly within this and the following papers. However, we emphasise that applications of ^{18}O , D, and T in hydrology often require a multi-disciplinary approach, in collaboration with geologists, hydrologists, hydrochemists, oceanographers, atmospheric scientists, and others. We shall show that measurements of ^{18}O , D, and T often give information about hydrological systems which is not readily obtainable by other methods.

Table 1 lists mean abundances and ranges of variation of some environmental stable isotopes used in hydrology. The abundance variations are caused by physical-chemical processes, and are often applicable as source indicators which tag specific components within water systems. The abundance of a radiogenic stable isotope such as ${}^3\text{He}$

Element and common isotope	Rare isotope	Mean abundance of rare isotope	Range of Variation in waters
Hydrogen ^1H	$\text{D} = ^2\text{H}$	1.56×10^{-4}	$(0.8-1.6) \times 10^{-4}$
Helium ^4He	^3He	1.4×10^{-6}	$(0.1-30) \times 10^{-6}$
Oxygen ^{16}O	^{18}O	2.00×10^{-3}	$(1.90-2.02) \times 10^{-3}$
Carbon ^{12}C	^{13}C	1.12×10^{-2}	$(1.02-1.14) \times 10^{-2}$
Nitrogen ^{14}N	^{15}N	3.6×10^{-3}	$(3.5-3.7) \times 10^{-3}$
Sulphur ^{32}S	^{34}S	4.4×10^{-2}	$(4.2-4.6) \times 10^{-2}$
Argon ^{40}Ar	^{36}Ar	4.0×10^{-2}	$(0-4) \times 10^{-2}$

Table 1 Environmental stable isotopes used in hydrological studies. Abundances and ranges of variation are given as atom ratios.

or ^{40}Ar is related to the accumulation time, which is the basis for its use in dating. Information on environmental radioactive isotopes is given in Table 2; generally the concentrations are extremely low, but may vary over several orders of magnitude. Tritium is particularly useful for study of hydrological phenomena with time scales less than about 50 years (e.g., atmospheric mixing, exchange between ocean surface and deeper layers, groundwater recharge, lake residence times), because of its short half-life (12.43 a) and the recent transient due to thermonuclear HTO (Table 3). Although the other environmental radioactive isotopes can complement tritium in some hydrological systems, such measurements have not yet been applied to a significant extent in New Zealand.

OXYGEN-18 AND DEUTERIUM IN HYDROLOGY

Units

Oxygen-18 and deuterium concentrations are given as δ values (in parts per thousand, ‰) where

$$\delta(\text{‰}) = \left(\frac{R_{\text{sample}}}{R_{\text{V-SMOW}}} - 1 \right) \times 1000 \quad (1)$$

and R is the $^{18}\text{O}/^{16}\text{O}$ or D/H ratio. V-SMOW is Standard Mean Ocean Water held at IAEA, Vienna (see Part 2 of this series for further details). Measurement errors are $\pm 0.15\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 1.0\text{‰}$ for δD (95% confidence level).

Range of δ values in environmental waters

Fig. 1 shows the range of $\delta^{18}\text{O}$ and δD encountered in various categories of environmental water. Compared to all other water, the ocean is effectively uniform in isotopic composition, and it may therefore be conveniently considered as the starting point for discussion of the hydrological cycle of ^{18}O and D . (Nevertheless, the small variations of oceanic δ values are significant for oceanography. Craig & Gordon (1965) found that the deep water masses show a range of variation about 0.3‰ for ^{18}O and 3‰ for D).

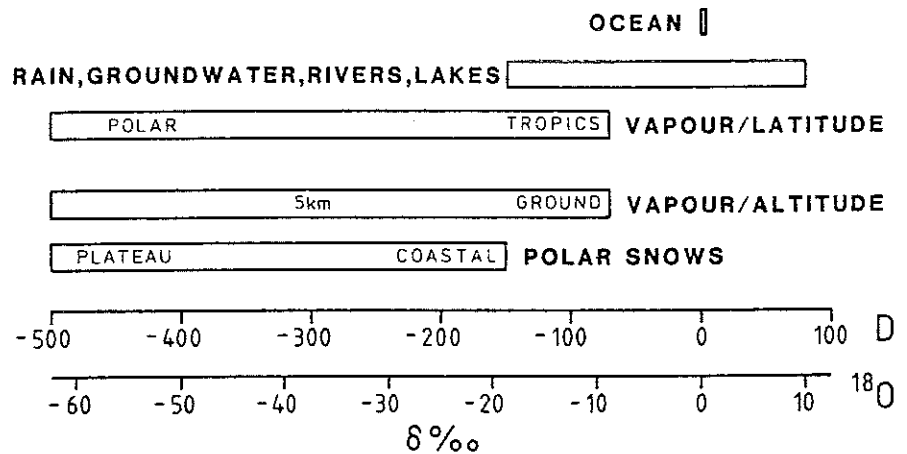
Isotope fractionation

The δ values of any atmospheric vapour or non-oceanic water are the end result of successive processes of evaporation, condensation, mixing, and (occasionally) isotopic exchange with chemical forms other than chemically free water. Most of these processes involve some degree of isotope separation (fractionation). The object of hydrological studies using ^{18}O and D is to understand the

Element	Radioactive isotope	Range of variation in environmental waters (various units)	Half-life (a)
H	$\text{T} = ^3\text{H}$	$\text{T}/\text{H} = 0-10^{-14}$	12.33
C	^{14}C	$^{14}\text{C}/^{12}\text{C} = 0-10^{-12}$	5730
Si	^{32}Si	$0-0.3$ (dpm/ 10^3 L H_2O)	280
Cl	^{36}Cl	$^{36}\text{Cl}/\text{Cl} = (0-5) \times 10^{-17}$	3.0×10^5
Ar	^{39}Ar	$0-0.1$ (dpm/L Ar)	269
Kr	^{85}Kr	$0-1000$ (dpm/mmol Kr)	10.75
Rn	^{222}Rn	$10^{-4}-3 \times 10^{-2}$ ($\mu\text{Ci}/\text{L}$ H_2O)	3.824 days
U	$^{234}\text{U}/^{238}\text{U}$	1-6 (activity ratio)	-

Table 2 Environmental radioactive isotopes used in hydrological studies. Units given are those used by workers in the field.

Fig. 1 Ranges of $\delta^{18}\text{O}$ and δD in environmental waters.



nature and magnitude of the isotope separations, and to apply this knowledge to trace the origin and movement of environmental waters.

The most fundamental causes of ^{18}O and D variations in environmental waters are the separation or fractionation effects which prevail during evaporation and condensation, and the quantitative variation of these fractionations with temperature. The heavy molecules H_2^{18}O and HDO occupy the condensed phase preferentially. Already in the first step of the cycle, evaporation from the ocean surface, appreciable isotope separation occurs with the result that oceanic vapour is strongly depleted in ^{18}O and D relative to the ocean surface. (The balancing increase in ^{18}O and D concentration of the surface ocean is negligible, due to its immense water content relative to the amount of evaporation and the closed nature of the cycle; only very shallow basins show significant enrichment).

An isotope fractionation is described quantitatively by a fractionation factor (symbol α), which is the ratio of isotope concentrations in two interacting phases (e.g., water/vapour or ice/vapour). The most fundamental of these factors is the equilibrium fractionation factor

$$\alpha_e = R_c/R_v \tag{2}$$

where R_c , R_v are the $^{18}\text{O}/^{16}\text{O}$ (or D/H) ratios of the condensed and vapour phases, respectively, when isotopic equilibrium exists across a plane phase boundary. α_e equals the ratio of vapour pressures of the normal component (H_2O) to the heavy component (H_2^{18}O or HDO).

Temperature variations of α_e for liquid/vapour and ice/vapour equilibria are depicted in Fig. 2; the isotope separation increases with decreasing temperature. Note that α is close to unity; it is often more convenient to work with the increment ϵ where $\epsilon = \alpha - 1$.

Evaporation from the ocean is *not* an equilibrium process. Over a short distance of order 1 mm above the ocean surface, the relative humidity drops sharply to about 80%. Differing molecular diffusion coefficients affect the various isotopic vapour molecules as they diffuse across this humidity gradient (Craig & Gordon 1965). Other separation effects may occur at the interface itself, and turbulent diffusion always plays a role in the atmosphere. Moreover, atmospheric mixing ensures that, even close to the surface, atmospheric vapours contain at least a minor component of vapour which has already participated in condensation higher in the atmosphere (Taylor 1972). The net result of all these effects is that actual near-surface marine vapours are depleted in ^{18}O and D relative to equilibrium vapour. The extra fractionation due to the near-surface effects is called kinetic fractionation, and the overall separation factor α is given by

$$\alpha = \alpha_e \alpha_k \quad (\text{or } \epsilon = \epsilon_e + \epsilon_k) \tag{3}$$

where $\alpha_k = 1 + \epsilon_k$ is the kinetic fractionation factor.

Marine vapours sampled at Baring Head, near Wellington (Fig. 3), illustrate the consequence of kinetic fractionation; these samples are all depleted in ^{18}O and D relative to equilibrium vapour. It is apparent that the kinetic separation for D is smaller relative to the equilibrium effect than is the case for ^{18}O . Fig. 3 is an example of the linear δ -diagram commonly used to show isotope relationships in hydrological studies, δD being plotted as ordinate and $\delta^{18}\text{O}$ as abscissa. Ocean water occupies a small region close to the origin, and most other waters occupy the negative quadrant.

Atmospheric condensation processes: isotopic composition of precipitation

When condensation occurs from vapours such as those of Fig. 3, the condensates lie nearer to the

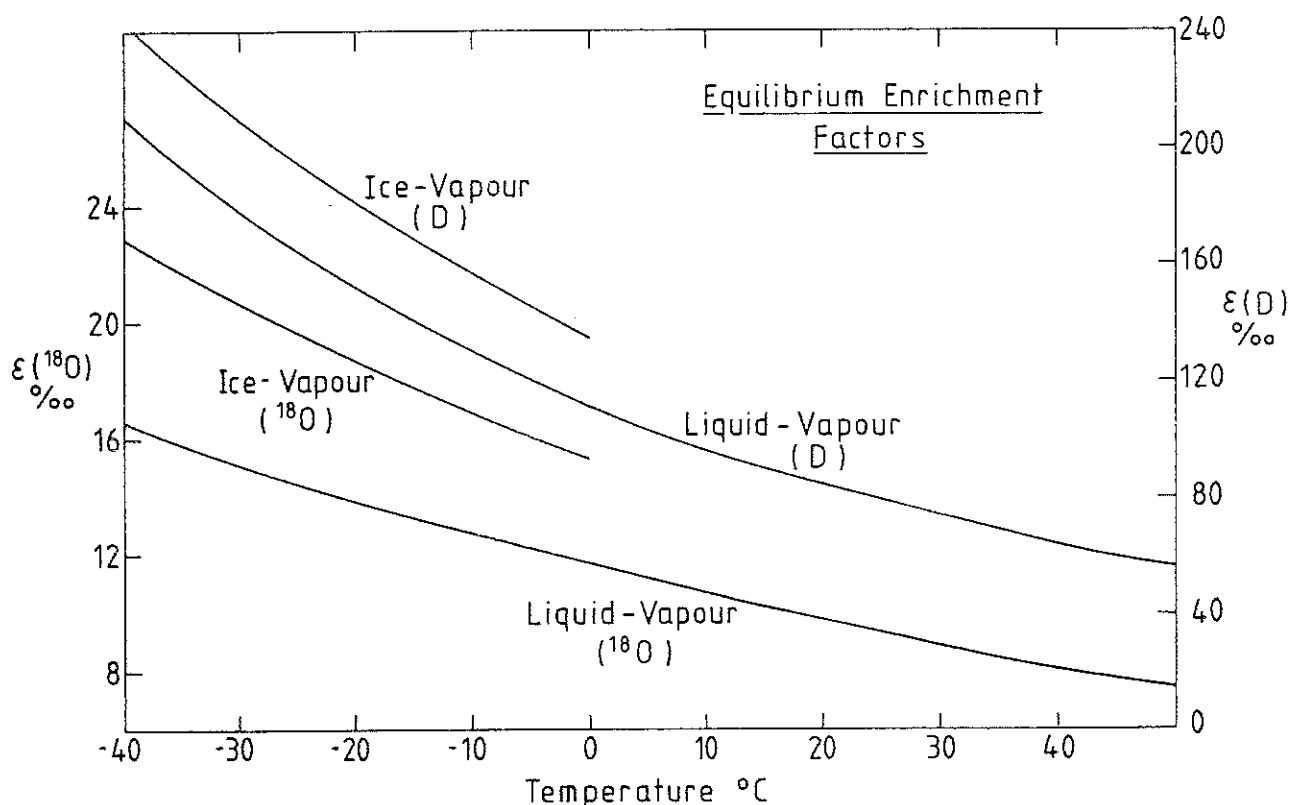


Fig. 2 Enrichment factors for oxygen-18 and deuterium between liquid/vapour and ice/vapour phases (from Majoube 1971) as a function of temperature T . The scale for ^{18}O is on the left side of the diagram and that for D on the right.

origin of the δ -diagram, and the remaining vapour shifts farther away from the origin. The fractionation factors pertaining in atmospheric condensation processes approximate closely to equilibrium factors, and the relative changes of δD and $\delta^{18}\text{O}$ correspond to the ratio $\epsilon_e(\text{D})/\epsilon_e(^{18}\text{O})$, which is close to 8 over the range of atmospheric temperature. As a consequence, both condensates and depleted vapours occupy a thin pencil of slope about 8 in the δ -diagram. However, the 'memory' of the extra kinetic fractionation during the evaporation from the ocean surface is not lost, so that the pencil of the δ -diagram occupied by condensates and vapours does not pass through the origin, but has a positive intercept (symbol d) on the δD axis. From global measurements Dansgaard (1964) determined $\delta\text{D} = 8\delta^{18}\text{O} + 10$ as a global average (see also Friedman 1953). We have found that d is about +13‰ for the New Zealand region.

Taylor (1972) measured highly depleted vapour samples of varying origin at heights up to 5 km over Germany, and found that the gradient 8 relationship does indeed apply for vapours down to $\delta^{18}\text{O} \approx -50$, $\delta\text{D} \approx -390$; the isotopic composition of the vapours from which atmospheric condensation processes occur is thus clearly characterised within the δ -diagram.

An infinitesimal stage of an atmospheric condensation process involving immediate removal of condensate may be described by the equation

$$dN_i = \alpha R_v dN \quad (4)$$

where dN_i , dN are respectively the number of isotopic and normal water molecules condensing, and α is the instantaneous separation factor. α increases during most atmospheric condensations, because the temperature must be progressively lowered to promote further condensation (Fig. 2). Integration of Equation 4 gives

$$R_v = R_{0v} F^{\bar{\epsilon}} \quad (5)$$

where R_{0v} is the initial isotope ratio of the vapour ($F = 1$), and F is the fraction of original vapour remaining. $\bar{\epsilon}$ is defined by Equation 5, as a mean over the condensation process. The isotopic ratio of the instantaneous condensate is, from Equation 5

$$R_c = \alpha R_{0v} F^{\bar{\epsilon}} \quad (6)$$

As the air mass is cooled, and provided it is isolated from input of other vapour, R_c decreases (i.e., δ_c becomes more negative) because F decreases, even though α (and $\bar{\epsilon}$) increase. This is the basis for the general rule that δ values of

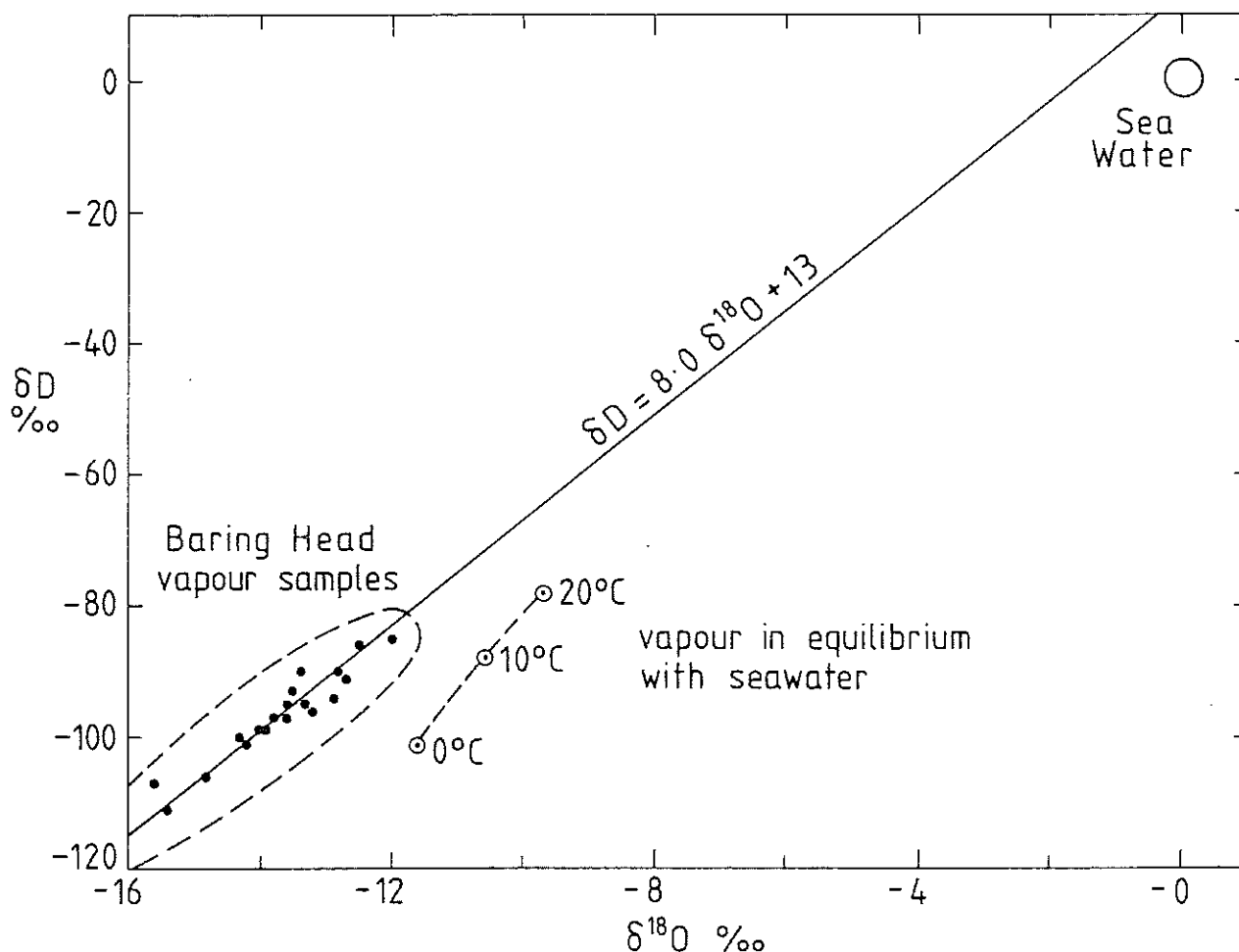


Fig. 3 Plot of $\delta^{18}\text{O}$ versus δD for ocean water, water vapour in isotopic equilibrium with sea water at the indicated temperatures, and actual atmospheric water vapour sampled at Baring Head, near Wellington. The line is an average straight line through points for many New Zealand precipitation samples (not plotted).

precipitation are more negative at lower temperature, which, like the gradient 8 and positive intercept d , is a fundamental feature in applying ^{18}O and D as water tracers. As a consequence of this, δ values of precipitation vary with

- season, with more negative δ values in winter (We note also that the isotope separation during evaporation from the oceans is enhanced during winter, so that δ_{0v} is also more negative.);
- altitude, with more negative δ values at higher altitudes; and
- mean temperature change, with more negative δ values during colder periods at a specific location.

A further effect on the δ values of rain due to interaction with atmospheric vapour must be considered. Raindrops formed at low temperatures within clouds can be isotopically enriched by exchange with warmer atmospheric vapour, or if the

air is not saturated, by evaporation, as they fall between the cloud and the ground (Stewart 1975). The exchange effect is greatest for light rain and oceanic locations, while evaporation from falling raindrops is most common in arid regions.

A typical example of seasonal variation is shown by $\delta^{18}\text{O}$ variation in precipitation at Takaka (Nelson Province) (Fig. 4). Just as ambient temperatures do not conform exactly to mean patterns, the isotopic compositions of individual storms do not correspond exactly to their mean seasonal patterns. Because of greater amplitude of seasonal temperature variations, the amplitudes of the seasonal δ value variation are more pronounced at higher latitudes and altitudes.

The altitude effect is especially important in New Zealand hydrology. Much groundwater derives from rivers whose flow originates predominantly as precipitation in mountain areas. The Waimakariri River (see Fig. 5) is a good example. Its δ values are

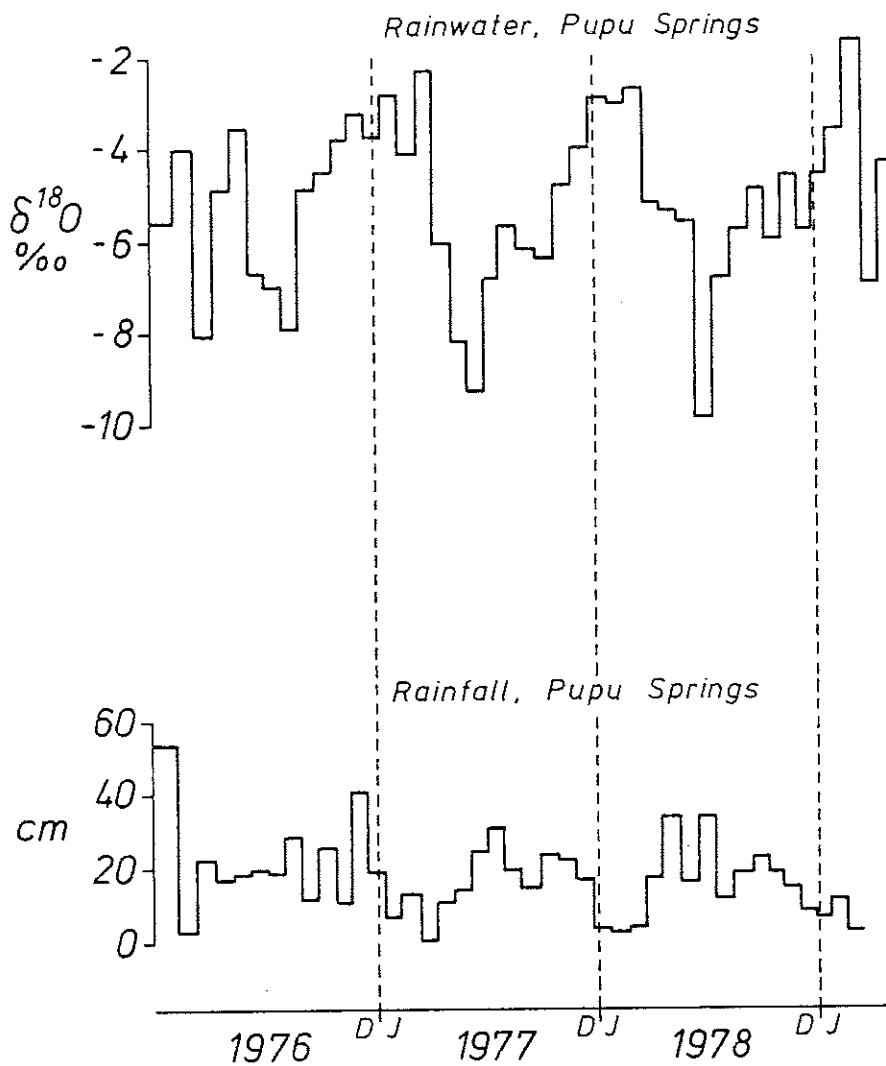


Fig. 4 $\delta^{18}\text{O}$ value and amount of rainfall in 4 weekly samples collected at Puppu Springs, near Takaka (northwest Nelson).

significantly more negative than those of precipitation falling on the Canterbury Plains. Measurements of groundwater indicate that the Waimakariri and other major rivers are the main sources of groundwater in the gravel aquifers underlying the Canterbury Plains.

Dansgaard (1964) derived the relationships

$$\delta^{18}\text{O} = 0.695T_m - 13.6 \quad (7)$$

$$\delta\text{D} = 5.6T_m - 100$$

for mean δ values of precipitation at many stations at mid and high latitudes. Approximate predictions can therefore be made about locations where isotope measurements of precipitation are not made. The range of isotope composition predicted for sea level locations in New Zealand is between $(-3.0, -14)$ for Kaitaia ($T_m = 15.3^\circ\text{C}$) to $(-7.1, -48)$ for Invercargill ($T_m = 9.3^\circ\text{C}$). This range is supported by groundwater measurements. (We note here that many of the monthly δ values reported

from Kaitaia and Invercargill within the auspices of the IAEA/WMO network are unreliable due to excessive evaporation from the collection pot.) Closer to the equator (Pacific islands), mean precipitation lies closer to the origin, and there is little seasonal variation.

Because altitude-temperature relationships vary widely from place to place, no uniform δ value-altitude coefficients can be applied. However, -0.23‰ per 100 m for $\delta^{18}\text{O}$, and -1.8‰ per 100 m for δD may be taken as tentative guidelines for New Zealand studies (Taylor & Stewart 1979).

To conclude this discussion of the isotopic composition of atmospheric vapour and precipitation, we emphasise that detailed treatment of the topic involves greater complexity than we have indicated. We have here summarised only the essential features necessary to adequate understanding of the application of these isotope variations once precipitation has reached the ground surface.

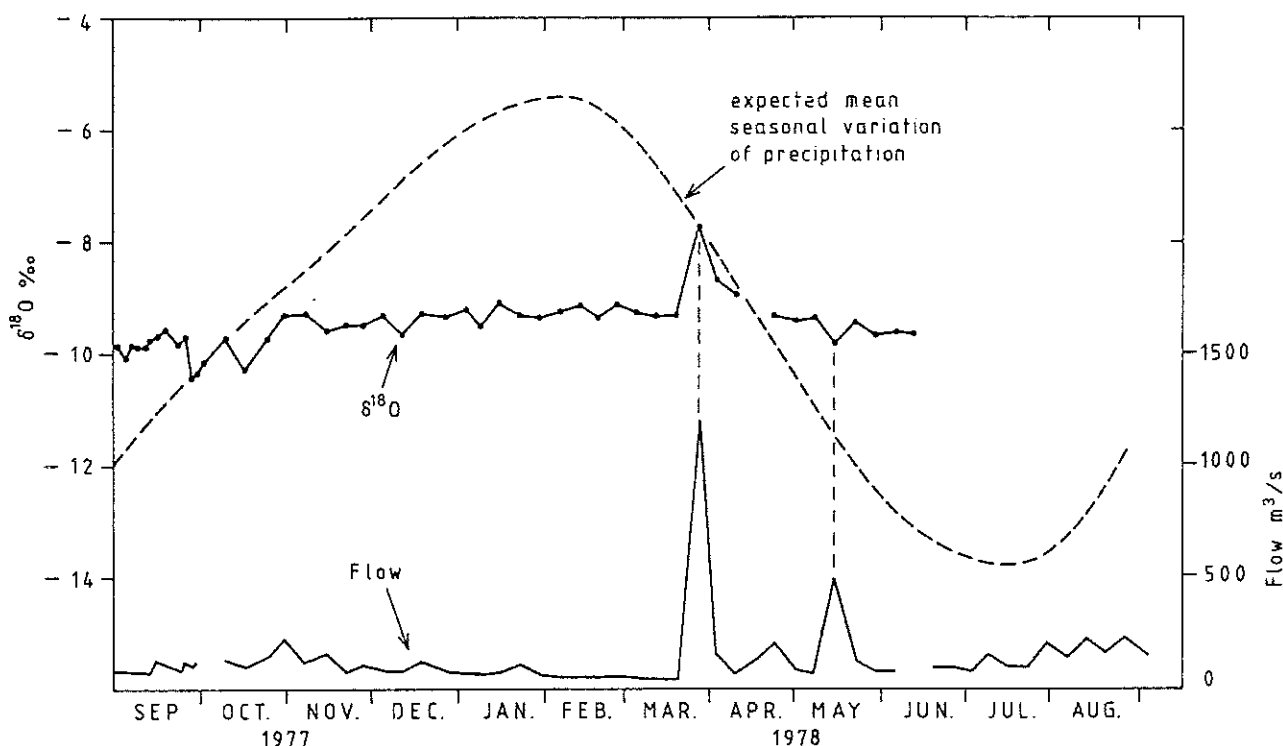


Fig. 5 $\delta^{18}\text{O}$ and flow in the Waimakariri River during 1977–78. The expected mean seasonal variation of $\delta^{18}\text{O}$ in precipitation in the catchment is also shown.

Applications of ^{18}O and D in New Zealand surface and groundwater hydrology

We have shown above that the isotopic composition of precipitation usually occupies a narrow pencil of slope 8 and positive intercept d on the δ -diagram; from our measurements, $d = 13\text{‰}$ appears to apply in New Zealand. This linear relationship between $\delta^{18}\text{O}$ and δD is frequently referred to in the literature as the meteoric water line.

Once precipitation reaches the ground, mixing processes begin which tend to smooth out the δ value variations within and between individual precipitation events, and also the general seasonal trends.

Much of New Zealand (over 50%) is classified as steep (slopes greater than 30°) (Leamy & Fieldes 1976). The soil cover is usually shallow in these areas unless forested and covers predominantly low-permeability rock (greywacke, schists); there is little hold-up capacity for the relatively large amounts of precipitation. (Snow and glacier areas, and deep, porous volcanic deposits constitute exceptions.) Precipitated water is usually transmitted through the soil cover over a period of days to weeks and drained towards the coast in rivers which exhibit damped seasonal isotope variations. In Fig. 5, we

show the severely damped variation (apart from flood events) in the Waimakariri River (sampled near Christchurch).

Snow and ice constitute sizeable reservoirs for water in the Southern Alps, and contribute to spring peak flows in many South Island rivers. Fitzharris (1979) estimated that snow storage supplies 10–25% of annual streamflow for some of these catchments. The δ values of snow range from $(-7, -46)$ at low altitudes to $(-16, -126)$ on the highest peaks. However, on the basis of our measurements for several South Island rivers, we believe that the contribution of highly isotopically depleted snow melt to such rivers is not significant in most cases. In the lower reaches, the δ values in such rivers broadly reflect the mean altitude of the contributing catchments.

At any particular location, an important reference isotopic composition (usually on the meteoric line) is that pertaining to groundwater derived by direct infiltration of local precipitation. In most cases, the isotopic variations in precipitation are completely smoothed out below the water table. However, much of the summer precipitation may be returned to the atmosphere by evapotranspiration, which is essentially non-fractionating; as a result, the

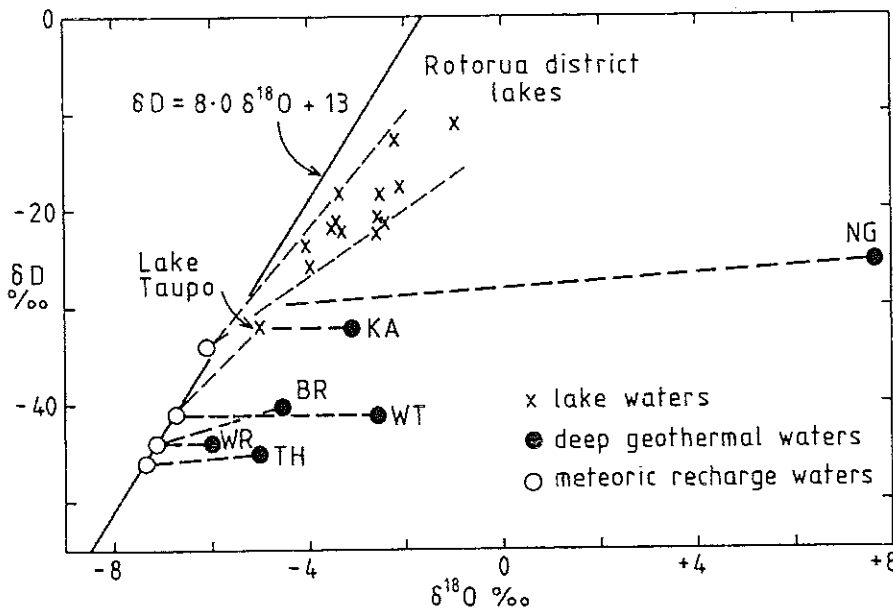


Fig. 6 Plot of $\delta^{18}\text{O}$ versus δD for 13 lakes in the Rotorua district, Lake Taupo, and deep geothermal waters from a number of New Zealand geothermal areas. The Rotorua lakes (and Lake Taupo) show enrichment in ^{18}O and D compared to their source waters because of evaporation, and the geothermal waters are enriched in ^{18}O compared to local groundwaters because of water-rock interaction. (WR is Wairakei, BR is Broadlands, TH is Tauhara, WT is Waitotapu, KA is Kawerau, and NG is Ngawha.)

recharge water may be more representative of winter rather than of mean annual precipitation, but it will still lie on the meteoric line.

Following Gat (1971), we may list the following effects which cause the isotopic composition of waters at any locations to differ from that of mean local recharge.

- A Geographic displacement by surface or subsurface flow (water falls as precipitation at another location).
- B Water derives from evaporating surface water bodies, such as lakes or swamps.
- C Recharge during earlier climatic periods (temperature effect in precipitation, changed oceanic composition during ice ages).
- D Mixing with other waters (e.g., seawater intrusion, subsurface brines).
- E Chemical interaction of water with aquifer materials, involving isotope exchange which changes $\delta^{18}\text{O}$ (particularly at elevated temperatures in geothermal systems).
- F Isotope separation during water transport (mainly diffusion).

Apart from D and F, these mechanisms play a major role in New Zealand. Mechanisms B, D, E, and F shift the isotopic composition of water away from the meteoric water line.

An example of A is the previously mentioned recharge of plains aquifers by river water originating as high-altitude precipitation.

Whereas we saw that evaporation (mechanism B) does not significantly affect the isotopic composition of ocean water, it does produce measurable ^{18}O and

D enrichment of many lakes. In the δ -diagram, evaporation displaces the isotope composition of lakes away from the meteoric water line along lines of slope 3–6 relative to their mean recharge water. Fig. 6 shows this effect for 13 lakes in the Rotorua region (Taylor et al. 1977). Our measurements indicate that New Zealand lakes do not develop significant isotope–depth gradients, whether they are seasonally stratified or not. Evaporation shifts such as those of Fig. 6 effectively tag lake water. This property was used to determine the proportions of lake drainage and precipitation-derived water in springs near several of the Rotorua lakes. In the same way, we know that Lake Taupo is not a significant recharge source for the deep geothermal water in the Wairakei area (Stewart 1978). Although stable isotopes can assist in determining the water balance of lakes, this aspect is usually complex and provides only limited results.

Mechanism C appears to operate in New Zealand, at least as regards short-term climatic fluctuations (over several years). We believe that at least part of the 'noise' measured in the δ values of regional groundwaters is due to short-term (i.e., over several years) climatic changes; evidence for this was found in $\delta^{18}\text{O}$ and catchment temperatures for the Waimakariri River (Taylor & Stewart 1979). These short term fluctuations appear to be less than 1‰ in $\delta^{18}\text{O}$.

Isotopic compositions of thermal waters are affected by oxygen exchange between water and hot rock (mechanism E); this results in a horizontal shift of $\delta^{18}\text{O}$, in a direction depending on the isotopic composition of the exchanging rock component and on temperature. (^{18}O shifts are normally positive in

New Zealand geothermal systems; examples are given in Fig. 6.) The amount of hydrogen in rocks is low, and D shifts due to hydrogen exchange are usually negligible. Phase separation (water/vapour) effects in thermal waters are complex and are discussed elsewhere (e.g., Giggenbach 1971; Stewart 1978).

TRITIUM HYDROLOGY

Introduction

Environmental HTO can be studied in separate, but often mutually interacting compartments or reservoirs, e.g., lakes, aquifers, river basins, surface and deep ocean, stratosphere and troposphere. Each reservoir is characterised by water quantity, inputs and outputs, internal structure, and dynamic characteristics. HTO enters a reservoir by one or more inputs, whose magnitudes (rates of water input) and tritium concentrations vary with time. The internal reservoir processes (advection, dispersion and other mixing processes, possible chemical exchange) produce a tritium distribution which varies with location and time. This distribution can be measured at suitable sampling points, some or all of which may be natural outputs; analysis of measured distributions takes account of other available information (e.g., hydrology, hydrochemistry, temperatures) to attempt to deduce unknown features of the reservoir hydrology. A frequently adopted approach is to establish likely reservoir models and to determine which of these are consistent with both tritium distribution and other information.

Concentration units

Our earlier tritium results were all published in Tritium Units (TU), where 1 TU represents a T/H ratio of 10^{-18} . Since 1980, we have replaced TU by Tritium Ratio (TR), with the same meaning. TR = 1 corresponds to specific activity 0.1181 Bq/(kg H₂O), assuming half-life 4540 d = 12.43 a. Details of measurement scales and units are given in Part 2 of this series.

Tritium in precipitation

Measurements of tritium in precipitation give a reliable indication of ambient concentration levels in the local troposphere, and assess the input to land-based hydrological systems. This aspect is so vital to the application of tritium in hydrology that we consider it in detail in this introductory paper. Fig. 7 shows mean annual Tritium Ratios (from monthly samples) at Kaitoke, near Wellington; this is the longest record for any Southern Hemisphere (SH) station. In SH, annual averages are compiled from July to June, because this best reflects the seasonal cycle and year-to-year variations of stratosphere-troposphere HTO exchange. The bulk of SH thermonuclear HTO fallout originated from stratospheric injections from testing in the Northern Hemisphere (NH) (Table 3). About 5% of total global HTO fallout mixed to the southern stratosphere, and thence into the south polar troposphere (Taylor 1964, 1966). During July–October, tropospheric tritium concentrations peak, as a further batch of thermonuclear HTO is released from the stratosphere. The mean residence time before release from the southern stratosphere is several years, but removal from the troposphere takes only a few days to weeks. The stratospheric

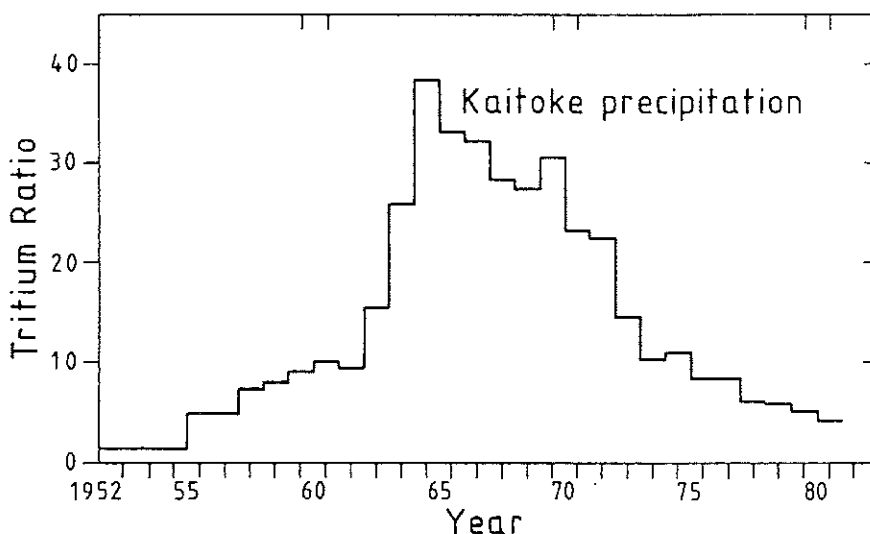


Fig. 7 Mean annual tritium ratios in precipitation at Kaitoke. Ordinates are mean TR values from monthly samples running from July to June. The record prior to 1960 was not obtained by direct measurement of precipitation samples but is based on evidence from Hutt River and groundwater data, and tritium profiles in Antarctic snow. The value TR = 1.5 prior to July 1955 represents our best estimate of the pre-thermonuclear (cosmic ray) level.

Period	1945-51	1952-54	1955-56	1957-58	1959-60	1961	1962
Tritium released (kg)	0.05	24	16	60	0	105	155

Table 3 Bomb tritium: estimated atmospheric releases 1945-1962.

A fusion device produces about 70 kg tritium/MT yield; a fission device about 2 g tritium/MT yield. Data from NCRP 1979.

injections and transport processes are reflected by the irregular year-to-year changes; the stratosphere-troposphere exchange produces a marked seasonal variation in the tropospheric concentrations, which has been quite closely repeated year-by-year (Fig. 8).

In addition to thermonuclear HTO, the tritium fallout also includes cosmic ray produced tritium (about TR = 1.5), and tritium re-evaporated from the ocean surface (never greater than TR = 3); it is clear from Fig. 7 that thermonuclear HTO dominated during the 1960s and early 1970s, but is now no greater than the cosmic ray level. At least for the present, the period of significant thermonuclear HTO fallout in SH is essentially over.

In the troposphere, descending HTO is diluted in concentration by admixture of ocean- and land-derived vapour, and is removed by precipitation and vapour exchange across the ocean surface. In the southern troposphere, the dominant input of HTO is at high latitudes, whereas that of water vapour is at low and middle latitudes. Consequently, the net latitudinal fluxes of HTO and HHO occur in opposite directions, producing a marked latitudinal variation of tritium concentrations (Fig. 9). In the polar regions, the dilution effect is at a minimum. Tritium concentrations in SH precipitation are greatest in the dry environment of the Antarctic polar plateau. Moving downward and equatorward, tritium concentrations decrease by increasing dilution and removal to the ocean surface; near the equator they reach a minimum. The equatorial rain belts have consistently acted as an effective barrier preventing trans-equatorial penetration of the higher HTO levels from the northern troposphere. Fig. 10 compares (on a logarithmic scale) the records of tritium at Kaitoke and Valentia, Ireland, which are both mid-latitude island stations.

Since the late 1970s, nuclear industry has provided another significant source of HTO, and also of HT, in the northern troposphere. Although the industrial HT has penetrated the equator, oxidation to HTO appears to be negligible, and there is no evidence yet that this contributes to the present low concentrations of HTO in the southern troposphere. But it is noteworthy that already in 1975 the inventory of tritium as HT in the southern troposphere greatly exceeded that in the water from

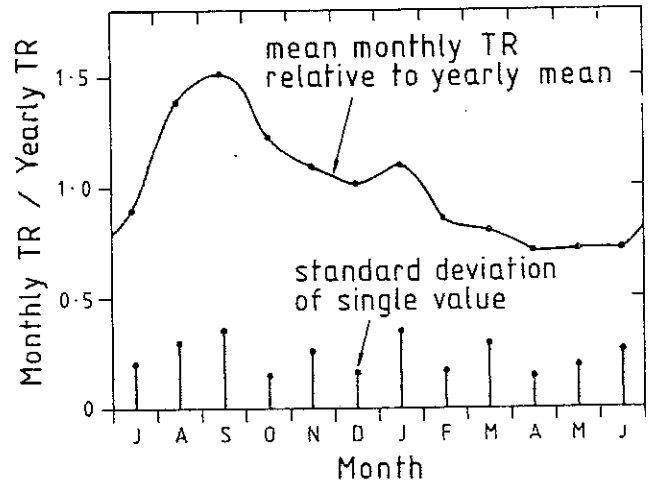
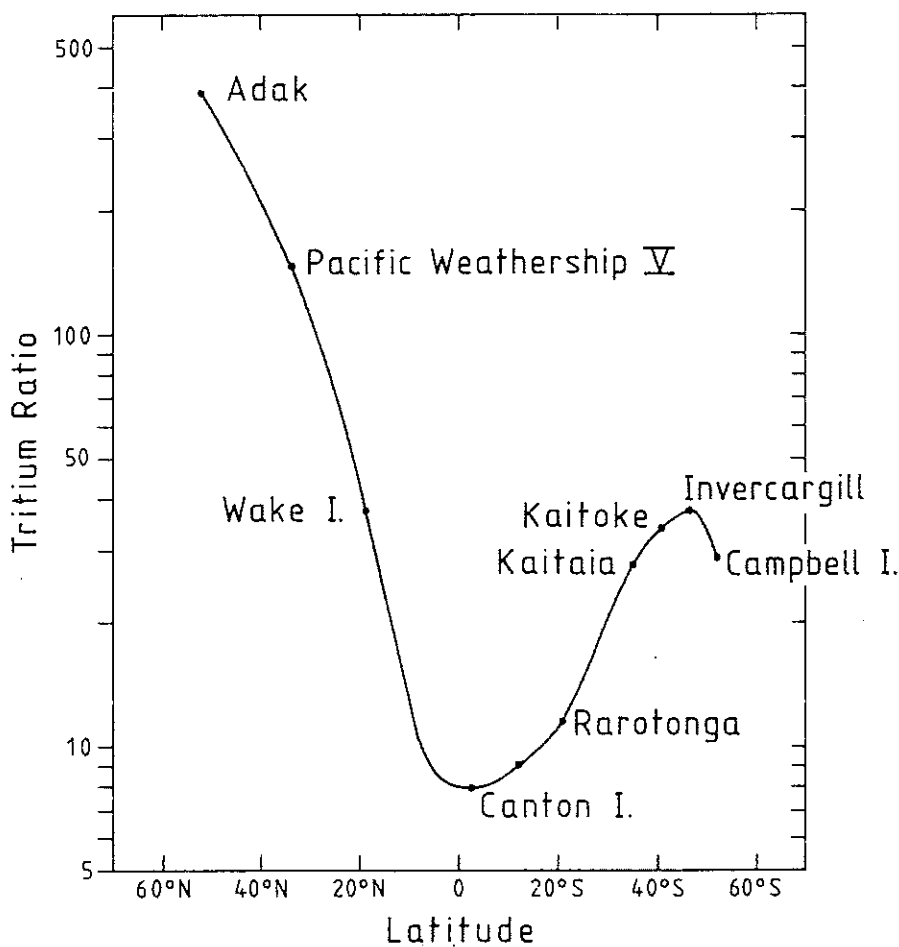


Fig. 8 Average seasonal variation of tritium concentration in precipitation at Kaitoke, based on data for the period 1961-81. Ordinate is mean ratio of monthly TR to annual mean TR; standard deviations of individual monthly values are shown at foot of diagram.

HTO (Mason & Östlund 1978); in continuing absence of significant thermonuclear detonations, this imbalance will continue, the tropospheric residence time of HT being several years.

So far as SH oceanic locations are concerned, a regular latitude variation of tritium concentration in precipitation prevails. Stations at corresponding latitudes have closely similar tritium records; moreover the ratio of mean annual concentrations at any two stations does not vary substantially. This allows approximate reconstruction of incomplete tritium records, or extrapolation to localities where no record exists. Another important phenomenon is the tendency of continental areas to exhibit higher concentrations than those of oceanic stations at similar latitudes; this is due to the return of recently precipitated HTO to the lower troposphere by evapotranspiration, in contrast to the tritium-diluted feedback from the ocean surface. New Zealand is essentially an oceanic environment in this sense; air masses moving in predominantly W-E direction across New Zealand do not acquire significant amounts of re-evaporated HTO from the land surface. But the effect is significant over much of Australia.

Fig. 9 Latitudinal variation of tritium concentration in precipitation at Pacific Island stations during 1965, when both NH and SH concentrations were near their peak.



In the global network for isotopes in precipitation (monthly samples) established by IAEA/WMO in the early 1960s, our laboratory has participated in the tritium measurements for New Zealand, Australian, and Pacific island stations since its inception. Following changes agreed recently, our future commitment will comprise the chain of island stations Tarawa, Funafuti, Rarotonga, Kaitaia, Kaitoke, and Invercargill. Network data is published regularly by IAEA (Environmental Isotope Data Nos 1-6).

Within New Zealand, the concentration differences Kaitoke:Invercargill are on average about 1:1.1, and Kaitoke:Kaitaia about 1:0.75. As a first approximation, the Kaitoke record is assumed to be typical for the latitude band (38-43)°S; a linear gradient between Kaitoke and Kaitaia values is assumed for the band (38-35)°S; a record mid-way between Kaitoke and Invercargill is assumed for the band (43-45)°S, and the Invercargill record for the band (45-47)°S. This division of the tritium record is sufficiently accurate for most purposes.

Tritium input to hydrological systems and response to thermonuclear tritium transient

It was shown in the preceding section that the SH thermonuclear HTO atmospheric transient is essentially finished. More than 90% of all undecayed thermonuclear HTO is now in the oceans. Although HTO is still being added to SH reservoirs, it does not balance the output and rate of decay, so that their total tritium content is presently declining. This can be demonstrated by examining what happens if the Kaitoke tritium loss is by radioactive decay. This corresponds to a reservoir with no water output, i.e. infinite water residence time. Fig. 11 shows that the total amount of tritium is indeed declining; hence the total must also be declining in any natural reservoir with non-zero water output. But we shall see that it is still possible for the tritium content to be increasing at specific reservoir locations if water originating as precipitation in the 1950s and 1960s moves past that location in a predominantly advective situation (i.e., piston flow). After a few more decades, thermonuclear

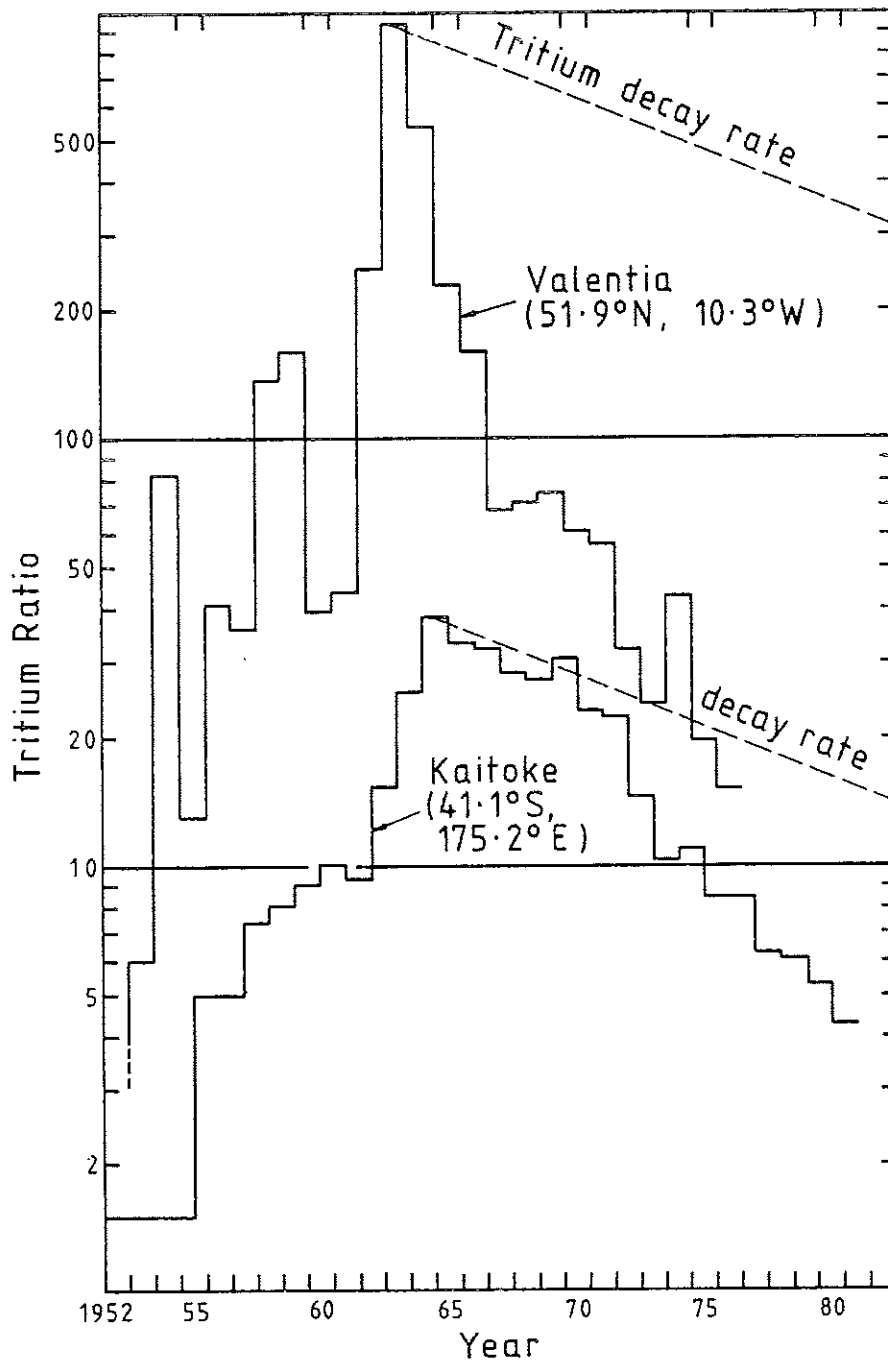


Fig. 10 Comparison between mean annual values of TR in precipitation at Valentia and Kaitoke, illustrating the imbalance between NH and SH. Following virtual cessation of testing in 1962, NH concentrations decayed much more sharply than the tritium decay rate (stratospheric residence time about 16 months), whereas the decline of SH concentrations was comparable to the decay rate, indicating much longer stratospheric hold-up. After 1972 the decline of SH concentrations became much steeper.

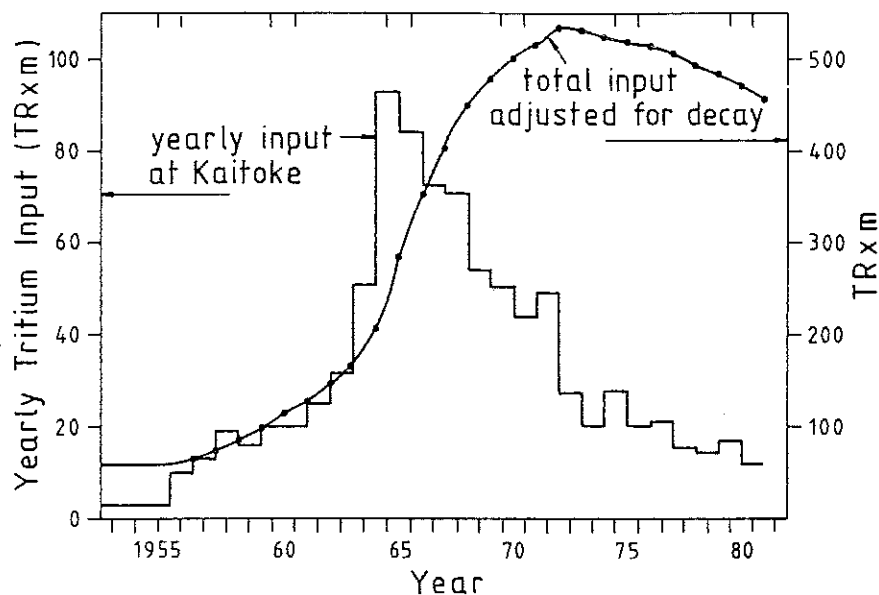
HTO will have decayed to insignificant levels; unless nuclear industry provides significant HTO release, only cosmic ray produced HTO will remain, at low concentration levels which will severely limit its application in environmental hydrology.

In the case of most freshwater systems, the chain of HTO input starts with the fall of precipitation; for the ocean, and also for many large lakes, vapour exchange constitutes an HTO input of usually

somewhat greater magnitude (by a factor 2-3) than that by direct precipitation.

Two important mechanisms of groundwater recharge in New Zealand are by infiltration from major rivers into gravel aquifers and by direct infiltration of precipitation. Overlying successions of aquifers and aquicludes are a common feature of coastal plains and valleys. These aquifers are often river-laid gravels, intersecting present-day rivers

Fig. 11 Yearly total input of tritium (in units TR × metres) by precipitation at Kaitoke and the total tritium input adjusted for decay. From the latter curve we deduce that the total tritium in all SH reservoirs has been declining since 1972.



which supply the main recharge (e.g., lower Hutt valley, Canterbury, Wairau, and Heretaunga Plains). In this situation, tritium may indicate (a) the extent of hold-up of water in the river basin (for the Hutt River it is only days to weeks, whereas the average hold-up period for the Waimakariri River appears to be about 3 years); (b) different velocities of travel in overlying or adjacent aquifers, or in different areas of the same aquifer; (c) whether water withdrawal significantly alters the natural flow of water through the aquifer; (d) whether the aquifer system has a natural discharge (particularly important in coastal aquifers); or (e) areas in which direct precipitation recharge may contribute. Such studies now invariably include ^{18}O and/or D measurements (e.g., Brown & Taylor 1974).

Within New Zealand's volcanic regions, there are extensive areas and depths of porous deposits and volcanic rock which are recharged predominantly by direct infiltration of precipitation. Most rivers and streams in such areas are fed from groundwater, the contribution of surface runoff and lateral near-surface flow being minimal; the ready response of streams to precipitation is often a pressure response, with older water being displaced to springs and streams in response to a remote input of newer water at the top of the reservoir. Tritium concentrations have shown that the release of water from volcanic rock to springs and streams often takes several decades or longer; this is a very important finding for catchment management policy, particularly in terms of water supply potential and long-term effects of pollution in the catchment areas. If the evidence of such long drainage times is combined with flow measurements, an estimate is obtained of

the quantity of water in the reservoir feeding the discharge; for example, if the average flow of a spring is 100 L/s, and the average drainage period of the discharge turns out to be greater than 10 years, the reservoir must contain at least 0.03 km^3 of water.

Tritium levels in geothermal bores are generally less than $\text{TR} = 1$; with our presently available measurement technique, the high measurement error in this range often prevents a definite decision on the presence or absence of tritium. More sensitive gas proportional counting techniques are being developed at INS to give better sensitivity in the range below $\text{TR} = 1$. The same situation applies in oceanographic measurements. In the South Pacific mixed layer, TR has apparently not exceeded 3, and concentrations fall to very low levels below the thermocline. Fig. 12 shows two South Pacific tritium profiles obtained by Östlund et al. (1979), one in a region of stable mixed layer, and the second in a region where vertical mixing is more intense.

Age spectra

Mixing of the inputs inside water reservoirs produces an age spectrum $f(t)$ of the water at any location, where $f(t)dt$ is the fraction of water in the age interval $t \rightarrow t + dt$. Age in this sense means the time since any water component entered the reservoir. The age spectrum extends over the time range $t = 0 \rightarrow \infty$, and

$$\int_0^{\infty} f(t)dt = 1 \quad (8)$$

The mean residence time τ is defined by

$$\tau = \frac{Q}{I} = \int_0^{\infty} t f(t)dt \quad (9)$$

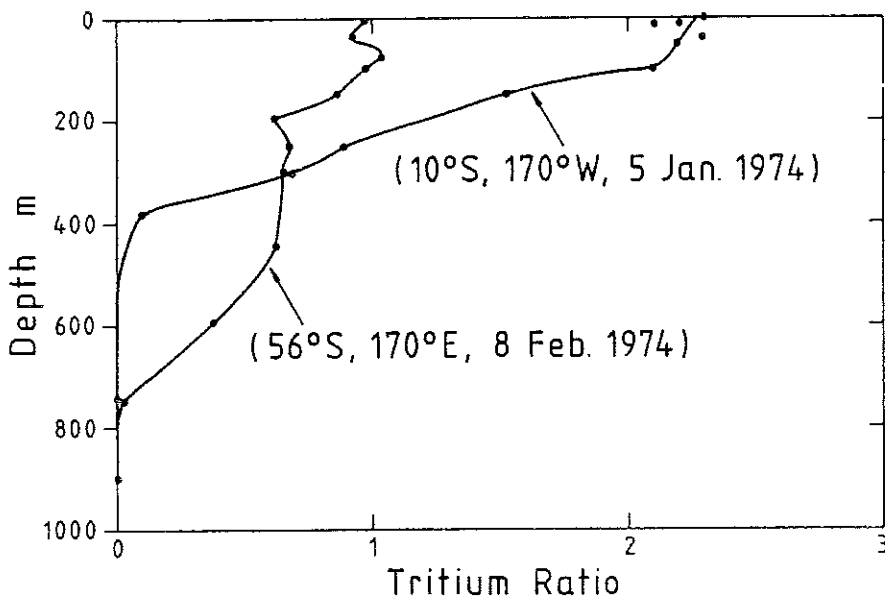


Fig. 12 Two GEOSECS South Pacific Ocean tritium profiles, illustrating varying depths of penetration of thermonuclear HTO.

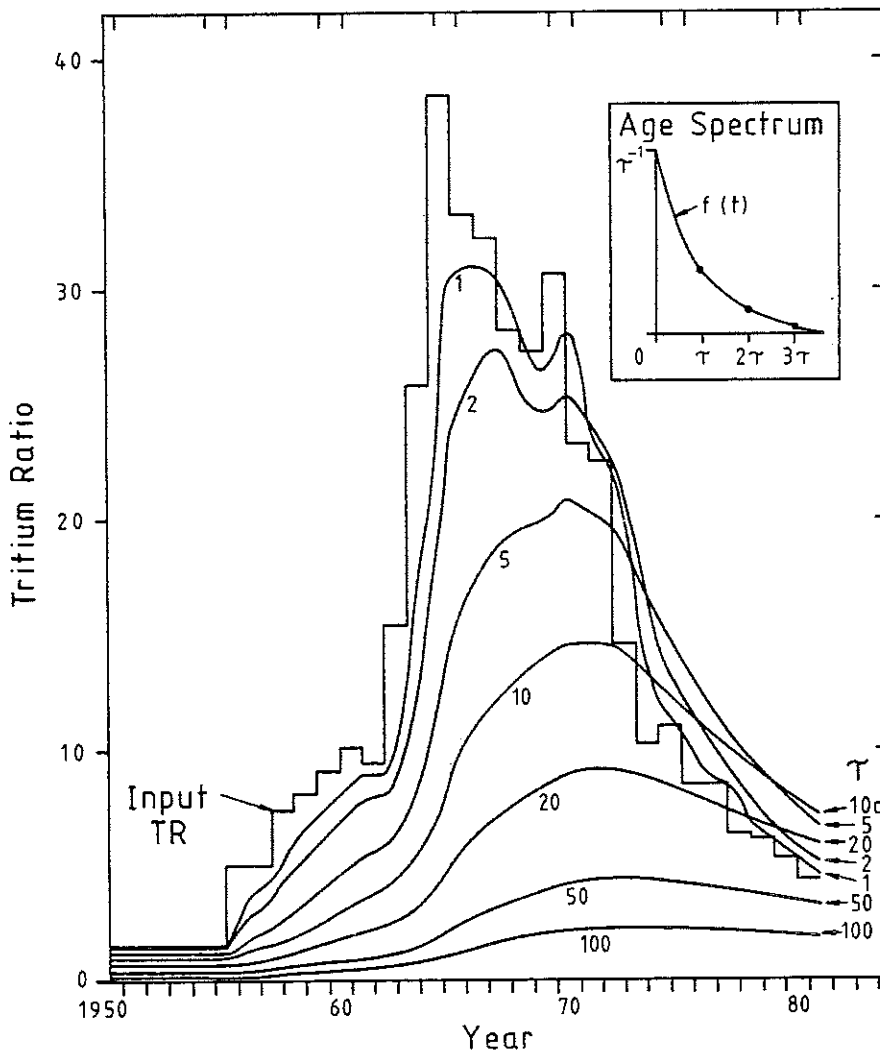
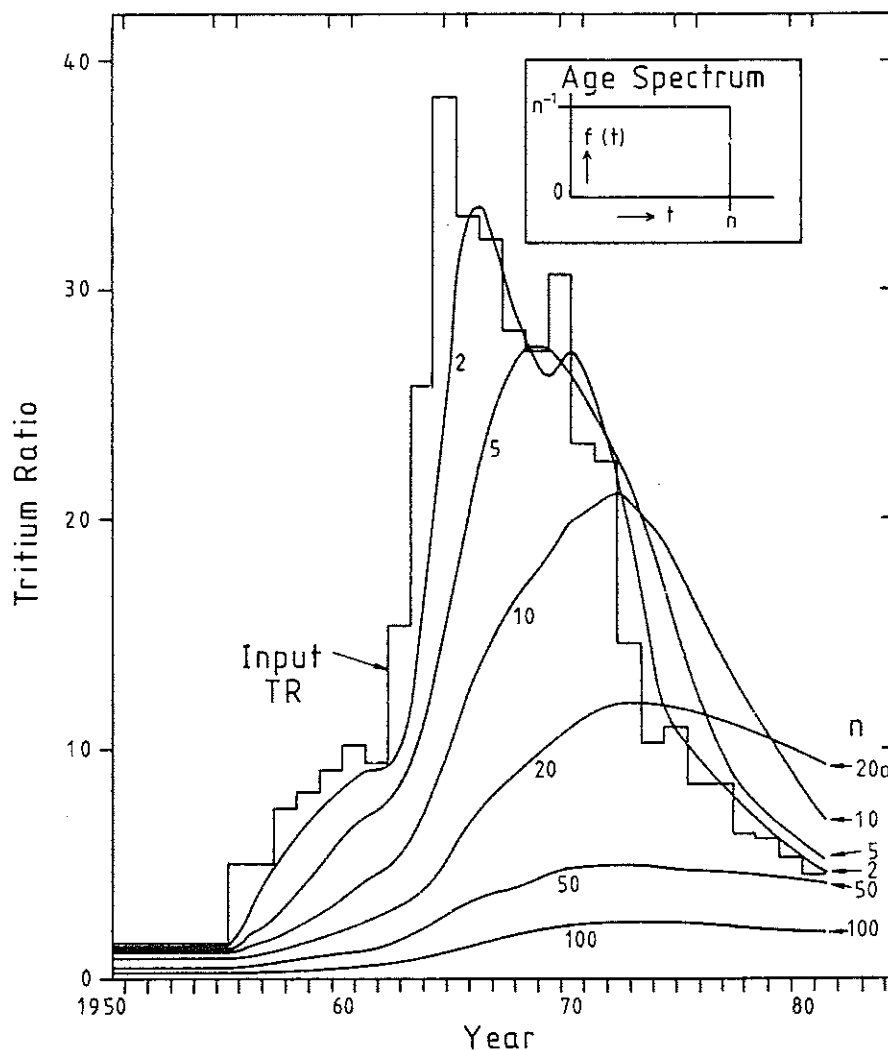


Fig. 13 Response of well-mixed reservoirs to constant yearly input of water with TR matching that of Kaitoke precipitation, for several values of mean residence time τ . Note the overlapping of responses for widely differing τ since 1972.

Fig. 14 Response of reservoir output delivering equal fractions of water with ages dating back n years, shown for $n = 2, 5, 10, 20, 50, 100$ years. Initial TR values match those of Kaitoke precipitation.



Where Q is the quantity of water in the reservoir and I is the input rate (= output rate).

It is an easy matter to deduce the tritium response of an output with arbitrarily chosen age spectrum to a known or specified tritium input. Usually, however, we are in the opposite situation, i.e., trying to deduce the age spectrum, or at least the mean residence time, from a measured tritium response. Detailed treatment of this topic is beyond the scope of this introductory paper. Nevertheless, some simple cases will be discussed, and the manner of extension to more complex systems indicated.

The well-mixed reservoir is a case which appears frequently in the literature. Some hydrological reservoirs are well-mixed in tritium. The ocean mixed layer and many lakes are good examples. If such a reservoir is considered to have an essentially constant water throughput rate, its response to the thermonuclear HTO transient can be calculated for various values of mean residence time τ without

having to insert any quantitative assessments of the throughput rate or water quantity. The well-mixed reservoir has an age spectrum

$$f(t) = \frac{1}{\tau} \exp(-t/\tau) \quad (10)$$

Fig. 13 shows such calculated tritium responses for tritium inputs matching those of Kaitoke precipitation.

It is rare to follow an actual system over long periods. Usually we are faced with measurements over a limited period. In Fig. 13, the overlapping of responses over the last 8–10 years illustrates an interpretation problem for recent measurements. Nevertheless, it is generally applicable that concentrations presently less than TR = 3 indicate mean residence times greater than 50 years.

Fig. 14 gives an indication of tritium response when the age spectrum is more evenly distributed. In this case, equal age fractions $1/n$ are assumed up

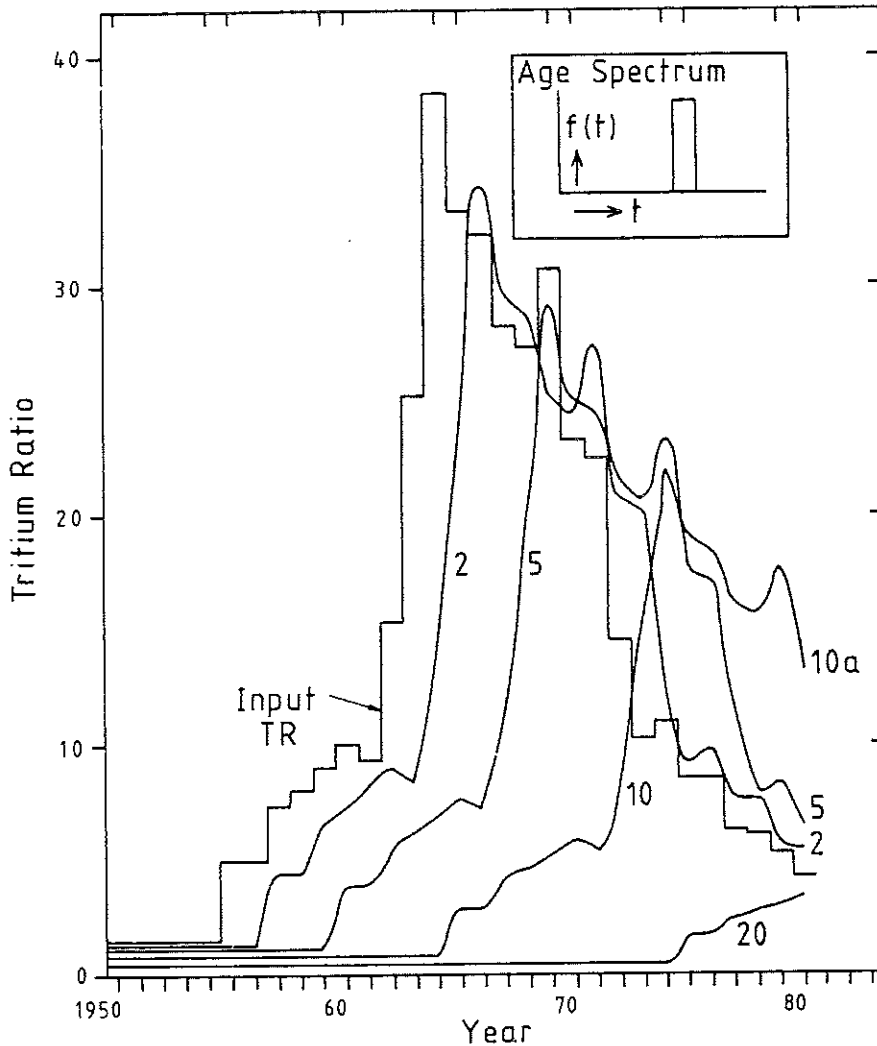


Fig. 15 Response at sampling point to piston flow of ages 2, 5, 10, and 20 years, originating with TR values matching those of Kaitoke precipitation.

to a maximum age n years. Compared to Fig. 13, the responses are more marked before and immediately after the peak in rainwater concentrations, but there is not much difference when the age interval is greater than 50 years.

As a final example, Fig. 15 shows tritium responses to piston flow of various ages. The piston flow situation is evaluated by assuming no mixing between the inputs of adjacent years. The case for piston flow of age 10 years presently produces much higher concentrations than the other model types. That for 20 years will rise within the next few years.

How do these situations apply in actual hydrological reservoirs? Do systems exist which closely correspond to ideal situations? A situation corresponding to piston flow exists in many gravel aquifers fed from rivers. The nature and hydraulic properties of the deposits produce fairly well-defined age fronts as the water advances towards points of discharge, without too much dispersion

along the flow direction. The lower Hutt valley aquifer is a case in point; during 1959–62, the tritium response at a pumping station drawing from the main aquifer indicated a travel time of 40 months without much dispersion (Grant-Taylor & Taylor 1967).

Other groundwater reservoirs correspond more closely to the well-mixed reservoir. These reservoirs are not well-mixed in the physical sense, but components of all ages combine near the output point to produce a well-mixed output. Vogel (1967) demonstrated this for a homogeneous aquifer of constant depth, uniformly recharged by precipitation over its entire area, and flowing away from a watershed. There is good reason to consider that the passage of water through many deep-seated systems such as sandstones, volcanic rocks (e.g., ignimbrite near Rotorua), and some karsts produces outputs which approximate to the well-mixed situation. In New Zealand, the base flow discharges or bore

samplings of such systems exhibit in many cases concentrations less than $TR = 2$, indicating that the bulk of the water circulates at least for many decades before reaching the sampling point.

SUMMARY

This paper contains general information relevant to the use of environmental isotopes in New Zealand hydrology and a more detailed survey of the variations of oxygen-18, deuterium, and tritium in precipitation, surface, and groundwaters. Future papers in the series will describe applications of the environmental isotopes to specific hydrological problems.

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