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Inferring groundwater influences on surface water in montane catchments from hydrochemical surveys of springs and streamwaters

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Summary Streamwaters and emergent groundwaters in springs and seeps were sampled over the 2003–2004 hydrological year in a geologically complex 31 km^2 catchment. Samples were analysed for Gran alkalinity and chloride; tracers that would respectively indicate the provenance and residence times of water. Streamwaters were sampled at the catchment outfall and in nine sub-catchments. Streamwater Gran alkalinity showed predictable fluctuations with flow, with high flows and baseflows exhibiting low and high alkalinity respectively. During storm flow conditions the nine monitoring points exhibited similar levels (0–50 μeq l^{-1}), whilst under baseflows alkalinity was highly variable (300–1000 μeq l^{-1}), depending upon catchment geology. Comprehensive spatial surveys of springs and seeps in 6 of the sub-catchments during a typical summer low flow period revealed marked differences in groundwater chemistry. This broadly related to sub-catchment geology and geochemistry, but local variability implied marked differences in groundwater flow paths, residence times and geochemical reactions. Chloride data indicated a high degree of synchronicity between concentrations in precipitation and streamwaters. In contrast, concentrations in groundwaters were more consistent. This implies that Cl concentrations in the stream depend upon the relative contribution of groundwaters and soil waters where Cl concentrations are respectively more stable and more dynamic. In general, at the catchment scale, mean water residence times appear to be relatively short which appears to relate to the low permeability of soils and bedrock.

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Introduction

Despite longstanding assumptions that groundwater had a negligible role in upland catchments, recent studies have demonstrated its major influence on the hydrology and hydrochemistry of streams (McDonnell, 2003). These have shown that fracture systems in hard rocks and more permeable drifts can comprise small, but significant aquifers (Neal et al., 1997; Vitvar and Balderer, 1998; Soulsby et al., 1998; Shand et al., 1999; Uhlenbrook et al., 2002; Rodgers et al., 2004a; Haria and Shand, 2004). Furthermore, the ecological implications of groundwater discharge into upland watercourses are increasingly recognised (Findlay, 1995; Brunke and Gonser, 1997); perhaps most notably the issue of low oxygen levels in the hyporheic zone of salmonid streams (Sowden and Power, 1985; Malcolm et al., 2003, 2004, 2005). Although investigations into upland groundwater–surface water interactions are relatively scarce and focused in few catchments, the spatial and temporal variability in groundwater hydrology and chemistry has been acknowledged (e.g. Kirchner et al., 1993); even in small catchments that are relatively uniform in a geological sense (Hill and Neal, 1997; Soulsby et al., 1999; Shand et al., 2006). The spatial and temporal variability of groundwater influences on surface waters in larger scale (>10 km^2) catchments that are geologically complex are poorly understood: in addition, the interactions between flow patterns in soils, drift and bedrock are not well-defined (Smart et al., 2001; Soulsby et al., 2005). Remoteness, accessibility and costs dictate that drilling programmes in such catchments are very rare. This may be further constrained by conservation designations which may preclude destructive environmental monitoring (e.g. drilling and borehole installation). These facts, together with the complex, heterogeneous nature of groundwater movement in upland environments, means that non-invasive approaches – such as direct sampling of springs and seeps – may help gain qualitative insights into groundwater–surface water (GW–SW) interactions in upland streams (Rodgers et al., 2004a).

Geochemical and isotopic tracers have provided some of the most important insights into catchment hydrological processes over the past two decades. These range from the geographical sourcing of waters, to assessing dynamic source contributions to stream flow and age dating of groundwaters (Kendall and McDonnell, 1998; Uhlenbrook et al., 2002; Vitvar et al., 2002; Soulsby et al., 2004; Rodgers et al., 2005). Sampling springs and seeps; locations where sub-surface water sources are emerging above ground level, often close to streams, offers the opportunity to use natural tracers to assess water sources in geologically complex catchments and help make inferences about the nature of GW–SW interactions (Edmunds and Savage, 1991; Soulsby et al., 1999; Manga and Kirchner, 2004). Such understanding is needed to help protect water resources and the ecological status of rivers and wetlands as required by environmental legislation such as the EU Water Framework Directive.

The Girnock Burn is a Scottish experimental catchment, established to monitor Atlantic salmon (*Salmo salar*) populations in the mid-1960s. Recently, process-based investigations have examined the influence of groundwater on the chemistry of the hyporheic zone and the survival of salmon embryos (Malcolm et al., 2002, 2003; Youngson et al., 2004). This led to a re-assessment of the role of groundwater in the hydrological functioning of the catchment (Soulsby et al., 2005). The Girnock has a very complex geology, which results in marked spatial and temporal variability in GW–SW interactions and stream chemistry (Malcolm et al., 2005, 2006). The aim of this paper is to present the results of an intensive sampling programme of streamwaters and groundwaters (primarily from springs and seepages), in order to gain a better insight into the spatial and temporal variability of GW–SW interactions at the catchment scale. The main objectives of the paper are to: (1) characterise the behaviour of certain tracers – Gran alkalinity and chloride – in the surface waters of the Girnock and its major sub-catchments over a hydrological year to assess the geographic sources of water generating streamflows and their residence time; (2) establish the spatial and temporal variability of the tracer characteristics of groundwater discharges in major sub-catchments; and (3) use this data to inform a qualitative conceptual model of catchment scale GW–SW interactions and their influence on streamwater chemistry and hydrology. Achieving these objectives will help provide a basis for more detailed field and modelling investigations for testing hypotheses about the role of groundwater in this particular catchment.

Study area

Topography and land use

The Girnock Burn drains a catchment of ca. 31 km^2 whose characteristics are summarised in Table 1. Briefly, the altitude ranges from 230 to 862 m (Fig. 1a), though most of the catchment lies below 500 m. The stream drains a *Calluna*-dominated moorland environment that has some small areas of forestry on the lower hillslopes (Fig. 1b). The main economic activity is the management of moorlands for shooting red deer (*Cervas elaphus*) and grouse (*Lagopus lagopus*) – activities common to much of the Scottish highlands. This involves the burning of moorland vegetation to create a mosaic of habitats that can be used by grouse and red deer at different life stages (Thompson et al., 2001). The catchment forms a large basin with a wide and gently sloping valley bottom, reflected by a modest mean stream gradient of 28.9 m km^{-1}. The highest elevations are to be found at the south western edge of the catchment, and the basin interfluves to the east and west are generally at above 500 m.

Geology

The geology of the Girnock is complex (Soulsby et al., 2005). Granite and granite-like (granodiorite and diorite) rocks associated with a regional batholithic intrusion dominate the south western sector of the catchment and a smaller area in the north (Fig. 1c). The granitic rocks are generally base poor, though the CaO and MgO content increases in the granodiorite and diorite as the SiO_2 content falls (Table 2). The granites are fringed by a complex suite of meta-sediments, ranging from base poor quartzite and psammite, to more calcareous strata, including bands of metamorphosed

Table 1 Characteristics of the Girnock and associated sub-catchments

	IB	Bov	S/E B	SB	EB	HB	Ca	BB	L
Area (km^2)	9.07	1.81	12.35	4.52	3.16	20.40	1.07	3.44	31.05
Topography									
Mean elevation (m)	469	397	445	415	420	432	396	354	405
Min elevation (m)	350	329	321	320	321	311	304	248	233
Max elevation (m)	852	500	852	552	593	852	517	536	852
Mean slope [deg]	8.7	6.6	7.8	7.4	11	8.2	11.7	12.3	9.4
Max slope [deg]	28	14	28	24.6	27.9	28	24.2	35.8	46
Drainage density (km^1 km^2)	1.16	1.42	1.23	1.12	0.96	1.17	1.36	1.01	1.10
Soils [%]									
HOST 5	0	0	0	0	0	0	0	0	2
HOST 15	86	94	88	84	38	78	11	20	60
HOST 17	7	0	4	1	49	11	75	34	24
HOST 22	0	6	1	0	14	3	14	23	5
HOST 27	7	0	5	0	0	3	0	18	4
HOST 29	0	0	2	15	0	5	0	6	4
Geology [%]									
Granite	86.0	67.3	80.7	27.3	0.0	55.0	0.0	45.7	45.6
Granodiorite	14.0	10.7	12.3	2.2	0.0	7.9	0.0	0.0	5.2
Diorite	0.0	0.0	0.0	0.0	0.0	0.0	0.3	5.1	0.9
Amphibolite	0.0	1.1	0.2	23.3	38.8	11.2	15.4	0.9	11.9
Serpentinite	0.0	0.0	0.0	0.0	11.8	1.8	0.0	0.0	1.2
Quartzite/Psam.	0.0	0.0	0.0	5.6	0.0	1.2	0.0	0.0	0.8
Dior./Amphibolite	0.0	0.0	0.0	18.5	0.0	4.1	0.0	0.0	2.7
Quartz./Psam./Pelite	0.0	15.0	3.8	9.9	47.5	12.1	1.4	45.3	16.3
Quartz./Psam./Calc.	0.0	5.9	3.1	13.2	1.9	6.6	82.9	2.9	15.5
Groundwater contribution to annual flow 2002-2003[a]									
% annual runoff	30–41	23–32	29–36	31–39	28–32	29–36	55–59	24–32	27–33

IB – Iron Bridge, Bov – Bovaglie, S/EB – upstream of the South and East Burn, SB – South Burn, EB – East Burn, HB – Hampshires Bridge, Ca – Camlet Burn, BB – Bruntland Burn, L – Littlemill. This includes estimated range of groundwater contributions to annual runoff from chemical hydrograph separations.

[a] Estimated by hydrograph separation (see Tetzlaff et al. (2006) for detail).

limestone and amphibolite. The units containing bands of limestone have much higher CaO contents, comprising 20% of the whole rock chemistry. Elsewhere, the areas of quartzite and psammite can be comprised of 88% SiO_2. Close to the south-eastern tip of the catchment the metamorphic rocks include an outcrop of ultra-basic Mg-rich serpentenite.

Much of the catchment is covered by drift deposits (Soulsby and Boon, 2001). These range from low permeability lodgement till in the valley bottoms, to moranic deposits, fluvio-glacial sands and glacio-lacustrine materials. The Girnock lies perpendicular to the main directions of ice flow during the last glaciation (Moir et al., 2004). Thus the catchment is mainly characterised by depositional landforms.

Soils

Soil distribution in the catchment reflects the interactions between geology, drift cover and topography (Fig. 1d) and is a very good predictor of catchment hydrology in Scotland (Soulsby et al., 2006a). The hydrological characteristics of soils are most effectively mapped using the UK HOST (Hydrology Of Soil Type) system (Boorman et al., 1995; Dunn et al., 2003; Soulsby et al., 2005) which classifies soils according to dominant hydrological processes (Fig. 2). The most extensive soils are peaty gleys which – along with much smaller areas of peaty podzols – form HOST class 15 which covers 60% of the catchment (Table 1). These are found on the low gradient lower hillslopes and interfluves that cover a large proportion of the Girnock. They are mainly derived from the granitic rocks, though some are also derived from meta-sediments. Process studies 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 (Soulsby and Reynolds, 1993). Infiltration excess overland flow may be important where such soils are extensively burnt as part of moorland management programmes as the organic surface horizon can become very thin and hydrophobic.

HOST class 17 is the second most extensive and covers around 24% of the catchment. This class comprises freely draining brown soils, humus iron podzols and deeper sub-alpine soils. These tend to occupy steeper slopes and are derived from a wide range of geologies. Vertical water

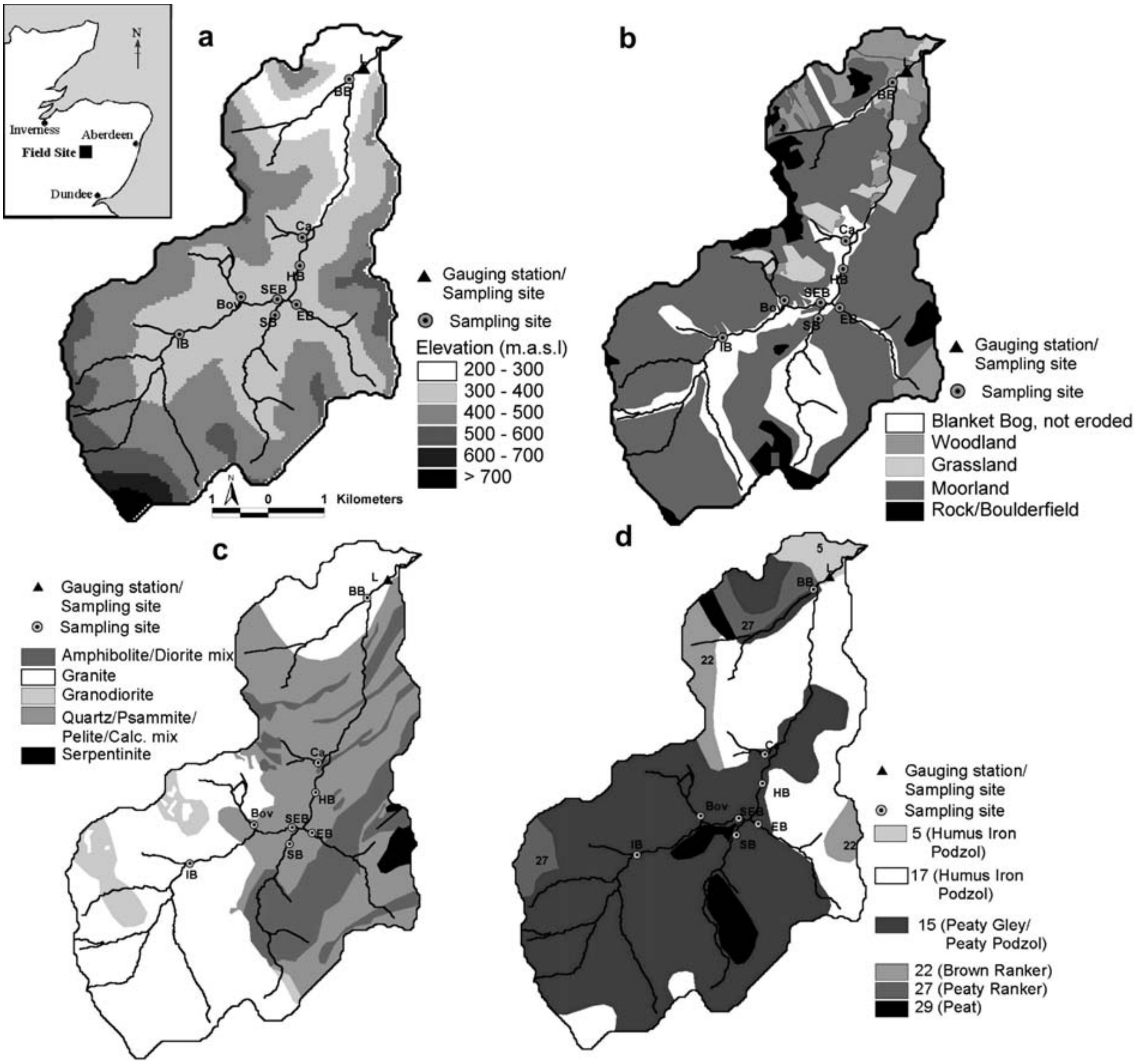

Figure 1 Girnock Burn catchment: (a) topography, showing Littlemill gauging site and sampling locations (Nested mainstem: IB — Iron Bridge, S/EB — upstream of the South and East Burn, HB — Hampshires Bridge, L — Littlemill; tributaries: Bov — Bovaglie, SB — South Burn, EB — East Burn, Ca — Camlet Burn, BB — Bruntland Burn); (b) Landuse; (c) Geology; (d) HOST classes.

Table 2 Hard rock geochemistry [% content] of major geological units in the Girnock catchment (after Smart et al., 2001)

	SiO_2	$CaCO_3$	MgO	Na_2O	K_2O
Lochnagar Granite	73.3	1.12	1.00	3.73	4.22
Granodiorite	66.8	2.81	1.65	4.25	3.12
Diorite	57.1	5.62	4.50	3.33	1.95
Amphibolite, Hornblende, Schist	49.6	9.43	5.53	3.05	0.66
Serpentinite	38.85	1.07	36.07	0.15	0.05
Quartzite, Psammite	82.5	0.73	0.62	1.53	1.87
Granite/Granodiorite	53.3	7.55	5.02	3.19	1.30
Quartz/Psammite, Semipelite/Pelite	77.0	0.96	1.30	1.25	2.25
Quartz/Psammite, Calc. geol.	51.3	20.44	4.00	0.88	1.25

movement facilitates groundwater recharge in such soils and in some instances deeper sub-surface flow at the soil-bedrock interface (Soulsby, 1992; Wheater et al., 1993; Soulsby et al., 1998). In the main river valley near the catchment outlet, freely draining alluvial deposits and soils (HOST 5) are to be found. Blanket peat (HOST class 29) and shallow

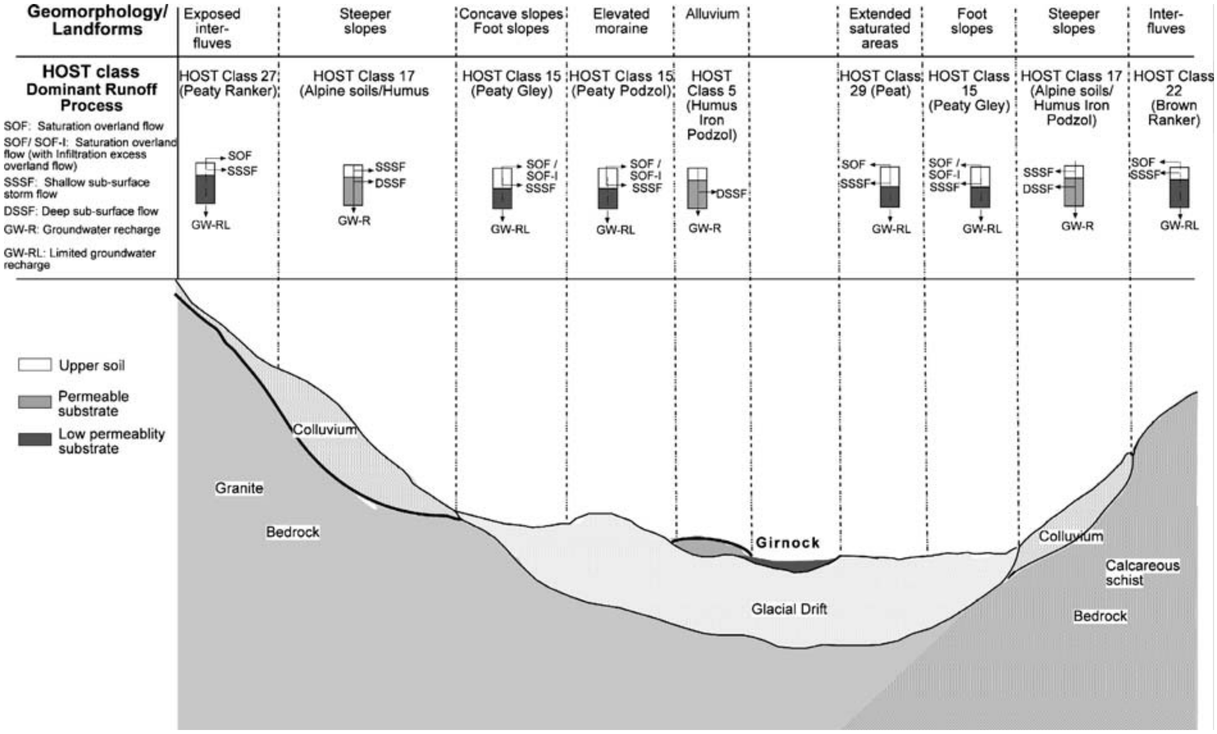

Figure 2 A conceptual model of soil distributions in the Girnock according to the HOST classification.

alpine soils/peaty rankers (HOST class 22 and 27) cover 4% and 9% of the catchment respectively. The alpine soils and rankers are found on the higher altitude slopes in the upper catchment and fractured bedrock outcrops suggest these may be important recharge zones. The deeper peats are mainly found in the two most southerly tributaries, fringing the stream channels and draining the higher altitude headwaters of the catchment. Both soils types generate saturation excess overland flow during storm events (Davies et al., 1993; Holden and Burt, 2003).

Hydrology

Discharge is measured by the Scottish Environment Protection Agency (SEPA) in a natural rated section at Littlemill, a short distance upstream from the confluence with the river Dee (Fig. 1a). Annual precipitation in the catchment is around 1100 mm with annual runoff about 700 mm. Snow — mostly falling between November and February — comprises less than 10% of annual precipitation. Mean annual discharge at Littlemill is 0.52 $m^3 s^{-1}$ (1969—2001). However, instantaneous flows varied between ca. 0.04 $m^3 s^{-1}$ in the summer to over 50 $m^3 s^{-1}$ during floods (Malcolm et al., 2003; Tetzlaff et al., 2005). The gleyed and peaty soils which fringe the stream channel give the Girnock a very responsive hydrological regime compared with many other upland catchments in Scotland (Soulsby et al., 2006a). Event runoff coefficients are generally between 0.3-0.7, though they can be as low as 0.1 in substantial events following long dry periods (Tetzlaff et al., 2006). Chemically-based hydrograph separations on long-term flow data indicate that 25—35% of annual runoff from the catchment is derived from higher alkalinity groundwaters.

Sub-catchments

For monitoring purposes, the Girnock catchment was divided into nine main sub-catchments (Fig. 1a and Table 1). The upper catchment was delimited by Iron Bridge (IB), the highest road crossing on the Girnock. Downstream of this, five main tributaries drain into the Girnock; on the western side of the river, the Bovaglie (Bov), Camlet (Ca) and Bruntland Burn (BB) are found. On the eastern side, the South Burn (SB) and East Burn (EB) are the main tributaries whilst the lower eastern hillslope is a large area drained by a number of first order streams, springs and seeps with poorly defined topographic catchments. The main stem of the Girnock was further subdivided by points above the south burn confluence (S/EB) and at Hampshires Bridge (HB) below the East Burn.

The sub-catchments generally have distinct landscape characteristics. Upstream of Iron Bridge, granite dominates, shallow alpine soils cover steeper slopes, with peats and peaty gleys in the valley bottoms. The Bovaglie Burn mainly drains granite, though calcareous meta-sediments outcrop in the north east. Peaty gleys dominate, though some alpine soils mantle the meta-sediments. The geology of the South Burn sub-catchment is complex; the central valley is underlain by diorite and amphibolite, the west is underlain by granite, and amphibolites and meta-sediments outcrop in the east. Peats and peaty gleys cover the till-dominated valley bottom. The East Burn is distinguished by a serpentinite outcrop in the east edge; meta-sediments fringe this and amphibolite covers the lower area. The serpentinite is covered by shallow sub-alpine soils which grade into humus iron podzols on the lower slopes. Peaty podzols dominate the west. The Camlet sub-catchment is underlain by calcareous meta-sediments. Alpine and podzolic soils dominate the upper slopes with peaty gleys in the valley bottom. The Bruntland Burn is dominated by granite, with meta-sediments in the south-west. Alpine soils mantle to granite whilst the meta-sediments have freely draining humus iron podzols. The Eastern hillslopes of the Girnock are underlain by calcareous meta-sediments. Soils range from freely draining humus iron podzols on the upper slopes to peaty gleys in the valley bottom.

Methodology

To characterise the tracer hydrology of the Girnock, streamwater and precipitation samples were collected from the gauging station and the catchment outfall at routine weekly or twice-weekly intervals between October 2003 and September 2004. In order to collect as comprehensive a set of samples as possible, stream samples were also collected whenever staff were at the site, thus in the spring and summer samples were collected 2–5 times a week. Streamflows were measured in a rated natural section in the lower catchment. In addition, the five major sub-catchments were sampled at approximately fortnightly intervals between January and August 2004 (Fig. 1). This time period was considered to be sufficient to capture the seasonality associated with variability between high flow conditions during the winter and low flow conditions during the summer. At the same time, sampling sites on the main stem of the Girnock were collected at Iron Bridge, upstream of the South Burn confluence and downstream of the East Burn at Hampshires Bridge. Flows at all sampling sites were estimated scaling the Littlemill flow data according to catchment area and altitude as described by Wade et al. (1999).

In addition to routine samples, detailed spatial surveys of hillslope seepages and groundwater springs were also undertaken. In January and February 2004, the springs and seeps draining into the mainstem of the Girnock between Littlemill and Iron Bridge were sampled on days when stream discharge was close to the mean annual flow. In June 2004, following a typical summer dry period for the catchment, springs and seeps in the main sub-catchments of the Bruntland Burn, Camlet Burn, Bovaglie Burn, South Burn and East Burn were sampled. A further set of samples had also been collected from the Bruntland Burn in May 2004 when flows in the stream were still fairly high. Additionally, the Eastern hillslopes draining into the main stem of the Girnock between the East Burn confluence and Littlemill (which had already been sampled in January) were re-sampled in late July. As part of a separate study (see Malcolm et al., 2005), a streambed piezometer close to the HB sample point, was used to sample groundwater from 0.5 m depths between November 2003 and March 2004 for Cl analysis to compare with precipitation and streamwater.

Samples were analysed for pH, conductivity and Gran alkalinity using a Radiometer Combination electrode and a Jenway 3020 pH meter. The main focus was on measuring Gran alkalinity by acidimetric titration as this is easily determined and closely approximates acid neutralising capacity (ANC), which is a conservative tracer that differentiates between acidic soil waters and more alkaline groundwaters and as such has proven utility in the hydrological studies in the UK uplands (Neal, 2001). This was used as a basis for classical 2-component hydrograph separation at each sampling site, using low flow chemistry as a groundwater end member and soil water samples as the soil water end member as described by Tetzlaff et al. (2006). Chloride concentrations were also measured in each sample of precipitation and streamwater by colorimetric analysis using a Foss autoanalyser to provide a measure of how a passive tracer varied as it move through the catchment. Cl input fluxes were estimated by multiplying the concentration and equivalent volume of effective precipitation for each sample. Similarly, Cl output fluxes from the catchment between sampling occassions were estimated from the measured concentration and accumulated flow volume (Neal and Rosier, 1990). Thus, by focusing on Gran alkalinity and Cl, it was anticipated that a preliminary insight could be gained into the geological sources of water, and the nature of residence times.

Catchment characteristics were analysed by applying GIS ARCVIEW (Rodgers et al., 2004b). This included a 10 m DTM, together with the HOST soil classes and underlying geology. The GIS provided a means of analysing how the hydrological and hydrochemical functioning varied with landscape characteristics in each of the sub-catchments (Tetzlaff et al., 2006).

Results and discussion

Catchment hydrology

Fig. 3a shows the flows in the Girnock stream over the 2003–2004 hydrological year. This followed a very dry summer and early autumn in 2003 where rainfall values had been 50% of their long-term average (Tetzlaff et al., 2005). A flow increase is evident from mid-October and distinct hydrological events occurred in November and December; thereafter, the winter and early spring were moderately wet. The early summer was characterised by a sustained period of low flows, that was punctuated only by small events in late June and early July. Re-wetting of the catchment occurred in early August which preceded the largest event of the year in Mid-August. Following two further events, streamflows commenced a late summer recession.

Catchment stream hydrochemistry

Fig. 3b also shows the Gran alkalinity of the Girnock as a time series. Initial low flows had Gran alkalinities of ca. 700 μeq l^{-1}, though these reduced as flows increased in late October. During the high flows of January, the Gran alkalinity dropped to 0 μeq l^{-1} and generally remained below 200 μeq l^{-1} until flows receded in early summer. Very small events in June and July had a dramatic effect in temporarily lowering alkalinity, before low flows in late July subsequently produced alkalinities exceeding 600 μeq l^{-1}. Low values were again observed during the August high flows and recovered again through September.

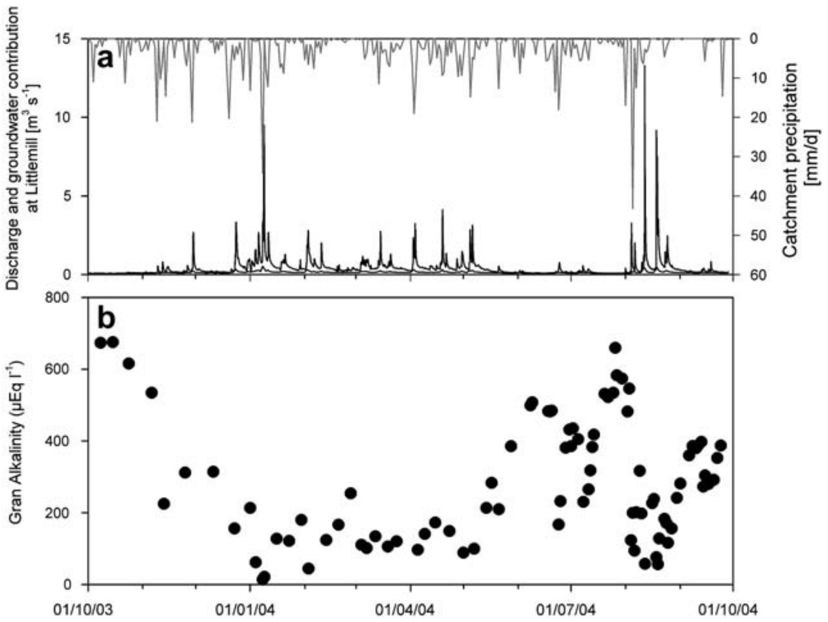

Figure 3 (a) Hydrograph (showing groundwater contributions below lower line) and precipitation and, (b) Gran alkalinity at the catchment outlet at Littlemill 2003–2004.

This temporal variability in alkalinity is common in the British uplands, as alkaline groundwaters increasingly dominate streamflows during drier periods, but are diluted by acidic soil waters during events (Wade et al., 1999). Studies in the Scottish highlands have indicated that soil water from intensively leached upland soils generally has a low alkalinity typically between −100 and 50 µeq l^{-1} (Soulsby and Dunn, 2003; Soulsby et al., 2003). Groundwater is much more variable in composition, depending upon residence times and the geochemistry of the geology and drifts. In less weatherable rocks like granite and psammite, it may be ~100 µeq l^{-1}, but is likely to exceed 1000 µeq l^{-1} where ultra-basic rocks, or deep groundwater flow paths occur (Smart et al., 2001). As a consequence, high flow stream chemistry in upland catchments tends to be soil-derived and relatively similar, whilst baseflow chemistry is dependent on dominant catchment geology (Smart et al., 2001). Fig. 3a also indicates the chemically-based separation of groundwater from the stream hydrograph (see Tetzlaff et al., 2006 for details), which estimates that groundwater accounted for around 30% of the stream flow during this particular hydrological year. This is slightly higher than the long-term average, mainly as the year was drier than normal.

Sub-catchment stream hydrochemistry

Fig. 4 shows spatial variations of Gran alkalinity ranges in the main sub-catchments of the Girnock between January and October 2004. All sites show broadly similar, flow-related patterns to the Girnock at Littlemill, in terms of low alkalinity from high flow samples and higher alkalinity levels during baseflows. Whilst alkalinities of high flows converge, there is marked spatial variability in low flow chemistry reflecting the influence of sub-catchment geology, geochemistry and the dominance of longer residence water under low flow conditions. These effects are most clearly marked in East Burn and the Camlet Burn. In contrast, the Iron Bridge site has the lowest alkalinity range, with the lowest high flow and low flow alkalinities. Downstream, along the mainstem of the Girnock, mean and maximum alkalinity values gradually increase from Iron Bridge to the South Burn confluence, Hampshires Bridge and Littlemill.

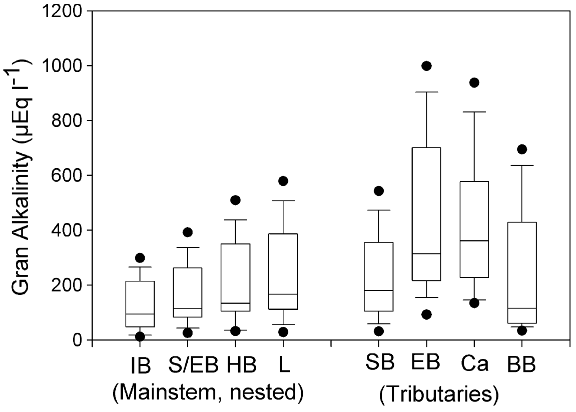

Figure 4 Gran alkalinity of streamwaters of the Girnock (nested mainstem: IB, SEB, HB, L) and associated sub-catchments (SB, EB, Ca, BB) showing median, 5th/95th percentiles (outlying points), 10th/90th percentiles (whiskers) and 25th/75th percentiles (box boundaries).

There are clear links between these spatial patterns and the sub-catchment geologies. Most obvious are the influences of the serpentinite and calcareous meta-sediments on the high baseflow alkalinities of the East Burn and the Camlet Burn respectively. In contrast, the granite-dominated sub-catchment upstream of Hampshires Bridge (including samples taken at the Iron Bridge and upstream of the South and East Burns) is reflected in low baseflow alkalinity. The Bruntland Burn exhibits intermediate characteristics, reflecting its mixed granitic/metamorphic geology. Changes to main stem chemistry between Iron Bridge and Littlemill, reflect the progressive influence of mixing from different sub-catchment sources. Interestingly, the alkalinity responses for the South Burn are very similar to Littlemill reflecting a broad mix of geologies and soils like the Girnock as a whole (Table 1).

Table 1 shows the likely range of groundwater contributions to the annual runoff for each sub-catchment estimated from chemical hydrograph separation. These were generally in the range 30—40%, and broadly similar to that estimated for Littlemill. Camlet had the highest estimated groundwater contribution (55—59%) probably reflecting the high coverage of HOST class 17 which are freely draining soils facilitating greater groundwater recharge. In general however, the predominant cover of hydrologically responsive soil types facilitate low groundwater recharge and a flashy hydrological regime.

Chemistry of springs and seeps

Broad scale spatial surveys of springs and seeps were undertaken to improve understanding of the sources of water that influence the observed sub-catchment scale patterns of stream chemistry. Fig. 5 summarises an initial alkalinity survey of major springs and seeps discharging into the Girnock undertaken in February 2004 (to indicate wet winter conditions when flows were close to the mean annual) between Littlemill and the Iron Bridge. In some places, the influence of low alkalinity (<~50 μeq l^{-1}) near-surface soil waters mainly draining peaty gley soils are evident. Elsewhere, deeper groundwaters discharging downslope from more freely draining soils and more calcareous geologies have much higher alkalinities (>~200 μeq l^{-1}). Clearly, complex spatial patterns are evident indicating a wide range of water sources and chemistries comprising groundwater discharges.

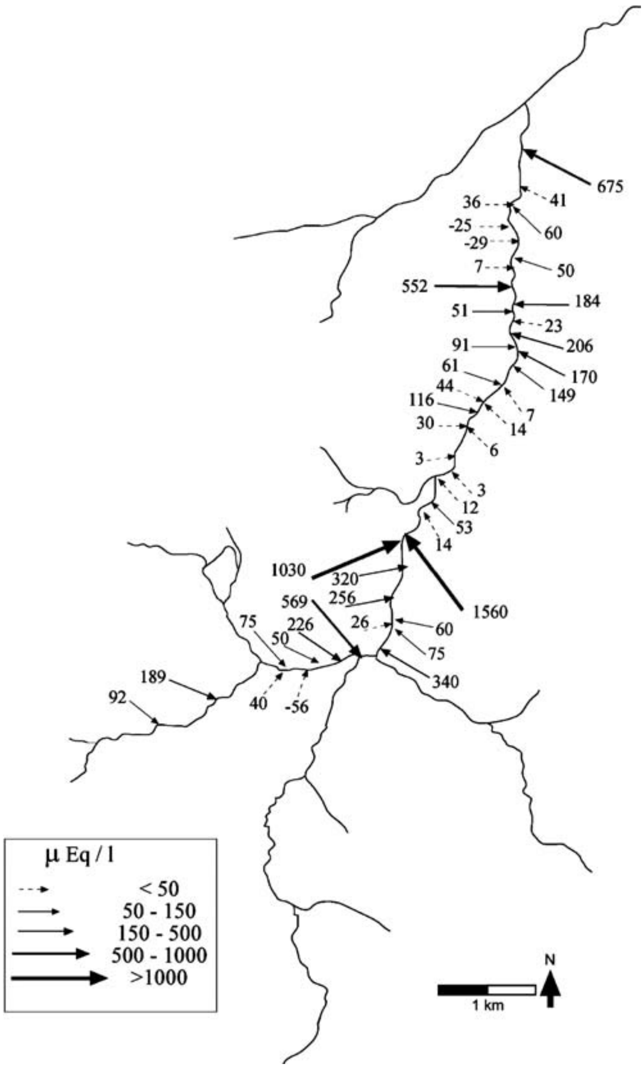

Figure 5 Gran alkalinity distribution in springs and seeps between Iron Bridge and Littlemill on 20/02/04.

A more systematic, detailed survey of springs and seeps was undertaken in June 2004 and provided details of sub-catchment hydrochemistry at a much finer spatial resolution (Figs. 6). In such summer low flow conditions, as flows approach the long-term Q_{95}, most seepage from all but the wettest catchment soils largely ceases. The springs and seeps in the Bovaglie sub-catchment (Fig. 6c), generally exhibit relatively low alkalinity waters (50—300 μeq l^{-1}), presumably reflecting the influence of slow weathering granitic rocks. Highest values were recorded in valley bottom springs (>300 μeq l^{-1}) or in the upper catchment to the north east, where alkalinities exceeded 400 μeq l^{-1}. In the valley bottom, this would be consistent with the re-emergence of water recharging the outcrops of calcareous metamorphic rocks in the north east (Smart et al., 2001). The high alkalinity in the west is less obviously related to geology, issuing from an area of granite and granodiorite. This water may be affected by local mineralization in these geological units, or may be water that has followed a deeper flow path (Shand et al., 2006).

The springs and surface waters in the South Burn (Fig. 6d) exhibited complex patterns of alkalinity. Most of the lower alkalinity springs (100—300 μeq l^{-1}) emerge in the west, originating from areas underlain by granite and quartzite/psammite. However, a high alkalinity seep (>600 μeq l^{-1}) also emerges here, whilst the lowest alkalinity seep (just under 100 μeq l^{-1}) emerges within 100 m on the opposite side of the stream. Water emerging in the east tends to be of higher alkalinity (up to 1000 μeq l^{-1}), reflecting the influence of recharge in areas underlain by calcareous meta-sediments and amphibolite. However, the patterns are not systematic, and the relative influence of provenance in areas of different geological units and the depth of groundwater flow paths are unclear from alkalinity data alone.

In the East Burn (Fig. 6e), the influence of the Mg-rich serpentinite is immediately obvious. The alkalinities of springs emerging to the east of the stream are amongst the highest observed in the catchment (Fig. 7). Springs on the western side of the stream exhibit lower alkalinities, though these are still relatively high, apparently influenced by the amphibolite. Only one small seep had an alkalinity lower than 100 μeq l^{-1}.

The Camlet sub-catchment (Fig. 6b) also had complex patterns of alkalinity. A striking feature was the combination of low (<50 μeq l^{-1}) and high (>600 μeq l^{-1}) alkalinity

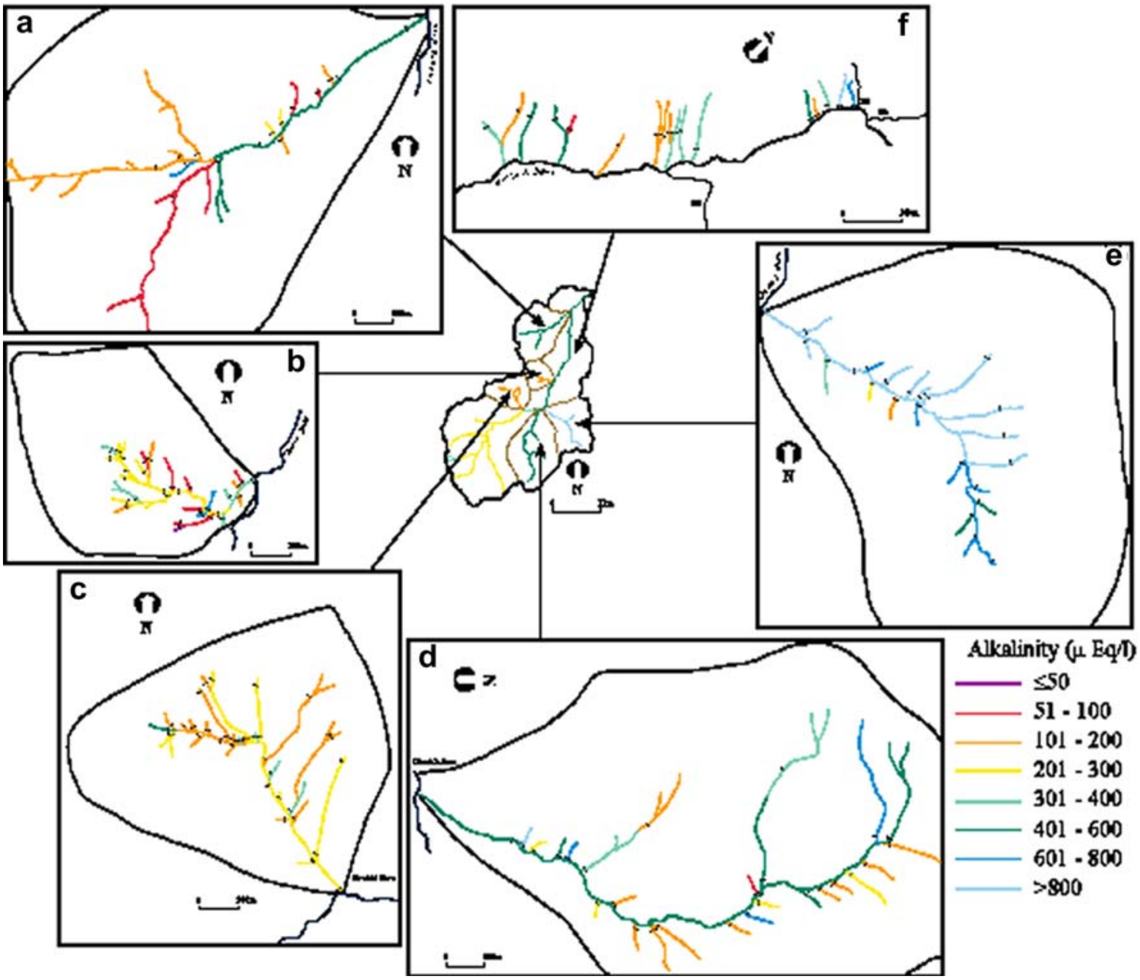

Figure 6 High resolution Gran alkalinity distribution in major sub-catchments; (a) Bruntland Burn, (b) Camlet Burn, (c) Bovaglie, (d) South Burn, (e) East Burn, (f) eastern hillslopes.

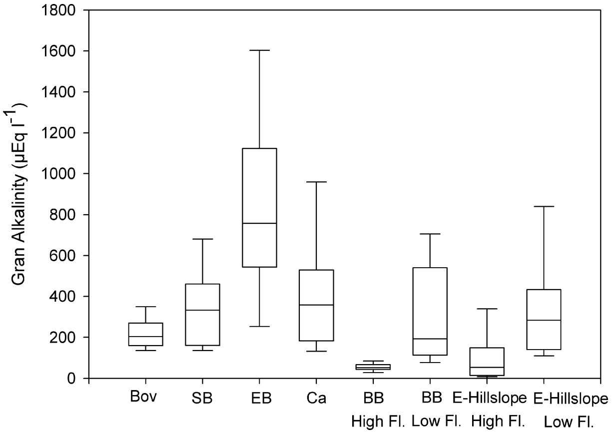

Figure 7 Gran alkalinity distribution of springs and seeps for the sub-catchments of the Girnock Burn showing median, 10th/90th percentiles (whiskers) and 25th/75th percentiles (box boundaries) (Bov — Bovaglie Burn, SB — South Burn, EB — East Burn, Ca — Camlet Burn, BB — Bruntland Burn) (High Fl = high flow in May 2004; Low Fl = low flow in July 2004), E-Hillslope — Eastern hillslopes (High Fl = high flow in May 2004; Low Fl low flow in July 2004).

waters emerging in lower slope areas in close proximity. This sub-catchment is underlain by calcareous meta-sediments, which outcrop in the western upper slopes and appear to act as recharge areas. However, the lower catchment is covered by peaty gley soils which are poorly drained and characterise the areas where most springs re-emerge (Fig. 1b). Drainage from these wet, acidic soils appears to influence the chemistry of some of these seepages resulting in low alkalinities, though the effect on the Camlet stream is limited implying volumes are low.

The alkalinities in the Bruntland Burn sub-catchment were comparatively low (Fig. 6a). Only one small spring in the lower catchment had an alkalinity exceeding 600 μeq l^{-1}. Elsewhere, most springs had alkalinities <200 μeq l^{-1}, reflecting the dominance of groundwater derived from granite and siliceous meta-sediments. The eastern slopes of the lower catchment of the Girnock form a series of small streams, spring and seeps draining hillslopes which fringe the lower 5 km of the Girnock. The alkalinities of these waters are highly variable ranging from 50 to 600 μeq l^{-1} (Fig. 6f). The geology is mainly dominated by calcareous meta-sediments with some areas of amphibolite. However the lower slopes are covered by drifts with peaty gley soils; this again probably implies some mixing of soil water drainage and water from deeper groundwater sources.

The nature of such groundwater and soil water mixing under contrasting hydrological conditions becomes clearer when the February 2004 surveys of the eastern hillslope waters are compared with those taken in the summer (Fig. 7). In February (high flow) samples, most of the alkalinities are below 100 μeq l^{-1}. Similarly, the influence of geology in the Bruntland Burn is masked under higher flows in May 2004, when a water quality survey showed all waters to have alkalinities <100 μeq l^{-1}. This clearly contrasts with the situation later in the summer when soil water seepages appear to be less influential and deeper, well-buffered groundwater sustains flows.

Influence of groundwater on stream hydrochemistry

Results clearly show that the spatial variability of groundwater chemistry in emergent springs and seeps in the Girnock is highly variable and complex at localised scales. At a broader scale, inter-sub-catchment contrasts in geology explain the main differences in stream chemistry at low flows. However, at finer spatial scales, differences in flow path depths, reaction kinetics and water residence times are probably interacting to explain local variability. Under high flow conditions, considerably less alkaline waters are evident at many of these springs and seepages. This low alkalinity water dominates the stream flow response at high flows throughout the catchment (eg January 2004 in Fig. 8). This reflects the influence of overland flow and shallow subsurface storm flow from upslope, which then dominates the storm hydrograph at such times (Newson et al., 2001; Holden et al. (2002); Soulsby et al., 2004). However, process studies elsewhere have shown that it is also possible that there is an influence of rapidly recharged groundwater – largely reflecting soil water chemistry – moving quickly through shallow fracture systems or freely draining glacial deposits, to discharge in valley bottom areas where saturated drifts cause return flows back to the soil surface (Shand et al., 2006). It is not yet known whether such processes are also important in the Girnock. The progressive lessening of soil water influences on the river network hydrochemistry is evident as flows decline through April, May and June and the imprint of catchment geology on stream chemistry becomes more strongly defined (Fig. 8b–d).

To provide additional insight into the hydrological pathways routing rainfall to streams, precipitation and streamwater samples collected at Littlemill were analysed for chloride (Fig. 9) to assess the behaviour of a passive tracer which can be used to infer the timescales over which precipitation directly influences runoff (Kirchner et al., 2000). During the monitoring period, the degree of damping observed in streamwater relative to precipitation is less marked than reported in many other studies (cf. Neal et al., 1988; Soulsby, 1995; Kirchner, 2003). Unfortunately, the relatively coarse and uneven sampling intervals means that detailed modelling of precipitation inputs and streamflow outputs to estimate residence times accurately is not possible. Nevertheless, there is a fairly high degree of general synchronicity between precipitation Cl concentrations and those in the stream, implying responsive hydrological flow paths which transfer Cl out of the catchment relatively rapidly. In many cases the streamwater Cl signal is damped and often lags that of precipitation, indicating mixing in the catchment soils and hillslopes.

Streamwater Cl concentrations are fairly constant in the first month of the investigation, but increase in mid-November in response to the first hydrologically effective precipitation inputs. Streamwater concentrations fall in December and January when levels in precipitation decline. They then increase through March and April in response to high rainfall inputs. However, declining Cl concentrations in rainfall in April and May, prompted streamwater levels to fall before recovering in May and June. Some very high Cl spikes in streamwater were observed in the second half of June and mid-July in response to very minor increases in stream flow. Unfortunately, the resolution of rainfall samples was poor at this time, though a high Cl sample collected in mid-July corresponded to very high Cl level in the stream on the recession of a very small event.

Fig. 10 shows the Cl response for the month of August in more detail. Following the high Cl spike in July, concentrations in rainfall and streamwater generally fell in early August, as did levels in the stream. The dynamics around particular events appear to be complex, suggesting our coarse sampling is missing much of the detailed event-scale variation in precipitation and streamwater levels (cf. Soulsby, 1995; Kirchner et al., 2000). Despite this, the Gran alkalinity variability shows consistent response to a range of hydrological events as acidic soil-derived water dominates the storm hydrograph.

At present groundwater sampling in the catchment is limited to shallow hyporheic zone piezometers that are often influenced by surface waters (Malcolm et al., 2005). Hence the chemistry of deeper groundwater sources are unknown. However, a 0.5 m deep piezometer close to the HB sampling point in Fig. 1, is known to sample upwelling groundwater. Samples were collected from this piezometer for Cl analysis at fortnightly intervals over a period of 4 months between November 2003 and March 2004. These are plotted against mean daily flows at Littlemill, along with streamwater and precipitation Cl values in Fig. 11. The groundwater concentrations are remarkably constant, despite variations in those in precipitation and streamwaters, and marked hydrological variability. This implies that these deeper valley bottom sources have a relatively large store of groundwater that mixes only slowly with new recharge. Thus it appears that the streamwater represents a mixture of groundwaters with relatively stable Cl concentrations and soil-derived water which has much more dynamic variation in Cl levels which reflects precipitation inputs. The rapid hydrological pathways that dominate the responsive peaty soils which cover much of the Girnock catchment probably allow this Cl signal in precipitation to be transported to the stream relatively quickly.

Fig. 12 shows the cumulative Cl flux estimated between sampling occasions in precipitation and streamwater. As this method is quite basic (for example occult or dry deposition were not assessed, thus streamwater output fluxes were some 20% higher than inputs) the fluxes are expressed as a cumulative percentage of the total annual flux. The high input fluxes in December/January and July/early August are evident, and matched by marked output fluxes that are

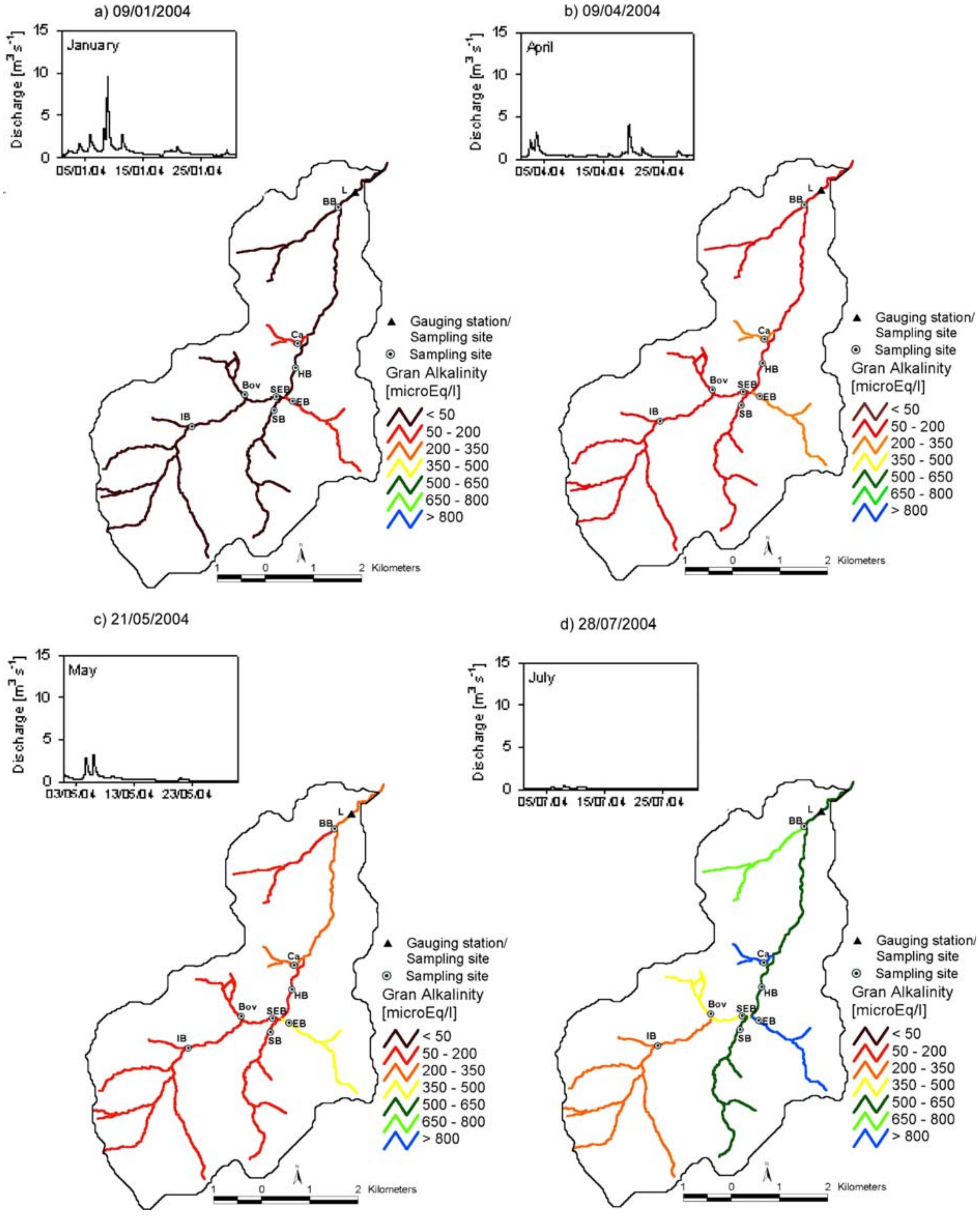

Figure 8 Spatial variability of Gran alkalinity at four selected dates: (a) during high flow conditions (09/01/04); (b) and (c) moderate flow conditions (09/04/05 and 21/05/04); (d) low flow conditions (28/07/04).

lagged by a month or two. This is especially notable when the high Cl concentrations in inputs (which increase from around 65—95% of the annual total) in June and July in small rainfall events with low runoff coefficients seemed to correspond to high outputs in mid- to late August. This would be consistent with the Cl inputs being stored in relatively dry catchment soils and then being remobilized along hydrological flow paths which re-connect to the stream as the catchments re-wets. The Cl concentrations and flux estimates in streamwater at Littlemill were representative of the other sampling locations (not shown). Recent work by Tetzlaff et al. (2006) used variations in oxygen isotope ratios to estimate mean residence times of around 4-5 months for streamwaters at all the sampling points in the Girnock.

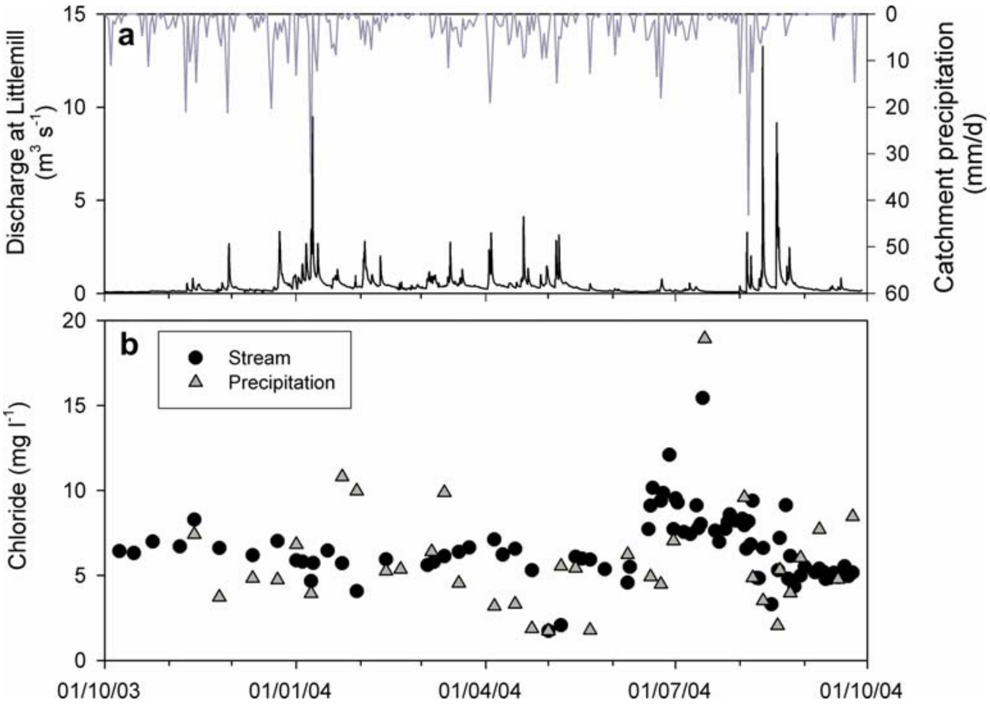

Figure 9 (a) Stream hydrograph and (b) chloride distribution in precipitation and stream at Littlemill 2003–2004.

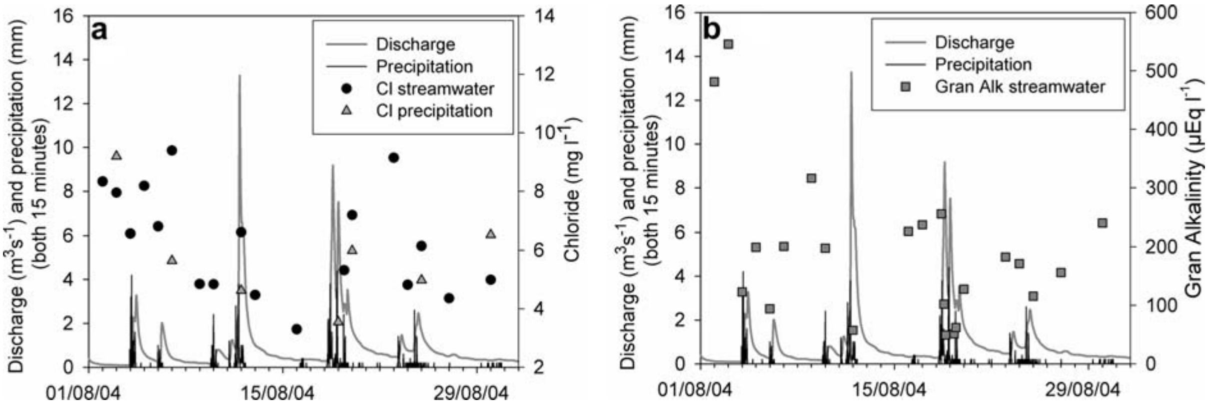

Figure 10 Temporal distribution of (a) Cl in precipitation and streamwater and (b) alkalinity in streamwater during August 2004.

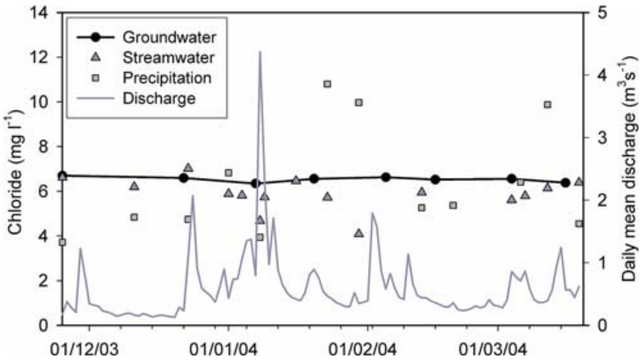

Figure 11 Cl variations in groundwater in hyporheic well near Hampshires Bridge relative to streamwater and precipitation November 2003–March 2004.

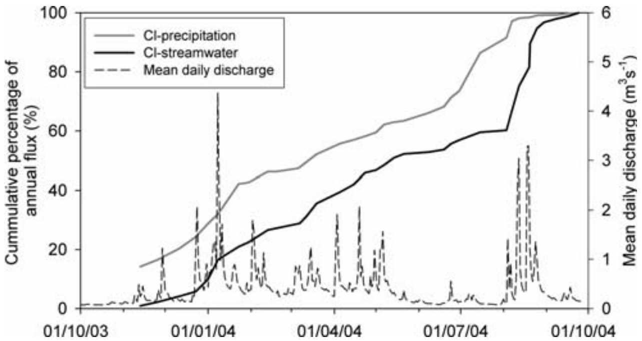

Figure 12 Cumulative percentage fluxes of Cl in precipitation and streamwater in the Girnock 2003–2004.

The Cl and alkalinity data presented in this paper suggests that this represents the integration of much shorter residence times in responsive catchments soils and longer residence times in groundwaters. However these tentative hypotheses need to be tested by more direct observations of Cl in soils and groundwaters.

Implications

The data presented in this paper provide some insights into the nature of groundwater influences on the Girnock catchment. At a broad scale, the integrated effects of groundwater contributions to temporal variations in flow in the Girnock can be explained conceptually by a simple two component mixing model which views higher alkalinity groundwater sources, with stable Cl concentrations, dominating baseflows, and a low alkalinity soil-derived water source, with variable Cl concentrations, dominating high flows (Fig. 3). However, this simple temporal variation is underpinned by marked spatial variation in the nature, geochemistry and residence times of different groundwater sources. The ''snap shot'' surveys of springs, seeps and surface waters shown in Figs. 5 and 6, helps conceptualise the nature of this spatial variation in chemistry, which – at a relatively coarse (sub-catchment) scale – reflects an expected geological influence. At finer scales of individual seeps and springs, heterogeneity is apparent often even within the same geological units.

The detailed interactions between soil water, groundwater and streamwater remain obscure in larger heterogenous catchments like the Girnock. In the surveys of seeps and springs under wet and dry antecedent conditions, the mixing of soil water and groundwater discharges in the riparian zone becomes readily apparent (eg Fig. 7). This can be conceptualised by the same 2-component mixing at the hillslope scale as is apparent at the catchment scale. However, the extensive distribution of springs and seeps in the wide, flattish valley bottom of the Girnock implies that a significant proportion of groundwater discharges away from the main river channel network rather than through the bed and banks of the stream. A recent examination of groundwater–surface water interactions in the hyporheic zone at a site close to Hampshires Bridge was carried out by Malcolm et al. (2006). At this location, which is known to the characterised by groundwater upwelling, piezometers indicated relatively small and transient positive (streamward) heads following hydrological events. For long periods positive heads indicated little groundwater discharge through the streambed. Moreover, the alkalinity of deeper waters was generally greater than that observed in the stream (Soulsby et al., 2005). The presence of poorly drained glacial drift in the valley bottom appears to create zones of extensive saturation, but low sub-surface permeability causes groundwater to re-emerge in the springs and seeps at some distance from the stream channel (see Fig. 2). In this area, emergent groundwaters can mix with acidic soil waters in the peaty soils which dominate these locations.

The saturated areas appear to be fed by upslope drainage, mainly from water recharging through the more permeable soils on the catchment hillslopes. Recharge appears to be a smaller component of Girnock's hydrology than in other upland catchments in the UK; in the Girnock chemically-based hydrograph separations indicate that groundwater comprises about 30-40% of the annual runoff in almost all the sub-catchments, elsewhere – even in montane catchments in the Cairngorms – groundwater contributions comprise as much as 50–60% of annual runoff (Soulsby et al., 2005). A recent tracer-based assessment of 25 catchments in the Scottish Highlands – ranging in scale from 1 to 230 km^2 – indicated that catchment soil cover was a first order control on groundwater recharge and catchment mean water residence times (Soulsby et al., 2006a). Put simply, this work implies that catchments with a high coverage of freely draining soils on steep hillslopes or overlying alluvial aquifers are characterized by high groundwater (>40%) contributions and long mean residence times (>1 yr^{-1}). In contrast, catchments dominated by responsive peaty soils or skeletal montane soils have low groundwater contributions (<35%) and short residence times (<0.5 yr^{-1}) (Soulsby et al., 2006b). The landscape of the Girnock and its major sub-catchments appears to conform to the latter case (Tetzlaff et al., 2006), with over 75% of the catchment being covered by responsive soils (Table 1). The major zones of recharge are likely to be the areas occupied by the freely draining HOST class 17 and 5 podzolic soils. Over much of the catchment, where coverage of peats (HOST class 29) and peaty gley (HOST class 15) soils predominate, significant deeper recharge is unlikely as the permeability of the upper soil horizons is too low. However, it is likely that some recharge occurs below the shallow ranker soils (HOST classes 22 and 27) as fractures at the soil/bedrock interface will transmit recharge.

The data collected here demonstrate the insights into catchment hydrology that can be gained from tracer studies of stream networks and groundwater seeps and springs. The use of GIS to plot the chemistry of groundwater discharges and stream chemistry shown in Figs. 6 and 8 provides a valuable insight into the spatial heterogeneity of groundwater. To gain insight into groundwater heterogeneity through extensive drilling programmes (cf. Shand et al., 2006) would generally be prohibitively expensive, even where it is logistically possible. There is, therefore, considerable potential in using tracers as tools in rapid appraisals of catchment hydrology in ungauged, or sparsely gauged basins. This is of relevance to the current Predictions in Ungauged Basins (PUB) initiative of the International Association of Hydrological Sciences (IAHS) is seeking to develop such techniques to aid conceptualization of catchment functioning to aid modelling and management goals (Sivapalan et al., 2003).

The implications of this work for modellers depends upon the purpose of modelling. Heterogeneity in groundwater discharge and chemistry and its influence on the quality and quantity of surface water is unimportant if rainfall-runoff modelling is concerned with simulating the stream hydrograph. However, when modelling for hydrochemical purposes, the simple lumped approaches of many catchment models would be unable to incorporate the spatial heterogeneity and temporal dynamics that is indicated by Figs. 6 and 7. This may not be so important in the case of end member mixing analysis, where a catchment-average groundwater chemistry is often used to conceptualise a groundwater source and predict plausible groundwater contributions to flow (Wade et al., 1999); though it is important to recognise that the groundwater end member probably comprises a range of discrete sources with differing characteristics (Haria and Shand, 2004). However, in the case of the more complex hydrochemical models applied to upland catchments, such as those used to predict the chemical and ecological effects of changing patterns of S and N driven acidic deposition and/or land management, such heterogeneity in groundwater hydrochemistry has major implications for spatial variability in resultant streamwater quality which models would be unable to simulate (Wade et al., 2001a,b; Haria and Shand, 2004; Malcolm et al., 2006). Spatially extensive data sets – such as the tracer-based one presented here – provide a valuable resource that can be used in distributed modelling studies to understand the complex interactions occurring at larger catchment scales and assist in modelling them in a more feasible and meaningful way.

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