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## Using tracers to upscale flow path understanding in mesoscale mountainous catchments: two examples from Scotland

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### Abstract

Natural geochemical tracers were monitored over a hydrological year in the Feshie (231 km<sup>2</sup>) and Feugh (233 km<sup>2</sup>) catchments in the Cairngorm Mountains, Scotland. The monitoring sought to assess the utility of tracers in upscaling flow path understanding in mesoscale catchments. A spatially and temporally nested sampling approach was adopted involving hydrochemical monitoring of sub-catchments ranging from 1 to  $\approx$  100 km<sup>2</sup> in area. This allowed chemically-based hydrograph separations to be made and facilitated catchment-wide prediction of stream chemistry at a high and low flows. Differences in catchment geology were the main controls on baseflow chemistry, which was spatially variable in both catchments. However, acidic, organic soils produced the majority of storm runoff at all scales monitored, though its contribution was determined by the soil distributions of particular sub-catchments. Given the practical difficulties associated with comprehensive hydrometric monitoring at large spatial scales, it is argued that focused tracer studies can provide both an invaluable insight into the hydrological functioning of mesoscale catchments and a useful additional method for evaluating the structure and performance of distributed hydrological models. In addition, such tracer data provides important information on hydrological pathways that can aid catchment management.

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### 1. Introduction

There is a major contemporary research focus in attempting to bridge the gulf between hydrological process understanding gained in small (< 10 km<sup>2</sup>) research catchments and the needs of water managers who make decisions, and, therefore, require

functional understanding of hydrological systems at the larger mesoscale (> 100–1000 km<sup>2</sup>) (Montgomery et al., 1995; Cooper et al., 2000; Naiman et al., 2001; Wade et al., 2001; Soulsby et al., 2003a). There are major scientific challenges associated with scaling process understanding in catchment hydrology. Meeting such challenges will develop better communication at the interface between catchment science and watershed management; this is an essential prerequisite to developing sustainable approaches to a range of

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water resource problems (Falkenmark, 1990; Healey, 2001). The importance of these two research themes in contemporary hydrology is evident in a range of initiatives at the local (Eden et al., 1999), regional (Allan et al., 1997; Langan et al., 1997; Neal et al., 1998), national (Gupta et al., 1999) and international (HELP, 1999) scales. All of which seek to integrate scientific understanding with practical catchment management.

Extrapolating process understanding of terrestrial hydrological pathways often involves some kind of distributed modelling which needs to be based on conceptual understanding of catchment hydrological functioning (Bloschl and Sivaplan, 1995; Kilsby et al., 1999). There are methodological problems in that traditional hydrometric-based studies usually employ techniques that are scale specific, and even when methods have been developed to allow wider extrapolation, these usually involve only a few square kilometres (Beven, 1993, 2000). In order to develop more integrated approaches to understanding catchment functioning, the past two decades have seen widespread application of tracer studies which use the hydrochemical ‘fingerprints’ of various biogeochemical processes to identify chemically distinct hydrological source areas and flow paths (Kendall et al., 1995; Neal, 1997; Hoeg et al., 2000). There is now considerable evidence that tracers can be used to assess the relative importance of different hydrological sources in contributing to stream runoff at different spatial and temporal scales (Kendall and McDonnell, 1998; Wade et al., 1999; Smart et al., 2001; Soulsby et al., 2003a).

It follows that there is considerable potential in using tracer studies to help conceptualise catchment hydrological functioning within the structures of rainfall–runoff models and provide alternative objective functions with which to test modelling predictions (Uhlenbrook and Leibundgut, 2002; Soulsby and Dunn, 2003). Despite a relatively long-history of integrating tracer studies within hydrological models (Kleissen et al., 1990; Robson et al., 1992), the potential of this approach remains largely underdeveloped. However, with increasing interest in upscaling, it may be that tracer based approaches to understanding the hydrological functioning of larger catchment systems, may aid significant progress in hydrological modelling at

different spatial and temporal scales (Kirchner et al., 2000; Rodriguez-Iturbe and Rinaldo, 2001).

In this paper we examine the tracer hydrology of two contrasting mesoscale catchments in the Scottish Highlands that are the foci of current research initiatives. These are the Feshie and the Feugh catchments which lie in the Cairngorm and East Grampian mountains, respectively. The Feshie is the more mountainous of the two with high altitude (>1000 m) headwaters and a snowmelt-influenced hydrological regime (Soulsby and Dunn, 2001). The Feugh catchment, whilst still upland in nature, only reaches maximum elevations of approximately 770 m and is characterised by extensive areas of peatlands which experience less snow (Soulsby et al., 2003a). Both catchments have significant water management issues that are of concern to regulatory agencies. Important Atlantic salmon populations are present in each river system and both catchments are sensitive to surface water acidification. Consequently, there has been concern over the impact of acidification on the fish stocks and other components of freshwater biodiversity (SEPA, 2000; Davidson et al., 2002). Both rivers have major flooding problems in their lower reaches which has been attributed, in some quarters, to the hydrological effects of land management (e.g. afforestation, high grazing pressures; Walker, 2000). Both rivers are also important recreational and amenity resources. Finally, the Feugh is also an important local resource for drinking water (Soulsby et al., 2003a). Thus, in addition to the sites being of scientific interest in terms of upscaling hydrological understanding, tracer information can play a key role in contributing to the solution of applied catchment management problems.

Both catchments have had a long history of hydrological research, initially based on relatively small scale hydrometric, hydrochemical and modelling studies (Reid et al., 1981; Cresser et al., 1987; Wheeler et al., 1993; Jenkins et al., 1994). More recently, the UK’s Catchment Hydrology And Sustainable Management (CHASM) research initiative, of which the Feshie forms part, has focused on developing methods for larger-scale extrapolation. This paper follows on from more recent tracer investigations that have been used to infer the hydrological functioning of the catchments at different spatial and temporal scales (Dunn et al.,

2003; Soulsby et al., 2003a). Specifically, the paper aims to contribute to a better understanding upscaling using tracers by: (a) examining the hydrochemical behaviour of nested sub-catchments in the Feshie and Feugh to identify the significance of different hydrological processes in runoff generation at a range of spatial and temporal scales; (b) assessing the results of two extensive hydrochemical surveys to examine the spatial variation in catchment hydrochemical functioning at average flows and (c) using this data in conjunction with GIS-based knowledge of catchment characteristics to model catchment-wide hydrochemistry at low and high flows. Finally, the paper discusses ways in which such information can be used in providing more realistic models of catchment hydrology and contributing to catchment management problems.

## 2. Study areas

### 2.1. Feshie catchment

The Feshie catchment drains an altitudinal area of 231 km<sup>2</sup> on the western side of the Cairngorm massif (Fig. 1 and Table 1). The catchment covers some of the steepest, most mountainous terrain in the UK with an altitudinal range from 230 to 1115 m, and a mean elevation of 617 m (Fig. 1a). The highest parts of the catchment are associated with granite batholiths which were intruded 435–390 million years ago (Fig. 1b). These were intruded into the Moinian schists which underlie most of the catchment and were metamorphosed in the Grampian Orogeny, 550–450 million years ago (Brown and Clapperton, 2002). Dykes and sills of diorite and felsite are present, particularly in the headwaters of the Allt Chomraig and Upper Feshie.

The topography of the catchment also reflects the glacial history of the area, which resulted in a river capture of the Upper Feshie, which formerly flowed east to the Dee catchment, but was diverted west by a low ridge of glacial deposits to flow into the Spey (Werritty and McEwan, 1993). Thus the Upper Feshie itself undergoes an 180° turn, just upstream of its confluence with the Eidart, the second main headwater tributary of the main stem of the river Feshie (Fig. 1a). These two headwaters drain catchments of

contrasting character (Table 1). The Upper Feshie drains a lower area (mean altitude 686 m), mainly underlain by schists, which despite having a number of peaks exceeding 800 m, mainly comprises a flattish basin, covered by peat soils (up to m deep) which occupy approximately 65% of the sub-catchment (Fig. 1c). The Eidart drains part of the Cairngorm granite above altitudes of 900 m (mean altitude 865 m) and flows south through a steep, incised, glaciated valley. The dominant soils are shallow (<0.5 m deep) alpine soils or bedrock which cover 63% of the sub-catchment, though some peat occurs (28% of area) in the lower areas and on the upper north west fringe.

Downstream of the Upper Feshie-Eidart confluence, the river flows westwards and becomes increasingly incised as it flows through the glaciated trough of Glen Feshie. Just upstream of the Lorgaidh, a large south bank tributary (Fig. 1a), alluvial deposits (in places deeper than 10 m) become more extensive (Fig. 1b), as the Feshie flows north through a braided section, which is some 4 km in length (Rodgers et al., 2002). Downstream of the braids, the valley widens out, and extensive alluvial and fluvio-glacial terrace deposits cover the valley floor (Werritty and Ferguson, 1980). A large west bank tributary, the Allt Chomraig, enters the main stem of the Feshie, whilst five smaller east bank tributaries, including the Allt a' Mharcaidh experimental catchment, drain the main area of Cairngorm granite and enter the river between the braids and the catchment outfall at Feshie Bridge (Soulsby et al., 2001). The Allt Chomraig is similar to the upper Feshie, being relatively low-lying (mean altitude 490 m) and having extensive peat soils covering the upper sub-catchment. 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.

From previous work done in the area, the peats and peaty soils are known to generate large volumes of storm runoff via overland flow and shallow sub-surface storm flow (Soulsby et al., 2000). The thin alpine soils and areas of bare bedrock are also likely to be responsive during rainfall and snowmelt events. Groundwater flow systems in the catchment are relatively shallow (<10 m), but significant. The largest aquifers are found in the valley alluvium in

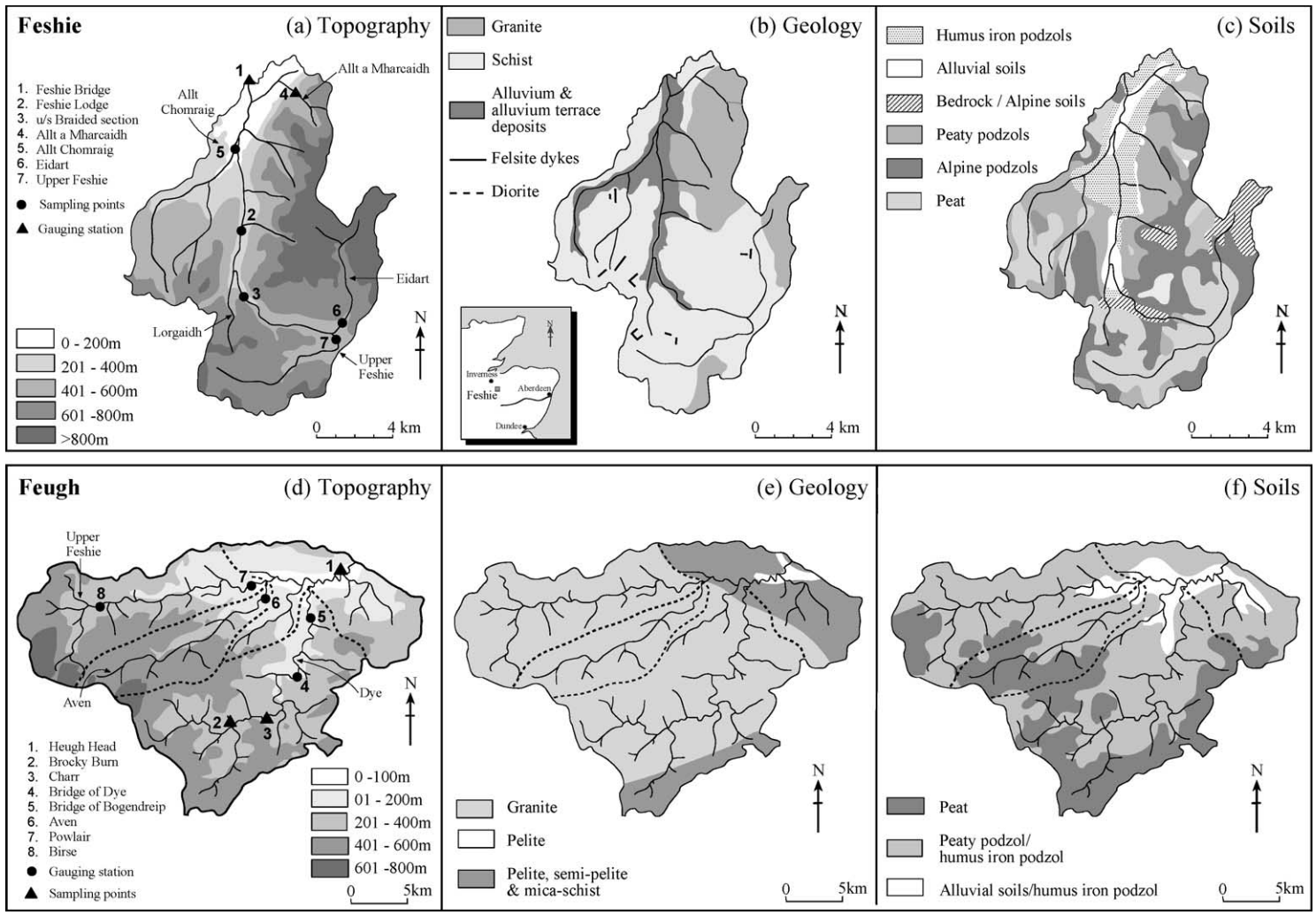


Fig. 1. The Feshie and Feugh catchments, showing (a and d) topography and monitoring networks, (b and e) geology and (c and f) main soil coverage.

Table 1  
Characteristics of the Feshie and Feugh catchments

	Topography		Hydrology			Geology		Main soil sub-groups					Main land use				
	Area (km <sup>2</sup> )	Mean altitude (m)	Precipitation (mm)	Long term mean flow <sup>a</sup> (m <sup>3</sup> s <sup>-1</sup> )	Long term $Q_5^a$ (m <sup>3</sup> s <sup>-1</sup> )	Long term $Q_{95}^a$ (m <sup>3</sup> s <sup>-1</sup> )	Granite (%)	Metamorphic, e.g. pelites and schists (%)	Peat (%)	Peaty Podzol (%)	Alpine (%)	Shallow alpine/rock (%)	Alluvial (%)	Woodland (%)	Heather moor/blanket bog (%)	Montane/rock (%)	Grassland (%)
<i>Feshie</i>																	
Feshie Bridge	230.7	617	1598	8.0	26.5	1.7	27.0	60.5	32.6	21.4	8.2	28.2	8.5	11.8	68.6	12.1	5.7
Allt Chomraig	44.9	490	1344	1.2	4.1	0.3	0	77.9	34.7	38.1	2.1	14.7	10.4	16.0	73.5	6.0	4.5
Feshie Lodge	114.6	715	1795	4.6	15.3	1	5	81.5	41.1	9.2	2.8	45.5	1.0	0.7	81.1	11.3	5.6
Upstream Braids	88.1	743	1853	3.7	12.2	0.8	17.6	80.2	45.4	7.7	2.8	44.1	0	0	84.7	11.2	3.4
Eidart	29.9	865	2095	1.5	4.8	0.3	43	57	27.6	9.6	3.4	59.5	0	0	79.1	19.4	0.5
Upper Feshie	32.3	686	1743	1.3	4.1	0.3	9	91	65.6	10.1	4.5	19.7	0	0	89.5	5.7	4.8
Allt a' Mharcaidh	10.0	699	1150	0.25	0.7	0.07	100	0	24.9	35.3	30.2	8.4	1.1	4.2	59.0	34.5	0
<i>Feugh</i>																	
Heugh Head	232.8	329	1130	5.3	20.1	0.9	83.9	5.0	32.3	67.3	0	0	0.4	18.1	68.2	0	10.7
Brocky Burn	1.3	419	1230	0.04	0.16	0.005	100	0	51.6	48.4	0	0	0	0	100	0	0
Charr	41.8	420	1280	1.3	4.7	0.2	72.1	21.5	65.0	35.0	0	0	0	0	99.4	0	0.6
Br. Dye	70.6	386	1244	2.1	7.8	0.3	77.8	16.5	54.8	45.2	0	0	0	9.7	87.2	0	2.8
Br. Bogendreip	90.1	357	1211	2.2	9.7	0.4	82.5	12.9	49.0	51.0	0	0	0	22.1	72.4	0	4.2
Aven	30.1	427	1236	0.8	2.8	0.1	100	0	56.9	43.1	0	0	0	5.6	92.7	0	1.6
Birse	27.1	456	1206	0.8	2.9	0.1	100	0	31.1	68.9	0	0	0	0.4	95.1	0	4.5
Powlair	61.1	356	1108	1.4	5.2	0.23	94.8	5.2	19.4	80.6	0	0	0	10.1	74.2	0	9.5

<sup>a</sup> Estimated values except Heugh Head, Charr, Brocky Burn, Feshie Bridge and Allt a' Mharcaidh which are flow gauged.

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

Land use in the Feshie is mainly characterised by alpine heath at higher altitudes in the mountainous headwaters above 800 m, heather (*Calluna*) moorland covers the steeper slopes, with boreal blanket bog vegetation covering the peat soils (Table 1). Forest cover is restricted to some small areas of native woodlands of Scots pine (*Pinus sylvestris*) in the lower catchment and some small areas of commercial forest. Almost the entire catchment lies within the Cairngorms National Nature Reserve, so conservation is a major management priority (Matthew, 2002). However, Glen Feshie Estate, which owns much of the land, is managed as a working highland estate, with shooting of Red Deer (*Cervus elaphus*) and fishing for Salmon (*Salmo salar*) being important management objectives. Salmon are distributed throughout the main stem of the Feshie and the lower part of all the main tributaries, except the Eidart (Gardiner and Mackay, 2002).

Mean annual precipitation is estimated for the catchment at 1600 mm mainly derived from the prevailing westerly weather systems. It has been estimated that snow accounts for around 30% of annual precipitation (Soulsby et al., 1997). The mean flow at Feshie Bridge is  $8.01 \text{ m}^3 \text{ s}^{-1}$ , with the long-term (10 year)  $Q_{95}$  at  $1.71 \text{ m}^3 \text{ s}^{-1}$  and the  $Q_{10}$   $16.28 \text{ m}^3 \text{ s}^{-1}$ . Mean monthly temperatures at 575 m vary between  $1.2^\circ \text{C}$  in February and  $10.3^\circ \text{C}$  in July. Evapotranspiration rates vary between ca. 300 and 400 mm, being highest in the lower, forested parts of the catchment (Haria and Price, 2000; Dunn et al., 2003).

## 2.2. Feugh catchment

At  $233 \text{ km}^2$ , the Feugh catchment is almost identical in size to the Feshie; however with a mean altitude of 329 m, the catchment has a much lower elevation though the altitudinal range is 80–788 m (Fig. 1d and Table 1). The Mount Battock granite underlies most of the catchment and is of similar age to the Cairngorm granite in the Feshie (Fig. 1e). On

the southerly edge of the catchment, schists (mainly psammite) occur at the contact, whilst in the lower catchment metamorphic rocks ranging from psammite to graphitic schists outcrop (Smart et al., 2001).

The Feugh is formed by three tributaries (the Dye, Aven and Upper Feugh) of similar area, which are confluent some 4 km upstream of Heugh Head (the gauging station at the catchment outfall) (Fig. 1d). The largest of these sub-catchments (at  $90 \text{ km}^2$ ), the Water of Dye, is the most southerly and drains a granite-dominated area, although there is a significant outcrop of schist in its headwaters. The sub-catchment is characterised by extensive plateau areas on the interflues above 450 m that are dominated by peats (up to 5 m deep) and peaty podzols (ca. 1 m deep; Fig. 1f). Only on the more incised catchment slopes do more freely draining podzols (<1 m deep) occur and the main river valleys generally have alluvial deposits and soils. The Water of Feugh sub-catchment is the most northerly with granite-dominated headwaters grading to metamorphic rocks in the lower catchment near Powlair. In comparison with the Dye, the catchment has been over widened by glacial erosion and meltwater action, with more restricted plateau areas, lower peat coverage and larger areas of more freely draining podzols (Fig. 1f). More extensive alluvial deposits (>10 m deep) occupy the valley floor, especially in the Powlair area. The smallest sub-catchment ( $30 \text{ km}^2$ ) is occupied by the Water of Aven, which lies between the Dye and Upper Feugh. The upper sub-catchment drains an extensive peat-covered plateau underlain by granite, but downstream the valley is very steeply incised, mainly due to erosion by meltwaters. In the lowest part of the sub-catchment, extensive alluvial deposits form a fan, where the Aven confluences with the upper Feugh, and further extensive deposits fill the valley floor between this confluence and the gauging station of Heugh head.

As with the Feshie, the extensive peat soils have been shown to be the dominant source of storm runoff in the catchment (Soulsby et al., 2003a). Valley bottom alluvial deposits (in places over 20 m deep) include extensive sands and gravel aquifers that constitute the main catchment groundwater reservoirs that sustain baseflows.

Land management activities in the Feugh catchment are more intensive and varied than in the Feshie

(Table 1). The open moorlands which occupy the higher altitude parts of the catchment are mainly managed for grouse (*Lagopus lagopus*) shooting. Thus, the moors are regularly burned to create the patchwork of different aged heather (*Calluna*) stands that grouse utilise at different stages in their life cycle (Hudson, 2002). There are extensive areas of forestry; in the Water of Dye sub-catchment, this predominantly comprises commercial forest of pre-felling age whilst, in the Water of Feugh sub-catchment, an important area of native woodland is actively regenerating and managed for conservation purposes (Callander, 2000). Only in the lower catchment, on the extensive alluvial deposits does agriculture become spatially extensive and this mainly involves areas of arable farming and improved grazing.

Precipitation for the catchment is estimated around 1200 mm, being less exposed to westerly weather systems than the Feshie. Snow generally accounts for 10–15% of catchment precipitation and mean monthly air temperatures in Banchory 1 km south of the catchment range from 4 °C in February to 13 °C in July (Warren, 1985). The mean annual runoff at Heugh Head, the catchment outfall, is  $5.55 \text{ m}^3 \text{ s}^{-1}$ , with a range between a  $Q_{95}$  of  $0.9 \text{ m}^3 \text{ s}^{-1}$  and a  $Q_{10}$  of  $11.4 \text{ m}^3 \text{ s}^{-1}$ . Water balances estimates suggest annual evaporation estimates of 350–400 mm.

### 3. Methodology

In order to assess the tracer hydrology of the two catchments, a combination of hydrometric methods and hydrochemical surveys were used. In the Feshie catchment, pre-existing gauging stations at the Allt a' Mharcaidh and Feshie Bridge have flow records exceeding 10 years in length. This gives flow data at the 10 and 231 km<sup>2</sup> scales, respectively. In October 2000, fortnightly sampling commenced at these sites and the main tributaries of the Eidart, upper Feshie and Allt Chomraig, as well as two main stem sites upstream and downstream of the main Feshie braided section (Fig. 1a and Table 1) to give seven sites in total. Unfortunately, access restrictions resulting from the outbreak of Foot and Mouth Disease in the UK resulted in sampling ceasing in February 2001. A second hydrological year was

fully sampled at fortnightly intervals between October 2001 and September 2002. At these sites, mean daily flows during sampling were modelled using data from Feshie Bridge and adjusted to altitude as described by Wade et al. (1999); current metering at low and moderate flows confirmed accuracies to within  $\pm 10\%$  which is within typical gauging errors (8–10%).

To supplement this temporal sampling strategy, a major spatial survey was undertaken on 27th May 2002. This involved the collection of 140 samples from most of the main headwater tributaries of the Feshie, a range of main stem sites, various groundwater springs and overland flows from peaty soils. Flows on the sampling day were at the long-term  $Q_{55}$ , close to the median. Samples collected at Feshie bridge and analysis of the hydrograph confirmed stable hydrological and hydrochemical conditions during sampling. As road access is restricted to the lower part of the catchment, these samples were collected during four person days of work over a 24 h period that involved around 90 km of walking.

Pre-existing gauging stations in the Feugh catchment were located on the Water of Charr and Brocky Burn in the Water of Dye sub-catchment, and the catchment outfall at Heugh Head. Thus, flow data were available at scales of 1, 40 and 230 km<sup>2</sup> (Table 1 and Fig. 1). These sites, together with the five others on the main tributaries shown in Fig. 1d, were sampled at weekly or fortnightly occasions throughout the 2001–2002 hydrological year. Flows were again estimated for these sites using existing flow gauges, adjusting for altitude as described by Wade et al. (1999) and checked by spot gauging. An extensive spatial survey of the three main sub-catchments and their headwater tributaries was undertaken on 8th August 2002. As with the Feshie, flows and hydrochemical conditions were stable during sampling and flows equated to the  $Q_{47}$ . Although vehicular access in the Feugh is better than the Feshie, to collect the 135 samples involved six person days of effort over a 24-h period and approximately 92 km of walking.

All samples were analysed for pH, conductivity, and Gran alkalinity. In addition, silicate concentrations were determined for the samples collected during the spatial surveys. All of these parameters are relatively easy and cheap to measure, furthermore

they have proven utility as natural geochemical tracers, particularly in the UK uplands as they distinguish waters derived from acidic, organic soils and deeper, longer-residence time groundwaters in the deeper mineral soil and parent materials (Hill and Neal, 1997; Wade et al., 1999; Soulsby and Dunn, 2003). In particular, Gran alkalinity, which was determined by acidimetric titrations to end points of 4.5, 4, and 3, gives a directly measurable value that is very close to the chemically conservative parameter of acid neutralising capacity in catchments where aluminium concentrations are low (Neal, 2001; Stutter et al., 2001). This makes it useful for end member mixing studies, and a number of investigations have used this to differentiate between different source areas within catchment systems (Neal, 1997; Hill and Neal, 1997; Wade et al., 1999; Soulsby et al., 2003a). Silicate also gives a useful indicator of weathering reactions/residence times in catchment soils and bedrock (Hoeg et al., 2000; Smart et al., 2001).

A GIS was developed for both catchments. This incorporated a range of digital data sets including a Digital Elevation Model, soil cover, land use

and geology. This allowed catchment characteristics to be summarised for any sub-catchment greater than ca. 1 km<sup>2</sup> in area (Langan et al., 1997; Soulsby and Dunn, 2001).

#### 4. Catchment hydrology

Standardised flow duration curves for the Allt a' Mharcaidh and Feshie Bridge provide a summary of the runoff characteristics of the Feshie catchment at the 10<sup>1</sup> and 10<sup>2</sup> km<sup>2</sup> scales, respectively, and these can be compared for similar scales in the Feugh at Charr and Heugh head (Fig. 2). This gives some insight into the changing hydrological characteristics with spatial scale. At flows greater than  $Q_{40}$ , standardised flows (flow/mean flow) at Feshie Bridge are generally greater than the Mharcaidh, with a higher specific discharge (not shown), implying a more marked storm runoff response. Conversely, at lower flows standardised flows and specific discharges are greater in the Allt a' Mharcaidh implying greater groundwater contributions.

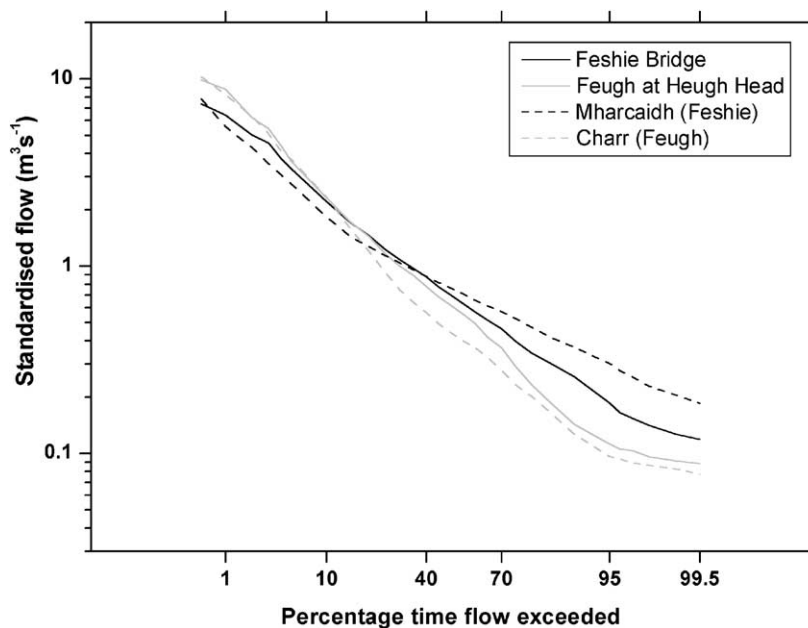


Fig. 2. Flow duration curves for the Feshie and Feugh catchments along with the Allt a' Mharcaidh and the water of Charr.

In the Feugh catchment, the standardised flow duration curves for the Charr and the Feugh at Heugh head are similar above the  $Q_{10}$ . Specific discharges at high flows (not shown) are higher at Charr (Soulsby et al., 2003a), implying a more marked storm runoff response, whilst standardised low flows and specific discharges over the remainder of the flow duration curves are higher for the Feugh at Heugh Head suggesting greater groundwater contributions.

These flow duration curves indicate some significant contrasts in functioning between the two catchments, and show, in the case of the Feshie, that anticipated increased baseflow contributions in larger catchments are not necessarily as expected. The greater importance of groundwater contributions in the Feshie catchment compared with the Feugh is evident from Fig. 2; at Feshie Bridge, this probably reflects the importance of groundwater in the alluvium which covers extensive valley bottom areas and other glacial and periglacial drift deposits (Fig. 1b). The greater groundwater storage in the Allt a' Mharciadh, is less related to alluvium, but instead reflects relatively high recharge from the relatively deep periglacial drift beneath alpine soils which cover the 30% upper catchment and storage in extensive glacial drifts in the lower catchment (Soulsby et al., 1998, 1999). In contrast, the greater coverage of peat in the catchment at Feshie Bridge (33% compared with 25% in the Mharciadh) and shallow alpine soils, bedrock and gleys (31% compared with 8%) results in a more marked storm response in larger catchment.

In the Feugh, both catchments upstream of Charr and Heugh head have extensive coverage of peat soils (65 and 32%, respectively) to generate similar storm responses, although the lower part of the catchment immediately upstream of Heugh head has the more extensive alluvial deposits to facilitate groundwater storage. This gives a more classical pattern of increased groundwater contribution with catchment size. In contrast to the Feshie, storm flows appear to be more responsive and groundwater contributions more limited.

### 5. Stream chemistry—temporal variations and hydrological pathways

Fig. 3a and b shows the time-series of discharge and the fortnightly stream alkalinity samples collected

from the seven locations in the Feshie catchment. These time series are supplemented by plots of concentration against flow for selected sampling points (Fig. 4). The most salient features of these plots are the wide range of alkalinities observed at the various sampling points during low flow periods and the lowering and convergence of concentrations at relatively high flows. This reflects the increasing acidity of stream waters in storm events as soil-derived flow paths become increasingly important. In general, low flow alkalinities were ordered as Allt Chomraig > Upper Feshie > Feshie Bridge > Feshie Lodge > u/s braids > Eidart > Allt a' Mharciadh. At higher flows, alkalinities became negative at all sites, with the Upper Feshie and Eidart generally having the lowest storm flow alkalinities, though negative alkalinities were observed at Feshie bridge as flows approached the  $Q_5$  ( $25 \text{ m}^3 \text{ s}^{-1}$ ; Fig. 4).

Fig. 3c and d shows equivalent time series plots for the Feugh catchment, together with plots of alkalinity concentration against flow for selected sites in Fig. 5. Again, widely varying baseflow chemistries were observed, ranging from  $\cong 70 \mu\text{equiv. l}^{-1}$  in the Water of Aven (Balblythe) to  $\cong 300 \mu\text{equiv. l}^{-1}$  in the Water of Charr. Generally, base flow alkalinities follow the pattern Charr > Powlair > Birse > Heugh head > Bogendreip > Dye > Brocky > Balblythe (Aven) (Fig. 1). However, at high flows, negative alkalinities are observed at all sites except Powlair.

In both catchments, these broad patterns reflect the influence of soils and geology. Differences in geology govern the degree of groundwater recharge, storage and geochemistry of water–rock interaction (Wade et al., 1999). Thus groundwater, and hence base flow, alkalinities are higher in catchments where more reactive, metamorphic rocks are present (e.g. the Allt Chomraig and the Water of Charr) rather than granite (Water of Aven, the Eidart and the Allt a' Mharciadh). Storm flow chemistry is also influenced by the coverage of acidic peaty, shallow alpine soils and bedrock. These areas generate storm runoff peaks comprised of low alkalinity waters like in the Eidart, Upper Feshie, Brocky and the Water of Aven (Soulsby and Dunn, 2003). At anytime, the interaction between the volume of acidic soil waters and the degree of groundwater buffering determines stream chemistry.

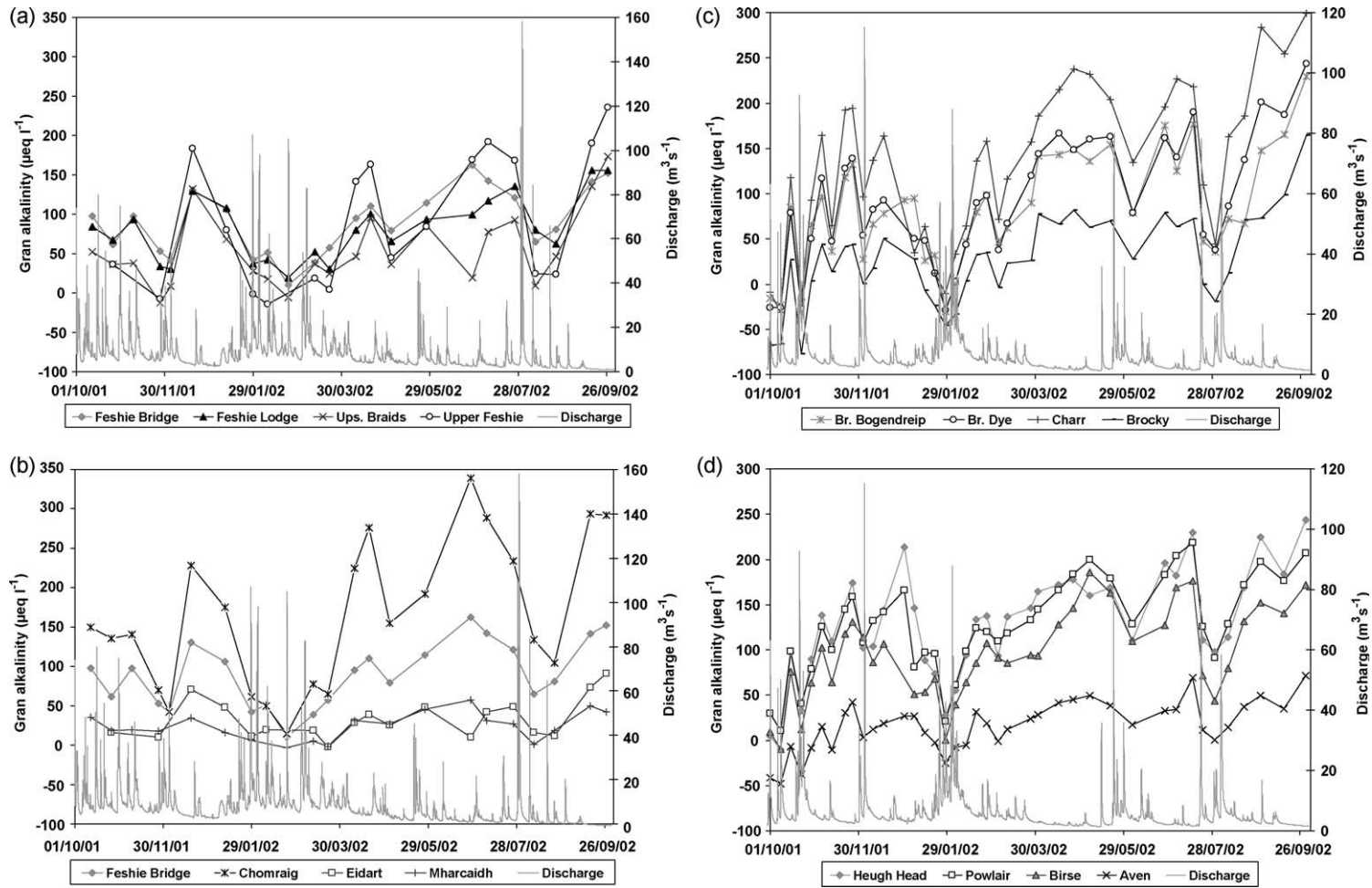


Fig. 3. Time series of alkalinity over the 2001–2002 hydrological year for the main sub-catchments of the (a and b) Feshie and (c and d) Feugh.

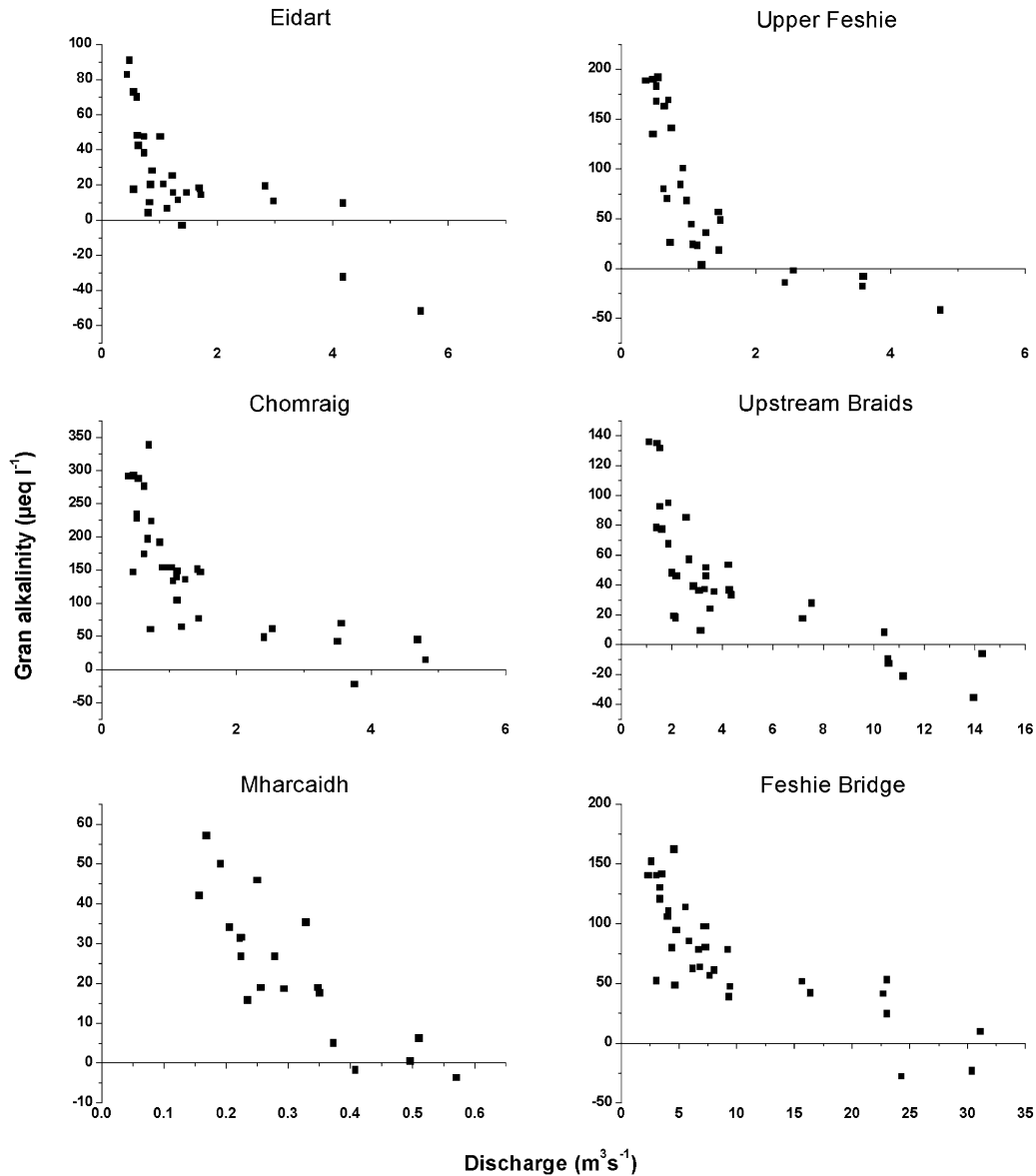


Fig. 4. Concentration vs. flow plots for selected Feshie sub-catchments.

In this context, two component end member mixing has been shown to be a useful approach to chemically-based hydrograph separation in mountainous catchments in Scotland (Wade et al., 1999; Soulsby et al., 1998). Storm runoff from overland flow or shallow sub-surface storm flows in peaty soils and shallow alpine soils/bedrock tends to discharge directly into first and second order channels,

and originating from acidic soil horizons, has broadly similar chemical characteristics of low alkalinity and silica concentrations. This provides a soil-water based storm flow end member for hydrograph separation. In contrast, deeper sub-surface hillslope drainage tends to be hydrologically de-coupled from stream channels as it mainly serves to mix with, and displace groundwater in alluvium or other drift that

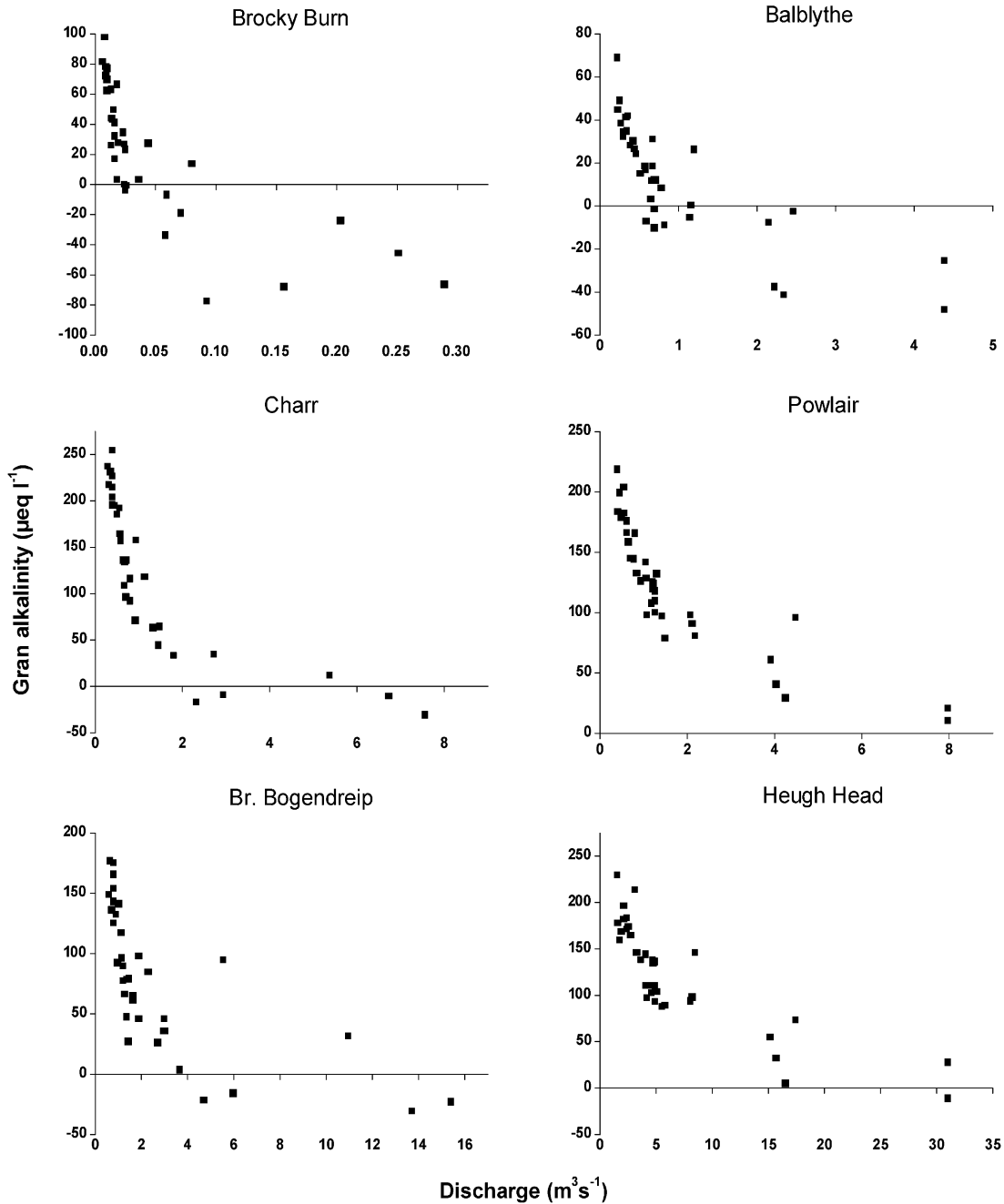


Fig. 5. Concentration vs. flow plots for the selected Feugh sub-catchments.

stores ground water in valley bottom areas (Smart et al., 2001). Thus baseflow chemistry provides an integrated measure of groundwater for mixing analysis.

Table 2 shows the result of a simple two component hydrograph separation at the seven Feshie monitoring sites. Fig. 6a shows the separation for Feshie Bridge at the catchment outfall. An integrated

Table 2  
Hydrograph separation results for Feshie and Feugh sub-catchments

	Flow ( $\text{m}^3 \text{s}^{-1}$ )		Groundwater contribution to annual flow (%)		
	$Q_5$	$Q_{95}$	<i>Alpine</i> soil water end-member ( $-25 \mu\text{equiv. l}^{-1}$ )	<i>Peat</i> soil water end-member ( $-48 \mu\text{equiv. l}^{-1}$ )	
<i>Feshie</i>					
1. Feshie Bridge	26.5	1.7	46.7	51.2	
2. Allt Chomraig	4.1	0.3	48.5	51.6	
3. Feshie Lodge	15.3	1.0	43.5	49.5	
4. Upstream Braids	12.2	0.8	31.2	37.2	
5. Eidart	4.8	0.3	31.2	40.8	
6. Upper Feshie	4.1	0.3	31.9	36.8	
7. Allt a' Mharcaidh	0.7	0.07	46	67	
	$Q_5$	$Q_{95}$	<i>Mean peat</i> soil water end-member ( $-49 \mu\text{equiv. l}^{-1}$ )	+ St. dev. <i>peat</i> soil water end-member ( $-31 \mu\text{equiv. l}^{-1}$ )	- St. dev. <i>peat</i> soil water end-member ( $-67 \mu\text{equiv. l}^{-1}$ )
<i>Feugh</i>					
1. Heugh Head	20.1	0.9	54.6	51.0	57.8
2. Brocky Burn	0.16	0.005	24.3	19.3	30.0
3. Charr	4.7	0.2	37.3	34.3	40.1
4. Br. Dye	7.8	0.3	35.1	31.3	38.7
5. Br. Bogendreip	9.7	0.4	35.8	31.6	39.9
6. Aven	2.8	0.1	41.4	32.5	49.4
7. Birse	2.9	0.1	47.9	43.3	51.9
8. Powlair	5.2	0.23	54.7	51.2	57.7

estimate of groundwater alkalinity was derived from the mean of the lowest three flows sampled at each point (Neal, 1997). Two estimates of soil water alkalinity were used at  $-48$  and  $-25 \mu\text{equiv. l}^{-1}$  which represent the mean of overland flow samples collected from peats and shallow alpine soils, respectively. These two soil types are the main sources of storm runoff generation in the Feshie catchment and, thus, provide an appropriate range of soil water end members to assess variability in groundwater contributions. According to the resulting separations (Table 2), the Upper Feshie and Eidart have the lowest groundwater contributions over the hydrological year with 32–37% and 32–41%, respectively. This is consistent with the high peat coverage in the upper Feshie and thin soils in the Eidart, together with the limited storage in drift deposits and the bedrock. In contrast, the Allt a' Mharcaidh had groundwater contributions of 46–57%

of annual flows, reflecting greater recharge of shallow, but significant groundwater bodies in the deeper alpine soils (on periglacial drifts) and drift deposits in the lower catchment (Fig. 2). In the main stem of the Feshie, modelled groundwater contributions increased from 32 to 37% upstream of the braids to 44–50% downstream, to 47–51% at Feshie Bridge (Table 1). Clearly, the greater groundwater storage in the alluvial deposits of the lower Feshie valley and the Allt Chomraig, together with storage in the western Cairngorm streams like the Mharcaidh, increase downstream contributions. At all sites however, substantial groundwater contributions need to be invoked to explain storm flow chemistries showing mixing with, and displacement by hillslope drainage occurring during storm events.

A similar picture emerges in the Feugh catchment when the annual hydrograph was separated using end member mixing (see Heugh Head example in Fig. 6b).

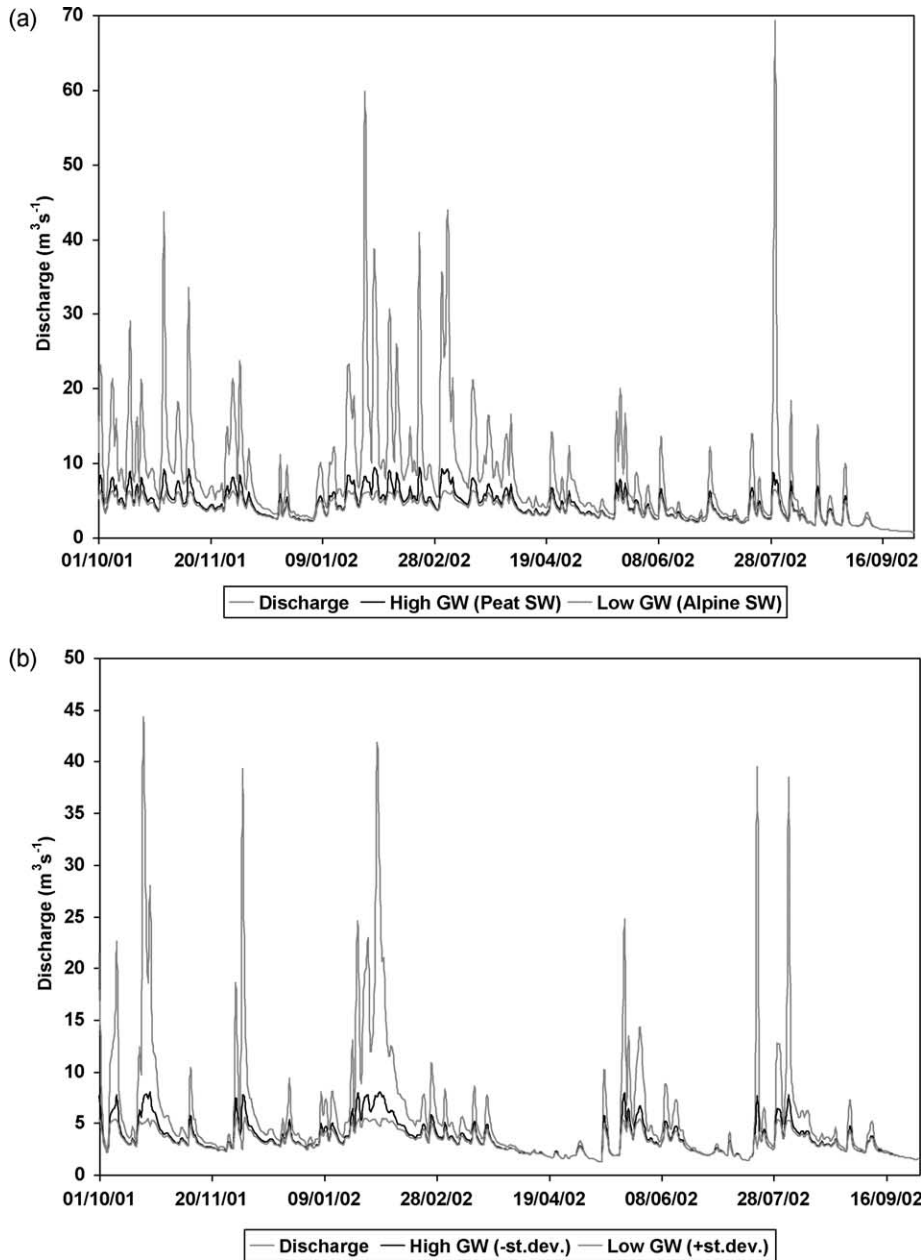


Fig. 6. Hydrograph separations for the (a) Feshie and (b) Feugh catchments.

Again, the three lowest flows were used to characterise catchment groundwater alkalinity, whilst the standard deviations of collected peat overland flow samples were used to estimate the upper and lower alkalinities of soil waters (Table 2). The metamorphic

rocks at the head of the Water of Dye produce the most marked baseflow buffering in stream chemistry at Charr, which declines downstream at Bridge of Dye and Bogendreip as granite becomes increasingly dominant as the catchment bedrock. Groundwater

contributions are lowest in small headwater streams like Brocky burn (19–30%), and then increase with catchment scale to 34–40% at Charr. There is no estimated increase from here downstream to Bridge of Bogendreip (32–40%), despite the catchment area doubling. The smaller Water of Aven at Balblythe, the reflects its shallow soil coverage and granitic bedrock, by having a limited range of alkalinities and larger uncertainties over the hydrograph separations (33–49%). The more permeable Upper Feugh also produces relatively high baseflow alkalinities, presumably as a result of greater groundwater storage and greater recharge resulting from the lower peat coverage, which give predicted groundwater contributions of 51–58% at Powlair. At Heugh head the flow path contributions in the three sub-catchments are integrated and the model indicates 51–58% groundwater contributions over the hydrological year, which is slightly higher than for the Feshie at Feshie Bridge. Comparison of the separated hydrographs in Fig. 6 suggests a more gradual recession control by groundwater in the Feugh catchment, probably reflecting lower hydraulic gradients resulting from the larger areas of flatter ground and more subdued topography (Fig. 1).

## 6. Stream chemistry—spatial variation and hydrological sources

Although investigating temporal changes in tracer hydrology within nested sub-catchments provided considerable insight into hydrological and hydrochemical functioning, further data are needed to identify how different hydrological sources at smaller spatial scales aggregate to underpin the sub-catchment response. The results of the spatial survey (27th May 2002) of the Feshie hydrochemistry are shown in the interpolated spatial distribution of Gran alkalinity in Fig. 7a. Flows on this day equated to the  $Q_{55}$  and followed some relatively heavy rain in the preceding week. It is immediately apparent that the relatively simple flow concentration plots observed at an individual sampling point belie a wide range of source chemistries. Alkalinity concentrations in the upper Eidart are the lowest, reflecting the shallow granitic alpine soils and peats that form the headwaters. Flows from the schist headwaters in

the northwest of the sub-catchment result in alkalinity concentrations increasing downstream. A more marked downstream decline in alkalinities occurs in the upper Feshie as groundwaters draining the schist-derived soils in the catchment headwaters mix with more acidic, low alkalinity waters derived from the extensive peatlands which cover the lower catchment slopes (Fig. 1).

Downstream of the Eidart/upper Feshie confluence, the alkalinity of the main stem of the Feshie declines slightly towards the braided section. This reflects the influx of acidic tributaries from the south bank of the Feshie where peaty soils predominate; this masks the high alkalinity inputs from some of the small tributaries on the northern side of the Feshie gorge. However, through the braided reach, groundwater inflows and inputs from relatively alkaline tributaries such as the Lorgaidh increase the main stem alkalinity. Downstream of the braids, further groundwater inputs from the alluvial deposits in the lower Feshie valley, together with flows from the 45 km<sup>2</sup> Allt Chomraig sub-catchment cause further alkalinity increases along the main stem, despite the low alkalinity inputs from the western Cairngorm streams like the Allt a' Mharcaidh.

Plotting two flow-variant tracer concentrations against each other reveals significant structure to the data sets for each sub-catchment (Fig. 8a). Both alkalinity and silicate measurements provide independent indexes of the degree of weathering and organic-soil derived waters. Samples collected from the Eidart sub-catchment and the Upper Feshie exhibit similar ranges of Gran alkalinity and silica concentrations and samples lie on a line of similar slope (Fig. 8a). The upper Feshie samples exhibit more scatter and have a greater proportion of samples with high alkalinity and high silica concentrations. In addition, samples of first order peat streams which cover an extensive proportion of the Upper Feshie headwaters have very low silica and alkalinity concentrations, similar to storm runoff samples. Samples collected from the Allt Chomraig tend to have higher alkalinity and silica concentrations than the Eidart and Upper Feshie, though the samples collected spanned a similar range. The most variable population of samples collected were those of small first–third order tributaries of the main stem of the Feshie, which exhibited widely varying chemical

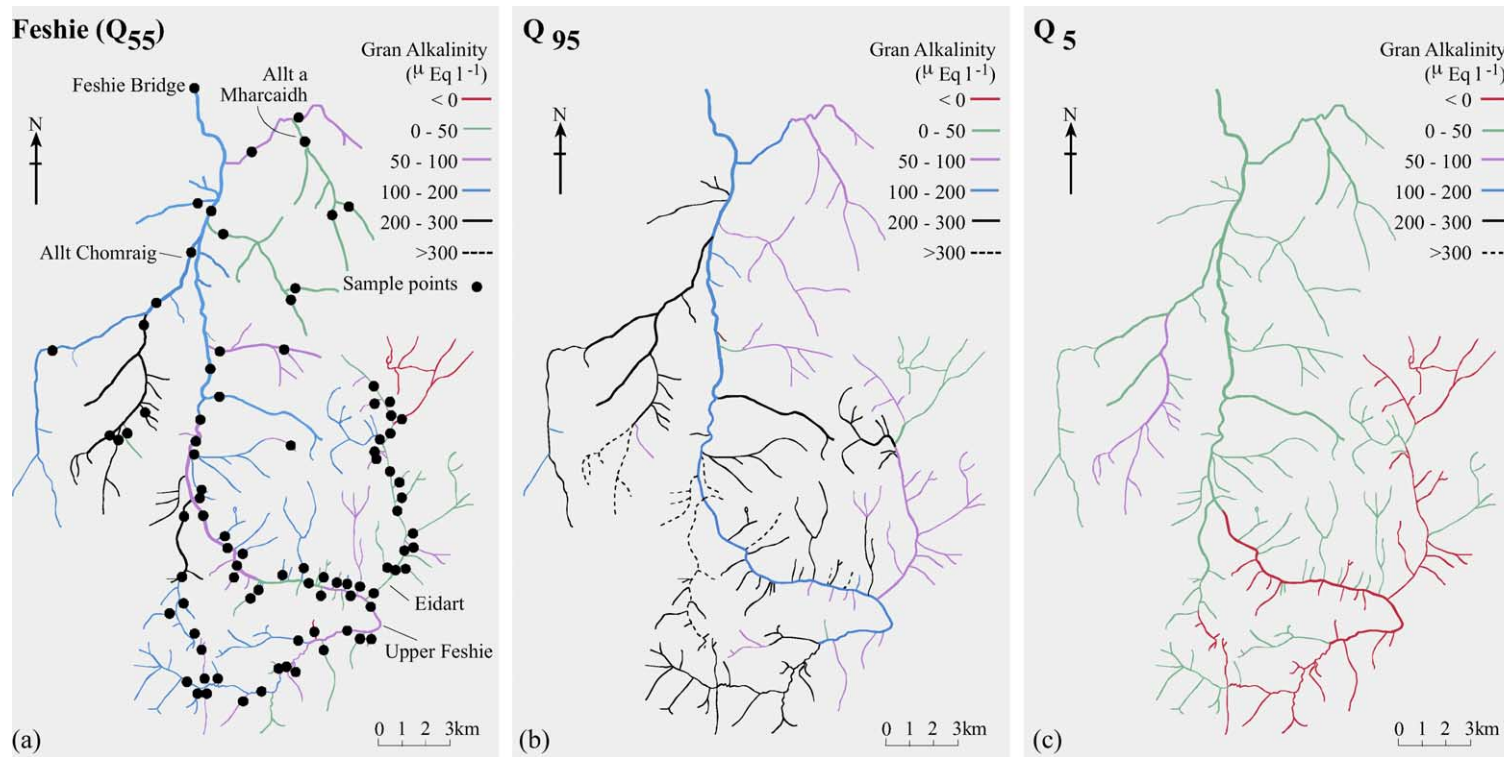


Fig. 7. Spatial variation in Gran alkalinity in the Feshie catchment (a) May 2002, (b)  $Q_{95}$ , (c)  $Q_5$ .

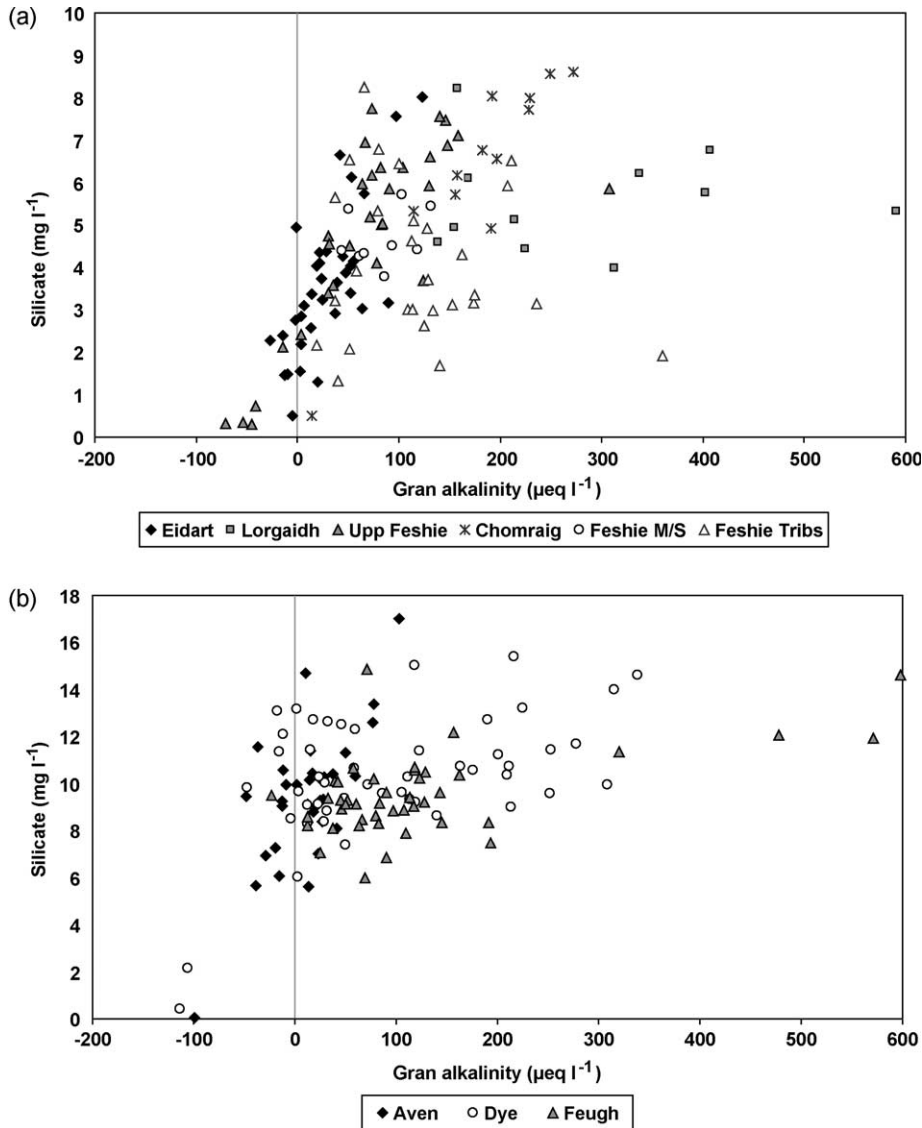


Fig. 8. Alkalinity and silicate concentrations in major sub-catchments of the (a) Feshie and (b) Feugh catchments.

characteristics. Moreover, the Allt Lorgaidh tributary samples had a wide range of alkalinity concentrations. Due to the mixing of contrasting source waters, the mainstem Feshie samples plot within the cloud of samples collected from throughout the catchment.

These differences in sub-catchment hydrochemistry reflect the interaction of soil-derived and ground-water-derived hydrological sources upstream of each individual sampling point. Fig. 9 shows

the generalised conceptual hydrological pathways and their characteristic chemistries (based on samples collected) of the main soil types in the Feshie catchments. Thus, the schist-dominated and felsite/diorite influenced catchments of the Allt Chomraig and Upper Feshie have the highest baseflow alkalinities, reflecting more rapid weathering reactions than in the granite-influenced Eidart and Allt a' Mharcaidh. Although the Eidart has large areas of schist, the soils

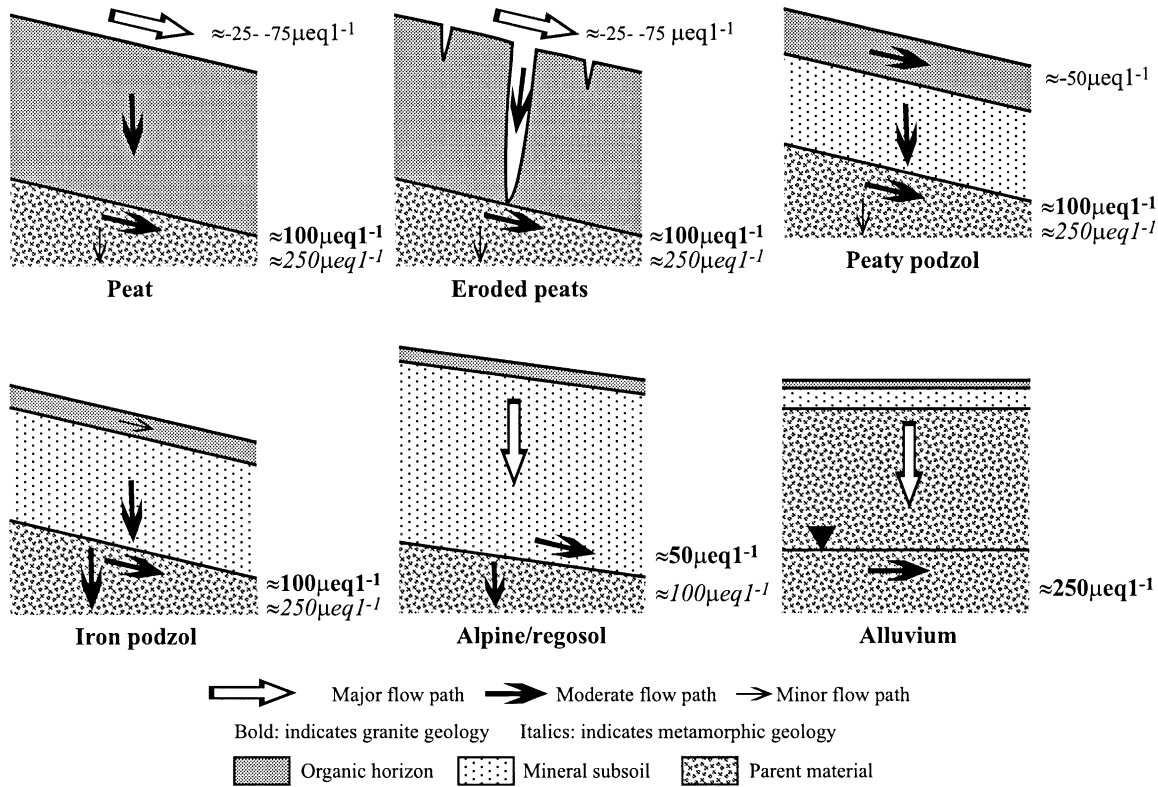


Fig. 9. Conceptual flow paths in main hydrological response units for the Feshie and Feugh catchments.

are very thin and drifts only occupy the lower catchments, reducing residence times. The baseflow alkalinities along the main stem of the Feshie, generally show increasing trends downstream, presumably reflecting greater groundwater inputs from alluvial aquifers in the lower catchment, and the influence of the Chomraig. In contrast, at high flows, this groundwater influence is masked by the influence of rapid runoff generated from the peats and other shallow organic soils, which generally has alkalinity values of  $-75-25 \mu\text{equiv. l}^{-1}$  (Fig. 9). Obviously, the effect of this hydrological flow path on stream water chemistry depends largely on the area of peat coverage and the degree of buffering available from groundwater.

Fig. 10a shows the spatial variation in Gran alkalinity in the Feugh catchment as sampled on the 8th August 2002. Flows on this day equated to the  $Q_{47}$  and followed some intensive convective rainfall the preceding week. The highest alkalinities were measured in headwater streams in the southern part

of the Dye sub-catchment, where streams drained areas underlain by schists and other metamorphic rocks (Fig. 1e). The northern headwaters of the Dye drain granitic areas and have much lower alkalinities. Thus, alkalinities in the mainstem of the Dye decline downstream towards the Charr Flume, a trend which continues in the lower sub-catchment as more inflows from the granite derived soils occurs. The Water of Aven also shows a downstream decline in alkalinity, despite its catchment being entirely underlain by granite. The headwaters of the sub-catchment drain the mineral slopes of Mount Battock and heavily eroded peatbogs that allow recharge of groundwater in the underlying mineral soils. The lower catchment becomes increasingly incised, with peats and thinner soils that produce drainage waters with low alkalinities. Thus, a slight, but detectable downstream decline is observed. In contrast, the alkalinities in the upper Feugh increase downstream. The greater coverage of podzolic soils and glacial drift material in the valley bottoms results in larger groundwater

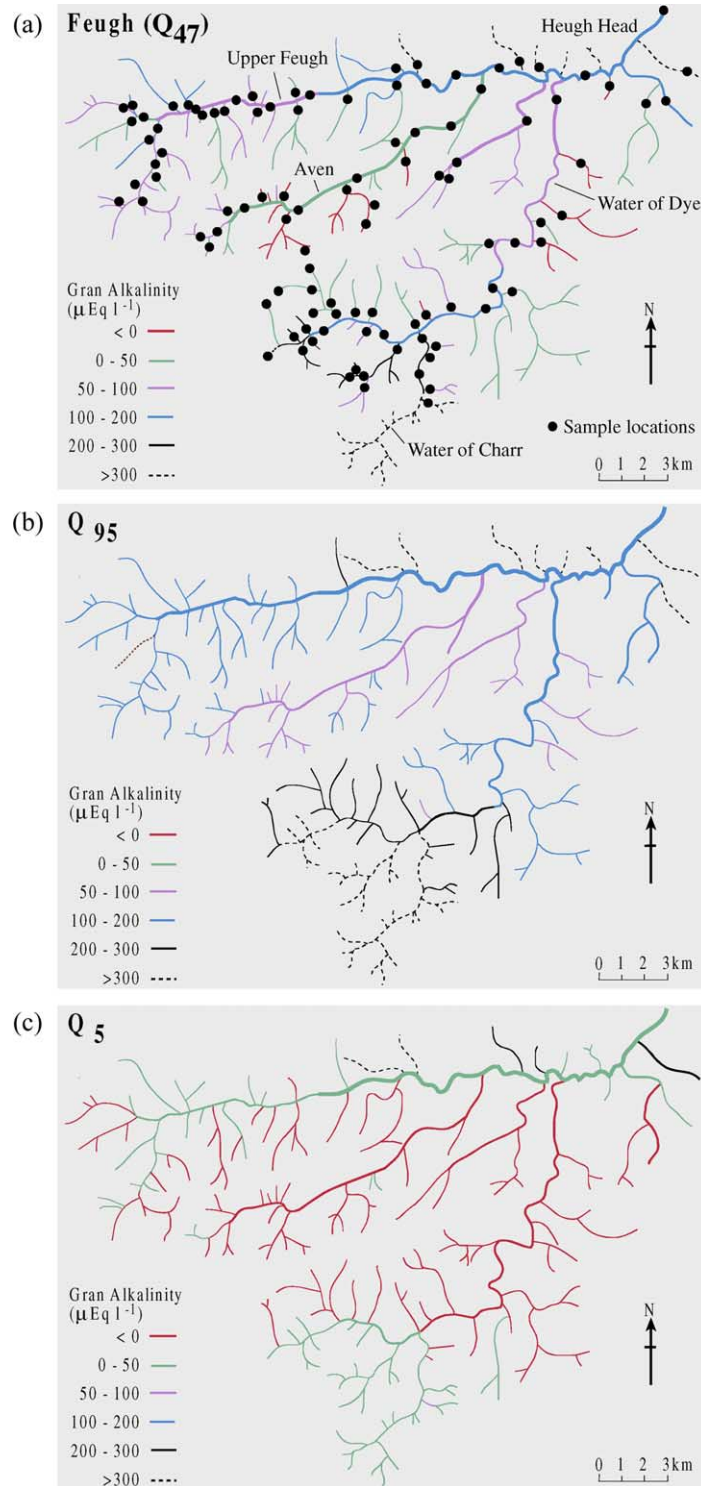


Fig. 10. Spatial variation in Gran alkalinity in the Feugh catchment (a) August 2002, (b) Q<sub>95</sub>, (c) Q<sub>5</sub>.

influences on flows, with a concomitant increase in alkalinity to Heugh head, despite inflows from the Aven and Dye. It is notable that some small high alkalinity tributaries enter the lower Feugh from areas of metamorphic rocks in the lower catchment, most notably a small south bank tributary just upstream of Heugh head which drains from an area underlain by the Deeside limestone (Fig. 1f).

The same data are plotted as alkalinity-silica relationships for the three main sub-catchments in Fig. 8b. Again, wide-ranging chemistries were observed in each sub-catchment, but some structure, albeit less marked than for the Feshie, emerged. The Water of Dye samples showed the largest scatter with higher alkalinity and silica levels in the metamorphic upper headwaters and more acidic waters draining the granite in the northern parts of the sub-catchment. The Water of Aven samples span a similar range to the Eidart in the Feshie, being relatively low in alkalinity and silica. The Upper Feugh samples still exhibited considerable scatter compared with the Aven, though less marked than Charr. Lower alkalinity/silica samples were observed in the most upstream headwaters. Again these patterns are consistent with the combined soil and geological influence on the chemistries of different hydrological pathways as shown in Fig. 9.

### 7. Predicting catchment scale hydrochemistry under contrasting flow conditions

In considering the likely flow path combination and end member chemistry for the main sampling points, the series of concentration–discharge plots shown in Figs. 4 and 5 provides a family of curves that can be used as a basis for a scale-independent method for classifying the other streams sampled during the spatial surveys of the Feugh and Feshie. These can aid prediction of flow-related chemistry changes, which can provide a basis for conceptualising catchment-wide hydrochemistry variations at different flows. Soil water and groundwater end members (three highest and lowest flows) for each of these routine sites in the Feshie and the Feugh were related by multiple regression to their respective soil and geology coverage determined

through a GIS (Smart et al., 1998; Wade et al., 1999). Example regression equations used for the Feshie were:

Groundwater EM

$$= 52.2 - 1.1 (\% \text{Peat}) + 0.23 (\% \text{Granite}) \\ - 289 (\% \text{Felsite} + \text{Diorite}) : R^2 = 0.99$$

Soil Water EM

$$= -51.8 + 1.43 (\% \text{Peaty podzol}) \\ + 0.64 (\% \text{Alpine}) : R^2 = 0.79$$

The likely high and low flow alkalinities for each spatial survey sample site shown in Figs. 8 and 10 were then predicted using the same two component end member mixing technique used previously in this paper. The stream water alkalinities sampled under average flow conditions (Figs. 8 and 10) were used as a check on the general validity of these predictions. Extensive historic data collection in the western Cairngorm streams (Soulsby et al., 2001), the Water of Dye sub-catchment of the Feugh (Dawson, 1999) and the Upper Feugh (Soulsby et al., 1995) also corroborated these predictions as being a good indication the range of measured high flow and low flow chemistries at various sites.

At low flows the influence of the catchment geology of the hydrochemistry is readily evident. Thus, in the Feshie, the Upper Feshie, Allt Chomraig and Lorgaidh have the highest alkalinities ( $> 300 \mu\text{equiv. l}^{-1}$ ), compared with the granite derived streams like the Mharcaidh and Eidart ( $< 100 \mu\text{equiv. l}^{-1}$ ; Fig. 7b). This reflects the metamorphic rocks present in the catchment and the presence of diorite and/or felsite that buffers groundwater chemistry. Moreover, under such low flow conditions, drainage from the acidic soils in the catchment will exert a small influence on stream chemistry. Conversely at high flows, the dominance of acidic, low alkalinity ( $< 50 \mu\text{equiv. l}^{-1}$ ) storm runoff is predicted to dominate stream flows throughout the river network, with only groundwater in the headwaters of the Allt Chomraig sustaining stream chemistry above  $50 \mu\text{equiv. l}^{-1}$  (Fig. 7c).

Similarly in the Feugh, baseflows show the low levels of buffering ( $< 100 \mu\text{equiv. l}^{-1}$ ) in the granite-dominated Water of Aven sub-catchment (Fig. 10b) compared with the base-rich sub-catchments of

the upper Dye and lower Feugh where alkalinities are well-above 200  $\mu\text{equiv. l}^{-1}$ . However, at high flows, the influence of acidic runoff from the greater coverage of peaty soils is more dramatic than for the Feshie, with only the lower stretches of Feugh and the most southerly headwaters of the Dye maintaining positive alkalinities (Fig. 10c).

## 8. Discussion

By combining relatively high-resolution temporal and spatial sampling in mesoscale catchments, tracer hydrology provides considerable insight into catchment hydrological functioning in a way that small-scale hydrometric studies could never do. Despite marked heterogeneity in catchment characteristics, flow-related water quality variations are very predictable for certain tracers in upland catchments (Hoeg et al., 2000). The degree of variation observed clearly related to geology, drift cover and catchment soil characteristics. As such, the tracers indicate the degree of groundwater recharge, the geochemistry of the catchment groundwater stores, and the relative importance of peats and thin acidic soils in generating storm runoff and contributing to catchment recession flows. This gives a predictability to tracer behaviour that could be used to model internal catchment-wide hydrochemistry to supplement the information already gained from routine monitoring. Although, the results of this analysis are only preliminary, they nonetheless provide a useful additional tool for dis-aggregating the hydrological and hydrochemical behaviour observed at the catchment scale. Further work is underway to assess more thoroughly the accuracy of these predictions against the observed spatial survey results. Comparable studies from other mesoscale catchments combining field tracer studies and GIS techniques are clearly also required in order to establish whether this particular approach has wider applicability to other mesoscale catchments. For example, the clear chemical gradients observed in upland soils and groundwaters may be lost in agricultural catchments where ploughing and fertiliser application may homogenise end member chemistry (Soulsby et al., 2003b).

The advantages of the insights gained from this study include two key aspects. The first, which is important from a management perspective, is that

the hydrochemical functioning at the catchment scale can be understood. For example, the two catchments studied have very important salmonid fisheries. Salmon are known to be sensitive to stream acidity and yet this study has shown that large parts of both catchments have negative alkalinity waters at high flows. Whilst these clearly do not constrain salmon populations surviving at the catchment scale, the spatial variations in water quality will have important implications for the hydroecology of the two catchments and its internal structure (SEPA, 2000). This is invaluable information where catchment management strategies such as afforestation and liming could be usefully guided by identifying sensitive parts of catchments (Wade et al., 2001).

The second main insight is that hydrochemical tracer work can help underpin modelling studies in mesoscale catchments by providing an alternative means for model validation, and confirmation that distributed model structures give a reasonable representation of catchment flow paths (Guenter et al., 1999). It is recognised that this is not a panacea; modelling flow path partitioning at daily time steps in such a similar manner will miss a lot of event-specific variability in event characteristics, and other factors such as the importance of spatial variability in precipitation. Nevertheless, the value of larger scale hydrochemical tracer studies in catchment modelling deserves further assessment. To this end, future work in the Feshie and Feugh catchments will focus on the potential of stable isotope tracers ( $\text{O}^{18}$ ) in complementing hydrochemical tracer insights to provide information on catchment mixing and residence time variation. Together, this in-depth tracer-based understanding will be used as the basis for the application and validation of distributed hydrological modelling in both catchments.

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