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Truncation of stream residence time: how the use of stable isotopes has skewed our concept of streamwater age and origin

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Abstract:

Although early studies of streamwater residence time included the use of stable isotopes (deuterium, oxygen-18) and tritium, work in the last decades has largely relied on stable isotopes (or chloride) alone for residence time determination, and derived scaling relations at the headwater and mesoscale watershed scale. Here, we review critically this trend and point out a significant issue in our field: truncation of stream residence time distributions because of only using stable isotopes. When tritium is used, the age distributions generally have long tails showing that groundwater contributes strongly to many streams, and consequently that the streams access considerably larger volumes of water in their catchments than would be expected from stable isotope data use alone. This shows contaminants can have long retention times in catchments, and has implications for process conceptualization and scale issues of streamflow generation. We review current and past studies of tritium use in watersheds and show how groundwater contributions reflect bedrock geology (using New Zealand as an example). We then discuss implications for watershed hydrology and offer a possible roadmap for future work that includes tritium in a dual isotope framework. Copyright © 2010 John Wiley & Sons, Ltd.

KEY WORDS streamflow; residence time; groundwater; tritium; oxygen-18; chloride

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INTRODUCTION

The field of watershed hydrology concerns itself with questions of where water goes when it rains, what flowpaths the water takes to the stream and how long water resides in the watershed. Although basic and water-focused, these questions often form the underpinning for questions of plant water availability, biogeochemical cycling, microbial production and other water-mediated ecological processes (Kendall and McDonnell, 1998). The use of stable isotope tracers (^{2}H and ^{18}O) [and in some cases chloride (Cl)] more than any other tools has influenced the development of the field since their first use in the 1970s (Dinçer *et al.*, 1970). Sklash and Farvolden (1979) were among the first hydrologists to quantify the composition of stream water and its temporal and geographical sources in small watersheds. Since then, watershed-scale stable isotope hydrology has blossomed (McGuire and McDonnell, 2006), and today, stable isotope-derived interpretations inform watershed rainfall-runoff concepts (Weiler and McDonnell, 2004), development (Uhlenbrook *et al.*, 2002b) and testing (Vache and McDonnell, 2006).

But what if the information gleaned from stable isotopes has actually biased our understanding of how catchments store and transmit water? What if our now, almost exclusive use of stable isotopes has led us down a path that has skewed our view of streamwater residence time? Here, we show that deeper groundwater contributes more to streamflow than we are able to ascertain using conventional stable isotope-based hydrograph separation and streamflow residence time approaches. We examine critically our reliance on ^{18}O-based estimates of residence time and explore the implications for the recent relationships discovered between residence time and topography (McGuire *et al.*, 2005), soil drainage class (Tetzlaff *et al.*, 2009) and soil depth and climate (Sayama and McDonnell, 2009).

In many ways, this is hydrology back to the future. Some of the earliest benchmark work in watershed residence time analysis used both stable isotope and tritium (^{3}H) analysis of streamwater (Maloszewski and Zuber, 1982; Maloszewski *et al.*, 1983) and showed quite clearly how faster and slower components of watershed residence time could be deduced by the separate residence time estimates of the different tracers. Since then, the use of ^{3}H has become more problematic, particularly in the Northern Hemisphere, because the year-by-year decrease in ^{3}H concentrations in precipitation has mimicked the radioactive decay of ^{3}H, i.e. the ^{3}H concentration in precipitation several decades after the bomb peak of the

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1960s has been falling at the same rate as ^{3}H decays by radioactivity. As a result, different transit time waters can have the same ^{3}H concentrations, because their reduced initial concentrations in time compensate for the radioactive decay in waters already in the catchment. The result is ambiguous ages, which can often be resolved by using gas tracers (^{3}H/^{3}He, CFCs, SF_6, ^{85}Kr), although for streams their use can be limited by exchange with the atmosphere (Busenberg and Plummer, 1992; Bohlke and Denver, 1995; Solomon and Cook, 2000). In recent years, the prospects for using natural precipitation ^{3}H for transit time determination have actually improved because the bomb peak influence is largely gone and concentrations in precipitation have stopped falling from their 1960s peak (with precipitation ^{3}H levelling out in the last 5 years in the Northern Hemisphere and for the last 15 years in the Southern Hemisphere).

Here, we make the case for increased use of ^{3}H for estimation of residence time in watersheds, in order to reveal the *real age and origin of streamwater*, and in particular the important role of deep groundwater. While perhaps not a new message, these ideas are consistent with the growing recent literature on the role of deep groundwater in contributing to streamflow based on groundwater–streamflow hydrometrics (Kosugi *et al.*, 2008) and physics-based model analysis (Ebel *et al.*, 2008). Our main message is that there is a continuum of surface and subsurface processes by which a hillslope or watershed responds to a storm rainfall (Beven, 1989), and that a focus on these processes with stable isotopes alone truncates our view of the transit time, effectively removing the long tails in the transit time distribution. Many more estimates of stream transit times have been made using ^{18}O (or chloride) variations because the measurements and age interpretation process are more straightforward (McGuire and McDonnell, 2006). This paper counters this growing trend by showing how ^{3}H-based analyses differ from ^{18}O-based analyses when the two are performed together, and providing a review of ^{3}H-based studies to recall their findings and significance. We then show how groundwater contributions to streamflow (revealed via ^{3}H) relate to bedrock geology patterns (using New Zealand as an example). We summarize the work in the context of: implications for watershed hydrology, how tritium can be utilized as an essential tool alongside stable isotopes in watershed studies, and a future, useful direction for the field.

^{18}O MEAN TRANSIT TIMES CAN BE DIFFERENT FROM ^{3}H MEAN TRANSIT TIMES

Why are they different?

Residence time is the time spent in the catchment since arriving as rainfall. Transit time is the time taken to pass through the catchment and into the stream. The transit time distribution of a catchment is difficult to measure directly, and is usually estimated from time series of tracers in precipitation and streamflow, using lumped parameter models (Maloszewski and Zuber, 1982). Such models integrate transport of tracer through the whole catchment or system under study. The varied flowpaths that water can take through a catchment mean that outflows (i.e. streams) contain water with different transit times (i.e. the water in a sample of the stream does not have a discrete age, but has a distribution of ages). This distribution is simulated by a steady-state flow model, which is intended to reflect the average conditions in the catchment.

Both ^{18}O and ^{3}H are used to estimate transit times in catchments by transforming the input series of concentrations (in the recharge) to match the output series of concentrations (in the stream), with an assumed transit time distribution. The variations of ^{18}O are altered (and usually damped) by mixing of precipitation from the succession of storms with different tracer signatures. This damping allows the transit time distribution to be extracted from the time series by convolution using a lumped parameter model. ^{3}H while passive, differs from ^{18}O by being radioactive and its decay is the basis for dating. Rainfall incident on a catchment can be affected by immediate surface or near surface runoff and longer-term evapotranspiration loss. The remainder becomes recharge to the subsurface water stores. Tracer input to the subsurface water stores is modified by passing through the hydrological system (as represented by the flow model) before appearing in the output. The convolution integral and an appropriate flow model are used to relate the tracer input and output. The convolution integral is given by

$$C_{\text{out}}\ (t) = \int_0^{\infty} C_{\text{in}}\ (t-\tau)h(\tau)\exp(-\lambda\tau)\mathrm{d}\tau \qquad (1)$$

where C_{in} and C_{out} are the concentrations in the recharge and stream, respectively. t is calendar time and the integration is carried out over the transit times τ. $h(\tau)$ is the flow model or response function of the hydrological system. The exponential term accounts for radioactive decay of ^{3}H {λ is the ^{3}H decay constant [$= \ln 2/T_{1/2}$, where $T_{1/2}$ is the half-life of ^{3}H (12·32 years)]}.

Simulation via the convolution integral causes a decrease in the range of variation of ^{18}O in streamflow in comparison with the range in rainfall. It can be shown that the maximum mean residence time that can be determined using ^{18}O is about 4 years with the exponential flow model (EM), longer if a more peaked model is used (e.g. deWalle *et al.*, 1997; McGuire and McDonnell, 2006). Depending on the variation, which usually follows a seasonal pattern, the maximum could be smaller. Thus, water resident in the catchment for longer than about 4 years is not expected to show detectible variation in ^{18}O (i.e. variation greater than the measurement error) and therefore is effectively invisible to the method.

On the other hand, ^{3}H decay with half-life 12·32 years allows for age dating covering several half-lives, and therefore much longer mean transit times (MTTs) can be determined. The maximum age that can be determined depends on the ^{3}H level in precipitation, the measurement precision of the tritium laboratory at the background level and the flow model applied. The ^3H level in precipitation differs between the Northern and Southern Hemispheres (see discussion below), and different laboratories have different measurement precisions. MTTs of up to 200 years can often be determined with the EM.

How can their differences be quantified?

So how do we quantify the residence time of these different components? Two flow models are commonly used in environmental tracer studies (Maloszewski and Zuber, 1982). The exponential-piston flow model (EPM) combines a volume with exponentially distributed transit times followed by a piston flow volume to give a model with two parameters. The response function is given by

$$h(\tau) = 0 \qquad \text{for } \tau < \tau_m\ (1-f) \tag{2}$$

$$h(\tau) = (f\tau_m)^{-1}.\exp\left[-\left(\frac{\tau}{f\tau_m}\right) + \left(\frac{1}{f}\right) - 1\right] \quad \text{for } \tau \geq \tau_m\ (1-f) \tag{3}$$

where τ_m is the mean residence time, and f the ratio of the exponential volume to the total volume. Maloszewski and Zuber (1982) used the parameter η, $f = (1/\eta.)$ $\tau_m(1-f)$ is the time required for water to flow through the piston flow section. [In abbreviated form, EPM ($f = 0{\cdot}9$) signifies an EPM with $f = 90\%$. The EM is EPM ($f = 1{\cdot}0$).]

The EM (introduced by Eriksson, 1958) is often misleadingly referred to in this context as the one-box or well-mixed model, which is analytically the same. However, Eriksson clearly envisaged flowlines with different transit times combining in the outflow to give the exponential transit time distribution rather than instantaneous mixing within the ground. The combination of the EM and PFM (in the EPM) gives a wide range of possible transit time distributions. The EM and EPM are especially suitable for interpreting transit time distributions of streamflow, because the stream integrates the total flow out of the catchment [i.e. combines water originating from near (streamside) to far (catchment boundary)].

The dispersion model (DM) is based on a solution to the dispersion equation which describes the flow in porous media (the C_{FF} case from Maloszewski and Zuber, 1982). The equation is

$$h(\tau) = \frac{1}{\tau\sqrt{4\pi \mathrm{DP}(\tau/\tau_m)}} \exp\left[-\frac{(1-\tau/\tau_m)^2}{4\mathrm{DP}(\tau/\tau_m)}\right] \tag{4}$$

where the parameters are τ_m and DP (the dispersion parameter, defined as the mass of the variance of the dispersive distribution of the transit time). Although apparently less suitable conceptually for application to transit time determination of streamflow, the DM has proven to be useful in practice. The DP effectively describes dispersion resulting from the extended recharge zone (catchment area), which is much greater than dispersion due to flow within the ground. The model gives a wide range of transit time distributions, which have realistic-looking shapes (no sharp edges like the EPM transit time distributions).

Combinations of these models can be used to simulate more complicated transit time distributions, for example, where there are several distinct flow components contributing to the streamflow. Michel (1992) and Taylor *et al.* (1992) applied two EM models in parallel to identify fast and slow components of flow to rivers. Their combined models have three parameters, the MTTs of the two EMs and the fraction of the rapid component. Likewise, Stewart and Thomas (2008) used two DM models in parallel to identify two groundwater components feeding the Waikoropupu Springs in New Zealand. Identification of distinct flow components and their average proportions generally requires streamflow and/or geochemical records for the streams.

Examples that show their difference

Four key studies from the literature using both ^{18}O and ^3H are highlighted here to contrast the two methods, and illustrate how ^{18}O produces a truncated version of the transit time distribution. Results of the studies are summarized in Table I. In the first example, Maloszewski *et al.* (1983) used ^2H and ^3H to study runoff in the Lainbach Valley (670–1800 m a.s.l, 80% forested) in the Bavarian Alps. Geological substrates are Pleistocene glacial deposits, Triassic calcareous rocks and Cretaceous sandstones and marlites. They examined transit times for three runoff conceptualizations assuming contributions from different flow components in each (illustrated in Figure 1a). In the first, the whole system was treated as a black box where only the input and output concentrations were known. The MTTs found using ^2H and ^3H were 1·1 and 1·8 years, respectively. In the second, 70% of the flow went through a subsurface reservoir while the remainder was direct runoff with very short residence time. The subsurface water was found to have MTTs of 2·1 years (^2H) and 2·3 years (^3H). In the third, the subsurface 'box' was split into an upper reservoir with short turnover time (taking 52·5% of the total flow), and a lower reservoir with longer turnover time (17·5% of the flow) based on the streamflow record. The MTTs for the reservoirs were found to be 0·8 and 7·5 years using ^3H. The transit time distribution of the subsurface system is illustrated in Figure 1b. With ^2H, only the short transit time could be estimated (0·6 year) when allowance for the old component with no ^2H variation was made.

The second study was by Uhlenbrook *et al.* (2002a), who applied ^3H with other measurements in the Brugga Basin in Germany. In a detailed study, they used several tracers (^{18}O, ^3H, silica) and the flow record to show that runoff sources or main flowpaths could be separated into three components: short-term runoff (comprising 11·1% of annual runoff, with MTT of days or weeks), shallow groundwater (69·4% and MTT 2·3–3 years)

Table I. Summary of the four key examples of the difference between ^{18}O- and ^{3}H-based mean transit times (MTTs). The flow components and their MTTs were identified from hydrometric, isotopic and chemical measurements by each author. The blackbox MTTs are those given by ^{18}O or ^{3}H simulations assuming different blackbox models of the streams fitted to the data or by calculation assuming ^{18}O MTTs $\leq$4 years

Catchment	Flow components			Blackbox MTTs (year)	
	Type	MTT (year)	%	$^{18}O/^{2}H$	^{3}H
Lainbach Valley[b]	Surface runoff	~0·01	30	*All flow* 1·1 (1·1[a])	1·8 (1·7[a])
	Upper reservoir	0·8	52·5	*Subsurface flow* 2·1 (1·6[a])	2·3 (2·5[a])
	Lower reservoir	7·5	17·5		
Brugga Basin[c]	Event water	~0·01	11·1	*All flow* 2 · 6[a]	3·3[a]
	Shallow groundwater	2·3–3	69·4	*Subsurface flow* 2·9[a]	3·7[a]
	Deep groundwater	6–9	19·5		
Pukemanga Catchment[d]	Direct runoff	~0·1	15	*All flow* 3·4[a]	9·0[a]
	Groundwater	10·6	85	*Subsurface flow* 4	10·6
Waikoropupu Spring[e]	Shallow groundwater	1·2	26	*Subsurface flow* 2·6–3·9 (3·3[a])	7·9 (7·9[a])
	Deep groundwater	10·2	74		

[a] Calculated by combining the flow components in the indicated proportions.
[b] Maloszewski *et al.* (1983).
[c] Uhlenbrook *et al.* (2002a)
[d] Stewart *et al.* (2007)
[e] Stewart and Thomas (2008).

and deep groundwater (19·5% and MTT 6–9 years). Shallow groundwater resides in upper drift and debris cover, and deep groundwater in deeper drift, weathering zone and hard rock (gneiss) aquifers. In the third study, Stewart *et al.* (2007) reported on the small (3·8 ha), steep Pukemanga Catchment on highly weathered greywacke in New Zealand. The perennial stream flows from a small wetland at the bottom of a gully. Baseflow comprises 85% of the annual flow and shows no significant ^{18}O variation, indicating that it has a minimum MTT of 4 years. The ^{3}H results show an MTT of 10·6 years (from Stewart *et al.*, 2007 and a later result).

The fourth example was by Stewart and Thomas (2008), who used ^{18}O and ^{3}H to study the flow to the Waikoropupu Spring, the source of the Waikoropupu River, in NW Nelson, New Zealand. Analysing the whole system as a black box gave MTTs of 7·9 years with ^{3}H, and 2·6–3·9 years with ^{18}O (Figure 2a). However, hydrometric, Cl and ^{18}O measurements showed that there were two groundwater systems or components feeding the springs and established their proportions. The ^{3}H results allowed these to be characterized as shallow (26% of the flow with MTT 1·2 years) and deep (74%, and 10·2 years) components. The flow components and transit time distribution are illustrated in Figure 2a and b. When allowance is made for the 10·2 years component (which would have had no significant ^{18}O variation), the ^{18}O data identified a 1·0-year component (i.e. the shallow groundwater). In this case, the presence of the dominant deep groundwater component was evident from the ^{3}H, but not from the ^{18}O.

Table I gives a summary of the four cases. The flow components supplying each stream and their MTTs based

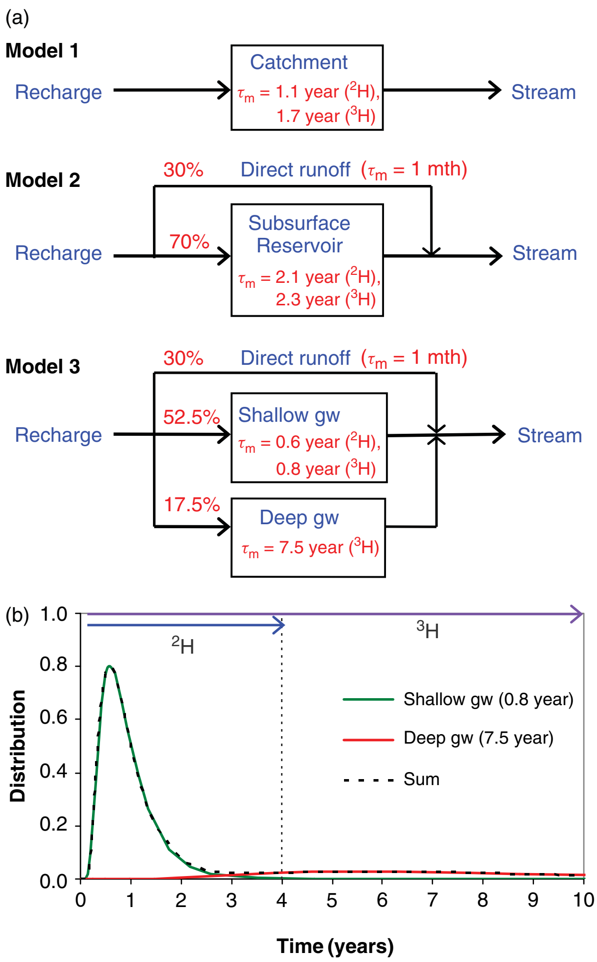

Figure 1. (a) Conceptual flow models, and (b) distribution of transit times for model 3 (excluding direct runoff), for Lainbach Valley (Maloszewski *et al.*, 1983)

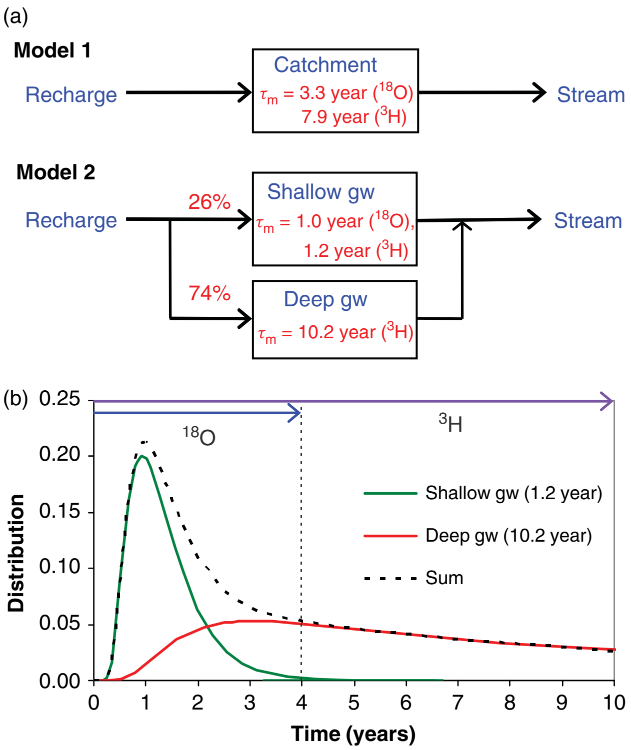

Figure 2. (a) Conceptual flow models, and (b) distribution of transit times for model 2, for Waikoropupu Stream (Stewart and Thomas, 2008)

on ^{3}H are listed in Table I, as determined by each author from hydrometric and geochemical measurements. The blackbox values on the right side of the table are those derived by assuming different blackbox models of the flow systems, as described above and illustrated in Figures 1 and 2. The calculated blackbox values (starred) were obtained by combining the flow components in the indicated proportions, recognizing that ^{18}O cannot give ages greater than 4 years. Although there is a component of older (7·5 years) water present at both Lainbach Valley and Brugga Basin, it is not very apparent from the blackbox values except that the ^{3}H values are consistently older than the ^{18}O values. The old water components are more apparent from the marked differences between the ^{18}O and ^{3}H blackbox values at Pukemanga Catchment and Waikoropupu Spring. It is usually necessary to understand the flow components feeding the stream when interpreting the ^{3}H results; but such understanding does not prevent truncation of the transit time distribution with ^{18}O if there is no ^{3}H data.

A SURVEY OF ^{3}H STREAMFLOW STUDIES

So how common are old water components in streams? Or, components that are too old to be seen by ^{18}O? This section aims to establish how likely it is that old water components are common, and possibly dominant, in rivers and streams, by surveying the literature on ^{3}H studies in catchments. The studies are listed in Tables II and III.

Headwater catchments

Baseflow proportions and ages in smaller catchments are expected to reflect more faithfully their widely varying geography and lithology (Tague and Grant, 2004). Dinçer *et al.* (1970) used ^{18}O and ^{3}H to study runoff in the alpine Modry Dul basin in the present Czech Republic (altitude range 1000–1554 m a.s.l.). They showed that two-thirds of the snowmelt infiltrated the soil, and had an MTT of 2·5 years. Storage of water was attributed to subsurface reservoirs in relatively large amounts of unconsolidated glacial deposits (up to 50 m thick) on a crystalline basement. Maloszewski and Zuber (1982) later revised the estimate of MTT to 3·6–5·5 years based on more detailed lumped parameter modelling of the ^{3}H concentrations.

Martinec *et al.* (1974) used ^{3}H to show that most of the runoff (64%) from the high alpine Dischma basin in Switzerland (1668–3146 m a.s.l.) had MTT 4·5–4·8 years. ^{18}O showed a very subdued variation in the runoff in comparison with the precipitation; no estimate of MTT from the ^{18}O data was given. The catchment contains unconsolidated glacial and avalanche deposits, as described above. Behrens *et al.* (1979) reported isotope studies on the Rofenache Catchment in the Austrian Alps (1905–3772 m a.s.l.). The ^{3}H measurements in winter runoff showed a 4-year MTT, which was attributed to storage in groundwater aquifers in morainal material.

Zuber *et al.* (1986) determined a 2·2-year MTT for 89% of the total flow in the Lange Bramke catchment in Germany (543–700 m a.s.l., 90% forested). The authors obtained the same result with both variable flow and steady-state models, concluding that 'the latter is applicable even for systems with highly variable flow, if the variable part of the system is a small fraction of the total water volume'. The subsurface reservoir consists of the unsaturated zone (residual weathering and allochthonic Pleistocene solifluidal materials), and saturated zone (fractured Lower Devonian sandstones, quartzites and slates, and gravels, pebbles and boulders in the valley bottom). Maloszewski *et al.* (1992) used ^{18}O and ^{3}H to determine the MTT of runoff (4·2 years) in the Wimbachtal Valley in Germany (636–2713 m a.s.l.). Direct runoff was considered negligible (<5%). The three aquifer types were a dominant porous aquifer (debris from dolomite), a fractured dolomite aquifer and a karstified limestone aquifer.

Matsutani *et al.* (1993) used ^{3}H in the Kawakami Basin in Japan (1500–1680 m a.s.l., mountainous) to characterize the baseflow component (identified as groundwater) with MTT 19 years comprising 33% of the annual runoff. The remainder (identified as soil water) had MTT 4 months. The bedrock is late-Tertiary volcanic deposits. Rose (1993) applied ^{3}H to estimate the MTT of baseflow in large nested gneiss catchments (6·5, 109 and 347 km^2) in the Georgia Piedmont Province. The streams were baseflow dominated, and ^{3}H concentrations in the baseflow were very significantly greater than the precipitation at the time (about double). He estimated baseflow

Table II. Summary of published field studies for headwater catchments using ^{3}H

Reference	Region	Catchment	Bedrock	Area (km^2)	Mean transit time		Fraction of total runoff	
					Model	^{3}H (year)	(%)	Description
Dincer *et al.* (1970)	Czech Republic	Modry Dul	Gneiss/granite	2·65	BN	2·5	67	Subsurface flow
Martinec *et al.* (1974)	Switzerland	Dischma		43·3	EM, DM	4, 4·8	64	Subsurface flow
Behrens *et al.* (1979)	Austria	Rofenache		96·2	EM	4		Baseflow
Maloszewski and Zuber (1982)	Czech Republic	Modry Dul	Gneiss/granite	2·65	DM	5·5–3·6	67	Baseflow
Maloszewski *et al.* (1983)	Germany	Lainbach	Pleistocene glacial	18·7	DM	7·5	17·5	Deep reservoir
Zuber *et al.* (1986)	Germany	Lange Bramke		0·76	EM	2·2	89	Baseflow
Maloszewski *et al.* (1992)	Berchtesgaden Alps	Wimbachtal	Limestone/dolomite	33·4	EM/DM	4·2	>95	Groundwater
Matsutani *et al.* (1993)	Central Japan	Kawakami	Tertiary volcanics	0·14	BN	19	33	Groundwater
Rose (1993)	Piedmont Province, GA	Three streams	Gneiss	6·5–347	ND	15–35	67	Baseflow
Bohlke and Denver (1995)	Coastal plain, MD	Chesterville Br	Sediments	32·9		~20	59	Baseflow
Rose (1996)	Piedmont Province	Falling Creek	Gneiss	187	ND	10–20	67	Baseflow
Herrmann *et al.* (1999)	Vallcebre, Spain	14 streams	Paleocene	0·6–4·2	EM	8–13·5		Low flows
Taylor (2001)	NW Nelson, NZ	Upper Takaka	Paleozoic schist		EM	0·2	80	Runoff less peaks
Uhlenbrook *et al.* (2002a)	SW Germany	Brugga	Gneiss	40	DM	6–9	19·5	Groundwater
Stewart *et al.* (2002)	N. Auckland, NZ	Mahurangi	Tertiary		EM	2	60	Baseflow
McGlynn *et al.* (2003)	Maimai, NZ	Four streams	Tertiary glacial sediment	0·03–2·8	EM	1·1–2·1	60	Baseflow
Morgenstern *et al.* (2005)	Rotorua, NZ	Six streams	Welded ash flows		EPM	30–145	100	Spring-fed streams
Stewart *et al.* (2005a)	NW Nelson, NZ	Upper Motueka River	Tertiary		EM	0·3	40	Baseflow
Stewart *et al.* (2005b)	Glendhu, NZ	GH5	Schist	0·036	DM	16	60	Groundwater
Morgenstern (2007)	Taupo, NZ	Eight streams	Unwelded ash flow		EPM	40–84	90	Baseflow
Stewart *et al.* (2007)	Waikato, NZ	Pukemanga	Greywacke	0·038	EM	10·6	85	Baseflow
Stewart and Thomas (2008)	NW Nelson, NZ	Waikoropupu	Marble	450	DM	10·2	74	Groundwater
22 papers		22 catchments		Averages		15 ± 22 years	60 ± 22%	

See original references for details.

Table III. Summary of published field studies for macroscale catchments using ^{3}H

Reference	River (sample point)	Bedrock	Area (km^2)	Mean transit time		Fraction of total runoff	
				Model	^{3}H (year)	(%)	Description
Begemann and Libby (1957)	Upper Mississippi River (Rock Island, IL)			Mass balance	15		Baseflow
Eriksson (1958)	Upper Mississippi River (Rock Island, IL)			EM	8	~90	Baseflow
Taylor *et al*. (1989)	Waimakariri River (Halkett, NZ)	Greywacke	2 600	EM	>3	90	Runoff less floods
Taylor *et al*. (1992)	Wairau River (Renwick, NZ)	Greywacke	2 600	EM	8	40	Baseflow
Michel (1992)	Colorado River (Cisco, UT)		75 000	EM	14	60	Groundwater
Michel (1992)	Mississippi River (Anoka, MA)		53 000	EM	10	36	(The remainder in all cases is runoff resident for less than 1 year in the catchment)
Michel (1992)	Neuse River (Vanceboro, NC)		11 000	EM	11	27	
Michel (1992)	Potomac River (Point of Rocks, MD)		27 000	EM	20	54	
Michel (1992)	Sacramento River (Sacramento, CA)		67 000	EM	10	65	
Michel (1992)	Susquehanna River (Harrisburg, PA)		70 000	EM	10	20	
Michel (1992)	Kissimmee River (L. Okeechobee, FL)		4 500	EM	2·5	6	
Yertsever (1999)	River Danube (Vienna)		101 700	EM	11·7	36	Subsurface runoff
Michel (2004)	Ohio River (Markland Dam, KY)		215 400	EM	10	60	Baseflow
Michel (2004)	Missouri River (Nebraska City, NE)		1 073 300	EM	4	90	Baseflow
Koeniger *et al*. (2005)	Weser-1 River (Karlshafen, Germany)	Consolidated rock	15 320	EM	13	55	Groundwater
Eight papers	14 catchments			Averages	10 ± 5 years	$52 \pm 26\%$	

See original references for details.

MTTs of 15–35 years, and observed that the baseflow MTT varied during the year, being older (with higher ^{3}H) during lower flow periods in summer. ^{3}H was also used to show an MTT of 10–20 years for baseflow in another large Piedmont catchment (187 km^2) (Rose, 1996).

Bohlke and Denver (1995) used ^{3}H (together with CFCs) to date water in two small agricultural watersheds on Tertiary sediment on the Atlantic Coastal Plain, MD, USA. The study on the history and fate of nitrate in the watersheds revealed baseflow comprising 59% of annual flow had MTT 20 years. Herrmann *et al*. (1999) applied ^{3}H to determine MTTs for streams (8·5–13·0 years), springs (10·5–13·5 years) and wells (8·0–11·5 years) during summer low-flows in the Vallcebre basins in the Pyrenees of Spain. The substrate comprised four Paleocene units (limestone, clay, silt and limestone from bottom to top). Altitude range was 960–2245 m a.s.l. ^{3}H measurements in subcatchments in the Mahurangi Catchment (New Zealand) suggested short MTTs (about 2 years), but data are limited and not fully evaluated yet (Stewart *et al*., 2002). The catchments are underlain by Tertiary sediment. McGlynn *et al*. (2003) reported ^{3}H measurements for four nested Maimai catchments (New Zealand). The estimated ages ranged from 1 to 2 years and correlated with median subcatchment areas of the sampled catchments rather than with their overall areas. Previous ^{18}O measurements at a nearby small catchment had given an age of 4 months (Stewart and McDonnell, 1991). The substrate is Tertiary sediment (a firmly compacted conglomerate known as the Old Man Gravel).

Estimated ages for six streams flowing into Lake Rotorua were given by Morgenstern *et al*. (2005) based on ^{3}H. Earlier results were given by Taylor and Stewart (1987). The spring-fed streams drain Mamaku Ignimbrite (a welded volcanic ash-flow deposit with no surface water flows) on the west side of the lake. MTTs ranged from 30 to 145 years, showing that the very porous ignimbrite constitutes a very large reservoir. The largest and oldest stream (Hamurana Spring, mean flow 3·5 m^3/s) has mean age 145 years indicating water storage of 5 km^3, far greater than Lake Rotorua itself. Morgenstern (2007) gave ^{3}H data for eight streams draining into Lake Taupo from unwelded volcanic ash-fall deposits north of the lake. The deposits have remarkable porosity. Estimated MTTs for baseflow ranged from 40 to 84 years and baseflow comprises 90% of the annual flow. A more detailed study at Tutaeuaua Stream (also in the North Taupo region feeding Lake Taupo) revealed a baseflow MTT of 45 years (Stewart *et al*., unpublished).

The Upper Takaka River discharges very young water on average—the MTT from ^{3}H was 2 months (Taylor, 2001). The bedrock is Paleozoic schist with very low porosity. ^{3}H measurements show that the Upper Motueka River has an MTT of about 4 months (Stewart *et al*., 2005a). The catchment geology is varied with strongly indurated ultramafics and sediments of Permian age in the headwater, and Tertiary sediment (Moutere Gravel) with a shallow overlay of permeable Holocene gravels in the middle reach. The river dominates the interaction with groundwater in the Holocene gravels. Stewart *et al*. (2005b) reported on ^{3}H measurements at Glendhu Catchment (schist bedrock). At GH5 (a perennial stream flowing out of a wetland), the MTT of baseflow (60% of the flow) was 16 years.

Table II shows that the MTTs of these catchments vary greatly, but the results (and average) show that many streams discharge large proportions of old water.

Macroscale catchments

The first application of ^{3}H dating to a river catchment was by Begemann and Libby (1957). They used the ^{3}H released by the Castle test in 1954 (along with the assumption of instantaneous mixing of ^{3}H delivered by rainfall into the groundwater aquifer, i.e. a one-box model) to estimate an MTT of 15 years for water through the Upper Mississippi catchment. This estimate was refined by Eriksson (1958) to 8 years, by using a smaller value for the ^{3}H fallout. Eriksson established some important points in his treatment: (1) Recharge and ^{3}H input to the aquifer is from precipitation minus evapotranspiration, (2) while instantaneous mixing *does not occur* in groundwater (or soil water), the assumption of instantaneous mixing can appear to be correct when water following different flowpaths through the catchment combines in the outflow (stream), thus approximating the EM, (3) different flow models can give similar results when MTTs are short compared with the half-life of ^{3}H (Eriksson suggested up to $0{\cdot}6 \times T_{1/2}$ or 7 years).

Taylor *et al*. (1989, 1992) reported ^{3}H measurements for two large greywacke catchments in New Zealand (both with catchment areas of 2600 km^2). The Waimakariri River results (which omitted peak flows) were fitted with a single exponential component with MTT of 3 years (90% of flow). The Wairau River data were fitted with two EM components, the older of which had an MTT of 8 years and comprised 40% of the annual streamflow. The younger component was essentially direct runoff (MTT 0·2 year and 60% of the flow).

Michel (1992) reported monthly ^{3}H measurements on six large US rivers, with catchment areas ranging from 11 000 to 75 000 km^2. His model to simulate the ^{3}H concentrations had two components, 'quick' runoff with transit times less than 1 year, and 'slow' runoff (groundwater). The slow runoff had MTTs ranging from 10 to 20 years, and supplied 20–65% of the annual flows in the six catchments. A smaller karstic catchment (Kissimmee River, Florida) had a younger (2·5 years) and smaller (6%) groundwater component.

In a further study, Michel (2004) reported on ^{3}H in rivers at four locations within the Mississippi River basin. The two-component mixing model was applied to the Ohio and Missouri Rivers; the components were quick runoff (MTT less than 1 year) and water from groundwater reservoirs, as described above. The modelling yielded groundwater components with MTT 10 years comprising 60% of the flow at Ohio River and MTT 4 years comprising 90% of the flow at Missouri River. Using these results, Michel demonstrated that the rivers will require 20–25 years to fully respond to a change in the input of a conservative pollutant.

Monthly data since 1968 for the River Danube at Vienna (catchment area 101 700 km^2) was analysed by Yertsever (1999). He applied a two-component compartmental (mixing cell) model, and derived a surface flow component with MTT of 0·83 year (64% of annual flow) and a subsurface component with MTT 11·7 years (36% of flow). An ANN model had previously yielded an MTT of 4·8 years for the total flow, in good agreement with the compartmental model.

Koeniger *et al.* (2005) applied 50 years of ^{3}H data to estimate the MTTs of three large subcatchments in the Weser River catchment. The largest (Weser-1, 15 320 km^2) is representative of the three. Direct runoff (supplying 45% of the flow on average) and two groundwater components ('quick' and 'slow', each with mobile and immobile fractions) were used for modelling. Quick groundwater (26% of flow and thought to result from flow in fissured rock) had MTTs 5–7 years (mobile fraction 5 years, immobile fraction 7 years). Slow groundwater (29% of flow and flowing in porous rock) had MTTs 12–28 years (mobile fraction 12 years, immobile fraction 28 years).

These studies demonstrate that large rivers generally discharge large proportions of old water. Most of the studies cover some of the bomb peak years, when ^{3}H data were most effective for determining ages, so the age estimates are considered very reliable. The average MTT of the old water component from Table III is 10 ± 5 years, and comprised $52 \pm 26\%$ of annual streamflow. The results are relatively homogeneous, which is probably related to the catchments being humid and large enough to average out diverse landscape elements.

Figure 3a shows conceptual flow models representing the average from Table III. Note that treating the entire flow as one exponential component (model 1) still produces different results for ^{18}O and ^{3}H. With two exponential components (model 2), 18·5% of the water would be older than 10 years and 7% older than 20 years (see distributions in Figure 3b). It is clear that there must be substantial storage volumes for this water in the catchments. Most of the authors ascribe this storage to groundwater aquifers. (Some refer to the water as 'subsurface runoff'.) Although most subsurface flowpaths are likely to pass through both the unsaturated and saturated zones, there must also be substantial access to deep groundwater systems.

Other more minor factors potentially affecting the baseflow age include the presence of lakes or storage dams in the catchments. As noted by Michel (2004), storage of water in lakes and dams would reduce the amount of immediate runoff and increase the delayed runoff. However, storage time of water in lakes or dams is likely to be much shorter than that in groundwater systems, so the delayed fraction would be greater, but its age would be less. Extraction of water from the river

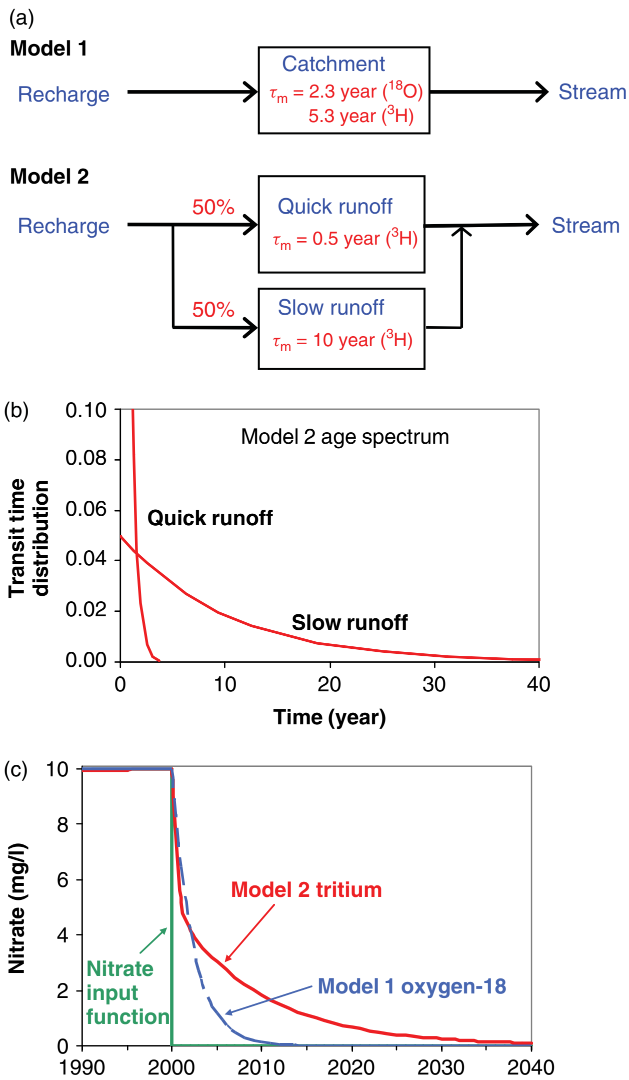

Figure 3. (a) Conceptual flow models, and (b) distribution of transit times for model 2, for the average of the large rivers from Table III. (c) The consequent nitrate response of the average river to a decrease of nitrate in its input

for agricultural or urban use can also affect the mean residence time at the macroscale. As the water drains back to the river, it would increase the apparent age of the river water. Similarly, artificial drainage of agricultural lands could short-circuit the groundwater pathways and reduce the apparent age of the river water.

Groupings by geological class in New Zealand

Recent studies have shown that topography (McGuire *et al.*, 2005), soil drainage class (Soulsby and Tetzlaff, 2008) and drainage density (Hrachowitz *et al.*, 2009) may control the spatial pattern of stream residence time within particular classes of rocks. Here we contend that geology (and deep groundwater as evidenced by ^{3}H-based residence time) may define an overarching control at the scale of the country of New Zealand. Figure 4 is a generalized geological map of New Zealand showing bedrock geology and the locations of studied streams (Tables II and III). The various classes of rocks provide a guide to streamflow characteristics, despite considerable

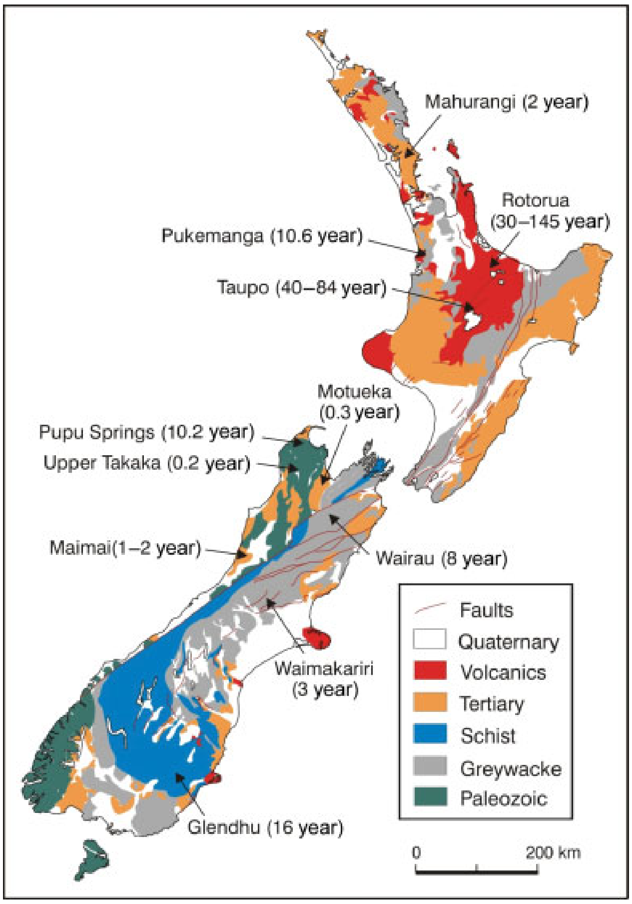

Figure 4. Generalized geological map of New Zealand showing locations of studied catchments and their baseflow MTTs based on ^{3}H

variations in hydrological properties within classes in some cases.

Paleozoic rocks are present in the South Island (Figure 4). The Upper Takaka River drains Paleozoic schist of very limited porosity and permeability and has very short MTT (2 months). In contrast, the Waikoropupu Springs (Pupu Springs on Figure 4) drain Paleozoic marble; the MTT of old water is 10·2 years and comprises 74% of the flow. (This is a rare case where the age of the water becomes younger as flow decreases; Stewart and Thomas, 2008.) Greywacke is the true basement of both islands. The Waimakariri (90% of flow has 3 years MTT) and Wairau (40% has 8 years MTT) rivers rising in the Southern Alps drain greywacke, which against expectation provides considerable storage of old water. For the Wairau, Taylor *et al.* (1992) commented that 'large deposits of scree in higher-lying, formerly glacial catchments appear to be the major factor in the surprisingly large quantity of stored water implied'. There may also be storage in fractured greywacke aquifers. Pukemanga Stream drains from highly weathered greywacke on the west of the North Island. The old age (10·6 years MTT on 85% of streamflow) appears to reflect the weathered (clay-rich) nature of the substrate above bedrock as well as groundwater flow within the bedrock. Weathered hard rocks in Japan (Kosugi *et al.*, 2008) and USA (piedmont gneiss, Rose, 1993, 1996) may also show similar properties. Glendhu (16 years MTT on 60% of streamflow) also shows considerable storage, indicating groundwater flow within the schist bedrock. The streams in this group of old rocks are highly variable, but most show large fractions of old water (generally older than can be seen by ^{18}O).

Tertiary sediments underlie streams in a considerable part of the country. Maimai Catchment and part of the Upper Motueka River catchments are on Tertiary sediments laid down during an intense mountain building episode of the Southern Alps. Mahurangi Catchment is also on Tertiary sediment, but not related to the Southern Alps. MTTs in these environments appear to be short (up to 2 years) reflecting low permeability of these rocks. In contrast, the young volcanic rocks covering a large part of the central North Island of New Zealand have streams with very long transit times. Ash-fall deposits form large sheets at Rotorua and Taupo; these have remarkable hydrological properties as shown by MTTs of 30–145 years on nearly all the streamflow in six streams at Rotorua and eight streams at Taupo. Elsewhere in the world, older volcanic rocks at Kawakami Catchment in Japan discharge streamflow with MTT 19 years on 33% of the flow. Young volcanic ash-flow deposits also occur in Southern Chile, where they cover 62% of the area (Blume *et al.*, 2008). Although no ^{3}H measurements have been made, it is likely that the streams also discharge water with very long MTTs. It is believed that young ash-flow rocks anywhere are likely to have the ability to store very large quantities of water and produce very old streamflow, but other eruptive (but non-explosive) igneous rocks (rhyolites, andesites, basalts) can have very different hydrological properties and responses.

DISCUSSION AND CONCLUSIONS

On the implications of stream residence time truncation in watershed hydrology

The current largely sole focus on streamwater residence time deduced from ^{18}O studies has truncated our view of streamwater residence time and skewed our understanding of how catchments store and transmit water. This truncated view of streamwater residence time is problematic because most of the work that now strives to develop relationships between catchment characteristics and streamwater residence time (e.g. McGuire *et al.*, 2005; Soulsby and Tetzlaff, 2008; Tetzlaff and Soulsby 2008; Hrachowitz *et al.*, 2009) do so solely on the basis of ^{18}O (and in some cases Cl) records. Similarly, the many new model approaches that include representations of residence time for model testing and development (Vache *et al.*, 2004; Vache and McDonnell, 2006) have relied to date on the truncated residence time from ^{18}O-derived field studies. The use of these convolution-based estimates in watershed rainfall-runoff models for transport in the subsurface could be severely compromised by their clipped residence times. Similarly, if we used these models to calculate the response of a stream to a decrease in nitrate recharge (following Michel, 2004), then our estimates of stream chemistry could be quite different. For instance, if a shift in nitrate concentration from 10 to 0 mg/l occurred at the start of 2000 (as illustrated for the large river average in Figure 3c), the nitrate in the stream would be predicted to fall rapidly with a truncated ^{18}O-based streamwater residence time estimate of 2·3 years (model 1). By 2010, nitrate would apparently have been almost entirely removed from the stream. With the ^{3}H-based estimate (model 2), streamwater nitrate concentrations would initially decrease rapidly to around 5 mg/l by the end of the first year, because of the quick runoff component, but then the rate of decrease would slow as longer-retained nitrate-bearing groundwater (i.e. the slow runoff component) continues to flow into the stream. By 2010, for instance, predicted stream concentration would be 2·0 mg/l; by 2020 it would still be 0·7 mg/l.

Our comments here are not new. Benchmark papers in the field of residence time analysis in watersheds used both stable isotope and tritium analysis of streamwater (Maloszewski and Zuber, 1982; Maloszewski *et al.*, 1983). This re-focusing on the role of deep groundwater coincides with recent hydrometric-based observations of the role of deep groundwater on hillslope and headwater catchment response (e.g. Kosugi *et al.*, 2008). Indeed many of the key hillslope studies in the past decade have implicated deep groundwater in hillslope response (e.g. Montgomery and Dietrich, 2002; Uchida *et al.*, 2004; Ebel *et al.*, 2008). The combination of these new hydrometric-based approaches to quantifying the role of deep groundwater (especially in the headwaters) with ^{3}H-based streamwater residence time estimates seems like a particularly good way forward.

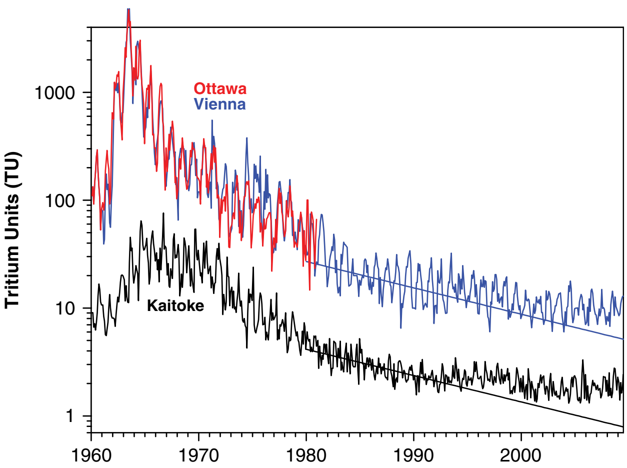

Figure 5. Tritium concentration in precipitation at Ottawa, Canada and Vienna, Austria (Northern Hemisphere) and Kaitoke, New Zealand (Southern Hemisphere). Tritium concentrations are expressed as tritium units (TU) with 1 TU corresponding to a ratio of tritium/total hydrogen = T/H = 10^{-18} (Morgenstern and Taylor, 2009). The straight lines show the effects of radioactive decay of tritium in groundwater recharged in 1980s

On the use of ^{3}H in a post-bomb world

So how can we use ^{3}H in future studies even though ^{3}H concentrations in precipitation have declined so greatly after the 1960s? Figure 5 shows representative ^{3}H records for precipitation in the Northern and Southern Hemispheres. The main features in both curves are the pronounced bomb peaks due to nuclear weapons testing mainly in the Northern Hemisphere during the 1950s and 1960s. The peak was much larger in the Northern Hemisphere than in the Southern Hemisphere. Since then there has been a steady decline due to leakage of ^{3}H from the stratosphere into the troposphere from where it is removed by rainout, together with radioactive decay of ^{3}H. Difficulties with using ^{3}H for dating have resulted from the similarity in the slope of the decline to the decrease due to radioactive decay of ^{3}H. The straight lines in the figure illustrate ^{3}H decay in groundwater recharged in 1980s.

However, it can be seen that the rain record has begun to diverge from the straight lines in recent years. In the Southern Hemisphere, this has been for about the last 15 years, while for the Northern Hemisphere it is for about 5 years. This already allows young and older groundwater to be distinguished, and the situation will improve in time with further decay of the remaining bomb ^{3}H. The rain record for the Southern Hemisphere is from Kaitoke, New Zealand, and that for the Northern Hemisphere is from Vienna, Austria. The North American representative record from Ottawa is shown only until 1981 because later it was influenced by local ^{3}H sources. However, the good agreement between the Ottawa and Vienna records prior to 1985 shows that the Vienna record can be used as an approximation for Northern Hemisphere sites.

To demonstrate the ^{3}H output of a catchment, Figure 6 shows the ^{3}H outputs for the Northern and Southern Hemispheres based on the EM. The current outputs (marked 2010) are shown together with the outputs 10 years ago (2000) and in 15 years time (2025) to demonstrate the situation with ambiguous age interpretations due to the interference of bomb ^{3}H. The curves in 2000 showed a large amount of bomb ^{3}H leading to ambiguous age interpretations in the age range 0 to about 50 years for both hemispheres. For the current ^{3}H output, the Southern Hemisphere already shows a monotonous decline with age which enables unique ages to be determined (and in principle for single ^{3}H measurements to be usable for age determinations). In the Northern Hemisphere, the much larger input of bomb ^{3}H to the hydrologic systems still causes an ambiguous ^{3}H output within the age range 0–50 years at present. But the remaining bomb ^{3}H is expected to decrease, resulting in a monotonously declining ^{3}H output within a few years. It needs to be noted that despite the ambiguous ages due to bomb ^{3}H obtainable at present, collecting ^{3}H data now will be valuable in a few years. This is because the bomb peak has advantages as well as disadvantages for dating—dating now requires time-separated

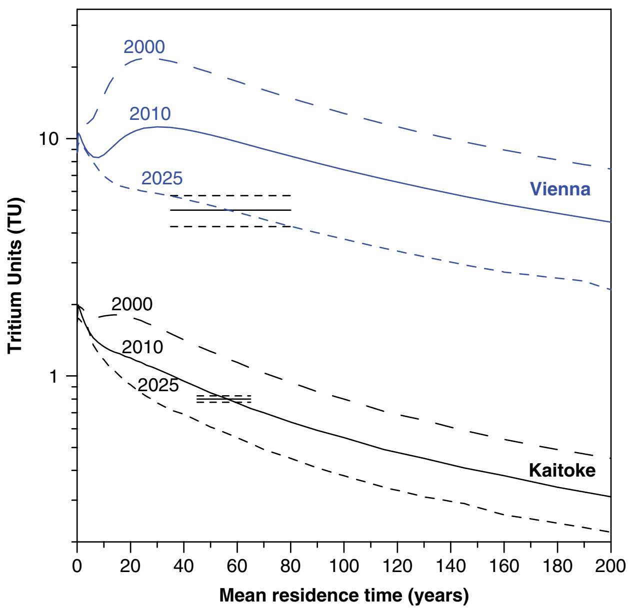

Figure 6. Tritium concentrations predicted in groundwater after applying an EM to tritium inputs measured at Vienna, Austria (Northern Hemisphere) and Kaitoke, New Zealand (Southern Hemisphere). Tritium concentrations are expressed as tritium units (TU) with 1 TU corresponding to a ratio of tritium/total hydrogen = T/H = 10^{-18} (Morgenstern and Taylor, 2009). Ambiguous ages (i.e. two or more possible ages) arise for the parts where the curves rise or are level. The horizontal lines show average measurement errors (one sigma) of the ten best Northern Hemisphere laboratories (Groening *et al*., 2007) for the Northern Hemisphere, and the New Zealand laboratory (Morgenstern and Taylor, 2009) for the Southern Hemisphere

data. After re-sampling, such time series data will be able to resolve the ambiguity and establish accurate transit time distributions, pinpointing both parameters (the mean residence time and the exponential fraction).

It is seen from Figure 6 that the ^3H concentrations in hydrologic systems in the Southern Hemisphere are much smaller than those in the Northern Hemisphere, so more sensitive and accurate measurements are required. The error bar (horizontal line with broken lines showing one-sigma measurement error) illustrates the current measurement precision in New Zealand (Morgenstern and Taylor, 2009). The high precision is sufficient to constrain robust age interpretations with 2–3 years accuracy. Figure 6 also shows the error bar for Northern Hemisphere ^3H laboratories. The indicated error is the average of the ten best NH ^3H laboratories (Groening *et al*., 2007). Although the predicted ^3H output for NH systems in 15 years will be a similar monotonous gradient to that of the current SH, the measurement accuracy of Northern Hemisphere laboratories is not yet sufficient for accurate age dating and needs to be improved. Note also that the ^3H input is not known sufficiently for many locations. However, the ^3H input function for catchments can usually be established by measuring ^3H in rainwater for 1 or 2 years in order to scale the ^3H input function of the nearest long-term ^3H monitoring station.

The ^3H studies cited have generally used series of measurements on streams covering a number of years (the longer the better) to determine MTTs. The most effective studies have used data from during and shortly after the bomb peak years. Future studies will preferably use a number of years of data (e.g. decadal scale data, Rose, 2007). Although the cost of individual measurements is relatively high, the method only requires measurements at long intervals so the number of samples is likely to be low and overall cost will be inexpensive (depending on the objectives of the study). Sample collection is straightforward and best coordinated with on-going streamflow and geochemical measurements, in particular ^{18}O and other age dating methods (CFCs, etc.).

Future directions

The foregoing has shown that a substantial fraction of the water in many streams is very old. What does this mean for interpretation of flow pathways through the catchments? The results certainly confirm that groundwater contributes strongly to many streams, a result which has been well-known by some (e.g. Sklash and Farvolden, 1979; Winter, 2007; Lerner, 2009; Tellam and Lerner, 2009), although is disputed by others. The nature of the groundwater system feeding the stream is the point of interest. Long transit times would indicate that there is considerable storage within catchments. Taking the average for the large rivers studied (MTT 10 years on about 50% of streamflow, Table III), we can explore the storage amounts required. For annual precipitation 1000 mm with evapotranspiration 600 mm, recharge and therefore annual streamflow is 400 mm/year. The storage requirement to supply 10 years of 50% of the annual flow is therefore 2 m. With total porosity 0·2, this requires an aquifer thickness of 10 m over the whole watershed.

The presence of groundwater in streams is often attributed to flow over the regolith/bedrock interface, where it is assumed there is a strong permeability contrast (see Weiler *et al.* 2005, for a review). The above calculation shows that this explanation can be ruled out by the storage requirements of the ‘average’ model from Table III. What is now needed are process studies that relate deeper groundwater flow processes to watershed response. Indeed, this has begun with hydrogeophysics approaches that examine deep groundwater response (Robinson *et al*., 2008), hydrochemical approaches to understanding groundwater–streamwater interactions (Anderson and Dietrich, 2001), sprinkling experiments to examine the loss to deep groundwater from transient saturation at the soil–bedrock interface (Tromp van Meerveld *et al*., 2007) and wellfield analysis of deep groundwater dynamics in headwater areas (Kosugi *et al*., 2008). Notwithstanding, these new approaches need to be carried out in concert with tracers that can reveal and help quantify long tails of the residence time distribution. Although studies have previously advocated greater use of hydrogeologically oriented tracers in watershed hydrology (Devine and McDonnell, 2005), our work here shows a rather glaring issue requiring concerted effort by the watershed hydrology community. Truncated residence times pose a threat to useful and accurate model development and testing by providing skewed targets and benchmarks for model calibration.

An especially useful approach will be to intercompare and contrast geology between different catchments to understand what conditions give rise to big and small differences between ^{3}H-based and ^{18}O-based approaches. In fact, something like this could serve as a new ratio by which to classify catchments in terms of their amounts of deep groundwater contributions to flow.

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REFERENCES

Anderson SP, Dietrich WE. 2001. Chemical weathering and runoff chemistry in a steep headwater catchment. *Hydrological Processes* **15**: 1791–1815.

Begemann F, Libby WF. 1957. Continental water balance, groundwater inventory and storage times, surface ocean mixing rates and world-wide circulation patterns from cosmic-ray and bomb tritium. *Geochimica et Cosmochimica Acta* **12**: 277–296.

Behrens H, Moser H, Oerter H, Rauert W, Stichler W. 1979. Models for the runoff from a glaciated catchment area using measurements of environmental isotope contents. Isotope Hydrology 1978. In *Proceedings of the I.A.E.A. Symposium in Neuherberg, IAEA*, Vienna.

Beven KJ. 1989. Changing ideas in hydrology: the case of physically based models. *Journal of Hydrology* **105**: 157–172.

Blume T, Zehe E, Bronstert A. 2008. Investigation of runoff generation in a pristine, poorly gauged catchment in the Chilean Andes II: Qualitative and quantitative use of tracers at three spatial scales. *Hydrological Processes* **22**: 3676–3688.

Bohlke JK, Denver JM. 1995. Combined use of groundwater dating, chemical and isotopic analyses to resolve the history and fate of nitrate contamination in two agricultural watersheds, Atlantic coastal plain, Maryland. *Water Resources Research* **31**: 2319–2339.

Busenberg W, Plummer LN. 1992. Use of chlorofluorocarbons (CCl_3F and CCl_2F_2) as hydrologic tracer and age-dating tools: the alluvium and terrace system of Central Oklahoma. *Water Resources Research* **28**: 2257–2283.

Devine C, McDonnell JJ. 2005. The future of applied tracers in hydrogeology. *Hydrogeology Journal* **13**: 255–258.

deWalle DR, Edwards PJ, Swistock BR, Aravena RJ, Drimmie RJ. 1997. Seasonal isotope hydrology of three Appalachian forest catchments. *Hydrological Processes* **11**: 1895–1906.

Dinçer T, Payne BR, Florkowski T, Martinec J, Tongiorgi E. 1970. Snowmelt runoff from measurements of tritium and oxygen-18. *Water Resources Research* **6**: 110–124.

Ebel BA, Loague K, Montgomery DR, Dietrich WE. 2008. Physics-based continuous simulation of long-term near-surface hydrologic response for the Coos Bay experimental catchment. *Water Resources Research* **44**: W07417. DOI: 10.1029/2007WR006442.

Eriksson E. 1958. The possible use of tritium for estimating groundwater storage. *Tellus* **10**: 472–478.

Groening M, Dargie M, Tatzber H. 2007. *7th IAEA Intercomparison of Low-Level Tritium Measurements in Water (TRIC2004)*. http://www-naweb.iaea.org/NAALIHL/docs/intercomparison/Tric2004/TRIC2004-Report.pdf.

Herrmann A, Bahls S, Stichler W, Gallari F, Latron J. 1999. Isotope hydrological study of mean transit times and related hydrological conditions in Pyranean experimental basins (Vallcebre, Catalonia). *Integrated Methods in Catchment Hydrology—Tracer, Remote Sensing and New Hydrometric Techniques*. IAHS-Pub. No. 258: Wallingford; 101–110.

Hrachowitz M, Soulsby C, Tetzlaff D, Dawson JJC, Malcolm IA. 2009. Regionalization of transit time estimates in montane catchments by integrating landscape controls. *Water Resources Research* **45**: W05421. DOI: 10.1029/2008WR00749.

Kendall C, McDonnell JJ. 1998. *Isotope Tracers in Catchment Hydrology*. Elsevier Science BV: The Netherlands; 839.

Koeniger P, Wittmann S, Leibundgut Ch, Krause WJ. 2005. Tritium balance modelling in a macroscale catchment. *Hydrological Processes* **19**: 3313–3320.

Kosugi K, Katsura S, Mizuyama T, Okunaka S, Mizutani T. 2008. Anomalous behavior of soil mantle groundwater demonstrates the major effects of bedrock groundwater on surface hydrological processes. *Water Resources Research* **44**: W01407. DOI: 10.1029/2006WR005859.

Lerner DN. 2009. Groundwater matters. *Hydrological Processes* **23**: 3269–3270.

Maloszewski P, Rauert W, Stichler W, Herrmann A. 1983. Application of flow models in an alpine catchment area using tritium and deuterium data. *Journal of Hydrology* **66**: 319–330.

Maloszewski P, Rauert W, Trimborn P, Herrmann A, Rau R. 1992. Isotope hydrological study of mean transit times in an alpine basin (Wimbachtal, Germany). *Journal of Hydrology* **140**: 343–360.

Maloszewski P, Zuber A. 1982. Determining the turnover time of groundwater systems with the aid of environmental tracers, 1. Models and their applicability. *Journal of Hydrology* **57**: 207–231.

Martinec J, Siegenthaler U, Oeschger H, Tongiorgi E. 1974. New insights into the runoff mechanism by environmental isotopes. Isotope Techniques in Groundwater Hydrology. In *Proceedings of a Symposium Organised by the I.A.E.A.* Vienna; 129–143.

Matsutani J, Tanaka T, Tsujimura M. 1993. Residence times of soil water, ground and discharge waters in a mountainous headwater basin, central Japan, traced by tritium. *Tracers in Hydrology*. IAHS: Yokohama; 57–63.

McGlynn BL, McDonnell JJ, Stewart MK, Seibert J. 2003. On the relationships between catchment scale and streamwater mean residence time. *Hydrological Processes* **17**: 175–181.

McGuire KJ, McDonnell JJ. 2006. A review and evaluation of catchment transit time modelling. *Journal of Hydrology* **330**: 543–563.

McGuire KJ, McDonnell JJ, Weiler M, Kendall C, Welker JM, McGlynn BL, Seibert J. 2005. The role of topography on catchment-scale water residence time. *Water Resources Research* **41**: W05002. DOI: 10.1029/2004WR00365.

Michel RL. 1992. Residence times in river basins as determined by analysis of long-term tritium records. *Journal of Hydrology* **130**: 367–378.

Michel RL. 2004. Tritium hydrology of the Mississippi River basin. *Hydrological Processes* **18**: 1255–1269.

Montgomery DR, Dietrich WE. 2002. Runoff generation in a steep soil-mantled landscape. *Water Resources Research* **38**: 1168. DOI: 10.1029/2001WR000822, 2022.

Morgenstern U. 2007. Lake Taupo Streams: Water age distribution, fraction of landuse impacted water, and future nitrogen load. Environment Waikato Technical Report 2007/26. Environment Waikato: Hamilton, New Zealand; 21.

Morgenstern U, Reeves RR, Daughney CJ, Cameron S, Gordon D. 2005. Groundwater age and chemistry, and future nutrient load for selected Rotorua lakes catchments. Institute of Geological & Nuclear Sciences science report 2004/31; 73.

Morgenstern U, Taylor CB. 2009. Ultra low-level tritium measurement using electrolytic enrichment and LSC. *Isotopes in Environmental and Health Studies* **45**: 96–117.

Robinson DA, Binley N, Crook N, Day-Lewis FD, Ferr'e TPA, Grauch VJS, Knight R, Knoll M, Lakshmi V, Miller R, Nyquist J, Pellerin L, Singha K, Slater L. 2008. Advancing process-based watershed hydrological research using near-surface geophysics: a vision for, and review of, electrical and magnetic geophysical methods. *Hydrological Processes* **22**: 3604–3635.

Rose S. 1993. Environmental tritium systematics of baseflow in Piedmont Province watersheds, Georgia (USA). *Journal of Hydrology* **143**: 191–216.

Rose S. 1996. Temporal environmental isotopic variation within Falling Creek (Georgia) watershed: implications for contributions to streamflow. *Journal of Hydrology* **174**: 243–261.

Rose S. 2007. Utilization of decadal tritium variation for assessing the residence time of base flow. *Ground Water* **45**: 309–317.

Sayama T, McDonnell JJ. 2009. A new time-space accounting scheme to predict stream water residence time and hydrograph source components at the watershed scale. *Water Resources Research* **45**: W07401. DOI: 10.1029/2008WR007549.

Sklash MG, Farvolden RN. 1979. The role of groundwater in storm runoff. *Journal of Hydrology* **43**: 45–65.

Solomon DK, Cook PG. 2000. ^{3}H and ^{3}He. In *Environmental Tracers in Subsurface Hydrology*, Cook PG, Herczeg AL (eds). Kluwer Academic Publishers: Boston (MA); 397–424.

Soulsby C, Tetzlaff D. 2008. Towards simple approaches for mean residence time estimation in ungauged basins using tracers and soil distributions. *Journal of Hydrology* **363**: 1–4, 60–74.

Stewart MK, Bidwell V, Woods R, Fahey BD, Basher L, Bowden B. 2002. Water residence times at different scales in the Mahurangi Catchment, New Zealand. *Eos Trans. AGU, 83, Western Pacific Geophysics Meeting Supplement*, Abstract H21A-02, 2002.

Stewart MK, Cameron SC, Hong TY-S, Daughney CJ, Tait T, Thomas JT. 2005a. Investigation of groundwater in the Upper Motueka River Catchment. GNS Science Report, 2003/32; 47.

Stewart MK, Fahey BD, Davie TJA. 2005b. New light on streamwater sources in the Glendhu Experimental Catchments, East Otago, New Zealand. In Proceedings: *'Where Waters Meet' Conference (NZ Hydrological Society, International Association of Hydrologists (Australian Chapter) & NZ Society of Soil Science)*. Auckland, New Zealand; 11.

Stewart MK, McDonnell JJ. 1991. Modeling baseflow soil water residence times from denterium concentrations. *Water Resources Research* **27**(10): 2681–2693.

Stewart MK, Mehlhorn J, Elliott S. 2007. Hydrometric and natural tracer (^{18}O, silica, ^{3}H and SF_6) evidence for a dominant groundwater contribution to Pukemanga Stream, New Zealand. *Hydrological Processes* **21**: 3340–3356 DOI: 10.1002/hyp.6557.

Stewart MK, Thomas JT. 2008. A conceptual model of flow to the Waikoropupu Springs, NW Nelson, New Zealand, based on hydrometric and tracer (^{18}O, Cl, ^{2}H and CFC) evidence. *Hydrology and Earth System Sciences* **12**: 1–19.

Tague C, Grant G. 2004. A geological framework for interpreting the low flow regimes of Cascades streams, Willamette River Basin, Oregon. *Water Resources Research* **40**: W04303. DOI: 10.1029/2003WR002629.

Taylor CB. 2001. Contributing sources to Waikoropupu Springs, Takaka, NW Nelson: a new assessment. In *New Zealand Hydrological Society 2001 Symposium Proceedings*, NZHS: Palmerston North; 38–39.

Taylor CB, Brown LJ, Cunliffe JJ, Davidson PW. 1992. Environmental isotope and ^{18}O applied in a hydrological study of the Wairau Plain and its contributing mountain catchments, Marlborough, New Zealand. *Journal of Hydrology* **138**: 269–319.

Taylor CB, Stewart MK. 1987. Hydrology of Rotorua geothermal aquifer, New Zealand. In *Isotope Techniques in Water Resources Development. IAEA-SM-299/95*, Vienna; 25–45.

Taylor CB, Wilson DD, Brown LJ, Stewart MK, Burdon RJ, Brailsford GW. 1989. Sources and flow of North Canterbury Plains groundwater, New Zealand. *Journal of Hydrology* **106**: 311–340.

Tellam JH, Lerner DN. 2009. Management tools for the river-aquifer interface. *Hydrological Processes* **23**: 2267–2274 DOI: 10.1002/hyp.7243.

Tetzlaff D, Seibert J, McGuire KJ, Laudon H, Burns DA, Dunn SM, Soulsby C. 2009. How does landscape structure influence catchment transit time across different geomorphic provinces? *Hydrological Processes* **23**: 945–953.

Tetzlaff D, Soulsby C. 2008. Sources of baseflow in large catchments—using tracers to develop a holistic understanding of runoff generation. *Journal of Hydrology* **359**: 287–302.

Tromp van Meerveld I, Peters NE, McDonnell JJ. 2007. Effect of bedrock permeability on subsurface stormflow and the water balance of a trenched hillslope at the Panola Mountain Research Watershed, Georgia. *Hydrological Processes* **21**: 750–769.

Uchida T, Asano Y, Mizuyama T, McDonnell JJ. 2004. Role of upslope soil pore pressure on lateral subsurface storm flow dynamics. *Water Resources Research* **40**: W12401. DOI: 10.1029/2003WR002139.

Uhlenbrook S, Frey M, Liebundgut C, Maloszewski P. 2002a. Hydrograph separations in a mesoscale mountainous basin at event and seasonal timescales. *Water Resources Research* **38**: 10.1029/2001WR000938.

Uhlenbrook S, Steinbrich A, Tetzlaff D, Leibundgut C. 2002b. Regional analysis of the generation of extreme floods. *International Association of Hydrological Sciences* **274**: 243–250.

Vaché KB, McDonnell JJ. 2006. A process-based rejectionist framework for evaluating catchment runoff model structure. *Water Resources Research* **42**: W02409. DOI: 10.1029/2005WR004247.

Vaché KB, McDonnell JJ, Bolte JP. 2004. On the use of multiple criteria for a posteriori parameter estimation. *Geophysical Research Letters* **31**: W05421. DOI: 10.1029/2004GRL021577.

Weiler M, McDonnell JJ. 2004. Virtual experiments: a new approach for improving process conceptualization in hillslope hydrology. *Journal of Hydrology* **285**: 3–18.

Weiler M, McDonnell JJ, Tromp van Meerveld I, Uchida T. 2005. Subsurface stormflow runoff generation processes. In *Encyclopedia of Hydrological Sciences*, Anderson MG (ed.). Wiley: Chichester; 1719–1732.

Winter TC. 2007. The role of groundwater in generating streamflow in headwater areas and in maintaining base flow. *Journal of the American Water Resources Association* **43**: 15–25.

Yertsever Y. 1999. Use of environmental tritium to study catchment dynamics: case study from the Danube River basin. *Integrated Methods in Catchment Hydrology—Tracer, Remote Sensing and New Hydrometric Techniques*. IAHS-Pub. No. 258: Wallingford; 167–174.

Zuber A, Maloszewski P, Stichler W, Herrmann A. 1986. Tracer relations in variable flow. In *5th International Symposium on Underground Water Tracing. Institute of Geology and Mineral Exploration*. Athens; 355–360.

