Image analysis was used at the scale of the hillslope plots to quantify surface characteristics including the tortuosity of inter-hummock channels from a particle tracking procedure. Image analysis was also used at the scale of soil thin sections for analysis of porous media properties that control subsurface flow rates.

The relatively low cost of producing the chloride-sensing micro electrodes enabled the deployment of a large number of them on the hillslopes. Since they provide continuous measurements, water sampling and subsequent analysis was not necessary. During the study periods, neither the reference nor the sensing electrodes required maintenance, and by the end of the study, the electrodes showed very little drift from their initial calibrations. Under certain conditions however, the electrodes did not perform well. For example, erroneous readings occurred when the electrodes were exposed to sunlight (since their tips are coated with silver chloride), frozen into the ground, or when the soil around the sensor fell below saturation for an extended period (hours). The limited occurrence of these conditions resulted in only minimal disruption to the tracer monitoring programme.

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A combined tracer–hydrometric approach to assess the effect of catchment scale on water flow path, source and age

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Abstract The scaling of water source contributions to channel streamflow is not well understood. We collected rainfall–runoff data along with streamfl and rainfall 818O information for four nested catchments in the Main watershed, South Island, New Zealand. The catchments ranged in size from 0.1 to 920 ha. Water source contributions and water age spectra were assessed for an 87 mm rainfall event using a new model by Stewart & Rowe (1998). We found that (a) the source contributions of new water increased v-increasing catchment area for catchment scales above the representative elementary area of the system, and (b) water age (flow time) showed a larger increase with increasing catchment size (beyond the zero-order catchment scale), and peak water fraction increased linearly with catchment area. This work has implications for how we model stream water chemistry since it is affected by the mixing of different catchment end members and contaminant in the subsurface.

INTRODUCTION
The effect of catchment scale on water age and water source is poorly understood. Although there has been considerable recent interest in the scaling of hydrologic behaviour, much of the work to date has been highly theoretical (Bloschl & Svapalal, 1997). Few process studies have addressed this issue and Bonell (1998) notes that it is one of the major challenges in runoff generation research. One of the best developed for process-level exploration of water age and water sources scaling isotope tracing (Kendall & McDonnell, 1998). Whilst isotopic tracing has been used in many studies for determining geographic and time sources of runoff at specie catchment scales (Buttle, 1994; many others), few studies have used isotopic tracers a means to assess scale-dependency in runoff formation.

In this paper we present some of the first data that explore the relationship between catchment size and water source contributions and age spectra of surface waters. We base our source water and age estimates on a new model of Stewart & Rowe (1998) that overcomes many of the limitations of the traditional two-component hydrogra.
separation approach by using a simple transfer function to determine water source and age from temporal variations in rainfall $\delta^18$O. We test two null hypotheses:

1. source contributions of new water do not change with increasing catchment area, and
2. the distribution and age of source waters do not change with increasing catchment area.

We hope that this short paper, and its test of basic scale-related research hypotheses, will be a useful first step in the mechanistic assessment of scale issues on runoff processes.

WATER SOURCE AND AGE SPECTRA MODEL

Stewart & Rowe (1999) developed an alternative to the standard two-component mixing model that combines rainwater with different flow paths/times through the catchment. The model does two things: first it allows one to quantify the old/new water ratio through the event and second, it provides a residence time distribution, or age spectrum, for new waters through the event. Assuming that the old water term is constant, the stream concentration is determined by:

$$\delta_S(t) = x(t) \delta_s(t) + [1 - x(t)] \delta_O(t)$$

where $x(t)$ is the fraction of storm water in the stream, i.e. flows are:

$$Q_S(t) = x(t) \, Q(t)$$
$$Q_O(t) = [1 - x(t)] \, Q(t)$$

where $Q$ is discharge, $\delta$ is oxygen-18 concentration and the subscripts $S, N$ and $O$ designate stream, new and old waters respectively. In general, these quantities can vary during the event. Measurements of $\delta_S(t)$ and $Q(t)$ are made at intervals during the event.

The simulated $\delta_S(t)$ is matched to the observed stream concentrations by finding the parameters of the mixing model and the new water fraction ($x$) that produce the best fit between simulated and observed stream data. It should be noted that unlike the traditional two-component separation, the Stewart & Rowe (1999) model takes advantage of the varying rainfall $\delta^18$O composition in the model solution—an event analogy to the time series approach of Stewart & McDonnell (1991). Variation of $\delta_O$ also occurs in time and likely in space, but as Stewart & Rowe (1999) argue, it is much less than that observed in the rainfall, especially at individual sites. Thus it is neglected in the new model.

The age spectra part of the model is essentially a transfer function based on the assumption of steady-state well mixed flow. This approach was outlined by Zuber (1986) and Kreft & Zuber (1978) and used widely in the hydrological literature for assessing residence times of soil water (Stewart & McDonnell, 1991) and groundwater (Maloszewski et al., 1983). To model rainwater $\delta^18$O concentrations in the stream ($\delta_S(t)$), the convolution integral is used:

$$\delta_S(t) = \int_0^{\infty} g(t') \, \delta_S(t - t') \, dt'$$

where $\delta_S(t)$ is the $\delta^18$O concentration of the rainfall at any time and $g(t)$ is the system response function, which specifies the transit time distribution of water within the system (Zuber, 1986). Calendar time is represented by $t$ and the integration is carried out over the transit times ($t'$) (Stewart & Rowe, 1999). Stewart & McDonnell (1991) found that a dispersion model led to the best system response function that would reproduce the most reasonable residence time parameters based on physical measurements in the Maimai watershed. We use the system response function given by:

$$g(t) = (16 \pi Dp)^{1/2} (v/\alpha)^{1/2} \exp[-(1 - t/\alpha)^2/(4Dp\alpha)]$$

where $t$ is the time increment, $\alpha$ is the mean residence time of the system and $Dp$ is the dispersion parameter described by Stewart & McDonnell (1991), $Dp = D/v\alpha$, where $D$ is the dispersion coefficient (square metres per second), $v$ is the mean travel velocity of water in the system (metres per second) and $\alpha$ is the length of the line of flow (metres). This dispersion model is flexible because it permits a wide variation of residence time distributions. Consequently, Zuber (1986) found it to be an effective simulator for a wide variety of hydrological systems. The only real difference here, is that we are applying this model on an event time scale; taking advantage of the very large cosine function that is the rainfall $\delta^18$O. The weighting of input data in the simulations and its quality measures for the model are the same as those reported in Stewart & McDonnell (1991) and not repeated here.

CATCHMENT CHARACTERISTICS AND METHODS

Hydrological research at Maimai, South Island, New Zealand has been ongoing since 1974. The work has been directed mainly at the impacts of land-use change (Rowe et al., 1994). However, many studies have focused on subsurface stormflow processes, old water ratios in small subcatchments (Pearce et al., 1986), the role of preferential flow and water mixing in the subsurface soil layers. Here, we present the first multi-scaling data from the site, beyond the small first and second order catchment scale. We present data for four subcatchments: T8 (0.1 ha), M8 (3.8 ha), PL14 (80 ha) and MAW (920 ha) (Fig. 1).

The nested catchments receive 2500 mm of rainfall per year with little seasonal variation. Slopes are short (<100 m) and steep (average 35°) in the headwater sections and grade abruptly to flat valley bottom zones. Soils are shallow (25–130 cm deep, average 60 cm) podzolized yellow brown earths and have a litter and humus layer averaging 17 cm thick. These soils are formed on early Pleistocene Old Man gravels, a moderately weathered, firmly compacted conglomerate that is poorly to moderately permeable.

We sampled storm hydrographs for the four catchment outlets described in Table 1 for an 87 mm rainfall event in February 1995. Rainfall was collected with a standard collector and streamflow was sampled manually at irregular intervals through the storm. No pre-event soil water was available for this event. The pre-storm baseflow composition was used as the pre-event end member for application of the Stewart & Rowe (1999) model. Additional longitudinal sampling of the main stream channel baseflow was made to determine the field-based representative elementary area of the
RESULTS AND DISCUSSION

Event summary

Time series of flow and isotopic composition of rain and streamflow are shown in Fig. 2. Eighty-seven millimetres of rain fell within a 24-h period on 1 February 1995. Rain $\delta^{18}O$ followed a monotonic decline through the first 12 h of the event and then progressive enrichment through the second half of the storm. Each of the subcatchments showed similar patterns of stream $\delta^{18}O$ deflection. The sensitivity of the stream response is indicative of some new water input to the channel—the smaller subcatchment showed much more response to within-storm oscillations. Hydrograph shapes, time-to-peak and recession limb characteristics were remarkably similar across catchment scales. These findings are consistent with early work at the site by Mosley (1979) who commented "...the most striking feature of the hydrographs is the close coincidence of peaks (Mosley, 1979, p. 798).

New water scaling

The Stewart & Rowe (1999) model was able to simulate the time series of stream $\delta^{18}O$ well (Fig. 2(a)–(d)). New water contributions were calculated based on equation (4). Table 2 shows that the new water fraction was 30% for T8, 10% for M8, 9% for PL14 and 17% for MAW. T8 new water percentage was very high. McDonnell et al. (1998) showed that for a range of trough sections, new water varied across the trench face from about 3 to 40%. Similarly, Sklash et al. (1986) showed new water percentage variation at the hillslope trench scale at Maimai ranged from 1 to 25%. These data underscore the variation encountered at individual hillslope segments at scales less than the REA. If one discounts the T8 value because it falls below the REA, the data in our study show a weak trend of increasing new water percentages with increasing catchment area (Table 1). Such trends can be attributed to increased amounts of saturation overland flow from valley bottom zones. Topographic data appear to corroborate this—valley bottom % (computed from a 10 m digital elevation model (DEM) where % slope < 5°) was 3% for both M8 (Fig. 2(b)) and PL14 (Fig. 2(c)) and 14% for MAW (Fig. 2(d)). This increase in valley bottom zone at the 920 ha catchment scale (MAW) reflects the emergence of wide valley-bottom flats beyond the second-order catchment scale. This feature is readily observable on the DEM and in the field. This effect appears to be closely related to surface saturation propensity, whereby the valley bottom wet area may partition new water inputs directly into the stream. At the hillslope scale (T8), no surface saturation occurs (Woods & Rowe, 1996). The magnitude of new water increases from M8 to MAW is in keeping with the change in flat zones accumulated with increasing catchment area. PL14 and M8 have essentially the same new water percentages and the same percentages of flat valley-bottom zones.

Event water age spectra

Event water age spectra are plotted as insets in Fig. 2(a)–(d). A frequency distribution model for a hypothetical water age spectrum is plotted in Fig. 3 and shows the key
Table 2: New water scaling relationships for the four subcatchments

<table>
<thead>
<tr>
<th>Catchment</th>
<th>Initial δ¹⁸O (%)</th>
<th>Final δ¹⁸O (%)</th>
<th>Change time (h)</th>
<th>Fraction (%)</th>
<th>New water peak time (h)</th>
<th>Peak height (Fp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T8</td>
<td>-4.67</td>
<td>-3.00</td>
<td>8</td>
<td>30</td>
<td>3.4</td>
<td>0.16</td>
</tr>
<tr>
<td>MR</td>
<td>-5.26</td>
<td>-4.84</td>
<td>6</td>
<td>10</td>
<td>1.1</td>
<td>0.30</td>
</tr>
<tr>
<td>PL14</td>
<td>-5.85</td>
<td>-5.10</td>
<td>9</td>
<td>9</td>
<td>2.6</td>
<td>0.27</td>
</tr>
<tr>
<td>MAW</td>
<td>-5.52</td>
<td>-5.00</td>
<td>20</td>
<td>17</td>
<td>2.5</td>
<td>0.12</td>
</tr>
</tbody>
</table>

* The T8 site was ephemeral and did not flow prior to the rainfall event and ceased flowing well before the cessation of the stream recession in MR, PL14 and MAW.

The peak water fraction (Fp) is the “highest frequency” residence time (i.e., the residence time which applies to the largest fraction of water) or the mode (Fig. 3). The distribution for a system where there is no mixing is a delta-function, so the higher the peak the less mixing there is. The T8 peak value of 0.3 in Fig. 2(a) is quite high and suggests that the water is delivered predominately by a single type of pathway (we hypothesize preferential flow based on our earlier published work—see McDonnell, 1990). As this water mixes with matrix water (or water with longer residence times) the peak will become lower. The trend for sites MR to MAW to lower Fp values at larger scales seems logical. Fp varied systematically with catchment area: 0.3 for M8, 0.27 for PL14 to 0.12 for MAW.

The time axis on the age spectrum in Fig. 3 is the residence time of “young” water or “new” water—i.e., water which has a varying isotope concentration. Old water (baseflow) is assumed to have a constant isotopic composition on the time scale of the rainfall event in order to distinguish it from the young water. We use the term young water here because some of it must originate before the rainfall event starts according.
to equations (4) and (5). The age spectrum time scale is drawn backwards but with the same time divisions as the calendar time axes of the plots in Fig. 2, in order to show the fraction of new water from any previous calendar times which is present at the origin (intersection of axes) of the age spectrum. The actual age spectrum/distribution of water at any calendar time point can be seen by placing the origin of the age spectrum at that point. The age spectra in Fig. 2(a)-(d) are shown only for 0–12 h because after 12 h the fraction is quite small. The shape of the age spectra are meaningful in comparison with the shapes of well-mixed simple models (e.g. a piston-flow model) and the single delayed spike (Stewart & McDonnell, 1991). A completely mixed model would have an exponential shape with the highest fraction with zero residence time. Each of the catchments show a partially mixed model (Fig. 2(a)-(d)), with the most peaked shape (7B) showing that most of the water is delivered via a single (average) pathway and the least peaked shape (MAW) showing a wide range of residence times and pathways. The long tail for the MAW distribution exceeding 12 h indicates that some of the water is delayed for longer in soil with either great depth or lower hydraulic conductivity. It is important to note for each of the plots that the old water store is about 5–10 times greater than the young water input (based on data presented in Pearce et al., 1986).

CONCLUSIONS AND FUTURE RESEARCH DIRECTIONS

We can address the hypotheses described at the beginning of this paper: (1) the source contributions of new water do appear to increase with increasing catchment area. This pattern however is only consistent for catchment scales above the REA. The increase in new water with catchment scale was not linear, but appears to follow closely the increase in measured valley-bottom flat zones extracted from the DEM, and (2) water age (flow time) showed some increase with increasing catchment size (beyond the 18 hillslope). Peak water fraction increased with catchment area. Similarly, the age distribution function showed patterns consistent with the notion of increased amounts of older waters at increased catchment scales. The largest third-order catchment (MAW) was the only site to show amounts of water in the age spectra greater than 12 h.

The results from this study are preliminary. To date, only one storm has been analysed. Clearly, additional storms need to be examined to explore such effects as antecedent wetness, storm size, intensity and duration. It remains uncertain whether or not scaling behaviour exhibited in conservative isotopic tracers is useful for addressing water quality parameters. One area of considerable research need is the examination of riparian zone volume, as contrasted with the areal measure used in this study. The use of multiple tracers may prove useful in this context.

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