Assessing the value of Cl^- and $\delta^{18}O$ data in modelling the hydrological behaviour of a small upland catchment in northeast Scotland

Sarah M. Dunn and Jeffrey R. Bacon

ABSTRACT

Model simulation of Cl^- and $\delta^{18}O$ in stream waters has been investigated as a means of improving interpretation of catchment-scale hydrological processes. The procedure has been evaluated for a small upland catchment which is one of the UK Environmental Change Network sites. Precipitation and stream samples have been analysed for hydrochemical determinands since the mid 1990s and, since November 2004, measurement of $\delta^{18}O$ has also been undertaken. A conceptual hydrological model STREAM (STorage REsidence times And Mixing) was applied to the catchment to simulate the hydrology and responses of Cl^- and $\delta^{18}O$. Results from model simulations confirmed that the catchment generally behaves as a well-mixed system. The feasibility of flow contributions from a deep groundwater source and infiltration excess runoff was examined, in addition to the apparently dominant shallow groundwater response. The ability to estimate mean residence times and draw strong conclusions about catchment processes was limited by the range of uncertainties in the experimental data and modelling. Integration of the tracer data in the model was found to be of value for probing model sensitivities and developing hypotheses that inform the design of further field experimentation. In this way, the modelling provides key feedback within a catchment learning framework.

Key words | chloride, $\delta^{18}O$, flow path, model, residence time, tracer, uncertainty

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NOMENCLATURE

A	amplitude of the annual variation in tracer concentration (mg l^{-1})
A_p	amplitude of precipitation concentration (mg l^{-1})
A_s	amplitude of stream water concentration (mg l^{-1})
AvSlope	slope from model cell to stream
c	radial frequency of annual tracer fluctuations (0.017214 rad d^{-1})
C	fitted tracer concentration
C_{ero}	expected mean Cl^- concentration in runoff (mg l^{-1})
C_{mi}	measured precipitation Cl^- concentration (mg l^{-1}) of sample i
CalibGw	shallow groundwater rate parameter (m s^{-1})
CelWidth	size of model cell (m)
DrainGw	drainage to shallow groundwater (m)
DSlope	slope from model cell to immediately adjacent down-slope cell
EffPore	effective porosity (–)
ET_j	evapotranspiration rate (m s^{-1})
F	output flux of tracer (kg)
Factor	topographic weighting factor (–)
Flow	water flow rate ($m^3 s^{-1}$)

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GwStore	shallow groundwater storage (m)
i	cell label (−)
j	sample label (−)
MRT	mean residence time (s)
n	number of samples in a year (−)
NearS	drainage to near-surface store (m)
Qgw	shallow groundwater flow rate ($m^3\ s^{-1}$)
P_i	precipitation (m)
$PNet$	net precipitation (precipitation − evapotranspiration) (m)
R_m	ratio of measured $^{18}O/^{16}O$
R_s	ratio of the $^{18}O/^{16}O$ in VSMOW (Vienna Standard Mean Ocean Water)
SoilStore	soil storage for model cell (m)
Surf	loss by saturation excess surface runoff (m)
t	time (s)
TStore	tracer stored in model cell (kg)
USlope	slope uphill of model cell (−)
X	annual mean tracer concentration (mg l^{-1})
Δt	time-step (s)
θ	phase lag (rad)

INTRODUCTION

Responses of hydrological systems to environmental changes such as land use, management or climate change remain poorly understood. A major limitation is the importance of sub-surface runoff generation processes in controlling not just the flow pathways of water, but also the degree of mixing and residence times within the system. If predictive capabilities are to be improved, it is important that these processes are adequately represented within models. However, there are difficulties in obtaining data that can help to define the processes at appropriate spatial scales.

Historically, catchment scale models have tended to focus on reproduction of observed time-series of streamflows, with minimal regard to the internal behaviour of the model (Nash & Sutcliffe 1970). More recent studies have demonstrated the potential problems associated with different sets of model parameters leading to the same end prediction (Freer *et al.* 1996), and there have been attempts to develop multi-objective criteria for model simulations using additional types of data (e.g. Franks *et al.* 1998; Guntner *et al.* 1999). The drawback of many hydrological data (e.g. groundwater levels and soil moisture) is that they are point specific and potentially highly variable at the sub-metre scale, making it problematic to use them for model calibration at catchment scales. Data that provide spatially integrated information, for example in-stream, are more likely to prove useful in this respect. The study presented here explores the utility of natural tracers as a means of providing information to support the structure and parameterization of a conceptual hydrological model, with the objective of integrating it as part of a catchment learning framework.

Recent studies have highlighted the opportunity for greater utilization of hydrochemical and isotopic tracer data within catchment modelling studies (Soulsby *et al.* 2006; Vache & McDonnell 2006). Tracers have been widely used as a means of disaggregating streamflow into two or three components to represent different flow paths within catchments (e.g. Christophersen *et al.* 1990; Robson *et al.* 1992). Some tracers can also be used to infer information about how long water has been stored in a catchment (Maloszewski *et al.* 1983). Analysis of catchment mean residence time (MRT) is of particular interest for predicting future water quality of catchments (Zoellmann *et al.* 2001), since the transport of pollutants from the land to surface waters is inextricably linked to the movement of water itself. In addition, the concept of MRT probes a new axis of behaviour, namely that of particle transport as opposed to pressure wave propagation, and can therefore potentially provide data that are not cross-correlated with other observations. The fact that tracer data can provide spatially integrated information is also an added benefit.

While tracers have been widely used to help interpret hydrological processes, there have been few studies that have attempted to integrate tracers directly within a conceptual modelling framework. An early set of studies by de Grosbois *et al.* (1988) using the Birkenes model highlighted the potential for tracer data to assist with identification of parameter values, although Hooper *et al.* (1988) concluded that the data were still insufficient to uniquely identify values for a six parameter model. Dunn *et al.* (2003, 2006) and Stadnyk *et al.* (2005) used tracer data to verify the hydrograph separation within a streamflow model. Uhlenbrook & Leibundgut (2002) used a tracer analysis as the basis for designing the structure of a semi-distributed conceptual hydrological model, based around the idea of functional units. None of these examples used the tracer data to examine residence times within the modelling procedure, but a recent study by Vaché & McDonnell (2006) found that residence time could be usefully included as a means of evaluating model structure and reducing uncertainty in parameter values.

Previous studies of catchment residence times have mostly involved the application of a range of black-box models to represent catchment response functions and evaluate residence times (Maloszewski *et al.* 1983; Asano *et al.* 2002; McGuire *et al.* 2005). Applications of this type are based on comparison of tracer input and output signals with no direct linkage to conceptual hydrological processes. An alternative approach is to use conceptual hydrological modelling to investigate the nature of the tracer response and examine how it is controlled by different internal processes represented within the hydrological model. The same conceptual model can be applied using different parameterizations to generate a degree of flexibility in the structure of the catchment response function. This approach has the advantage that the model can be interpreted using tracer responses in conjunction with other hydrological data, thus creating a multi-objective methodology.

The primary objective of the analysis presented in this paper was to evaluate the utility of two different natural tracers in modelling the hydrological behaviour of a small upland catchment in northeast Scotland. Secondary objectives included quantification of the MRT for the catchment and an investigation of the mechanisms that control the MRT and the residence time distribution (defining the age distribution of water that reaches the catchment outlet) through the model analysis.

STUDY AREA

The study was based at the Glensaugh experimental research station, which lies on the southern and eastern fringe of the Grampian Mountains 40 km southwest of Aberdeen. The research station incorporates one of the monitoring sites of the UK Environmental Change Network (ECN) (Sykes & Lane 1996) which was established in 1993. Sampling within the ECN programme includes continuous stream discharge measurements and monitoring of meteorological variables as well as weekly dip samples for water chemistry analysis. The catchment upstream of the ECN gauging structure covers an area of 0.77 km^2, comprising rough grazing land (Figure 1).

The elevation of the catchment ranges from 225 to 435 m with the main stream (the Birnie Burn) draining from north to south. The area has been extensively glaciated, resulting in rounded hilltops and the main stream is incised into a narrow valley 5–10 m deep in places. The area lies just to the north of the Highland Boundary fault, with soils of the Strichen Association developed on glacial drifts. The depth of the glacial deposits varies with topography, with generally deeper deposits down-slope. At the top of the catchment, the soils are mainly hill peats that are up to 5 m deep in places and around 2 m deep on average (Miller & Hirst 1998), whereas peaty podzols and more freely drained humus–iron podzols predominate at lower altitudes. The podzolic soils overlie thin drift. Many small surface channels are sourced from springs on the main hillslope. Some of these flow permanently whereas others are more intermittent, appearing only after periods of wet weather.

The catchment receives around 1,000 mm mean annual precipitation and produces approximately 700 mm of run-off. There is little variability in precipitation volumes throughout the year, but some of the winter precipitation falls as snow. The amount of snow is highly variable from year to year, and the snow rarely lies in the catchment for more than 1 or 2 weeks. Peaks in streamflow occur within a few hours of a precipitation event.

METHODOLOGY

Field measurements

Routine weekly sampling of precipitation and stream water has been undertaken as part of the ECN data collection procedures since 1993. Stream levels are logged every 15 min and converted to discharge using the established stage-discharge relationship for the weir. Meteorological observations are recorded hourly at an automatic weather

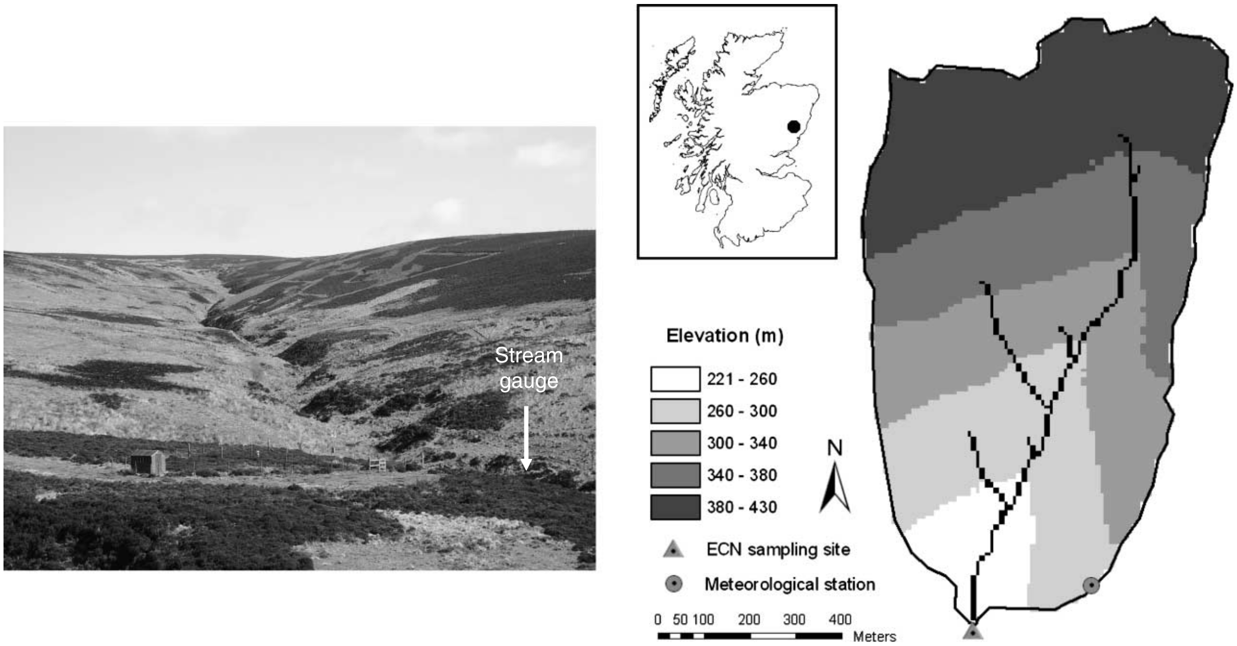

Figure 1 | Map and photograph of the ECN catchment at Glensaugh, showing topography, streams and monitoring sites.

station. All data have been subjected to standard procedures for data quality control in accordance with the protocols developed for the ECN.

The analysis presented in this paper focuses on the use of Cl^- and $\delta^{18}O$ as tracers. The water samples are filtered through 0.45 μm membrane filters and analysed for 15 chemical determinands by a range of techniques including inductively coupled plasma–opticial emission spectometry (ICP-OES), inductively coupled plasma–mass spectrometry (ICP-MS), and ion chromatography. Uncertainty in measurement of Cl^- concentrations is around 3% (at the 95% confidence level). Precipitation samples are taken from bulk collectors and the chemistry therefore represents the composite mean from the preceding week. Streamflow samples are grab samples and the chemistry therefore represents instantaneous conditions.

From the beginning of November 2004, water samples were also taken for measurement of $\delta^{18}O$ using isotope ratio mass spectrometry. The measurement of $\delta^{18}O$ is accurate to $\pm 0.1‰$. No long term $\delta^{18}O$ data were available, although some spot samples were taken for a range of different catchment waters (including precipitation, soil, spring, groundwater and streamflow) in spatial surveys carried out during 2002 and 2003 (Dunn *et al.* 2006).

Tracer data and residence time calculation

Cl^- and $\delta^{18}O$ have commonly been used as effective natural tracers of hydrological pathways and transit times within catchments (e.g. Neal & Rosier 1990; Kirchner *et al.* 2000; Soulsby *et al.* 2000) because they are non-reactive under typical catchment conditions (Kendall & Caldwell 1998). Although commonly used as a tracer, a number of studies involving Cl^- have experienced difficulties due to problems of accurately measuring the solute inputs and outputs (Neal & Rosier 1990; Miller & Hirst 1998; Peters & Ratcliffe 1998), and in particular the dry deposition component. Analyses based on $\delta^{18}O$ are also subject to the limitations of routine monitoring programmes in terms of bias towards baseflow conditions (Littlewood & Marsh 2005) and its comparison with composite precipitation samples, that could also lead to mass balance issues. Given these uncertainties, it is of value to use more than one tracer for interpretation of catchment processes and in this study both Cl^- and $\delta^{18}O$ data have been used.

Many studies have shown that the signals of natural tracers observed in stream water are often highly damped by comparison with the input precipitation signals (e.g. Pearce *et al.* 1986; Neal *et al.* 1990). The level of damping represented by the signals is indicative of the amount of mixing in the catchment and, consequently, the catchment mean residence time. In some catchments, certain tracers exhibit strong seasonal trends in precipitation concentrations which are reflected, albeit in a highly damped manner, in streamflow concentrations. Maloszewski *et al.* (1983) demonstrated a simple methodology for utilizing this behaviour to develop catchment models for evaluating mean transit times and storage volumes. This methodology has since been widely applied as a means of estimating catchment MRT (DeWalle *et al.* 1997; Soulsby *et al.* 2000; Asano *et al.* 2002), and is summarized below.

Seasonal trends in tracer concentrations are modelled using periodic regression analysis to fit sine curves to the seasonal variations of the tracer in precipitation and stream water:

$$C = X + A[\cos(ct - \theta)] \tag{1}$$

where C is the fitted tracer concentration (or the isotope ratio $^{18}O/^{16}O$), X is the annual mean tracer concentration, A is the amplitude of the annual tracer variations, c is the radial frequency of annual fluctuations ($0.017214\,\mathrm{rad\,d^{-1}}$), t is the time in days from start of measurements and θ is the phase lag (rad).

If an exponential model is used to represent the catchment response, Maloszewski *et al.* (1983) show that the mean residence time T of water leaving the system can be calculated as:

$$T = c^{-1}\left[\left(\frac{A_s}{A_p}\right)^{-2} - 1\right]^{0.5} \tag{2}$$

where A_p is the amplitude of precipitation and A_s is the amplitude of the stream water, both estimated from Equation (1) above.

Since this method assumes that the ages of water reaching the catchment outlet are exponentially distributed, it is only appropriate as a first estimate of the catchment MRT or, in situations where the catchment has been demonstrated through other analysis, to conform to exponential behaviour. Equally, the equations can only be applied if the input and output tracer signals demonstrate strong seasonal variability. Utilization of the procedure was investigated in this analysis to give a first approximation of the catchment MRT.

Model theory and implementation

In this study, the STREAM model (STorage REsidence times And Mixing) has been used to model the behaviour of Cl^- and $\delta^{18}O$ tracers in the Glensaugh catchment. STREAM is a semi-distributed conceptual hydrological model that includes a means of simulating the transport of a conservative solute tracer in conjunction with water flows and calculating the residence time distribution for water in the catchment (Dunn *et al.* 2007). The key features of the model code are presented below.

The catchment is represented in STREAM by a grid of square cells, each of which is characterized by a range of properties including elevation, soil type and several topographic descriptors. The topographic descriptors define how the hydrology of each cell is linked with the remainder of the catchment, as well as the routing of flows from the land to the stream. A 10 m digital elevation model was used to derive the topographic descriptors for this study.

For each grid cell, effective precipitation (rainfall − evapotranspiration) is added to a soil store, where a water balance is calculated at each time-step. A fraction of the soil water drains to both a near-surface and sub-surface store, at a rate dependent on the soil water store. If the soil is fully saturated, or if its infiltration capacity (*InfThresh*) is exceeded, infiltration excess runoff also occurs. The full set of equations for the soil water balance is detailed in Dunn *et al.* (2004). The water balance equation for the soil store is:

$$\begin{aligned}\mathrm{SoilStore}_{i,t} = {} & \mathrm{SoilStore}_{i,t-1} + P\mathrm{Net}_{i,t} - \mathrm{Near}S_{i,t-1} \\ & - \mathrm{DrainGw}_{i,t-1} - \mathrm{Surf}_{i,t-1}\end{aligned} \tag{3}$$

where $\mathrm{SoilStore}_{i,t}$ is the soil storage for cell i at time t (m), $P\mathrm{Net}_{i,t}$ is the net precipitation (precipitation − evapotranspiration) (m), NearS is the drainage to the near-surface store (m), DrainGw is the drainage to the shallow groundwater (m) and Surf is the loss by saturation excess surface runoff (m). The near-surface store (NearS) represents water that is rapidly transported to the stream network via macropores, rills and small channels, at a rate that is sufficiently rapid to neglect the detailed routing of the flow down the hill-slope. The infiltration excess runoff (Surf) is also assumed to be transported at this rate.

Water from the sub-surface store of each grid cell generates shallow groundwater flow. The flow is routed to a surface stream via a series of hill-slope cells, defined according to the topographic location of the grid cell. The simulation for each individual grid cell can be performed independently of all other cells in the catchment, as the routing function for each cell is disaggregated from neighbouring cells. The approach is very similar to that applied within the Distributed Ythan (DIY) model (Dunn *et al.* 1998) except that within STREAM the routing equation includes a weighting factor to account for the position of each hill-slope routing cell in relation to the remainder of the catchment. The shallow groundwater flow is defined by

$$QGw_{i,t} = \mathrm{CalibGw} \times Gw\mathrm{Store}_{i,t} \times D\mathrm{Slope}_i \times \mathrm{CelWidth} \times \mathrm{Factor}_i \tag{4}$$

where $QGw_{i,t}$ is the flow for cell i at time t ($m^3\,s^{-1}$), CalibGw is the shallow groundwater rate parameter ($m\,s^{-1}$), $D\mathrm{Slope}_i$ is the slope from cell i to the immediately adjacent down-slope cell, CelWidth is the dimension of the cell (m) and $\mathrm{GwStore}_{i,t}$ is the sub-surface store. This is calculated for each routing cell by:

$$\mathrm{GwStore}_{i,t} = \mathrm{GwStore}_{t-1} + (Q\mathrm{Gw}_{i-1,t-1} - Q\mathrm{Gw}_{i,t-1}) \times \Delta t/\mathrm{Celwidth}^2 \tag{5}$$

The topographic weighting factor *Factor* is defined for each cell i by:

$$\mathrm{Factor}_i = \frac{D\mathrm{Slope}_i}{(D\mathrm{Slope}_i + (U\mathrm{Slope}_i \times U\mathrm{Area}_i))} \tag{6}$$

The variable Factor accounts for the influence of topographic location in modifying the dynamics between the flow rate Qgw and the shallow groundwater storage GwStore. The greater the up-slope contributing area of a cell, the greater will tend to be the storage in the cell. However, the discharge rate depends on the trade-off between the slope uphill of the cell (USlope), compared with that downhill of the cell (DSlope). If USlope is large relative to DSlope, then the cell will tend to accumulate greater storage than if the reverse scenario is true. Where there is a uniform gradient, the only influencing topographic factor becomes the up-slope contributing area. The initial conditions for GwStore are calculated to account for these dynamics by weighting the storage by 1/Factor.

The shallow groundwater flow is routed through the appropriate number of cells to correspond to its physical location in the catchment relative to the stream network. Thus, the transport occurs over a lateral distance equivalent to the flow length from each cell to the stream. The flow calculated for the final hill-slope routing cell in each case is assumed to be the discharge to the stream cell (or riparian cell if a riparian storage is included in the model).

An additional deep groundwater flow can also be modelled. This is produced by a steady uniform recharge from the soil store to a deep groundwater store. The deep groundwater is routed down a simplified hill-slope (defined for each cell by the mean slope, *AvSlope*, and the flow length) to the stream.

The total catchment streamflow is calculated by simple summation of the routed flows originating from each cell in the catchment. In-stream routing of flows within the catchment is not included in the model.

A set of equations defining the transport of a conservative solute tracer are associated with each of the flow equations. The tracer is assumed to be fully mixed within each of the stores through which it passes. However, if infiltration excess runoff occurs, then the fraction of precipitation that does not infiltrate the soil is assumed to retain the same concentration of tracer as the incoming precipitation. An optional effective porosity term is also included to account for the potential influence of immobile water on tracer movement. For each modelled flow, the associated flux of tracer TFlux (kg) is defined by:

$$TFlux_{i,t} = \frac{TStore_{i,t} \times Flow_{i,t} \times \Delta t \times EffPore}{SoilStore_{i,t} \times CelWidth^2} \tag{7}$$

where $T\mathrm{Store}_{i,t}$ is the tracer stored in cell i at time t (kg), $\mathrm{Flow}_{i,t}$ is the water flow from cell i at time t ($m^3\,s^{-1}$), Δt is the time-step (s), EffPore is the effective porosity for transport through the cell, $\mathrm{Store}_{i,t}$ is the depth of water stored in cell i at time t (m) and CelWidth is the size of the cell (m). This form of equation applies to the fluxes from the soil storage, the shallow sub-surface flow, the near-surface flow and the deep groundwater storage, although in many cases the value of EffPore will be assumed to be equal to one.

Residence times for the catchment model are calculated by introduction of a pulse input of tracer over the whole catchment at the start of a simulation. The residence time of the tracer in the catchment is calculated from the output flux of this tracer F (kg) by

$$\mathrm{MRT} = \frac{\int_0^\infty tF\,\mathrm{d}t}{\int_0^\infty F\,\mathrm{d}t} \tag{8}$$

In order to achieve full tracer recovery, long model simulations are usually necessary and are achieved by repeated cycling of meteorological data to extend the length of the simulation as required. The MRT calculated using this method is an approximation to the long-term MRT, because the response is affected by the specific hydrological conditions at the time of the pulse tracer application. The sensitivity to timing of the pulse application can be tested during the model application.

There are a total of 13 parameters in the STREAM model which are summarized in Table 1, together with details of how the parameters are determined. In theory, some of the parameters could take spatially varying values, although where calibration is required there is little sense in implementing this. Some of the parameters are based on experimental data, others are derived from observed hydrological characteristics for the catchment and some are based solely on the model calibration.

The STREAM model was applied in this study to simulate the response of two tracers (Cl^- and $\delta^{18}O$) and compare the results with observed streamflow responses. A 1 year simulation was performed for $\delta^{18}O$ (for Oct 2004–Oct 2005) using a 4-hourly time-step. A 9 year simulation of Cl^- (for Oct 1996–Oct 2005) was undertaken using a daily time-step, to compare with available long-term data. Sensitivity analysis of key parameters was carried out to evaluate the principal controls on the modelled tracer response, and to evaluate the quality of information that could be gleaned from the modelled tracer response. The catchment MRT was also calculated by the model and an estimate of the uncertainty in MRT values was made on the basis of the sensitivity analysis results.

Table 1 | Parameters of the STREAM model

Variable	Units	Description	Model component	Identification methodology
fieldCap	m	Soil field capacity	Soil water balance	Based on physical data
satCap	m	Soil saturated capacity	Soil water balance	Based on physical data
porosity	%	Soil porosity	Soil water balance	Based on physical data
infThresh	$\mathrm{m\,s^{-1}}$	Infiltration capacity	Soil water balance	Calibration including timing of storm runoff
calibV	$\mathrm{s^{-1}}$	Sub-surface drainage parameter	Soil water balance	Calibration including data on flow path proportions
calibL	$\mathrm{s^{-1}}$	By-pass flow loss parameter	Soil water balance	Calibration including data on flow path proportions
effPoreUz	%	Effective porosity	Soil water balance	Calibration including MRT
calibSF	$\mathrm{m\,s^{-1}}$	Near-surface rate parameter	Near surface flow routing	Calibration including high streamflow response
calibGw	$\mathrm{m\,s^{-1}}$	Shallow groundwater rate parameter	Groundwater hill-slope routing	Calibration using streamflow response
effPoreGw	%	Effective porosity	Shallow groundwater flow	Calibration including MRT
rech	$\mathrm{m\,s^{-1}}$	Recharge rate of deep groundwater	Deep groundwater	Estimation from stream baseflow
dGwSInit	m	Initial depth of deep groundwater store	Deep groundwater	Estimation in conjunction with *dGwK* from baseflow
dGwK	$\mathrm{m\,s^{-1}}$	Groundwater conductivity	Deep groundwater	Estimation in conjunction with dGsInit from baseflow

ANALYSIS OF DATA

Hydrological data

Measured precipitation, air temperature and streamflow for Glensaugh, for the period October 2004–October 2005, are shown in Figure 2. The total precipitation was 1,100 mm and measured flow was 700 mm. Evapotranspiration rates calculated using the Penman–Monteith formula (Monteith 1965) from data measured at the Glensaugh meteorological station were equivalent to 370 mm, demonstrating a good balance in terms of the catchment water budgets (<3% error in relation to incoming precipitation). Snow processes were not included in the present analysis, but were of minimal significance during the winter of 2004–2005 with no prolonged periods of snow lying in the catchment. After a wet month in Oct 2004 the winter was very dry, with a wetter spring from March to May, followed by a relatively dry summer. The 90 percentile flow for 9 years from 1996–2005 was exceeded only 83% of the time in 2004–2005, due to the extended period of dry weather during the summer.

The 2004–2005 data compare with a 9 year average from October 1996–October 2005 of 1025 mm precipitation, 850 mm streamflow and 250 mm calculated evapotranspiration. It should be noted that the catchment automatic weather station was moved at the beginning of June 2004 to a new site in the catchment, approximately 90 m higher, which may record slightly enhanced precipitation more likely to be representative of the catchment mean. However, the catchment water balance falls well

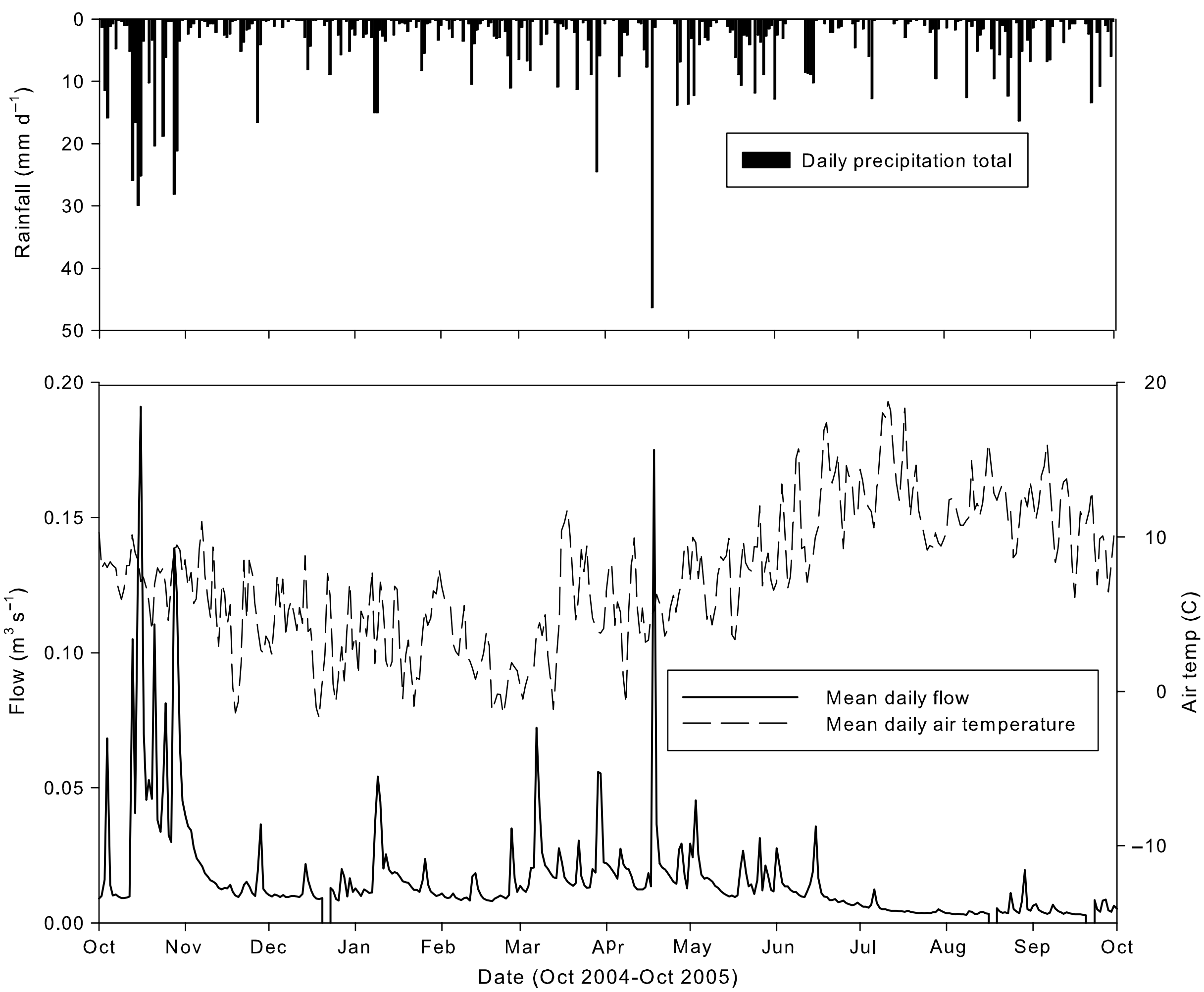

Figure 2 | Measured precipitation, air temperature and streamflow data for Glensaugh, for the period October 2004–October 2005.

within the expected bounds of error on measured variables (Harmel *et al.* 2006) over the full period.

Analysis of $\delta^{18}O$ data

The measured $\delta^{18}O$ in precipitation and streamflow are shown in Figure 3 for the period November 2004–October 2005. The flow data demonstrate a high degree of damping of the precipitation signal, despite the small size of the catchment. Whereas the precipitation signal varied between −14.3‰ and 1.1‰, the streamflow only varied between −9.0‰ and −7.9‰. This variability of ±0.6‰ compares with other studies in the northeast of Scotland which have displayed variability of ±1–2‰ (Soulsby *et al.* 2006) in similar weekly sampled datasets. Based on volume-weighted averages, the mean precipitation input for the period was −7.8‰ (standard deviation 3.0‰) compared with −8.6‰ (standard deviation 0.3‰) for the streamflow.

Taking into account the potential errors in measurement of precipitation volumes and the high variability in $\delta^{18}O$, together with poor capture of snowfall during a short period in the winter, it is feasible that these mean values are effectively in balance. However, it is also possible that the precipitation data collected over the period of monitoring were not characteristic of the long-term $\delta^{18}O$ input to the catchment. Measurements of $\delta^{18}O$ collected from a range of different soil and groundwater sources in the catchment during 2002 and 2003 (Dunn *et al.* 2006) show values that are largely in balance with the observed streamflow (Table 2).

In order to apply the method of periodic regression analysis to estimate the MRT of the catchment, the data should display clear seasonal variability. This attribute was not apparent from the measured $\delta^{18}O$ data, shown in Figure 3, and therefore the approach was not applied to the $\delta^{18}O$ data.

Analysis of Cl^- data

The long-term record of measured Cl^- in precipitation and streamflow is illustrated in Figure 4 for the period October 1996–October 2005. As with $\delta^{18}O$, the Cl^- signal in the streamflow is damped by comparison with the precipitation signal. Both the precipitation and streamflow Cl^- signals display a strong seasonal cycle with mean concentrations of 5.8/8.2 mg l^{-1} January–March, 4.0/7.2 mg l^{-1} April–June,

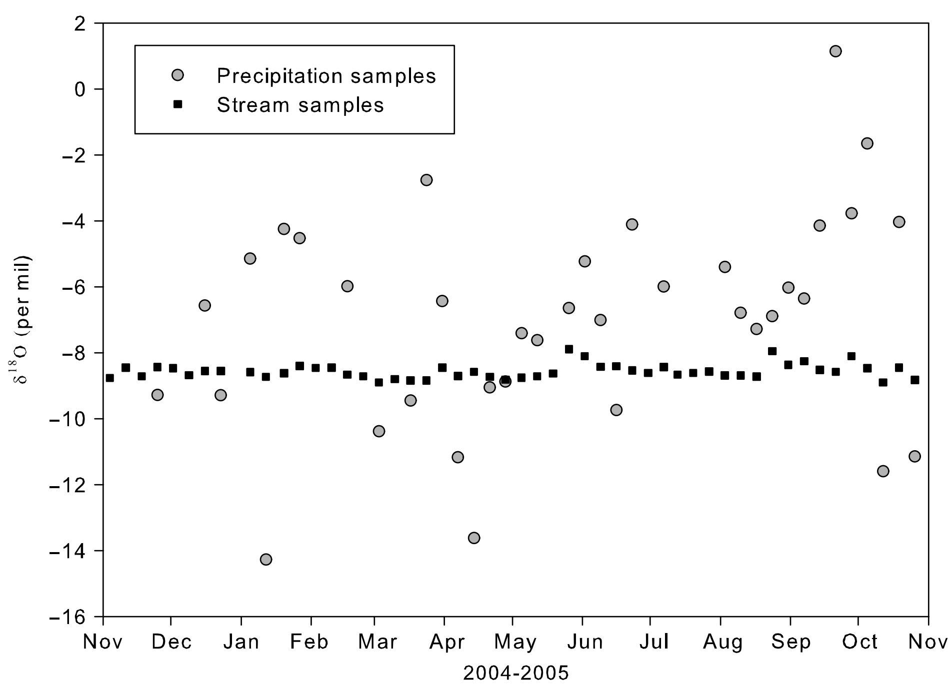

Figure 3 | Measured $\delta^{18}O$ in precipitation and streamflow for the period November 2004–October 2005.

Table 2 | Mean values of δ^{18}O (‰) in Glensaugh soils and groundwaters measured during 2002–2003 (standard deviation in brackets)

Source	15/07/2002	15/10/2002	07/01/2003	30/04/2003
Hill-slope springs (10 sites)	−8.7 (0.2)	−8.8 (0.2)	−8.7 (0.2)	−8.8 (0.1)
Deep groundwater source (1 site)	−8.8	−8.8	−8.8	−8.7
Soil water through-flow (3 pits, 2 − 4 horizons)	−8.4 (0.4)	−9.0 (0.4)	−9.9 (0.8)	−9.7 (0.6)

1.6/7.3 mg l^{-1} July–September and 4.3/8.2 mg l^{-1} October–December for the precipitation/streamflow. The overall amplitude of precipitation Cl^- varied from 0–20 mg l^{-1} and streamflow from 5–11 mg l^{-1}. The mean concentration of Cl^- in precipitation (3.9 mg l^{-1} with standard deviation of 2.5 mg l^{-1}) is significantly lower than that measured in streamflow (7.6 mg l^{-1} with standard deviation of 0.9 mg l^{-1}). Increased concentrations of the precipitation Cl^- are expected in runoff because of a decrease in water volumes through evapotranspiration (ET) (Neal & Rosier 1990). However, the discrepancy in this case is very large. An estimate of the expected mean Cl^- concentration in runoff (as calculated by precipitation less ET) C_{ero} can be made by applying a weighting factor based on the water budget:

$$C_{\mathrm{ero}} = \sum_{j=1}^{n} C_{mj} P_j \Big/ \sum_{t=1}^{365} (P_t - ET_t) \tag{9}$$

where n is the number of samples in a year, $C_{\mathrm{m}j}$ is the measured precipitation Cl^- concentration (mg l^{-1}) of sample j and P_j is the precipitation (m) during the period of collection of sample j. P_t and ET_t are the daily precipitation and evapotranspiration values.

Equation (9) was applied to 9 years of data from 1996–2005. This gave a mean value of the expected Cl^- concentration in runoff of 4.8 mg l^{-1}. This value is significantly lower than the mean concentration observed in the stream water, indicating that evaporative effects alone are inadequate to account for the higher concentrations in stream water compared to precipitation.

An additional factor that has been found to be significant in other studies is that rainfall collectors do not adequately capture dry and occult deposition of Cl^- (e.g. Neal *et al.* 1990; Peters & Ratcliffe 1998). During 2002 and 2003, some water samples were collected from two interception gauges

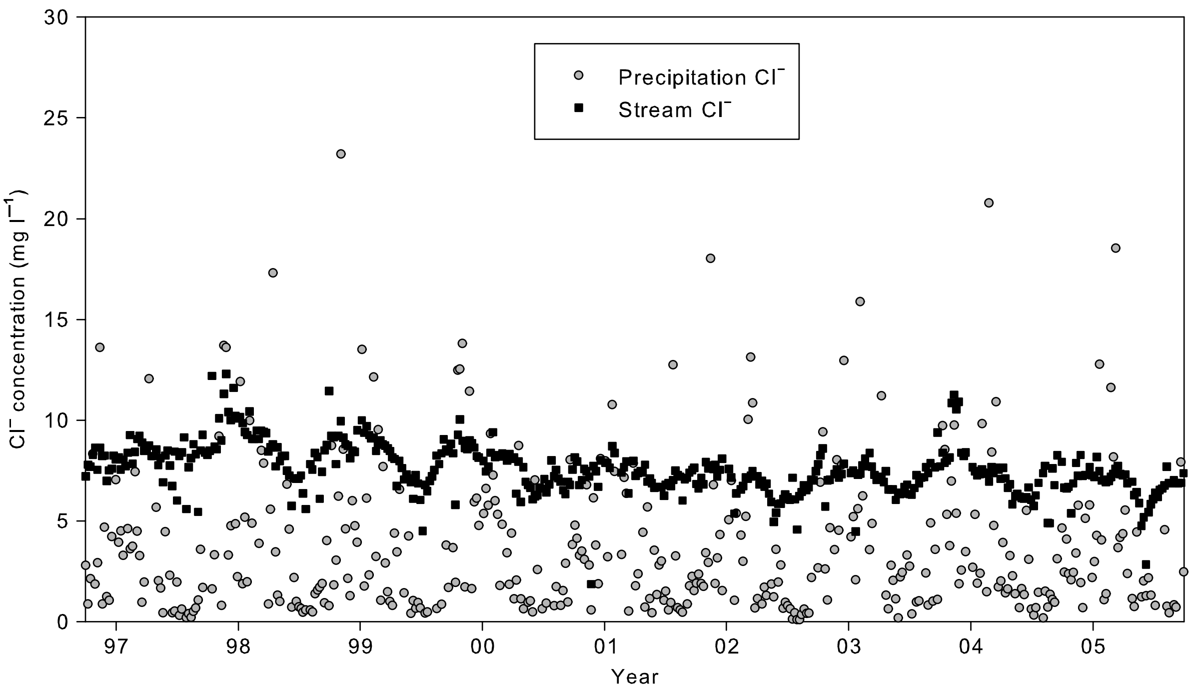

Figure 4 | Measured Cl⁻ in precipitation and streamflow for the period October 1996–October 2005.

immediately adjacent to two rainfall collectors in the Glensaugh catchment. The Cl^- concentrations of the interception water are compared with those of the rainwater in Table 3. These values show that the water captured by the interception collectors had much higher Cl^- concentrations and therefore that the remaining imbalance in the Cl^- rainfall–runoff budget is most probably due to additional Cl^- deposition inputs. The volume of dry deposition inputs is likely to be highly variable in time, as well as their Cl^- content, depending on meteorological conditions and seasonality. However, quantification of this temporal variability is not possible from the limited available data.

For the purposes of this analysis (including the model application), a uniform weighting factor of 1.55 was calculated by comparing precipitation Cl^- and stream Cl^- fluxes, to increase the Cl^- inputs to the level required to create a mass balance. This dry deposition contribution of around 35% is comparable with estimates of between 33% and 50% made in other studies (Peters & Ratcliffe 1998; Lovett *et al.* 2005), albeit in forested catchments where dry deposition is expected to be greater than the short vegetation present in the Glensaugh catchment.

The strong seasonality in observed Cl^- concentrations in Glensaugh means that the application of periodic regression analysis to estimate the MRT of water in the catchment can be undertaken. Best fits of Equation (1) to measured precipitation and streamflow Cl^- data were evaluated and then used to apply to Equation (2) to calculate the MRT. To give a measure of the uncertainty in the calculated MRT as a function of uncertainty in the Cl^- inputs, three different forms of the Cl^- input data were used to estimate the MRT. The three datasets were:

(1) measured concentrations from precipitation samples;
(2) measured concentrations adjusted to account for the effect of ET; and
(3) measured concentrations adjusted to account for ET and weighted to account for the additional input of dry and occult deposition.

Figure 5 shows the sinusoidal curves fitted to the weighted precipitation data (dataset (3) above) and the streamflows. The catchment MRT values calculated using this technique were 260 days, 288 days and 420 days using datasets (1), (2) and (3), respectively.

MODEL RESULTS

Flow simulation

The STREAM model was first calibrated to streamflow before examining the tracer behaviour. The model calibration simulations were based on one year of data from October 2004–October 2005, using a time-step of 4 hours. Given the uncertainty in parameter values and the issue of equifinality (Freer *et al.* 1996), the calibration simulations aimed to identify sets of parameter values that give acceptable measures of performance according to three criteria for simulation of streamflows:

(1) Nash–Sutcliffe (NS) efficiency of flow predictions ≥ 0.75
(2) NS efficiency based on log (flow) values ≥ 0.75
(3) ratio of groundwater hill-slope runoff to near-surface flow $\geq 40\%$ and $\leq 60\%$.

The NS efficiency (Nash & Sutcliffe 1970) gives a measure of the closeness of fit between the modelled and observed time-series of flows, evaluated against the mean flow. Since the NS efficiency tends to bias model evaluation towards accurate prediction of high flows, the NS based on log flows is also used to ensure that low flows are also acceptably simulated. The third criterion was based on the results of a previous hydrological study of the Glensaugh catchment which utilized hydrochemical data to partition the sources of runoff into two flow paths (Dunn *et al.* 2006). All parameter sets that satisfied these three criteria were used to identify uncertainty bounds for the simulations, according to the method described in Dunn (1999).

Table 3 | Mean Cl^- concentrations (mg l^{-1}) in rainwater and interception water measured during 2002–2003

Source	15/07/2002	15/10/2002	07/01/2003	30/04/2003	22/07/2003
Rain water (2 sites)	1	6	5	1	3
Interception water (2 sites)	2	35	60	14	16

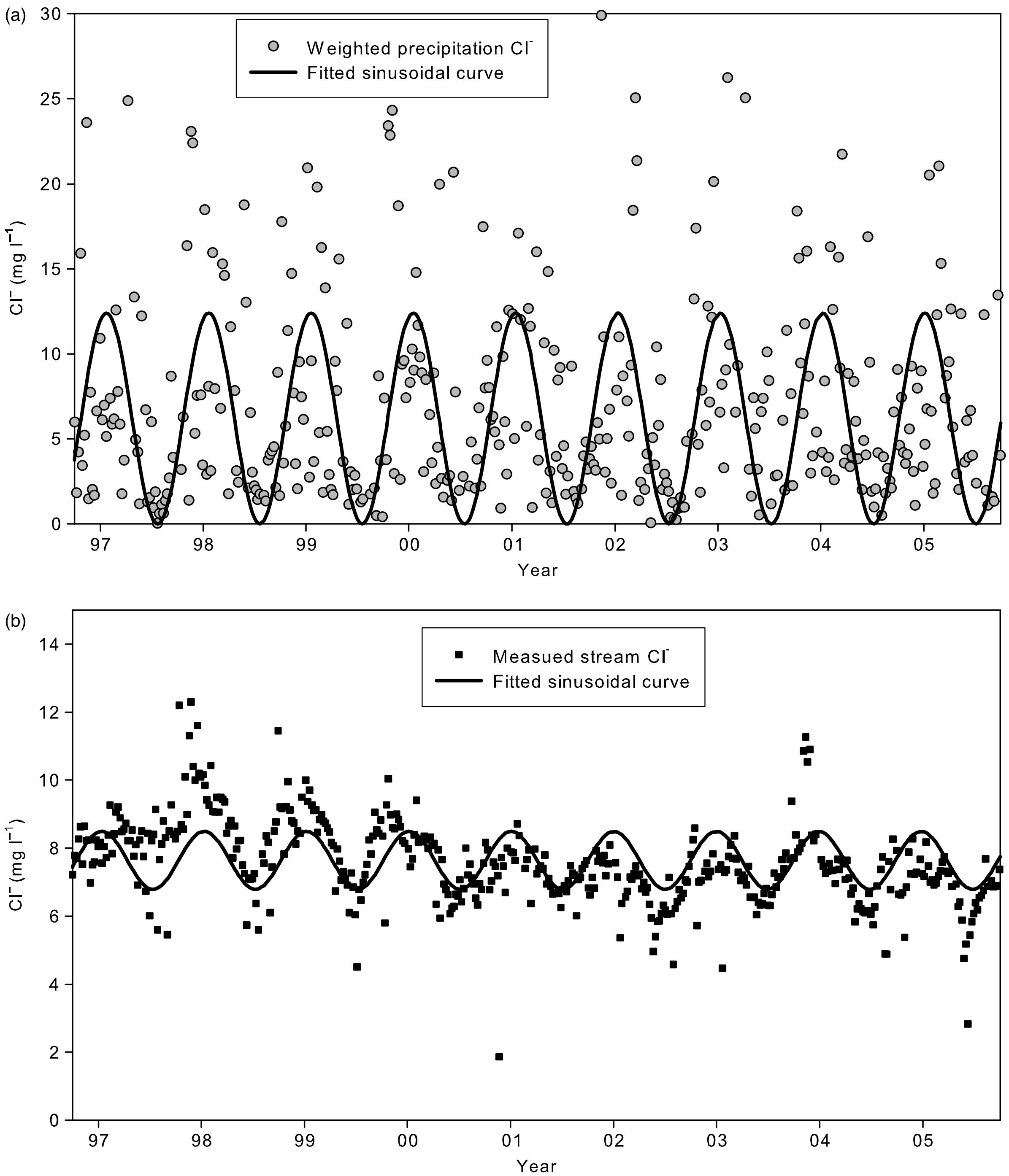

Figure 5 | Sinusoidal curves fitted to weighted precipitation Cl^- data and stream Cl^- data.

Table 1 summarizes the methodology used for identification of each of the parameters. For the initial simulations there was assumed to be no deep groundwater flow (*rech* = 0, *dgwsInit* = 0) and values for *effPoreUz* and *effPoreGw* were set = 1. The latter two parameters do not affect the flow simulations. Values for *fieldCap*, *satCap* and *porosity* were identified from soil physical data for two soil types: deep peat above 400 m elevation and a peaty podzol below 400 m. However, in order to simplify the calibration procedure, uniform values were used for the lateral and vertical drainage parameters *calibL* and *calibV*. Initial conditions for the water balance stores were estimated by pre-running three months of meteorological data through the model.

One thousand simulations were performed varying values of the five parameters *infThresh*, *calibV*, *calibL*, *calibSF* and *calibGw* within broad ranges defined by previous experience of the model application. A random number generator was used to select parameter values within the defined ranges, in order to test the full parameter space. From the results of these simulations, the parameter ranges were narrowed down to: $infThresh = 0.5–2.0$ mm h^{-1}; $calibV = 0.005–0.01\,h^{-1}$; $calibL = 0.03–0.4\,h^{-1}$; $calibSF = 1–5\,m\,h^{-1}$ and $calibGw = 25–100\,m\,h^{-1}$. A further 500 simulations were performed using these parameter bounds.

From this set of simulations, only 22 parameter sets satisfied the three criteria defined above. These parameter sets constituted the acceptable set of parameters on the basis of the flow calibration. Upper and lower bounds of predictions have been extracted from the results based on the maximum and minimum flow calculated at each time from each of the acceptable simulations. These results are compared to the measured streamflow in Figure 6(a). There is a notable difference between the upper and lower bounds of simulated peak flows with maximum simulated flows (not shown) exceeding those of the measured data by up to 50%. This reflects the sensitivity of the simulations to the *infThresh* parameter.

Simulation of $\delta^{18}O$

The measured $\delta^{18}O$ in weekly precipitation samples was used to provide a time-series input of tracer to the STREAM model. A constant concentration was assumed to apply to the period between each sample. For modelling purposes, values were converted to the ratio of $^{18}O/^{16}O$ (R_m), using the conversion equation:

$$\frac{^{18}O}{^{16}O} = R_s \times \left(\frac{\delta^{18}O}{1000} + 1\right)$$

where R_s is the ratio of the $^{18}O/^{16}O$ in VSMOW (Vienna Standard Mean Ocean Water) which equals 0.0020052. The isotope ratios can then be treated as concentrations for the purposes of the model calculations (Genereux & Hooper 1998).

The initial condition for R_m in stored catchment water was set to 0.0019873 (which is equivalent to $\delta^{18}O$ of −8.9‰), based on data from previous sampling of soil water and groundwater in the catchment (Table 2).

Simulations of stream $\delta^{18}O$ for each of the 22 acceptable flow parameter sets were collated to generate the upper and lower bounds of prediction for tracer concentration simulated at each time-step. These results are compared with the measured stream $\delta^{18}O$ signal in Figure 6(b). The precipitation $\delta^{18}O$ is also shown. The modelled streamflow signal demonstrated damping of the precipitation signal with a maximum simulated value of −5.8‰ and a minimum value of −10.1‰. This compared with −7.8‰ and −9.0‰ for the measured streamflow data and +1.1‰ and −14.3‰ for the measured precipitation data. Due to their temporal resolution, the sample data provide only limited information regarding the temporal variability in $\delta^{18}O$ and the stream $\delta^{18}O$ data would be expected to be less variable than the modelled time-series data. However, it is clear that the overall variability in $\delta^{18}O$ was not captured by any of the models that were deemed acceptable in terms of their flow calibration, although some of the temporal dynamics of the $\delta^{18}O$ response appeared to be successfully mimicked.

Simulation of Cl^-

Simulation of stream Cl^- concentrations was also attempted with the STREAM model. Long-term Cl^- data were available from the ECN dataset, enabling a 9 year simulation to be undertaken from October 1996 to October 2005. The measured Cl^- concentration in weekly precipitation samples was used to generate a time-series input of tracer for the STREAM model, again with an assumption of constant concentration applied to the period between each sample. Based on the analysis of the Cl^- budget, a uniform weighting factor of 1.55 was derived from the mean measured streamflow concentration ($7.6\,mg\,l^{-1}$) divided by the expected mean Cl^- concentration in runoff

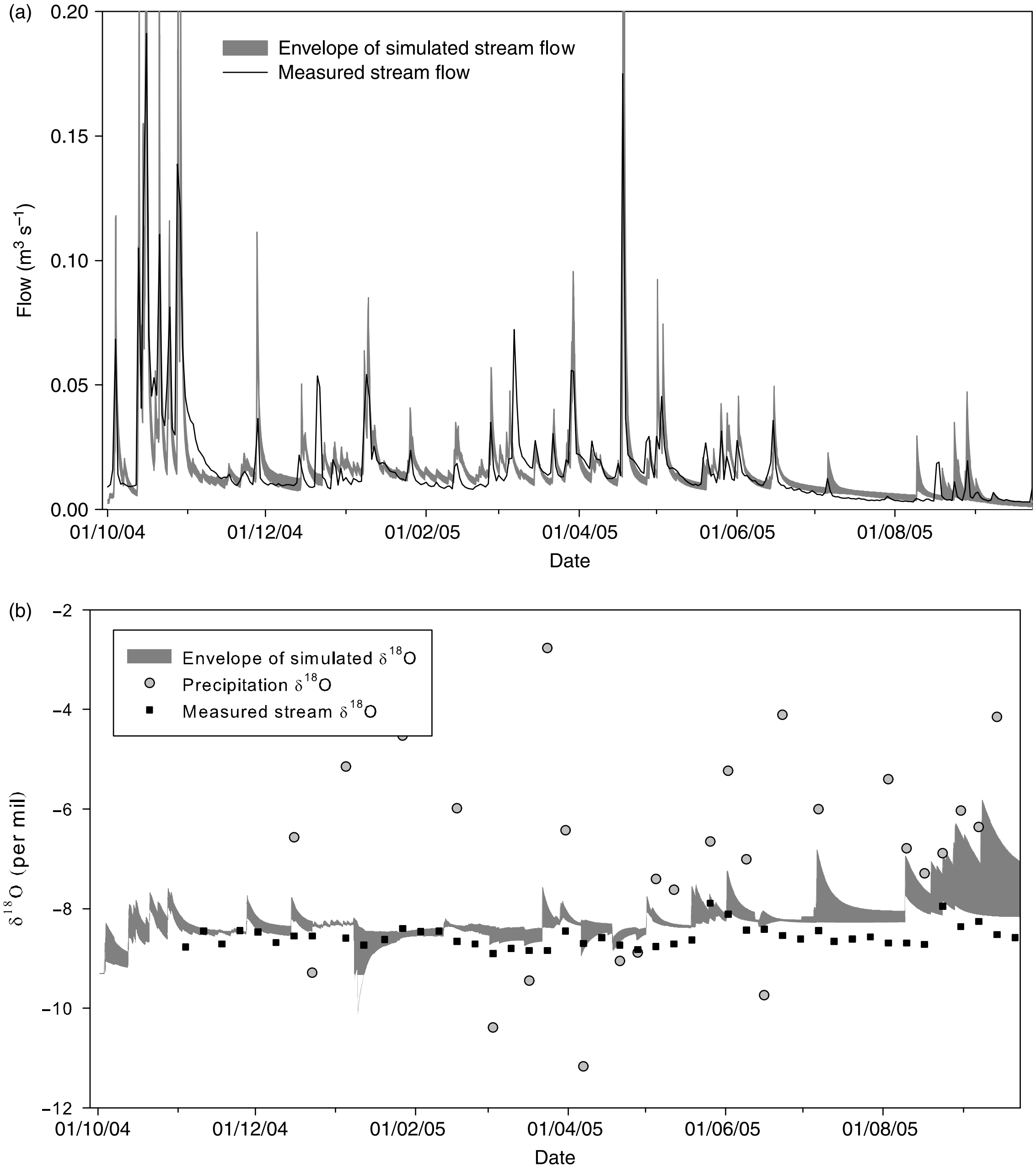

Figure 6 | Upper and lower bounds of simulations from 22 acceptable flow parameter sets with no deep groundwater flow (a) for streamflow compared with measured stream data and (b) for $\delta^{18}O$ compared with measured precipitation and stream data.

($4.8\,mg\,l^{-1}$). This factor was applied to the measured precipitation concentrations to account for the additional estimated input from dry and occult deposition. In addition, no Cl^- was removed with ET water in the model. The initial conditions for Cl^- concentrations were set to $7.5\,mg\,l^{-1}$ for the soil and deep groundwater. These values were based on Cl^- concentrations previously measured in soils and groundwaters in the catchment (Dunn *et al.* 2006).

A daily time-step was used within the model and 9 year simulations were run for each of the 22 parameter sets deemed acceptable from the flow simulations. The results are presented in Figure 7, where the upper and lower

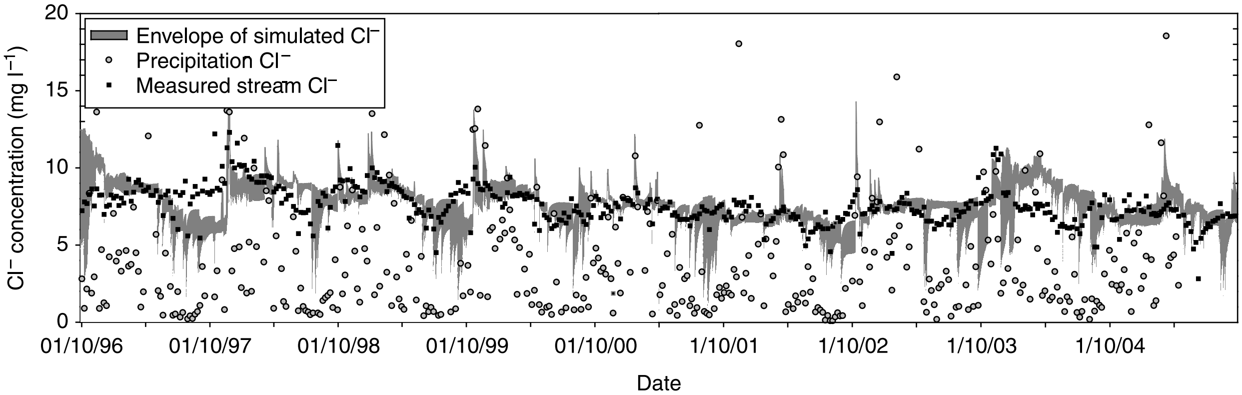

Figure 7 | Upper and lower bounds of Cl^- simulations from 100 acceptable flow parameter sets for 1996–2005 using a daily time-step model.

bounds of simulated response are compared with both the measured precipitation signal and the measured stream water signal. In general, the bounds of predicted Cl^- concentrations followed the same seasonal patterns as the measured data with a comparable mean (7.7 mg l^{-1} simulated, 7.6 mg l^{-1} measured). The standard deviation of the median value from the 100 simulations (1.5 mg l^{-1}) was slightly greater than for the measured data (1.2 mg l^{-1}); a result that would be expected given the weekly sampling resolution of the measured data. The standard deviations of the upper and lower predicted bounds were only slightly greater than the median at 1.6 mg l^{-1}.

Although the seasonal variability of the simulations was acceptable, the short-term variability in the Cl^- response was often poorly represented.

Model sensitivity to inclusion of deep groundwater

The previous simulations for $\delta^{18}O$ and Cl^- were based on a conceptual model that included two main runoff mechanisms: near-surface runoff (including infiltration excess) and shallow groundwater hill-slope flow. The presence of deep groundwater flow, even as a small contribution, has the potential to significantly alter the observed tracer response and MRT of a catchment. Inclusion of deep groundwater flow as a third flowpath in the STREAM model was therefore investigated in order to examine the sensitivity of the simulations and gain a better understanding of the uncertainty inherent in the results. This required the estimation of three parameter values: *rech*, *dGwSInit* and *dGwK*. From the stream baseflow, a maximum value of *rech* of 0.015 mm h^{-1} could be assigned. Setting values for *dGwSInit* of 500–1,500 mm, approximate values for *dGwK* were estimated to balance the recharge rate (thus effectively adding only two further degrees of freedom with the deep groundwater model). These figures were used as bounds for the deep groundwater parameters and an additional set of 750 model simulations was run using the same ranges for other parameters as previously defined. From these simulations, 100 satisfied the three flow criteria (NS efficiency, NS efficiency of log flow, flow proportion), compared with 22 out of 500 simulations when deep groundwater was excluded, indicating a general improvement in model fit. The upper and lower bounds predicted by these 100 parameter sets are shown in Figure 8(a) for flow and in Figure 8(b) for $\delta^{18}O$. Qualitative comparison of this figure with Figure 6 indicates that inclusion of the deep groundwater component gave at least as good a prediction of both the stream baseflows and the temporal dynamics of the $\delta^{18}O$ response, compared to the model with only two flow paths. However, the bounds of predicted $\delta^{18}O$ still failed to fully enclose the observed values and generally over-predicted the response to the summer high-flow events.

Model sensitivity to mixing of infiltration excess water

All of the preceding $\delta^{18}O$ simulations tended to result in over-prediction of the dynamics of the stream response during the summer high-flow events. Comparison of the values for the infiltration capacity parameter *infThresh* with the sum of square errors for each of the 100 simulations

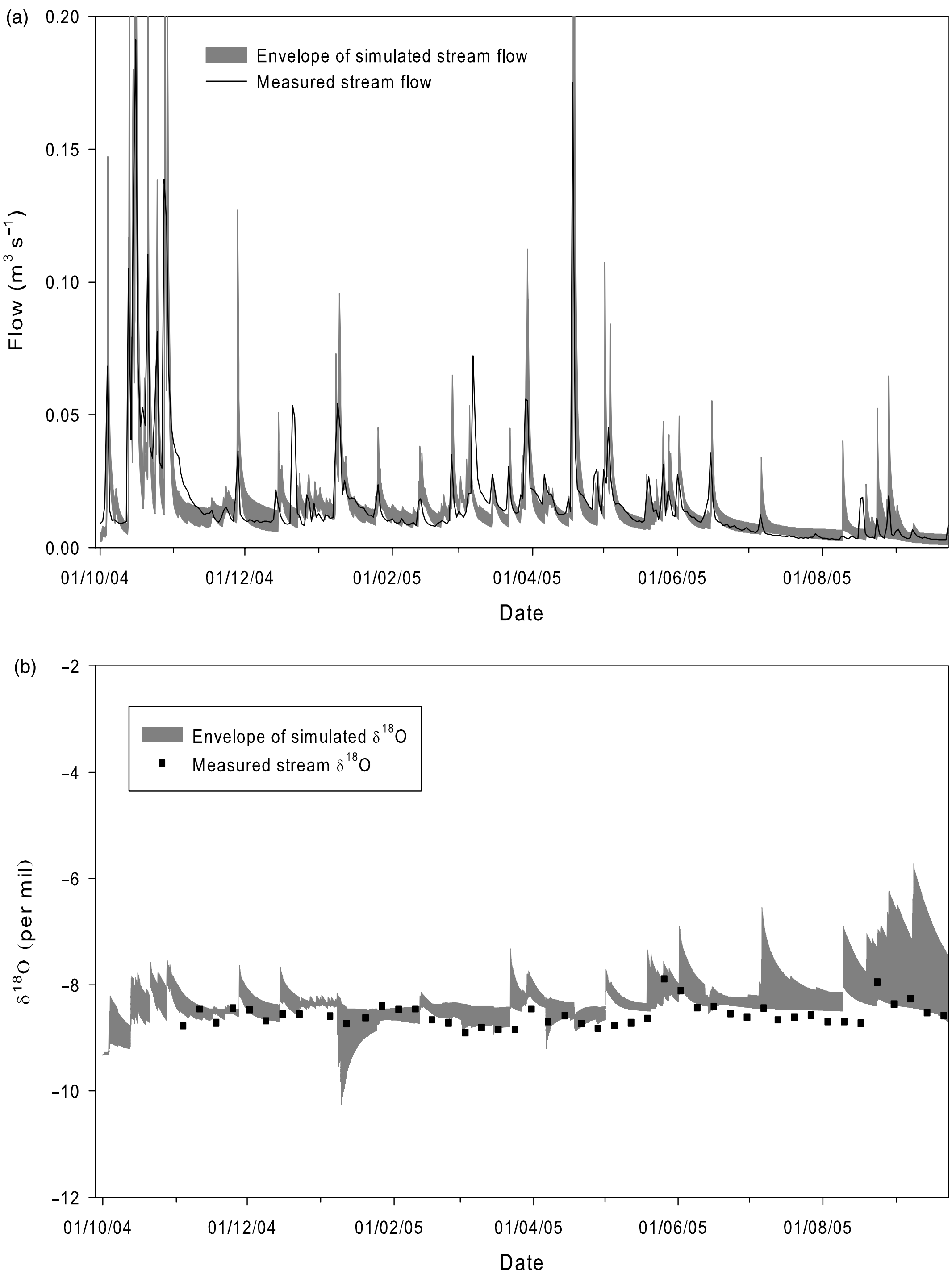

Figure 8 | Upper and lower bounds of simulations from 100 acceptable flow parameter sets including deep groundwater flow (a) for streamflow compared with measured stream data and (b) for $\delta^{18}O$ compared with measured precipitation and stream data.

carried out above showed a strong linear relationship (Figure 9(a)). The smallest error in the $\delta^{18}O$ simulations corresponded to those parameter sets with the highest value of infiltration capacity, representing the model simulations with least infiltration excess runoff. The same relationship did not hold true for prediction of flow, as shown by the plot of NS efficiency values against *infThresh* (Figure 9(b)). This suggested that the presence of infiltration excess runoff improves the simulation of streamflows in terms of the temporal dynamics of the runoff generation. However, the $\delta^{18}O$ carried with the infiltration runoff does not transfer the signature of rainwater to the stream. Hence, the data indicate that infiltration excess runoff has been at least partially mixed with other water prior to reaching the stream.

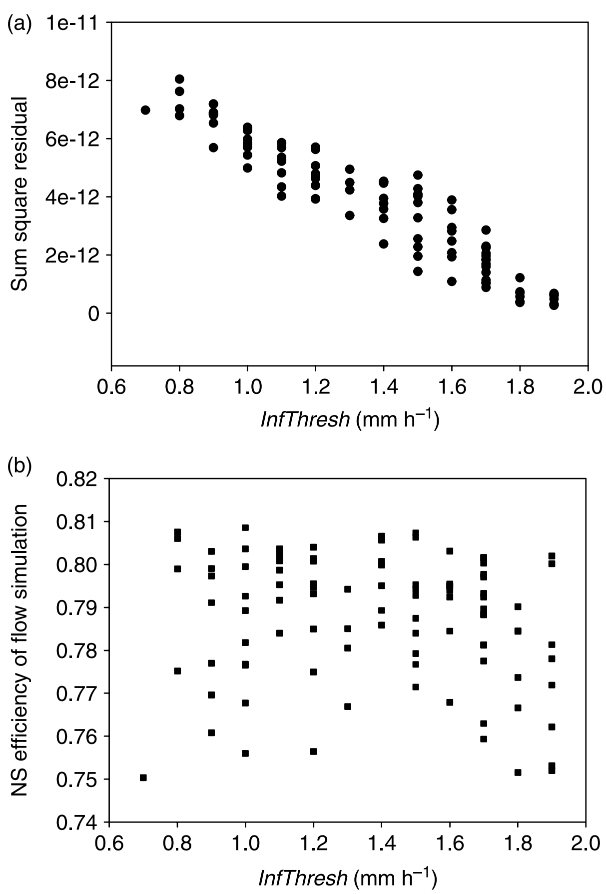

Figure 9 | Influence of *infThresh* parameter value for 100 model simulations on (a) sum of squares for $\delta^{18}O$ simulation and (b) NS efficiency value for flow simulation.

This was examined by re-coding the STREAM model such that all $\delta^{18}O$ associated with incoming precipitation was mixed within the soil store before being lost by any runoff mechanism, including infiltration excess (thus representing the alternative extreme scenario of full mixing). The same 100 simulations (including deep groundwater) were then re-run, and the resulting $\delta^{18}O$ predictions are shown in Figure 10. As expected, the bounds of simulated response were damped compared to the previous simulations. The $\delta^{18}O$ response during the summer events was closer to the observed values. However, these improvements appeared to be at the expense of a loss in the ability to predict the dynamics at other stages of the simulation.

Model estimation of MRT

The MRT of the catchment simulations can be evaluated from the model, but require long model runs to achieve full tracer recovery. For the model representation with no groundwater, only around 63% of a pulse tracer applied 31 days after the start of the simulation is recovered within 1 year. Time-series input data were therefore cycled to generate longer simulations. Using 10 years of data, around 97% of the pulse input of tracer was recovered and the MRT was evaluated for each of the 22 acceptable parameter sets. These simulations gave MRT values for the catchment ranging from 258 to 338 days. The residence times of the two main flowpaths ranged from 228 to 321 days for the near-surface runoff (including the infiltration excess component, which itself has a very short residence time) and 285 to 345 days for the groundwater hill-slope runoff.

The MRT for the catchment simulations including deep groundwater was also calculated in a similar way, except that in this case a time-series of 100 years was necessary to recover most of the pulse input of tracer. Values for the MRT were found to range from 1.1 to 8.5 years with between 93 and 97% recovery of the pulse input. Breaking the MRT down into its three flow components gave 311–418 days for the near-surface runoff, 367–425 days for the groundwater hill-slope flow and 12–48 years for the deep groundwater flow. The difference between these figures and those calculated for the model without deep groundwater demonstrate that the available tracer data cannot be used to estimate the catchment mean residence

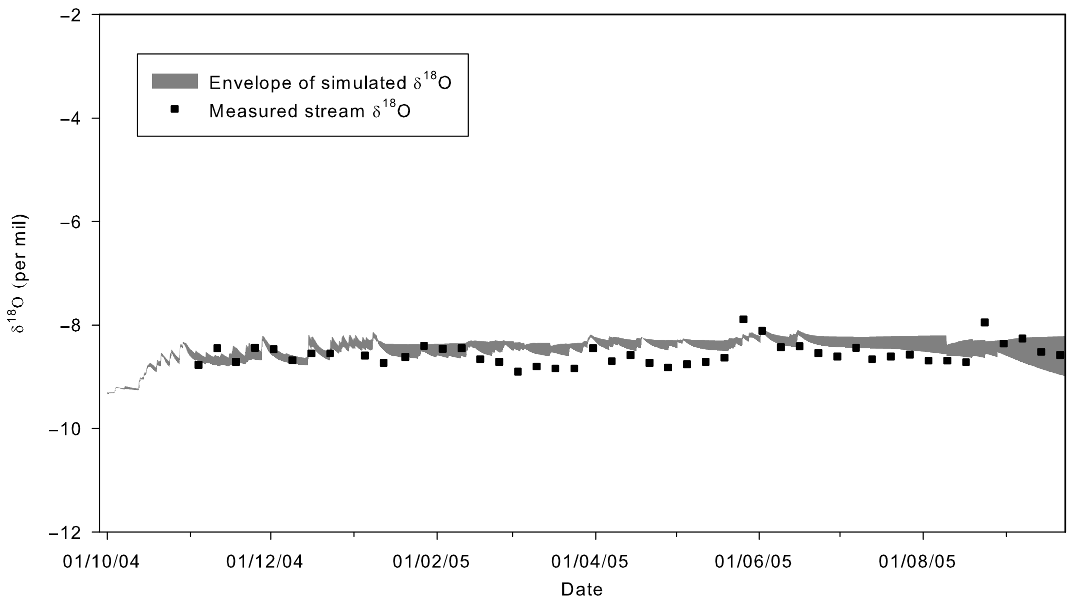

Figure 10 | Upper and lower bounds of δ^{18}O simulations from 100 acceptable flow parameter sets including deep groundwater flow, using assumption of complete mixing of δ^{18}O between infiltration excess water and soil water.

time with any certainty. Not only is there a strong influence of the deep groundwater on the mean value, but its presence also modifies the residence times of both the near-surface runoff and the groundwater hill-slope flow. This is because the leakage to groundwater reduces the runoff by surface and shallow groundwater pathways, thus increasing the turnover time of the water in the soil profile.

The nature of the infiltration excess mixing also affects the MRT of near-surface runoff and groundwater hill-slope flow. An assumption of full mixing of infiltration excess water leads to a more rapid turnover of the water in the soil profile, and hence reduces the residence times. This is counter-intuitive to what one would expect since the infiltration excess itself has an increased residence time.

DISCUSSION

A modelling study was undertaken to investigate how successfully two natural tracers, δ^{18}O and Cl^-, could be utilized to improve the understanding of hydrological behaviour in a small upland catchment in the northeast of Scotland. The study achieved some success in modelling the data, but also encountered a range of practical difficulties.

Data issues

The clearest example of problems associated with the data was the difficulty in achieving a simple balance between the inputs and outputs to the catchment for both the tracers. For δ^{18}O, the volume-weighted mean of the precipitation input was calculated as 9% higher than the mean of the stream measurements. This discrepancy can be accounted for by errors in the measurement of precipitation volumes, missing data points and unmonitored spatial variability in the data. Less important errors are caused by unmonitored temporal variability in the stream δ^{18}O (small compared with the variability in the precipitation input) and the analytical measurement of δ^{18}O (accurate to $\pm$ 0.1‰).

It is also possible that the precipitation inputs were not in balance with the outputs measured in the stream over the relatively short period of one year. The mismatch of 9% was believed to be acceptable for use within the conceptual modelling. However, a greater potential issue in this respect was found to be the limitation of using a step function to define the precipitation δ^{18}O input, with a uniform value applied to each period between samples. This arose from the temporal resolution of the experimental sampling, demonstrating the need to increase the temporal resolution of precipitation sampling (e.g. Shand *et al.* 2005).

The errors in the Cl^- mass balance were more serious, and could not be accounted for by evapotranspiration losses coupled with similar measurement errors to δ^{18}O. Limited data indicated that an important source of the error was due to dry and occult deposition of Cl^-. Quantification of such inputs is problematic (Wesely & Hicks 2000; Peters *et al.* 2006). Although the concentrations of the intercepted water could easily be measured on a more frequent basis, the actual volumes are difficult to determine. However, regular sampling of the intercepted water would enable temporal variability in the concentrations to be characterized, which could be used to develop a temporally varying weighting function to estimate the Cl^- inputs to the catchment. Integration of the Cl^- data within a conceptual model gave acceptable simulations of the response with regard to the degree of damping and seasonal variability, but poor representation of the short-term variability reflecting the limitations of the input data. The results of the model analysis were comparable to the recent findings of Page *et al.* (2007) who found difficulty in simulating the stream Cl^- signal in the Plynlimon catchment despite the availability of daily precipitation Cl^- data.

The regular sampling strategy was also found to be problematic in terms of the model evaluation, because of its bias towards monitoring of baseflow conditions. This made it difficult to assess whether short-term variability simulated by the model is incorrect, or simply not reflected by the monitored data.

Model structure

Aside from the limitations of data in achieving good model simulations, the analysis demonstrated the importance of some of the uncertainties inherent in the model structure and parameterization. The potential role of a deep groundwater source in runoff generation in the catchment was investigated, and the simulations indicated that such a contribution was feasible. However, because of the low sensitivity of the simulated hydrograph to this flow path, and the relatively poor simulation of the tracer response, it is not possible to confirm either the characteristics of such a flow path or even its existence by this experiment alone.

Given the uncertainties in the data, and apparent inconclusiveness of the model results with regard to process definition, the question arises as to the merit of undertaking such a conceptual modelling exercise. The value of the insights from the model will reflect the quality of the model itself. However, we argue that these insights can be extremely useful provided that the modelling is seen as a tool for probing sensitivities and developing hypotheses for further testing, rather than as a definitive representation of the catchment processes. The modelling procedure demonstrates how different processes can interact and mix and the outcomes that this generates in terms of catchment responses. Such understanding is very difficult to develop without an underpinning numerical basis. Simpler approaches, for example based on statistical relationships between inputs and outputs, yield single-step associations that provide minimal interpretation of the complex multi-response systems that are known to exist.

Tracer data and MRT estimation

Tracer data provide an orthogonal dataset to streamflows for interpretation of catchment processes and, as such, have great potential to supplement understanding. In this example, it was clear from the strongly damped stream δ^{18}O signal that water within the system must be well mixed and the model was therefore structured to represent this. In other catchments, the degree of mixing may be less clear and is likely to be temporally variable. Other types of tracer data and analysis, such as end-member mixing using hydrochemical tracers (Hooper *et al.* 1988), can also be employed to improve understanding of these mixing processes and how they vary with time. Information of this type is extremely important in terms of the manner in which a catchment will respond to changes in external drivers; stream hydrographs alone do not provide sufficient information about catchment behaviour to enable these processes to be identified. Thus, even if the uncertainties in the tracer data only enable them to be used as soft data, they are still of value for improving interpretation of behaviour.

Adequate representation of catchment mixing processes and flow pathways is essential for estimating mean residence times. Modelling the δ^{18}O variability in the Glensaugh catchment was particularly difficult because fluctuations around the mean value of the stream δ^{18}O are small. Consequently, it also makes it extremely difficult to assess the MRT of the water. If we neglect a potential influence of deep groundwater, the δ^{18}O simulations estimated an MRT of the order of 9–12 months which was consistent with the estimate from the Cl$^-$ data, based on the *a priori* assumption of an exponential distribution. However, the potential influence of deep groundwater increased the modelled MRT estimate to 11–14 months for the near-surface and hill-slope runoff.

The modelled MRT is also affected in a similar way by changing the assumption of how infiltration excess water mixes. Given the well-mixed nature of the system, the primary control on the MRT becomes the size of the soil/groundwater store, a parameter which has been estimated from soil physical data. The uncertainty associated with this value could be significant, particularly in terms of the unknown spatial variability of soil depth across the catchment. The potential influence of a small fraction of deep groundwater on the MRT also skews the estimated catchment MRT to be much older. Since the conceptual modelling illustrated that the presence or absence of such a flow path is very difficult to validate, this raises questions about the value of MRT, alone, as a catchment descriptor. A similar hypothetical analysis of the components of catchment MRT in the Maimai catchment has previously flagged up the same issue (Dunn *et al.* 2007). In practice, it would appear that knowledge of the residence time distribution is necessary to provide more meaningful information about how a catchment behaves.

Catchment learning framework

The modelling philosophy described here is one where conceptual models are seen as one tool in an iterative process that involves experimental design, implementation and assessment to generate a 'learning framework' methodology for understanding catchment processes. The integration of tracers within such a methodology is believed to be of value, despite the additional uncertainties that they introduce to the modelling procedure.

In this example, the modelling has stimulated two further field experiments to further probe the nature of the tracer response and water residence times, as well as highlighting the limitations of the available experimental data. The first of these experiments aims to test the hypothesis that a small fraction of old water (with a mean residence time of greater than 10 years) contributes to streamflow in the catchment. This will be examined through collection and analysis of groundwater samples from a range of sources in the catchment to estimate their age using chlorofluorocarbons (CFC) and sulphur hexafluoride (SF_6) dating techniques. The second experiment will test the hypothesis that during high-flow events, a small fraction of the incoming precipitation reaches the stream without having been mixed with pre-event water. This will be achieved through the collection and analysis of tracer data for precipitation and streamflow during a storm event.

CONCLUSIONS

The objective of this study was to evaluate the utility of two different natural tracers in modelling the hydrological behaviour of a small upland catchment in northeast Scotland and to assess the residence time of water in the catchment. A novel conceptual hydrological modelling framework that integrates simulations of tracer behaviour was applied and found to have limited success in simulating the responses of δ^{18}O and Cl$^-$ in streams. However, the study presented a number of technical difficulties that arose from the many uncertainties inherent in the data and modelling procedure.

Notwithstanding this, the tracer data were believed to be of value for interpretation of catchment runoff generation mechanisms, by providing an orthogonal type of data to streamflows. Integration of the tracer data within the model permitted the exploration of different runoff processes and assessment of their feasibility. For the Glensaugh catchment, the potential occurrence of a small contribution of deep groundwater to streamflow was examined. The sensitivity of the model to this flow path was found to be low and consequently the available data were insufficient to either confirm or reject the runoff mechanism. This was shown to be important in terms of evaluating catchment mean residence times, as the deep groundwater flow path significantly altered the residence time distribution of catchment waters. In addition to contributing a small fraction of very old water, the presence of the deep groundwater recharge modified the dynamics of the soil profile in the model, leading to an increase in the mean residence times of runoff generated by the near-surface flow path and groundwater hill-slope flow.

The model showed that waters in the catchment are generally well mixed within the soil profile prior to runoff, but gave an indication of a small contribution of new water to streamflow from infiltration excess runoff during storm events. The modelling has stimulated two further field experiments to further probe the presence of the deep groundwater contribution and the presence of some new water during storm events. Through this approach, the model simulations have provided a feedback loop to inform the design of appropriate field experimentation, thus completing the formation of a catchment learning framework.

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