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Hydrometric and natural tracer (oxygen-18, silica, tritium and sulphur hexafluoride) evidence for a dominant groundwater contribution to Pukemanga Stream, New Zealand

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Abstract:

Pukemanga is a small (3 ha) steep headwater catchment at the Whatawhata Research Station near Hamilton, New Zealand. The water balance (1996–2002) shows average annual rainfall of 1640 mm producing annual runoff of 440 mm (baseflow 326 mm, stormflow 114 mm) and 'deep seepage' loss of 450 mm (i.e. 450 mm of water not appearing in the stream). Oxygen-18 (^{18}O) concentrations were measured at weekly intervals for 8–15 months at six sites, ranging from Pukemanga Stream baseflow through wetland seepage to ephemeral streams and surface runoff. The first two showed no significant ^{18}O variations. Inferred mean residence times within the catchment ranged from at least 4 years (for the stream baseflow and seepage) to a few weeks (for the ephemeral flows and surface runoff). Silica concentrations could also be used to distinguish deep flowpath water from near-surface flowpath water. Tritium concentrations gave an estimated mean residence time of 9 years for Pukemanga Stream baseflow. Sulphur hexafluoride tended to give younger ages, while the chlorofluorocarbon ages were older, but are not considered as reliable for dating streamflow in this time range. These results show that deep pathways predominate with over 74% of runoff deriving from deep hillslope flowpaths via the wetland, and 87% of total drainage (baseflow and deep seepage) travelling via deep hillslope flowpaths. Our conception of the deep drainage process is that there is a large volume of slowly moving water in the system (above and below the water table), which reaches the wetland and stream via an unconfined groundwater system. Subsurface water equivalents are estimated to be 2·9 m for drainage at the weir and 4·1 m for drainage bypassing the weir, giving a total of 7 m depth over the catchment. The unsaturated zone plays an important role in storing water for long periods (about 4 years), while linking the surface with the groundwater water table to contribute to the fast streamflow response to rainfall. A schematic model of the various pathways with indicative residence times is given. Copyright © 2006 John Wiley & Sons, Ltd.

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INTRODUCTION

Streamflow generation processes in catchments have been the subject of many papers in the last 50 years. The important role of subsurface stormflow (SSSF) has been recognized since Hewlett and Hibbert (1967). Field studies by many workers have established that subsurface flow is generally the major source of both quickflow and baseflow in moderate to steep soil-mantled catchments. Montgomery and Dietrich (2002) noted some of the many mechanisms proposed to explain how SSSF produces stream discharge responses to storms. These include lateral throughflow in hillslope soils, lateral unsaturated flow, macropore flow, displacement of old water at the base of slopes in response to upslope additions of new water, saturation overland flow in valley bottoms, and groundwater ridging near streams. Although the topic is still controversial, runoff generation by SSSF in steep to moderate terrain is probably most often assumed to be due to development of a perched water table at a conductivity barrier, such as the soil–bedrock interface, causing lateral flow to a channel at the base of the slope.

However, a number of recent studies have demonstrated the involvement of groundwater flow in many catchments. A recent special issue of *Ground Water* (2003. **41**(7): 881–1007) highlighted the significance of groundwater in small watershed studies. Montgomery *et al*. (1997) showed that phreatic water flowing in colluvium and near-surface bedrock dominated runoff production in their steep Oregon Coast Range catchments. In the same catchments, Anderson *et al*. (1997a,b) concluded from chemical evidence that nearly all the runoff passed through the underlying bedrock, rather than perching and discharging through the soil. They also found from tracer evidence that rapid flow to the catchment outlet occurred in bedrock fractures (shown by bromide), that (vertical) plug flow occurred in the vadose zone (shown by

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deuterium (^{2}H)), and that the channel head became a subsurface variable source area where the groundwater emerged. Torres *et al.* (1998) studied the unsaturated zone in the same catchment and concluded that 'once soil attained near-zero pressure head, the unsaturated zone, saturated zone, and (stream) discharge became delicately linked' so that any sudden increase in rainfall intensity led to rapid release of stored soil-water, which increased delivery of water to the underlying saturated zone and increased stream discharge.

Tracer hydrological investigations provide information on the hydrodynamics of catchments such as residence times and sources of runoff. Naturally occurring stable isotopes, such as ^{18}O and ^{2}H, have been widely used to separate event hydrographs into old and new water contributions (e.g. Sklash *et al.*, 1976) and to determine the residence time of water in hydrological systems (e.g. Maloszewski and Zuber, 1982; Maloszewski *et al.*, 1983; Stewart and McDonnell, 1991). The advantage of using $H_2{}^{18}O$ or $HD^{16}O$ as tracers is their conservative behaviour, which is almost the same as that of $H_2{}^{16}O$ during passage of water through hydrological systems. Silica (SiO_2) provides a contrasting tracer because its concentration is related to the contact time of water with soils and rocks.

The radioisotope tritium (^{3}H) is also a component of the water molecule. ^{3}H is produced naturally in the atmosphere by cosmic rays, and large amounts were released into the atmosphere by nuclear weapons tests in the late 1950s–early 1960s, giving rain and surface water a relatively high ^{3}H concentration. However, the bomb peak in groundwater systems is now much smaller, because of radioactive decay and dispersion, or has almost completely passed through short-residence-time hydrological systems. ^{3}H dating of streamflow has been reported by Maloszewski *et al.* (1983), Uhlenbrook *et al.* (2002) and Burns *et al.* (2003). Cosmic ray ^{3}H can now be used for dating groundwater if sufficiently precise ^{3}H measurements are available (McGlynn *et al.*, 2003; Morgenstern and Taylor, 2005). Other tracers (chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF_6)) are providing new methods of age-dating groundwater (Plummer and Busenberg, 1999). The steady increases of CFCs and SF_6 in the atmosphere since 1940 and 1970 respectively potentially tag subsurface waters with their dates of last exposure to the atmosphere. Dating streamflow with the gas methods is more challenging because of the possibility of gas exchange with the atmosphere after the water has emerged from the ground.

Research effort to characterize the hydrology and biogeochemistry of the Pukemanga catchment area has been carried out for a number of years at the Whatawhata Research Station, because of the importance of agriculture in such areas to New Zealand (Smith *et al.*, 1993; Nguyen *et al.*, 1999; Elliott and Ibbitt, 2000; Quinn and Stroud, 2002). This paper uses ^{18}O, highly precise ^{3}H, and SF_6/CFC measurements to determine the residence times and nature of the flowpaths of water within catchments. The purpose is to provide an improved understanding of the processes involved in generating streamflow in the Pukemanga catchment, and in particular to show the importance of groundwater discharge in producing runoff.

METHODS

Study catchment

The study was carried out in the small (3 ha) hill-country Pukemanga headwater catchment located 30 km west of Hamilton in New Zealand's North Island (latitude 37°88′S, longitude 175°5′E; Figure 1). Samples were also collected from the adjacent Mangaotama catchment (259 ha) to provide a larger scale comparison. The topography is steep (>30°) to hilly (17–20°). Both catchments were converted to pasture from native forest (podocarp-hardwood) about 75 years ago. Headwater streams in the area (such as the Pukemanga Stream) often start as small valley-bottom wetlands (Quinn and Stroud, 2002).

The underlying greywacke/argillite bedrock at Pukemanga and Mangaotama is the Hakarimata Formation, described as poorly bedded well-jointed indurated siltstone with sandstone more common near the top (Kear and Schofield, 1978). Also, it is 'deeply weathered in the top 10–20 m and extensively fractured' (S. Edbrooke, personal communication, 2004). The area is strongly faulted. A recent drill hole in the upper section of the Pukemanga catchment showed that the substrate is clay down to 11 m, then clay with weathered rock to 26 m, then weathered rock with clay, becoming hard at 27 m (R. Stenger, personal communication, 2004). The well is screened from 27 to 30 m and the water level was 20 m below ground in March 2004, rose to less than 16 m below ground in August 2004 and then fell to 18·5 m below ground in December 2004. The upper soil layer (average depth 0·1–0·2 m) has an effective porosity of about 40%, the lower soil layer (to depth 1·2–1·5 m) around 20%, and deeper layers possibly 10–20%.

The topography of Pukemanga catchment (Figure 2) is dominated by a steeply incised gully surrounded by active slump areas. The elevation ranges from 72 to 146 m above sea level, and the slope ranges from flat near the outlet to 60° on the gully sides. The soils in the study basin in the main are the Waingaro series (typic yellow ultic soil) on the steep gully sides, the Kaawa series (also typic yellow ultic soil) on gentler slopes above the gully, and the Naike series (typic orthic granular soil) located towards the tops of ridges, all above weathered greywacke (Müller *et al.*, 2004). The ultic soils are imperfectly drained, with typically silt loam in the topsoil and silty clay below. Measured total porosities in the soil horizons down to 120 cm depth ranged from 48 to 66%. Macroporosity ranged from 0·9 to 11·3%. The Naike series is described as strongly leached, having firm compact subsoils and sticky when wet due to the high content of kaolin-type clays, especially halloysite. They are moderately well drained (Müller *et al.*, 2004; R. Stenger,

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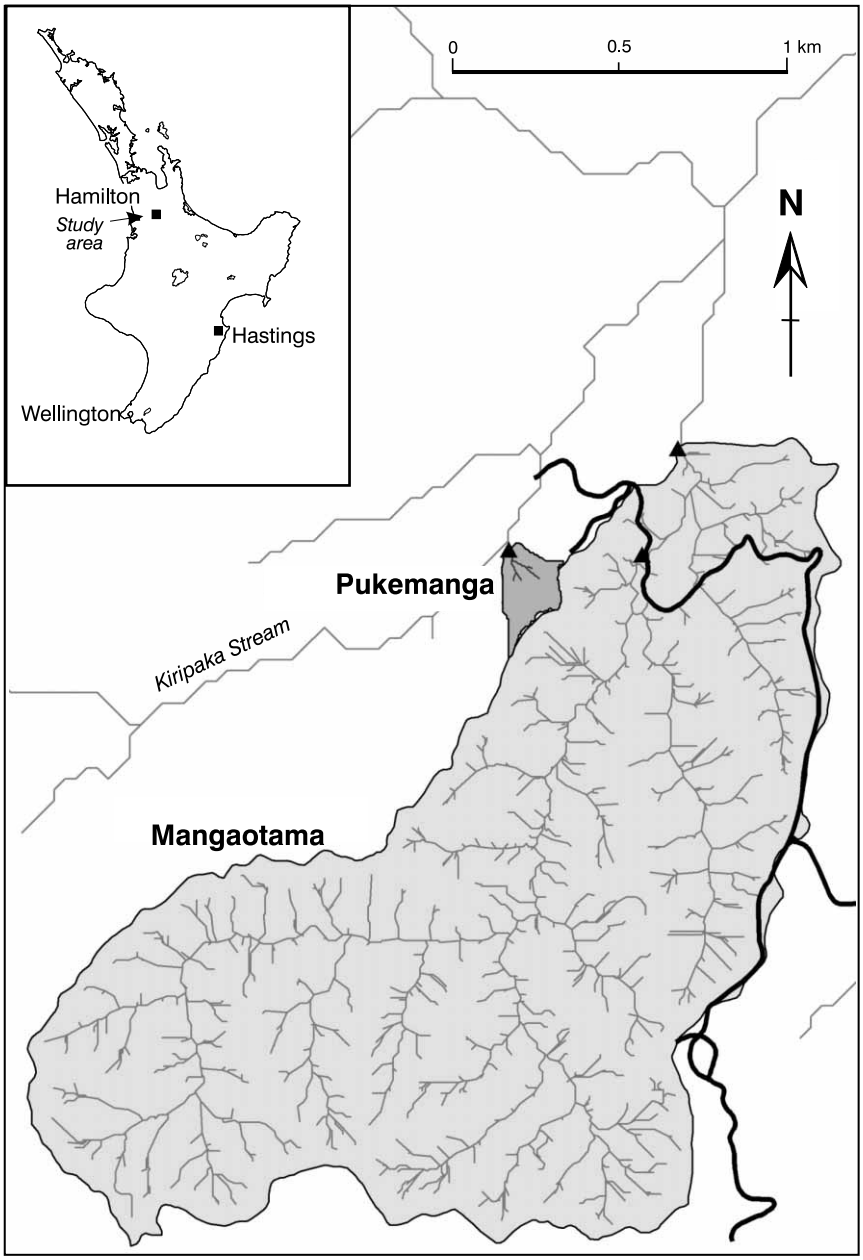

Figure 1. The Pukemanga and Mangaotama catchments. The inset shows the location of the study area near Hamilton, and the location of Hastings, in the North Island of New Zealand

personal communication, 2004). The vegetation consists of grazed perennial pasture, which has annually received superphosphate applications (200–300 kg ha^{-1} $year^{-1}$). Pastures are rotationally grazed by sheep (and at times cattle) throughout the year.

The wetland is a 62 m^2 riparian wetland zone located in the gully of the catchment (Figure 2). A small perennial stream (Pukemanga) drains the discharged groundwater at the wetland. Two tributaries at 'Waterfall' and 'Poplar' provide flow to the wetland during and after rainfall (generally when rainfall rate is more than 20 mm day^{-1}). 'Below Waterfall' and 'Below Poplar' are groundwater seepages on the edges of the wetland.

Rainfall and runoff monitoring were carried out using a tipping bucket rain gauge and a weir at the basin outlet (site 1, Figure 2). Rainfall and streamflow were logged at 5 min intervals.

The water balance at Pukemanga, based on a 6-year (1996–2002) record of rainfall and outlet streamflow (Elliott and Ibbitt, 2000) and assuming no long-term change in the volume of stored water, is

$$\text{Precipitation (1640 mm)} - \text{PET (750 mm)} = \text{Streamflow (440 mm)} + \text{Loss (450 mm)}$$

Here, PET refers to potential evaporation and transpiration; the actual evaporation and transpiration (AET) may be less. (The Penman PET was 826 mm $year^{-1}$, Priestly–Taylor PET 760 mm $year^{-1}$, for 1997–1999 at Whatawhata Research Station.) The current best estimate is that the 'Loss' component comprises about 50% of the

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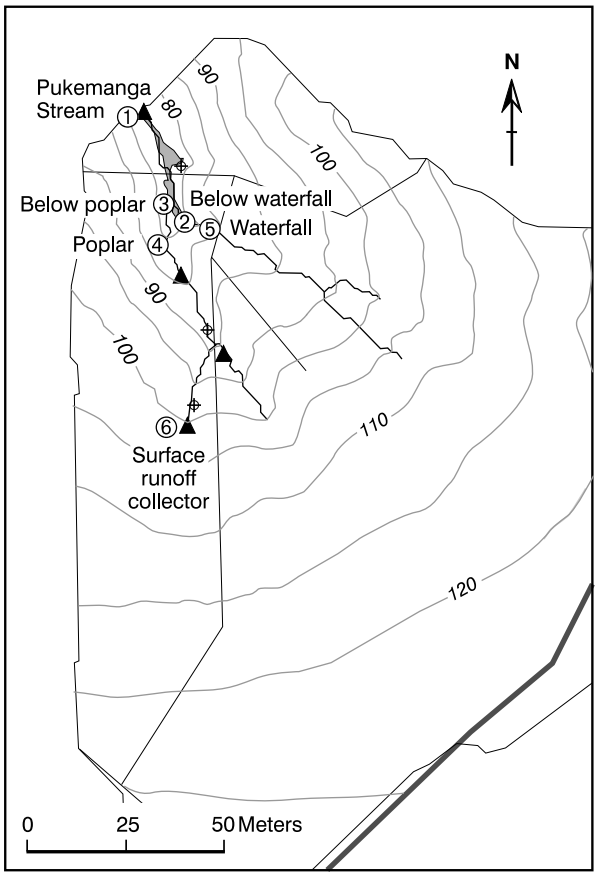

Figure 2. Map of Pukemanga catchment showing sample collection sites and topographic contours

total drainage from the catchment. Because of the contour of the catchment (Figure 2), it is considered probable that most of this lost water drains into the adjacent Kiripaki Stream by flowing under the narrow ridge separating the Pukemanga and Kiripaka catchments.

Oxygen-18

Bulk samples of rainfall and grab samples of streamflow were collected each week at the catchment outlet (site 1, Figure 3) below the wetland from August 1997 to October 1998. Samples were also collected from groundwater seepage/flow at 'Below Waterfall' (site 2) and 'Below Poplar' (site 3), from ephemeral tributaries 'Poplar' (site 4) and 'Waterfall' (site 5), and from surface runoff at 'Surface Runoff Collector' (SRC, site 6) from March 1998 to October 1998 (see locations in Figure 2).

^{18}O measurements of the water samples were carried out by equilibrating the water with carbon dioxide (CO_2) according to the method of Brenninkmeijer and Morrison (1987), and analysing the CO_2 using an NAA mass spectrometer.

The concentration of ^{18}O in water samples is expressed in the δ notation as per mil difference between the $^{18}O/^{16}O$ ratio of the sample and the international standard Vienna standard mean ocean water (VSMOW):

$$\delta^{18}O = \left(\frac{^{18}O/^{16}O_{Sample}}{^{18}O/^{16}O_{VSMOW}} - 1 \right) \times 1000 \qquad (1)$$

The $\delta^{18}O$ of VSMOW is zero. Depletion of ^{18}O in the sample is expressed in negative δ values and enrichment in positive δ values. The measurement error is $\pm 0{\cdot}10‰$ (standard error based on analysis of duplicate samples).

Silica

A selection of the samples collected for measurement of ^{18}O were analysed for SiO_2 concentration. SiO_2 was analysed by inductively coupled plasma optical emission spectroscopy at the GNS Water Lab, Wairakei.

SiO_2 concentrations are normally low in rainfall, but become higher in water infiltrating the ground because of dissolution or interaction with silicate minerals underground. The longer the residence time of the water in the ground, the greater the SiO_2 concentration (e.g. Burns *et al.*, 2003). SiO_2 concentrations can, therefore, be used to distinguish rainfall, soil water or short-residence-time shallow groundwater from long-residence-time deeper groundwater. Other chemical constituents, such as sodium, calcium and bicarbonate, have also been used in this way.

Tritium

^{3}H samples were collected in 1·1 l glass bottles, which were allowed to overflow before being tightly capped, in order to minimize contact with the atmosphere. The samples were electrolytically enriched in ^{3}H by a factor of 70, and counted in an ultra-low-background Quantalus liquid scintillation counter (Taylor, 1994; Morgenstern and Taylor, 2005). The results are based on the new radioactive half-life of ^{3}H of 12·32 years, and new calibration of standard water SRM4926C ($1{\cdot}100\,462 \pm 0{\cdot}366\%$ at 3 September 1998; Morgenstern and Taylor, 2005).

The natural variation of ^{3}H in New Zealand is not large, so use of ^{3}H for dating requires very precise measurements. The precision of the measurements reported in this paper have been extensively documented by Taylor (1994), Östlund *et al.* (1995), and Morgenstern and Taylor (2005). Measurement errors (1σ) on samples at the ambient ^{3}H level are $\pm 2{\cdot}8\%$ (about $\pm 0{\cdot}04$ TU (tritium unit)).

Chlorofluorocarbons and sulphur hexafluoride

CFC and SF_6 samples were collected air free in 2·5 l glass bottles according to methods developed by van der Raaij (2003). The bottles were rinsed in the water to be collected, then filled smoothly from the bottom and allowed to overflow. Care was taken to ensure that there were no small bubbles adhering to the inner sides of the bottle. After overflowing for some time, the tube was slowly removed, leaving a convex meniscus on the top of the bottle. The cap was filled with water, then placed over the meniscus and firmly secured. A shaped nylon liner within the cap expelled any surplus water as the cap was being tightened. Then the bottle was tipped upside down and closely observed to see if any bubbles rose up through the water in the bottle. If any did, the sample

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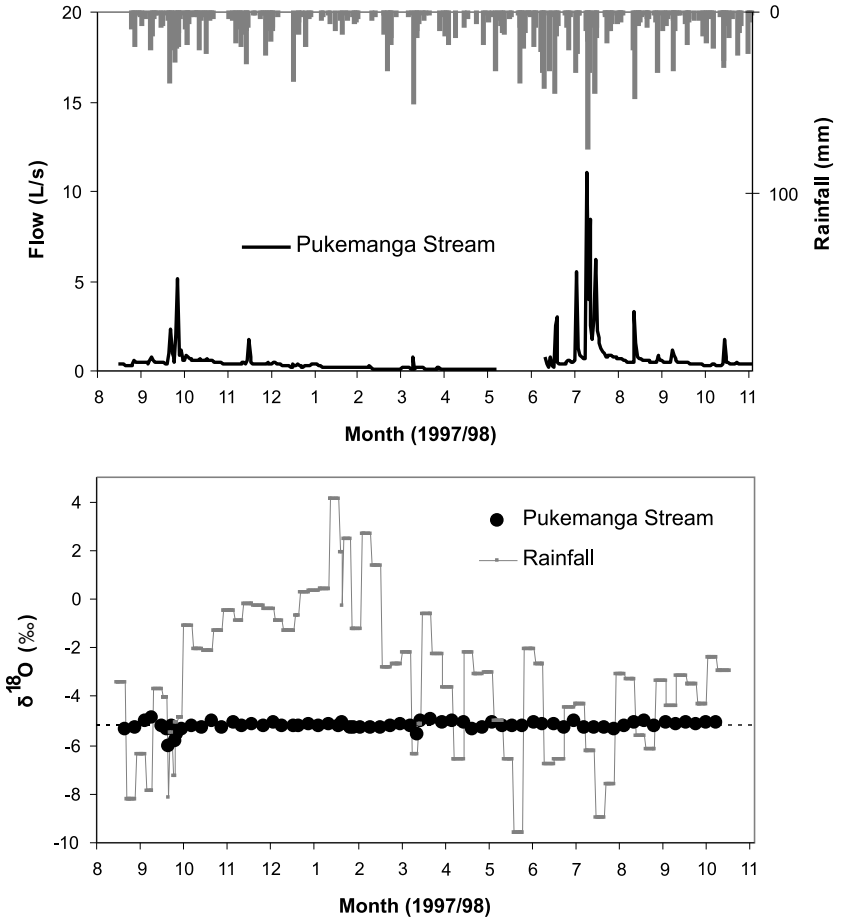

Figure 3. Daily rainfall, runoff and δ^{18}O values of stream and rainfall at Pukemanga catchment from 15 August 1997 to 14 October 1998

was discarded and a new sample was collected. Samples were stored at constant temperature.

Two of the present samples were from streams. In these cases, the samples were taken from deep slow-moving portions of the streams (in the case of Pukemanga Stream near the spring inflow), from as deep as practicable below the surface (about 60 cm). The bottles were held under water and allowed to fill, then a pump was used to suck fresh water into the bottles while they were still under water, then the bottles were tightly capped still under water. The bottles were tested to ensure that there were no air bubbles in the sample.

Dissolved CFC and SF_6 concentrations were measured by gas chromatography using a purge and trap method, and electron capture (EC) detector (van der Raaij, 2003). Dissolved argon and nitrogen concentrations were also measured by gas chromatography on the same water as used for the CFC measurements of the later samples.

Residence time determination

The different flowpaths of water through the unsaturated and saturated zones of catchments means that outflows contain water with different residence times. The water in a sample does not have a discrete age, but has a distribution of ages. This distribution is described by a conceptual flow or mixing model, which reflects the average conditions in the catchment.

Rainfall incident on the catchment is affected by immediate surface/near-surface runoff and longer term evapotranspiration (ET) loss. The remainder constitutes recharge to the subsurface water stores; these are accounted for in the ^{18}O and ^{3}H results sections below (Maloszewski and Zuber, 1982; Viville *et al.*, 2006). The tracer inputs to the subsurface water stores (i.e. the temporal ^{18}O variations, ^{3}H, CFC or SF_6 concentrations in the recharge water) are 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

$$C_{\text{out}}(t) = \int_0^\infty C_{\text{in}}(t-\tau)h(\tau)\exp(-\lambda\tau)\,\mathrm{d}\tau \qquad (2)$$

where C_{in} and C_{out} are the input and output concentrations in the precipitation and baseflow 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. $\lambda = \ln 2/T_{1/2}$ is the ^{3}H decay constant, where $T_{1/2}$ is the half-life of ^{3}H (12·32 years).

Two flow models are commonly used in stable isotope studies. The exponential piston-flow model (EPM)

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combines a volume with exponential transit times followed by a piston-flow volume to give a model with two parameters (Maloszewski and Zuber, 1982). The response function is given by

$$h(\tau) = 0 \qquad \text{for } \tau < \tau_m(1-f) \tag{3a}$$

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

where τ_m is the mean residence time and f is 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 exponential model (EM) is EPM($f = 1{\cdot}0$).)

The dispersion model assumes a tracer transport that is controlled by advection and dispersion processes (Maloszewski and Zuber, 1982):

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

where D is the longitudinal dispersion coefficient, v is the flow velocity and x is the flow distance.

RESULTS

Flow measurements

The water balance measurements in the Pukemanga catchment showed that streamflow at the outlet weir represents only about 50% of the drainage from the basin. The other 50% apparently drains underground, bypassing the weir entirely and only emerging into the stream or other streams at lower altitude. Hydrograph analysis (method of Hewlett and Hibbert (1967)) showed that the total annual streamflow could be separated into 74% baseflow and 26% quickflow (Elliott and Ibbitt, 2000). Therefore, the annual catchment outflows are

Stream quickflow:	114 mm (13%)
Stream baseflow:	326 mm (36%)
Deep groundwater seepage:	450 mm (51%)

This grouping suggests that groundwater pathways contribute at least 87% of the annual flow out of the catchment (some of the quickflow also derives from groundwater, as evidenced by ^{18}O values and the fact that flows measured in the ephemeral streams do not account for all of the quickflow (Elliott and Ibbitt, 2000)). Deep groundwater thus plays a dominating role in the catchment drainage.

The deep groundwater system was recently accessed via a well in the upper section of the Pukemanga catchment (R. Stenger, personal communication, 2004). Large fluctuations in the water level measured in the well (from 20 m below ground in March 2004 to less than 16 m in August 2004, and then to 18·5 m in December 2004) show that groundwater recharge is substantial and that the unsaturated zone (at least in its lower parts) is close to saturation.

Mangaotama catchment has similar land cover and geology to Pukemanga catchment, and the stream has a similar flow regime. This suggests that similar baseflow generation pathways may also operate in that catchment.

Oxygen-18 and silica data

Daily rainfall and streamflow, and the weekly $\delta^{18}O$ values for bulk rainfall and stream at the catchment outlet are shown in Figure 3 for the period of sampling from August 1997 to October 1998. The $\delta^{18}O$ values of the rainfall show a wide variation from $-9{\cdot}6$ to $+4{\cdot}1‰$. Lower values are recorded during winter. The values increase in spring and, particularly, during summer. From the middle of February (end of summer–early autumn) the values decrease again. In contrast, the $\delta^{18}O$ values in the stream at the weir show a much smaller variation. They change only from $-6{\cdot}0$ to $-4{\cdot}9‰$. The largest variations are caused by runoff events (Figure 3). If these values are not included, then the change of $\delta^{18}O$ in the stream is only from $-5{\cdot}3$ to $-5{\cdot}0‰$. This strong damping, from the $\delta^{18}O$ variation of the rainfall input to that in the baseflow, shows that baseflow water is drawn from a large store of water and has a substantial mean residence time within the catchment in agreement with the flow results. The mean $\delta^{18}O$ values of the rainfall and baseflow show that groundwater supplying the latter is recharged disproportionately by winter rainfall. The weighted mean $\delta^{18}O$ of the rainfall is $-4{\cdot}36‰$, whereas that of Pukemanga Stream baseflow is $-5{\cdot}17‰$ (Table I).

The SiO_2 concentrations of a number of samples are plotted against $\delta^{18}O$ in Figure 4. Rainfall has low concentrations of SiO_2 ($0{\cdot}09$ mg l^{-1}), but very variable $\delta^{18}O$. Samples from the runoff collector (SRC), and the ephemeral streams at Waterfall and Poplar, also have low SiO_2 and variable $\delta^{18}O$. Below Poplar, Below Waterfall and Pukemanga Stream baseflow have higher SiO_2 concentrations and less variable $\delta^{18}O$ values because of their dominant deep groundwater contributions. The SiO_2 concentration of deep groundwater is identified as being in the range 20–25 mg l^{-1}.

Residence time calculations using oxygen-18

The record of ^{18}O concentration in water infiltrating the ground and recharging the subsurface water stores is required in order to estimate water residence times within the catchment using the convolution integral approach (Equation (2)). The longer the residence time, the longer the input record of ^{18}O needed before the stream samples were collected. Determining the ^{18}O input function consists of two parts:

1. determining the ^{18}O concentration in rainfall incident on the catchment;
2. accounting for losses by ET and surface runoff as rainfall infiltrates into the ground, i.e. as rainfall is converted into groundwater recharge (e.g. we have

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Table I. Mean $\delta^{18}O$ values and ranges of $\delta^{18}O$ and SiO_2 values from weekly samples (August 1997 to October 1998), with quality of fit and parameters of the best-fit simulations using the EPM. (See text for model descriptions)

Feature (site no.)	$\delta^{18}O$ (‰)		SiO_2 range (mg l^{-1})	EPM f	Quality of fit, SD (‰)	Groundwater MRT (weeks)	Rainfall fraction (%)
	Mean	Range					
Rainfall (1)	−4·34[a]	−9·60 to 4·08	0·05–0·09				
Recharge	−5·13[a]	−9·60 to −0·18	—				
Pukemanga Stream (1)	−5·17 ± 0·10	−5·31 to −4·97	20–25	1·0	±0·10	≥208	0
Below Waterfall (2)	−5·11 ± 0·08	−5·26 to −5·03	21–25	0·6	±0·04	208	0
Below Poplar (3)	−5·00 ± 0·29	−5·35 to −4·30	10·9–24	0·8	±0·25	≥156	10
Waterfall (5)	−4·99 ± 0·59	−5·70 to −3·83	0·05–4·5	0·8	±0·47	12	12
Poplar (4)	−4·99 ± 0·61	−5·61 to −3·81	0·87–4·1	0·8	±0·44	12	21
SRC (6)	−4·32 ± 1·86	−7·85 to −1·03	2·4–4·5	0·8	±1·46	12	66

[a] Weighted means by rainfall or recharge amounts.

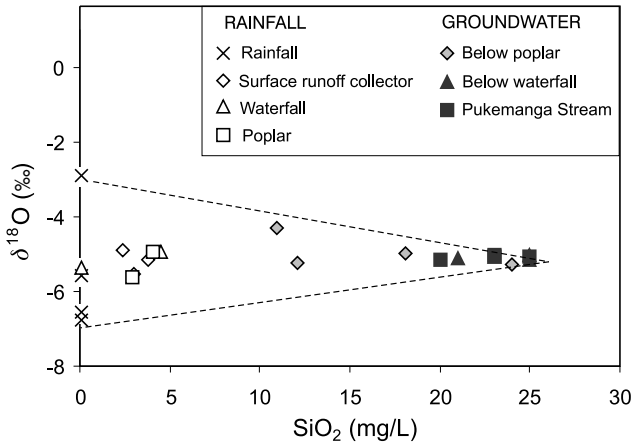

Figure 4. SiO_2 concentrations and $\delta^{18}O$ values in runoff at Pukemanga catchment

already noted that winter rainfall contributes proportionally much more to baseflow than summer rainfall).

^{18}O measurements were made on bulk weekly rainfall samples collected between 15 August 1997 and 14 October 1998 at Pukemanga catchment (Figure 3). This record has been extended by using ^{18}O measurements in weekly rainfall samples from Hawkes Bay, New Zealand (near Hastings), collected between 30 October 1995 and 4 June 1997 (Figure 5a). The latter record was adjusted by adding 1·11‰ to the $\delta^{18}O$ values, to produce the same mean value as for the Pukemanga record. The daily rainfall is available for Pukemanga in this 3-year period. (Using rainfall $\delta^{18}O$ data from Hawkes Bay is not ideal, as Hawkes Bay is on the east coast of the North Island and Pukemanga is on the west coast. Nevertheless, the New Zealand climate tends to be dominated by westerly influences, so the substitution is reasonable.) The record was extended to 6 years (November 1992 to October 1998) using the monthly averages from the 3 years of data (November 1995 to October 1998, Figure 5b).

To account for losses as rainfall infiltrates the ground, a weighting procedure is required. The main loss is by ET within the soil, but there is also surface/near-surface runoff during heavier rainfall. A suitable weighting formula for the input function was introduced by Bergmann *et al.* (1986); also see Vitvar and Balderer (1997). (An alternative weighting procedure, which involved introducing a weighting factor into the convolution integral, was used by Stewart and McDonnell (1991) to account for throughfall losses in forest at Maimai catchment.) The Bergmann *et al.* (1986) formula is

$$\delta_w = \frac{N\alpha_i P_i}{\sum \alpha_i P_i}(\delta_i - \delta_{mean}) + \delta_{mean} \quad (5)$$

where δ_w and δ_i are the weighted and measured $\delta^{18}O$ values respectively, and α_i and P_i are respectively the groundwater recharge parameter and precipitation amount in the ith week. N is the number of measurements and δ_{mean} is the long-term mean input $\delta^{18}O$ value (taken as the mean for Pukemanga Stream baseflow, i.e. −5·17‰). We can substitute R_i (groundwater recharge) for $\alpha_i P_i$ and substitute R_{mean} for $(\sum a_i P_i)/N$ (mean weekly recharge).

R_i values were estimated by subtracting the estimated weekly ET from the rainfall, with ET losses in excess of the rainfall in one week being subtracted from rainfall in subsequent weeks. Rainfall in excess of 53 mm $week^{-1}$ was considered to be removed as surface or near-surface runoff (quickflow). This scheme, with ET varying by month, approximately replicates the 6-year average water balance observed, i.e. ET of 744 mm $year^{-1}$ is removed, quickflow of 109 mm $year^{-1}$ runs off and recharge is 840 mm $year^{-1}$ over the 3-year period. The resulting groundwater recharge estimates are given in Figure 5a. It can be seen that, generally, there is little recharge in the summer–autumn periods (November to April, i.e. weeks 1–26, 53–78 and 106–131). Recharge mainly occurs during winter–spring (May to October, i.e. weeks 27–52, 79–105 and 132–155).

Figure 5a also shows the rainfall $\delta^{18}O$ (Pukemanga and adjusted Hawkes Bay values) and recharge $\delta^{18}O$ (i.e. the 'weighted' values from Equation (5)). Using the recharge amounts gives a recharge-weighted mean $\delta^{18}O$ of −5·13‰, which is close to the Pukemanga baseflow mean value of −5·17‰, and that of the perennial spring

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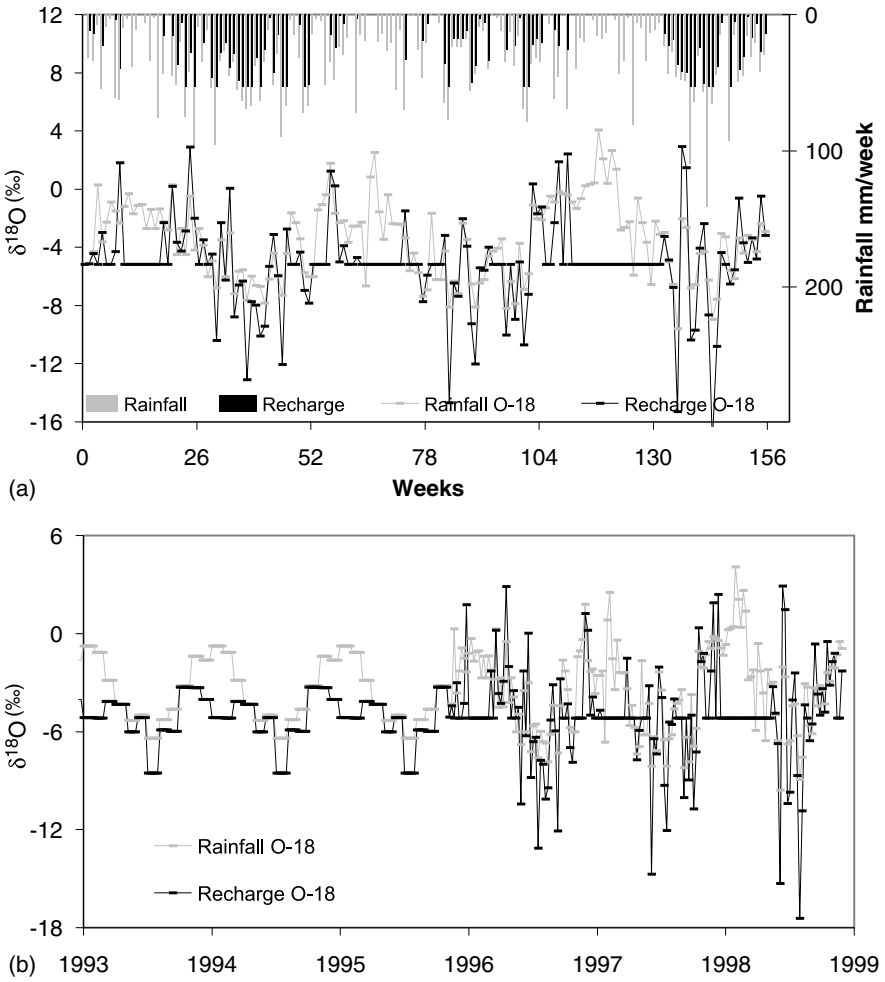

Figure 5. (a) Amounts and δ^{18}O values of rainfall and recharge in the period 30 October 1995 to 14 October 1998 (156 weeks). The summers are 1–26, 53–78 and 106–131 weeks, and winters are 27–52, 79–105 and 132–155 weeks, respectively. (b) δ^{18}O values of rainfall and the 6-year input function (i.e. recharge)

Below Waterfall (−5·11‰). The seepage at Below Poplar had mean δ^{18}O of −5·00‰, the ephemeral streams at Poplar and Waterfall −4·99‰, and SRC −4·32‰. The latter is close to the rainfall-weighted mean δ^{18}O of −4·34‰.

To simulate the ^{18}O variations of the diverse features sampled, we assumed input of two types of water, i.e. 'old' groundwater and 'young' rainfall. The old component was water with some residence time within the ground, which had been affected by ET. The old water variations were modelled using an EPM. The value of f (the ratio of the exponential volume to the total volume of the system) was considered in relation to the ^{3}H results (below) and to results in the literature (see 'Discussion' section). The young component was rainfall from the immediate week (i.e. input of rainfall by direct incidence or surface/near-surface flow, not affected by ET). Least-squares regression was used to optimize the fits to the data (expressed as the standard deviation (SD) of the δ^{18}O simulation about the δ^{18}O measurements, i.e.

$$\mathrm{SD} = \sqrt{\sum[(\delta_{si} - \delta_i)^2/(N-1)]} \qquad (6)$$

where δ_{si} and δ_i are the simulated and measured δ^{18}O values respectively).

Three adjustable parameters were used to simulate the ^{18}O variations of the three perennial sites: f, the mean residence time of the old water (MRT), and the fraction of young water (RF). Pukemanga Stream baseflow shows a marked predominance of deep groundwater input with a very limited δ^{18}O range of −5·0 to −5·3‰, and SiO_2 range of 20–25 mg l^{-1} (Table I). Sampling was from August 1997 to October 1998; seven samples were omitted because the streamflow was above baseflow when they were collected. The standard deviation of the measurements about the mean (±0·10‰) was the same as the measurement error; hence, no significant variation in the results is proven. The quality of fit as a function of the MRT is shown in Figure 6a for values of f between 0·6 and 1·0. f = 1·0 gives the best fits, and the quality of fit closely approaches the standard deviation of the measurements for MRT = 4 years (208 weeks) or greater. The fit to the data for MRT = 4 years is shown in Figure 6b. The optimum rainfall fraction was 0%.

Below Waterfall (Table I, Figure 6c and d) had fewer measurements and a shorter sampling period (8 months).

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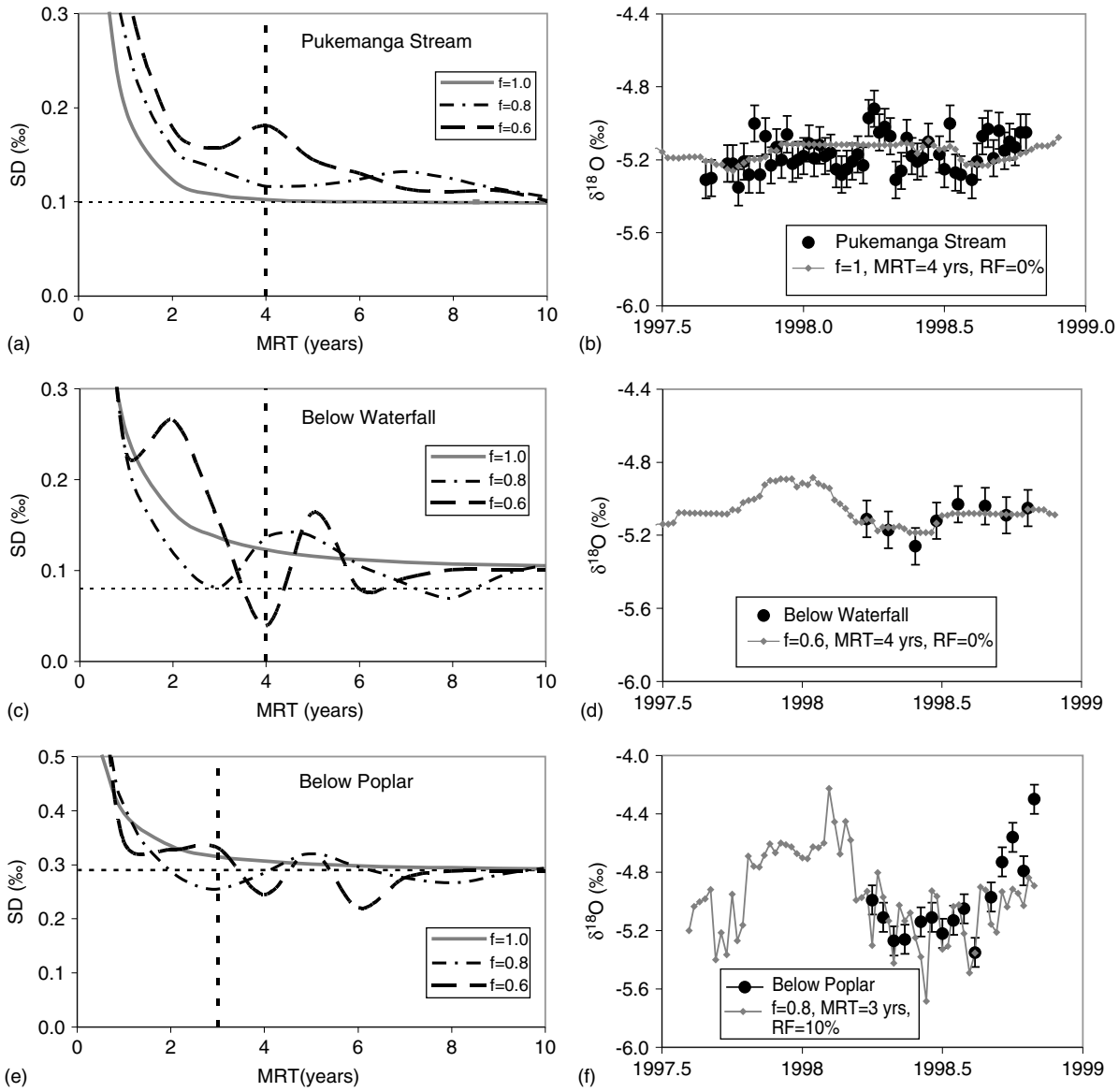

Figure 6. Variation of the ^{18}O goodness-of-fit criterion (SD) with f and MRT, and selected best-fit positions (vertical dashed lines) for (a) Pukemanga Stream baseflow, (c) Below Waterfall spring, and (e) Below Poplar spring. (b, d, f) $\delta^{18}O$ measurements and simulations based on the selected best-fit parameter values

The data also show no significant variation compared with the measurement error (the standard deviation of the measurements was ±0·08‰). The $\delta^{18}O$ range was −5·0 to −5·3‰, and the SiO_2 range was 20–25 mg l^{-1}. The quality of fit as a function of the MRT is shown in Figure 6c for values of f between 0·6 and 1·0. The best-fitting simulation was for $f = 0{\cdot}6$, MRT = 204 weeks, RF = 0% (this case is shown in Figure 6d). This fit is almost too perfect (with SD = ±0·04‰). Other poorer fits (subsidiary minima) are possible (i.e. $f = 0{\cdot}6$, MRT = 6 years, and $f = 0{\cdot}8$, MRT = 3 years or 8 years). No satisfactory fits are possible with $f = 1{\cdot}0$, and $f = 0{\cdot}8$ did not give good simulations to the ^3H data, so the best fit at $f = 0{\cdot}6$, MRT = 4 years is taken as the mean residence time. The optimum rainfall fraction was 0% in all cases.

The Below Poplar site has a $\delta^{18}O$ range of 1‰ and SiO_2 range from 10·9 to 24 mg l^{-1} (Table I), showing that groundwater predominates, but up to 50% of low-SiO_2 water can be present on occasions. The best-fit simulations have 10% rainfall. There are minima at 4 and 6 years for $f = 0{\cdot}6$, and at 3 and 8 years for $f = 0{\cdot}8$ (Figure 6e). The fit for $f = 0{\cdot}8$, MRT = 3 years is taken as the minimum MRT. Most of the variation is due to the input of direct rainfall; a couple of points lie off the curve, indicating occasional input of larger amounts of rainfall than 9%. Nevertheless, the majority of the water, on average (91%), is from long-residence time groundwater with MRT of 3 years or greater.

The remaining three sites have ephemeral flows after rainfall. Three adjustable parameters were used: the groundwater MRT, the rainfall fraction and the 'long-term' mean $\delta^{18}O$ of the groundwater (δ_{mean}, see Equation (6)). (f was taken as 0·8.) In these cases, the description 'long term' was not appropriate, as these features discharged little deep groundwater. The Waterfall

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site has a $\delta^{18}O$ range of 1·9‰ and SiO_2 range from 0 to 5 mg l^{-1} (Table I), showing that rainwater or shallow groundwater predominates. The best match to the data had 12% rainfall and groundwater with MRT = 12 weeks and $\delta^{18}O_{mean} = -6{\cdot}52‰$ (Figure 7a). The $\delta^{18}O_{mean}$ is quite negative, probably reflecting soil water affected by short-residence-time winter rainfall. It appears that Waterfall is substantially from short-residence-time soil water displaced by rainfall in addition to direct rainfall, suggesting that saturation overland flow near the top of the waterfall is the source mechanism.

The Poplar site has a $\delta^{18}O$ range of 1·8‰ and SiO_2 range of 1 to 4 mg l^{-1} (Table I). A simulation with 21% rainfall and groundwater with MRT = 12 weeks and $\delta^{18}O_{mean} = -5{\cdot}50‰$ gives the best match to the data (Figure 7b). These support saturation overland flow as the source mechanism.

The SRC site has a $\delta^{18}O$ range like that of rainfall (7‰) and SiO_2 range of 2 to 4 mg l^{-1} (Table I). A simulation with 66% rainfall and groundwater with MRT = 12 weeks and $\delta^{18}O_{mean} = -4{\cdot}34‰$ gives the best match to the data (Figure 7c), indicating that this site is dominated by direct rainfall, although some short-residence-time soil water is present.

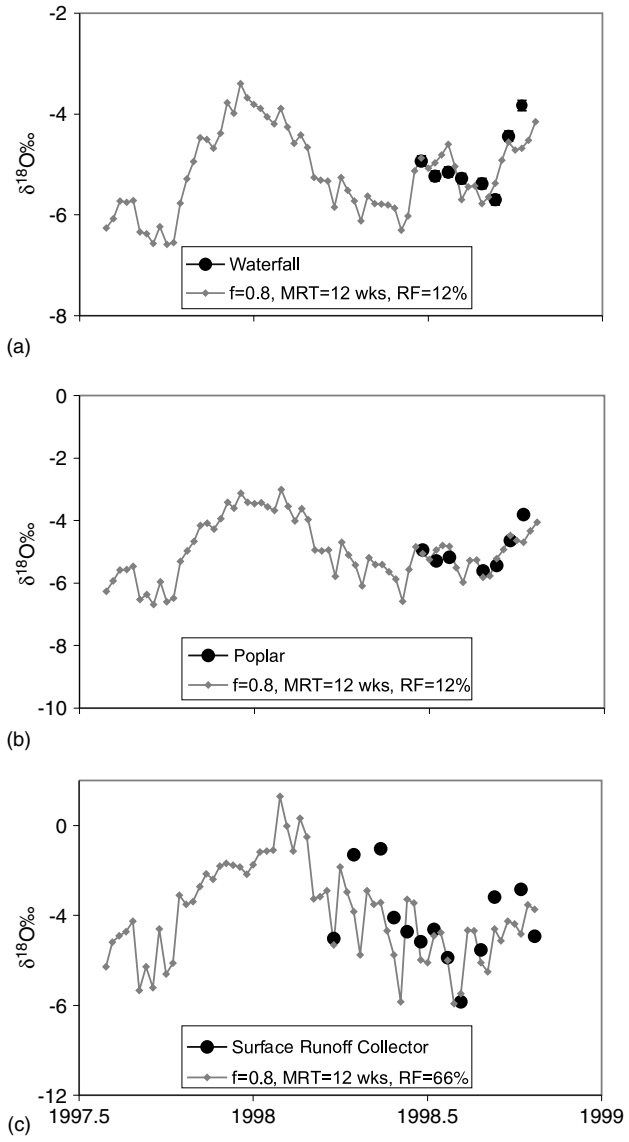

Figure 7. $\delta^{18}O$ measurements and simulations based on best-fit parameter values for (a) Waterfall, (b) Poplar, and (c) SRC

Simulation results using the dispersion model are not presented, but fits of similar quality and yielding similar MRTs are also obtainable with the dispersion model.

Residence time calculations using tritium

The ^3H measurements are given in Table II. Interpretation of ^3H ages is complicated because of the complicated ^3H input function (Figure 8). This is partly due to the bomb ^3H input in the 1960s and 1970s, although this is less of a factor for young waters now because bomb ^3H will mostly have passed through such systems. Further complication for dating young waters is caused by the seasonal variation in ^3H: the ^3H concentrations in precipitation are generally higher in spring than in the rest of the year because ^3H from the stratosphere leaks into the troposphere each spring in the Southern Hemisphere (Stewart and Taylor, 1981). This variation is illustrated by the six-monthly data in Figure 8.

Another complication is caused by the preferential removal of summer rainfall by ET during infiltration into the ground as described above for ^{18}O. The average monthly recharge amounts were determined from the 3-year rainfall record and estimated monthly ET rates, and used to determine the six-monthly ^3H averages in the recharge using

$$C_{in} = \sum_{i=1}^{6} C_i R_i / \sum_{i=1}^{6} R_i \tag{7}$$

where C_i and R_i are the ^3H concentrations in rainfall and the recharge amounts for the ith month. C_i are taken from monthly ^3H measurements at Kaitoke, near Wellington, adjusted by a scale factor of 0·9. (The scale factor adjusts precipitation data for well-known latitudinal variations over New Zealand; Stewart and Taylor, 1981) These adjusted ^3H concentrations are given in Figure 8.

To simulate the ^3H concentrations of the baseflows and spring, we assumed input of only the 'old' groundwater component because the ^{18}O results showed that the direct rainfall input was negligible. As before, least-squares regression was used to optimize the fits to the data (expressed as the standard deviation of the ^3H simulation about the ^3H measurements). The adjustable parameters were f and MRT.

For Pukemanga Stream baseflow the best fit is obtained with $f = 1{\cdot}0$, which gives a broad minimum centred around MRT = 9 years (Figure 9a). This is the same model as was used for the ^{18}O measurements. $f = 0{\cdot}8$ gives a similar, but less well fitting result. $f = 0{\cdot}6$ has a sharp minimum at MRT = 7 years. The three ^3H measurements on Pukemanga Stream (Table II) are plotted in Figure 9b, with the input curve and simulation for EPM($f = 1{\cdot}0$, MRT = 9 years). The major source of

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Table II. ^{3}H concentrations and age interpretations

Site	Sampling date	^{3}H concentration (TU)	EPM f	MRT (years)
Pukemanga Stream (1)	18 Oct 2002	1·44 ± 0·03	1·0	9
	12 Jul 2004	1·19 ± 0·04		
	15 Dec 2004	1·35 ± 0·04		
Below Waterfall (2)	18 Oct 2002	1·49 ± 0·03	0·6	3
	15 Dec 2004	1·38 ± 0·05		
Mangaotama Stream	18 Oct 2002	1·54 ± 0·04	1·0	2
	12 Jul 2004	1·31 ± 0·04		
	15 Dec 2004	1·48 ± 0·04		

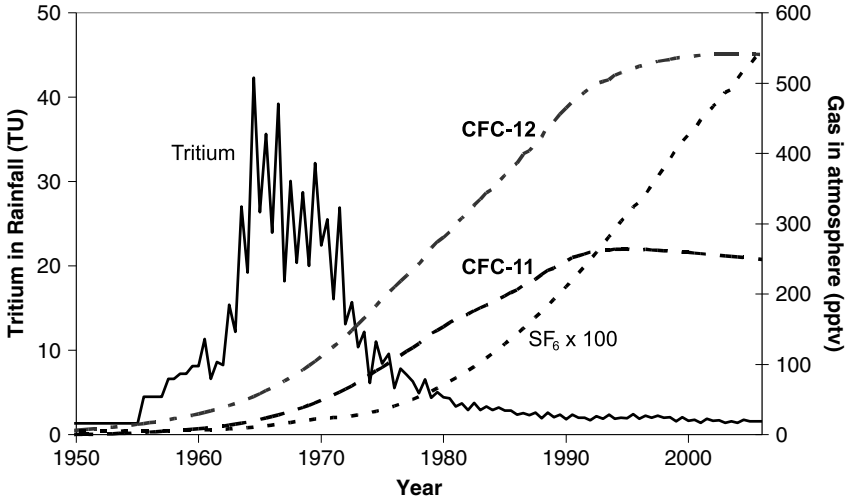

Figure 8. Estimated six-monthly mean ^{3}H concentration in groundwater recharge at Pukemanga (scaled from monthly rainfall data measured at Kaitoke, near Wellington, New Zealand, and weighted by monthly recharge), and CFC and SF_6 concentrations in the Southern Hemisphere atmosphere

possible error in the MRT is due to the ^{3}H measurement errors. This is estimated by combining the measurement errors of the three points (using the expression $(1/N)\sqrt{\sum \sigma_i^2}$, where σ_i are the measurement errors) and fitting curves to the high and low values of the measurements. This gives a possible age range of 6–14 years. It is also noted that the 2004 sample points do not lie on the optimum simulation within the 1σ measurement error (and barely within 2σ). This suggests that the July 2004 sample, which was collected during winter when the groundwater table was relatively high, may have contained some older water. Fitting the model to the points separately would give an MRT of 5 years for the October 2002 and December 2004 points, and 24 years for the July 2004 point. Investigating this observation more thoroughly will require more data.

Only two ^{3}H measurements were obtained from Below Waterfall (Table II). Excellent fits were obtained with $f = 1{\cdot}0$ and $f = 0{\cdot}6$; both indicate MRT = 3 years (Figure 9c). The points are plotted in Figure 9d with the input curve and simulation for EPM($f = 0{\cdot}6$, MRT = 3 years). The fit with $f = 0{\cdot}6$ is preferred. Combining the ^{3}H errors, as above, gives a possible age range of 1–6 years. Poorer fits were obtained with $f = 0{\cdot}8$, but the minimum occurs at the same MRT of 2–4 years. No sample was collected in the winter at this site, which may have contributed to the very good fit and young age. (The winter samples at Pukemanga and Mangaotama Streams appeared to have lower ^{3}H concentrations and older ages.)

The Mangaotama Stream ^{3}H results (Table II) yield a best fit at about MRT = 2 years with the EPM($f = 1{\cdot}0$) model (Figure 9e). The data are plotted in Figure 9f, with the input and simulation (EPM($f = 1{\cdot}0$, MRT = 2 years)) curves. Combining the measurement errors gives a possible age range of 1–3 years. Simulations with $f = 0{\cdot}8$ have a broad minimum at MRT = 0–2 years, and $f = 0{\cdot}6$ has minima at 1 and 4 years. As before, the winter point appears to have lower ^{3}H (and, therefore, greater age) than the spring/summer points.

Residence time calculations using chlorofluorocarbons and sulphur hexafluoride

CFCs are entirely man-made contaminants of the atmosphere and hydrological systems. Their concentrations in the atmosphere have gradually increased from zero in about 1940 to the present levels of several hundred parts per trillion by volume (or 10^{-12}). SF_6 concentrations in the atmosphere have increased from low values in 1970 to the present, because of its use in electrical switchgear. CFC-11, CFC-12 and SF_6 concentrations in the Southern Hemisphere are shown in Figure 6. Because the gases are relatively long-lived, they are widely distributed in the atmosphere. CFCs and SF_6 are slightly soluble in

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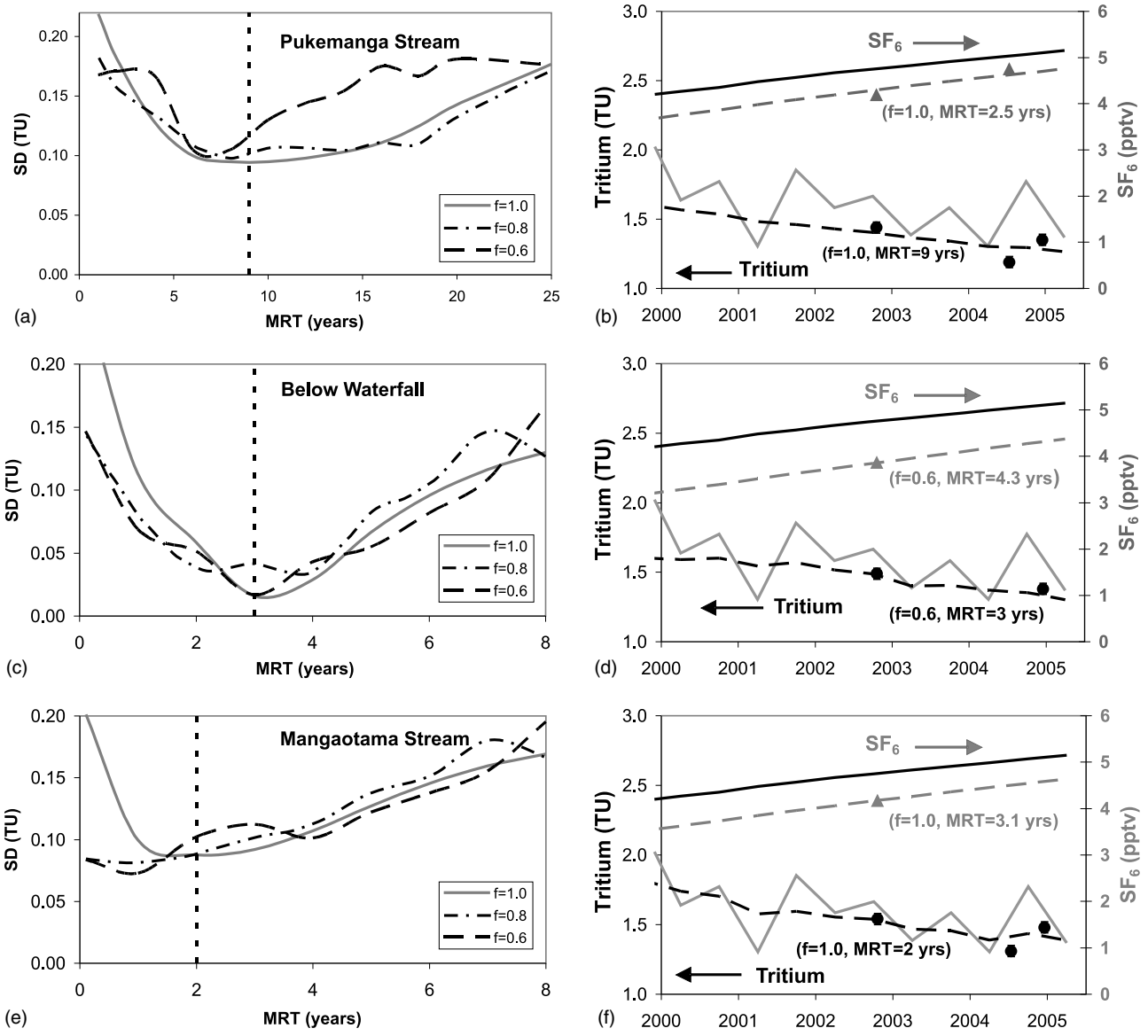

Figure 9. Variation of the ^{3}H goodness-of-fit criterion with f and MRT, and ^{3}H and SF_6 concentrations of measurements, input functions and best-fit simulations, for (a, b) Pukemanga Stream baseflow, (c, d) Below Waterfall spring, and (e, f) Mangaotama Stream

water and enter groundwater systems during recharge. Assuming that they were in solubility equilibrium, their concentrations in groundwater record the atmospheric concentrations when the water was recharged, thus allowing the recharge date of the water to be determined.

The concentrations of the gases in groundwater can be affected by several processes, which can make age interpretation complicated (Plummer and Busenberg, 1999). The most important of these in the present context are:

1. Possible degradation or absorption in anaerobic conditions underground; CFC-11 is more susceptible to this than CFC-12, and SF_6 is rarely affected.
2. Possible contamination from local sources, such as organic liquids. CFC-12 is more prone to this than CFC-11, and SF_6 is hardly ever affected; however, SF_6 can be affected by natural sources such as volcanic rocks.
3. Possible presence of excess air in solution; SF_6 is much more sensitive to this, CFC-12 mildly sensitive, and CFC-11 much less.

A further complication is that:

4. In comparison with ^{3}H, which travels with the water, the gases can travel with air through the unsaturated zone, thereby shortcutting the water. This means that gas ages may be expected to be younger than ^{3}H ages in systems with substantial unsaturated zones.

Finally:

5. Because some of these measurements are on stream waters, the dissolved gases could be affected by exchange with the atmosphere after the water has emerged from the ground. This is a formidable list of potential problems.

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Table III. Recharge temperatures and excess air concentrations (either assumed values for sampling on 18 October 2002 or calculated from Ar and N_2 concentrations for 12 July 2004), calculated atmospheric SF_6 and CFC concentrations during recharge, and mean residence times (MRT)

Sample ID	Sampling date	Recharge temp. (°C)	Excess air (ml(STP) kg^{-1})	Calc. atmospheric partial pressure (pptv)[a]			MRT (years)		
				SF_6	CFC-11	CFC-12	SF_6	CFC-11	CFC-12
Pukemanga Stream (1)	18 Oct 2002	12·5	0	4·19	ns	ns	2·5	15	7
	12 Jul 2004	13·7	0·1	4·75	220·9	519·5			
Below Waterfall (2)	18 Oct 2002	12·5	0	3·86	200·6	427·0	4·3	17	14
Mangaotama Stream	18 Oct 2002	12·5	0	4·17	219·0	488·1	3·1	13	9
	12 Jul 2004	8·0	0·1	ns	247·0	C			

[a] ns: not sampled; C: concentration greater than the concentration in the present atmosphere; pptv: parts per trillion by volume, where 1 pptv signifies a ratio of 1×10^{-12}.

CFC and SF_6 samples were collected from Pukemanga and Mangaotama Streams on 18 October 2002 and 12 July 2004, and from Below Waterfall on 18 October 2002 (Table III). The 12 July 2004 analyses included measurements of the dissolved Ar and N_2 concentrations to give an independent measure of the recharge temperature (i.e. the temperature at which the groundwater was last in equilibrium with the atmosphere) and the excess air concentration at that time (i.e. the amount of air, if any, in excess of the equilibrium amount dissolved in the water). The atmospheric partial pressures have been calculated from the concentrations in the samples assuming a recharge temperature of 12·5 °C (mean soil temperature in the region) and absence of excess air for the 18 October 2002 samples, and using the Ar/N_2-determined values for the 12 July 2004 samples. Ages have been calculated based on the EPM, using $f = 1{\cdot}0$ for Pukemanga and Mangaotama Streams and $f = 0{\cdot}6$ for Below Waterfall.

The CFC and SF_6 ages show a consistent pattern, with CFC-11 ages oldest, CFC-12 ages next, and SF_6 ages youngest. Because CFC-11 concentrations in the atmosphere have been almost constant for the last 12–13 years (Figure 8), and CFC-12 concentrations for the last 8–9 years, they are not very effective for dating in these time ranges, and hence are given little weight in the discussion. However, SF_6 concentrations have been increasing rapidly in the atmosphere in recent years, so SF_6 should be useful for dating young waters. Figure 9b, d and f includes the SF_6 concentrations, atmospheric concentrations and simulations for several of the sites. Two samples for Pukemanga Stream fit the model (EPM($f = 1{\cdot}0$)) with MRT of 2·5 years. One sample for Below Waterfall fits the model (EPM($f = 0{\cdot}6$)) with MRT of 4·3 years. One sample from Mangaotama Stream fits the model (EPM($f = 1{\cdot}0$)) with MRT of 3·1 years. The SF_6 ages are almost independent of the value of f, i.e. the fits are very insensitive to f.

DISCUSSION

Meaning of the age results

The hydrological balance shows clearly that deep subsurface flowpaths predominate in the Pukemanga catchment. Various natural tracer methods have been used to probe the nature of the flowpaths. The mean residence times obtained by the various methods are summarized in Table IV.

Pukemanga Stream baseflow. The ^{18}O results are remarkable, in that the baseflow shows no significant variation (i.e. the ^{18}O variation is no greater than that expected from the measurement error) despite the small size of the catchment. This may be partly because the sampling period (14 months) was relatively short. However, the sampling period was long enough to cover at least one of the expected annual cycles. Apart from any modelling, the lack of variation shows that there must be a large volume of stored water and a wide range of flowpaths and water residence times in the catchment.

Modelling gives an estimated MRT of at least 4 years with the optimum model (EPM($f = 1{\cdot}0$), i.e. the EM). Previous workers have often found that the EPM (with f close to 100%) gives better fits to streamflow $\delta^{18}O$ data than the dispersion model. They derived best-fit exponential fractions f ranging from 78 to 97% (Vitvar and Balderer, 1997; McGuire *et al*., 2002; Uhlenbrook *et al*., 2002; Viville *et al*., 2006). The optimum rainfall fraction RF was 0% (i.e. adding any direct rainfall made the fit worse). This is partly expected, because samples collected during higher streamflows were excluded.

The minimum MRT of 4 years from ^{18}O is consistent with the MRT of 9 years derived from the ^{3}H measurements. The accuracy of the age estimation with ^{3}H is expected to depend mainly on the accuracy of the measurements; taking into account the measurement error gives a possible range of 6–14 years.

Table IV. Summary of mean residence times

Sample ID	EPM f	MRT (years)				
		^{18}O	^{3}H	SF_6	CFC-11	CFC-12
Pukemanga Stream (1)	1·0	≥4	9	2·5	15	7
Below Waterfall (2)	0·6	4	3	4·3	17	14
Below Poplar (3)	0·8	≥3	—	—	—	—
Mangaotama Stream	1·0	—	2	3·1	13	9

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The CFC age estimations are not expected to be particularly accurate, because CFC concentrations have not been changing much in the atmosphere in recent years (Figure 8). However, the CFC-11 (15 years) and CFC-12 (7 years) results are close to the possible ^{3}H age range. The SF_6 age observed is much shorter at 2·5 years. Of the five possible processes that could change the concentrations of SF_6 in groundwater or streamwater discussed above, two are likely to be more important (these would also affect the CFCs, but to a lesser extent). These are:

1. SF_6 can travel more rapidly through the unsaturated zone than ^{3}H because SF_6 is mainly contained in the gas phase.
2. Atmospheric SF_6 can interact with the stream after the water has emerged from the ground.

The mean residence time determined for Pukemanga catchment baseflow appears to be comparable to or somewhat longer than some reported in the literature. Using ^{3}H and ^{2}H, Maloszewski *et al.* (1983) estimated MRTs of 0·8 years and 7·5 years for upper and lower subsurface reservoirs supplying the creek draining the 18·7 km^2 Lainbach Valley in the Bavarian Alps. The lower subsurface reservoir was considered to supply the baseflow. Vitvar and Balderer (1997) reported MRTs of baseflow from an upper sub-basin (24·5 months) within the Rietholzbach basin and from the basin itself (12·5 months). Mehlhorn *et al.* (1999; Mehlhorn and Leibundgut, 1999) found an MRT of 4 years for the Brugga basin, a 39·8 km^2 subalpine catchment, a result amplified by Uhlenbrook *et al.* (2002), who determined MRTs of 28–36 months for shallow groundwater and 6–9 years for deep groundwater components in the Brugga basin stream. Burns *et al.* (2003) reported stream baseflow residence times of 1·5 and 4·5 years for nested 10 and 41 ha portions of the Panola Mountain granite catchment based on chemical weathering rates.

Within New Zealand, ^{3}H measurements have been used to estimate MRTs of 1–2 years for several headwater streams at Maimai (McGlynn *et al.*, 2003) and 2–4 months in the Upper Motueka River upstream of the confluence with the Wangapeka River (Stewart, unpublished data). At Glendhu catchment, the presence of bomb-^{3}H revealed a 27-year old water component comprising 60% of the flow of the headwater stream GH5 at the time of sampling (Stewart *et al.*, 2005). Longer catchment residence times are found where the catchment bedrock is highly porous. Ignimbrite volcanics in the Lake Taupo catchment and Mamaku ignimbrite in the Rotorua lake catchments have high porosities (up to 90%), and streams draining the areas have baseflows making up 90% of their total annual flows. The MRTs of the baseflows are 60 years or more (Morgenstern and Stewart, 2004). These long catchment residence times in areas that were developed for pastoral farming in the 1960s and 1940s indicate that the quality of streamflows and downstream lakes will be deteriorating for many years into the future.

Below Waterfall spring. The ^{18}O results again showed no significant variation in the 8 months of sampling. Modelling the variation that was observed gives a best-fit simulation with MRT = 4 years with the EPM(f = 0·6) model. The ^{3}H measurements yield an MRT of 3 years with the same model. Taking into account the ^{3}H measurement error gives a possible MRT range of 1–6 years.

The value of f used (60%) is lower than values commonly found for springs. Other workers have found optimum values in the range 81 to 95% (Vitvar and Balderer, 1997; McGuire *et al.*, 2002; Uhlenbrook *et al.*, 2002; Viville *et al.*, 2006).

The single measurement for SF_6 gave an MRT of 4·3 years, which is very comparable to the ^{18}O and ^{3}H results. Water collected from a spring is not likely to have gained SF_6 by exchange with the atmosphere in the same way that a stream might have. This suggests that the lower MRT for SF_6 from the Pukemanga Stream is due to atmospheric exchange after emergence from the ground. The CFC measurements gave longer MRTs (17 and 14 years), which do not agree with the other measurements.

The difference between the MRTs for Pukemanga Stream baseflow and Below Waterfall spring is interesting, but may be partly a result of the time of sampling as pointed out above. If the two stream ^{3}H samples collected at the same time as the spring samples are used (Table II), then the stream MRT would be 5 years, which is closer to the spring age. While it is likely that Pukemanga Stream baseflow and Below Waterfall spring draw on much the same body of water, it is considered that the stream receives water with a wider distribution of ages (both younger and older).

Below Poplar spring. The ^{18}O results showed moderate variation that could be mostly accounted for by input of an average of 10% direct rainfall/near-surface runoff. The last few samples showed larger deviations from the simulation that are attributed to larger inputs of direct rainfall. The 90% average remainder is from long-residence-time water (i.e. groundwater) within the catchment.

Ephemeral flows. The ^{18}O results for Waterfall, Poplar and SRC showed larger variations, but the simulations were only able to capture general aspects of the variations. The difficulty with lumped-parameter modelling of ephemeral flows is that steady-state conditions are assumed, and ephemeral flows are anything but steady. The objective in applying the steady-state approach is to extract average values of the parameters in order to illuminate the underlying processes, but accurate simulation is not to be expected.

Nevertheless, the processes assumed do manage to reproduce general patterns of the variations (Figure 7).

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The flows occur following rainfall, and more frequently during winter. Large portions of the flows at Waterfall and Poplar on average (88% and 79% respectively) appear to be derived from the soil and to be mobilized by temporary saturation following rainfall. The low values of $\delta^{18}O_{mean}$ (−6·52‰ and −5·52‰) show that the deep groundwater is not involved (that would have $\delta^{18}O_{mean}$ of −5·17‰). The MRTs of the subsurface water at all three features was 12 weeks. Waterfall and Poplar are within the incised gully from which the Pukemanga Stream and perennial springs originate, but their waters flow over and emerge from higher levels in the sides.

The SRC is much more dominated by the immediate rainfall (66%), and its $\delta^{18}O_{mean}$ value of −4·34‰ is the same as the weighted average of the rainfall. This site is located on the slope above the gully.

Mangaotama Stream. No ^{18}O data are available for the larger scale Mangaotama catchment, but the ^{3}H result of 2 years (or range of 1–3 years considering the measurement error) agrees with the SF_6 result of 3·1 years. The CFC ages are longer at 13 and 9 years. The water in this larger stream appears to have a shorter MRT than the Pukemanga Stream; this is an unexpected result. This may be due to more of the streamflow being derived from lower altitude and flatter portions of the catchment.

Nature of the subsurface system and conceptual model

The 9-year mean residence time and exponential fraction near 100% obtained for Pukemanga Stream baseflow in this study indicate that the water age varies widely, with a distribution peaking somewhere near zero age, and with a long tail of older ages. The deep seepage that bypasses the outlet weir is likely to have a similar age distribution and similar or older mean age. The implied subsurface water storage equivalents are 2·9 m and 4·1 m depths respectively (Table V), or a total of 7·0 m depth averaged over the catchment. If different parts of the catchment supplied these flows, then the water equivalents of each would be larger over smaller areas. It is clear that this amount of water cannot be stored in soil layers 1·5 m thick or in a small area near the wetland. The reservoir thicknesses implied are 19 m and 27 m, assuming effective porosity (i.e. specific yield) of 15%. (The latter number is quite uncertain.)

The well in the upper part of the catchment showed that the water table was at 15–20 m depth; this indicates that the unsaturated zone constitutes an important part of the water storage reservoir. The flow characteristics of the catchment, as well as the results of some earlier studies (Anderson *et al*., 1997b; Asano *et al*., 2002), indicate that flow in the unsaturated zone is predominantly vertical (at least in the upper part of the catchment). Vertical transport in the unsaturated zone will impose a considerable time delay in water following flowpaths through the unsaturated and saturated zones to the stream. With porosity of 15%, the recharge of 776 mm year^{-1} would produce an average vertical velocity of 5 m year^{-1}, indicating mean residence time of about 4 years in the unsaturated zone.

Table V. Groundwater drainage components of the Pukemanga catchment

Component	Flow (mm year^{-1})	MRT (years)	Water depth[a] (m)	Aquifer thickness[b] (m)
Stream baseflow	326	9	2·9	19
Deep seepage	450	9	4·1	27

[a] Flow times MRT.
[b] Aquifer thickness calculated assuming effective porosity of 15%.

The streamflow integrates flowpaths from all parts of the catchment (except that which bypasses the stream). Flowpaths originating in and close to the gully will reach the stream with only short delays. Flowpaths originating further away will have much longer delays in the unsaturated and saturated zones. This is believed to be the reason for the exponential fraction being near 100%. The springs, however, are fed from groundwater aquifers, and young water is more likely to be excluded (thus $f \approx 60–80\%$).

Montgomery and Dietrich (2002) studied the time lag between rainfall and streamflow response for a range of catchments drawn from the literature. They found that the lag did not depend on catchment slope, and concluded that the 'controlling timescale is that of the vertical unsaturated flow'. Lateral pressure waves in the saturated zone have been identified as a possible mechanism causing rapid water table rise and fast runoff following rainfall (Beven, 1989; Wenninger *et al*., 2004). For this catchment, it is suggested that the time lag of about 2 h between rainfall and streamflow response is due to the time required for a pressure wave to travel vertically through the unsaturated zone to the water table. Rainfall impacting on the surface (or increase in the intensity of rainfall) causes a vertical pressure wave to travel down through the unsaturated zone. The vertical velocity of such a pressure wave will be governed by the slope of the hydraulic conductivity versus water content relationship in the unsaturated zone (Bidwell, personal communication, 2005). Near the water table, the pressure wave generates sudden recharge to the saturated zone nearly simultaneously over the whole water table. This produces an immediate increase in streamflow via subsurface partial source areas (described by Montgomery and Dietrich (2002)) near the stream. Note that it is not suggested that the current rainfall recharges the water table, but that (old) unsaturated zone water near the water table is incorporated into the saturated zone by water table rise brought about by the pressure wave.

Our conception of the deep drainage process is that there is a large volume of slowly moving water in the system contained in the unsaturated and saturated zones. The clay-rich substrate has the ability to hold large amounts of water, which drains slowly through the unsaturated zone. The transport time in the unsaturated zone is estimated to be about 4 years. Although slow, drainage is

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sufficient to allow the incident rainfall (minus ET and a small proportion of surface/near-surface runoff during heavy rainfall) to reach the underlying water table. Transport in the saturated zone is more uncertain, but the dating evidence indicates additional substantial time delay before the water reaches the stream that depends on flowpath length. High hydraulic heads due to the steepness of the country and low permeability near the water table due to the clay-rich nature of the deeply weathered greywacke are likely to promote deeper penetration of water into the saturated zone. A schematic model of the various pathways with indicative mean residence times is given in Figure 10. The mean residence times given for the deep flowpaths are based on the recharge rate of 776 mm year^{-1} and porosity of 15%, giving vertical velocity of 5 m year^{-1}. Ephemeral surface/near-surface flows are indicated near the gully area.

CONCLUSIONS

Measurements of the water balance components at Pukemanga catchment have shown that deep groundwater discharge supplies more than 74% of streamflow via the wetland. In addition, since 50% of the drainage from the catchment bypasses the Pukemanga weir, more than 87% of the total catchment drainage is via groundwater flow.

Mean catchment residence times were estimated from the weekly variations in ^{18}O concentrations, and from ^{3}H, CFC and SF_6 concentrations, for sites ranging from Pukemanga Stream baseflow, through perennial seepage (Below Waterfall spring), to ephemeral flows after rainfall. Input functions for ^{18}O and ^{3}H to the deep subsurface water stores were determined from measured rainfall data, adjusted for immediate runoff and ET. Baseflow and perennial seepage had mean residence times of 4 years or greater, whereas the ephemeral flows had varying amounts of short-residence-time soil water and immediate rainfall. SiO_2 concentrations were used to identify flowpaths, with rainfall/surface runoff having concentrations of 0–5 mg l^{-1} and deep groundwater seepage having 20–25 mg l^{-1}.

The mean residence time of the Pukemanga Stream baseflow was 9 years from the ^{3}H measurements, with a wide distribution of ages peaking at close to zero years and a long tail of older water. CFC dating was not effective in this time range. The SF_6 MRT was 2·5 years, but was thought to have been affected by exchange with atmospheric SF_6. The perennial seepage had a concordant MRT of 3–4 years (with ^{18}O, ^{3}H and SF_6). The adjacent 259 ha Mangaotama catchment had a mean baseflow residence time of 2 years from ^{3}H.

A conceptual model of the deep drainage process is given that shows flowpaths and indicative residence times based on the hydrometric and dating results. The unsaturated and saturated zones hold large volumes of slowly moving water that give long residence times within the catchment. The unsaturated zone is considered to impose a delay of about 4 years on the water moving vertically through it, but to rapidly transmit rainfall-induced pressure fluctuations that contribute to fast stormflow response following rainfall (along with ephemeral surface/near-surface flows). Transport in the saturated zone increases water drainage times depending on flowpath lengths. Subsurface water equivalents are estimated to be 2·9 m for drainage at the weir and 4·1 m for drainage bypassing the weir, giving a total of 7 m.

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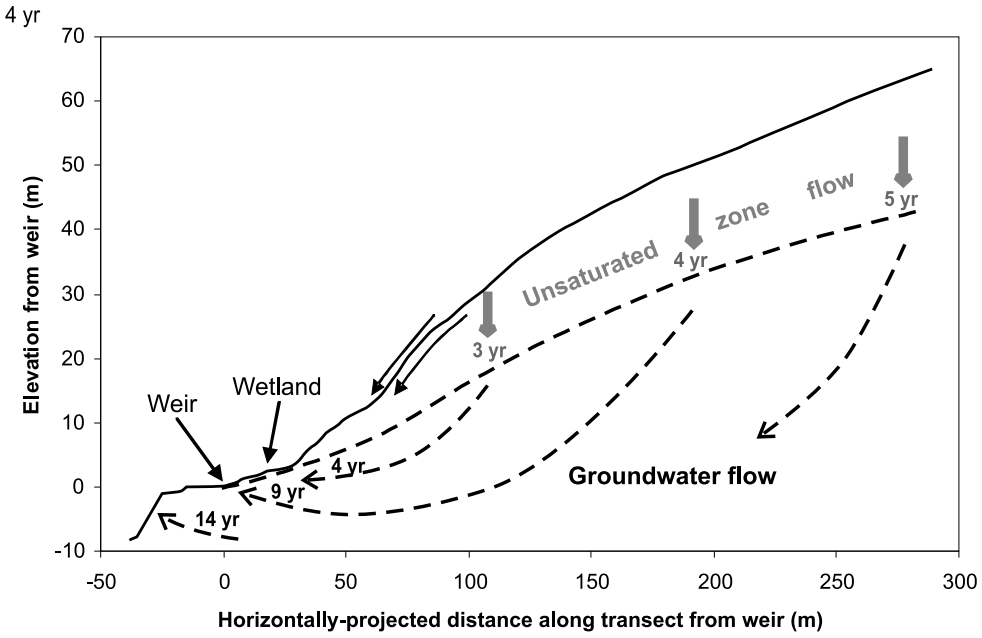

Figure 10. Conceptual model of water flowpaths in the Pukemanga catchment

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