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Relative influence of upland and lowland headwaters on the isotope hydrology and transit times of larger catchments

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ABSTRACT:

In four comparatively large catchments in north-eastern Scotland, the weekly fluctuation of d18O in precipitation and river water was studied over a period of two years. The majority of the River Dee's 1712 km2 is upland, with impassible bedrock and hydrologically responsive soils. Similar to the River North Esk's (732 km2) headwaters, the lower third of the catchment is lowland (i.e., less than 300 m above sea level) in character and is submerged by a significant sandstone aquifer. The majority of the River Don catchment (1273 km2) is lowland with easily draining soils that replenish significant groundwater reservoirs in suprafinancial drifts. The upper 20% of this area is upland. The entire lowland (662 km2) River Ythan watershed is comparable to the lower Don. The upland region of the catchments had a direct impact on how hydrologically responsive they were, with the Dee and the North Esk producing the largest specific discharges during high flow occurrences. In contrast, the Don and Ythan had hydrological regimes that were more restrained yet had higher specific discharge under baseflows. Ythan > Don > North Esk > Dee was the order in which the variability of stream flows was gradually dampened despite broadly similar d18O fluctuation in precipitation inputs. Using the isotope data, Mean Travel Times (MTTs) for the four catchments were estimated using convolution integral models. For the Dee and the North Esk, they were reas- sonably well-constrained at roughly 2 and 3 years, respectively. Estimates for the Don and Ythan are both likely to last longer then 10 years but were poorly limited, making them extremely uncertain. MTTs in highland catchments in the Scottish Highlands are demonstrated to be substantially linked with soil hydrology, topographic indices, and precipitation intensity, although being very brief (between 2 months and 4 years). These correlations alter in lowland regions, where deeper mixing mechanisms and larger groundwater storage lead to significantly higher MTTs and catchments that are less dominated by surface water. Nonetheless, there is still a strong relationship between soil cover and MTT.

1. Introduction

Recent years have seen significant progress applying methods to quantify the mean transit time (MTT) of stream water and identify associated landscape controls (McDonnell et al., 2010). The concept of transit times provides an integrative tool for understanding the emergent behaviour of mixing processes at larger catchment-scales (McDonnell et al., 2007). MTTs are usually estimated by modelling input–output relationships of conservative tracers such as stable isotopes or chloride according to various assumed Transit Time Distributions (e.g. Hrachowitz et al., 2009a; Kirchner et al., 2010). The integrating nature of tracers dictates that transit times have considerable potential as metrics in aiding process-based catchment classification and facilitating cross-regional inter-comparison (Tetzlaff et al., 2009a; Soulsby et al., 2010a,b). In turn, inter-catchment comparison studies provide a stronger sci- entific basis for identifying first-order controls on hydrological pro- cesses and facilitate synthesis and understanding of how catchment behaviour varies in different geographical regions (Carey et al., 2010).

Combining transit time estimates with GIS-based landscape analysis has helped demonstrate how landscape controls on MTTs vary in different geographical environments. For example, work by McGuire et al. (2005) has identified the link between transit times and topographic indices in the steep landscape of the Western Cascades, USA. Conversely, hillslope lithology and catchment exposure were shown to be the dominant controls on MTTs in other mountainous areas in Arizona (Troch et al., 2009). In glaciated catchments in Scotland and Sweden, studies by Soulsby et al. (2006) and Laudon et al. (2007) have emphasised the importance of soil hydrology as the main control on MTTs. More recent work has successfully modelled the integrated influence of soils, topography

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and climate on transit times (Hrachowitz et al., 2009b). Apparent contrasts in the identification of first-order controls on transit times seem to reflect geographic differences in key climatic forcing factors and catchment landscape characteristics (e.g. Tetzlaff et al., 2009b). Despite such progress, it is still the case that most transit time studies focus on relatively small (<10 km^2) experimental catchments in headwater regions, although some studies have examined mesoscale (>100 km^2) and macroscale (>1000 km^2) catchments (e.g. Soulsby and Tetzlaff, 2008; Ogrinc et al., 2008; Rank et al., 1998; Koeniger et al., 2009; Speed et al., 2010). Thus, there is comparatively little information on how tracer dynamics and subsequent MTTs estimates evolve in larger scale catchments and how the relative importance of landscape controls change as lowland landscape features become more important, associated groundwater inputs increase, land becomes increasingly cultivated and climatic contrasts are enhanced (e.g. Kendall and Coplen, 2001).

In the Scottish Highlands, the scaling of MTTs and their landscape controls has been examined: long-term (up to 20 years) Cl data were used to constrain MTT estimates in 21 montane headwater catchments (mostly <10 km^2) where MTTs estimates varied between ca. 2 months and ca 5 years (Hrachowitz et al., 2009b). These were used to develop a robust multiple-regression model based on soil cover, drainage density, topography and precipitation which could explain around 90% of the variation in MTT. This was successfully tested for 12 further sites in the river Dee catchment in North East Scotland at scales up to 1700 km^2 (Hrachowitz et al., 2010). Here, MTTs varied from around 18 months to 3.5 years in tributaries, but converged to around 2 years in the lower main stem of the river, reflecting the strong influence of the montane headwater tributaries. However, this upscaling focused on a relatively undisturbed montane catchment lying within a single geomorphic province with a broadly consistent climate. Nevertheless, other large scale studies have similarly emphasised a strong influence of montane headwaters on downstream MTTs. For example, Rank et al. (1998) used long-term stable isotope and tritium data for the 100,000 km^2 Danube basin at Vienna to tentatively conclude that river water had a mean age of around 3 years, with high flow waters having an age of 1 year, reflecting the significance of alpine snowmelt in dominating the downstream flow regime. Similarly, Ogrinc et al. (2008) showed a strong mountainous headwater influence on the input–output relationships for stable isotopes at 21 nested sites in the 11,000 km^2 Sava catchment in Slovenia. Preliminary estimates of Mean Transit Times varied between 0.5 and 2.1 years in different montane tributaries, converging to around 1.5 years at the most downstream site. In contrast, Koeniger et al. (2009) used stable isotopes and tritium in the 46,000 km^2, mainly lowland, Weser catchment in Germany, and concluded that water ages were 14–50 years, generally increasing downstream as inputs from lowland aquifers became the increasingly important dominant source of runoff, despite a relatively small area of mountainous headwaters.

In this paper, we examine the interplay of upland and lowland headwaters in four larger scale catchments in North East Scotland. Building on the recent examination of tracer hydrology and MTTs in the upland Dee catchment by Hrachowitz et al. (2010), we examine three other adjacent catchments ranging between 682 and 1273 km^2 in area. These catchments increase in their proportion of lowland areas as they encompass different geomorphic and geologic provinces. This results in drier climatic conditions, increasing proportions of freely draining soils and greater groundwater inputs. The present study sought to use stable isotope tracer data over a period of 2 years to explore what can be inferred from rainfall-runoff relationships in terms of transit times and their first-order controls. The study tests the following hypotheses: 1. Different larger scale catchments show contrasting tracer dynam-

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ics that are consistent with landscape characteristics. 2. Catchment MTTs increase as the landscape becomes more lowland in charac- ter with increased free draining soil cover and larger groundwater inputs. 3. Landscape controls on MTTs in upland areas are less rel- evant in lowland environments.

2. Study sites

The study sites form four adjacent catchments in the north east of Scotland (Fig. 1 and Table 1). The Dee catchment (1712 km^2 at the gauging station Banchory) is upland in character; over 60% of the area lies above 300 m and much of the river drains the Cairn- gorm Mountains (Tetzlaff and Soulsby, 2008). The montane head- waters reach up to 1300 m and are dominated by crystalline bedrock – mainly granite and associated metamorphic rocks – and have steep slopes (Speed et al., 2010). Precipitation is high here; over 1500 mm each year falls with ca. 30% as snow (Soulsby et al., 1998). The headwaters are dominated by hydrologically responsive soils: regosols, peaty gleys (gleysols) and deep peats (histosols) which generate rapid overland flow and shallow sub- surface storm flow in response to precipitation and snowmelt events (Tetzlaff et al., 2007). In the east, the geology is similar, but the topography is much more subdued with wider valleys and gentle hills. Precipitation falls to around 800 mm per annum. Extensive drift deposits mantle the bedrock and form locally important aquifers, especially where alluvial deposits fill the main valleys (cf. Chen et al., 1997). Freely draining podzols and alluvial soils increasingly dominate in the east of the catchment and mainly contribute to groundwater recharge via slower flow paths compared to the hydrologically responsive soils. Land use in mon- tane headwaters ranges from alpine health, to heather moorland and blanket bog as altitudes decline (Soulsby and Tetzlaff, 2008). In contrast, the eastern lowlands are mainly managed for agricul- tural practices (mainly grazing), with Scots Pine (*Pinus sylvestris*) forests common on the steeper slopes at lower altitudes (Wade et al., 2001). Anthropogenic influences on the river regime and its water quality are limited compared to most UK rivers of similar size, with only four small towns (each with a population <2000) in the upper catchment.

The river North Esk (749 km^2) lies to the south of the Dee and also has headwaters in the Cairngorm Mountains, which are broadly comparable to the Dee in terms of climate, geology, topog- raphy and soils, though they lack extensive areas above 1000 m (Table 1 and Fig. 1). The lower third of the catchment is lowland in nature – here defined as <300 m altitude and underlain by a large sandstone aquifer (Capell et al., in press) that forms a region- ally important water resource (Ó Dochartaigh et al., 2006). The lowlands are milder and drier, with mean annual precipitation fall- ing to around 700 mm. The upland vegetation is similar to the Dee, whilst the lowlands have intensive agricultural land use. One rela- tively small town (population ca. 3500) is located in the lowland area.

In contrast to the Dee and North Esk catchments, the Don – which covers an area of 1270 km^2 at the sampling site – is predom- inantly lowland in character with approximately 80% lying below 300 m. However, the upper part of the catchment also has small areas of headwaters in the Cairngorm mountains which although only reaching an altitude of 872 m, have broadly similar environ- mental characteristics to the headwaters of the other two catch- ments. The geology of the Don is dominated by metamorphic rocks (some of which are derived from base-rich formations) which are covered by thick layers of locally-derived coarse- textured drift which form significant aquifers (Soulsby et al., 2003). In the lowlands, humus–iron podzols predominate on freely draining slopes with smaller areas of gleysols which occur locally

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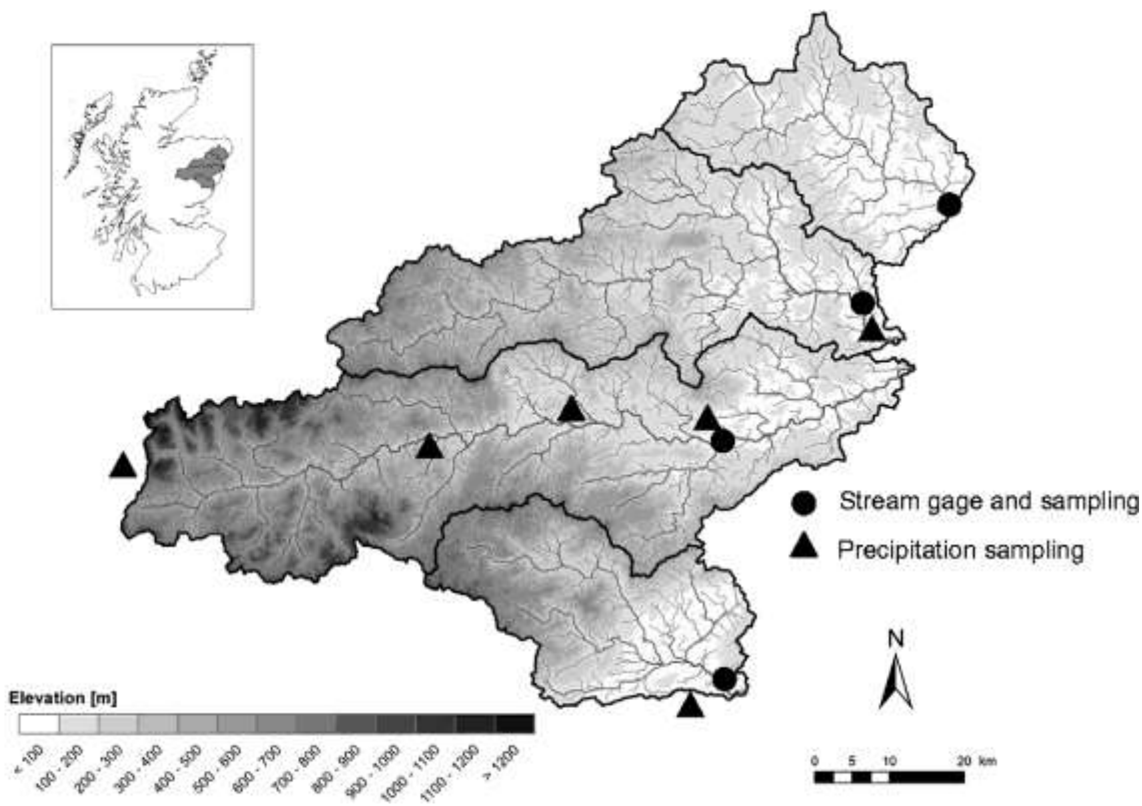

Fig. 1. Catchment characteristics of the catchments showing topography and sampling location. From south to north: North Esk, Dee, Don, Ythan.

Table 1
Characteristics of the four study catchments.

Site	Dee	North Esk	Don	Ythan
Hydrology				
Area (km^2)	1712	732	1273	682
Annual rainfall (mm)	1130	1074	885	826
Mean annual flow* ($l\ s^{-1}\ km^{-2}$)	20.1	14.8	14.7	13.5
Q_{95}* ($l\ s^{-1}\ km^{-2}$)	7.0	5.2	8.5	8.4
Q_{10}* ($l\ s^{-1}\ km^{-2}$)	48.2	47.9	32.3	31.0
Topography				
Drainage density ($km\ km^{-2}$)	1.25	0.73	0.73	0.61
Median slope (°)	10.5	8.3	6.3	2.6
Max slope (°)	78.3	78.0	53.2	22.2
Mean elevation (m)	467	306	255	97
Max elevation (m)	1305	939	872	286
Min elevation (m)	44	4	15	3
Soils				
Alluvial soils (%)	7	3	4	6
Mineral gleys (%)	2	34	7	22
Peaty gley/podzol (%)	24	25	15	2
Podzol (%)	43	20	56	60
Regosols (%)	12	0.5	4	1
Peats (%)	11	17	14	9
Geology				
Igneous – granites/diorite (%)	51	7	15	0
Metamorphic – quartzite/psammite/schist (%)	45	55	82	94

grazing which extend to an elevation of 450 m. The catchment also has a relatively large town (ca. 11,500 population) upstream of the sampling location.

In contrast to the other three catchments, the Ythan (682 km^2) is entirely lowland in character. It has a gently rolling topography with a maximum elevation of 300 m (Dunn et al., 1998). Mean annual precipitation is lowest of all catchments with ca. 820 mm. Most of the underlying bedrock is impermeable; sedimentary rocks and deep groundwater resources are only to be found in an area of Old Red Sandstone in the north-west of the catchment. However, the catchment is mantled by deep coarse-textured drift deposits that provide extensive shallow aquifers (Robins, 1990). The soils are primarily freely draining podzols and facilitate recharge of groundwater in the drifts. However, in the lower slopes the soils are less permeable and seasonally waterlogged in places. As a consequence of the nature of the soils and the relatively dry climate, around 85% of the catchment is cultivated for arable crops. The remaining area is predominantly improved grassland. There are only small urban areas within the catchment. Thus, the Ythan is atypical of Scottish catchments in terms of its physical characteristics because it is relatively homogeneous in land use, lowland topography and soils.

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3. Data and methods

Sedimentary (%)	4	38	3	6
Montane, moorland and bog (%)	63	50	25	2
Forestry (%)	17	7	15	7
Arable/improved pasture (%)	19	43	58	90

* Mean annual flow, Q_{95} and Q_{10} figures from SEPA (1985–2006).

in poorly drained areas (Hope et al., 1997; Soulsby et al., 2003). The higher base status of many of the soils in the Don catchment results in cultivated soils under arable cropping and improved

To establish the tracer composition of precipitation and stream waters, sampling was conducted over two hydrological years (October 2007–September 2009). Weekly grab samples, for d^{18}O and Gran alkalinity analysis, were collected at the outlets of the four catchments. The sample sites were located at Scottish Environment Protection Agency (SEPA) gauging stations to relate samples to discharge. Daily precipitation amounts were measured by SEPA at a total of 29 sites in and around the catchments.

Precipitation samples were collected at weekly intervals at Ballater, Banchory, Aberdeen and Lunan to estimate d^{18}O inputs in precipitation by spatial and altitudinal weighting.

All samples were refrigerated until d^{18}O was measured using a gas source isotope ratio mass spectrometer. Ratios of $^{18}O/^{16}O$ are expressed in delta units, d^{18}O (‰, parts per mille) defined in relation to V-SMOW (Vienna Standard Mean Ocean Water), with an analytical precision of approximately 0.1‰. Gran alkalinity of stream waters were measured by acidimetric titration which closely approximates acid neutralising capacity (ANC); a conservative tracer useful in differentiating between acidic soil derived water sources and more alkaline groundwaters in UK catchments (Robson and Neal, 1990; Soulsby and Dunn, 2003).

The spatial characteristics of the study catchments were analysed by applying a Geographic Information System (GIS) ESRI ARCMAP. This included 10×10 m Digital Terrain Models together with digital maps of geology, land use and soils, thus providing a means to analyse how the hydrological, hydrochemical and isotopic functioning varied with landscape characteristics. Soils were mapped and grouped according to the UK's Hydrology of Soil Types (HOST) data set (Boorman et al., 1995). These were divided into responsive soils which dominate rapid runoff responses (e.g. peats, gleys, regosols etc.) and more slower responding permeable soils which facilitate deeper recharge (e.g. podzols, alluvium and brown soils).

MTT estimates were obtained for each catchment using weekly d^{18}O stream water samples and bulk precipitation samples during the observation period. The d^{18}O in precipitation for each catchment was derived using a fixed elevation correction factor of 0.25‰ per 100 m, based on the low flow stream water d^{18}O elevation gradient, which was in the range of what was reported by earlier studies (e.g. Lachinet and Patterson, 2006). For the upland-dominated Dee and North Esk, precipitation amounts were estimated from catchment-scale, GIDS interpolation (Nalder and Wein, 1998; Stahl et al., 2006), which uses catchment topography in an inverse distance weighted multiple linear regression approach, based on the SEPA ground stations. In the more lowland Don and Ythan catchments, where topographic influences on precipitation inputs are less marked, a simple average was estimated from SEPA ground stations.

Using a transit time distribution, mean catchment d^{18}O precipitation concentrations were convoluted over time as suggested by Maloszewski and Zuber (1982):

$$c_{out}(t) = \int_0^{\infty} g(S)\, c_{in}(t - S)\, dS \qquad (1)$$

where S is the transit time, t is the time of exit from the system and (t–S) represents the time of entry into the system. Thus, the d^{18}O output composition, $c_{out}(t)$, of the stream water at time t equals the integrated input concentrations from any time (t–S) in the past, weighted by the transfer function $g(S)$, which represents the time-invariant, lumped transit time distribution (TTD) of tracers in the catchment. The TTDs act as transfer functions in the convolution integral and they conceptualize the internal catchment functioning. In this case, a Gamma distribution was used as the transfer function:

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catchments in the Scottish Highlands by Hrachowitz et al. (2009a,b). The available data were looped in a 4-year cycle as asuitable time period for the modelling (cf. Hrachowitz et al., 2011).The Generalized Likelihood Uncertainty Estimation (GLUE) framework (Beven and Bingley, 1992) was used to estimateuncertainties introduced by model identifiability. Parameterswere sampled from a pre-defined uniform distribution with10,000 Monte-Carlo realizations and Nash–Sutcliffe efficiencyNSE (Nash and Sutcliffe, 1970) was used as a likelihood measure.All realizations with NSE >0.4 were retained as ''acceptable'' andused for the construction of the likelihood-weighted 90% uncertainty.

4. Results

Differences in flow regimes

Flow duration curves show that the highest variability in hydro- logical regime occurs in the North Esk with the steepest curve and lowest specific discharge below the Q_{70} (Fig. 2). At

$$g(s) = \frac{s^{a-1}}{b^{a} C(a)} e^{\left(-\frac{s}{b}\right)} \qquad (2)$$

Within the distribution, a is the shape, b is the scale parameter and C is the gamma function. As shown by Kirchner et al. (2000) using spectral analysis, the Gamma distribution model (GM) with a shape parameter a = 0.5 is the mathematically ideal representa- tion of stream signals. Previous work showed that it was the most identifiable distribution for parsimonious estimation of MTTs in high flows $>Q_5$ the specific discharge of the North Esk is only slightly lower than the Dee, which has a less steep curve. The Don and Ythan have the flattest flow duration curves, with mostly low specific dis- charges that are generally higher in the Don. However, for low flows $<Q_{80}$ the specific discharges of the Ythan and Don are higher than both the Dee and North Esk.

These flow duration curves are consistent with differences in precipitation and the landscape characteristics of the different catchments (Table 1). Highest precipitation and the highest per- centage of upland areas, dominated by hydrologically responsive soils which activate rapid flow paths, are characteristic of the Dee and North Esk. This results in high specific discharges particu- larly for lower frequency high flows. In contrast, the lowland, more-groundwater dominated Don and Ythan catchments with higher percentages of more freely draining podzols and alluvial soils appear to have greater water storage to sustain low flows via slower flow paths despite the lower precipitation. Although there is greatest groundwater storage in the deep sandstone aqui- fers of the lower North Esk catchment, groundwater fluxes seem to be compromised by the low precipitation totals and the flat topog- raphy in the lower catchment. The latter would be expected to re- sult in lower hydraulic gradients which help explain the lower specific discharges at low flows.

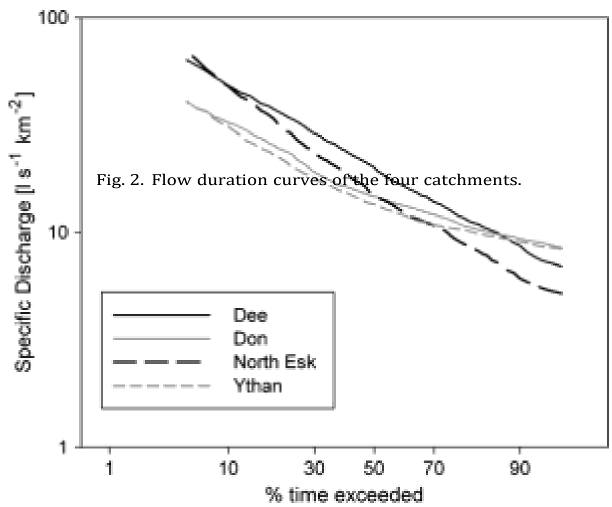

Fig. 2. Flow duration curves of the four catchments.

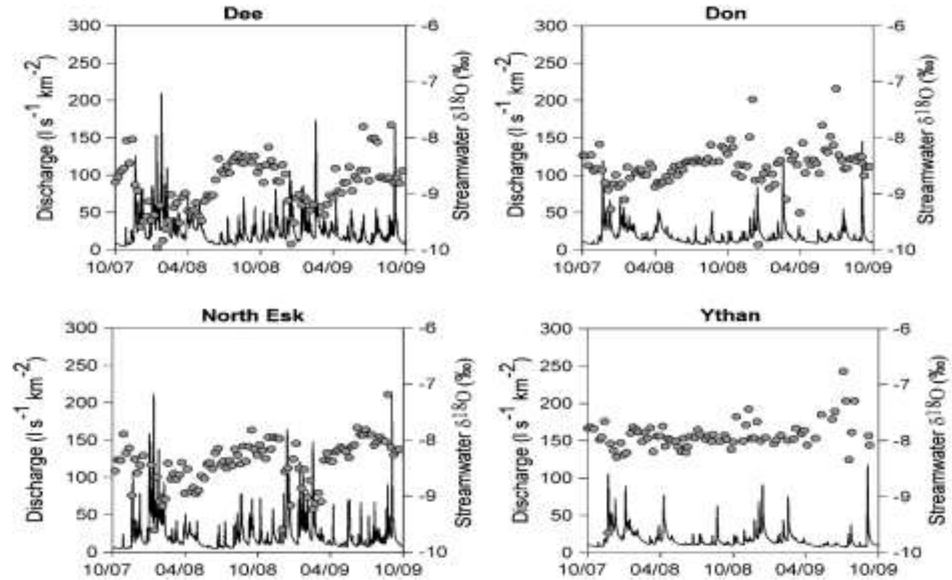

Fig. 3. Daily specific discharge and d18O in streamwater for all catchments (for October 2007–September 2009).

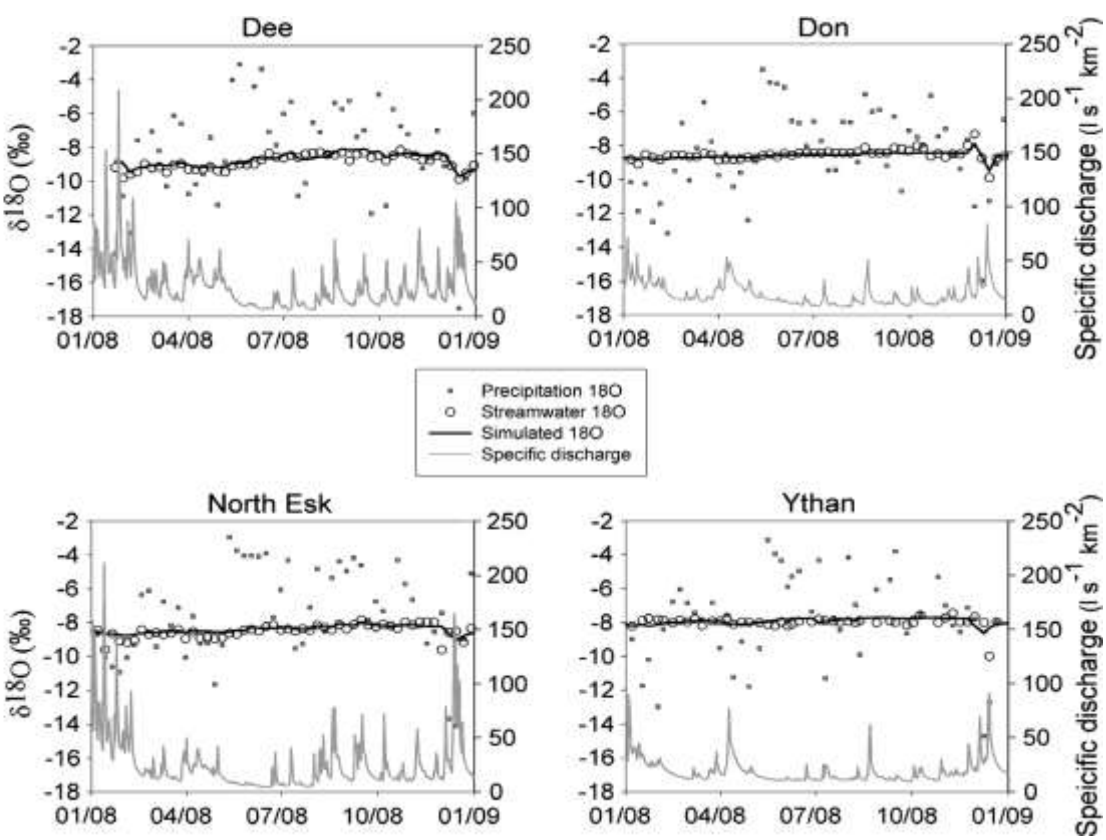

Fig. 4. Time series of d18O input and output signatures and the best fit of the modelled d18O stream signature for the behavioural models using the Gamma distribution model for each of the catchments (for year 2008).

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Table 2
Statistics of isotopic signature d18O in precipitation (*P*) and stream water (*Q*) (observation period October 2007–September 2009).

	Dee		North Esk		Don		Ythan	
	P	*Q*	*P*	*Q*	*P*	*Q*	*P*	*Q*
Mean	—7.9	—8.9	—7.8	—8.4	—8.7	—8.5	—8.2	—8.0
Max	—1.9	—7.8	—2.9	—7.2	—3.5	—7.1	—3.1	—6.8
Min	—18.7	—10.8	—14.1	—9.6	—16.7	—10.1	—14.7	—9.9
St. Dev.	2.45	0.50	2.59	0.41	2.71	0.35	2.70	0.28
95th	—3.4	—8.1	—4.0	—7.9	—4.6	—8.0	—4.3	—7.5
5th	—14.3	—9.6	—11.9	—9.1	—13.5	—9.1	—13.6	—8.3

Table 3
Summary of MTT estimations and range and gamma model parameters.

	E_{max}	a_{med}	b_{med}	MTT_{max}	5th Percentile	95th Percentile
Dee	0.63	0.557	1481	741	242	1441
North Esk	0.66	0.651	1639	953	325	1871
Don	0.56	0.511	28,790	>5000	n.a.	n.a
Ythan	0.18	0.406	28,811	>6000	n.a.	n.a

n.a. – Not definable.

Differences in hydrology and isotope response

As indicated by their flow duration curves, the hydrological responses of the Dee and North Esk are notably flashy during high flow events, with high discharges distributed throughout both of the study years (Fig. 3). Prolonged low flow periods of more than a few weeks are restricted to short spells in autumn 2007 and early summer 2008. However, the isotopic response of these two catchments to flow variability is markedly different. Precipitation inputs to both catchments exhibited seasonal variation in d18O, tending to be more enriched in summer and more depleted in the winter (Fig. 4). The stream water response in the Dee is the most isotopically depleted and the most variable with a d18O range of 3‰ and a standard deviation of 0.5 (Table 2), showing clear seasonality with depleted signatures in winter and enriched signatures in summer clearly reflecting precipitation (Fig. 3). Signature extremes occur during high flow events with contrasting precipitation inputs, especially in snowmelt in January 2008 and summer precipitation in summer 2009. Despite similar seasonal variation in d18O precipitation inputs (ca. 14.1 to 2.9‰), the isotopic response of river water in the North Esk only exhibits a d18O range of 2.4‰ and a standard deviation of 0.5 (Table 2). It is also notable that periods of depleted samples in the winters of 2007/8 and 2008/9 are shorter than those in the Dee and recover more rapidly. In addition, enriched summer events are less evident in the North Esk, especially in 2009.

Consistent with the flow duration curves, the hydrograph of the Don is less flashy than the Dee and the North Esk, though the timings of the highest flows in winter 2007/8 and 2008/9 and September 2009 are broadly similar (Fig. 3). However, the response to smaller precipitation events during summer is much more subdued, presumably reflecting the lower precipitation and greater freely draining soil cover in the lowland areas, which are likely to have higher moisture deficits. Although the general isotope response is more damped than in the North Esk – with a d18O standard deviation of 0.38, higher winter and summer flows can higher ET outputs compared to the other three catchments. The isotopic response in stream water is similarly subdued and d18O is the most enriched and remains close to —8‰ during the whole of the investigation period with a range of only 0.5‰ between the 5th and 95th percentile samples and a standard deviation of 0.28. Only very occasional extreme inputs result in very transient periods of more depleted stream water in a single sample in winter 2007 and more enriched values during summer 2009, though produce greater extremes in depleted and enriched signatures respectively.

The Ythan is characterised by the most markedly subdued hydrological response to precipitation, especially during summer. Again, this probably reflects lower precipitation inputs, greater freely draining soil cover and groundwater recharge, as well as somewhat paradoxically this gives a large overall range.

Inferring transit times from d18O data

Fitting a gamma distribution to the d18O input–output relation- ships in the four catchments had variable success in terms of con- straining MTT estimates (Fig. 4 and Table 3). In the Dee, estimates were relatively well-constrained with a highest NSE achieved (0.63) for a MTT estimated at 741 days. This captures the main sea- sonal variability quite well. In the North Esk, the maximum NSE was 0.66, giving a MTT estimate of 953 days, though minima in early and late 2008 were not well captured by the model (Fig. 4). In the Don and the Ythan, the very constrained variability in stream water d18O made modelling much more difficult and relatively few models were behavioural, particularly for the Ythan. For the Don, the models with the highest efficiencies (NSE 0.56) equate to a MTT of ca. 5000 days, but, the median of the relatively few behav- ioural models implied a MTT greater than this. For the Ythan, no models were behavioural, in terms of a NSE >0.4, largely because the stream water variability was so damped. The best fit models (which had an NSE statistic of 0.1) were ca. 7000 days; though this estimate is clearly, at best, indicative, it is consistent with a greater domination of older, well-mixed groundwater. In all cases the *a* va- lue of the gamma model was close to the theoretical ideal of 0.5 suggested by Kirchner et al. (2001) for advective–dispersive sys- tems. This also corresponds to empirical work by Godsey et al. (2010) on a major international inter-catchment comparison study looking at input–output relationships for conservative tracers.

Insights from dual tracers

Using alkalinity as a geographic source tracer has proved highly complementary to using isotopes as time domain tracers in terms of understanding catchment runoff processes and mixing (Birkel et al., in press). In all four catchments, alkalinity is inversely corre- lated with flow (Fig. 5). In the Dee alkalinity is low; high flow val- ues are close to zero and low flow concentrations are ca. 400 leq l−1. This reflects acidic soil waters which mix with rela- tively poorly buffered groundwater in the granitic/metamorphic- dominated catchment (Tetzlaff and Soulsby, 2008). The North Esk is characterised by high flow alkalinities of ca. 200 leq l−1, but base flows reach 1000 leq l−1. Here, acid soil waters from the catchment's headwaters, which are similar in composition to those in the Dee, mix with relatively mineralised groundwater from deep sandstone aquifers in the lowland part of the catchment (Ó Dochartaigh et al., 2006; Capell et al., in press). Acidic upland

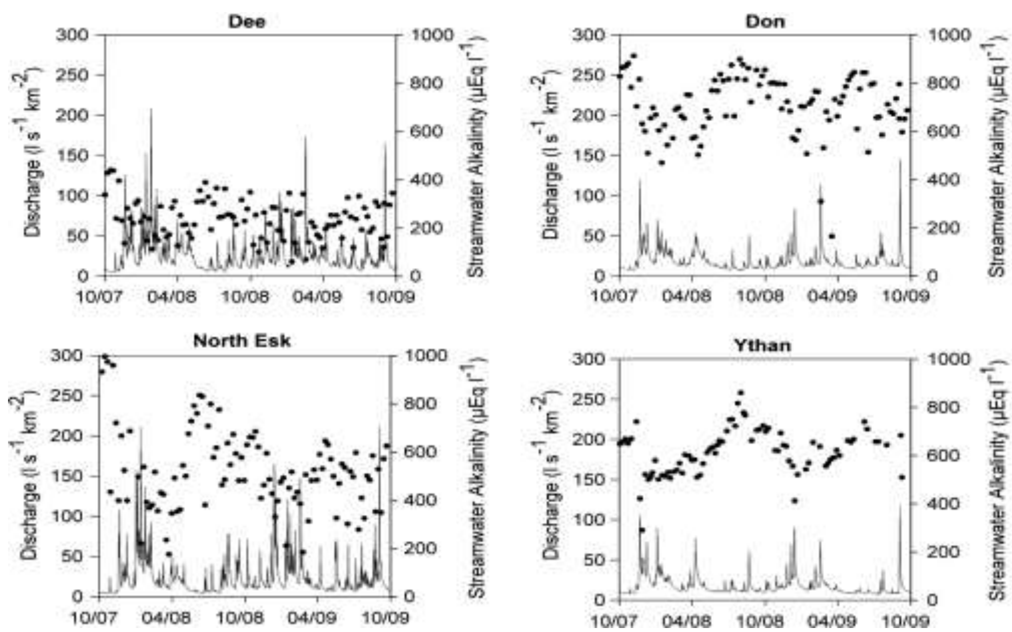

Fig. 5. Daily specific discharge and alkalinity for all catchments (for October 2007–September 2009).

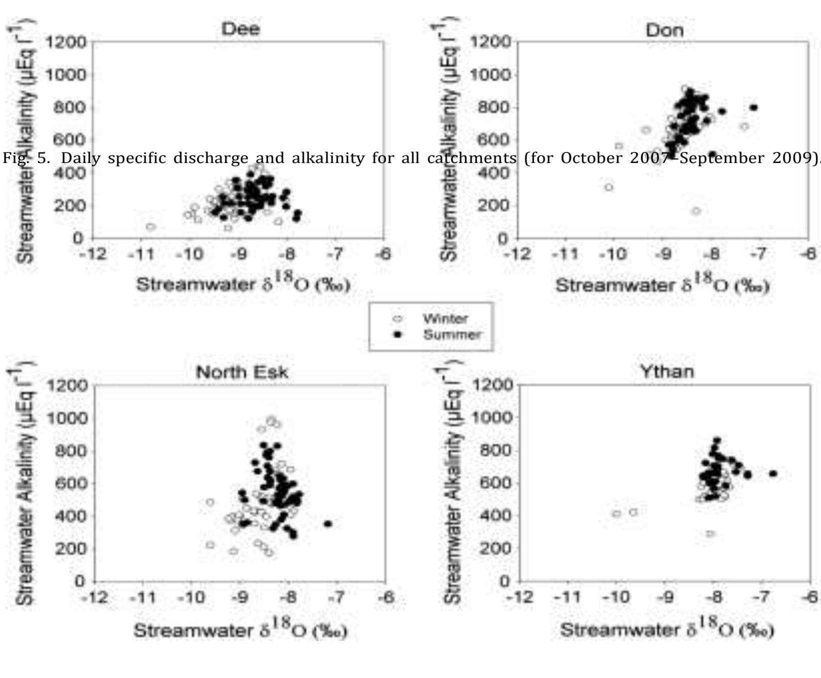

Fig. 6. Mixing plots for streamwater d18O (‰), showing flow (alkalinity, leq l^{-1}) related variation for all catchments.

soil waters dominate high flows, but their influence decreases in drier periods as the relative importance of lowland groundwater increases. In the Don high flows are well-buffered; concentrations fall below 300 leq l^{-1} only once in a large, rapid snowmelt in February 2009 while baseflows are ca. 900 leq l^{-1}. This is consistent with the presence of base-rich geology in parts of the catchment, and its influence on soil acidity and groundwater buffering, even when upland headwaters influence storm runoff (Soulsby et al.,

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2003). The Ythan is most seasonal in its alkalinity response reflecting the marked seasonality in its hydrological regime. It may also reflect high concentrations of agricultural pollutants in the Ythan.

In Fig. 6, d^{18}O is plotted against alkalinity for each of the sites to infer the relationship between sources of runoff, their temporal dynamics and the degree of mixing. From Fig. 5, it is clear that the highest alkalinities reflect baseflows in all catchments with intermediate d^{18}O levels consistent with well-mixed groundwater sources. However, low alkalinity waters with depleted d^{18}O signatures generally show winter high flows while low alkalinity with enriched d^{18}O signatures rather reflect summer high flows. The plots for Dee and North Esk are roughly triangular in shape, though the Dee has a broader base reflecting the higher variability in d^{18}O at high flows. Both catchments also show a greater frequency of higher flows in winter when d^{18}O is depleted. In contrast, the Don and Ythan are much more constrained for d^{18}O across a range of alkalinities, consistent with greater mixing of precipitation inputs reflected in Fig. 3. For both the Don and Ythan, occasional samples, collected at high flows in winter and summer, had extreme d^{18}O values. In the Don catchment, these most frequently corresponded with more moderate events where alkalinities were still relatively high, whereas in the Ythan the extremes tended to be in winter high flows. Both catchments, although intensively cultivated, have large areas of minerogenic gley soils which are prone to overland flow generation in precipitation events. Connection of such areas to the channel network is often facilitated by agricultural drainage (Birkel et al., 2010) and this probably contributed to the rare, extreme values.

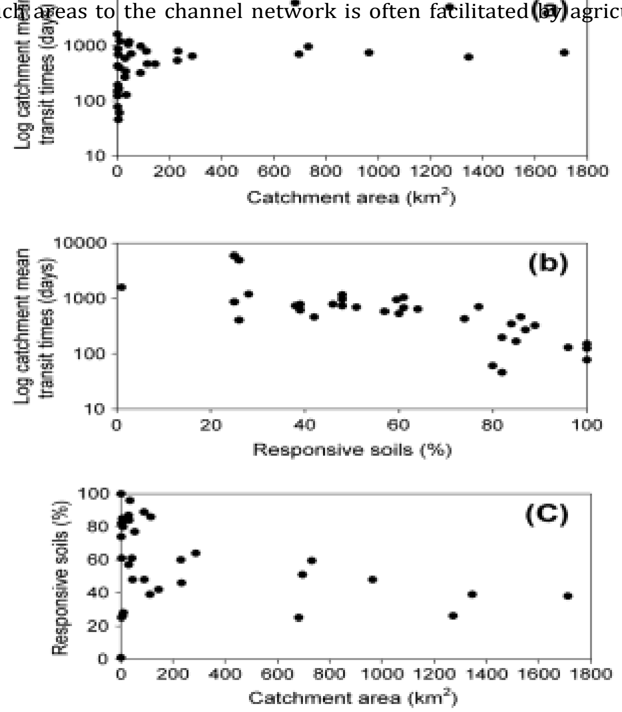

Fig. 7. Integration of data from this study with the data from Hrachowitz et al. (2010) for Scottish catchments to show the relationships between (a) catchment size and estimates of MTT; (b) percentage of responsive soils and estimates of MTT; and (c) catchment size and percentage of responsive soils.

Comparison to other MTT studies in Scotland

Despite the tentative nature of the estimates for the Don and Ythan, Fig. 7a shows the MTT results for the four catchments plotted against the relatively well-constrained estimates for ca. 50 other Scottish sites derived by Hrachowitz et al. (2009b, 2010). These covered a range of scales, though they are mostly in Highland catchments with limited anthropogenic influence. Furthermore, these estimates were mainly carried out for surface water dominated catchments without major aquifers and estimated MTTs varied from 1–2 months to over 4 years. Whilst results for the Dee and North Esk fall within this range, the Don and Ythan appear to have much greater MTTs consistent with their more stable, well-mixed water sources and greater ground-water influence. Despite this, there remains a strong relationship between MTT and percentage responsive soil cover when the larger scale sites are included (Fig. 7b). This is probably because of the general tendency, in this particular geomorphic province, for responsive soil cover to decrease as the proportion of lowland areas in catchments increases and the influence of montane headwaters decreases accordingly (Fig. 7c).

5. Discussion

This study sought to extend our knowledge of MTT estimates beyond smaller experimental catchments to larger river basin scales. It also shifted focus from headwater catchments in the Scottish Highlands to lowland environments with increased groundwater stores and greater anthropogenic influences on land use. In montane catchments with responsive soil cover, high drainage densities, steep topography and high rainfall intensities, MTTs are relatively short (Fig. 7). These are typically less than 2 years and in some cases just a few months (Hrachowitz et al., 2009b). In the case of the Dee, it is clear that such headwater catchments still dominate the hydrology of the river downstream and result in a 2-year transit time at the most downstream sampling site (Hrachowitz et al., 2010). The North Esk data imply a subtle change as lowland groundwater mixes with water from more montane headwaters to increase the MTT to almost 3 years. The low precipitation in the lowlands, coupled with higher evaporation, results in modest groundwater recharge. Thus, fluxes of groundwater – which has been dated with CFCs as having a residence time of around 30 years (Ó Dochartaigh et al., 2006) – into the river result in a relatively limited dilution of the much larger volumes of ''younger'' runoff derived from the catchment headwaters which underlines the downstream ''ecosystem service'' provided by small upland aquifers in montane environments (Capell et al., in press). The damped d^{18}O response in the Don catchment shows the opposite effect, with groundwater inflows from the larger lowland part of the catchment, moderating much of any variability in response from the upland headwaters. The influence of winter precipitation and snowmelt from the headwaters is apparent in the depressed d^{18}O signatures during the winter of both years, but summer high flows have a much more muted response. Despite uncertainty over the resulting MTT estimates, it is clear from the d^{18}O damping in stream water relative to precipitation, that they are likely to be much longer than those for the Dee and North Esk. This is consistent with previous work using water isotope in a 14 km^2 agricultural tributary of the Don which tentatively sug- gested MTTs in excess of 5 years (Soulsby et al., 2003). The Ythan, lacking any montane headwater influence, has the most stable d^{18}O time series. However, occasional extreme values can occur in large events, or smaller events when baseflows are low, both of which can translate the precipitation isotope signature rapidly into the stream. This probably reflects the influence of areas of overland flow, or where agricultural drainage can route precipitation rapidly to streams when intensities are high (Birkel et al., 2010). Nevertheless, the overall MTT is likely to be greater than 10 years.

These new results from larger catchments indicate that the multivariate models used to predict MTTs in upland catchments (e.g. Hrachowitz et al., 2010) cannot be extended into the Scottish lowlands. The greater influence of groundwater inputs weakens the significance of the influence of topographic controls and differences in precipitation intensity on MTTs. Nevertheless, the importance of soil hydrology clearly remains (Fig. 7b) in this part of Scotland where freely draining soils overlay lowland aquifers and facilitate recharge. At these larger scales, the correlation between catchment area and increasing cover of freely draining soils (Fig. 7c) begins to suggest a stronger positive correlation between catchment size and MTT, though the lack of larger catchments in the relatively small area of the North East Scotland precludes testing this hypothesis.

The inability of conservative tracers, such as stable isotopes, to constrain MTT estimates beyond around 4 years highlights the importance of using other tracers for estimating longer residence times in catchments where a large component of the runoff is old. The long memory of catchments to conservative tracer inputs was highlighted by Kirchner et al. (2000), and it has recently been re-emphasised that in catchments with longer transit times other tracers such as ^{3}H may be needed to avoid misleading truncation of the TTD and erroneous MTTs (Stewart et al., 2010). However, for MTTs up to 3 years, ^{3}H and ^{18}O have been shown to give comparable results (Rank et al., 1998; Koeniger et al., 2009). Nevertheless, it is clear that a major challenge in using tracers to upscale process understanding in larger catchments with significant ''old'' water contributions is to integrate insights from conservative tracers such as stable isotopes which label more recent waters and those which date older waters (McDonnell et al., 2010).

Such integration would seem essential for advancing understanding of how water moves through larger heterogeneous catchments and integrates with upscaling. In addition to being an essential prerequisite to fundamental process understanding in catchment hydrology, such insights are crucial in many applied aspects of hydrology. Perhaps most obviously, transit times of water within the catchment landscape are often closely correlated with the clean up time needed for natural attenuation of diffuse pollutants such as nitrate which have accumulated in different catchment sources waters (Dunn et al., 2010). However, transit times may also have a wider utility as metrics of hydrological function. For example, Soulsby et al. (2010a) show how there can be strong correlations between MTTs and hydrometric design statistics such as the mean annual flood or the Q_{95} of catchments. As MTT can be, in certain situations, reliably predicted from catchment characteristics for ungauged basins, particularly in upland environments, it may be a useful tool for estimating design flows from different landscape types in terms of flood risk or water resource provision (Soulsby et al., 2010b). Clearly extending such analysis to lowland landscapes would require better constraints on MTTs for older groundwaters, but it would appear that the potential utility of transit times would warrant further investigation in larger heterogeneous catchments.

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