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## Dating of streamwater using tritium in a post-bomb world: continuous variation of mean transit time with streamflow

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Tritium measurements of streamwater draining the Toenepi catchment, a small dairy farming area in Waikato, New Zealand, have shown that the mean transit time of the water varies with the flow of the stream. Mean transit times through the catchment are 2-5 years during high baseflow conditions (in winter), becoming older as streamflow decreases (in summer), and then guite dramatically older during drought conditions, with ages of more than 100 years. Older water seems to be gained in the lower reaches of the stream, compared to younger water in the headwater catchment. The groundwater store supplying baseflow was estimated from the mean transit time and average baseflow to be  $15.4 \times 10^6 \,\mathrm{m}^3$  of water, about 1 m water equivalent over the catchment and 2.3 times total annual streamflow. Nitrate from recent intensified land use is relatively high at normal streamflow, but is low at times of low flow with old water. This reflects both lower nitrate loading in the catchment several decades ago, and active denitrification processes in older groundwater. Silica, leached from the aquifer material and accumulating in the water in proportion to contact time, is high at times of low streamflow. There was a good correlation between silica and streamwater age, which potentially allows silica concentrations to be used as a proxy for age when calibrated by tritium measurements. This study shows that tritium dating of stream water is possible with single tritium measurements now that bomb-test tritium has effectively disappeared from hydrological systems in New Zealand, without the need for time-series data.

### 1 Introduction

The source of the baseflow component in streams is usually groundwater. This truism and the fact that baseflow is often the dominant component of streamflow (Hewlett and Hibbert, 1967) shows that in order to understand the quantity and quality of streamflow, we need to understand the dynamics and volumes of the underlying groundwater resource feeding the stream.

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We still have limited understanding of the dynamics of the groundwater component that is transmitting much of the water from rainfall to streams. According to the dynamics of these underlying groundwaters, the streams' response is modulated in flow and strongly damped and delayed in hydrochemical composition compared to rainfall (Kirchner, 2003). The age distribution of the groundwater is a fundamental parameter of the groundwater dynamics, and accurate groundwater ages can greatly improve our conceptual understanding of streamflow generation. We show with data from the small Toenepi catchment in New Zealand how the streamwater age illumines these dynamics.

Accurate groundwater ages can significantly improve conceptual flow models and allow direct calibration of numerical flow models (e.g. Bethke and Johnson, 2008) for detailed understanding of the groundwater resource, of water flow paths that describe the pathway along individual flow lines for certain points in the catchment, and delays in transporting contaminants from the land into streams. However, this paper does not aim to establish a detailed groundwater flow model for the Toenepi catchment.

Rather than elucidating in detail the various groundwater flow paths within the catchment, this paper focuses on deriving the fundamental model parameters of groundwater, the mean transit time and volume, from baseflow tritium signatures in the stream at the catchment outflow. The resultant mean transit times and groundwater volumes therefore provide measures of groundwater dynamics integrated over the whole catchment. Water transit time, and amount of water stored in the catchment, rather than only fluxes, are crucial for water management issues and understanding the response of the stream to environmental change and pollution.

Many previous studies have used environmental isotopic or chemical tracers to determine transit time distributions and mean transit times for catchments (references in McGuire and McDonnell, 2006). Often these studies derive a single mean transit time to characterise the streamflow (or sometimes only the baseflow), although it is intuitively likely for example that the mean transit times of high flows will be different from those of low flows in many catchments. It has been difficult to probe the likely different Discussion Paper











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mean transit times at different parts of the hydrograph with the most-used methods (i.e. variations of stable isotopes and chemicals). However, other studies using tritium have been able to look at several components in streamflow and show that their mean transit times can be very different (Maloszewski and Zuber, 1982; references in Stewart et al., 2010). This work at Toenepi reveals a continuous variation of mean transit time with streamflow. And, in particular, it establishes the possibility and importance of being able to estimate ages from individual tritium measurements for given streamflow rates.

This paper represents one of the early detailed results of stream water age derived from tritium data in the post-bomb world of the Southern Hemisphere (McGlynn et al., 2003; Stewart et al., 2007; Stewart and Fahey, 2010; Morgenstern, 2007). It gives a preview of what will also become possible in the Northern Hemisphere in the future for assessment of groundwater dynamics and volumes, after further decline of nuclear weapons test tritium there, and after analytical techniques have been improved to provide better measurement accuracy for age interpretation (Morgenstern and Taylor, 2009).

### 2 Water dating

Dating of groundwater relies on the measurement of tracer substances that have time-dependent input functions into the groundwater system or well-defined decay terms (e.g., radioactive decay). Tritium (along with oxygen-18 and deuterium) is the most direct dating tool for groundwater because it is part of the water molecule, and ages include the travel time through the unsaturated zone. For streamwater dating, tritium is applicable to estimating older ages (>1 year), while methods using the variations of stable isotopes and chemicals are more suitable for younger ages (<3 years). The latter methods are likely to truncate the age distributions and not show older age water (Stewart et al., 2010). Gas tracers such as helium-3, chlorofluorocarbons, and sulphur hexafluoride equilibrate with air once old groundwaters have entered the stream and

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thus have very limited use for streamwater dating. Tritium can be used for dating young water with mean transit times ranging from recent to several hundred years (Stewart et al., 2010). For improved understanding of older water components with mean transit times of up to 1000 years, silicon-32, another non-gaseous tracer, has potential for dating of water within various types of aquifer if the exchange processes of the silica in the groundwater with the aquifer material can be better understood (Morgenstern et al., 1995, 1996; Fifield and Morgenstern, 2009).

Major ion concentrations which are easier to measure than tritium concentrations, have the potential to complement tritium dating, and help us understand the ground-water dynamics (Morgenstern et al., 2004; Daughney et al., 2010). Major ion concentrations increase with groundwater age due to mineral dissolution during water–rock interactions. In several previous investigations major ion concentrations were found to increase with groundwater age (Edmunds and Smedley, 2000; Katz et al., 2004; Zuber et al., 2005), although the relationships between groundwater age and ion concentrations can be complicated. In several studies of New Zealand catchments, we found reasonably good correlations between mean residence time of the water in the groundwater system and silica concentration of the water (Morgenstern et al., 2004, 2009). Therefore we tested if silica concentration in stream water is sufficiently correlated to water transit time to be used as a proxy for tritium age.

Tritium dating in New Zealand has become more straightforward now that tritium from atmospheric nuclear weapons tests has decayed below the natural cosmogenic tritium level. It is now more than four decades after levels of atmospheric tritium spiked from nuclear weapons testing during the 1950s and 60s. That nuclear test tritium, mostly released in the Northern Hemisphere, had caused problems for tritium-dating over the past decades because the year-by-year decrease in atmospheric <sup>3</sup>H concentration occurred at a rate similar to that of radioactive <sup>3</sup>H decay. Figure 1 shows representative tritium records for precipitation in the Northern and Southern Hemispheres, together with lines showing radioactive decay of a water sample infiltrated in 1980. The nuclear test tritium in the atmosphere steadily declined due to the combined effect of removal

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of <sup>3</sup>H by rain and radioactive decay of <sup>3</sup>H. The similarity in the slope of the decline of tritium in precipitation to the decrease due to radioactive decay of <sup>3</sup>H caused waters with different transit times to have the same <sup>3</sup>H concentration, leading to ambiguous age interpretations that needed tritium time series data for resolution.

Tritium has declined to such low levels now that recent rain water has a higher <sup>3</sup>H concentration than water recharged during the nuclear-weapons-testing period (decay lines in Fig. 1 now fall below levels in recent rain). In the Southern Hemisphere this has occurred for about the last fifteen years, while for the Northern Hemisphere it has occurred for about five years. There is now a difference in tritium signature between young and old water, thus allowing young and older groundwater to be distinguished. The situation will improve over time with further decay of the remaining nuclear test <sup>3</sup>H, so that tritium can be used in a straightforward way for groundwater dating.

Figure 2 shows the respective tritium output curves versus mean residence time for Kaitoke and Vienna. In New Zealand there is already a monotonous decrease of the tritium concentration with mean residence time observed because of the much lower weapons-test tritium input to the Southern Hemisphere. This steady decrease, together with the high measurement accuracy in New Zealand (horizontal line with broken lines show one-sigma measurement error, Morgenstern and Taylor, 2009), allows a dating accuracy of 1-3 years with single tritium measurements, even though the <sup>3</sup>H concentrations in hydrologic systems in the Southern Hemisphere are much smaller than those in the Northern Hemisphere and require more sensitive and accurate measurements. The predicted <sup>3</sup>H output for Northern Hemisphere hydrologic systems will also start to have a steady gradient similar to the current situation in the Southern Hemisphere in about ten years (Stewart et al., 2010).

### Site description and catchment characteristics

The Toenepi catchment (15.1 km²) is situated in a dairy farming area near Morrinsville, Waikato, North Island of New Zealand. Detailed catchment characteristics are given

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in Stenger et al. (2008). The elevation of the catchment ranges from approximately 40 to 130 m above mean sea level, reflecting the transition from alluvial plains to rolling downlands. Mean annual rainfall is approximately 1280 mm and mean annual air temperature is 14°C.

The alluvial plains have developed on Pleistocene rhyolitic alluvium with a varying thin cover of Holocene rhyolitic and andesitic volcanic ash. The downlands are characterised by 1-2 m thick Holocene to late Pleistocene volcanic ash beds of silt loam to fine sandy loam texture, overlying older strongly argillised Pleistocene ash beds (Wilson, 1980).

Streamflow was recorded and water samples for silica and tritium analyses were taken at the catchment outflow weir maintained by New Zealand's National Institute of Water & Atmospheric Research (NIWA), and at the headwater weir maintained by Lincoln Ventures Ltd. The headwater sub-catchment has an area of 1.6 km<sup>2</sup> and the headwater weir site is located approximately 5.5 km upstream of the catchment outflow weir site (Fig. 3).

### Age interpretation and mean transit time

Groundwater at its discharge point is a mixture of water from short and long flowlines, and therefore has a distribution of ages rather than a single age. Various response functions describe the distribution of ages within the water sample (Maloszewski and Zuber, 1982, 1991; Goode, 1996; Weissman et al., 2002; Zuber et al., 2005). The two most commonly employed response functions are the dispersion model and the exponential piston flow model (Zuber et al., 2005). The exponential piston flow model is a combination of the piston flow model, which assumes piston flow with minimal mixing of water from different flow lines at the discharge point, as might occur in a narrow confined aquifer, and the exponential model, which assumes that transit times are exponentially distributed at the groundwater discharge point, as might occur for mixing of stratified groundwater at the discharge point in unconfined aguifers. These

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response functions each have two parameters-one specifying the mean and the other the spread of transit times. The parameters are determined by convoluting the input (rainfall) tritium concentrations (to simulate passage through the hydrological system) in such a way as to match the output (stream) tritium concentrations.

Stenger et al. (2009) identified strong redox gradients in the groundwater underlying the well-drained soils that dominate in the Toenepi catchment. The uppermost oxidised groundwater was nitrate-bearing, while the deeper reduced groundwater was nearly devoid of nitrate. Silica concentrations increased with depth, with the greatest increases coinciding with the location of the redox line. This observation suggested that the reduced groundwater was markedly older than the oxidised groundwater.

The total flow in the stream reflects water flow paths integrated over the whole catchment area, with a continuum of flow lengths from the points of infiltration to the stream. Therefore, we used a flow model with a continuous age distribution. While the short time-series tritium data from the Toenepi stream preclude pinpointing the flow model, we used the exponential-piston flow model for age interpretation because this model produced good matches of long-term tritium data in similar hydrogeologic situations, with data from other catchments showing that the exponential fraction is significantly less than 100% (Morgenstern and Stewart, 2004; Morgenstern, 2007). We tested the sensitivity of the mean transit time (MTT) to the exponential fraction by using models with 70, 80, and 90% fractions. For young water (MTT ≤ 5 years), the choice of exponential fraction has relatively little effect on the mean transit time, with an insignificant difference in mean transit times of 0-0.5 years between the three models. Also, for the medium-age water (MTT 30-40 years), the difference in mean transit time of one year for the different models is insignificant. Only for the old water (MTT > 100 years) is there a significant difference of 15-30 years. For the Toenepi data we used an exponential-piston flow model with an exponential fraction of 80%.

For the tritium input function we used the tritium record from Kaitoke near Wellington (Fig. 1), with a scaling factor 0.90 to account for the latitude of the Toenepi catchment (400 km north of Kaitoke, Fig. 4a) (Stewart and Taylor, 1981; Stewart and Morgenstern,

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2001). Seasonal variations of tritium concentration in rain, and rate of precipitation and infiltration modify the average tritium concentration between rain and recharging groundwater. For example, evapotranspiration preferentially removes summer precipitation during the recharge process. Using climate data from the meteorological station in the Toenepi catchment (Fig. 3), we corrected the annual tritium input concentration  $C_{\rm in}$  by weighting the tritium concentration  $C_i$  of the ith month by the monthly infiltration rate  $\alpha_i$  and the monthly precipitation rate  $P_i$ :

$$C_{\text{in}} = \frac{\sum_{i=1}^{12} C_i * \alpha_i * P_i}{\sum_{i=1}^{12} \alpha_i * P_i}$$
 (1)

The change in tritium input is insignificant because rain is relatively evenly distributed through the year, and the seasonal variation in tritium concentration of rain and infiltration rate are in phase (Fig. 4b) in such a way that the low infiltration in summer does not change the mean seasonal tritium signal. The average annual tritium concentration of rain and the corrected tritium input concentration are shown in Fig. 5c for comparison. The differences would result in an age difference of only a few months. Uncertainties in the correction process have an insignificant effect on the dating result.

### Results and discussion

Table 1 lists streamflow, silica and tritium concentrations, and mean transit times for the water samples from Toenepi Stream at the catchment outflow weir and the headwater weir. The samples were collected during baseflow conditions, with summer baseflows being generally much lower than winter baseflows (Figs. 5a and 7a). In particular, the January and March 2008 samples were collected at extremely low flow (drought) conditions. No sample could be collected from the headwater weir sampling point during March 2008 because the stream at the headwater weir had almost dried up.

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Figure 5 shows flow, and silica and tritium concentrations over time for the catchment outflow weir and the small headwater sub-catchment weir. At reasonably high winter base flow conditions (>100 L/s), the tritium concentration in the stream at the catchment outflow weir is slightly below that of recent rain (annual average TU shown as dotted line in Fig. 5c, together with corrected annual tritium input), indicating that at winter baseflow the stream contains mostly young water with mean transit times of between 2.5–4 years (see Table 1). It is important to note that even within the range of uncertainty, the water has a mean transit time of greater than one year at reasonably high winter flow conditions. At extreme low-flow conditions in early 2008, the tritium concentration in the stream at the catchment outflow weir decreased to below 0.3 TU, indicating discharge of very old water (MTT > 100 years). Tritium concentrations during summer and autumn with flow below 100 L/s dropped to near or below 1 TU, indicating old water with mean transit times of 30–40 years in the stream discharge.

Tritium concentrations at the headwater catchment weir at reasonable flow conditions (>0.6 L/s) are just below those of present-day rain, indicating young water with mean transit times of 1.5–3 years in this upper part of the catchment (Table 1). Note that the first value of 4 years in July 2004 is slightly ambiguous in age interpretation due to declining tritium concentration in rain prior to 2004. In early 2008, at very low flow during drought conditions, the tritium concentration at this site also decreased significantly below that of the previous rain, indicating slightly older water with a mean transit time of 5 years.

Figure 6 shows tritium concentrations versus silica. The good correlation of the raw tritium data with silica shows that silica correlates to age; the oldest water samples with the lowest tritium concentrations have significantly higher silica concentrations. The correlation of the raw tritium data with silica also shows that ambiguity in age interpretations in New Zealand has decreased because the small amount of remaining nuclear test tritium has decayed to below the natural cosmogenic tritium level for more than a decade (Fig. 1). If nuclear test tritium were still present in significant amounts similar to that of the Northern Hemisphere, all waters with mean transit times between

### 6 Conceptual groundwater flow model

Figure 7a shows streamflow versus mean transit time. The results demonstrate that the water in the stream becomes older as streamflow decreases, and is quite dramatically older at very low flow conditions.

There is an excellent correlation between mean transit time (MTT) and streamflow (Q) at the catchment outflow weir:

$$Ln(MTT) = -1.16Ln(Q) + 6.36, R^2 = 0.964(N = 6)$$
(2)

At relatively high winter baseflow, mainly young water (MTT < 5 years) discharges into the stream. At significantly lower summer baseflow, mainly old groundwater (MTT > 30 years) discharges into the stream.

The data at the headwater weir also indicates the trend of older water at low flow conditions. However, the correlation is very weak because young waters with mean transit times of  $\sim 0-4$  years are nearly indistinguishable from each other.

The significantly older water at low flow conditions at the catchment outflow weir (MTT > 30 years) compared to the headwater catchment with water of MTT = 5 years indicates that older water is gained in the lower reaches of the catchment. This finding may have been expected because in dry conditions the streams maintain their flow longer in the lower reaches. However, until very recently the ambiguity caused by remaining bomb tritium prevented the accurate determination of mean transit times with single tritium measurements necessary to substantiate the hypothesis. Detailed studies of changes of transit time of the water over time scales of decades are only now becoming possible as the influence of bomb tritium wanes.

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To estimate the volume of water that is stored in the groundwater reservoir and actively contributing to the baseflow, we approximate the groundwater flow by the average baseflow  $Q_{\rm BF}$ , and the time by the mean transit time of the water at average baseflow condition MTT<sub>BF</sub>:

$$V = Q_{\rm BF} \times MTT_{\rm BF} \tag{4}$$

Baseflow separation was carried out using the method of Hewlett and Hibbert (1967). The baseflow and quickflow components are shown in Fig. 8a, together with rainfall. The baseflow fraction was 76%, using hourly flow data during the 6-year period 2004–2009. This value is comparable with the estimates of 85% for 2003 and 71% for 2004 reported by Stenger et al. (2005) and derived using a groundwater discharge model (Bidwell, 2003). While there is a year-to-year variation, it is evident that Toenepi streamflow is dominated by groundwater discharge.

To estimate the mean transit time of the stream water at average baseflow we used the correlation between mean transit time and flow (Eq. 2). All tritium samples for age determinations were collected from the stream in baseflow conditions (see Fig. 8a, crosses indicate time of tritium sampling), so the calculated mean transit times for the various flow conditions characterise the groundwater reservoir that feeds the baseflow.

Using an average baseflow of  $165\,\text{L/s}$  and the calculated mean transit time of the water at average baseflow of 3.0 years, we estimate the groundwater volume that contributes to the baseflow of the stream as  $15.4\times10^6\,\text{m}^3$ . No pump test data are available in this catchment for comparison.

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Figure 9 shows the schematic flow model (9a), the parameters of the quickflow and baseflow components (9b), and the volume of the groundwater reservoir in relation to the volume of annual quickflow runoff and annual baseflow discharge (9c). The size of the boxes in Fig. 9c is proportional to the volume of the various components. Out of a total active groundwater volume of 15.4×10<sup>6</sup> m<sup>3</sup>, 5.2×10<sup>6</sup> m<sup>3</sup> are being turned over every year feeding the baseflow. The volume of guick runoff over one year (1.6×10<sup>6</sup> m<sup>3</sup>) is relatively small compared to the groundwater volume. The groundwater volume that feeds the baseflow of the stream contains about 3 times the volume of the annual baseflow, and about 2.3 times the annual total flow volume of the stream. Such a groundwater volume between the rain input and the streamflow explains the damping of the variations in the chloride concentration between rain and the stream water (e.g. Kirchner, 2003). Even at reasonably high winter baseflows, the discharging water is several years old.

With a catchment area of 15.1 km<sup>2</sup>, storage of water in the Toenepi groundwater is 1.02 m water equivalent over the catchment. This is about mid-range compared with values found in a study by Soulsby et al. (2009) for 32 Scottish catchments. They found mean transit times and storage amounts varying between 0.1 and 4.4 years and 0.3 and 2.5 m, respectively. They noted that their longer mean transit times, which were estimated from seasonal tracer variations, will have the greater errors.

### Dissolved SiO<sub>2</sub> as a secondary age tracer

Strong correlations of hydrochemical components with groundwater age allow the components to be used as proxies for age. This could help in understanding the dynamics of groundwater and streamflow by allowing better spatial and time resolution because chemical analyses are easier and cheaper to carry out than tritium analyses. Therefore we tested if chemical data can complement tritium data for age determination of the discharging groundwater. The SiO<sub>2</sub> concentrations in groundwater are expected to increase with increasing time the water is in contact with the aquifer material due to

$$SiO_2 = 10.3 \times Ln(MTT) + 16.3; R^2 = 0.972(N = 5)$$
 (5)

This relationship is derived from the data of the outflow of the total catchment. The data from the headwater catchment also match this trend (Fig. 7b). Data from other catchments follow similar trends of increasing SiO<sub>2</sub> with increasing mean transit time, however the correlation parameters are different depending on the aguifer lithologic units.

With this excellent correlation between mean transit time and SiO<sub>2</sub>, easily measured SiO<sub>2</sub> data can be used to estimate the age of the water with a higher time resolution once the SiO<sub>2</sub> concentration versus tritium age data is calibrated. This allows detailed study of contaminant flow paths and high-resolution time-series stream water ages for assessing the connection between the groundwater and the water in the stream. More detailed data on silica concentrations found in the vadose zone-aquifer-surface water continuum in the Toenepi catchment will be reported elsewhere (Stenger et al., 2010).

### Changing stream water quality with changing water source

Figure 8b shows the simulated mean transit time versus calendar time using the relationship given in Eq. (2). The source of the water changes seasonally depending on the climatic water balance, with increasingly older groundwater water discharging into the stream in low-flow summer conditions. Note that the simulated mean transit time in Fig. 8b represents only the transit time of the baseflow component. Mean transit time (MTT) is shown with a full line only for the parts where MTT > 2 years; there is negligible quick flow in these flow conditions. At MTT < 2 years there is considerable quickflow,

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The chemical composition of the streamwater changes with changing water transit 5 times. Old water, which was recharged before any contamination event or recent intensification in land use, is expected to have lower concentrations of contaminants or plant nutrients than younger water. Conversely, concentrations of compounds that are leached from the soil and aquifer material and accumulate in the groundwater (e.g. silica) are expected to be higher in the older water.

Figure 8c shows the simulated silica concentrations according to Eq. (5), together with measured data. Full circles indicate the data that were used to establish Eq. (5), and hollow circles are additional data. The figure shows how SiO<sub>2</sub> varies over time according to water age and flow.

Phosphate, which we often found to be leached from the aguifer in groundwater systems (Morgenstern et al., 2004), does not show a clear correlation to mean transit time and flow at Toenepi, because there is an additional source of PO₄ from fertiliser surface runoff superimposed on the PO<sub>4</sub> component of old groundwater. However, the highest PO₄ concentrations are observed at the lowest flows and highest mean transit times (Fig. 8c).

A good correlation with flow was found for nitrate (Wilcock et al., 1998), because it travels via the groundwater from the farms to the stream. For more recent data (Wilcock, pers. comm.) we found for the periods 2004-2005 and 2006-2010 the following correlations:

$$2004 - 2005 : NO_3 - N = 0.642 \times Ln(Q) - 1.15; R^2 = 0.62$$
 (6a)

$$2006 - 2010: NO_3 - N = 1.036 \times Ln(Q) - 2.21; R^2 = 0.80$$
 (6b)

Figure 8c shows the simulated NO<sub>3</sub> concentration in the stream (Eqs. 6a and b), together with the measured data. Clearly, high NO<sub>3</sub> concentrations occur at times of high flow with young water, while NO<sub>3</sub> is nearly zero at low stream flow with old water.

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The lower nitrate concentrations in the older water are likely to be a result of a combination of effects, namely lower nitrate loading in the catchment several decades ago and groundwater nitrate concentrations in the Toenepi catchment being substantially affected by denitrification in the older water (Stenger et al., 2008). Redox profiles in multi-level wells revealed that the uppermost, youngest groundwater layer is oxidised and contains nitrate, while the deeper, reduced groundwater is nearly devoid of nitrate (Stenger et al., 2010).

The data show clearly that the transit time of the water in the stream changes with flow. As the age changes, so its chemical composition changes according to the characteristics of the various chemicals and hydrochemical processes occurring along the different flowpaths.

### **Conclusions**

Accurate tritium dating of stream water is now possible with single tritium measurements in the post-nuclear testing era in New Zealand. This enables high-resolution age dating for assessing stream water generation processes and groundwater stores.

The results demonstrate that the streamwater baseflow component has mean transit times of 2-5 years at high baseflow conditions in winter, and water becomes older as streamflow decreases, and is quite dramatically older at very low flow summer drought conditions, with ages of more than 100 years. Older groundwater is gained in the lower reaches of the stream, compared to younger groundwater in the headwater catchment.

The groundwater store was estimated from the mean transit time and flow of average baseflow to be 15.4×10<sup>6</sup> m<sup>3</sup> of water, about 1 m water equivalent. The groundwater store that feeds the baseflow is about 2.3 times the total annual streamflow volume.

Accurate transit times of the stream water help us to understand concentrations of contaminants that enter the stream via different pathways with different lag-times, and can explain the variation in hydrochemical composition of the streamwater as a result of the contact time of the water with the aquifer material. Nitrate, which originates

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from recent intensified land use and is relatively high at normal streamflow, is low at times of low flow with old water. This probably reflects both the lower nitrate loading in the catchment several decades ago, and the more evolved denitrification processes in older groundwater. Silica that is leached from the aquifer material and accumulates in the water in proportion to contact time is high at times of low streamflow with old water.

We found a good correlation between SiO<sub>2</sub> and groundwater age, which allows analysis of SiO<sub>2</sub> to complement age dating and to be used to understand the dynamics of older groundwater. SiO<sub>2</sub> is simple to sample, cheap to measure, and does not rely on variations in input for its interpretation.

This paper adds another piece of information to the search for understanding the dynamics of catchment hydrology. We show that the concentration discharge relationship is explainable by a continuum of ages in the streamwater, with higher silica concentrations at lower streamflow with older water (see Fig. 7b). The tritium data show that, even at high baseflow, the mean transit time is greater than one year (Fig. 7a), and the relevant large groundwater volumes (Fig. 9c) explain the highly damped tracer responses.

Acknowledgements. The work in the Toenepi catchment was funded by the Foundation for Research, Science and Technology (FRST) as part of the Groundwater Quality Protection Programme of Lincoln Ventures Ltd (8137-ASXS-LVL). We wish to thank the farmers in the catchment for their support and Aaron Wall, Juliet Clague, and Brian Moorhead for excellent technical assistance. We are grateful to Bob Wilcock (National Institute of Water and Atmospheric Research, NIWA) for providing the streamflow, nitrate, and phosphate data from the catchment outflow weir. Financial support for this study was also provided by FRST through grants to GNS Science (C05X0706, "New Zealand Groundwater Quality") and NIWA (C01X0304, "Water Quality and Quantity") via a subcontract to GNS Science.

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**Table 1.** Streamflow, silica and tritium concentrations, and mean transit times (MTT) for the Toenepi stream at the catchment outflow weir (COW) and at a headwater weir (HWW). Catchment outflow weir streamflow data from NIWA, headwater weir streamflow data from Lincoln Ventures Ltd. ±TU is the one-sigma standard error for the measured tritium concentrations, and ± MTT describes the MTT deviation which would still match the measured tritium concentration within its standard error.

Date	Streamflow	$SiO_2$	TU	±TU	MTT	±MTT
	L/s	mg/L			у	у
Toenepi catchment outflow weir COW at Tahuroa Road bridge						
14/07/2004	172	29	1.32	0.04	4	2
1/02/2005	8.99		1.06	0.05	34	2
27/08/2007	240	22.7	1.4	0.04	2.5	1.5
25/01/2008	2.54	55				
26/03/2008	1.6	68	0.265	0.02	157	4
24/04/2008	10.1	54	0.87	0.04	39	2
4/06/2009	52	37	1.32	0.04	4.5	1.5
Weir at headwater sub-catchment HWW						
14/07/2004	17	25	1.32	0.04	4	2
1/02/2005	0.87		1.41	0.04	2	1
27/08/2007	21.36	25.6	1.48	0.04	1.5	1
25/01/2008	0.09	26				
26/03/2008	stream ran dry					
24/04/2008	0.51	32	1.27	0.04	5	1
4/06/2009	3.4	30	1.45	0.04	3	0.5

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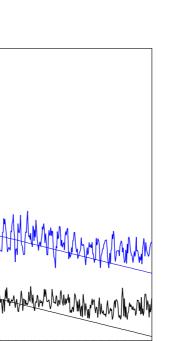
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2000

**Fig. 1.** Tritium in precipitation. The rain record for the Southern Hemisphere is from Kaitoke, New Zealand, and that for the Northern Hemisphere is from Vienna, Austria. Data for Vienna are from Global Network of Isotopes in Precipitation (GNIP), with data for recent years from Manfred Groening, IAEA (personal communication). One TU corresponds to an atomic ratio of tritium/total hydrogen of 10<sup>-18</sup>, and a massic tritium concentration of 0.11919 Bq/kg (Morgenstern and Taylor, 2009).

1980

1990

1000

100

1960

Tritium Units [TU]

Vienna

1970

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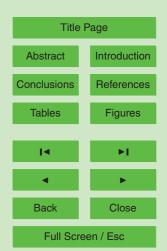




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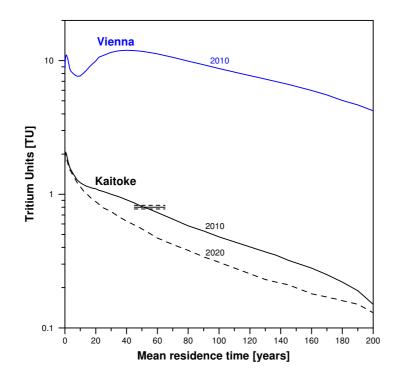


Fig. 2. Tritium output for a typical groundwater flow model of 80% exponential flow within an exponential piston flow model. Solid lines are current tritium outputs for the year 2010. For New Zealand (Kaitoke), the predicted output for 2020 (dashed line) is shown for comparison.

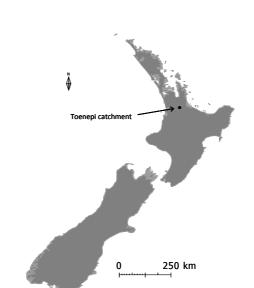


Fig. 3. Map showing Toenepi catchment boundary, 20 m-contour lines, and stream sampling sites at the catchment outlet weir (COW) and headwater weir (HWW).

Metstation

1000 m

LEGEND

Catchment Boundary

Stream

20 m Contour Line

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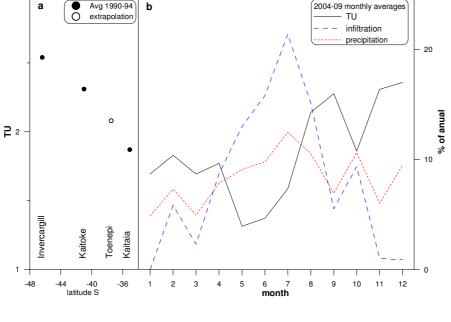
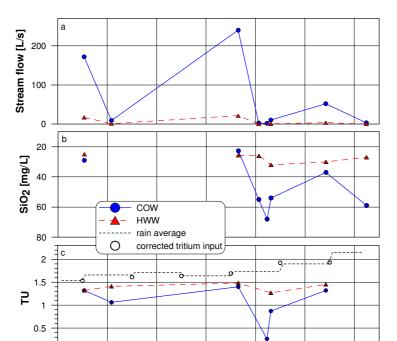


Fig. 4. (a) Average tritium concentration in rain of three reference stations (Invercargill, Kaitoke, Kaitaia) with the extrapolated value for Toenepi using a scaling factor 0.9 to the Kaitoke master reference record, and (b) seasonal variation of tritium concentration in Kaitoke, and precipitation and infiltration (as defined by precipitation – evapotranspiration) in the Toenepi catchment. Monthly values of precipitation rate and infiltration coefficient are shown as % of the annual total. Meteorological data are from the Lincoln Ventures Ltd meteorological station in the Toenepi catchment (see Fig. 3).

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**Fig. 5.** (a) Streamflow, (b)  $SiO_2$ , and (c) tritium concentration versus time for Toenepi catchment. Note the inverse axis for  $SiO_2$ . Graph (c) shows, for comparison, the average tritium concentrations in rain (Kaitoke data scaled by a factor 0.9 to account for the lower latitude at Toenepi, see Fig. 4a), and the corrected annual tritium input. The currently rising tritium concentration in rain is caused by variation in cosmogenic tritium production, which is modulated by cosmic rays and reflects varying solar activity.

2007

2008

2009

2010

0

2004

2005

2006

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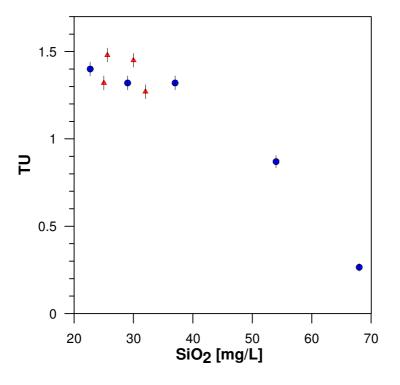
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**Fig. 6.** Tritium versus SiO<sub>2</sub> concentration.



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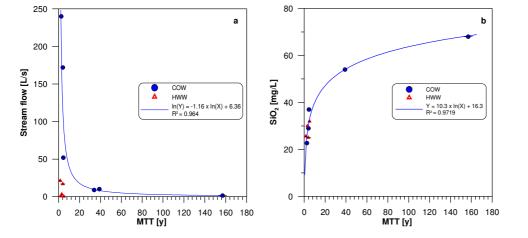


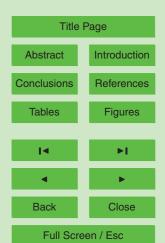
Fig. 7. (a) Streamflow and (b) SiO<sub>2</sub> concentration versus mean transit time (MTT). Correlations are deduced from data from the catchment outflow weir (COW) only.



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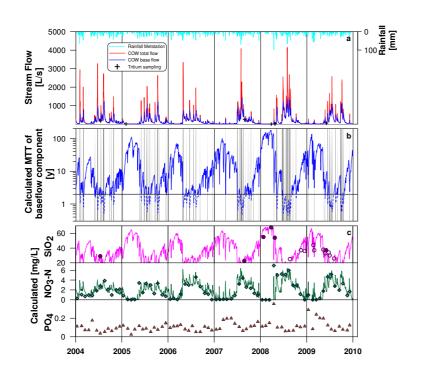


Fig. 8. Toenepi baseflow and quickflow components, together with (a) rainfall, (b) simulated mean transit time of the baseflow component, and (c) simulated (curves) and measured (points) silica, nitrate, and phosphate concentrations. Shaded areas in (b) indicate periods with quickflow run-off. Data points in (c) are measured data; full circles for SiO<sub>2</sub> are data points with age data listed in Table 1; hollow circles are additional SiO<sub>2</sub> data from Stenger et al. (2010), and NO<sub>3</sub> and PO<sub>4</sub> are data measured at the catchment outflow weir by NIWA.



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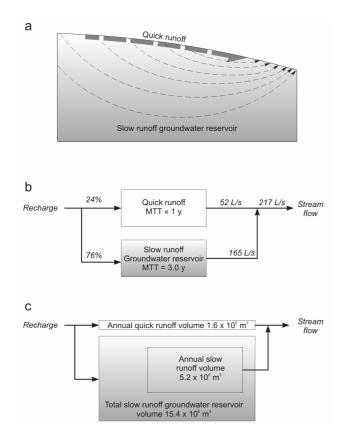


Fig. 9. (a) Conceptual flow model, (b) fractions of guick- and base-flow, and (c) comparison of water volumes. The size of the boxes in (c) is proportional to the volume of the various volumes.