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Using tracers and soil distributions, we work towards straightforward methods for mean residence time estimation in ungauged basins.

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Abstract:

Summary Recent studies have demonstrated that the mean residence time (MRT) of water in catchments serves as a helpful indicator of hydrological function and a useful tool for comparing different catchments. This study develops simplified methods for predicting MRTs for 22 montane catchments with sizes ranging from 1 km2 to 293 km2, using the conservative tracer chloride and digital soil mapping. The Scottish Cairngorm Mountains' sub-catchments of the River Dee served as the study's base of operations. Stable isotopes were previously utilised in this geomorphic province to calculate catchment MRTs, which were found to be predicted from catchment soil properties. These linkages served as the foundation for the creation of transferrable strategies for two streamlined techniques of MRT estimation. Originally, basic input-output connections based on the ratio of the normalised standard deviation of Cl in streamwater to that of precipitation were employed as an MRT surrogate (MRTCl). Second, using catchment soil maps produced from the UK hydrology of soil type (HOST) digital data set, MRTs were projected from the percentage coverage of hydrologically responsive soils (MRTsoil). The two methods were demonstrated to produce results that were largely equal, however in five of the study catchments, estimates produced from Cl data compared better with estimates independently derived using isotopic MRTd18 O data. The ability of free-draining soils to dampen the tracer response or the connectedness of responsive soils with channel networks were also improved predictions when only riparian soil cover was taken into account. Since the computed MRTs and mean catchment slope have a substantial correlation, topographic maps alone may be useful in projecting residence periods in ungauged basins in some geographic locations.

Introduction

There is growing awareness that methodologies commonly used for characterising catchments are often very simplistic (Tetzlaff et al., 2008a). Consequently, there have been calls for classification schemes that facilitate inter-catchment comparisons that are based on metrics reflecting behavioural traits (McDonnell and Woods, 2004; Wagener et al., 2007). Reliance on measuring inputs and outputs, together with technological constraints in monitoring at the appropriate spatial and temporal scales, has dictated that limited progress has been made in conceptualising and characterising the stores and fluxes of water in catchments; particularly in the subsurface (McDonnell et al., 2007). These limitations mean that there are still major problems associated with understanding the hydrological functioning of even well-monitored catchments (Soulsby et al., 2008). This, in turn, constrains transferable predictive tools for use in ungauged basins where many applied issues in hydrology emerge (Kirchner, 2007). These problems are particularly acute in montane catchments where data collection is difficult (Winter, 2007; Soulsby et al., 2007; Tetzlaff et al., 2008b). Despite such knowledge gaps, in many parts of the world, montane areas are important runoff source areas – generating floods, sustaining base flows and regulating the hydrological regime that maintains freshwater ecosystems (Messerli et al., 2004; Bales et al., 2006; Tetzlaff et al., 2007a).

Recent years have seen the development of methods that characterise aspects of hydrological functioning of montane catchments: thus, enhancing understanding; having utility across spatial and temporal scales; and aiding management decisions (Viviroli and Weingartner, 2004; Lovett et al., 2007). The concept of mean residence time (MRT) or mean transit time (MTT) has been identified as a valuable hydrological descriptor that integrates aspects of hydrological routing and mixing processes across scales from tracer data (McGuire and McDonnell, 2006). This uses the variation in input-output relationships for natural tracers, such as water isotopes (^{18}O and ^{2}H) or Cl, along with residence time models (e.g. Kirchner et al., 2001) to identify the likely residence time distributions of water within a catchment and estimate the MRT of water molecules between the timing of precipitation and streamflow outputs (see Fig. 1 in McGuire and McDonnell, 2006).

Inter-catchment comparisons have identified some of the important controls on MRT in different geographical regions. The importance of geology has long been recognised (Maloszewski et al., 1992; Vitvar and Balderer, 1998; Viville et al., 2006), whilst the role of topography and catchment structure has been demonstrated in recent work in steep terrain in New Zealand and the Cascades in the western USA (McGlynn et al., 2003; McGuire et al., 2005). In glaciated mountains, complex drift distributions may over-ride topographic and geological differences with the result that soil hydrology can also be a useful predictor of MRT (Rodgers et al., 2005a,b; Soulsby et al., 2006a,b; Tetzlaff et al., 2007b). In other areas where the topography is more subdued and soils are relatively uniform, the topology of landscape features adjacent to the River channel network are more important (Buttle, 2006). Overarching all of these, climatic differences and variability may have an important influence on MRT estimates (Tetzlaff et al., 2007c). In most situations these controlling factors interact and other authors have looked at the generic macroscale characteristics of residence time distributions. For example, Kirchner et al. (2000, 2001) have shown how catchment-scale advection–dispersion processes result in partitioning of flow paths between more dynamic, rapidly responding ones and longer-term turnover within the catchment system giving a wide range of residence time distributions.

Increasing recognition of the importance and influence that soil coverage can have on catchment hydrology in certain geographical settings has resulted in numerous recent initiatives that have sought to develop approaches to utilise soil information in application to problems in ungauged basins. These include developing approaches to soil classification and mapping that are hydrologically meaningful (e.g. Scherrer and Naef, 2003) and can be used in a wide range of applications from flood prediction (Schmocker-Fackel et al., 2007), water quality forecasting (Wade et al., 2001a) and low flow assessment (Schneider et al., 2007). In the UK, the Hydrology of Soil Types (HOST) system was developed over a decade ago as a digital data set based on a national hydrological classification scheme (Boorman et al., 1995; www.macaulay.ac.uk/host/). In upland areas, the HOST system has been shown to be a useful means of grouping soils on the basis of hydrological flow paths. Thus, soils that can generate overland flow (such as peats and gleys) and shallow subsurface storm flow (such as regosols) can be classed as being ''responsive'' in that they rapidly generate storm runoff. Conversely, more ''freely-draining'' soils (such as podzols and alluvium) which facilitate groundwater recharge or generate deeper subsurface can be hypothesised as the main sources of baseflow generation (e.g. Tetzlaff et al., 2007b; Tetzlaff and Soulsby, 2008). This in turn has allowed catchment HOST maps to be used as apparently good predictors of MRTs estimated from tracer data, with MRT's decreasing with increasing coverage of responsive soils (Soulsby et al., 2006b).

In this paper we use these soil-based relationships – for the geomorphic province of the Cairngorms Mountains in the Scottish Highlands – to develop transferable approaches to estimating MRTs in other catchments, including ungauged ones. Although isotope data have provided a useful means of estimating residence times in this region (e.g. Soulsby et al., 1999, 2000, 2006a; Rodgers et al., 2005a,b; Tetzlaff et al., 2007b; Tyler et al., 2007); such data sets are scare and expensive to generate. In contrast, chloride – an equally useful conservative tracer in unpolluted maritime environments – is much more frequently measured in precipitation and runoff as part of numerous monitoring schemes such as the UK Environmental Change Network (ECN) and the UK Acid Waters Monitoring Network (UKAWMN) (e.g. Miller et al., 2001; Evans et al., 2001; Hrachowitz et al., submitted for publication). Such data sets provide a resource that can be used to test – much more generally – hypotheses regarding the role of soils and other landscape controls in influencing MRTs and aid the development of approaches to be used in ungauged basins. Here, we use data from a 12 month, fortnightly sampling programme in a large 1849 km^2 catchment, which generated 59 records of Cl in streamwaters. A subset of 22 of these (at sites free from anthropogenic sources of Cl) was used in this paper to test the following three hypotheses: (1) that fortnightly variation of Cl in precipitation and streamflow can be used to calibrate estimates of catchment MRTs using simple, transferable techniques; (2) that catchment soil cover can be used as a means of predicting MRTs; which can be improved by examining soil distributions in terms of their proximity to the stream network; and (3) that simple topographic indices are also correlated with soil distributions in this region and may therefore also be useful in MRT estimates.

Study area

The Dee drains a total area of ca. 2000 km^2 and is an important resource in terms of supplying drinking water for over 300,000 people, biodiversity conservation and has an economically important Atlantic salmon fishery. The catchment is described in detail elsewhere (e.g. Smart et al., 1998); a brief summary follows. The headwaters are at ca. 1220 m.a.s.l in the Cairngorm mountains with extensive parts (ca. 60%) of the catchment being above 300 m in altitude (Fig. 1a). In the east, the topography is much more lowland in character. The Dee flows east from the Cairngorm headwaters into the North Sea at a distance of ca. 140 km downstream at the city of Aberdeen.

The general catchment characteristics of the sampling sites used in this study (Fig. 1b) are shown in Table 1. Annual precipitation ranges from 800 mm (in the east) to ca. 1500 mm (in the west). The upland region of the Dee can be classified as sub-arctic and snow can be an important component of the water balance (Dunn et al., 2001). Annual flow at Park, the lowest gauging station at the Dee at 1845 km^2, is ca. 806 mm (Scottish Environment Protection Agency, SEPA). Specific high flows (Q_{10}) and low flows (Q_{95}) at Mar Lodge (ID = 4, Table 1), the gauging station located furthest west within the Dee catchment, are 88 $l\ s^{-1}\ km^{-2}$ and 7 $l\ s^{-1}\ km^{-2}$, respectively. Specific discharges decline downstream (Tetzlaff and Soulsby, 2008).

The geology is characterised by a dominance of Precambrian metamorphic and igneous rocks. Granite batholiths dominate the areas of higher relief and the surrounding rocks were mainly sandstones that have been metamorphosed into siliceous schists, though some schists include calcareous strata (Smart et al., 2001). Despite these units being usually considered as aquitards with very low primary porosity, fractures in the upper 10 m or so of the granites are important groundwater flow paths (Soulsby et al., 1998). Although fractures in the schists also occur, the intensity is usually lower. The solid geology is overlain by a range of drift deposits reflecting the complex glacial history of the Cairngorms. Alluvium and fluvio-glacial deposits fill the bottom of many main river valleys, till covers the low slopes of many valley sides and a range of periglacial deposits occur at altitude above the glacial trimline (Gordon and Wignall, 2006). Many of the drifts have significant water storage and are important sources of groundwater.

Soils in the catchment have been mapped and grouped according to the UK's Hydrology of Soil Types (HOST) (www.macaulay.ac.uk/host/) digital data set (Fig. 2). Soil cover is dominated by freely-draining humus iron podzols in the eastern parts of the Dee catchment (HOST class 17) whilst towards the west, more hydrologically responsive soils, which can generate saturation overland flow and/or shallow subsurface storm flow, dominate. These mainly comprise peaty gleys (HOST class 15) and blanket peat soils (HOST class 29) where low permeability till forms the main parent material. At altitudes over 800 m, thin alpine soils (HOST classes 19 and 22) are also responsive to precipitation and snowmelt generating shallow subsurface storm flow or overland flow if frozen. Larger valley bottoms have alluvial soils (HOST classes 5 and 7) which are free-draining, facilitating groundwater recharge.

Reflecting the geology, soils coinciding with granites or quartzites are mainly acidic with pH < 4.0 in near surface horizons and increasing to 5.0 in deeper horizons. The low fertility soils in the upland parts of the catchment are dominated by semi-natural landcover, such as montane and alpine heath type vegetation, blanket bog and heather moorland (*Calluna vulgaris*). The lower, eastern parts of the catchment contrast, being characterised by more intensively managed agricultural land. Here, the agriculture is mainly mixed grassland with some arable land. The steeper valley sides of the mid-catchment include significant areas of forestry (Wade et al., 2001b).

Data and methodology

A total of 59 sites in the Dee catchment were sampled (by instantaneous grab samples) at fortnightly intervals between June 1996 and June 1997. Chloride was included amongst the suite of determinants analysed and was measured using liquid chromatography (Dionex) (Smart et al., 1998). Inspection of the catchment characteristics of the 59 sites revealed that 37 were unsuitable for investigating in terms of input-output relationships due to being contaminated by Cl from drainage of road salts (determined by being downstream of major roads), agricultural fertilizers (if agricultural land comprised >10% of the catchment area) and/or sewage discharges (if downstream from sewage treatment works) (Smart et al., 2001). Thus, 22 sites were included in the analysis for this paper (Fig. 1b). Bulk precipitation (fortnightly) was collected in integrated samples at four points during the study year at Mar Lodge, Lochnagar, Banchory and Glen Dye (Fig. 1b).

The 22 sites that were investigated grouped into four geographical regions in the Dee catchment: (1) the Cairngorm Headwaters, (2) Upper Deeside, (3) sites in Mid-Deeside and (4) catchments in the Feugh tributary in Lower Deeside (Table 1). The catchments ranged from 1 to 293 km^2 in area and were generally steep, with median slopes above 9° in most cases. Soil cover varied (Fig. 2 and Table 2). In general, the Cairngorm Headwater sub-catchments were relatively steep and had a high proportion of montane soils such as alpine podzols (HOST class 17) and more responsive rankers (HOST classes 19, 22 and 27). In the Upper and Mid-Deeside groups, more freely-draining podzol soils (HOST classes 15 and 17) tended to be more prevalent. The Lower Deeside sites in the Feugh catchments, were notable for having a high coverage of peat soils (HOST class 29).

Time series analysis of chloride in rainfall and runoff in upland catchments has been widely used to explore residence times and residence time distributions (Kirchner

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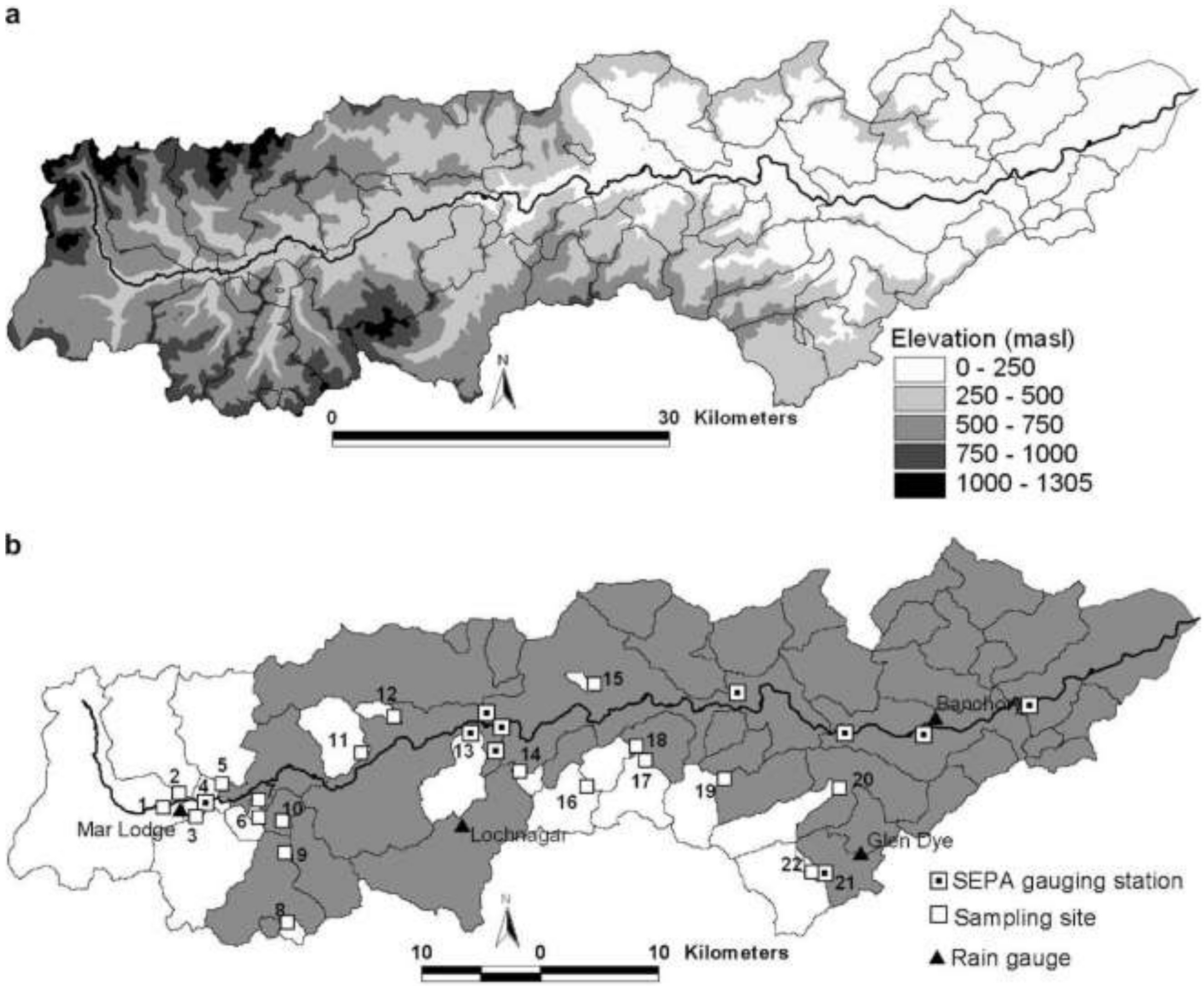

Figure 1 Catchment characteristics of the Dee catchment: (a) topography and (b) catchments investigated and sampling network.

et al., 2001; Page et al., 2007; Tetzlaff et al., 2007c). This usually involves using tools such as convolution integral methods in various residence time models or spectral analysis which are data intensive and thus time consuming. Consequently, there is attraction in developing simpler residence time proxies that can be readily applied to different sites. Earlier work by the authors identified strong relationships between catchment soil cover (mapped from the HOST data base) and MRTs based on $d^{18}O$ tracers $MRT_{d^{18}O}$. This found that the use of simple analysis of input–output relationships using various residence time models for $d^{18}O$ worked well in the Scottish context as precipitation inputs and streamwater outputs follow distinct seasonal patterns (Soulsby et al., 2000; Rodgers et al., 2005a,b; Tetzlaff et al., 2007b).

The $MRT_{d^{18}O}$ (+5th and 95th percentiles) estimated from fitting sine waves to weighted precipitation inputs and streamflow outputs were strongly, negatively correlated with percentage cover of responsive soils; notably peats (HOST class 29), peaty gleys (HOST class 15), peaty rankers (HOST class 22) and lithosols (HOST classes 19 and 27). $MRT_{d^{18}O}$ estimates have least uncertainty where residence times were relatively low and seasonal variations in $d^{18}O$ were most apparent in the stream (Fig. 3a). In catchments dominated by more freely-draining soils and with more damped $d^{18}O$ signals in streamwaters, estimates were more uncertain as model parameters are less well-identified (e.g. McGuire et al., 2005; Tetzlaff et al., 2007c). In addition to the relationship with soil cover, $MRT_{d^{18}O}$ estimates also correlated well with the ratio of the normalised standard deviation of $d^{18}O$ streamflow samples to the normalised standard deviation of $d^{18}O$ in the precipitation samples (Fig. 3b). This suggests that this simple statistic may be a convenient, transferable residence time proxy which can be derived much more quickly for large numbers of catchments with more limited data sets. Of course, caution must be exercised as standard deviations will be influenced by sampling intervals and the length of sampling period, which

Table 1 Catchment characteristics of the 22 sampling sites in the Dee; all sites are sorted along a west/east direction.

ID	Site	Area (km^2)	Annual rainfall (mm)	Mean annual flow ($m^3 s^{-1}$)	Median slope (deg)	Mean elev. (m)	Responsive soils (%)	Responsive riparian soils (%)
Cairngorm headwaters								
1	Dee, linn of Dee	157.5	1355	5.75	9	689	53.9	53.0
2	Lui, Water Br.	63.5	1383	2.36	12	706	50.7	7.7
3	Ey, Br.	63.8	1287	2.21	14	675	58.0	29.5
4	Dee, Mar Lodge	293.4	1336	10.55	11	683	50.0	50.0
5	Quoich, Linn of Quoich	59.6	1340	2.15	11	723	22.3	1.8
Upper Deeside								
6	Linn of Corriemulzie	7.0	1143	0.12	11	615	32.9	20.5
7	Coire Allt a' Chlair	1.6	1101	0.03	14	643	9.7	0
8	Clunie, Allt Coire Fionn	4.0	1583	0.17	14	789	53.8	18.1
9	Clunie, S. Newbigging	1.0	1229	0.01	16	650	21.8	0.0
10	Coire na Meanneasg	1.4	1220	0.01	14	650	0	0.0
11	Feardar, Inver	27.7	990	0.40	9	515	35.1	22.0
Mid-Deeside								
12	Crathie	4.4	992	0.08	4	546	95.0	95
13	Girnock, Littlemill	29.6	934	0.41	8	409	79.9	78.8
14	Aultonrea	4.6	1025	0.07	8	490	48.5	41.5
18	Burn O Vat	2.6	856	0.03	9	375	23.3	0
15	Tanar, Etnach Br.	21.7	1223	0.75	9	583	20.5	37.2
16	Tanar, Forest Br.	41.6	1152	1.08	10	521	25.4	32.0
17	Allachy, Forest Br.	28.0	1189	0.75	11	489	21.1	21.8
Lower Deeside								
19	Feugh, Birse	27.1	1206	0.50	9	456	31	25.6
20	Aven	30.1	1236	0.57	7	427	55.7	56.3
21	Dye, Charr	41.8	1280	0.81	7	420	72.3	66.0
22	Dye, Brocky	1.3	1230	0.02	3	419	91.0	92.0

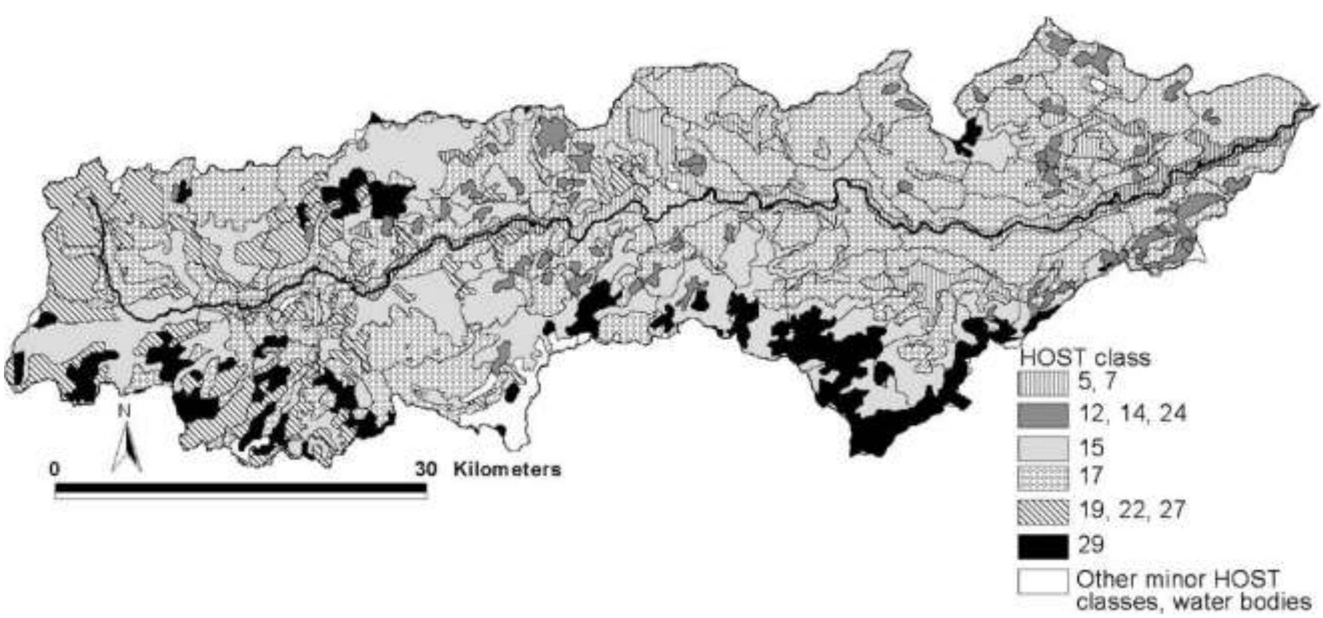

Figure 2 HOST classes of the Dee catchment (HOST classes 5, 7: alluvial soils; HOST classes 12, 14, 24: gleysols; HOST class 15: peaty podzols and peaty gleys; HOST class 17: humus iron podzol; HOST classes 19, 22, 27: rankers; HOST class 29: blanket peats).

may be affected by anomalous periods in the sampling period.

In this study, we therefore sought to utilise the Cl input-output data in a similar way, assuming that as an alternative

Table 2 Percentage soil distributions mapped according to HOST classes[a] in the 22 catchments.

ID	HOST class	4, 5, 7	14/24	15	17	19	22	27	29	Total responsive soil cover
Cairngorm headwaters										
1	Dee, Linn of Dee			30.7	15.3	17.5	26.7		9.7	53.9
2	Lui, Water Br.	0.1	0.1	18.4	30.8	7.1	43.2		0.2	50.7
3	Ey, Br.			19.5	22.6	1.9	32.3		23.7	58.0
4	Dee, Mar Lodge			25.0	24.0	12.0	27.0		11.0	50.0
5	Quoich, Linn of Quoich			24.0	53.7	21.7			0.6	22.3
Upper Deeside										
6	Linn of Corriemulzie				67.1		8.2		24.7	32.9
7	Coire Allt a' Chlair	0.7		37.4	52.2		9.7			9.7
8	Clunie, Allt Coire Fionn			46.2		43.3			10.5	53.8
9	Clunie, S. Newbigging			52.7	25.8		21.6			21.6
10	Coire na Meanneasg				100.0					0.0
11	Feardar, Inver	8.8	4.2	16.3	39.9	9.3	5.5		16.1	35.1
Mid-Deeside										
12	Crathie			67.2	0.7				32.0	32.0
13	Girnock, Littlemill	0.1	9.1	53.5	26.1		4.7	6.4		20.2
14	Aultonrea		37.1	18.7	32.8				11.4	48.5
15	Burn O Vat		6.9	66.1	10.6				16.3	23.3
16	Tanar, Etnach Br.			15.8	63.7				20.5	20.5
17	Tanar, Forest Br.		3.4	30.2	44.4				22.1	25.4
18	Allachy, Forest Br.		7.0	34.9	44.1				14.1	21.1
Lower Deeside										
19	Feugh, Birse			56.5	12.4				31.0	31.0
20	Aven			30.3	13.2				55.7	55.7
21	Dye, Charr	3.6	1.9	32.2	2.4		4.5		65.9	72.3
22	Dye, Brocky	2.1		20.5	1.7		18.0		58.0	76.0

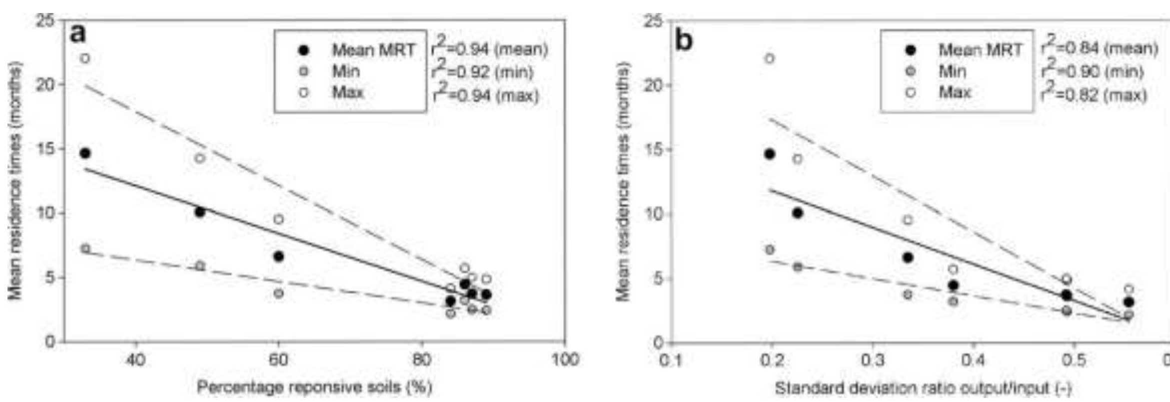

Figure 3 Relationship between (a) $d^{18}O$ based MRT and percentage soil cover in the Feshie and its sub-catchments and (b) $d^{18}O$ based MRT and standard deviation ratios of stream water: precipitation.

conservative tracer, the Cl damping within catchments would be equivalent to that of $d^{18}O$ and be an indication of hydrological function. As contemporaneous Cl and $d^{18}O$ data were not available for the 1996/1997 sampling year, more recent data (2003–2007) collected from Glen Girnock, a tributary of the Dee, was used to assess the validity of this assumption (cf. Soulsby et al., 2007; Tetzlaff et al., 2007b). Weekly precipitation (integrated) and streamflow (grab) samples were analysed for Cl and $d^{18}O$ and the ratios of the standard deviation of streamwater to the standard deviation of precipitation – when normalised relative to the weighted mean of each – were very close at 0.47 and 0.42, respectively (Fig. 4). Also, mean residence times for the Girnock estimated from sine wave application to the

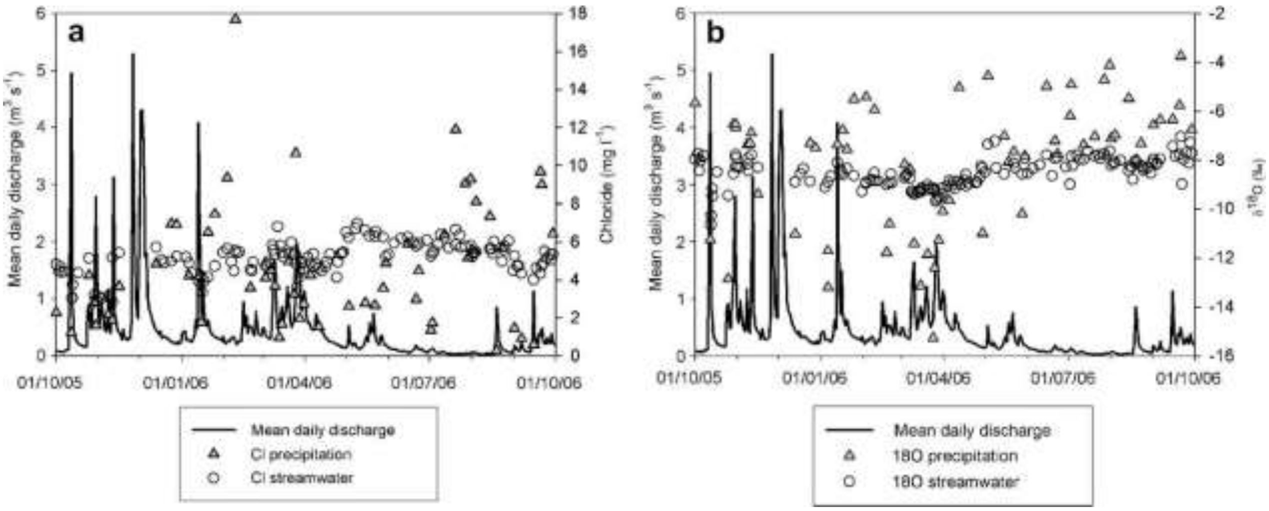

Figure 4 (a) Cl and (b) d^{18}O in weekly precipitation and streamwater samples in the Girnock tributary of the Dee catchment.

d^{18}O signal and convolution integral methods applied to the Cl data revealed similar mean residence times of 4 months and 5 months, respectively (Tetzlaff et al., 2007b). This supports the assumption that using the standard deviation of Cl has potential in using the metrics of tracer damping as a simple surrogate of mean residence times (MRT_{CL}).

The four precipitation samplers gave similar ranges and standard deviations, though, as noted by Smart et al. (2001), there was an eastward increase in mean weighted Cl concentrations in the order Mar Lodge < Lochnagar < Banchory < Glen Dye, reflecting precipitation gradients and increased sea-salt influence near the coast. Some samples from the Mar Lodge gauge were contaminated by wind-blown salt applied as a de-icing agent to an adjacent road, therefore the Lochnagar gauge was used for the Cairngorm Headwater, Upper Deeside and Mid-Deeside sites; and the Glen Dye gauge was used for the Lower Deeside sites in the Feugh catchment.

A GIS of catchment characteristics was available for the Dee including the HOST class distributions for the 22 study catchments (Fig. 2). The HOST database is adapted from mapped soil associations, which each have a proportion of different soil types (i.e., HOST classes) associated with them. These were tallied for each mapping unit to give the distributions in each catchment shown in Table 2. Thus, the maps are derived and give a simplified perspective on catchment soil distributions. For example, previous work has shown that HOST class 15 is ambiguous in terms of hydrological responsiveness. The original HOST classification scheme (Boorman et al., 1995) groups peaty gleys and peaty podzol soils together at the scale of the UK, whereas process studies in the Cairngorms and elsewhere (e.g. Soulsby and Reynolds, 1992, 1993; Tetzlaff et al., 2007b) have shown that peaty gleys are far more responsive. Thus, the original soil association data were used to classify HOST class 15 as being responsive when peaty gley soils were present, but not when peaty podzols predominated. In addition, for some experimental catchments (e.g. Brocky, Dye and Girnock) more detailed soil maps were available, and where possible the HOST maps were enhanced with such additional information (Table 2).

In addition, within the GIS, riparian soil distributions were estimated by assuming the riparian zone was delineated within 50 m of the river channel network. Fig. 5 shows the resulting riparian soil cover map for the Girnock as one example. Although relatively simple, this

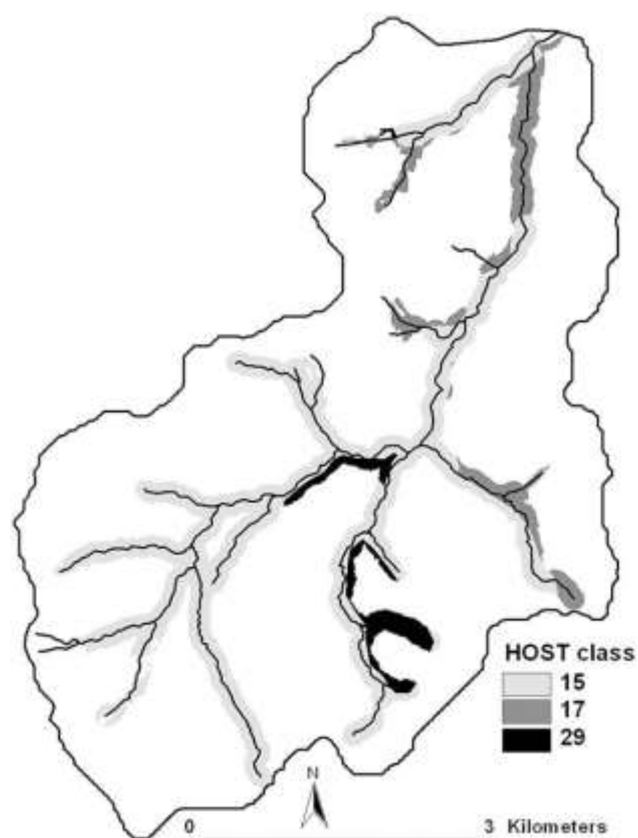

Figure 5 Girnock catchment, HOST classification in riparian zone – defined as 50 m either side of the stream (HOST class 15: Peaty Podzols and Peaty Gleys; HOST class 17: Humus Iron Podzol; HOST class 29: Blanket Peats).

allowed the topology of responsive riparian soils to be analysed to see whether this improved representation of the connectivity between responsive soil and the river channel network could be used as a better predictor of MRT than catchment soils data alone.

Results

Using Cl data to predict MRT

Table 3 shows the mean Cl concentrations, ranges and standard deviations for streamwater at the 22 sites and precipitation at Lochnagar. In general, the concentrations increase along a west – east gradient. Within that, there are higher concentrations in a few westerly catchments such as Burn O'Vat and the Fearder where there is a higher tree cover (ca. 10–5%) which may have increased dry and occult deposition, or increased evapotranspiration effects, though this did not appear to produce any exceptional differences in the standard deviation. The temporal variability of Cl in streamwaters was damped compared with precipitation characteristics at all of the Dee sample sites. The degree of damping is reflected in the standard deviations shown in Table 3. Fig. 6 shows how the Girnock (see also Fig. 4 for much finer resolution sampling) was an example of catchments where streamwater concentrations were responsive to variable precipitation inputs in large hydrological events, whilst other catchments such as the Clunie tributary at Newbiggin (which is also shown) was much more damped.

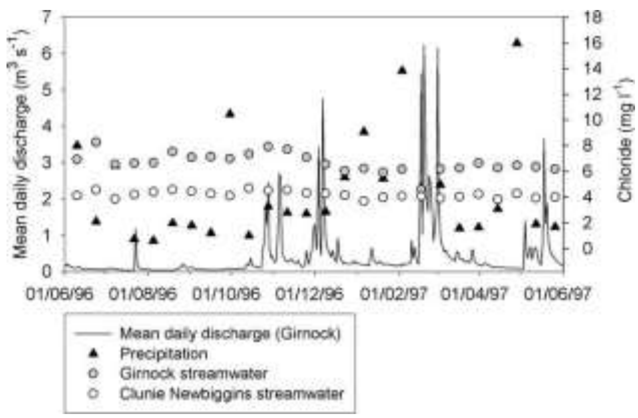

Figure 6 Examples of chloride time series (1996–1997) in the Girnock (example for variable streamwater signature) and Clunie, Newbiggin (example for damped streamwater signature).

Table 3 Mean, range and standard deviation of chloride in precipitation and stream waters at each site (mg l^{-1}) and the ratio of the normalised standard deviation ratio to that of precipitation.

ID	Site	Mean	Min	Max	Standard deviation	Standard deviation ratio to precipitation
Precipitation						
	Lochnagar	2.89	0.2	15.3	1.52	–
	Cairngorm headwaters					
1	Dee, Linn of Dee	3.76	2.89	5.99	0.65	0.42
2	Lui, Water Br.	3.91	3.33	4.66	0.38	0.25
3	Ey, Br.	3.50	3.0	4.16	0.32	0.21
4	Dee, Mar Lodge	3.86	3.0	5.14	0.50	0.33
5	Quoich, Linn of Quoich	4.05	3.36	5.20	0.41	0.27
Upper Deeside						
6	Linn of Corriemulzie	4.42	3.66	5.42	0.39	0.26
7	Coire Allt a' Chlair	4.54	3.72	6.32	0.48	0.31
8	Clunie, Allt Coire Fionn	2.89	2.08	3.85	0.39	0.25
9	Clunie, S. Newbigging	4.20	3.69	4.69	0.26	0.17
10	Coire na Meanneasg	4.07	3.41	4.82	0.37	0.24
11	Feardar, Inver	6.73	5.63	7.97	0.6	0.39
Mid-Deeside						
12	Crathie	6.07	4.2	7.71	0.8	0.52
13	Girnock, Littlemill	6.69	4.61	8.28	0.75	0.48
14	Aultonrea	5.89	5.34	6.98	0.45	0.29
15	Burn O Vat	10.41	9.29	11.12	0.47	0.31
16	Tanar, Etnach Br.	4.99	4.12	5.85	0.41	0.26
17	Tanar, Forest Br.	5.54	4.84	6.50	0.46	0.30
18	Allachy, Forest Br.	5.95	4.94	7.05	0.46	0.31
Lower Deeside						
19	Feugh, Birse	6.62	5.75	7.88	0.49	0.32
20	Aven	7.08	8.03	11.49	0.57	0.37
21	Dye, Charr	7.07	5.75	8.29	0.60	0.39
22	Dye, Brocky	7.40	4.99	8.72	0.89	0.58

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Residence times (MRT_{Cl}) estimated from the relationships between the ratio of the streamwater standard deviation: precipitation standard deviation from Fig. 3b, are shown in Table 4. These are plotted against percentage cover of catchment responsive soils (Fig. 7). A reasonable general relationship was observed ($r^2 = 0.603$, $p < 0.001$). Given the relationships in Fig. 3, the estimates were, unsurprisingly, well constrained for sites with low residence time estimates, but increasingly uncertain for longer MRTs, suggesting that the method may be better suited to catchments with short residence times, rather than ones with longer residence times where subsurface mixing damps out the tracer signal.

Lowest estimated mean residence times (in the order of 1–4 months) were observed in catchments with over 75% responsive soil cover. This was mainly where peats (HOST class 29) and peaty gleys (HOST class 15) dominate the Brocky Burn sub-catchment (within the Lower Deeside Feugh group), and the Crathie and Girnock Burns (in the Mid-Deeside group). The longest residence times, in the order of 11–13 months, were estimated for catchments dominated by more freely-draining soils (<35% responsive soils). These included the Clunie tributaries at South Newbiggin and Coire na Meannseag in the Upper Deeside group where more freely-draining podzols (HOST class 17) prevail, or the Ey in the Cairngorm Headwater group of catchments which has a more limited coverage of freely-draining soils, but a complex, fractured geology.

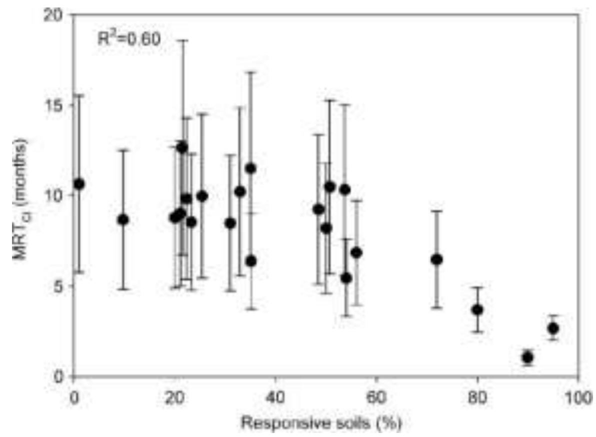

Figure 7 Relationship between MRT_{Cl} and percentage cover of responsive soils.

In catchments with similar coverage of responsive and freely-draining soils, the MRT_{Cl}'s exhibited considerable scatter (Fig. 7). For example, in the Cairngorm Headwater group of catchments, relatively short residence times (ca. 5 months) were estimated for the Upper Dee at the Linn

Table 4 Mean residence time (months) estimated for the 22 sub-catchments from Cl data (MRT_{Cl}) and soil maps (MRT_{soil}).

ID	Site	Cl			Soil maps		
		Mean	Lower	Upper	Mean	Lower	Upper
Cairngorm headwaters							
1	Dee, Linn of Dee	5.4	3.3	7.7	9.5	5.2	13.8
2	Lui, Water Br.	10.4	5.7	15.4	10.1	5.5	14.8
3	Ey, Br.	11.4	6.2	16.9	13.1	6.8	19.3
4	Dee, Mar Lodge	8.2	4.6	11.9	10.3	5.5	15.0
5	Quoich, Linn of Quoich	9.8	5.4	14.4	15.4	7.8	23.0
Upper Deeside							
6	Linn of Corriemulzie	10.2	5.6	14.9	13.4	6.9	19.9
7	Coire Allt a' Chlair	8.7	4.8	12.6	17.7	8.9	26.6
8	Clunie, Allt Coire Fionn	10.3	5.6	15.1	9.6	5.2	13.9
9	Clunie, S. Newbigging	12.7	6.7	18.6	15.6	7.9	23.2
10	Coire na Meanneasg	10.7	5.8	15.6	19.4	9.6	29.1
11	Feardar, Inver	6.4	3.8	9.1	13.0	6.8	19.3
Mid-Deeside							
12	Crathie	2.7	2.0	3.5	1.0	1.3	0.6
13	Girnock, Littlemill	3.7	2.5	5.0	4.7	3.0	6.4
14	Aultonrea	9.2	5.1	13.5	10.5	5.6	15.4
15	Burn O Vat	8.8	4.9	12.8	15.8	8.0	23.6
16	Tanar, Etnach Br.	10.0	5.5	14.6	14.8	7.6	22.1
17	Tanar, Forest Br.	9.0	5.0	13.1	15.6	7.9	23.3
18	Allachy, Forest Br.	8.5	4.8	12.4	15.2	7.8	22.7
Lower Deeside							
19	Feugh, Birse	8.5	4.8	12.3	13.8	7.1	20.5
20	Aven	6.8	4.0	9.8	9.1	5.0	13.3
21	Dye, Charr	6.5	3.8	9.2	6.2	3.7	8.7
22	Dye, Brocky	1.1	1.3	1.1	2.8	2.2	3.5

of Dee, where responsive soils (mainly peats (HOST class 29) and lithosols (HOST classes 19 and 22)) cover 54% of the catchment. In contrast, the Lui, with similar (51%) responsive soil cover has a longer MRT_{Cl} estimate of ca. 10 months. These Upper Headwaters show the effects of averaging at larger scales, as the site at Mar Lodge shows the integrated influences of the Linn of Dee, Lui and Ey tributaries with a MRT_{Cl} of ca. 8 months (Table 4).

The Upper Deeside group of catchments show broadly similar and longer residence times (>9 months) reflecting the responsive soil cover being generally low (<35%). Allt Coire Fionn was unusual in having a high (54%) coverage of responsive soils, but a relatively high MRT_{Cl} (10 months). Conversely, the Fearder Burn had a relatively short estimated MRT_{Cl} (6 months) but only 35% responsive soil coverage.

Estimates of MRT_{Cl} for the Mid-Deeside group of catchments divided into the aforementioned shorter ones (ca. 4 months) for the Crathie and Girnock Burns and longer ones (8–10 months) for the other catchments with more freely-draining soil cover. The three sites in the Tanar catchment and the Burn O'Vat had similar residence time estimates, consistent with their relatively limited (ca. <25%) coverage of responsive soils and a dominance of more freely-draining podzols (HOST class 17). The Muick at Aultonrea was unusual in having relatively high coverage of responsive soils (48%) – mainly gleys (HOST class 24) and peats (HOST class 29) but relatively long residence time estimates (9 months).

Finally, in the four Feugh sub-catchments (Lower Deeside) high coverage of responsive soils at Brocky corresponded to the shortest MRT_{Cl} estimates. The relatively short residence times for the Water of Aven and Dye at Charr (ca. 6–7 months) are also consistent with relatively high responsive soil coverage (56% and 72%, respectively) with Birse having longer residence times (9 months) and a higher coverage of more freely-draining soils.

As both $d^{18}O$ and Cl data are available for the Feugh sites, along with the Girnock, this provides an opportunity to compare the MRT_{Cl} estimates with those estimated independently using $d^{18}O$ in earlier work (Rodgers et al., 2005b; Tetzlaff et al., 2007b). Fig. 8a shows both MRT_{Cl} and MRT_{d18O} (+5th and 95th percentile) for the five of the catchments (Girnock, Brocky Burn, Water of Dye, Water of Aven and the Water of Feugh). The results compare reasonably well ($r^2 = 0.762$, $p < 0.0001$), though residence times appear to be under-predicted in Brocky and the Water of Aven, though estimates for the latter site were highly uncertain, even with the $d^{18}O$ data.

MRT predictions from soil maps

The relationships derived from Fig. 3a allowed an alternative estimate of mean residence times to be calculated for each of the 22 sub-catchments based on percentage responsive soil cover (MRT_{soil}) given in Table 2, see Table 4. Although not independent of the estimates derived from the Cl data, being both derived from the Feshie data sets shown in Fig. 3, they provide a potential means of assessing residence time predictions in ungauged catchments. The resulting MRT_{soil} estimates are, once again, most well constrained for short residence times, and vary from 1 month in the peat-dominated Crathie Burn to >18 months in Coire na Meanneasg. The relationship between the MRT_{soil} estimated from soil maps and the MRT_{Cl} estimated from the Cl data show reasonable general agreement ($r^2 = 0.604$, $p < 0.001$), though the soil-based estimates tend to produce higher predictions (Table 4). Comparison of the predictions from the HOST maps with those derived from the time series analysis of $d^{18}O$ data by Rodgers et al. (2005b) and Tetzlaff et al. (2007b) also show comparable results (Fig. 8b), but indicate that the Cl-based MRTs are more strongly correlated than those from the soil maps ($r^2 = 0.702$). Although good predictions for the MRT of Brocky, the Girnock and the Dye were achieved, those for the Aven and Birse were less satisfactory.

Does topology of soil cover improve predictions?

When only the percentage of responsive soils in the riparian zone was used, the correlation with the MRT_{Cl} was improved compared to whole catchment soil distributions with an r^2 of 0.710 ($p < 0.001$) (Fig. 9). This seems to confirm that the topology of a catchment's soil distribution is an important control on MRTs, with soil cover in the riparian zone

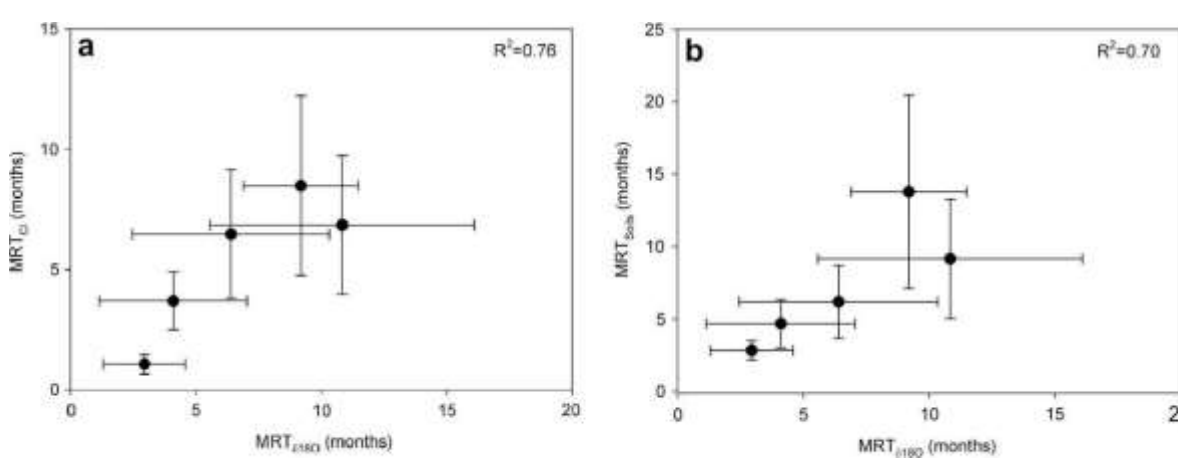

Figure 8 Correlations of (a) MRT_{Cl} predicted from Cl standard deviations and MRT_{d18O} and (b) MRT_{soil} and MRT_{d18O}. The MRT_{d18O} estimates were derived from earlier work in the Feugh (Rodgers et al., 2005b) and Girnock (Tetzlaff et al., 2007b).

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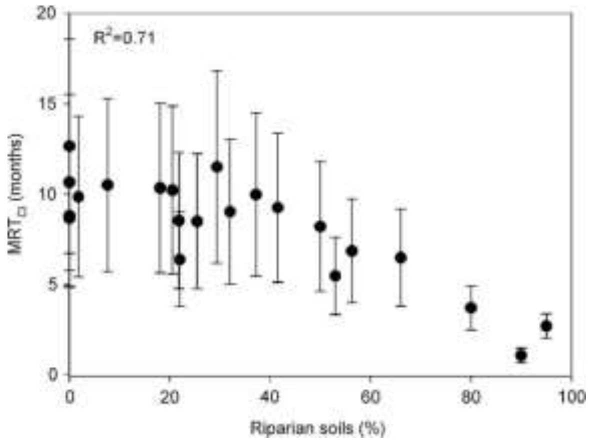

Figure 9 Relationship between MRT_{Cl} and percentage cover of responsive soils in the riparian zone.

being important, probably as a proxy for the connectivity of responsive soils with the channel network. The relationship is sharpened mainly as a result of some of the catchments with intermediate and longer residence times which have relatively high catchment coverage of responsive soils, have reduced responsive soil cover in the riparian zone.

Influence of topography, scale and comparison with other sites

The original work in the Feshie indicated that soil cover correlated more strongly with MRT than simple topographic indices (Soulsby et al., 2006a,b). However, Fig. 10 shows that the correlations for MRT_{Cl} derived for the Dee sites in the present study and simple topographic descriptors such as mean catchment slope ($r^2 = 0.670$, $p < 0.0001$), were comparable to the soil-based catchment and riparian descriptors. Somewhat counter-intuitively, the correlation is negative predicting shorter residence times in catchments with lower gradients. However, this is consistent with the dominant coverage of responsive peats and peaty gleyed soils (HOST classes 29 and 15) in flatter valley bottoms (e.g. the Girnock and Crathie Burns) or low gradient catchment interfluves (e.g. Brocky Burn and the Water of Dye). Conversely, the dominance of free-draining podzols (HOST class 17) on steeper slopes (e.g. Coire na Meanneasg and the Quoich) facilitate greater mixing, more damped Cl stream concentrations and longer residence time estimates. Despite the strong correlations between MRT and both slope and percentage responsive soil cover, the correlations between slope and responsive soil cover was much weaker ($r^2 = 0.45$).

Fig. 11a shows the lack of relationship between catchment size and MRT estimates, that has been noted by researchers elsewhere (e.g. McGlynn et al., 2003; McGuire et al., 2005). To provide greater context, the data from the Dee catchment are plotted together with those estimated as part of independent studies in catchments in the Cairngorm or near by in the Scottish Highlands. These include the ones already mentioned in the Feshie (Rodgers et al., 2005a), Feugh (Rodgers et al., 2005b) and Girnock (Tetzlaff et al., 2007b) where $d^{18}O$ has been used to estimate MRT; and those where Cl has been similarly used such as Glensaugh (Dunn et al., 2006) and Loch Ard (Tetzlaff et al., 2007c). The data show that variability is most marked at smaller scales, with averaging occurring at larger (ca 150 km^2) scales. The relationship with percentage responsive soil coverage is reasonably consistent though there is considerable scatter (Fig. 11b). Of course, as the Dee estimates were derived from the Feshie relationships, it is unsurprising that the relationship plots along a line of similar gradient. However, the independent MRT estimates calculated for the Feugh, Girnock, Glensaugh and Loch Ard give a fairly consistent picture of MRT in the order 2–4 months in catchments dominated by responsive soils, increasing to 10–14 months where freely-draining soils predominate. The relationship with mean catchment slope (Fig. 11c) is less sharply defined; for example, catchments with a mean slope of 10° can vary between 3 and 14 months limiting its general transferability.

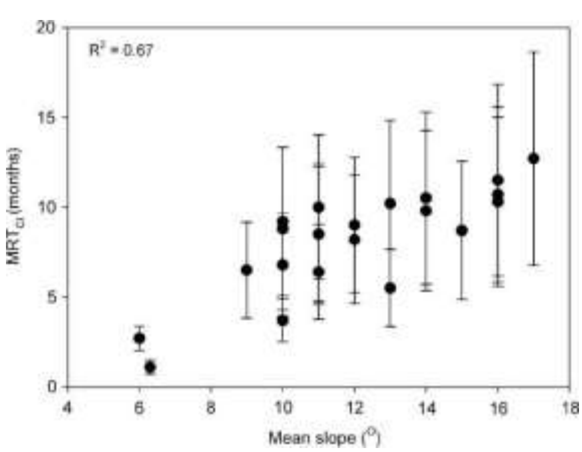

Figure 10 Relationship between MRT_{Cl} and mean catchment slope.

Discussion

This study sought to test three hypotheses: firstly, that fortnightly variation of Cl in precipitation and streamflow can be used as a simply proxy to calibrate estimates of catchment MRTs. Secondly, that catchment soil cover can be used as a reliable means of predicting MRTs in ungauged catchments and that these predictions can be improved using soil distributions in riparian zones. Finally, that simple topographic indices may also provide useful predictors of MRT.

It is clear that the methods used are very simplistic and the results can only be regarded as preliminary, and should therefore be treated with caution. Nevertheless, they do provide some evidence that simple metrics derived from Cl input–output ratios can provide insightful MRT estimates, at least within this particular geographical region where more detailed studies allow calibration. That said, there are a number of simplifying assumptions in the method which need to be emphasised to ensure that any interpretation is suitably circumspect. Firstly, the Cl data were only collected at fortnightly intervals, so the high frequency dynamics in short-term Cl signals reported by others in response to precipitation events (e.g. Soulsby, 1995; Kirchner

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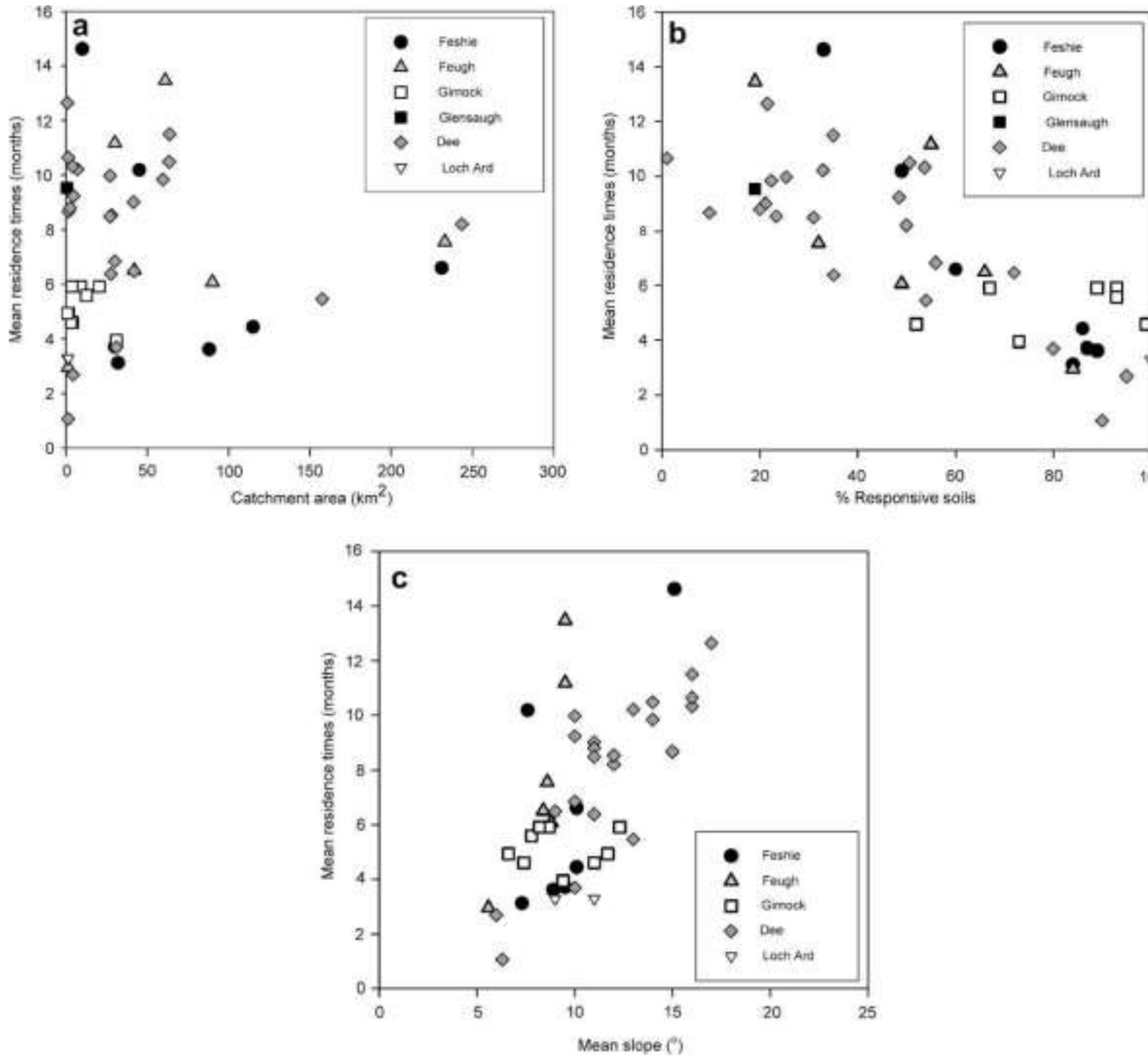

Figure 11 Regionalised relationships between MRT and (a) catchment size, (b) soil cover and (c) mean slope in the Dee sites and others in the Scottish Highlands. MRTs at other sites were estimated from sine wave or convolution integral approaches.

et al., 2000; Tetzlaff et al., 2007c) will be not be sampled or well-represented. This means the MRTs estimated will be biased towards source waters with longer residence times, akin to the notion of baseflow residence times advocated by others using a similarly coarse sampling frequency such as McGuire et al. (2005) or McGlynn et al. (2003). Secondly, recent work has also shown that using MRTs estimated from typically 1–2 years of tracer data may not provide a representative perspective on the way in which climatic influences dictate that MRTs are non-stationary on an annual basis (Hrachowitz et al., submitted for publication). Thus, MRT estimates can vary markedly between wet and dry years. For example, Tetzlaff et al. (2007c) note how MRTs of 4–6 months estimated from 15 years data for one of the Loch Ard catchments in the central Scottish Highlands masked the fact that estimates for individual years could range between 2 and 12 months in wet and dry years respectively. Consequently, the results collected from a given study year, may not be more broadly representative, especially given the relatively wide 5th and 95th percentiles around the estimates as MRTs increase.

However, whilst the absolute values of the MRTs should be treated cautiously, comparison with other Scottish studies shown in Fig. 11 indicates that the estimates probably give useful first approximations at least for catchments in the Scottish Highlands. Moreover, it is perhaps the relative contrasts between different sites that are most important in terms of using a metric to define behavioural characteristics of a catchment that might contribute to a more generic classification scheme. Finally, perhaps the large uncertainty ranges – although unsatisfactory – may give some indication of how the MRT may change between wetter and drier years and underline the way in which temporal variability in MRT estimates may be as important as spatial ones.

The reasonable relationship between MRT_{Cl} estimates derived from the Cl input–output ratios and MRT_{soil} estimated from percentage responsive soil cover, imply that catchment soil maps can be used in the Cairngorm regions to gain a useful prediction of the MRT of ungauged basins. The similar quality of the predictive relationships between the estimated $MRT_{\delta^{18}O}$ for the Girnock, Birse, Aven, Charr and Brocky, and those predicted from both Cl input–output ratios and from soil maps (c.f. Fig. 8), indicate the potential utility of catchment soil maps as a basis for a first approximation of the MRT of ungauged basins in montane areas where soil maps are available. Whilst the transferability of this approach beyond the geomorphic province of the Cairngorms remains unproven, the usefulness of a relatively small number of research catchments where such behavioural knowledge can be defined seems to allow broader prediction within a comparable geographical area. Despite this, the estimates are not particularly well defined, especially where catchments have soils that are dominated by subsurface flow paths, which may restrict the potential transferability of this approach to more responsive, montane catchments. This may mean that the utility of such estimates is more qualitative than quantitative and this underlines the need for better understanding of subsurface flow paths and their influence on MRTs (McGuire et al., 2005).

Mean residence times were more closely correlated with riparian soil cover – even quite simply defined as that within 50 m of the river channel – than total cover of responsive soils. This relationship is consistent with the importance of the topology of catchment soil distribution, particularly in relation to the connectivity between more responsive soils and the River channel network (Buttle, 2006). Conversely, this may also reflect the ability of more free-draining riparian soils to damp tracers more effectively (Laudon et al., 2004, 2007). These findings are consistent with previous work in the Dee that has highlighted the importance of riparian zones in governing the hydrology and hydrochemistry of high and low flows (Smart et al., 2001; Tetzlaff et al., 2008b). Both the good relationships between MRT and percentage responsive soils in the catchment as a whole and within the riparian zone suggest that the HOST system is a useful process information carrier that can be used in catchment-scale assessment of hydrological function. It is likely that this could be improved further if – rather than the relatively crude riparian metric used – the riparian area could be accurately mapped in a more physically meaningful way (McGlynn et al., 2003).

Indeed the relationship between MRT and simple topographic metrics such as mean catchment slope shown in Fig. 10 suggest more sophisticated topographic characterisation of catchments may offer significant potential in predictions for ungauged basins. It has been noted that topographic maps are usually more readily available in mountainous areas and recent work that has linked topographic indices to MRT estimates is promising in terms of more readily available means of predicting and aiding catchment management (McGuire et al., 2005). Of course topography is a major influence on pedogenesis and so may be autocorrelated with soil coverage and further work is needed to evaluate the extent to which the soil-related influences on catchment hydrology can be captured by more sophisticated terrain indices derived from DTMs (Seibert and McGlynn, 2007). In particular, the subtle interplay between soil and topographic factors which may contribute to the scatter shown in Fig. 11b and c need to be more fully understood and characterised.

The utility of the link between MRT and catchment soil characteristics and topography in catchment management is ambiguous. The value of a MRT metric has been questioned in terms of its limited insight into the residence time distribution; the ways in which combinations of very different residence time distributions can give rise to similar MRT and large uncertainties (Dunn et al., 2006, 2008). Nevertheless, insight into how the MRT relates to the catchment coverage or riparian distribution of responsive soils may help guide management and provide a metric that is useful for classifying catchments in the way envisaged by Wagener et al. (2007). For example, responsive soils are likely to be the ones where high flows may be most sensitive to certain hydrological impacts and may be areas where particular activities could have disproportionately adverse impacts on surface waters. Conversely, freely-draining soils are often areas where groundwater recharge is important and certain impacts may adversely affect baseflows. Thus, using soil maps in catchment management could be valuable for guiding land use activities in montane areas in terms of, for example, planning various developments, forestry operations, roads construction etc. in such ways as to avoid adverse impacts (Wemple et al., 2007). Of course, the UK is fortunate in having relatively high quality digital soil maps available for mountainous areas which may not be the case in many other countries, hence the need for better understanding of topographic controls where maps are usually available.

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