HYDROLOGICAL PROCESSES
Hydrol. Process. **18**, 1315–1332 (2004)

Groundwater–surface-water interactions in a braided river: a tracer-based assessment

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Abstract:

Natural tracers (alkalinity and silica) were used to infer groundwater–surface-water exchanges in the main braided reach of the River Feshie, Cairngorms, Scotland. Stream-water samples were collected upstream and downstream of the braided section at fortnightly intervals throughout the 2001–2002 hydrological year and subsequently at finer resolution over two rainfall events. The braided reach was found to exert a significant downstream buffering effect on the alkalinity of these waters, particularly at moderate flows (4–8 $m^3 s^{-1}$/$\cong Q_{30-70}$). Extensive hydrochemical surveys were undertaken to characterize the different source waters feeding the braids. Shallow groundwater flow systems at the edge of the braided floodplain, recharged by effluent streams and hillslope drainage, appeared to be of particular significance. Deeper groundwater was identified closer to the main channel, upwelling through the hyporheic zone. Both sources contributed to the significant groundwater–surface-water interactions that promote the buffering effect observed through the braided reach. Their impact was less significant at higher flows (>15 $m^3 s^{-1}$/$>Q_{10}$) when acidic storm runoff from the peat-covered catchment headwaters dominated, as well as under baseflow conditions (<4 $m^3 s^{-1}$/$<Q_{70}$), when upstream alkalinity was already buffered owing to headwater groundwater sources assuming dominance. The significant temporally and spatially dynamic influence of these groundwater–surface-water interactions was therefore seen to have important implications for both catchment functioning and instream ecology. Copyright © 2004 John Wiley & Sons, Ltd.

KEY WORDS groundwater–surface-water interactions; tracers; braided rivers; hydrology; hydroeocology; Cairngorms; Scotland

INTRODUCTION

Braided rivers are amongst the most dynamic type of riverine environments, with rapidly changing channel characteristics occurring to accommodate flood flows and sediment delivery (Poole *et al.*, 2002). Thus braided rivers have had intrinsic geomorphological interest as locations where the link between fluvial processes and channel evolution can be readily observed (Nanson and Knighton, 1996). Moreover, the dynamic, diverse abiotic environment of braided channels has provided a focus for ecological studies, which have highlighted their rich biodiversity (Malard *et al.*, 2002; Robinson *et al.*, 2002). Increasingly, however, interdisciplinary investigations of fluvial hydrosystems have sought to understand the interlinkages between river channels, floodplains, alluvial aquifers and freshwater/riparian ecosystems (Brunke and Gonser, 1997; Petts, 2000). Braided rivers are of particular interest in this respect as their large heterogeneous morphology results in marked physical, chemical and biological gradients between river channels, associated floodplain wetlands and groundwaters in alluvial aquifers (Stanford and Ward, 1993). The large surface area of braided channels, together with localized topographic gradients, facilitates extensive interactions between surface water and groundwaters throughout braided reaches (Poole *et al.*, 2002). Thus, influent channels occur where groundwater or hyporheic water emerges, and effluent flows occur where surface waters drain into the alluvial

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Received 23 December 2002
Accepted 7 May 2003

aquifer. The interrelationships between surface water and groundwater are not stable, with dynamic and rapid channel changes occurring to create constantly evolving gradients between groundwater and surface waters (Wondzell and Swanson, 1999; Soulsby *et al.*, 2001; Malcolm *et al.*, 2003a). These changes and gradients also exert a profound impact on stream ecology and biodiversity (Fowler and Death, 2001; Fowler and Scarsbrook, 2002; Robinson *et al.*, 2002).

This paper examines groundwater–surface-water interactions in a braided section of the River Feshie, probably the largest and best-known section of braided river in the UK (Werrity and McEwen, 1993). This lies within the Feshie catchment, which is one of four mesoscale catchments being investigated as part of the CHASM (Catchment Hydrology and Sustainable Management) initiative. The Feshie braids form part of a Site of Special Scientific Interest (SSSI) and also fall within the Cairngorms National Nature Reserve (NNR), which also forms part of the Cairngorms National Park. In view of this high conservation value, it important that any preliminary assessment of groundwater–surface-water interactions applies non-intrusive techniques that avoid any harm to the conservation interest of the site.

Tracer technologies for understanding groundwater–surface-water interactions are well established (Walker and Krabbenhoft, 1998). Use of natural geochemical and isotopic tracers can help identify hydrological source areas and residence times in groundwater and stream-water systems (Kendall and McDonnell, 1998). In particular, tracers such as alkalinity and silica can usefully distinguish acidic, organically enriched soil water, and more alkaline groundwater in upland catchments where soil and groundwater systems have stratified chemical characteristics (Neal, 1997; Soulsby *et al.*, 1998, 2000, 2003). This allows assessment of groundwater influence on stream flows in catchments, and can also indicate effluent conditions where stream waters may be recharging groundwaters and influent situations where groundwaters emerge and mix with surface waters (Wroblicky *et al.*, 1998).

In this study, natural tracers are used to investigate groundwater–surface-water interactions in a braided river. Specifically, this paper aims to: (i) assess the temporal change in stream water chemistry through a braided river section over a range of flows during the hydrological year, and the finer resolution event scale; (ii) characterize the tracer chemistries of the different source waters contributing to flows through the braids and (iii) assess their relative influence on stream-water chemistry in terms of groundwater–surface-water interactions.

STUDY AREA

The River Feshie drains 231 km^2 of the western Cairngorm Mountains in the Scottish Highlands (Figure 1a). The catchment is mountainous, spanning an altitudinal range from 232 to 1115 m. The highest parts of the catchment are underlain by granite batholiths that are *c.* 400 million years old. Moinian schists, mainly psammite, comprise most of the remainder of the catchment (Figure 1b). There are also diorite and felsite dykes and sills, particularly in the headwaters of the Allt Chomraig and upper Feshie. There are three important braided sections of the Feshie; at the confluence with the Spey, at the Allt Chomraig confluence and at Feshie lodge (Werrity and McEwen, 1993). The most extensive are at Feshie lodge, and these provide the focus for this study (Figure 1a).

The topography of the Feshie catchment bears the strong imprint of its glacial history (Sissons, 1974). Immediately upstream of the braided section at Feshie lodge, erosion by ice and meltwaters has sculpted a 3 km long gorge with oversteepened side walls up to 250 m high. High volumes of coarse sediment enter the channel in this reach via active slope–channel linkages at the base of scree slopes, truncated debris cones fed by steep tributary streams and, in places, the erosion of alluvial fill (Brazier and Ballantyne, 1989). In the lower section of the gorge the valley gradient decreases and alluviation becomes more marked and the river begins to braid. In addition, mid-way through the braided section, the Allt Lorgaidh, a major south bank tributary, enters the Feshie. The Lorgaidh also flows out of an oversteepened gorge and a large alluvial fan has splayed over the southern edge of the Feshie floodplain (Werrity and McEwen, 1993). The valley

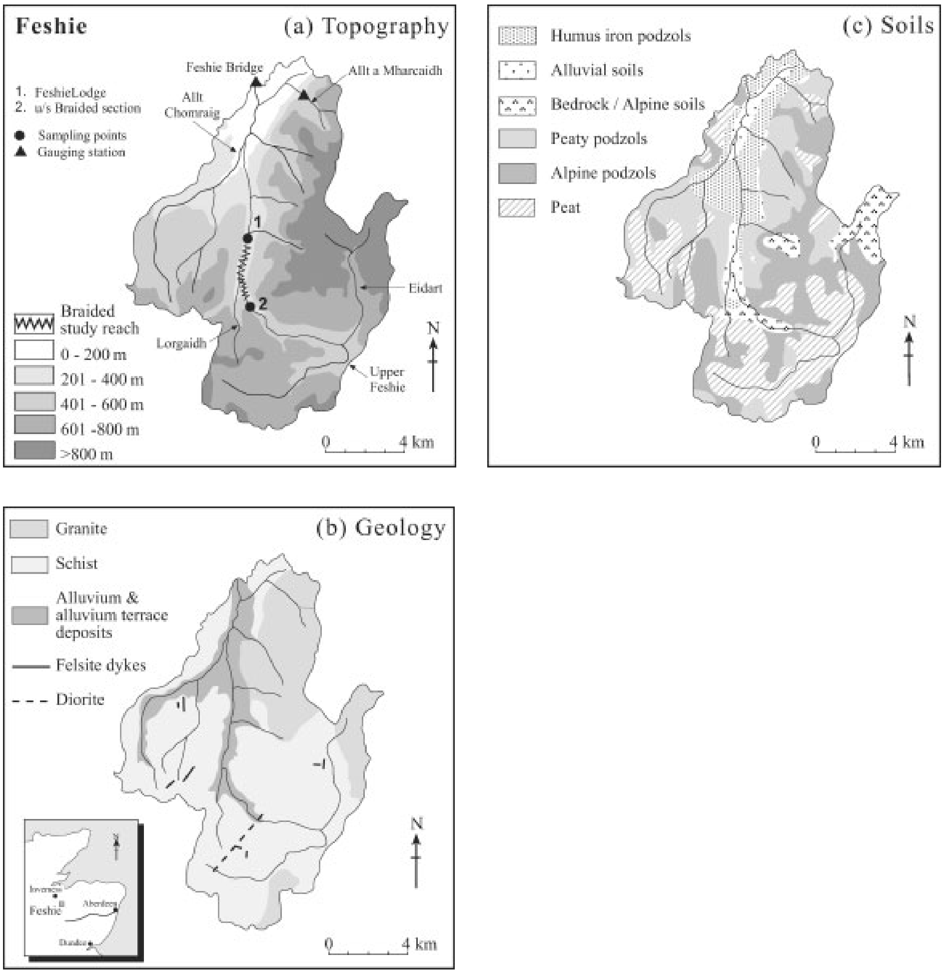

Figure 1. Catchment map of Feshie; (a) topography, (b) geology and (c) soils

becomes much wider and the gradient declines in the area of the Feshie–Lorgaidh confluence leading to more extensive deposition. The braids are bounded, particularly on the western valley sides, by a number of terrace features, indicating that the river has cut into older glacio-fluvial deposits (Young, 1976). In addition to the Lorgaidh, a number of smaller tributaries also flow into the Feshie through the braided reach. Many of them drain relatively small catchments and are, for much of the year, effluent channels that flow into the Feshie via subsurface flow paths. A second major alluvial fan encroaches on to the Feshie floodplain at the downstream eastern side of the braids at the outfall of Allt Choire Chaoil (Robertson-Rintoul, 1986).

The catchment receives a mean annual precipitation of around 1400 mm. With an average catchment altitude of 700 m, a significant proportion of this usually falls as snow (Soulsby *et al.*, 1997). As a result, the flow regime of the Feshie reflects the influence of snowmelt, particularly between January and May (Ferguson, 1984). Mean annual flows at Feshie Bridge gauging station are 8·01 m^3 s^{-1}, with the Q_{95} at 1·71 m^3 s^{-1} and the Q_{10} 16·28 m^3 s^{-1}. In addition to being mountainous, the headwaters of the Feshie have extensive coverage of peat soils (Figure 1c). These are particularly important in generating flood peaks in response to both rainfall and snowmelt events. As storm runoff tends to originate from the acidic peaty soils in the catchment headwaters, it is typically acidic with a very low alkalinity (e.g. <0 μeq l^{-1}), whereas baseflows, derived from deeper groundwater sources, are relatively well-buffered (e.g. 150–300 μeq l^{-1}) (Soulsby *et al.*, in press).

The variable snowmelt-driven flow regime, together with the rivers abundant bedload in a low gradient valley, creates conditions well suited to the development of braided channels (Werrity and Ferguson, 1980). Nevertheless, it is probable that deforestation of the catchment has accentuated the degree of braiding and accelerated the rates of channel change. Although some mature woodland remains on the upper braided floodplain and the slopes of the Feshie gorge, historic forest clearance and limited regeneration owing to deer grazing, has created a heather–grassland vegetation over much of the braided reach. The absence of deep rooting vegetation has probably exacerbated bank erosion rates along the reach.

METHODS

As part of a routine hydrochemical study in 2000 in the wider Feshie catchment, samples collected upstream (2) and downstream (1) of the braids at Feshie lodge (Figure 1a) revealed notable changes in stream chemistry across a range of flows (Rodgers *et al.*, 2002). Alkalinity was regularly found to double through the braided reach. This provided some evidence that the channel was receiving a significant influx of groundwater through the braided section. To investigate this further, fortnightly samples were collected at the same upstream and downstream locations of the braids throughout the 2001–2002 hydrological year.

In addition, extensive hydrochemical surveys of the braids were carried out in December 2001 and April 2002 to sample surface waters, floodplain springs and emergent hyporheic flows in flood channels. These were undertaken to characterize the chemistry of different source waters throughout the braids, and to qualitatively assess their influence on surface-water chemistry. A third spatial survey was undertaken in May 2002 to focus sampling around particular features within the braided reach to try and use natural tracers to gain some more detailed insight into the groundwater-surface water interactions occurring. Finally, at the routine upstream (2) and downstream (1) sites used throughout the hydrological year, automated samplers were used to examine surface water hydrochemical changes over the duration of individual rainfall events. These were sampled at 2-h intervals for a period of 7 days in November 2002. Although the Feshie has a very flashy storm response and 1-h samples may have provided greater detail on rising limb hydrochemistry, 2-h intervals were nonetheless effective in ensuring complete coverage of the range of flows and hydrochemical changes that occurred over the 7-day sampling period. Finer temporal resolution would have been prohibitive in terms of analytical demands and logistical difficulties associated with the inaccessibility of the site.

As part of the routine fortnightly sampling and the first spatial survey, samples were analysed for pH, conductivity and Gran alkalinity. Silica and dissolved oxygen (DO) concentrations were also determined for the second and third survey occasions. The event samples for November 2002 were analysed for all these determinands except DO. Gran alkalinity was determined by acidimetric titration with 0·005 M H_2SO_4 in the pH ranges of 4·5–4·0 and 4·0–3·0, giving approximations of the bicarbonate and organic acid contributions to alkalinity respectively. The DO concentrations were measured *in situ* using a portable DO meter. Silica concentrations were determined by flow injection analysis using a FIAstar 5000 water analyser system (detection limit: 15 μg).

Conductivity, pH and DO are commonly used parameters with proven utility in investigations of groundwater–surface-water exchange (e.g. Fowler and Death, 2001). Natural geochemical tracers such as Gran alkalinity and silica provide further information in distinguishing different catchment water sources. Gran alkalinity is particularly useful in that it provides a directly measurable, close approximation to the chemically conservative parameter acid neutralizing capacity (ANC), which to a first approximation can be used as an assumed conservative tracer (Neal, 2001). Strictly, ANC also depends on Al and DOC concentrations (Neal *et al.*, 1997) but in the Feshie concentrations of Al are generally very low (McMahon and Neal, 1990) and given the titration to pH 3, the Gran alkalinity and charge balance ANC are strongly and linearly correlated within the pH range observed in stream waters. Gran alkalinity is therefore extremely useful for end-member mixing analysis (EMMA), and a number of investigations have used this to differentiate between different source areas within catchment systems (Hill and Neal, 1997; Neal, 1997; Wade *et al.*, 1999; Soulsby *et al.*, 2003). The simple two-component approach adopted here is considered reasonable owing to the important role that riparian zones play in effectively decoupling subsurface storm flow in hillslopes from the channel network (Smart *et al.*, 2001). Using soil-water and groundwater end members to account for catchment hydrochemistry is therefore justified given that subsurface storm flows commonly displace or mix with groundwater stored in these riparian zones (Cresser *et al.*, 2000).

HYDROCHEMICAL CHANGES IN A BRAIDED RIVER

Spatial variation

Figure 2 shows the changes in stream-water alkalinity through the braided reach for the two spatial sampling surveys in December 2001 and April 2002. On the first of these, when flows at Feshie Bridge averaged 22 $m^3 s^{-1}$ ($\cong Q_7$), alkalinity was 9 μeq l^{-1} upstream of the braids. At the downstream site at Feshie lodge, alkalinity had increased to 31 μeq l^{-1}. In April 2002, when flows at Feshie Bridge were considerably lower (5·3 $m^3 s^{-1}$, $\cong Q_{60}$), upstream alkalinity was 44 μeq l^{-1}, increasing to 83 μeq l^{-1} downstream of the braided section. Particularly evident on this occasion was the marked increase in alkalinity between 2 and 2·5 km along the braided section (Figure 2), the section through which an important west bank tributary (Fionntag Burn) enters the Feshie as well as various groundwater springs and seepage flows originating from the significant area of alluvial deposits downstream of the Lorgaidh tributary.

Temporal variation

The basic upstream–downstream changes in alkalinity through the braided reach are plotted as a time-series for the 2001–2002 hydrological year in Figure 3a. Upstream alkalinity ranges between −12 and 173 μeq l^{-1}, with a mean value of 54 μeq l^{-1}, whereas downstream of the braids the range is from 20 to 156 μeq l^{-1} with a mean of 81 μeq l^{-1}. When plotted against flows at Feshie Bridge, both sites show the classic decline in alkalinity with increasing flows as acidic soil waters increasingly dominate alkaline groundwater as the

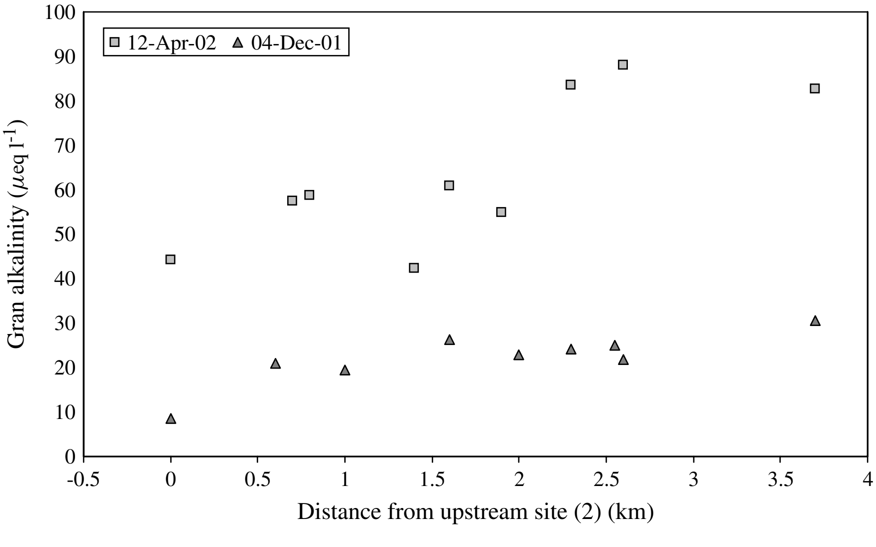

Figure 2. Stream-water alkalinity change with distance downstream through Feshie braids

main source of runoff (Figure 3b). The downstream alkalinity increase clearly reflects a buffering through the braids. This buffering is greatest (*c*. 30–80 μeq l^{-1} increase) at moderate flows, between *c*. 4–8 m^3 s^{-1} ($\cong Q_{30-70}$). Figure 3c shows the actual net change in alkalinity through the braided section against flow and provides a better insight into the influence of varying hydrological conditions. In contrast with the marked buffering at moderate flows, higher flows (>15 m^3 $s^{-1}/>Q_{10}$) produce a much less marked buffering effect on the alkalinity of stream water flowing through the braids (*c*. 20 μeq l^{-1}). The lowest flows (<4 m^3 $s^{-1}/<Q_{70}$) generally produce a more negligible change between upstream and downstream alkalinities, although it is clear that there can be significant variation between samples taken at similar flows, indicating potential hysteresis in hydrochemical response on the rising and recession limbs.

The classification of each sample in terms of the specific hydrological conditions during sampling (Figure 3c) allows further insight into this variation in hydrochemistry. The small number of samples obtained during the rising limb of the hydrograph generally display the highest buffering through the braids, whereas towards peak flows and high recession flows, the downstream increase in alkalinity is lower. This may be the result of stream-water alkalinity above the braids responding more rapidly to relatively minor volumes of acidic runoff from the extensive peat soils in the catchment headwaters associated with either modest rainfall events or the early stages of larger ones. Such modest flows may attenuate through the braided section, given the likelihood of significant recharge into the extensive and highly permeable braid bars and banks that characterize this reach. This therefore would lead to a more negligible flow increase and subsequent hydrochemical response below the braids, and indeed the rest of the catchment down to its outlet at Feshie Bridge, with groundwater inputs through the braids still exerting a significant buffering effect on the relatively low volume acidic flows from the upper catchment.

Hydrochemical change through the braids also appears to be variable at baseflows, with the responsiveness of stream-water alkalinity above the braids leading to varying degrees of buffering even at relatively similar low flows. The two lowest flow samples taken towards the end of September 2002 (6 and 17 days since any increase in flow) are particularly interesting in that alkalinity below the braids remained unchanged for both samples (156 μeq l^{-1}) but upstream alkalinity increased from 135 to 174 μeq l^{-1}, leading to an actual decrease in alkalinity through the braids (Figure 3a and c). This probably reflects the influence of higher alkalinity groundwater contributions from the upper Feshie headwater subcatchment assuming dominance over those from the Eidart headwaters (Soulsby *et al*., in press). Routine hydrochemical data collected for the same period shows the groundwater end-member alkalinity value (mean of three lowest flow samples) for the upper Feshie to be 204 μeq l^{-1}, whereas the Eidart's was only 82 μeq l^{-1}. Moreover, the estimated groundwater contributions to annual flow for the upper Feshie are lower than for the Eidart (Soulsby *et al*., in press), suggesting that its more buffered influence on stream-water alkalinity is relatively slow in taking effect, as reflected in the prolonged alkalinity increase above the braids.

Event-scale temporal variation

Figure 4a and 4b display the time-series for alkalinity and silica values sampled upstream and downstream of the Feshie braids between the 7 and 14 November 2002. The 15-min flow data were modelled using the stream stage record from the downstream braids sampling site at Feshie lodge alongside the gauged flows at Feshie Bridge and confirmed with spot gauging. The flow record for this period of sampling shows two notable events as well as more minor fluctuations in flow (Figure 4a and b). The peak discharge for these two events fall closely either side of the corresponding long-term Q_{10} flow measured at Feshie Bridge, with the second being the larger and more prolonged of the two. Indeed, the contrast in hydrochemical response between the two events sampled is notable. The first, more modest flow rise resulted in a fairly sharp decrease in alkalinity upstream of the braids, falling from 68 to 3 μeq l^{-1} in 6 h. Downstream of the braids, however, stream water remained relatively well-buffered in comparison, even though the equivalent drop in alkalinity was of similar magnitude to that seen upstream (110–54 μeq l^{-1}). Figure 4b indicates a similar response in silica values. In this instance, as suggested from the previous routine-sampled data, it would appear that flow

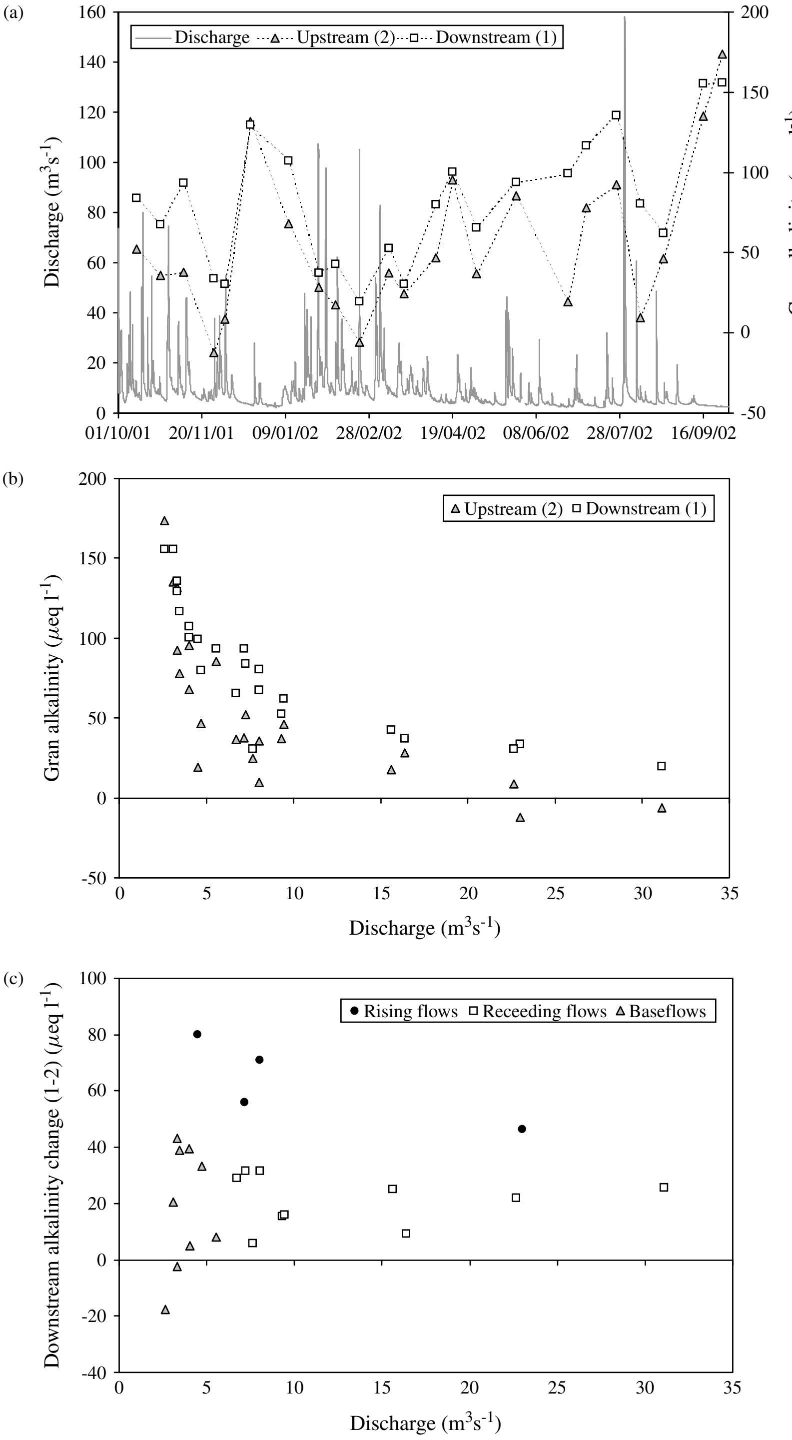

Figure 3. 2001–2002 stream-water alkalinity variation with flow: (a) upstream and downstream alkalinity time series, (b) upstream and downstream flow-concentration plot and (c) downstream alkalinity change against flow

attenuation owing to bank recharge, as well as high alkalinity and silica groundwater inputs through the braids, effectively damp the hydrochemical response at the downstream extent of the braids. This is clearly reflected in that downstream alkalinity also appears more stable compared with upstream in the period between the two events, with much larger fluctuations upstream in response to relatively minor changes in flow. Indeed, Figure 4a shows that the lowest alkalinity recorded for the upstream site (-14 μeq l^{-1}) was in response to only a very small flow increase and this corresponds to a high net change through the braids (60 μeq l^{-1} increase), given the more modest response in downstream alkalinity observed.

The second main rainfall event that started on 13 November 2002 exerted a very different impact on stream-water hydrochemistry compared with that seen for the smaller and shorter first event. Upstream alkalinity responded similarly, again declining by 50 μeq l^{-1}. Downstream of the braids, however, alkalinity fell from 96 to 4 μeq l^{-1}, converging with the low alkalinity values upstream (Figure 4a). On this occasion, therefore, with higher flows, negligible buffering through the braids was observed with the net alkalinity change falling to zero during peak flows. Figure 4c emphasizes the overall difference in response between the two events, showing hysteresis curves for rising and falling limbs of each event. The first event shows a buffering of alkalinity through the braids (*c*. 30 μeq l^{-1} increase) being maintained at the highest flows, whereas for the second event the typical buffering effect is cancelled out by the substantial volumes of acidic runoff from the upper catchment. It is interesting to note that stage data recorded for the two headwater subcatchments (not shown) indicates a much more pronounced hydrological response for the upper Feshie for the first event compared with the Eidart, given its much higher proportion of responsive peat soils. In contrast, the second event shows a more comparable stream stage response from the Eidart subcatchment reflecting more prolonged and widespread rainfall across the Feshie as a whole. Furthermore, the more responsive nature of the upper Feshie subcatchment, particularly to smaller catchment inputs, appears to help substantiate the more variable pattern of alkalinity upstream of the braids, which is not as obvious from the more subdued and lagged downstream flow record presented in Figure 4a.

The upstream and downstream silica concentrations shown in Figure 4b reveal a slightly contrasting overall response compared with alkalinity. Although both mirror alkalinity behaviour quite closely for the first event, they then converge during the reasonably high post-event flows at the start of 11 November 2002 (Figure 4b). From this point onwards, upstream and downstream silica behave similarly to each other with little overall increase through the braids, signifying a marked response to more sustained moderate flows, yet conversely, less sensitivity to minor flow changes.

GROUNDWATER, HYPORHEIC-WATER AND STREAM-WATER CHEMISTRY

Table I shows the hydrochemistry for selected samples of groundwater springs, emergent hyporheic waters, tributary streams and main stem river water for the April 2002 spatial survey. These different source waters exhibit clear variation in their respective hydrochemistry, particularly in terms of alkalinity. Predictably, main stem samples can be seen to have the lowest alkalinity (mean 64 μeq l^{-1}) in contrast with groundwater samples, which have the most consistently high alkalinities (mean 178 μeq l^{-1}) and can be up to five times greater than main stem samples. Surface water tributaries showed significant variation in alkalinity, ranging from 72 to 316 μeq l^{-1}, although the mean value of 139 μeq l^{-1} shows them to be more buffered than main stem surface waters. Hyporheic samples seem to be intermediate between main stem river water and groundwater (mean 79 μeq l^{-1}).

Plotting silica against alkalinity for the April 2002 survey samples (Figure 5a) highlights these distinctions further. Main stem river samples plot with the lowest silica (mean 3·9 mg l^{-1}) and alkalinity and display relatively limited variation. In general, groundwater samples are higher in silica concentration (4·6 mg l^{-1}) as with alkalinity, but they also display much greater variation. Silica concentrations for hyporheic samples are generally similar to those of main stem waters (3·7 mg l^{-1}) but are distinguished by their slightly elevated alkalinity. Surface water tributaries encompass a wide range of silica concentrations and alkalinity.

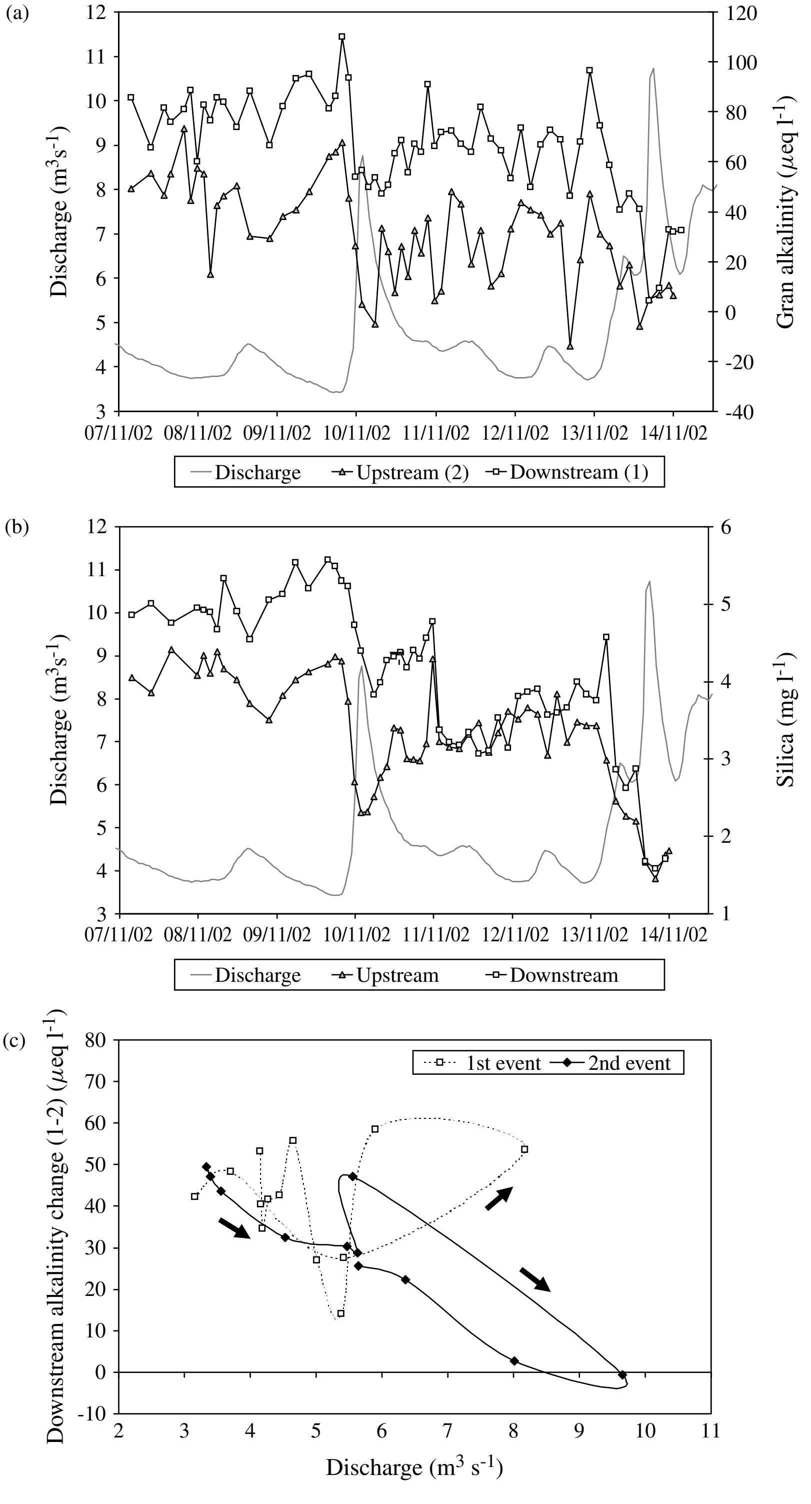

Figure 4. Event-based stream-water alkalinity variation with flow: (a) upstream and downstream alkalinity time series, (b) upstream and downstream-silica time-series and (c) event hysteresis curves

Table I. Summary of selected hydrochemical characteristics of surface-water, groundwater and hyporheic flows within the Feshie braids: April 2002

Sample Group	Gran alkalinity (μeq l^{-1})	Si (mg l^{-1})	DO (mg l^{-1})	Conductivity (μS)
Main stem (1)	44·2	3·85	12	21·2
Main stem (2)	58·7	3·85		23·2
Main stem (3)	60·9	3·93	13·4	21·0
Main stem (4)	88·0	3·71	11·6	30·0
Main stem (5)	82·7	4·35	10·2	25·0
East tributary (6)	204·3	5·36	13·1	41·5
East tributary (7)	71·9	3·75	9·3	27·8
East tributary (8)	123·8	4·77	9·5	29·5
West tributary (9)	147·0	3·80		42·4
West tributary (10)	127·8	5·71	11·2	32·6
West tributary (11)	316·1	7·13		53·0
West tributary (12)	222·5	3·52	12·9	34·1
Hyporheic (13)	83·7	3·44	10·9	24·4
Hyporheic (14)	112·0	3·50	7·7	27·6
Hyporheic (15)	52·7	3·79	0·7	22·5
Hyporheic (16)	92·7	4·07	1·2	27·7
Groundwater (17)	183·4	5·34	6	44·3
Groundwater (18)	181·6	5·03	11·8	42·8
Groundwater (19)	225·7	4·39	6·8	40·1
Groundwater (20)	250·4	4·82	7·4	42·4

The DO content of the samples, plotted once again against alkalinity, reveal more structure to the data (Figure 5b). The most well-oxygenated waters are the low alkalinity, main stem surface waters. Again surface water tributaries and groundwaters exhibit considerable scatter, although the highest alkalinity groundwater samples generally have the lowest DO. Hyporheic samples are again intermediate, although it is notable that certain samples have particularly low levels of DO. Although it is likely that temperature differences between the different source waters sampled has an important influence on DO solubility, this in itself reflects their different hydrological sources and flow paths. In general, the overall variation in DO was found to be greater than the temperature-related effect that might be expected from the relatively narrow natural temperature range of different source waters in the Feshie (e.g. ±3 mg l^{-1}).

These spatial differences in hydrochemistry highlight the various source areas in the catchment and their associated hydrological flow paths. Near-surface hydrological pathways in organic soils with short residence times in the upper catchments are consistent with the sources of the well-oxygenated, low alkalinity, low silica main stem river water. Surface water tributaries exhibit the hydrochemical influence of more variable geochemical conditions and hydrological source areas, as might be expected, given that many drain small headwater catchments (e.g sites 7–10, Table I). However, there are also some notable tributary flows entering the braids that have much higher alkalinity and silica concentrations (e.g. sites 6, 11 and 12), signifying greater influence of groundwater sources. Groundwater springs and seepage zones on the floodplain surrounding the braids exhibit a clear elevation in alkalinity and silica, but the lowest DO, reflecting the longer residence times and greater buffering in deeper drifts and bedrock. The intermediate alkalinity values for hyporheic waters sampled suggests a mixing of deeper groundwater with river waters, implying that upwelling groundwater in the central part of the floodplain mixes with river waters in the hyporheic zone.

Figure 6 shows selected samples collected in April 2002 plotted on a concentration map of the braided reach in order to emphasize the spatial pattern of hydrochemistry. Especially prominent is the high alkalinity groundwater emerging towards the edge of floodplain in marked contrast with the much lower alkalinity, central main stem samples. Intermediate of these, both spatially and in terms of alkalinity, are hyporheic

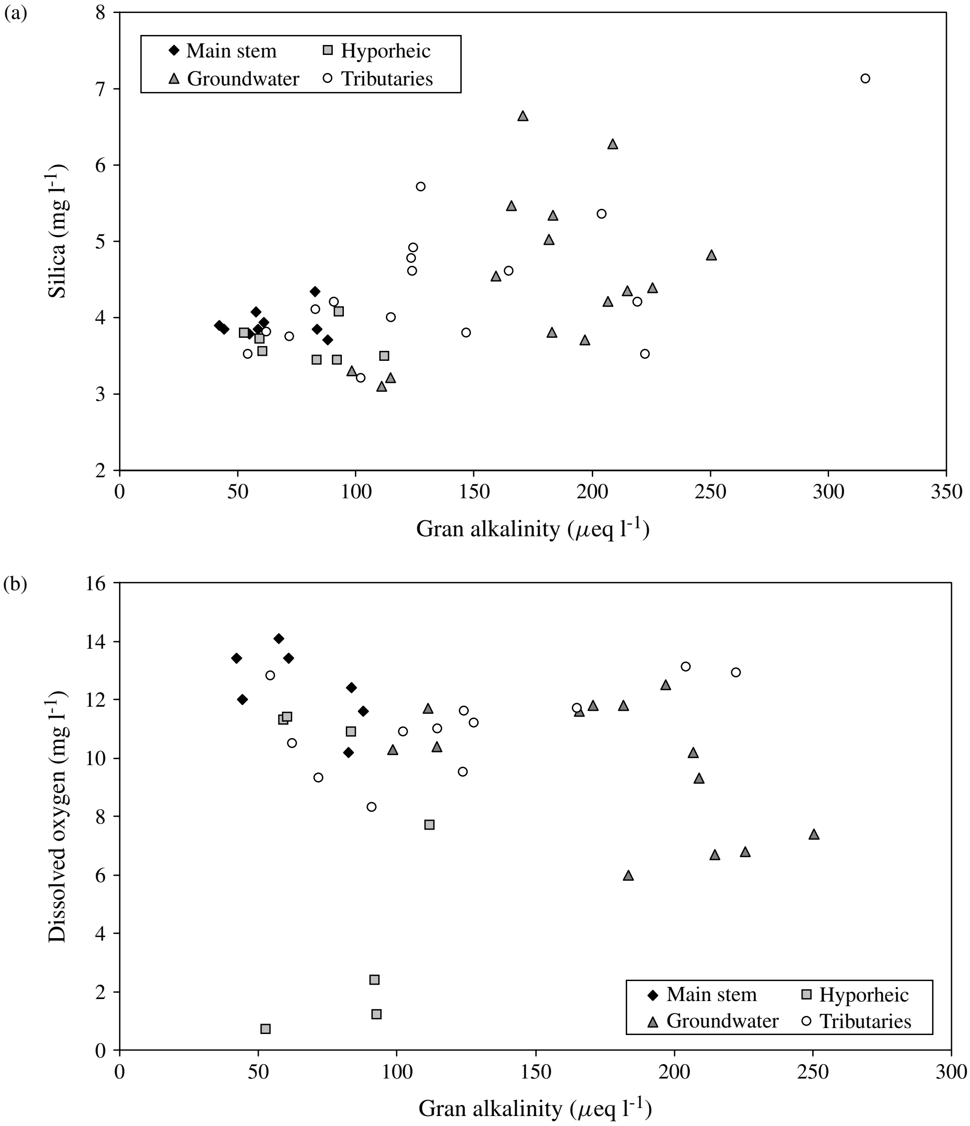

Figure 5. End-member chemistries for different source waters in the Feshie braids: (a) alkalinity against silica and (b) alkalinity against DO

waters emerging in partially dry channels that were disconnected from the main river channel when sampled. Also notable are the highly variable and elevated alkalinity, surface water tributaries. The overall buffering of stream-water alkalinity through the braids therefore can be seen to reflect the mixing of these various inputs.

GROUNDWATER–SURFACE-WATER INTERACTIONS

The more focused spatial survey in May 2002 highlighted more clearly some of the interactions between the alkalinity, silica and DO concentrations of surface, hyporheic and groundwaters through the Feshie's braided section. Four different sites were monitored, including a relatively small braid bar within the main stem of the river (see Figure 8), as well as a more extensive part of the floodplain encompassing the large alluvial fan

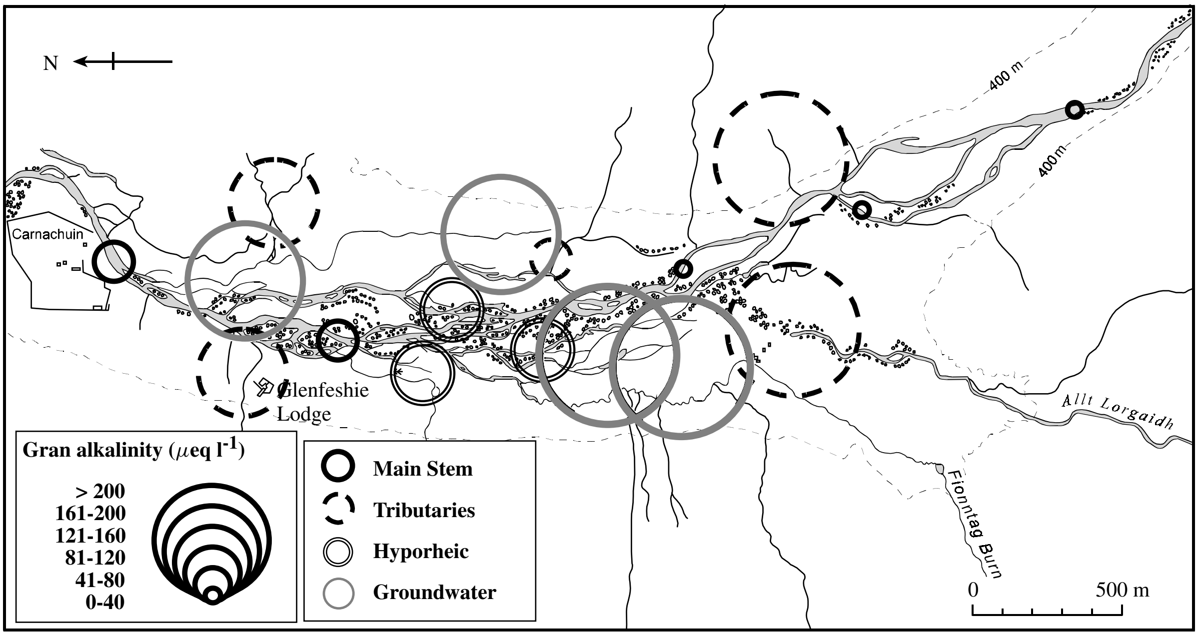

Figure 6. Spatial variation in alkalinity for selected sample sites in the Feshie braids: April 2002

of the Allt Lorgaidh tributary (Figure 7). It appears that the Lorgaidh effluent stream provides an important source of (shallow) groundwater recharge to the alluvial aquifer. This gives rise to a fairly extensive network of groundwater springs and seepages owing to localized topographic and hydraulic gradients. These flow alongside, and eventually mix with, hillslope tributaries, buffering their alkalinity. Also noteworthy is the pattern of increasing alkalinity and lower DO with proximity to the main stem (Figure 7a and b). This is consistent with the influence of upwelling groundwater with longer residences times from greater depths. This would corroborate the explanation of hyporheic hydrochemistry as resulting from the mixing of main stem river waters and deeper, upwelling groundwater in the hyporheic zone, beneath and fringing the river channel.

Figure 8 allows a more detailed examination of these hyporheic zone interactions and shows a typical hyporheic channel emerging on a braid bar and then mixing with a groundwater spring before entering the main stem of the Feshie. These samples highlight clearly the transitional chemistry of hyporheic flows in that they are initially low in alkalinity, indicating a dominance of main stem surface water (Figure 8a). However, as they flow through the hyporheic environment they are subject to increasing groundwater influence. These flows are then further buffered by high alkalinity groundwater spring flows before entering the main channel of the Feshie. Figure 8b shows DO concentrations for the same samples. Most evident is the rapid decline in DO in the first hyporheic sample compared with that for the main stem of the Feshie. The DO levels then increase as surface hyporheic flow accumulates. This is likely to reflect marked biological activity in the hyporheic zone, which rapidly consumes oxygen (Fowler and Death, 2001).

TRACER-BASED HYDROGRAPH SEPARATIONS

The utility of natural tracers, such as alkalinity, in assessing the relative importance of different hydrological sources in controlling stream hydrochemistry has been demonstrated already. End-member mixing was used to perform hydrograph separations for the upstream and downstream sampling sites to help quantify the observed groundwater inputs through the braided section. An integrated estimate of groundwater alkalinity was derived from the mean of three lowest flows sampled for each site (Neal, 1997) alongside two different estimates

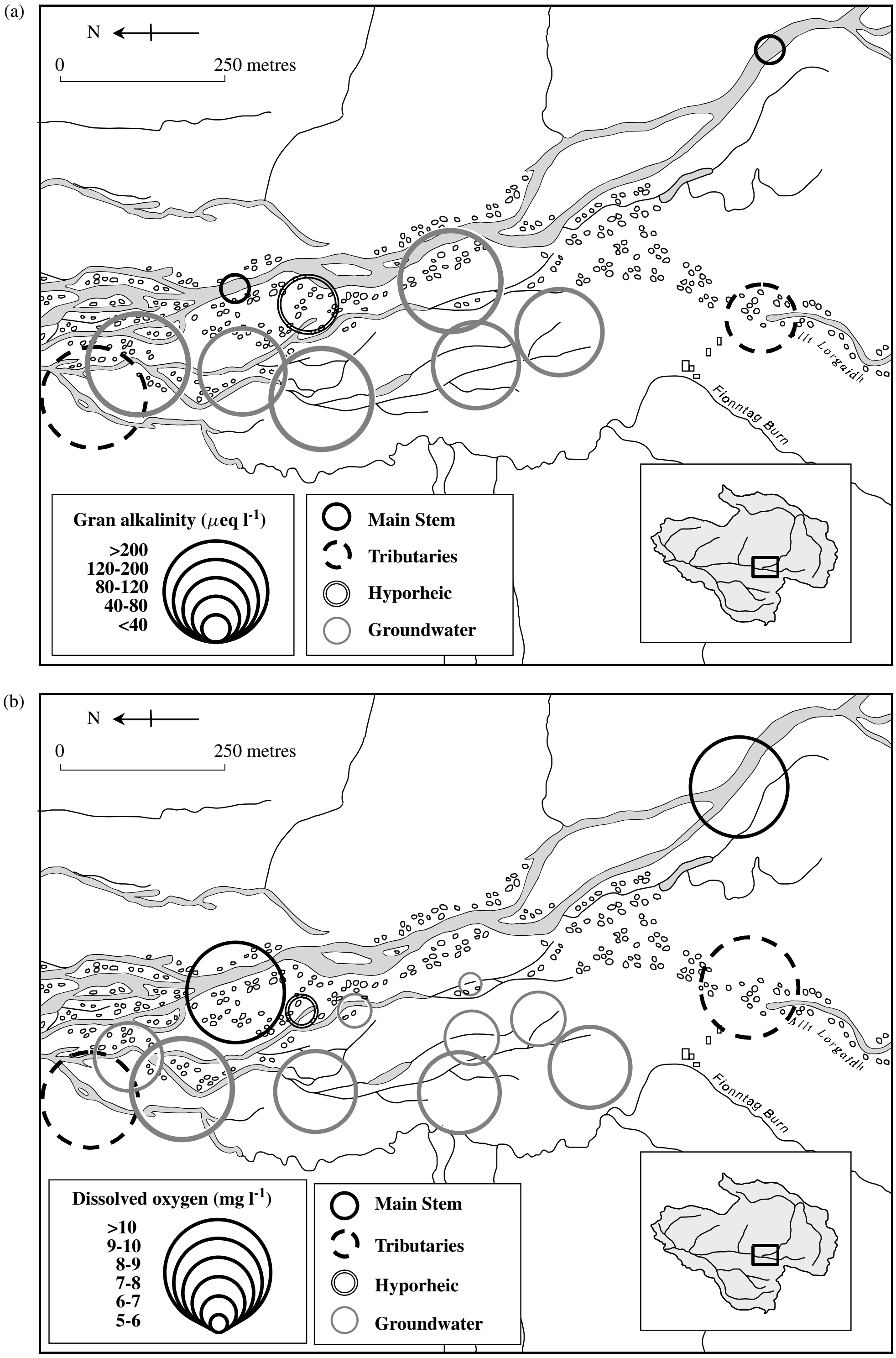

Figure 7. Spatial variation in (a) alkalinity and (b) DO for the Lorgaidh alluvial fan

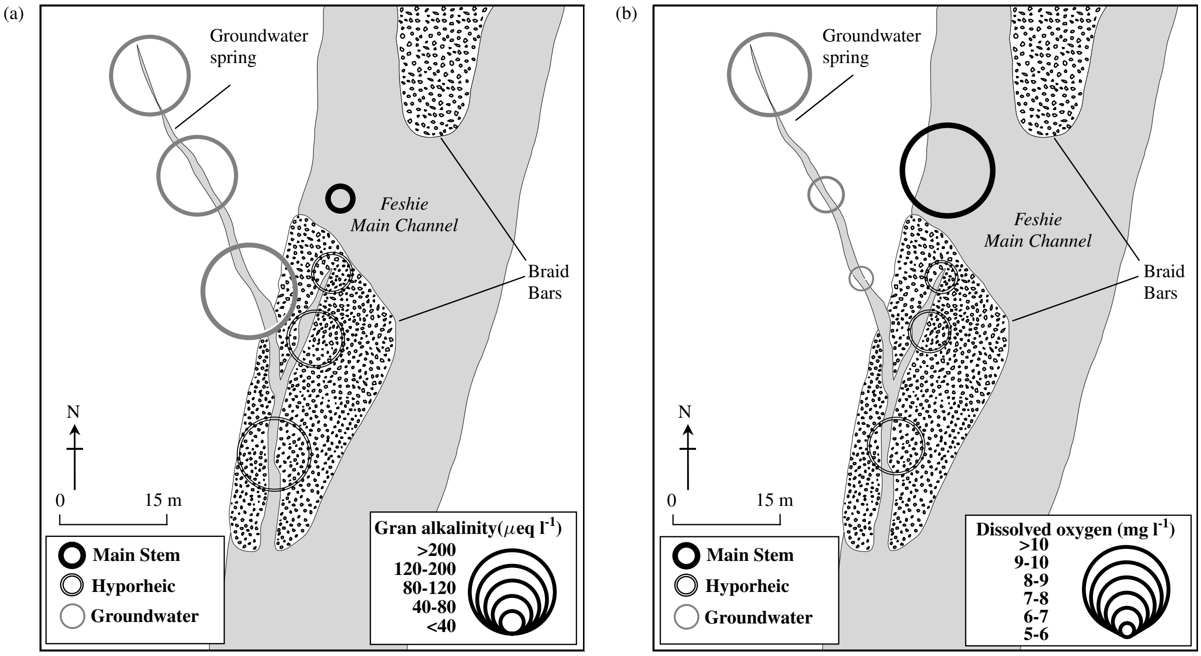

Figure 8. Spatial variation in (a) alkalinity and (b) DO for a main stem braid bar

of soil-water alkalinity (−48 and −25 μeq l^{-1}) that represent the mean of overland flow samples collected from the two dominant soil types, peats and shallow alpine soils respectively (Soulsby *et al.*, in press). These two soil types represent the main sources of storm runoff generation in the catchment and therefore provide an appropriate range of soil-water end members to assess the variability in groundwater contributions. The annual hydrograph was then separated according to a classic two-component mixing model

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

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

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

According to the resulting separations, at the upstream site, groundwater is modelled as contributing 31–37% of annual flows whereas some 4 km further downstream at the braids lowest extent, groundwater is estimated to account for 44–55% (Figure 9). Although only a relatively crude first approximation owing to the potential for end-member variability, these proportions seem to be consistent with the increased groundwater storage expected in the alluvial deposits of the braided section that appear to make significant and variable contributions to main stem surface waters.

DISCUSSION

This study clearly demonstrates the highly significant and dynamic influence that groundwater–surface-water exchange in the Feshie's braided section has on the hydrochemistry of surface waters flowing through it. This influence is temporally significant in response to seasonal variations in flow conditions over the

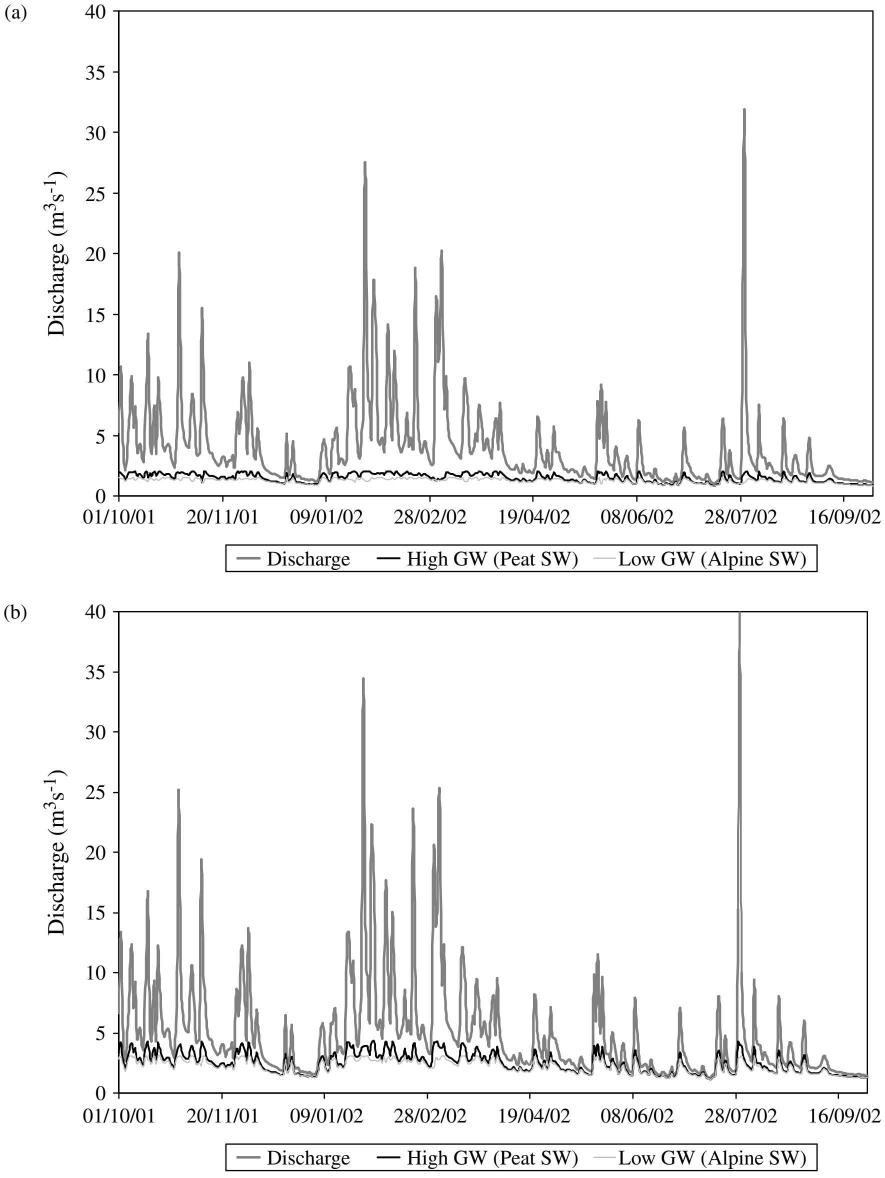

Figure 9. Hydrograph separations for (a) upstream of the braided section and (b) downstream

hydrological year as well as at the shorter, event scale and both provide valuable insight into the processes affecting the buffering of surface water hydrochemistry. In particular, upstream alkalinity, and therefore upstream–downstream change, is seen to be highly responsive to minor changes in flow. It would also appear that there is a relatively narrow high flow threshold beyond which upstream and downstream stream-water chemistries converge and any high-alkalinity groundwater inputs through the braids become insufficient to buffer stream-water alkalinity. This pattern can be mirrored at the lowest flows as high-alkalinity groundwater sources from the upper catchment dominate flows entering the braids, making them less susceptible to change. Moderate flows lead to the greatest contrast in alkalinity through the braids given the flow attenuation and hydrochemical buffering possible under such conditions.

In addition to the distinct temporal variability, groundwater–surface-water exchanges through the braids also displayed a significant spatial pattern. In particular, extensive shallow groundwater flow systems at the edge of the braided floodplain that are recharged by effective precipitation, hillslope inflows and effluent streams such as the Allt Lorgaidh, were seen to be highly significant. However, alkalinity and DO concentrations also indicated the presence of deeper, longer residence time groundwater upwelling closer to the main channel through the hyporheic zone, accounting for the more transitional chemistry of these waters.

The results demonstrate the utility of Gran alkalinity as an effective tracer in identifying clearly the different hydrological sources contributing to runoff through the Feshie's braided section. Furthermore, its conservative behaviour in this setting allows for estimates of contributions from different hydrological sources to be made, as in this study, using EMMA. Reasonable confidence can be attached to these estimates given the amount of detailed information on the spatial and temporal variability of these different hydrochemical sources built up over the intensive fieldwork detailed here. Thus, longer term, routine sampling throughout the hydrological year (Soulsby *et al.*, in press) and the detailed spatial surveys carried out in this study are increasingly feasible given the relative simplicity and low cost of the Gran alkalinity method. Unfortunately, it was not possible to attain the same coverage of silica samples in this particular instance given that silica measurements were only available in the latter stages of the research. This has therefore prevented it being used more fully in this study given the greater confidence in the Gran alkalinity data. Additionally, although as a generally unreactive solute, silica is commonly used to distinguish between different catchment hydrological source waters (Hoeg *et al.*, 2000), it can in certain situations be affected by biological uptake. Diatomaceous algae, for example, can exert an important impact on flux rates and concentrations of silica in lakes and streams and are also known to be abundant in the sediments of freshwater ecosystems. In upland Scottish rivers, though, it is not anticipated that there is sufficient level of diatom activity and any partial seasonal decline owing to diatom uptake would be expected only during summer months (Benzie *et al.*, 1991), when conditions are most suited to diatom growth. However, more data collection is clearly needed to further establish the utility of silica as a conservative tracer in this setting and to allow it to complement and validate the Gran alkalinity information more fully.

The significant findings regarding the quality of stream flows through the braided section also raise some important hydroecological implications. The Feshie braids are an important area for Atlantic salmon spawning, where eggs are laid in redds (or nests) in the river gravels in the autumn for juvenile fish to emerge the following spring. To survive, the eggs must be subject to well-oxygenated and circumneutral waters in the hyporheic zone for a period of around 6 months (Malcolm *et al.*, 2003b). Acid waters are detrimental to salmonids generally, and in particular to fish eggs (Harriman *et al.*, 1990). The success of spawning and the maintenance of healthy salmon populations in the Feshie braids therefore may be influenced by the discharge of alkaline groundwater through the river bed to buffer the acidity of the hyporheic zone, given the strongly acidic, negative alkalinity, high flows that can occur in the Feshie.

More generally, the dynamic morphology of braided rivers such as the Feshie, with frequent channel changes and cycles of inundation and drying of side channels, creates a dynamic, physico-chemical environment that probably exerts a profound impact on stream ecology and biodiversity (Fowler and Death, 2001; Robinson *et al.*, 2002). The shift from well oxygenated, acidic and effluent streams feeding the braided channels at high flows to deoxygenated, alkaline groundwater creates a diverse range of habitats, with obvious implications for aquatic organisms (Fowler and Scarsbrook, 2002). The work detailed here therefore may provide a useful basis for future research into the structure and stability of hyporheic communities within the Feshie's braided section in response to these hydrochemical changes given that there has been no published research in this area to date.

In addition to its hydroecological importance, it is clear that the Feshie's extensive braided section represents an integral control on the overall hydrological and hydrochemical functioning of the catchment. In terms of the former, floodplain storage and subsequent discharge moderates most flood events, whereas groundwater sustains low flows. In terms of hydrochemical functioning, the loss of DO implies rapid carbon processing and respiration by organisms in the hyporheic zone. While the results presented here are preliminary, they clearly point to the need for further investigation. Ongoing work is being conducted to assess the changes in flow through the braids, with flow gauging being carried periodically at the upstream and downstream sites as part of more general hydrometric work in the catchment. This should give some idea of the potential for flood attenuation/bank recharge relative to the expected area increase in flow. Furthermore, as part of the CHASM project, boreholes and peizometers are to be used to provide a more detailed assessment of the effect of groundwater–surface-water exchange on the quantity and quality of surface flows. Moreover, it is also hoped that the initial tracer-based attempts to identify and model groundwater–surface-water interactions detailed in this study will contribute to future application at the wider mesoscale, a major research aim within the CHASM initiative.

ACKNOWLEDGEMENTS

The authors are grateful to NERC for funding this work through the CHASM initiative and a studentship for PJR (award reference GT 4/00/02/). Glen Feshie Estate is thanked for providing access and other support to the work, and David Duncan and colleagues at Scottish Natural Heritage have kindly issued permits to carry out the research. The assistance of Maureen Lamb for laboratory analysis and Jenny Johnston and Alison Sandison for cartographic presentation is gratefully acknowledged. Finally, Paul Younger is thanked for providing the original inspiration for this study.

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