Quantifying the differential contributions of deep groundwater to streamflow in nested basins, using both water quality characteristics and water balance

M. C. Ockenden, N. A. Chappell and C. Neal

ABSTRACT

This paper describes use of a hydro-chemical mixing model and a water budget to investigate the presence of deep runoff pathways in two small, nested sub-catchments of the Eden basin, UK (8.8 km^2 Blind Beck and 1.0 km^2 Low Hall stream). A linear relationship between bicarbonate concentration and electrical conductivity was used in a two-component mixing model. End-members were identified as a high-solute, deep groundwater and a low-solute, soil-water. The mixing model indicated 69% $\pm$ 10% deep groundwater in Low Hall for September–December 2008 and 46% $\pm$ 8% in Blind Beck for the same period. The water budget also indicated more deep groundwater in Low Hall stream. These results were consistent with the findings of rainfall–runoff models which also indicated the presence of high storage, deeper pathways.

Key words | bicarbonate, Eden catchment, electrical conductivity, end-member mixing, hydrological pathway, interbasin groundwater flow

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INTRODUCTION

Knowledge of hydrological pathways is fundamental in addressing environmental problems of water quality, and chemical characterisation of stream waters makes an important contribution in understanding these pathways. Deep groundwater returning to the surface may make an important contribution to the stream hydrograph in some catchments. This is important for water resources worldwide, as deep groundwater is responsible for sustaining flows during dry periods and buffering streams against some agricultural impacts on water quality in soils. In order to understand the physical and chemical processes that cause stream water quality to change through time, it is necessary to determine where the water has come from and what interactions may have taken place along the dominant hydrological pathways from the source of the water to its arrival in the stream channel. Different water pathways may bring water into contact with different subsurface strata, and for different durations, thus giving the water a different chemical signature. The amount of deep

groundwater returning to the surface may be quite different in adjacent catchments, and, from some surface-defined catchments, interbasin groundwater flow (IGF) may take place (Genereux et al. 2005). Deep groundwater is defined here as water which has travelled through a rock aquifer. Deep groundwater is important for water resources as it is the slow store which sustains base flows in dry conditions, when other sources are contributing little or nothing to the flow. It is important because of its different chemistry: it is often both base-rich and well buffered, with implications for mitigation of acidification and the subsequent effects on aquatic ecology. McDonnell (2003) argued that rather than trying to understand a catchment based on physical data alone or on chemical data alone, a more robust process description of catchment function is gained by combining physical and chemical data to give information on the water flow, source and age together.

Mixing models can be used to estimate the proportions of water from two or more sources of contrasting chemistry

(e.g., Christophersen *et al.* 1990; Burns *et al.* 2001; Dunn *et al.* 2006). If end-members with distinct and constant chemical composition can be identified, then the stream-water chemistry can be described in terms of a mixture of end-members. The end-members are identified by a tracer which can be a natural chemical tracer such as chloride (Genereux *et al.* 2002; Hrachowitz *et al.* 2009) or a stable iso-tope (Sklash 1990; Rodgers *et al.* 2005; Genereux *et al.* 2009) or an added tracer such as bromide or dye (Collins *et al.* 2000; Joerin *et al.* 2005). A critical feature is that this tracer must act conservatively when mixed. Genereux *et al.* (2002) used chemical tracers and water budgets (Genereux *et al.* 2005) to identify and quantify IGF. In that case, the high-solute, deep groundwater was identified as one end-member of a mixing model, representing IGF, with soil-water representing the other end-member.

To investigate the presence of groundwater in the streamflow of small catchments where high frequency dynamics occur, high temporal resolution data are required. Most ions within streamwater cannot be measured easily *in situ* or at a high temporal resolution. Therefore, a combi-nation of discrete sampling for detailed chemical analysis and correlation with *in situ* high frequency measurements of physico-chemical parameters such as electrical conduc-tivity and pH can be used to quantify the high frequency dynamics.

Acid neutralising capacity (ANC), defined as the sum of the strong base cations minus the strong acid anions, has also been used to identify water from shallow and deep sources (e.g., Robson & Neal 1990; Robson *et al.* 1992; Soulsby *et al.* 1998; Tetzlaff *et al.* 2007), notably shallow acidic waters with high aluminium concentrations versus deep sources low in acidity and aluminium. Although ANC was not continuously monitored in these previous studies, relationships were found with continuous measure-ments of pH (Robson 1993). Similarly, both Gran alkalinity (Soulsby *et al.* 2003b, 2004; Capell *et al.* 2011) and electrical conductivity (Wetzel 2003; Tetzlaff *et al.* 2007; Pellerin *et al.* 2008) have been used as continuously sampled tracers to investigate runoff sources.

This paper describes how hydro-chemical data and water budgets were used to investigate the presence of deep runoff pathways in two sub-catchments of the Eden basin, UK. The objectives were: (1) to identify the main contributing end-members to the stream using spot sampled data; (2) to quantify the proportions of deep groundwater and soil-water in the two catchments using high frequency temporal data in a mixing model; (3) to compare water bud-gets for the two sub-catchments; (4) to compare the results of this study with the published estimates of flow pathway proportions identified from a rainfall–runoff modelling study (Ockenden & Chappell 2011).

METHODS

Study catchments

The study area was the 8.8 km^2 Blind Beck sub-catchment of the River Eden basin in northwest England (Figure 1), with the 1.0 km^2 Low Hall sub-catchment nested within Blind Beck. The Eden is one of four UK catchments in the Catchment Hydrology and Sustainable Management (CHASM) programme, a catchment research framework addressing issues such as water quality, flooding and ecology at a range of spatial and temporal scales (Quinn *et al.* 2000). The Eden is also one of three UK catchments chosen for the UK Department for Environment, Food and Rural Affairs (DEFRA) Demonstration Test Catchments Project to assess mitigation measures for diffuse pollution (Davey 2010), so a knowledge of the deep groundwater contribution would be valuable.

Elevations within Blind Beck range from around 140 m at the catchment outlet to 390 m in the headwaters (Figure 1(a)). Average annual rainfall is approximately 1,300 mm. Land use in Blind Beck is predominantly live-stock farming, with sheep on the upland areas of unimproved pasture and beef or dairy cattle on the lowland improved pasture. The geology in the catchments is shown in Figure 2. In Blind Beck the valley floor comprises Triassic Penrith sandstone underlain by Carboniferous limestone, and the valley slopes comprise Carboniferous limestone (Figure 2(a)). The valley floor is covered by regolith of vari-able thickness that is mostly glacial till, with only small areas of glacio-fluvial deposits and alluvium (Geological Survey of Great Britain 1974; British Geological Survey 1997), whereas the upper slopes lack a significant regolith cover (Figure 2(b)). In contrast, the small 1.0 km^2 catchment of the Low Hall
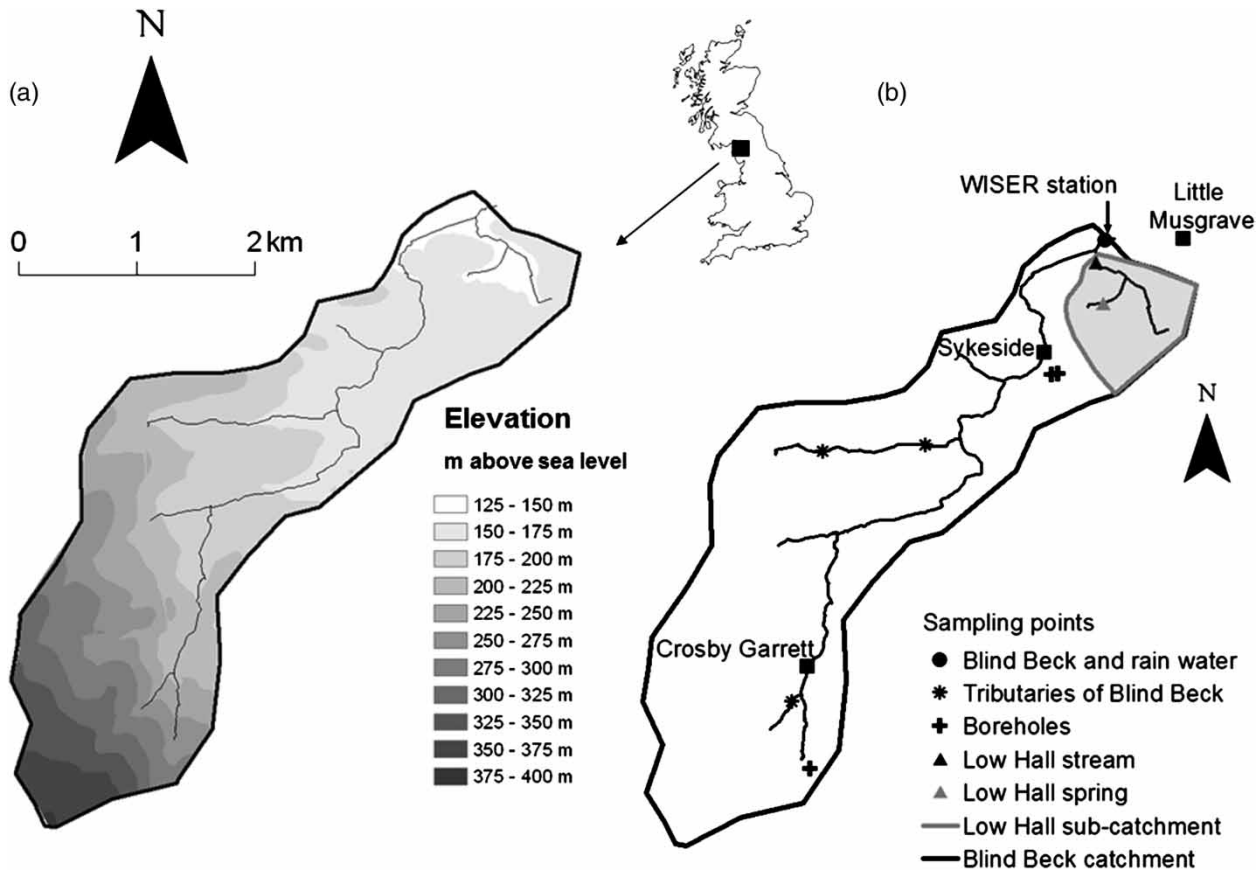
Figure 1 │ The location of Blind Beck catchment within the UK with (a) the topography of Blind Beck catchment and (b) the location of the Low Hall sub-catchment (shaded) and sampling locations.

stream, nested within Blind Beck catchment, lies entirely on the sandstone and is covered largely by alluvial and glacio-fluvial deposits with little glacial till.

Identification of end-members

Rainfall and stream water samples for the determination of major ions were collected to identify chemical signatures to use as end-members. Samples were collected approximately fortnightly from January to October 2008 from Blind Beck, Low Hall stream and a bulk rain water collector at Little Musgrave (Figure 1(b)). Spot samples were also collected from three points on tributaries joining Blind Beck in its headwaters. For the deep groundwater, samples were collected from an 18 m borehole (screened 0–18 m below ground) in the sandstone at Sykeside and a 100 m borehole (screened 0–100 m below ground) in the limestone at Crosby

Garrett (Figure 1(b)). Before sampling, the boreholes were purged using a bailer. Samples were also taken from a 6 m deep borehole (piezometer, screened 4–6 m below ground) in the drift geology at Sykeside Farm.

All samples were filtered on site through sterile cellulose nitrate membrane filters (0.45 μm pore size: type WCN, Whatman International Ltd, Maidstone, Kent, UK) into polyethylene bottles. The bottles were stored in the dark in a refrigerator (at 4 °C) before being transported to CEH Wallingford for analysis by CEH laboratory staff. Fluoride, chloride, nitrate and sulphate were determined by ion chromatography using a Dionex AS50 system. Sodium, potassium, calcium and magnesium were determined by inductively coupled plasma optical emission spectroscopy using a Perkin-Elmer 3300 Dual View instrument. All analysis was undertaken using UK accredited laboratory methods.
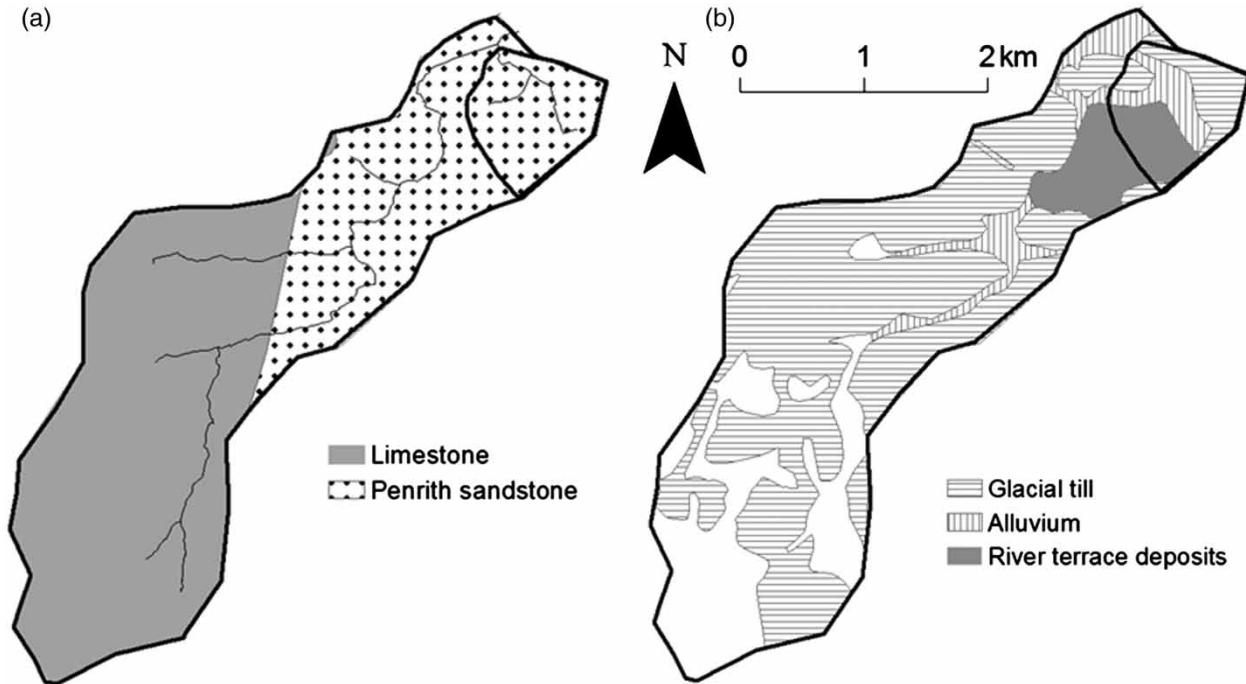
Figure 2 | Geology within Bind Beck: (a) solid geology and (b) drift geology.

Soil-water data were taken from the study of Simon *et al.* (2004) collected in the Helm Beck sub-catchment of the Eden basin, 5 km from Blind Beck.

For circum-neutral to alkaline systems (pH 6–10), the relative contribution of carbonate ions versus bicarbonate ions is heavily dominated by bicarbonate (Neal 2001). For the alkaline waters in this study (minimum pH 7.6; pH > 8.0 for approximately 90% of the time), the difference in charge balance of the major ions was therefore attributed to bicarbonate ions, i.e.:

$$[\text{HCO}_3^-] = [\text{Ca}^{2+}] + [\text{Mg}^{2+}] + [\text{Na}^+] + [\text{K}^+] - [\text{Cl}^-] - [\text{NO}_3^-] - [\text{SO}_4^{2-}] \tag{1}$$

where all concentrations are in micro-equivalents per litre (μEq L^{-1}). Chemical equivalents are commonly used in expressing concentrations of ions in natural waters to allow the calculation of a charge balance (sum of anions = sum of cations).

Cross-correlations of all ions were investigated to try to identify end-members.

Electrical conductivity measured to derive a high resolution bicarbonate time series

Electrical conductivity of the Blind Beck and Low Hall streams and the rainwater at Little Musgrave was recorded during the period December 2007–December 2008. In Blind Beck at Little Musgrave (NY 753130), a YSI 600R sonde (Sontek/YSI Inc., San Diego, CA, USA) was used to measure electrical conductivity and water temperature, with data-logging to a Campbell Scientific CR10X data logger (Campbell Scientific Ltd, Loughborough, UK) at 15 min intervals. This sonde was part of a WISER (Wallingford Integrated System for Environmental monitoring in Rivers) system (Evans *et al.* 1997) installed in July 2003 under the CHASM project (Quinn *et al.* 2000), but serviced by this project. The YSI sonde from the WISER system was exchanged at approximately fortnightly intervals with a sonde which had been cleaned and calibrated in the laboratory. Following recalibration, drift over 2 weeks was found to be <3% in the conductivity measurements. In the Low Hall stream at Little Musgrave an ABB 3-ring conductivity probe (model 2022-680; ABB Kent-Taylor Limited,

St Neots, UK) was installed for high temporal resolution measurements of electrical conductivity. Data were recorded with a Campbell Scientific CR10 data logger at 15 min intervals.

The conductivity of the rainfall was measured at Little Musgrave using a large funnel (376 mm diameter) connected to a specially made sealed cup containing another conductivity probe (model 2022-680). The connecting tubing was arranged to minimise the storage volume (40 mL) to ensure that the fluid around the probe was quickly replaced during rain events. The storage volume equated to approximately 0.36 mm of rainfall. The conductivity of the rainwater in the cup was recorded by a CR10 data logger at 15 min intervals. Outflow from the cup was collected in a large carboy to enable a bulk measurement of conductivity to check the datalogged data at approximately fortnightly intervals. The carboy was wrapped in a black plastic bag to reduce algal growth. The cup and adjoining plastic tubes were insulated to reduce the possibility of freezing during the winter months. The rim of the funnel was protected with short plastic spikes to prevent birds from perching and defecating in the sample.

The temperature dependency of electrical conductivity at all sites was removed by converting to a specific electrical conductivity at a temperature of 25 °C (the temperature used for calibration).

Specific conductivity depends on both the amount of charge in solution and the electrostatic interactions between the ions, so every constituent ion contributes to the total conductivity. This relationship is approximated by Kohlrausch's law:

$$\text{Conductivity} = \sum_i \Lambda_i c_i \tag{2}$$

where Λ_i (constant) is the equivalent conductance (Scm^2/Eq) of the ith ion (i.e., the conductance of that volume of solution that has one equivalent of the ith ion dissolved in it) and c_i is the equivalent concentration of the ith ion (Robson 1993). Apart from the hydrogen ion, which has an equivalent conductance of 350 Scm^2/Eq, the major ions found in upland streams have equivalent conductance at 25 °C in the range 45–80 Scm^2/Eq (Thomas 1986).

For the alkaline waters in this study the hydrogen ion concentrations were negligible compared to the other ions,

and, therefore, made an insignificant contribution to the conductivity.

Bicarbonate concentration was chosen as the tracer for the end-member mixing analysis as the bicarbonate concentration, as calculated according to Equation (1) is approximately the same as the ANC, which is known to be conservative (Neal 2001). A linear relationship was sought between electrical conductivity (from the time series) and bicarbonate concentration (from the spot samples) in order to create a time series of bicarbonate concentration.

Mixing model

A two-component mixing model was used to identify the proportion of deep groundwater. Two distinctive end-members, soil-water and deep groundwater, with fixed compositions were defined, and the stream water was then considered to be made up of different proportions of these two end-members. The proportion of deep groundwater is given by:

$$\frac{Q_{\text{deep}}}{Q_s} = \frac{(C_s - C_{\text{soil}})}{(C_{\text{deep}} - C_{\text{soil}})} \tag{3}$$

where Q_{deep}, Q_{soil} and Q_s, are the deep groundwater, soil-water and total stream discharges and C_{deep}, C_{soil} and C_s, are concentrations of a tracer in the deep groundwater, the soil-water and the stream, respectively.

Provided that the end-members C_{deep} and C_{soil} are fixed, time series of Q_s and C_s can be used to create a time series of Q_{deep}. In this case, the tracer used was the bicarbonate concentration, as calculated from the time series of electrical conductivity. The bicarbonate concentrations of the end-members were chosen such that the soil-water end-member covered the range measured (from Simon *et al.* 2004) for soil waters (0–1,000 $\mu\text{Eq L}^{-1}$) and the deep groundwater end-member (from boreholes in the rock) exceeded the maximum value measured in Blind Beck and Low Hall stream at low flow (7,400–9,400 $\mu\text{Eq L}^{-1}$). The mixing model was run for January to February 2008 and September to December 2008 as these periods had the most reliable and continuous conductivity record. The proportion of deep groundwater was calculated by integrating Q_{deep} and Q_s over the analysis period and taking the quotient.

Water budget comparison of Blind Beck and nested Low Hall basin

A water budget for each catchment, defined by its surface topography, was calculated for 1 December 2007 to 30 November 2008 using:

$$P - Q_s - ET \pm \Delta S + IGF = 0 \qquad (4)$$

where P is precipitation, Q_s is stream discharge at the catchment outlet, ET is evapotranspiration, ΔS is the change in water storage within the basin and IGF is the net inflow of IGF (net gains of groundwater across a topographic boundary). Precipitation was measured using one gauge at Sykeside, within the Blind Beck catchment (Figure 1(b)). Walsh & Kilsby (2007) reported that rainfall in the Eden catchment was linearly related to elevation, so the total rainfall for each sub-catchment (including Low Hall) was corrected for mean elevation based on GIS analysis. Q_s was calculated from high temporal resolution (15 min) measurements of water level and a stage–discharge relationship measured during this study (reported in Ockenden & Chappell (2011)). Evapotranspiration was not measured during this study, but was estimated by Walsh & Kilsby (2007) to be approximately 450 mm per year at a weather station within 10 km of Blind Beck, where land use and climatic conditions were similar. Changes in storage and IGF were not measured directly during this study as there are no satisfactory methods to do this, so $\Delta S + IGF$ was calculated as the residual to balance the budget. Uncertainty of $\pm 7\%$ was included in P, $\pm 5\%$ in Q_s and $\pm 20\%$ in ET, based on estimations by Winter (1981). The uncertainty was propagated through to the calculation of $\Delta S + IGF$ as the square root of the sum of squared uncertainties in each of the other terms. The water budget is useful for comparing catchments and in cases where the IGF component is large and exceeds the uncertainty in the other components.

Comparison with results of rainfall–runoff modelling

The proportion of water in each pathway, identified by the mixing model was compared with the proportion of water on each of two pathways identified in a parallel rainfall–runoff modelling study of the Upper Eden (Ockenden 2010; Ockenden & Chappell 2011). In the rainfall–runoff study, models based on discrete-time, linear transfer functions (TF) were used to investigate the dominant components generating the stream hydrograph and to see if and how these changed with catchment scale and underlying geology. TF-based models are considered to be among the most parsimonious for investigating rainfall–streamflow dynamics (Young 2003). The time constants and the relative proportions of water taking each defined pathway are obtained from model-derived parameter estimates. Discrete-time TF models could be used given that the time-step in the modelled time-series ($\Delta t = 1$ h) was significantly smaller than the time constant. If this had not been the case, continuous-time TF models would have been needed (Littlewood & Croke 2008; Littlewood *et al.* 2010; Chappell *et al.* 2012).
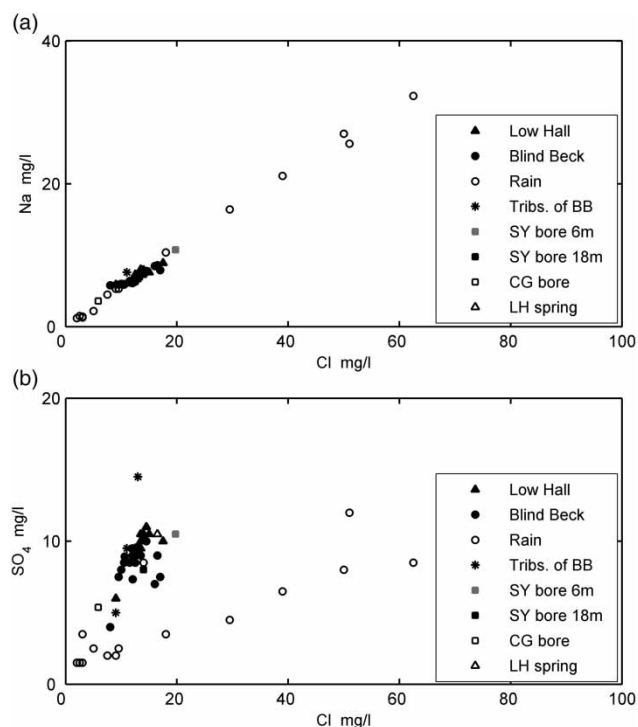
RESULTS AND DISCUSSION

End-member identification from hydrochemical analysis

The minimum, median, arithmetic mean and maximum concentrations of the major ions in Blind Beck, Low Hall stream and the rainwater are given in Table 1. The major components of the rainwater were sodium and chloride (derived from sea salt), whereas a dominant component of both the Blind Beck and Low Hall stream waters was the cation calcium, followed by magnesium. The concentrations of most ions were higher for Low Hall stream than for Blind Beck, with nitrate twice as high in Low Hall stream as in Blind Beck. Concentrations of fluoride were consistently lower in Low Hall stream. The high ratio of nitrate concentrations between Low Hall and Blind Beck may indicate that the Low Hall stream has a more dominant input of water from the sandstone aquifer in the bottom of the Eden Valley, which is known to have a rising nitrate concentration (Butcher *et al.* 2006), with a significant number of boreholes in the Eden Valley approaching or exceeding the EC maximum admissible concentration of 50 mg L^{-1} nitrate.

Cross-correlations between ions showed a very strong correlation ($R^2 = 0.99$) between chloride and sodium (Figure 3(a)), with no significant difference between the ratio for the stream waters or the rainfall. In contrast, while there was a correlation between sulphate and chloride (Figure 3(b))

Table 1 | Minimum, median, arithmetic mean and maximum values of major ions in stream water in Blind Beck and Low Hall stream, and rainwater collected at Little Musgrave, January–October 2008. Arithmetic mean has not been calculated where more than half the samples were below the level of detection. Bicarbonate concentrations have been calculated from ion balance

Location	Catch size km²	No. in sample		F mg L⁻¹	Cl mg L⁻¹	NO₃ mg L⁻¹	SO₄ mg L⁻¹	Na mg L⁻¹	K mg L⁻¹	Ca mg L⁻¹	Mg mg L⁻¹	HCO₃ from ion balance mg L⁻¹
Blind Beck at Little Musgrave	8.8	21	Min.	0.09	8.0	3.5	4.0	5.8	1.5	58.0	13.7	229
			Median	0.12	12.0	7.5	8.5	6.4	2.0	77.7	23.5	338
			Arith. mean	0.12	12.4	7.6	8.4	6.7	2.6	76.0	22.4	327
			Max.	0.14	17.0	10.0	10.0	8.6	6.4	86.1	26.6	365
Low Hall stream at Little Musgrave	1.0	20	Min.	0.08	9.0	7.5	6.0	5.9	2.5	56.0	17.0	267
			Median	0.11	13.8	16.0	10.0	7.7	2.8	97.2	25.1	391
			Arith. mean	0.10	13.7	15.6	10.0	7.6	2.9	95.4	24.1	385
			Max.	0.12	17.5	18.0	11.0	8.9	3.7	117.7	26.3	459
Rain from bulk collector at Little Musgrave	–	14	Min.	<0.05	2.0	<1.0	1.5	1.2	1.9	1.1	0.4	3
			Median	<0.05	9.25	<1.0	3.0	5.3	3.6	1.8	1.0	7
			Arith. mean	–	20.8	–	4.3	11.1	4.9	2.2	1.5	9
			Max.	0.12	62.5	8.5	12.0	32.3	12.5	3.8	4.0	26

Figure 3 | Concentration inter-relationships for (a) chloride (Cl) and sodium (Na), and (b) chloride (Cl) and sulphate (SO₄) within the Blind Beck (BB) basin.

another source. Some of this could have been from dry deposition between rainfall events. Sulfur deposition has been described as a legacy of atmospheric pollution (Daniels et al. 2008), particularly in regions such as the South Pennines, UK where acid deposition was severe (Evans et al. 2000).

There is evidence for bedrock weathering processes from the high concentrations of magnesium and bicarbonate in the streamwater (Drever 1997). Magnesium ions result from the weathering of the mineral biotite into a clay mineral, kaolinite. Bicarbonate ions are produced in this weathering reaction, with all of the carbon coming from carbon dioxide in the atmosphere. Bicarbonate is also produced in the weathering of the mineral calcite ($CaCO_3$) that is dominant in the aquifers of limestone areas, and in this case only half the carbon comes from the atmosphere (Drever 1997). There was very little magnesium (Mg) in the rainfall (average Mg 1.5 mg L⁻¹), but the concentrations in the stream waters were higher by a factor of approximately 15. The highest concentrations of magnesium were observed in the Sykeside boreholes, with the concentration in the deeper (18 m) borehole higher than the shallower (6 m) borehole (35 mg L⁻¹ in the deeper borehole, 30 mg L⁻¹ in the shallower one). Higher magnesium concentrations in Low Hall stream indicated greater reactivity with the rock suggesting that more of the Low Hall water came via a deep pathway. The low concentrations of magnesium and calcium in high flows in the stream

the ratio was different for stream waters and rain water. This suggested that the major source of sodium and chloride in stream waters was from precipitation, but that the sulfate in the stream waters came both from precipitation and

indicate the greater influence of the soil-water component at high flows (e.g., Hooper *et al.* 1990; Robson *et al.* 1992; Genereux *et al.* 1993).

The concentrations in Low Hall stream were higher, by an average of 7% for magnesium and 26% for calcium. The concentration inter-relationship between calcium and magnesium (Figure 4) suggested that the water in Blind Beck basin was a mixture made from three distinct end-members. The end-members were indicated by the vertices of the dashed triangle in Figure 4, which encloses data for both Blind Beck and Low Hall. Although samples of soil water were not analysed in this study, soil waters from nearby sites (within 5 km) were analysed by Simon *et al.* (2004) and are included in Figure 4. One end-member appeared to be a soil-water, with very low concentrations of both calcium and magnesium. A second end-member had high concentrations of both calcium (~130 mg L^{-1}) and magnesium (~27 mg L^{-1}). The sample from the 6 m borehole at Sykeside (which is in the drift layer) was similar to this and suggested the water travelling through the drift only as a separate end-member. The third end-member also had high magnesium concentration (~27 mg L^{-1}) but lower calcium concentration (~50 mg L^{-1}) and was closest to the water in Low Hall stream at low flows. The water from the 18 m borehole at Sykeside (which is in the sandstone) was similar to this, indicating water from the deeper sandstone geology as the third
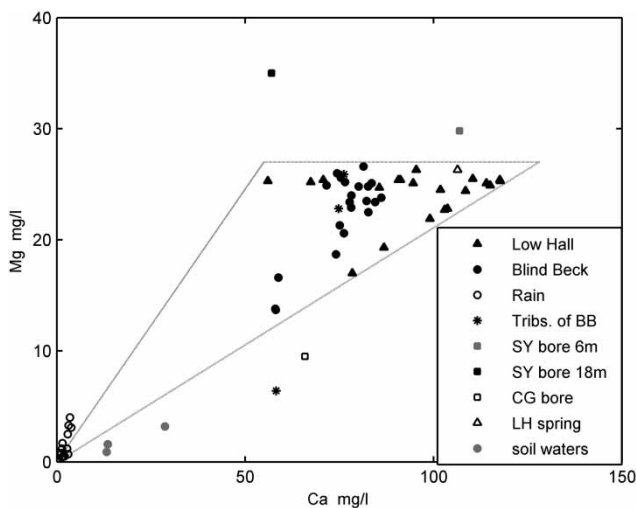
end-member. In contrast, water from a borehole at Crosby Garrett, in the limestone, and water from the higher tributaries of Blind Beck both had low concentrations of magnesium.

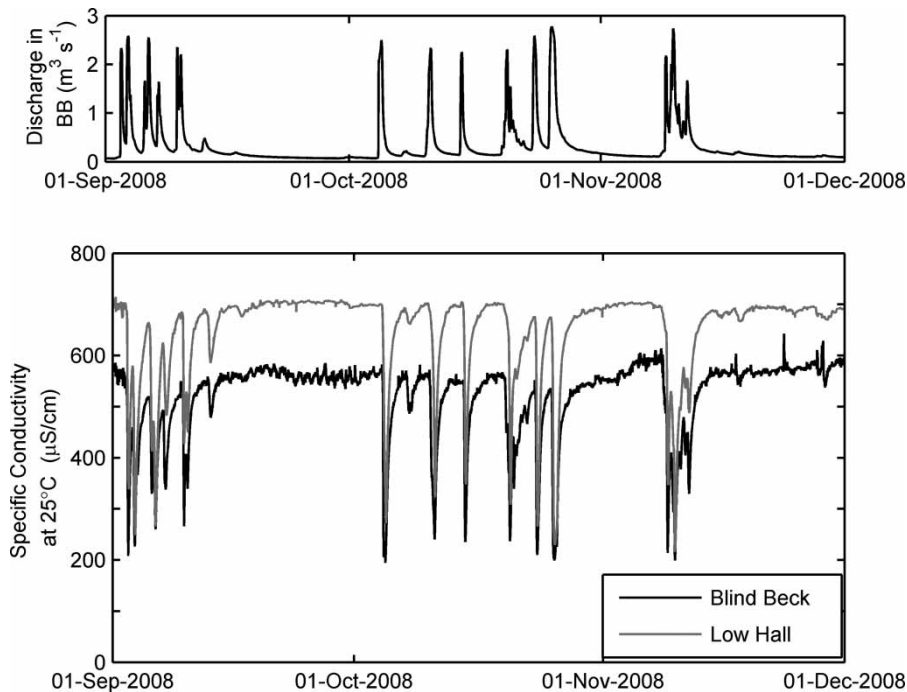## Specific conductivity and bicarbonate concentration

The specific conductivity in Low Hall and Blind Beck mirrored the stream water levels extremely well, with the conductivity dropping sharply as rainfall caused a rise in the water level and then rising again as the water levels fell. The specific conductivity of Low Hall stream was higher than in Blind Beck at all times apart from at extremely high flows, when Blind Beck burst its banks and spilled down the road, overflowing into Low Hall stream. The discharge in Blind Beck and specific conductivity in Blind Beck and Low Hall are shown in Figure 5. The conductivity in Blind Beck fell from about 600 to 200–250 μS cm^{-1} during storms. It indicates that the rain water, which had a very low specific conductivity throughout the 12-month monitoring period (typically <100 μS cm^{-1}, measured at 15 min intervals in a rain gauge at Little Musgrave, the Blind Beck catchment outlet), reached the stream via relatively fast pathways and did not increase its dissolved solids content significantly.

Figure 6 shows the bicarbonate concentration in μEq L^{-1}, calculated from the charge balance, plotted against the specific conductivity (μS cm^{-1}) of all the samples of stream water, rain water and borehole water. Figure 6 also includes a shaded area which represents the range of conductivity and alkalinity measured by Simon *et al.* (2004) for the nearby soil waters. For these waters, alkalinity is approximately equivalent to bicarbonate concentration. For rain water, the estimate of bicarbonate will be inexact because of the influence of other significant ions, such as ammonium, that were not measured. However, the sum of cations and anions in rainwater was very small anyway, as reflected by the low specific conductivity.

Figure 6 shows a linear relationship between the bicarbonate concentration and the specific conductivity. The relationship, with standard errors on the coefficients, is given by:

Figure 4 │ Concentration inter-relationship for magnesium (Mg) and calcium (Ca) for waters within the Blind Beck basin. The vertices of the dashed triangle indicate the calcium and magnesium concentrations of end-members.

Bicarbonate concentration =
$$(10.7 \pm 0.4) * \text{Conductivity} - (425 \pm 200) \qquad (5)$$

Figure 5 | Discharge from Blind Beck basin (upper panel) and specific conductivity of the Blind Beck and Low Hall streams, September–December 2008 (lower panel).
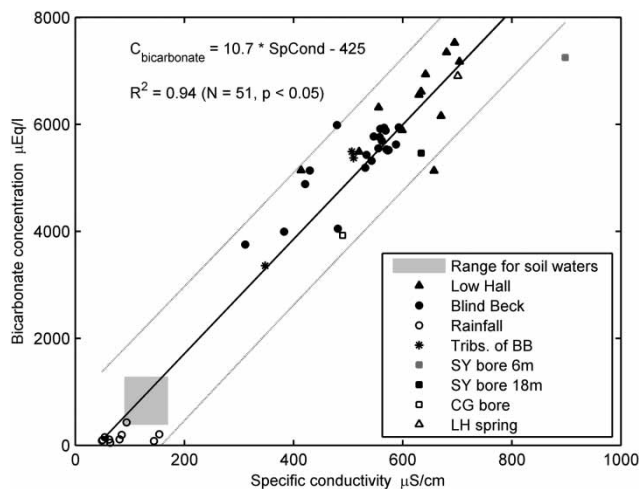

Figure 6 | Concentration of bicarbonate (from charge balance) against specific conductivity, showing a linear relationship with coefficient of determination $R^2 = 0.94$. Number of samples, $N = 51$; the relationship is significant at the 95% level ($p < 0.05$). The grey lines show 95% confidence intervals on the regression.

where the bicarbonate concentration has units of $\mu Eq\ L^{-1}$ and conductivity has units of $\mu S\ cm^{-1}$, giving $R^2 = 0.94$ ($N = 51$, $p < 0.05$). The highest bicarbonate concentrations were in Low Hall stream and the 6 m borehole at Sykeside.

## End-member mixing analysis (EMMA) based on bicarbonate concentration

Two end-members were used for the mixing model rather than the three suggested by Figure 6 because of the absence of time series data for separate Ca and Mg concentrations; specific conductivity gave a better linear relationship with bicarbonate (approximately equal to the sum of Ca^{2+} and Mg^{2+} in terms of charge balance as these two ions made up over 90% of the cations in stream water) than with either Ca or Mg separately. The end-members were a low-solute, soil-water (bicarbonate concentration of $500 \pm 500\ \mu Eq\ L^{-1}$) and a high-solute, deep groundwater, as measured in the Low Hall stream at low flow (bicarbonate concentration of $8,400 \pm 1,000\ \mu Eq\ L^{-1}$). Figure 7 shows the total discharge and the estimated contribution from the deep groundwater, from the end-member mixing model for Low Hall stream. The lower edge of the grey band represents the minimum contribution of deep groundwater, while the upper edge represents the maximum contribution of deep groundwater. For September to December 2008, the deep groundwater contribution averaged $69\% \pm 10\%$, while for January to February 2008, the same
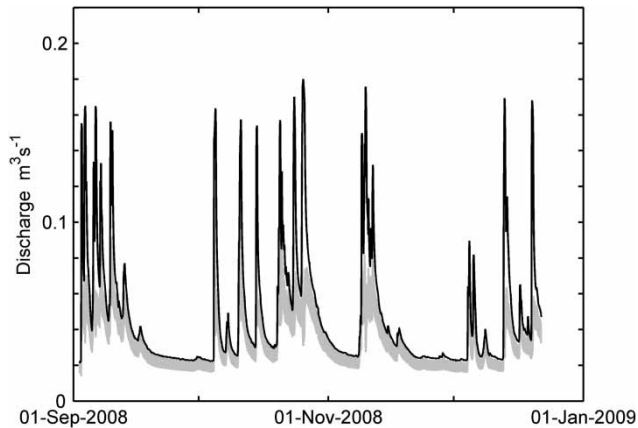
Figure 7 | Total discharge ($m^3 s^{-1}$) (solid black line) and estimated contribution from deep groundwater, from end-member mixing model, for Low Hall stream, September–December 2008. The lower edge of the grey band represents the minimum contribution of deep groundwater while the upper edge represents the maximum contribution of deep groundwater. This range is derived from the range in each end-member (i.e., 0–1,000 μEq L^{-1} bicarbonate for soil-water and 7,400–9,400 μEq L^{-1} bicarbonate for deep groundwater).

mixing model suggested 61% ± 9% deep groundwater. The proportion of deep groundwater in Low Hall stream varied through time, with a maximum of around 85% in periods of low flow, which fell to 20–40% during storm peaks.

Using the same two end-members, the contribution of deep groundwater in Blind Beck was estimated to be 46% ± 8% for September to December 2008 (Figure 8), and 41% ± 7% for January to February 2008. The proportion of
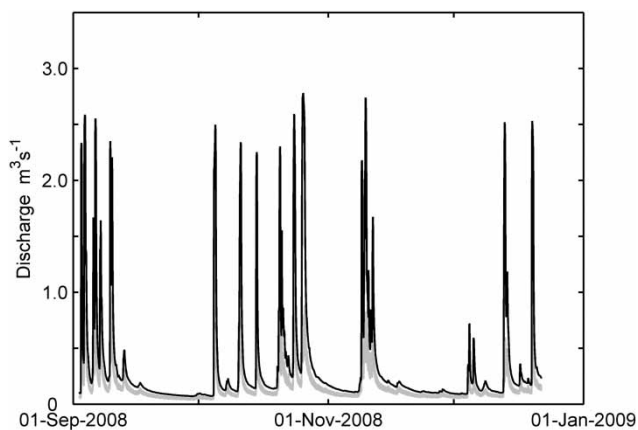
Figure 8 | Total discharge ($m^3 s^{-1}$) (solid black line) and estimated contribution from deep groundwater, from end-member mixing model, for Blind Beck, September–December 2008. The lower edge of the grey band represents the minimum contribution of deep groundwater while the upper edge represents the maximum contribution of deep groundwater. This range is derived from the range in each end-member (i.e., 0–1,000 μEq L^{-1} bicarbonate for soil-water and 7,400–9,400 μEq L^{-1} bicarbonate for deep groundwater).

deep groundwater in Blind Beck was around 65% in periods of low flow, and 10–20% during storm peaks.

Water budget

Table 2 shows the water budget calculation for the year 1 December 2007–30 November 2008 for both sub-catchments. Even allowing for the uncertainty in each of the estimated or measured quantities, the high total stream discharge in Low Hall, which exceeds the precipitation, strongly supports the presence of a large component of deep groundwater which enters the catchment across the topographic boundary. This is in marked contrast to Blind Beck, where the net gains across the boundary are very much smaller and within the uncertainty propagated by the measured or estimated quantities. This does not preclude the presence of deep groundwater in the streamflow of Blind Beck, but rather indicates that, unlike Low Hall catchment, the deep groundwater has been generated from within the catchment and the net gains from outside the catchment boundary are small.

Comparison with rainfall–runoff modelling

In a previous study of rainfall–runoff modelling (Ockenden & Chappell 2011) for the catchments of Blind Beck and Low Hall stream, a second-order linear transfer function was identified to relate the rainfall to the streamflow. This could be decomposed by partial fraction expansion into a parallel model composed of a fast and a slow pathway (see, e.g., Box *et al.* 2008).

The rainfall–runoff modelling suggested 75.6% ± 1% (based on 1,000 Monte Carlo realisations) of water on a

Table 2 | Water budget for Blind Beck and Low Hall sub-catchments for the year 1 December 2007–30 November 2008. Precipitation (P) was measured at one location within Blind Beck and corrected for mean elevation of each sub-catchment. Evapotranspiration (ET) is an estimate from Walsh & Kilsby (2007). The stream discharge (Qs) is the flow measured at the outlet of each catchment, integrated over the year and divided by the catchment area. The net inflow of IGF plus the change in storage (ΔS) is the balance. All quantities are measured in mm yr^{-1}. Positive quantities indicate water entering the catchment, negative quantities indicate water leaving the catchment

	P	ET	Qs	IGF + ΔS
Blind Beck	1,440 ± 100	−450 ± 90	−980 ± 50	−10 ± 140
Low Hall	1,360 ± 100	−450 ± 90	−1,580 ± 80	670 ± 160

slow pathway in Low Hall basin for a period January to February 2008. The mixing model results from this physico-chemical study, based on the chemical composition of the stream water in Low Hall stream, estimated $61\% \pm 9\%$ deep groundwater (i.e., a slow pathway) for January to February 2008. Similarly, for Blind Beck, the rainfall–runoff model indicated $46\% \pm 10\%$ of water on a slow pathway for January to February 2008, while the mixing model estimated $41\% \pm 7\%$ deep groundwater for the same period. The model-identified proportions of flow along different pathways are known to be uncertain when using either the mixing model (Soulsby *et al.* 2003a) or the TF model decomposition (Young 1992, 2003). However, these two methods were consistent in indicating that within the sub-catchment of Blind Beck there was a substantial contribution to the stream from water which had travelled by longer residence time pathways (e.g., lateral water flow through a rock aquifer), and that this input was even larger in Low Hall stream. In particular, it highlighted the importance of deep water pathways returning water to the surface even in small catchments.

CONCLUSIONS

The use of both streamwater chemistry and water balance has been shown to be a useful technique to quantify the contribution of deep groundwater to streamflow. This is important for water resources worldwide, particularly in catchments with a large component of deep groundwater, as this deep groundwater is responsible for sustaining flows during dry periods and buffering streams against some agricultural impacts on the quality of shallow groundwater within soils. The water quality of two nested catchments on a major rock aquifer, Blind Beck and its Low Hall tributary, indicates the value of EMMA based on bicarbonate concentration, as derived from a linear relationship with specific conductivity (i.e., Bicarbonate concentration = 10.7 * Conductivity – 425; $R^2 = 0.94$, $N = 51$, $p < 0.05$). The work indicates the importance of both rapid and slow transit pathways, notably the importance of deep water pathways such as those in the sandstone aquifer beneath the lower slopes of the whole (2,288 km^2) Eden basin. It highlights the value of using both spot and more

continuous measurements. The study also gives findings consistent with a parallel analysis based on rainfall–runoff modelling of the same catchments for the same period; both of which indicated a higher proportion of longer residence time water in Low Hall stream than in Blind Beck (despite the uncertainties in the respective methods).

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