

Towards integrating tracer studies in conceptual rainfall-runoff models: recent insights from a sub-arctic catchment in the Cairngorm Mountains, Scotland

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Abstract:

Hydrochemical tracers (alkalinity and silica) were used in an end-member mixing analysis (EMMA) of runoff sources in the 10 km² Allt a' Mharcaidh catchment. A three-component mixing model was used to separate the hydrograph and estimate, to a first approximation, the range of likely contributions of overland flow, shallow subsurface storm flow, and groundwater to the annual hydrograph. A conceptual, catchment-scale rainfall-runoff model (DIY) was also used to separate the annual hydrograph in an equivalent set of flow paths. The two approaches produced independent representations of catchment hydrology that exhibited reasonable agreement. This showed the dominance of overland flow in generating storm runoff and the important role of groundwater inputs throughout the hydrological year. Moreover, DIY was successfully adapted to simulate stream chemistry (alkalinity) at daily time steps. Sensitivity analysis showed that whilst a distinct groundwater source at the catchment scale could be identified, there was considerable uncertainty in differentiating between overland flow and subsurface storm flow in both the EMMA and DIY applications. Nevertheless, the study indicated that the complementary use of tracer analysis in EMMA can increase the confidence in conceptual model structure. However, conclusions are restricted to the specific spatial and temporal scales examined. Copyright © 2003 John Wiley & Sons, Ltd.

KEY WORDS hydrograph separation; flow paths; end-member mixing analysis; conceptual; modelling; hydrology; Cairngorms; Scotland

INTRODUCTION

Using insights from tracer studies to validate rainfall-runoff models is a promising field in catchment research (Turner and Barnes, 1998; Genereux and Hooper, 1998). Tracers can be used as constraints in model calibration or for defining alternative objective functions for validation (Lundquist *et al.*, 1990; Mehlhorn and Leibundgut, 1999). Over the past decade, advances in tracer technologies and readily available conceptual models have underpinned the evolution of this integrated approach (Robson *et al.*, 1992). For example, a recent application of end-member mixing analysis (EMMA) in tracer studies has helped highlight the associated methodological limitations and contributed to methods for estimating uncertainty in model predictions (Genereux, 1998). Similarly, the increasing availability of digital data sets within a geographical information system (GIS), and the increasing processing capacities of computers, have contributed to the development of conceptual semi-distributed models that can account for spatial heterogeneity in catchment characteristics. Such models can incorporate a feasible representation of hydrological flow paths needed to predict stream chemistry without being too highly parameterized, and thus provide alternative objective

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functions that can be used to explore the model behaviour and structure (Dunn *et al.*, 1998; Gunter *et al.*, 1999; Uhlenbrook and Leibundgut, 1999). Such approaches offer flexible tools that can aid the understanding and modelling of catchment systems. Given recent cautions against the problems of equifinality and uncertainty in hydrological modelling (e.g. Beven, 1996, 2001), such tools are valuable in critically evaluating the results of modelling studies.

In this paper, we present a study that has sought to integrate the insights of tracer studies and conceptual modelling in the 10 km² Allt a' Mharcaidh catchment in Scotland. The catchment has a long history of hydrological research, and a detailed knowledge gained during many years of fieldwork provided a suitable context for such integration. Hydrometric studies initially identified some of the key processes involved in the production of storm runoff in different parts of the catchment (Wheater *et al.*, 1991, 1993). Tracer studies were subsequently used to examine the influence of different hydrological pathways, including those involving snowmelt, on runoff generation (Jenkins *et al.*, 1993, 1994; Ogunkoya and Jenkins, 1993). These earlier studies helped to develop a conceptual catchment model that could also simulate tracer (alkalinity) concentrations on the basis of soil water chemistry (Wheater *et al.*, 1990). The model had some success in simulating the chemistry during high and moderate flows, but was less successful during base flow periods. Subsequently, geochemical tracer studies of groundwater in boreholes and emerging from springs identified the important contribution of groundwater to the catchment response during both high and low flows (Jenkins *et al.*, 1994; Soulsby *et al.*, 1998, 1999). Increasingly, the complexity of the catchment response, in terms of intra-storm and inter-annual variation, has become apparent through the use of mixing models, both during individual events and over the hydrological year (Jenkins *et al.*, 1994; Soulsby *et al.*, 1998). Recent studies with ¹⁸O have indicated that widely varying residence time spectra have been identified for different hydrological stores in the catchment—these show mean residence times of weeks to months for soil water, and *ca* 2 year⁻¹ and >5 year⁻¹ for shallow and deeper groundwater respectively (Soulsby *et al.*, 2000).

Using complementary methods of tracers and a conceptual rainfall-runoff model to test hypotheses relating to the catchment's hydrological functioning, the study had three specific aims. First, to develop a three-component mixing model based on identifiable end members to separate the annual hydrograph of the Allt a' Mharcaidh on the basis of the two geochemical tracers (Gran alkalinity and silica). Secondly, to apply a conceptual rainfall-runoff model (DIY) to the Mharcaidh at the catchment scale, use it, in combination with knowledge gained in previous process studies, to partition runoff according to flow paths and compare this with the results of mixing analysis (Dunn *et al.*, 2001). Thirdly, to adapt the conceptual model to predict the chemistry of stream water. Throughout the study, attention was paid to assessing the uncertainty and sensitivity of the model predictions.

STUDY AREA AND DATA SOURCES

The Allt a' Mharcaidh catchment lies within the Cairngorm mountains of Scotland. The catchment is underlain by granite and spans an altitudinal range from 330 to 1118 m (Figure 1). Mean annual precipitation is 1200 mm, much of which falls as snow, particularly at the higher altitudes. A substantial snow pack can be present between November and May (Soulsby *et al.*, 1997). The catchment is covered by three main soil types, which have distinct hydrological characteristics (see Dunn *et al.* (2001) for details). These characteristics exert strong controls on catchment hydrological pathways (Figure 1). At altitudes above 800 m, freely draining alpine soils overlie extensive periglacial deposits. These are characterized by vertical flow paths to the bedrock interface, and water subsequently discharges at high-altitude springs, or flows laterally down slope in the deeper subsurface (Wheater *et al.*, 1991). In this down-slope area, hillsides steepen and podzolic soils predominate. These are characterized by transient lateral flow paths (subsurface stormflow) in the more permeable organic surface horizon during storm events, and, during large storms, for prolonged periods after storms in the deeper subsurface in the soil mineral horizons (Wheater *et al.*, 1993). These soils are highly heterogeneous and preferential flow is important in delivering hillslope waters to the channel network (Jenkins *et al.*, 1990).

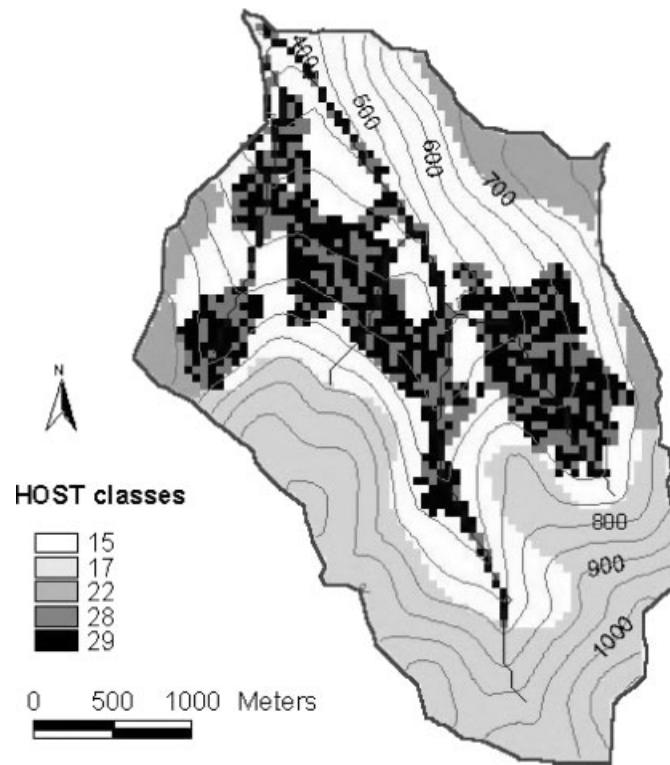


Figure 1. Allt a' Mharcaidh catchment showing topography and soil cover according to HOST classes. The soils are classified in a 50 m × 50 m grid used in DIY and show podzols (15), alpine soils (17 and 22) and deep peats (28 and 29)

In the valley bottom area, extensive areas of blanket peat (in places over 2 m deep) cover slopes of lower gradient where deep (>10 m) glacial and periglacial drift overlay the granite. Overland flow from these, often saturated, areas is the main contributor to the storm response of the catchment (Wheater *et al.*, 1991). In some places, return flow from the upslope podzolic soils also contributes to storm runoff, though deeper subsurface flow that contributes to groundwater recharge through the drift also occurs. In the 10 m or so fringing the river channel, a narrow strip of alluvial soils predominate. Groundwater discharges in the riparian zone either via springs or by seepage into the bed of the stream (Soulsby *et al.*, 1998).

Flows in the stream have been monitored since 1985 using a pressure transducer in a natural rated section, together with parameters like pH, conductivity, and temperature. Stream water samples have been collected weekly or bi-weekly and analysed for a range of determinands, including Gran alkalinity (determined by titration to an end point of 3.0 to account for organic anions (Hill and Neal, 1997), silica (expressed as SiO₂), and ¹⁸O isotopes (Ferrier and Harriman, 1990). In addition, soil waters have been sampled in the main catchment soil units (Ferrier *et al.*, 1990), and groundwaters have been sampled from both boreholes and springs (Soulsby *et al.*, 1998, 1999).

MODELLING APPROACH

EMMA

Based on previous hydrometric and tracing studies, three main hydrological flow paths have been postulated to conceptualize the hydrological and hydrochemical response of the catchment (Wheater *et al.*, 1990; Jenkins

et al., 1994; Soulsby *et al.*, 1998). The contrasting hydrochemical characteristics of these flow paths have been used to identify three end members for EMMA diagrams (see example in Figure 2). Storm runoff from overland flow (OF) and shallow subsurface storm flow in organic soil horizons have low alkalinity and low silica concentrations. In contrast, average groundwater (GW) composition has much higher alkalinity and silica concentrations, with subsurface storm flow (SSF) in the mineral horizons of the catchment soils being intermediate between the two.

The spatial and temporal variation that can occur in end-member composition is well established in catchment studies (Hooper *et al.*, 1990), and the Allt a' Mharcaidh is no exception, with both soil water and groundwater exhibiting marked variability (Table I), often over short spatial and (during storm events) temporal scales (Jenkins *et al.*, 1994). However, differences between end members are generally greater than their variability; moreover, this study aimed to separate the hydrograph at the catchment scale for daily time steps, thus reducing the effect of variation in end-member composition on modelling results. In many ways, this application of the EMMA approach is consistent with the notion of conceptualizing the emergent properties of processes operating at the catchment scale over the course of the hydrological year (Barnes,

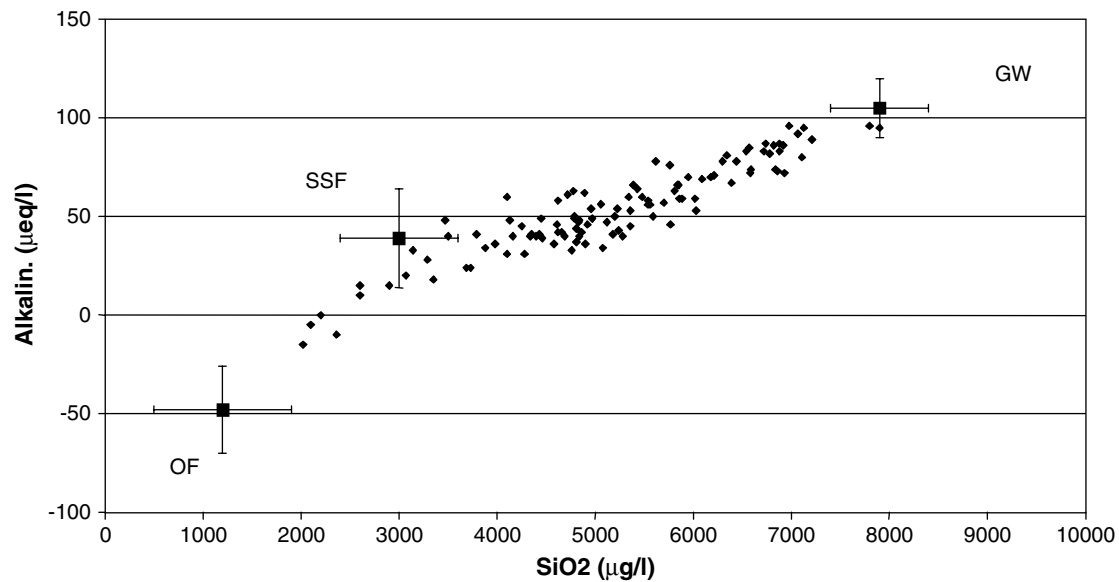


Figure 2. An example of an EMMA diagram for the Mharcaidh. Stream water chemistry is shown in relation to the mean (and standard deviations) overland flow (OF), subsurface storm flow (SSF) and groundwater alkalinity ($\mu\text{eq l}^{-1}$) and silica ($\mu\text{g l}^{-1}$) concentrations

Table I. Variation in end-member composition (mean and range) for various Allt a' Mharcaidh source waters

		Gran alkalinity ($\mu\text{eq l}^{-1}$)	Silica (as SiO_2) (mg l^{-1})
Organic soil	Mean	-48	1.2
	Range	-75 to 24	0.1-2.1
Mineral soil	Mean	40	3.1
	Range	14-69	2.3-5.78
Shallow spring	Mean	18	3.35
	Range	20-55	2.18-3.73
Boreholes	Mean	105	7.98
	Range	32-210	4.46-9.05

2001). Whilst it is recognized that process complexity, and thus variability in end-member composition, is much greater than is incorporated in the model, the conceptualization is deemed appropriate for the spatial and temporal scales of interest (Wade *et al.*, 2001). In this way, EMMA remains a pragmatic approach to hydrograph separation that can help estimate the contribution of water from different flow paths (Hoeg *et al.*, 2000).

A classical three-component mixing approach was applied, at daily time steps, to the hydrograph for the 1991–92 hydrological year using the method described by Jenkins *et al.* (1994). To overcome the problem of heterogeneity in end-member composition, low flow stream water samples ($<Q_{95}$) were used to define an integrated measure of the groundwater end member. Similarly, the overland flow end member was defined by the mean chemistry of high-flow surface waters from peat soils overlying granite (Dawson, 1999). Previous studies have demonstrated the utility of this pragmatic approach to overcome problems of soil and aquifer heterogeneity when defining end members (Wade *et al.*, 1999). Spatially weighted soil water chemistry collected from the mineral horizons of podzols and alpine soils was used to estimate the soil water end member (Ferrier *et al.*, 1990). To allow for uncertainty in end-member characterization, repeated hydrograph separations were carried out using EMMA; the end-member alkalinities for overland flow and subsurface storm flow (the most variable end members) were varied by one standard deviation of the measured chemistries, as indicated in Figure 2 (Foster, 2000). Whilst not a fully quantitative assessment of uncertainty in the EMMA separation (see Uhlenbrook and Hoeg 2003, this issue), the range of predictions indicate the potential variations of end-member contributions to the annual hydrograph.

As Gran alkalinity or silica in stream waters were only measured in weekly or bi-weekly spot samples, daily water quality time series had to be reconstructed. Minimum daily alkalinity concentrations were derived using the strong relationship ($r^2 = 0.859$) between the continuous pH record and the spot samples of alkalinity over part of the 15 year data record (cf. Wade *et al.*, 1999) (Figure 3). Secondly, the similarly good relationship between mean daily flow and minimum silica concentrations ($r^2 = 0.821$) was used to construct a daily time series of stream water chemistry. In both cases, independent periods were used for developing the regression model and predicting the time series. Minimum values were used to identify high-flow chemistries better and aid hydrograph separation.

DIY

The original development of the conceptual rainfall-runoff model, DIY, applied to the Allt a' Mharcaidh is described by Dunn *et al.* (1998). More recent developments of the model have also been presented. The

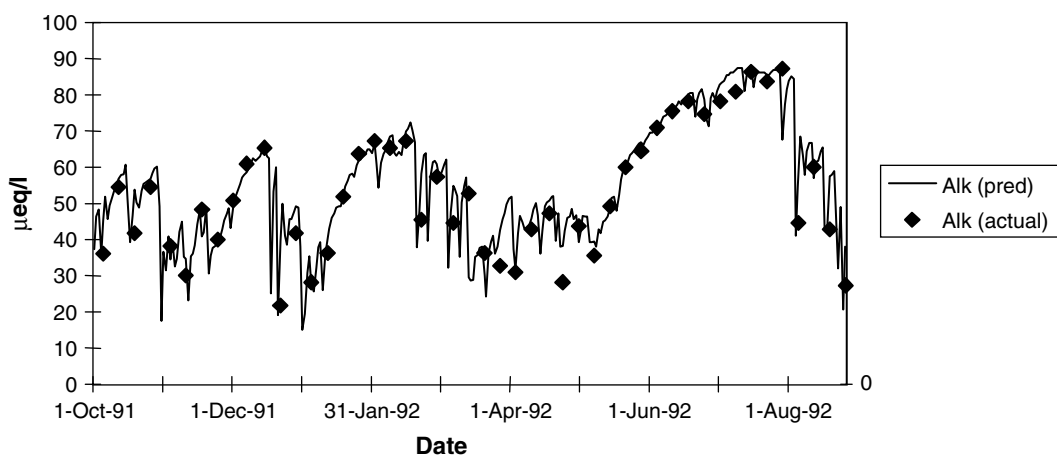


Figure 3. Constructed daily alkalinity ($\mu\text{eq l}^{-1}$) time series (based on continuous pH records) for the 1991–92 hydrological year, together with measured values

addition of a snowmelt subroutine is described by Dunn and Colohan (1999) and the use of a Monte Carlo framework for parameter identification is described by Dunn (1999). A methodology for linking parameters of the model to a soil classification has also been investigated (Dunn and Lilley, 2001). The version of the model used for this analysis is described by greater detail by Dunn *et al.* (2003, this issue) and illustrated in Figure 4.

Briefly, the model is based on a cell by cell storage balance linked to a hillslope routing function. Time series of flow contributions to the stream network are calculated for each characteristic cell within a catchment, typically defined at a resolution of $50 \times 50 \text{ m}^2$. Characteristic cell categories are defined by combining geographical information system layers, including topographic analyses and a range of other spatial classifications of physical properties, such as soil type, land use, and rainfall distributions, as appropriate for the model application. This approach permits characterization of hydrological properties at a relatively small scale whilst still enabling scaling-up to the catchment by combining the response of hydrologically similar areas (Dunn, 1998).

For each characteristic cell, meteorological inputs, in the form of net precipitation, are partitioned into three different stores, generating different runoff mechanisms. The runoff from each cell is routed to the stream using a disaggregated hillslope flow model controlled by two topographic parameters, viz. slope and flow path distance to the stream. The topographic parameters are derived from a digital elevation model. A further six model parameters relate to soil hydrological processes and are defined as: active zone conductivity, total soil porosity, threshold soil storage for fast response flow, fast response distance, groundwater conductivity, and a groundwater recharge fraction. These parameters control the distribution of the runoff between the three different flowpaths, as well as the runoff rates.

Dunn and Lilley (2001) have developed a preliminary methodology for linking the soil-related parameters to a hydrology of soil types (HOST) classification, described by Boorman *et al.* (1995). This methodology involves an inverse modelling approach whereby the distributions of HOST classes in different catchments are

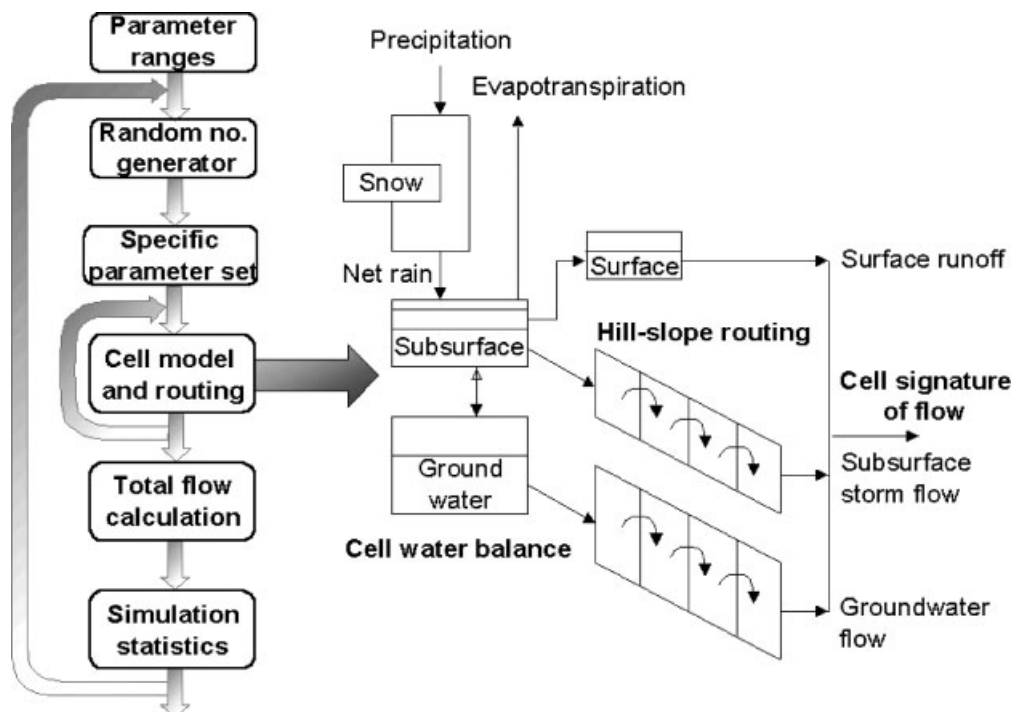


Figure 4. Structure of the DIY model showing the partitioning of flows into overland flow, subsurface storm flow, and groundwater

used to infer values of the model parameters. Initially, each of the DIY soil-related parameters was assigned a value of 'high', 'medium', or 'low' for each HOST class, on the basis of its conceptual functioning within DIY. An application of Monte Carlo simulations to two separate catchments was then employed to quantify values for 'high', 'medium' and 'low'. Results from this study are of a preliminary nature, but have been used and tested in the DIY application to the Allt a' Mharcaidh described here, and in more detail in Dunn *et al.* (2003, this issue). The HOST classification for the Mharcaidh is shown in Figure 1.

DIY also includes a simple module for snow accumulation and melt, with five parameters. These relate to critical snowfall temperatures, critical snowmelt temperatures, a degree-day factor to relate snowmelt to temperature, the fraction of the catchment area where snow accumulates in gullies, and a fraction to define how much snow is redistributed to gully areas by windblow (Dunn and Colohan, 1999). The parameters of the snowmelt module were calibrated for the Allt a' Mharcaidh using a period of streamflow record for the winter months, as well as observations of snow cover in the catchment.

The DIY simulations are run using a daily time step and evaluated through comparison of the predictions of streamflow with measured flows. Two measures of Nash and Sutcliffe efficiency are used to evaluate the quality of the simulations: one calculated using the full streamflow record and one calculated using data for days when streamflow is dominated by baseflow conditions, as in Dunn (1999). In this application, the period from 1 October 1991–1 October 1992 was studied because of the availability of good quality streamflow and hydrochemical data. A start date of 1 October minimizes problems with initial conditions for the model in terms of snow cover and soil moisture deficits. A suite of DIY simulations was performed for the Allt a' Mharcaidh using different parameter sets, the derivation of which are described in Dunn *et al.* (2003, this issue). The upper and lower extremes of prediction for each of the three runoff components are extracted from these simulations to provide output prediction bands from the model.

RESULTS

Figure 5a and b shows the EMMA-derived hydrograph separation for the study year investigated and Figure 5c gives the average predicted flow partitioning predicted by the EMMA approach. As previously identified by Soulsby *et al.* (1998), the high alkalinity, high silica groundwater end member contributes a relatively constant, though responsive, source of stream flows that rarely exceeds $0.2 \text{ m}^3 \text{ s}^{-1}$ and which is generally less than $0.1 \text{ m}^3 \text{ s}^{-1}$ (Figure 5b). This end member can account for virtually all of the low flow from the catchment, and rapid, transient contributions to relatively high flows need to be invoked to explain stream water chemistry. The model predicts that 35–47% of total runoff is derived from this end member over the hydrological year (see Figure 5c). In contrast, the low silica, low alkalinity overland flow end member is predicted to be the largest source of storm runoff (Figure 5a), accounting for 40–70% of flows during the largest rainfall and snowmelt events and between 13 and 32% of annual runoff (Figure 5c). Meanwhile, the intermediate alkalinity and silica hillslope water has a more subdued response, but appears to control the recession limb of the storm hydrograph (Figure 5b and c). The contribution of this conceptual flow path is predicted to lie between 27 and 42%.

Clearly, this modelling approach only represents a first approximation of flow path partitioning, but the results are consistent with the findings of previous hydrometric and tracer investigation (cf. Ogunkoya and Jenkins, 1993) and give a useful conceptual picture of runoff processes at the catchment scale over the hydrological year. This highlights the importance of overland flow from the valley bottom peats and upper organic horizons. These soils remain saturated, or close to saturation, for much of the year, and isotope studies (Soulsby *et al.*, 2000) have indicated that it is mainly pre-event water that is displaced during storm events. The estimated mean residence time for storm runoff is <6 months, with obviously much shorter residence times (hours or days) occurring during storm events. In addition, substantial, but less responsive, subsurface storm flow in the podzolic and alpine soils characterizes the recession, whereas deeper, longer residence time contributions (<5 years) from shallow groundwater in various drift deposits sustain base flows.

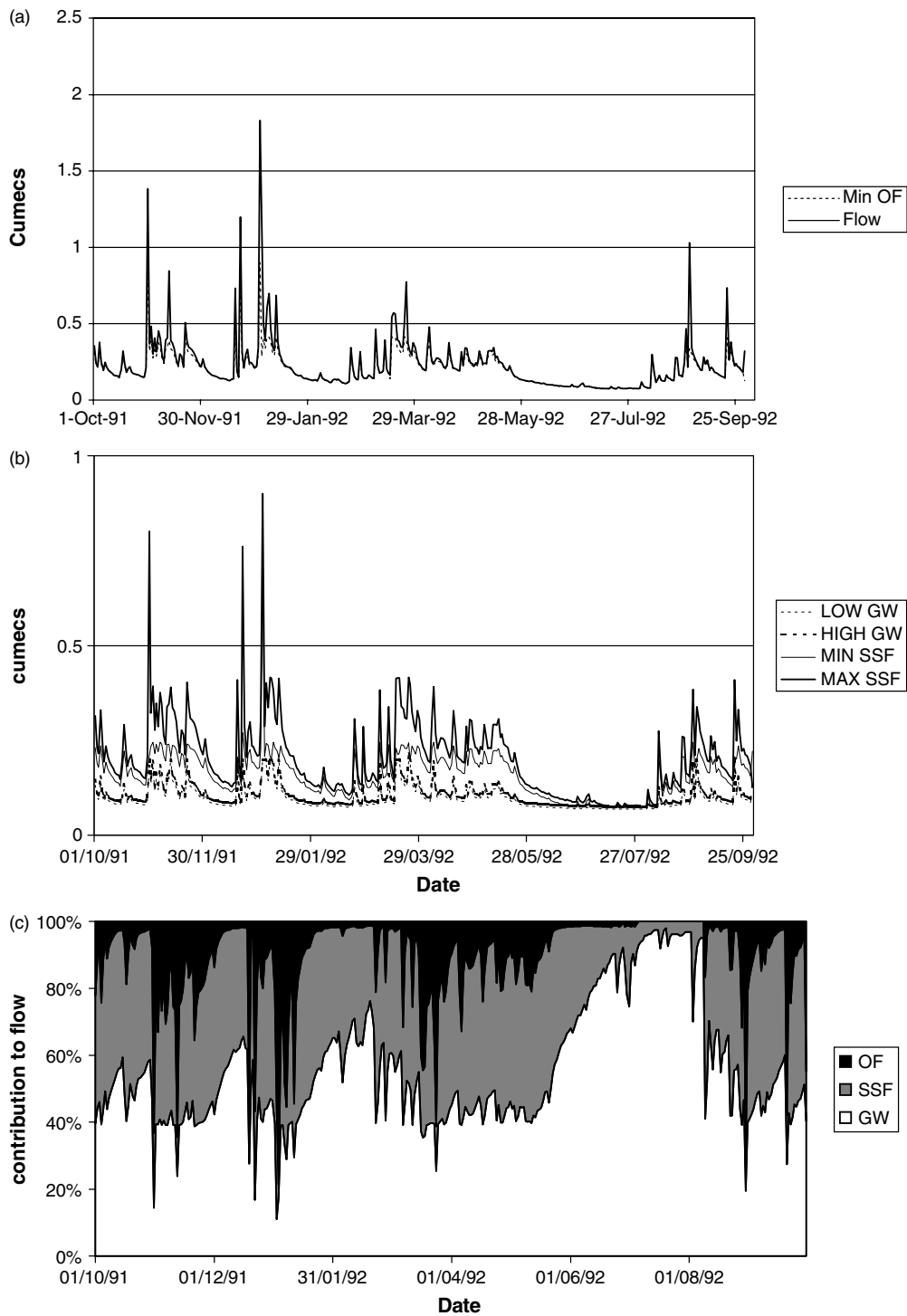


Figure 5. Results of EMMA prediction for the Allt a' Mharcaidh over the hydrological year, showing (a) overland flow (difference between flow and minimum OF line), (b) the maximum and minimum subsurface flow and groundwater contributions, and (c) average flow path partitioning by percentage

The mixing analysis indicated that groundwater contributions are relatively insensitive to variations in end-member composition; however, much greater uncertainty characterizes the separation of the overland flow and subsurface flow end members (Figure 5a and b). In part this reflects the continuum in chemistries observed in the catchment soils and their likely spatial and temporal variation (Figure 2). Moreover, although overland flow and subsurface storm flow are relatively easy to conceptualize in theory, there are identifiability problems when end-member chemistries can overlap, as is the case in this analysis and the flow paths are interdependent. Despite these uncertainties over the precise partitioning of flows, the results are consistent with hydrometric studies, which show that the storm hydrograph response is controlled by a peak produced by overland flow, with the recession controlled by deeper subsurface flow paths (Wheater *et al.*, 1991).

The application of DIY to the Allt a' Mharcaidh is described in detail by Dunn *et al.* (2003, this issue). The application was carried out without any reference to the results of the mixing model analysis. These were later used to provide an alternative objective basis to assess the structural uncertainty associated with the representation of the catchment in DIY. Generic soil parameters derived from studies elsewhere were successful at simulating total flows in the Mharcaidh, but failed to simulate base flows (Dunn *et al.*, 2001). Consequently, the groundwater recharge parameter had to be adjusted and was randomly selected from a constrained range between 0.12 and 0.28 to produce feasible simulation results (Dunn *et al.*, 2001). This is consistent with the significant groundwater storage in various drift deposits in the catchment, which has been implied in earlier studies (Soulsby *et al.*, 1998).

Following such adjustment, Figure 7 (see later) shows that the model was generally successful in simulating the hydrograph response of total stream flow, resulting in a Nash and Sutcliffe (1970) efficiency of 0.74 for the best simulations. The total annual runoff was predicted to within 6% and the upper and lower ranges of predicted flows generally envelope the measured flow (see Dunn *et al.* (2003, this issue) for more detail). These values are acceptable for such a topographically complex catchment with marked spatial variations in precipitation, snow accumulation and snowmelt (cf. Uhlenbrook and Leibundgut, 1999). However, significant variations in efficiency statistics were observed in 500 simulations, which allowed parameter values to vary within constrained ranges (Dunn *et al.*, 2003, this issue). Consequently, the DIY application also suffers from the problem of equifinality that characterizes most hydrological models (Beven, 1996). The greatest divergence occurred during the snowmelt period (February–March) and in the summer (July–August), where the model is not predicting snowmelt (and subsequent routing) accurately or the re-wetting of catchment soils.

The hillslope-based structure of DIY allowed disaggregation of the runoff response into the three main hydrological flow paths also identified in the EMMA. The Monte Carlo analysis provided a range of values, according to the different parameter sets used in DIY, that yielded high efficiency statistics (Figure 6). The models predicted that between 27 and 55% of annual runoff was contributed by groundwater, 35–56% by surface storm flow contributions and 7–24% from overland flow. The average predicted proportions of individual flow path contributions are shown in Figure 6c. In general, the main features of the geochemical hydrograph separation are reflected by the semi-distributed model, though important differences emerge (Figure 6a and b). The most obvious is the higher range of possible groundwater contributions, together with the slightly lower prediction of overland flow and higher prediction of subsurface storm flow by DIY (Figure 6c). This probably reflects identifiability problems resulting from the similar chemical composition of storm runoff originating from organic soils that may include both surface and subsurface components, which are differentiated by DIY but not by EMMA. However, the subsurface flow control on the recession characteristics is evident in both approaches. The groundwater component predicted by DIY is much more constant (reflecting the recharge factor) and shows no response to individual storm events, though seasonal differences are apparent (Figure 6b).

It is likely that the chemical basis of the mixing model is more sensitive to changes reflecting heterogeneities in catchment response. For example, the groundwater peaks predicted during events in Figure 5b could be explained by discharge of subsurface flow through riparian areas, which could result in mixing and

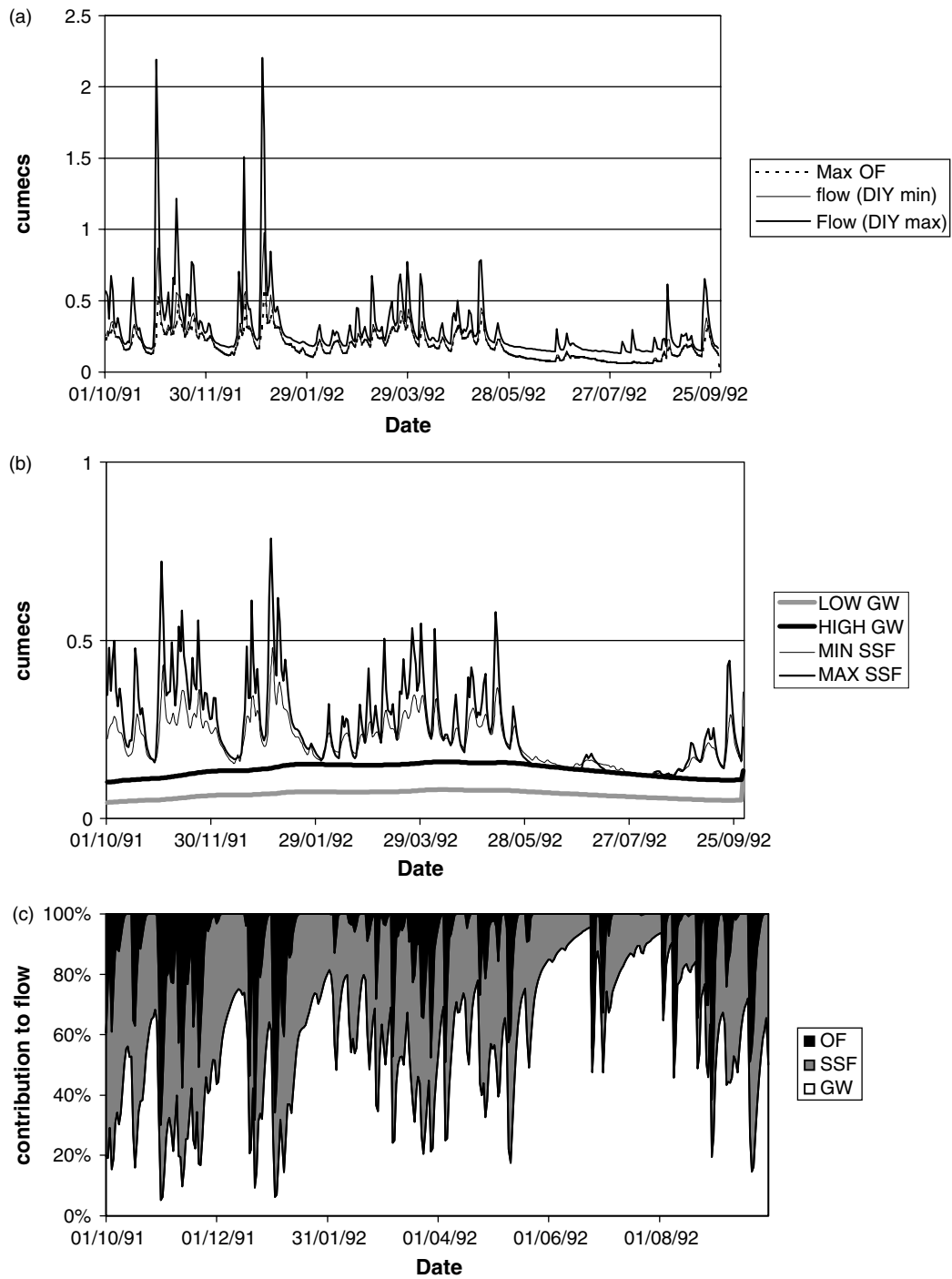


Figure 6. Results of DIY predictions showing (a) upper and lower stream flow estimates, with prediction of maximum overland flow contributions (difference between flow and DIY maximum lines), (b) maximum and minimum subsurface storm flow and groundwater flow predictions from DIY, and (c) average flow path partitioning by percentage

displacement that would imprint a groundwater chemical signature during the storm response (Smart *et al.*, 2002). Such fine process resolution, known from field studies to be highly heterogeneous, would be difficult to incorporate within a catchment-scale model like DIY (Beven, 2001).

The output of DIY was adapted to utilize the predicted flow partitioning, along with associated end-member chemistries to simulate stream water chemistry as a further objective function in model validation. Figure 7 shows the results of this exercise and indicates that the rainfall-runoff model simulates stream water chemistry reasonably well ($r^2 = 0.70$). The main deviations again relate to periods where flows were not well reproduced by the model (in spring and summer), and thus appear to reflect the fundamental problems of handling highly heterogeneous hydrological processes in a relatively large catchment with marked environmental gradients. A high degree of uncertainty remains over the partitioning of the two soil-related flow paths, and clearly the DIY application suffers from the problem of equifinality in parameter selection. However, for the spatial and temporal scales of relevance in this investigation, the favourable comparisons of DIY output with that of the EMMA, and the subsequent simulation of alkalinity, increases confidence that the structural representation of catchment hydrology incorporated within DIY seems feasible and is consistent with previous process-based hydrometric and tracer studies within the catchment.

DISCUSSION

These results demonstrate the utility in comparing tracer-based hydrograph separation with that predicted by a semi-distributed model. Though these modelling results apply to a particular spatial (10 km² catchment) and temporal (daily) scale, one can envisage a range of applications for such a tracer-validated model in catchments that require predictions with assessments of uncertainties (e.g. flood warning, estimating flows in ungauged catchments with similar characteristics, etc.). Also, by providing a semi-distributed model that

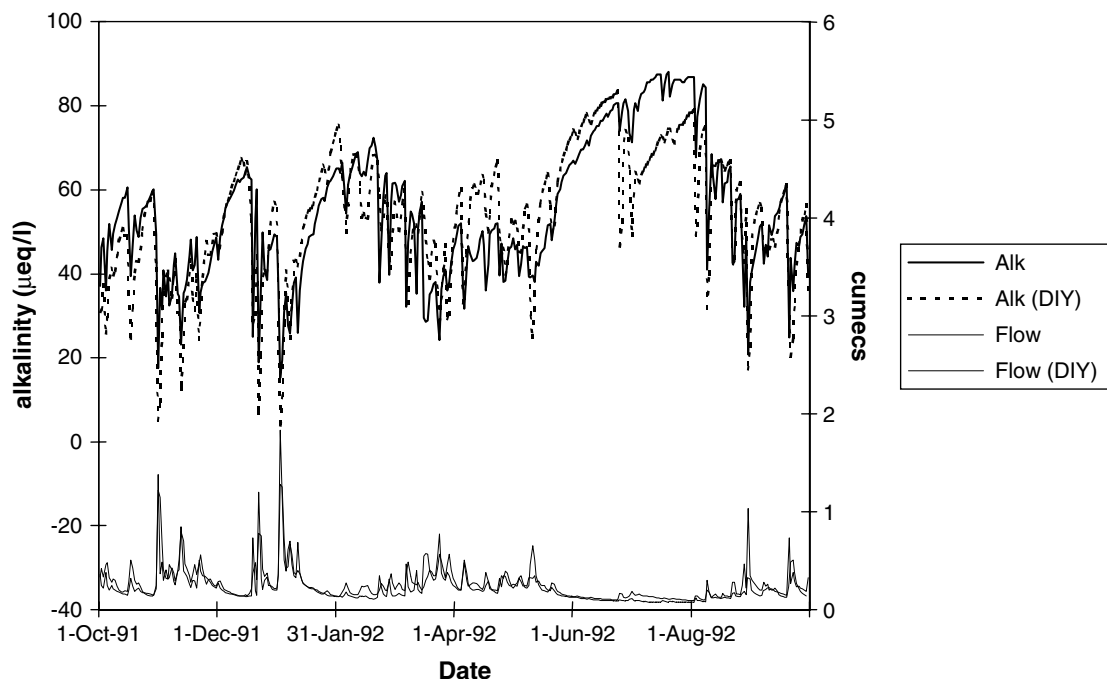


Figure 7. Actual mean daily flows with DIY predictions and the daily alkalinity time series ($\mu\text{eq l}^{-1}$) in comparison with predictions from DIY flow path partitioning and end-member chemistry values

facilitates the identification of conceptual hydrological pathways, the model can handle the emergence of processes apparent at this scale, without necessarily conceptualizing the more detailed suite of processes at the smaller scale that underpin such emergent properties (Wade *et al.*, 2001). As such, the results of this study are comparable to those of similar attempts to integrate tracer understanding in rainfall-runoff models (Robson *et al.*, 1992; Uhlenbrook and Leibundgut, 1999).

However, in addition to identifiability problems at finer scales of resolution, the problem of equifinality in parameter sets is clearly likely to be a major constraint on applications that seek to understand hydrological processes and biogeochemical interactions (e.g. in modelling pollutant transport) at finer spatial and temporal resolutions. Other studies have shown the great difficulties associated with modelling the response of a smaller catchment at shorter (e.g. hourly) time steps (Peters *et al.*, 2001) even where an EMMA application has successfully identified conceptual flow paths (Hooper *et al.*, 1990). Such problems in moving between scales have frustrated attempts to implement the results of this study into the DIY; for example, an attempt to use the results of EMMA in further constraining the generic, soil-related parameters to improve applicability to other catchments proved unsuccessful (Dunn *et al.*, 2003, this issue).

Given that DIY has had some success in modelling the catchment response and that corroboration by tracer studies has increased confidence in the model structure, it is envisaged that further tracer studies, including use of ^{18}O , can be applied to estimate mixing volumes which determine the residence times calculated for different conceptual catchment stores. This could, in turn, help provide insight into the mixing processes and associated residence times occurring in the subsurface, which recent studies have indicated may be extremely long (Kirchner *et al.*, 2000). DIY used in combination with tracers could also improve upscaling capabilities from the experimental catchment scale (*ca* 10 km²) of the Allt a' Mharcaidh to the larger mesoscale (>200 km²) catchment of the river Feshie, which the Mharcaidh forms a tributary of. Work towards this end is currently under way as part of the CHASM (Catchment Hydrology And Sustainable Management) initiative, part of NICHE (National Infrastructure for Catchment Hydrology Experiments), a major UK programme in catchment hydrology research.

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