

Hydrogeochemistry of montane springs and their influence on streams in the Cairngorm mountains, Scotland

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Abstract

Springs are important groundwater discharge points on the high altitude (>800m) plateaux of the Cairngorm mountains, Scotland and form important wetland habitats within what is often a dry, sub-arctic landscape. The hydrogeochemistry of a typical spring in the Allt a' Mharcaidh catchment was examined between 1995–98 in order to characterise its chemical composition, identify the dominant controls on its chemical evolution and estimate groundwater residence time using ¹⁸O isotopes. Spring water, sustained by groundwater flow in shallow drift deposits and fractured bedrock, was moderately acidic (mean pH 5.89), with a very low alkalinity (mean 18 $\mu\text{eq l}^{-1}$) and the ionic composition was dominated by sea-salts derived from atmospheric sources. Geochemical modelling using NETPATH, predicted that the dissolution of plagioclase mainly controls the release of Si, non-marine Na, Ca, K and Al into spring waters. Hydrological conditions influenced seasonal variations in spring chemistry, with snowmelt associated with more rapid groundwater flows and lower weathering rates than summer discharges. Downstream of the spring, the chemistry of surface waters was fundamentally different as a result of drainage from larger catchment areas, with increased soil and drift cover, and higher evaporation rates. Thus, the hydrogeochemical influence of springs on surface waters appears to be localized. Mean $\delta^{18}\text{O}$ values in spring water were lower and more damped than those in precipitation. Nevertheless, a sinusoidal seasonal pattern was observed and used to estimate mean residence times of groundwater of around 2 years. Thus, in the high altitude plateau of the Cairngorms, shallow, coarse drift deposits form significant aquifers. At lower altitudes, deeper drift deposits, combined with larger catchment areas, increase mean groundwater residence times to >5 years. At high altitudes, the shallow, permeable nature of the drifts dictates that groundwater is vulnerable to impacts of environmental changes that could be usefully monitored at spring sites.

Introduction

The Cairngorm mountains in northern Scotland comprise the largest high altitude area in the British Isles with upland plateaux forming an extensive area of land above 1000m altitude (Gordon *et al.*, 1998). High altitude springs (above 800 m) are common in the Cairngorms; these are found at zones of perennial groundwater discharge from shallow aquifers comprised of various glacial and periglacial deposits (Soulsby *et al.*, 1998). These springs are thought to be recharged by the substantial volumes of meltwater released from the ablation of large winter snowpacks (Rodwell, 1991; Soulsby *et al.*, 1997a, 1999a). The springs are an extremely important and distinct component of the functional ecology of montane habitats in the Cairngorms (Gordon *et al.*, 1998). The mountain plateaux

are characterised by freely draining regosols, and experience high wind speeds (frequently in excess of 40 m s^{-1}) and sub-zero temperatures for much of the year (Nethersole-Thompson and Watson, 1981). Thus, moisture is often limiting and the springs form wetland habitats for a number of rare plants such as the moss *Pohlia wahlenbergii* var. *glacialis* (McVean and Ratcliffe, 1962; Rodwell, 1991). Moreover, these wetter areas support a range of invertebrates which provide a major food resource for many of the arctic bird species that contribute to the conservation value of the Cairngorm region (Thompson and Whitfield, 1993).

The hydrological and ecological importance of high altitude springs is by no means unique to the Cairngorms; the presence of highly fractured rocks and shallow drifts that characterise many temperate mountain regions creates

similar conditions for both perennial and ephemeral groundwater discharge areas (Hill and Neal, 1997; Hudson and Golding, 1997; Decker *et al.*, 1998). Consequently, in addition to their ecological value, springs can contribute significantly to the quantity and quality of streamflows in headwater areas that often support public water supplies further downstream. Despite this, Leibundgt (1998) notes that shallow upland aquifers with poor soil cover and short transit times render springs vulnerable to the effects of atmospheric air pollutants, such as acidic oxides and heavy metals, and of climate change. There is growing recognition that holistic investigations of groundwater-surface water interactions at high altitude spring-fed wetlands can be diagnostic tools to examine the environmental sensitivity of mountain landscapes (Williams, 1991; Cantonati and Ortler, 1998). Unfortunately, the remoteness of many areas and resource constraints dictate that such studies are relatively scarce.

Recent research has indicated that groundwater resources in upland areas in the British Isles are often larger and more extensive than previously realized (Edmunds and Savage, 1992; Jenkins *et al.*, 1994; Neal *et al.*, 1997). More specifically, hydrogeochemical studies have shown that groundwater contributions to streamflows in the Cairngorms are substantial at both high and low flows (Soulsby *et al.*, 1998; Wade *et al.*, 1999). Recent developments in the application of stable isotope tracers such as oxygen-18 (^{18}O), have also been shown to be extremely useful in catchment hydrology in identifying water flow paths and estimating residence times in major water stores (Kendall *et al.*, 1995; Soulsby *et al.*, 1999a, In press). In this study, such hydrogeochemical techniques are applied in order to examine in more detail the hydrological and hydrochemical processes influencing shallow springs in the Allt a' Mharcaidh catchment in the Cairngorms. Specifically, the objectives of the paper are to; (i) characterise the seasonal features of spring water chemistry and assess the effect on surface waters further downstream, (ii) identify the main controls on the evolution of spring water using the hydrogeochemical code NET-PATH and (iii) apply stable isotope tracers to identify the recharge mechanisms and residence time of water in high altitude aquifers. The significance of the findings are then discussed in relation to the sensitivity of upland water resources to environmental change such as acid deposition, climate change, overgrazing and recreational pressure, all of which are important in the Cairngorm region (Conroy *et al.*, 1990; Watson, 1990; Soulsby *et al.*, 1997a; Dunn, and Langan, 1997)

Study area

The Allt a' Mharcaidh drains a 10 km² experimental catchment on the western side of the Cairngorm mountains, which ultimately discharges into the river Spey (Fig. 1).

The catchment spans an altitudinal range from 320 m at the gauging station to 1111 m at the summit of Sgoran Dubh Mor, and is underlain by an intrusive biotite granite associated with the later stages of the Caledonian Orogeny. The dominant minerals that comprise the granite are plagioclase, K-feldspar, biotite, chlorite, kaolinite and quartz. The granite is covered by a variety of locally-derived drift deposits ranging from glacial boulder fields to moraines and gelifluction deposits (Gordon *et al.*, 1998). At high altitudes (> ca. 800 m), these drifts tend to be shallow (<5 m) and relatively coarse. In the lower parts of the catchment, colluvial processes have resulted in much deeper accumulations of relatively fine drift which may exceed 10 m. Although a massive rock, the upper granite is weathered and dense networks of fractures are present where the granite is exposed. It is believed that this results from deep chemical weathering during the Tertiary, though in places the weathered granite has been exposed by successive glaciations and the weathered regolith has been incorporated into various drift deposits.

At high altitudes, poorly developed alpine podzols are the dominant soils; these lie on top of the freely draining drifts and shattered bedrock which characterise the higher altitude plateau of the Cairngorm region. Many small springs are present at these high altitudes (>800 m) where groundwater re-emerges at discharge sites which may be perennial or ephemeral (Rodwell, 1991). Around the spring discharge points, rich bryophyte and vascular plant assemblages are found dominated by species such as *Pohlia wahlenbergii* var. *glacialis*, *Deschampsia cespitosa* and *Saxifragia stellaris* (Rodwell, 1991); such sites generally form the source of first order streams draining from the high altitude plateaux. At lower altitudes, the deeper drift deposits are usually less freely draining and are overlain by more mature soil profiles, with peaty podzols covering steeper slopes and deep peats mantling flatter valley bottom areas (Soulsby *et al.*, 1999b). A narrow band of alluvial soils fringes the main stream channel of the Allt a' Mharcaidh where it has incised into various valley bottom drifts. The main vegetation assemblages reflect these soil-topographic units; with lichen-*Azalea* heaths mantling the alpine soils, northern blanket bog vegetation characterising the peats and lichen-rich boreal heather (*Calluna*) dominating the peaty podzols. Like much of the Cairngorm region, the semi-natural habitats in the catchment are primarily managed for nature conservation and are part of a proposed National Park. However, most of the Cairngorms are in private ownership and have been managed as part of highland estates for sporting interests, particularly shooting. Consequently, red deer populations in the area are maintained at un-naturally high levels. However, the mountain area is also being increasingly used for various recreational pursuits including climbing and hillwalking.

Mean annual precipitation in the Allt a' Mharcaidh catchment is around 1,200 mm, with as much as 40% of this falling as snow during the winter (Soulsby *et al.*,

1997). Mean monthly temperatures (at 575 m) range from 1.2 °C in February to 10.3 °C in July. The mean daily flow of the catchment at the G1 gauging station is approximately 0.25 m³ s⁻¹, giving a mean annual runoff of ca. 800 mm, with annual evaporation estimated at around 350 mm (Soulsby *et al.*, 1999b). Low flows fall below 0.1 m³ s⁻¹, whilst flood peaks may exceed 15 m³ s⁻¹. The annual hydrograph reflects the importance of snowmelt, with March generally being the month with the highest mean daily flow, whilst June and July experience the driest conditions and lowest streamflows (Dunn and Langan, 1998). Hydrogeochemical and hydrometric analysis has shown that, over the course of the year, groundwater sources account for 40–50% of streamflows, whilst near-surface hydrological pathways in peaty soils are the main sources of storm runoff (Soulsby *et al.*, 1998).

Methodology

The extensive data collection programme in the Allt a' Mharcaidh has been described elsewhere (Ferrier and Harriman, 1990; Soulsby *et al.*, 1999b). The key data collected as part of this project was gathered between March 1995 and April 1998. Spring water was collected at fortnightly intervals from the site G4 in a groundwater discharge zone at an altitude of 970 m. Observations since 1985 show that the spring is perennial and drains a hillslope mantled with various coarse, shallow drift deposits that are subject to freeze thaw action (Soulsby *et al.*, 1998). Unfortunately, the remoteness of the spring and resource constraints prevented continuous flow measurement at the site. Nevertheless, the spring effectively forms the source of one of the major tributaries of the Allt a' Mharcaidh and spot gaugings show that flows range from <5 l s⁻¹ in summer to > 50 l s⁻¹ in the late spring/early summer when snowmelt is occurring. The tributary was also sampled at G3 approximately 1.5 km further downstream at an altitude of 530 m where its catchment area is some 2.96 km². Weekly samples were also collected from the Allt a' Mharcaidh gauging site at G1 (altitude of 330 m) as part of long-term monitoring. In addition, precipitation was collected at 4 sites around the catchment, with rainfall (bulk deposition) being collected throughout the year and additional snow samples being collected during the winter months. Precipitation samples were usually collected fortnightly, though severe winter weather sometimes resulted in a 3 week interval. All samples were analysed for pH, alkalinity and major cations and anions, as well as having the oxygen isotope (¹⁸O/¹⁶O) ratio being measured. Charge balance was carried out on all samples that were used for geochemical modelling and showed less than 5% difference between anions and cations. This was important to ascertain as the geochemical modelling package is based on a mass balance approach. All analyses were carried out according to standard procedures at the laboratories of the Macaulay Land Use Research Institute in Aberdeen.

Ratios of ¹⁸O/¹⁶O are expressed on delta units δ¹⁸O parts per mille (‰) defined in relation to SMOW (standard global mean ocean water) (Craig, 1961a,b). Hydrometric data from the catchment automatic weather station (AWS) and gauging station (G1) were also used for precipitation and streamflow measurements.

The NETPATH computer code was used to model the major hydrogeochemical reactions contributing to the evolution of spring water chemistry over the year. The model is described in detail by Plummer *et al.* (1991). Briefly, it is an interactive code that reconstructs mass balance reactions to identify possible geochemical processes that are consistent with the evolution of the water chemistry observed between two or more points along a flow path. The model can be constrained by identifying minerals and processes that are thought/known to be important at a particular site. Typically a range of models is produced by NETPATH from which it is usually possible to identify the most feasible prediction on the basis of thermodynamic and kinetic considerations. Despite limitations in this modelling approach (see Appelo and Postma, 1993; Drever, 1997) it can provide a useful insight into the probable processes governing groundwater chemistry (Chen *et al.*, In press; Soulsby *et al.*, 1998; Malcolm and Soulsby, In press).

Seasonal trends in δ¹⁸O values were modelled in precipitation and groundwater using sine functions of appropriate amplitude and frequency for the three study years between 1995–98. Details of the technique are given by Dewalle *et al.* (1997) and only a brief description follows. Periodic regression analysis was used to fit a seasonal sine wave model to annual δ¹⁸O variations as;

$$\delta^{18}\text{O} = X + A [\cos(ct - \theta)] \quad (1)$$

where δ¹⁸O is the predicted oxygen-18 level in ‰, X is the mean annual value in ‰, A is the δ¹⁸O annual amplitude in ‰, c is the radial frequency of annual fluctuations, t is the time in days after the start of the period under investigation, and θ is the phase lag or time of the annual peak oxygen-18 values in radians.

Mean residence times for water to move through the groundwater system were also estimated using a simple steady-state, well-mixed model in which precipitation is assumed to mix rapidly with resident water in major catchment stores (Maloszewski *et al.*, 1993; Stewart and McDonnell, 1991). The model assumed that the decrease in the amplitude of outputs relative to inputs provides a basis for determining residence times (Unnikrishna *et al.*, 1995). Thus, sine waves are fitted to input and output water δ¹⁸O concentrations and an exponential distribution of transit times is assumed. The mean residence time (T) or the mean age (in years) of water leaving the system is calculated as;

$$T = c^{-1}[(Az2/Az1)^{-2} - 1]^{0.5} \quad (2)$$

where $Az1$ is the amplitude of the initial water and $Az2$ is the amplitude of the resulting water. Given the simple

nature of the model, the size and complexity of the Allt a' Mharcaidh catchment and data limitations (particularly for precipitation inputs), the results were taken only as indicating residence time to a first approximation (Unnikrishna *et al.*, 1995). Nevertheless, studies elsewhere suggest that the model should be reasonable for such preliminary assessment in montane catchments (Maloszewski and Zuber, 1993).

Results

HYDROGEOCHEMICAL CHARACTERISTICS OF SPRING WATER

The ionic concentrations measured in the spring are low and are indicative of shallow groundwater circulation (Edmunds and Savage, 1992). Groundwater discharging from the spring at G4 was enriched in most elements compared to precipitation (Table 1). The mean pH of spring

water was 5.87 compared with 4.88 for precipitation. In both precipitation and spring water, ions derived mainly from marine sources, Na and Cl, form the dominant cation and anion respectively (Fig. 2). Despite enrichment of weathering-derived elements such as Si, excess-Na and Mg, Fe and Al, concentrations are very low and alkalinity generation is extremely limited at $18 \mu\text{eq l}^{-1}$. Chloride concentrations are similar to those measured in precipitation, probably reflecting low evaporation rates at high altitudes, where soils are freely draining and short, patchy vegetation cover minimizes interception and transpiration rates. The SO_4 enrichment in spring water probably reflects enhanced inputs in occult and dry deposition at high altitudes, particularly on winter snowpack surfaces (Helliwell *et al.*, 1998). Concentrations of N, both as $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$, are very low in springwater, and below detection for much of the year. It does appear, however, that some atmospheric N is retained within the vegetation and soils of the spring catchment, particularly as bulk precipitation

Table 1. Mean and range (in brackets) of spring water chemistry ($\mu\text{eq l}^{-1}$), along with that of streamwater in G1 and G3 and precipitation 1995–98.

	Precipitation	Spring (G4)	G3 stream	Allt a Mharcaidh (G1)
pH	4.88 (3.97–5.91)	5.87 (4.93–7.00)	5.93 (5.12–6.51)	5.97 (5.01–6.83)
Alkalinity	–1 (–3–0)	18 (20–54)	36 (22–85)	59 (24–117)
Cl	64 (1–283)	64 (51–90)	83 (50–216)	98 (63–165)
SO_4	21 (2–122)	41 (37–79)	43 (27–68)	44 (27–67)
$\text{NO}_3\text{-N}$	3 (0.3–16)	3 (<1–9.4)	2 (<1–13.6)	2 (<1–12)
$\text{NH}_4\text{-N}$	6 (1–76)	4 (<1–114)	3 (<1–85)	1 (<1–11)
Na	56 (1–247)	79 (67–91)	106 (70–207)	132 (85–180)
K	2 (1–44)	4 (1–4)	4 (2–7)	6 (3–12)
Ca	8 (1–44)	17 (12–23)	30 (12–21)	43 (28–62)
Mg	13 (1–57)	17 (11–19)	25 (17–59)	29 (21–47)
Si	—	240 (179–272)	300 (129–395)	393 (155–540)
Al	—	4 (0.6–11)	6 (1–39)	8 (1–42)
Fe	— (0.04–3)	0.1 (0.04–1.81)	0.2 (0.04–2.6)	0.4

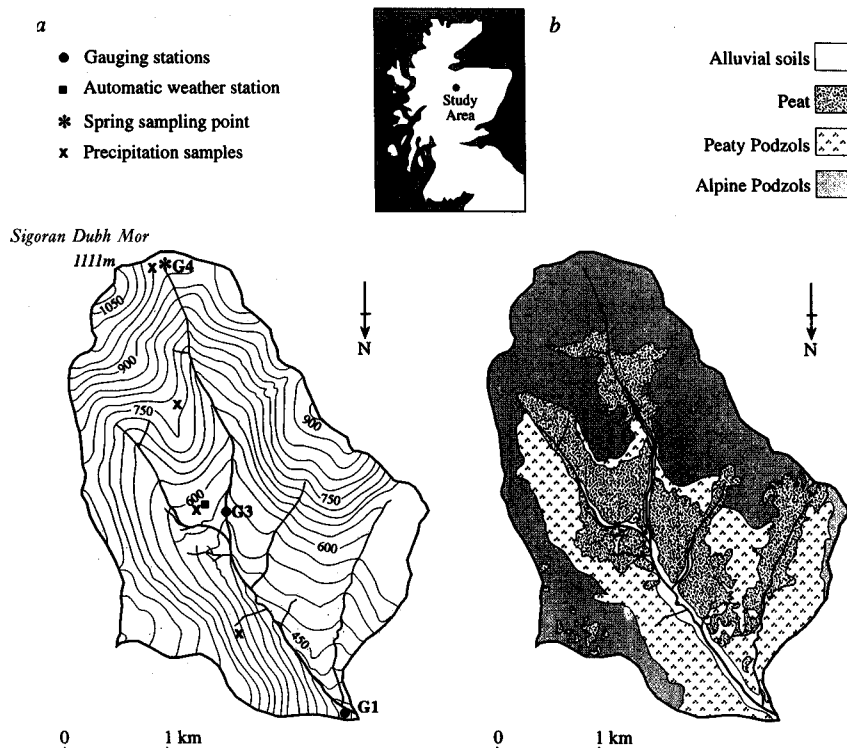


Fig. 1. Allt a' Mharcaidh catchment showing (a) topography and main sampling points and (b) soil distribution.

collectors will underestimate dry and occult inputs (Helliwell *et al.*, 1998). Highest concentrations of N species tend to occur during the snowmelt period where preferential elution has been observed (Jenkins *et al.*, 1993).

HYDROGEOCHEMICAL CHARACTERISTICS OF STREAMWATER

Downstream of the spring, stream water chemistry at G3 and G1 reflect additional hydrological inputs from acidic soil waters and deeper groundwaters, which enhance many of the patterns observed at G4 (Fig. 2 and Table 1). Thus, the mean concentrations of weathering derived ions increased by as much as 50% and alkalinity generation was significantly greater (approximately 200% increase) though still modest. This presumably reflects the higher temperatures, larger catchment area and increased water residence times that would be anticipated as one moves downstream. Average Cl concentrations increased by almost a third at G3, which would be consistent with increased evaporation rates in the lower catchment. Sulphate levels increased only slightly downstream, despite likely increases in evaporation, probably reflecting the decrease in atmospheric inputs with decreasing altitude. Similar patterns of change were observed between G3 and G1, though a reduction in N species was observed at G1 which may reflect lower inputs or greater retention in the lower catchment.

In addition to these spatial differences, spring water exhibits a much less variable chemistry compared to surface water at G1 and G3 (Figs. 2 and 3). This appears primarily to reflect the more complex hydrological pathways that occur as the catchment size increases, and soil and drift cover change. Thus, at the catchment (G1) and sub-catchment (G3) scale, runoff during storm events is generated mainly by near-surface hydrological pathways in peaty soils that reduce the alkalinity of streamwaters as well as diluting most other species (Wheater *et al.*, 1991, 1993; Ogunkoya and Jenkins, 1993). The decrease in alkalinity is particularly evident in the Piper diagram in Fig. 2. In contrast, baseflows are derived mainly from deeper groundwater sources which have a more constant chemistry with higher concentrations reflecting the longer residence times (Soulsby *et al.*, 1998). Thus spring discharges, though responsive to precipitation events (particularly snowmelt) are less flashy than streamwaters and are attenuated by the nature of deeper flow paths through coarse drift material. Consequently, a much more stable chemical composition appears to result. However, these comments are tentative in the light of the under-representation of samples during the spring snowmelt period when inaccessibility or avalanche risk precluded sample collection (*cf.* the spring period of 1995 and 1996 in Fig. 3), though samples from 1997 and 1998 appear to support this view.

The time series plots in Fig. 3 show the increasing concentrations moving downstream, particularly for Cl, Si and

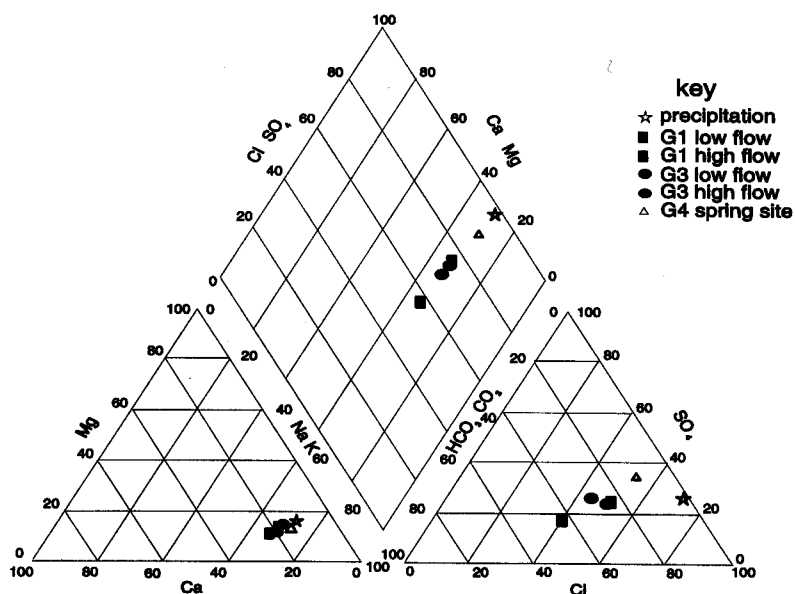


Fig. 2. Piper diagram showing the composition of spring water in the Allt a' Mharcaidh in relation to precipitation and streamwater chemistry at G1 and G3 at high ($> Q_{10}$) and low ($< Q_{95}$) flows.

Ca. Seasonality is much more pronounced for Si and Ca in stream waters presumably reflecting the seasonal switch between summer baseflows and winter storm events though some instream biological influence on Si may occur. Nevertheless, spring waters do exhibit some seasonality with low Si concentrations in February 1997 during the melt period when the low temperatures and presumably shorter residence times reduce weathering rates. Higher concentrations subsequently occurred later in the summer. The variability of SO_4 reflects preferential elution in the snowmelt period, particularly in 1995/96 when high concentrations were observed. However, variability was generally damped and SO_4 concentrations increased slightly downstream probably reflecting evaporation effects.

MODELLING THE HYDROGEOCHEMICAL CONTROLS OF SPRING WATER CHEMISTRY

The evolution of springwater chemistry was examined using the NETPATH model. Precipitation inputs were compared with spring water outflows during the autumn (Sept–Nov), winter (Dec–Feb), spring (Mar–May) and summer (Jun–Aug) periods. The model was constrained by examining only the weathering derived elements Si, Al, Ca, Mg, Na and K. In addition, the main mineral phases known to be important in Cairngorm granite were identified as plagioclase, K-feldspar, biotite and kaolinite. Although these phases were specified, none was forced in the simulations.

Very low weathering rates were predicted by the model, consistent with the low solute concentrations observed in spring water (Fig. 4). The model predicts that plagioclase

weathering is by far the most dominant control on the release of elements, with only minor contributions from K-feldspar and biotite. Kaolinite was predicted as being the main weathering product being precipitated within the aquifer. Seasonal NETPATH simulations predicted that weathering rates are approximately 15–30% higher during the summer and autumn, compared to winter and spring. This appears to reflect hydrological and climatic differences with more rapid rates of groundwater throughput and colder temperatures during the winter period, even when snowmelt is occurring at relatively higher temperatures. Overall, the low mineral dissolution rates probably reflect the dominance of relatively insoluble minerals resulting from the long history of weathering since the Tertiary, cold temperatures and the coarse nature of the drifts.

ISOTOPE HYDROLOGY OF SPRING AND STREAMWATERS

The $\delta^{18}O$ values measured in spring water were extremely damped compared with those of precipitation (Table 2 and Fig. 5). As anticipated, spatially averaged precipitation $\delta^{18}O$ values (which showed no consistent spatial variation) exhibited a roughly sinusoidal pattern, with water enriched in ^{18}O dominating summer precipitation, whilst winter snow inputs were depleted in ^{18}O , in agreement with Dansgaard (1964). In comparison, the oxygen-18 content of spring waters varies little throughout the year implying a well-mixed groundwater source (McDonnell *et al.*, 1991). However, higher $\delta^{18}O$ values reflect more enriched, well-mixed water discharging during the summer and autumn, whilst isotopically depleted water was observed

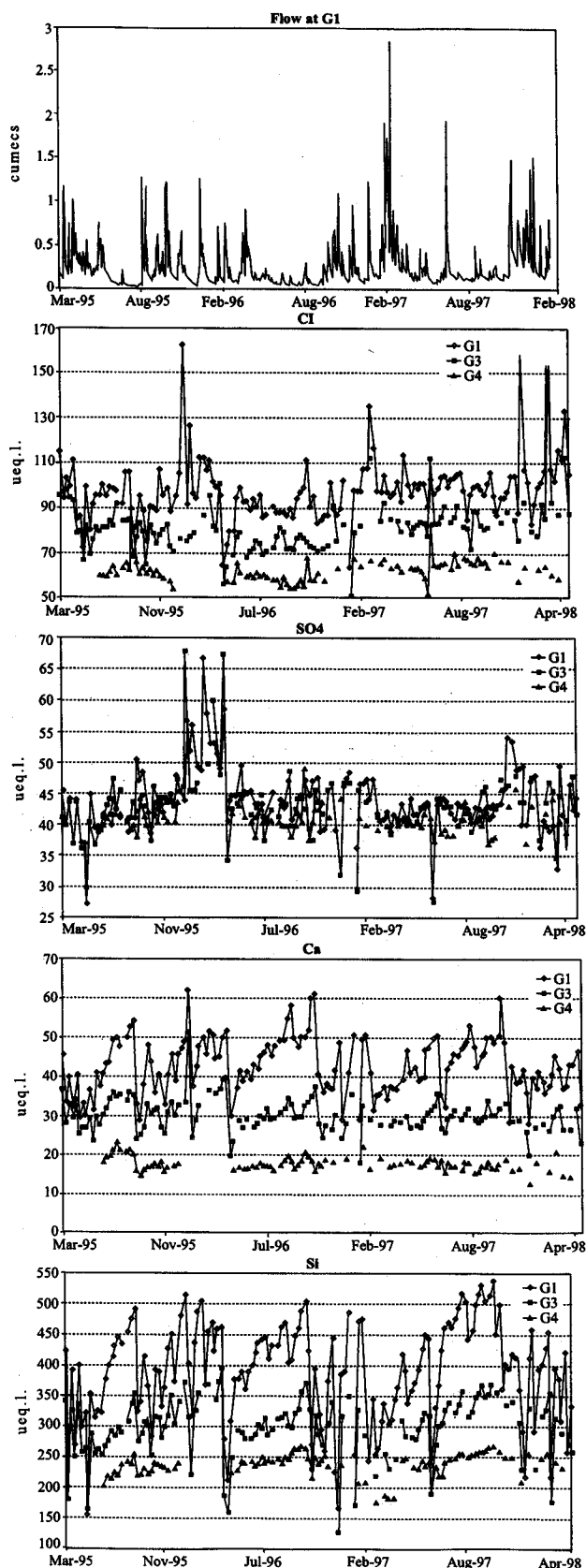


Fig. 3. Time series plots of (a) flow, (b) Cl (c) SO₄, (d) Ca and (e) Si in spring water and stream water at G1 and G3 in the Allt a Mharcaidh catchment 1995-98.

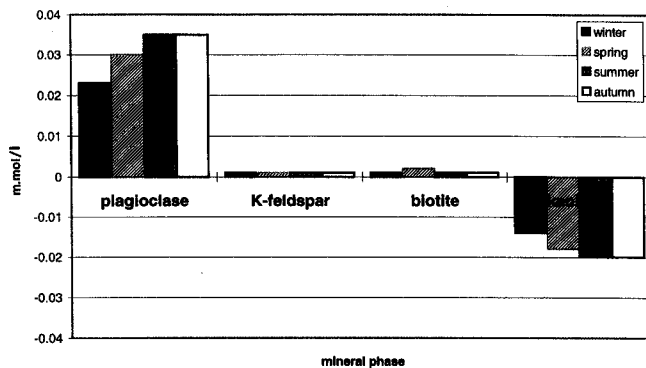


Fig. 4. NETPATH predictions of seasonal mineral dissolution/precipitation rates (mmol l⁻¹) controlling the hydrogeochemistry of spring waters.

during the late winter and early spring. Again this is consistent with snowmelt recharging the shallow aquifers in the drift, resulting in less thorough mixing. The isotope values of spring water are much closer to those of winter precipitation throughout the year, implying that most recharge is facilitated by winter rainfall and snowmelt.

Compared to the damping and limited range in $\delta^{18}\text{O}$ values at G4, $\delta^{18}\text{O}$ values in stream water at both G3 and G1 are more variable (Table 2 and Fig. 5). This is consistent with a more attenuated groundwater response to hydrological events at G4, and the more dynamic mixing of groundwater and soil water sources in storm event runoff in G1 and G3 (Soulsby *et al.*, 1999a). Nevertheless, $\delta^{18}\text{O}$ values in G1 and G3 baseflows exhibited even less variability than G4, indicating an extremely well-mixed groundwater source in the lower catchment.

These seasonal patterns of $\delta^{18}\text{O}$ values were used to estimate the mean residence time of groundwater for each individual year by fitting a sine-wave to the annual cycle

Table 2. Mean, maximum and minimum $\delta^{18}\text{O}$ (‰) values for precipitation, streamwaters and springwaters in the catchment 1995-98 (baseflow = flow <0.10 m³ s⁻¹).

	Mean	Min	Max
PRECIPITATION			
Summer rainfall	-6.82	-16.04	-2.47
Winter snow	-8.84	-20.93	-4.55
GROUNDWATER			
G4 Spring	-9.19	-9.74	-8.86
G3 baseflow	-9.46	-9.83	-8.99
G1 baseflow	-9.44	-9.69	-9.16
STREAMWATER			
G3	-9.61	-10.55	-8.43
G1	-9.28	-10.44	-8.45

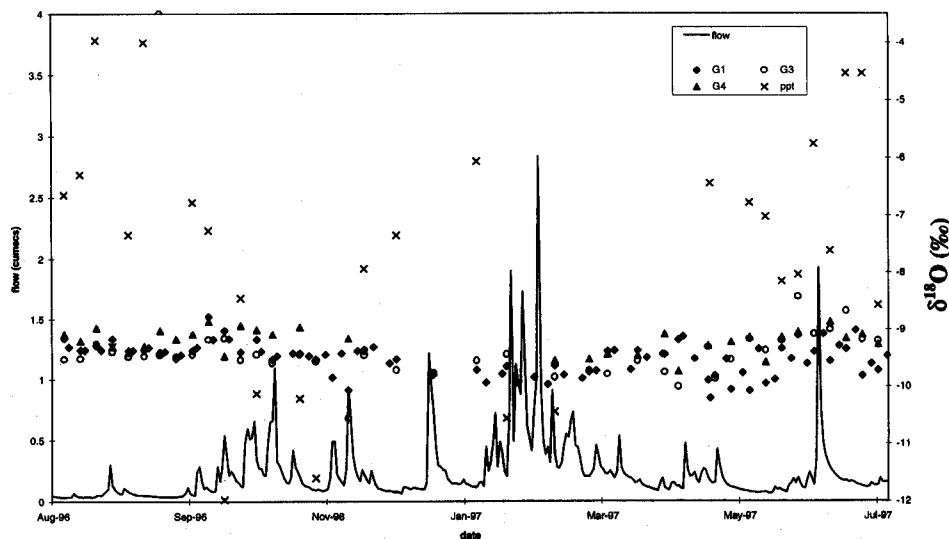


Fig. 5. Oxygen-18 variations in G1, G3 and G4 in the hydrological year 1996–97.

(using weighted monthly mean concentrations) of precipitation and groundwater variations using Eqn. 1. Figure 6 shows the model simulations plotted against the raw data sets to show the degree of variability more clearly. The degree of damping was then examined by comparing the amplitude in modelled groundwater $\delta^{18}\text{O}$ values with those in precipitation using Eqn. 2. Given the relatively crude fit of the model to the precipitation data ($p \leq 0.05$), the residence time estimates are considered as first estimates from the available data, providing previously unknown insight into probable mean water residence times in the catchment. The model simulates the monthly variation in isotope signatures of springwater at G4 ($p \leq 0.01$) and baseflows in G3 and G1 reasonably well, though the

latter were not statistically significant. To a first approximation, the model suggests a mean residence time of 2 years for springwaters suggesting that even at altitudes above 900 m, fractured bedrock and shallow superficial drifts form significant aquifers that sustain spring-fed wetlands and initiate first order streams. Clearly the mean residence time belies the fact that a spectrum of flow paths with a range of residence times is likely to sustain spring flows.

Further downstream, modelled baseflow $\delta^{18}\text{O}$ values at G1 and G3 were extremely damped with mean residence times estimated in excess of 5 years (Table 3). The longer mean residence times reflect the deeper and less permeable drifts in the lower catchment, and the larger drainage

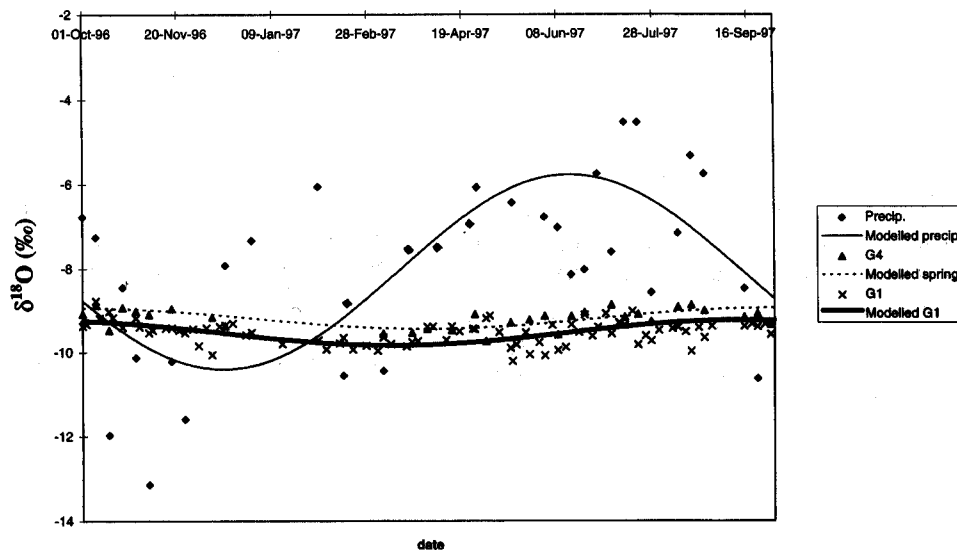


Fig. 6. Sine wave regression models of precipitation, spring water and streamwater oxygen-18 levels.

Table 3. Predicted mean $\delta^{18}\text{O}$ levels and mean estimated residence times (years) of spring water and stream water in the Allt a' Mharcaidh catchment from sine wave regression analysis, 1995–98.

	Mean (%)	Amplitude (%)	Residence time (yr ⁻¹)	n
PRECIPITATION	-7.61	1.47		84
GROUNDWATER				
G4 Spring	-9.21	0.1	2.3	73
G3 Baseflows	-9.47	0.03	>5.0	53
G1 Baseflows	-9.44	0.02	>5.0	104

areas. This is consistent with hydrometric data which show that the specific discharge of the lower catchment (downstream of the G2 and G3 confluence) during low flows ($3 \text{ l}^{-1} \text{ s}^{-1} \text{ km}^2$) is less than half that of the G3 sub-catchment ($8 \text{ l}^{-1} \text{ s}^{-1} \text{ km}^2$). These residence time estimations for groundwater in the Allt a' Mharcaidh imply that significant recharge must occur through the freely draining alpine soils that cover 40% of the catchment. Some of this recharge then emerges at relatively localised spring discharge point. However, it appears that a significant amount of this recharge follows relatively long and/or slow flow paths to sustain groundwater-surface water interactions along the main channel network in the valley bottom.

Discussion

The springs of the Cairngorm mountains are hydrological features that have unique ecological characteristics and provide the sources of many upland streams. The chemical composition of the Allt a' Mharcaidh spring is extremely dilute and slightly acidic, resulting from the highly weathered nature of the drift aquifer. The perennial nature of the spring and the damping of ^{18}O isotopes implies that surprisingly large amounts of groundwater storage exist in high altitude drifts and fractured rocks of the Cairngorm plateaux. The main recharge mechanism seems to be via snowmelt through freely draining alpine soils. As the geology, soils and topography of the catchments of other high altitude springs in the Cairngorms are comparable, it is reasonable to speculate that other spring sites have similar hydrochemical characteristics, though more extensive sampling is required to confirm this (*cf* Hill and Neal, 1997; Neal, *et al.*, 1998). These high altitude aquifers of the Cairngorms are not common in other mountain areas in the British Isles, where peat coverage is greater or more peaked mountains have limited high altitude drift (Rodwell, 1991).

Comparison of the chemical characteristics of the spring with downstream surface waters shows that these chemical features are localized to the headwaters of mountain

streams and emphasises their conservation importance in the Cairngorm area. The wetlands that they support are isolated features in the Cairngorm plateau and the combination of cold snowmelt and ultra-oligotrophic water appears to sustain the relatively rare assemblages of flora and fauna that contribute to the biodiversity importance of the area (Gordon *et al.*, 1998).

The shallow nature of the drift aquifer, thin soil cover and relatively short residence times of spring waters demonstrate that these areas are vulnerable to environmental change, including acidic deposition, climate change and land use changes (Ramspacher *et al.*, 1992; Leibundgt, 1998). In particular, pollutants such as acidic oxide and heavy metals from atmospheric sources can readily contaminate groundwater and rapidly be routed to downstream freshwater environments via such shallow aquifer systems. Regarding acid deposition, although sulphur deposition in the Cairngorms has declined over the last decade-or-so (Soulsby *et al.*, 1997b), N deposition is still increasing, although actual deposition rates are relatively low. The sequestration of N by terrestrial or aquatic ecosystems, as implied by this and other more detailed studies, may lead to fundamental changes to their nutrient status. In such oligotrophic systems, modification to the structure, functioning and composition of terrestrial and freshwater communities could occur (Pitcairn and Fowler, 1989). In areas of such high conservation importance, these changes would generally be undesirable, though further work is required to ascertain the current and likely future extent to which systems are approaching N-saturation.

Shallow groundwater systems are also vulnerable to the effects of climate change, especially if snowpack accumulation is reduced and temperatures increase as predicted (Gordon *et al.*, 1998). The NETPATH simulations presented here suggest that higher weathering rates might be expected if future predictions of warmer and wetter climatic conditions in the Cairngorms are correct. These may in turn alter the chemical composition of water (by increasing base cation concentrations) in spring-fed plant communities. These are believed to be highly sensitive to water quality and may also change in composition as a result (Rodwell, 1991). Although little can be done to manage such large scale environmental change, there is a need for conservation management to recognise that montane ecosystems are dynamic and responsive to climatic change.

Other threats to shallow groundwater systems include the potential for bacterial contamination from both high deer populations and human activities in the mountains. In parts of North American mountain areas, such as the Rockies, water courses and springs can be unfit for consumption as a result of bacteria from large mammals and human recreationalists. High deer densities in the Cairngorms have the potential to contaminate water sources with bacteria in faeces. Intensive recreational use of the Cairngorms, together with the growing international mobility of mountain recreationalists has also increased the

range of bacterial agents that can be introduced into the upland environment. In particular, the increasing popularity of wild camping and overnight bivouacs in certain 'honey pot' locations carries a potential pollution threat (Soulsby *et al.*, 1999c). Shallow aquifers, thin soils and relatively rapid rates of transit dictate that montane groundwaters may be particularly vulnerable and, although little evidence of contamination is currently available, studies to date have been sparse.

Remote high altitude springs are potentially vulnerable to many such pressures and monitoring of their hydro-geochemical and ecological conditions could provide extremely useful indicators of environmental change. The rapid turnover of water in spring/aquifer systems dictates that they should exhibit rapid responses to any such changes, and they provide a setting where integrated assessment of physical, chemical and ecological effects could be examined. Thus, more extensive and detailed work on a wider range of spring sites is a research priority in the Cairngorm region.

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References

- Appelo, C.A.J. and Postma, C., 1993. *Geochemistry, Groundwater and Pollution*. Blakema, Rotterdam.
- Cantonati, M. and Ortler, K., 1998. Using spring biota of pristine mountain areas for long-term monitoring. *IAHS Publ.*, 248, 379–385.
- Chen, M., Soulsby, C. and Younger, P.L. (In press) Modelling the evolution of minewater pollution at Polkemmet Colliery. *Quart. J. Engng Geol.*
- Conroy, J., Watson, A. and Gunson, A.R., 1990. *Caring for the High Hills: the conservation of the Cairngorms* ITE, Banchory.
- Craig, H., 1961a. Standard for reporting concentrations of deuterium and oxygen-18 in natural waters. *Science*, 133, 1833
- Craig, H., 1961b. Isotopic variations in meteoric water. *Science*, 133, 1702–3
- Dansgaard, W., 1964. Stable isotopes in precipitation. *Tellus*, 16, 436–468
- Decker, K., Heinrich, M., Klein, P., Kociu, A., Lipiarski, P., Pirkel, H., Rank, D. and Wimmer, H., 1998. Karst springs, groundwater and surface runoff in the calcareous alps: assessing quality and reliance of long-term water supply. *IAHS Publ.*, 248, 149–156.
- Dewalle, D.R., Edwards, P.J., Swistock, B.R., Aravena, R. and Drimmie, R.J., 1997. Seasonal hydrology of three Appalachian forest catchments. *Hydrol. Process.*, 11, 1895–1906.
- Drever, J., 1997. *The Geochemistry of Natural Waters*. Prentice Hall.
- Dunn, S.M. and Langan, S.J., 1998. Climate, snow and the water resources of a major Scottish river. In: Lemmela, N. and Helenius, N. (eds) *Proceedings of the Second International Conference on Climate and Water*. Espoo, Finland. 178–187.
- Edmunds, W.M. and Savage, D., 1992. Geochemical characteristics of groundwater in granites and related crystalline rocks. In: *Applied groundwater hydrology*, Wilkinson, W.B. and Downing, R.A., Oxford University Press. 266–282.
- Ferrier, R.C. and Harriman, R., 1990. Scottish catchment studies. In: Mason, B.J. (ed) *The Surface Water Acidification Programme*. Cambridge University Press. 8–17.
- Gordon, J.E., Thompson, D.B.A., Haynes, V., Brazier, V. and MacDonald, R., 1998. Environmental sensitivity and conservation management in the Cairngorm mountains, Scotland, *Ambio*, 27, 335–344.
- Helliwell, R.C., Ferrier, R.C., Jenkins, A. and Soulsby, C., 1998. Influence of altitude on bulk and enhancement deposition in the Cairngorm mountains, Scotland. *Headwaters 98*. Proceedings of International Conference, Merano, Italy, 209–212.
- Hill, T. and Neal, C., 1997. pH, alkalinity and conductivity in runoff and groundwater for the Upper River Severn catchment. *Hydrol. Earth Systems Sci.*, 1, 697–715.
- Hill, T. and Neal, C., 1997. Spatial and temporal variation in pH, alkalinity and conductivity in surface runoff and groundwater of the upper River Severn catchment. *Hydrol. Earth Systems Sci.*, 1, 549–556
- Hudson, R.O. and Golding, D.L., 1997. Controls in groundwater chemistry in subalpine catchments in the southern interior of British Columbia. *J. Hydrol.*, 201, 1–20.
- Jenkins, A., Ferrier, R.C. and Harriman, R., 1993. Meltwater chemistry and its impact on stream water quality. *Hydrol. Process.*, 8, 335–349.
- Jenkins, A., Ferrier, R.C., Harriman, R. and Ogunkoya, Y.O., 1994. A case study in catchment hydrochemistry: conflicting interpretations from hydrological and chemical observations. *Hydrol. Process.*, 8, 335–349.
- Kendall, C., Sklash, M.G. and Bullen, T.D., 1995. Isotope tracers of water and solute sources in catchments. In: *Solute modelling in catchment systems*, Trudgill, S.T. (ed), Wiley, 261–303.
- Leibundgt, C., 1998. Tracer based assessment of vulnerability in mountainous headwaters. *IAHS Publ.* 248, 317–323.
- Malcolm, R. and Soulsby, C. (In press) Hydrogeochemistry of groundwater in a coastal wetland in NE Scotland. *Sci. Total Environ.*
- Maloszewski, P. and Zuber, A., 1993. Principles and practice of calibration and validation of mathematical models for the interpretation of environmental tracer data in aquifers. *Advances in Water Resources*, 16, 173–190.
- Maloszewski, P., Rauert, W., Stichler, W. and Herrman, A., 1983. Application for flow models in alpine catchment area using tritium and deuterium data. *J. Hydrol.*, 66, 319–330.
- McDonnell, J.J., Stewart, M.K. and Owens, I.F., 1991. Effects of catchment scale subsurface mixing on stream isotopic response. *Wat. Resour. Res.*, 27, 3065–3073.
- McVean, D. and Ratcliffe, D.A., 1962. *Plant Communities of the Scottish Highlands*. HMSO, London.
- Neal, C., Hill, T., Hill, S. and Reynolds, B., 1997. Acid neutralization capacity measurements in surface and groundwaters in the upper River Severn, Plynlimon: from hydrograph splitting to water flow pathways. *Hydrol. Earth System Sci.*, 3, 687–696.

- Neal, C., Reynolds, B., Adamson, J., Stevens, P.A., Neal, M., Harrow, M. and Hill, S., 1998. Analysis of the impacts of major anion variations on surface water acidity particularly with regard to conifer harvesting: case studies from Wales and Northern England. *Hydrol. Earth System Sci.*, 2, 303–322
- Nethersole-Thompson, D. and Watson, A., 1981. *The Cairngorms*. Melven Press, Perth. (2nd Edn).
- Ogunkoya, O.O. and Jenkins, A., 1993. Analysis of storm hydrograph and flow separations using a three-component hydrograph separation model. *J. Hydrol.*, 142, 71–88.
- Pitcairn, C.E.R. and Fowler, D., 1989. Changes in species composition of semi-natural vegetation associated with increase in nitrogen deposition. *Report to NCC/NERC Project No. To705il*, NERC/ITE, Edinburgh, UK.
- Plummer, L.N., Prestemon, E.C. and Parkhurst, D.L., 1991. An interactive code for modelling net geochemical reactions along a flow path. *USGS Water Resource Inventory*, 91–4078. USGS, 100pp.
- Ramsbacher, P., Zojeer, H., Frochlich, K. and Stichler, W., 1992. The recharge of large springs from a carbonate aquifer near Innsbruck: applying environmental tracers. In Hotzel, H. and Werner, A. *Tracing Hydrological Processes*, 6th International Symposium on Water Tracing. AA Balkema, Rotterdam. 251–257.
- Rodwell, D., 1991. *British Plant Communities: Mires and Heaths*, Cambridge University Press.
- Soulsby, C., Helliwell, R.C., Ferrier, R.C., Jenkins, A. and Harriman, R., 1997a. Seasonal snowpack influence on the hydrology of a sub-arctic catchment in Scotland. *J. Hydrol.*, 192, 17–32.
- Soulsby, C., Turnbull, D.A., Hirst, D., Langan, S.J. and Owen, R., 1997b. Reversibility of stream acidification in the Cairngorm region of Scotland. *J. Hydrol.*, 195, 291–311.
- Soulsby, C., Chen, M., Ferrier, R.C., Helliwell, R.C., Jenkins, A. and Harriman, R., 1998. Hydrogeochemistry of shallow groundwater in an upland Scottish catchment. *Hydrol. Process.*, 12, 1111–1118.
- Soulsby, C., Malcolm, R., Ferrier, R.C., Helliwell, R.C., and Jenkins, A., 1999a. Isotope hydrology of the Allt a' Mharcadh catchment, Cairngorm mountains, Scotland: assessing hydrological pathways and residence times. *Hydrol. Process.* (In press)
- Soulsby, C., Ferrier, R.C., Helliwell, R.C. and Jenkins, A., 1999b. Hydrological research in the Cairngorms: 15 years of research in the Allt a' Mharcadh catchment. *Scottish Geographical Magazine*. In press.
- Soulsby, C., Hunter, C. and Petry, J., 1999c. Faecal bacteria in the river Dee, NE Scotland. *Sci. Total Environ.* In press.
- Stewart, M.K. and McDonnell, J.J., 1991. Modelling base flow soil water residence times from deuterium concentrations. *Wat. Resour. Res.*, 27, 2681–2693.
- Thompson, D.B.A. and Whitfield, T.P.P., 1993. Research on mountain birds and habitats. *Scottish Birds*, 17, 1–9.
- Unnikrishna, P.V., McDonnell, J.J. and Stewart, M.L., 1995. Soil Water Isotope Residence Time Modelling. In: Trudgill, S.T. (ed) *Solute Modelling in Catchment Systems*. Wiley, Chichester, UK. 237–260.
- Wade, A.J., Neal, C., Soulsby, C., Smart, R.P., Langan, S.J. and Cresser, M.S., 1999. Modelling streamwater quality under varying hydrological conditions at different spatial scales. *J. Hydrol.* 217, 266–283.
- Watson, A., 1990. Human impact on the Cairngorm environment above timberline. Conroy, J., Watson, A. and Gunson, A.R. (1990) *Caring for the High Hills: the conservation of the Cairngorms* ITE, Banchory.
- Wheater, H.S., Langan, S.J., Brown, A. and Beck, M.B., 1991. Hydrological response of the Allt a' Mharcadh catchment— inferences from experimental plots. *J. Hydrol.*, 123, 163–199
- Wheater, H.S., Tuck, S., Ferrier, R.C., Jenkins, A., Kleissen, F.M., Walker, T.A.B., and Beck, M.B., 1993. Hydrological flow paths at the Allt a' Mharcadh catchment: an analysis of plot and catchment scale observations. *Hydrol. Process*, 7, 359–371.
- Williams, D.D., 1991. The spring as an interface between groundwater and lotic faunas and as a tool in assessing groundwater quality. *Verh. Int. Verin. Limnol.* 24, 1621–1624.