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Land cover influence on catchment scale subsurface water storage investigated by multiple methods: Implications for UK Natural Flood Management

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ABSTRACT

Study region: United Kingdom (UK).
Study Focus: 'Natural flood management' (NFM) schemes manipulating land use and other catchment features to control runoff are increasingly promoted across the UK. Catchment water storage and mixing processes influence runoff, but our understanding of the effects of land cover change on these processes is still limited. This study combined hydrometric, isotopic and geochemical measurements to investigate land cover versus potential topographic, soil and geological controls. It compared storage-discharge dynamics in nine nested catchments within a 67 km^2 managed upland catchment in southern Scotland. Storage and mixing dynamics were characterised from hydrometric data using recession analysis and from isotopic data using mean transit time and young water fraction estimates. To give information on water sources, groundwater fraction was estimated from end member mixing analysis based on acid neutralising capacity.
New hydrological insights: The analysis showed low but variable sub-catchment scale dynamic storage (16–200 mm), mean transit times (134–370 days) and groundwater fractions (0.20–0.52 of annual stream runoff). Soil hydraulic conductivity was most significantly positively correlated with storage and mixing measures, whilst percentage forest cover was inversely correlated. Any effects of forest cover on increasing catchment infiltration and storage are masked by soil hydraulic properties even in the most responsive catchments. This highlights the importance of understanding dominant controls on catchment storage when using tree planting as a flood management strategy.

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1. Introduction

The way in which catchments store, mix and release water has a strong influence on runoff mechanisms and the flow paths water takes from hillslopes to streams. Understanding controls on catchment storage and mixing is therefore fundamental to improving our knowledge of catchment hydrological processes (McNamara et al., 2011). Indeed it has been suggested that this could help address fundamental challenges in hydrology, such as bridging across scales (Spence, 2010) and underpinning improvements in hydrological modelling (Birkel et al., 2015). It could also help in developing new and more unified theories of hydrological processes in the critical zone, which converge on a need to understand the amount and residence time of subsurface water (Brooks, 2015). Quantifying these processes is also crucial from an environmental management perspective, including the regulation of stream flow, contaminant transport, predicting the impacts of land use, climate and ecological changes, and understanding catchments' "hydrologic resistance" to change (Carey et al., 2010).

Many studies have investigated the controls on catchment storage and mixing inferred through hydrometric, isotopic and hydrochemical data. Hydrometric approaches have used various forms of recession analysis (Birkel et al., 2011; Kirchner, 2009) or water balance approaches to estimate "dynamic" storage (Sayama et al., 2011) or "total" storage (Pfister et al., 2017). Studies using isotopic and other tracers (e.g. chloride ions) have often used metrics such as mean transit time (MTT) (McGuire and McDonnell, 2006), young water fraction (Kirchner, 2016), and other measures of isotopic damping (Tetzlaff et al., 2009a) to infer storage and mixing dynamics (Ali et al., 2012), and quantify partitioning between surface and subsurface stores (Klaus and McDonnell, 2013). Nevertheless, few studies have attempted to combine all these measures to relate storage estimates based on water balance methods with estimates derived from conservative tracers (Buttle, 2016).

These investigations into storage and mixing processes have identified a wide range of process controls including bedrock geology (Capell et al., 2011; Cartwright et al., 2018; Hale and McDonnell, 2016; Haria and Shand, 2004; Pfister et al., 2017), soil type and depth (Dunn et al., 2008; Muñoz-Villers et al., 2016; Soulsby et al., 2006b; Tetzlaff et al., 2007b), topography (Buttle, 2006; McGlynn et al., 2003; McGuire et al., 2005), and land use change and urbanisation (Ma and Yamanaka, 2016; Soulsby et al., 2015; Yu et al., 2019). They have also highlighted the non-stationarity of storage and mixing processes, meaning that the relative importance of different controls may vary with time (Geris et al., 2015). Many studies have been conducted in catchments with limited human impacts, but there is increasing recognition that land management could alter some of these controls (Dimitrova-Petrova et al., 2020). Understanding these processes in catchments subject to human induced changes is therefore crucial, given the complex and scale-dependent nature of the changes, combined with increasing pressures of urbanisation, agricultural intensification and climate change on catchments worldwide (Bosmans et al., 2017).

One fundamental challenge in this area surrounds the relationship between forest cover change and other catchment properties that control runoff mechanisms. Vegetation has been shown to influence the fluxes, flow pathways and timing of water movement through soils, through impacts on interception, evapotranspiration, throughfall, infiltration, and rooting systems altering soil hydraulic properties (Thompson et al., 2010; Zimmermann et al., 2006). The effects of forest cover on subsurface storage can be significant, particularly through enhanced infiltration rates that enable water to pass into soil storage (Archer et al., 2013); enhanced connection to groundwater storage (e.g. through penetrating compacted soil horizons) (Neal et al., 1997a); enhanced soil porosity to greater depths than other vegetation types (Peña-Arancibia et al., 2019); and seasonal pumping effects of evapotranspiration (Ellison et al., 2012). At the catchment scale, impacts of vegetation cover on catchment runoff have mainly been explored through paired catchment studies (PCS). Despite decades of research, reviews of PCS have generally concluded that the influence of forest cover on catchment hydrology is unclear and unpredictable, leading to an inability to generalise their results (Barrientos and Iroumé, 2018; Goeking and Tarboton, 2020). It has been suggested that one of the key reasons for such variable effects may be due to a lack of understanding of subsurface storage and how this interacts with forest cover change and other factors such as geology and soil type to influence runoff response (McDonnell et al., 2018). Concepts of subsurface storage have arguably been overlooked in conceptual models of catchment forest treatment response (Barrientos and Iroumé, 2018). This underlines the importance of investigating human induced changes to catchments from a storage and mixing perspective, and in understanding their relative importance compared to other catchment properties (Geris et al., 2015).

From a practical perspective, understanding the links between land use change and other properties that control catchment storage, mixing and release, is not only important in quantifying unintended human impacts on catchment hydrological processes, but also increasingly in evaluating the efficacy of planned catchment-wide interventions to manage hydrological response. 'Green infrastructure' projects in the water resources sector, often focussed on catchment land management, are now being mainstreamed into national and local policy in many countries (EEA, 2017; World Bank, 2018). In the UK, for example, 'Natural Flood Management' (NFM) has become a key aspect of national flood risk management strategies, with a growing number of schemes being established nationwide (Kay et al., 2019). NFM promotes a number of different measures for controlling runoff, including those aimed at water retention in the landscape through the management of infiltration and overland flow, managing connectivity and conveyance within rivers, and increasing floodplain water storage (Dadson et al., 2017).

Forest and woodland planting is now widely promoted as an NFM strategy based on the following hydrological processes: 1) the potential for trees to intercept precipitation and reduce water fluxes to rivers; 2) enhancing infiltration and 'creating' subsurface storage, and; 3) slowing the conveyance of water (Environment Agency, 2017; Geris et al., 2015; Lane, 2017). The second suggested alteration in processes raises questions about the primary controls on catchment storage, the degree to which forest cover can influence catchment storage, and how these controls might vary through space and time.

To our knowledge there have been few studies investigating catchment scale storage and mixing processes in an NFM context. Storage and mixing processes are hard to measure, but by combining hydrometric and tracer based methods new insights can be gained

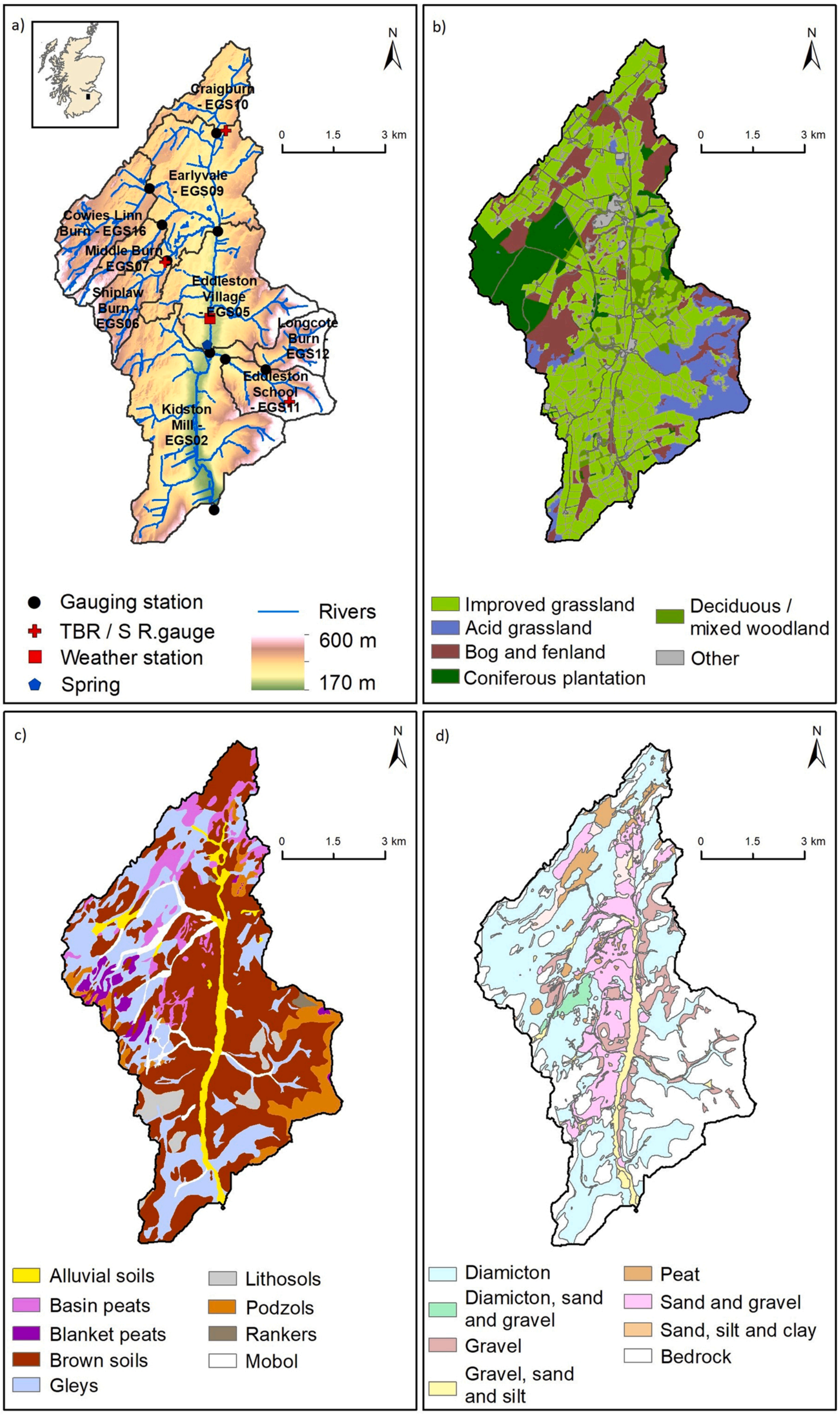

Fig. 1. a) The Eddleston Water location and map showing catchment topography, the river network, monitoring network, and the nine sub-catchments examined in this study. TBR / S R.gauge: paired tipping bucket rain gauges and storage rain gauges used in the study. Base mapping derived from Ordnance Survey (2016). b) Land cover map of the Eddleston Water catchment with simplified land cover classification based on Medcalf and Williams (2010). Due to the low percentage of deciduous woodland in the catchment, woodland was grouped into a single woodland category for analysis. c) Soil map showing major soil groups (MSG) in the Eddleston Water catchment. 'Mobol' is 'Mixed Bottom Land' as defined in the 1:25,000 soil map of Scotland (Soil Survey of Scotland Staff (, 1970–, 1987)). d) Superficial geology map of the Eddleston Water catchment based on survey conducted for the Eddleston Water NFM project in 2011 (Auton, 2011). Mapping units are based on the British Geological Survey Rock Classification Scheme.

(Geris et al., 2015). This paper quantifies catchment water storage and identifies key controls on catchment storage and mixing using combined hydrometric and tracer-based approaches in an NFM context. Storage estimates are made with both hydrometric data using recession analysis and isotope data based on transit time calculations, whilst mixing processes are evaluated through estimates of transit times and groundwater fractions. The focus is on the relative role of vegetation cover compared to soils and geology, to give insights into the potential impacts of forest cover change on runoff mechanisms. We investigated this through a cross-catchment comparison of nine sub-catchments sharing similar bedrock geology, but with varying superficial geology, soils and land use. The catchment is an important UK NFM pilot site and the relatively dense hydrometric monitoring network, paired with tracer data and new data on superficial geology, enabled investigation using methods that have not been widely applied in a flood management context in the UK.

The questions addressed by the study were:

1. What are the subsurface water storage capacities of different upland catchments?
2. What are the primary catchment characteristic controls on catchment water storage and mixing?
3. Does land cover have a discernible impact on catchment water storage and mixing?

2. Methods

The research focussed on nine sub-catchments of the 67 km^2 Eddleston Water river catchment in the Scottish Borders, UK (Fig. 1a), which is typical of many northern temperate upland catchments. The catchment has variable forest cover (with some sub-catchments extensively forested and others with minimal cover), variable soil types and an extensive hydrological monitoring network, making it ideal for investigating the variability of storage in the catchment and its relationship to land cover. It is the site of a major NFM pilot project aiming to inform national and European water policy (under the EU Water Framework Directive and EU Floods Directive) (Tweed Forum, 2019; Werritty et al., 2010). We used hydrometric, isotopic and acid neutralising capacity (ANC) sampling data to quantify water storage and mixing dynamics in the different sub-catchments and compared these with GIS-derived metrics of catchment topography, land cover, soils and geology to investigate controls on storage.

2.1. Study site

Elevation ranges between 180 and 600 masl across the Eddleston Water catchment. At Eddleston Village mean annual precipitation (2011–2017) is ~900 mm, falling mainly as rainfall; monthly mean air temperatures are 3–13 °C; and actual daily evapotranspiration ranges from 0.2 mm in winter to 2.5 mm in summer (estimated using methods of Granger and Gray, 1989 from weather station data at Eddleston Village).

Land cover (Fig. 1b) is mainly improved or semi-improved grassland on the lower slopes, rough heathland at higher elevations and marshy ground in hollows (Medcalf and Williams, 2010). Forest cover was historically limited in most of the catchment, but extensive coniferous plantations (primarily Sitka spruce, *Picea sitchensis*) were established in the 1960 s and 1970 s in some of the western sub-catchments, with up to 90% forest cover (Fig. 1b) (see Peskett et al., 2021 for a more detailed description of forestry practices). Forest cover in other parts of the catchment is typically mixed coniferous and deciduous woodland, concentrated along field boundaries.

Soils in the western sub-catchments include extensive areas of poorly permeable gley soils and peats, but also areas of more freely draining brown soils, whilst the east is dominated by brown soils with some peaty and gley soils on hilltops (Fig. 1c). Soil median field saturated hydraulic conductivities measured in the wider catchment in a separate study (Archer et al., 2013) were 0.50–0.94 m d^{-1} for improved grassland sites, 1 m d^{-1} for ~50 year old plantation forest, and 2.86–4.18 m d^{-1} for broadleaf forests > 180 years old. Soils and underlying geology are strongly associated. The western catchments are dominated by poorly permeable glacial till (Aitken et al., 1984) with pockets of permeable glacio-lacustrine sands and gravels (Fig. 1d). The estimated hydraulic conductivity of the glacial till is < 0.001–1 m d^{-1} (MacDonald et al., 2012). The eastern catchment is mostly rock head overlying bedrock, with smaller areas of glacial till mantling some of the main streams. The hydraulic conductivity of the Silurian greywacke bedrock was not measured, but Silurian greywacke aquifers elsewhere in southern Scotland have low productivity (Ó Dochartaigh et al., 2015), with an estimated average transmissivity of 20 m^2 d^{-1} (Graham et al., 2009).

2.2. Field methods

2.2.1. Hydrometric monitoring

Rainfall has been measured since April 2011 at four locations using stainless steel Octapent storage rain gauges and tipping bucket rain gauges (RIM8020) recording at 15-minute intervals and in increments of 0.2 mm (Fig. 1a). Air temperature, solar radiation, relative humidity and wind speed and direction have been measured at the same frequency over the same period at a weather station (Campbell CR1000 Automatic Weather Station) located at the centre of the catchment (Fig. 1a).

Stream water levels have been measured every 15 min (Hobo U20 0–3.5 m unvented pressure-based water level recorders) in each catchment since April 2011, except for Cowieslinn sub-catchment where gauging began in 2014. Discharge was calculated at the same time step using rating curves derived from applying the mid-section method (Dingman, 2014) to velocity-area gauging at natural rated sections approximately eight times a year under a range of conditions. We calculated several hydrograph response metrics for the whole time series (October 2011-September 2016) as part of our initial data analysis. These included: median daily runoff (Median_R);

standard deviation in daily runoff (SD_R); coefficient of variation in daily runoff (COV_R); mean annual peak runoff (MAPR); mean annual minimum runoff (MAMR); Richards-Baker flashiness index (RB), calculated according to Baker et al. (2004); and Baseflow index (BFI) calculated according to Gustard et al. (1992).

2.2.2. Rainfall and stream water sampling for isotopic and geochemical analysis

Water samples for isotopic and geochemical analysis (^{2}H, ^{18}O, acid neutralising capacity (ANC), conductivity, pH) were collected for analysis on a weekly basis between 2 September 2015 and 26 August 2016. Three storage rain gauges, nine rivers, and one spring were sampled. The samples for isotopic analysis were collected in two dry 15 mL HDPE sample bottles, with the second as a backup sample. Samples for geochemical analysis were collected in 1 L HDPE bottles that were rinsed three times with sample water before collection and then filled completely with minimal headspace. Rainfall samples for isotopic analysis were collected directly from the Octapent storage rain gauges to minimise any contamination. Given that the collectors were buried (~0.5 m depth), have a minimal aperture (~15 mm), are in a region with low average temperatures and high humidity, and weekly collection was undertaken, no further evaporation prevention measures were put in place. However, prior to sampling for this study, we checked for evidence for evaporation using data from 10 previous sampling rounds carried out during summer 2015. These data showed no significant deviation of δ^{18}O and δ^2H values compared to the Local Meteoric Water Line (LMWL).

River water samples were collected as grab samples from locations close to the gauging stations, away from any inflows and as far from the bank as possible. The spring water sample was collected from a spring close to the Eddleston Village river gauge and at the site of detailed floodplain and hillslope hydrogeological research described in Ó Dochartaigh et al. (2018) and Archer et al. (2013). Conductivity of river water samples was measured in-situ using a Mettler Toledo conductivity meter, whilst pH was measured in the laboratory using a Fisherbrand Hydrus 300 pH meter prior to titration for ANC determination.

2.3. Laboratory methods

Precipitation and stream samples were analysed for H and O isotope compositions using a Los Gatos Research liquid water Off-Axis Integrated-Cavity Output Spectroscopy (Off-Axis ICOS) laser absorption spectrometer at the University of Saskatchewan, Canada. We used standard analytical methods (IAEA, 2009) and report δ^2H and δ^{18}O values relative to V-SMOW; precision was ± 1.0‰ and ± 0.2‰, respectively.

Table 1

Summary of the topographic, soils, geology and land cover metrics selected to compare catchment hydrology. Drainage density (T_DD) was calculated as the total length of all rivers / area. Topographic wetness index (T_TWI) was calculated as ln(a/tan B), where a is upstream contributing area in m^2 and B is local slope (see e.g. Ali et al., 2012). HWC_1/2: HOST wetness classes 1&2/3&4; G_Di/G_SG: Diamicton and Sand and Gravel. LU_Gi/LU_F/LU_M: Land use improved grassland/Plantation Forest/Modified bog and fenland.

Variable	Code	Kidston (EGS02)	Eddleston (EGS05)	Earlyvale (EGS09)	School (EGS11)	Cowieslinn (EGS16)	Craigburn (EGS10)	Shiplaw (EGS06)	Longcote (EGS12)	M. Burn (EGS07)
Topographic indices										
Area (km^2)	T_A	59.5	35.3	25	6.8	5.6	3.5	3.1	2.7	2.4
Drainage density (km km^2)	T_DD	0.0008	0.0009	0.0012	0.0012	0.0030	0.0032	0.0031	0.0020	0.0027
Topographic wetness index (ln (m))	T_TWI	6.39	6.6	6.79	5.86	6.97	7.02	6.51	5.69	6.69
Soils (% cover)										
HOST wetness 1&2	HWC_1	56.7	49.8	37.1	80.2	26.9	57.0	35.4	78.4	11.6
HOST wetness 3&4	HWC_2	23.5	23.1	26.8	8.1	30.5	9.1	22.9	8.1	18.1
Geology (% cover)										
Glacial till and peat	G_Di	43.4	51.8	60.9	12.0	72.3	66.8	62.6	8.0	75.9
Sand and Gravel	G_SG	23.8	28.1	22.6	7.8	9.1	7.0	16.0	8.3	12.1
Land cover (% cover)										
Improved and semi-improved grassland	LU_Gi	54.5	51.4	45.0	29.0	38.6	58.9	28.4	10.7	2.4
Woodland – all	LU_F	16.1	24.3	26.5	0.5	37.7	3.8	41.0	0.5	94.3
Dry/wet modified bog and fenland	LU_M	15.0	16.9	21.2	10.6	18.5	31.2	26.6	22.2	0.0

ANC was determined in stream water samples using acidimetric titration with H_2SO_4 in accordance with Rounds (2012) to end-points of pH 4.5, 4.1, 4.0 and 3.5 within 48 h of returning from the field. In natural waters where aluminium concentrations are low this method has been shown to give a good approximation of ANC (Neal, 2001).

2.4. Landscape analysis

Landscape analysis comprised investigation of topographic, geological, soil and land use metrics of potential hydrological importance using existing 5 m x 5 m resolution datasets in ArcMap 10.3. Topographic data were derived from Ordnance Survey maps (Ordnance Survey, 2016). Geological data were derived from a 1:25,000 geological map of the catchment produced for the Eddleston Water flood management project by the British Geological Survey (BGS). Soils data were derived from the 1:25,000 soils map of Scotland (Soil Survey of Scotland Staff, 1970). Land cover data were derived from a 2010 survey commissioned by the Scottish Borders Council (Medcalf and Williams, 2010) with corrections to plantation forest area estimated from more recent Google Earth aerial imagery.

The analysis of soil types was based on the 'Hydrology of Soil Types' (HOST), which classifies soils according to their hydrological properties (Boorman et al., 1995) and has been used in a number of studies investigating landscape controls on catchment mixing processes (e.g. Hrachowitz et al., 2009a; Tetzlaff et al., 2007b). It is directly related to soil type as the HOST class codes are linked to each soil type classification. HOST Classes 1 and 2 are freely draining soils (e.g. brown earths); Classes 3 and 4 are medium draining (e.g. gleyed mineral soils); and Classes 5 and 6 are poorly draining (e.g. peats and gleys).

The number of variables in the landscape analysis dataset was initially simplified through re-categorisation of variables to reduce the number within the geology, soil HOST class and land cover groups. A correlation matrix constructed using Spearman rank's correlation coefficient was used to check for co-linearity between independent variables (Table S1.1). Most co-linear variables were removed, except for those with high catchment coverage or of relevance to the study. Table S1.2 describes the independent variables used in the final analysis and their rationale for inclusion. A summary of final metrics is given in Table 1.

2.5. Calculation of transit times, storage and groundwater fraction

2.5.1. Mean transit time and fraction young water calculations

The relationship between the seasonal variation in isotopic composition of rainfall inputs and the variation in river water outputs was used to estimate catchment mean transit time (MTT) (McGuire and McDonnell, 2006). In this method, seasonal variations in δ^2H and $\delta^{18}O$ are approximated to a sinusoidal seasonal signal and the regression coefficients used to estimate the amplitude and phase lag. We assumed a catchment transit time distribution governed by an exponential flow model for an open, unconfined aquifer system in each of the sub-catchments and used this to calculate the transit time parameter of the exponential flow model (see S1.2 for summary of methodology). Studies have shown that this method provides similar estimates of MTT compared to more complex transit time distribution models when applied in upland Scottish catchments (Tetzlaff et al., 2009b). A number of studies have also demonstrated the utility of MTT estimates for giving an 'indicative estimate' of mean transit times and, when combined with discharge data, a proxy for catchment storage (Soulsby et al., 2006b; Soulsby et al., 2009).

Applying such residence time models to stream water data requires several assumptions that have been widely reviewed (McGuire and McDonnell, 2006) and we discuss briefly in the context of this study in S1.2. MTT estimates can be subject to large errors due to aggregation bias in heterogeneous catchments. This problem occurs because of the strong nonlinearity between the tracer cycle amplitude and mean travel time (Kirchner, 2016). We therefore also calculated the 'young water fraction' (F_{yw}) as an alternative metric (see S1.2) – the proportion of catchment outflow younger than ~2.3 months. This is less subject to aggregation bias and has been used in more recent cross catchment comparison studies (Dimitrova-Petrova et al., 2020; Jasechko et al., 2016). In practice the cross comparisons in this study using either MTT or F_{yw} gave similar results, so only those based on MTT are discussed. This also enabled comparison with results from similar studies in Scotland that have used MTT.

Uncertainty in both MTT and F_{yw} was estimated based on 95% confidence intervals for the parameters obtained from the model used to fit the isotopic data.

2.5.2. Dynamic storage

Catchment dynamic storage (S) was estimated for each sub-catchment using the discharge sensitivity approach developed by Kirchner (2009), which assumes that discharge depends entirely on storage in the catchment (see S1.3 and S1.4 for a summary of the methodology). This assumption has been found to be a valid approximation in catchments with similar properties to the study area. For example, Kirchner (2009) showed that it holds for the Plynlimon catchments in Wales with similar properties to those in Eddleston. The same approach has also been applied elsewhere in Scottish catchments (Birkel et al., 2011). In this method, least squares regression of the relationship between recession rate and discharge, often expressed as a power law relationship, is used to estimate the coefficients of the relationship between storage and discharge. Whilst there are many ways of filtering data in this fitting process (Stoelzle et al., 2013), we used the approach in Kirchner (2009) to maximise the data available and to reduce bias.

Uncertainty in storage estimates was calculated based on 95% confidence intervals for the parameters obtained from the model used to fit the $-dQ/dt$ vs. Q data.

2.5.3. Groundwater fraction

ANC-discharge relationships were determined for each river sampling location and fitted using non-linear least squares regression based on a power law relationship, as in other studies (Capell et al., 2012). The data were also used to develop end members for a simple two-component mixing model for each catchment to estimate the groundwater fraction in runoff during the sampling period:

$$F_{gw} = \frac{A_r - A_s}{A_r - A_{gw}} = \frac{Q_{gw}}{Q_t} \tag{2.5.3}$$

where F_{gw} is groundwater fraction, Q_t is stream discharge, Q_{gw} is groundwater discharge, A_s is ANC of stream discharge, A_r is ANC of surface runoff end member, and A_{gw} is ANC of groundwater end member. Hydrograph separation relies on a number of assumptions and has limitations that have been extensively reviewed elsewhere (Klaus and McDonnell, 2013). Despite its limitations, tracer-based hydrograph separation is considered more objective than separation methods based on hydrometric data alone and provides a useful first approximation of runoff components operating at the catchment scale (Klaus and McDonnell, 2013).

The groundwater end member was defined as the mean ANC of the five lowest flows in each sub-catchment for the period September 2015-August 2016 (based on weekly sampling) similar to other studies (Neal et al., 1997b; Soulsby et al., 2003). The surface runoff end member was defined as zero, as this approximates the ANC of rainfall. The stream water end member was taken as the ANC at the time of sampling. Uncertainty in the groundwater fraction was estimated based on 95% confidence intervals for the regression parameters obtained from the models fitted for the ANC-discharge relationships.

2.6. Relating transit times, storage and groundwater fraction to catchment characteristics

Spearman rank correlation was used to analyse relationships between MTT, S and F_{gw} estimates and different landscape characteristics. This was considered most appropriate given the small sample size and that four of the catchments were nested. The approach has been used in other catchment comparison studies (e.g. Tetzlaff et al., 2009b).

3. Results

3.1. Seasonal hydrological and hydrochemical dynamics

Metrics of catchment hydrological response indicated distinct differences between the eastern, western and main stem sub-catchments (Table 2). Mean annual minimum runoff, median daily runoff and baseflow index (BFI) were higher, and flashiness lower, in the eastern Longcote (EGS12) and School (EGS11) catchments suggesting higher baseflow and less responsive catchments. The western catchments (EGS06, EGS07, EGS16) had more variable flow characteristics and were more responsive.

The mean isotopic composition of rainfall data (Table S1.1) suggest there was little variation in the rainfall isotopic signature across the catchment during the study (annual volume-weighted mean values for δ^2H are within ~2.5‰ for the three gauges). There was also little indication of any elevation effect. Volume-weighted δ^2H varied seasonally, with depletion during winter and enrichment during summer. These changes approximate a sine wave (amplitude 14–16‰) with a good fit for the three rain gauges (r^2 ranged 0.60–0.67 – Fig. S2.2).

River isotopic samples plotted close to the global meteoric water line (GMWL) and the local meteoric water line (LMWL) determined from rainfall isotopic data in the catchment (Fig. 2). However, there was divergence from the LMWL in some catchments, particularly during summer, indicative of evaporation in catchments where discharge becomes extremely low and in which wetland/open water areas are more extensive. Temporal changes in the δ^2H of rivers followed rainfall but with different degrees of damping (Fig. 3, Fig. S2.3). Damping was lowest in the west and north (Standard Deviation (SD): 7.94–8.43‰, Amplitude (A): 4–6‰), intermediate in the nested catchments (SD: 6.64–8.81‰, A: 3.2–4.2‰) and greatest in the east (SD: 4.46–4.87‰, A: 2.3–2.7‰).

Median ANC also varied between catchments. There were significant differences between most of the headwater catchments and the main stem ($p < 0.05$, except for Cowieslinn) and the most significant differences ($p < 0.001$) between the headwater catchments in the east and west (Fig. 4). The ANC in river water data also showed clear seasonal trends, with ANC strongly negatively correlated with discharge, as reported in other catchments (Neal et al., 1997b) (Fig. S2.4). This relationship followed a power law (Fig. S2.5), with a good fit for most catchments ($r^2 > 0.62$). At high flows, soil waters with lower ANC dominated the chemistry of most sub-catchments, particularly those in the west. Catchments with higher baseflow ANC were generally better buffered during higher flow periods,

Table 2
Summary of catchment hydrometric responses based on daily discharge data for October 2011-September 2016. Median_R: median daily runoff; SD_R: standard deviation in daily runoff; COV_R: coefficient of variation in daily runoff; MAPR: mean annual peak runoff; MAMR: mean annual minimum runoff; RB: Richards-Baker flashiness index; BFI: Baseflow Index. See Section 2.2.1 for more information on variable calculations.

Variable	EGS 02	EGS 05	EGS 09	EGS 11	EGS 16	EGS 10	EGS 06	EGS 12	EGS 07
Median_R (mm day^{-1})	0.945	0.986	0.794	1.42	0.578	0.949	0.349	1.48	0.587
SD_R (mm day^{-1})	2.34	1.84	4.31	2.24	3.25	4.26	2.38	2.17	2.06
COV_R (%)	132	115	217	104	176	207	172	101	136
MAPR (mm day^{-1})	18.4	14.7	44.1	16.9	31.8	41.9	16.1	14.1	13.3
MAMR (mm day^{-1})	0.204	0.251	0.232	0.449	0.0627	0.143	0.0065	0.51	0.164
RB	0.326	0.288	0.509	0.195	0.491	0.396	0.593	0.179	0.426
BFI	0.46	0.55	0.38	0.59	0.30	0.47	0.21	0.61	0.35

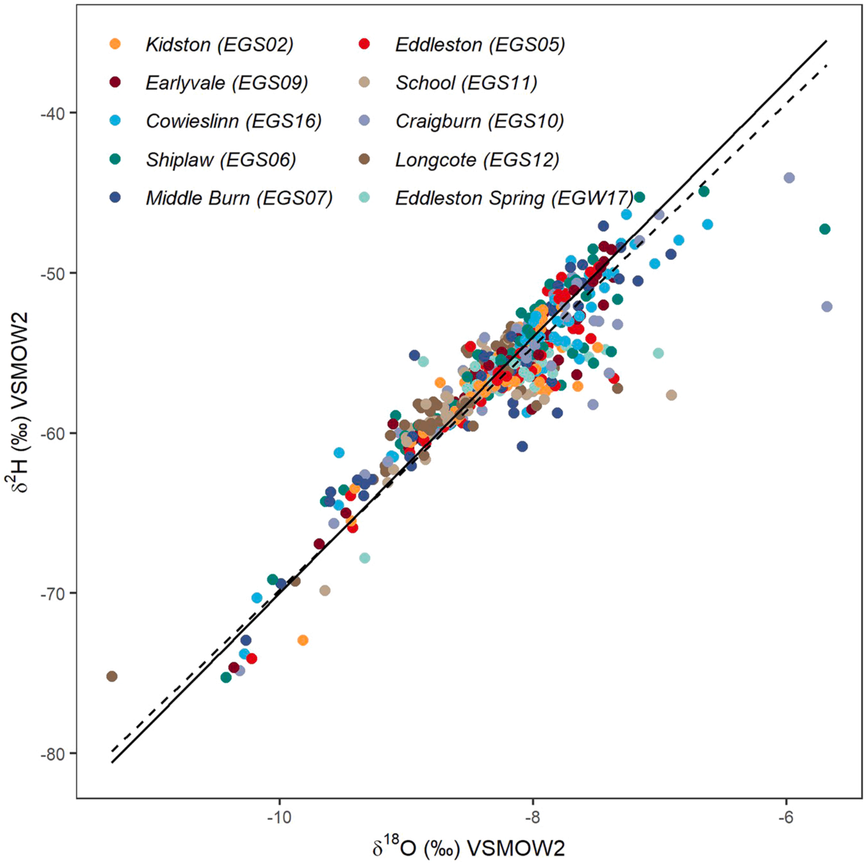

Fig. 2. Dual isotope plot for all catchments and Eddleston Spring. The solid black line is the global meteoric water line (GMWL) and the dotted line is the local meteoric water line (LMWL).

indicative of greater groundwater contributions in these catchments.

3.2. Catchment MTT, water storage and groundwater estimates

MTT estimates indicated large differences between the eastern and western catchments, as well as increasing transit times down the main river stem (Table 3). These differences were significant between the eastern catchments and Middle Burn (EGS07) in the west based on 95% confidence intervals. As noted in other studies (Rodgers et al., 2005; Soulsby et al., 2006b) these transit time estimates are only indicative, given the large confidence intervals, especially in catchments with significant damping, where r^2 values for the regression are lower. The F_{yw} showed a similar, although inverse, pattern between catchments, with much lower F_{yw} in the east, higher F_{yw} in the west and intermediate values in the main stem catchments.

Dynamic storage estimates based on the Q0.1 and Q99.9 discharge rates for each catchment ranged from 16 to 22 mm in the western catchments and 159–202 mm in the eastern catchments, although the confidence intervals were large in the east due to the high degree of scatter at low flows (Table 3). Storage estimates down the main river stem were 28–43 mm, between the values in the east and west, with increases downstream reflecting catchment nesting. The inferred passive storage estimates (S_{MTT}) made using the isotopic data were much higher as expected, but followed the same pattern.

There were also differences in groundwater fraction estimates between catchments (Table 3). The largest differences between catchments of similar area were between the eastern/northern (0.48–0.52 groundwater fraction) and the western catchments (0.20–0.36 groundwater fraction). Groundwater fraction was intermediate (0.41) at Earlyvale (EGS09), which is the smallest nested catchment on the main river stem, mixing inputs from the west and north. It was higher for the larger nested catchments on the main river stem (0.50–0.51) but did not increase consistently with scale.

3.3. Relationships between catchment characteristics and hydrological responses

Catchment hydrological response variables were significantly correlated with several catchment characteristics and MTT and S behaved in a similar way (Table 4). The percentage of more freely draining HOST classes (HWC_1) had the highest correlation coefficients, with significant positive correlations across all dependent variables, suggesting that coverage of more freely draining soils is

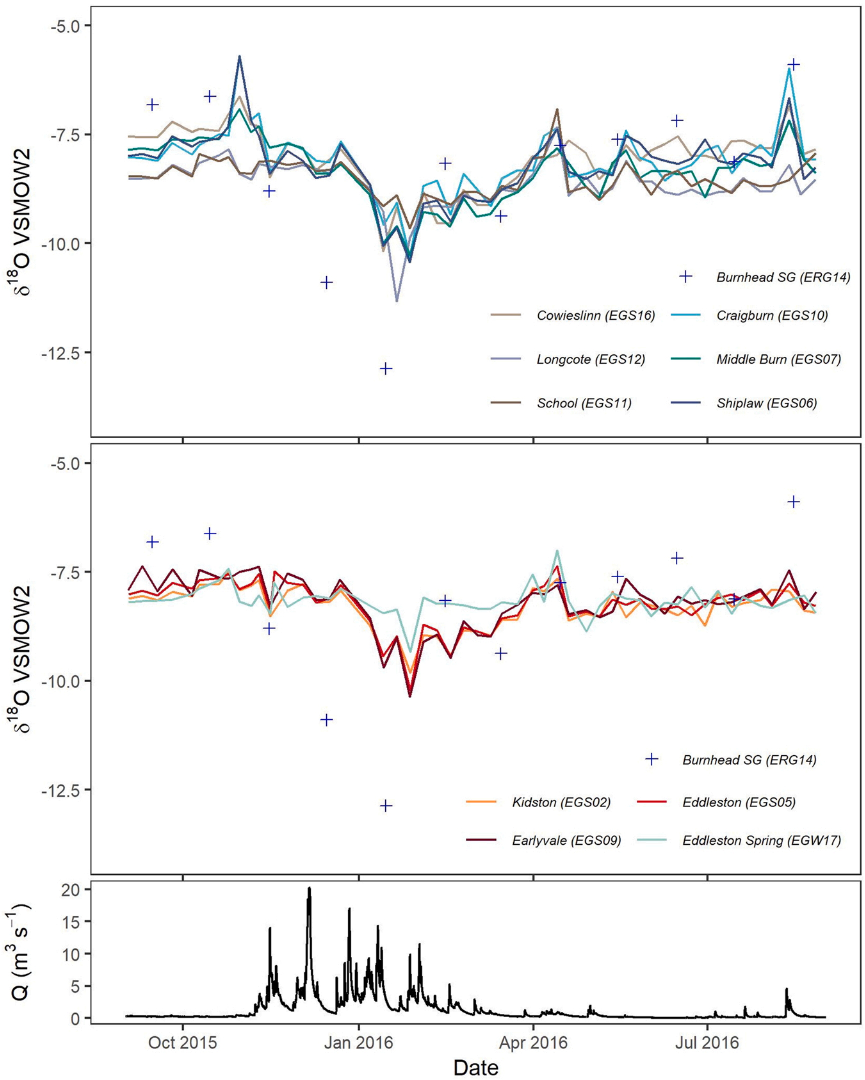

Fig. 3. Time series of isotopic composition of river water in headwater catchments, on the main river stem and at the spring site. Monthly volume-weighted rainfall data shown by the blue crosses from one rain gauge (Burnhead), as values are similar for the other rain gauges.

related to greater MTT, S and F_{gw}. The percentage Diamicton and Peat (G_Di) was also an important influence on MTT, with a strong inverse correlation. Given there is a high level of co-linearity between the soils and geology, it was difficult to distinguish the relative role of soil type and geology with this dataset, but HOST class appears to be a stronger control across all the dependent variables. The percentage forest cover (LU_F) was also significantly inversely correlated across all dependent variables, suggesting that higher forest cover is related to lower MTT, S and F_{gw}. There were generally weaker correlations between the topographic metrics and catchment hydrological response. The topographic wetness index (TWI) was weakly inversely correlated with MTT and S, but catchment area and drainage density were not significantly correlated with any of the response variables.

x-y scatterplots of the correlations indicate that there is some clustering of catchments, with the eastern catchments skewing the correlations for some of the comparisons, which reduces the power of the Spearman ranking method (Fig. 5). Re-running the correlations without these catchments showed there was little change for most of the variables, although the relationships with improved grassland became significant (Table 4). However, improved grassland and forest cover are inversely co-linear for the subset of catchments.

The lower correlation coefficients between F_{gw} and catchment characteristics, suggest that there are more complex controls on the fraction of groundwater in streams in the catchment. While the eastern catchments have longer residence times, they have a similar F_{gw} to the main stem (including a lower F_{gw} than the similarly sized headwater catchment on the main stem, Craigburn).

Comparisons between the different response variables help to summarise these different relationships. S and MTT (Fig. 6a) are correlated across the catchments but F_{gw} and MTT (or S) are not so well correlated (Fig. 6b). These relationships suggest clustering of catchments into three main groups between the east, west and main stem. Given the large confidence intervals for both MTT and

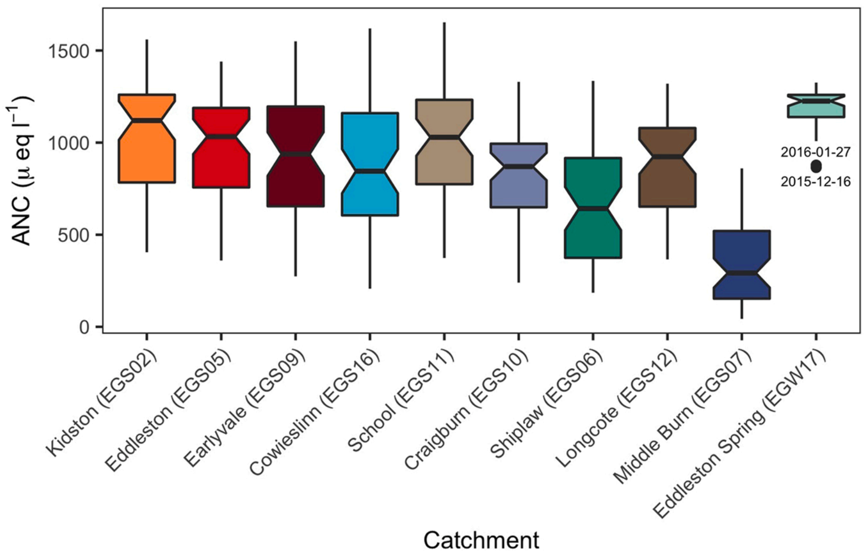

Fig. 4. Boxplots of ANC during the sampling period, ordered from largest to smallest catchment. Horizontal line inside the box represents the median and the lower and upper hinges correspond to the first and third quartiles. The upper and lower whiskers depict the largest and smallest values respectively within 1.5 * the interquartile range (IQR). The notches extend 1.58 * IQR / sqrt(n). This gives a roughly 95% confidence interval for comparing medians. Dots are outliers. There are no significant differences between the three main stem catchments (at the left of the plot) but significant differences between most of the other catchments ($p < 0.001$).

storage estimates, these patterns are only indicative. However, the fact that there are similar findings for relatively independent metrics, suggests that the relationships reflect the underlying processes.

4. Discussion

4.1. Catchment water storage

The results indicate that catchment dynamic storage is generally low in the Eddleston Water catchment but that it is variable across the different sub-catchments. There was a significant contrast between the western catchments where dynamic storage estimates were 16–22 mm and the eastern catchments, where estimates were 159–202 mm, although with substantial uncertainty, particularly in the east. Estimates for the main stem catchments were 28–43 mm. These estimates are much lower than some published work in catchments with thick weathered bedrock geology (e.g. Sayama et al., 2011) but of a similar order of magnitude to other studies in UK catchments. For example, Birkel et al. (2011) reported mean values of 15 mm and 35 mm based on a similar approach for catchments in Scotland with 73% and 61% responsive soil cover respectively. Capell et al. (2013) reported a similar range of dynamic storage estimates based on modelling for a range of Scottish catchments. Kirchner (2009) calculated dynamic storage estimates of 68 mm and 95 mm for two catchments in Wales, UK, (with similar soils and geology but much higher precipitation) using a similar method but based on the means of annual maximum and minimum flows over five years. Estimates for the western catchments in Eddleston Water are lower, which could be partly due to catchment properties as discussed below but will also be due to the use of the 0.1 and 99.9 percentiles to define maximum and minimum flows and the shorter timeframe of the dataset. The estimates are sensitive to the precision of low flow estimation, so are only an initial quantification, given the use of natural rated sections in Eddleston Water (Buttle, 2016). They are also sensitive to the length of the dataset. Kirchner (2009) found that estimates increased with a longer (27 year) time series and this would be expected in Eddleston Water under a larger range of flow conditions.

The inferred ‘passive’ storage estimates based on MTT were higher, as expected, and ranged from 209 to 253 mm in the west, 487–596 mm on the main stem to 766–870 mm in the east. Estimates for the main stem and the east are within a similar range to those in other parts of Scotland using similar methods, while those in the west are slightly lower than reported for other areas of Scotland (Birkel et al., 2011; Capell et al., 2013; Soulsby et al., 2009). The differences may arise because there are few estimates for streams in the Scottish Borders where mean annual precipitation and runoff are typically lower than in northern and western Scotland. Again, there are large uncertainties in these estimates due to the limitations of the method for estimating MTT in more highly damped catchments, the short timeframe of the dataset, and MTT being a poor representation of ‘mean’ water storage time given the nature of the residence time distribution. However, these estimates give a first indicative estimate of catchment storage.

4.2. Catchment characteristic controls on storage and mixing

Soil type, as expressed here by HOST class, is the strongest and most consistent explanatory variable for MTT, dynamic storage and

Table 3
Catchment dynamic storage estimated using the method described in the text. Summary of Dynamic storage (S), amplitudes (A), mean transit times (MTT), implied storage based on MTT estimates (S_{MTT}), and young water fraction (F_{yw}) determined from the fitted data for all streams, with 95% confidence intervals (CI) determined from the regression. Groundwater fractions (F_{gw}) estimated from 15-minute discharge data for the sampling period September 2015–August 2016 using ANC-discharge relationships and end member definition reported in the text. Storage estimates were not made for the Cowieslinn catchment because of the much shorter discharge time series.

	Recession analysis			*Transit time*					*Young water fraction*			*Groundwater fraction*		
Catchment	*S (mm)*	*S 2.5% CI (mm)*	*S 97.5% CI (mm)*	*A (‰)*	*MTT (days)*	*MTT 2.5% CI (days)*	*MTT 97.5% CI (days)*	S_{MTT} *(mm)*	*Fyw (-)*	*Fyw 2.5% CI (-)*	*Fyw 97.5% CI (-)*	*Fgw (-)*	*Fgw 2.5% CI (-)*	*Fgw 97.5% CI (-)*
Kidston (EGS02)	43	36	52	3.16	269	176	440	596	0.21	0.1	0.32	0.5	0.43	0.57
Eddleston (EGS05)	36	25	50	3.79	222	148	359	444	0.25	0.13	0.37	0.51	0.44	0.58
Earlyvale (EGS09)	28	20	40	4.24	197	132	304	487	0.28	0.15	0.41	0.41	0.33	0.49
School (EGS11)	202	161	313	2.33	370	235	742	766	0.15	0.06	0.24	0.48	0.39	0.57
Cowieslinn (EGS16)	NA	NA	NA	5.68	142	103	191	509	0.37	0.23	0.5	0.36	0.29	0.43
Craigburn (EGS10)	46	38	57	3.95	213	139	324	548	0.26	0.14	0.39	0.52	0.41	0.63
Shiplaw (EGS06)	16	14	18	4.92	167	114	241	209	0.32	0.19	0.46	0.27	0.19	0.35
Longcote (EGS12)	159	52	789	2.66	323	191	647	870	0.18	0.07	0.29	0.48	0.41	0.55
Middle Burn (EGS07)	22	19	25	5.96	134	97.5	189	253	0.39	0.24	0.52	0.2	0.08	0.32

Table 4
Spearman rank correlation coefficients between catchment characteristics and hydrological response variables, mean transit times (MTT), dynamic storage (S) and groundwater fraction (F_{gw}). Significance levels: * *(p < 0.05); ** (p < 0.01); *** (p < 0.001)*. The subset of northern and western catchments includes Middle Burn (EGS07), Shiplaw (EGS06), Craigburn (EGS10), Cowieslinn (EGS16), Earlyvale (EGS09), and Eddleston Village (EGS05).

Variable	*Code*	*All catchments (n = 9)*			*Northern and western catchments (n = 6)*		
		MTT	S	F_{gw}	MTT	S	F_{gw}
Glacial till (Diamicton) and Peat (%)	G_Di	-0.930 **	-0.690	-0.460	-0.829 *	-0.200	-0.543
Sand and Gravel (%)	G_SG	-0.150	-0.500	-0.0586	0.371	-0.100	-0.0286
HOST wetness classes 1 & 2 (%)	HWC_1	0.950 ***	0.980 ***	0.711 *	0.943 **	0.900 *	0.943 **
HOST wetness classes 3 & 4 (%)	HWC_2	-0.510	-0.610	-0.193	-0.0857	-0.200	-0.0857
Woodland – coniferous plantation (%)	LU_F	-0.920 ***	-0.950 ***	-0.728 *	-0.886 *	-0.900 *	-1.00 ***
Improved and semi-improved grassland	LU_Gi	0.230	0.260	0.787 *	0.886 *	0.900 *	1.00 ***
Dry/wet modified bog and fenland (%)	LU_M	-0.033	-0.024	0.243	0.371	0.300	0.486
Area (km^2)	T_A	0.400	0.170	0.536	0.714	0.600	0.657
Drainage density ($km\ km^2$)	T_DD	-0.570	-0.260	-0.301	-0.200	0.00	0.0286
Topographic wetness index	T_TWI	-0.680 *	-0.450	-0.00837	0.0286	0.700	0.486

to a lesser extent groundwater fraction across the catchments. More permeable soil types are associated with longer MTTs, higher storage and higher groundwater fractions, suggesting that soil permeability is the primary control on runoff mechanisms in Eddleston Water. These findings are consistent with many other studies, particularly in Scotland, that have examined relationships between MTTs / inferred storage, and HOST classes (Hrachowitz et al., 2009b; Laudon et al., 2007; Soulsby et al., 2006b; Tetzlaff et al., 2007b).

Soil type is co-linear with geology in the catchment, which is not surprising given that the evolution of soils is strongly influenced by parent materials (Huggett, 1998; Lacoste et al., 2011). This makes it difficult to distinguish the relative role of soils and geology in controlling subsurface flow. However, the lower correlation coefficients for the geological variables, combined with relatively low storage and MTT estimates, suggest that subsurface flow systems are relatively shallow in the catchment. This is consistent with observations of thin soil profiles overlying glacial till in much of the north, west and central parts of the catchment (Peskett et al., 2020), and soils in the east overlying relatively impermeable bedrock. Nevertheless, there is considerable variation, particularly between the east and west, which might be due to distinct differences in superficial geology. While the west of the catchment is dominated by impermeable till, which is often associated with short MTTs (Dimitrova-Petrova et al., 2020; Pfister et al., 2017) there are likely to be significant areas of relatively thin (< 2 m) highly permeable weathered rock head underlying soils in the central and eastern areas of the catchment. These have been observed on slopes in the central parts of the catchment (Ó Dochartaigh et al., 2018) but are probably most extensive in area in the east.

Catchment area and topographic characteristics have some influence on MTT, storage and groundwater fraction but do not appear to be primary controls. Catchment area scaling helps to explain the pattern of increasing MTT, S and F_{gw} for nested catchments on the main stem. The same pattern is found in many other studies, with more heterogeneity at small catchment scales but convergence at larger scales (Hrachowitz et al., 2010; Soulsby et al., 2006a; Soulsby et al., 2009). However, given the distinct differences between similarly sized catchments in the east, west, and north, this is clearly not a primary control. In terms of topographic variables, correlations are generally weak, although the topographic wetness index shows some inverse correlation with MTT. Interestingly the steeper parts of the catchment, are associated with longer MTTs and higher storage. More rapid runoff might be expected in these areas, shortening MTTs, as has been identified in some studies (McGuire et al., 2005). This pattern is, however, consistent with other studies in Scotland (though in different geomorphic settings), where such behaviour has been attributed to the permeability of soils on steep slopes and potentially the presence of permeable superficial geological deposits (Tetzlaff et al., 2009b, 2009a). This fits with observations of catchment geology discussed above.

Forest cover has a strong inverse correlation with MTT, S and F_{gw}. This is surprising, given the large area of forest cover in some of the catchments, combined with highly responsive catchments in which identifying effects due to the forest might be more likely. These findings suggest that catchment responses are dominated by soils and geology, which are inversely co-linear with forest cover. A complicating factor, which requires further research, is the role of forest management approaches in Eddleston Water. The historical focus has been on coniferous plantation forests, which contain drainage ditches and trees with shallower rooting systems that will affect infiltration and runoff. However, similar to our study, other studies examining the influence of forest cover on catchment MTTs and water storage have also found limited impacts of forests, with differences attributed to soils and topography (Geris et al., 2015; Tetzlaff et al., 2007a).

The impact of improved grassland on runoff mechanisms also requires further research. Improved grassland could have variable impacts on MTT, S and F_{gw}. For example, under-drainage could lower water tables and increase soil moisture storage capacity but also facilitate rapid runoff, whilst field compaction could increase surface runoff. When analysing all catchments in our study, the correlation coefficients between the response variables and improved grassland were not significant, suggesting that soils are a primary control.

The generally weaker correlations between F_{gw} and the different explanatory variables, compared to MTT and S, suggest a more complex set of controls on ANC, linked to both residence times and source area chemistry. Higher F_{gw} in the east of the catchment can be explained most easily by the longer MTTs. The high F_{gw} on the main stem is partly explained by the larger catchment areas, but the most northerly headwater catchment has the highest F_{gw}. This may be linked to higher alkalinity source rocks of the glacially derived

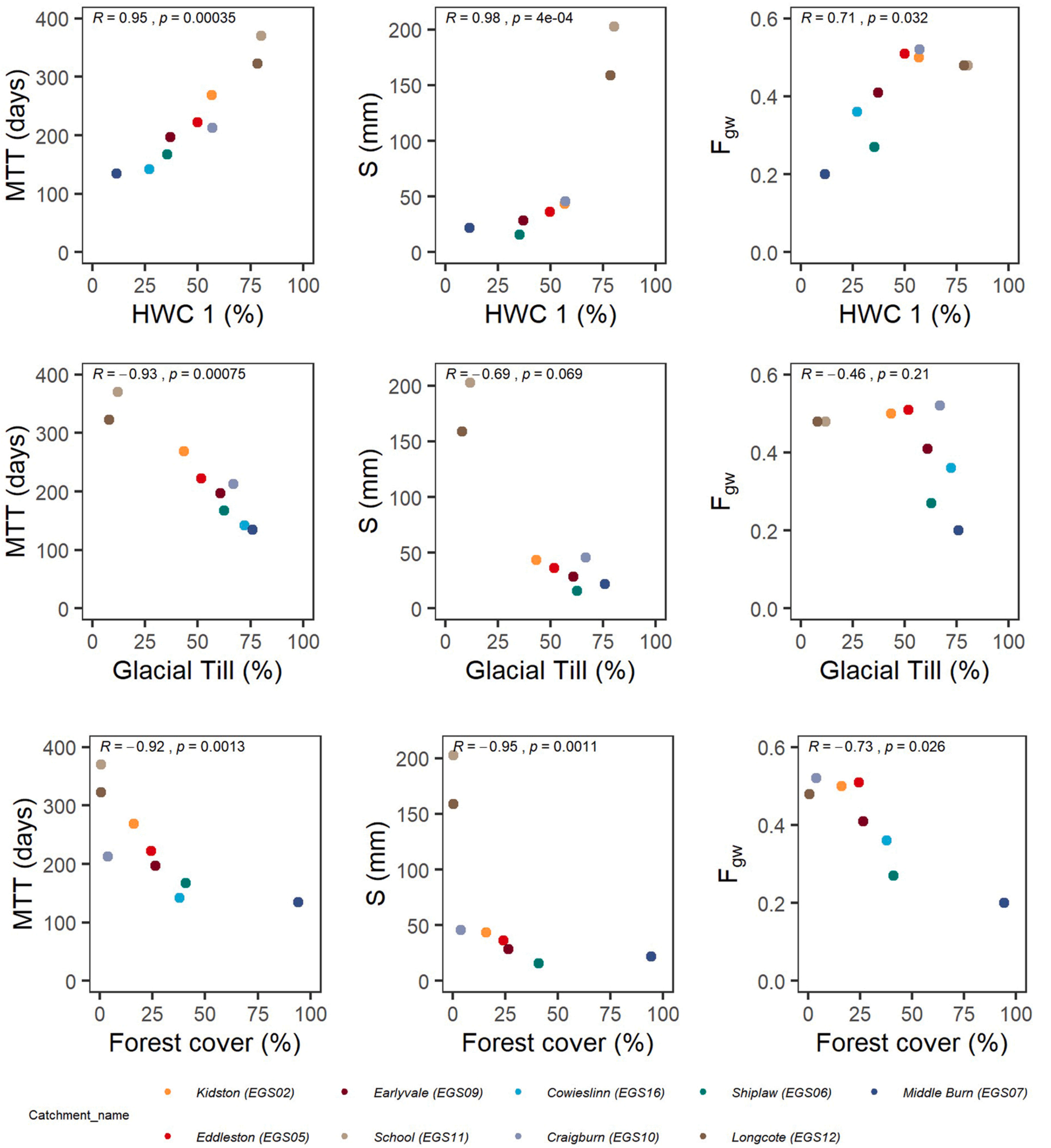

Fig. 5. x-y scatter plots and Spearman rank correlations between hydrological response variables (MTT: mean transit time; S: dynamic storage; F_{gw}: groundwater fraction) and explanatory variables (HWC 1: HOST wetness class 1; Glacial Till; Forest cover) in the nine study catchments.

superficial deposits in the north of the catchment (Auton, pers. comm.). The lower F_{gw} estimates in the western catchments are partly explained by the lower residence times and soil types. However, there is considerable variability, which could be due to the effect of forest cover on lowering ANC (Nisbet and Evans, 2014). Localised heterogeneity in the superficial deposits might also contribute to more variability in ANC: while the northwestern catchments are underlain by thick till, there is considerable heterogeneity, with isolated areas of thinner relatively permeable gravels and impermeable peats overlying the till. Such sequences are typical of post-glacial landscapes in this area and are likely to locally influence HOST class development and land cover (Lacoste et al., 2011; Natural England, 2015), affecting ANC but having a potentially less discernible impact on transit times and storage.

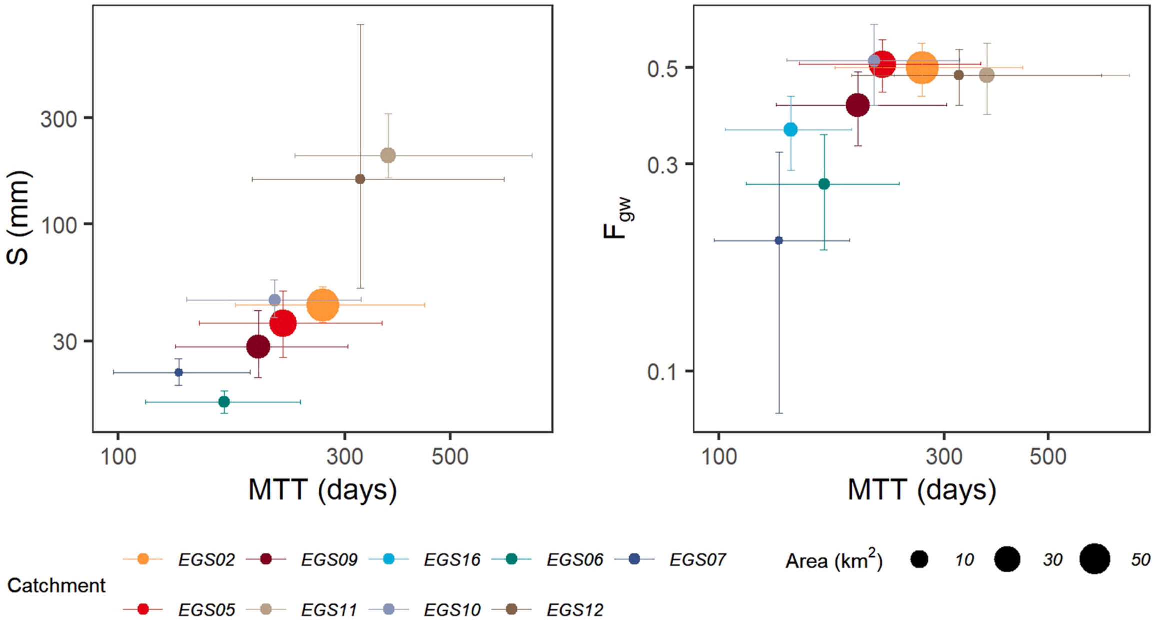

Fig. 6. Relationships between a) storage (S) and mean transit time (MTT), and b) groundwater fraction (F_{gw}) and MTT. Note the use of logarithmic axes to improve the clarity of the plot and help distinguish between catchments with lower MTTs.

4.3. *Conceptual model of runoff mechanisms and implications for NFM*

Fig. 7 proposes a conceptual model of the runoff mechanisms operating in the three catchment groups:

1. The eastern catchments (Fig. 7a) have thin freely draining soils overlying extensive areas of weathered bedrock which dominate hydrological responses, resulting in long MTTs, high storage, and a high groundwater fraction. Deeper subsurface flow through weathered bedrock and bedrock fractures dominates the transit time distribution and groundwater fraction. Limited rapid surface runoff occurs in till mantled areas and field drains close to the main streams.
2. Western catchments (Fig. 7b) have responsive soils underlain by extensive impermeable glacial till result in infiltration-excess and saturation-excess overland flow, as well as rapid subsurface flow in near surface horizons as found in other northern catchments (Tetzlaff et al., 2015). Deeper but rapid (relative to the eastern catchments) subsurface flow occurs in isolated, permeable superficial deposits. The relatively impermeable glacial till has a dominant effect on the transit time distribution. However, the variable soil types and land cover have a more discernible impact on ANC, which is more variable across the western catchments.
3. Catchments on the main river stem (Fig. 7c) have a higher proportion of improved grassland, freely draining soils and glacial sand and gravel deposits. They also have significant areas of floodplain. Research on runoff mechanisms in these areas suggests that hillslopes are dominated by shallow subsurface flow due to high infiltration rates on the freely draining soils and underlying head deposits with high hydraulic conductivities (Archer et al., 2013; Ó Dochartaigh et al., 2018). In areas where glacial till overlies weathered bedrock similar mechanisms appear to exist, although the lower permeability soils and glacial till can lead to saturation excess overland flow in the wettest periods (Peskett et al., 2020).

While we do not investigate the high frequency response of the catchments here (i.e. runoff from individual storm events that usually cause flooding), this was examined previously using hydrograph separation in a subset of catchments (Peskett et al., 2021). The current study builds on this by looking at the lower frequency response across a greater number and range of catchments to identify controlling catchment characteristics. Storage, transit time and groundwater fraction indicators are influenced particularly by processes that enable percolation into the subsurface (i.e. hydraulic conductivity and the presence of impermeable horizons) and the capacity of the subsurface to hold water (i.e. porosity and degree of saturation). The indicators therefore give an insight into processes that will have a direct impact on the higher frequency response. The findings in Peskett et al., 2021 align with the findings in this study, as both indicate that soils and geology exert a greater influence than land cover on high flows and catchment storage and mixing.

These findings are important in the context of current debates about NFM in the UK and global interest in nature-based solutions. They illustrate the importance of understanding dominant catchment characteristic controls on catchment storage, the subsequent limits of land use change as an NFM measure in many catchments, and the need for targeted tree planting (Cooper et al., 2021; Soulsby et al., 2017). They also illustrate the complexity of catchment runoff processes and the potential role that tracers can play in providing independent insights on runoff mechanisms that could help better constrain catchment hydrological models (Kuppel et al., 2018; Neill et al., 2021).

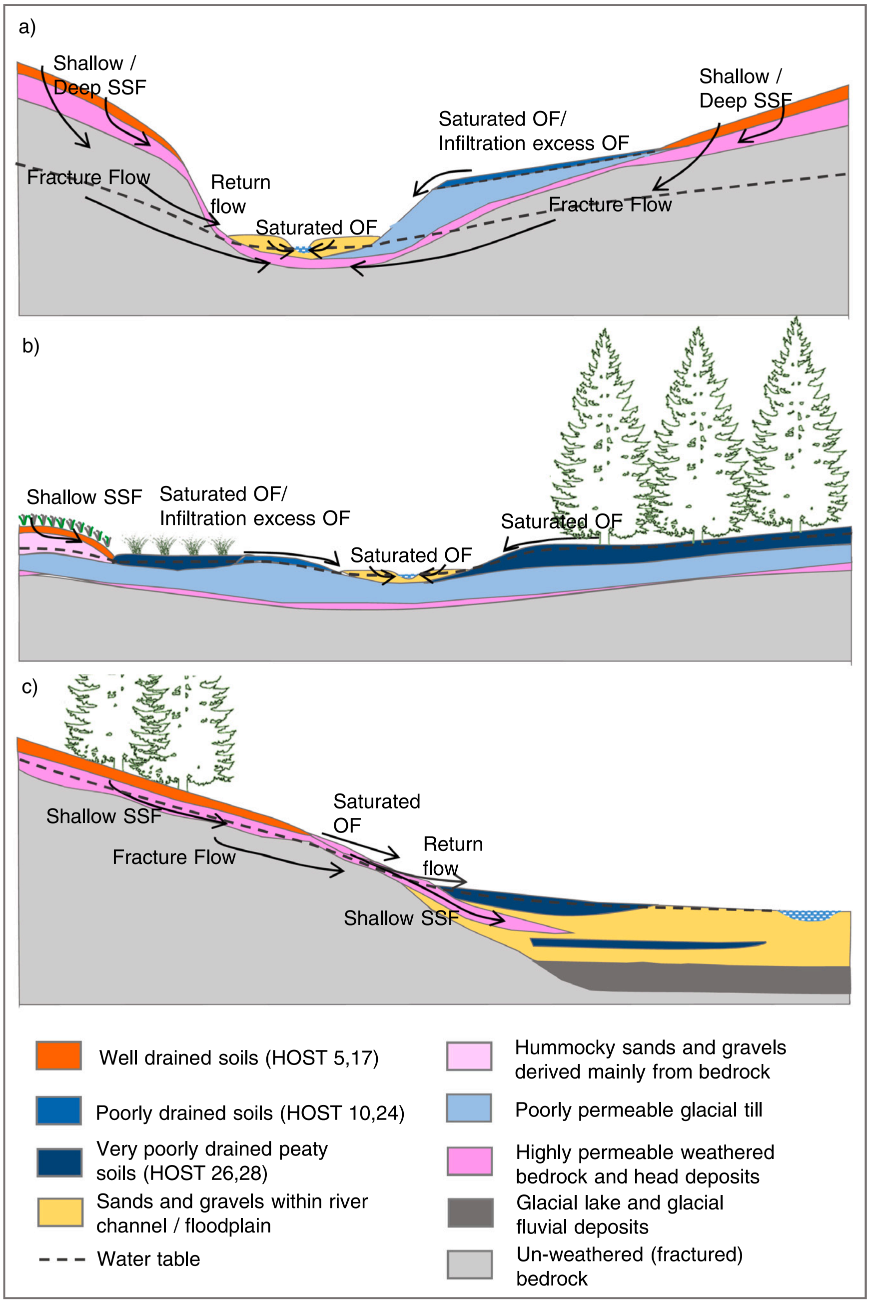

Fig. 7. Conceptual model of runoff mechanisms in the a) eastern, b) western, and c) main stem catchments. SSF: Subsurface Flow; OF: Overland Flow; HOST: Hydrology of Soil Types. Floodplain structure in c)
Adapted from Ó Dochartaigh (2018).

5. Conclusions

Catchments worldwide are undergoing rapid changes in land use and management. Concurrently, concerns about the role of climate change in increasing flood risk and drought are fueling a new wave of policies aimed at returning catchments to a more 'natural' state as a means of regulating stream flows more effectively. While difficult to investigate, quantifying catchment scale mixing and storage is crucial to these efforts, particularly in terms of better conceptualising flow paths and quantifying the relative impacts of interventions that are geographically dispersed such as changes in land management. This study demonstrated the generally low but variable storage that exists in a typical upland landscape in the UK, and the dominance of soil and geological hydraulic properties in controlling storage and mixing dynamics. Correlations between different metrics of water storage and mixing, and different physical catchment characteristics, suggest that any impacts that land cover may have on increasing catchment water storage or altering catchment mixing processes in this environment are masked by soil and geological properties. These findings suggest limitations on the potential of large-scale tree planting to reduce flood risks in similar upland settings, at least from the perspective of their impacts on infiltration and storage, and highlight the need for careful targeting taking into account existing catchment properties.

CRediT authorship contribution statement

Leo Peskett: Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft, Writing – review & editing, Funding acquisition. **Kate Heal:** Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Funding acquisition. **Alan MacDonald**: Conceptualization, Methodology, Writing – original draft, Funding acquisition. **Andrew Black:** Investigation, Data curation, Writing – review & editing. **Jeffrey McDonnell***:* Conceptualization, Writing – review & editing, Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ejrh.2023.101398.

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