HYDROLOGICAL PROCESSES
Hydrol. Process. **17**, 759–777 (2003)

A tracer-based assessment of hydrological pathways at different spatial scales in a mesoscale Scottish catchment

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Abstract:

Geochemically based hydrograph separation techniques were used in a preliminary assessment to infer how runoff processes change with landscape characteristics and spatial scale (1–233 km^2) within a mesoscale catchment in upland Scotland. A two-component end-member mixing analysis (EMMA) used Gran alkalinity as an assumed conservative tracer. Analysis indicated that, at all scales investigated, acidic overland flow and shallow subsurface storm flows from the peaty soils covering the catchment headwaters dominated storm runoff generation. The estimated groundwater contribution to annual runoff varied from 30% in the smallest (*ca* 1 km^2) peat-dominated headwater catchment with limited groundwater storage, to >60% in larger catchments (>30 km^2) with greater coverage of more freely draining soils and more extensive aquifers in alluvium and other drift. This simple approach offers a useful, integrated conceptualization of the hydrological functioning in a mesoscale catchment, which can be tested and further refined by focused modelling and process-based research. However, even as it stands, the simple conceptualization of system behaviour will have significant utility as a tool for communicating hydrological issues in a range of planning and management decisions. Copyright © 2002 John Wiley & Sons, Ltd.

KEY WORDS hydrology; runoff processes; flow paths; EMMA; catchment; Scotland

INTRODUCTION

Recent years have seen a gradual change of emphasis in hydrology as environmental management requires that hydrological understanding gained at the small (<10 km^2) experimental catchment scale is applied to solving a range of problems that are manifest at the larger (>100 km^2) mesoscale (Falkenmark, 1990; Naiman *et al.*, 1995; Law, 2001). This alignment of scientific research to scales commensurate with environmental planning and management represents a significant challenge to hydrologists, as heterogeneity in catchment characteristics, non-linearities in catchment behaviour, and the scale issue often limits the extrapolations that can be made from traditional reductionist approaches to process understanding (Beven, 2001a; Healy, 2001; Naiman *et al.*, 2001). Consequently, there is a need to develop tools and approaches that are integrative and hierarchical, yet allow the internal functioning and behaviour of catchment systems to be investigated (Kendall and McDonnell, 1998; Beven, 2001b). Moreover, interests in catchment functioning are no longer restricted to traditional hydrological routing issues, such as flood generation or low-flow assessments (Gleick, 1993). The increasingly interdisciplinary nature of catchment science dictates that the hydrological influences on water quality and stream ecosystems need to be understood if catchments are to be managed to meet human needs and maintain ecological integrity in a sustainable manner (He *et al.*, 2000; WCD, 2000; Ward and Tockner, 2001).

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Received 11 February 2002
Accepted 16 May 2002

Despite this changing agenda, published work looking at the hydrological and hydrochemical functioning of larger, mesoscale catchments in an integrative manner remains relatively scarce (Allan and Johnston, 1997). Consequently, a gulf generally separates the practical concerns of managers and the research interests of freshwater scientists (Naiman *et al.*, 1995). Paradoxically, many early integrated studies of catchment hydrological and hydrochemical functioning focused on relatively large river systems (e.g. Webb and Walling, 1983; Kennedy *et al.*, 1986), though the need for process understanding of issues such as acidification subsequently focused efforts into reductionist approaches in smaller headwater basins (e.g. Bishop *et al.*, 1990; Soulsby and Reynolds, 1993; Hooper 2001). Amongst a range of initiatives targeted at understanding the hydrological and hydrochemical functioning of larger catchments (e.g. Allan *et al.*, 1997; Neal *et al.*, 1997, 1998; Cooper *et al.*, 2000) has been a major programme of research in the Dee catchment in northeast Scotland (Langan *et al.*, 1997; Smart *et al.*, 1998). As part of this study, the hydrology and hydrochemistry of the 230 km^2 Water of Feugh sub-catchment has been intensively studied at a range of spatial scales (Figure 1).

This sub-catchment of the Dee is particularly interesting from a management perspective, in that it is an important multi-use resource for the local community that is subject to a range of pressures and problems (SEPA, 2000). The river system is an important source of potable water for public supplies, and many of the widely distributed properties have private wells (Figure 1d). Water quality problems of discoloration and

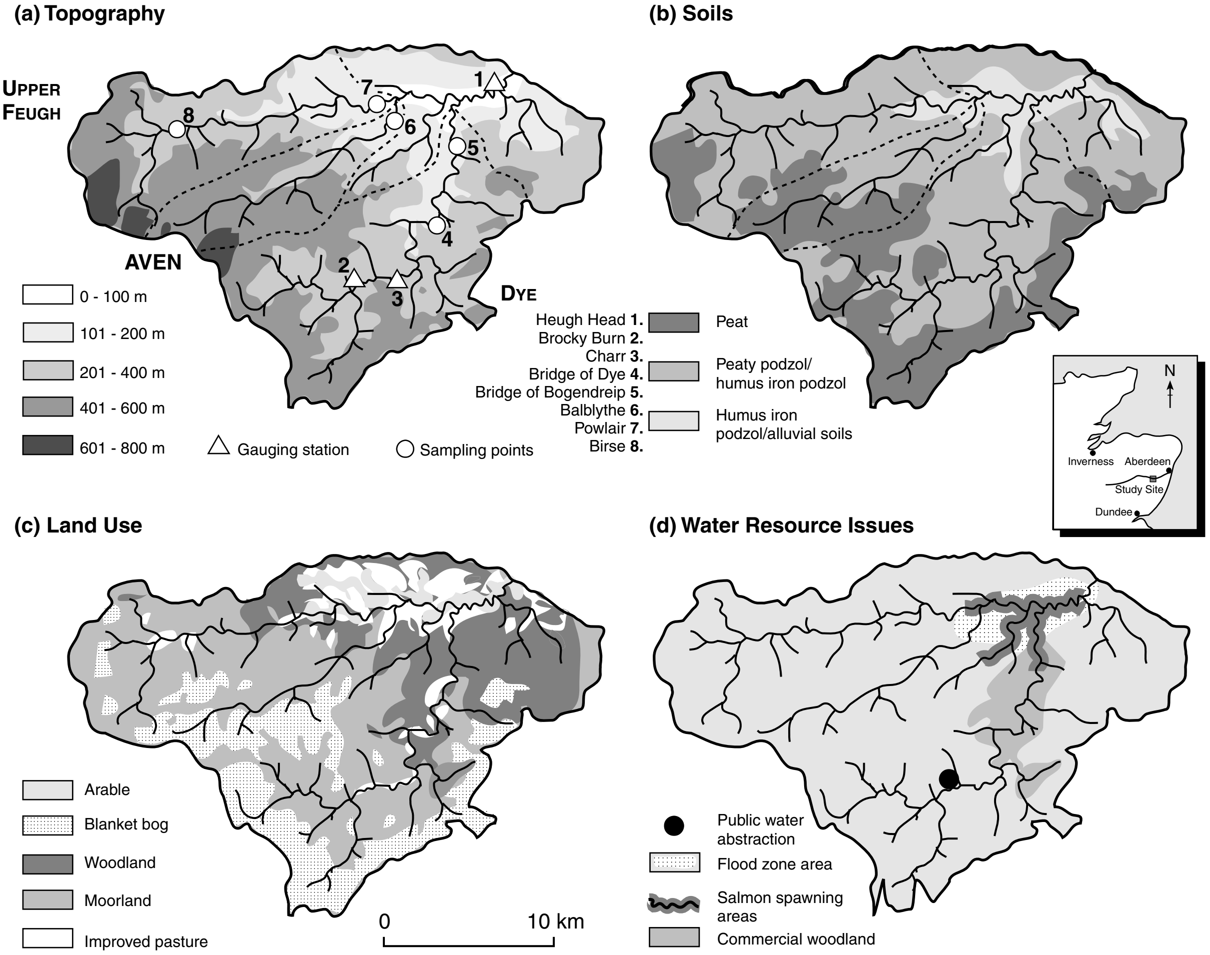

Figure 1. The Feugh catchment showing (a) topography, (b) soil coverage, (c) land use, and (d) water resource issues

microbiological pollution are common, particularly the former at direct public supply abstractions (Gidney, 2001). The lower river has a significant flood problem that inundates agricultural land and blocks transport routes. A significant salmonid fishery utilizes the river for spawning and juvenile habitat, but there is concern that acidification and sediment fluxes from commercial forestry may be compromising the fishery (Wade *et al.*, 2001). In many instances these problems are manifest at specific locations, and decisions regarding resource allocation in management responses are often based on piecemeal and fragmented approaches (SEPA, 2000). These usually lack a catchment context and fail to appreciate how the overall hydrological functioning of the catchment system underpins many of these problems (see Bellman, 2000). Despite this, such understanding is fundamental to the evolution of sustainable management strategies, and there is growing general awareness that environmental scientists need to be more proactive in communicating their knowledge to managers, policy makers, and the wider public (Lubchenco, 1998).

In this paper, the signatures of geochemical tracers are used to examine the varying sources of stream flow in the Feugh catchment at different spatial scales over the hydrological year. The approach is based upon the relatively simple technique of end-member mixing analysis (EMMA) in order to identify hydrological source areas dominating runoff at different flows (Hooper *et al.*, 1990; Genereux, 1998). The paper has three main aims: (a) to examine the spatial variability in storm flow and baseflow chemistry within the mesoscale Feugh catchment; (b) to use this information to identify how the relative importance of hydrological flow paths varies with scale as consideration moves from the headwater (*ca* 1 km^2) to the whole catchment; and (c) assess the utility of such understanding for management purposes. The paper uses relatively simple data analysis techniques, but the methods are underpinned by insights from a series of detailed process studies undertaken at smaller scales, either within the same catchment (e.g. Reid *et al.*, 1981; Billett and Cresser, 1992; Hope, 1995; Aitkenhead *et al.*, 1999; Dawson *et al.*, 2001) or in proximal locations in the Scottish highlands (e.g. Soulsby *et al.*, 1998, 2000; Soulsby and Dunn, 2003).

STUDY AREA: THE WATER OF FEUGH CATCHMENT

The Water of Feugh drains a 232·8 km^2 area in northeast Scotland (Figure 1). The catchment is predominantly upland in character, and the altitude ranges from 70 to 776 m. The climate is cool and wet, with an estimated mean annual precipitation of 1130 mm, which mainly falls as rain (Table I), though snow does occur during the winter months and significant snow pack accumulation can occur in cold years (Soulsby *et al.*, 1997). The catchment is mainly (*ca* 85%) underlain by granite, though the southern edge of the catchment boundary in the Water of Dye subcatchment is underlain by metamorphic rocks (mainly pelites and schists) (Table I).

The catchment is composed of three main sub-basins: the Water of Dye, the Aven, and the upper Feugh. The sub-basins have different glacial histories (Bremner, 1912) and, therefore, contrasting characteristics, particularly in relation to topography, drift cover, and soil distribution (Figure 1b). The southerly Water of Dye sub-basin comprises an extensive upland plateau with widespread coverage of peat. Even on valley slopes incised into the plateau, peaty podzols predominate. Freely draining humus iron podzols only become more common on steeper hillslopes in the lower catchment where the main river valleys become more entrenched. In contrast, the valley of the northerly upper Feugh is less incised, with smaller areas of peat-covered plateau (Figure 1b). The more extensive coverage of steeper hillslopes dictates larger distribution of more freely draining humus iron podzols. Between these two sub-basins, the Water of Aven has a much more linear drainage (Figure 1), with an extensive blanket bog in the upper catchment, which drains into a very steeply incised lower area. Soil coverage changes to freely draining podzols on the more steeply incised slopes.

Downstream of the confluence of the three sub-basins, freely draining podzolic alluvial soils predominate, which have formed on a range of fluvio-glacial and floodplain deposits. Such drift deposits are generally composed of freely draining sands and gravels (MacMillan and Aiken, 1981). All three sub-basins exhibit evidence of post-glacial modification by melt waters. The Water of Aven, for example, is largely devoid of drift deposits, presumably due to meltwater erosion. In both the lower parts of the Water of Dye and,

Table I. Catchment characteristics: area, mean altitude, precipitation, flow, geology, soil subgroup, and land use

	Topography		Hydrology				Geology (%)		Soil subgroup (%)			Land use (%)				
	Area (km^2)	Mean altitude (m)	Average SAAR (mm)	Long-term mean flow[a] (m^3/s^{-1})	Long-term Q_{10}[a] (m^3/s^{-1})	Long-term Q_{95}[a] (m^3/s^{-1})	Granite	Semi-pelite, pelite & mica-schist	Blanket peat	Humus iron podzol	Peaty podzol	Heather moorland	Blanket bog and peat	Improved grassland	Arable	Woodland
Water of Feugh																
1. Heugh Head	232·8	329	1130	5·3	10·7	0·8	83·9	5·0	32·3	33·8	33·5	44·5	23·7	7·7	17·2	18·1
Water of Dye																
2. Brocky Burn	1·3	419	1230	0·04	0·1	0·005	100	0·0	51·6	0·0	48·4	44·1	55·8	0·0	0·0	0·0
3. Charr	41·8	420	1280	1·3	2·6	0·2	72·1	21·5	65·0	0·0	35·0	47·3	52·1	0·1	0·0	0·0
4. Bridge of Dye	70·6	386	1244	2·1	4·3	0·3	77·8	16·5	54·8	6·1	39·1	44·9	42·3	1·1	0·1	9·7
5. Bridge of Bogendreip	90·1	357	1211	2·2	4·4	0·3	82·5	12·9	49·0	14·1	36·9	35·9	36·5	2·5	0·3	22·1
Water of Aven																
6. Balblythe	30·1	427	1236	0·8	1·5	0·1	100·0	0·0	56·9	17·0	26·1	46·9	45·8	1·4	0·0	5·6
Upper Feugh																
7. Powlair	61·1	356	1108	1·4	2·8	0·2	94·8	0·0	19·4	41·7	38·9	62·6	11·6	6·6	5·6	10·1
8. Birse	27·1	456	1206	0·8	1·6	0·1	100·0	0·0	31·1	12·4	56·5	76·1	19·0	2·2	0·0	0·4

[a] Estimated values except for Brocky Burn, Charr, and Heugh Head, which are flow gauged.

particularly, the upper Feugh sub-catchments, the lower hillslopes are covered by a range of drift deposits and the main river valleys have alluvial flood plains and gravel-dominated channels, though in many places the bedrock is intermittently exposed.

Given the topography and soil coverage in the catchment, land use is largely restricted to grouse (*Lagopus lagopus)* and deer (*Cervus elaphus*) shooting on heather moorland in the upper reaches of all three sub-basins. The moorlands are managed by regular burning to retain the mosaic of habitats required by grouse. The long history of burning may have contributed to peat erosion, as the peat is extensively 'hagged' in many places (Thompson *et al*., 2001). This dictates that a high density of ephemeral drainage channels covers the peat, connecting it to the perennial stream channel network. In all three sub-basins, agriculture occupies the better floodplain soils, though this mainly comprises livestock grazing (Figure 1c). The more extensive coverage of freely draining soils in the upper Feugh sub-basin and the lower catchment below the tributary confluences is the main area where arable farming occurs (Table I). Some of the valley hillslopes are forest covered, most notably in the lower valleys of the Water of Dye and upper Feugh. In the former case, the forestry is mainly commercial woodlands, whilst in the latter, semi-natural forests of Scots Pine (*Pinus sylvestris*) predominate.

The major water resource issues in the watershed include the flood risk area in the lower catchment, the public water supply abstraction in the Water of Dye, the main salmon spawning areas, and main area of commercial forestry (Figure 1). These have been identified in a catchment management plan for the River Dee (SEPA, 2000), and strategies for sustainable management objectives are being pursued in a number of community-based rural development initiatives (BCT, 2000).

DATA SOURCES

Between 1996 and 1997, an extensive hydrochemical sampling programme involved the establishment of eight monitoring sites in the catchment (Figure 1). The location of these was largely dictated by ease of access, but, in addition to sampling the catchment outfall at Heugh head, included points on the lower Dye, Aven, and upper Feugh at Bogendreip, Balblythe, and Powlair respectively. In addition, sampling points on the upper Dye at Bridge of Dye and Charr Flume were included, as was Brocky Burn, a 1·3 km^2 headwater stream, assumed to be characteristic of the peat-dominated upper catchment. Unfortunately, the upper Aven is inaccessible, but a sampling point on the upper Feugh at Birse was included in the study. As detailed by Smart *et al.* (1998), samples were analysed for pH, Gran alkalinity, major cations, major anions, and total organic carbon (TOC), which was measured in the supernatant solution of settled samples and thus approximates dissolved organic carbon (DOC). Of particular importance was the determination of Gran alkalinity by acidimetric titration in the pH ranges 4·5–4 and 4–3. This gives approximations of the bicarbonate and organic acid contributions to alkalinity respectively. As described by Wade *et al.* (1999), Gran alkalinity gives a directly measurable close approximation to the chemically conservative parameter acid neutralizing capacity (ANC), which to a first approximation can be used as an assumed conservative tracer (Neal, 2001). Strictly, ANC also depends on aluminium and DOC concentrations (Neal *et al*., 1999), but in the Feugh the aluminium concentrations are generally very low (Stutter *et al*., 2001) and, given the titration to pH 3, the Gran alkalinity and the charge balance ANC are strongly and linearly correlated within the pH range observed in stream waters.

Stream flow in the catchment was measured at Heugh Head and Charr flume. These sites are part of the UK national hydrometric network and are monitored by the Scottish Environment Protection Agency (SEPA). Further flow records were collected from Brocky Burn, where a flume and pressure transducer were established by the University of Aberdeen (Dawson, 1999). This gave accurate flow records for 233 km^2, 42 km^2, and 1·3 km^2 for the Feugh, Charr, and Brocky Burn respectively. Resources were not available for measuring flows at other sites, but, as part of a hydrological modelling study for the whole Dee basin, Wade (1999) found that mean daily flows could be predicted to ±7% by extrapolating from measured flow data at Charr (for Bridge of Dye, Bogendreip, Balblythe, and Birse) and Heugh Head (for Powlair) and adjusting for altitudinal influences on precipitation.

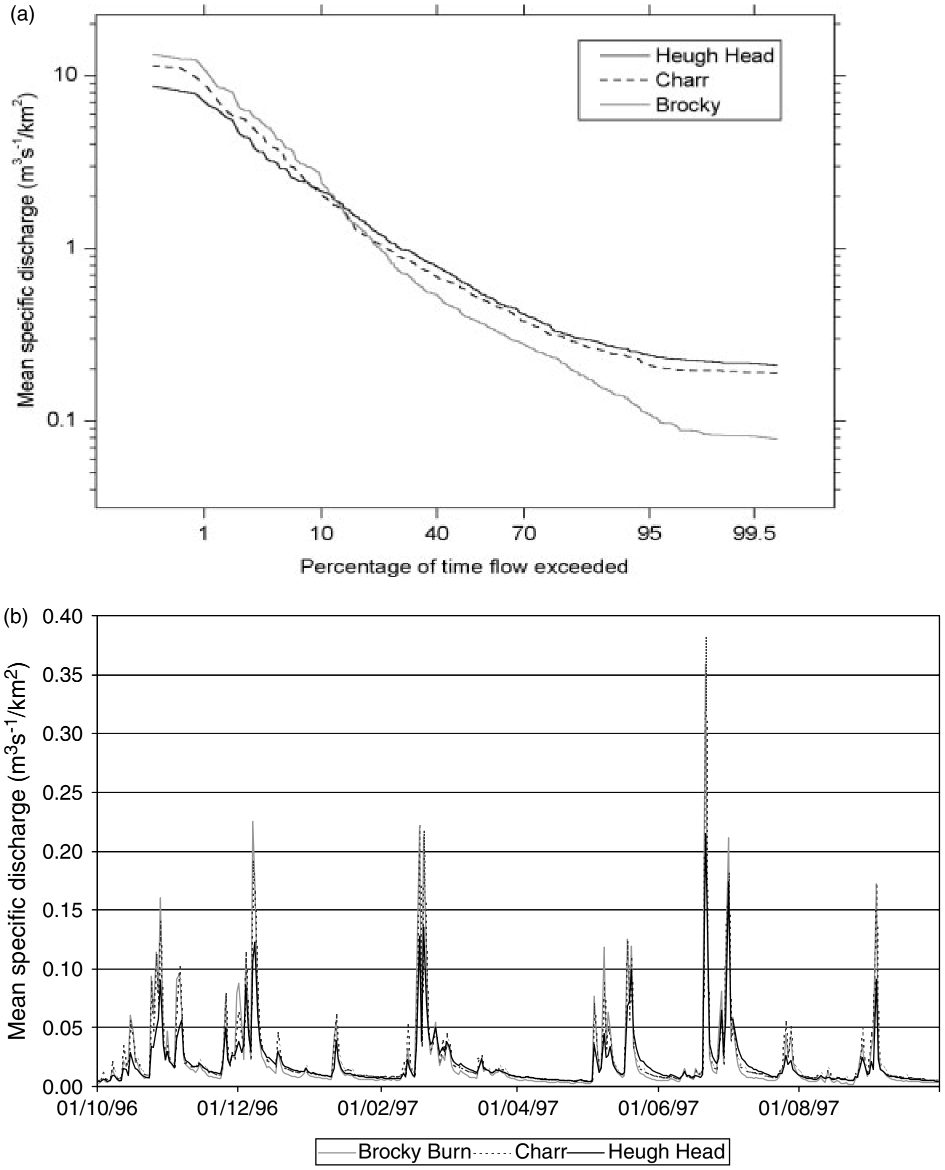

Figure 2. (a) Standardized flow duration curves and (b) specific mean daily discharge for 1996–97 for Brocky Burn, Charr flume and Heugh Head

HYDROLOGY

Standardized flow duration curves derived for the gauging stations at Brocky Burn, Charr flume, and Heugh Head give a useful insight to the effects of catchment characteristics on the flow regimes (Figure 2a). The steep flow duration curve for Brocky Burn implies limited groundwater storage for sustaining baseflows, but a more marked response at high flows. At the larger scale of Charr flume, a similar flow duration curve is produced, but a lower high-flow contribution is evident and contributions to baseflows are greater. Further downstream, at Heugh Head, the larger catchment shows a more marked groundwater influence and a more subdued response at high flows.

The same variation is evident when mean daily flows at the three scales are compared in terms of specific discharge time series (Figure 2b). The dominance of the upper catchment in producing hydrograph peaks is apparent in the time series for Brocky and Charr. However, at both of these sites the hydrograph recession is extremely steep compared with Heugh Head, which has a more gradual and sustained recession to baseflows, implying greater groundwater storage. There appears to be some seasonality in the behaviour of the recession curves for Charr. In the summer, recessions are steeper, like Brocky, whereas in winter they are more gradual like Heugh Head, possibly indicating a seasonally replenished groundwater store, most probably in alluvial aquifers in the valley bottom.

This changing hydrological behaviour with scale is not surprising, and it is generally consistent with catchment characteristics and processes anticipated from other process studies. The blanket peats, which cover 51·6% and 65% of the Brocky and Charr catchments respectively, clearly dominate the storm response, generating storm runoff by saturation overland flow (Reid *et al.*, 1981; Dawson *et al.*, 2001; Soulsby and Dunn, 2003). As the soil coverage and topography of these two streams are representative of much of the headwaters of the Feugh system as a whole, the effects propagate downstream to Heugh Head. However, increasing coverage of more freely draining alluvial gravels and humus iron podzols on extensive drifts, together with the declining gradient in the lower catchment, dictate lower specific yields during storm events, but facilitate a larger, more slowly responding storage that can control the hydrograph recession and sustain baseflows.

HYDROCHEMISTRY

Spatial variation

The catchment characteristics that influence hydrological behaviour also affect hydrochemical conditions in the Feugh watershed (Table II). In general, stream waters are acidic, with a low ionic strength that is dominated by atmospherically derived Cl^- and Na^+ as the main anion and cation respectively (Smart *et al.*, 2001a). In common with upland catchments elsewhere (Neal, 1997; Soulsby *et al.*, 1998), a number of determinands are strongly correlated with flow (Figures 3–5). Figure 3 shows the flow–concentration relationships at the Heugh Head site for the main hydrochemical parameters monitored in the study. In general, the patterns are similar for all the monitoring sites. Baseflows reflect weathering influences in the groundwater zone, and are relatively alkaline, and enriched in base cations and silica, whereas storm runoff is acidic, enriched in TOC, and diluted in weathering-derived solutes. This reflects the well-established influence of soil waters on stream chemistry at high flows in acid and acid-sensitive upland catchments (Robson and Neal, 1990; Soulsby, 1992).

Despite these simple patterns of flow-related variation observed throughout the catchment, spatial variations in stream chemistry are evident. With the exception of Brocky Burn, the alkalinity levels, particularly at baseflows, are highest in the Water of Dye sub-basin, most notably at Charr, then decline downstream at the Bridges of Dye and Bogendreip sampling sites (Figure 4). This is explained by the influence of metamorphic rocks in the upper part of the Dye catchment, which are more weatherable than the granite that underlies the other sub-catchments (Smart *et al.*, 2001b). The effect of the granite and lack of drift deposits is particularly evident in the chemistry of the Water of Aven, where baseflow alkalinities and base cation concentrations are very low at Balblythe (Figure 4).

Concentrations of TOC reflect peat coverage (Aikenhead *et al.*, 1999), with the mean and maximum values being highest at Brocky and Charr in the headwater of the Dye sub-basin, whereas they are lower at Birse and Powlair due to lower peat coverage in the upper Feugh (Figure 5). All sites show low TOC concentrations at lower flows.

Nitrate concentrations reflect soil coverage and agricultural land use (Wade *et al.*, 1998). Only downstream of large areas of arable land do nitrate concentrations increase, though they remain at fairly low levels (Edwards *et al.*, 2000). This reflects the relatively low intensity of farming, even on the better soils, and the more limited inputs of artificial fertilizers.

Table II. Mean concentration and range of major chemical determinands in the Feugh

		Gran alkalinity (μeq l^{-1})	pH	Concentration (mg l^{-1})							
				TOC	Ca^{2+}	Mg^{2+}	SiO_2	Cl^-	Na^+	SO_4^{2-}	NO_3^-
Water of Feugh											
1. Heugh Head	Mean	141·2	6·66	5·91	3·99	1·20	8·29	10·24	6·69	6·61	0·65
	Range	28·4–242·1	5·48–7·48	2·08–17·61	2·61–5·71	0·78–1·78	4·46–11·79	8·14–11·23	4·37–8·01	5·20–7·55	0·31–1·23
Water of Dye											
2. Brocky Burn	Mean	74·0	5·99	12·17	2·03	0·70	7·82	7·43	5·22	3·64	0·05
	Range	−44·7–188·1	4·24–6·87	5·60–31·05	1·04–3·41	0·44–1·00	2·99–11·86	4·99–8·72	2·71–6·32	2·30–5·10	<0·0–0·21
3. Charr	Mean	196·9	6·83	7·50	3·38	1·09	8·82	7·10	5·57	4·55	0·11
	Range	9·8–380·3	4·77–7·96	2·41–29·77	1·83–5·59	0·62–1·66	4·24–12·88	5·75–8·29	3·16–6·75	3·30–5·77	<0·0–0·35
4. Bridge of Dye	Mean	145·9	6·68	7·55	2·98	1·07	8·45	8·47	6·08	5·09	0·14
	Range	8·4–303·2	4·84–7·74	2·85–19·73	1·82–4·98	0·61–1·60	4·92–12·57	6·64–9·69	3·47–7·39	3·53–6·14	<0·0–0·42
5. Bridge of Bogendreip	Mean	126·3	6·62	7·79	3·03	1·10	8·49	9·31	6·52	5·79	0·26
	Range	12·9–260·7	4·85–7·76	2·91–19·31	1·74–4·48	0·74–1·67	5·10–12·57	7·42–10·48	4·07–7·52	4·09–8·71	<0·0–0·51
Water of Aven											
6. Balblythe	Mean	47·2	6·32	4·87	1·59	0·70	8·61	7·10	5·29	5·21	0·16
	Range	−6·9–99·7	4·60–7·28	1·86–15·46	1·18–2·97	0·42–0·95	4·58–12·25	5·64–8·19	3·16–6·29	3·73–6·11	<0·0–0·50
Upper Feugh											
7. Powlair	Mean	154·4	6·82	3·24	4·20	1·09	8·70	9·05	5·91	5·99	0·62
	Range	46·5–235·1	6·04–7·19	1·11–10·26	2·89–5·97	0·68–1·54	6·39–10·77	8·03–11·49	4·37–7·23	4·51–6·96	0·31–1·00
8. Birse	Mean	132·7	6·93	3·32	3·10	0·78	8·49	6·66	4·84	4·84	0·14
	Range	30·4–218·1	5·81–7·68	1·18–10·71	2·14–4·36	0·51–1·47	5·64–10·77	5·75–7·88	3·32–6·41	3·40–5·72	<0·0–0·36

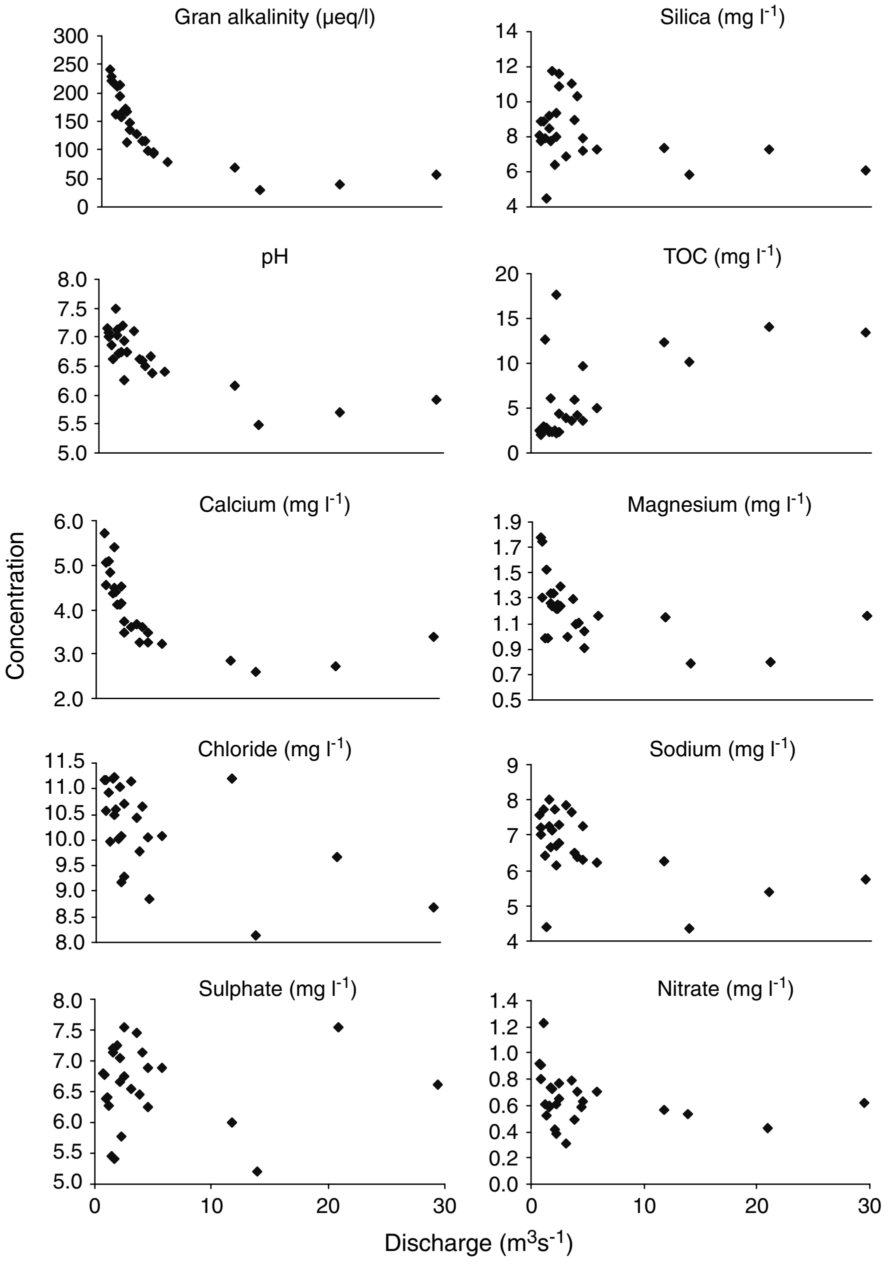

Figure 3. Concentration–flow relationships for selected determinands at Heugh Head

Temporal variation

Hydrochemical variations with flow reveal that, despite inter-site variations in baseflow chemistry reflecting differences in geology and soil type proportions, storm flow chemistry tends to converge, reflecting the dominant source area of storm runoff on the peatlands in the catchment headwaters. This is particularly evident when two flow-dependent species are plotted together for all of the study sites (Figure 6). Moreover, the shapes of the flow–concentration plots in Figure 4 all reveal roughly linear relationships

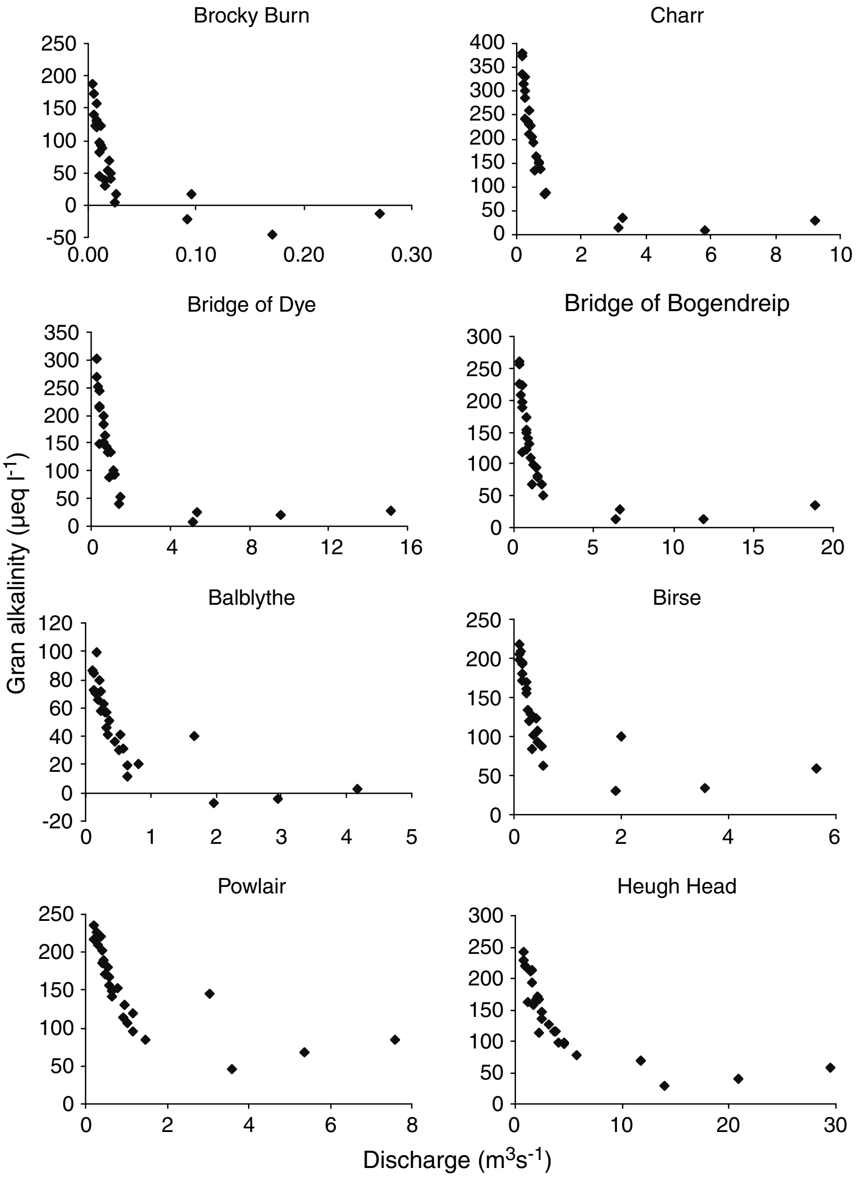

Figure 4. Concentration–flow relationships for Gran alkalinity in the Feugh catchment

between flow and alkalinity for all but the four highest flow samples collected for each sample site. This relationship breaks down at higher flows, presumably as low alkalinity soil water, derived mainly from overland flow, dominates the storm hydrograph (Soulsby and Dunn, 2003). This break is most abrupt for Brocky, Charr, Bridge of Dye, and Bogendreip, but is still evident, albeit smoothed, for Balblythe, Birse, Powlair, and Heugh Head. Nevertheless, the degree of baseflow buffering by groundwater sources clearly influences storm flow chemistry, as catchments such as Brocky and the Water of Aven appear to lack major groundwater sources in drifts and so have very low, or even negative, storm flow alkalinities. In contrast, even high flows remain relatively well-buffered, with positive alkalinity at sites like Powlair and Heugh Head.

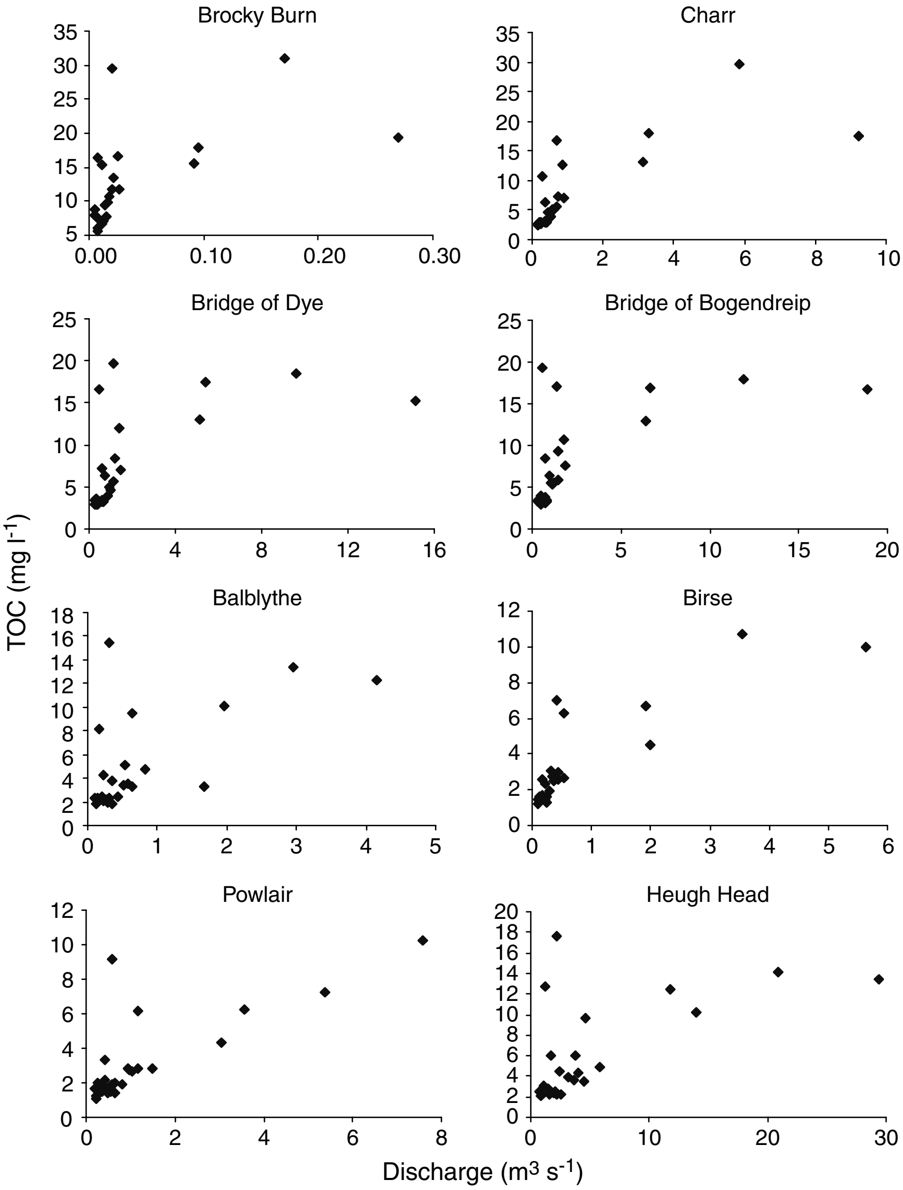

Figure 5. Concentration–flow relationships for TOC in the Feugh catchment

Similar patterns are evident in the concentration discharge relationships for calcium, magnesium, sodium, and silicon (not shown, but see Figure 3). Once again, the abrupt transition is more marked for the sites on the Water of Dye system; however, the relationship at Balblythe is less clear. These patterns are roughly reciprocated in the concentration–flow relationship for TOC (Figure 5). Here, concentrations generally increase with flows, reflecting source areas in organic soils, although other non-hydrological factors, such as temperature and biological processes, have an important influence on TOC concentrations (Hope, 1995), as seen from the varying degrees of scatter in the Figure 5 concentration plots.

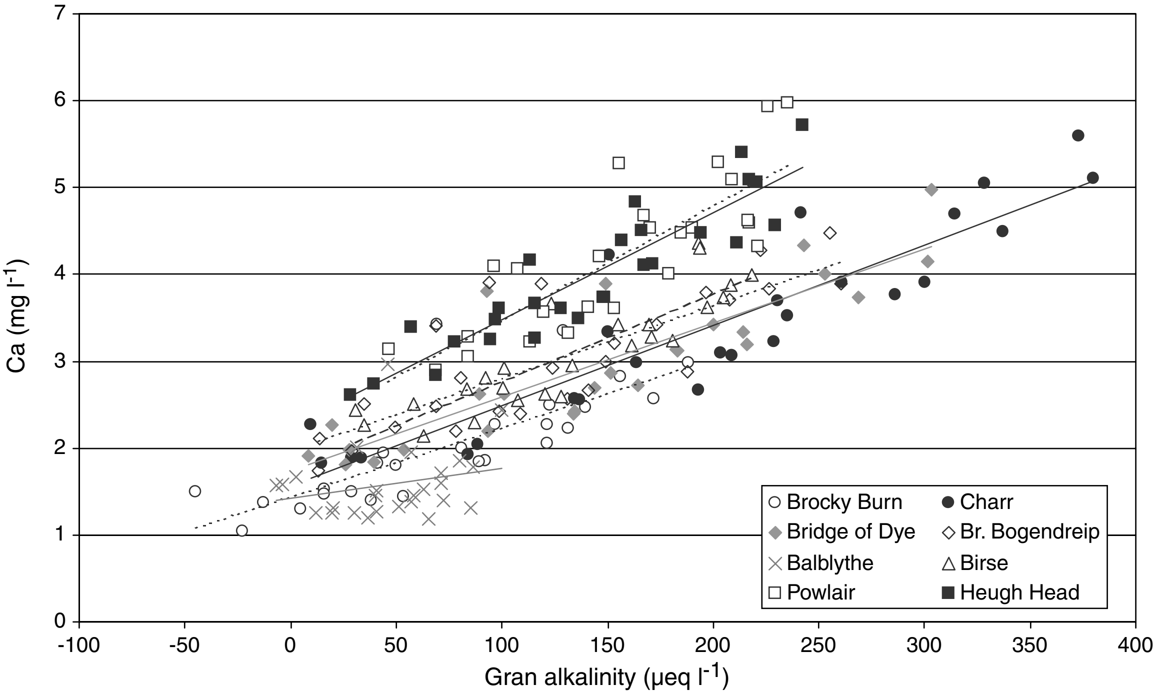

Figure 6. Relationships between Gran alkalinity and calcium for sampling sites in the Feugh catchment

HYDROGRAPH SEPARATION USING EMMA

The relatively simple relationships between flow and alkalinity in the Feugh catchment indicated that EMMA would probably be a useful diagnostic tool in exploring conceptual hydrological pathways in a more quantitative manner. This would provide a basis for assessing how different hydrological flow paths contribute to flows at different scales within the catchment.

In this case, a two-component EMMA was deemed appropriate using Gran alkalinity, as an approximation for ANC, as a conservative tracer. Previous work in the Dee catchment has shown that two-component mixing models have utility at a range of spatial scales (Billett and Cresser, 1992; Wade *et al.*, 1999). Although this contrasts with process studies in other catchments in the Scottish uplands which used three components (Jenkins *et al.*, 1994), subsequent work by Cresser *et al.* (2000) suggested that this could be partly explained by the important role of riparian zones in effectively decoupling subsurface storm flow in hillslopes from the channel network. Further work by Smart *et al.* (2001b) has indicated that this relates to the importance of groundwater storage in alluvial aquifers, which is either displaced by subsurface storm flow from adjoining hillslopes or mixes to limit the hydrochemical influence of hillslope water on stream flows. Thus, Smart *et al.* (2001b) showed that groundwater influence is evident in stream water chemistry at a range of spatial scales at both high and low flows. Only in small first-order catchments, where overland flow from peats collects in channels, is there an absence of riparian areas and groundwater inputs. These observations have been supported by process studies (Soulsby *et al.*, 1998) and the integrated application of EMMA and rainfall-runoff models (Dunn and Soulsby, 2003) in the Allt a' Mharcaidh catchment, a similar upland environment to the Feugh. Moreover, work at a number of other catchments has identified the decoupling of hillslopes from the channel networks due to the influence of riparian groundwater (Hooper *et al.*, 1998; McGlynn *et al.*, 1999; Burns *et al.*, 2001).

The strong correlations between stream Gran alkalinity and discharge were used as a basis for constructing a daily Gran alkalinity time series. At each site, the annual hydrograph was then separated according to a classical two-component mixing model:

$$C_t Q_t = C_s Q_s + C_g Q_g$$

where Q_t is stream flow, Q_s and Q_g are the contributions of soil water and groundwater respectively, and C is the concentration of conservative tracer in each component. From this, the groundwater contribution ($\%_g$) at any time can be estimated:

$$\%_g = 100(C_s - C_t)/(C_s - C_g)$$

The recorded flows at the three gauging stations and modelled flows at the remaining five were used to reconstruct the stream water time series. Although soil and groundwater samples have been collected in the Feugh catchment, spatial heterogeneity at small scales dictates that surface water samples often give better integrated measures of end-member chemistries at the catchment scale (Kendall *et al.*, 1995; Neal, 1997; Wade *et al.*, 1999). Thus, the groundwater end-member C_g was defined as the average Gran alkalinity of the three lowest flows recorded at each monitoring point. To define the soil water end member C_s, the chemistry of drainage water from an upland peat bog in the upper part of Brocky Burn was used (Dawson, 1999). Bi-weekly sampling over a coinciding 2 year period had collected low-alkalinity storm runoff from the peat bog on seven occasions, and the mean (-49 μeq l^{-1}) and standard deviation (18 μeq l^{-1}) were used to characterize the soil water end member for all the monitoring points. Given the similarity of the peat soils covering the headwaters of the three main sub-basins within the Feugh catchment, this was deemed a reasonable assumption. This has subsequently been confirmed by sampling other first-order streams draining the peat. Likewise, since the flows used to define the soil water and groundwater end-member chemistries were above and below the respective Q_{10} and Q_{95} of mean daily flows, this makes it reasonable to assume that they are at least characterized to a first approximation. The EMMA hydrograph separation was carried out for average end-member chemistries and then the soil water end member was varied by one standard deviation to give some indication of the sensitivity of hydrograph separation to the end-member composition (Foster, 2000). Obviously there is also uncertainty in the groundwater end member as well, though this was much less than for more reactive soil waters (Uhlenbrook and Hoeg, in press).

The separations for the eight sampling points are shown in Figure 7. In the Water of Dye sub-catchment, the increasing groundwater influence with catchment size is evident (Figure 7a). In Brocky Burn, the limited groundwater storage implied by the flow duration curve shown in Figure 2 is corroborated by the EMMA results. Groundwater inputs, although dominating base flows, appear to make a very limited response to the storm hydrograph. The slight increases that occur probably result from the displacement of groundwater as the subsurface storm flow from the steeper hillslopes enters the riparian zone in the lower reaches of the stream (Soulsby *et al.*, 1998). In contrast, the high-flow chemistry is dominated by overland flow from the extensive peat soils. Consequently, over the year, it is estimated that no more than 30% of runoff is generated from groundwater sources in the catchment.

A similar type of response can be observed at Charr flume, though the specific discharge at low flows is higher (Figure 2b) and greater groundwater inputs need to be invoked to explain the high-flow chemistry. Thus, it is estimated that 35–41% of runoff during the study year can be accounted for by groundwater sources. This probably reflects the presence of increased drift deposits and, crucially, more extensive alluvial aquifers in the 42 km^2 Charr catchment compared with the 1 km^2 Brocky watershed, as implied by Figure 2. In addition, the presence of metamorphic bedrock in the headwaters of the Charr sub-catchment probably has groundwater storage in fractures. These hypotheses are supported by the separations for the Bridge of Dye and Bogendreip sampling sites, where groundwater inputs of 34–41% and 36–44% respectively are required to account for the stream chemistry. These modest downstream increases in estimated groundwater contributions, as catchment size approximately doubles, suggest that although different landscape features (peat soils, alluvial aquifers, etc.) occupy varying proportions of the Dye catchment at the three sampling locations (Table I), the impact on the main hydrological flow paths is relatively limited.

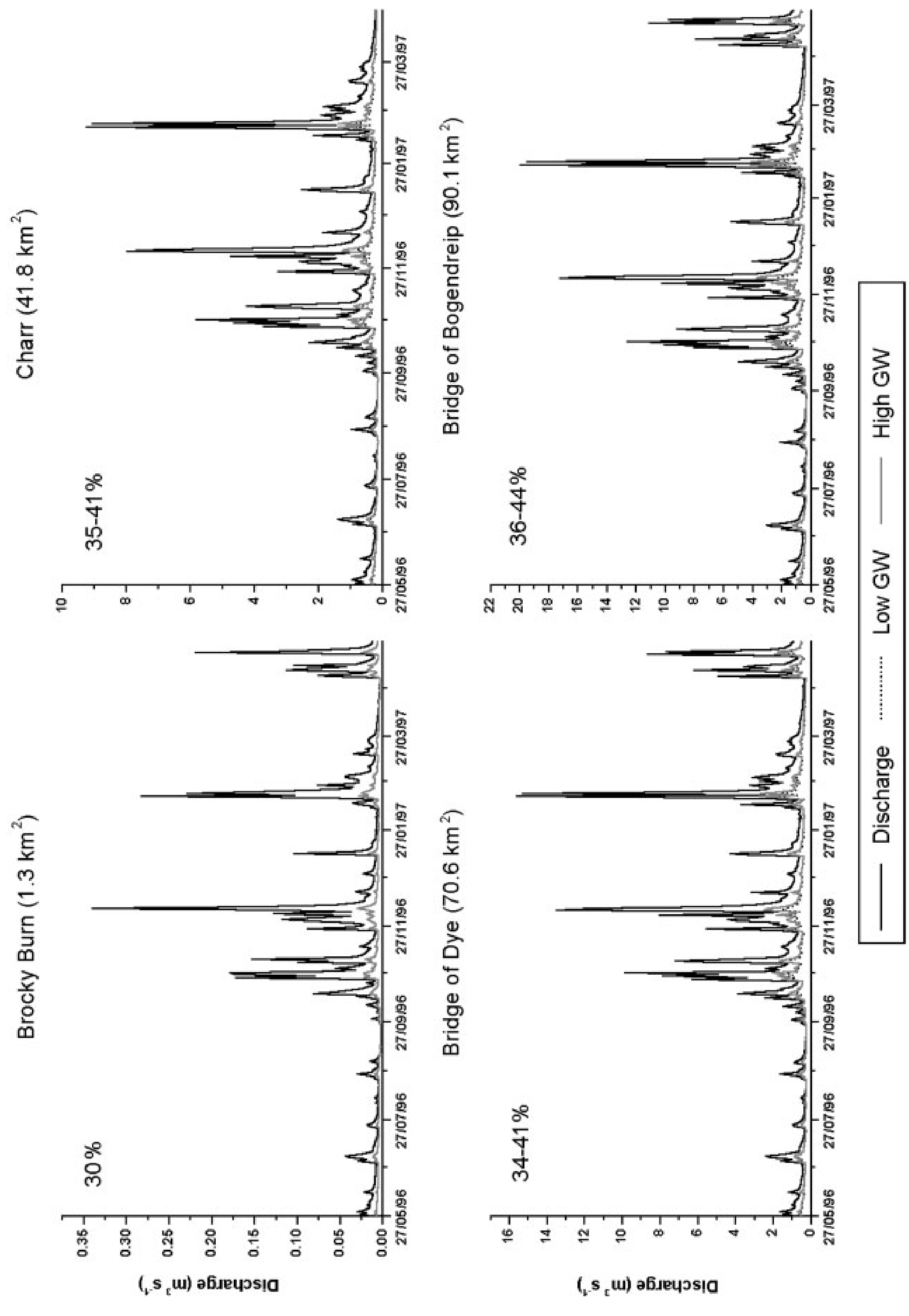

Figure 7. Hydrograph separations for sampling sites in the Feugh catchment

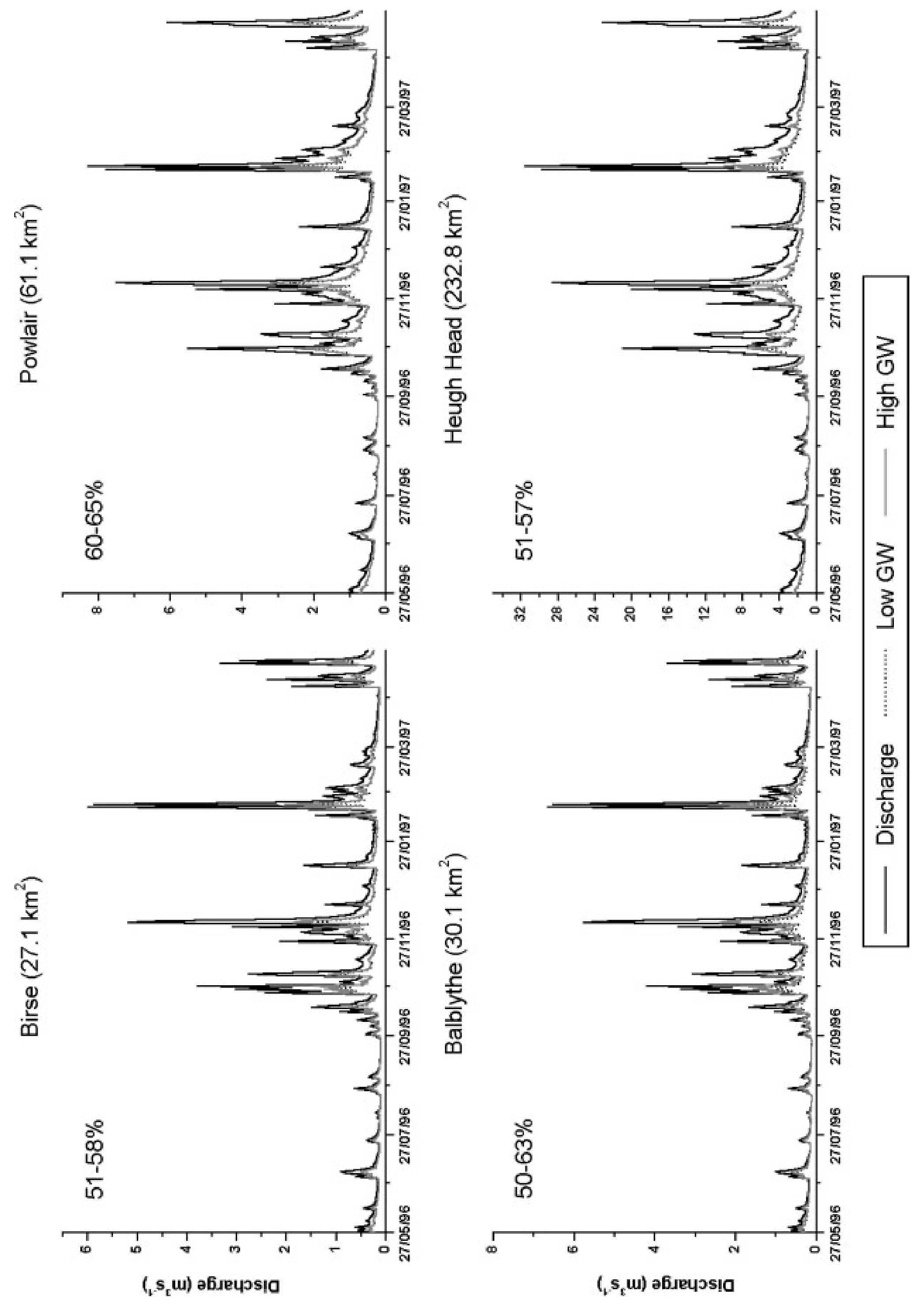

Figure 7. (*Continued*)

In contrast to the Dye, the EMMA result implies that the greater coverage of freely draining humus iron podzols in the Water of Aven and upper Feugh sub-basins reduces the influence of overland flow from peat soils, at the catchment scale, during storm events. The results must be interpreted with caution, as flows are modelled for these sites; nevertheless, storm-flow chemistry implies that, although overland flow is still the dominant source (*ca* >70%) of storm runoff, more buffered groundwater is displaced into the stream, again probably as a result of an influx of, and mixing with, hillslope water. Thus, estimates of groundwater contributions to annual runoff in the upper Feugh sub-basin increase from 51–58% at Birse to 60–65% at Powlair. Separations for the Water of Aven have the greatest uncertainty, probably due to the less marked differentiation of high- and low-flow chemistry (Figures 4 and 5), with estimated annual groundwater contributions of 50–61%. Given the absence of alluvial deposits in the incised valley of the Aven, this probably reflects the direct influence of hillslope waters on stream chemistry, that is indicated by the low alkalinity of baseflows (Figure 4).

Notwithstanding the uncertainty over the flow estimates in the ungauged catchments, the separation at Heugh Head is consistent with the mixing of water from the surface-water-dominated Water of Dye catchment, the more groundwater-dominated upper Feugh sub-basins, and the intermediate Water of Aven. Groundwater contributions are estimated at 51–57% of annual flows; again, this larger proportion than Brocky or Charr is consistent with the hydrological differences evident in Figure 2 and the known groundwater influences in the lower part of the catchment.

Although these separations are exploratory and a first approximation, the resulting groundwater and surface water contributions were used to model stream calcium concentrations and those of other weathering-derived species that had linear relationships with Gran alkalinity. As with Gran alkalinity, the groundwater and soil water calcium concentrations were estimated from baseflow and storm flow samples, and these were mixed according to the EMMA results and compared with measured stream flow samples. Coefficients of determinations ranged between 0·71 and 0·89, providing additional evidence that the separations predicted by EMMA appear to be feasible.

DISCUSSION

The Feugh catchment comprises three basic topographic units: the plateau peatlands that cover the headwaters, the steep, freely draining slopes on the incised valley sides, and the drift aquifers in the main river valleys. Generally, the hydrological and hydrochemical characteristics of the catchment reflect these basic upland–lowland transitions, with the plateau peatlands dominating storm runoff generation at all scales and with groundwater in valley bottom drifts, fed by hillslope drainage, sustaining baseflows. Implicit in this conceptual model is the influence of scale on the relative proportion of different landscape units, with the effect of the plateau peatlands decreasing with catchment size and the influence of aquifers in alluvium and other drifts becoming more marked. However, when individual sub-catchments are considered, catchment characteristics, rather than scale alone also become important.

The hydrograph separations presented here represent a first approximation of the changing groundwater influence with scale, and even the simple sensitivity analysis presented shows considerable uncertainty over the resulting separations. Nevertheless, the results are broadly consistent with the results of hydrometric investigations and modelling studies in the catchment and proximate locations. This basic conceptualization highlights the importance of emergent hydrological processes at different scales of enquiry (Neal, 1997). Thus simple behaviour (i.e. two-component mixing) at the catchment scale is underpinned by a myriad of complex processes at the hillslope scale that are difficult to elucidate (Barnes, 2001). However, this apparent influence of different landscape units on runoff generation and stream hydrochemistry in the Feugh catchment offers considerable potential for the application of semi-distributed modelling, informed by tracer behaviour, to show how the catchment response is integrated at different scales (cf. Uhlenbrook and Leibundgut, 1999; Soulsby and Dunn, 2003).

Despite this need for further research, the simple conceptualization of catchment functioning achieved so far has considerable utility as a tool to communicate the importance of hydrology to different stakeholders and policy makers concerned with various issues in the catchment. This communication may be simple and qualitative, allowing the hydrological context of many of the water resource problems highlighted earlier to be more easily understood. Thus, the responsive peat soils in the catchment explain the rapid flood period responses; they also account for discoloration problems and the rapid transmission of pathogens (from sheep and deer excrement) into stream channels and water supplies. In addition, to a large extent, the acidic storm runoff that characterizes the Feugh catchment can largely be ascribed to organic acids generated in the catchment's peatlands, rather than atmospherically derived acids. The extremely low alkalinities that occur in acidified sites such as Plynlimon (Neal *et al*., 1999) are not observed in the Feugh. This presumably reflects the influence of strong mineral acids reducing surface water alkalinity at acidified sites. Although in many ways such observations are obvious from basic watershed science, Lubchenco (1998) and Healy (1998) remind scientists that communicating such science is a non-trivial issue.

Not only are these explanations of catchment functioning useful at the interface between science and society, but, by providing a basic understanding of the underpinning hydrological processes, a more formal framework is provided for environmental planning and for modelling the possible impacts of a range of environmental changes (Bellman, 2000). Hydrological subroutines are increasingly incorporated into integrated decision support system models that can be used in environmental planning (WCD, 2000 Bellman, 2000). Combining the simple approach presented here with more comprehensive, processes-based models offers considerable potential for effectively integrating hydrological knowledge into management strategies for the Feugh and other similar mesoscale watersheds. No doubt the influence of spatial scale on the hydrology and hydrochemistry of the Feugh catchment is more complex than presented here. Thus, in addition to modelling, increasing our understanding of the spatial and temporal variability in the hydrological and hydrochemical functioning of the Feugh is also an aim of ongoing research. Particular attention is being given to providing a better resolution of sampling during storm events at different spatial scales to appreciate how the hydrological functioning of a mesoscale catchment operates on shorter time steps than the daily ones considered here.

ACKNOWLEDGEMENTS

Funding for this research has been provided by NERC through the Large Scale Processes in Ecology and Hydrology Special Topic, the NERC/JIF Catchment Hydrology and Sustainable Management (CHASM) Initiative and a studentship to PR.

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