HYDROLOGICAL PROCESSES
Hydrol. Process. **19**, 2291–2307 (2005)

Stable isotope tracers as diagnostic tools in upscaling flow path understanding and residence time estimates in a mountainous mesoscale catchment

P. Rodgers,[1]* C. Soulsby[1] and S. Waldron[2]

[1] *Department of Geography and Environment, University of Aberdeen, Elphinstone Road, Aberdeen AB24 3UF, UK*
[2] *Scottish Universities Environmental Research Centre, Scottish Enterprise Technology Park, East Kilbride, Glasgow G75 OQF, UK*

Abstract:

δ^{18}O measurements of precipitation and stream waters were used as a natural tracer to investigate hydrological pathways and residence times in the River Feshie, a complex mesoscale (231 km^2) catchment in the Cairngorm Mountains of Scotland. Precipitation δ^{18}O exhibited strong seasonal variation over the 2001–02 hydrological year, ranging from $-6{\cdot}9$‰ in the summer, to $-12{\cdot}0$‰ during winter snowfalls (mean δ^{18}O $-9{\cdot}59$‰). Although damped, this seasonality was reflected in stream water outputs at seven sampling sites in the catchment, allowing δ^{18}O variations to be used to infer hydrological source areas. Thus, stream water δ^{18}O was generally controlled by a seasonally variable storm flow end member, mixing with groundwater of more constant isotopic composition. Periodic regression analysis allowed the differences in this mixing process between monitoring subcatchments to be assessed more quantitatively to provide a preliminary estimate of mean stream water residence time. This demonstrated the importance of responsive hydrological pathways associated with peat and shallow alpine soils in the headwater subcatchments in producing seasonally variable runoff with short mean residence times (33–113 days). In contrast, other tributaries with more freely draining soils and larger groundwater storage in shallow aquifers provided more effective mixing of variable precipitation inputs, resulting in longer residence time estimates (178–445 days). The mean residence time of runoff leaving the Feshie catchment reflected an integration of these contrasting influences (110–200 days). These insights from δ^{18}O measurements extend the hydrological understanding of the Feshie catchment gained from other hydrochemical tracers, and demonstrate the utility of isotope tracers in investigating hydrological processes at the mesoscale. Copyright © 2005 John Wiley & Sons, Ltd.

KEY WORDS δ^{18}O; isotope; tracers; hydrology; mesoscale; residence times; runoff processes; Cairngorms; Scotland

INTRODUCTION

The hydrological research community is under increasing pressure to provide process understanding and quantitative knowledge at scales where water resource decision-making occurs (Healy, 2001; Naiman *et al.*, 2001; Soulsby *et al.*, 2003). Over the past two decades, interpretation of changes in the stable oxygen (^{18}O/^{16}O) and hydrogen (^{2}H/^{1}H) isotopic signatures of catchment waters have proved to be useful as tracers for identifying hydrological source areas/flow paths under different flow conditions and estimating catchment residence times (Sklash, 1990; Genereux and Hooper, 1998; Burns, 2002). To date, the majority of studies have focused on storm event sampling in relatively small (<10 km^2) catchments (Buttle, 1994). However, the use of isotope tracers to upscale flow path understanding in mesoscale (*c.* 10^2–10^3 km^2) catchments is less common (e.g. Skalsh *et al.*, 1976; Turner and Barnes, 1998; Frederickson and Criss, 1999; Uhlenbrook *et al.*, 2002), and the few investigations of scale on mean residence time of runoff have been restricted to small catchments (Brown *et al.*, 1999; McDonnell *et al.*, 1999; McGlynn *et al.*, 2003). This reflects the logistical

---

* Correspondence to: P. Rodgers, SEPA, Rivers House, Irongray Road, Dumfries DG2 OJE, UK. E-mail: paul.rodgers@sepa.org.uk

Received 18 January 2004
Accepted 25 May 2004

difficulties of sampling in larger watersheds, and also the potential loss of isotopic tracer signatures at larger spatial and temporal scales (Buttle, 1998).

This paper reports the use of $\delta^{18}O$ measurements as a natural tracer to provide insight into hydrological pathways in the mesoscale (231 km^2) Feshie catchment in the Cairngorm Mountains, Scotland. Extensive hydrological and hydrochemical research in a small 10 km^2 headwater subcatchment of the Feshie, the Allt a' Mharcaidh, has effectively conceptualized catchment hydrological functioning (e.g. Soulsby and Dunn, 2003), and allowed for the preliminary estimates of mean residence times in its main hydrological stores using $\delta^{18}O$ measurements (Soulsby *et al*., 2000). This provided the basis for more recent efforts to upscale hydrological understanding to the larger Feshie catchment, as part of the NERC-funded CHASM (Catchment Hydrology And Sustainable Management) initiative. The use of $\delta^{18}O$ measurements at this scale is expected to complement this recent hydrochemical tracer work (Rodgers *et al*., 2004a,b; Soulsby *et al*., 2004). The objectives of this paper are therefore to: (i) characterize spatial and temporal variation in $\delta^{18}O$ of catchment precipitation and stream waters; (ii) establish the main hydrological controls on stream water $\delta^{18}O$ using insights from other geochemical tracers; and (iii) produce preliminary estimates of the mean residence time of runoff in the catchment and its major subcatchments.

STUDY AREA

The River Feshie drains 231 km^2 of the western Cairngorm Mountains in Scotland, which includes some of the highest mountainous terrain in the UK with a mean elevation of 617 m and an altitudinal range of 230–1115 m (Figure 1a, Table I). The catchment is notable for its flashy, snowmelt-influenced flow regime (Ferguson, 1984) and geomorphological features of international conservation importance (Werrity and McEwan, 1993). The highest areas are associated with the main massif of Cairngorm granite that was intruded some 435–390 million years ago (Figure 1b). Surrounding these are Moinian schists that underlie most of the catchment and were metamorphosized around 550–450 million years ago (Brown and Clapperton, 2002). Dykes and sills of diorite and felsite (intermediate igneous rocks) are also present, notably in the headwaters of the Allt Chomraig and Upper Feshie. The Feshie has two main headwater subcatchments, the Eidart and the Upper Feshie. The River Eidart (30 km^2) drains the high altitude granite (Figure 1a), flowing south through a steep valley before widening out in its lower reaches with a range of glacial and fluvio-glacial landforms. The Eidart subcatchment is predominantly covered by shallow alpine soils, though it includes an extensive high altitude peat bog at 900 m (Figure 1c). The Upper Feshie drains a more subdued, lower altitude catchment (mean altitude 686 m), underlain by schists, with a dominant coverage of blanket peat soils (65%: Figure 1b and c).

Downstream of the Eidart–Upper Feshie confluence, the river becomes incised as it flows through the glaciated trough of Glen Feshie. Just upstream of the Lorgaidh, alluvial deposits (in places >10 m in depth) become more extensive (Figure 1b), as the Feshie flows north through a braided section (Rodgers *et al*., 2004a). Downstream of the braids, the valley widens out, and extensive alluvial and fluvio-glacial terrace deposits cover the valley floor (Werritty and Ferguson, 1980). The major west bank tributary, the Allt Chomraig (45 km^2), enters the Feshie, whilst five smaller east bank tributaries drain the main area of granite and enter the river between the braids and Feshie Bridge (Figure 1a). The Allt Chomraig is relatively low-lying (mean altitude 490 m) and has extensive peat soils covering its upper catchment, though the lower catchment has substantial coverage of alluvial soils (Figure 1c). The east bank tributaries, such as the Allt a' Mharcaidh, are much higher and alpine soils (often overlying deep, free-draining periglacial parent materials) and peaty podzols (approximately 1 m deep) predominate.

The peats and peaty podzol soils are highly responsive in generating large volumes of storm runoff via overland flow and shallow subsurface storm flow (Soulsby *et al*., 2000). The thin alpine soils and areas of bare bedrock are responsive during rainfall and snowmelt events (Soulsby *et al*., 2004). Groundwater flow systems in the catchment are quite shallow (<10 m), but significant. The largest aquifers are found in alluvium in

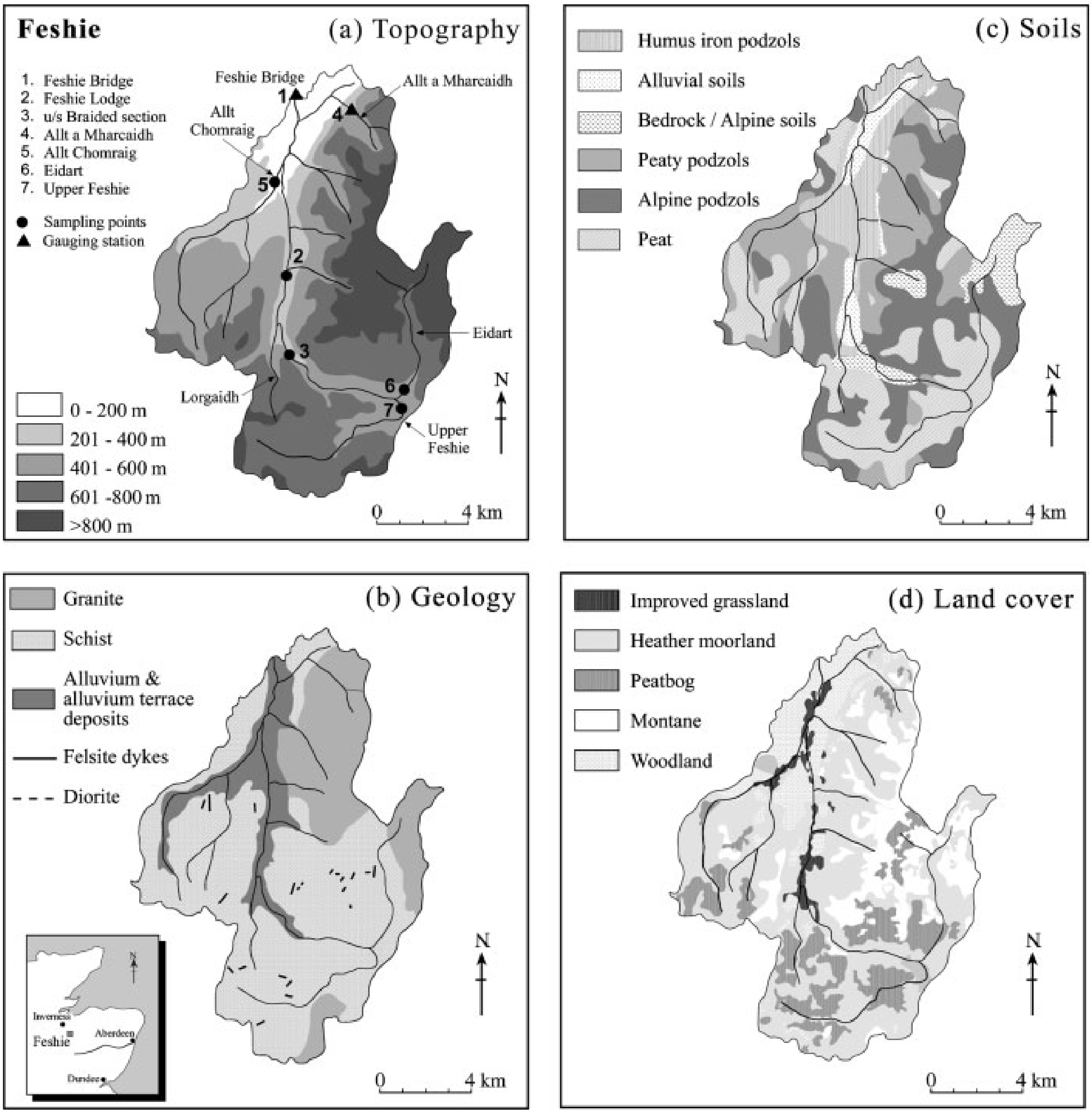

Figure 1. Catchment maps of the Feshie, showing (a) topography and monitoring network, (b) geology, (c) soil coverage and (d) land cover

the lower Feshie valley (Rodgers *et al*., 2002), though other glacial and periglacial drift deposits can provide important base flow contributions, even at altitudes above 800 m (Soulsby *et al*., 1998, 1999). In addition, flow in shallow fracture systems is probably important in areas of exposed granite and schists (Shand *et al*., 2001).

Vegetation cover in the Feshie is mainly characterized by alpine heath in the mountainous headwaters above 800 m, heather (*Calluna)* moorland covering the steeper slopes, with boreal blanket bog vegetation covering the peat soils (Figure 1d). Forest is restricted to small areas of native Scots pine (*Pinus sylvestris*) in the middle reaches of the catchment and commercial forestry in its lowest areas. Almost the entire catchment lies within the Cairngorms National Nature Reserve (NNR), so conservation is a major management priority (Matthew, 2002).

Table I. Characteristics of the Feshie catchment

	Topography		Geology		Soil subgroups				
	Area (km^2)	Mean altitude (m)	Granite (%)	Schist (%)	Peat (%)	Peaty Podzol/ Podzol (%)	Alpine (%)	Shallow alpine/ rock (%)	Alluvial (%)
1. Feshie Bridge	230·7	617	27·0	60·5	32·6	21·4	8·2	28·2	8·5
2. Allt Chomraig	44·9	490	0	77·9	34·7	38·1	2·1	14·7	10·4
3. Feshie Lodge	114·6	715	5	81·5	41·1	9·2	2·8	45·5	1·0
4. Upstream Braids	88·1	743	17·6	80·2	45·4	7·7	2·8	44·1	0
5. Eidart	29·9	865	43	57	27·6	9·6	3·4	59·5	0
6. Upper Feshie	32·3	686	9	91	65·6	10·1	4·5	19·7	0
7. Allt a' Mharcaidh	10·0	699	100	0	24·9	35·3	30·2	8·4	1·1

Mean annual precipitation for the catchment is estimated at 1600 mm, mainly derived from the prevailing westerly weather systems, with snow probably accounting for some 30% of this (Soulsby *et al.*, 1997). The mean flow at Feshie Bridge is 8·01 $m^3\ s^{-1}$, with the long-term (10-year) Q_{95} at 1·71 $m^3\ s^{-1}$ and the Q_{10} at 16·28 $m^3\ s^{-1}$. Mean monthly temperatures at 575 m vary between 1·2 °C in February and 10·3 °C in July. Evapotranspiration rates vary between *c*. 300–400 mm, being highest in the lower, forested parts of the catchment (Haria and Price, 2000; Dunn *et al.*, 2003).

METHODS

Fortnightly samples of stream water for the 2001–02 hydrological year were collected at seven sites in the catchment, with four sites corresponding to major tributaries (Upper Feshie, Eidart, Allt Chomraig and Allt a' Mharcaidh) and three sites on the main stem of the Feshie (upstream and downstream of the braids and the catchment outlet at Feshie Bridge) (Figure 1a). A river flow gauging station was also established at each sampling site. Precipitation was sampled at the same fortnightly intervals from a rain collector located in the Allt a' Mharcaidh subcatchment at an altitude of 350 m.

Fortnightly sampling was a compromise between characterizing isotopic variation during the hydrological year, and the logistical difficulties associated with access, particularly during winter, in a mountainous catchment with road access only available to Feshie Lodge. Samples were collected and stored according to standard procedures (cf. Clark and Fritz, 1997) and analysed at the Scottish Universities Environment Research Centre (SUERC) using a gas source isotope ratio mass spectrometer. Ratios of $^{18}O/^{16}O$ are expressed in delta units, $\delta^{18}O$ (‰, parts per mille) defined in relation to V-SMOW (Vienna standard mean ocean water). The analytical precision was ±0·1‰. Stream water samples were also analysed for Gran alkalinity as described by Soulsby *et al.* (2004).

Seasonal trends in $\delta^{18}O$ were modelled using periodic regression analysis to fit seasonal sine wave curves to annual $\delta^{18}O$ variations in precipitation and stream water (cf. DeWalle *et al.*, 1997), defined as:

$$\delta^{18}O = X + A[\cos(ct - \theta)] \tag{1}$$

where $\delta^{18}O$ is the modelled $\delta^{18}O$, X is the mean annual measured $\delta^{18}O$, A is the measured $\delta^{18}O$ annual amplitude, c is the radial frequency of annual fluctuations (0·017 214 rad d^{-1}), t is the time in days after the start of the sampling period (01/10/01) and θ is the phase lag or time of the annual peak $\delta^{18}O$ in radians.

To estimate mean residence times from these regression models, the commonly used exponential model approach was used in which precipitation inputs are assumed to mix rapidly with resident water in the major soil water and groundwater catchment stores (Maloszewski *et al.*, 1983; Stewart and McDonnell, 1991). This assumption is reasonable if soil water and groundwater are viewed as unconfined aquifers, allowing the decrease in amplitude of stream water outputs relative to precipitation inputs to be used as the basis for estimating residence time (Unnikrishna *et al.*, 1995). The seasonal sine wave models fitted to input and output water δ^{18}O variations were used and an exponential distribution of transit times was assumed. The mean residence time (T) of water leaving the system is calculated as:

$$T = c^{-1}[(Az2/Az1)^{-2} - 1]^{0\cdot5} \tag{2}$$

where $Az1$ is the amplitude of precipitation, $Az2$ is the amplitude of the stream water outputs and c is the radial frequency of annual fluctuations as defined in model (1). Given the relatively simple nature of this model, the size and complexity of the Feshie catchment and the fortnightly resolution of precipitation inputs in particular, the results can only be taken as preliminary estimates of mean residence times. Nonetheless, studies elsewhere (Maloszewski and Zuber, 1993) and earlier work in the Allt a' Mharcaidh (Soulsby *et al.*, 2000) have suggested that the model should be useful for such a first approximation.

RESULTS

Seasonal variation in precipitation inputs

Precipitation inputs to the catchment show distinct seasonal variation, with winter precipitation (November to April: mean −10·74‰) more ^{18}O-depleted than summer rainfall (May to October: mean −8·67‰) (Table II). This follows the anticipated, roughly sinusoidal, seasonal pattern of precipitation δ^{18}O, whereby winter months are dominated by colder northerly and easterly air masses that bring precipitation which, due to low temperatures, is more ^{18}O-depleted (Figure 2). In contrast, summer weather systems are predominantly southwesterly in origin, resulting in more ^{18}O-enriched inputs. Despite this seasonal pattern, substantial variation is observed in the δ^{18}O ranges for both summer (−10·3‰ to −6·9‰) and winter (−12·0‰ to −8·2‰) samples, with ^{18}O-depleted precipitation also occurring in summer. This variation reflects the diverse range of source areas for weather systems that the Cairngorms can experience within individual seasons. In particular, although some summer samples exhibit the enriched δ^{18}O signatures expected during summer months (e.g. −6·9‰: 09/08/02), there are notable periods when depleted rainfall dominated (e.g. −10·3‰: 26/07/02). This can be attributed to the particularly wet and unsettled conditions that characterized the summer of 2002, which therefore resulted in a less well-defined seasonal cycle of precipitation δ^{18}O compared with drier, warmer and more settled summers (cf. Soulsby *et al.*, 2000).

Table II. Mean, range and standard deviation of δ^{18}O (‰) in the Feshie catchment

	Mean	Minimum	Maximum	Standard deviation
Inputs:				
Winter precipitation	−10·74	−12·0	−8·2	1·40
Summer precipitation	−8·67	−10·3	−6·9	1·46
Stream water:				
1. Feshie Bridge	−9·59	−10·7	−8·3	0·58
2. Allt Chomraig	−9·34	−10·2	−8·3	0·39
3. Feshie Lodge	−9·55	−11·0	−8·4	0·66
4. Upstream Braids	−9·53	−11·3	−7·8	0·88
5. Eidart	−9·74	−11·3	−8·0	0·80
6. Upper Feshie	−9·45	−11·3	−7·6	0·86
7. Allt a' Mharcaidh	−9·96	−10·9	−9·1	0·34

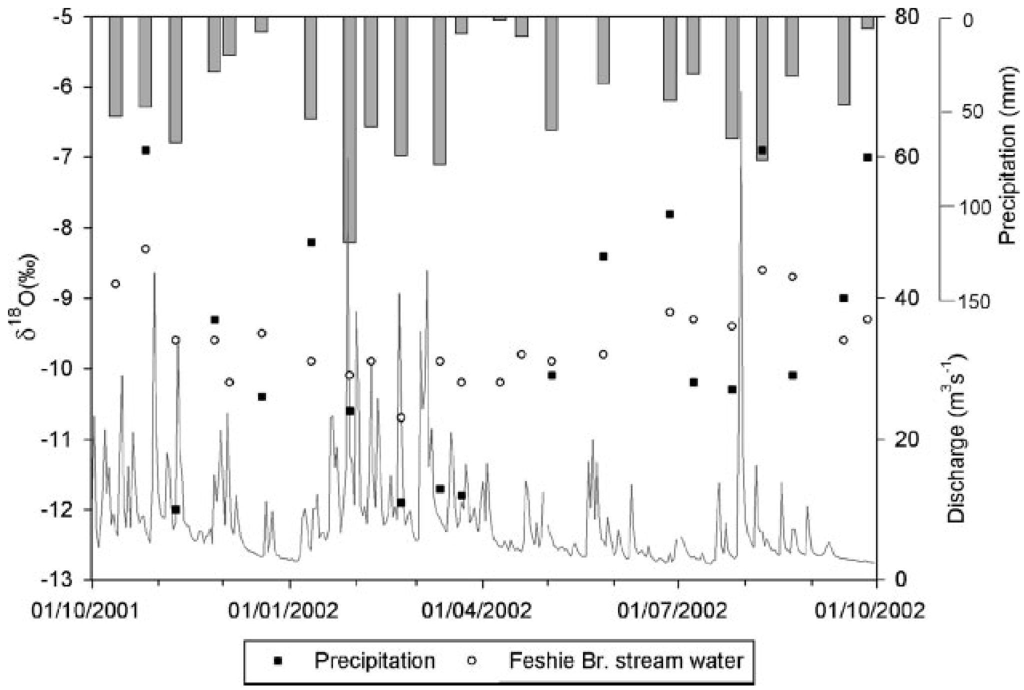

Figure 2. Temporal variation in precipitation and stream water δ^{18}O, annual run-off and rainfall for the Feshie catchment (01/10/01–30/09/02)

The fortnightly sampled pattern of precipitation δ^{18}O may underestimate the variation over shorter (e.g. daily or weekly) time scales (Darling and Talbot, 2003), but the main seasonal differences are nonetheless reasonably well defined. This approach also eliminates the need to use volume-weighted δ^{18}O measurements as the volume effect and intra-storm variability is generally integrated out over this longer time scale. Furthermore, the overall range and seasonal pattern observed during the sampling period compares closely with the overall variability observed in a 3-year precipitation δ^{18}O record for the Feshie catchment collected between 1995 and 1998 (Soulsby *et al.*, 2000).

Stream water outputs

There are notable differences between mean stream water δ^{18}O for the sites sampled in the Feshie during the hydrological study year (Table II). Stream water δ^{18}O from the main stem site upstream of the braids, and the Eidart and Upper Feshie headwater subcatchments, are all relatively similar, particularly the convergence of the minimum stream water δ^{18}O levels (−11·3‰) observed for the highest flow sampled. However, maximum stream water δ^{18}O upstream of the braids is intermediate between the Eidart and Upper Feshie subcatchments (−7·8‰ cf. −8·0‰ and −7·6‰, respectively).

As the Feshie flows through its main braided section, δ^{18}O ranges become increasingly damped with distance downstream, with a decrease at Feshie Lodge (2·6‰ cf. 3·5‰ upstream), followed by further reduction at the catchment outlet at Feshie Bridge (2·4‰). In contrast, the tributaries of the Allt Chomraig and the Allt a' Mharcaidh have the narrowest δ^{18}O ranges (1·9‰ and 1·8‰, respectively; Table II). Subcatchment mean stream water δ^{18}O also show spatial variation (Table II). The Allt a' Mharcaidh is most ^{18}O-depleted (−9·96‰), and closest in composition to more ^{18}O-depleted winter precipitation (mean −10·74‰), suggesting that greater recharge of the Allt a' Mharcaidh's groundwater and soil water stores occurs during this winter period when precipitation inputs are more ^{18}O-depleted (Soulsby *et al.*, 2000). The dominance of permeable alpine soils and lower peat coverage compared with elsewhere in the catchment (Table II) may facilitate greater winter recharge, but the relatively high mean altitude of the Allt a' Mharcaidh catchment (699 m) and its northerly aspect dictates that greater snow pack accumulation and snowmelt influence (Soulsby *et al.*, 1997) will also be important.

These factors are also important to the Eidart subcatchment, which has the highest mean altitude in the Feshie (865 m), and second lowest mean stream water δ^{18}O (−9·74‰). In comparison, mean δ^{18}O for the Upper Feshie and the Allt Chomraig are the highest (−9·45‰ and −9·34‰, respectively), reflecting less winter recharge due to a combination of less snowpack accumulation in these lower altitude catchments with more subdued topography, and greater peat coverage enhancing the delivery of precipitation to the stream channel via saturation overland flow. The main stem Feshie sites exhibit more comparable and intermediate mean stream water δ^{18}O; increasing from −9·53‰ to −9·55‰, then −9·59‰ from the upstream braids site down to Feshie Lodge and Feshie Bridge.

Hydrological controls on stream water $\delta^{18}O$

Figure 3 shows the stream water δ^{18}O time series for six of the seven Feshie subcatchment sampling sites during the 2001–02 hydrological year (Allt Chomraig not shown due to space limitations and its similarity to Allt a' Mharcaidh time series). As with the precipitation inputs, stream waters are most ^{18}O-depleted during the winter months when rainfall and snowmelt produce the highest flows (see Feshie Bridge: Figure 2). Conversely, under summer conditions, stream waters are generally more ^{18}O-enriched, reflecting the influence of ^{18}O-enriched precipitation (Figure 2). However, stream water δ^{18}O will also reflect where hydrological controls can lead to significant differences in isotopic composition between sites, a control easily examined by comparing δ^{18}O with corresponding stream water alkalinity time series (Figure 3). Gran alkalinity has proven utility as a tracer, particularly in the UK uplands as it effectively distinguishes between low alkalinity high flows derived mainly from acidic, organic soils and higher alkalinity water from lower soil horizons and/or groundwater which dominates base flows (Hill and Neal, 1997; Wade *et al.*, 1999). This alkalinity differentiation with flow is presented in Figure 4 for selected sampling sites.

Upper Feshie stream water δ^{18}O is the most variable out of the sites monitored (Figure 3). δ^{18}O declines from relatively enriched values in October to the most ^{18}O-depleted on 22/02/02 (−11·3‰), when significant snowmelt led to the highest flows sampled (31·1 m^3 s^{-1} measured at Feshie Bridge $\cong Q_2$: Figure 2) and subsequently lowest stream water alkalinities (Figure 3). The ^{18}O-depleted stream water reflects the depleted precipitation inputs driven by snowmelt. Stream water δ^{18}O then increases through March and April as sampled flows decrease, whilst isotopic composition over the remaining summer months reflects the response to more ^{18}O-enriched summer precipitation, particularly the two notable enriched peaks associated with the highest summer flows. The first of these on 27/06/02 (−8·4‰: Figure 3) was a relatively minor event measuring 4·6 m^3 s^{-1} at Feshie Bridge, exerting a minor effect on alkalinity concentrations. Later in the summer, on 09/08/02 and 23/08/02, the more marked low alkalinity stream water samples reflect the influence of higher summer flows again (Feshie Bridge mean daily flows of 6·8 and 7·3 m^3 s^{-1}, respectively; cf. <4·5 m^3 s^{-1} for other summer samples), and stream water δ^{18}O peaks for the year (−7·6‰ and −7·9‰). The remaining two samples from September 2002 correspond to the two lowest flows (3·0 and 2·6 m^3 s^{-1}, respectively) and show a return to more intermediate base flow δ^{18}O composition.

This marked stream water δ^{18}O response to both winter and summer storm flows is also evident for the Eidart subcatchment (Figure 3). It shows slightly lower stream water δ^{18}O for the two summer peaks compared with the Upper Feshie, with generally more ^{18}O-depleted base flow conditions (compare mean values, Table II). The stream water δ^{18}O time series for the upstream braids site reflects an integration of these two subcatchments (Figure 3). While these three sites are generally comparable in terms of their temporal response to hydrological variation over the year, the Feshie Lodge site 4 km downstream of the braids is more damped, as noted from Table II. Despite this, the same response to summer and winter storm events is evident, albeit subdued by the influence of increasing catchment size and the notable groundwater inputs through the braided reach (Rodgers *et al.*, 2004a). This downstream damping is continued to the catchment outlet at Feshie Bridge, where δ^{18}O

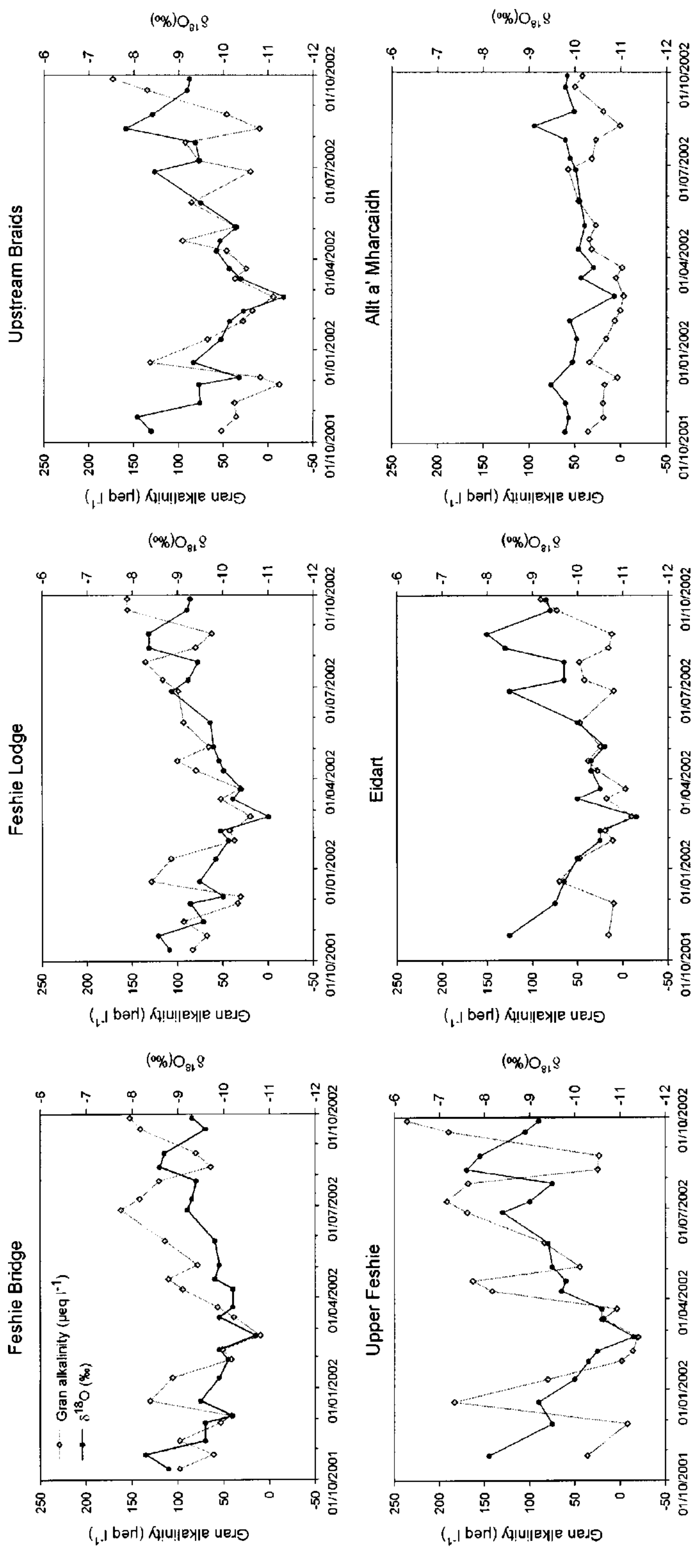

Figure 3. Temporal co-variation in stream water $\delta^{18}O$ and alkalinity for Feshie subcatchments

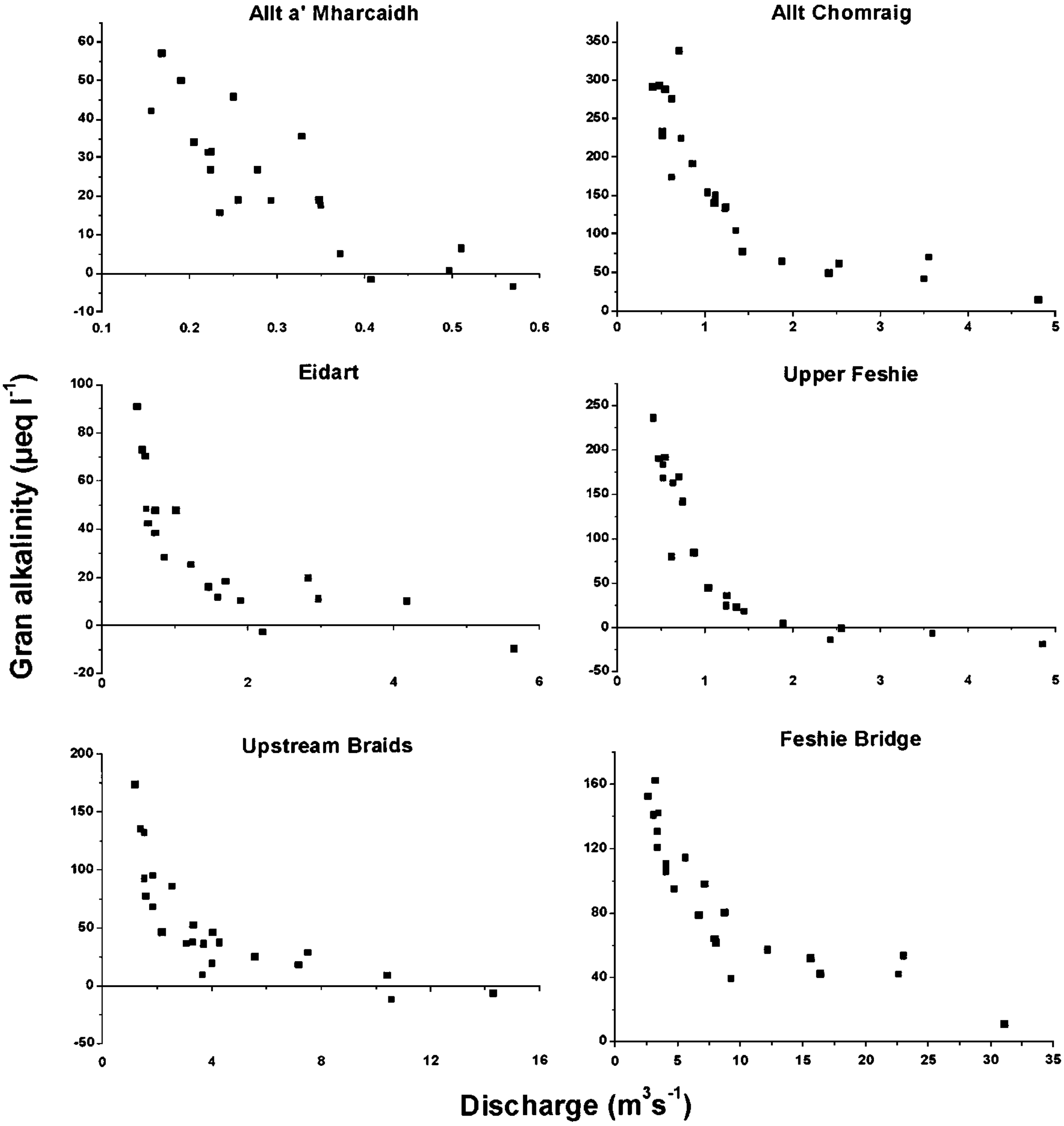

Figure 4. Alkalinity variation with flow for selected subcatchment sampling sites in the Feshie

is generally more consistent throughout the year (Figure 3), reflecting seasonally variable precipitation inputs becoming increasingly mixed with less isotopically variable water already present in the catchment at the larger spatial scale.

This is partly evident in the $\delta^{18}O$ time series for the lower catchment tributaries of the Allt a' Mharcaidh (Figure 3) and Allt Chomraig (not shown but generally similar: see Figure 6), which exhibit much less isotopic variation in response to hydrological variation over the year. In common with all other sites, stream water $\delta^{18}O$ is most depleted on the highest flow sampling day (22/02/02) and most ^{18}O-enriched for the summer peak on 09/08/02. In general though, variations in precipitation inputs seem to be well mixed in each catchment, leading to the damped stream water δ^{18}O output. These well-mixed stream waters appear, therefore, to have an influence on the increasingly damped main stem stream water δ^{18}O observed at Feshie Bridge (Figure 3).

These δ^{18}O and alkalinity variations in stream flows can be viewed conceptually as the combination of two components: a relatively stable base flow end member and a seasonally variable storm flow end member. This conceptualization is consistent with the two-component end member mixing previously used to assess the hydrology of the Feshie based on alkalinity tracer data alone (Soulsby *et al.*, 2004). Figure 5 shows this relationship more clearly, presenting seasonally differentiated δ^{18}O–alkalinity mixing plots. As in Figure 3, alkalinity measurements are used to provide a more direct indication of hydrological sources affecting measured stream water δ^{18}O. Theoretically, the influence of seasonally variable precipitation inputs should result in an approximately triangular-shaped plot of δ^{18}O and alkalinity measurements comprising a low alkalinity, seasonally variable storm flow end member (with low δ^{18}O during winter and higher δ^{18}O during summer), which mixes with higher alkalinity base flow waters with more intermediate δ^{18}O. At most sites this conceptual structure is apparent, although there are important differences.

The larger variability in Upper Feshie and Eidart stream water δ^{18}O is again evident (Figure 5), as is the greater variability in high alkalinity groundwater δ^{18}O observed in the Upper Feshie compared with the Eidart and other downstream sites. This reflects the more dominant influence of blanket peats in the Upper Feshie where recharge rates, and therefore groundwater influence, are likely to be more seasonally variable.

The main stem sites at Feshie Bridge and upstream and downstream of the braids all generally exhibit more clearly defined structure in terms of seasonally differentiated mixing lines compared with tributary sites. Unlike the Upper Feshie, the upstream braids site appears to have more constrained base flow stream water δ^{18}O, as do the sites downstream at Feshie Lodge and Feshie Bridge. Further, δ^{18}O contrast through the braided section corroborates similar findings from hydrochemical tracer data (Rodgers *et al.*, 2004a). Measured δ^{18}O at the downstream site shows less divergent summer and winter extremes and differences appear to be most marked for more moderate flow (intermediate alkalinity) samples. This presumably reflects the overall influence of well-mixed groundwater inputs through the braided reach, mixing with more ^{18}O-variable stream water from the catchment headwaters.

The mixing plot for the catchment outlet at Feshie Bridge (Figure 5) predictably reflects this upstream influence of greater groundwater influence from the braided section and is similar to Feshie Lodge, albeit exhibiting further reduced variability with greater mixing of hydrological source waters and damped inputs from downstream tributaries. Thus, mixing plots for the Allt a' Mharcaidh and Allt Chomraig (not shown) again highlight their relative lack of variability in δ^{18}O compared with the other sampling sites. Both are generally consistent with the conceptual model, though with summer samples from a range of different flows distributed towards higher δ^{18}O and winter samples being more ^{18}O-depleted.

Seasonal analysis of δ^{18}O patterns: preliminary estimate of mean residence times

The seasonal δ^{18}O trends of precipitation and stream water can be interpreted more quantitatively by use of periodic regression analysis to fit seasonal sine wave models to the annual δ^{18}O variations in precipitation and stream water (Figure 6). Although it is clear that the modelled curves oversimplify the patterns of variation, in particular for precipitation, the results are nonetheless statistically robust ($p < 0{\cdot}02$), with generally strong correlations between observed and modelled δ^{18}O for most sites (i.e. $r^2 > 0{\cdot}50$). These are comparable with correlations from similar studies (e.g. DeWalle *et al.*, 1997; McGuire *et al.*, 2002). Least well predicted is precipitation δ^{18}O, with the marked deviations from the sinusoidal seasonal pattern leading to a relatively weak r^2 of 0·28 (solid regression line: Figure 6). The model fit also produces a relatively low amplitude (1·16‰), which is the result of bias towards the more variable summer precipitation δ^{18}O caused by the particularly wet and unsettled summer.

Given the importance of obtaining a representative precipitation model for subsequent residence time calculations, in addition to counteracting loss of variability due to fortnightly sampling, it was considered prudent to produce a second regression fit weighted towards the more expected seasonal δ^{18}O extremes.

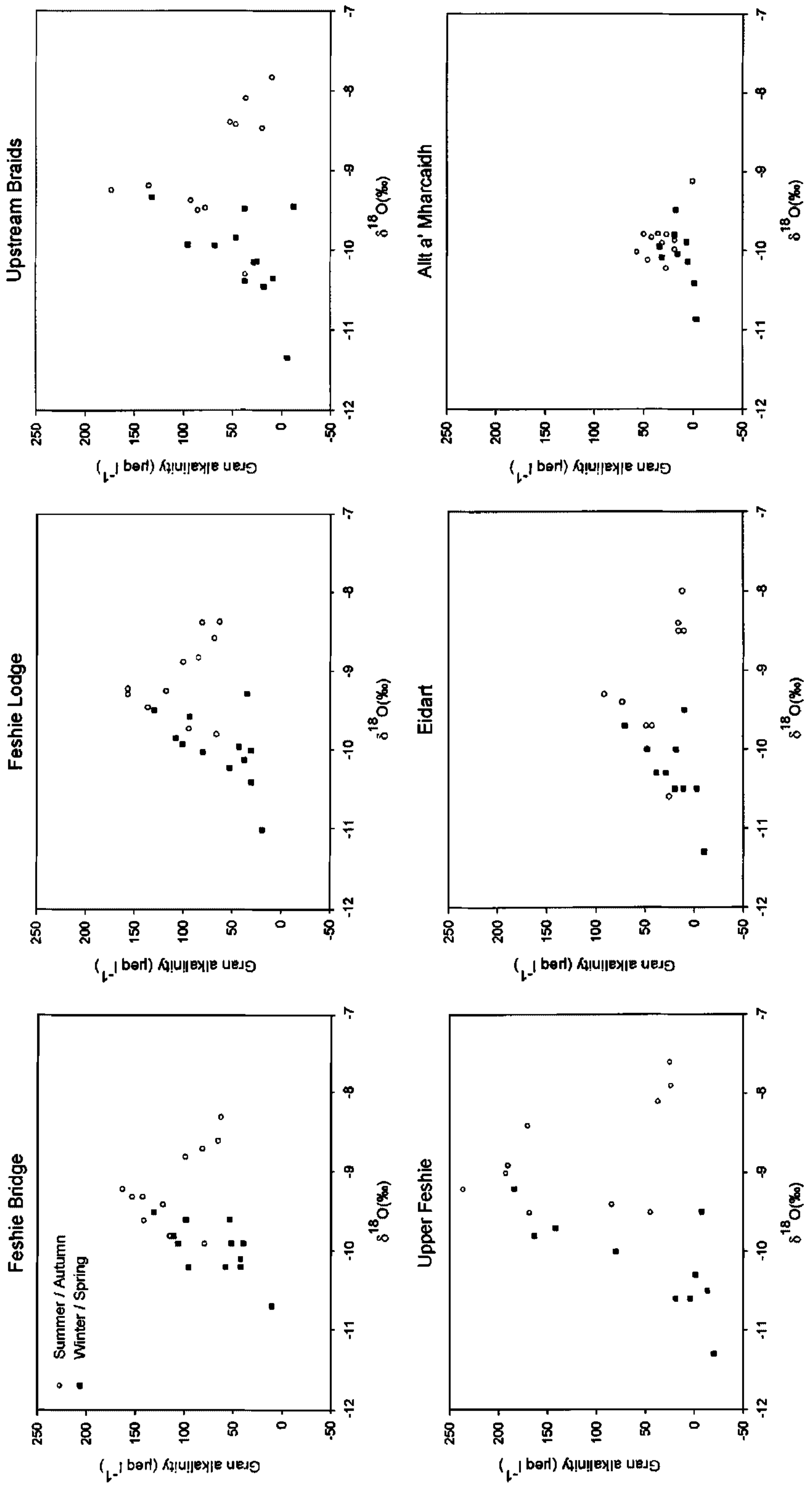

Figure 5. Mixing plots for stream water $\delta^{18}O$, showing seasonal and flow (alkalinity)-related variation

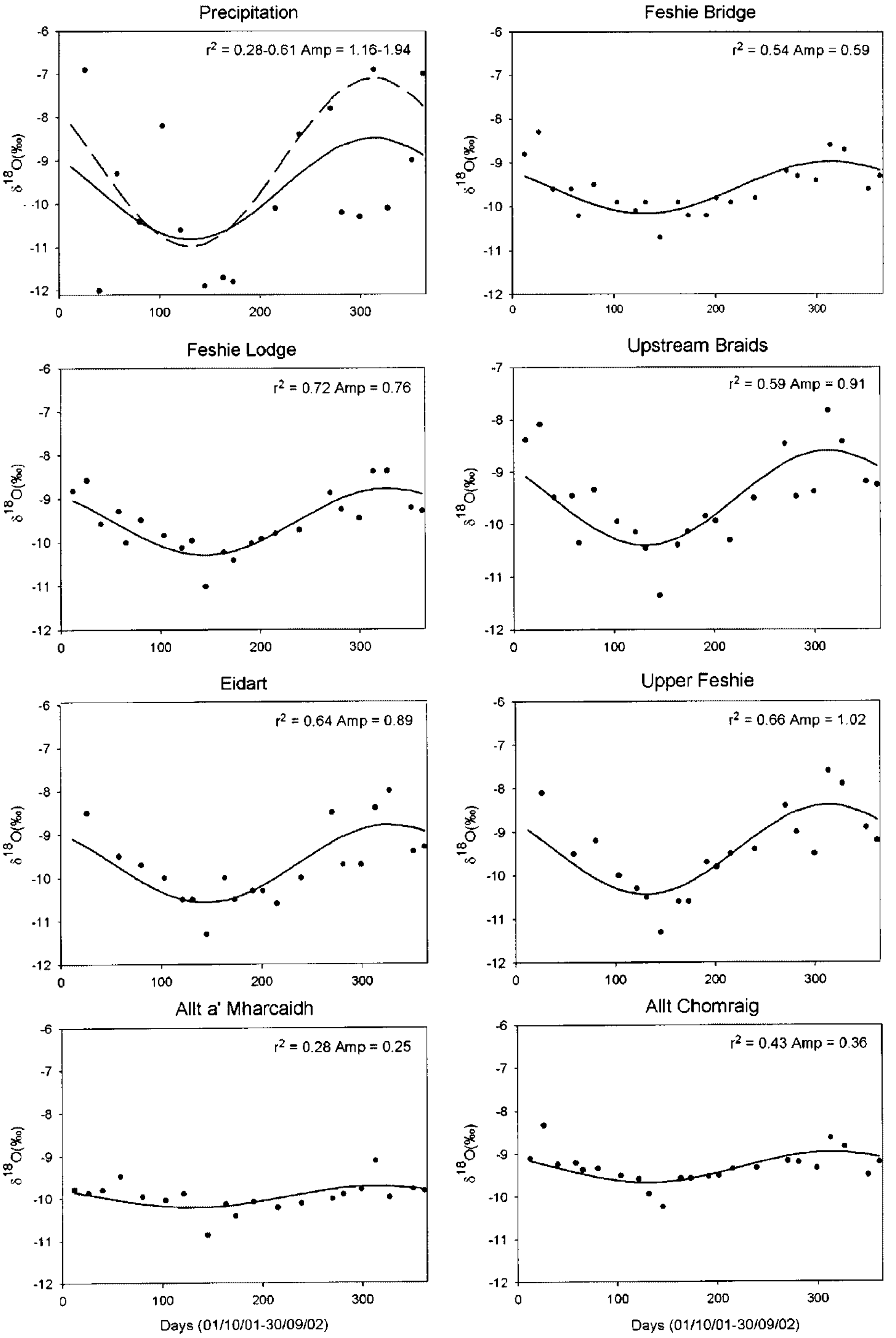

Figure 6. Fitted annual regression models to $\delta^{18}O$ for precipitation and stream water. Two precipitation models are presented, with the solid regression line based on the raw data series and the dashed regression line fitted to an optimized data set where depleted summer samples have been omitted in order to represent more typical seasonal variability

Depleted summer rainfall samples were therefore omitted in order to produce a more 'typical' model with a larger amplitude (dashed regression line, 1·94‰: Figure 6), which although only a first approximation, could be used as an upper estimate of the seasonal variability of precipitation δ^{18}O inputs (e.g. drier summer) in contrast with the lower variability model from the unweighted, raw data series. Furthermore, these two limits appear to represent reliable estimates given that they effectively bracket the modelled precipitation δ^{18}O monitored in the Allt a' Mharcaidh between 1995–98 (δ^{18}O amplitude 1·47‰; Soulsby *et al.*, 2000).

In general, the model fits are better for stream water sites, given the damping compared with precipitation. The modelled amplitudes reflect the observed patterns of variability between subcatchment sites that were identified from the δ^{18}O ranges in Table II, with the largest amplitudes for the Eidart, Upper Feshie and upstream braids site, becoming more damped further downstream (Figure 6). The site with poorest modelled stream water δ^{18}O was the Allt a' Mharcaidh ($r^2 = 0{\cdot}28$), on account of it displaying the least evident seasonal δ^{18}O variation. Previous work in the Allt a' Mharcaidh (Soulsby *et al.*, 2000), and other studies looking at residence time distribution of different catchment stores (e.g. DeWalle *et al.*, 1997), have inferred that the characteristic damping of seasonal variation in stream water δ^{18}O results from greater mixing and contributions of relatively isotopically constant groundwater sources; whereas seasonal variations in hydrologically reactive surface and near surface soil waters are far more significant with larger δ^{18}O amplitude, reflecting greater responsiveness to recent precipitation inputs. This characteristic catchment behaviour can therefore be used to infer the likely degree of influence of mixing in groundwater and soil water stores on the modelled stream water δ^{18}O for each subcatchment site in the Feshie.

Thus, the lowest amplitudes modelled for the Allt a' Mharcaidh and Allt Chomraig are consistent with significant groundwater storage and contributions in these two subcatchments (see Table III) previously implied from alkalinity-based end member mixing analysis (Soulsby *et al.*, 2004), implying δ^{18}O variations may be more subdued due to greater mixing. Both sites are more damped than the catchment outlet at Feshie Bridge, suggesting that such damped tributary inputs and further groundwater damping in the lower catchment have a moderating influence on the more marked seasonal variation of collectively larger volumes of runoff transferred down the Feshie's main stem from its main headwaters. Thus, the modelled amplitude for the Upper Feshie and the Eidart show a more variable seasonal response reflecting shorter hydrological pathways associated with the dominant and highly responsive blanket peat and shallow alpine soils in these headwaters areas. The resulting seasonal δ^{18}O models would therefore appear to be consistent with expectations based on these catchment characteristics providing more limited groundwater storage, as well as the lower groundwater contributions to flows (Table III) estimated for these subcatchments (Soulsby *et al.*, 2004).

The model described by Equation (2) was used to provide estimates of mean stream water residence time (Table III), which provide a very general but useful indication of the degree of mixing of hydrological sources in each subcatchment and thus offer a valuable integrated assessment of the differences in hydrological sources for the Feshie catchment. Given the wet nature of the study year, and the absence of a dry summer period, the lower estimates based on the unweighted precipitation model should also be taken as being close to minimum values for the catchment, whereas the upper values are probably closer to typical conditions.

The predominance of highly responsive peat and shallow alpine soils in the Upper Feshie and Eidart contribute to the relatively short mean residence times estimated; 33–95 and 47–113 days, respectively (Table III). The lower blanket peat coverage and comparatively larger groundwater influence predicted for the Eidart (41% cf. 29%: Table III) are consistent with the slightly longer mean residence time than in the Upper Feshie. In the main stem of the Feshie, the braided section influences the residence time of runoff over a relatively short distance, with an approximate 20% increase from 47–110 days to 66–135 days, mirroring the marked increase in groundwater contributions known to occur through this reach. Although this appears to be related to the increasing influence of older and deeper groundwater sources, the influence of the flashier, shorter residence time outputs from the two main headwater catchments is still dominant. The influence of the braided section is most important under moderate flow conditions, beyond which at higher flows it fails to exert a significant influence (Rodgers *et al.*, 2004a), and the same is most likely true in terms of mixing of different aged waters.

Table III. Mean and amplitude of modelled δ^{18}O, approximate mean residence times and estimated groundwater flow contributions for subcatchment sites in the Feshie (2001–02). Mean residence times range from a minimum estimate derived from the unweighted precipitation model, to a higher estimate based on more typical seasonal extremes. Groundwater proportions based on annual two-component mixing analysis using Gran alkalinity (see Soulsby *et al.*, 2004)

	Modelled mean (‰)	Amplitude (‰)	Mean residence time (days)	% Groundwater contribution to annual flow
Inputs:				
Raw precipitation	−9·70	1·16		
Weighted precipitation	−9·11	1·94		
Stream water:				
1. Feshie Bridge	−9·59	0·59	110–200	54·0
2. Allt Chomraig	−9·33	0·36	178–308	45·3
3. Feshie Lodge	−9·55	0·76	66–135	51·9
4. Upstream Braids	−9·53	0·91	47–110	37·0
5. Eidart	−9·70	0·89	47–113	40·9
6. Upper Feshie	−9·44	1·02	33–95	29·2
7. Allt a' Mharcaidh	−9·98	0·25	263–445	51·3

In contrast, the subcatchment tributaries of the Allt Chomraig and the Allt a' Mharcaidh can be seen as more distinct units which exhibit different behaviour to the two headwater subcatchments. As a result, the influence of more extensive mixing with groundwater is more tangible, as seen from the longer mean residence time estimates. The Allt a' Mharcaidh in particular has the longest mean residence time of the seven monitored sites (Table III). This appears reasonable as an integration of previously estimated residence times for the same site, which indicated that soil water had a mean residence time in the order of 0·2 years and groundwater mean ages ranging between 2·3 and >5 years (Soulsby *et al.*, 2000).

At the catchment outfall at Feshie Bridge, stream water is generally older than the upstream main stem sites (110–200 days), and thus integrates the wide range of subcatchment stream water ages, from the generally recent runoff from the main headwater subcatchments to older water from the larger groundwater sources which are more important as catchment scale increases downstream of the braids.

DISCUSSION

These results contribute to an improved understanding and conceptualization of catchment hydrology for the Feshie, previously based on hydrochemical tracer analysis (Soulsby *et al.*, 2004). Variation in stream water δ^{18}O is generally consistent with relatively simple two-component mixing, where well-mixed, longer residence time groundwater sustains base flows and more recent, seasonally variable precipitation inputs in soil waters mainly account for storm flow response. Over the course of the hydrological year, this mixing process resulted in a reasonably well-defined, seasonally evolving isotopic signature that reflects important differences in subcatchment hydrological processes, and allows intra-catchment differences in stream water residence times to be estimated.

While previous isotope-based residence time estimates have commonly compared the distribution of residence times between different hydrological stores based on direct sampling (e.g. DeWalle *et al.*, 1997; Soulsby *et al.*, 2000; McGuire *et al.*, 2002), this approach would have been impractical here given the much larger scale of the Feshie. However, the important subcatchment stream water δ^{18}O differences observed and modelled allowed a more pragmatic, scale-independent approach to be adopted to examine mean residence times at the mesoscale, allowing the conceptualization of hydrological functioning in response to different catchment characteristics over a range of scales.

These estimates, however, are recognized as a generalization of a much wider and more complex range of internal catchment residence time distributions that are currently unknown (Kirchner *et al*., 2000). Clearly, under base flows, much longer residence time waters would be expected to account for the majority of stream flow at downstream sites such as Feshie Lodge and Feshie Bridge, but this could not be characterized by the simple modelling approach used here, particularly in such a wet year. This points to the greater inherent uncertainty in the estimation of residence times of such averaged stream water, rather than component soil water and groundwater stores. Future work in the Feshie would therefore benefit from further assessment of different influences on the preliminary mean stream water residence times presented here, particularly in terms of groundwater residence times which are likely to be highly variable (Frederickson and Criss, 1999; Gonfiantini *et al*., 1998). These could be assessed indirectly through more intensive sampling of stream base flows or using other tracers such as tritium (cf. McGlynn *et al*., 2003) or CFCs (cf. Uhlenbrook *et al*., 2002).

The observed and modelled stream water δ^{18}O also display interesting patterns in relation to the scaling and integration of hydrological processes. In particular, the results for the largest scale (Feshie Bridge) indicate that the upstream influence of highly responsive headwater peat and shallow alpine soils has the dominant influence on the overall seasonal patterns and residence times observed at the larger catchment scale, despite significant downstream groundwater inputs. These findings may be consistent with the recent findings of McGlynn *et al*. (2003), that landscape organization rather than catchment area is more important as a first-order control on catchment residence times. In particular, their use of median subcatchment area to describe area accumulation patterns may have some significance in the Feshie when comparing the different estimated residence times of the four tributary subcatchments.

However, given the larger scale involved in the Feshie, such patterns of landscape organization generally reflect the contrasts already identified from catchment soil coverage (peat) and topography. Topography exerts a dominant control, resulting in shorter residence times in the Upper Feshie and Eidart headwaters compared with the larger groundwater stores in the Allt Chomraig and Allt a' Mharcaidh. However, beyond this topographic distinction, the more peat-dominated Allt Chomraig and Upper Feshie have denser drainage networks (lower median subcatchment areas) and thus shorter respective residence times compared with the Allt a' Mharcaidh and Eidart tributaries, respectively. These general observations suggest that catchment characteristics and landscape organization are therefore highly influential on the age distribution of catchment runoff at the mesoscale, issues that have received relatively limited attention given the small scale and relatively homogeneous character of many catchments conventionally studied in this field (Buttle, 1994). These results highlight the pragmatic utility of stream water oxygen isotope measurements as an analytical tool in the study of mesoscale catchments, given that they effectively integrate the influence of these complex catchment heterogeneities, as well as indicating the relative importance of different sources in runoff production. This further suggests that the potential of such an approach to improve current understanding of scaling in catchment hydrological processes remains largely underdeveloped (Brown *et al*., 1999; Genereux and Hooper, 1998; McDonnell *et al*., 1999), particularly at the mesoscale (Uhlenbrook *et al*., 2002). It is important, therefore, that tracer studies such as these are continued in order to refine our understanding of flow paths and residence times, and to help structure and validate more accurate hydrological models.

ACKNOWLEDGEMENTS

The authors are grateful for the support of NERC through the NERC/JIF CHASM initiative and for supporting PJR on his studentship (GT 4/00/02/). Scottish Natural Heritage are thanked for allowing permission to work in the Cairngorm National Nature Reserve as is Glen Feshie Estate, which provided site access and other support. SUERC is funded by a consortium of Scottish Universities and research council support.

REFERENCES

Brown IM, Clapperton CM. 2002. The physical geography. In *The Ecology, Land Use and Conservation of the Cairngorms*, Gimingham C (ed.). Packard: Chichester; 8–20.

Brown VA, McDonnell JJ, Burns D, Kendall C. 1999. The role of event water, rapid shallow flow paths and catchment size in summer storm flow. *Journal of Hydrology* **217**: 171–190.

Burns DA. 2002. Stormflow hydrograph separation based on isotopes: the thrill is gone—what's next? *Hydrological Processes* **16**: 1515–1517.

Buttle JM. 1994. Isotope hydrograph separation and rapid delivery of pre-event water from drainage basins. *Progress in Physical Geography* **18**: 16–50.

Buttle JM. 1998. Fundamentals of small catchment hydrology. In *Isotope Tracers in Catchment Hydrology*, Kendall C, McDonnell JJ (eds). Elsevier: Amsterdam; 1–43.

Clark ID, Fritz P. 1997. *Environmental Isotopes in Hydrogeology*. CRC Press: Boca Raton, FL; 328 pp.

Darling WG, Talbot JC. 2003. The O & H stable isotopic composition of fresh waters in the British Isles. 1. Rainfall. *Hydrology and Earth System Sciences* **7**: 163–181.

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

Dunn SM, Soulsby C, Lilley A. 2003. Parameter identification for conceptual modelling using combined behavioural knowledge. *Hydrological Processes* **17**: 329–343.

Ferguson RI. 1984. Magnitude and modelling of snowmelt runoff in the Cairngorm mountains, Scotland. *Hydrological Sciences Journal* **29**: 49–62.

Frederickson GG, Criss RE. 1999. Isotope hydrology and residence times of the unimpounded Meramec River Basin, Missouri. *Chemical Geology* **157**: 303–317.

Genereux DP, Hooper RP. 1998. Oxygen and hydrogen isotopes in rainfall–runoff studies. In *Isotope Tracers in Catchment Hydrology*, Kendall C, McDonnell JJ (eds). Elsevier: Amsterdam; 319–346.

Gonfiantini R, Frohlich K, Araguas-Araguas L, Rozanski K. 1998. Isotopes in groundwater hydrology. In *Isotope Tracers in Catchment Hydrology*, Kendall C, McDonnell JJ (eds). Elsevier: Amsterdam; 203–246.

Haria A, Price DJ. 2000. Evaporation from Scots pine following recolonisation of the Cairngorm mountains, Scotland. *Hydrology and Earth System Science* **4**: 228–249.

Healy J. 2001. Paradigms, policies and prognostications about the management of watershed ecosystems. In *River Ecology and Management*, Naiman RJ, Bilby RE (eds). Academic Press: London; 642–661.

Hill T, Neal C. 1997. pH, alkalinity and conductivity in runoff and groundwater. *Hydrology and Earth System Science* **3**: 381–394.

Kirchner JW, Feng X, Neal C. 2000. Fractal stream chemistry and its implications for contaminant transport in catchments. *Nature* **403**: 524–527.

Maloszewski P, Zuber A. 1993. Principles and practice of calibration and validation of mathematical models for the interpretation of environmental tracer data in aquifers. *Advances in Water Resources* **16**: 173–190.

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

Matthew EM. 2002. Nature conservation. In *The Ecology, Land Use and Conservation of the Cairngorms*, Gimingham C (ed.). Packard: Chichester.

McDonnell J, Rowe L, Stewart M. 1999. A combined tracer–hydrometric approach to assess the effect of catchment scale on water flow path, source and age. In *Integrated Methods in Catchment Hydrology–Tracer, Remote Sensing and New Hydrometric Techniques*, Leibundgut C, McDonnell J, Schultz G (eds). IAHS Publication no. 258; 265–274.

McGlynn B, McDonnell J, Stewart M, Seibert J. 2003. On the relationship between catchment scale and stream water mean residence time. *Hydrological Processes* **17**: 175–181.

McGuire KJ, DeWalle DR, Gburek WJ. 2002. Evaluation of mean residence time in subsurface waters using oxygen-18 fluctuations during drought conditions in the mid-Appalachians. *Journal of Hydrology* **261**: 132–149.

Naiman RJ, Bisson PA, Lee RG, Turner MG. 2001. Watershed management. In *River Ecology and Management*, Naiman RJ, Bilby RE (eds). Academic Press: London; 642–661.

Rodgers P, Soulsby C, Petry J, Gibbins C, Malcolm I, Dunn SM. 2002. A tracer-based investigation of groundwater–surface water interactions in a braided river: a case study of the river Feshie, Scotland. In *Proceedings of the 8th National Hydrology Symposium, BHS, Birmingham*; 183–189.

Rodgers P, Soulsby C, Petry J, Malcolm I, Gibbins C, Dunn S. 2004a. Groundwater–surfacewater interactions in a braided river: a tracer based assessment. *Hydrological Processes* **18**: 1315–1332.

Rodgers P, Soulsby C, Petry J, Dunn S. 2004b. Integrating tracers and GIS to assess the influence of landscape heterogeneity on runoff processes in a complex mountainous catchment. In *Proceedings of the BHS International Conference—Hydrology: Science and Practice for the 21st Century*; 458–467.

Shand P, Darbyshire DPF, Goody DC, Darling WG, Neal C, Haria AH, Dixon AJ. 2001. The application of Sr isotopes to catchment studies: the Plynlimon upland catchment of Central Wales. *Water–Rock Interaction* **1 & 2**: 1577–1580.

Sklash MG. 1990. Environmental isotope studies of storm and snowmelt runoff generation. In *Process Studies in Hillslope Hydrology*, Anderson MG, Burt TP (eds). John Wiley: Chichester; 401–435.

Sklash MG, Farvolden RN, Fritz P. 1976. A conceptual model of watershed response to rainfall developed through the use of oxygen-18 as a natural tracer. *Canadian Journal of Earth Science* **13**: 271–283.

Soulsby C, Dunn SM. 2003. Towards integrating tracer studies with a conceptual rainfall–runoff model; insights from a sub-arctic catchment in the Cairngorm Mountains, Scotland. *Hydrological Processes* **17**: 403–416.

Soulsby C, Helliwell RC, Ferrier RC, Jenkins A, Harriman R. 1997. Seasonal snowpack influence on the hydrology of a sub-arctic catchment in Scotland. *Journal of Hydrology* **192**: 17–32.

Soulsby C, Chen M, Ferrier RC, Helliwell RC, Jenkins A, Harriman R. 1998. Hydrogeochemistry of shallow groundwater in an upland Scottish catchment. *Hydrological Processes* **12**: 1111–1127.

Soulsby C, Malcolm R, Ferrier RC, Jenkins A. 1999. Hydrogeochemistry of montane springs and their influence on streams in the Cairngorm Mountains, Scotland. *Hydrology and Earth System Science* **3**: 409–419.

Soulsby C, Malcolm R, Helliwell RC, Ferrier RC, Jenkins A. 2000. Isotope hydrology of the Allt a' Mharcaidh catchment, Cairngorm mountains, Scotland: implications for hydrological pathways and water residence times. *Hydrological Processes* **14**: 747–762.

Soulsby C, Rodgers P, Smart R, Dawson J, Dunn S. 2003. A tracer based assessment of hydrological pathways at different spatial scales in a mesoscale Scottish catchment. *Hydrological Processes* **17**: 759–777.

Soulsby C, Rodgers P, Petry J, Hannah DM, Malcolm IA, Dunn SM. 2004. Using tracers to upscale flow path understanding in mesoscale mountainous catchments: two examples from Scotland. *Journal of Hydrology* **291**: 174–196.

Stewart MK, McDonnell JJ. 1991. Modelling base flow soil water residence times from deuterium concentrations. *Water Resources Research* **27**: 2681–2693.

Turner JV, Barnes CJ. 1998. Modelling of isotope and hydrogeochemical responses in catchment hydrology. In *Isotope Tracers in Catchment Hydrology*, Kendall C, McDonnell JJ (eds). Elsevier: Amsterdam; 723–760.

Uhlenbrook S, Frey M, Leibundgut C, Maloszewski P. 2002. Hydrograph separations in a mesoscale mountainous basin at event and seasonal timescales. *Water Resources Research* **38**: 1096–1110.

Unnikrishna PV, McDonnell JJ, Stewart ML. 1995. Soil water isotope residence time modelling. In *Solute Modelling in Catchment Systems*, Trudgill ST (ed.). John Wiley & Sons: Chichester; 237–260.

Wade AJ, Neal C, Soulsby C, Smart RP, Langan SJ, Cresser MS. 1999. Modelling streamwater quality under varying hydrological conditions at different spatial scales. *Journal of Hydrology* **217**: 266–283.

Werrity A, Ferguson RI. 1980. Pattern change in a Scottish braided river over 1, 30 and 200 years. In *Timescales in Geomorphology*, Cullingford RA, Davidson DA, Lewin J (eds). John Wiley & Sons: Chichester; 53–68.

Werrity A, McEwan LJ. 1993. Glen Feshie. In *Quaternary of Scotland*. Chapman & Hall: London; 298–303.