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Topographic, pedologic and climatic interactions influencing streamflow generation at multiple catchment scales

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Abstract:

Dominant flow pathways (DFPs) in mesoscale watersheds are poorly characterized and understood. Here, we make use of a conservative tracer (Gran alkalinity) and detailed information about climatic conditions and physical properties to examine how temporally and spatially variable factors interact to determine DFPs in 12 catchments draining areas from 3.4 to 1829.5 km^2 (Cairngorms, Scotland). After end-member mixing was applied to discriminate between near surface and deep groundwater flow pathways, variation partitioning, canonical redundancy analyses and regression models were used to resolve: (i) What is the temporal variability of DFPs in each catchment?; (ii) How do DFPs change across spatial scales and what factors control the differences in hydrological responses?; and (iii) Can a conceptual model be developed to explain the spatiotemporal variability of DFPs as a function of climatic, topographic and soil characteristics? Overall, catchment characteristics were only useful to explain the temporal variability of DFPs but not their spatial variation across scale. The temporal variability of DFPs was influenced most by prevailing hydroclimatic conditions and secondarily soil drainability. The predictability of active DFPs was better in catchments with soils supporting fast runoff generation on the basis of factors such as the cumulative precipitation from the seven previous days, mean daily air temperature and the fractional area covered by Rankers. The best regression model R^2 was 0.54, thus suggesting that the catchments' internal complexity was not fully captured by the factors included in the analysis. Nevertheless, this study highlights the utility of combining tracer studies with digital landscape analysis and multivariate statistical techniques to gain insights into the temporal (climatic) and spatial (topographic and pedologic) controls on DFPs.

KEY WORDS end-member mixing; dominant flow pathways (DFPs); Gran alkalinity; variation partitioning; canonical redundancy analysis; multiple linear regression

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INTRODUCTION

The interaction of topographic, pedologic and climatic factors to determine streamflow generation is poorly understood. During the First International Hydrological Decade (IHD), many early studies in catchment hydrology examined how such factors combined to influence headwater runoff across large numbers of catchments (e.g. Hewlett and Hibbert, 1967). Around that same time, other studies employed multiple regression and principal component analysis (PCA) to explore the relations between a host of catchment morphometric indices and streamflow behaviour (e.g. Morisawa, 1959; Gardiner, 1975). Since the IHD, however, most studies have given up this tradition and focused on an ever-more detailed field and process-based examination of internal runoff mechanisms specific to a given headwater research catchment (McDonnell *et al*., 2007). As a result, recent runoff generation studies have been mostly in single, iconic headwater catchments with little intercomparison among sites. While intercomparison studies are now gaining popularity (e.g. Carey *et al*., 2010), process-based model development continues to be the norm for understanding what factors might determine streamflow generation in different areas (Hopp *et al*., 2009).

Here, we return to some of the early IHD era research themes to explore the statistical relations between topographic, pedologic, climatic factors and streamflow generation across scales. Our approach is motivated by calls for a wider range of spatial and temporal scales to be considered in runoff generation studies (Shaman *et al*., 2004; Buttle, 2006). While there have been some mesoscale-focused statistical analyses of basin morphometric variables and water quantity and water quality measures (e.g. Fröhlich *et al*., 2008a; Barthold *et al*., 2010), there have been no studies that have yet examined the temporal variations in the partitioning of dominant flow pathways (DFPs) and how this partitioning is hydroclimatically influenced. We here define DFPs as the flow pathways that carry out most of the stormflow routing during an event. Of course, DFPs vary temporally largely in response to rainfall intensity and amount (e.g. Dunne, 1978) and antecedent catchment conditions (e.g. Elsenbeer *et al*., 1994; Grayson *et al*., 1997). For example Lana-Renault *et al*. (2007) found for a small catchment in the central Spanish Pyrenees that under dry antecedent conditions, runoff was dominated by infiltration excess

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overland flow while under wet conditions, saturated excess overland flow and subsurface flow dominated the runoff response. In contrast to this type of field-based work in headwater catchments, classifications of DFPs at the mesoscale are usually static in that they do not account for temporal variability. The United Kingdom's Hydrology of Soil Types (HOST) (Boorman *et al.*, 1995) is one example of such a classification scheme: it groups all UK soils into 29 classes that reflect different aspects of runoff generation and hydrological response. Tetzlaff *et al.* (2007a) combined HOST and topographic maps to identify likely DFPs; however these likely DFPs are only valid under average stormflow conditions and do not account for hydrological extremes. Outside of the UK, some authors have suggested the use of decision schemes to determine DFPs given specific information about soil or vegetation types (e.g. Scherrer and Naef, 2003; Schmocker-Fackel, 2004; Schmocker-Fackel *et al.*, 2007; Müller *et al.*, 2009). In these studies, runoff generation mechanisms were generally observed on several plots after rainfall events and then linked to soil, geological and land-use maps in order to establish a set of rules. These rules then were used to build an automated process determination of DFPs for more or less large areas. Such methods however tend to extrapolate plot scale observations to larger scales with no clear evidence of scale independence or scale invariance.

At the meso- and large scales, geochemical tracers have been the most widely used technique for quantifying DFPs, sometimes in combination with static decision schemes (e.g. Tetzlaff *et al.*, 2007a). The rationale behind the use of tracers is that they reflect the integration of smaller-scale hydrological processes (Tetzlaff and Soulsby, 2008) and that they can be used as proxies for large-scale hydrological dynamics (Frisbee *et al.*, 2011), thus capturing implicitly the upscaling of DFPs. Because different tracers can be associated with different flow pathways in a catchment, their mixture in stream waters constitutes a hydrochemical signature from which DFPs can be traced back (Kendall *et al.*, 1995; Neal, 1997; Kendall and McDonnell, 1998; Soulsby *et al.*, 2003; Tetzlaff and Soulsby, 2008). Hence, end-member mixing (EMM, sensu hydrograph separation) and end-member mixing analysis (EMMA, based on PCA) are especially useful when it comes to the testing of DFP-related hypotheses (e.g. Christophersen *et al.*, 1990; Hooper *et al.*, 1990; Christophersen and Hooper, 1992; Burns *et al.*, 2001). So far, the assumption of time-invariant DFPs has been implicit in EMM studies; multiyear datasets are usually fed into mixing models with no discrimination of climatic and flow conditions (Ali *et al.*, 2010), only with the hope that dominant end-members (i.e. median values) will emerge from the analysis. Brown *et al.* (1999) demonstrated that most EMM studies have focused on DFPs that are mainly active in wet conditions. To counteract such approaches, Tetzlaff and Soulsby (2008) specifically focused on low flow periods in a wide range of Scottish catchments in order to better understand DFPs under drier conditions. Soulsby *et al.* (2004) also explored mixing at the mesoscale under contrasting flow conditions; they used a spatially and temporally nested sampling approach in sub-catchments ranging from 1 to 100 km² to predict catchment scale hydrochemistry from soil and geological properties. More recently, Ali *et al.* (2010) further relaxed the assumption of time-invariant end-members by breaking down an 11-year stream chemistry dataset into 64 different hydrologic scenarios of antecedent precipitation and stream discharge to examine the variability of DFPs across various hydroclimatic conditions.

Here, we build upon previous work to understand how topographic, pedologic and climatic factors interact to determine DFPs at multiple basin scales. We examine 12 sub-catchments, all located within the Dee River basin in Scotland, that showcase a large range of physical characteristics. Our focus on the Dee river system is motivated by the fact that it is roughly comparable to many similar-sized catchments in upland parts of north-western Europe, with modest anthropogenic influences and clear landscape controls on hydrological processes (Tetzlaff and Soulsby, 2008). Specifically, the paper aims to provide insights into the following questions:

(i) What is the temporal variability of DFPs in each sub-catchment?
(ii) How do DFPs change across spatial scales and what factors control the differences in hydrological responses?
(iii) Can a conceptual model be developed to explain the spatiotemporal variability of DFPs as a function of climatic, topographic and soil characteristics?

Following an initial, simple one-tracer, two-component EMM for each sub-catchment, we proceed through several statistical techniques to investigate spatial and temporal controls on DFPs and answer our three research questions We approach the problem of determining DFPs by considering each stream chemistry sample as the integrated signature of a specific combination of climatic, pedologic and topographic interactions. We use Gran alkalinity (ALK) and detailed information about climatic conditions, topographic properties and soil cover. ALK is used here as a surrogate measure for acid neutralizing capacity, a conservative tracer with proven ability to differentiate between acidic soil water (i.e. near surface pathways) and alkaline groundwater pathways in the UK uplands (Robson and Neal, 1990; Wade *et al.*, 1999; Neal, 2001; Soulsby and Dunn, 2003).

STUDY CATCHMENTS

The Dee river basin covers approximately 2000 km². It is especially important for biodiversity conservation as it is an Atlantic salmon fishery and is designated a Special Area for Conservation under the EU Habitats Directive (Speed *et al.*, 2010). Its economical importance is also non negligible as the river supplies drinking water to over 300 000 people. In this study, six main stem sites as

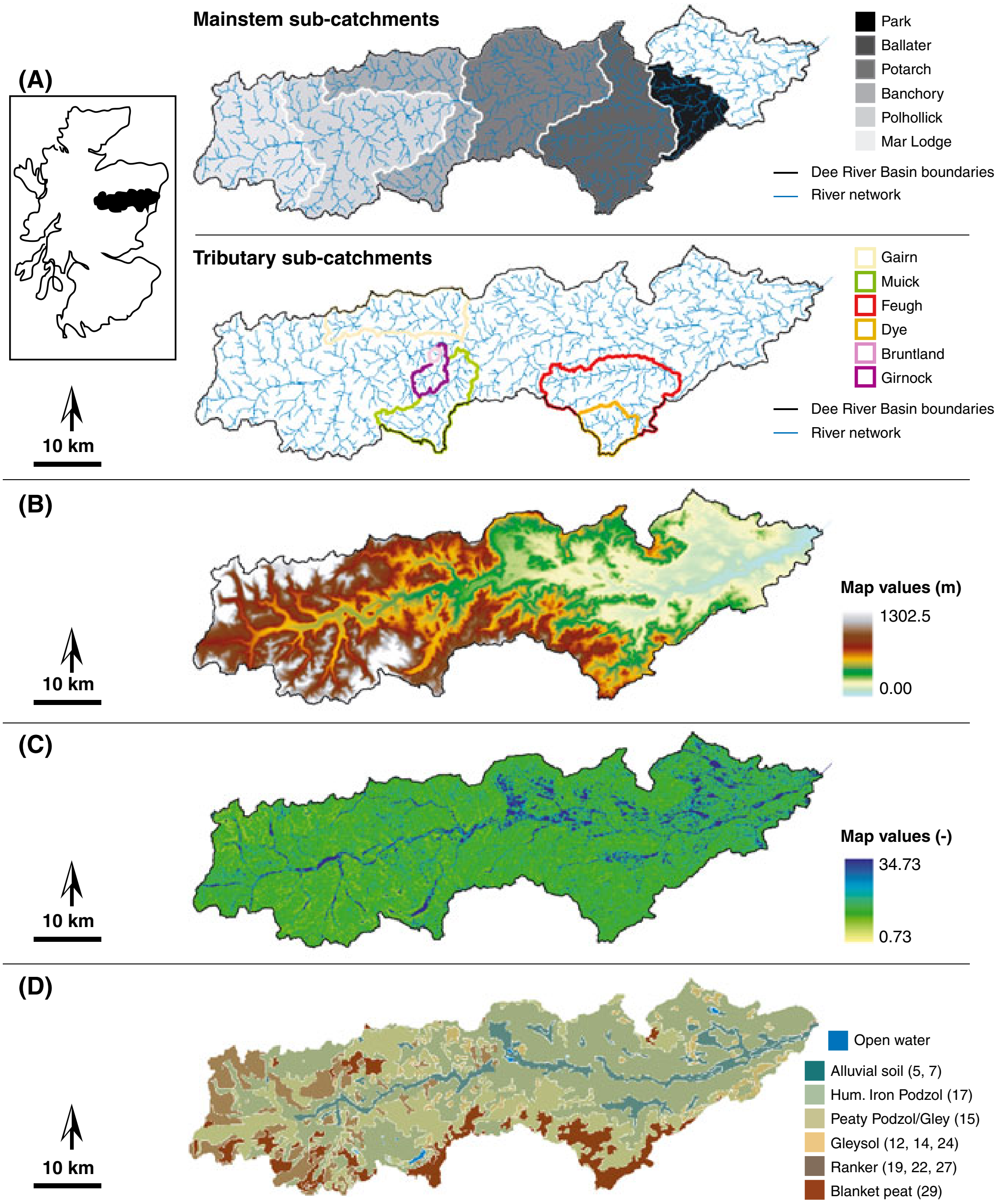


Figure 1. **(A)** Location of the Dee River Basin in Scotland, the mainstem and the tributary sub-catchments; spatial distribution maps of **(B)** Elevation; **(C)** Topographic index; and **(D)** HOST classes in the Dee River Basin

well as six tributaries (Figure 1 (A)) were investigated with drainage areas ranging from 3.4 to 1829.5 km² (Table I). In total, the Dee river basin includes 59% of mountainous headwaters originating from the Cairngorms and situated above 300 m a.s.l (Tetzlaff and Soulsby, 2008) (Figure 1 (B)).

Extensive descriptions of the 12 sub-catchments can be found elsewhere (e.g. Soulsby and Tetzlaff, 2008; Tetzlaff and Soulsby, 2008; Hrachowitz *et al.*, 2010; Speed *et al.*, 2010). Briefly, the headwater parts of the catchments in the West are mostly alpine with steep slopes and frequent bedrock outcrops, while surface topography is generally more subdued with wider valleys and rolling hills in the East. The Mar Lodge, Gairn and Muick sites are among the largest tributaries and drain the western montane headwaters, while the behaviour of the Feugh is more strongly determined by lowland influences (Rodgers *et al.*, 2005). Annual catchment precipitation for all 12 sub-catchments is 1100 mm in average; however, 53% of the catchment upstream of Ballater accounts for 58% of annual water inputs (Tetzlaff and Soulsby, 2008). Precipitation maxima of *ca*. 1500 mm are recorded in the most western sites and minima of *ca*. 800 mm are rather measured at the most eastern sites. Since the upland region of the Dee is classified as a sub-arctic climate, up to 20% of the annual precipitation amount can fall as snow in the western sub-catchments (Warren, 1985); snowfall, however, accounts for less than 10% of the annual water inputs in the eastern, lowland catchments (Soulsby *et al.*, 2004). Cool temperatures are usually

Table I. Topographic and soil characteristics for the 12 studied sub-catchments

TOPOGRAPHIC PROPERTIES

	Area (km^2)	Perimeter (km)	Minimum elevation (m)	Maximum elevation (m)	Mean elevation (m)	Maximum slope (deg)	Mean slope (deg)	Drainage density (km/km^2)	Mean flow path length (km)	Median Topographic wetness index (ln(m))	β coefficient (Hack's law)	Longest stream length (km)	Perimeter/Area
Brundtland	3.4	7.78	255.2	542.0	358.7	50.2	13.4	0.65	2.58	6.4	1.25	2.58	2.32
Girnock	30.4	30.22	230.1	861.0	406.8	61.4	9.9	0.83	12.87	6.43	1.66	12.87	0.99
Dye	53.3	34.76	197.5	774.6	408.9	41.2	9.0	0.91	14.46	7.44	1.33	14.46	0.65
Muick	111.7	77.33	200.2	1150.0	586.4	78.3	11.1	0.97	36.84	7.25	2.17	36.84	0.62
Gairn	146.1	69.45	216.0	1169.7	556.9	56.0	10.8	0.90	37.20	6.81	1.87	37.20	0.53
Feugh	232.5	81.23	72.3	774.6	329.0	51.7	9.0	0.93	33.16	7.1	1.26	33.16	0.35
Mar Lodge	288.1	105.6	337.7	1304.5	681.4	73.4	13.7	0.86	31.09	7.47	1.04	31.09	0.36
Polhollick	696.5	163.7	220.8	1304.5	619.6	75.3	12.9	0.89	69.48	7.1	1.37	69.48	0.24
Ballater	965.8	187.2	194.6	1304.5	602.6	78.3	12.3	0.90	75.77	7.06	1.23	75.77	0.19
Potarch	1346.4	243.2	83.9	1305.0	518.0	78.3	11.1	0.92	114.28	6.79	1.52	114.28	0.18
Banchory	1712.1	289.6	44.0	1304.5	466.9	78.3	10.5	0.93	128.99	6.8	1.48	128.99	0.17
Park	1829.5	307	24.1	1305.0	446.0	78.3	7.8	0.93	140.51	7.06	1.55	140.51	0.17

SOIL CHARACTERISTICS (fractional catchment area)

	Alluvial soils	Humus-iron podzols, alpine soils	Rankers	Peaty Podzols, peaty gleys	Peat	Gleysols	Open water	Freely draining soils	Responsive soils
Brundtland	0.00	0.39	0.61	0.00	0.00	0.00	0.00	0.39	0.61
Girnock	0.02	0.25	0.12	0.52	0.00	0.09	0.00	0.43	0.57
Dye	0.00	0.00	0.00	0.42	0.58	0.00	0.00	0.23	0.77
Muick	0.01	0.42	0.02	0.23	0.23	0.04	0.02	0.61	0.39
Gairn	0.02	0.38	0.06	0.41	0.07	0.06	0.00	0.58	0.42
Feugh	0.08	0.26	0.00	0.35	0.31	0.00	0.00	0.54	0.46
Mar Lodge	0.00	0.24	0.39	0.25	0.11	0.00	0.00	0.36	0.64
Polhollick	0.04	0.33	0.27	0.25	0.09	0.01	0.00	0.49	0.51
Ballater	0.04	0.35	0.21	0.27	0.10	0.02	0.00	0.52	0.48
Potarch	0.06	0.42	0.16	0.24	0.08	0.02	0.00	0.61	0.39
Banchory	0.07	0.43	0.12	0.24	0.11	0.02	0.00	0.63	0.37
Park	0.07	0.44	0.11	0.24	0.10	0.02	0.00	0.63	0.36

encountered with mean daily averages of 1 °C in January and 14 °C in July in the upper catchment (Speed *et al.*, 2010). It should be noted that for the Mar Lodge site located further west (Figure 1 (A)), specific high flows (Q_{10}) and low flows (Q_{95}) values are $88\,l.s^{-1}.km^{-2}$ and $7\,l.s^{-1}.km^{-2}$ respectively, and these values decrease as we move towards the Park site located further east (i.e. $Q_{10} = 52\,l.s^{-1}.km^{-2}$ and $Q_{95} = 46\,l.s^{-1}.km^{-2}$) (Tetzlaff and Soulsby, 2008).

Geological units are predominately made of Precambrian metamorphic and igneous rocks, except in areas of higher relief where granite batholiths are usually present (Tetzlaff and Soulsby, 2008). These granites form aquitards that are assumed to be subjected to low weathering rates (Soulsby *et al.*, 2007) and can host fractures in their upper 10 m which serve as preferential groundwater flow paths (Soulsby *et al.*, 1998). Glacial drift deposits of various types (e.g. alluvial, fluvio-glacial, till) and various thicknesses are superimposed on the solid geology; their influence on the overall hydrology of the catchments is important as they have significant potential water storage and are therefore important sources of groundwater (Soulsby *et al.*, 1999). Relying on topography alone is therefore misleading in this region. For example, the spatial patterns of the topographic wetness index (Beven and Kirkby, 1979) tend to highlight the difference between the Western and the Eastern parts of the Dee river basin when it comes to the presence of flow convergence zones with a higher probability of near-surface soil saturation (blue-colored areas in Figure 1 (C)). Figure 1 (D) however shows that these zones of high topographic index are mainly covered by alluvial soils, thus pointing towards greater vertical drainage and deeper water storage. Since soil covers are a result of the interactions between local topography, geology and superficial deposits (Soulsby and Tetzlaff, 2008), the HOST map presented in Figure 1 (D) is a static representation of likely DFPs under average conditions in all 12 sub-catchments. Shallow Regosols (Rankers) together with alpine soils dominate on steeper mountain slopes and in higher altitude areas (e.g. Mar Lodge), while peaty gley soils and peats (Histosols) are commonly found in the valley bottoms. Deep blanket peats are frequently present on gently sloping hilltops in central-southern regions of the Dee river basin. Humus-iron Podzols and alluvial soils are widespread in the East (e.g. lower portions of the Feugh and Dye catchments) and on steep slopes where superficial drifts are permeable. Peaty gleys, blanket peats and Rankers are labelled as ‘responsive soils’ since they remain close to saturation during much of the year in the wet Scottish climate (Hrachowitz *et al.*, 2010). Generally low in alkalinity and enriched in dissolved organic carbon in their upper horizons, these responsive soils are typically subjected to overland flow and shallow subsurface flow as DFPs, with flashier responses, lower contributions to annual runoff and shorter transit times encountered in sub-catchments where they are overly present (Tetzlaff *et al.*, 2007a). On the contrary, podzols and alluvial soils are rather termed ‘freely draining soils’ because they are subjected to higher vertical drainage and groundwater recharge, with an enhanced contribution to alkaline runoff (Tetzlaff *et al.*, 2007a). Vegetation-wise, western and southern upland areas above 800 m a.s.l are dominated by montane heath while semi-natural land cover such as heather moorland and blanket bog are present elsewhere. Anthropogenic influences in the Dee are relatively limited: eastern lowland catchments have higher fertility soils and are heavily managed for agricultural purposes; very few forestry activities (Scot Pine) exist on the steepest slopes at lower altitudes; and the largest settlement in the area is Banchory with a population of less than 6000 inhabitants.

DATA AND METHODS

Here, we use data from a weekly sampling programme in the Dee river basin which was conducted over 17 months. Stream water grab samples were collected at the outlet of the 12 studied sub-catchments where Scottish Environment Protection Agency (SEPA) gauging stations continuously record river discharges (15-min time step). Daily precipitation was measured by SEPA at 12 sites in and around the Dee river basin and further interpolated using the Gradient-Inverse-Distance-Squared (GIDS) method (Nalder and Wein, 1998; Stahl *et al.*, 2006). In our particular case, the GIDS method combined multiple regression and inverse-distance-squared weighting to model the spatial variability of daily precipitation as a function of five catchment parameters (i.e. elevation, slope, aspect, longitude and latitude). The multiple regression coefficients were changed on a daily time step and produced a mean *R*-squared (R^2) value of 0.72 (Speed *et al.*, 2010).

Stream water samples were refrigerated upon collection and analyzed within seven days for Gran alkalinity (ALK). The analyses were carried out by acidimetric titration to end points pHs of 4.5, 4 and 3 (Speed *et al.*, 2010). For each of the 12 studied sub-catchments, the ALK data were used in a one-tracer, two-component EMM model or hydrograph separation. The aim was to determine the time-variable, relative contributions of near surface soil water and groundwater that can be linked to different DFPs: overland and shallow subsurface flow in the former case and deep subsurface (groundwater) flow in the latter case. The classical two-component mixing model allows to compute the fraction of runoff that is made of groundwater as follows:

$$Groundwater\,fraction = \frac{C_s - C_t}{C_s - C_g} \qquad (1)$$

Where C_s is the ALK value of near surface soil water, C_g is the ALK value of groundwater and C_t is that of stream water. The definition of the near surface soil water and groundwater end-members was catchment specific (i.e. conducted independently for each sub-catchment) as we could not hypothesize the spatial consistency of C_s

and C_g over the whole Dee River Basin drainage area. Following the conclusions of previous studies in Scottish catchments (e.g. Soulsby *et al*., 2006), the groundwater end-member ALK value of a sub-catchment was set to the mean of the three samples associated with the three lowest flows recorded over the 17-month study period in that sub-catchment. Similarly, the near surface soil water end-member ALK value of a sub-catchment was set to the mean of the three samples associated with the highest flows recorded over the 17-month study period in that sub-catchment. For each site, the labelling of groundwater or near surface soil water as the DFP for each sampling step was done when their respective fractional contribution to runoff exceeded 0.5 (i.e. 50%). This labelling was only meant for interpretation purposes and was not used in any of the statistical analyses described below.

Once the relative runoff contributions of the groundwater and near surface soil water pathways were obtained for all sampling times and all 12 sub-catchments, a series of statistical analyses were carried out (Figure 2) so as to answer our three research questions. From here onwards in this paper, only the results associated with the groundwater contributions are presented as groundwater and near surface soil water contributions are complementary as expressed in Equation (1). First, we addressed the issue of the temporal variability of DFPs by looking at scatter plots of groundwater flow contributions *versus* discharge. As no grab samples were collected during flashy storm events, we chose to match each water sample (and computed groundwater contribution) to mean specific daily discharge. Seasonality effects in both catchment discharge and groundwater contributions were visually investigated by comparing winter and summer values. A climate variation partitioning was also achieved using groundwater flow contributions as a response variable, and associated AP_7 (e.g. cumulative sum of precipitation over the 7 previous days) and mean daily air temperature as explanatory variables. AP_7 is used here as a surrogate measure for antecedent conditions, while mean daily air temperature is used as a proxy for current evapotranspiration. Hence, both climatic variables are used to describe the overall state of wetness prevailing in each catchment. The algebra of variation partitioning is described in Borcard *et al*. (1992) and Legendre and Legendre (1998). Briefly, the method as applied here aims at partitioning the variation of a response variable among two sets of explanatory variables using a series of regressions. The adjusted R^2 values obtained from the analysis are combined to compute the amount of variation explained uniquely by each explanatory variable and jointly by the two variables (Figure 3). The use of adjusted R^2 values over non adjusted ones was motivated by the fact the former allows the comparison of analyses involving different numbers of objects and explanatory

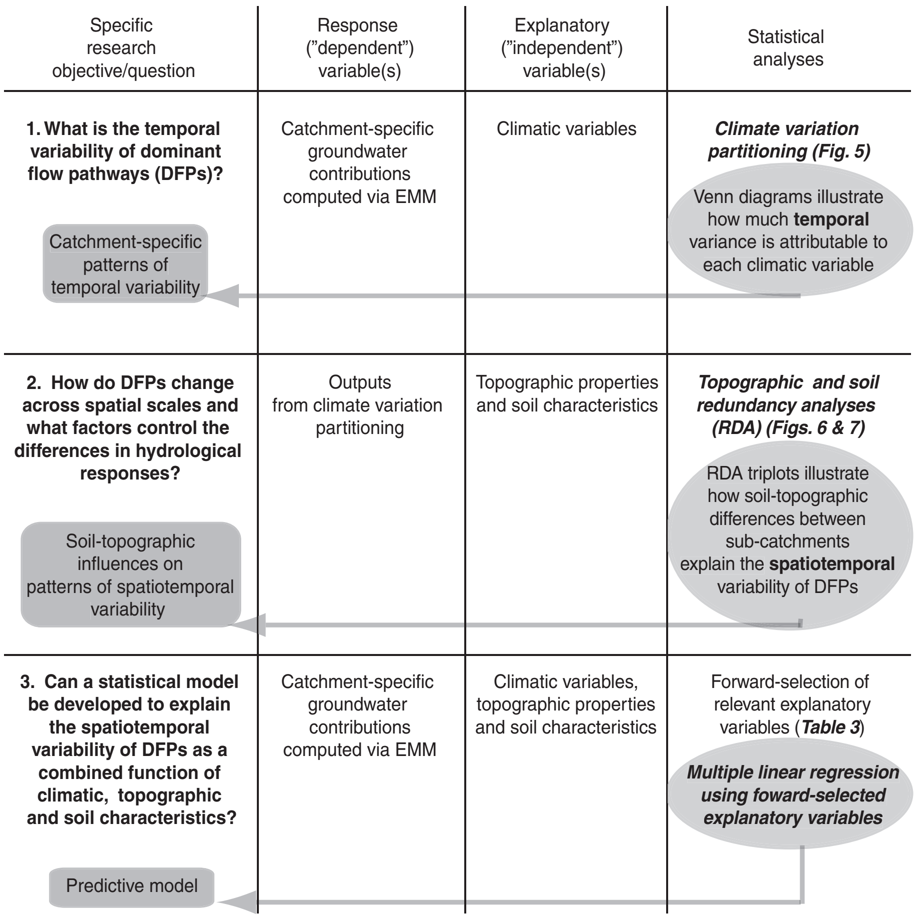
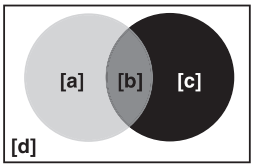


Figure 2. Links between the research questions investigated and the statistical analyses run in this paper



[a]
Proportion of variance in the response variable that is attributable to the first explanatory variable
[c]
Proportion of variance in the response variable that is attributable to the second explanatory variable
[b]
Proportion of variance in the response variable that is attributable to the joint influence of the first and the second explanatory variables
[d]
Proportion of variance in the response variable that cannot be explained by the influence of the two tested explanatory variables

Figure 3. Theoretical Venn diagram illustrating the different fractions of variance obtained from a variation partitioning analysis. The [a] to [d] notation illustrated here is used throughout the text and in further plots

variables, and its value only increases if a new explanatory variable improves the model more than would be expected by chance. We therefore relied on variation partitioning to understand how much of the (catchment-specific) temporal variance in DFPs could be attributed to: (1) the individual effect of antecedent conditions (AP_7, fraction [a], refer to Figure 3), (2) the individual effect of current evapotranspiration (air temperature, fraction [c]), and (3) the joint effect of antecedent conditions and current evapotranspiration (fraction [b]). Fraction [d] rather illustrated the amount of variance that could not be explained by the two climatic variables tested here. The results of these variation partitioning analyses were illustrated using Venn diagrams and individual fractions of variance were tested for significance ($p < 0.05$) using permutation tests. It should be mentioned that joint effects could not be tested for significance because they cannot be obtained directly.

As our second research question concerns how not only DFPs but also physical controls on hydrological response change across spatial scales (i.e. spatiotemporal variability), we calculated Spearman rank correlation coefficients between temporal statistics of groundwater flow contributions (i.e. minimum, maximum, mean, median, standard deviation and coefficient of variation) and catchment topographic and soil characteristics. Redundancy analysis (RDA) was also run to examine the cumulative effect of climate and physical catchment attributes on the spatiotemporal variability of groundwater flow contributions. There again, RDA is fully described in Legendre and Legendre (1998). In a nutshell, RDA is the constrained version of PCA. The two techniques differ in a fundamental way: PCA is a simple ordination method aiming at identifying gradients in a multivariate dataset and interpreting these gradients using loadings on the principal component axes; RDA is rather a canonical ordination method that is forced to express the gradients in a set of response variables as a function of another set of variables called 'explanatory'. In our case, the response variables are the climate influences on groundwater flow contributions as portrayed by variation partitioning fractions [a], [b], [c] and [d], and the explanatory variables are either the catchments' topographic characteristics or soil cover proportions. The performance of the RDA models was assessed using R^2 and adjusted R^2 values. RDA triplots were later built to visualize how the effects of topographic properties or soil cover were superimposed on climate influences to explain the temporal variability in DFPs. Indeed, triplots are scattergrams showing the catchments (illustrated as circles), response variables (i.e. variation partitioning fractions [a], [b], [c] and [d], illustrated as vectors) and explanatory variables (i.e. catchment physical attributes also illustrated as vectors) on the same diagram. These diagrams are interpreted according to the following rules:

(i) Distances among the catchments in the triplot are approximations of their Euclidean distances in multidimensional space;
(ii) Projecting a catchment at right angle on a response variable or an explanatory variable vector approximates the position of the catchment along that variable;
(iii) The angles among response vectors are meaningless; and
(iv) The angles between response and explanatory variables are proportional to their inter-correlations.

Lastly, we investigated whether a statistical model could be developed to explain the spatiotemporal variability of DFPs as a combined function of climatic, topographic and soil characteristics. Linear regression was used for that purpose. Data from all sampling dates and all catchments were combined in one single database. Groundwater flow fractions obtained from the two-component mixing modelling were used as response variables, while topographic, soil and climatic (e.g. AP_7 and air temperature) variables were included as potential explanatory factors. To assess possible linear and nonlinear controls on DFPs, the database included the following original and transformed variables:

$$x, x^2, x^3, \ \exp(x), \ \ln(x), \ \log_{10}(x), \ 10^x \qquad (2)$$

Where x is each topographic, soil or climate characteristic. This allowed us to use the very simple multiple linear regression technique while acknowledging the fact that some climatic and physical controls on DFPs might be nonlinear. Given that a large number of original and transformed potential explanatory factors were derived, a forward selection algorithm was run prior to regression to guide the identification of the most relevant topographic, soil and climatic controls. Forward selection means that initially, no explanatory variable is included in the regression model; the explanatory variables are rather tried out one by one and selected for inclusion in the regression analysis only if they are statistically significant. In its traditional form, the forward selection algorithm is known to overestimate the amount of explained variance R^2. To overcome this problem, the modified algorithm put forward by Blanchet *et al.* (2008) was used as it controls the end of the selection procedure via two stopping rules: a significance level, for example $p < 0.05$ as is usually the case, and the value of the adjusted R^2 for the subset of forward selected variables that must be higher than that of the whole set of explanatory variables. In the end, we used residuals diagnostics to assess whether the various assumptions behind multiple linear regression were reasonable for our dataset. For a given prediction model, the residuals are the differences between the observed values (i.e. the groundwater contributions obtained from EMM computations) and the regression fitted values. A scatter plot of the regression residuals against the regression fitted values was therefore built to determine whether there were any systematic patterns. The presence of a non-random structure in the residuals would be indicative of a regression model that fits the data poorly. In contrast, the absence of systematic structure in the residuals would indicate that the regression model fits the data well.

We should here mention that according to proper statistical reasoning, we could have used a mixed effects linear regression model to take into account potential nested catchment effects. Indeed, for data that are nested and hence usually correlated, mixed effects regression models are often used to incorporate and estimate the influence of random effects (Zuur *et al.*, 2009). However, previous studies have shown that in spite of their nested character, the Dee sub-catchments have quite different hydrological behaviours thanks to different spatial arrangements of topographic units and soil classes (e.g. Soulsby and Tetzlaff, 2008; Tetzlaff and Soulsby, 2008; Hrachowitz *et al.*, 2010; Speed *et al.*, 2010). As a result, we decided not to resort to mixed-effects models here and rather use classic linear regression.

Most statistical analyzes reported in this paper were done in R (R Development Core Team, 2010). Apart from some custom-made codes, we acknowledge the various R packages that were used, namely the *vegan* package (Oksanen *et al.*, 2010) for variation partitioning analyses, the *rdaTest* package (Legendre and Durand, 2010) for RDA and triplots, and the *packfor* package (Blanchet *et al.*, 2008) for the newest forward selection algorithm.

RESULTS

Temporal variation of DFPs

Simple statistics summarizing the range of groundwater contributions obtained from EMM computations are reported in Table II. All catchments showed similar standard deviations in their groundwater contributions. Groundwater contributions were not equally variable in all catchments as coefficients of variation exceeded 0.60 at some sites (e.g. Dye, Bruntland Burn) while they were below 0.40 at some other sites (e.g. Girnock, Polhollick).

Table II. Summary of unweighted groundwater contributions obtained from EMM computations in all 12 sub-catchments

	Mean	Median	Standard deviation	Coefficient of variation
Bruntland Burn	0.29	0.18	0.25	0.87
Girnock	0.71	0.82	0.25	0.36
Dye	0.43	0.36	0.27	0.62
Muick	0.57	0.64	0.27	0.46
Gairn	0.45	0.44	0.26	0.58
Feugh	0.55	0.56	0.26	0.48
Mar Lodge	0.41	0.39	0.23	0.55
Polhollick	0.59	0.61	0.23	0.39
Ballater	0.49	0.47	0.22	0.44
Potarch	0.51	0.53	0.22	0.43
Banchory	0.43	0.42	0.23	0.55
Park	0.57	0.58	0.23	0.41

Table III shows the Spearman correlation coefficients (significance level of 95%) obtained between temporal statistics of groundwater flow contributions and catchment topographic and soil characteristics. It is interesting to note that both topographic properties and soil characteristics were only useful in characterizing the temporal variability of groundwater flow contributions (e.g. standard deviation and coefficient of variation) rather than the mean or median values (Spearman rank correlation coefficients were not significant). Negative correlation coefficients were obtained between the coefficient of variation of groundwater flow contributions and catchment properties such as the drainage area, the perimeter, the mean flow path length and the longest stream length. This suggests that flow contributions are less temporally variable in larger catchments. Correlation coefficients also suggest that the higher the proportion of freely draining soils (and the lesser the proportion of responsive soils) in the studied catchments, the less temporally variable the fractional flow contributions.

The fractional contributions of groundwater flow to runoff obtained from EMM for the 68 sampling dates are shown in Figure 4 as a function of daily specific mean discharge. Seasonal effects in both discharge values and groundwater contributions could be observed for the Bruntland Burn and the Girnock sites with a rather clear break of slope delimiting winter dynamics (i.e. higher discharges and lower groundwater contributions) from summer dynamics (i.e. lower discharges and higher groundwater contributions) (Figure 4). Such clear seasonality effects could not really be observed at the remaining ten study sites (Figure 4). For all 12 sub-catchments, the Spearman rank correlation coefficients between groundwater contributions (and thus, also near surface soil water contributions) and discharge were very strong (significance level of 99%): they ranged from −0.66 for the Bruntland Burn to −0.95 for the Girnock, with an average value of −0.83. It was therefore possible to identify the threshold value of specific discharge from which groundwater fractional contributions fell below 50% and near surface soil water was the DFP in the

Table III. Spearman rank correlation coefficients between the temporal statistics of groundwater (GW) contributions and the catchments topographic properties or soil characteristics. 'Min', 'Max', 'Std' and 'CV' stand for minimum, maximum, (temporal) standard deviation and (temporal) coefficient of variation. Only statistically significant correlations (95% significance level) are shown

TOPOGRAPHIC PROPERTIES

	Min GW	Max GW	Mean GW	Median GW	Std GW	CV GW
Area					−0.78	−0.71
Perimeter					−0.76	−0.66
Minimum Elevation						
Maximum Elevation					−0.87	−0.65
Mean Elevation					−0.62	
Maximum Slope					−0.62	
Mean Slope						
Drainage Density						
Mean Flowpath Length					−0.71	−0.83
Median Topographic Index						
β coefficient (Hack's law)						
Longest Stream Length					−0.71	−0.83
Perimeter/Area					0.71	0.74

SOIL CHARACTERISTICS (Proportion of catchment with:)

	Min GW	Max GW	Mean GW	Median GW	Std GW	CV GW
Alluvial soils						−0.61
Podzols and subalpine soils						
Rankers						
Peaty Podzols and gleys						
Peat						
Gleysols						
Open water						
Freely draining soils						−0.67
Responsive soils						0.65

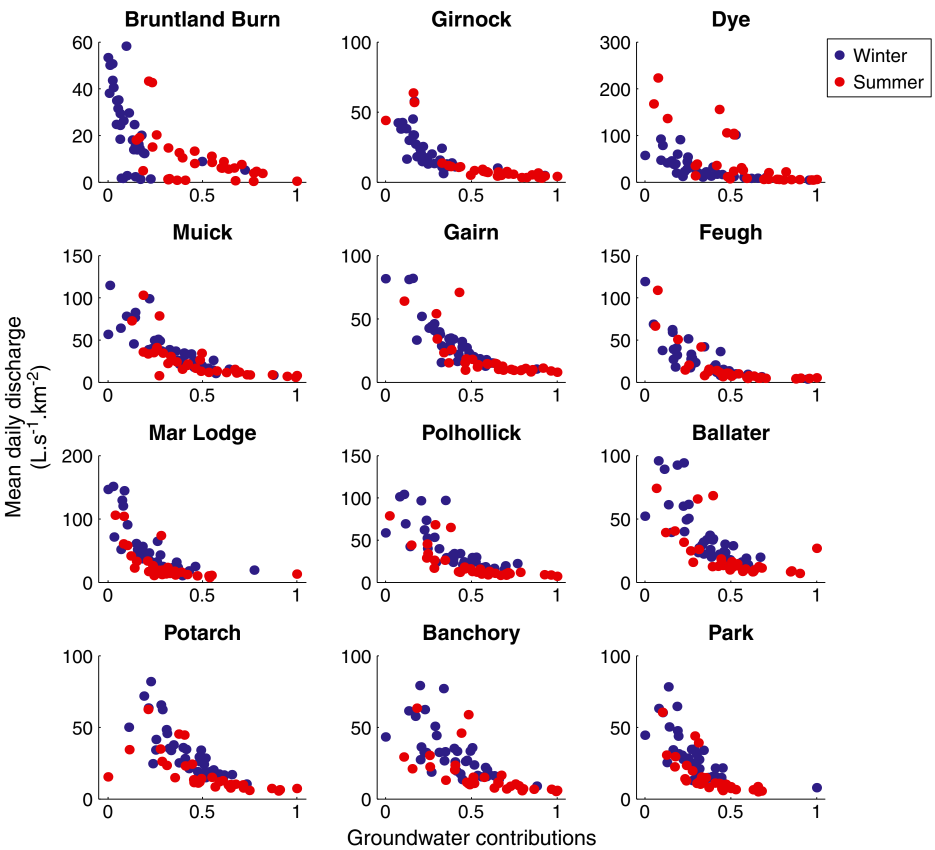


Figure 4. Groundwater fractional flow contributions determined via EMM as a function of catchment specific mean daily discharge

catchments. This threshold value was highly variable among the catchments, with an average of 15.93 L.s^{-1}.km^{-2}. The minimum threshold value was obtained in the Girnock catchment (i.e. 5.01 L.s^{-1}.km^{-2}) where responsive soils are overly dominant and, as a result, surface and shallow subsurface runoff are typical DFPs across a wide range of conditions. The maximum threshold value was rather observed for the Dee at Banchory (i.e. 33.45 L.s^{-1}.km^{-2}); that is also in accordance with the much higher proportion of freely draining soils that favour deep subsurface runoff generation processes.

Figure 4 clearly shows that even though the relationships between groundwater contributions and discharge had similar decreasing exponential shapes among all sub-catchments, not only the 50% contribution threshold but also the scatter around the exponential trend were highly variable. Variation partitioning analyses and subsequent Venn diagrams provided useful insights into this variability. Indeed, Figure 5 reveals that the 12 study sites are subjected to contrasting patterns of climatic influences. In the Bruntland Burn, the Girnock, the Dye and the Feugh sub-catchments, the temporal variance in groundwater contributions was explained by the two tested climatic influences in a proportion of 40% to 56%. Venn diagrams suggest that for the Bruntland Burn and the Girnock, air temperature was the more influential of the two climatic variables while for the Dye and the Feugh it was rather AP_7. For all other sub-catchments, however, the two tested climatic variables were rather inefficient in describing the temporal variability in groundwater contributions: the Venn diagrams associated with the six main stem sites (i.e. Mar Lodge, Polhollick, Ballater, Potarch, Banchory, Park) and two of the tributary sites (i.e. Muick and Gairn) show that the proportion of climatically unexplained temporal variance in groundwater contributions consistently exceeded 69% and could reach 87% (i.e. Mar Lodge).

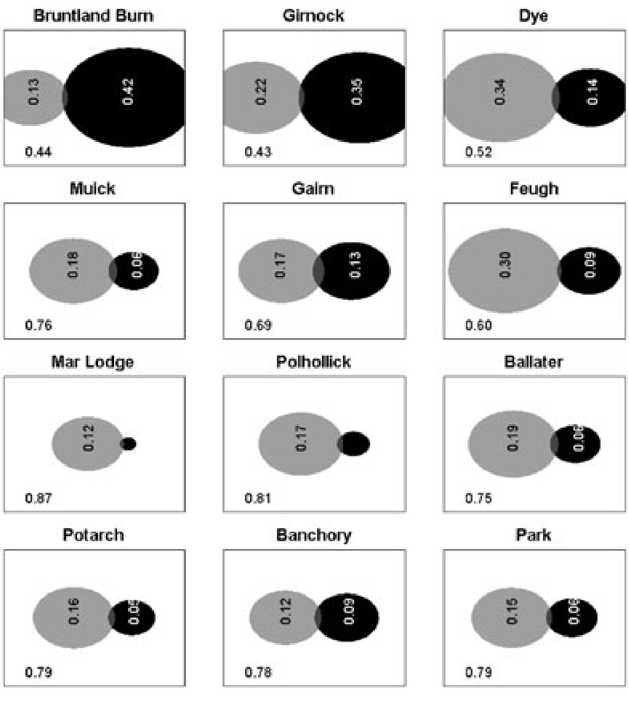


Figure 5. Venn diagrams illustrating the relative importance of AP_7 (light grey circles) and mean daily air temperature (black circles) on the temporal variability of groundwater flow contributions to runoff. The joint effect of AP_7 and air temperature is illustrated by the overlapping dark grey areas. For each catchment, the blank area delimitated by the black rectangle is the proportion of variance in the groundwater water flow contributions that cannot be explained using only AP_7 and air temperature. Variation partitioning fractions that are not explicitly quantified (i.e. labelled) on the Venn diagrams are not statistically significant at the 95% level

Spatiotemporal variation of DFPs across scale

RDA triplots are presented in Figures 6 and 7 to investigate the reasons behind the presence or absence of strong climatic controls on the temporal variability of groundwater contributions. With Figure 6 in particular, topographic properties were very effective ($R^2 = 0.99$, adjusted $R^2 = 0.88$) in explaining the contrasting patterns of climatic influences previously identified among the study sites. Three groups of sites could be distinguished in the canonical space (Figure 6), and they reflect what was observed in Figure 5 with (i) sub-catchments whose temporal dynamics was explained by air temperature in a proportion of 35% to 42% (i.e. Bruntland and Girnock), (ii) sub-catchments whose temporal dynamics was explained by AP_7 in a proportion of 30% to 34% (i.e. Dye and Feugh), and (iii) the others in which most of the temporal variance in groundwater contributions was not explained by the two tested climatic variables. The topographic triplot suggests that the highest variation partitioning fractions [d], which illustrate the relative lack of climatic influences on groundwater contributions, were associated with large or steep catchments. This is revealed by the graphical cluttering of the drainage area, perimeter, mean flow path length and maximum slope vectors with the fraction [d] vector in Figure 6. The soil RDA performed equally well as the topographic RDA in explaining the contrasting patterns of climatic influences observed among the study sites ($R^2 = 0.98$, adjusted $R^2 = 0.92$). The triplot in Figure 7 suggests that the strongest climatic influences (i.e. fraction [a] and [c] vectors) on the variability in flow contributions occurred when there was a higher proportion of peat, peaty podzols and gleys and other responsive soils in the studied sub-catchment as is the case with the Bruntland Burn, Girnock, Dye and Feugh sites. The strongest influences from air temperature occurred when there was a high proportion of gleysols and rankers in the sub-catchments (refer to the angles between the gleysols and rankers vectors and the variation partitioning fraction [c] in Figure 7). As for the lack of climatic influences on groundwater contributions (i.e. variation partitioning fraction [d]), it especially concerned sites in which podzols, alluvial, subalpine and other freely draining soils were common. These results therefore led us to the formulation of a working hypothesis: DFPs might be predictable on the basis of topographic, soil and climatic properties for sub-catchments located in the left portion of the triplots in Figures 6 and 7; however, achieving such predictions might not be possible for the larger sub-catchments located in the right portion of the triplots and

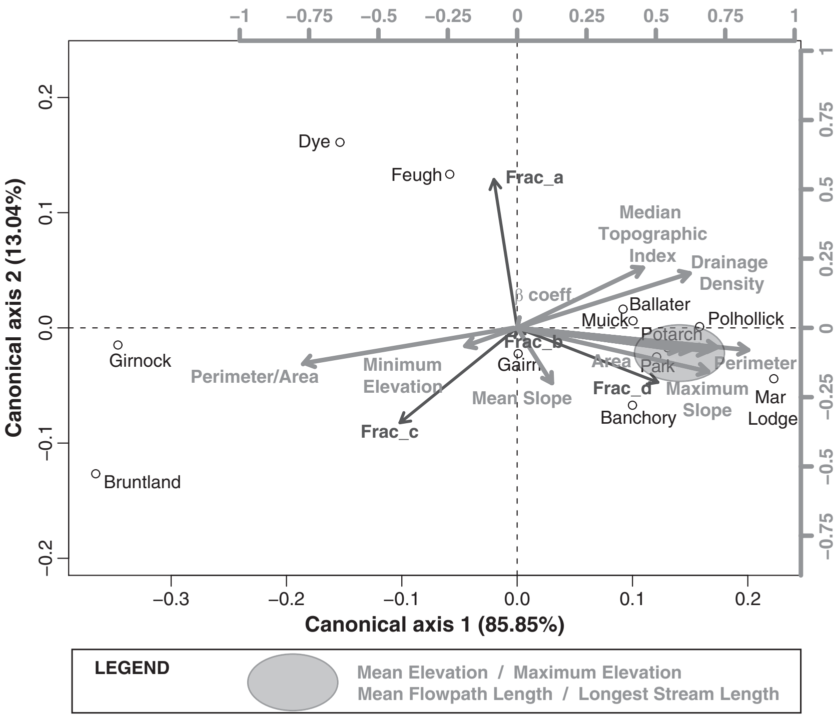


Figure 6. RDA triplot (canonical axes 1 and 2) used to evaluate how the effects of topographic properties are superimposed on climate influences to explain the spatiotemporal variability in groundwater flow contributions. This plot shows the 12 studied sub-catchments (open circles), the four variation partitioning fractions (response variables, black arrows) illustrating the climate controls (or lack thereof) on the magnitude of groundwater water flow contributions, and 12 topographic properties (explanatory variables, grey arrows). Note that the values of the response (black) and the explanatory (grey) variables are illustrated using two sets of axes (displayed in black and grey, respectively, on the triplot). The grey ellipse flags an area of the triplot where many arrows are cluttered; the topographic variables associated with these arrows are listed at the bottom of the diagram

which also happen to be main stem sites with a high proportion of freely draining soils for the most part. Hence in connection to our third research question, we tried to establish a general statistical model linking flow contributions to climatic, topographic and soil properties, and we assessed its performance across the two groups of sub-catchments.

Predictability of DFPs in space and time

Two regression models linking flow contributions to climatic, topographic and soil factors were built: the first one included data from all 12 study sites, while the second only focused on the Bruntland Burn, Girnock, Feugh and Dye sub-catchments which laid in the left portion of the triplot space in Figures 6 and 7. The

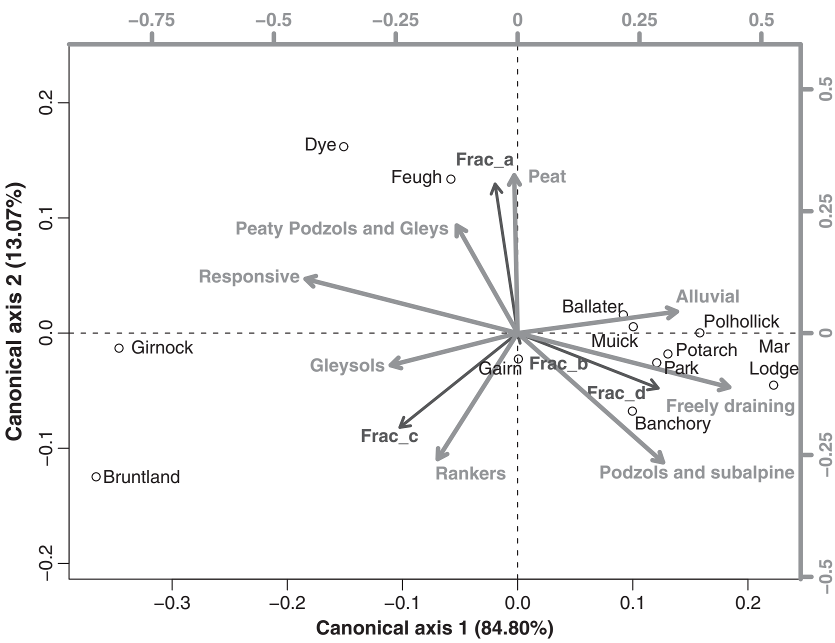


Figure 7. RDA triplot (axes 1 and 2) used to evaluate how the effects of soil characteristics are superimposed on climate influences to explain the spatiotemporal variability in groundwater/near surface soil water flow contributions. Notations are the same as in Figure 6 except that eight soil cover proportions are now used as explanatory variables

different explanatory variables added at each step of the forward selection procedure are reported in Table IV, together with the amount of variance explained by each variable as expressed by the R^2 and the adjusted R^2. In the end, the equation of the linear regression prediction model fitted using all 12 sub-catchments was as follows:

$$\begin{aligned} \text{GW} = & -0.08 \cdot \ln(AP_7) + 0.001 \cdot (Temperature)^2 \\ & -0.72 \cdot Rankers + 0.10 \cdot Mean\ slope \\ & -0.43 \cdot Median\ topographic\ index \\ & +0.75 \cdot Peat - 0.09 \cdot \frac{Perimeter}{Area} + 2.57 \end{aligned} \quad (3)$$

Where GW is the fractional groundwater contribution to runoff. The R^2 of the model was 0.3527, while the adjusted R^2 was 0.3471. It should be noted that the regression coefficients in Equation (3) (and Equation (4)) are very small because the target variable, namely the fractional groundwater contribution to runoff, only ranges from 0 to 1. The model fitted using only four sub-catchments yielded a higher R^2 of 0.5260 and an adjusted R^2 of 0.5189 and is formulated in Equation (4):

$$\begin{aligned} GW = & \, 0.02458 \cdot Temperature - 0.01219 \cdot AP_7 \\ & -0.00007746 \cdot (AP_7)^2 - 0.2664 \cdot Rankers \\ & +0.4829 \end{aligned} \quad (4)$$

Figure 8 however reveals that the regression residuals showed an apparently random pattern for the model based on all 12 sub-catchments (i.e., Equation (3)) but a rather structured pattern for the model based on only four sub-catchments (i.e., Equation (4)); this suggests that even though the R^2 associated with Equation (4) was higher, this model badly fitted the data. Some variables were recurrent in Equations (3) and (4), for instance both climatic variables *Temperature* and AP_7 and the proportion of the catchment that is covered by *Rankers*. Since the order in which the variables were included in the models is important, it was interesting to observe that the first three variables were always the same (Table IV), even though their associated regression coefficients and weighing (i.e. linear *vs* nonlinear) were different (Equation (3) and (4)). When Equation (4) derived based on the Bruntland Burn, Girnock, Feugh and Dye sub-catchments only was applied to the eight remaining sites, the prediction R^2 only reached 0.31. This tended to confirm the hypothesis that was formulated based on the RDA triplots that the prediction of DFPs is not equally feasible depending on the characteristics of the sub-catchments.

DISCUSSION

On the variability of DFPs across scale and under varying hydroclimatic conditions

Runoff generation studies to date have been mostly in single, headwater catchments, and very few have looked at interactions between controlling factors or the temporal variations in the relative flow path partitioning and how

Table IV. Results of the forward selection procedure towards building statistical prediction models of groundwater flow contributions

Step in forward selection procedure	Explanatory variable added	R^2	Cumulative R^2 (**Cumulative adjusted R^2**)
MODEL FITTED ON ALL 12 SUB-CATCHMENTS			
1	$\ln(AP_7)$	0.1589	0.1589 (**0.1579**)
2	$(Temperature)^2$	0.1059	0.2648 (**0.2630**)
3	Rankers (fraction)	0.0431	0.3079 (**0.3054**)
4	Mean Slope	0.0127	0.3206 (**0.3173**)
5	Median topographic index	0.0117	0.3323 (**0.3282**)
6	Peat (fraction)	0.0077	0.3399 (**0.3351**)
7	Ratio 1	0.0127	0.3527 (**0.3471**)
MODEL FITTED ON BRUNTLAND BURN, GIRNOCK, DYE AND FEUGH ONLY			
Step in forward selection procedure	Explanatory variable added	R^2	Cumulative R^2 (**Cumulative adjusted R^2**)
1	Temperature	0.2024	0.2024 (**0.1994**)
2	AP_7	0.2090	0.4114 (**0.4071**)
3	Rankers (fraction)	0.074	0.4854 (**0.4797**)
4	$(AP_7)^2$	0.041	0.5260 (**0.5189**)

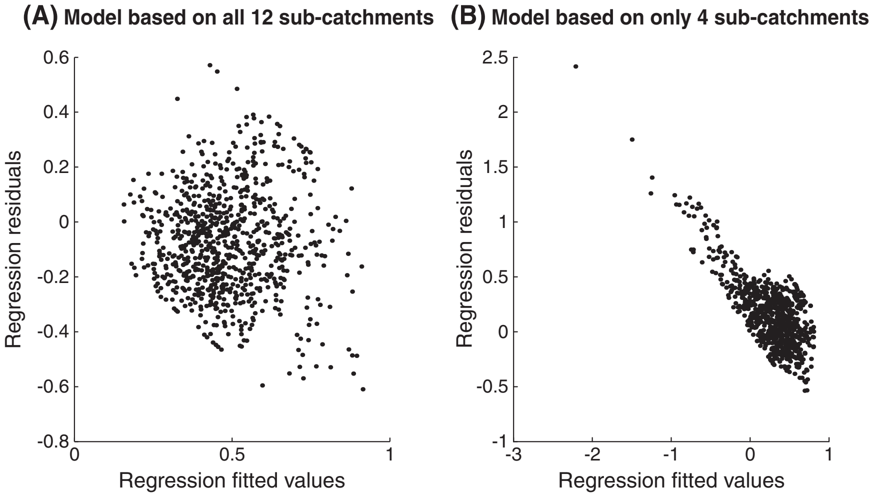


Figure 8. Residual diagnostics plots for the regression (prediction) models based on (A) all 12 sub-catchments, and (B) only four sub-catchments

this is hydroclimatically influenced. Our findings across a wide range of spatial scales suggest that the temporal variability in the relative contributions of quick flow/near surface soil water and slow flow/groundwater DFPs depends, in part, on hydroclimatic factors (i.e. AP_7 and temperature). The importance of hydroclimatic factors in the determination of temporally variable DFPs is however greater in catchments dominated by responsive soils than it is in catchments with more freely draining soils.

Figure 9 summarizes schematically how topographic features, soil drainability and hydroclimatic conditions interact to determine DFPs in the 12 studied sub-catchments. All 12 study sites were characterized by strong exponential relations between groundwater contributions and discharge. Hydrological functioning of all 12 catchments was controlled by the alternation between the same two DFPS: deep groundwater and near surface soil water. The 50% fractional contribution threshold and the scatter around the exponential trend in Figure 4 were however variable among the sites; since the same data collection methods were used at all sites, we believe that this variability is not entirely the result of measurement uncertainty and that both the 50% fractional contribution threshold and the scatter around the exponential trend were effective indicators of catchment internal process variability. The variation partitioning and the RDA results then revealed contrasting patterns of influences and led to a classification of catchments in two major groups (Figure 9): those climatically influenced, to a certain extent, with 40% to 56% of the temporal variance in groundwater contributions explained by AP_7 and air temperature, and those non-climatically influenced. By ‘non-climatically influenced’, we mean sites in which short-term climatic variations are strongly filtered or averaged out. Our results show that such dynamics are a result of catchment organization. The effect of catchment size and soil cover resulted in less temporally variable flow contributions in larger catchments and catchments with higher proportions of freely draining soils. These catchments were also those in which we observed no correlation between air temperature, AP_7 and groundwater contributions (Figure 9). It is important to note that the more climatically influenced sites (i.e. Bruntland, Girnock, Dye and Feugh catchments) have the most easterly, lowest altitude catchments of Dee tributaries and the driest climate. Conversely, the Mar Lodge, Gairn and Muick headwaters are higher, steeper and wetter. The main stem sites integrate all these inputs but are disproportionately influenced by the wetter headwaters; this explains why the main stem sites lay on the same side as the Gairn and Muick tributaries in the triplots shown in Figures 6 and 7. When two regression models linking flow contributions to climatic, topographic and soil variables were built, the model fitted using only four highly responsive sub-catchments (Equation (4)) yielded a higher R^2 than the model built using data from all 12 sub-catchments (Equation (3)) but still badly fitted the data (Figure 8). Even though three variables were included in both models, namely *Temperature*, AP_7 and *Rankers*, the four-catchment based model (Equation (4)) was poorly transferable to the remaining eight catchments. In both regression models, topographic effects were always linear, while climatic ones were often nonlinear (Figure 9) as illustrated by the natural logarithm and the quadratic functions applied to the *Temperature* and AP_7 variables (Equations (3) and (4)). While this observation seems to give very different weights to climatic and topographic controls, there is unfortunately not enough data to run a cross-validation test.

On the consistency with findings elsewhere

Our main finding was that the temporal variability of DFPs is first influenced by hydroclimatic factors and enhanced further by soil drainability properties; this is consistent with previous mean transit time studies in the region which have shown that water residence time is highest when freely draining soils dominate the catchment landscape and DFPs are deep subsurface storm flow and groundwater discharge (Soulsby and Tetzlaff, 2008; Hrachowitz *et al.*, 2010). We attribute the statistically significant, yet moderate influences of AP_7 and air

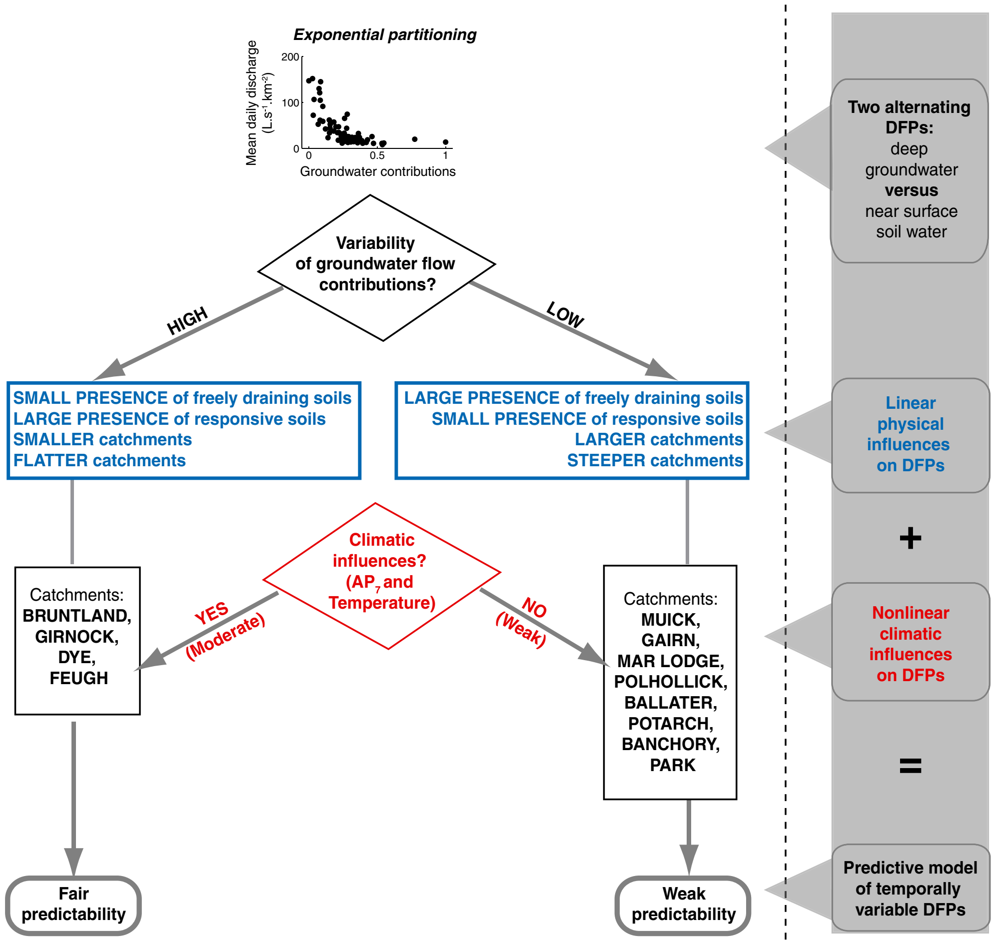


Figure 9. Conceptual diagram illustrating how topographic features, soil drainability and hydroclimatic conditions interact to determine dominant flow pathways (DFPs) in the 12 studied sub-catchments.

temperature on flow contributions in the Bruntland Burn, Girnock, Dye and Feugh sub-catchments to (i) the capacity of the predominant responsive soils to dynamically store and release water over short time periods, and (ii) the effect that evapotranspiration might have on the spatial connectedness of surface and near-surface flow pathways – particularly in a Scottish context. Our identification of non-climatically influenced sub-catchments could be a methodological artifact where AP_7 was an ineffective surrogate measure for antecedent conditions and hence did not capture the influence of climate variability on DFPs. There is precedence in using AP_7 and temperature-based measures as proxies for antecedent conditions (see Ali and Roy, 2010 for a review) since they are easy to derive given widely available meteorological data. These measures might however not be appropriate in continuously wet environments such as Northeast Scotland. It is also possible that the explanation for the non-climatically influenced catchments might be physically based rather than being a simple artefact of our methodological approach. Indeed, we can hypothesize that short-term climatic effects such as those portrayed by air temperature and AP_7 can only be perceived in smaller catchments and in areas prone to near-surface runoff generation mechanisms whereas they are strongly modulated or damped out in regions where deeper subsurface processes and storage dynamics occur. In the Dee basin in particular, higher proportions of freely draining soils are especially encountered in the larger sub-catchments with outlets located on the main stem of the river. This can be linked to the presence of relatively important lowland aquifers in these larger sub-catchments because of the accumulation of alluvial deposits in the valleys (Tetzlaff *et al.*, 2011). Our broad conclusions are therefore in accordance with previous studies which have advocated that catchment attributes in general (e.g Worrall *et al.*, 2003; McGuire *et al.*, 2005; Shand *et al.*, 2006; Stutter *et al.*, 2006; Fröhlich *et al.*, 2008a) and catchment typology and topology in particular (e.g. Fröhlich *et al.*, 2008a) can be used to infer first-order controls on stream chemistry and to explain the complex hydrological behaviours observed at the mesoscale. Our results are also aligned with previous investigations which showed the high temporal variability of end-member concentrations in streamflow when a range of climatic conditions are considered (e.g. Bernal *et al.*, 2006; Liu *et al.*, 2008; Barthold *et al.*, 2010).

With regards to the derivation of regression-based prediction models, similar regression equations were previously derived for another Scottish catchment, the Feshie (Soulsby *et al.*, 2004) but only in order to relate near surface soil water and groundwater end-members (i.e. three highest and lowest flows) to physical properties:

$$\text{Groundwater EM} = 52.2 - 1.1(\%\text{Peat}) + 0.23(\%\text{Granite}) - 289(\%\text{Felsite} + \text{Diorite}) \quad (5)$$

$$\text{Soil water EM} = -51.8 + 1.43(\%\text{Peaty Podzols}) + 0.64(\%\text{Alpine}) \quad (6)$$

These regression models included explicit information on catchment geology but did not consider any climatic factors, and Equations (5) and (6) were associated with R^2 values of 0.99 and 0.79, respectively. Regression models linking land cover (cultivation) and soil type characteristics to end-member composition were also derived by Wade *et al.* (1999) with R^2 values between 0.74 and 0.85. These R^2 values are considerably higher than those obtained in this paper and are probably attributable to the fact that only extreme flow conditions were included in the prediction models. Our current analysis rather focused on intermediate conditions; hence, it is worth asking why prediction R^2 rarely exceeded 0.5 even when only four responsive sub-catchments were considered for the regression. Our analyses are not able to directly answer to this question, but insights from previous studies (i.e. Wade *et al.*, 1999; Soulsby *et al.*, 2004) suggest that the explicit consideration of catchment geological properties and/or land cover might have contributed to higher prediction R^2 in our study. Indeed, spatially variable solid geology and drift deposits could have been used as proxies for aquifer properties. Water transit times may be decadal or longer in sub-catchments with extensive fracture systems (Speed *et al.*, 2010), which is then indicative of dominant groundwater pathways. Fluvio-glacial sediments made of sand and gravel can also act as important aquifers as is the case in the Feugh catchment (Speed *et al.*, 2010), a factor that we did not take into account here. The selective glacial erosion processes that took place in this region of Scotland also had a strong impact on the presence of wide and deep valleys in some areas (Tetzlaff *et al.*, 2009), a landscape characteristic which influences water routing but was not explicitly illustrated by any of the topographic variables in Table I. Besides, none of the topographic variables in Table I depicted the presence of relict paraglacial features; such features are known to influence the distribution of wetlands and zones of internal drainage (Gordon and Wignall, 2006) which can be topographically isolated from the drainage network, and runoff generated on these areas might therefore never reach the stream but via groundwater pathways. We could also hypothesize that the effects of climatic, soil and topographic factors on hydrological functioning might not be additive and hence cannot be captured by simply collating or adding terms in a regression model as we did in this study.

On the robustness of the EMM methodology

Our reliance on a one-tracer, Gran alkalinity, two-component EMM model constrained us to assume the equivalence of overland and shallow subsurface flow pathways in contrast to deeper groundwater. One might argue that it may be more appropriate to rely on a two-tracer, three-component EMM model to be able to distinguish between these three different pathways. We decided not to do so based on a previous analysis by Soulsby and Dunn (2003) who worked in the Allt a'Mharcaidh catchment, a neighbouring site west of Mar Lodge, and found that a third end-member was difficult to identify with the use of alkalinity and silica as conservative tracers. There is also strong precedence for using two-component mixing models with Gran alkalinity or ^{18}O as conservative tracers at a range of spatial scales in the Dee river basin (e.g. Soulsby *et al.*, 2000, 2003, 2004, 2006).

By adopting a catchment-specific definition of end-members, we hypothesized that end-members are spatially consistent in nature (i.e. near surface soil water *vs* groundwater) but spatially variable in value (i.e. alkalinity values). Indeed, it is known that granite dominated sub-catchments such as Mar Lodge and the Feugh have low maximum alkalinity values whereas sub-catchments such as Girnock and Gairn have higher alkalinities because of small areas of calcareous schist or other rocks bearing base-cations (Speed *et al.*, 2010). If a single definition of end-members had been adopted for all 12 sub-catchments (i.e. extreme values of alkalinity had been selected from the entire dataset), this would have led to greater (structural) uncertainty as some catchments would have had a much stronger influence on the definition of the end-members and hence affected the reliability of our EMM results. With regards to input data uncertainty, we acknowledge that both the scatter and also the trends in chemical records make the definition of end-members difficult (Tetzlaff *et al.*, 2007b). Soulsby *et al.* (2004) allowed the near surface soil water end-member ALK value to vary so as to illustrate the range of conditions present among acidic, near surface soil water draining both shallow alpine soils and peat soils; upper and lower boundaries for estimates of groundwater contributions to stream flow were then used as surrogate measures for hydrograph separation uncertainty. On another front, Bayesian analysis has been used to facilitate the chemical hydrograph separation procedure (Brewer *et al.*, 2005), especially in Scottish forested catchments where a systematic temporal change in end-member composition was associated with reduced acid deposition (Tetzlaff *et al.*, 2010). Earlier work across the River Dee and its tributaries however showed that the three lowest (highest) flows provide a reasonable approximation of groundwater (near surface soil water) contributions at larger scales (e.g. Wade *et al.*, 1999; Rodgers *et al.*, 2004; Soulsby *et al.*, 2004, 2006). In following this same simple approach, we relied on the very common assumption in EMM studies that end-member compositions are stable, time-invariant, or at least showcase a temporal variability in chemical concentrations that is significantly less important than that observed in streamflow. While this assumption is often violated in catchments exhibiting strong seasonality (e.g. Hooper, 2003; James and Roulet, 2006; Ali *et al.*, 2010) and/or when using multiyear datasets that reflect long-term climatic or management-induced changes (e.g. Tetzlaff *et al.*, 2007b), our simple assumption is plausible here given the lack of seasonality observed in most of our instrumented sub-catchments (Figure 4).

CONCLUSION

We sought to understand how topographic, pedologic and climatic factors interact to determine DFPs across 12 contrasting mesoscale sub-catchments all located within the Dee River basin. We found that topographic properties and soil characteristics were only useful to explain the temporal variability of DFPs but not their spatial variation across scale. Different groups of sub-catchments showcasing contrasting patterns of temporal variability in their DFPs could be identified: DFPs appeared to be less temporally variable in larger catchments dominated by freely draining soils in comparison to smaller ones where responsive soil cover was more extensive. The predictability of temporally variable DFPs was also slightly better in responsive catchments on the basis on factors such as AP_7, air temperature and the fractional area covered by Rankers.

While trying to mimic early IHD studies which explored the relationships between catchment morphometric properties and streamflow generation, this study went further in illustrating the utility of combining tracer studies with digital landscape analysis and multivariate statistical techniques to gain insights into the climatic, topographic and pedologic controls on DFPs. It however falls short of providing a robust predictive model of DFPs across all catchments, thus highlighting the need to further investigate the contrasting dynamics of the different systems and the complex processes that lead to the spatially and temporally variable emergence of DFPs.

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