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Regionalization of transit time estimates in montane catchments by integrating landscape controls

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[1] Mean transit time (MTT) is being increasingly used as a metric of hydrological function in intercatchment comparisons. Estimating MTT usually involves relating the temporally varying input concentration of a conservative tracer to the signal in the stream using various transfer functions as transit time distributions (TTDs). Most studies have been confined to data collection periods of 1–2 years at single sites, often limiting the transferability of the findings as such short periods usually only capture a narrow range of climatic variability within a spatially restricted area. In this study, we use longer-term (up to 17 years) weekly input-output relationships of Cl^- to estimate MTTs using a range of TTD models in 20 headwater catchments (ranging from <1 to 35 km^2) in seven geomorphologically and climatically distinct parts of the Scottish Highlands. The MTTs obtained from a Gamma distribution model were the best identified and ranged from about 50 to 1700 days for individual catchments. The MTTs, in conjunction with GIS analysis of landscape characteristics and climatic indices, allowed the development of a robust multiple-regression model to establish the relative importance of different landscape and climate controls on MTTs. The best model combines the prediction variables percent responsive soil cover, drainage density, precipitation intensity, and topographic wetness index and yields $R^2_{\mathrm{adj}} = 0.88$. Cross validation shows small absolute error, suggesting that the model can be used to estimate MTTs in ungauged headwater catchments throughout the Scottish Highlands and potentially in similar regions where comparable information is available.

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1. Introduction

[2] Recent research has highlighted two important priorities for catchment hydrology: (1) identification of behavioral metrics that facilitate process-based approaches to intercatchment comparison [*McDonnell et al.*, 2007] and (2) the development of tools to upscale understanding from small experimental catchments to the mesoscale (10^1–10^3 km^2) where management decisions are made [*Tetzlaff et al.*, 2008]. Progress in both of these research areas, which essentially involve understanding the relationships between catchment form and hydrological function, will also help fulfill a wider need to provide predictive tools that can be used in ungauged watersheds, where many issues in applied hydrology occur [*Wagener et al.*, 2007].

[3] Natural conservative tracers are invaluable tools for understanding hydrological processes at larger scales. As tracer variations represent the integrated effect of catchment processes at multiple scales, they can be used to determine the age and identify the geographical sources of streamflow [*Soulsby et al.*, 2003, 2008]. Consequently, they can be used as a basis for determining metrics which can be applied in intercatchment comparisons and upscaling studies [e.g., *Shaman et al.*, 2004; *Soulsby et al.*, 2006a]. In recent years, mean transit time (MTT), i.e., the average time a water molecule takes to travel through a catchment system, has increasingly been applied as a behavioral metric that can be used to characterize and compare different hydrological systems in an integrated manner [*McGuire and McDonnell*, 2006]. For estimating MTT, inverse modeling using lumped parameter convolution models is usually applied [*McGuire and McDonnell*, 2006]. This relates the degree of attenuation and time lag of the stream water levels of conservative tracers, such as Cl^- [e.g., *Kirchner et al.*, 2000; *Hrachowitz et al.*, 2009] or stable isotopes (^2H or ^{18}O) [*Stewart and McDonnell*, 1991; *Soulsby et al.*, 2000; *Uhlenbrook et al.*, 2002], to their changing input levels compared with different assumed transit time distributions (TTDs) for the catchment.

[4] Theoretical studies have provided insight into the physical processes that explain why tracer variations correspond to certain TTDs in certain situations [*Małoszewski et al.*, 1983, *Kirchner et al.*, 2001; *Cardenas*, 2007]. Additionally, numerous empirical studies have applied such models to catchment data, and tried to identify landscape controls on MTTs and associated TTDs. If landscape controls on MTT can be established, these can be used in the prediction of MTTs of ungauged basins and their sensitivity to environmental change [*Soulsby and Tetzlaff*, 2008]. For example, *McGuire et al.* [2005], working in the steep Western Cascades of Oregon, emphasized the usefulness

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of topographic indices for prediction, showing that the ratio of median flow path length to median flow path gradient has strong positive correlations with MTT. *McGlynn et al.* [2003] in steep montane catchments in New Zealand and *Laudon et al.* [2007] in more subdued catchments in northern Sweden also noted that topographic indices related to MTT, but found median subcatchment area appeared to be the strongest control. Others have found that catchment characteristics that reflect the permeability of the subsurface and connectivity of hydrological sources are the strongest controls on MTTs. For example, in glaciated landscapes in Scotland, the hydrological characteristics of catchment soils are closely related to MTT [*Rodgers et al.*, 2005a, 2005b; *Soulsby et al.*, 2006b; *Tetzlaff et al.*, 2009a]; elsewhere the deeper subsurface appears to be more important and catchment geology is the key determinant of MTT [*Vitvar and Balderer*, 1997; *Viville et al.*, 2006]. In addition to catchment characteristics, several studies have emphasized how climate, particularly precipitation amounts in certain years, can cause significant interannual and intersite variability in MTT [*Tetzlaff et al.*, 2007a; *McGuire et al.*, 2007; *Hrachowitz et al.*, 2009]. The influence of catchment size on MTT is not entirely clear yet; smaller catchments exhibit more marked heterogeneity, which averages at larger scales [*Shaman et al.*, 2004; *Soulsby et al.*, 2006a; *Laudon et al.*, 2007], but few studies have looked at larger catchments (>10^2 km^2) to see how MTTs change as more lowland landscape features may become influential.

[5] To date, most empirical investigations of MTTs have focused on small catchments of broadly similar structure within the same geomorphologic and climatic region. Intercatchment comparisons on a larger supraregional scale, spanning several geomorphic and climatic provinces, play a key role in enhancing understanding of the processes driving hydrological systems and how, and why, the landscape controls on metrics such as MTT change [*Tetzlaff et al.*, 2009b]. Such regionalization has the potential to provide insights as to how landscape controls integrate in different geographical regions and may provide a basis for developing predictive models which can be applied to ungauged basins. An essential prerequisite for such regionalization is high-quality and long-term tracer data at a supraregional scale from which to derive MTT estimates. Funding constraints and limited accessibility frequently prevent long-term monitoring in montane areas, and most empirical studies to date are typically restricted to 1–2 years of data.

[6] In this study we examine longer-term tracer data sets (2–17 years) for 20 watersheds in seven climatically and geomorphologically different regions of Scotland. In addition to topographic and climatic differences, the catchments also have contrasting soil cover, geology and land use. The objectives were (1) to constrain MTT estimates using longer-term data in these contrasting catchments, (2) to identify the most important landscape controls on these constrained MTT estimates, and (3) to use these to develop a simple tool to regionalize MTT predictions on the basis of catchment characteristics that could be applied to ungauged basins.

2. Study Sites

[7] The 20 study catchments range from 0.3–35 km^2 in area (Figure 1). Geographically, they include steeper, montane catchments in the maritime northwest (Strontian), southwest (Loch Dee), the Central Highlands (Balquhidder), and the subarctic Cairngorms (Allt a'Mharcaidh). Other catchments were of lower altitude, though still montane in nature including those in south Central Highlands (Loch Ard), northern Scotland (Halladale) and in the Cheviot Hills in the southeast (Sourhope) (Tables 1a and 1b). Frontal systems from the Atlantic, mainly moving from the southwest, result in annual precipitation of more than 2000 mm along the west coast, compared to around 1000 mm in the rain shadow to the east [*Bain et al.*, 1998; *Harriman et al.*, 2001]. The mean annual temperature, which mainly reflects elevation and to a smaller extent latitude, ranges from 4.7°C for the highest to 8.8°C for the lowest catchment. The geology of most of the sites is characterized by low-permeability igneous and metamorphic rocks which dominate the Scottish Highlands [*Robins*, 1990]. At the west coast sites (Strontian) the bedrock is composed of schist and gneiss [*Monteith and Evans*, 2005], granite dominates in the Green Burn and Dargall Lane at Loch Dee, while in the White Laggan metamorphic rocks dominate in the lower catchment [*Harriman et al.*, 1987; *Williams*, 1991; *Nisbet et al.*, 1995]. Granite also dominates the Allt a'Mharcaidh [*Soulsby et al.*, 2000] and Halladale sites [*Bain et al.*, 2001], while the Balquhidder [*Johnson*, 1991] and Loch Ard [*Harriman and Morrison*, 1982; *Wilson et al.*, 1984] sites are mainly underlain by metamorphic rocks. At Sourhope fractured volcanic rocks are dominant [*Bain et al.*, 1998]. At most sites superficial drifts cover much of the solid geology. Where the drift is fine textured, peats and peaty gley soils are dominant, particularly in valley bottoms and gentle slopes at sites like Loch Ard, Strontian and Halladale. As these soils remain close to saturation throughout the year and generate overland flow as a dominant runoff mechanism [*Tetzlaff et al.*, 2007b] we labeled them as "responsive soils" in the subsequent analysis. Where slopes are steeper or drifts are more permeable, coverage of more freely draining soils such as humus-iron podzols and subalpine podzols predominate, resulting in deeper subsurface flow paths and greater groundwater recharge at sites like the Allt a'Mharcaidh and Balquhidder [*Soulsby et al.*, 1998, 1999; *Hrachowitz et al.*, 2009]. Most catchments at Loch Ard, Balquhidder, Loch Dee, Strontian and Halladale are, at least at lower elevations, partly forested, while the Allt a'Mharcaidh and Sourhope are mainly characterized by moorland.

3. Data and Methods

3.1. Hydrological and Hydrochemical Data

[8] At each site daily streamflow and precipitation amounts were available for the entire observation periods (>4 years in Table 1a and <4 years in Table 1b, ranging from 2 to 17 years). Precipitation gauges were generally located within 1 km of the catchment main outlets, where stream gauges were operated by the Scottish Environment Protection Agency. Precipitation was generally sampled on a weekly (Loch Ard, Halladale, Allt a'Mharcaidh and Sourhope) or fortnightly basis (Strontian, Balquhidder, Loch Dee) using open funnel bulk deposition samplers. Stream water dip samples were taken at the same dates as the precipitation samples at the individual catchment outlets

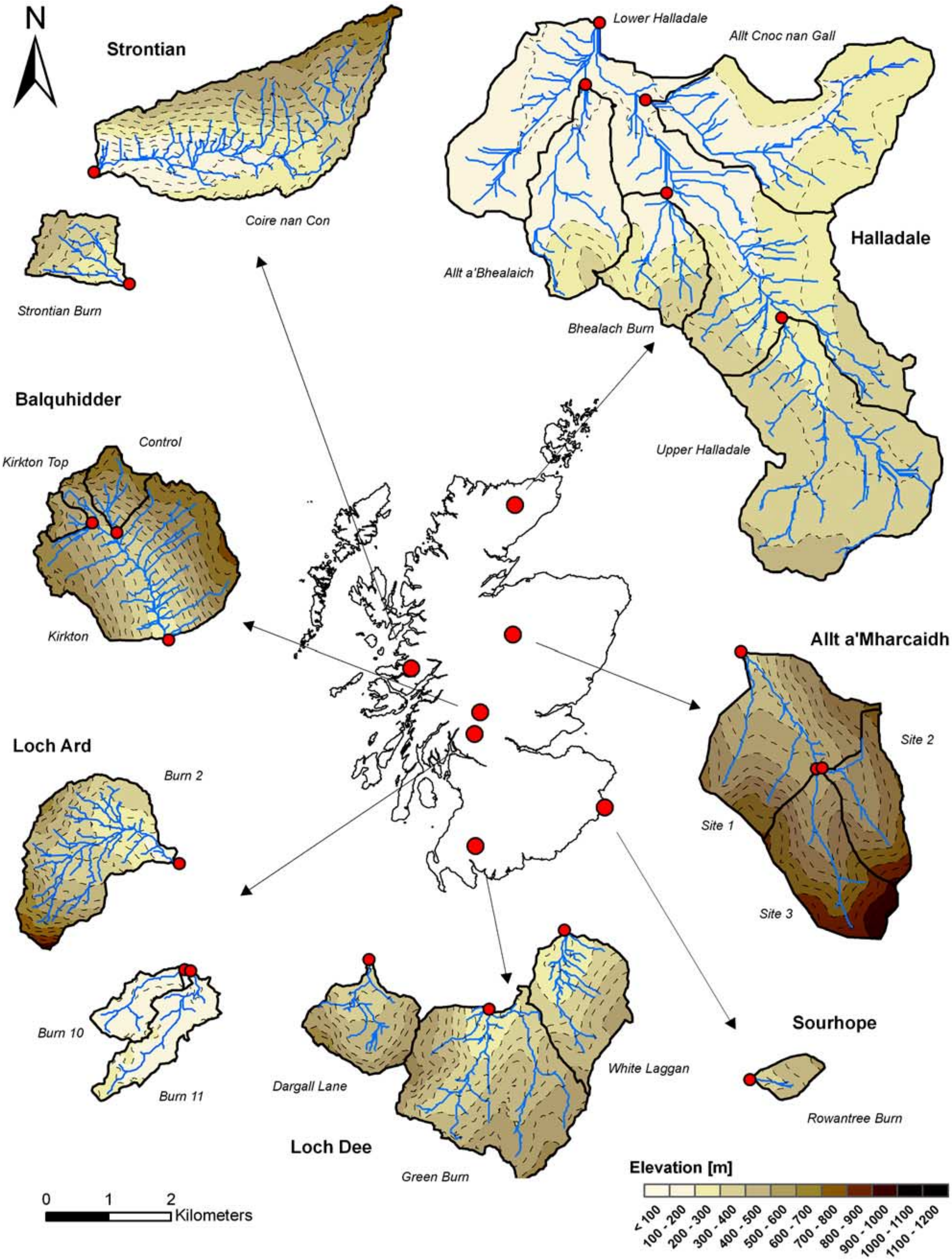

Figure 1. Location and elevation of the 20 study catchments in seven regions of Scotland.

Table 1a. Summary of Catchment Climatic, Topographic, and Pedologic Characteristics for Data Sets >4 years

	Strontian		Loch Ard			Balquhidder			Allt a'Mharcaidh			Sourhope[a]
	Coire nan Con	Strontian Burn	Burn 2	Burn 10	Burn 11	Control	Kirkton	Kirkton Top	Site 1	Site 2	Site 3	Rowantree Burn
Grid reference	NM 793 688	NM 824 652	NN 388 043	NS 469 988	NS 470 988	NN 524 237	NN 533 220	NN 520 238	NH 882 043	NH 894 026	NH 893 026	NT 860 204
Observation period												
Start	9 May 1986	9 May 1986	7 Jan 1988	7 Jan 1988	7 Jan 1988	14 Nov 1984	16 Oct 1987	22 Jan 1986	1 Jan 1990	22 Oct 1998	24 Sep 1998	1 Jun1994
End	11 Jul 2003	11 Jul 2003	15 May 2002	15 May 2002	15 May 2002	1 Mar 2000	1 Mar 2000	1 Feb 1995	31 Dec 2003	22 Sep 2005	22 Sep 2005	1 Jan 2003
Land cover[b]	F/M	M	M	F	F	F/M	M	M	F/M	M	M	M
Climatic indices												
Mean annual precipitation (mm)	2690	2690	2200	2200	2200	2720	2720	2720	1100	1100	1100	876
Mean rain intensity (mm d^{-1})	10.70	10.60	12.67	9.23	9.23	10.29	10.29	10.29	6.28	6.32	5.92	6.25
Mean annual temperature (deg C)	7.18	7.17	7.21	8.80	8.70	5.38	5.88	5.75	5.38	5.11	4.66	7.50
Mean annual wind speed (m s^{-1})	3.16	3.09	10.49	5.80	5.80	6.66	6.66	6.66	6.54	6.67	5.39	6.68
Topographic indices												
Area (km^2)	7.97	1.39	4.04	0.87	1.42	0.82	6.80	0.31	9.61	2.03	3.07	0.44
Perimeter (km)	14.20	5.56	9.48	4.88	7.54	3.96	11.17	2.67	13.29	7.25	7.55	2.94
Minimum elevation (m)	18	149	154	98	99	375	248	421	332	549	539	297
Maximum elevation (m)	755	502	971	220	282	787	849	654	1111	1022	1111	508
Mean elevation (m)	339	340	411	166	183	622	545	566	704	746	815	430
Maximum slope (deg)	54.0	44.0	59.0	41.0	39.0	58.0	65.0	56.0	52.0	36.0	42.0	32.0
Mean slope (deg)	17.0	14.0	18.0	11.0	9.0	22.0	19.0	18.0	16.0	15.0	17.0	12.0
Drainage density (km km^{-2})	3.80	3.85	4.33	2.82	2.87	3.41	3.88	2.07	2.14	2.41	1.88	2.09
Median upslope area (m^2)	300	200	300	200	200	300	300	300	500	600	600	400
Median flow path length (m)	195	162	183	128	134	185	230	173	270	267	266	218
Median flow path gradient (m m^{-1})	0.31	0.26	0.33	0.18	0.15	0.38	0.33	0.30	0.29	0.28	0.32	0.14
L/FG (m)	624	619	561	711	879	481	702	581	927	953	840	1543
Median subcatchment area (ha)	13.9	16.1	13.1	49.1	33.5	11.7	11.1	7.7	26.5	13.8	25.5	30.7
Topographic wetness index (ln(m))	5.29	5.29	5.16	5.61	5.87	4.99	5.32	5.15	5.86	5.95	5.79	5.87
Soil type												
Alluvial soils[c]	-	-	0.01	-	-	-	-	-	-	-	-	-
Humus-iron podzols[c]	-	-	-	-	-	0.42	0.60	0.45	0.30	0.33	0.61	-
Rankers[d]	-	-	-	-	-	-	-	-	0.07	0.11	-	-
Subalpine soils[c]	0.21	-	0.07	-	-	0.08	0.14	-	-	-	-	-
Peaty podzols[c]	-	-	-	-	-	-	-	-	0.35	0.22	0.28	1.00
Peaty gleys[d]	0.79	1.00	0.77	1.00	0.98	0.50	0.22	0.55	-	-	-	-
Peat[d]	-	-	0.15	-	0.02	-	0.04	-	0.28	0.34	0.11	-

[a] Sourhope data are from *Hrachowitz et al.* [2009].

[b] Land cover is classified as forest (F) or moorland (M).

[c] Freely draining soil.

[d] Responsive soil.

Table 1b. Summary of Catchment Climatic, Topographic, and Pedologic Characteristics for Data Sets <4 years

	Loch Dee			Halladale				
	Dargall Lane	Green Burn	White Laggan	Allt a'Bhealaich	Allt Cnoc nan Gall	Bhealach Burn	Upper Halladale	Lower Halladale
Grid reference	NX 451 787	NX 481 791	NX 468 781	NC 892 433	NC 902 430	NC 905 416	NC 924 395	NC 894 443
Observation period								
Start	4 May 1998	4 May 1998	4 May 1998	2 Mar 1993	2 Mar 1993	2 Mar 1993	2 Mar 1993	2 Mar 1993
End	9 Jan 2001	9 Jan 2001	9 Jan 2001	10 May 1994	10 Sep 1994	10 Sep 1994	10 Sep 1994	10 Sep 1994
Land cover[a]	F/M	F/M	F/M	M	M	M	M	F/M
Climatic indices								
Mean annual precipitation (mm)	3400	3400	3400	1300	1300	1300	1300	1300
Mean rain intensity (mm d^{-1})	10.10	10.33	10.33	5.72	5.51	5.51	5.95	5.72
Mean annual temperature (deg C)	5.93	6.54	6.06	6.81	6.73	6.51	5.79	6.49
Mean annual wind speed (m s^{-1})	7.46	6.72	6.72	4.80	4.93	4.93	6.60	4.80
Topographic indices								
Area (km^2)	1.97	2.59	5.76	3.68	6.77	2.35	8.40	34.97
Perimeter (km)	7.02	7.25	10.94	9.25	13.56	7.10	14.07	36.19
Minimum elevation (m)	265	230	229	128	145	158	221	118
Maximum elevation (m)	684	550	668	338	300	366	433	433
Mean elevation (m)	466	372	446	198	211	245	356	247
Maximum slope (deg)	48.0	32.0	56.0	32.0	17.0	31.0	32.0	34.0
Mean slope (deg)	18.0	11.0	15.0	5.0	3.0	8.0	4.0	4.0
Drainage density (km km^{-2})	2.91	3.26	2.62	2.96	2.96	3.26	2.93	3.21
Median upslope area (m^2)	400	400	300	400	500	400	300	400
Median flowpath length (m)	233	261	210	232	268	214	239	242
Median flowpath gradient (m m^{-1})	0.36	0.21	0.28	0.08	0.05	−0.13	0.06	0.06
L/FG (m)	654	1266	760	2941	4883	1619	3740	3930
Median subcatchment area (ha)	11.4	10.5	22.5	24.6	12.9	10.7	18.7	14.8
Topographic wetness index (ln(m))	5.30	5.96	5.50	7.50	8.24	6.54	7.60	7.80
Soil type								
Alluvial soils[b]	-	-	-	-	-	-	-	-
Humus-iron podzols[b]	-	-	-	-				
Rankers[c]	0.82	-	0.14	-	-	-	-	-
Subalpine soils[b]	-	-	-	-	-	-	-	-
Peaty podzols[b]	0.18	0.08	0.15	0.24	-	0.08	-	0.04
Peaty gleys[c]	-	0.78	0.70	0.76	0.30	0.77	0.25	0.48
Peat[c]	-	0.14	0.01	-	0.70	0.14	0.75	0.48

[a] Land cover is classified as forest (F) or moorland (M).

[b] Freely draining soil.

[c] Responsive soil.

(Figure 1). All water samples were filtered through a 0.45 μm polycarbonate membrane filter. Cl^- concentrations were determined by ion chromatography (Dionex DX100/DX120).

3.2. Transit Time Estimation

[9] The mean transit time (MTT) of a water molecule is the average time elapsed between the moments of entry to and exit from a catchment [*Etcheverry and Perrochet*, 2000]. It is widely used as a descriptor of catchment functioning and can be conceptualized as the time integrated response of a catchment assuming no zones of immobile water are present [*Rodhe et al.*, 1996]. MTT was estimated using weekly and fortnightly samples of Cl^- concentration in precipitation and stream water convoluted over time as suggested by *Małoszewski and Zuber* [1982]:

$$c_{out}(t) = \int_0^\infty g(\tau) c_{in}(t-\tau) d\tau \qquad (1)$$

where τ is the transit time, t is the time of exit from the system and $(t - \tau)$ represents the time of entry into the system. Thus, the Cl^- output concentration $c_{out}(t)$ in the stream water at any time t equals the combined Cl^- input concentrations from any time $(t - \tau)$ in the past, weighted by the transfer function $g(\tau)$, which represents the assumed time-invariant, lumped transit time distribution (TTD) of tracers in the catchment.

[10] Although developed for quasi–steady state groundwater systems, this time invariant approach has proved useful in many surface water studies [*Kirchner et al.*, 2001; *McGuire et al.*, 2005]. This is especially true for wet regions like the Scottish Highlands, where the soils remain close to saturation throughout the year and precipitation is distributed rather evenly [*Tetzlaff et al.*, 2007a].

[11] As the streamflow tracer signal depends on the actual tracer mass flux, this mass weighted input, rather than the input concentration alone, can be used to estimate the stream water Cl^- concentration [cf. *Stewart and McDonnell*, 1991; *Weiler et al.*, 2003]:

$$c_{out}(t) = \frac{\int_0^\infty g(\tau) w(t-\tau) c_{in}(t-\tau) d\tau}{\int_0^\infty g(\tau) w(t-\tau) d\tau} \qquad (2)$$

Table 2. Descriptions of Applied Transit Time Distributions

Model	TTD g(τ)	MTT	Parameter Description
Exponential	${\tau_m}^{-1}\exp\left(-\frac{\tau}{\tau_m}\right)$	τ_m	-
Two parallel linear reservoirs	$\frac{\phi}{\tau_f}\exp\left(-\frac{\tau}{\tau_f}\right)+\frac{1-\phi}{\tau_s}\exp\left(-\frac{\tau}{\tau_s}\right)$	$\phi\tau_f+(1-\phi)\tau_s$	τ_f is mean transit time of fast reservoir; τ_s is mean transit time of slow reservoir; ϕ = volume of fast reservoir/total volume
Gamma	$\frac{\tau^{\alpha-1}}{\beta^{\alpha}\Gamma(\alpha)}\exp\left(-\frac{\tau}{\beta}\right)$	$\alpha\beta$	α is shape parameter; β = scale parameter

where $w(t-\tau)$ is the mass weighting factor. Depending on the antecedent conditions, varying proportions of precipitation inputs become hydrologically effective and contribute to catchment turnover: storage in the unsaturated zone and subsequent evapotranspiration increase Cl^- concentrations in the system. Thus, effective precipitation p_{eff} as an estimate of the mass flux of water actually contributing to runoff generation was used as weighting factor $w(t-\tau)$. A nonlinear loss function based on the antecedent wetness index $s(t)$ is used to determine p_{eff} [*Jakeman and Hornberger*, 1993; *Weiler et al.*, 2003]:

$$p_{eff}(t)=p(t)s(t) \tag{3}$$

where $p(t)$ is the measured precipitation at any time t and $s(t)$ is the antecedent precipitation index at any time t, calculated by exponentially weighting precipitation backward according to b_2:

$$s(t)=b_1p(t)+\left(1-b_2^{-1}\right)s(t-\Delta t) \tag{4}$$

Parameter b_1 closes the water balance, i.e., $\Sigma p_{eff}=\Sigma Q$, and is therefore not a free but merely a normalizing parameter. The initial antecedent precipitation index $s(t=0)$ and parameter b_2 are obtained by calibration.

[12] As shown by others [e.g., *Neal et al.*, 1988], stream water Cl^- flux usually exceeds the precipitation Cl^- flux, indicating the importance of dry and occult Cl^- deposition. These inputs vary depending on vegetation, topography and climatic conditions and may be temporally decoupled from the measured wet inputs, though this is of minor concern in wetter parts of Scotland. Therefore, lumped adjustment factors were applied to maintain the Cl^- balance. Such lumped adjustment factors should be treated cautiously in regions with a more marked seasonal change of climate as they might cause serious errors in Cl^- inputs and associated uncertainty in MTT estimates. The factors applied ranged from about 1.0 to 2.2, which are similar to adjustment factors reported by others: 1.55 for a moorland catchment [*Dunn and Bacon*, 2008], 1.9–2.8 for forested catchments [*Tetzlaff et al.*, 2007a; *Shaw et al.*, 2008]. High adjustment factors were needed where catchments had some forest cover which enhanced deposition or where the gauge was in the lower catchment and there was a marked deposition gradient.

[13] Transit time distributions (TTD) act as transfer functions in the convolution integral and they conceptualize the internal catchment functioning in different ways. The details of the three TTDs used in this study are summarized in Table 2. The exponential model (EM) is a basic and widely used [e.g., *Małoszewski et al.*, 1983; *Stewart and McDonnell*, 1991; *McGuire et al.*, 2002] one-parameter model, conceptualizing the catchment as well mixed linear reservoir. The two parallel linear reservoir (TPLR) model, as applied by *Weiler et al.* [2003] and on the basis of three parameters, allows separating the system into a fast and a slow component according to the partition parameter Φ. As shown by *Kirchner et al.* [2000] using spectral analysis, the Gamma distribution model (GM) with a shape parameter $\alpha = 0.5$ is the mathematically ideal representation of stream signals exhibiting $1/f$ noise. The long tail of the gamma distribution enables this model to reproduce the long internal memory of many catchments.

[14] It is problematic to compare MTTs estimated with data sets of varying length or resolution because of the fact that they capture different levels of climatic variability, as shown by *Hrachowitz et al.* [2009]. They not only demonstrated that the variability in MTT estimates increases with decreasing length of observation periods but that MTT estimates themselves tend to increase with decreasing length of observation periods. Therefore all MTTs estimated in this study were adjusted to the level of the longest data set using the power law suggested by *Hrachowitz et al.* [2009].

3.3. Uncertainty Estimation

[15] In catchments with long MTTs, the tracer signal in the stream is extremely attenuated, which frequently results in poor model fits and, despite the low number of parameters in the TTDs, equifinality in the determination of the best parameter set [cf. *Dunn et al.*, 2008]. The generalized likelihood uncertainty estimation (GLUE) framework developed by *Beven and Binley* [1992] was therefore used to estimate the uncertainty introduced by limited model identifiability. On the basis of the idea of a set of "equally good" parameters, this concept yields upper and lower bounds for the modeled stream water Cl^- time series [*Freer et al.*, 1996]. In this study, parameters were sampled from a predefined uniform distribution with 2500 Monte Carlo realizations. Considering the contrasting nature of the study catchments, the chosen likelihood measure was a combination of Nash-Sutcliffe efficiency NSE [*Nash and Sutcliffe*, 1970] and normalized 1 − RMSE [cf. *Weiler et al.*, 2003], where a value of 1 would indicate a perfect fit. Therefore models were retained as "behavioral" only if they showed both: RMSE <2.5 mg L^{-1} and $E > 0.15$. As GLUE assumes the absence of a single best model structure, MTTs used in the analysis are median rather than best fit values of the retained subsets.

3.4. Topographic Analysis

[16] For all catchments 10 × 10 m digital terrain models (DTMs) were available from which various catchment

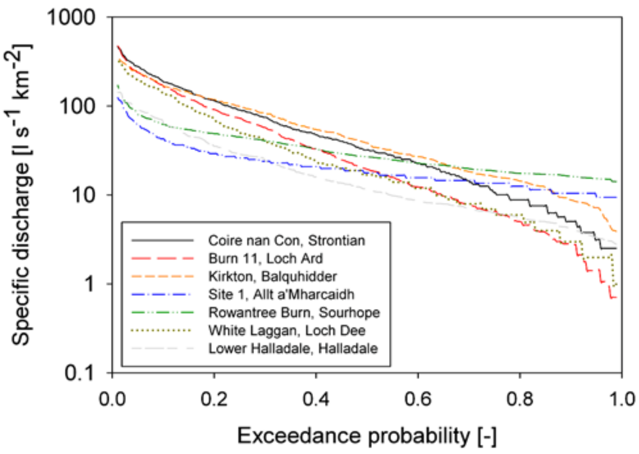

Figure 2. Median annual flow duration curves for one selected catchment in each region based on the individual observation periods.

characteristics were extracted. The stream network was derived from the DTM with a D8 flow direction algorithm [*Jensen and Domingue*, 1988] on the basis of the channel threshold method. In correspondence with the mapped stream networks (Ordnance Survey, 1:50 000) and the upslope area over local slope ratio suggested by *Tarboton et al.* [1991] a stream initiation threshold of 5 ha upslope area was defined as threshold for all sites, which is in the range of what has been reported by *Montgomery and Dietrich* [1988] and was shown to be for other Scottish sites in previous studies [*Tetzlaff et al.*, 2009b]. The DTM and the derived stream networks were then used as a basis for calculating catchment attributes including area (A), perimeter (PE), mean slope (S), median upslope area (UA), computed as the median of contributing areas to all cells of the DTM, drainage density (DD), median flow path length (L), computed as the median of all flow path lengths from the respective source to the stream, median flow path gradient (FG), the median topographic wetness index (TWI) [*Beven and Kirkby*, 1979], the ratios PE/A and L/FG as well as the median subcatchment area (A_{msc}). In contrast to UA, A_{msc} is calculated as the median of the upstream contribution areas for each cell flagged as a stream cell [*McGlynn et al.*, 2003; *Laudon et al.*, 2007]. It is a metric for catchment structure, having higher values for linear and lower values for more dendritic stream networks [*Tetzlaff et al.*, 2009b].

3.5. Multiple-Regression Analysis

[17] To identify the relative significance of various climatic, pedological and topographic catchment characteristics for MTTs, a stepwise backward multiple linear regression analysis (MLR) with $p_{out} = 0.10$ was carried out. The climatic descriptors included mean annual precipitation, mean precipitation intensity (calculated as the ratio of precipitation amount over the number of days with precipitation), mean annual temperature and mean annual wind speed, with the latter two used as proxies for evapotranspiration. The pedological descriptors used were percent peat soil cover, percent responsive soil cover (i.e., generating overland flow) and percent freely draining soil cover. The class "responsive soils" combined peat, peaty gleys and rankers, while "freely draining soils" included podzolic and alluvial soils.

[18] The results of the MLR models were evaluated by cross validation to test robustness and to estimate the prediction error expected when applying the model to estimate MTT in similar catchments not used in the initial model definition. The method used is the "leave-one-out cross validation" (LOOCV) [e.g. *Stone*, 1974; *Efron and Gong*, 1983], which is a special case of the *k*-fold cross validation, with $k = n$ and n is the number of data points [*Shao*, 1993]. One catchment at a time is removed and the best fit MLR model is computed from the remaining catchments. The model is then used to predict the MTT at the removed catchment and to determine the absolute error between predicted and "known" MTT. This is repeated in turn for all catchments and the mean absolute error is calculated. As most of the seven regions contain a different number of catchments, leaving one catchment out at a time might give biased results. To avoid this bias, a second cross-validation analysis was done, leaving one entire region out at a time. To avoid the adverse influence of highly correlated descriptor variables, the best MLR models were examined for multicollinearity using the variance inflation factor (VIF), the determinant of the correlation matrix, the condition number (CN) and the proportion of variance [*Belsey*, 1991; *Mueller and Pierce*, 2003].

4. Results

4.1. Catchment Hydrology

[19] The mean annual precipitation totals during the observation periods (Tables 1a and 1b) are in the range of long-term mean annual precipitation reported in earlier studies [*Harriman et al.*, 2001], with the exception of the Loch Dee region, which experienced an unusually wet period. The median annual flow duration curves for one catchment in each region are shown in Figure 2. Streams such as Coire nan Con (Strontian, northwest Scotland) and burn 11 (Loch Ard, central Scotland) show a very flashy response to precipitation events (with Q_5 exceeding 276 and 224 $l\ s^{-1}\ km^{-2}$) and low base flows (Q_{95} around 3.1 and 1.4 $l\ s^{-1}\ km^{-2}$). At the other extreme, sites such as the Allt a'Mharcaidh (Cairngorms) and Rowan Tree Burn (South East Scotland) are less flashy with a Q_5 of about 59 and 78 $l\ s^{-1}\ km^{-2}$, respectively, and a stronger base flow component (Q_{95} around 9.4 and 15.2 $l\ s^{-1}\ km^{-2}$). This suggests that deeper subsurface flow pathways dominate the latter rather than near-surface, well-connected flow pathways in the former catchments. The other catchments are intermediate or more complex in response. Balquhidder (Central Highlands) and Loch Dee (southwest Scotland) have marked storm responses, but the former has a much stronger base flow component. High flows at Halladale are modest (presumably reflecting the lower precipitation), but the base flow is component is much weaker.

4.2. Chloride Concentrations and Transit Time Estimation

[20] As Cl^- in precipitation is generally marine derived, the clear and fairly consistent seasonal variation for all regions is explained by stormy weather conditions in the north Atlantic which increase the amount of sea salt being sprayed into the atmosphere [*Neal and Kirchner*, 2000].

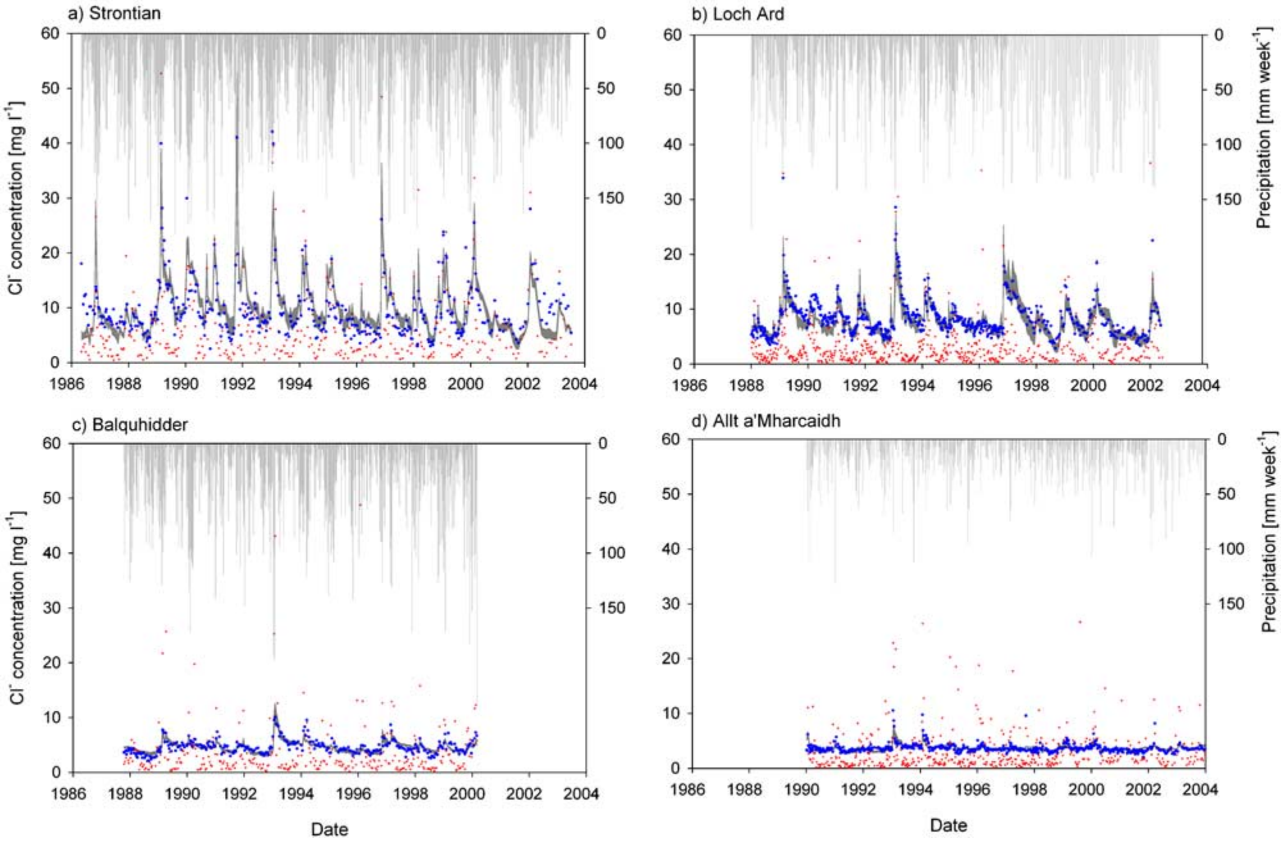

Figure 3. Time series of precipitation and Cl⁻ input and output concentrations at (a) Coire nan Con (Strontian), (b) burn 11 (Loch Ard), (c) Kirkton (Balquhidder), and (d) site 1 (Allt a'Mharcaidh). Inverted triangles are observed Cl⁻ concentrations in precipitation, circles are observed Cl⁻ concentrations in the stream water, and the gray shaded area shows the modeled Cl⁻ stream concentration as GLUE uncertainty bounds for the behavioral models using the Gamma distribution model.

This is shown for selected sites in Figure 3 that also indicates that the level of Cl⁻ concentration in precipitation is strongly dependent on the distance of the region to the coast, with the west coast sites in the Strontian region showing the highest Cl⁻ input concentration levels while the Allt a'Mharcaidh region in central Scotland receives lowest.

[21] Compared to Cl⁻ precipitation concentrations, the observed Cl⁻ concentrations in stream water are much less variable (Figure 3), indicating that the fluxes from the catchment comprise a mix of waters of different "age" [cf. *Feng et al.*, 2004]. The varying levels of damping in the individual catchments are generally consistent with the conceptualizations inferred from the flow duration curves (Figure 2) and those reported by other studies [e.g., *Neal and Rosier*, 1990; *Soulsby et al.*, 2006a]: little damping at the site in the Strontian region with a suspected predominance of overland and preferential flow pathways, becoming slightly more attenuated at sites at Loch Ard and then increasingly attenuated at Balquhidder, and almost complete loss of the seasonal signal at the Allt a'Mharcaidh site, indicating the dominance of well-mixed water routed through slower pathways [*Soulsby et al.*, 1998].

[22] As anticipated, the use of the TPLR and GM as transfer functions consistently produces better fits of modeled stream water Cl⁻ concentration than the EM, which tends to predict low MTTs (Figure 3 and Tables 3a and 3b). The TPLR model produces the highest Nash-Sutcliffe efficiencies for burn 2 (Loch Ard) (NSE = 0.82) and the lowest efficiencies (NSE = 0.20) for site 2 at the Allt a'Mharcaidh. The GM yields equally good or marginally lower efficiencies throughout, with efficiencies falling as tracer damping (and MTT) increases (Tables 3a and 3b and Figure 3). Thus, the median MTTs for the GM range between 47 days at burn 2 (Loch Ard) and over 1000 days at sites like the Allt a'Mharcaidh. The median fast and slow transit times, τ_f/τ_s, computed with the TPLR for the same catchments, are 22/300 and 43/1021 days, respectively. Although the TPLR allows a slightly better representation of the stream water Cl⁻ concentrations, limited identifiability of the best fit parameter sets becomes a concern. Figure 4 shows dotty plots (2500 Monte Carlo realizations) of the MTT obtained from the GM (i.e., MTT = $\alpha\beta$) and the TPLR models (i.e., MTT = $\Phi\tau_F + (1 - \Phi)\tau_S$) plotted against efficiency for the same catchments shown in Figure 3. The range of best parameter sets is better constrained for the GM than for the TPLR model, where similar efficiencies can be obtained using parameters within a wider range. Furthermore, Figure 4 reflects the decreasing parameter identifiability with increasing MTT noted by *Dunn et al.* [2008]. The Cl⁻ concen-

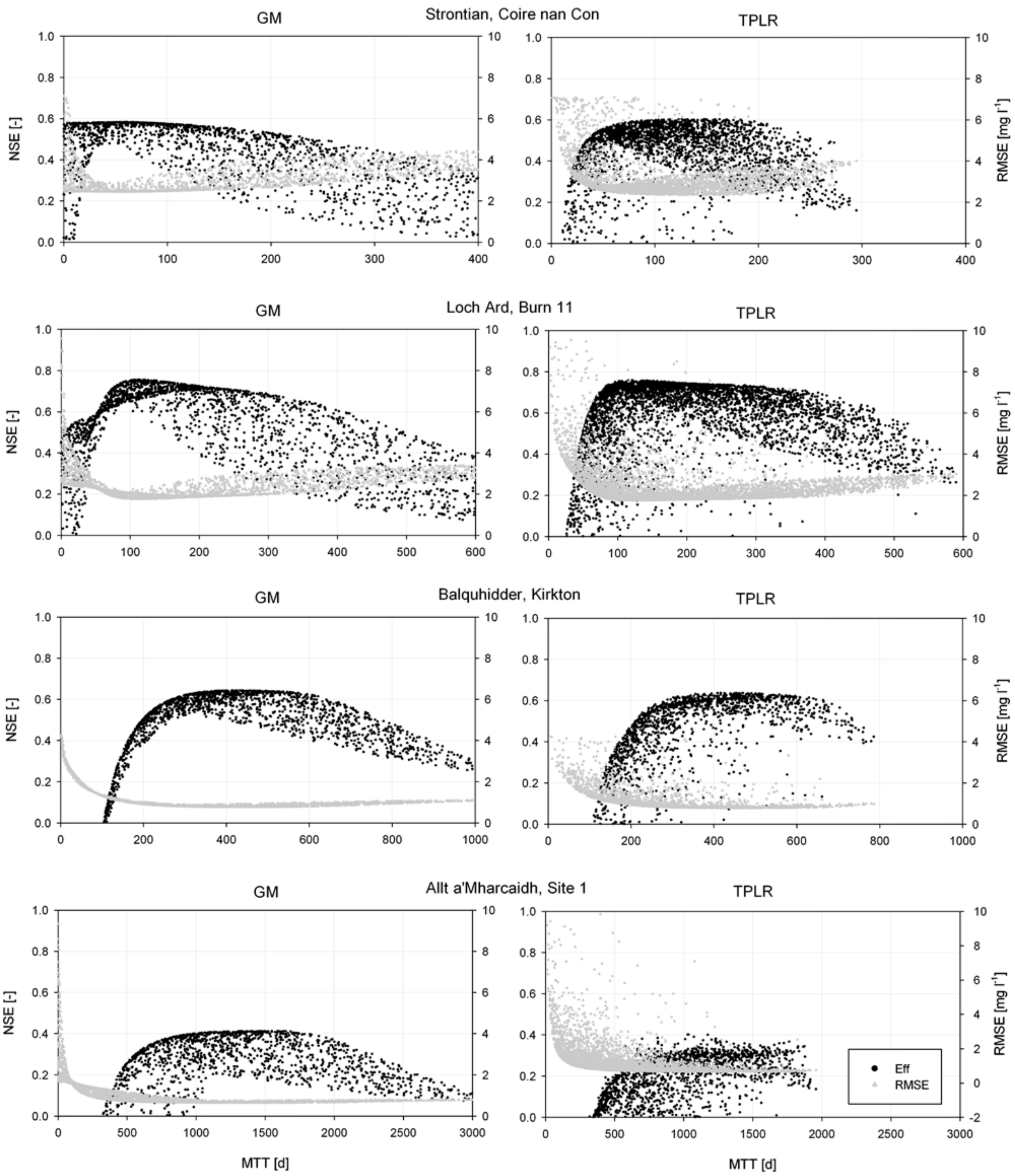

Figure 4. Dotty plots of MTT against Nash-Sutcliffe efficiency NSE (circles) and RMSE (triangles, 2500 Monte Carlo realizations) for one catchment in (top to bottom) the Strontian, Loch Ard, Balquhidder, and Allt a'Mharcaidh regions. (left) Gamma distribution model (MTT = $\alpha\beta$) and (right) two parallel linear reservoir model (MTT = $\Phi\tau_F + (1 - \Phi)\tau_S$).

trations in such catchments become attenuated to the point where fluctuations are extremely limited. Therefore, MTT can only be identified to be within a wide range: around 1200–1700 days at site 1 (Allt a'Mharcaidh). At other sites, the resulting MTTs fell between these extremes: at Strontian and the other Loch Ard catchments the GM predicted MTTs of 2–3 months. The Halladale and Loch Dee estimates were 3–6 months, while at Balquhidder MTTs were in the order of 1 year. As previously shown, the Sourhope site was even more extreme than the Allt a'Mharcaidh in terms of tracer damping [*Hrachowitz et al.*, 2009]. Despite identifiability problems, the TPLR models are useful in terms of conceptualizing the MTTs of more rapidly responding flow paths. All the catchments have a fast component with a characteristic MTT of a few days/weeks, with this component accounting for between 1 and 67% of the flow routing. Note that in spite of very low NSE at Allt a'Mharcaidh and Sourhope, these models have not been rejected as "nonbehavioral" because of the very low RMSE compared to all other catchments (Tables 3a and 3b and Figure 4).

4.3. Topographic Analysis

[23] The topographic indices derived from DTMs highlight the contrasting nature of the study catchments (Tables 1a and 1b). The lowest drainage densities are found in catchments in the Allt a'Mharcaidh (1.88–2.41 km^{-1}) where the percentages of responsive soils are also low. Drainage densities increase in catchments with a higher percentage of responsive soil cover as rapid routing via overland and preferential flow pathways enhances connectivity between the catchment hillslopes and stream channel network (Strontian: 3.80–3.85 km^{-1}, Loch Ard: 2.82–4.33 km^{-1}). Values found for median flow path lengths range from 128 to 270 m. Only the lowest median flow paths lengths, found in the Loch Ard (128–183 m) and Strontian (162–195 m) regions, are consistent with the high proportions of responsive soils in these catchments, while the higher flow path lengths at the other study sites do not seem to be related to responsive soils. The median upslope areas tend to decrease with increasing percentage of responsive soil cover and drainage density with a range from 200 (Loch Ard) to 600 m^2 (Allt a'Mharcaidh). Values for median slope range from 0.06 (Halladale) to 0.39 m m^{-1} (Balquhidder). The fact that higher median slopes are found in catchments with a lower percentage of responsive soils cover is consistent with the distribution of responsive peat and gley soils on flat hilltops or valley bottoms, while freely draining soils are more likely to be found on steeper hillslopes. The median topographic wetness index reaches minimum values in the Balquhidder region (4.99–5.32 $\ln(\text{m}^2)$) and maximum values in the Halladale region (6.54–8.24 $\ln(\text{m}^2)$), reflecting their steep, upland-type and subdued, wetland-type characteristics respectively. The ratio of catchment perimeter to area roughly distinguishes between elongated and rather circular catchment shapes, ranging from 1.6 km^{-1} at the Kirkton catchment (Balquhidder) to 5.6 km^{-1} at the burn 11 catchment (Loch Ard). The flow path length over gradient ratio has its minimum in the Balquhidder region (481–702 m) and reaches maximum values in the Halladale region (1619–4883 m), while the median subcatchment area ranges from 7.7 ha (Kirkton Top catchment) to 49.1 ha (burn 10), reflecting the degree of branching in the individual catchments.

4.4. Landscape Controls on MTT: A Regression Analysis

[24] Because of better identifiability, only the results from the GM were used in the subsequent MLR analysis. The topographic, pedologic and climatic indices were correlated with the data set length adjusted median MTTs from the subset classified as behavioral in the GLUE analysis. Because of the MTTs spanning 3 orders of magnitude, log(MTT) was used in the analysis. Table 4 and Figure 5 summarize the results of the univariate analysis. The landscape characteristic exhibiting the strongest correlation with log(MTT) was the percentage responsive soil cover. Coverage of responsive soils was negatively correlated with log(MTT) ($R^2 = 0.80$, $p < 0.001$), while freely draining soils were positively correlated ($R^2 = 0.80$, $p < 0.001$). This reflects rapid routing through surface and preferential flow pathways in responsive soils and the matrix and deep subsurface flow controlled freely draining soils as previously suggested by *Soulsby et al.* [2006a, 2006b] and *Laudon et al.* [2007].

[25] Drainage density ($R^2 = 0.59$, $p < 0.001$) and upslope area ($R^2 = 0.25$, $p = 0.02$) are the only topographic indices which are significantly correlated with log(MTT). Both have been identified as possible controls on MTT in Scottish uplands in earlier studies by *Soulsby et al.* [2006a] and *Tetzlaff et al.* [2009a], respectively. However, topographic indices which have been identified as controls on MTT in other regions, such as the median subcatchment area [*McGlynn et al.*, 2003; *Laudon et al.*, 2007] and the flow path length over flow path gradient ratio [*McGuire et al.*, 2005], did not show significant relationships with log(MTT) using the entire data set. Interestingly, the correlations between log(MTT) and indices of landscape organization become more robust when the data from the regions with the shortest data sets (Halladale, Loch Dee) are removed from the analysis, making the initial L/FG ratio ($R^2 = 0.01$, $p = 0.70$) significant ($R^2 = 0.34$, $p = 0.03$; not shown). Although several studies have hypothesized that MTT may be positively correlated with catchment area [*DeWalle et al.*, 1997; *Soulsby et al.*, 2000], the results of this study ($R^2 = 0.13$, $p = 0.11$) and other more recent studies suggest the absence of such a scaling relationship [*McGlynn et al.*, 2003; *Rodgers et al.*, 2005a; *Laudon et al.*, 2007; *Tetzlaff et al.*, 2009b].

[26] The climatic indices showed varying correlations with log(MTT). Mean annual precipitation totals exhibit a negative correlation with log(MTT) ($R^2 = 0.25$, $p = 0.02$) as high precipitation amounts are likely to raise water tables in soils and accelerate tracer flux rates. The mean precipitation intensity is not significantly correlated with log(MTT) ($R^2 = 0.14$, $p = 0.09$), which is rather counterintuitive, as high precipitation intensities might be expected to trigger infiltration and saturation excess overland flow, particularly in catchments with responsive soils. As also observed for the topographic indices, correlating precipitation and precipitation intensity with log(MTT) leaving out the two shortest data sets shows that there are highly significant negative relationships: for precipitation $R^2 = 0.61$, $p < 0.001$ and for precipitation intensity $R^2 = 0.76$, $p < 0.001$. This might once more highlight the uncertain nature of MTT estimates from short data sets. No significant relationships between log(MTT) and mean annual temperatures ($R^2 = 0.09$, $p = 0.18$) or wind speeds ($R^2 = 0.03$, $p = 0.42$) as proxies for evapotranspiration were found. It was hypothesized that evapotranspiration is positively correlated with log(MTT) for reasons contrary to precipitation amounts, but it seems as if the evapotranspiration gradients in Scotland are not sufficiently high to have a major impact.

[27] As noted by others [e.g., *Kirchner et al.*, 1996; *Laudon et al.*, 2007; *Tetzlaff et al.*, 2009b], the complex structure of cocorrelations between variables frequently

Table 3a. Model Parameters for Individual TTDs >4 years[a]

	Strontian		Loch Ard			Balquhidder			Allt a'Mharcaidh			Sourhope[b]
	Coire nan Con	Strontian Burn	Burn 2	Burn 10	Burn 11	Control	Kirkton	Kirkton Top	Site 1	Site 2	Site 3	Rowantree Burn
EM												
NSE	0.50	0.54	0.70	0.74	0.71	0.46	0.56	0.63	0.25	0.20	0.26	0.15
RMSE (mg L^{-1})	2.72	2.69	2.02	1.77	2.02	1.29	1.26	1.20	1.03	1.09	0.87	0.85
MTT (d)	45	54	39	95	105	181	275	320	758	752	605	1283
MTT, 5–95% (d)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
TPLR												
Median NSE	0.58	0.60	0.82	0.73	0.72	0.57	0.64	0.69	0.40	0.20	0.26	0.16
RMSE (mg L^{-1})	2.44	2.12	1.91	1.84	1.97	1.12	0.96	0.99	0.92	1.10	0.87	0.87
Median MTT, fast/slow (d)	21/181	28/189	22/300	57/219	54/281	84/504	85/548	94/513	87/1486	43/1021	42/931	803/1994
MTT fast/slow, 5–95% (d)	12–35/ 95–270	19–46/ 82–264	6–43/ 79–521	28–69/ 94–546	17–71/ 112–534	38–136/ 303–666	20–154/ 331–793	25–149/ 310–771	13–183/ 846–1957	11–49/ 907–1112	14–59/ 807–1076	376–993/ 1232–2968
Median proportion fast	0.51	0.57	0.65	0.61	0.53	0.38	0.24	0.24	0.14	0.01	0.03	0.37
Proportion fast, 5–95%	0.23–0.72	0.28–0.75	0.32–0.89	0.12–0.90	0.13–0.78	0.15–0.66	0.05–0.48	0.04–0.46	0.04–0.26	0.01–0.03	0.00–0.05	0.05–0.86
GM												
Median NSE	0.58	0.59	0.82	0.74	0.71	0.59	0.64	0.69	0.40	0.20	0.26	0.16
RMSE (m gL^{-1})	2.46	2.12	1.79	1.78	2.03	1.11	0.90	0.92	0.78	0.98	0.88	0.87
Median MTT (d)	61	78	46	124	149	347	405	402	1275	1013	871	2141
MTT, 5–95% (d)	12–117	46–133	6–102	62–203	83–247	232–501	290–584	289–562	885–1725	669–1501	552–1268	1172–2920

[a] Median values and 5–95% percentiles from the behavioral subsets are shown. Also shown are the goodness of fit for the associated models expressed as Nash-Sutcliffe efficiency (NSE) and RMSE for data sets. NA means no GLUE uncertainty bounds are available as EM is a model with only one parameter.

[b] Sourhope analysis is from *Hrachowitz et al.* [2009].

Table 3b. Model Parameters for Individual TTDs <4 years[a]

	Loch Dee			Halladale				
	Dargall Lane	Green Burn	White Laggan	Allt a'Bhealaich	Alt cnoc nan Gal	Bhealeach Burn	Upper Halladale	Lower Halladale
EM								
NSE	0.60	0.64	0.69	0.40	0.33	0.26	0.26	0.27
RMSE (mg L^{-1})	1.90	2.10	1.96	2.40	2.54	2.78	2.81	2.75
MTT (d)	172	153	139	75	35	54	58	45
MTT, 5–95% (d)	NA	NA	NA	NA	NA	NA	NA	NA
TPLR								
Median NSE	0.63	0.65	0.70	0.41	0.45	0.34	0.41	0.42
RMSE (mg L^{-1})	1.48	1.90	1.63	2.35	2.27	2.45	2.33	2.29
Median MTT, fast/slow (d)	58/267	60/250	56/230	56/245	19/342	9/391	9/286	16/331
MTT fast/slow, 5–95% (d)	22–76/147–483	24–77/134–481	21–73/116–466	35–71/84–483	6–30/125–483	3–18/172–493	2–14/101–464	3–26/138–478
Median proportion fast	0.27	0.30	0.35	0.64	0.40	0.10	0.15	0.25
Proportion fast, 5–95%	0.05–0.58	0.02–0.59	0.03–0.67	0.14–0.93	0.10–0.65	0.04–0.23	0.06–0.24	0.06–0.45
GM								
Median NSE	0.63	0.65	0.70	0.41	0.45	0.34	0.42	0.41
RMSE (m gL^{-1})	1.40	1.95	1.70	2.33	2.27	2.42	2.32	2.27
Median MTT (d)	196	226	167	120	100	260	140	129
MTT, 5–95% (d)	119–298	109–357	90–263	73–183	69–161	189–334	90–232	95–211

[a] Median values and 5–95% percentiles from the behavioral subsets are shown. Also shown are the goodness of fit for the associated models expressed as Nash-Sutcliffe efficiency (NSE) and RMSE for data sets. NA means no GLUE uncertainty bounds are available as EM is a model with only one parameter.

conceals the actual relationships. If these cocorrelations are not too strong, more information about relationships can be extracted from data with MLR analysis. Using a stepwise MLR with backward selection method we found that the best fit model for log(MTT) consists of four predictor variables (Table 5): percentage responsive soil cover, log(drainage density), precipitation intensity and topographic wetness index (R^2_{adj} = 0.88, $p < 0.001$). Soil type and drainage density are first-order controls for small-scale catchments all over Scotland, explaining together more than 85% of the total variance in log(MTT). In contrast to the univariate analysis, precipitation intensity becomes significant ($p_{\mathrm{individual}}$ = 0.03) in combination with soil type and drainage density, making it the strongest climatic descriptor index though only accounting for 2% additional explained variance. The fourth descriptor variable in the MLR model is the topographic wetness index, increasing the explained variance by 1%. As expected from the univariate analysis, uncertainties in MTT estimates from short data sets equally influence the MLR model. Leaving the shortest two data sets out, MLR analysis produces a similar model of equal strength but with a higher relative importance of precipitation intensity at the expense of drainage density (not shown).

[28] All three multivariate models were tested for multicollinearity between the descriptor variables, which, if present, would make interpretation difficult. In all three cases, the collinearity diagnostics imply that no multicollinearity is present; that is, the determinant of the correlation matrices are >0.001, the variance inflation factors <10, and the condition numbers below 30.

[29] Cross validation revealed that the median absolute errors range from 32 days for the 4 predictor model to 66 days for the univariate model, when leaving one catchment out in turn (Table 6). To avoid the bias of higher errors for increasing MTTs, caused by the fact that the least squares fit was made on logarithmic MTT, we also used median absolute percentage error. Depending on the model, this error ranges from 0.26 to 0.37, indicating that a predicted MTT is likely to be within 26% to 37% of the "actual" MTT. Cross-validation errors are in a similar range when leaving one region out in turn (Table 6). The same applies for MLR models excluding the shortest data sets (not shown). The low cross-validation errors and comparable results for the two cross-validation approaches suggest that the presented MLR model is relatively robust and may potentially give good results for independent MTT prediction.

5. Discussion

[30] In this study we explored the utility of using an integrated model of catchment descriptors for predicting MTT in catchments across several geomorphic regions with contrasting pedologic and climatic characteristics. In comparison to univariate relationships, the integrated model derived from MLR analysis provides insight into the interactive nature of landscape controls. It was shown that a combination of percentage responsive soil cover, drainage density, precipitation intensity and topographic wetness index can explain almost 90% of the variance in MTT estimates across the very distinct regions investigated. Soil hydrology has been identified as a principal control on hydrological response in catchments in northern Europe

Table 4. Correlation Matrix of Data Set Length Adjusted Median MTT and Pedologic, Topographic, and Climatic Indices Using the Pearson Correlation Coefficient[a]

	log(MTT)	log(A)	log(P)	log(L/FG)	log(DD)	Percent Peat	Percent Freely Draining Soil	Percent Responsive Soil	log(PE/A)	log(A_{msc})	WS	L	S	UA	T	PI	TWI
log(MTT)	1.00	−0.36	**−0.50**	0.09	*−0.77*	−0.18	*0.89*	*−0.89*	0.29	0.11	0.18	0.40	0.35	**0.50**	−0.35	−0.37	−0.24
log(A)	−0.36	1.00	−0.10	0.29	0.34	*0.58*	−0.33	0.29	*−0.98*	−0.04	−0.16	**0.46**	−0.28	0.23	−0.23	−0.23	**0.51**
log(P)	**−0.50**	−0.10	1.00	*−0.66*	**0.56**	−0.41	**−0.51**	**0.45**	0.10	−0.32	0.08	**−0.50**	0.43	*−0.60*	0.07	*0.88*	**−0.54**
log(L/FG)	0.09	0.29	*−0.66*	1.00	−0.33	**0.52**	0.08	−0.02	−0.25	0.05	−0.16	**0.51**	*−0.74*	0.30	0.14	*−0.73*	*0.80*
log(DD)	*−0.77*	0.34	**0.56**	−0.33	1.00	0.04	*−0.72*	*0.63*	−0.32	−0.30	−0.07	−0.35	0.00	**−0.49**	0.19	**0.53**	−0.04
Percent peat	−0.18	*0.58*	**−0.41**	**0.52**	0.04	1.00	−0.25	0.29	**−0.54**	−0.11	−0.01	**0.49**	**−0.54**	0.36	−0.26	**−0.52**	*0.76*
Percent freely draining soil	*0.89*	−0.33	**−0.51**	0.08	*−0.72*	−0.25	1.00	*−0.99*	0.23	0.11	0.19	0.41	0.39	**0.51**	−0.37	−0.33	−0.24
Percent responsive soil	*−0.89*	0.29	0.45	−0.02	*0.63*	0.29	*−0.99*	1.00	−0.19	−0.06	−0.18	−0.39	**−0.46**	**−0.46**	0.37	0.25	0.30
log(PE/A)	0.29	*−0.98*	0.10	−0.25	−0.32	**−0.54**	0.23	−0.19	1.00	0.08	0.11	**−0.53**	0.19	−0.27	0.33	0.21	**−0.45**
log(A_{msc})	0.11	−0.04	−0.32	0.05	−0.30	−0.11	0.11	−0.06	0.08	1.00	−0.12	−0.24	−0.27	−0.11	**0.45**	−0.26	0.09
WS	0.18	−0.16	0.08	−0.16	−0.07	−0.01	0.19	−0.18	0.11	−0.12	1.00	0.06	0.29	0.05	−0.13	0.30	−0.29
L	0.40	**0.46**	**−0.50**	**0.51**	−0.35	**0.49**	0.41	−0.39	**−0.53**	−0.24	0.06	1.00	−0.10	*0.86*	*−0.62*	*−0.59*	0.45
S	0.35	−0.28	**0.43**	*−0.74*	0.00	**−0.54**	0.39	**−0.46**	0.19	−0.27	0.29	−0.10	1.00	0.01	−0.41	*0.60*	*−0.88*
UA	**0.50**	0.23	*−0.60*	0.30	**−0.49**	0.36	**0.51**	**−0.46**	−0.27	−0.11	0.05	*0.86*	0.01	1.00	*−0.61*	*−0.63*	0.33
T	−0.35	−0.23	0.07	0.14	0.19	−0.26	−0.37	0.37	0.33	**0.45**	−0.13	*−0.62*	−0.41	*−0.61*	1.00	0.18	0.02
PI	−0.37	−0.23	*0.88*	*−0.73*	**0.53**	**−0.52**	−0.33	0.25	0.21	−0.26	0.30	*−0.59*	*0.60*	*−0.63*	0.18	1.00	*−0.75*
TWI	−0.24	**0.51**	**−0.54**	***0.80***	−0.04	***0.76***	−0.24	0.30	**−0.45**	0.09	−0.29	**0.45**	***−0.88***	0.33	0.02	***−0.75***	1.00

[a]For bold values $p < 0.05$, and for italic values $p < 0.001$. Matrix shows area (A), mean annual precipitation (P), perimeter (PE), median subcatchment area (A_{msc}), wind speed (WS), median flow path length (L), mean slope (S), upslope area (UA), mean annual temperature (T), mean annual precipitation intensity (PI), and topographic wetness index (TWI).

with substantial coverage of peat soils [e.g., *Soulsby et al.*, 2006a, 2006b; *Laudon et al.*, 2007; *Tetzlaff et al.*, 2009a]. Percentage responsive soil cover reflects a conceptualization of flow path partitioning and subsoil permeability. While a higher proportion of responsive soils tends to increase the proportion of water routed rapidly through overland or shallow preferential flow pathways to the stream network, a higher proportion of more permeable, freely draining soils is more likely to cause delayed and damped stream response generated in deep-subsurface zones and routed through matrix flow pathways. Drainage density, although to a certain extent cocorrelated to the dominant soil types and precipitation, is mainly a measure of catchment structure that reflects the degree of connectivity between the catchment landscape and channel network [*Soulsby et al.*, 2006a]. Precipitation amounts and intensities on the other hand are essential for activation of fast responding flow paths and will have an overarching influence on catchment wetness, connectivity and resulting MTT [*Tetzlaff et al.*, 2007a; *Hrachowitz et al.*, 2009]. The subtle interplay between precipitation, soil hydrology and drainage density therefore seems to best capture the landscape controls that determine the characteristic MTT of water in these catchments.

[31] The fact that the same variables have been identified and reported in various studies in different montane regions suggests that they might be generally valid descriptors of catchment functioning in other regions that have climatic, geomorphic and pedological similarities. Certainly, it is now a priority to test the approach in other catchments in the Scottish Highlands where independent MTT estimates are available. However, care is always needed in making such extrapolations, especially when landscape characteristics begin to change markedly. For example, *McGuire et al.* [2005] report a dominating influence of the flow path length over flow path gradient ratio on MTT in catchments with steep slopes in the Pacific Northwest where, in spite of high rainfall amounts and intensities, highly permeable soils are characteristic and soil cover is a poor means of discriminating catchment differences in a region where topography is the dominant control. Moreover, *Tetzlaff et al.* [2009b] used intercatchment comparisons to show that different landscape controls can act differently in different regions. Hence in areas like the Cascades, MTT is negatively correlated with slope parameters as these mainly reflect hydraulic gradients. In contrast, positive correlations were found in Scottish catchments where flatter areas tend to have coverage of peat soils which generate overland flow and reduce TTs. Nevertheless, applying such multivariate approaches to understanding the interactive controls on MTTs in other catchments is likely to be instructive.

[32] One of the strengths of the analysis used here was that at most sites a long-term record of tracer fluctuations was invaluable for constraining the MTT estimates which helps identify landscape controls and facilitates intercatchment comparisons. As shown by *Hrachowitz et al.* [2009], MTT estimates from data sets of less than 4 years can have a very high uncertainty associated with them. In this study most topographic and climatic indices have shown improved correlations with MTT when leaving out the two data sets <4 years. Assuming that the suggested conceptualization of flow processes is correct, this further supports

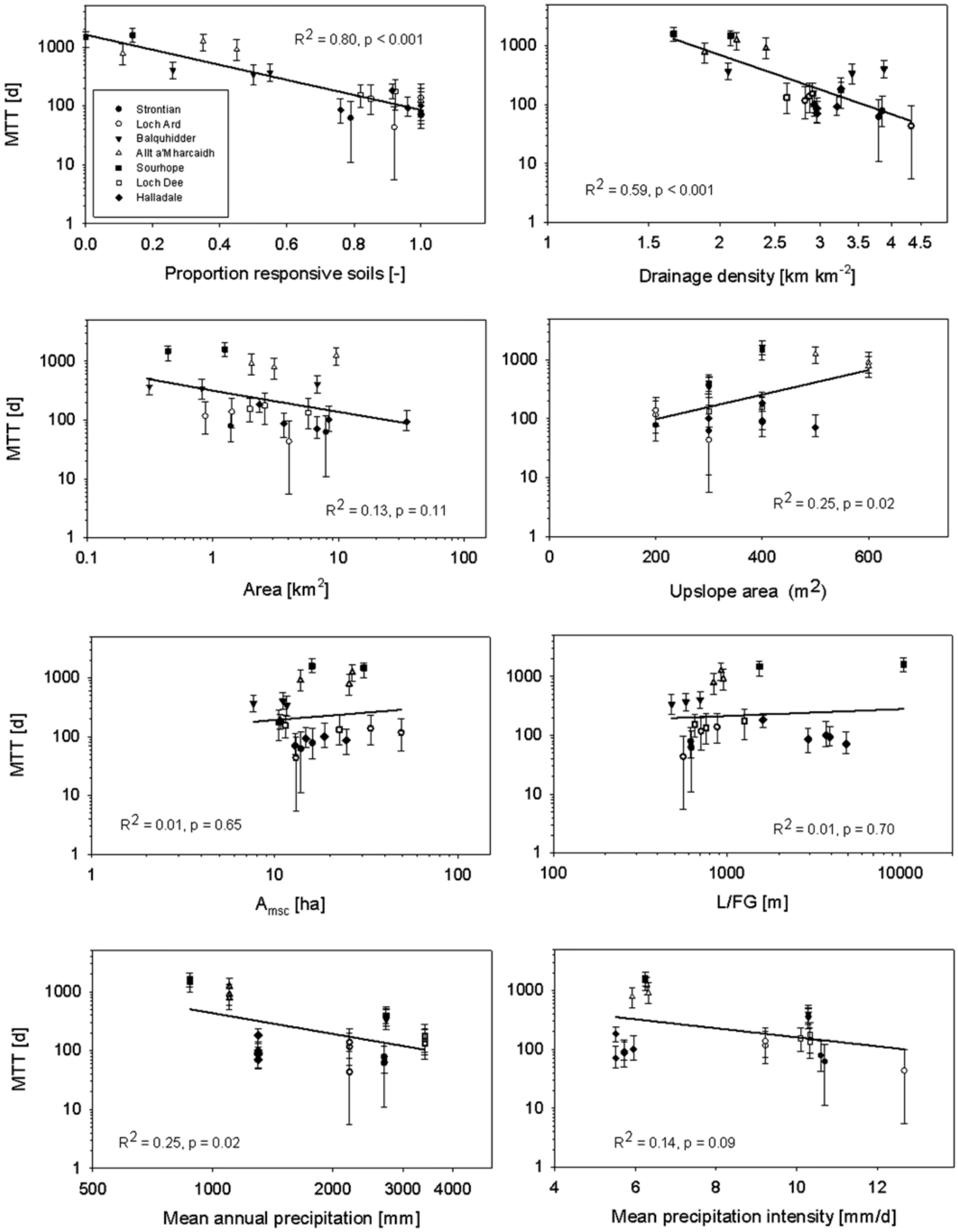

Figure 5. Plots of various selected pedologic, topographic, and climatic indices from all catchments against the data set length adjusted median MTTs including their GLUE bounds computed from the Gamma distribution model (A_{msc}, median subcatchment area; L/FG, flow path length over flow path gradient).

Table 5. Stepwise Multiple Linear Regression Results Including the Best Fit MLR Models and Collinearity Diagnostics[a]

R^2	R^2_{adj}	*p* value	Predictor Variable 1	Predictor Variable 2	Predictor Variable 3	Predictor Variable 4	Det	VIF	CN	MLR Model
0.80	0.78	<0.001	responsive soil cover				-	-	-	$\log(\mathrm{MTT}) = -1.28 \times (\text{responsive soil cover}) + 3.21$
0.87	0.85	<0.001	responsive soil cover	log(drainage density)			0.60	1.65	2.09	$\log(\mathrm{MTT}) = -0.97 \times (\text{responsive soil cover}) - 1.49 \times \log(\text{drainage density}) + 3.67.$
0.89	0.87	<0.001	responsive soil cover	log(drainage density)	precipitation intensity		0.43	1.65	2.58	$\log(\mathrm{MTT}) = -0.98 \times (\text{responsive soil cover}) - 1.41 \times \log(\text{drainage density}) - 0.01 \times (\text{precipitation intensity}) + 3.69$
0.91	0.88	<0.001	responsive soil cover	log(drainage density)	precipitation intensity	TWI	0.07	2.27	5.30	$\log(\mathrm{MTT}) = -0.72 \times (\text{responsive soil cover}) - 1.04 \times \log(\text{drainage density}) - 0.09 \times (\text{precipitation intensity}) - 0.22 \times (\mathrm{TWI}) + 5.37$

[a] Shown are the determinant (Det), the variance inflation factor (VIF), and the condition number (CN).

the hypothesis that short data sets produce poorly constrained MTT estimates because of the limited climatic variability during short observation periods.

[33] The GM and the TPLR models proved to be superior to the EM in this study. While this is mathematically not surprising, as the former two have more degrees of freedom using two and three parameters, respectively, compared to only one in the EM, they also allow a more realistic conceptualization of flow generating processes. *Kirchner et al.* [2001] demonstrated that the effectiveness of GM model can be theoretically related to the likely physical flow mechanisms producing advection-dispersion at the catchment scale, which are particularly effective at capturing the long-term memory of catchments, which causes the characteristic $1/f$ scaling in tracer outputs. The TPLR model, as applied by *Weiler et al.* [2003], on the other hand is a conceptually very appealing alternative. The separation of the flow system in two or more flow generating reservoirs is a simplistic concept widely used in rainfall-runoff models, though sometimes criticized [*Turner and Barnes*, 1998]. The TPLR may therefore be useful in certain cases to determine the MTTs of simplified flow processes at the catchment scale. This might potentially allow the application of predicted MTTs as a criterion for model parameterization and evaluation in rainfall-runoff models [e.g., *Vaché and McDonnell*, 2006]. However, given the poor identifiability of the TPLR model at higher MTT, it may be that such applications will be limited to catchments with short transit times.

[34] The modeling approaches used here may also have potential use in predicting MTT in ungauged basins in montane areas. Most catchments are ungauged particularly in the hydrologically sensitive headwaters of basins, and it is the integrated response of these that is responsible for generating flows, sustaining water supplies during dry periods and downstream aquatic ecosystems [*Soulsby and Tetzlaff*, 2008]. Montane headwaters in many areas are currently subject to marked environmental change as a result of land use change, developments or climatic change [*Viviroli and Weingartner*, 2003]. Often hydrological information on such catchments is severely limited, not least because monitoring networks in remote montane areas are poorly developed [*Lovett et al.*, 2007]. The simple tool for modeling MTT on a regional scale, using readily available topographic, pedologic and climatic data has considerable potential in identifying sensitive catchments. For example, catchments with short MTTs are likely to respond more rapidly to certain types of input, while longer MTTs may have delayed but equally significant response. The relatively low cross-validation errors suggest that the model is reasonably robust and can potentially be used to predict MTT in catchments all over Scotland and possibly in similar regions elsewhere. However, independent testing of the model's predictive capabilities is necessary to gain insight on its performance and the actual prediction errors to be expected. Given the fuzzy nature of MTTs and their relatively wide uncertainty bounds, there can be considerable uncertainty with MTT estimates that are obtained from both, lumped convolution integral and MLR methods. Therefore, the results should be seen as an order of magnitude estimates rather than actual values.

Table 6. Residuals and Cross-Validation Results for the Best MLR Models[a]

	Mean Absolute Residual[b] (d)	Median Absolute Cross-Validation Error[b] (d)		Median Absolute Percentage Cross-Validation Error (%)	
Number of Predictor Variables	All Stations	Leaving One Station Out	Leaving One Region Out	Leaving One Station Out	Leaving One Region Out
1	61 (9/88)	66 (10/95)	75 (27/111)	37	41
2	48 (20/90)	64 (25/108)	67 (27/125)	35	39
3	47 (20/89)	60 (27/117)	63 (31/155)	35	38
4	26 (7/71)	32 (9/83)	50 (29/131)	26	36

[a] One, two, three, and four predictor variables are shown as median absolute and median absolute percentage errors for leaving one catchment out in turn and leaving one region out in turn.
[b] The 25th and 75th percentiles are shown in parentheses.

[35] The dominant controls of MTT identified in this study tie in well with the T^3 concept suggested by *Buttle* [2006], which identifies three first-order controls, typology, topography and topology, on streamflow in any given basin. While percent responsive soil cover is an indicative of typology, drainage density can be associated with topology and TWI with topography. This might support the assumption that the suggested T^3 approach is a valid tool for catchment conceptualization: the Scottish catchments in this study are predominantly controlled by typology and topology, with only secondary influence of topography.

[36] A further need, however, is to assess the degree to which these results from small (<35 km^2) headwater catchments can be upscaled. This is important as many catchment processes are often only observed and understood at the hillslope or small experimental catchment scale ($<10^1$ km^2). In contrast, catchment management decisions are taken at larger scales ($>10^2$ km^2). A key question therefore is whether the integrated downstream response of a stream is the sum of the responses in the headwater catchments or if the processes which control the MTT change as catchment size increases, and if so, whether thresholds where new landscape control emerge can be identified. *Shaman et al.* [2004] and *Soulsby et al.* [2006b] have shown that the response of larger catchments is the combination of headwater catchment responses while *Uchida et al.* [2005] additionally showed how the hydrology of a small catchment integrates and attenuates hillslope responses. However, these studies have only upscaled as far as $\sim$200 km^2 and testing this modeling approach on larger (i.e., 10^3 km^2) Scottish catchments is a further research priority.

6. Conclusions

[37] In this study MTTs for 20 catchments in seven contrasting regions of Scotland were obtained from long-term tracer data sets (up to 17 years). It was shown that pedologic, topographic and climatic catchment characteristics can act as proxies to predict MTT over several geomorphic and climatic regions in the Scottish uplands and potentially in similar regions. This may be of significance in the light of prediction in ungauged basins, especially as the presented model may facilitate MTT estimation in areas without tracer information and preliminary conceptualization of catchment processes.

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References

Bain, D. C., A. J. Midwood, and J. D. Miller (1998), Strontium isotope ratios in streams and the effect of flow rate in relation to weathering in catchments, *Catena*, *32*, 143–151, doi:10.1016/S0341-8162(97)00055-6.

Bain, D. C., M. J. Roe, D. M. L. Duthie, and C. M. Thomson (2001), The influence of mineralogy on weathering rates and processes in an acid-sensitive granitic catchment, *Appl. Geochem.*, *16*, 931–937, doi:10.1016/S0883-2927(00)00071-8.

Belsey, D. A. (1991), A guide to using the collinearity diagnostics, *Comput. Econ.*, *4*(1), 33–50.

Beven, K. J., and A. M. Binley (1992), The future of distributed models: Model calibration and uncertainty prediction, *Hydrol. Processes*, *6*, 279–298, doi:10.1002/hyp.3360060305.

Beven, K. J., and M. J. Kirkby (1979), A physically based, variable contributing area model of basin hydrology, *Hydrol. Sci. Bull.*, *24*, 43–69.

Buttle, J. (2006), Mapping first-order controls on streamflow from drainage basins: The T^3 template, *Hydrol. Processes*, *20*, 3415–3422, doi:10.1002/hyp.6519.

Cardenas, M. B. (2007), Potential contribution of topography-driven regional groundwater flow to fractal stream chemistry: Residence time distribution analysis of Tóth flow, *Geophys. Res. Lett.*, *34*, L05403, doi:10.1029/2006GL029126.

DeWalle, D. R., P. J. Edwards, B. R. Swistock, R. Aravena, and R. J. Drimmie (1997), Seasonal isotope hydrology of three Appalachian forest catchments, *Hydrol. Processes*, *11*, 1895–1906, doi:10.1002/(SICI)1099-1085(199712)11:15<1895::AID-HYP538>3.0.CO;2-#.

Dunn, S. M., and J. M. Bacon (2008), Assessing the value of Cl− and δO^{18} data in modeling the hydrological behaviour of a small upland catchment in north-east Scotland, *Hydrol. Res*, *39*, 337–358, doi:10.2166/nh.2008.134.

Dunn, S. M., J. R. Bacon, C. Soulsby, D. Tetzlaff, M. Stutter, S. Waldron, and I. A. Malcolm (2008), Interpretation of homogeneity in isotopic signatures of stream water in a nested sub-catchment system, *Hydrol. Processes*, *22*, 2389–2393, doi:10.1002/hyp.7070.

Efron, B., and G. Gong (1983), A leisurely look at the bootstrap, the jackknife and cross-validation, *Am. Stat.*, *37*, 36–48, doi:10.2307/2685844.

Etcheverry, D., and P. Perrochet (2000), Direct simulation of groundwater transit-time distributions using the reservoir theory, *Hydrogeol. J.*, *8*(2), 200–208.

Feng, X., J. W. Kirchner, and C. Neal (2004), Measuring catchment-scale chemical retardation using spectral analysis of reactive and passive chemical tracer time series, *J. Hydrol.*, *292*, 296–307, doi:10.1016/j.jhydrol.2004.01.012.

Freer, J., B. Ambroise, and K. J. Beven (1996), Bayesian estimation of uncertainty in runoff prediction and the value of data: An application of the GLUE approach, *Water Resour. Res.*, *32*, 2161–2173.

Harriman, R., and B. R. S. Morrison (1982), Ecology of streams draining forested and non–forested catchments in an area of central Scotland subject to acid precipitation, *Hydrobiologia*, *88*, 251–263, doi:10.1007/BF00008505.

Harriman, R., B. R. S. Morrison, L. A. Caines, P. Collen, and A. W. Watt (1987), Long-term changes in fish populations of acid streams and lochs in Galloway south west Scotland, *Water Air Soil Pollut.*, *32*, 89–122, doi:10.1007/BF00227686.

Harriman, R., A. W. Watt, A. E. G. Christie, P. Collen, D. W. Moore, A. G. McCartney, E. M. Taylor, and J. Watson (2001), Interpretation of trends in acidic deposition and surface water chemistry in Scotland during the past three decades, *Hydrol. Earth Syst. Sci.*, *5*, 407–420.

Hrachowitz, M., C. Soulsby, D. Tetzlaff, J. J. C. Dawson, S. M. Dunn, and I. A. Malcolm (2009), Using long-term data sets to understand transit times in contrasting headwater catchments, *J. Hydrol.*, *367*, 237–248.

Jakeman, A. J., and G. M. Hornberger (1993), How much complexity is warranted in a rainfall-runoff model?, *Water Resour. Res.*, *29*, 2637–2649, doi:10.1029/93WR00877.

Jensen, S. K., and J. O. Domingue (1988), Extracting topographic structure from digital elevation data for geographic information system analysis, *Photogramm. Eng. Remote Sens.*, *54*(11), 1593–1600.

Johnson, R. C. (1991), Effects of upland afforestation on water resources, *Rep. 116*, Inst. of Hydrol., Wallingford, U. K.

Kirchner, J. W., R. P. Hooper, C. Kendall, C. Neal, and G. Leavesley (1996), Testing and validating environmental models, *Sci. Total Environ.*, *183, 33–47, doi:10.1016/0048-9697(95)04971-1.*

Kirchner, J. W., X. Feng, and C. Neal (2000), Fractal stream chemistry and its implications for contaminant transport in catchments, *Nature*, *403*, 524–527, doi:10.1038/35000537.

Kirchner, J. W., X. Feng, and C. Neal (2001), Catchment scale advection and dispersion as e mechanism for fractal scaling in stream tracer concentrations, *J. Hydrol.*, *254*, 82–101, doi:10.1016/S0022-1694(01)00487-5.

Laudon, H., V. Sjöblom, I. Buffam, J. Seibert, and M. Mörth (2007), The role of catchment scale and landscape characteristics for runoff generation of boreal streams, *J. Hydrol.*, *344*, 198–209, doi:10.1016/j.jhydrol.2007.07.010.

Lovett, G. M., D. A. Burns, C. T. Driscoll, J. C. Jenkins, M. J. Mitchell, L. Rustad, J. B. Shanley, G. E. Likens, and R. Haeuber (2007), Who needs environmental monitoring?, *Front. Ecol. Environ*, *5*, 253–260, doi:10.1890/1540-9295(2007)5[253:WNEM]2.0.CO;2.

Małoszewski, P., and A. Zuber (1982), Determining the turnover time of groundwater systems with the aid of environmental tracers. 1.Models and their applicability, *J. Hydrol.*, *57*, 207–231, doi:10.1016/0022-1694(82)90147-0.

Małoszewski, P., W. Rauert, W. Stichler, and A. Herrmann (1983), Application of flow models in an alpine catchment area using tritium and deuterium data, *J. Hydrol.*, *66*, 319–330, doi:10.1016/0022-1694(83)90193-2.

McDonnell, J. J., et al. (2007), Moving beyond heterogeneity and process complexity: A new vision for watershed hydrology, *Water Resour. Res.*, *43*, W07301, doi:10.1029/2006WR005467.

McGlynn, B., J. J. McDonnell, M. Stewart, and J. Seibert (2003), On the relationships between catchment scale and streamwater mean residence time, *Hydrol. Processes*, *17*, 175–181, doi:10.1002/hyp.5085.

McGuire, K. J., and J. J. McDonnell (2006), A review and evaluation of catchment transit time modelling, *J. Hydrol.*, *330*, 543–563, doi:10.1016/j.jhydrol.2006.04.020.

McGuire, K. J., D. R. DeWalle, and W. J. Gburek (2002), Evaluation of mean residence time in subsurface waters using oxygen-18 fluctuations during drought conditions in the mid-Appalachians, *J. Hydrol.*, *261*, 132–149, doi:10.1016/S0022-1694(02)00006-9.

McGuire, K. J., J. J. McDonnell, M. Weiler, C. Kendall, B. L. McGlynn, J. M. Welker, and J. Seibert (2005), The role of topography on catchment-scale water residence time, *Water Resour. Res.*, *41*, W05002, doi:10.1029/2004WR003657.

McGuire, K. J., M. Weiler, and J. J. McDonnell (2007), Integrating tracer experiments with modelling to assess runoff processes and water transit times, *Adv. Water Resour.*, *30*, 824–837, doi:10.1016/j.advwatres.2006.07.004.

Monteith, D. T., and C. D. Evans (2005), The United Kingdom Acid Waters Monitoring Network: A review of the first 15 years and introduction to the special issue, *Environ. Pollut.*, *137*, 3–13, doi:10.1016/j.envpol.2004.12.027.

Montgomery, D. R., and W. E. Dietrich (1988), Where do channels begin?, *Nature*, *336*, 232–234, doi:10.1038/336232a0.

Mueller, T. G., and F. J. Pierce (2003), Soil carbon maps: Enhancing spatial estimates with simple terrain attributes at multiple scales, *Soil Sci. Soc. Am. J.*, *67*, 258–267.

Nash, J. E., and J. V. Sutcliffe (1970), River flow forecasting through conceptual models part I—A discussion of principles, *J. Hydrol.*, *10*, 282–290, doi:10.1016/0022-1694(70)90255-6.

Neal, C., and J. Kirchner (2000), Sodium and chloride levels in rainfall, mist, streamwater and groundwater at the Plynlimon catchments, mid-Wales: Inferences on hydrological and chemical controls, *Hydrol. Earth Syst. Sci.*, *4*, 295–310.

Neal, C., and P. T. W. Rosier (1990), Chemical studies of chloride and stable oxygen isotopes in 2 conifer afforested and moorland sites in the British uplands, *J. Hydrol.*, *115*, 269–283, doi:10.1016/0022-1694(90)90209-G.

Neal, C., N. Christopherson, R. Neale, C. J. Smith, P. G. Whitehead, and B. Reynolds (1988), Chloride precipitation and streamwater for the upland catchment of River Severn, Mid-Wales: Some consequences for hydrochemical models, *Hydrol. Processes*, *2*, 155–165, doi:10.1002/hyp.3360020206.

Nisbet, T. R., D. Fowler, and R. I. Smith (1995), An investigation of the impact of afforestation on streamwater chemistry in the Loch Dee catchment, SW Scotland, *Environ. Pollut.*, *90*, 111–120, doi:10.1016/0269-7491(94)00081-N.

Robins, N. (1990), *Hydrogeology of Scotland*, Her Majesty's Stationery Off., London.

Rodgers, P. J., C. Soulsby, and S. Waldron (2005a), Using stable isotopes as diagnostic tools in upscaling flow path understanding in mesoscale catchments in the Scottish Highlands, *Hydrol. Processes*, *19*, 2291–2307, doi:10.1002/hyp.5677.

Rodgers, P. J., C. Soulsby, S. Waldron, and D. Tetzlaff (2005b), Using stable isotope tracers to assess hydrological flow paths, residence times and landscape influences in a nested mesoscale catchment, *Hydrol. Earth Syst. Sci.*, *9*, 139–155.

Rodhe, A., L. Nyberg, and K. Bishop (1996), Transit times for water in a small till catchment from a step shift in the oxygen 18 content of the water input, *Water Resour. Res.*, *32*, 3497–3511.

Shaman, J., M. Stieglitz, and D. Burns (2004), Are big basins just the sum of small catchments?, *Hydrol. Processes*, *18*, 3195–3206, doi:10.1002/hyp.5739.

Shao, J. (1993), Linear model selection by cross-validation, *J. Am. Stat. Assoc.*, *88*, 486–494, doi:10.2307/2290328.

Shaw, S. B., A. A. Harpold, J. C. Taylor, and T. M. Walter (2008), Investigating a high resolution, stream chloride time series from the Biscuit Brook catchment, Catskills, NY, *J. Hydrol.*, *348*, 245–256, doi:10.1016/j.jhydrol.2007.10.009.

Soulsby, C., and D. Tetzlaff (2008), Towards simple approaches for mean residence time estimation in ungauged basins using tracers and soil distributions, *J. Hydrol.*, *363*, 60–74, doi:10.1016/j.jhydrol.2008.10.001.

Soulsby, C., M. Chen, R. C. Ferrier, A. Jenkins, and R. Harriman (1998), Hydrogeochemistry of shallow groundwater in a Scottish catchment, *Hydrol. Processes*, *12*, 1111–1127, doi:10.1002/(SICI)1099-1085(19980615)12:7<1111::AID-HYP633>3.0.CO;2-2.

Soulsby, C., R. Malcolm, R. Helliwell, and R. C. Ferrier (1999), Hydrogeochemistry of montane springs and their influence on streams in the Cairngorm mountains, Scotland, *Hydrol. Earth Syst. Sci.*, *3*, 409–419.

Soulsby, C., R. Malcolm, R. C. Helliwell, R. C. Ferrier, and A. Jenkins (2000), Isotope hydrology of the Allt a' Mharcaidh catchment, Cairngorm mountains, Scotland: Implications for hydrological pathways and water residence times, *Hydrol. Processes*, *14*, 747–762, doi:10.1002/(SICI)1099-1085(200003)14:4<747::AID-HYP970>3.0.CO;2-0.

Soulsby, C., P. Rodgers, R. Smart, J. Dawson, and S. M. Dunn (2003), A tracer-based assessment of hydrological pathways at different spatial scales in a mesoscale watershed in NE Scotland, *Hydrol. Processes*, *17*, 759–777, doi:10.1002/hyp.1163.

Soulsby, C., D. Tetzlaff, S. M. Dunn, and S. Waldron (2006a), Scaling up and out in runoff process understanding—Insights from nested experimental catchment studies, *Hydrol. Processes*, *20*, 2461–2465, doi:10.1002/hyp.6338.

Soulsby, C., D. Tetzlaff, P. Rodgers, S. M. Dunn, and S. Waldron (2006b), Runoff processes, stream water residence times and controlling landscape characteristics in a mesoscale catchment: An initial evaluation, *J. Hydrol.*, *325*, 197–221, doi:10.1016/j.jhydrol.2005.10.024.

Soulsby, C., C. Neal, H. Laudon, D. A. Burns, P. Merot, M. Bonell, S. M. Dunn, and D. Tetzlaff (2008), Catchment data for process conceptualization: Simply not enough?, *Hydrol. Processes*, *22*, 2057–2061, doi:10.1002/hyp.7068.

Stewart, M. K., and J. J. McDonnell (1991), Modeling base flow soil water residence times from deuterium concentrations, *Water Resour. Res.*, *27*, 2681–2693, doi:10.1029/91WR01569.

Stone, M. (1974), Cross-validatory choice and assessment of statistical predictions, *J. R. Stat. Soc., Ser. B*, *36*, 111–147.

Tarboton, D. G., R. L. Bras, and I. Rodriguez-Iturbe (1991), On the extraction of channel networks from digital elevation data, *Hydrol. Processes*, *5*, 81–100, doi:10.1002/hyp.3360050107.

Tetzlaff, D., I. A. Malcolm, and C. Soulsby (2007a), Influence of forestry, environmental change and climatic variability on the hydrology, hydrochemistry and residence times of upland catchments, *J. Hydrol.*, *346*, 93–111, doi:10.1016/j.jhydrol.2007.08.016.

Tetzlaff, D., C. Soulsby, S. Waldron, I. A. Malcolm, P. J. Bacon, S. M. Dunn, and A. Lilly (2007b), Conceptualisation of runoff processes using GIS and tracers in a nested mesoscale catchment, *Hydrol. Processes*, *21*, 1289–1307, doi:10.1002/hyp.6309.

Tetzlaff, D., J. J. McDonnell, S. Uhlenbrook, K. J. McGuire, P. W. Bogaart, F. Naef, A. J. Baird, S. M. Dunn, and C. Soulsby (2008), Conceptualising catchment processes: Simply too complex?, *Hydrol. Processes*, *22*, 1727–1730, doi:10.1002/hyp.7069.

Tetzlaff, D., J. Seibert, and C. Soulsby (2009a), Inter-catchment comparison to assess the influence of topography and soils on catchment transit times in a geomorphic province, *Hydrol. Processes*, in press.

Tetzlaff, D., J. Seibert, K. J. McGuire, H. Laudon, D. A. Burns, S. M. Dunn, and C. Soulsby (2009b), How does landscape structure influence catchment transit time across different geomorphic provinces?, *Hydrol. Processes*, *23*, 945–953, doi:10.1002/hyp.7240.

Turner, J. V., and C. J. Barnes (1998), Modeling of isotope and hydrogeochemical responses in catchment hydrology, in *Isotope Tracers in Catchment Hydrology*, edited by C. Kendall and J. J. McDonnell, pp. 723–760, Elsevier Sci., Amsterdam.

Uchida, T., Y. Asano, Y. Onda, and S. Miyata (2005), Are headwaters just the sum of hillslopes?, *Hydrol. Processes*, *19*, 3251–3261, doi:10.1002/hyp.6004.

Uhlenbrook, S., M. Frey, C. Leibundgut, and P. Maloszewski (2002), Hydrograph separations in a mesoscale mountainous basin at event and seasonal timescales, *Water Resour. Res.*, *38*(6), 1096, doi:10.1029/2001WR000938.

Vaché, K. B., and J. J. McDonnell (2006), A process-based rejectionist framework for evaluating catchment runoff model structure, *Water Resour. Res.*, *42*, W02409, doi:10.1029/2005WR004247.

Vitvar, T., and W. Balderer (1997), Estimation of mean water residence times and runoff generation by ^{18}O measurements in a pre-Alpine catchment (Rietholzbach, eastern Switzerland), *Appl. Geochem.*, *12*, 787–796, doi:10.1016/S0883-2927(97)00045-0.

Viville, D., B. Ladouche, and T. Bariac (2006), Isotope hydrological study of mean transit time in the granitic Strengbach catchment (Vosges massif, France): Application of the FlowPC model with modified input function, *Hydrol. Processes*, *20*, 1737–1751, doi:10.1002/hyp.5950.

Viviroli, D., and R. Weingartner (2003), The hydrological significance of mountains: From regional to global scale, *Hydrol. Earth Syst. Sci.*, *8*, 1016–1029.

Wagener, T., M. Sivapalan, P. Troch, and R. Woods (2007), Catchment classification and hydrologic similarity, *Geogr. Compass*, *1*(4), 901–931, doi:10.1111/j.1749-8198.2007.00039.x.

Weiler, M., B. L. McGlynn, K. J. McGuire, and J. J. McDonnell (2003), How does rainfall become runoff? A combined tracer and runoff transfer function approach, *Water Resour. Res.*, *39*(11), 1315, doi:10.1029/2003WR002331.

Williams, T. M. (1991), A sedimentary record of the deposition of heavy metals and magnetic oxides in the Loch Dee basin, Galloway, Scotland, since c. AD 1500, *Holocene*, *1*, 142–150, doi:10.1177/095968369100100206.

Wilson, M. J., D. C. Bain, and D. M. L. Duthie (1984), The soil clays of Great Britain: II. Scotland, *Clay Miner.*, *19*, 709–735, doi:10.1180/claymin.1984.019.5.03.

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