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Assessing nested hydrological and hydrochemical behaviour of a mesoscale catchment using continuous tracer data

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Summary High resolution (15 min) continuous environmental tracer data (conductivity, pH and derived Gran alkalinity) were used to investigate the hydrological functioning of the 233 km^2 Feugh catchment in NE Scotland and two of its nested sub-catchments (42 km^2 and 1 km^2). Over the 2003–2004 hydrological year, a fine resolution Gran alkalinity time series was derived and indicated detailed and subtle changes in stream chemistry. Diurnal variation in alkalinity and flow were observed under low flow conditions, attributed to instream-respiration and riparian-evapotranspiration respectively. At high flows, abrupt threshold-like behaviour was evident during storm events as hydrological sources in the acidic surface horizons of the catchment soils replace groundwater as the dominant source of runoff. Using Gran alkalinity to define end-member compositions, chemically-based hydrograph separations revealed that as catchment scale increased, groundwater contributions to annual runoff increased from 52 ± 10%, to 67 ± 6%, to 70 ± 11%. This is consistent with previous mean residence times (MRT) estimated from weekly δ^{18}O data which respectively increased from 1.3–4.7 months^{-1} to 2.4–10.6 months^{-1} to 2.5–11.1 months^{-1}. Linking continuous tracer data with GIS interpretation of landscape characteristics increased the sophistication of our conceptual model of catchment processes. Increasing dominance of responsive peaty soils leads to more saturation overland flow, increased flashiness of runoff, reduced groundwater recharge, reduced MRTs and more marked diurnal variations in flow, which drive concomitant difference in hydrochemistry. Conversely, increased cover of free-draining soils and aquifers in drift, reduced flashiness, increased groundwater contributions and increased MRTs. It is proposed that high resolution tracer data, in conjunction with other measurements defining catchment characteristics, represent a resource and challenge to modellers if models can be produced which

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use tracer data, as well as physical parameters as objective functions in model evaluation.

Introduction

Hydrologists are increasingly challenged to provide process-based understanding of catchment behaviour at larger scales, commensurate with the concerns of river basin managers (Bonell, 2004). This requires the development and use of new tools that can offer integrated perspectives on how catchments route water to river networks at larger spatial scales (Soulsby et al., 2006a). Two obvious technologies that can aid this task are the use of natural tracers, such as stream-water chemistry composition, which can provide integrated insights into the emergent hydrological processes that characterise larger scale catchment functioning; and the use of Geographical Information Systems (GIS) which can be used to examine the influence of catchment landscapes on these processes (McGlynn et al., 2003). The utility of tracers in contributing to process understanding at larger scales is widely recognised (Weiler et al., 2003). However, recent work by Kirchner et al. (2004) highlights the fact that the relatively poor temporal resolution of tracer data (typically weekly) – particularly when compared with flow measurement (typically sub-hourly) – normally leads to considerable uncertainty over its interpretation.

The potential of continuous water quality monitoring to overcome this problem of poor temporal resolution of tracer samples has long been recognised (Robson et al., 1992; Hodgson and Evans, 1997; Jarvie et al., 2001; Peterson et al., 2005) but appears under-utilised, possibly as a result of expense and/or unreliability of field instruments. However, recent technological developments mean that such data can now be collected more easily, cheaply and reliably than ever before (Malcolm et al., 2005). Likewise, as GIS facilitates greater availability of spatially distributed digital data sets, catchment behaviour can more readily be related to catchment characteristics to improve process understanding (Rodgers et al., 2004; Tetzlaff et al., 2007) and allow extrapolation to other ungauged basins (e.g. Soulsby et al., 2006b).

This paper reports the results of data collected by continuous water quality monitoring in the Feugh catchment, Cairngorms, NE Scotland used to examine the tracer response at fine temporal resolution. Previous studies in the Feugh have utilised routine (weekly or fortnightly) sampling of tracer data to infer hydrological functioning at different spatial scales (Soulsby et al., 2003, 2004) and begun to relate this to landscape characteristics using GIS (Rodgers et al., 2005). Deployment of continuous water quality loggers in the catchment has provided the opportunity to enhance our understanding of catchment hydrochemical response and, by inference, hydrological processes. In this paper data from continuous water quality monitoring are used to derive tracer data at fine (15 min) temporal resolution at two spatial scales – at 1 km^2 and 42 km^2, supplemented by inferred composition at 233 km^2 – in order to gain insight into the changing nature of hydrochemical response with increasing spatial scales.

Within an over-arching aim of examining how high frequency tracer data can enhance understanding of the hydrological and hydrochemical functioning of nested catchments, a GIS of catchment characteristics is used to identify landscape controls on catchment hydrological behaviour. In conjunction with continuous tracer data, the paper aims to use to assess specifically:

(i) The scaled hydrological and hydrochemical response of catchments over a hydrological year.
(ii) The changing importance of different hydrological sources of runoff at different spatial scales, providing more insightful estimation of uncertainties.
(iii) The scaled influence of hydrological conditions on stream hydrochemistry under high and low flows.

Study catchment

The Water of Feugh, a tributary of the River Dee, is located in the eastern Cairngorm Mountains of NE Scotland and drains a catchment of 233 km^2 to the gauging site at Heugh Head (Fig. 1). River discharge was measured at three spatial scales: 233 km^2, 42 km^2 and 1.3 km^2 for the Water of Feugh at Heugh Head, at Charr and Brocky Burn respectively (Soulsby et al., 2003). The landscape characteristics of the Feugh catchment and its associated sub-catchments have been derived from detailed GIS analysis and are summarised in Table 1.

The altitude ranges from 69 m to 775 m with a mean elevation just over 300 m (Fig. 1a, Table 1). Highest elevations occur at the western edge of the catchment. The mean slope is 8.6° with maximum slopes of >40° occurring in the north-western parts of the Water of Feugh catchment (Fig. 1b). Higher elevation areas are associated with granite (which cover ca. 78% of the catchment), although the most southern parts of the catchment are underlain by metamorphic rocks (mainly pelites and psammites) and thus, strongly influence the hydrochemistry of the Water of Dye sub-catchment (Fig. 1c). The poor aquifer characteristics of these metamorphic rocks render fracture flow likely to be the main mechanism of bedrock groundwater movement (cf. Haria and Shand, 2004). In the northern parts, the lower Feugh catchment has been over widened by glacial erosion and meltwater action. Extensive alluvial deposits of sands and gravels (>10 m deep) occupy the valley bottoms.

Soil cover, whilst complex, reflects the organisation of topography, geology and drift cover. Recent studies have shown that it is a very good predictor of catchment hydrology in Scotland (Soulsby et al., 2006b). The UK HOST (Hydrology Of Soil Type) system (Boorman et al., 1995) groups all soils of the UK into 29 classes and characterises them according to dominant hydrological processes (e.g. Dunn et al., 2003). Hence, HOST provides a convenient classification for identifying hydrological similarities (Dunn et al., 2003; Soulsby et al., 2006a; Tetzlaff et al., 2007)

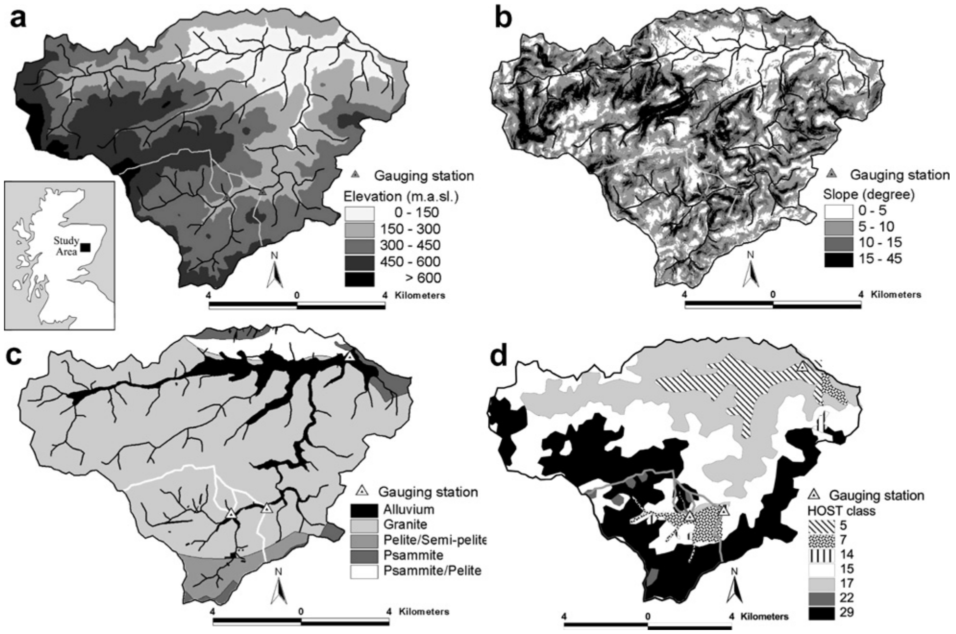

Figure 1 The Feugh catchment: (a) topography, gauging sites and sampling locations; (b) slope; (c) geology; (d) HOST classes (5 = Humus Iron Podzol; 7 = Alluvial Soils; 14 = Gley; 15 = Peaty Gley, Peaty Podzol; 17 = Alpine soils, Humus Iron Podzol; 22 = Brown Ranker; 29 = Peat).

Table 1 Characteristics of the Feugh and associated sub-catchments Water of Dye and Brocky Burn

Catchment	Feugh	Water of Dye	Brocky Burn
km^2	233	42	1.3
Topography			
Mean slope (°)	8.6	8.4	5.6
Max. slope (°)	43.7	32.9	25.8
Mean elevation (m)	328	422	415
Min. elevation (m)	69	246	257
Max. elevation (m)	775	773	532
Drainage density (%)	0.71	0.65	0.66
Flat area (slope < 4°)(%)	28	21	47
Geology (%)			
Alluvium	8.3	2.4	0
Granite	78.4	74.4	100
Pelite/semi-pelite	4.8	20.1	0
Psammite	3.6	3.0	0
Psammite/pelite	4.9	0	0
HOST class (%)			
* BFI, base flow index			
** SPR, standard percentage runoff coefficient			
5 (Humus Iron Podzol; BFI*1.0; SPR**14.5)	6.6	0	0
7 (Alluvial soils; BFI*0.725; SPR**44.3)	1.6	3.6	2.1
14 (Gley; BFI*0.219; SPR**25.3)	0.8	1.9	0
15 (Peaty Gley, Peaty Podzol; BFI*0.387; SPR**48.4)	33.4	32.8	20.5
17 (Alpine soils, Humus Iron Podzol; BFI*0.613; SPR**29.2)	26.5	2.4	1.7
22 (Peaty Ranker; BFI*0.294; SPR**60.0)	1.0	4.5	18.1
29 (Peat; BFI*0.232; SPR**60.0)	30.0	54.8	57.5
Landcover (%)			
Woodland	18.1	0	0
Moorland/peat	68.2	99.4	100
Grassland	10.7	0.6	0

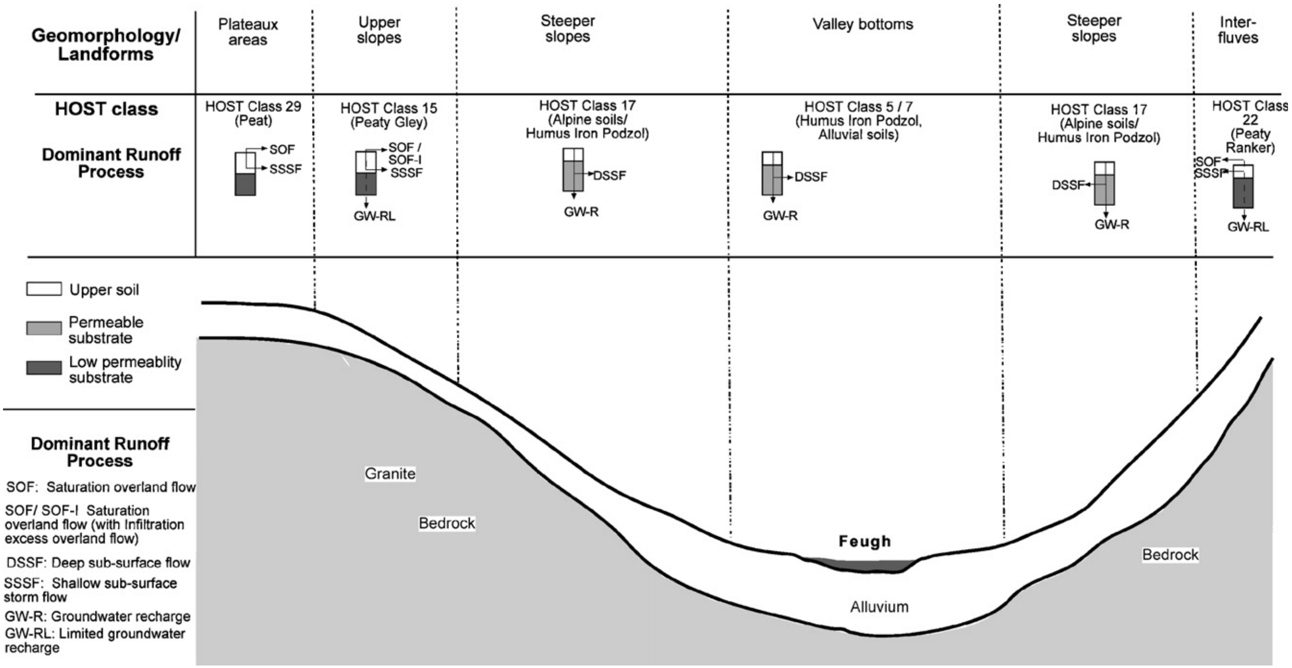

Figure 2 Conceptual model of the Feugh catchment showing distribution of dominant HOST classes and corresponding dominant runoff generation processes.

which complements existing soil classification schemes. In the Feugh catchment, the interaction between geology and topography results in seven different spatially-distributed HOST classes occurring that can be used to inform a conceptual model of catchment hydrological response (Figs. 1d and 2).

Higher elevation areas are characterised by extensive plateaux areas, covering >60% of the Feugh catchment and dominated by HOST class 29 (peats (histosols) up to 5 m deep), and additionally HOST class 15 (peaty gleys (histic gleys) ca. 1 m deep). Process studies (e.g. Soulsby and Reynolds, 1993) have shown that such soils are saturated for much of the year and generate substantial amounts of saturation excess overland flow and shallow lateral flow in organic surface horizons (Fig. 2). On steeper catchment slopes HOST class 17 (<1 m deep) comprises freely-draining brown soils, humus iron podzols (haplic podzols) and deeper sub-alpine podzols which cover 27% of the catchment. In addition, in the main river valleys freely-draining alluvial soils (fluvisols) (HOST 5 and 7) are to be found (Fig. 2). Vertical water movement in these hillslope and valley bottom HOST classes facilitates groundwater recharge and in some instances deeper sub-surface flow at the soil-bedrock interface (Soulsby, 1992, 1998; Soulsby and Reynolds, 1992; Wheater et al., 1993).

From the HOST data base, the base flow index (BFI: the proportion of annual runoff totals that are ascribed to more slowly responding hydrological stores) and standard percentage runoff (SRP: the typical percentage of storm precipitation that appears as runoff) can be determined. Values imply greatest groundwater recharge and base flow contributions for alluvial soils (class 7), humus iron podzols (class 5) and deeper subalpine soils (class 17). Peats (class 29), peaty gleys and peaty podzols (HOST class 15), gleys (HOST class 14) and shallow alpine soils (class 22) are the most responsive to storm events with more limited baseflow contributions (Table 1). These responsive soils cover 65%, 94% and 96% of the Feugh, Water of Dye and Brocky catchment respectively. In general, soils are acidic, ranging in pH from 3.5 to 4.0 in top-soils and 4.0–5.0 in the sub-soils (Reid et al., 1981).

Landcover is dominated by heather (*Calluna vulgaris*) moorland used for deer stalking and grouse shooting. These activities are common to much of the Scottish highlands and the moorlands are managed by regular burning to retain the mosaic of habitats required by grouse and deer (Thompson et al., 2001). This long history of burning may have contributed to the erosion of peaty soils (Thompson et al., 2001). The peat is extensively ''hagged'' or degraded in many places which in turn dictates that a high density of ephemeral drainage channels covers the peat, connecting it to the perennial stream channel network. Over substantial areas, both deliberate and accidental burning has resulted in the severe depletion of organic horizons of peaty soils and prone to the development of drying cracks and hydrophobic conditions after dry periods (e.g. Stutter et al., 2006). In such places, infiltration-excess overland flow and macropore flow can be important. The more fertile floodplain soils are occupied by agriculture. This mainly comprises livestock grazing with some arable land. Some of the valley hillslopes are forest-covered. The forestry is a mixture of commercial woodlands and semi-natural forests of Scots Pine (*Pinus sylvestris*) predominate (Table 1).

The climate is cool and wet, with an estimated mean annual precipitation of 1130 mm, mainly derived from prevailing westerly weather systems and falling as rain, though snow does occur during the winter months and in extreme years may account for 10–20% of annual precipitation inputs (Soulsby et al., 1997). At the gauging station at the 233 km^2 catchment outlet, mean annual discharge is

Table 2 Characterisation of hydrological regime for the hydrological year 2003/2004

Catchment	Feugh	Water of Dye	Brocky Burn
km^2	233	42	1.3
Mean flow ($l\ s^{-1}\ km^{-2}$)[a]	24.8 (1985–2003)	30.9 (1957–2003)	40 (1999–2003)
Mean annual precipitation (1961–1990) (mm)[a]	1130	1278	1050
Mean ($l\ s^{-1}\ km^{-2}$)	19.5	25.3	31.0
Median ($l\ s^{-1}\ km^{-2}$)	12.5	13.7	14.6
Max. ($l\ s^{-1}\ km^{-2}$)	396.7	693.7	922.6
Min. ($l\ s^{-1}\ km^{-2}$)	2.2	2.6	1.2
Q_{95} ($l\ s^{-1}\ km^{-2}$)	2.5	2.9	1.5
Q_5 ($l\ s^{-1}\ km^{-2}$)	55.8	78.4	119.1
Coefficient of variation (–)	1.4	1.9	2.0

[a] Long term data from UK National Water Archive (www.ceh.ac.uk/data/nrfa).

$24.8\ l\ s^{-1}\ km^{-2}$ (1985–2003, Table 2). Previous work – based on weekly samples – used chemical hydrograph separation to show that groundwater contributed 19–30% to annual runoff in Brocky Burn, 34–40% at Charr and 51–58% at Heugh Head in the 2001–2002 hydrological year (Soulsby et al., 2004). This was comparable to earlier estimations for 1996–1997 (30%, 35–41% and 51–57% respectively) by Soulsby et al. (2003).

Methodology

Discharge was calculated from stage records in rated river sections, continuously monitored by the Scottish Environment Protection Agency (SEPA), both at the catchment outlet at 233 km^2 at Heugh Head and at Charr, the gauging station of the sub-catchment Water of Dye (42 km^2). Further flow records were also collected for 1.3 km^2 from Brocky Burn, where a flume and pressure transducer was established by the University of Aberdeen (Dawson, 1999). All discharge was recorded at 15 min resolution. Rainfall data were also recorded at 15 min resolution by SEPA at Charr, located at ca. 300 m, reasonably close to the mean catchment altitude of 328 m.

Catchment characteristics were analysed by applying the GIS ARCVIEW. This included an Ordnance Survey Profile dataset, which is a 1:10,000 scale Digital Terrain Model (DTM). This dataset comprises 25 m × 25 m grid cells each of which have an elevation value in metres. Additionally, digital coverage of soil types, underlying geology and land use was derived from previous work (Dawson, 1999; Rodgers et al., 2005). The GIS provided a means of assessing how the hydrological and hydrochemical functioning varied in each of the sub-catchments in relation to readily quantifiable catchment characteristics.

Using Troll 9000XPE data loggers (In-Situ, Inc.) deployed at both sites, pH was continuously logged (at 15 min resolution). The pH sensor was a gel-filled probe supplied by In-Situ specially designed for use with this field equipment. The manufacturer's specification of probe performance is a measurement resolution of 0.01 pH units, with an accuracy of ±0.09 pH units, over the pH range 0–12. In the field, equipment was recalibrated at approximately monthly intervals. A two buffer calibration (4 and 7) was employed. Prior to pH recalibration, the pH 4 buffer was measured to assess if there had been probe drift. The measured response was always $\leqslant 0.2$ pH units of the laboratory determined value, a precision we consider satisfactory for field measurements. Thus, no correction was applied to the data for drift between calibration intervals and we estimate precision of field measurement to be better than ±0.2 pH units. The accuracy of the pH of the calibration buffers had been assessed in the laboratory prior to the field visit. Hence, we consider measurements to be accurate. Similarly specific conductivity was logged at 15 min intervals.

Gran alkalinity closely approximates the chemically conservative parameter of acid neutralising capacity (ANC) in waters with low aluminium concentrations (such as those in the Feugh). It can be used as a conservative tracer to differentiate between acidic soil-waters and more alkaline groundwaters considering their mixing (Robson and Neal, 1990). Using Gran alkalinity as a measure of ANC has proven utility in chemically-based hydrograph separations catchments in the UK uplands (Wade et al., 1999; Neal, 2001; Soulsby et al., 2005) and, previous work albeit from temporally poorer data, has allowed us to develop an understanding of how the Feugh catchment functions (Soulsby et al., 2003a, 2004). Gran alkalinity is an easily measured determinant by sequential acidimetric titration to end-point pHs of 4.5, 4.0 and 3.0, but as titration is required, thus unsuitable for in-situ measurement. However, applying the method of Neal et al. (1990) the empirical relationship between H^+ activity and Gran alkalinity can be used to convert continuous pH records (Hodgson and Evans, 1997). This used the relationship between H+ and Gran alkalinity in spot samples spanning the range of flows from $>Q_1$ to $<Q_{99}$ (Rodgers, 2004). The resulting equations used a least squares fit for a constrained minimisation method for two exponential curves for each site and produced R^2 values of 0.89 and 0.93 for Brocky and Charr respectively (Fig. 4).

Data capture during the year was good: 93% at Charr and 86% at Brocky Burn. Data from the latter site were lost, with the record incomplete due to technical problems over a few weeks in December 2003 and January 2004, May 2005 and maintenance of both loggers mid July 2004. Financial constraints limited deployment of a third water chemistry logger at 233 km^2. Thus, the strong relationship between Gran alkalinity and flow in weekly samples (Soulsby et al., 2003a, 2004) was used to estimate Gran alkalinity for the purpose of providing a large scale comparison with the Brocky and Charr sites.

The focus of the Gran alkalinity-based hydrograph separation was to distinguish the relative importance of responsive hydrological pathways sourced by the acidic, organic surface horizons of the soils and the role of deeper groundwater sources, which sustain baseflows. The contributions of two end members – soil water and groundwater – were derived by compositional analyses (Brewer et al., 2005). For all three sites, for each time point, the proportion of the source, the standard deviation and the limits of the 95% credible interval for the proportions were estimated (Soulsby et al., 2003b). Credible intervals are the Bayesian equivalent of confidence intervals, and should be interpreted as meaning that there is a 95% chance of the true proportion lying within the range (Brewer et al., 2005).

Quantifying the uncertainties associated with chemically-based hydrograph separations has recently become a major research theme (e.g. Genereux, 1998; Uhlenbrook and Hoeg, 2003; Joerin et al., 2002; Soulsby et al., 2003b). To give an indication of the uncertainty in the separations, soilwater alkalinity was estimated to lie within a range between -123 and -8.2 μeq l^{-1} following previous studies, which have extensively sampled over 100 soil waters from peaty soil horizons in the Cairngorms and show that it has a low alkalinity in this range (Soulsby and Dunn, 2003; Soulsby et al., 2004). Choosing end members is always problematic. In particular, the catchment-scale groundwater end member is usually impossible to sample. This end member usually represents a range of groundwater sources, some of which may have relatively short residence times and only be connected at high flows compared to groundwater sources which sustain flows in the very driest periods. On the basis of up to 40 baseflow samples, providing an integrated measure of the possible groundwater chemistries influencing stream water, groundwater alkalinity was estimated to range between 216 and 234 μeq l^{-1} (at Heugh Head), 304 and 343 μeq l^{-1} (at Charr) and 156 and 171 μeq l^{-1} (at Brocky Burn). Whilst local heterogeneity in end-member chemistry is well-known (cf. Stutter et al., 2005), our data indicate that this appears to be averaged at larger scales, thus justifying this two component approach. A precipitation end member was not included as the alkalinity of precipitation is usually close to zero and is rapidly depressed after contact with acidic organic surface horizons.

The data for each end member were considered as having Normal (Gaussian) distributions, and thus provide a basis for describing the uncertainty in the stream water data. The stream water compositions can be considered as proportional mixes of end member values. The use of variable soil water and groundwater end members, together with assessment of the measurement error (cf. Genereux, 1998), generates interval estimates of groundwater contributions to stream flow. This provides an indication of the uncertainty associated with the separations, whilst still revealing meaningful differences in catchment responses at larger spatial scales (Soulsby et al., 2006a).

Hydrological characteristics and response

Analyses of the long-term precipitation and flow data for the Feugh sites from the UK National Water Archive (www.ceh.ac.uk/data/nrfa) show that the highest variability in hydrological regime occurs at Brocky Burn (Fig. 3 and Table 2). Average specific discharge are ordered such that Brocky Burn > Charr > Heugh Head. Brocky Burn has the highest specific discharge at high flows and the lowest specific discharge at low flows. Heugh Head has the lowest specific discharge at high flows, but its specific discharge at low flows is slightly lower than that of the Water of Dye at Charr.

These responses are consistent with the catchment characteristics (Table 1): the predominance of hydrologically-responsive peaty soils in the catchments at Brocky Burn and the Water of Dye at Charr (HOST classes 15, 22 and 29) result in a ''flashy'' hydrological regime with high runoff coefficients during events (typically ca. 0.6). Conversely, the limited groundwater storage in the peaty soil-dominated Brocky catchment results in the lower specific discharges at low flows. The presence of alluvium in the valley bottoms of the 42 km^2 Water of Dye catchment (Fig. 1c) allows greater aquifer storage and sustains baseflows. The larger catchment at Heugh Head has greater cover of more freely draining podzolic soils (HOST classes 5 and 17) and a relatively damped hydrological response in comparison, though still reflects the influence of the responsive soils in the catchment headwaters. The slightly lower specific discharges at base flow at Heugh Head relative to Charr initially seem surprising, though the aforementioned alluvium in the valley bottom of the latter and higher mean annual catchment precipitation (Table 2) help explain this anomaly.

The hydrological year 2003–2004 followed an unusually hot and dry summer in 2003, which affected much of north west Europe (e.g. Tetzlaff et al., 2005). In the north east of Scotland precipitation was around 50% of the long-term average between May and September, thus mean flows in the catchment over this particular year were around 20% lower than the long-term average. Discharge increased from mid-October 2003 as the prolonged dry spell ended and distinct hydrological events occurred in November and December (Fig. 5). Thereafter, the winter and early spring were moderately wet. The late spring and early summer of May and June 2004 were characterised by a sustained period of

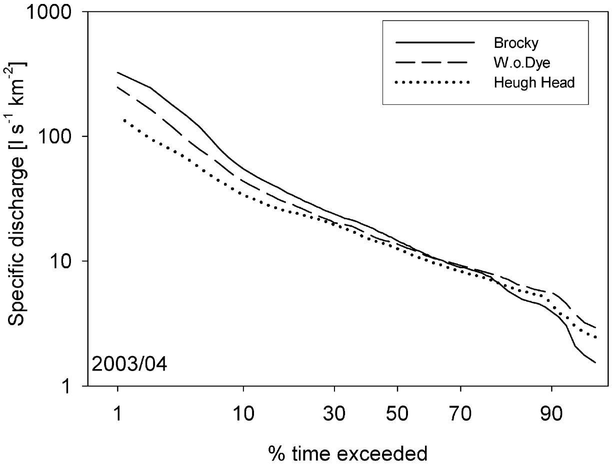

Figure 3 Flow duration curves at all three sites for hydrological year 2003–2004.

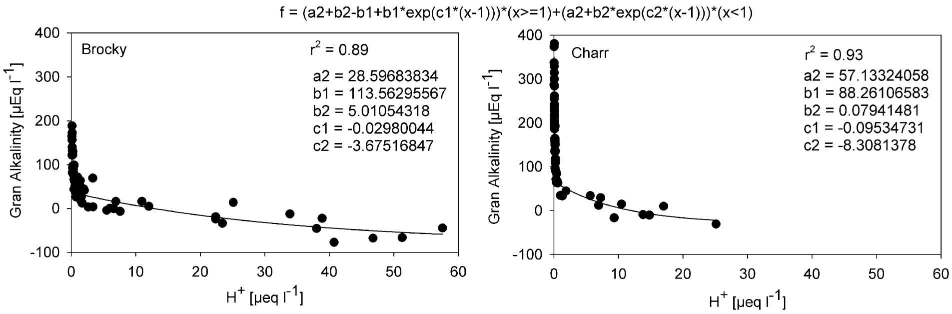

Figure 4 Relationships between H^+ and Gran alkalinity at (a) Brocky and (b) Charr.

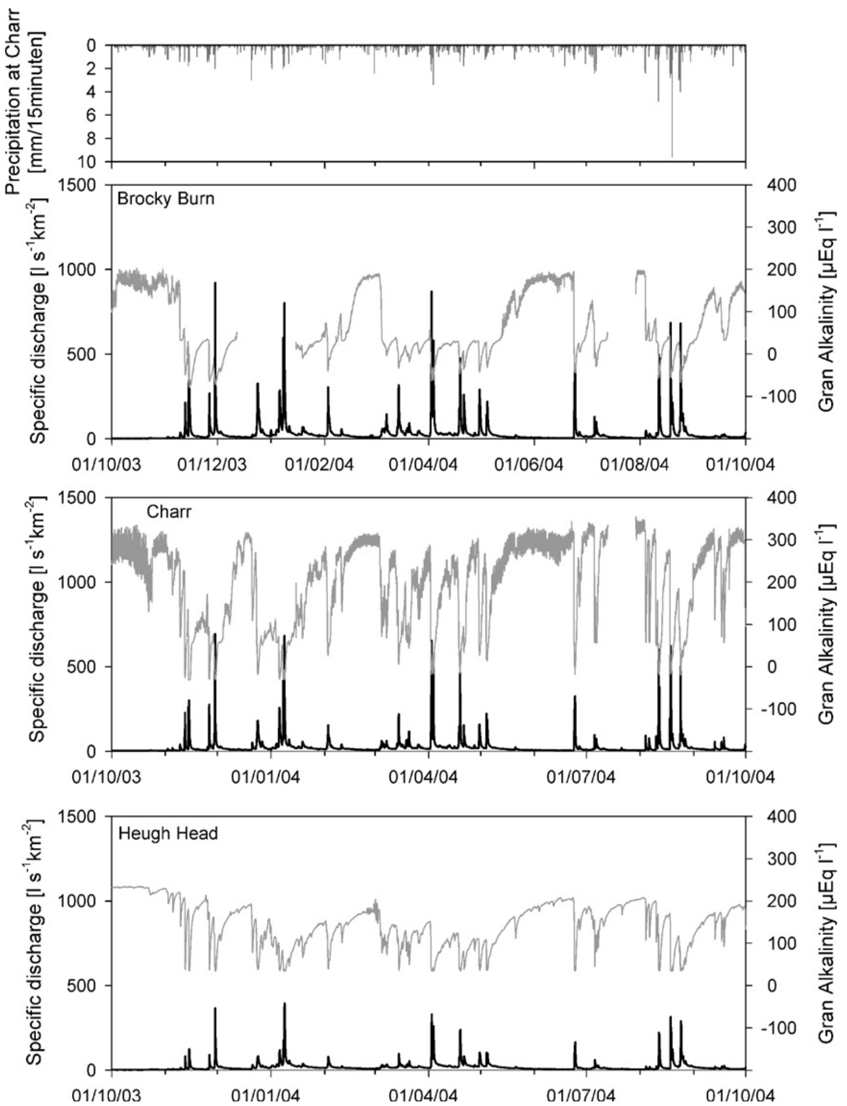

Figure 5 Specific discharge and continuous Gran Alkalinity at (a) Brocky Burn, 1.3 km^2; (b) at Charr, 42 km^2 and (c) at Heugh Head, 233 km^2(c), showing precipitation at station at Charr.

low flows. Re-wetting of the catchment occurred in early July, which preceded the largest rainfall event of the year in Mid-August. The hydrographs show all three sites highly responsive to precipitation (Fig. 5). This is most notable in Brocky where specific discharges for large events are more than double those at Heugh Head and the difference can be even greater for small and moderate events. However, in most cases, flows respond to precipitation within hours at all three sites and the rising limb of the storm hydrograph is very steep. The hydrograph of the Water of Dye catchment — which is topographically steepest — generally responds first followed by Brocky Burn within an hour or two. Channel routing dictates that hydrograph rise at Heugh Head is a few hours later. The early phase of the hydrograph recession is similarly steep at all three sites, with flows approaching baseflows within a few days. In general, given the 233 km^2 catchment area, all sites were affected by individual rainfall events. However, spatially discrete events – such as convectional cells – do occur, for example in mid-September 2004 rainfall influences the Water of Dye more markedly than the other two sites, indicating quite localised rainfall.

Hydrochemical time series

Inspection of the pH-derived continuous Gran alkalinity time series provided spatially-nested and fine temporal resolution insight into runoff sources at Brocky Burn and the Water of Dye site (Fig. 5). This Figure also shows the estimated alkalinities at Heugh Head, which are based on the strong relationship between Gran alkalinity and flow which have been previously established for this site (Soulsby et al., 2003).

Gran alkalinity exhibits a clear relationship with flow at both Brocky and Charr; respectively decreasing to $-70\ \mu eq\ l^{-1}$ and $-30\ \mu eq\ l^{-1}$ in events and increasing to ca. 225 $\mu eq\ l^{-1}$ and ca. 350 $\mu eq\ l^{-1}$ at low flows (Fig. 5). This reflects the common origins of storm runoff as overland flow and shallow subsurface storm flow from the acidic surface horizons of peats and peaty soils (Wade et al., 1999; Soulsby et al., 2003a, 2004). Low flow Gran alkalinity is more divergent between the subcatchments reflecting the strong influence of geology and geochemistry, in particular the presence of more base-rich metamorphic rock in the Water of Dye sub-catchment which buffers both baseflows, and – to a lesser extent – storm flows (Smart et al., 2001; Soulsby et al., 2004).

Despite these general patterns, the continuous time series provide detailed insight into the variations in hydrochemistry with flow. For example, both sites exhibited diurnal variations in derived Gran alkalinity during the low flows at the start of the study year; evident in the ''noisy'' nature of the low flow alkalinity trace (Fig. 5). Similar diurnal variation has been reported from this site (Dawson, 1999) and elsewhere (e.g. Jarvie et al., 2001); alkalinity falls during the night time and increases during the day. In the derived data, this reflects diurnal changes in pH which reflects the relative influences of photosynthesis and respiration on increasing the availability of free CO_2 during dark hours and in turn, as carbonic acid is generated, decreasing the pH of the stream. Dawson (1999) has showed by direct measurements that diurnal variation in Gran alkalinity does occur at these sites, though the timing does not simply match that of pH as alkalinity is conserved as pCO_2 changes.

Both the derived data and Dawson (1999) direct measurements showed that the diurnal response is more marked in the Water of Dye at 42 km^2 where variations in Gran alkalinity can exceed 60 $\mu eq\ l^{-1}$, though even at Brocky where the range can still be 30 $\mu eq\ l^{-1}$. This may reflect the more base-rich water and wider, less-shaded channel in the Dye. The derived data – being dependent on pH – must be viewed cautiously, and taken only as a crude indicator of the likely range of alkalinity variability. In reality the situation will be more complex as alkalinity may be influenced by loss of carbon as CO_2 shifting the carbonate equilibria (Cresser and Edwards, 1987), some biotic uptake of HCO_3- and diurnal variability in flow (see below). This biogeochemical interpretation of in-stream processing is the focus of another manuscript (Waldron et al., in review).

As the first marked hydrological events occur in November 2003, low alkalinities, characteristic of high flow are observed. Due to the higher antecedent alkalinity levels at baseflows, the subsequent depression during events is generally most marked at Charr. However, the alkalinity recovery on the hydrograph recession is also most rapid at Charr, particularly notable in March and April 2004 events. The diurnal variation in pH-derived Gran alkalinity is evident, albeit less pronounced, during winter low flows (for example in February 2004) most obviously in the Water of Dye at Charr, though also at Brocky Burn at 1.3 km^2. For much of the winter hydrological variability disrupts these biogeochemical patterns or masks their influence. However, in late May and early June 2004, low flows predominate again and high alkalinities with diurnal variations are evident at both sites. Subsequently, this summer was much wetter than the preceding one, and storm events in late June, early July and August resulted in marked depressions in Gran alkalinities, before drier conditions returned in September.

Clearly, as Kirchner et al. (2004) note, such fine resolution data reveal patterns and the effects of processes that are simply not available from the more typical weekly or fortnightly sampling periods used in many hydrochemical studies. To illustrate the scale of information loss by less frequent sampling, compare box plots (Fig. 6) which, using 100 random repeat samples from the continuous time series (cf. Malcolm et al., 2005), illustrate the information available from monthly, weekly, or daily sampling strategies at Brocky and Charr. Monthly and weekly samples portray general seasonal patterns of alkalinity, but only crudely. Daily sampling provides greater insight into event-based changes, but no insight into diurnal changes.

Resource limitations precluded deployment of continuous water quality monitors at Heugh Head, however historic data showed that the site has a very good relationship between Gran alkalinity and flow, and the continuous flow record was used to derive a continuous Gran alkalinity time series which is shown in Fig. 5, to provide some context at the larger scale. Although it is obvious that this lacks the detail of the time series for Brocky and Charr, it shows a generally smoother hydrological and hydrochemical response at the larger catchment scale. Previous work has shown that this probably reflects the averaging of different inputs from the Water of Dye tributary with those from the other tributaries of the Water of Aven and the Upper Feugh (Rodgers et al., 2005).

As an additional tracer, the data loggers used provided a continuous electrical conductivity time series (Fig. 7). Although not a conservative tracer per se, electrical conductivity can provide insights into the nature of the catchment hydrological response (Robson et al., 1995). Unlike pH or Gran alkalinity, the relationship between conductivity and discharge was usually distinctly different for Brocky and Charr: at Brocky, conductivity generally increased with discharge, whilst at Charr, it decreased (Fig. 7a and b). This is consistent with the geological differences between the two catchments (Soulsby et al., 2004). Baseflow conductivity at Brocky is 40–50 $\mu S\ cm^{-1}$, indicating quite dilute waters; at

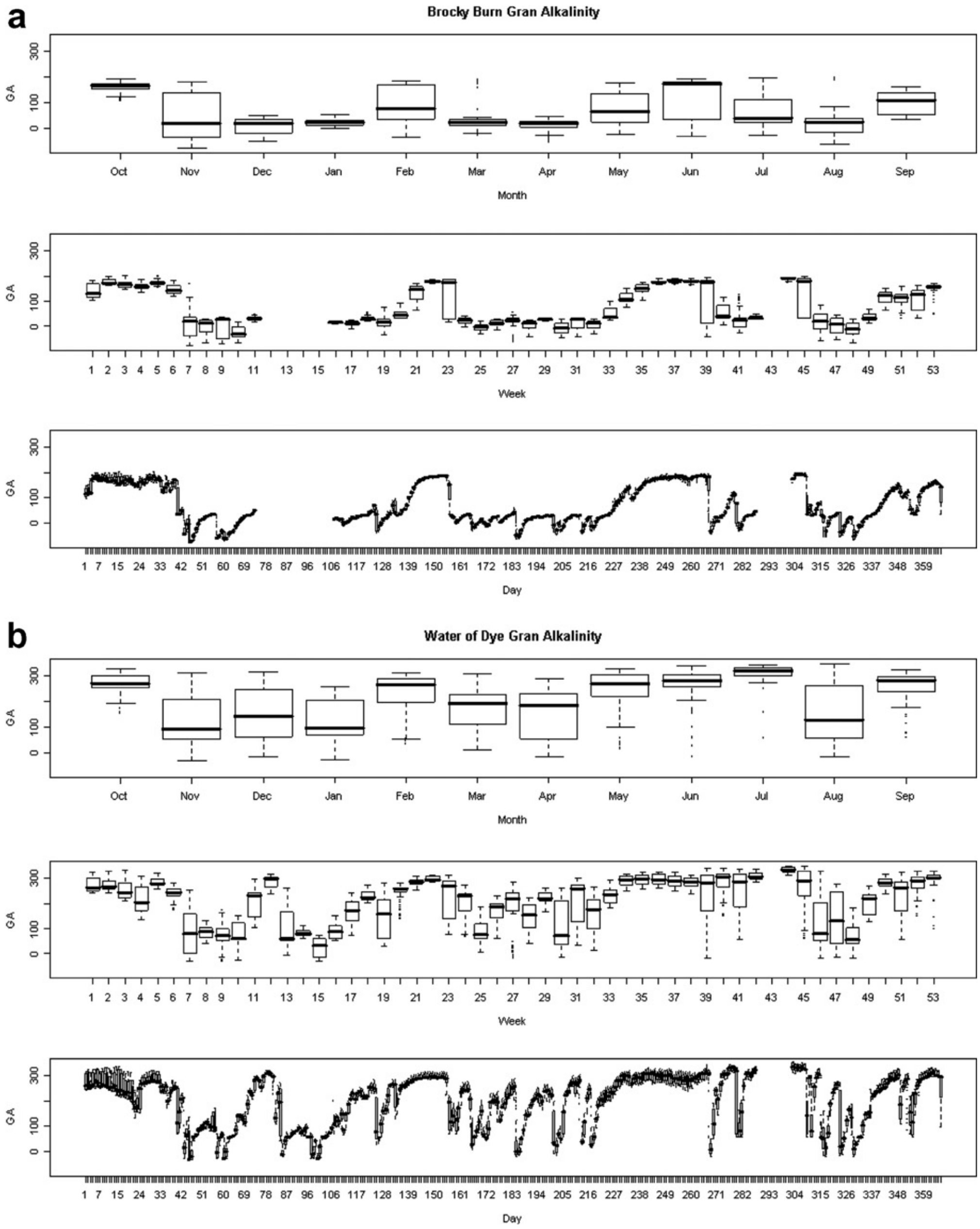

Figure 6 Effect of sampling resolution on variability in Gran Alkalinity: (a) Brocky Burn and (b) Water of Dye.

Charr it is 60–70 μS cm^{-1}, indicating a greater solute concentration and reflecting greater ionic input from metamorphic rocks in the upper Dye compared with the granite underlying Brocky. H^+ ions have a disproportionate effect on electrical conductance. Thus, at higher flows, acidic soil-derived waters have a pronounced effect on conductivity: in the low ionic strength Brocky catchment waters conductivity increases, but the higher ionic strength baseflow in the Water of Dye is reduced (Fig. 7b and d). The main exceptions to this generalised response occur after prolonged dry spells; for example in the first events after the summer 2003 conductivities in Brocky double (Fig. 7a), presumably as accumulated solutes are flushed from the catchment soils, and in response the conductivity did not fall. A further exception occurs in Brocky in June 2004 when, after a two-month long dry spell with low flows and increasing base flow conductivities, an event flow increase depresses conductivity, returning to pre-dry spell composition. The conductivity time series also shows the diurnal variations in stream chemistry under low flow conditions, which again likely reflect the changing ionic strength of the waters due to changing dominance of photosynthesis and respiration affecting pCO_2 levels and pH.

High flow and low flow variability

Focusing on individual storm events to explore the hydrochemical response in more detail reveals relatively simple and consistent patterns. A typical event response for Brocky Burn and the Water of Dye is shown in Fig. 8. Baseflow con-

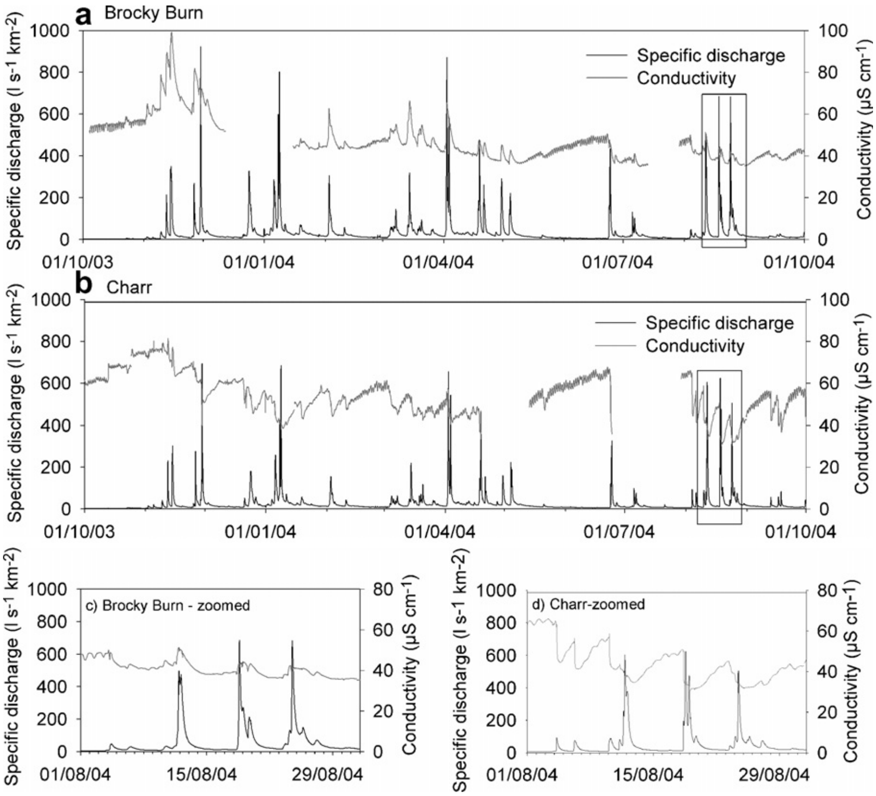

Figure 7 Continuous conductivity time series at (a) Brocky Burn and (b) at Charr (Water of Dye).

ditions are dominated by circum-neutral groundwater (pH c. 6 in Brocky and pH c.7 at Charr). At both sites, pH decreases rapidly as flows increase, whilst electrical conductivity falls at Charr but increases at Brocky. As with other events examined, Gran alkalinity plotted against discharge shows very limited hysteresis, which reflects a constant storm event hydrochemistry dominated by acidic soil water of relatively constant composition with limited divergence in the

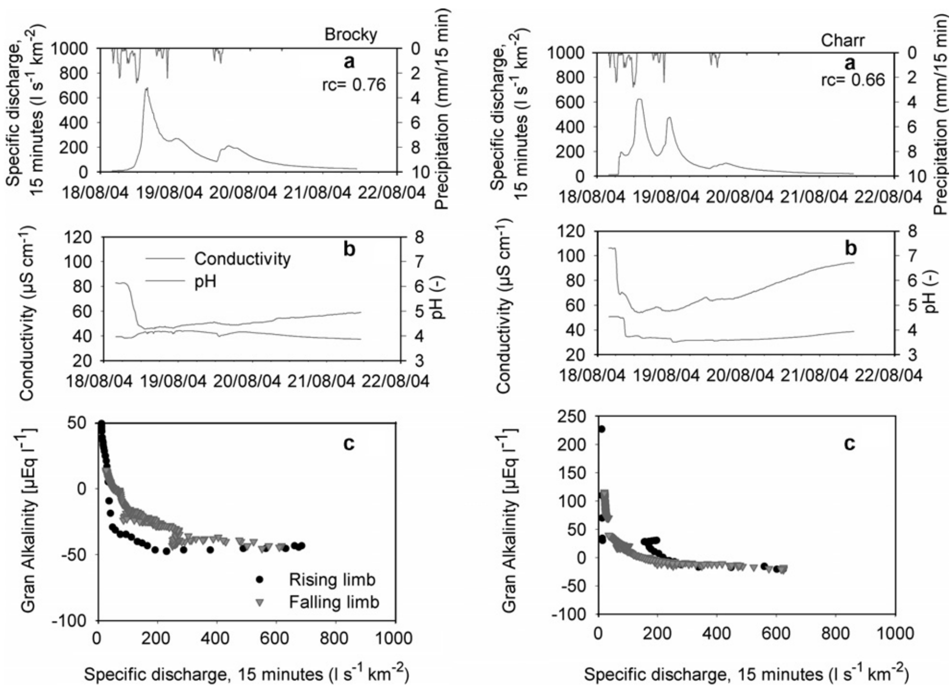

Figure 8 Storm flow dynamics for an exemplary event showing (a) hydrographs and runoff coefficients; (b) conductivity, pH and (c) Gran alkalinity distribution at Brocky Burn and Charr (Water of Dye).

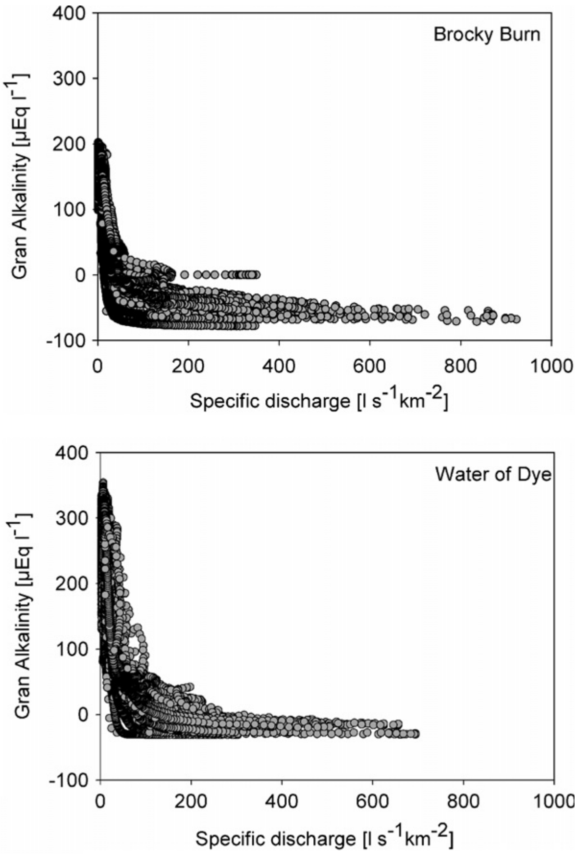

Figure 9 Flow concentration plot of Gran Alkalinity at Brocky Burn and at Charr (Water of Dye).

response during recession. The consistency of such hysteresis is apparent from Fig. 9 where the continuous Gran alkalinity data is plotted against flow for the whole monitoring period. At both sites Gran alkalinity exhibits a threshold-like response; up to specific discharges of around 50—100 l s^{-1} km^{2}, Gran alkalinity decreases linearly with flow, above this concentrations are relatively constantly <0 μeq l^{-1}. Although antecedent conditions, storm event rainfall characteristics and atmospheric deposition result in some variability in the storm response, the lack of marked hysteresis is consistent with a threshold response to dominance runoff sources in acidic peaty soils being activated.

Figs. 5 and 7 indicated diurnal variability in stream hydrochemistry particularly at low flows. Closer inspection of such periods showed that in addition to any diurnal cycles in stream biogeochemistry, diurnal variability in flow was also evident (Fig. 10). This was most marked at Brocky and most damped at Heugh Head. Flows were lowest during the day and increased during the night. Likewise, conductivity tended to be lowest during the day and highest over night, reflecting the greater influence of H$^+$ ions on electrical conductance. The causes of diurnal variations in flow are unclear, though given the restriction of this response to hot, dry periods, it may well involve increased capillary tensions in riparian groundwater arising from high rates of potential evapotranspiration restricting seepage during the day when transpiration rates are highest (Bond et al., 2002). Alternatively, it may reflect the influence of direct evaporative losses from the stream network and riparian vegetation during the day. In extreme cases such as the summer of 2003, such daily losses could reduce stream flows by some 20—30% at Brocky and Charr. It may be the case that these diurnal hydrological changes — along with biogeochemical processes — partly explain the changes in hydrochemical parameters such as alkalinity. Clearly the data indicate that hydrological and biogeochemical processes are extremely complex — even at low flows when the hydrological system is usually assumed to be fairly stable — and warrant more detailed investigation.

Estimation of groundwater contributions and mean residence times

Using the high resolution tracer profile, and accommodating appropriate uncertainty analysis (cf. Brewer et al., 2005), a

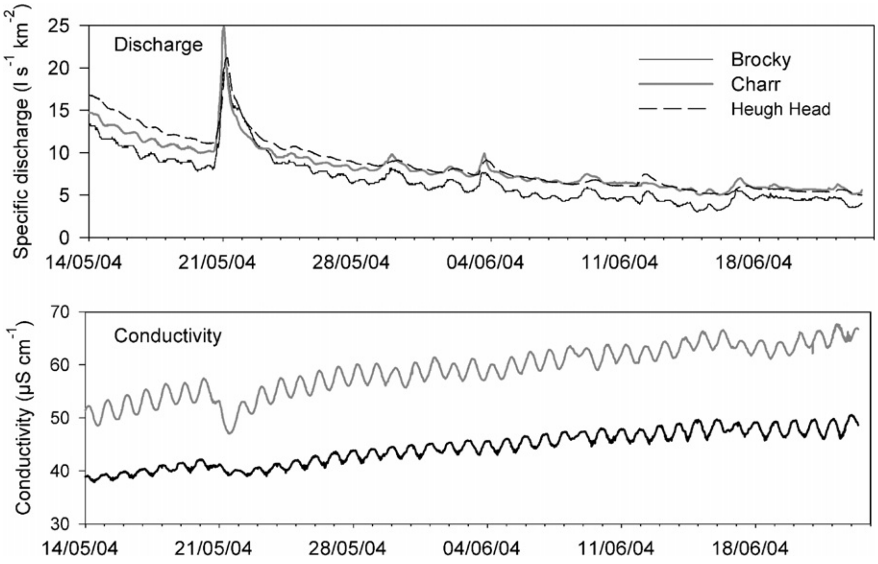

Figure 10 Baseflow diurnal variability: (a) specific discharge and (b) conductivity (no conductivity measurements at Heugh Head).

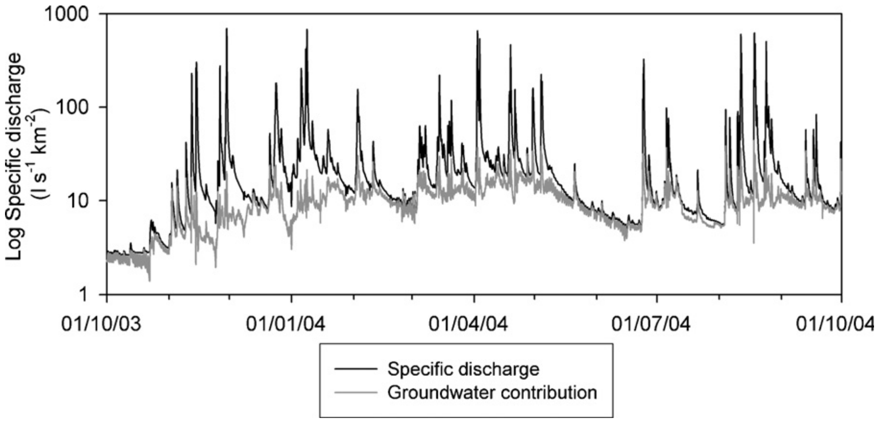

Figure 11 Tracer-based hydrograph separation at Charr.

two-component mixing analysis was carried out to estimate the relative importance of soilwater and groundwater components to stream discharge for the whole record. Fig. 11 shows the resulting chemically-based separation of groundwater from the stream hydrograph in Water of Dye. This analysis indicated that groundwater contributions accounted for 61–72% (95% credible intervals) of the stream flow during the hydrological year 2003–2004 (Table 3). Groundwater contributions at Heugh Head and Brocky Burn are 59–81% and 42–62% respectively (Table 3). This is similar to, but greater than, contributions previously estimated (Soulsby et al., 2003, 2004), presumably reflecting the drier conditions decreasing the contribution of hydrological sources of storm flow. However, the uncertainty analysis which was adopted here is more robust, and thus, suggests that previously the groundwater contribution were probably slightly under-estimated. Percentage of near surface runoff increases during storm events when soil water contributions can exceed 95% of flows in Brocky Burn.

In addition to the continuous data, the abundance of ^{18}O in precipitation and streamwater – at all three sites – in the Feugh catchment has been monitored, albeit on a weekly basis in the 2001–2002 hydrological year, which allowed mean residence times of water to be calculated for the three catchments (Rodgers et al., 2005). Comparison of δ^{18}O of the three sites relative to precipitation indicates that δ^{18}O damping of streamwater composition was Heugh Head > Water of Dye > Brocky Burn, from which respective mean residence times were estimated (Rodgers et al., 2005) to be 205, 195 and 90 days, respectively (Table 3). Although collected from a much wetter year, these spatial differences are likely to be constant over longer timescales (cf. Soulsby et al., 2000) and are consistent with the increasing importance of groundwater in the larger scale catchments that we have estimated by hydrograph separations.

Concluding comments

This paper aimed to examine how high frequency tracer data can enhance understanding of the hydrological and hydrochemical functioning – as advocated by Kirchner et al. (2004) – of nested catchments in the Feugh watershed. In so doing it was anticipated that this study would expand upon earlier tracer studies within the catchment (Soulsby et al., 2003, 2004; Rodgers et al., 2005) and contribute to the development of transferable approaches to tracer-based conceptualisation of streamflow generation processes at larger scales. Such process-based conceptualisation is needed for assessing and modelling the implications of environmental change on catchment hydrology and water resources (Wade et al., 2001).

The continuous tracer data provided detailed insight of the scaled hydrological and hydrochemical response of these nested catchments under high flow and low flow conditions. In conceptualising the dominant runoff sources, the continuous tracer data largely confirmed the insights gleaned from coarser sampling. However, as shown in Figs.

Table 3 Estimated percentage soil water and groundwater contributions in the Feugh and associated sub-catchments calculated from chemical hydrograph separations and mean residence times

Catchment	Feugh	Water of Dye	Brocky Burn
km^2	233	42	1.3
Mean groundwater contribution (%)	70	67	52
GW-contribution – 95% credible interval, lower	59	61	42
GW-contribution – 95% credible interval, upper	81	72	62
Mean residence time (days)[a]	205	195	90
±95% Confidence interval to mean residence time[a]	129	123	51

[a] From Rodgers et al. (2005).

8 and 9, the threshold behaviour of runoff processes in larger storm events became clearer, and the lack of strong hysteresis revealed dominance of hydrochemically similar storm runoff sources in acidic, peaty soils. The importance of antecedent conditions and event characteristics in determining the specific features of the hydrochemical response to individual events could also be identified, particularly clearly from conductivity profiling. The increasing groundwater contribution to flows with increasing catchment scale is consistent with the mean residence time estimates previously derived from isotope data and the catchment characteristics as the proportion cover of freely draining soils increases (Rodgers et al., 2005). Recent work in other Scottish catchments has shown that any scale-dependency in hydrological behaviour reflects catchment characteristics – particularly soil hydrology – rather than scale per se (Soulsby et al., 2006b).

Diurnal variation in low flows observed during hot, dry periods may be a more widespread feature of Scottish peat-covered catchments (Soulsby, unpublished data) and further research to define mechanistic causes would be useful for further refining catchment understanding, particularly as drier summers are predicted from climate change scenarios (Werritty, 2002). The continuous data also revealed that in-stream biogeochemical processes affect stream hydrochemistry at low flows, and this is prevalent at different spatial scales (e.g. Waldron et al., in review). The potential diurnal variation in derived-Gran alkalinity observed at both sites during summer dry periods was expected from pH variations (e.g. Jarvie et al., 2001), but perhaps it is clear that pH variations can also occur during winter periods when flows were stable. Thus, stream biogeochemical process can influence stream hydrochemistry throughout the year. It seems that only higher event flows reduce – or mask – the influence of these processes.

The availability of continuous water quality data for the Feugh greatly enriches our understanding of catchment hydrological and hydrochemical behaviour. Such tracer data also represents a resource – and challenge – to hydrological modellers to incorporate this, in addition to flow or other physical parameters, as an objective function in model evaluation (e.g. Dunn et al., 2003; Soulsby and Dunn, 2003). Characteristic flow-related responses are important, but high resolution profiles such as those which were presented here also reveal subtlety that may need to be incorporated into a wider range of water quality models pertinent to the influence of environmental change in upland catchments (Peterson et al., 2005).

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