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Conceptualization of runoff processes using a geographical information system and tracers in a nested mesoscale catchment

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Abstract:

Tracer investigations were combined with a geographical information system (GIS) analysis of the 31 km^2 Girnock catchment (Cairngorm Mountains, Scotland) in order to understand hydrological functioning by identifying dominant runoff sources and estimating mean residence times. The catchment has a complex geology, soil cover and topography. Gran alkalinity was used to demonstrate that catchment geology has a dominant influence on baseflow chemistry, but flow paths originating in acidic horizons in the upper soil profiles controlled stormflow alkalinity. Chemically based hydrograph separations at the catchment scale indicated that ~30% of annual runoff was derived from groundwater sources. Similar contributions (23–36%) were estimated for virtually all major sub-basins. δ^{18}O of precipitation (mean: $-9\cdot4$‰; range: $-16\cdot1$ to $-5\cdot0$‰) and stream waters (mean: $-9\cdot1$‰; range: $-11\cdot6$ to $-7\cdot4$‰) were used to assess mean catchment and sub-basin residence times, which were in the order ~4–6 months. GIS analysis showed that these tracer-based diagnostic features of catchment functioning were consistent with the landscape organization of the catchment. Soil and HOST (Hydrology of Soil Type) maps indicated that the catchment and individual sub-basins were dominated by hydrologically responsive soils, such as peats (Histosol), peaty gleys (Histic Gleysols) and rankers (Umbric Leptosols and Histosols). Soil cover (in combination with a topographic index) predicted extensive areas of saturation that probably expand during hydrological events, thus providing a high degree of hydrological connectivity between catchment hillslopes and stream channel network. This was validated by aerial photographic interpretation and groundtruthing. These characteristics of hydrological functioning (i.e. dominance of responsive hydrological pathways and short residence times) dictate that the catchment is sensitive to land use change impacts on the quality and quantity of streamflows. It is suggested that such conceptualization of hydrological functioning using tracer-validated GIS analysis can play an important role in the sustainable management of river basins. Copyright © 2006 John Wiley & Sons, Ltd.

KEY WORDS dominant runoff processes; environmental tracers; geographical information system; HOST classification; isotopes; landscape organization; mean residence times; mesoscale; terrain analyses

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INTRODUCTION

The need to upscale hydrological understanding has become a central research issue in recent years (Bonell, 1998). A number of initiatives have challenged hydrologists to extrapolate their understanding of runoff processes from hillslope and small catchment (>1 km^2) scales to larger mesoscale basins (>10 km^2), where catchment and water management issues become apparent (Sivapalan, 2003). International research programmes have emerged, such as the International Association of Hydrological Sciences (IAHS) Prediction in Ungauged Basins (PUB) initiative, which seeks to develop new tools to transfer hydrological conceptualization to sparsely instrumented basins in order to underpin more robust modelling methodologies (Sivapalan *et al.*, 2003). Similarly, the UNESCO Hydrology, Environment, Life and Policy (HELP) agenda urgently calls upon catchment scientists to find tools that help translate their understanding of biophysical processes in ways that can aid catchment and water managers develop more sustainable approaches to resource utilization as required by legislation such as the European Union's Water Framework Directive (Bonell, 2004; Takeuchi, 2004). In response to such challenges, the catchment hydrology research community is looking afresh at how the spatial arrangement of watershed characteristics (i.e. topography, geology and soils), or landscape organization, determines the variability in water flow paths, storage and residence times at larger spatial scales (Beighley *et al.*, 2005; McGuire *et al.*, 2005). Two approaches with particular potential to aid this upscaling involve the use of readily available geo-spatial data, which can be easily

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integrated within a geographical information system (GIS), and environmental tracer studies (Rodgers *et al.*, 2005a; Soulsby *et al.*, 2006a).

Multiple digital data sets are often available for catchments characteristics and GIS techniques are now widely used to combine and integrate data layers in terrain and landscape analyses, which facilitate visualization of spatially distributed catchment features and processes at larger scales (Fluegel, 1995; Richards and Brenner, 2004). In order to use GIS in upscaling the transfer of process knowledge, simple tools are needed that allow generalizations that aid the understanding of hydrological functioning in a scale-independent manner (Bongartz, 2003). For example, new high-resolution approaches to terrain analysis have been used to consider topographic indices of hydrological similarity in order to give more realistic assessments of hillslope connectivity to improve the predictions of traditional rainfall-runoff models (Lane *et al.*, 2004). Similarly, digital soil data may have advantages over topographic approaches alone, as soils (in addition to topography) also integrate the influence of geology, land use and climate in a way that helps define areas of hydrological similarity (e.g. Scherrer and Naef, 2003; Weiler and Naef, 2003; Uhlenbrook *et al.*, 2004). In the UK, for example, the Hydrology of Soil Type (HOST) classification system (Boorman *et al.*, 1995) is based on soil characteristics, which infer aspects of hydrological response and dominant runoff processes. This enables the delineation of such information and allows it to be extrapolated to a range of catchment scales to understand the controls on catchment hydrological response (Soulsby *et al.*, 2006a). Other researchers have used geological maps to characterize geological influences at different scales in similar way (Smart *et al.*, 2001; Beighley *et al*, 2005).

As it is often difficult to extrapolate from traditional (typically hillslope scale) hydrometric process studies, environmental tracers have been viewed as useful tools in field studies that can provide an integrated insight into hydrological functioning at larger catchment scales (Kendall and McDonnell, 1998; Stutter *et al.*, 2005). Tracers, if their behaviour is close to conservative, can provide insights into runoff sources and catchment residence times, and thus have proven utility in aiding conceptualization of hydrological functioning at larger spatial scales (Kendall and Coplen, 2001; Soulsby *et al.*, 2004; Uhlenbrook *et al.*, 2004). Geochemical tracers such as silicon (Si) and other weathering-derived elements can be useful in identifying the provenance of waters; in certain situations alkalinity can be also useful, as it is reflects the integration of weathering reactions and can be helpful in distinguishing acidic soil-derived waters and more buffered groundwater (Neal *et al.*, 1997). Isotopes ratios of hydrogen (^{2}H) and oxygen (^{18}O) within water molecules themselves are also particularly useful, as comparison of stream waters with precipitation can indicate the nature and timing of catchment flow paths. Clearly, combining GIS and tracer studies has considerable potential in fulfilling the objectives of initiatives such as PUB and HELP.

An advantage of using GIS in applied catchment management is its obvious utility in allowing watershed analysis with readily communicable understanding of hydrological functioning as a visual mapped output (Montgomery *et al.*, 1995; Lyon, 2003). Mapping areas of different types of environmental sensitivity can greatly aid land managers in providing a rationale for zoning certain activities (Montgomery *et al.*, 1998). These are extremely useful tools, given that preventative strategies are often the key to avoiding and mitigating many human impacts on water resources (Brooks *et al.*, 2003). Moreover, extensively managed headwater catchments are increasingly identified as important source areas in river basins that are subject to a range of pressures that need to be carefully managed (Langan *et al.*, 1997; Brandt *et al.*, 2004).

The Girnock Burn is a 31 km^2 experimental catchment in northeast Scotland. Originally established to monitor Atlantic salmon (*Salmo salar*) populations in the mid-1960s, it is now the focus of a wide range of interdisciplinary freshwater research (Youngson and Hay, 1996). Its landscape is typical of much of the Scottish Highlands, and thus experiences a number of issues that result in potentially conflicting land and water management concerns (e.g. Soulsby *et al.*, 2002). In recent years, a GIS of the catchment characteristics has been developed and a number of different investigations have provided a wealth of tracer-based knowledge about hydrological functioning (Malcolm *et al.*, 2004a; Soulsby *et al.*, 2006b). This paper attempts to extend this understanding of how catchment characteristics and landscape organization influence runoff sources and water residence times. In so doing, the work also seeks to highlight some land-use issues that are relevant to sustainable watershed management in the Scottish Highlands. Thus, this paper has three specific aims:

1. to develop a GIS approach to identify likely landscape controls on runoff dynamics and contribute to the development of a transferable approach to conceptualizing streamflow generation processes at larger scales;
2. to use environmental tracers (stable isotopes and geochemistry) to examine characteristics of streamflow generation processes at the catchment and subcatchment scale in relation to landscape controls hypothesized from the GIS;
3. to use this information to assess the implications of current land management activities in the Scottish Highlands on catchment hydrology and water resources.

STUDY AREA

Catchment characteristics

The Girnock Burn, a subcatchment of the River Dee, is located in the Cairngorms National Park, northeast Scotland and drains a catchment of 31 km^2 to the gauging site at Littlemill (L; Figure 1). For monitoring purposes, the Girnock catchment was nested into three further main stem sites and five subcatchments. Iron Bridge (IB) was selected as the upper catchment of the Girnock stream. Additionally, the main stem was sampled upstream (S/EB) and downstream (at Hampshires Bridge, HB) of South (SB) and East Burn (EB) tributary confluences. Three further main tributaries drain into the Girnock from the Bovaglie (Bov), Camlet (Ca) and Bruntland Burn (BB) subcatchments. The characteristics of the Girnock and its associated subcatchments are summarized in Table I.

The altitude ranges from 230 to 862 m (Figure 1a), although mean elevation is just over 400 m. The highest elevations occur at the southwestern edge of the catchment upstream of Iron Bridge. Slopes show more distinct differences in the several subcatchments (Figure 1b), with mean slopes ranging between 6·6° at Bovaglie and >11° in the steeper basins of East Burn, Camlet and Bruntland Burn. The gently sloping valley bottom is reflected by a modest average channel slope of 28·9 m km^{-1} (Moir *et al.*, 1998), though some of the steepest hillslopes are found on the eastern side of the lower catchment.

The geology is complex (Figure 1c), which results in marked spatial variability in groundwater–surface water interactions and stream chemistry (Malcolm *et al.*, 2005). Higher elevation areas are associated with granite and granite-like rocks (granodiorite and diorite), whereas in lower elevation areas the bedrock is composed of schists and other metamorphic rocks (Soulsby *et al.*, 2006b). The northern edge of the catchment in the Bruntland Burn also consists of granite. The granite is predominantly fringed by formations of metasediments ranging from base-poor quartzite and psammite, to more calcareous strata, including bands of metamorphosized limestone

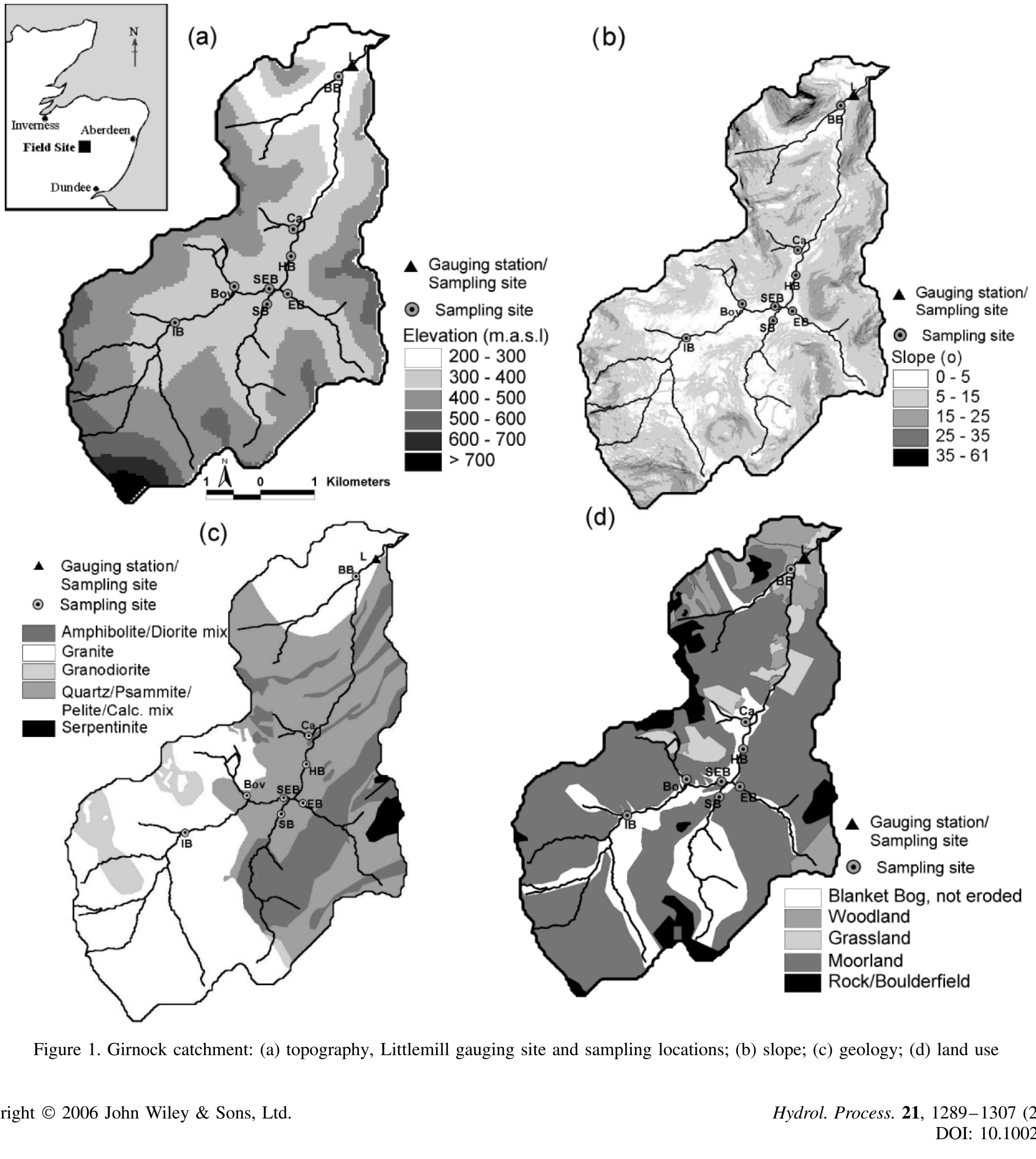


Figure 1. Girnock catchment: (a) topography, Littlemill gauging site and sampling locations; (b) slope; (c) geology; (d) land use

Table I. Characteristics of the Girnock and associated subcatchments (IB: Iron Bridge; S/EB: upstream of South and East Burn; HB: Hampshires Bridge; L: Littlemill (catchment outlet) and tributaries Bovaglie (Bov), South Burn (SB), East Burn (EB), Camlet Burn (Ca), Bruntland Burn (BB))

	IB	S/EB	HB	L	Bov	SB	EB	Ca	BB
Area (km^2)	9·11	12·58	20·42	31·05	1·84	4·21	3·25	0·99	3·62
Topography									
Mean elevation (m)	469	445	432	405	397	415	420	396	354
Min. elevation (m)	350	321	311	233	329	320	321	304	248
Max. elevation (m)	852	852	852	852	500	552	593	517	536
Mean slope (°)	8·7	7·8	8·2	9·4	6·6	7·4	11	11·7	12·3
Max. slope (°)	28	28	28	46	14	24·6	27·9	24·2	35·8
Drainage density	1·16	1·23	1·17	1·10	1·42	1·12	0·96	1·36	1·01
Geology									
Granite (%)	86·0	80·7	55·0	45·6	67·3	27·3	0·0	0·0	45·7
Granodiorite (%)	14·0	12·3	7·9	5·2	10·7	2·2	0·0	0·0	0·0
Diorite (%)	0·0	0·0	0·0	0·9	0·0	0·0	0·0	0·3	5·1
Amphibolite (%)	0·0	0·2	11·2	11·9	1·1	23·3	38·8	15·4	0·9
Serpentinite (%)	0·0	0·0	1·8	1·2	0·0	0·0	11·8	0·0	0·0
Quartzite/psam. (%)	0·0	0·0	1·2	0·8	0·0	5·6	0·0	0·0	0·0
Dior./amphibolite (%)	0·0	0·0	4·1	2·7	0·0	18·5	0·0	0·0	0·0
Quartz./psam./pelite (%)	0·0	3·8	12·1	16·3	15·0	9·9	47·5	1·4	45·3
Quartz./psam./calc. (%)	0·0	3·1	6·6	15·5	5·9	13·2	1·9	82·9	2·9
Landcover									
Heather moorland (%)	77	74	66	63	75	40	69	35	20
Peat bog (%)	20	19	24	18	21	50	6	31	13
Woodland (%)	0	0	3	8	0	0	16	2	34
Grassland (%)	0	3	2	5	2	0	0	21	4
Rock, boulder field (%)	3	4	5	6	2	10	9	11	29
HOST type									
HOST 5 (%)	0	0	0	2	0	0	0	0	0
HOST 15 (%)	86	88	78	60	94	84	38	11	20
HOST 17 (%)	7	4	11	24	0	1	49	75	34
HOST 22 (%)	0	1	3	5	6	0	14	14	23
HOST 27 (%)	7	5	3	4	0	0	0	0	18
HOST 29 (%)	0	2	5	4	0	15	0	0	6

and amphibolite. These predominate on the lower catchment slopes downstream of Hampshires Bridge, and in the subcatchments of Camlet and the South Burn. The East Burn is distinct in having a large outcrop of serpentinite in its headwaters. In most cases these rocks have poor aquifer characteristics, and fracture flow seems likely to be the main mechanism of bedrock groundwater movement (Haria and Shand, 2004).

Much of the catchment bedrock in the valley bottom is covered by glacial drift deposits with gleyed and peat soils fringing the stream channel and sustaining blanket bog vegetation (Figure 1d). However, land use is dominated by heather (*Calluna vulgaris*) moorland used for deer stalking and grouse shooting, with smaller areas of abandoned rough grazing and a gradually increasing coverage of forestry on the lower hillslopes. These activities are common to much of the Scottish Highlands and have historically involved the burning of moorland to create a mosaic of habitats for grouse and deer (Thompson *et al.*, 2001).

Soil cover and Hydrology of Soil Type classification

Soil cover is complex and reflects the organization of topography, geology and drift cover (Figure 2). The UK HOST system (Boorman *et al.*, 1995) groups all soils of the UK into 29 classes and characterizes them according to the dominant pathways of water movement through the soil layer and underlying parent material. Hence, HOST provides a convenient classification for identifying hydrological similarities (Dunn *et al.*, 2003; Soulsby *et al.*, 2006a). In the Girnock, the complex geology and topography results in six different HOST classes occurring (Figure 2). HOST class 15 (mainly peaty gleys (Histic Gleysols), but some peaty podzols (Histic Podzols)) is most extensive (covering 60% of the catchment) and is found on the more subdued hillslopes and interfluves. They have mainly developed over granitic rocks, although some are also derived from metasediments. The peaty gleys form on flatter areas and valley bottoms and are generally saturated for much of the year (Soulsby and Reynolds, 1993). On steeper slopes within HOST class 15, peaty podzols form extensive tracts of heather moorland, which is often subject to regular burning. Over substantial areas, a long history of both deliberate and accidental burning has resulted in the severe depletion of organic horizons, and hydrophobic conditions are prone to develop after dry periods. Blanket peat (Histosols) (HOST class 29) also occupies small valley bottom areas, fringing the stream channels in upper Girnock, South Burn and Bruntland Burn. On steeper hillslopes in the lower catchment, deeper, freely draining brown soils (Cambisols), humus iron (Haplic Podzol) and

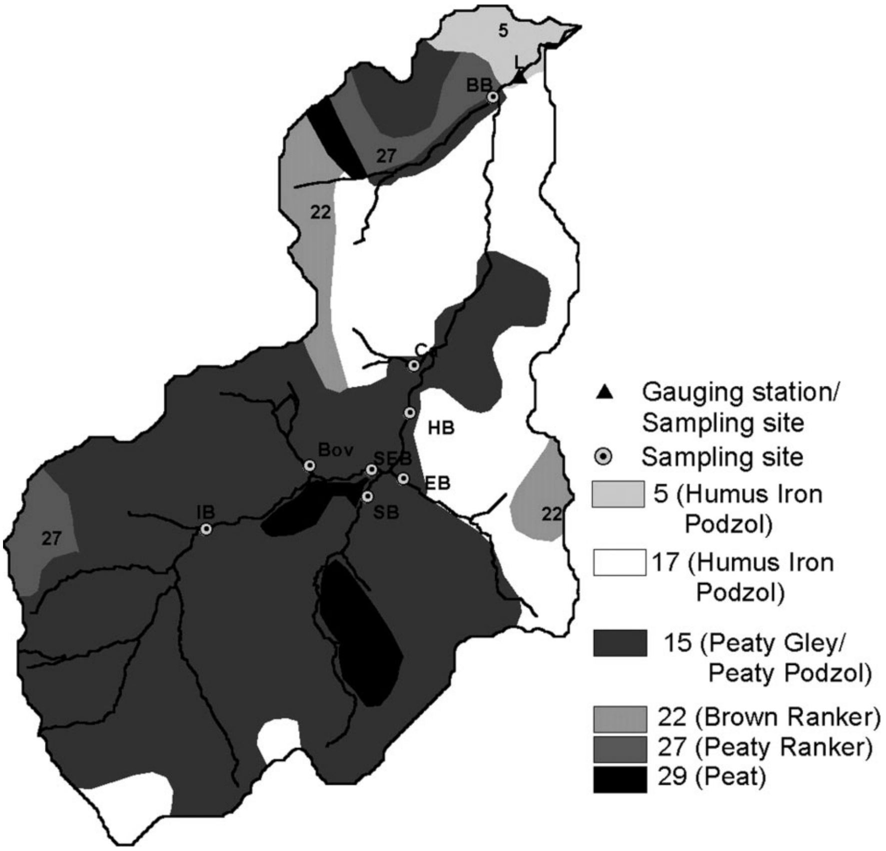


Figure 2. Distribution of HOST classes in the Girnock catchment (5: humus iron podzol; 15: peaty gley, peaty podzol; 17: alpine soils, humus iron podzol; 22: brown ranker; 27: peaty ranker; 29: peat)

subalpine podzols (Fragic Podzols) form HOST class 17, the second most extensive class, covering around 24% of the catchment. These soils have developed in drifts from a wide range of bedrock types, including the serpentinite. At the main river valley near the catchment outlet, freely draining alluvial deposits and soils (fluvisols) (HOST class 5) are to be found. On the upper slopes on the northwestern and southwestern parts of the catchment, shallow brown rankers (Umbric Leptosols) (HOST class 22) and peaty rankers (Histosols) (HOST class 27) occur.

Hydrology and runoff generation processes

Previous hydrological studies have shown that the Girnock Burn is characterized by high variability in discharge dynamics (Tetzlaff *et al.*, 2005a; Soulsby *et al.*, 2006b). Catchment average annual precipitation is 1100 mm, with annual runoff about 700 mm (1961–1991, Scottish Environmental Protection Agency, SEPA) with the summer months (May–August) generally being driest. At the gauging station at Littlemill (Figure 1) the mean annual discharge is $0{\cdot}52\ m^3\ s^{-1}$ (1969–2001), although discharge between June and August is often below $0{\cdot}1\ m^3\ s^{-1}$ (Moir *et al.*, 1998). Instantaneous discharges have varied between $\sim 0{\cdot}04\ m^3\ s^{-1}$ in the summer (Malcolm *et al.*, 2003) and $>50\ m^3\ s^{-1}$ during floods (Tetzlaff *et al.*, 2005b). Most high-discharge events occur between late autumn and early spring, though they can occur throughout the year (Tetzlaff *et al.*, 2005b). The peaty gley and peaty soils that fringe the stream channel have been identified as contributing to the Girnock's responsive hydrological regime (Soulsby *et al.*, 2005).

Previous investigations have shown that five dominant runoff generation processes are characteristic of Cairngorm catchments such as the Girnock (Soulsby *et al.*, 2004). These are shown in Table II. Overland flow can occur by two mechanisms: saturation overland flow from peats (HOST class 29) and peaty gley soils (HOST class 15) is most common, though infiltration excess overland flow can occur from burned peaty podzols (within HOST class 15) where a depleted, thin organic horizon (often in combination with hydrophobic conditions developing after dry periods) overlies a continuous iron pan within mineral subsoil that restricts infiltration (Wheater *et al.*, 1991; Rodgers *et al.*, 2005a). Overland flow and shallow subsurface storm flow are dominant runoff processes where upper organic soil horizons overlie low-permeability rock, e.g. HOST classes 22 and 27 (Wheater *et al.*, 1993; Boormann *et al.*, 1995), though recharge in to bedrock fracture systems can also occur under these soils. In freely draining soils, such as humus iron podzols or subalpine soils (HOST classes 5 and 17), deep subsurface storm flow and groundwater recharge dominates runoff generation (Davies *et al.*, 1993).

In spite of the influence of overland flow or shallow subsurface storm flow in dominating the storm hydrograph, Soulsby *et al.* (2005) have indicated that groundwater recharge, mainly through more freely draining soils

Table II. Description of major runoff processes in the Girnock catchment

Process	Criteria description
Saturation overland flow	Low antecedent soil moisture deficit and limited storage capacity
Infiltration excess overland flow	Precipitation intensity exceeds infiltration capacity of the soil (bedrock surfaces and soils with impeded infiltration, e.g. burnt soils, shallow drift, road and track surfaces, etc.)
Shallow subsurface storm flow	Effective lateral flow paths in macropores and/or permeable surface horizons overlying less permeable subsoils
Deep subsurface storm flow	Soils with macropore-dominated vertical infiltration to permeable zones at soil–bedrock or soil–drift interface
Groundwater recharge	Permeable soils with vertical drainage to deeper water stores

(especially those in HOST class 17), occurs throughout the catchment. A fraction of recharge may move quickly through shallow fracture systems or freely draining glacial deposits, to discharge in valley bottom areas either back to the surface of gleyed and peat soils (Shand *et al.*, 2006; Soulsby *et al.*, 2006b) or through the bed and banks of the stream (Malcolm *et al.*, 2006). Groundwater influence on runoff generation appears less important than responsive hydrological flow paths. Chemical hydrograph separation showed an ∼32% groundwater component of mean daily flows (10-year average, 1994–2004; Soulsby *et al.*, 2005). This low groundwater component also appears to contribute to a thermal regime throughout the Girnock river system, which is prone to strong climatic influence with cold winter and warm summer temperatures (Hannah *et al.*, 2004; Malcolm *et al.*, 2004b).

METHODOLOGY

Given the complexity of the Girnock catchment, it would be unrealistic to carry out a large number of traditional plot-scale investigations of hillslope hydrology to develop an understanding of catchment functioning. Thus, basic catchment hydrometrics were combined with tracer studies, GIS analysis and a synthesis of previous hillslope studies in the dominant soil types to develop a process understanding at the catchment scale.

Hydrometric data

Discharge was calculated from a rated natural section of the river, continuously monitored by SEPA, at Littlemill (Figure 1). Mean daily flow in the ungauged subcatchments was estimated from the mean daily gauged flow at Littlemill, weighted by the topographic area contributing to flow using

$$Q_u = Q_g(A_u/A_g) \tag{1}$$

where Q (m^3 s^{-1}) is mean daily flow, A (m^2) is the topographic area contributing to flow and the subscripts 'u' and 'g' refer to ungauged and gauged catchments respectively. Previous studies have validated the general utility of this approach to assessing ungauged flows in the wider Dee catchment (Wade *et al.*, 1999). Current metering at low and moderate flows confirmed that the method was accurate to within ±10%, which is around typical gauging errors.

Rainfall data were derived from a ground station at Hampshires Bridge, centrally located within the catchment at 311 m, reasonably close to the mean catchment altitude of 405 m. Estimated long-term annual catchment precipitation from water balance considerations is around 1100 mm, whereas annual precipitation at Hampshires Bridge (2001–2004) is about 900 mm. Therefore, to derive a time-series of weighted catchment precipitation, rainfall data at Hampshires Bridge were multiplied by a factor of 1·22. Comparison with surrounding gauges from the Meteorological Office UK network, using the automated optimization procedure of Tetzlaff and Uhlenbrook (2005), suggested these estimates were representative of the wider area around the catchment.

Geographical information system application and landscape analyses

Catchment characteristics were analysed by applying the GIS Arcview. This included an Ordnance Survey Profile data set that is a 1 : 10 000-scale digital terrain model (DTM). This dataset comprises 10 m × 10 m grid cells each of which have an elevation value in metres. Additionally, digital coverage of soil types, underlying geology and land use were available from previous work (Wade *et al.*, 1999; Smart *et al.*, 2001). The GIS provided a means of assessing how the hydrological and hydrochemical functioning varied in each of the subcatchments by allowing quantification of catchment characteristics. In addition, analyses of aerial photographs, taken on June 1994 flights at a scale of 1 : 10 000, provided further insight into landscape organization that could be used to validate aspects of the digital representation of catchment characteristics from the GIS.

For specifying water flow directions within the GIS, the ESRI GIS extension tool Hydrology Modelling was used. Based on the elevation data grid, the *flow direction* from each cell to its steepest downslope neighbour was derived by using the slope and aspect values for each grid cell to compute the direction of flow (Jenson and Domingue, 1988). This was then coded using the summed number of cells that are upstream from each cell. The resulting *flow accumulation* grid defined the ultimate downslope drainage point of water where it enters the stream. This procedure requires a preprocess of the DTM to identify any sinks in the DTM and fill these in by, for example, increasing the elevation of these grid cells that are fictitious terrain pits (Wolock and Price, 1994). From the slope and upslope contributing area, the distribution of topographic index ($\ln(A/\tan B)$) was determined, which predicts likely saturation areas (Quinn *et al*., 1991; Wolock, 1995; Beven, 2001).

Rationale for linking hydrological process knowledge and Hydrology of Soil Type classification

The methodology to combine the GIS and the existing HOST classification was as follows:

1. The spatial delineation of HOST classes was validated against land use, topography and geology maps and aerial photographs.
2. As the HOST classification does not explicitly capture topographic controls of hydrological pathways and source areas, flow accumulation and slope maps were combined to derive a topographic index assigned as 'low', 'medium' and 'high' and from this the likely spatial patterns of water movement and saturation were identified.
3. The distribution of HOST types and areas of differing topographic index were used to produce a preliminary map of likely dominant runoff processes that produce storm flow generation under typical conditions.

This provided a means of assessing patterns of water movement that could be compared with the insights gained from the tracer monitoring to conceptualize catchment-scale distribution of runoff processes, water sources and residence times.

Tracer analyses to estimate runoff components and indicative residence times

To establish the tracer characteristics of precipitation and stream waters and assess the likely validity of the inferences of hydrological functioning from the GIS, an extensive sampling regime was put in place. Samples were generally taken from Littlemill at weekly or biweekly intervals between October 2003 and September 2004. For certain periods, when staff were on site, daily sampling was possible, and sub-daily sampling in a few events. The additional main stem sampling locations (and the five subcatchments) were also sampled at approximately fortnightly intervals. Samples were refrigerated after collection and analysed within 7 days.

Samples were analysed for alkalinity by acidimetric Gran titration to end points of 4·5, 4·0 and 3·0; the resulting Gran alkalinity closely approximates acid neutralizing capacity (ANC, a conservative tracer) with proven utility to distinguish hydrological sources in the UK uplands (Neal, 2001). The Gran alkalinity data were used to carry out chemically based hydrograph separations to determine contributions of groundwater and soil-derived waters. To provide an integrated estimate of groundwater alkalinity, this end member was estimated from the three lowest flows sampled for each site (Neal *et al*., 1997). To give an indication of the uncertainty in the separations, soil water alkalinity (which encompasses both overland flow and shallow subsurface storm flow) was estimated at 0 and -50 μeq l^{-1} following previous studies indicating that soil water from upland soils has a low alkalinity typically in this range (Soulsby and Dunn, 2003; Soulsby *et al*., 2003a). The hydrograph was then separated into soil water and groundwater contributions at daily time-steps using a classic two-component mixing model (Rodgers *et al*., 2004).

Given the time-steps and the coarse temporal sampling, no attempt was made to distinguish 'old' water and 'new' water. The focus was on distinguishing (more generally) the relative importance of responsive hydrological pathways over and through the acidic near-surface soil horizons and the role of deeper flow paths that sustain baseflows. Thus, the local heterogeneity in end-member chemistry was recognized (Stutter *et al*., 2005); but this appears to be damped at larger scales, as the alkalinity of drainage water from peaty soils in the Cairngorms is remarkably consistent (Soulsby *et al*., 2003a, 2004). Three-component approaches to end-member mixing were considered, but earlier work indicated poor success in characterizing a third (mineral soil) component (Soulsby and Dunn, 2003). It was recognized that using the three lowest flows to approximate a groundwater end-member is arbitrary and provides additional uncertainty. Again, there is an identifiability problem in characterizing groundwater at the catchment scale, particularly if a number of groundwater sources of highly contrasting chemistry are important (Shand *et al*., 2006). However, earlier work in Cairngorm catchments has shown that the three lowest flows provide at least a minimum approximation of groundwater contributions at larger spatial scales (Wade *et al*., 1999; Rodgers *et al*., 2004, Soulsby *et al*., 2004).

Quantifying the uncertainties associated with chemically based hydrograph separations has recently become a major research theme (e.g. Genereux, 1998; Joerin *et al*., 2002; Soulsby *et al*., 2003b; Uhlenbrook and Hoeg, 2003). In this study, given the paucity of data, the use of variable soil water end-members, together with assessment of the measurement error (Genereux, 1998), were used to provide upper and lower boundaries for estimates of groundwater contributions to stream flow. This gives an indication of the uncertainty associated with the separations, though such simplification at these larger spatial and temporal (daily) scales has still been shown to provide meaningful differences in catchment responses (Wade *et al*., 1999).

To provide additional insights into the hydrological pathways routing precipitation to streams, samples were also analysed for oxygen isotope ratios 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 δ units, $\delta^{18}O$ (‰, parts per mille) defined in relation to Vienna standard mean ocean water (V-SMOW). The analytical precision was ±0·1‰. Additional to stream water, precipitation was collected for $\delta^{18}O$ analysis at Littlemill. $\delta^{18}O$ is a useful passive tracer that can infer the time-scale over which precipitation influences runoff generation by comparing ratios.

A range of models are available for assessing catchment residence times using tracer data (McGuire and McDonnell, 2006). Given the basic data set available, together with clear seasonal trends, the sine wave method was used for the Girnock data. This compares the amplitude of seasonal variations in $\delta^{18}O$ in precipitation and stream flow, and uses the degree of damping to estimate residence time (Burns and McDonnell, 1998). It assumes an exponential distribution of residence times and is particularly useful in catchments with a preponderance of short residence time flow paths, such as overland flow (Stewart and McDonnell, 1991; Maloszewski and Zuber, 1993; Rogers *et al.*, 2005b). The short (1 year) run of data precluded the application of the convolutional integral approach, where antecedent precipitation inputs would need to be modelled accurately (Vitvar and Balderer, 1998). In the context of the simpler sine wave method, the short run of data was less problematic. Earlier work in the region showed that the range and seasonal pattern of $\delta^{18}O$ in observed precipitation during the study year were representative of those in a total of five other years (Soulsby *et al.*, 2000).

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

$$\delta^{18}O = X + A[\cos(ct - \theta)] \qquad (2)$$

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 ($0{\cdot}017\,214$ rad day^{-1}), t is the time in days after the start of the sampling period (1 October 2003), and θ is the phase lag or time of the annual peak $\delta^{18}O$ in radians. The mean residence time T of water leaving the system is estimated as

$$T = c^{-1}[(\mathrm{Az2}/\mathrm{Az1})^{-2} - 1]^{0{\cdot}5} \qquad (3)$$

where Az1 is the amplitude of precipitation, Az2 is the amplitude of the stream water outputs (both estimated from Equation (2)) and c is the radial frequency of annual fluctuations.

Application of residence-time models to stream water data is problematic. The models often assume some steady-state condition in catchment function, which is obviously unrealistic in dynamic upland catchments. In some studies this results in high flow samples being omitted from the analysis and baseflow residence times being estimated (e.g. McGlynn *et al.*, 2003). In this context, the precipitation $\delta^{18}O$ inputs are accordingly weighted to try to reflect the signature of recharge, particularly in catchments with marked seasonality (e.g. Uhlenbrook *et al.*, 2002). However, in a flashy catchment, such as the Girnock, where precipitation is relatively evenly distributed in most years, meaningfully defining 'baseflow' is difficult. Moreover, high soil moisture deficits are not common in the wet, cool montane climate. Given this context and the fortnightly sampling regime, all the stream $\delta^{18}O$ data were used to fit curves to give a snapshot first approximation of mean residence times at the catchment scale.

RESULTS AND DISCUSSION

Identification of topographic controls on hydrological functioning

Despite the utility of tracers in geographically sourcing runoff and estimating residence times, the detailed spatial distribution of flow paths, such as areas of overland flow or shallow subsurface storm flow, will be unknown from tracer data alone. Topographic gradients underpin a number of other environmental gradients, and topography, together with geology, is a major influence on soil distributions and hydrological flow paths. This is shown clearly if the DTM of the Girnock is used to map out topographically induced areas of low, medium and high flow accumulation (Figure 3a). Validation against aerial photographs and field mapping suggests that even this simple topographic analysis can provide a reasonable indication of the distribution of saturated and near-saturated areas in the Girnock.

As a precursor to the interpretation of tracer data and the distributed modelling of catchment hydrology, these areas of topographic index were combined with HOST classes within the GIS to provide a preliminary delineation of units for which similar dominating runoff processes can be assumed (Table III). This simple decision scheme allows mapping areas of dominant runoff processes, i.e. the main runoff process in typical storm events, at the catchment scale (Figure 3b). The spatial distribution of dominant runoff processes helps to explain the flashy, responsive nature of the Girnock, as saturation overland flow prevails in many parts of the catchment, most notably where peaty gley and peaty soils fringe the channel network. Shallow subsurface flow from upslope areas contributes to this. Additionally, peaty podzols (within HOST class 15) can generate large volumes of infiltration-excess overland flow where burning has reduced the extent of organic horizons that overlay impermeable iron pans. In contrast, low flows are probably sustained by groundwaters, which are primarily recharged through more freely draining soils (e.g. humus iron podzols and alpine soils, HOST class 17) and exposed/near-surface bedrock in the areas of rankers (regosols) in HOST classes 22 and 27.

Catchment-scale tracer hydrology

Daily precipitation, mean daily flow, Gran alkalinity and the estimated groundwater contribution (from chemically based hydrograph separation) during the 2003–2004 hydrological year at Littlemill are shown in Figure 4. Gran alkalinity and its relationship with flow

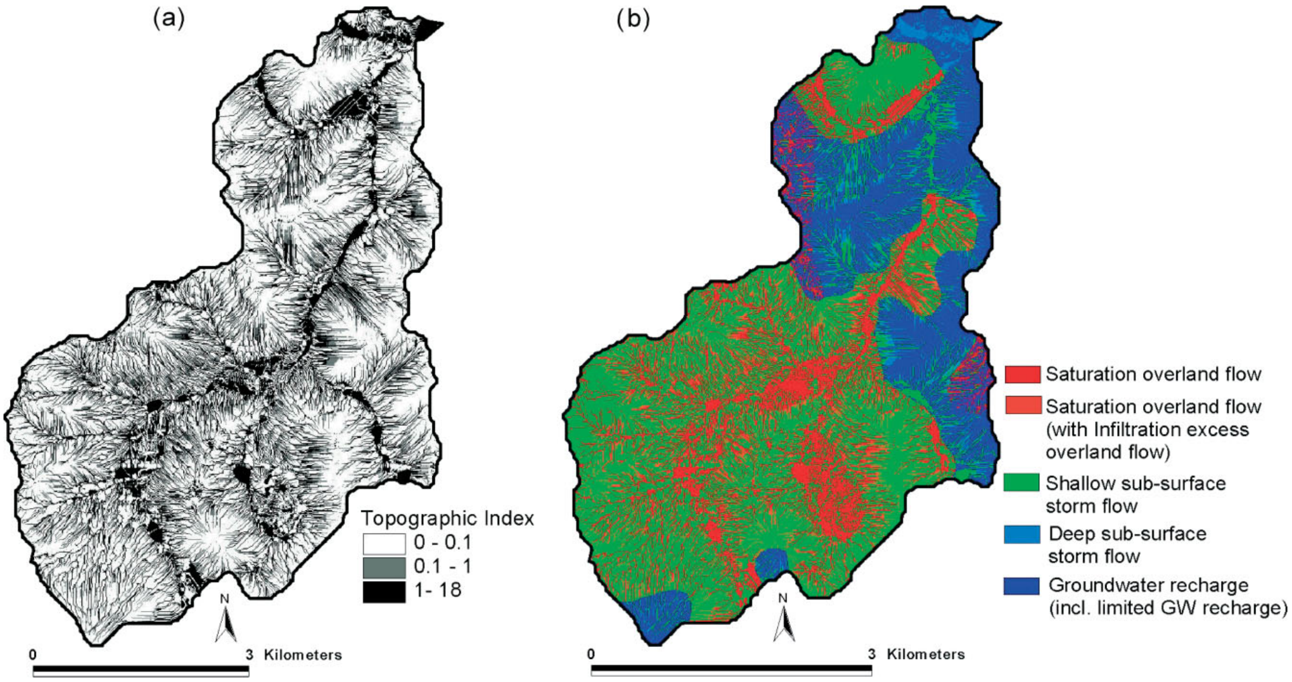


Figure 3. (a) Topographic index in the Girnock catchment. (b) Distribution of dominant runoff processes in the Girnock using topographic index and HOST class distribution

Table III. Determination of dominant runoff processes in the Girnock catchment from HOST type and topographic index

HOST (BFI)[a]	Soils	Responsiveness	Topographic index	Percentage area topographic index per HOST class	Dominant runoff process
5	Humus iron podzol	Freely draining	Low	45	Groundwater recharge
(0·9)			Medium	7	Groundwater recharge
			High	49	Deep subsurface storm flow
17	Alpine soil/ humus iron podzol	Freely draining	Low	66	(Limited) groundwater recharge
(0·69)			Medium	13	Deep subsurface flow
			High	21	Shallow subsurface storm flow
15	Peaty gley/ peaty podzol	Responsive/ freely draining	Low	60	Shallow subsurface flow
(0·38)			Medium	11	Saturation overland flow (with infiltration excess overland flow)
			High	29	Saturation overland flow
22	Brown ranker	Responsive soils	Low	78	(Limited) groundwater recharge
(0·315)			Medium	9	Shallow subsurface storm flow
			High	13	Saturation overland flow
27	Peaty ranker	Responsive soils	Low	67	Shallow subsurface storm flow
(0·259)			Medium	10	Shallow subsurface flow
			High	23	Saturation overland flow
29	Peat	Responsive soils	Low	52	Shallow subsurface storm flow
(0·26)			Medium	8	Saturation overland flow
			High	40	Saturation overland flow

[a] BFI: base flow index = the fraction of annual runoff totals that are ascribed to more slowly responding hydrological stores.

are also shown. The investigation period followed an unusually dry summer and early autumn in 2003, where precipitation had been 50% of the long-term average. Initial base flows, therefore, had Gran alkalinities of ~700 μeq l^{-1}. To re-wet the catchment, a few periods of rainfall were necessary before flows increased in late October. Gran alkalinities were slowly reduced and then markedly decreased during November in higher flows. After a substantial flood yielding a mean daily flow of over 4·5 m^3 s^{-1} in January 2004, the catchment was

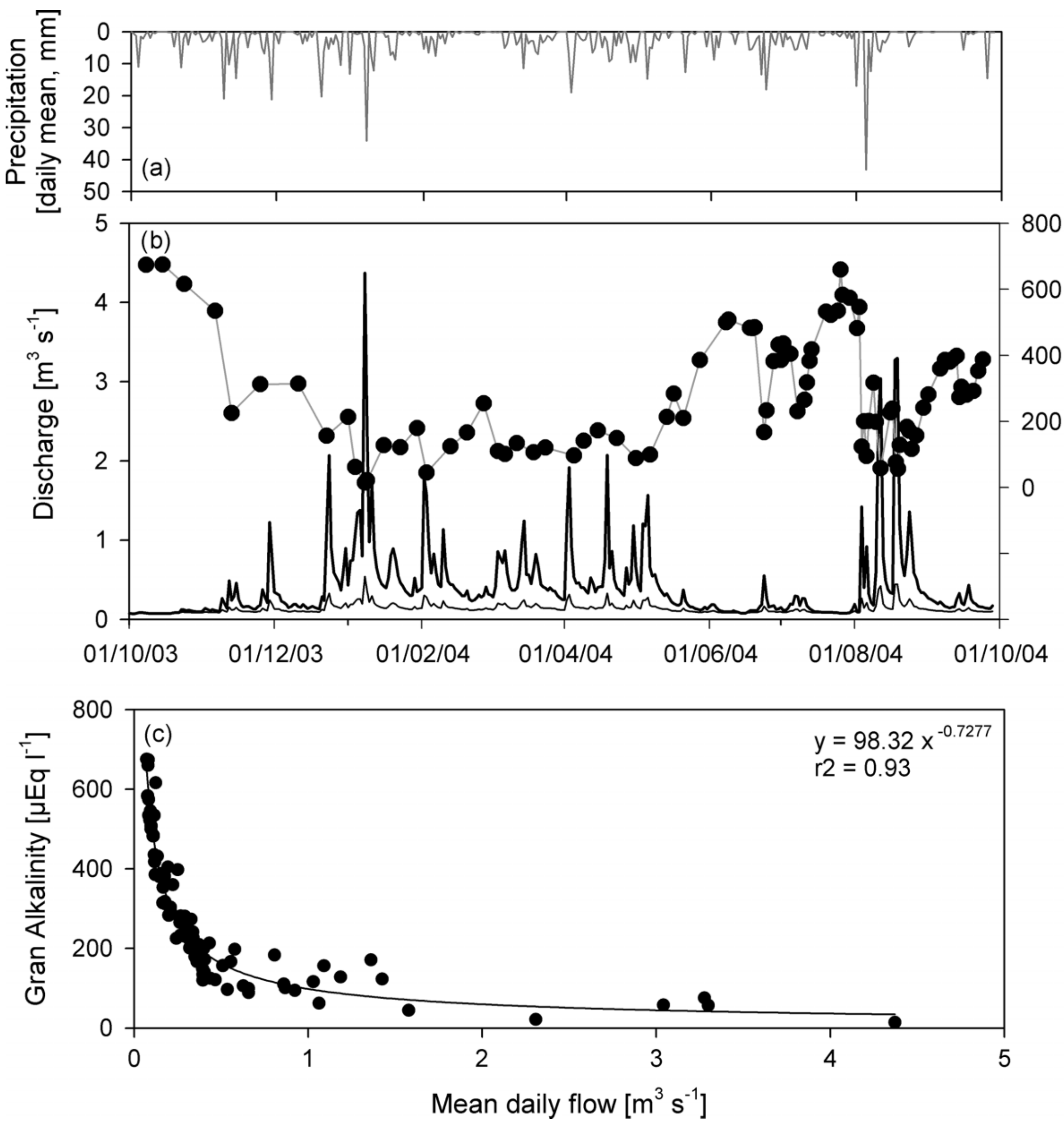


Figure 4. (a) Mean daily precipitation, (b) mean daily flow, groundwater contribution and Gran alkalinity and (c) flow concentration plot of Gran alkalinity at Littlemill

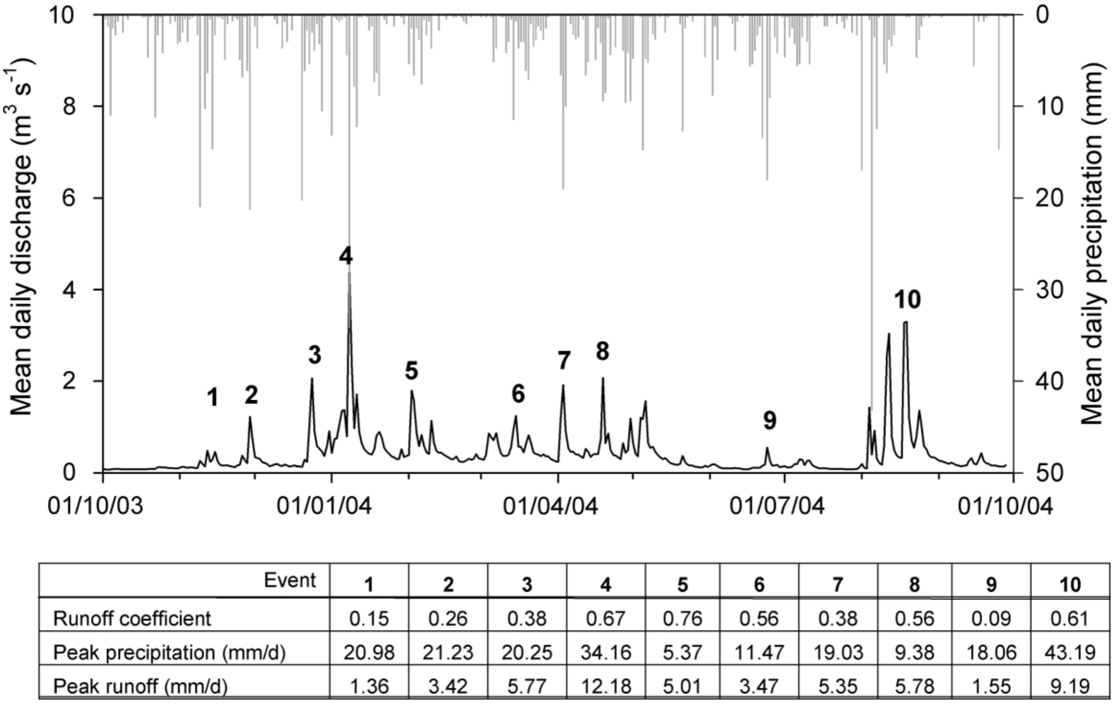
moderately wet in late winter and early spring and relatively small rain events resulted in a sustained period of flows above the mean of 0·52 m^3 s^{-1}. In the peak flow of January, the Gran alkalinity dropped close to 0 µeq l^{-1} and generally remained below 200 µeq l^{-1}, until higher concentrations were observed as flows receded in May and June. Following a modest event in early May, the early summer was characterized by a sustained period of low flows, with only small events ($<$1 m^3 s^{-1}) in late June and early July quickly lowering stream water alkalinity. Low flows in late July subsequently produced alkalinities exceeding 600 µeq l^{-1}. Rapid re-wetting of the catchment occurred in early August, which preceded the largest instantaneous flow of the year in mid-August. Following two further events in late August, stream flows commenced a late-summer recession, though some detectable increases in flow occurred in mid-September.

In many parts of the British uplands, these temporal patterns of alkalinity variations with flow are common, as alkaline groundwater dominates streamflows during drier periods. This is diluted by large volumes of acidic soil waters during hydrological events (Wade *et al*., 1999). At Littlemill, the groundwater contribution is relatively low: hydrograph separation suggests 27–33% for this particular year (Table IV). The flashiness in the hydrograph is likely to be explained by source areas delivering soil-derived overland flow and shallow subsurface storm flow into the stream, which is consistent with the well-connected network of flow paths shown in Figure 3b.

To gain further insights into the dynamics of catchment response, runoff coefficients (the fraction of event precipitation that is equivalent to event runoff) were calculated on an event basis for 10 storms (Figure 5).

Table IV. Estimated percentage groundwater contributions in the main subcatchments of the Girnock calculated from chemical hydrograph separations with groundwater end-member equal to the mean Gran alkalinity of the three lowest flows and soil water range of -50 to 0 μeq l^{-1}

Subcatchment	Gran alkalinity groundwater (μeq l^{-1})	GW contribution (%)	
		Soil water $= -50$ μeq l^{-1}	Soil water $= 0$ μeq l^{-1}
IB	269	41	30
SEB	348	39	31
HB	465	36	29
L	625	33	27
Bov	372	32	23
SB	496	36	30
EB	934	32	28
Ca	597	59	55
BB	440	32	24



Event	1	2	3	4	5	6	7	8	9	10
Runoff coefficient	0.15	0.26	0.38	0.67	0.76	0.56	0.38	0.56	0.09	0.61
Peak precipitation (mm/d)	20.98	21.23	20.25	34.16	5.37	11.47	19.03	9.38	18.06	43.19
Peak runoff (mm/d)	1.36	3.42	5.77	12.18	5.01	3.47	5.35	5.78	1.55	9.19

Figure 5. Runoff coefficients and event characteristics for selected events

Although the relationships between precipitation amount, intensity and antecedent conditions dictate that the precise nature of stream response is complex, some general patterns emerge. These show a seasonal pattern being low ($<0{\cdot}3$) after dry periods (events 1, 2 and 9), then gradually increasing ($\geq 0{\cdot}38$) with increased catchment wetness (events 3, 4, 5 and 8). In particular, during winter months, when the catchment is very wet, even relatively small rainfall events can result in high runoff coefficients (event 5). These decrease again after a short drier period in March (prior events 6 and 7).

The runoff coefficients are consistent with the alkalinity data, suggesting that (particularly with wet antecedent conditions) the responsive soils of the Girnock catchment generate significant volumes of overland flow and rapidly route water via hydrologically connected hillslope drainage networks to the stream channel and limit levels of groundwater recharge. In general, this is also indicated in the response of the $\delta^{18}O$ of stream water at Littlemill relative to precipitation (Figure 6). In October 2003, stream $\delta^{18}O$ under baseflow conditions was $-8{\cdot}6$‰, gradually falling in response to depleted $\delta^{18}O$ inputs in early winter precipitation. The most $\delta^{18}O$-depleted stream samples of $-11{\cdot}7$‰ were observed in response to the large event in January 2005, when antecedent precipitation was also depleted at $-16{\cdot}1$‰ and event precipitation averaged $-11{\cdot}2$‰. Stream $\delta^{18}O$ levels then recovered, as the $\delta^{18}O$ of spring and summer precipitation was more ^{18}O enriched. The subarctic climate of Scotland and the potential influence of polar air masses throughout the year mean that there is often variability around the general seasonal patterns in precipitation $\delta^{18}O$ that can influence stream waters (in this case, most notably in the depleted precipitation sample in May). Nevertheless, enriched summer storms in August 2005 were

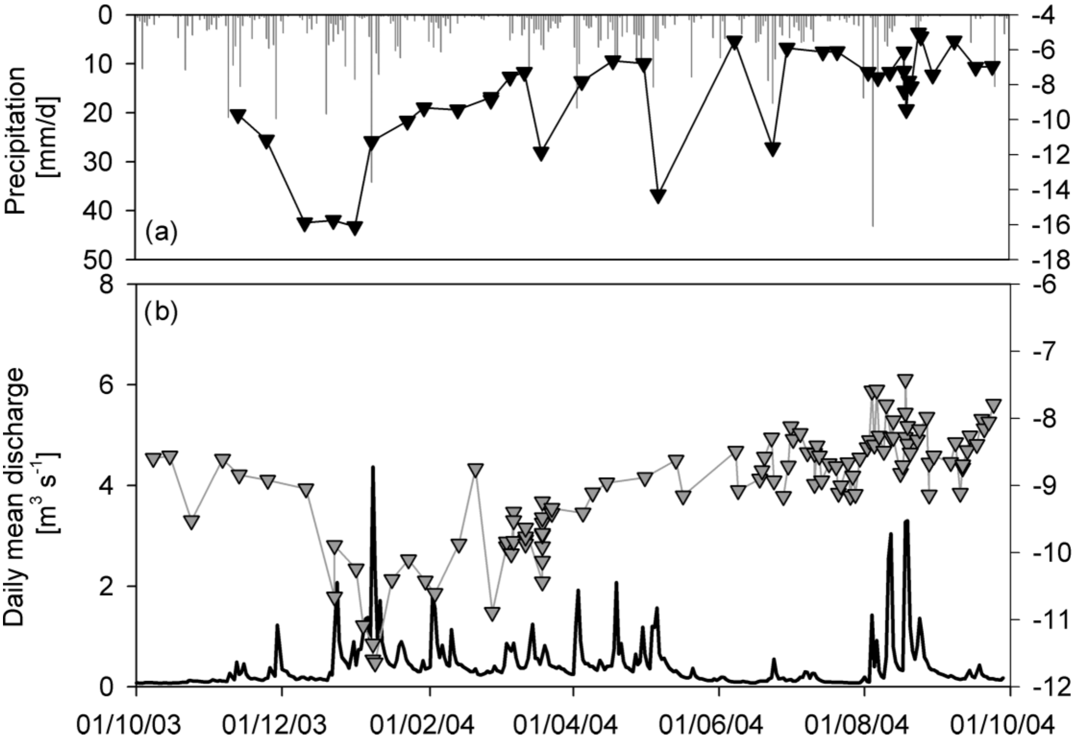


Figure 6. (a) Mean daily precipitation and $\delta^{18}O$ (‰). (b) Mean daily flow and streamwater $\delta^{18}O$ (‰) at Littlemill

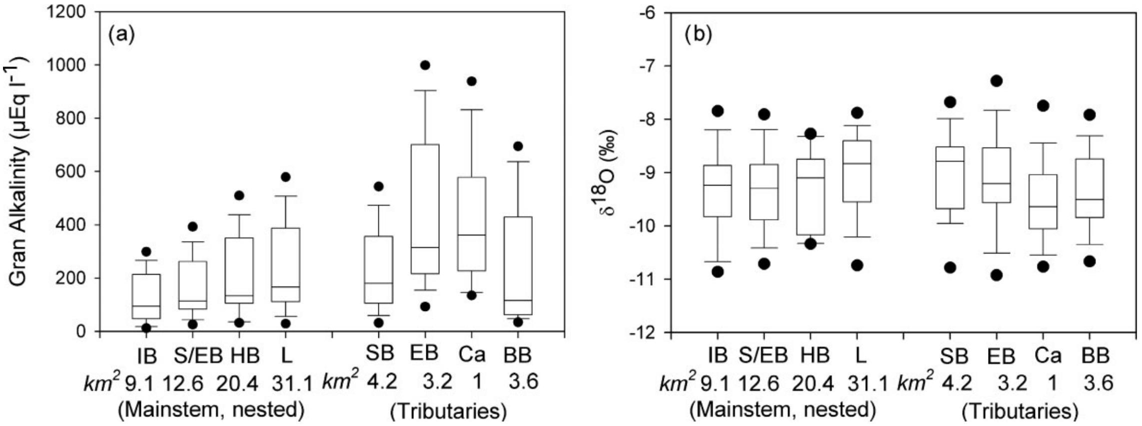


Figure 7. Hydrochemistry of the Girnock (mainstem, nested: IB, SEB, HB, L) and associated subcatchments (SB, EB, Ca, BB) showing median, 5th/95th percentiles (outlying points), 10th/90th percentiles (whiskers) and 25th/75th percentiles (box boundaries): (a) Gran alkalinity (µeq l^{-1}); (b) $\delta^{18}O$ (‰)

clear, when precipitation $\delta^{18}O$ in large events peaked at $-6\cdot1$‰, yielding stream waters of $-7\cdot4$‰. Unlike the highly damped rainfall–runoff relationships of $\delta^{18}O$ in some other catchments in the UK uplands (e.g. Neal and Rosier, 1990; Kirchner *et al.*, 2000; Soulsby *et al.*, 2000), where annual $\delta^{18}O$ in stream waters is within 2‰, the response of the Girnock showed there to be limited damping at Littlemill, with annual variability of 4‰. This implies a relatively direct, rapid link between precipitation and stream flow, with responsive hydrological pathways dominating in the catchment as a whole.

Subcatchment-scale tracer hydrology

Focusing on the subcatchments gives a more direct insight into the influence of spatial differences in landscape organization on hydrological and tracer response. Gran alkalinities show a marked spatial variability in low flow chemistry, and alkalinities at high flows are relatively similar (Figure 7a). This reflects the strong influence of subcatchment geology on stream chemistry at low flow conditions (Smart *et al.*, 2001; Soulsby *et al.*, 2004). Most obviously, East Burn (EB) and Camlet (Ca) appear to be well buffered because of the high percentage of calcareous geology. The downstream change in geology from granite to calcareous metasediments is evident in the systematic increase in baseflow alkalinity along the main stem from Iron Bridge (IB) to Littlemill (L). High flows, in contrast, are relatively uniform and low, similarly reflecting the common origins of storm runoff in acid soil horizons (Soulsby *et al.*, 2003a).

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Temporal variations in δ^{18}O responses at the subcatchment monitoring sites were comparable to Littlemill. However, in contrast to alkalinity, spatial differences in δ^{18}O of stream waters are less well-marked, implying similar δ^{18}O in precipitation inputs across the catchment (Figure 7b and Table IV). Littlemill has the largest δ^{18}O range, though this primarily reflects the greater sampling frequency of high flow events. From the fortnightly samples at all sites, the range in δ^{18}O is generally 3–4‰. Although substantially damped compared with the 11·1‰range in precipitation, the stream water ranges are relatively large, consistent with a significant proportion of rainfall reaching the stream rapidly during and shortly after precipitation events.

The seasonality of the δ^{18}O response at each site is evident when plotted against alkalinity for equivalent sampling dates (Figure 8). Within the plots the data points are spread in a roughly triangular manner: high flow (low alkalinity) samples separate into winter and summer events on the basis of depleted and enriched δ^{18}O signatures respectively. In contrast, baseflow (high alkalinity samples) exhibit much lower variability in δ^{18}O, implying a groundwater sources with less variable δ^{18}O characteristics.

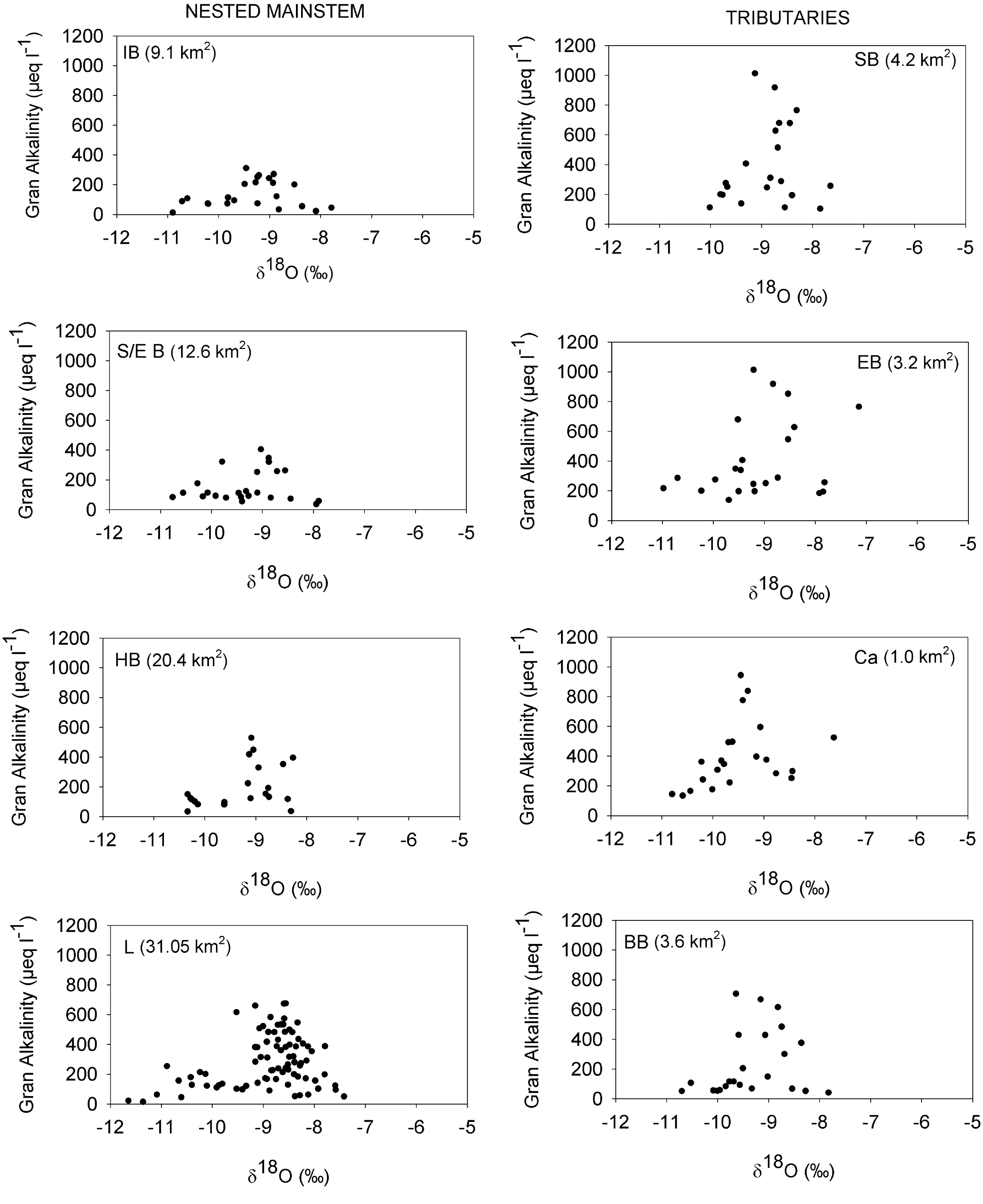

Figure 8. Mixing plots for streamwater δ^{18}O (‰), showing flow (alkalinity, μeq l^{-1}) related variation for the Girnock (mainstem, nested: IB, SEB, HB, L) and associated subcatchments (SB, EB, Ca, BB)

The resulting spatial patterns are evident in Figure 9, which maps out the seasonality of Gran alkalinity and δ^{18}O response throughout the stream network in relation to hydrological variability. Under summer low flow conditions the alkalinities reflect the highest buffering in the East Burn and Camlet and the lower buffering upstream of Iron Bridge (Figure 9a). The geological imprint is most clear at such times. Spatial variability of δ^{18}O is restricted to between $-9{\cdot}6$ and $-8{\cdot}8$‰ under baseflows (Figure 8b). Under both two summer and winter high flows that were sampled, the alkalinity at all sites is low, though again the geological influence of the East Burn and Camlet is evident (Figure 8c and e). Under high flows, the patterns of δ^{18}O in stream water reflect the seasonal variations in inputs. Under winter high flows, the δ^{18}O of the river network was restricted to $-10{\cdot}7$ to $-9{\cdot}6$‰; the range is similarly low under summer high flows, but the δ^{18}O values

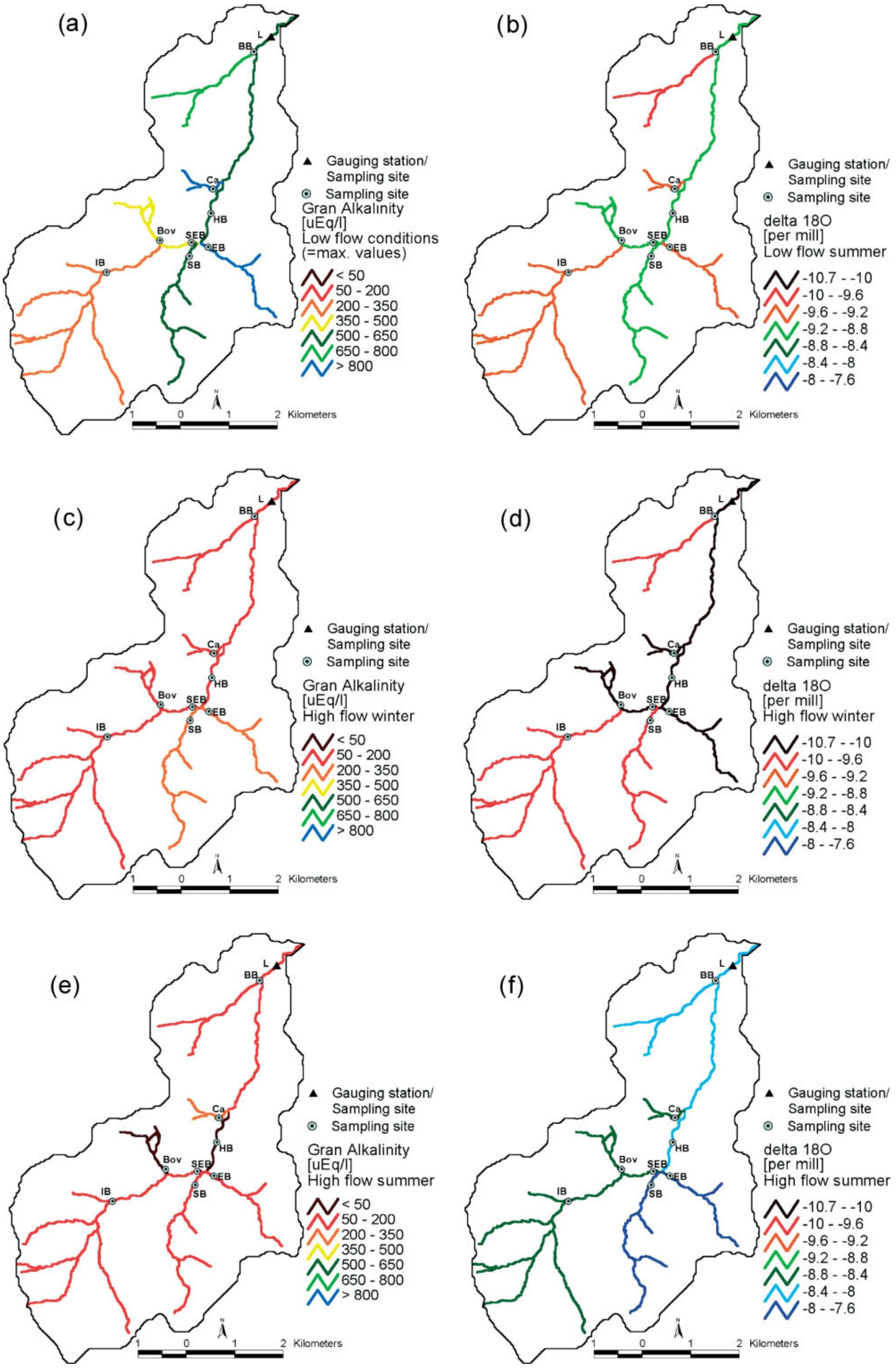

Figure 9. Spatial distribution of Gran alkalinity (μeq l^{-1}) and δ^{18}O (‰) during (a, b) summer low flow conditions (28 July 2004); (c, d) winter high flow conditions (30 January 2004) and (e, f) summer high flow condition (13 August 2004)

are enriched to between −8·7 and −7·6‰ (Figure 8d and f).

Estimating groundwater contribution and stream residence times

Table IV shows the results of the chemically based hydrograph separations for each of the subcatchments during the study year. In general, most subcatchments are predicted to have 23–40% of flows derived from groundwater sources. These lower groundwater contributions are similar to Littlemill, again implying that surface and near-surface hydrological pathways dominate the catchment response. The highest groundwater contributions are predicted for the Camlet Burn, with approximately 60% of flows being attributed to groundwater. This subcatchment has a high coverage of freely draining humus iron podzols and freely draining alpine soils, which would be consistent with higher groundwater recharge (Table I).

Figure 10 shows the fitted sine wave regressions (from Equation (2)) to weighted monthly precipitation (to show seasonal changes more clearly) and the Littlemill stream water data. Mean residence times calculated according to Equation (3) from modelled amplitudes and weighted means come out at 4·1 ± 3·3 months for Littlemill (Table IV). Mean residence times for all other main stem sites are estimated at around 4·7–5·9 months. These slightly higher figures partly reflect the less intense sampling at these sites, but still indicate low residence times, which, given the approximate nature of the sine wave method and the large 95% confidence limits, indicates statistically similar mean residence times to Littlemill. The same was evident for the subcatchments. It is interesting that, despite the major differences in subcatchment size and characteristics, the mean residence times of the Girnock sites were all so similar, and (with the exception of Camlet) consistent with the low groundwater contributions predicted by the chemically based hydrograph separations. The Camlet anomaly indicates that, despite higher groundwater contributions, this groundwater flow path is relatively rapid and not causing a difference in the seasonal patterns of δ^{18}O variations. This may reflect the combination of freely draining soils and steep catchment gradient at this site. As with recent work by McGuire *et al.* (2005) and Soulsby *et al.* (2006a), it appears that catchment characteristics are better indicators of mean residence time than scale.

WIDER IMPLICATIONS AND CONCLUSIONS

This paper aimed to develop a GIS approach to identify likely landscape controls on runoff dynamics and then use environmental tracers to assess streamflow generation processes independently at the catchment scale in relation to the landscape controls hypothesized from the GIS analysis. In so doing, it was hoped that this would contribute to the development of a transferable approach to conceptualizing streamflow generation processes at larger scales and allow this information to be used to assess the implications of current land management activities on catchment hydrology and water resources. The combination of tracers and landscape analysis within a GIS has provided a preliminary (though apparently effective) conceptualization of hydrological processes at the catchment and subcatchment scales. The Girnock appears to be very responsive to precipitation events, with hydrometric and tracer data inferring high runoff coefficients, limited (∼30%) groundwater contributions to stream flow and relatively short mean residence times (∼4–5 months). Dry spells are generally quite short and replenishment of soil and groundwater storage is relatively rapid. Consideration of these results in the context of the GIS analysis suggests that landscape organization (particularly the spatial distribution of soils and hillslope topography) interact as the first-order controls on catchment flow paths, residence times and storage (e.g. McGlynn *et al.*, 2003; Uhlenbrook *et al.*, 2004).

This spatially explicit conceptualization of runoff sources and hydrological flow paths provides a much more effective approach to understanding catchment functioning than can be gained from tracer studies alone. Interestingly, the analysis shows that the short residence time, dynamic soil-influenced hydrological response that is apparent for the catchment as a whole, and most subcatchments, depends on subtle interplay of different aspects of landscape organization. For example, the South Burn and East Burn have quite different catchment characteristics (Table I) but very similar mean residence times and groundwater contributions, which are comparable to

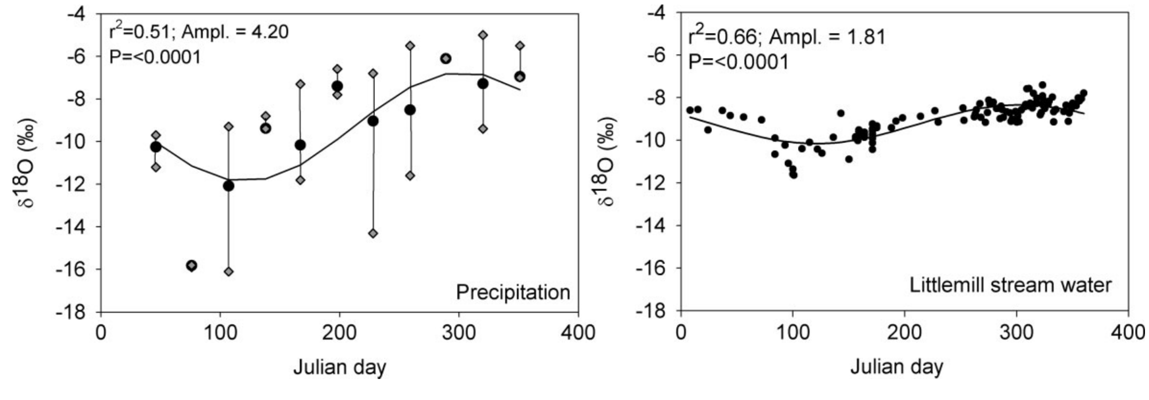

Figure 10. Fitted annual sine wave regression models to δ^{18}O in precipitation and stream water at Littlemill

Table V. Weighted mean and range of $\delta^{18}O$ in the Girnock precipitation and streamwaters together with modelled residence times (±95% confidence limit) from sine wave method

	$\delta^{18}O$ (‰)					Mean residence time (months)	±95% confidence interval (months)
	Mean	Min.	Max.	Modelled mean	Amplitude		
Precipitation	−9·36	−16·10	−5·02	−9·36	4·20	—	—
IB	−9·35	−10·90	−7·79	−9·35	1·31	5·9	3·1
SEB	−9·31	−10·76	−7·90	−9·31	1·34	5·8	3·7
HB	−9·29	−10·34	−8·27	−9·29	1·31	5·9	3·5
L	−9·11	−11·65	−7·42	−9·10	1·81	4·1	3·3
SB	−9·00	−10·92	−7·65	−9·01	1·38	5·6	3·2
EB	−9·10	−10·98	−7·14	−9·15	1·59	4·7	2·6
Ca	−9·52	−10·80	−7·63	−9·53	1·49	5·1	3·1
BB	−9·34	−10·70	−7·83	−9·37	1·33	5·8	3·5

the Girnock as a whole (Tables IV and V). The South Burn has a high coverage of responsive peat and peaty gley soils (99%) and the East Burn has 49% coverage of freely draining podzols of HOST class 17. Despite a lower coverage of responsive soils, the East Burn is the third steepest subcatchment with a highly connected flow path network (Figure 3b); thus, the soil and topographic characteristics together help to account for the hydrological characteristics. Camlet has a similar low residence time, despite 75% coverage of freely draining soils of HOST class 17, which seems to help explain the 55–59% groundwater contribution. However, Camlet has the second steepest catchment, and this, together with the free-draining soil dominance, may explain the paradox of high groundwater contributions but low residence times.

In general, however, the Girnock is notable for its responsive hydrological characteristics. Previous tracer-based work in the other montane catchments in the Cairngorm region of Scotland by Soulsby *et al.* (2006a) and Rodgers *et al.* (2005a) has shown that differences in soil cover (mapped by HOST classes) can be a powerful predictor of catchment hydrology at a range of scales. Where hydrologically 'responsive' soils, such as peats (HOST class 29), rankers (HOST classes 22 and 29) and peaty gleys (HOST class 15) are prevalent, catchments have a more 'flashy' hydrological regime. Thus, like the Girnock, mean residence times are generally in the order of a few months and groundwater recharge is low, typically resulting in groundwater contributing <40% of annual runoff (Rodgers *et al.*, 2005b). In contrast, where more freely draining soils, such as humus iron or subalpine podzols (HOST classes 5 and 17) prevail, the hydrological response is characterized by longer mean residence times, perhaps of a year or so, and greater groundwater contributions (>50%) to the annual hydrograph (Soulsby *et al.*, 2000, 2004). Recent work in the Plynlimon catchment has showed that groundwater in bedrock fractures may play an important role in storm runoff generation (Haria and Shand, 2004). Here, freely draining soils on steep hillslopes facilitate rapid groundwater recharge and lateral movement of groundwater to river channels during storm events. Paradoxically, catchments with steeper hillslopes often have such freely draining soils, so clear positive correlations between slope gradients and residence times, which have been demonstrated in other montane areas (McGuire *et al.*, 2005), are not always evident in the Scottish UK uplands.

The conceptualizations from combined GIS and tracer analysis provide us with a platform for advancing a number of research questions. First, the interrelationships between catchment characteristics and hydrological descriptors, such as mean residence time, or average groundwater contributions to flow offer potential in understanding being transferred to ungauged basins (McDonnell, 2003). In particular, use of the HOST system appears to provide a means of transferring process understanding across a range of spatial scales and to ungauged sites, where (as emphasized by the PUB initiative) predictions are increasingly required (McDonnell, 2003; Sivapalan *et al.*, 2003). Additionally, the tracer-based conceptual model of catchment hydrological functioning provides a framework for subsequent distributed modelling (Uhlenbrook *et al.*, 2004). Further research is needed to improve the spatial and temporal resolution of tracer responses to allow a more comprehensive understanding of the hydrological functioning of catchments like the Girnock. However, existing hydrological models can play an important role in assessing how the temporal variability in hydrological response would change the distribution of runoff generation processes shown in Figure 3b (Soulsby and Dunn, 2003).

A final use of the conceptualization of catchment functioning, such as presented in this paper, is to aid catchment management. As with many UK upland catchments, a striking feature of the Girnock is the dynamic nature of the hydrological response, the high degree of catchment connectivity and the relatively short residence times between hillslopes and the stream network. Such upland catchments will be sensitive to management activities, because any impacts can rapidly affect the quantity and quality of water reaching the river network (Lane *et al.*, 2004). This is a pertinent issue, as there is increased awareness that both traditional and new management activities in upland catchments may adversely impact upon water courses. Historically, much of the Girnock catchment (like large areas of upland Scotland) would have been forest covered (Smout, 2000). Forest clearance was followed by grazing by deer and sheep, which has prevented regeneration over the past few hundred years. Traditional burning of moorlands to create habitat for grouse has inhibited forest regeneration and in some areas has contributed to severe soil erosion and probably enhanced runoff (Watson, 1990). Road construction to access hunting grounds has also probably increased the hydrological responsiveness of catchments by intercepting flow paths and routing water more rapidly to streams, as well as generating infiltration-excess overland flow. Of course, the cumulative impacts of this long history of human management on watercourses are not well understood, though it is recognized that montane rivers of Scotland are highly simplified compared with the past (Montgomery *et al.*, 1998; Soulsby and Boon, 2001). Historic land management was generally carried out without any awareness of impacts on water resources, and even now the traditional burning regimes and land management activities often fail to recognize their potential impacts (Brogan and Soulsby, 1996). Clearly, tracer-validated GIS output has tremendous potential in aiding management in terms of understanding past and future impacts. Brandt *et al.* (2004) have already demonstrated this with respect to the afforested Plynlimon catchments, where, as with many traditional UK plantations, the forest is being restructured, and more sensitive protection and management of key hydrological source areas is being advocated as a means of avoiding problems, such as acidification, increased runoff rates and enhanced sediment delivery. Approaches such as those presented in this paper have considerable potential to contextualize land management decisions and foster precautionary approaches that can underpin more sustainable approaches to catchment management in upland watersheds.

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REFERENCES

Beighley RE, Dunne T, Melack JM. 2005. Understanding and modelling basin hydrology: interpreting the hydrogeological signature. *Hydrological Processes* **19**: 1333–1353.

Beven KJ. 2001. *Rainfall-Runoff Modelling: The Primer*. Wiley: Hoboken, NJ.

Bonell M. 1998. Selected challenges in runoff generation research in forests from the hillslope to headwater drainage basin scale. *Journal of the American Water Resources Association* **34**(4): 765–786.

Bonell M. 2004. How do we move from ideas to action? The role of the HELP programme. *International Journal of Water Resources Development* **20**(3): 283–296.

Bongartz K. 2003. Applying different spatial distribution and modelling concepts in three nested mesoscale catchments of Germany. *Physics and Chemistry of the Earth* **28**: 1343–1349.

Boorman DB, Hollis JM, Lilly A. 1995. *Hydrology of soil types: a hydrological classification of the soils of the United Kingdom*. Institute of Hydrology Report 126, Institute of Hydrology, Wallingford, UK.

Brandt C, Robinson M, Finch JW. 2004. Anatomy of a catchment: the relation of physical attributes of the Plynlimon catchments to variations in hydrology and water status. *Hydrology and Earth System Sciences* **8**: 345–354.

Brogan J, Soulsby C. 1996. Managing riparian tree cover in the Scottish Highlands: a study of Glen Tanar. *Scottish Forestry* **50**: 133–144.

Brooks KN, Folliott PF, Gregersen HM, DeBano LF. 2003. *Hydrology and the Management of Watersheds.* 3rd edn. Iowa State Press.

Burns DA, McDonnell JJ. 1998. Effects of a beaver pond on runoff processes: comparison of two headwater catchments. *Journal of Hydrology* **205**: 248–264.

Davies TD, Tranter M, Blackwood IL, Abrahams PW. 1993. The character and causes of a pronounced snowmelt-induced 'acidic episode' in a stream in a Scottish subarctic catchment. *Journal of Hydrology* **146**: 267–300.

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, Lilly A. 2003. Parameter identification for conceptual modelling using combined behavioural knowledge. *Hydrological Processes* **17**: 329–343.

Fluegel WA. 1995. Delineating hydrological response units by geographical information system analyses for regional hydrological modelling using MRMS/MMS in the drainage basin of the River Brol, Germany. *Hydrological Processes* **9**: 423–436.

Genereux D. 1998. Quantifying uncertainty in tracer-based hydrograph separations. *Water Resources Research* **34**: 915–919.

Hannah DM, Malcolm IA, Soulsby C, Youngson AF. 2004. Heat exchange and temperature behaviour in a salmon spawning stream in the Cairngorms, Scotland: seasonal and sub-seasonal dynamics. *River Research and Application* **20**: 635–652.

Haria AH, Shand P. 2004. Evidence for deep sub-surface flow routing in forested upland Wales: implications for contaminant transport and stream flow generation. *Hydrology and Earth Systems Science* **8**: 334–344.

Jenson SK, Domingue JO. 1988. Extracting topographic structure from digital elevation data for geographic information system analysis. *Photogrammetric Engineering and Remote Sensing* **54**: 1593–1600.

Joerin C, Beven KJ, Iorgulescu I, Musy A. 2002. Uncertainty in hydrograph separations based on geochemical mixing models. *Journal of Hydrology* **255**: 90–106.

Kendall C, Coplen TB. 2001. Distribution of oxygen-18 and deuterium in river waters across the United States. *Hydrological Processes* **15**: 1363–1393.

Kendall C, McDonnell JJ. 1998. *Isotope Tracers in Catchment Hydrology*. Elsevier: New York.

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

Lane SN, Brookes CJ, Kirkby MJ, Holden J. 2004. A network-index-based version of TOPMODEL for use with high-resolution digital topographic data. *Hydrological Processes* **18**: 191–201.

Langan SJ, Wade AJ, Smart R, Edwards AC, Soulsby C, Billett M, Jarvie H, Cresser MS, Owen R, Ferrier RC. 1997. The prediction and management of water quality in a relatively unpolluted major Scottish catchment: current issues and experimental approaches. *Science of the Total Environment.* **194**(5): 419–435.

Lyon J. 2003. *GIS for Water Resources and Watershed Management*. Taylor and Francis: UK.

Malcolm IA, Youngson AF, Soulsby C. 2003. Survival of salmonid eggs in a degraded gravel bed stream: effects of groundwater—surface water interactions. *River Research and Application* **19**: 303–316.

Malcolm IA, Soulsby C, Youngson AF, Hannah DM, McLaren IS, Thorne A. 2004a. Hydrological influences on hyporheic water quality: implications for salmonid survival. *Hydrological Processes* **18**: 1521–1542.

Malcolm IA, Hannah D, Donaghy M, Soulsby C, Youngson AF, Bacon P. 2004b. Influence of riparian woodland on water temperatures in an upland salmon stream. *Hydrology and Earth System Sciences* **8**: 449–459.

Malcolm IA, Soulsby C, Youngson AF, Hannah DM. 2005. Catchment scale controls on groundwater—surface water interactions in salmon spawning gravels. *Rivers Research and Management* **21**: 977–989.

Malcolm IA, Soulsby C, Youngson AF. 2006. High frequency logging technologies reveal state dependence of hyporheic process dynamics: implications for hydroecology. *Hydrological Processes* **20**: 615–622.

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.

McDonnell JJ. 2003. Where does water go when it rains? Moving beyond the variable source area concept of rainfall-runoff response. *Hydrological Processes* **17**: 1869–1875.

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

McGuire KJ, McDonnell JJ. 2006. A review and evaluation of catchment transit time modelling. *Journal of Hydrology* DOI: 10.1016/j/jhydol.2006.04.020.

McGuire KJ, McDonnell JJ, Weiler M, Kendall C, McGlynn BL, Welker JM, Seibert J. 2005. The role of topography on catchment-scale water residence time. *Water Resources Research* **41**(5): W05002.

Moir H, Soulsby C, Youngson AF. 1998. Hydraulic and sedimentary characteristics of habitat utilized by Atlantic salmon for spawning in the Girnock Burn, Scotland. *Fisheries Management and Ecology* **5**: 241–254.

Montgomery DR, Grant GE, Sullivan K. 1995. Watershed analysis as a framework for implementing ecosystem management. *Water Resources Bulletin* **31**: 1–18.

Montgomery DR, Dietrich WE, Sullivan K. 1998. The role of GIS in watershed analysis. In *Landform Monitoring, Modelling and Analysis*, Lane SN, Richard KS, Chandler JH (eds). Wiley: Chichester; 241–268.

Neal C. 2001. Alkalinity measurements within natural waters: towards a standard approach. *Science of the Total Environment* **265**: 99–113.

Neal C, Rosier PTW. 1990. Chemical studies of chloride and stable isotopes in two afforested and moorland sites in the British uplands. *Journal of Hydrology* **115**: 269–283.

Neal C, Hill T, Hill S, Reynolds B. 1997. Acid neutralizing capacity measurements in surface waters and groundwaters in the upper Severn, Plynlimon: from hydrograph splitting to water flow pathways. *Hydrology and Earth System Science* **3**: 687–696.

Quinn P, Beven K, Chevallier P, Planchon O. 1991. The prediction of hillslope flow paths for distributed hydrological modelling using digital terrain models. *Hydrological Processes* **5**: 59–79.

Richards PL, Brenner AJ. 2004. Delineating source areas for runoff in depressional landscapes: implications for hydrologic modelling. *Journal of Great Lakes Research* **30**: 9–21.

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

Rodgers P, Soulsby C, Waldron S, Tetzlaff D. 2005a. Using stable isotope tracers to assess hydrological flow paths, residence times and landscape influences in a nested mesoscale catchment. *Hydrology and Earth System Sciences* **9**: 139–155.

Rodgers P, Soulsby C, Waldron S. 2005b. Using stable isotopes as diagnostic tools in upscaling flow path understanding in mesoscale catchments in the Scottish Highlands. *Hydrological Processes* **19**: 2291–2307.

Scherrer S, Naef F. 2003. A decision scheme to indicate dominant hydrological flow processes on temperate grassland. *Hydrological Processes* **2**: 391–401.

Shand P, Haria AH, Neal C, Griffiths KJ, Goody DC, Dixon AJ, Hill T, Buckley DK, Cunningham JE. 2006. Hydrochemical heterogeneity in an upland catchment: further characterisation of the spatial, temporal and depth variations in soils, streams and groundwaters of the Plynlimon forested catchment. *Hydrology and Earth System Sciences* **9**(6): 621–644.

Sivapalan M. 2003. Process complexity at hillslope scale, process simplicity at the watershed scale: Is there a connection? *Hydrological Processes* **17**: 1037–1041.

Sivapalan M, Takeuchi K, Franks SW, Gupta VK, Karambiri H, Lakshmi V, Liang X, McDonnell JJ, Mendiondo EM, O'Connell PE, Oki T, Pomeroy JW, Schertzer D, Uhlenbrook S, Zehe E. 2003. IAHS decade on Predictions in Ungauged Basins (PUB), 2003–2012: shaping an exciting future for the hydrological sciences. *Hydrological Sciences Journal* **48**: 857–880.

Smart RP, Soulsby C, Cresser MS, Wade A, Townend J, Billett MF, Langan SJ. 2001. Riparian zone influence on stream water chemistry at different spatial scales: a GIS based modelling approach, an example for the Dee, NE Scotland. *Science of the Total Environment* **280**: 173–193.

Smout TC. 2000. *Nature Contested*. Edinburgh University Press.

Soulsby C, Boon P. 2001. Freshwater environments in Scotland: an earth science perspective on the natural heritage of Scotlands rivers. In *Earth Science and the Natural Heritage*, Gordon JE, Leys KF (eds). Stationary Office: London; 82–104.

Soulsby C, Dunn SM. 2003. Towards integrating tracer studies in conceptual rainfall-runoff models: recent insights from a subarctic catchment in the Cairngorm Mountains, Scotland. *Hydrological Processes* **17**: 403–417.

Soulsby C, Reynolds B. 1993. Influence of soil hydrological pathways on stream aluminium chemistry at Llyn Brianne, mid-Wales. *Environmental Pollution* **81**: 51–60.

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, Gibbins CN, Wade A, Smart R, Helliwell RC. 2002. Water quality in the Scottish uplands: a hydrological perspective on catchment hydrochemistry. *Science of the Total Environment* **294**: 73–94.

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

Soulsby C, Brewer M, Petry J, Dunn SM, Ott B. 2003b. Identifying catchment scale hydrological pathways using a novel approach to end member mixing in a small agricultural catchment. *Journal of Hydrology* **274**: 109–128.

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.

Soulsby C, Malcolm IA, Youngson AF, Tetzlaff D, Gibbins CN, Hannah DM. 2005. Groundwater–surface water interactions in upland Scottish rivers: hydrological, hydrochemical and ecological implications. *Scottish Journal of Geology* **41**(1): 39–49.

Soulsby C, Tetzlaff D, Rodgers P, Dunn SM, Waldron S. 2006a. Runoff processes, stream water residence times and controlling landscape characteristics in a mesoscale catchment: an initial evaluation. *Journal of Hydrology* **325**: 197–221.

Soulsby C, Tetzlaff D, van den Bedem N, Malcolm IA, Bacon PJ, Youngson AF. 2006b. Inferring groundwater–surface water interactions in montane catchments from hydrochemical surveys of springs and streamwaters. *Journal of Hydrology* (in press).

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

Stutter MI, Deeks LK, Billett MF. 2005. Transport of conservative and reactive tracers through a naturally structured upland podzol field lysimeter. *Journal of Hydrology* **300**: 1–19.

Takeuchi K. 2004. Hydrology as a policy-relevant science. *Hydrological Processes* **18**: 2967–2976.

Tetzlaff D, Uhlenbrook S. 2005. Significance of spatial variability in precipitation for process-oriented modelling: results from two nested catchments using radar and ground station data. *Hydrology and Earth System Sciences* **9**: 29–41.

Tetzlaff D, Soulsby C, Gibbins CN, Bacon PJ, Youngson AF. 2005a. An approach to assessing hydrological influences on feeding opportunities of juvenile Atlantic salmon (*Salmo salar*): a case study of two contrasting years in a small, nursery stream. *Hydrobiologia* **549**: 65–77.

Tetzlaff D, Soulsby C, Youngson AF, Gibbins CN, Bacon PJ, Malcolm IA, Langan SJ. 2005b. Variability in stream discharge and temperature: a preliminary assessment of the implications for juvenile and spawning Atlantic salmon. *Hydrology and Earth Systems Science* **9**: 193–208.

Thompson DBA, Gordon JE, Horsfield D. 2001. Montane landscapes in Scotland: are these natural, artefacts or complex relics. In *Earth Science and the Natural Heritage*, Gordon JE, Leys KF (eds). Stationary Office: London; 105–119.

Uhlenbrook S, Hoeg S. 2003. Quantifying uncertainties in tracer-based hydrograph separations: a case study for two-, three- and five-component hydrograph separations in a mountainous catchment. *Hydrological Processes* **17**: 431–453.

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**: 1–14.

Uhlenbrook S, Roser S, Tilch N. 2004. Hydrological process representation at the meso-scale: the potential of a distributed, conceptual catchment model. *Journal of Hydrology* **291**: 278–296.

Vitvar T, Balderer W. 1998. Estimation of mean residence times and runoff generation by stable isotope measurements in a small prealpine catchments. *Applied Geochemistry* **12**: 787–796.

Watson A. 1990. Human impact in the Cairngorms environment above timberline. In *Caring for the High Mountains—Conservation of the Cairngorms*, Conroy JWH, Watson A, Gunson AK (eds). Centre for Scottish Studies, University of Aberdeen; 61–82.

Wade A, Neal C, Soulsby C, Smart R, Langan S, Cresser M. 1999. Modelling stream water quality under varying hydrological conditions at different spatial scales. *Journal of Hydrology* **217**: 266–283.

Weiler M, Naef F. 2003. Simulating surface and subsurface initiation of macropore flow. *Journal of Hydrology* **273**: 139–154.

Wheater HS, Langan SJ, Brown A, Beck MB. 1991. Hydrological response of the Allt a' Mharcaidh catchment—inferences from experimental plots. *Journal of Hydrology* **123**: 163–199.

Wheater HS, Tuck A, Ferrier RC, Jenkins A, Kleissen FM, Walker TAB, Beck MB. 1993. Hydrological flow paths in the Allt a' Mharcaidh catchment: an analysis of plot and catchment scale observations. *Hydrological Processes* **7**: 359–371.

Wolock DM. 1995. Effects of subbasin size on topographic characteristics and simulated flow paths in Sleepers River watershed, Vermont. *Water Resources Research* **31**: 1989–1997.

Wolock DM, Price CV. 1994. Effects of digital elevation model map scale and data resolution on a topography-based watershed model. *Water Resources Research* **30**: 3041–3052.

Youngson A, Hay D. 1996. *The Lives of Salmon—an Illustrated Account of the Life-History of the Atlantic Salmon*. Swan Hill Press: Shrewsbury.