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**Catchment Subsurface Water Storage,
Mixing and Flowpaths: Implications for
Land Cover Change as a Natural Flood
Management Strategy**



THE UNIVERSITY
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Lay summary

The main cause of flooding in river valleys occurs when large amounts of water flows off the land surrounding rivers during wet periods with high rainfall and the river can no longer hold all of the water in its channel. When it rains during these periods, water can take many different pathways to travel from hills to rivers. Some of it may flow over the land (surface flow) because the ground does not have many spaces to let the water in quickly, or the ground is already full of water (it is saturated). Some water may seep into the ground and flow through soils or the rocks beneath them (subsurface flow), or it may even 'push' out water that was already in the soil further downhill, a bit like a piston. All of these processes can occur in river valleys, but some may be much more important than others and this depends on factors such as the type of soils and rocks, the land cover (e.g. is it grass or trees), the steepness of the hill slopes and climatic factors (e.g. differences in rainfall between seasons).

A big area of interest worldwide surrounds whether it is possible for humans to alter the balance of these processes in order to prevent flooding. Over many centuries, humans have altered river valleys in significant ways, removing forests, draining land and straightening rivers, often in an effort to get water off the land quickly to enable more intensive agriculture. However, it is thought (though not proven) that such changes may have made flooding worse and there are now efforts in many countries to 'return river valleys to nature' by planting forests, removing drainage and re-meandering rivers. These 'natural flood management' (NFM) schemes may also offer other benefits (e.g. for wildlife) and be cheaper than building large concrete flood defences in towns and cities down river.

This study focussed on the potential effectiveness of tree planting within NFM schemes. There is some evidence that trees can help more water to get into soils, for example, due to the roots breaking up the surface and creating more spaces to store water. It is hoped that by enhancing these processes, NFM tree planting schemes might reduce the amount of water that travels quickly to rivers during storms. However, there are still large uncertainties about the effects of tree planting on river flows, which make it difficult to evaluate the effectiveness of NFM. This study looked at the following questions through detailed investigation of a pilot NFM project in Scotland. What are the main controls on the amount of water river valleys

can store and the time it takes for water to reach rivers, and do greater forest areas help to increase water storage and residence time in the landscape? During storm events, how much water follows surface pathways and how much follows subsurface pathways, and how does the forest area affect this? If small areas of forest are planted on the boundaries between agricultural fields, could they change significantly the pathways water takes from hills to rivers?

One experiment used water samples and data on the amount of water flowing in nine rivers over the course of a year to investigate how much water can be stored in the different river valleys and the different pathways it takes to get from hills to rivers. It found that the type of soils and rocks were the main controls on water storage and pathways, and forest cover had no obvious effect. River water samples were then collected in three of the river valleys during four storm events to investigate the amount of water flowing in surface versus subsurface pathways from the hills to the river. It found that, while the forested river valley had slightly more water from subsurface sources, climatic factors, such as the amount of rainfall, were the most important control on how much water flows via subsurface pathways. Finally, a much smaller scale experiment investigated how a strip of forest planted on the boundary between two fields changed the amount and movements of water stored in the soils compared to the surrounding grasslands. It found that there were some differences in the drier summer months, but in wetter winter periods and storm events, there was little difference in water storage between the forest and grassland soils.

Overall, the study suggests that forests are likely to have small impacts on water storage in river valleys and lead to limited reductions in river flows during flood events in regions like the UK uplands. Nevertheless, there may be some localised situations where forests have a greater impact and a number of other benefits from increased tree cover, especially in these areas which were once highly forested. So, while tree planting may not be the most effective approach to protect against flooding, it should be considered as part of ongoing efforts to plan landscapes to fulfil multiple purposes.

Abstract

Efforts are increasing globally to harness the potential of forests to alter catchment water runoff and storage dynamics as a 'natural flood management' (NFM) strategy, particularly given a projected rise in the frequency and severity of floods with climate change. Despite decades of research on forest hydrology, knowledge of how forests and land use control catchment runoff is still limited, especially in relation to important, though less investigated, subsurface runoff processes.

This PhD research aimed to examine how forest cover interacts with soils and geology to influence runoff pathways at different spatial and temporal scales, focusing on the 67 km² Eddleston Water NFM pilot site in the Scottish Borders. At the catchment scale, isotopic (²H and ¹⁸O) and geochemical tracers (Acid Neutralising Capacity (ANC)), conductivity and pH) were used to investigate whether forest cover is a significant control on water storage and mixing over seasonal and storm event timescales. At the hillslope scale, dense subsurface monitoring (soil moisture, groundwater and time-lapse electrical resistivity tomography (ERT)) compared improved grassland to an across-slope forest strip, similar to those promoted in NFM schemes to control runoff, to reveal water storage potential in soil underneath the forest and the downslope extent of any impacts on subsurface hydrological dynamics.

The results revealed complex interactions between land cover and runoff processes at different scales. At the catchment scale, soil type and superficial geology were found to be more dominant controls on catchment storage over seasonal timescales, with land cover playing a secondary role. Dynamic storage estimates for headwater catchments underlain predominantly by glacial till were low, ranging from ~16 mm to 46 mm, and were correlated with low mean transit times, ranging from ~130 to ~210 days. There were no differences in these estimates, within the bounds of error, between catchments with up to 90% forest cover and those with much lower cover (<50%). However, there were significant differences compared to steeper catchments with low glacial till cover. In these catchments dynamic storage estimates ranged from ~160 mm to ~200 mm, and were correlated with high mean transit times, ranging from ~320 to ~370 days.

At the storm event timescale, and comparing two adjacent catchments with similar superficial geology and soils but differences in land cover, forest cover reduced the event water runoff fraction for four high flow events. The fraction of event water runoff at peak discharge during the largest event monitored was 0.37 for the forested catchment but 0.54 for the adjacent partially forested catchment. A third catchment, with minimal glacial till and low forest cover, demonstrated very different dynamics, with much lower runoff ratios for all events, higher groundwater fractions (0.21-0.55 at peak), and 'double-peak' hydrographs, illustrating the impacts of geology on runoff processes. Similar relative differences in runoff fractions were found between catchments across the three winter events, with differences between storms greater than differences between catchments. These findings suggest that while catchment characteristics mediate event responses, the characteristics of the event (rainfall depth, intensity and antecedent conditions) may dominate responses, though it was not possible to disaggregate the different event characteristics with this dataset.

The hillslope scale work identified significant differences in subsurface moisture dynamics underneath the forest strip over seasonal timescales: drying of the forest soils was greater, and extended deeper and for longer into the autumn compared to the adjacent grassland soils. Water table levels were also persistently lower in the forest and the forest soils responded less frequently to storm events. Downslope of the forest, soil moisture dynamics were similar to those in other grassland areas and no significant differences were observed beyond 15 m downslope, suggesting minimal impact of the forest at shallow depths downslope. The depth to the water table was greater downslope of the forest compared to other grassland areas, but during the wettest conditions there was evidence of upslope-downslope water table connectivity beneath the forest. The results indicate that forest strips provide only limited additional subsurface storage of rainfall inputs in flood events after dry conditions in this temperate catchment setting.

In summary, the research results show that while forests have some seasonal impacts on subsurface moisture dynamics, soil type and underlying superficial geology are primary controls on catchment storage and mixing in temperate upland environments, suggesting limited impacts of changing land use. At storm event timescales increased forest cover has some impact on reducing the amount of event water runoff, but event characteristics are a more dominant control, so forest cover

alone is unlikely to lead to significant reductions in peak flows during large flood events. Strategically placed forest cover, such as field boundary planting on hillslopes has some impacts on subsurface moisture dynamics but the effects are spatially limited and not present in winter periods. The processes leading to these findings appear to be similar at the catchment and hillslope scales.

From an NFM policy perspective the findings suggest that while tree planting is not a flood management panacea, it may have benefits in certain situations, as well as significant co-benefits. This implies a need for a change in emphasis within flood risk management policy, which 'mainstreams' tree planting as a flood risk strategy into wider policy processes to create multifunctional landscapes. There are still many unknowns about the impacts of land cover on hydrological processes, particularly in the subsurface, and there is a need for enhanced research on these processes. This will also help to reduce some of the large uncertainties surrounding the impacts of NFM, which remain one of the key barriers to its wider implementation.

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List of abbreviations

ANC	Acid Neutralising Capacity
AWI	Antecedent Wetness Index
ERT	electrical resistivity tomography
ET	Evapotranspiration
FDC	Flow Duration Curve
GMWL	Global Meteoric Water Line
HOST	Hydrology of Soil Types
LMWL	Local Meteoric Water Line
NBS	Nature Based Solutions
NFM	Natural Flood Management
MTT	Mean Transit Time
RR	Runoff Ratio
TBR	Tipping Bucket Rain Gauge

1 Introduction

1.1 Context and rationale

Flooding is a major global hazard, and in the UK flood risk is thought to be increasing due to the combined effects of climate change and other human induced changes to river catchments (Pattison and Lane, 2012, Pitt, 2008). Climate change is projected to increase the frequency and severity of precipitation. Increases in winter precipitation have already been observed in upland areas of the UK over the last 45 years and, while these cannot be directly attributed to climate change, they are likely to have increased flood risk (Jenkins et al., 2007).

There have also been significant human alterations to river catchments stretching back for many centuries in the UK. Some of the largest changes have been in land cover and land use, particularly over the last 70 years. Here 'land cover' is defined as "the observed (bio)physical cover on the earth's surface" which is normally assumed to include water cover. 'Land use' is defined as "the arrangements, activities and inputs people undertake in a certain land cover type to produce, change or maintain it" (Di Gregorio and Jansen, 2005). Changes in rural land cover and land use that are considered to have most impact on runoff include land drainage, increasing field size through removal of hedgerows, deforestation, and soil compaction. Changes have also been made to river channels, including channel straightening, containment of rivers within manmade levees and construction of control structures such as dams. While there are still debates about the impacts of some of these changes to catchments and their combined effects (Pattison and Lane, 2012), many of them are likely to affect the frequency and severity of flooding. This is because of how they alter the volume of water entering river catchments, the rate at which water reaches the river network, and the ability of the channel to contain and convey water.

Globally, there is increasing interest in 'nature-based solutions' or 'green infrastructure' approaches for controlling various environmental hazards, including flooding (Seddon et al., 2020; World Bank, 2018). The drivers include: 1) a growing recognition that human induced changes are having negative impacts on human resilience; 2) recognition that the effectiveness of 'hard engineering' may be limited in some areas and needs to be complemented by more distributed approaches (Pitt,

2008); 3) the potential cost-effectiveness of nature-based solutions compared to hard engineered approaches (Dittrich et al., 2018); 4) interest in the 'co-benefits' of nature-based solutions, such as improved biodiversity; and 5) ideological drivers particularly among environmental NGOs calling for a return of environmental systems to a more 'natural' state. Nature-based solutions are now being promoted in global, regional and local policy processes, and have been incorporated into legislation in many countries (Cohen-Shacham et al., 2016; Maes and Jacobs, 2017; Sutton-Grier et al., 2018; World Bank, 2018).

In the UK, 'Natural Flood Management' (NFM) is one type of nature-based solution that has been incorporated into policy over the last decade (European Parliament and European Council, 2007; Johnson et al., 2007; Scottish Government, 2009a; UK Government, 2010). The main statutory instrument that initially guided the development of NFM in the UK was the EU Floods Directive (Directive 2007/60/EC on the assessment and management of flood risks), which entered into force on 26 November 2007. The Directive was incorporated into Scots law as the Flood Risk Management (Scotland) Act 2009, which specifically mentions the sustainable management of flood risk.

NFM seeks to manage flood risks through distributed 'natural' changes to catchment properties that help to attenuate flood peaks, such as reducing runoff through afforestation and altered farming practices, increasing catchment storage through the creation of temporary holding ponds, and reducing conveyance through re-meandering of river channels and construction of woody debris dams (Environment Agency, 2017). Many of these interventions are not new, having been tested in some catchments for at least the last 20 years (Wheater et al., 2008). However, their incorporation into policy is more recent and an increase in European, UK government and devolved government funding since 2010 means that there are currently at least 32 active NFM projects in the UK (Kay et al., 2019).

1.2 The scientific rationale for NFM

The magnitude of fluvial flooding is controlled by: 1) the rate of runoff from hillslopes into rivers; 2) the rate of propagation of the runoff downstream in river channels; and 3) how the runoff contributions from multiple hillslopes combine via the channel network to generate the downstream flood hydrograph (Dadson et al., 2017). NFM interventions aim to manipulate these processes, with most NFM schemes focussed

on reducing rapid hillslope runoff, increasing channel and floodplain storage, and reducing the rate of conveyance in river channels (Table 1.1). In small catchments (<20 km²) the peak of the hydrograph is dominated by runoff from hillslopes, whereas in larger catchments the geography of the stream network is important as it determines which areas contribute to flooding. Given this, the evaluation of NFM at large scales needs to take into account the location of interventions, channel geography and the size of the catchment (Dadson et al., 2017).

Table 1.1: Summary of NFM interventions and how they might help to attenuate discharge. Adapted from Lane (2017).

<i>Class of manipulation</i>	<i>Types of NFM intervention</i>	<i>How interventions might attenuate discharge</i>
Reducing rapid runoff	<ul style="list-style-type: none"> • Reduced livestock density • Changing tilling practices • Afforestation • Riparian planting • Hedgerow / forest strip planting • Reducing land drainage 	Increase infiltration (e.g. through reduced soil compaction); alteration of flow pathways (e.g. reducing the conveyance effects of tram lines); increased interception and evapotranspiration.
Increasing storage	<ul style="list-style-type: none"> • Temporary holding ponds • Floodplain storage • Wetland creation 	Temporarily increase catchment water storage by holding water back from reaching rivers or providing space for the river to flood.
Reducing conveyance	<ul style="list-style-type: none"> • Blocking drains • Debris dam construction • Re-meandering • Riparian planting 	Reduce connectivity between source areas and rivers; increase surface roughness by temporarily pushing flow across floodplains; increase travel times by lengthening river channels.

The potential effectiveness of NFM and individual NFM measures has been the subject of a number of recent reviews (Alaoui et al., 2018; Carrick et al., 2018; Dadson et al., 2017; Dawson et al., 2011; Environment Agency, 2018; Lane, 2017; Stratford et al., 2017). The most wide-ranging review by Dadson et al. (2017) concluded that “The hazard associated with small floods in small catchments may be significantly reduced by CBFM [Catchment Based Flood Management] and NFM

although the evidence does not suggest these interventions will have a major effect on the most extreme events.”. In this review, small catchments are defined as those less than 20 km² and, while ‘small flood’ is not defined, reference is made to smaller storms being <20% of the mean annual flood. However, the authors also suggest that much of the empirical evidence surrounding NFM interventions has been gathered from small catchments and small-scale experiments. Thus the lack of findings about impacts at larger scales (> 20 km²) could be a consequence of the limitations of current science, not necessarily that the mitigation effects of NFM could not be achieved at these scales.

1.3 Catchment hydrological processes and the role of hillslopes

The current study focusses mainly on NFM interventions aimed at reducing rapid runoff through land use and land cover change. These include tree planting at the catchment scale or in strips across improved grassland. Improved grassland is often extensively drained and, given its use for livestock grazing, soils can often be degraded and compacted, reducing their infiltration capacity. The effectiveness of NFM interventions is fundamentally linked to hillslope hydrology, the current understanding of which is reviewed below.

Fluvial flooding occurs when the river channel capacity is exceeded. Whether this occurs for a particular precipitation event is governed by the volume and timing of surface and subsurface runoff into the stream network as represented by the storm hydrograph (Shaw et al., 2010). Runoff volume and timing depend on the intensity of the precipitation event, evapotranspiration, the geometry of the stream network and the flow paths in operation. Hillslopes in catchments are fundamental for controlling catchment flow paths and are important as the source areas for much of the runoff that generates streamflow. Characteristics of hillslopes such as topography, geology and land use have long been known to influence fluvial processes, making hillslopes an important area of focus for catchment hydrological studies.

Characteristics of channels (and hillslopes) including their slope and roughness are also important in flood routing, as these factors control flood wave propagation. Flood waves can be identified as either dynamic or kinematic waves. Dynamic waves govern the movement of long waves in shallow water when inertial and pressure forces are important, for example for large floods in wide rivers. Dynamic waves have higher velocities but tend to attenuate rapidly. For kinematic waves,

inertial and pressure forces are not important; the weight of water flowing downhill is approximately balanced by the resistive force of bed friction, flows do not accelerate and flow remains approximately uniform along the channel. Flood flows are usually dominated by kinematic waves, particularly in smaller, steeper rivers and catchments. Kinematic wave approximations of the St Venant equations are often used in modelling hillslope surface runoff and flood propagation in such circumstances (Shaw et al., 2010; Sholtes and Doyle, 2011). For catchments and channels with lower slopes, diffusion approximations of the St Venant equations can also be used as kinematic wave theory is insufficient (Kazezyılmaz-Alhan and Medina, 2007).

Early hydrological process understanding was influenced strongly by the local environment within which hydrologists were working. This led to the development of different models, which are now recognised as forming part of a continuum of hydrological processes with the exact processes in operation varying spatially but also over time at the same location. Initially, concepts of hillslope hydrological processes focussed primarily on surface runoff as the primary contributor to streamflow. Horton's (1933) early work was highly influential in this regard. He proposed 'Hortonian overland flow' to occur when the rainfall intensity exceeded the infiltration capacity of the soil, leading to surface runoff. It is a model that is applicable in parts of the semi-arid south-western US where Horton was working, with barely-vegetated soils and intense rainfall events so infiltration rates decrease rapidly during storm events. A central criticism of this approach was that too much emphasis was placed on the water that does not infiltrate and not enough on the water that does infiltrate. A second criticism stemmed from the realisation by hydrologists working in forested catchments that overland flow was not being observed to the degree predicted by Horton, so other mechanisms must be contributing to storm flow.

The 'variable source area' concept developed from experiments conducted by Hursh and Brater (1941) examining storm hydrographs in the 16 ha Coweeta watershed, North Carolina, USA. Unlike the Hortonian concept, it starts with the assumption that all water infiltrates. Using hydrograph analysis and careful observation of overland runoff they showed that: 1) channel precipitation is the first in time contributor to storm flow; 2) areas of shallow water table near streams contribute second, with an actual increase in the effective width of the channel; and 3) storm water moving

through soils and talus slopes adjacent to streams could reach the stream in time to contribute to the hydrograph (Hibbert and Troendle, 1988). Dunne and Black (1970) pioneered much of the work to understand the variable source area concept in the 1960s through field experiments using analysis of groundwater levels near streams through storm events. The number of channels near streams was seen to expand and contract during storm events, indicating a rise in groundwater levels (Dunne and Black, 1970).

Possibly the most important outcome of this research was the increased recognition of the role of subsurface flow paths in the generation of stream flow during storm events, rivalling overland flow as a cause of flooding. Since the 1960s, this has led to more research focus on mechanisms that cause rapid lateral flow within hillslopes. These are more difficult to investigate than surface processes for the obvious reason that observations of the subsurface are more challenging.

Much of the early focus on subsurface runoff mechanisms was on flow along the soil-bedrock interface and interflow through macropores. Although these concepts helped to explain runoff generation processes in some environments, the work reported by Sklash and Farvolden (1979) in their seminal paper “the role of groundwater in storm runoff”, explained runoff generation processes in a completely different way. They used naturally occurring stable isotopes to show that most river water at high flows was actually ‘groundwater’ (subsurface water present in catchment soils and rocks before the rainfall event), which would not support the rapid lateral flow processes explained with soil pipes or along the soil-bedrock interface. To account for this observation they proposed a process of ‘groundwater ridging’ in which the water table on the lower hillslopes near streams rises quickly during rainfall events and the resulting hydraulic gradient drives groundwater discharge to the stream. Similar findings have been reported in more recent studies and in Scotland some studies have estimated that up to 50% of streamwater is older groundwater (Soulsby et al., 2006a).

If the water being delivered to streams really was groundwater, the problem this raised was how such large volumes of groundwater become mobilised so rapidly. Research in the 1990s helped to address this issue further by proposing mechanisms in which soil layers near the soil-bedrock interface become saturated and then hydraulically connect during storm events of long enough duration. This

process helps to mobilise old (pre-event) water towards the base of slopes through the development of a pressure head (McDonnell, 1990). This mechanism and a similar mechanism of 'transmissivity feedback' have helped explain the 'old water paradox' (Kirchner, 2003).

At the scale of whole hillslopes, experiments have shown evidence for these mechanisms leading to threshold behaviour, in which whole hillsides are 'switched on' during events of particular rainfall intensities (McDonnell, 2003). This is sometimes called 'fill and spill' since it is not the surface topography that determines flow paths, but the subsurface topography and/or impermeable soil horizons and their role in controlling the development of saturated conditions. The threshold is particularly controlled by soil permeability, bedrock permeability and slope angle (Jencso and McGlynn, 2011). It also depends on the nature of the precipitation event and antecedent conditions in the hillslope (e.g. soil moisture), which highlights the importance of examining the temporal dimension of these processes.

This significant body of research has led to a model of hillslope runoff mechanisms that includes overland flow due to infiltration excess, but emphasises flow processes within soils and bedrock, the interaction between processes (e.g. return flow and saturation overland flow), and how these vary through time (Figure 1.1).

While this conceptual model helps to explain many aspects of runoff generation mechanisms, a number of questions remain about these processes. One aspect that has not been fully resolved surrounds the relative roles of flow velocities (that control the tracer response) and the hydraulic response (often referred to as the 'celerity', or the speed at which perturbations are transmitted, which controls the hydrograph (McDonnell and Beven, 2014)) in producing storm runoff. This distinction is important because it fundamentally alters how we model runoff generation processes and it also has wider relevance, for example for modelling the movement and dilution of pollutants. There have been calls for better representation of both processes in hydrological modelling, particularly by combining hydrometric and tracer-based experimental techniques (McDonnell and Beven, 2014).

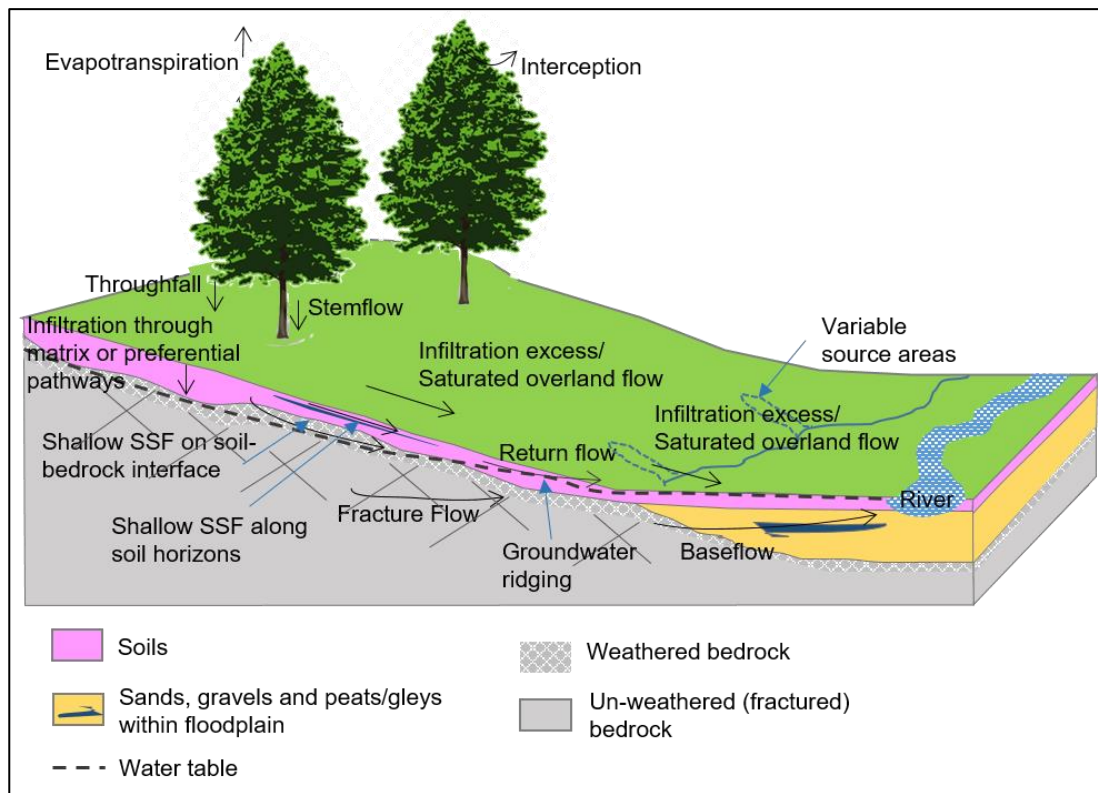


Figure 1.1: Schematic summary of different flow processes operating on and within hillslopes similar to those at the sites investigated in this research. SSF: Shallow subsurface flow.

Another related challenge is scaling up from individual hillslopes to the meso-catchment scale (50-100 km²) that is important in flood risk management. Kay et al. (2019) estimate that only around 25% of quantitative NFM studies in the UK are based on observational data but only three studies investigate catchments >20 km². Modelling studies are more common and many of these have addressed questions of scaling.

Hydrological modelling has developed significantly over the last 40 years with increasing ability to simulate runoff at larger catchment scales. The whole range of modelling approaches (including empirical, conceptual and physical models, as well as both lumped and distributed models) have been applied in an NFM context (e.g. Environment Agency, 2018; O’Connell et al., 2005; Stratford et al., 2017). Early reviews relevant to NFM, such as by O’Connell et al. (2005) on the impact of land use change on flooding, suggested that “there is no generally-accepted theoretical basis for the design of a model suitable to predict impacts, it is not known which data have the most value when predicting impacts, and there are limitations in the methods available for estimating the uncertainty in predictions”. They also

suggested that physically based and distributed models are needed so that the physical properties of landscapes, soils and vegetation can be modelled, but that this would require “a considerable amount of high-quality field data on impacts.” To a certain extent, little has changed, with more recent reviews highlighting continuing discrepancies between results from modelling studies and empirical studies for interventions such as catchment tree planting (Stratford et al., 2017), limited modelling studies in catchments > 100 km² (Kay et al., 2019), high uncertainties when using models to scale up (Dadson et al., 2017), and a lack of data for model validation at large catchment scales (Stratford et al., 2017).

To investigate NFM interventions such as changing land use management, physically based catchment scale models need to represent infiltration through a soil physics and hydrology component that partitions rainfall into surface flow, subsurface flow and evapotranspiration loss. It must also represent field scale surface flow and land drainage if these are not represented explicitly. However, these components are generally not capable of representing important details of water flow in soils such as the effects of mineralogy, natural vertical preferential flow path development, and rainfall impact, crust formation and degradation (O’Connell et al., 2005). It is also difficult to represent the heterogeneity of these factors across landscapes. This leads to a certain degree of lumping in the way that soil physics and hydrology are dealt with, meaning that many existing physically based rainfall-runoff models are over-parameterised and parameters do not represent observable properties once models have been optimised (Beven, 2011). Governing equations, such as the Richard’s equation that describes flow through porous media, are often used as the basis of soil physics modules. However, these do not necessarily represent processes such as the operation of preferential flow paths through soils and rocks at larger scales and complex geometries (Kirchner, 2009). These challenges have led to efforts to develop more general theories of hydrological processes that integrate across scales and heterogeneity. For example, the concept of ‘hydrological connectivity’ is increasingly used as a framework to study hillslope and catchment scale hydrological processes. It is conceived in various ways by different research groups (Bracken et al., 2013), but in essence describes the ability to transfer water from one part of a landscape to another (Bracken and Croke, 2007). It is hoped that incorporating connectivity into hydrological models may combine a number of complex processes, helping to improve process representation and overall predictive capability (Detty and McGuire, 2010).

1.4 Evidence for NFM effectiveness

Our understanding of hillslope and catchment scale hydrological processes fundamentally underpins our understanding of the potential effectiveness of NFM measures aimed at reducing rapid runoff. The catchment-scale effects of land use change on runoff remain a major research challenge (Dadson et al., 2017; O'Connell et al., 2007; Pattison and Lane, 2012). For most NFM interventions that aim to reduce rapid runoff, there is some evidence of their effectiveness at plot and hillslope scales in individual catchments, but the findings become less clear at larger scales. The main findings of a number of recent studies that have reviewed the evidence are:

- **Afforestation:** There is some evidence at the plot, hillslope and small catchment scales (< 10 km²) that afforestation can reduce peak flows, or that deforestation can increase peak flows. However, the effects are small and may be non-existent or undetectable within the bounds of error for larger floods (> 20% of the mean annual flood). Empirical evidence comes from very few sites and studies. For example, Dadson et al. (2017) found only three studies in the UK with quantitative empirical evidence. Stratford et al. (2017) identified 71 UK-relevant studies (in countries with the same Köppen climate classification), of which most were based on modelling; and Carrick et al. (2018) found only 7 empirical studies in Europe that met a strict framework to remove study bias. One of the main studies in Scotland looking at the effects of deforestation runoff was carried out in two small catchments in Balquhidder (6.85 and 7.70 km²). Clear-felling of 50% of the catchment was estimated (with the aid of a model) to have led to a small increase in total flow of approximately 3%. The calculated difference is likely to be within the range of model calibration uncertainty (Dadson et al. 2017). The study did not look at impacts on storm runoff.
- **Buffer strips/tree shelterbelts:** There is some empirical plot and hillslope scale evidence showing that buffer strips increase infiltration rates. However, the empirical evidence in the UK is limited to one study, which reported significant increases in the soil infiltration rate of tree shelterbelts on land used for sheep grazing at Pontbren in Wales (Carroll et al., 2004). The effects of scale in this study were explored by simulating (using a physically based model) a scenario in which all fields in a 6 km² area contain buffer strips at their lower altitude boundary. The results showed a 2-11% reduction in peak flows and no change

in time to peak for a simulated 70 mm d⁻¹ extreme rainfall event over a duration of two days (Jackson et al., 2008).

- **Soil compaction:** There is empirical plot and hillslope scale evidence that soil compaction increases surface runoff. However, there are still significant challenges in scaling up both in terms of understanding whether hydrological processes change at larger scales (e.g. infiltration excess mechanisms may switch to saturation excess mechanisms at larger scales) and in measurement techniques, such as how to map areas of compaction across large areas (Alaoui et al., 2018).
- **Field drainage:** Field drainage has variable effects on runoff depending on factors such as soil type, antecedent conditions, the type of drainage and drainage density. Drainage reduces peak flows from impermeable soils by increasing soil moisture storage capacity and infiltration rates, but increases peak flows from more permeable soils as drains allow infiltrating water to rapidly flow through subsurface pathways (Ballard et al., 2011; Dadson et al., 2017; Pattison and Lane, 2012). Antecedent conditions can alter these effects. Drains increase storage capacity during drier conditions but, if soils are saturated, drains may act to increase peak flows relative to similar undrained soils as both rapid surface and subsurface flow paths are activated. Open drains increase peak flows more than under-field drains due to attenuation effects during infiltration into subsurface drainage networks. A higher density of drainage networks and networks that are extended further upslope increase peak flows by increasing the rate of runoff to rivers. Most of the evidence for these effects is from plot scale studies; there are still few catchment scale experiments (Pattison and Lane, 2012).

The combined effects of NFM interventions are also poorly understood, particularly at larger scales. Three major studies in the UK have looked quantitatively at the impacts of land cover change and land management on downstream water flows and flood risk in large catchments (Dadson et al., 2017). The Sustainable Catchment Management Plan (SCaMP) in the Hodder catchment in Lancashire (260 km²) involved moorland ditch blocking in areas of blanket peat, tree planting and reduction in livestock stocking density. It found no significant effects at the scale of the whole catchment during large events (O'Donnell et al., 2011). The study on historical land use change in the Axe catchment in Devon (289 km²) looked at impacts on metrics of flow variability related to increased percentage cover of

autumn-sown and late-harvested cereals since the 1970s and increased stocking densities of sheep and cattle. It found the impacts limited to small events (10-30 mm of rain) after periods of dry weather (Archer et al., 2010; Climent-Soler et al., 2009). The Pontbren study in North Powys, Wales, also reported, as noted above, a modelled reduction in peak discharge for a 6 km² catchment, but suggested that uncertainties preclude further extrapolation to larger scales. Although the Pontbren results were derived from physically-based modelling, Pattison and Lane (2012) suggest that this study is the only reliable study assessing impacts at different scales in the UK.

The overall conclusion from existing studies of NFM interventions that aim to reduce rapid runoff, is one of considerable uncertainty. Some effects are observable at plot and hillslope scales. However, the effects can be unpredictable due to a continued lack of process understanding, varying for example on the age of planted trees or other underlying properties of catchments such as soil and geological hydraulic properties. There are clearly significant modelling challenges in extrapolating findings to determine larger scale impacts. In large scale empirical studies, there are challenges in the detection of impacts, even if they exist due to measurement uncertainties, and in the attribution due to the complex heterogeneity of catchment characteristics.

1.5 Research gaps in the current understanding of NFM effectiveness

As discussed above, the overarching challenge with NFM is the lack of evidence for its effectiveness, both in terms of what we know about the impacts of some individual measures (which are listed in recent studies, such as Dadson et al. (2017) and Environment Agency (2018)) and what happens at larger spatial scales (> 20 km²). These challenges are not new, and they can be clearly mapped on to more general debates about hillslope and catchment hydrology. The linking of runoff process understanding with NFM implementation is possibly one of the most pressing practical problems surrounding current NFM policy and practice. It has implications for determining NFM effectiveness, where to locate interventions, evaluating 'co-benefits' and assessing potential unintended consequences, such as impacts on the viability of different land uses. All of these aspects ultimately link to

NFM policy, as uncertainties in NFM outcomes are one of the key barriers to uptake (Waylen et al., 2017).

Much of the literature from NFM practitioners seeking to implement interventions that reduce rapid runoff is focused on reducing rapid overland 'Hortonian' flow. There are two key problems with this conceptualisation. Firstly, as discussed in Section 1.3, overland flow may be a consequence of either infiltration excess or saturation excess processes, which fundamentally alters the conceptualisation of flow paths, with implications for the design of interventions to manipulate these flow paths. In saturation excess situations, measures to increase infiltration are unlikely to work (Environment Agency, 2018). For example, tree planting may increase infiltration rates but the overall effect might be limited by the soil water storage capacity, which is linked to soil porosity, soil depth and the underlying geology.

Secondly, subsurface runoff through soils or the groundwater system may be an important contributor to storm flow and needs to be considered in assessing the impacts of NFM interventions. Channelling more runoff into the ground (e.g. through planting tree shelterbelts) does not mean it will just 'disappear', but may result in complex feedback processes linked to subsurface processes (Klaus and Jackson, 2018). For example, groundwater may be released rapidly downslope in certain environments due to celerity effects (McDonnell and Beven, 2014) or the slow exfiltration of groundwater could increase the extent of the downslope saturated area, promoting increased saturation excess runoff during sequences of storm events. There have been calls to consider the interaction of fluvial floods with other flood types such as groundwater flooding, and sequences of events also warrant further systematic study (Dadson et al. 2017).

The distributed nature and 'natural' form of many NFM measures is an additional challenge that makes the understanding of processes and their effects on flooding even more complex. Many NFM measures may be harder to model quantitatively compared to more traditional flood risk management interventions (Pappenberger et al., 2006). Debris dams, for example, pose challenges for hydraulic modeling individually, and these increase when many dams are put in place along river channels. This might require novel modelling methods and more comprehensive, or alternative, monitoring methodologies to establish impacts. These examples of the nuances of runoff mechanisms, combined with the distributed nature of NFM

measures also point to the need for much better process understanding about the 'hierarchy of influences' (Jencso and McGlynn, 2011) controlling runoff mechanisms and flow paths in catchments prior to implementation. This is of course one of the primary drivers of much hydrological research, but NFM and other nature-based solutions make this even more pressing.

To our knowledge, environmental tracers have not yet been investigated in UK NFM projects, but might help to address some of these challenges. Tracers can give information on the sources, pathways and residence times of water in catchments, thus contributing to process understanding and complementing hydrometric data on the 'celerity' of water movement with that on 'velocity' (McDonnell and Beven, 2014). At a practical level, this might help with questions about locating NFM measures, assessing their effectiveness, and quantifying co-benefits (e.g. pollution control). Tracers might also inform understanding of process scaling as they can be good process 'integrators', help with calibrating hydrological models and provide independent quantification from flow-based measurements (e.g. of event runoff fractions). Given that a key challenge with NFM is that effects at scale may not be measurable due to the high levels of uncertainty, tracers might also help to reduce such uncertainties.

1.6 Research aim, novelty and questions

The overarching aim of this research project was to investigate how NFM interventions using land cover change to reduce rapid runoff from hillslopes alter discharge dynamics and hydrological flow paths, with particular emphasis on partitioning between surface and subsurface flow. This responds to calls in the hydrological literature (Jencso and McGlynn, 2011) suggesting, in the context of our still limited understanding of first order controls on catchment runoff processes, that "further landscape-scale investigations are needed to evaluate the interplay between patterns of vegetation water-use efficiency, hydrologic connectivity, and runoff generation across finer space and timescales[...] Additionally, hillslope-scale studies that address both shallow subsurface and deeper groundwater flow components are needed to assess the impact of local disturbance in a larger watershed context." It also responds to some of the gaps outlined in Section 1.3 in the current understanding of NFM, in particular linking NFM interventions to a clear

understanding of runoff mechanisms and the need to incorporate knowledge of subsurface flow processes, including groundwater dynamics.

The study also uses techniques that, to our knowledge, have not been applied in an NFM context. These include isotopic and geochemical tracers (Chapters 3 and 4) and time-lapse electrical resistivity tomography (ERT) (Chapter 5) to help examine runoff sources and pathways, particularly in the subsurface.

The research aim was achieved through empirical research at both catchment and hillslope spatial scales, and storm event and seasonal timescales, in an experimental meso-scale catchment containing nested sub-catchments. The following questions were addressed. The conceptual model in Figure 2 illustrates how the different questions and scales of investigation are interlinked.

Catchment scale controls on storage and flow paths at seasonal timescales

- 1.A. *What are the dominant controls on catchment storage, mean transit times (MTTs) and groundwater fraction in rivers?*
- 1.B. *Does forest cover have a discernible impact on catchment storage, mean transit times (MTTs) and groundwater fraction in rivers?*

Catchment scale controls on runoff partitioning at the storm event timescale: the role of land cover

- 2.A. *What proportion of runoff in high flow events originates from water that was stored in the catchment prior to the event (pre-event water)?*
- 2.B. *Does the percentage of catchment forest cover have a discernible impact on the proportion of runoff during high flow events that is derived from pre-event water?*
- 2.C. *Are runoff mechanisms in catchments with different characteristics the same across events of different total rainfall depth, intensity and antecedent conditions?*

The impacts of forest cover on hillslope subsurface hydrological dynamics

- 3.A. *Does forest cover on hillslopes increase soil moisture storage capacity and reduce subsurface water table connectivity?*

3.B. *Does catchment forest cover have spatial dimensions such that fragments of forest cover on hillslopes have discernible hydrological impacts downslope?*

1.7 Thesis structure

The thesis has seven Chapters including this introduction. **Chapter 2** contains a detailed description of the research methodology, including the experimental design, details of the study site, and the field, laboratory and GIS methods used. **Chapters 3-5** are the results Chapters for the three main experiments which were structured around the three groups of questions defined in Section 1.6. The experiments spanned the catchment to hillslope scale as well as different temporal scales. The results Chapters are written in paper format, giving further details of methods specific to each experiment where necessary, presenting results and discussing the findings. **Chapter 3** focusses on the meso-catchment scale on questions related to catchment scale storage and seasonal storage dynamics (Questions 1A-1B). It compares nine sub-catchments across the 67 km² Eddleston Water catchment using weekly hydrometric and tracer data. **Chapter 4** focusses on the headwater (~3 km²) scale on understanding runoff dynamics and flow paths during high flow events (Questions 2A-2C). It compares three contrasting headwater sub-catchments in the Eddleston Water catchment using higher frequency hydrometric and tracer data. **Chapter 5** focusses on the hillslope scale, investigating tree shelterbelts as a specific NFM intervention. It looks at how such shelterbelts alter hillslope subsurface moisture dynamics compared to improved grassland, using soil moisture, groundwater and electrical resistivity tomography data to address Questions 3A-3B. **Chapter 6** discusses the results from all three experiments, the limitations of the research, and future research needs. **Chapter 7** summarises overall conclusions from the work including the main scientific findings, priority areas for further research, and policy implications.

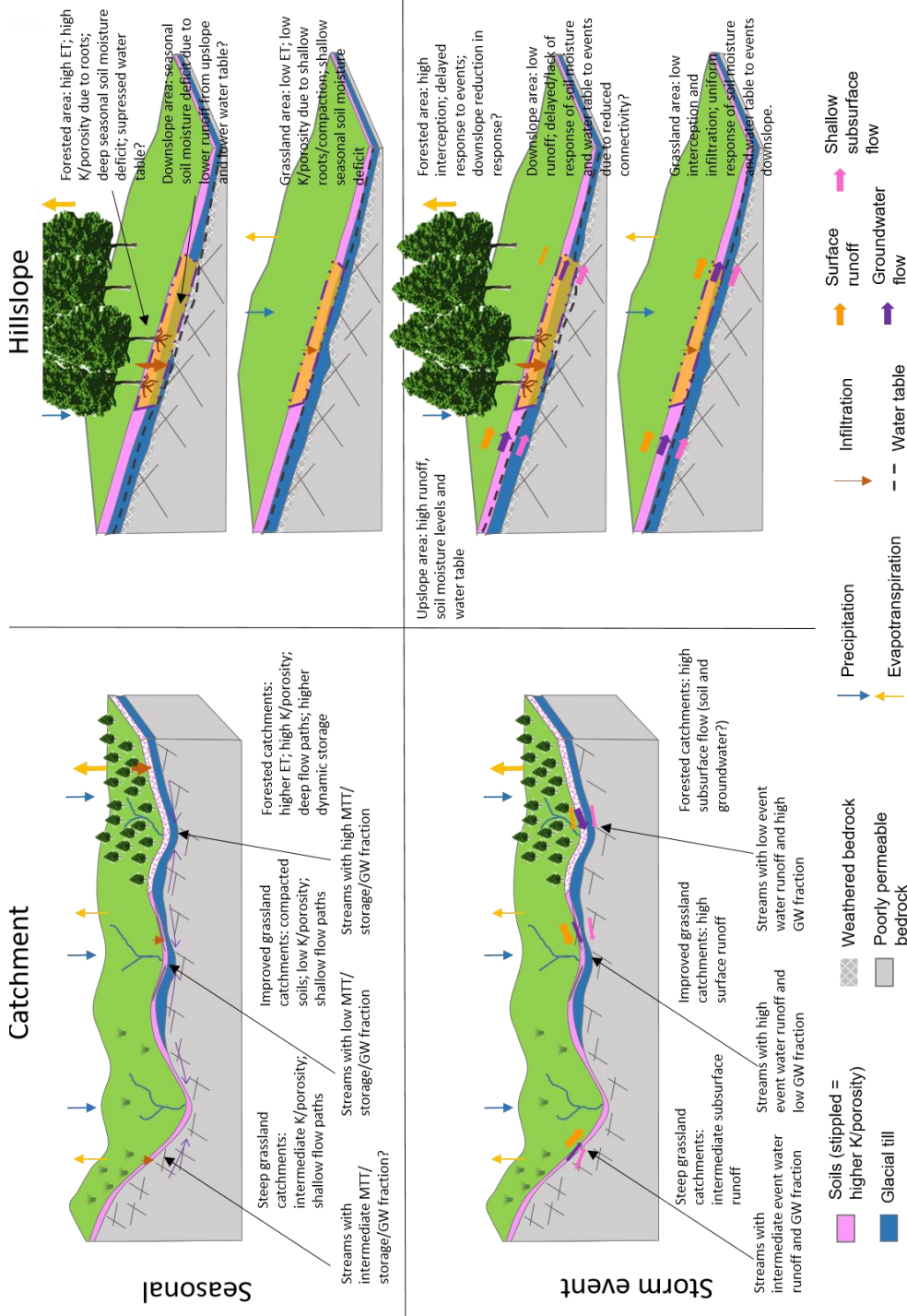


Figure 1.2: Conceptual model linking the main research questions across different temporal and spatial scales in a typical upland temperate catchment. Arrow sizes approximate the relative scale of different fluxes. Soil depth not to scale and some fluxes omitted for clarity (e.g. throughfall).

2 Methods

This Chapter contains methods relevant to all Chapters including a description of the study site, the experimental setup, and the field, laboratory and desk-based methods used. Data analysis methods specific to each results Chapter are included in the relevant Chapter.

2.1 Site description

The research was conducted in the 67 km² Eddleston Water catchment, a tributary of the River Tweed in the Scottish Borders, UK. The Eddleston Water river flows due south and is fed by a number of small streams draining from the west, north and east from distinctly different sub-catchments (Figure 2.1). The catchment hosts a project initiated in 2010 with support from the Scottish Government, European Union and a local implementing NGO (the Tweed Forum), to investigate the impact of natural flood management (NFM) measures aimed at controlling runoff from farmland and forest land (Werritty et al., 2010).

Catchment characteristics are typical of much of the UK uplands. Topography is varied with elevations of 180-600 m (Figure 2.1) and the climate is cool with mean annual precipitation of 1180 mm (at Eddleston Village, 2011-2017), falling mainly as rainfall. Mean daily temperatures range from 3 °C in winter to 13 °C in summer. Actual daily evapotranspiration ranges from 0.2 mm in winter to 2.5 mm in summer (estimated using the Granger-Gray method (Granger and Gray, 1989) using data from the weather station in the catchment at Eddleston Village).

Land cover (Figure 2.2) is mainly improved or semi-improved grassland on the lower slopes, rough heathland at higher elevations and marshy ground in the hollows (Medcalf and Williams, 2010). Forest cover was historically limited in most of the catchment, but extensive coniferous plantations were established in the 1960s and 1970s in some of the western sub-catchments, with up to 90% forest cover (Table 2.1). Forest cover in other parts of the catchment is typically mixed coniferous and deciduous woodland, concentrated along field boundaries.

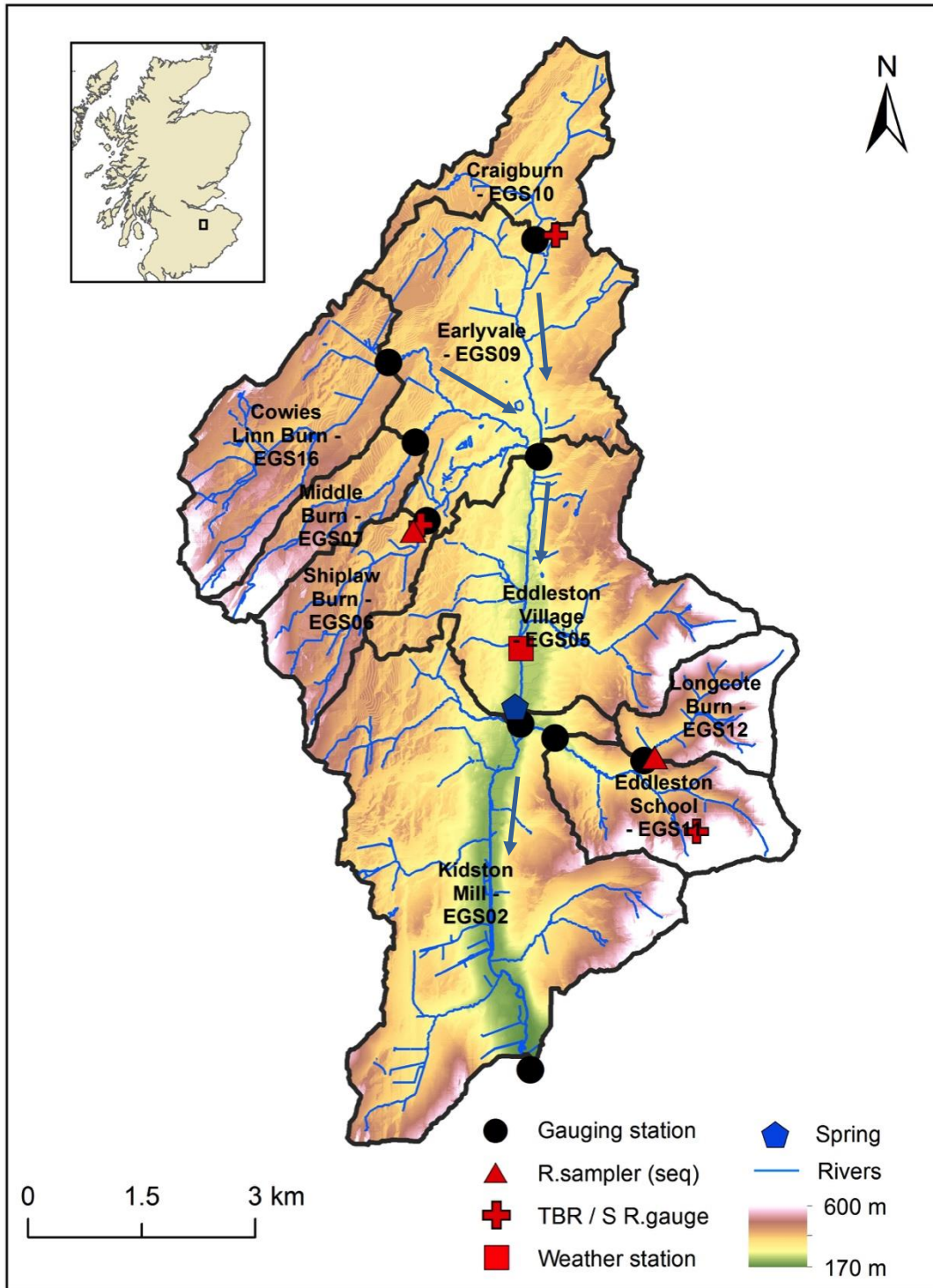


Figure 2.1: The Eddleston Water location and map showing catchment topography, the river network, the monitoring network, and the nine sub-catchments examined in this study. R.sampler (seq): location of sequential rainfall samplers used in Chapter 4. TBR / S R.gauge: paired tipping bucket rain gauges and storage rain gauges used in the study. Blue arrows indication direction of river flow. The weather station at the centre of the catchment near Eddleston Village is located at 55.717° N -3.208 W°.

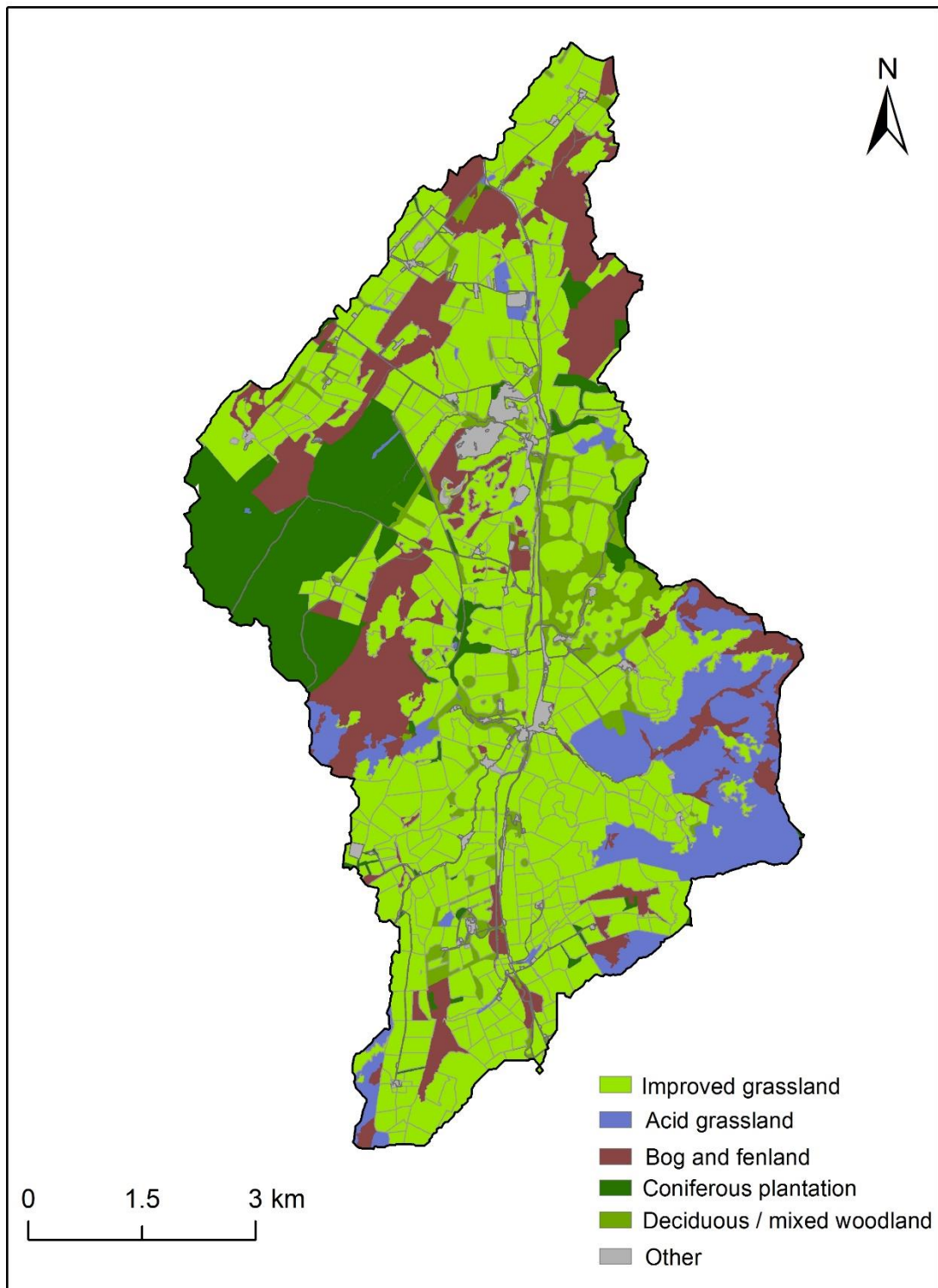


Figure 2.2: Land cover map of the Eddleston Water catchment with simplified land cover classification as described in Section 2.5. Note that the map distinguishes between coniferous and deciduous woodland for illustration purposes only. Due to the low percentage of deciduous woodland in the catchment, it was grouped into a single woodland category for analysis.

Soils on steeper hillsides are typically freely draining brown soils overlying silty glacial till, rock head or weathered head deposits (Figure 2.3 and Figure 2.4). Towards the base of the hillslopes the ground is typically wetter and soils comprise sequences of gleyed clays and peats on sub-angular head deposits or alluvial deposits closer to the river. Soil types reflect the underlying geology, with large differences between east and west (Soil Survey of Scotland Staff, 1970). The west has extensive areas of poorly permeable gleyed soils and peats, but also areas of more freely draining brown soils, whilst the centre and east of the catchment is dominated by brown soils but with some peaty and gleyed soils on hilltops. Hydraulic conductivity of soils overlying head deposits has been measured as part of the wider project on a hillslope to floodplain transect at the centre of the Eddleston catchment. This found median values of 21-39 mm h⁻¹ (0.50-0.94 m d⁻¹) for improved grassland and 42 mm h⁻¹ (1 m d⁻¹) for ~50 year old plantation forest, 119-174 mm h⁻¹ (2.86-4.18 m d⁻¹) for broadleaf forests > 180 years old (Archer et al., 2013), and 1-8 mm h⁻¹ (0.02-0.19 m d⁻¹) for floodplain soils.

Bedrock throughout most of the catchment is comprised of Silurian poorly permeable well-cemented, poorly sorted sandstone greywackes (Auton, 2011). Extensive glaciation during the last glacial maximum has affected the superficial geology and soil types (Ó Dochartaigh et al., 2018, 2012; Sissons, 1958). The western part of the catchment has extensive, thick and poorly permeable glacial tills (often > 5 m thick) (Aitken et al., 1984) but with some highly permeable glacio-lacustrine sands and gravels in isolated areas (Figure 2.5). The centre of the catchment has extensive alluvial and head sand and gravel deposits (up to 20 m thick) overlying bedrock or glacial till. The hydraulic conductivity of the glacial till is estimated to range from < 0.001 to 1 m d⁻¹ based on data from other locations in Scotland (MacDonald et al., 2012). Hydraulic conductivities of the sand and gravel alluvial and head deposits have been measured as 500 m d⁻¹ (Ó Dochartaigh et al., 2018). The east of the catchment is mostly thin soils and rock head overlying bedrock, with smaller areas of glacial till mantling some of the main streams. The hydraulic conductivity of the bedrock was not measured, but Silurian greywacke aquifers elsewhere in southern Scotland have been shown to have low productivity (Ó Dochartaigh et al., 2015), with an estimated average transmissivity of 20 m² d⁻¹ (Graham et al., 2009).

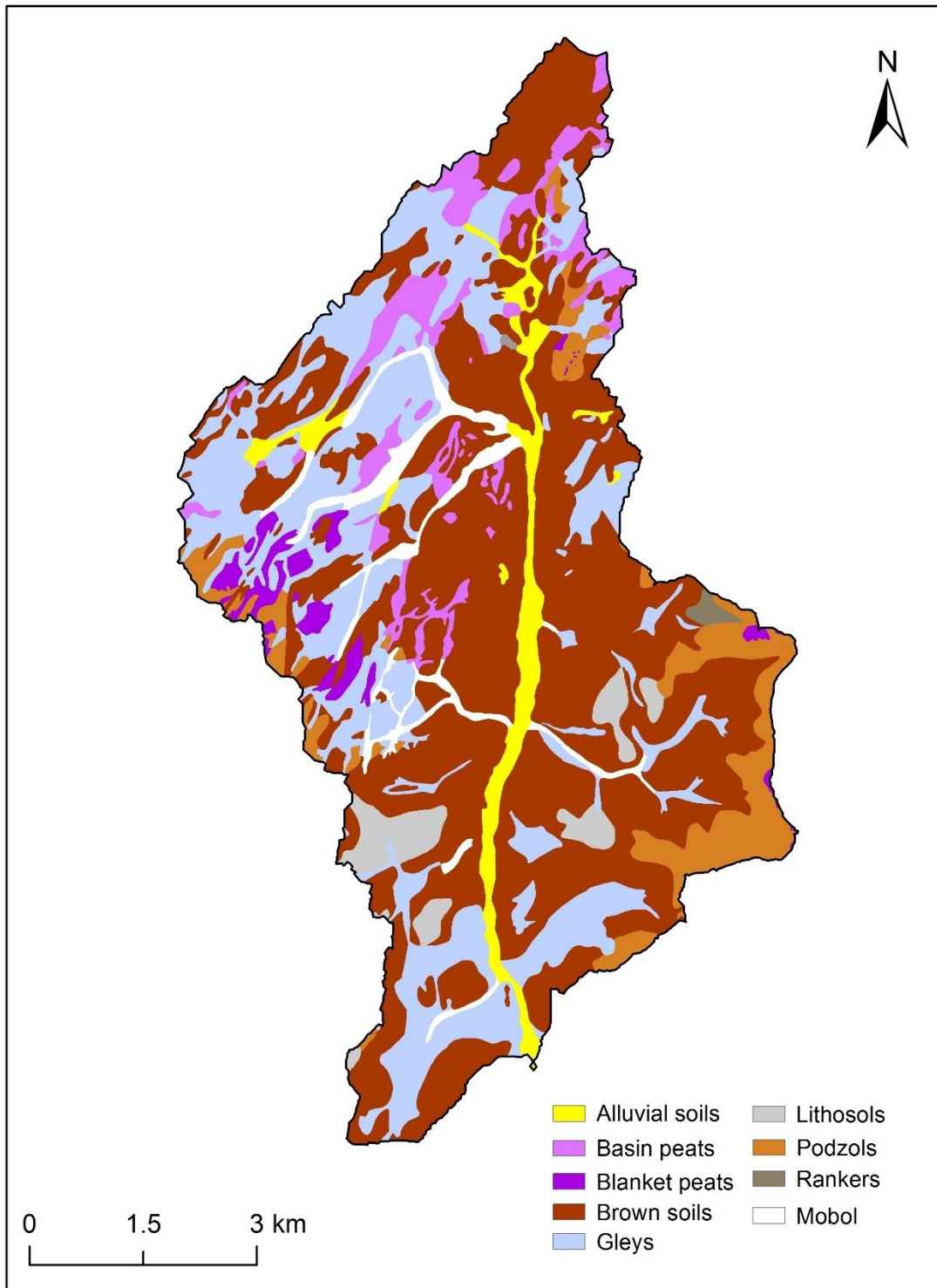


Figure 2.3: Soil map showing major soil groups (MSG) in the Eddleston Water catchment. 'Mobol' is 'Mixed Bottom Land' as defined in the 1:25,000 soil map of Scotland (2013 version).

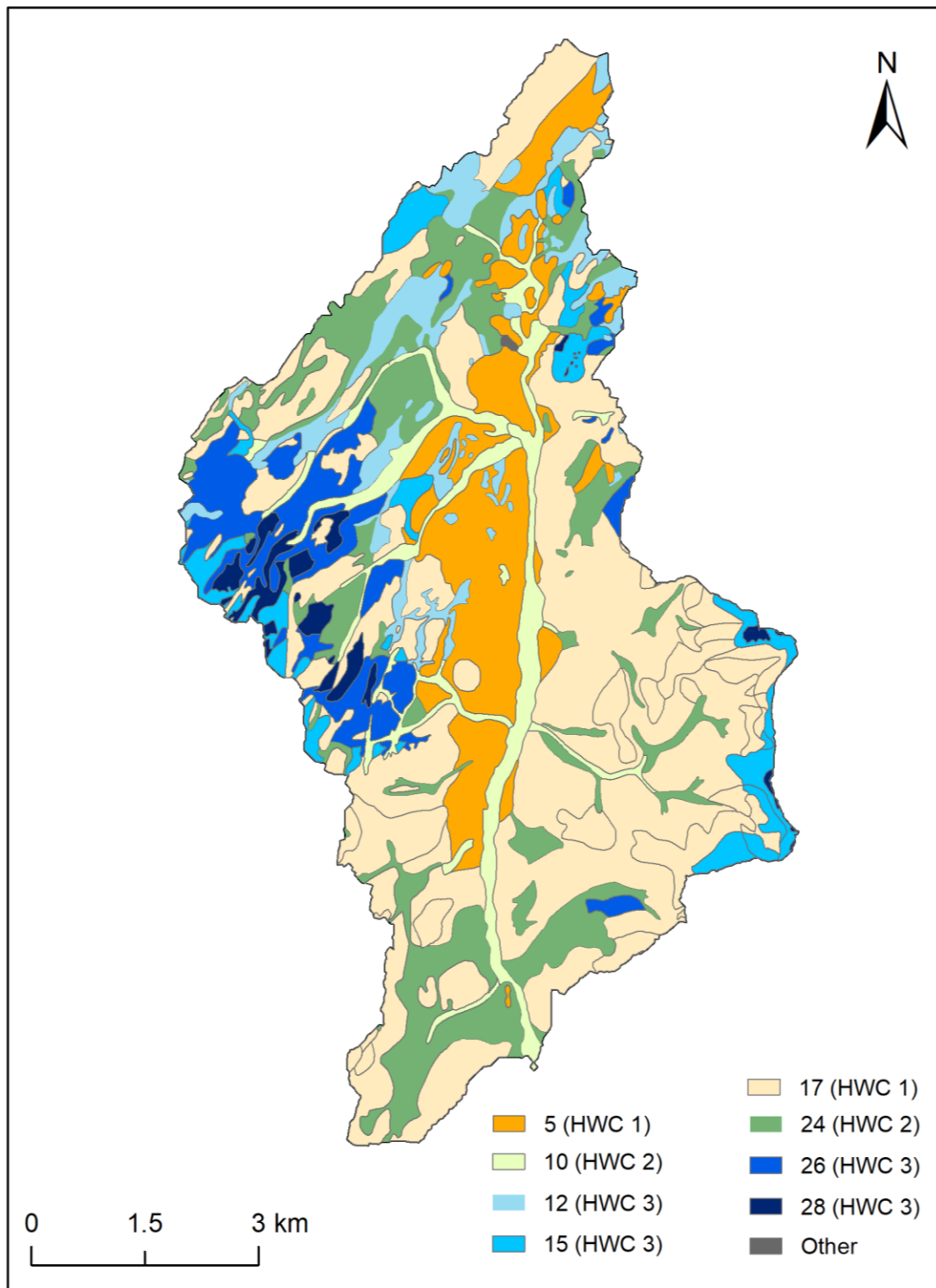


Figure 2.4: Soil HOST class map, showing the dominant soil types in the catchment based on their hydraulic properties. HWC defines the three different HOST wetness groupings used in the analysis in Chapter 3 with HWC 1 being the most freely draining soils and HWC 3 being the most poorly draining soils.

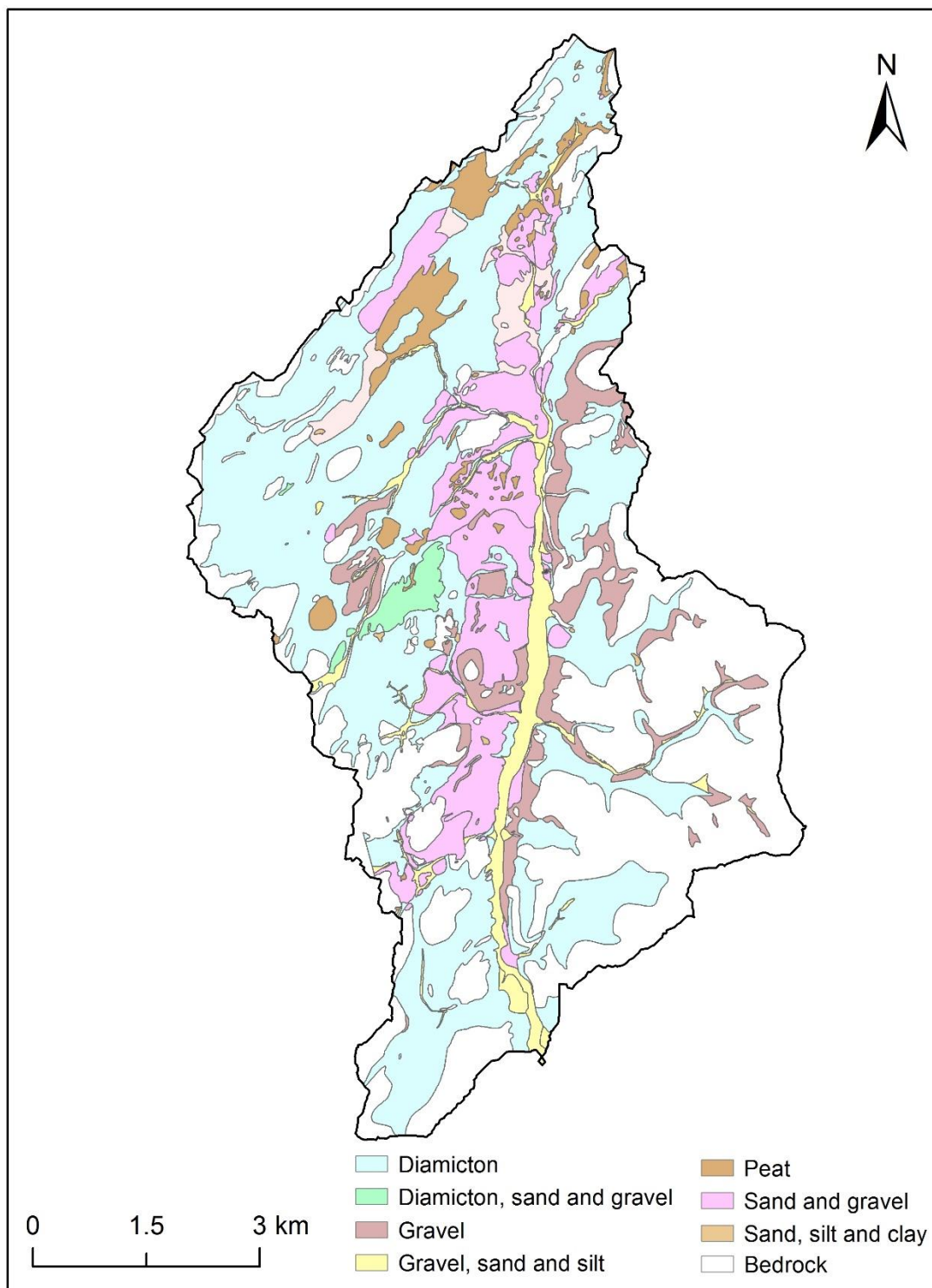


Figure 2.5: Superficial geology map of the Eddleston Water catchment based on survey conducted for the Eddleston Water NFM project in 2011 (Auton, 2011). Mapping units are based on the BGS Rock Classification Scheme.

The catchment has undergone extensive human-induced changes over the last 500 years including deforestation, land drainage, river straightening and afforestation (Harrison, 2012). These changes, combined with a risk of flooding to 500 houses in the valley, have made it a focus for a pilot natural flood management project (Werritty et al., 2010).

The majority of the NFM measures were installed between 2013 and 2015 and include: 1) tree planting (207 ha, ~233,000 trees); 2) establishment of 28 holding ponds (totalling around 0.8 ha of 'wetland') on farmland in some headwater catchments; 3) re-meandering 2.8 km of the Eddleston Water river; 4) removal of 2.9 km of flood embankment; 5) the construction of 116 wooden 'leaky' dams in some headwater sub-catchments; and 6) the construction of one large floodplain holding pond (Tweed Forum, 2019) (Figure 2.6). This study assumes that the catchment scale impacts of these measures on long-term storage dynamics (the subject of experiment 1 discussed in Chapter 3) are likely to be minimal. This is because the trees planted by the project were still young at the time of fieldwork and will take time to affect infiltration rates/soil porosity, and the holding ponds cover a small area of the whole catchment (and are designed to empty rapidly after events). The potential exception is the impact of the debris dams during high flow events. The dams are mainly brushwood laid over the channel, so only restrict flow at high flows and release water quickly as storms subside. Given this design and that little difference was found between total event water fractions and event water fractions at peak discharge during the storms observed in Chapter 4, we assume that they have little impact on partitioning. This may not be the case during larger events than those observed, but further event monitoring would be required to assess this.

2.2 Experimental design

The research was designed to investigate how catchment properties influence surface water-groundwater interactions in the context of upland landscapes that are target areas for UK natural flood management policies. It focussed on trying to establish at the meso-catchment scale, how land cover, topography, soils, and geology interact to control flow paths. The experiments covered three different spatial scales and two different time scales to help give insights into catchment processes and to address the question of scalability, which remains one of the main challenges for NFM (Dadson et al., 2017; Lane, 2017).

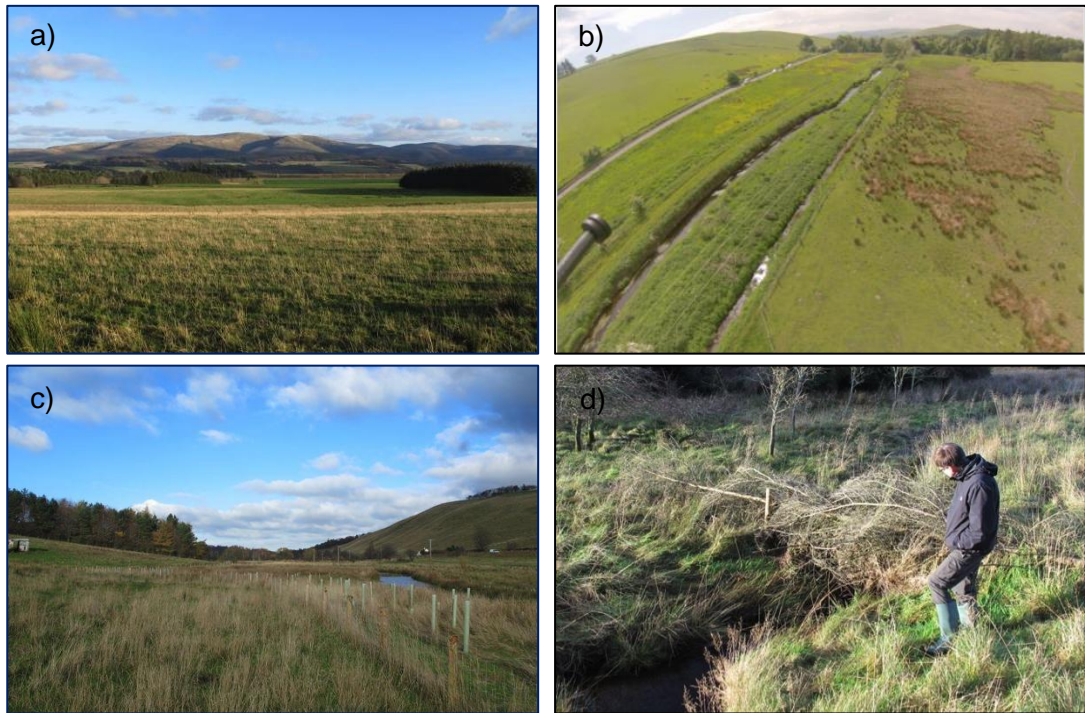


Figure 2.6: Examples of catchment characteristics and NFM interventions. a) view looking east across Cowieslinn and Earlyvale sub-catchments; b) aerial photo of Eddleston Water prior to re-meandering, showing extensive straightening of channel (source: Tweed Forum); c) riverside tree planting and wetland creation beside re-meandered section of Eddleston Water; d) debris dam in Middle Burn sub-catchment.

The Eddleston Water catchment is an appropriate field site for this analysis because of the dense hydrometric monitoring network (nine flow gauging stations and four tipping bucket rain (TBR) gauges (including the TBR at the weather station), described in Section 2.3 below) that delineates sub-catchments at a scale at which there is still much uncertainty about the effectiveness of NFM. The monitoring network is thought to be one of the densest in the UK at this scale. It has also been in place for a relatively long time (since April 2011) compared to other NFM pilot sites. Some sites with detailed monitoring in place, such as Pontbren in Wales, have existed for a long time (since 1997) (Marshall et al., 2009) but most others have only been established since 2017 with support from the Natural Environment Research Council (NERC). The Eddleston Water catchment is also a good site because it is typical of many upland areas in the UK but the sub-catchments have considerable diversity of land cover, soil types, geology and topography enabling cross-catchment comparison. At a practical level, the active engagement of the Scottish Government and the Tweed Forum, and buy-in from the local community, given that parts of Eddleston Village and Peebles are at risk of flooding, mean that access to existing

monitoring sites and permission to establish new sites was relatively easily sought. The experimental design is described in more detail below and summarised in Table 2.2.

2.2.1 Design of Experiment 1 (Chapter 3)

The first experiment (Chapter 3) looked broadly at hydrological processes operating across the majority of the 67 km² Eddleston Water catchment (a gauging station just north of the town of Peebles defined the largest nested catchment of 59.5 km²). It used continuous hydrometric and weekly isotopic/acid neutralising capacity (ANC) sampling data, to give insights into how catchments store and release water over seasonal timescales. These questions are important from an NFM perspective because catchment storage is a fundamental property underlying many other catchment processes, and many NFM interventions aimed at curtailing runoff before it reaches rivers (e.g. reduced soil compaction, tree planting) assume some degree of available catchment storage. The experimental design built on numerous studies that have used cross-catchment comparison of catchment properties and hydrological responses to give insights into hydrological processes (Ali et al., 2012b). However, such studies at this scale are still relatively rare in the UK, particularly where they combine hydrometric and tracer information, though a substantial body of work exists for areas further north in Scotland (e.g. Soulsby et al., 2006b; Tetzlaff et al., 2009b).

The experiment focussed on nine of the 12 sub-catchments in which there is hydrometric monitoring. Samples for isotopic and geochemical analysis (²H, ¹⁸O, acid neutralising capacity (ANC), conductivity, pH) were collected on a weekly basis over the course of a year from stream gauging sites adjacent to the stream gauging stations, one spring and three storage rain gauges. Analysis of these datasets, in combination with continuous (15 minute) discharge/rainfall measurements at each stream site/storage gauge site, and GIS datasets, enabled cross-catchment comparison.

The criteria for catchment selection were to include all of the headwater catchments (five catchments), given their diversity and similarities in catchment area, and four nested sub-catchments, as these could give insights into the scaling of hydrological processes. The spring samples were taken at a wetland site close to Eddleston Village to characterise the groundwater isotopic signature and chemistry. This

location was chosen given its situation at the centre of the catchment and extensive prior research undertaken at the site (Archer et al., 2013; Ó Dochartaigh et al., 2018). Three of the existing storage rain gauges were included in the monitoring to help characterise rainfall depths and the isotopic composition of rainfall. The three gauges were chosen to give good geographic coverage of the Eddleston Water catchment, particularly in the headwaters, and to include samplers in the east and west. The final selection of sub-catchments and rain gauges also met the sampling programme time constraints (each field outing for routine sampling took about 6 hours) and financial constraints for isotopic analysis of water samples (initially limited to 1000 samples).

Table 2.1: Summary of the land cover, soils and geology of the nine catchments selected for Experiment 1. Both catchment names and codes are given. Land cover and geology were re-classified as described in Section 2.5 to reduce the number of categories. Soil types are based on 'major soil groups' (MSG), though categories covering < 1% of any catchment (Quarries and Rankers) have been removed from summary data.

Characteristic	Acronym	Kidston EGS02	Eddleston EGS05	Earlyvale EGS09	Cowieslinn EGS16	School EGS11	Craigburn EGS10	Shiplaw EGS06	Longcote EGS12	M. Burn EGS07
% cover in catchment										
Land cover										
Acid grassland/ heathland	LU_Gui	10	2	1	0	58	0	3	64	1
Semi- and improved grassland	LU_Gi	55	51	45	39	29	59	28	11	2
Woodland	LU_F	16	24	27	38	1	4	41	0	94
Dry/wet bog and fenland	LU_M	15	17	21	18	11	31	27	22	0
Soils										
Alluvial soils	S_Alluv	4	5	5	4	0	0	0	0	1
Basin peats	S_B_peat	6	9	18	12	0	24	5	0	9
Blanket peats	S_Bl_peat	2	3	2	4	1	0	11	2	19
Brown soils	S_Brown	50	47	43	37	56	57	35	59	11
Gleys	S_Gleys	24	26	24	33	6	16	33	8	39
Lithosols	S_Lith	3	1	0	0	5	0	0	3	0
Mobol	S_Mob	3	4	2	5	2	0	6	0	15
Podzols	S_Podz	7	5	5	5	30	3	10	28	4
Geology										
Glacial till and peat	G_Di	43	52	61	72	12	67	63	8	76
Sand and Gravel	G_SG	24	28	23	9	8	7	16	8	12
Bedrock (Greywacke)	G_Br	33	20	17	19	80	26	21	84	12

2.2.2 Design of Experiment 2 (Chapter 4)

The second experiment (Chapter 4) focussed on three headwater catchments with contrasting catchment characteristics (Shiplaw Burn (EGS06), Middle Burn (EGS07) and Middle Longcote (EGS12)), investigating how they respond to storm events and combining hydrometric and tracer methods to quantify runoff sources. These questions are important for NFM because of the need to understand catchment runoff sources and pathways in order to select optimal locations for NFM interventions, particularly given that only marginal reductions to peak runoff might be expected under realistic scenarios of the extent of interventions (Dadson et al., 2017).

Storm samples from seven storms were collected at two hourly intervals during high flow events using automatic samplers (with the exception of one location for one event when a sampler was not available, so manual sampling was conducted at lower frequency) located near to the gauging station in each sub-catchment. Rainfall sampling used two sequential water samplers built for the experiment (see Section 2.3.1). Samples were used for isotopic and geochemical analysis (^2H , ^{18}O , acid neutralising capacity (ANC), conductivity, pH) to characterise water sources and mixing dynamics during events. These datasets were combined with continuous discharge data and GIS data to compare dynamics across the three catchments.

The three sub-catchments were selected based on their contrasting properties. Middle Burn and Shiplaw are adjacent catchments with similar geology, soils and topography but contrasting land cover (Middle Burn is over 90% forested, whilst Shiplaw has a mixture of forest, improved grassland and wetland) allowing a paired catchment approach. Longcote was also included as it has a markedly different hydrometric response and contrasting soils, superficial geology and topography. This means it could give insights into the heterogeneity within a meso-scale catchment, in particular into the hierarchy of controls on runoff response between land cover and the substrate.

2.2.3 Design of Experiment 3 (Chapter 5)

The third experiment (Chapter 5) investigated land cover and soils/geology interactions at the hillslope scale to give more detailed insights into their influence on subsurface moisture dynamics. By focussing on an across-slope forest strip the experiment was able to provide understanding of the operation of a specific NFM

intervention that is being suggested as part of current UK NFM policies (Environment Agency, 2018).

Table 2.2: Summary of the main research questions and the associated experimental design and methods used in each Chapter.

Questions	Experimental design	Methods
Chapter 3: How do catchment characteristics influence catchment storage, transit times and inferred runoff flow paths?	Cross-comparison of metrics of catchment storage with GIS derived catchment characteristics data for 9 sub-catchments.	<ul style="list-style-type: none"> • Recession analysis using 7 years of 15-min hydrometric data. • Mean transit time estimation using 1 year of weekly river and rainwater isotopic data. • Groundwater fraction estimation using 1 year of weekly ANC data. • GIS analysis of topography, land use, soils and geology data.
Chapter 4: How do catchment characteristics affect flow pathways during high flow events?	Cross-catchment comparison of high flow response of 3 similarly sized sub-catchments. 2 adjacent catchments with similar properties were paired to examine the influence of forest cover. A third catchment with different soils/geology allowed for relative influence of substrate to be considered.	<ul style="list-style-type: none"> • Analysis of hydrometric response during high flows using 15-min flow data (lag times, runoff coefficients etc.). • Two and three component hydrograph separation using 2-hourly isotopic and ANC data from 4 high flow events, and high frequency rainfall sampling for isotopic analysis. • GIS analysis of topography, land use, soils and geology data.
Chapter 5: How do forest strips on hillslopes affect subsurface moisture dynamics?	Comparison of two transects: one on improved grassland and one on improved grassland but crossing a mature mixed forest strip. Distributed monitoring to look at effects within and upslope/downslope of the strip.	<ul style="list-style-type: none"> • Seasonal and event analysis of 18 months of 15-min soil moisture data at different depths. • Seasonal and event analysis of 18 months of 15-minute groundwater level data at 2.5 m depth. • Bi-monthly repeat ERT (10 surveys) to look at inferred soil moisture dynamics in top 5 m.

Soil moisture and groundwater dynamics were compared on two transects spanning the same elevation on a 9° hillslope in a temperate UK upland catchment. One transect was located on improved grassland; the other was also on improved grassland but included a 14 m wide strip of 27-year-old mixed forest. Subsurface moisture dynamics were investigated upslope, underneath and downslope of the forest over 2 years at seasonal and storm event timescales. Continuous data from point-based soil moisture sensors and piezometers installed at 0.15, 0.6 and 2.5 m depth were combined with seasonal (~ bi-monthly) time-lapse electrical resistivity tomography (ERT) surveys.

The hillslope was selected through detailed examination of aerial photographs and walkover surveys of four shortlisted sites. The criteria for final site selection were: 1) the presence of a mature (> 25 years) forest strip of dimensions similar to NFM boundary planting interventions; 2) a strip sited on a uniform hillslope with adjacent improved grassland; 3) permission to install equipment, protect against farm animals and remove constraints (in particular the forest fence had to be insulated from the ground in order not to interfere with the ERT surveys); and 4) accessibility given the heavy drilling and ERT survey equipment needed for the research.

2.3 Field methods

2.3.1 Rainfall measurement

Rainfall has been measured continuously at four sites (including the weather station at Eddleston Village) set up in accordance with Met Office standards, since April 2011. No specific methods were deployed to quantify snowfall given the limited snowfall experienced in the catchment (an annual average of 10-20 days of snow lying based on 1981-2010 data (Met Office, 2020)) and that significant lying snow (~5 cm on ground > 350 m) was only observed during three of the weekly sampling field visits. However, in one of the high flow events (hereafter termed 'events') monitored for Chapter 4, which involved some snowfall, lying snow was used to characterise the snowfall input endmember.

Rainfall measurement uses RIM8020 tipping bucket rain gauges coupled with event recorders (recording at 15-minute intervals and in increments of 0.2 mm) and stainless steel Octapent storage rain gauges that meet UK Environment Agency requirements. TBR data have been downloaded approximately every 6 months (time

series is shown in Appendix A, Figure A.1) and the storage gauge volumes have been measured approximately monthly by the University of Dundee since 2011. During site visits all rain gauges are checked for obstructions and for the TBRs calibration checks are conducted occasionally. During the isotopic/geochemical sampling carried out in Chapters 3 and 4, storage rain gauges at the three sites (Shiplaw rain gauge (ERG06), Craighburn rain gauge (ERG10) and Burnhead rain gauge (ERG14) in Eddleston School catchment) were checked at least 2-weekly from May 2015 to May 2017 (weekly checks were undertaken between September 2015 and August 2016). This enabled the use of one year of higher resolution (weekly) sampling for the storage and transit time analysis in Chapter 3 and two years of lower resolution (2-weekly) sampling to contextualise the event analysis in Chapter 4.

All rainfall data were quality checked prior to any further analysis. Firstly, TBR data were compared to adjacent storage gauge data at each of the sites to check cumulative totals during the study period. These comparisons showed good consistency for the Shiplaw and Burnhead rain gauges, but considerable under-catch for the Craighburn rain gauge from September 2015. A correction was therefore made to the Craighburn TBR data after this date using the ratio of cumulative rainfall from the TBR and the adjacent storage gauge data over the study period; specifically, the step change in this ratio in September 2015 was used as a multiplier for each TBR reading after this date. Cumulative TBR totals were re-calculated and showed better correspondence with the storage gauge data (< 10% difference in cumulative total at any point in the time series), and the corrected values were used in subsequent analysis where necessary (see Appendix A, Figure A.2).

The TBR data were then checked for gaps at each site. There were some gaps in rainfall data during the period of this study (May 2015 – May 2017) although there was only one major gap (~ 1 month) at one site (Shiplaw) during the weekly sampling (Chapter 3) and event sampling (Chapter 4). There were larger gaps at some sites for the October 2011 – April 2015 data that were used as part of the catchment storage calculations in Chapter 3 (in order to determine dry night time periods as described in the Chapter). Given that data from the weather station had few gaps and at any one time at least two TBRs were working, this allowed an estimation of mean catchment rainfall and for infilling of data gaps. These infilled datasets were used in the storage calculations. Before any gap filling was

undertaken, a comparison of spatial variation in rainfall was made for all days on which all gauges were working. This showed some spatial variation across the catchments, with a 15% difference in total rainfall recorded over the period October 2011 – September 2017, compared to the mean total for this period and a maximum 25% difference for annual totals in any single year.

Given these variations in catchment rainfall, the distance-power method was used to infill missing data (arithmetic mean values are only considered suitable when differences are less than 10% (Chow et al., 1988)) using the distances between gauges. Regionalisation was also carried out using inverse distance weighting to further distribute rainfall across the different sub-catchments based on distances between catchment centroids, although in practice this made little difference to catchment totals.

2.3.2 River discharge measurement

Continuous flow measurements at the 9 sites used in this study have been made since April 2011 for 8 sites and since December 2014 for Cowieslinn. Water level measurement uses Hobo U20 0-3.5 m unvented pressure-based water level recorders (with error estimated at ± 5 -10 mm) installed in stilling wells in natural rated sections, each recording time, date, pressure and water temperature every 15 minutes. An identical Hobo is installed at the Earlyvale gauging station to compensate water depth pressure readings for barometric pressure.

Flow gauging has been carried out at each site by the University of Dundee approximately 8 times per year over a range of conditions including low flows and flood events in accordance with BS EN ISO 748:2007 (British Standards Institution, 2007). Velocities are measured using either an Ott MF Pro electromagnetic current meter (accuracy $\pm 2\%$ of measured value $\pm 0.015 \text{ m s}^{-1}$ (at velocities of 0 - 3 m s^{-1}) and $\pm 4\%$ of measured value $\pm 0.015 \text{ m s}^{-1}$ (at velocities of 3 - 5 m s^{-1})) or a SonTek FlowTracker ADV ($\pm 1\%$ of measured velocity of measured value $\pm 0.0025 \text{ m s}^{-1}$) in the smaller streams/low flow conditions. Between 8 and 20 verticals are used depending on stream width, with velocities measured at 0.6 of the water depth (1-point method) or at 0.2 and 0.8 of the water depth (2-point method) in high flow conditions. Discharge is calculated using the mid-section method (Dingman, 2014). A RDI Teledyne Rio Grande ADCP mounted on an Ocean Science boat is

occasionally used in the larger rivers during high flow conditions (velocity accuracy $\pm 0.25\%$ of the water velocity relative to the ADCP $\pm 2 \times 10^{-4} \text{ m s}^{-1}$).

The velocity-area measurements were used to generate ratings curves to enable discharge to be calculated from water depth measurements (stage) at each site. For some catchments two-stage ratings curves have been developed. The stage and discharge data are externally reviewed annually (most recently by Wallingford Hydro Solutions in April 2019), quantifying offsets between manual stage board readings on each stilling well during each discharge measurement site visit and the calculated water level reading from the Hobo pressure sensor after application of the calibration for each logger and correction for barometric pressure. The discharge data were corrected based on this review and these data are used throughout the study.

Discharge data were checked prior to analysis to identify any data gaps or potentially spurious data points. Time series plots for all discharge measurement sites are shown in Appendix A, Figure A.3. There are few gaps in the time series but where these occur (in the Shiplaw and School catchments) data were infilled using linear regression between all discharge data at the site and the nearest donor site (Shiplaw was paired with Middle Burn and the School was paired with Longcote) (Harvey et al., 2010). Flow duration curves (FDCs) were also plotted for each catchment as an initial comparison of discharge characteristics (see Appendix A, Figure A.4). Most catchments have similar FDCs and where differences occur these are consistent with our knowledge of the catchments under different conditions. However, the low flow FDC data for Shiplaw indicate considerably lower low flows than the adjacent Middle Burn catchment. In this case the discharge data for Shiplaw derived from the stage discharge relationships at low flows were checked against the raw gauging data. Since there was no apparent difference between the derived and the measured data, this difference in behaviour appears to be a feature of the catchment's discharge characteristics and no correction was applied.

For most of the analysis, discharge data in $\text{m}^3 \text{ s}^{-1}$ were normalised to depth values in mm based on catchment areas calculated from the 5 m x 5 m digital terrain model (DTM) (Ordnance Survey, 2016a) to remove some of the scaling effects of catchment area on discharge. Data were also converted to hourly or daily time steps where necessary.

2.3.3 Weather measurements

Weather data have been continuously measured in the catchment since April 2011 at a weather station close to Eddleston Village in the centre of the catchment (Campbell CR1000 Automatic Weather Station located at 55.717° N -3.208 W°). The station measures air temperature, solar radiation, relative humidity and wind speed and direction on a 15-minute time step. The station was equipped with telemetry in late 2012, since which time manual data collection has only been used when required.

Time series plots of all of the weather station datasets are given in Appendix A, Figures A.5 – A.8. Most of the datasets have only small gaps apart from in early 2013, when there are large gaps in the wind speed data. Where gaps exist data were infilled using monthly mean data for the same month in all other available years.

Potential and actual evapotranspiration (ET) were calculated using the weather station data aggregated to a daily time step. The ET data were used to quantify effective rainfall used in the analysis in Chapter 3 and potential ET fluxes from the forest strip investigated in the hillslope experiment in Chapter 5. The Penman-Monteith method (Allen et al., 1998) was used to calculate potential evapotranspiration and the Granger-Gray method (Granger and Gray, 1989) was used to calculate actual evapotranspiration. The R package 'Evapotranspiration' (Guo et al., 2016) was used for both calculations with initial parameters based on local data where appropriate (Table 2.3). The potential evapotranspiration estimates (Appendix A, Figures A.9 and A.10) compare well with estimates for Scotland in other studies (Bell et al., 2011). Potential evapotranspiration estimates were also regionalised for different catchments by weighting the vegetation (α) parameter according to the percentage area of different land covers (α estimates for different land covers were based on existing literature (Farmer and Cook, 2013; Saha, 2012)), and assuming the elevation parameter is defined by the median catchment elevation. The regionalised data had only small differences in daily and monthly evapotranspiration estimates compared to estimates based on the weather station alone, so the estimates based on parameters for the Eddleston Weather Station were used in subsequent analyses.

Table 2.3: Parameters used in catchment-wide potential evapotranspiration estimate.

<i>Parameter</i>	<i>Value</i>
Elevation	200 m
Height of wind measuring instrument, z	2 m
Stefan-Boltzmann constant	$4.903 \times 10^{-9} \text{ MJ.K}^{-4}.\text{m}^{-2}.\text{day}^{-1}$
Latitude (radians)	0.972
Solar constant (Gsc)	$0.0820 \text{ MJ.m}^{-2}.\text{min}^{-1}$
Soil heat flux (G)	$0 \text{ MJ.m}^{-2}.\text{day}^{-1}$ for daily time step
Vegetation (α)	FAO-56 hypothetical short grass

2.3.4 Routine water sampling for isotopic and geochemical analysis

Water samples for isotopic and geochemical analysis (^2H , ^{18}O , acid neutralising capacity (ANC), conductivity, pH) were collected on at least a 2-weekly basis between 21 May 2015 and 3 May 2017. Weekly routine sampling (data used primarily in Chapter 3) was conducted from 2 September 2015 to 26 August 2016 in which three storage rain gauges, nine rivers, and one spring were sampled (666 samples). Further routine samples were collected from the three storage rain gauges, the three sub-catchments that are the focus of Chapter 4, and the main Eddleston Water outlet (Kidston Mill) on a 2-weekly basis from 1 September 2016 to 3 May 2017 (126 samples) to help contextualise the event analysis (data used primarily in Chapter 4).

Rainfall samples for isotopic analysis were collected from the Octapent storage rain gauges, filling two dry 15 mL HDPE sample bottles (the second sample was collected as a backup) directly from the water in the gauge to prevent any contamination prior to measuring rainfall volume with a clean, dry 500 mL measuring cylinder. The body of each rain gauge is buried ~0.5 m into the ground and the rain gauge funnel has a small (~1.5 cm diameter) aperture. Fractionation due to evaporation in rain gauges needs to be considered in all isotopic studies, but is particularly important in hotter and more arid environments where comparisons of different evaporation prevention methods have shown that most approaches fail to prevent significant fractionation for monthly sampling (Michelsen et al., 2018). The most robust methods (addition of paraffin to the collector and tube dip in collector with pressure equalisation) were not options in this study using the existing rain gauge network and in any case the paraffin approach can cause complications with

isotopic analysis of rainfall samples. Given the fact that the collectors were buried, have a minimal aperture, 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. Furthermore, the following two checks showed no evidence of evaporation in terms of a significant deviation of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in rainfall samples from the Global Meteoric Water Line (GMWL) or available Local Meteoric Water Lines (LMWL). Firstly, a pilot study conducted prior to commencing the routine sampling programme in which results were compared for rainfall samples collected in December 2014 and June 2015. Secondly, results for rainfall samples collected in the early summer sampling rounds (May-August 2015), before weekly/2-weekly sampling was continued for the remainder of the study.

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 gauge and at the site of detailed floodplain and hillslope hydrogeological research described in Ó Dochartaigh et al. (2018) and Archer et al. (2013). 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 river water before collection of a sample with minimal headspace.

Conductivity was measured in the rivers and the spring in the field using a Mettler Toledo SG7 conductivity meter (Mettler Toledo, 2006) calibrated prior to each field visit using standard solutions of $84 \mu\text{S cm}^{-1}$ and $1413 \mu\text{S cm}^{-1}$, which span the typical range of conductivities across the Eddleston Water. The probe was inserted directly into the stream as far from the bank as possible, and rinsed with deionised water and wiped dry between sampling locations.

All samples for isotopic analysis were stored in cool, dark conditions to minimise evaporation. Samples for alkalinity analysis were refrigerated in the laboratory at 4°C prior to analysis and analysed within 48 hours of returning from the field.

2.3.5 Event rainfall and stream water sampling for isotopic and geochemical analysis

Event sampling was carried out over a 48-hour period in three sub-catchments (Shiplaw (EGS06), Middle Burn (EGS07) and Longcote (EGS12)) for seven events between December 2015 and February 2017. Detailed field sampling methods are described in Chapter 4, Section 4.2.3.

2.4 Water sample analysis methods

2.4.1 $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotopic composition

Water samples were analysed for their $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotopic composition in order to estimate the 'time source' components of runoff over seasonal and event time scales (Klaus and McDonnell, 2013; McGuire and McDonnell, 2006). Samples were analysed for both $\delta^{18}\text{O}$ and $\delta^2\text{H}$ as this can help with quality control of the sampling procedures (e.g. checking that samples plot close to the global meteoric water line), give further information on the importance of evaporation in different water sources (e.g. due to extensive wetlands) and the deuterium (d)-excess values ($\delta^2\text{H} - (8 \times \delta^{18}\text{O})$) can be used as an analytical tool for investigating transit times (McGuire and McDonnell, 2006).

All $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotopic analyses of water samples collected prior to 5 October 2015 were conducted at the NERC Isotope Geosciences Laboratory, Keyworth, UK by isotope ratio measurement on a VG-Micromass Optima mass spectrometer; measurement precision was $\pm 0.1\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 1.0\text{‰}$ for $\delta^2\text{H}$. All samples after that were analysed 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. Samples were filtered with a nylon 0.45 μm syringe filter into 2 mL glass autosampler vials and sealed with a solid 8 mm thread PTFE/silicone cap. Samples were analysed using the standard-sample bracketing method to control for drift and memory effects, in which standards were run for calibration, followed by 5 samples, and this sequence process was repeated. Each sample was injected nine times ignoring the first three injections and averaging the last six to obtain the sample value. Inter-injection standard deviation was $\leq \pm 1.0\text{‰}$ for $\delta^2\text{H}$ and $\pm 0.2\text{‰}$ for $\delta^{18}\text{O}$. In a run of 45 samples three control samples are run for QA/QC purposes at the beginning, middle and end of the run to check for any significant drift. If the drift is greater than the inter-injection standard deviation, the

run is repeated. All values are reported as permil (‰) according to the Vienna Standard Mean Ocean Water (VSMOW) scale. In addition to the known standard analytical uncertainty of the spectrometer reported above, seven of the backup duplicate samples from different catchments and sampling dates were analysed in order to estimate the variation between sub-samples and any effects of sample storage. The mean standard deviation for the differences in values between duplicates were 0.28 ‰ and 0.32 ‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively.

2.4.2 Acid neutralising capacity

Acid neutralising capacity (ANC) was measured in order to investigate the 'geographic source' of different runoff components in river flow, given that ANC is influenced mainly by the interaction of water with minerals on route to rivers. ANC has been used as a proxy for the groundwater fraction in a number of earlier studies because it is easily measured with high accuracy, it behaves conservatively on groundwater-soil mixing and it provides a clear marker between the soil and groundwater zone (Neal et al., 1997, 1990).

ANC was measured in all routine river and spring water samples and in river water samples from six of the events. The event in February 2016 was not included in the data analysis because it turned out to be a small event, with little rainfall or hydrograph response. Samples for ANC measurement in rainfall were collected once a month – the samplers were not designed to test for ANC in rainfall, so these samples were collected to give an indication of ANC values and to check how they compared to those in the literature. A value of $0 \mu\text{eq L}^{-1}$ for rainfall was used for the hydrograph separations in Chapters 3 and 4, based on the low value obtained from analysis of the monthly samples and values quoted in literature for rainfall in Scotland (Soulsby et al., 1999). Equivalence was assumed between total alkalinity and ANC, the only difference being that ANC is measured on unfiltered samples (Rounds, 2012).

Water samples for ANC measurement were allowed to come to room temperature before acidimetric titration in the laboratory. Initially a colorimetric approach was used to determine ANC (until September 2015), but during the first few sampling rounds this was found to be unreliable and the potentiometric approach was used instead, following cross-calibration of 10 samples to determine the pH of the colour change (found to be 4.1, which was therefore included as an endpoint in the

potentiometric titration). Titration was carried out with H_2SO_4 to endpoints of 4.5, 4.1, 4.0 and 3.5 within 48 hours of returning from the field. In dry periods when alkalinity was high, 1.6 N H_2SO_4 was used with 100 mL of sample and in wetter periods 0.16 N H_2SO_4 was used with 50 mL of sample. In natural waters where aluminium concentrations are low this method has been shown to give a good approximation of ANC (Neal, 2001).

Samples were measured using a 100 mL measuring cylinder and transferred to a glass beaker with a magnetic stirrer. All equipment was cleaned with deionised water then rinsed three times with the sample prior to each analysis. pH endpoints were measured using a Fisherbrand Hydrus 300 pH meter (with automatic temperature compensation) calibrated prior to each sample run using pH 7 and pH 4 standard solutions. The pH probe was rinsed in deionised water and dabbed dry between samples and, after insertion in the sample, was allowed to stabilise for 1 minute before the start of titration or until the meter indicated stabilisation. Acid was then delivered using a hand-held digital titrator (HACH 16900), which was carefully checked for air bubbles in the delivery tube before each titration. The number of digits on the titrator counter window was noted at each pH endpoint and a conversion to total alkalinity made based on the HACH titrator handbook (HACH, 2013). Two replicates were analysed for each sample and a mean alkalinity calculated. A further replicate was analysed if the digits at each endpoint differed by more than 10% and a mean value calculated for the values within 10%. Rainfall samples were analysed using the Gran Alkalinity method in accordance with procedures set out in Rounds (2012).

2.4.3 Conductivity

Conductivity, like ANC, can be a useful proxy for the 'geographic source' of different runoff components in river flow. However, while hydrograph separation studies using conductivity as a tracer have in some cases found similar results to more conservative tracers, there is some variation between studies, potentially due to the less conservative nature of the tracer (Pellerin et al., 2008). Given that conductivity is relatively easy to measure in the field, data were collected as a quality control measure and in case any substantial differences in dynamics from ANC gave insights into the nuances of runoff mechanisms.

As noted above, conductivity was measured in situ in the field during routine sampling. The conductivity of event river water samples was measured in the laboratory using the same Mettler Toledo conductivity meter. To prevent contamination, conductivity was measured in the remaining water sample after removal of sample volume for isotopic and ANC analyses, and the conductivity probe was cleaned with deionised water and dried between samples.

2.4.4 pH

pH was not a major focus of the study but it was measured to help characterise the chemistry of different sub-catchment waters and is useful as a check on the acidification effects of forest land cover.

pH was initially measured directly in the field using a SevenGo Duo pro pH meter (Mettler Toledo, 2008) but pH readings took too long to stabilise. pH measurements in water samples were therefore conducted in the laboratory as soon as possible after return from the field as the start point in the ANC titration.

2.5 GIS methods

2.5.1 Topographic mapping

Topographic analysis initially focused on catchment delineation, which was then used as a basis for summarising the topographic, land cover, soil and geological characteristics for each of the sub-catchments.

All catchment topographic analysis was based on a 5 m x 5 m resolution digital terrain model (DTM) (Ordnance Survey, 2016a) imported into ArcMap 10.3. Sinks in the DTM were first infilled using the Whitebox breach filling algorithm (Lindsay, 2016) with a depth threshold of 30 m. A flow direction raster was then created from the filled data (using the D8 algorithm) and a flow accumulation raster created, which served as a basis for delineating the river network. The sink infilling threshold was chosen after a number of iterations that were compared manually with some of the known sinks on the 1:25,000 scale Ordnance Survey map (Ordnance Survey, 2016b) and aerial photographs. The flow accumulation threshold was initially set to 100 pixels but prior to further topographic analysis was scaled up to an area of 5 ha (2000 pixels) on comparison with river delineation on the Ordnance Survey map and aerial photographs. The same threshold has been found to be a realistic

representation of stream initiation thresholds elsewhere in Scotland (Hrachowitz et al., 2009b; Tetzlaff et al., 2009b). Finally, sub-catchments were delineated using the GPS locations for river gauging stations as the sub-catchment outlets and taking all pixels draining to these locations as those within the sub-catchment area. The rasters of catchment boundaries and the stream network were converted to polygon files for use when necessary.

Table 2.4: Summary of topographic characteristics generated from the catchment DTM with examples of their use in other studies.

Characteristic	Acronym	Explanation	References using characteristics to investigate controls on catchment storage, MTT and/or groundwater fraction
Area (km ²)	T_A	Catchment area	Hrachowitz et al. (2010); McGlynn et al. (2004); Soulsby et al. (2006a)
Median elevation (m)	T_E	Median elevation	Staudinger et al. (2017)
Median slope (°)	T_S	Median slope	McGuire et al. (2005); Muñoz-Villers et al. (2016); Staudinger et al. (2017)
Drainage density (km km ⁻²)	T_DD	Drainage density calculated as total length of all rivers / area	Tetzlaff et al. (2009b); Muñoz-Villers et al. (2016); Staudinger et al. (2017)
Distance to stream (m)	T_DtS	Median distance of each pixel along flow path to stream	Tetzlaff et al. (2009b)
Downslope index (-)	T_DI	$\tan \alpha = d/L_d$, (L_d , [m]), (d , [m]) computed as the gradient to the nearest pixel at least 5 m below the pixel under analysis	Proposed by Hjerdt et al. (2004). Used in e.g. Tetzlaff et al. (2009b)
Elevation above stream (m)	T_EAS	Median elevation above stream of pixels on flow path to stream	Tetzlaff et al. (2009b)
Flowpath length over gradient (m)	T_FLG	Median flow path length / over gradient for all flow paths to stream	Tetzlaff et al. (2009b); Seeger and Weiler (2014)
Topographic wetness index (ln(m))	T_TWI	Median topographic wetness index (TWI). $TWI = \ln(a/\tan B)$, where a is upstream contributing area in m ² and B is local slope	Proposed by Beven and Kirkby(1979); Ali et al. (2012b); Seeger and Weiler (2014)
Gradient to stream (-)	T_GTS	Median gradient along the flow pathway to the stream	Tetzlaff et al. (2009b)

The master DTM and catchment delineation datasets were used to calculate basic catchment characteristics including catchment area (T_A), median elevation (T_E) and median slope (T_S), using the ArcToolbox Spatial Analyst extension. Drainage density (T_DD, defined as total stream length / catchment area) was calculated using the polygon data from the stream network layer and the catchment delineation layer. The data were imported into Whitebox (Lindsay, 2016) in order to calculate other metrics that have been linked to catchment water transit times in other studies (Table 2.4) including the elevation above stream (T_EAS), distance to stream (T_DtS), gradient to stream (T_GTS), downslope index (T_DI) and topographic wetness index (T_TWI).

2.5.2 Land cover mapping

Land cover in the catchment was mapped in 2010 as part of a wider land use mapping study commissioned by the Scottish Borders Council (Medcalf and Williams, 2010). A shapefile of this data provided by the Tweed Forum was used as the basis for analysis. The 28 land cover classes were reclassified by grouping those with low percentage (< 10%) catchment cover into similar classes and on their potential relevance to hydrological processes and the study objectives, focussing particularly on forest and improved grassland, which are the major land use types in different catchments. The final land cover classes used were: 1) acid grassland/bracken/heathland; 2) improved and semi-improved grassland; 3) woodland – coniferous plantation (including small areas of recently felled woodland and small areas of deciduous and mixed woodland); 4) dry/wet modified bog and fenland; and 5) other (including water and standing water).

To assess any potential changes in catchment land cover over the course of the study, high-resolution aerial photographs and Google Earth historic photographs taken before, during and after the study were compared. The most recent available images prior to the study in the western sub-catchments are 24/03/2014 and 07/09/2015 (which are identical over the area of interest) and 24/03/2014 for the eastern catchments. The next available images for both parts of the catchment are from 24/06/2018, approximately one year after the study ended. Few major long-term changes in land cover are evident in most sub-catchments apart from some felling and re-planting of forests in Middle Burn, Shiplaw and Cowieslinn. Felling and re-planting is most marked in the Middle Burn catchment. In September 2015 land cover comprised approximately 50% mature (40 year old) forest, 20% young forest

(< 10 years old), 25% recently felled forest, and 5% non-forest. By June 2018 these proportions had changed to an estimated 30% mature forest, 45% young forest, 20% recently felled and 5% non-forest. Given that a similar total area of land was under forest operations throughout the study and that most felled forest appears to have been re-planted, no differentiation was made between mature, recently felled or recently planted forest in the analyses in Chapters 3 and 4.

2.5.3 Soil mapping

Soils data were derived from the 1:25,000 soils map of Scotland (Soil Survey of Scotland Staff, 1970), downloaded as an ArcGIS layer file from the James Hutton Institute (JHI) on 10 January 2015. Soils were classified based on their 'Major Soil Group' (MSG) and colours used in mapping based on those specified in symbology metadata for the layer file.

In the UK, the Hydrology of Soil Types (HOST) system (Boorman et al., 1995) has proven useful in classifying and predicting the responsiveness of different soils and has been shown in a number of studies to be a key control on catchment mean transit time (MTT) (Hrachowitz et al., 2009a; Tetzlaff et al., 2007b, 2009b). HOST classes were derived from the 1:25,000 soils map and a list of associated HOST classes provided by JHI (Lilly, pers. comm.). Twenty-two HOST classes occur in the Eddleston catchment, which were reclassified for Chapter 3 of this study into three meaningful groups based on pre-defined wetness classes of the HOST class system. These include:

1. Freely draining soils– mostly brown earths with little or no gleying (wetness class I and II)
2. Medium draining soils – mostly gleyed mineral soils (wetness class III and IV)
3. Poorly draining soils – mostly peats and heavily gleyed mineral soils (wetness class V and VI)

2.5.4 Geological mapping

Geological classification was based on a 1:25,000 geological map of the catchment produced for the Eddleston Water flood management project by the British Geological Survey (BGS). BGS re-mapped superficial deposits in detail through walkover surveys, aerial photography and review of historical survey field slips (Auton, 2011). The map units were re-classified for the analysis in Chapter 3, based

on estimated hydraulic conductivities of geological materials and the coverage of the substrate in the catchment. Three main classes were defined:

1. Glacial till (diamicton) and peats > 1 m thickness assumed to be overlying glacial till, both of low hydraulic conductivity, estimated at < 0.001 to 1 m d^{-1} based on data from other locations in Scotland (MacDonald et al., 2012);
2. Sand and gravel with hydraulic conductivity values of $30 - 500 \text{ m d}^{-1}$ (Ó Dochartaigh et al., 2018); and
3. Bedrock (greywacke), with low estimated hydraulic conductivity. Bedrock hydraulic conductivity was not directly measured, but as noted in Section 2.1, Silurian greywacke aquifers elsewhere in southern Scotland have low productivity (Ó Dochartaigh et al., 2015) with an estimated average transmissivity of $\sim 20 \text{ m}^2 \text{ d}^{-1}$ (Graham et al., 2009).

3 Soils and geology dominate controls on storage and mixing in upland catchments: implications for Natural Flood Management

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The candidate, as lead author, conducted all the field work and laboratory analyses, with the exception of the isotopic analyses of water samples which were conducted by Melanie Leng (BGS) and Kim Janzen (University of Saskatchewan). All data analysis and the writing of the paper were carried out by the candidate. Co-authors provided guidance on the scope and design of the research, and contributed to the editing of the manuscript.

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Abstract

The way in which catchments store, mix and release water is a key control on how they respond to human-induced changes, such as land use change. But our understanding of controls on catchment storage and how these interact with human-induced changes is still limited, particularly in the subsurface, due to theoretical and methodological constraints. This study combined hydrometric, isotopic and geochemical measurements to investigate the role of land cover versus potential topographic, soil and geological controls. It compared storage-discharge dynamics in nine nested catchments within a 67 km² managed upland catchment in Southern Scotland to give insights into 'natural flood management' (NFM) measures being introduced across much of the UK. Storage and mixing dynamics estimates were derived from hydrometric data using recession analysis and from isotopic data using mean transit time (MTT) and young water fraction (F_{yw}) estimates. Groundwater fraction was also estimated from end member mixing analysis based on acid neutralising capacity (ANC) to give complementary information on water sources. The analysis showed low but variable sub-catchment scale dynamic storage capacities (16 – 200 mm), mean transit times (134 – 370 days) and groundwater fractions (0.20 – 0.52 of annual stream runoff). Soil hydraulic conductivity (expressed through HOST class) was most significantly positively correlated with measures of catchment scale storage and mixing, although it was highly co-linear with catchment superficial geology. Percentage forest cover was inversely correlated with measures of storage and mixing. This suggests that any effects of forest cover on increasing catchment infiltration and storage are masked by soil hydraulic properties even in the most responsive catchments. The study highlights the need for careful consideration of dominant controls on catchment storage and mixing in efforts to use tree planting to enhance catchment infiltration and transient storage in the context of flood management.

3.1 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 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 (Sayama 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., 2012a), and quantify partitioning between surface and subsurface stores (Klaus and McDonnell, 2013). Few studies have attempted 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 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., 2015a). 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). 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). 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 factors such as hydroclimate, topography, geology, and soil type conspire with catchment storage to define the watershed response to forest treatment” (McDonnell, 2017). 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., 2015a).

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 1) the potential for trees to intercept precipitation and reduce water fluxes to rivers; 2) to enhance infiltration and 'create' subsurface storage, and; 3) to slow the conveyance of water (Environment Agency, 2017; Geris et al., 2015a; Lane, 2017). This second objective 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. These questions are the focus of this chapter.

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 (Geris et al., 2015a). This chapter aims to quantify catchment water storage and identify key controls on catchment storage, mixing and release using combined hydrometric and tracer-based approaches in a natural flood management context. 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. This was investigated 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, enable investigation using methods that have not been widely applied in a flood management context in the UK.

The main questions the study sought to address 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, mixing and release?
3. Does land cover have a discernible impact on catchment water storage, mixing and release?

3.2 Methods

A detailed description of the study site and fieldwork methods is given in Chapter 2. This section summarises the relevant methods and provides further information where necessary.

3.2.1 Site description

Nine sub-catchments of the 67 km² Eddleston Water Catchment in Southern Scotland were compared in this chapter – five headwater catchments and four nested catchments, with the largest being 59.5 km² at Kidston Mill (hereafter referred to as Kidston) (Figure 2.1). Detailed descriptions of the monitoring network, catchment properties and GIS methods are given in Chapter 2, but are summarised below and in Table 3.1.

3.2.2 Hydrometric monitoring

River flows in the nine study catchments were monitored at flow gauging stations at the catchment outlets. Three tipping bucket rain gauges (TBR) with paired storage rain gauges were used to monitor rainfall (one within Eddleston School catchment, one within Craighburn catchment, and one within Shiplaw catchment). The weather station is at the centre of the wider Eddleston Water catchment (Figure 2.1).

Monitoring has been in operation since 2011 apart from in Cowieslinn catchment where the flow gauging station was installed in December 2014. The equipment and methods for gauging rainfall and stream flow are described in detail in Chapter 2, section 2.3.

3.2.3 Rainfall and stream water sampling for isotopic and geochemical analysis

Water samples for isotopic and geochemical analysis (^2H , ^{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. Sampling, storage and analytical methods are described in detail in Chapter 2, section 2.4.

3.2.4 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. The analysis of soil types was based on the 'Hydrology of Soil Types' (HOST) classification system, 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.

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. The procedures used for re-categorisation are outlined in Chapter 2, sections 2.5.2 to 2.5.4.

A correlation matrix constructed using Spearman rank's correlation coefficient was used to control for co-linearity between independent variables (Appendix B, Table B.1). Initially all co-linear variables within the different groups were removed (geology, soils, land cover and topographic indices), and then most co-linear variables between groups were removed. Some co-linear variables were retained because of their importance to the study and to examine their behaviour in relation to expected impacts on the dependent variables (e.g. to see whether forest cover was positively or negatively correlated with mean transit time (MTT)). The criteria used for removing co-linear variables were: 1) the extent of their catchment coverage (i.e. prioritising those with higher coverage within the geology, soils and land cover groups); 2) process understanding of their potential hydrological significance; and 3) the extent of their variation across the catchments (i.e. to avoid

clustered variables or those where the range was lower than the likely error in their measurement).

A summary of the independent variables used in this chapter to compare catchments is given in Table 3.1 and their justification for inclusion given in Appendix B, Table B.2.

Table 3.1: Summary of the topographic, soils, geology and land cover metrics selected to compare catchment hydrology. Methods for calculating these values are described in Chapter 2, Section 2.5.

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

3.2.5 Calculation of transit times, storage and groundwater fraction

Mean transit time and fraction young water

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). A number of studies have 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). Predicted δ is approximated to a sinusoidal seasonal signal given by:

$$\delta = \beta_0 + A[\cos(ct - \varphi)] \quad (\text{Eq. 3.1})$$

where δ is the predicted isotopic composition [‰], β_0 is the estimated weighted mean annual δ [‰], A is the annual amplitude of δ , φ is the phase lag of δ between the precipitation inputs and streamflow outputs in units of radians, c is the angular frequency constant ($2\pi/365$) in rad day^{-1} , and t is the time in days after the start of the sampling period. The terms in this equation were found using harmonic regression analysis of the volume weighted rainfall and river isotopic data (Bliss, 1970).

The regression coefficients were used to estimate the amplitude and the 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. The mean transit time parameter (τ_m) of the exponential flow model can be derived as (McGuire and McDonnell, 2006):

$$\tau_m = c^{-1} [f^{-2} - 1]^{1/2} \quad (\text{Eq. 3.2})$$

where f is the damping ratio between the input and output signals $f = \frac{A_{out}}{A_{in}}$, where A_{out} is the output amplitude and A_{in} is the input amplitude (McGuire and McDonnell, 2006). MTT estimates can also be used to infer 'passive' catchment water storage based on mean annual runoff (Birkel et al., 2011; Soulsby et al., 2009) and this method is used here as an initial estimate of water storage for the Eddleston Water catchment:

$$S_{MTT} = Q_t MTT \quad (\text{Eq. 3.3})$$

where S_{MTT} is storage based on the estimated MTT and Q_t is mean annual river runoff in mm yr^{-1} .

Applying such residence time models to stream water data has a number of complications that have been widely reviewed (McGuire and McDonnell, 2006). A key constraint is that they assume a steady state condition in catchments, which is not realistic in most catchments. Given the flashy nature of the catchment investigated here which makes baseflow sampling problematic, the relatively consistent precipitation throughout the year in southern Scotland, and the weekly sampling frequency, all stream water data were used to fit the regression models as in other studies in the region (Soulsby et al., 2006b).

A further complication with such models is that MTT estimates can be subject to large errors due to aggregation bias in heterogeneous catchments arising from differences in the transit time distributions (TTDs). This problem occurs because of the strong nonlinearity between the tracer cycle amplitude and mean travel time (Kirchner, 2016). The 'young water fraction' (F_{yw}) has been proposed as an alternative metric, which 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). Kirchner (2016) showed that this ratio accurately reflects F_{yw} , with errors of ~2% or less for TTD shape factors ranging from 0.3 to 2.0, spanning a wide range of plausible shapes of catchment TTDs. However, over this range of shape factors, the upper age threshold that defines young streamflow shifts by a factor of two, from 1.5 to 3.1 months, so F_{yw} has been defined as 2.3 ± 0.8 months for catchment comparison purposes (Jasechko et al., 2016). In this study F_{yw} has been calculated based on the amplitude ratio of the sinusoidal regressions described above, and the age threshold for F_{yw} defined as 2.3 ± 0.8 months. 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.

Dynamic storage

Catchment dynamic storage 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. This assumption is a valid approximation in many catchments. 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).

It can be shown (Kirchner, 2009) through the conservation of mass that during times when precipitation and evapotranspiration are minimal, catchment dynamic storage (S) can be estimated by:

$$S = \frac{1}{a} \cdot \frac{1}{(2-b)} \cdot Q^{(2-b)} + S_0 \quad (\text{Eq. 3.4})$$

where S_0 is a constant of integration related to the total storage in the catchment.

The constants a and b can be found through least squares regression of the relationship between recession rate and discharge, often expressed as a power law relationship:

$$-\frac{dQ}{dt} = aQ^b \quad (\text{Eq. 3.5})$$

where b is the slope of the log-log best fit line and $\log(a)$ is the intercept.

The practical application of this approach to discharge data requires defining an 'extraction procedure' to determine the data to analyse and a 'fitting procedure' to fit the data. As discussed in Stoelzle (2013) the choice of approach can have a significant impact on the results. Most studies have extracted discharge data for recession periods that fulfil certain conditions (e.g. number of dry days; removing the first few days or hours of each recession period) in order to analyse only data that are representative of baseflow. However, this can considerably reduce the number of data points and bias the analysis (Kirchner, 2009). We therefore used the approach proposed by Kirchner (2009) that uses minimal criteria for extracting data and a weighting procedure for both binning and curve fitting.

Recession rates were calculated by first converting 15-minute discharge data to hourly data and calculating change in discharge over each hourly time increment

using a three point method (i.e. based on discharges at $t \pm 1$ hour). Recession periods were then extracted as rainless periods at night. Rainless periods were defined as periods with no rain and where there had been no rain in the preceding 6 hours or the following 2 hours (Kirchner, 2009). Night-time periods were selected as times rounded up from the local sunset or down from the local sunrise times on each day of the year.

In order to determine the relationship between $-dQ/dt$ and Q , the data were binned using the approach outlined in Kirchner (2009). Bins were created that spanned at least 1% of the logarithmic range of the flow data and where the root mean squared error was less than half of the mean recession rate. As noted in Kirchner et al. (2009) this is a first-order Taylor approximation to the criterion $\text{std.err.}(\ln(-dQ/dt)) \leq 0.5$, which cannot be directly evaluated when dQ/dt has both positive and negative values. The binned averages reflect the average recession rate $-dQ/dt$ at each flow rate Q , without being unduly influenced by the stochastic scatter in $-dQ/dt$ when Q is small. Best-fit lines for the data were determined using weighted least squares regression and assuming a power law model for each catchment. The regression was weighted by the inverse square of the standard error for each binned mean in order to decrease the influence of the most uncertain points, especially at low discharge rates. Storage estimates for each catchment were then calculated using Eq. 3.4 above.

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

Groundwater fraction

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

$$F_{gw} = \frac{A_r - A_s}{A_r - A_{gw}} = \frac{Q_{gw}}{Q_t} \quad (\text{Eq. 3.6})$$

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 endmember, and A_{gw} is ANC of groundwater endmember.

The selection of endmembers to represent groundwater and surface runoff was based on previous studies in similar catchments and on assumptions about runoff mechanisms in the catchment. At small catchment scales surface water samples give better-integrated measures of endmember chemistry than point-based measurements (Neal, 1997). The groundwater endmember was defined as the mean ANC of the five lowest flows in each sub-catchment. Samples for ANC measurement in rainfall were collected once a month – the samplers were not designed to test for ANC in rainfall, so these samples were collected to give an indication of ANC values and to check how they compared to those in the literature. A value of $0 \mu\text{eq L}^{-1}$ for rainfall was used for the hydrograph separations, based on the low value obtained from analysis of the monthly samples and values quoted in literature for rainfall in Scotland (Soulsby et al., 1999). Other endmember definitions were explored, resulting in up to 25% variations in groundwater fraction estimates, but all gave similar relative estimates for the catchments so only figures based on the endmembers defined above are reported here.

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.

3.2.6 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.

3.3 Results

3.3.1 Catchment hydrology, MTT, F_{yw} , storage and groundwater fraction estimates

Overview of catchment hydrological responses

Metrics of catchment hydrological response indicated distinct differences between the eastern, western and main stem sub-catchments (Table 3.2). Mean annual minimum runoff, median daily runoff and baseflow index (BFI) were higher, and flashiness lower (as defined by the Richards-Baker Flashiness index – see Table 3.2), 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 are more responsive.

Table 3.2: 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, calculated as the sum, over one year, of the absolute values of day-to-day changes in daily discharge volumes, divided by the sum of the daily discharge volumes over the same period. It measures oscillations in discharge relative to total discharge and is an index of flashiness that is less subject to interannual variability compared to other indices (Baker et al., 2004); BFI: Baseflow index calculated according to Gustard et al. (1992); Lag time is between rainfall centroid and discharge peak for ~60 storm events (n differs by catchment) selected based on rainfall depth threshold of 15 mm and intensity threshold limiting gaps in rainfall to a minimum of one hour for any event.

<i>Variable</i>	<i>EGS 02</i>	<i>EGS 05</i>	<i>EGS 09</i>	<i>EGS 11</i>	<i>EGS 16</i>	<i>EGS 10</i>	<i>EGS 06</i>	<i>EGS 12</i>	<i>EGS 07</i>
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
Lag time (hours)	10.26	8.64	8.69	6.01	NA	6.80	5.91	6.27	8.60

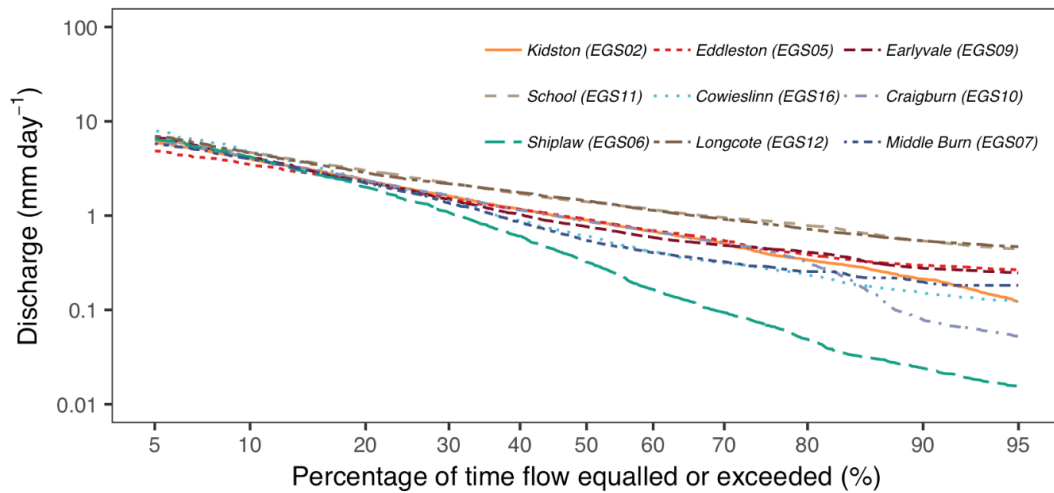


Figure 3.1: Flow duration curves for each catchment based on data from October 2011-September 2016. Lognormal probability plot used to highlight patterns at the extremes of the data after Searcy (1959).

Isotope dynamics, mean transit times and young water fractions

The mean isotopic composition of rainfall data (Appendix B, Table B.3) suggest there was little variation in the rainfall isotopic signature across the catchment during the study (annual volume-weighted mean values for $\delta^2\text{H}$ are within ~ 2.5 ‰). There was also little indication of a systematic elevation effect in the data, which is perhaps not surprising given that the gauges are within 100 m elevation of each other (literature estimates are $\delta^{18}\text{O}$: -0.1 to -0.6 ‰ per 100 m and $\delta^2\text{H}$: -0.5 to -4 per 100 m (Windhorst et al., 2013)), the short time series and the relatively infrequent sampling regime. There was, however, a notable difference between the volume-weighted mean values for the one and two year rainfall datasets (Appendix B, Table B.3), which gives insight into the annual variation of inputs into the catchment. Values in the two-year dataset were closer to those of the streams and groundwater, suggesting that these may be more indicative of long-term mean values and also highlighting the perturbation the wet 2015-2016 winter may have had on inter-annual water storage and cycling through the catchment (Appendix A, Figure A.1).

The weighted mean annual isotopic composition of stream waters suggest that they were generally more enriched than rainfall inputs (Figure 3.2a and Appendix B, Table B.3). The spring sample was also enriched compared to rainfall and rivers. There were some differences between the sub-catchments, with the eastern catchments (EGS11 and EGS12) more enriched compared to the other sub-catchments. Given the lack of any apparent elevation effect, these differences

probably reflect differences in groundwater inputs into the streams, combined with differences in residence times of water in the different sub-catchments. The western catchments had values closer to the one-year volume-weighted rainfall means, and the eastern catchments had values closer to those of the two-year weighted rainfall means and groundwater. The two catchments further downstream on the main stem (EGS05, EGS02) have values between those of the east and west suggesting some convergence in isotopic composition.

The annual variation in $\delta^2\text{H}$ also indicates differences between sub-catchments. The standard deviation of annual flow weighted $\delta^2\text{H}$ was greater in the northern and western sub-catchments, reflecting the flashier nature of these areas. There were intermediate values in the nested catchments and these decreased with increasing catchment area, suggesting mixing of inputs from either side of the catchment and the influence of higher groundwater contributions on the floodplains in the lowlands.

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 (Figure 3.2b). However, there was divergence from the LMWL in some catchments, particularly during summer, which is probably indicative of evaporation in catchments where discharge becomes extremely low and in which wetland/open water areas are more extensive (Appendix B, Figure B.2).

Similar patterns are also apparent temporally. Stream isotopic composition was closely aligned to rainfall isotopic composition and greater damping in the eastern catchments, at the spring site and downstream (Figure 3.2c). Rainfall and stream water isotopic composition varied seasonally, with depletion during winter and enrichment in summer due to differing condensation temperatures. Figure 3.2c shows the influence of the wet 2015-2016 winter on the catchment with a slight decrease in the long-term mean isotopic composition of the rivers following the winter, which did not appear to return to pre winter values within the one-year timeframe of this study.

The temporal variation in volume-weighted $\delta^2\text{H}$ approximated a sine wave, with a reasonably good fit for all three rain gauges (r^2 ranged 0.60 to 0.67 – Appendix B, Figure B.3). This sinuous pattern was also reflected in stream waters in different catchments (Appendix B, Figure B.4). The degree of damping varied across the sub-catchments in a similar pattern to the standard deviation of the annual weighted

mean data, with least damping in the west and north, intermediate values in the nested catchments and greatest damping in the east.

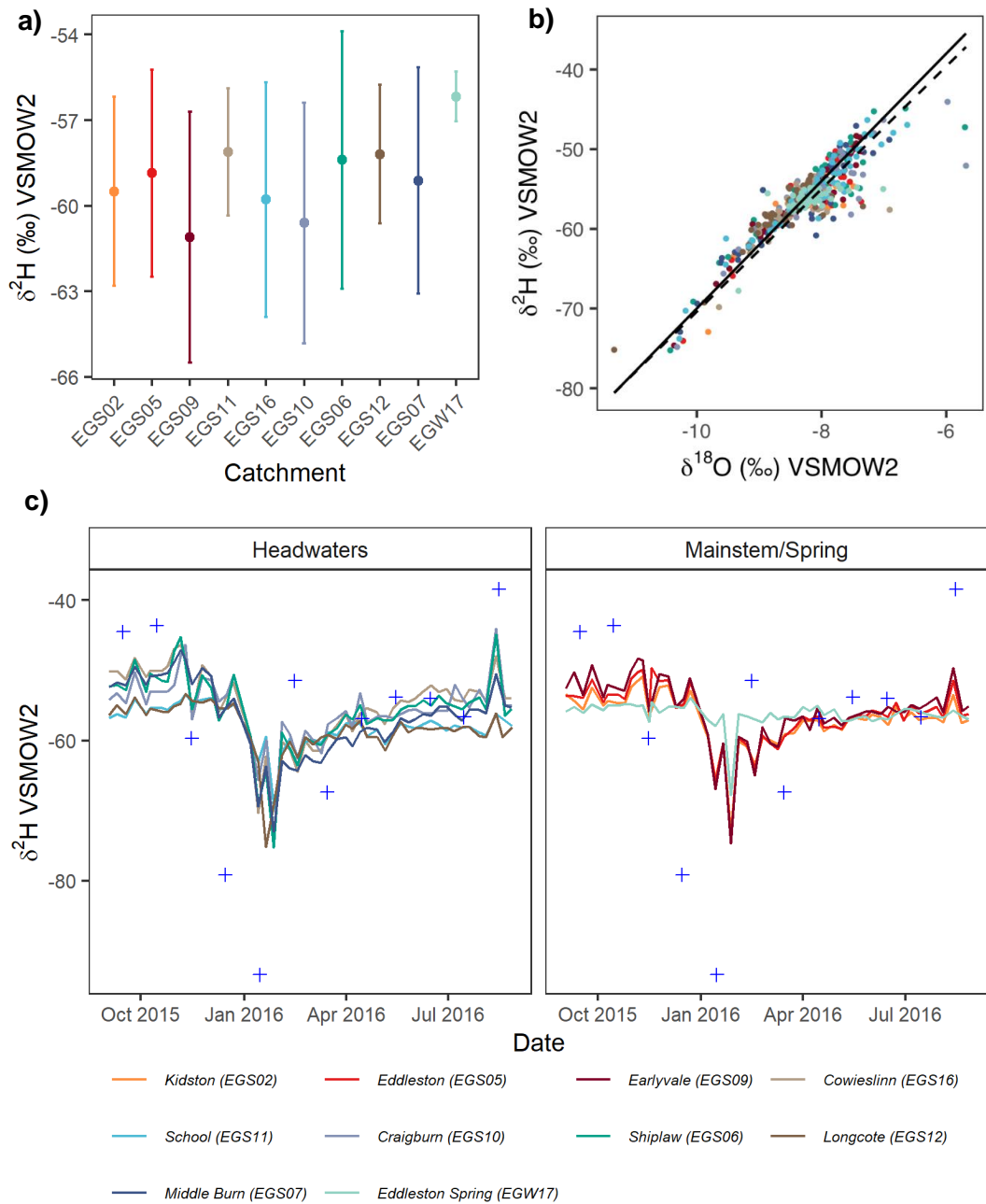


Figure 3.2: a) flow-weighted mean $\delta^2\text{H}$ and standard deviation of all stream data (and median $\delta^2\text{H}$ and interquartile range for Eddleston Spring). b) dual isotope plot for all catchments and Eddleston Spring – the solid black line is the global meteoric water line (GMWL) and the dotted line is the local meteoric water line (LMWL). c) Time series of isotopic composition of river water in headwater catchments and at the main river stem and spring sites. Monthly volume-weighted rainfall data from one rain gauge (ERG14) shown by the blue crosses.

The mean transit times calculated using these relationships indicate large differences between the eastern and western catchments, as well as increasing transit times down the main river stem (Table 3.3). These differences are 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} show 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.

Table 3.3: Summary of amplitudes (A), mean transit times (MTT), implied storage based on MTT estimates (S_{MTT}), and F_{yw} determined from the fitted data for all streams, with 95% confidence intervals (CI) determined from the regression.

Catchment	A (%)	MTT (days)	MTT 5% CI (days)	MTT 95% CI (days)	S_{MTT} (mm)	F_{yw} (-)	F_{yw} 5% CI (-)	F_{yw} 95% CI (-)
Kidston (EGS02)	3.16	269	176	440	596	0.21	0.10	0.32
Eddleston (EGS05)	3.79	222	148	359	444	0.25	0.13	0.37
Earlyvale (EGS09)	4.24	197	132	304	487	0.28	0.15	0.41
School (EGS11)	2.33	370	235	742	766	0.15	0.06	0.24
Cowieslinn (EGS16)	5.68	142	103	191	509	0.37	0.23	0.50
Craigburn (EGS10)	3.95	213	139	324	548	0.26	0.14	0.39
Shiplaw (EGS06)	4.92	167	114	241	209	0.32	0.19	0.46
Longcote (EGS12)	2.66	323	191	647	870	0.18	0.07	0.29
Middle Burn (EGS07)	5.96	134	97.5	189	253	0.39	0.24	0.52

Catchment dynamic storage

The relationships between dQ/dt and Q are shown for each catchment in Appendix B, Figure B.5. There was significant scatter at low flows, which will have been caused by the combination of random measurement noise, the limits of measurement in the pressure transducers, and impacts of precipitation and evapotranspiration that were not detected in the catchment. Additionally the use of natural rated sections at the gauging stations in this study, would have been subject

to greater random fluctuations at low flows due to, for example, shifts in profile or vegetation growth. Nevertheless, the binned means of the data (including negative recessions) formed an approximately log linear relationship for most catchments, suggesting a power law relationship between dQ/dt and Q over the range of flows. When these were converted to storage-discharge relationships for each catchment the relationships for Longcote and School catchments were less sharply curved, which is consistent with these catchments being less responsive.

Dynamic storage estimates based on the Q0.1 and Q99.9 discharge rates for each catchment ranged from 16 mm to 22 mm in the western catchments and 158 mm to 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 3.4). Storage estimates down the main river stem ranged from 28 to 43 mm, between the values in the east and west, with increases downstream reflecting catchment nesting.

Table 3.4: Catchment dynamic storage estimated using the method described in the text.

<i>Catchment_name</i>	<i>Storage (mm)</i>	<i>5% confidence interval</i>	<i>95% confidence interval</i>
Kidston (EGS02)	43	36	52
Eddleston (EGS05)	36	25	50
Earlyvale (EGS09)	28	20	40
School (EGS11)	202	161	313
Craigburn (EGS10)	46	38	57
Shiplaw (EGS06)	16	14	18
Longcote (EGS12)	159	52	789
Middle Burn (EGS07)	22	19	25

Geochemical tracers and geographic sources

The ANC in river water data showed clear seasonal trends, with ANC strongly negatively correlated with discharge, as reported in other catchments (Neal et al., 1997). Lower ANC was measured during the wetter winter and higher ANC during the drier summer periods (Figure 3.3). ANC increased gradually from the end of winter until the end of the water year, before decreasing considerably at the start of the new water year around October. In 2015-2016, this change was particularly marked due to a relatively dry autumn and a wet winter. These changes in ANC with discharge are consistent with baseflow chemistry being driven primarily by

weathering influences on groundwater, leading to water that is relatively alkaline and with higher conductivity compared to more acidic and low conductivity storm runoff.

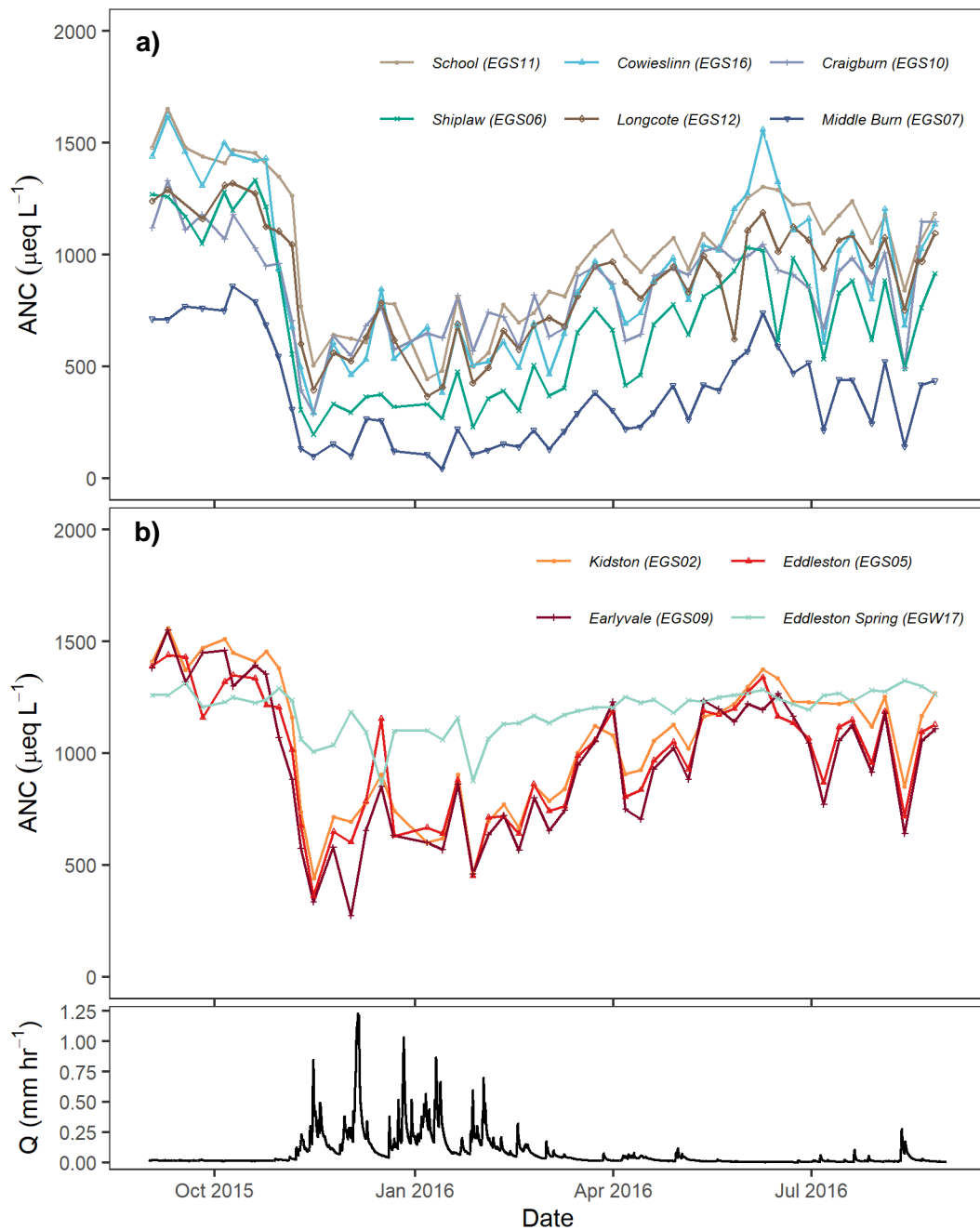


Figure 3.3: ANC time series for a) six headwater sub-catchments, and b) the three main stem nested catchments and a spring at the centre of the catchment. Flow time series (Q) is from the largest catchment, Kidston (EGS02).

Median ANC also differed significantly between catchments, particularly between the headwater catchments in the east and west (Figure 3.4), which probably reflects the fraction of groundwater in river flow and has some similarities with the isotopic

data. However, there were also significant differences (based on comparison of the notched boxplots in Figure 3.4) in ANC between the western Shiplaw and Middle Burn headwater catchments, the latter having particularly low ANC. Spring water ANC values on the main floodplain had a much lower interquartile range compared to any of the rivers. However, during very high flow periods floodplain inundation by the river caused sharp ANC decreases in the spring water (outliers in Figure 3.4), which quickly returned to base levels once floods had receded. There is evidence of nested scaling of ANC with catchment size on the main river stem, but much more variability at smaller headwater scales.

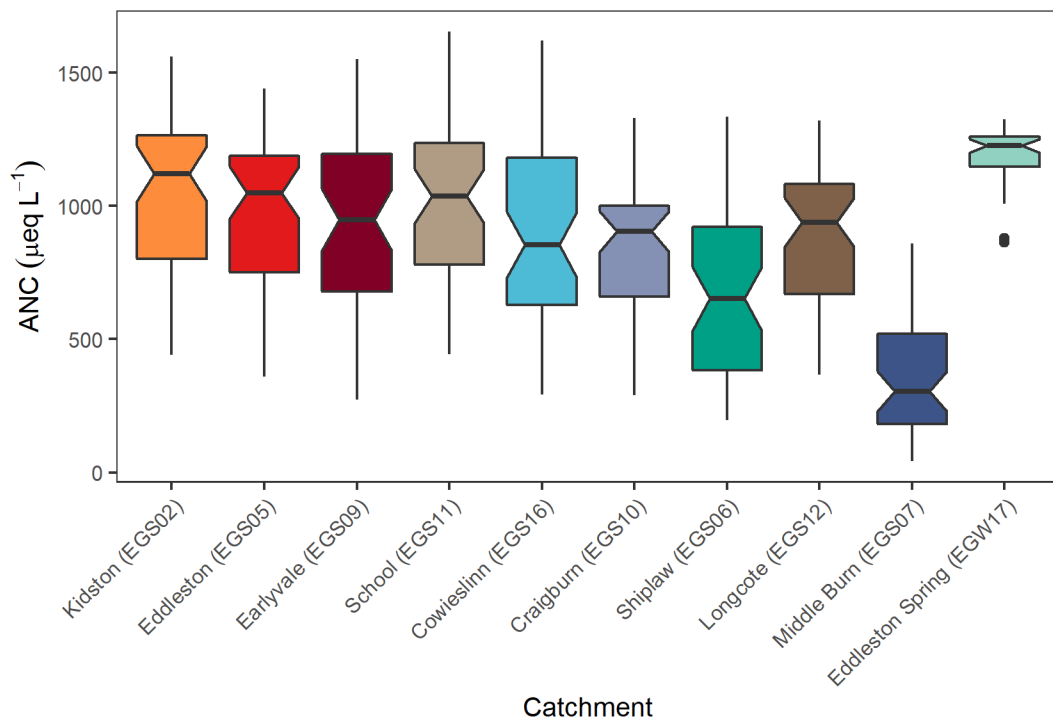


Figure 3.4: Boxplots of ANC during the sampling period. The horizontal line inside the box represents the median and the lower and upper hinges correspond to the first and third quartiles. The upper and lower whiskers depict the largest and smallest values respectively within $1.5 \times$ the interquartile range (IQR). The notches extend $1.58 \times \text{IQR} / \sqrt{n}$. This gives a roughly 95% confidence interval for comparing medians. Dots are outliers.

The relationship between ANC and discharge followed a power law relationship (Appendix B, Figure B.6), with a good fit for most catchments ($r^2 > 0.62$). At high flows, it appeared that 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, indicative of greater groundwater contributions in these catchments.

Two component hydrograph separation indicated differences in groundwater fraction estimates between catchments. 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 of intermediate values (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.

Table 3.5: Groundwater fractions estimated from 15-minute discharge data for the sampling period September 2015 – August 2016 using ANC-discharge relationships and endmember definition reported in the text.

<i>Catchment</i>	<i>Groundwater fraction (F_{gw}) [-]</i>	<i>95% confidence interval [-]</i>
Kidston (EGS02)	0.50	± 0.07
Eddleston (EGS05)	0.51	± 0.07
Earlyvale (EGS09)	0.41	± 0.08
Cowieslinn (EGS16)	0.36	± 0.07
School (EGS11)	0.48	± 0.09
Craigburn (EGS10)	0.52	± 0.11
Shiplaw (EGS06)	0.27	± 0.08
Longcote (EGS12)	0.48	± 0.07
Middle Burn (EGS07)	0.20	± 0.12

3.3.2 Relationships between catchment characteristics and hydrological responses

Catchment hydrological response variables were significantly correlated with a number of catchment characteristics and MTT and S behaved in a similar way (Table 3.6). 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 related to greater MTT, S and F_{gw} . The percentage Diamicton and Peat (G_Di) also appeared to be important in terms of its influence on MTT, with a strong inverse correlation. Given there is a high level of co-linearity between the soils and geology, it is 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 of 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 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 (Figure 3.5). 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 3.6). However, improved grassland and forest cover are inversely co-linear for the subset of catchments.

Table 3.6: Spearman rank correlation coefficients between catchments and hydrological response variables. 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	0.000	0.0286
Topographic wetness index	T_TWI	-0.680*	-0.450	-0.00837	0.0286	0.700	0.486

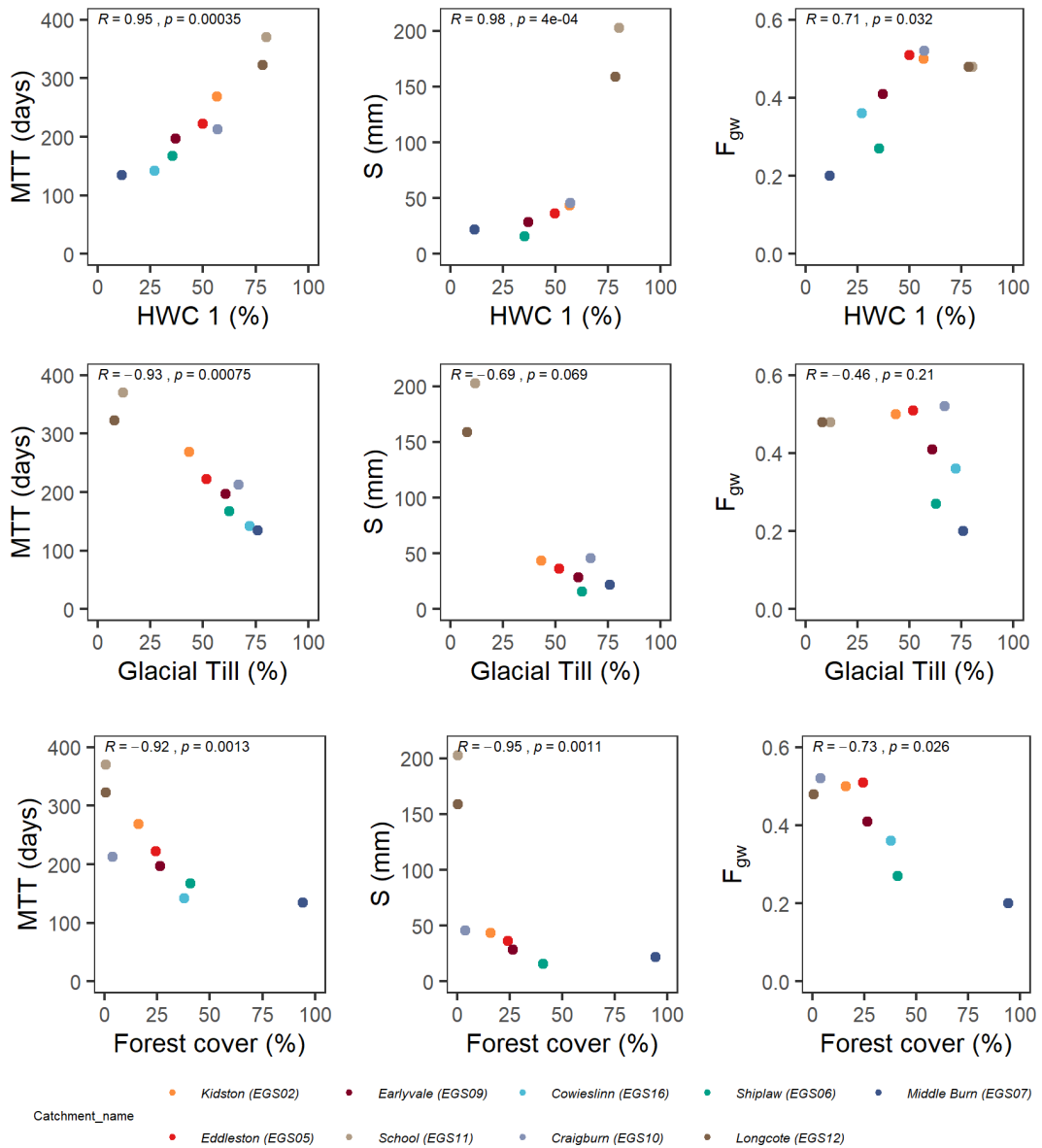


Figure 3.5: x-y scatter plots and Spearman rank correlations between hydrological response variables (MTT: mean transit time; S: dynamic storage; F_{gw} : groundwater fraction) and explanatory variables (HWC 1: HOST wetness class 1; Glacial Till; Forest cover) in the nine study catchments.

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, Craighburn).

Comparisons between the different response variables help to summarise these different relationships. S and MTT (Figure 3.6a) are correlated across the

catchments but F_{gw} and MTT (or S) are not so well correlated (Figure 3.6b). These relationships suggest clustering of catchments into three main groups:

1. Western catchments with shorter MTT, lower S, and low but variable F_{gw} .
 2. Eastern catchments with longer MTTs and higher S than the other catchments, and higher F_{gw} compared to the western catchments.
 3. Main stem catchments with intermediate MTTs, S and intermediate/high F_{gw} .
- MTT, S and F_{gw} generally increase downstream on the main stem, but Craighburn appears to be an outlier, suggesting some influence of scale but complex interaction with other landscape characteristics.

Given the large confidence intervals for both MTT and storage estimates, these patterns are only indicative. However, the fact that there are similar findings for relatively independent metrics, suggests that the relationships are a reflection of the underlying processes.

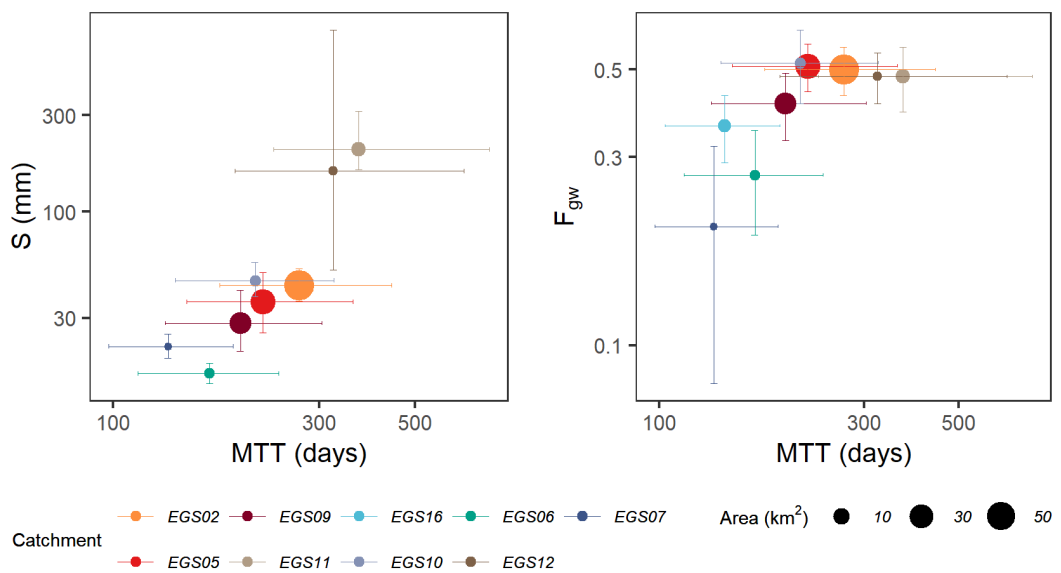


Figure 3.6: Relationships between a) Storage (S) and mean transit time (MTT), and b) Groundwater fraction (F_{gw}) and MTT.

3.4 Discussion

3.4.1 Catchment water storage

The results indicate that catchment dynamic storage is generally low in the Eddleston Water catchment but that it is quite 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 28-46 mm. These estimates are of a similar order of magnitude to other studies. Birkel et al. (2011) found 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. 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 – 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; 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.

These estimates relate well to observations based on simple measures of hydrometric response reported in section 3.3.1, which suggest large differences between the east and the west, and that the western catchments are relatively 'flashy' with large seasonal variations in discharge.

3.4.2 Catchment characteristic controls on MTT, S and F_{gw}

Soil type, as expressed here by HOST class, is the strongest and most consistent explanatory variable for MTT, storage and 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 looked at 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 (Peskest 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, and such an inverse correlation 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 focus has been on coniferous plantation forests, which contain drainage ditches and trees with shallower rooting systems, which will have an impact on infiltration and runoff. However, 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., 2015a; 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} depending, for example, on the extent of under-drainage (that could lower water tables and increase soil moisture storage capacity but also facilitate rapid runoff)

and of field compaction (that could increase surface runoff). Because the proportion of forest cover and improved grassland were inversely co-linear for the subset of catchments, this raises a question of whether improved grassland, rather than HOST class is a control on MTT, S and F_{gw} . However, when analysing all catchments the correlation coefficients between the response variables and improved grassland were not significant, providing further evidence that HOST class is 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 (linked to the Strathclyde Group) of the glacially derived 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 north western catchments are underlain by thick till, there is considerable heterogeneity, with isolated areas of thinner relatively permeable gravels and impermeable peats overlying the till. These are sequences that 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.

3.4.3 Conceptual model of catchment runoff mechanisms

As outlined in Section 3.3.2, the sub-catchments group into three main categories based on their hydrological responses and their catchment characteristics. Figure 3.7 proposes a conceptual model of the runoff mechanisms operating in these different catchment groups, which can be summarised as follows:

1. In the eastern catchments (Figure 3.7a), thin freely draining soils overlying extensive areas of weathered bedrock appear to dominate hydrological

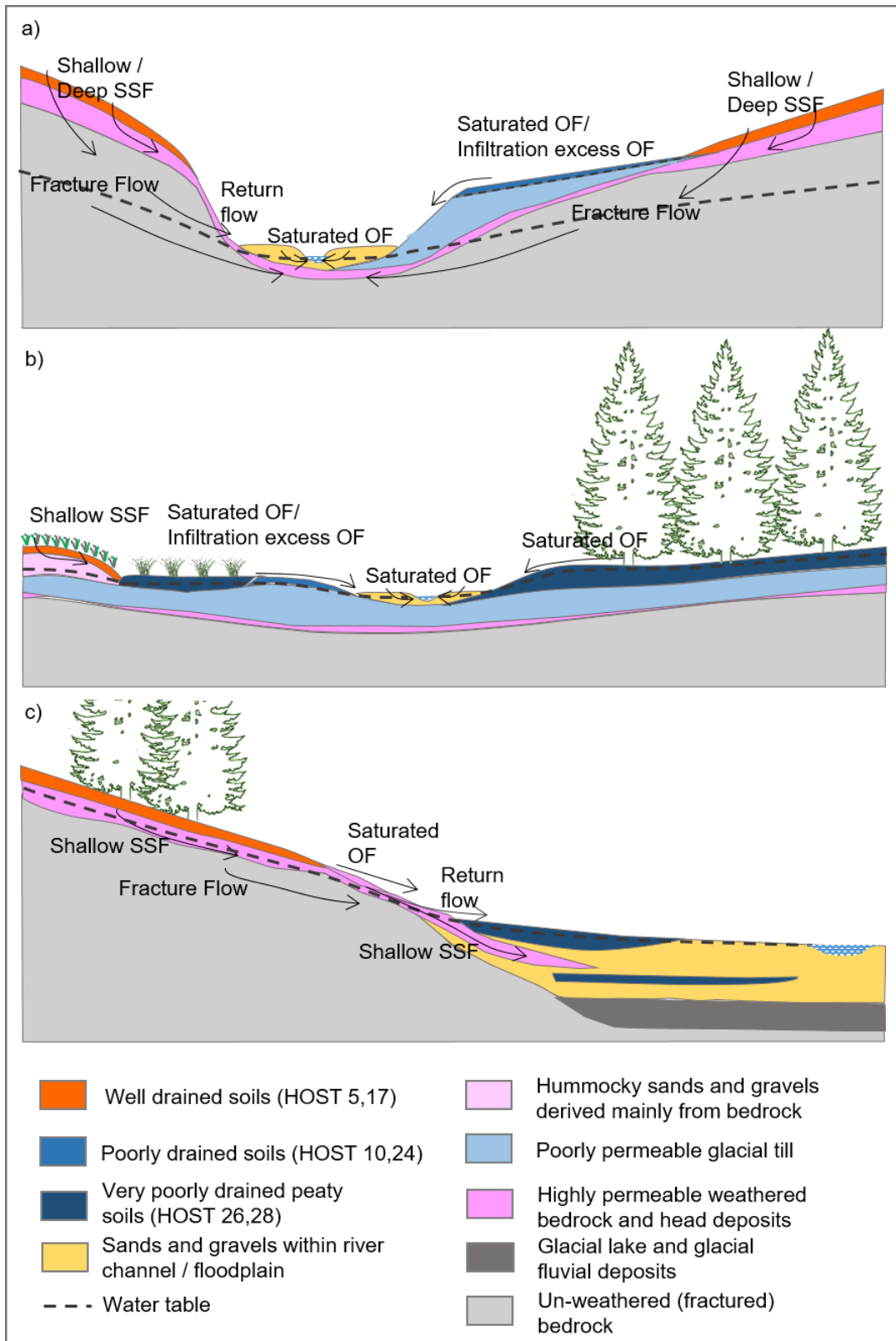


Figure 3.7: Conceptual model of runoff mechanisms in the a) eastern, b) western, and c) main stem catchments. SSF: Subsurface Flow; OF: Overland Flow; HOST: Hydrology of Soil Types. Floodplain structure in c) adapted from Ó Dochartaigh (2018).

responses, resulting in long MTTs, high storage, and a high groundwater fraction. Deeper subsurface flow through weathered bedrock and potentially through bedrock fractures dominates the transit time distribution and groundwater fraction, in a mechanism similar to that described by Sayama (2011). Some rapid surface runoff potentially occurs in till mantled areas and field drains close to the main streams, as will be discussed later in Chapter 4, but these areas cover a small proportion of catchment area so are likely to have minimal impact on longer term storage-discharge dynamics.

2. In the western catchments (Figure 3.7b) 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). There may also be some deeper but rapid (relative to the eastern catchments) subsurface flow in isolated, permeable superficial deposits. The relatively impermeable glacial till has a dominant effect on the transit time distribution, reducing the role of deeper subsurface flow pathways. However, the variable HOST classes and land cover have a more discernible impact on ANC, which is more variable across the western catchments. The ANC/groundwater fraction is generally higher in catchments with more extensive improved grassland and more permeable HOST classes and lower in forested catchments with more impermeable HOST classes.
3. The catchments on the main river stem (Figure 3.7c) 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 as discussed in Chapter 5 (Peskett et al., 2020). The floodplains are highly heterogeneous, but floodplain groundwater appears to be well connected to the river. A proportion of the water has mean residence times estimated at 20-30 years, but with fluctuating fractions of modern water at different times of the year, illustrating the event or seasonal scale inputs of water into aquifers (Ó

Dochartaigh et al., 2018). Permeable solifluction deposits at the base of hillslopes are also important pathways for groundwater flow from hillslopes into floodplains (Ó Dochartaigh et al., 2018).

3.5 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 using hydrometric and tracer-based data, 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.

4 Conceptualising storm runoff pathways at the catchment scale in the context of Natural Flood Management

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The candidate, as lead author, conducted the field work and undertook laboratory analyses. Kim Janzen conducted the isotopic analyses of all water samples. All other data analysis and the writing of the paper were carried out by the candidate. Co-authors provided guidance on the scope and design of the project, and contributed to the editing of the manuscript.

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Abstract

Landscape characteristics such as the type of vegetation cover or soil permeability can have a significant impact on hillslope runoff mechanisms. There is increasing global interest in the potential to manipulate such characteristics to reduce rapid runoff through 'natural flood management' (NFM) schemes that promote interventions such as afforestation and removing field drainage. Despite a growing number of NFM schemes globally, often accompanied by assertions about how they reduce flooding, evidence remains sparse for the effectiveness of NFM interventions and how they alter runoff processes in different contexts. The aim of this study was to investigate the sources and flow paths of runoff in the headwaters of a 67 km² temperate UK upland catchment to give insights into the potential impacts of NFM interventions aimed at reducing rapid hillslope runoff. The study compared three headwater sub-catchments (2.7-3.6 km²) with different characteristics (topography, land cover, soils and geology) and under a range of high flow event conditions. Rainfall and discharge monitoring data (2011-2017) were used to give initial insights into hydrometric responses during events. Measurements of isotopic (²H, ¹⁸O) and geochemical (acid neutralising capacity) tracers in stream water were then used to examine in more detail runoff partitioning for four high flow events between December 2015 and February 2017, using tracer-based hydrograph separation to determine the event water, soil water and the groundwater fractions in stream runoff. Streamflow during the events was sampled at 2-hourly frequency and sequential rainfall sampling was used to determine variation in rainfall endmember signatures. At the event timescale, and comparing two adjacent catchments with similar topography, soils and superficial geology, but differences in land cover, forest cover appeared to attenuate event water runoff in all high flow events. The fraction of event water runoff at peak discharge during the largest event monitored was 0.37 ± 0.04 for the forested catchment but 0.54 ± 0.14 for the adjacent partially forested catchment. A third catchment, with minimal glacial till and low forest cover, demonstrated different dynamics, with much lower runoff ratios for all events, higher groundwater fractions at peak discharge ($0.21 \pm 0.02 - 0.55 \pm 0.02$), and 'double-peak' hydrographs, illustrating the impacts of geology on runoff processes. Similar relative differences in runoff fractions were found between catchments across the three winter events, with differences between storms greater than differences between catchments. These findings suggest that while catchment characteristics mediate event responses, event characteristics (rainfall depth, intensity and

antecedent conditions) may dominate responses, though it was not possible to disaggregate between the effects of different event characteristics with this dataset. The findings highlight the need for a good characterisation of runoff processes in the design of NFM, the potential limitations of NFM in certain landscapes and for large events, and the utility of tracers in planning NFM interventions and monitoring their effectiveness.

4.1 Introduction

There is increasing interest globally in the use of 'nature-based solutions' for flood risk management and disaster risk reduction (EEA, 2017; World Bank, 2018). It is suggested that these approaches could provide significant 'co-benefits', for example through improvements in biodiversity (Iacob et al., 2014; Keesstra et al., 2018). They could also potentially reduce the costs associated with more traditional flood management (Waylen et al., 2017), particularly in the context of increased severity and frequency of extreme events due to climate change (Kay et al., 2019; Merz et al., 2010). In the UK, one manifestation of nature-based solutions is a new wave of policies and projects in support of 'natural flood management' (NFM) (Dadson et al., 2017; Kay et al., 2019; Lane, 2017). These policies promote a more catchment-wide approach to flood risk management, through interventions aimed at reducing runoff (e.g. tree planting and livestock management) and slowing the flow of water in rivers (e.g. ditch blocking and re-meandering) during flood events (Dadson et al., 2017; Environment Agency, 2017). Such approaches clearly require a detailed understanding of runoff mechanisms at multiple catchment scales and build upon decades of research on the impacts of catchment characteristics on runoff generation and flooding (Ali et al., 2012b; Wheater and Evans, 2009). This has demonstrated some relationships which, while still intensely debated (Alila et al., 2009; Carrick et al., 2018; Soulsby et al., 2017), are of relevance to NFM. For example, the potential for forest cover to alter the water balance through increased evapotranspiration and infiltration (Carroll et al., 2004), and the importance of soil management in controlling soil permeability and porosity (Alaoui et al., 2018).

Despite advances in our knowledge of runoff mechanisms, significant gaps still remain that are crucial for understanding the potential of NFM. These include fundamental questions, for example about whether there is evidence that tree cover can significantly reduce flood peaks (Carrick et al., 2018). Where NFM-type interventions have been demonstrated, this has mainly been at the plot or small catchment scale (< 10 km²), raising questions about scalability (Alaoui et al., 2018; Dadson et al., 2017). Catchment heterogeneity also poses problems for the transferability of findings between catchments. For example, the impact of forest cover or forest removal on flow may be highly variable depending on soil type, soil depth and bedrock permeability, which affect catchment storage (Pfister et al.,

2017). Modelling studies have tried to address some of these gaps, but suffer from difficulties in parameterisation at larger catchment scales (Wheater et al., 2008).

In the UK, approaches to NFM have tended to conceptualise event runoff as originating primarily as overland flow (either infiltration-excess or saturation-excess) with hydrographs dominated by surface runoff of 'event' water, a generalisation that has been highlighted in earlier waves of upland environmental management (e.g. to address stream water acidification – see Neal et al. (1997)) and in other landscapes (Ross, 2016). While the fraction of event water tends to increase on a continuum from forested to agricultural to urban landscapes (Buda and DeWalle, 2009; Buttle, 1994; Klaus and McDonnell, 2013; Wenjie et al., 2011), numerous studies have shown the importance of the rapid delivery of 'pre-event' water during storm events, often via subsurface flow paths (Kienzler and Naef, 2008; Sklash and Farvolden, 1979). Such findings have required a re-interpretation of runoff mechanisms (Alila et al., 2009).

In an NFM context it would seem important to try to apply these concepts about runoff mechanisms to management decisions, not only to determine whether subsurface flow paths are important in flood peaks, but in determining where and how to locate NFM interventions. Indeed, a number of hydrologists have argued more generally that integrating these concepts (and information from conservative tracers with which they are often studied) is essential in helping to develop more reliable hydrological models (Birkel and Soulsby, 2015; McDonnell and Beven, 2014; McGuire and McDonnell, 2015). Moreover, the limited scale of intervention that may be possible given practical limitations of local planning laws, public accessibility and cost (Waylen et al., 2017) means that the impacts of NFM on flood peaks may be so marginal as to be undetectable with standard hydrometric techniques. This raises a need for alternative and independent methods of monitoring impacts, or for helping to better model potential impacts (Roa-García and Weiler, 2010).

This study aims to better conceptualise runoff mechanisms in NFM by applying a combination of hydrometric and tracer-based approaches to high flow events (hereafter referred to as 'events', with event definition given in section 4.2.4) in three upland sub-catchments with different characteristics that form part of a relatively long running UK NFM pilot project. It investigates specifically the role of event/pre-

event and surface/groundwater during different events to give insights into flow sources and pathways. To our knowledge, none of the current NFM pilot projects in the UK has combined tracer and hydrometric information at the catchment scale and such studies in all contexts in the UK are limited to a few sites (e.g. Darling and Bowes, 2016; Neal and Rosier, 1990; Sklash et al., 1996; Soulsby et al., 2006b). At a global scale the study adds to the relatively few hydrograph separation studies in agricultural catchments (Klaus and McDonnell 2013) and studies that use high frequency sampling in multiple events and multiple catchments (Fischer et al., 2017; Holko et al., 2018; Hrachowitz et al., 2011; Jacobs et al., 2018; Klaus and McDonnell, 2013).

The main questions addressed in the research were:

1. Is pre-event water and groundwater important in high flow events in upland catchments?
2. How do event characteristics, antecedent conditions and catchment characteristics control event and surface water fractions in streams, of most significance for NFM?
3. What do these findings mean for the conceptualisation of natural flood management interventions?

4.2 Methods

A detailed description of the study site, and field and laboratory methods is given in Chapter 2, Sections 2.1, 2.3 and 2.4 respectively. This section gives a summary relevant for the event sampling work and provides further information where necessary.

4.2.1 Site description

Three sub-catchments of the Eddleston Water were selected for comparison in this study - two from the west and one from the east (Figure 4.1).

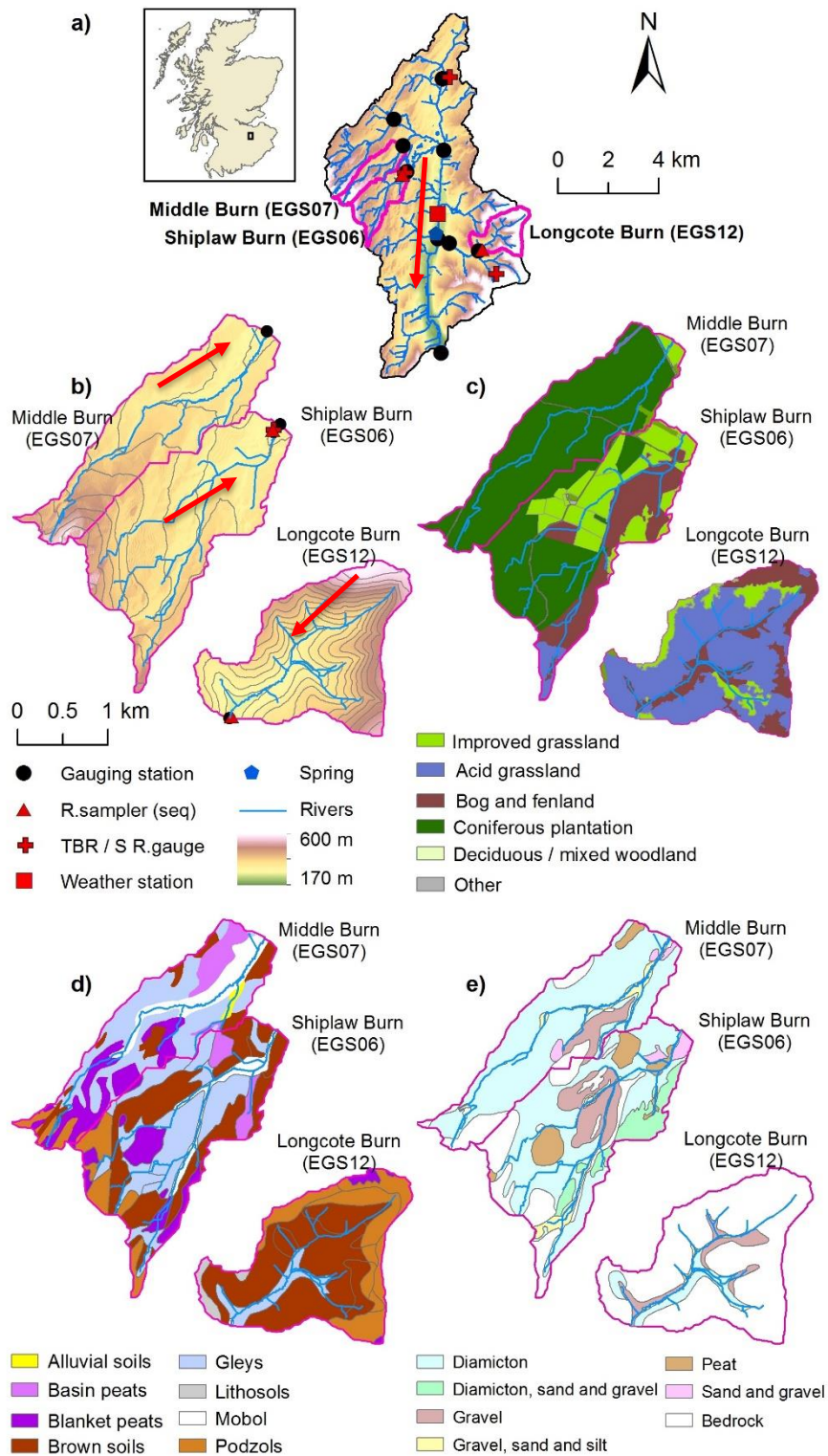


Figure 4.1: Maps of the study site. a) location of the Eddleston Water catchment (including TBR rain gauges and weather station locations) highlighting the three sub-catchments where event sampling was carried out (red arrow indicates stream flow direction); b) monitoring network in the three sub-catchments and sub-catchment topography (red arrows indicate stream flow direction); c) sub-catchment land use; d) sub-catchment soil cover ('Mobol' is undifferentiated mixed bottom land); e) sub-catchment geology. R. sampler (seq): sequential rainfall sampler; TBR / S R.gauge: paired tipping bucket and storage rain gauges.

Detailed descriptions of catchment properties are given in Chapter 2, but the main differences are summarised below and in Table 4.1:

- Middle Burn (EGS07) in the west: This catchment is dominated by poorly draining gleyed soils and peats overlying glacial till >1 m thick. It has a high percentage of coniferous forest cover (>90%, including ~20% recently felled forests).
- Shiplaw (EGS06) in the west: This catchment has similar soils and geology to Middle Burn, though is more typical of the wider landscape in terms of land cover, with a mixture of improved grassland, areas of wetland, and plantation forest on upland slopes.
- Middle Longcote (EGS12) in the east (hereafter named 'Longcote'): This catchment is defined by steeper slopes, more freely draining soils and a lower percentage glacial till cover compared to the western catchments.

Table 4.1: Summary of catchment characteristics for the three catchments. 'Mixed bottom land' soil type was reclassified into Alluvial soils and 'Lithosols' into Brown soils for clarity. Figures were derived from analysis of 5 m x 5 m resolution maps in ArcGIS.

<i>Characteristic</i>	<i>Middle Burn (EGS07)</i>	<i>Shiplaw (EGS06)</i>	<i>Longcote (EGS12)</i>
Topographic indices			
Area (km ²)	2.4	3.1	2.7
Median elevation (m)	313	324	376
Median slope (°)	5	5	16
Drainage density (km km ²)	0.0031	0.0020	0.0027
Elevation above stream (m)	15	15	60
Topographic wetness index (ln(m))	6.7	6.5	5.7
Soils			
Alluvial soils (%)	16	6	0
Basin peats (%)	9	5	0
Blanket peats (%)	19	11	2
Brown soils (%)	11	35	62
Gleys (%)	39	33	8
Podzols (%)	4	10	28
Geology			
Glacial till and peat (%)	76	63	8
Sand and gravel (%)	12	16	8
Bedrock (%)	12	21	84
Land cover			
Acid grassland/bracken/ heathland (%)	1	3	64
Improved and semi-improved grassland (%)	2	28	11
Woodland – all types (%)	94	41	1
Dry/wet modified bog and fenland (%)	0	27	22

4.2.2 Hydrometric monitoring

Discharge at the outlet of the three catchments was monitored at 15-minute frequency. Two tipping bucket rain gauges (TBR) with paired storage rain gauges were used to monitor rainfall (one close to Longcote catchment and one within Shiplaw catchment). Monitoring has been in operation since 2011. The equipment and methods for gauging rainfall and discharge are described in detail in Chapter 2, Sections 2.3.1 and 2.3.2.

4.2.3 Event rainfall and stream water sampling for isotopic and geochemical analysis

Event sampling was carried out over a 48-hour period in three sub-catchments (Shiplaw (EGS06), Middle Burn (EGS07) and Longcote (EGS12)) for seven events between December 2015 and February 2017. Events were targeted based on reviews of the weather forecast and predicted precipitation maps from the UK Met Office, and were only considered if total predicted event rainfall was above 15 mm with an average intensity of approximately 2 mm h⁻¹ (based on prior knowledge of the responsiveness of the catchment).

Event rainfall was sampled at a site in the east (within Longcote catchment) and a site in the west (within Shiplaw catchment) of the Eddleston Water catchment using sequential rainfall samplers built using a modified version of the method described in Kennedy et al. (1979), which were deployed a few hours prior to the start of the forecast event rainfall (Figure 4.2). The samplers enabled volume-based disaggregation of the rainfall isotope signature in 6 mm increments for the first three samples, 11 mm for the fourth sample (except for the Longcote gauge during the November 2016 event, where a larger ~ 30 mm bottle was used due to a broken seal discovered during deployment in the field) and then a bulk sample for the rest of the event. These volume increments were selected to balance the design and reliability of the instrument (which is easier to build and deploy with fewer bottles) with having some disaggregation of medium to large events (> 15 mm total rainfall). The volume increments were converted to time increments by pairing with the cumulative rainfall data from the closest TBR rain gauge. Bulk rainfall samples for the whole event were also collected from adjacent temporary storage gauges in case of failure of the sequential samplers. These were built with an aperture diameter identical to the sequential samplers, deployed at the same time and placed

approximately 2 m away. Following each event, rainfall samples were collected before any further rainfall (and within at most 12 hours of the end of each event), with isotopic samples transferred in the field into 2 x 15 mL HDPE bottles as outlined in the Section 2.3.4.

The sequential rainfall samplers proved to be quite reliable, but in one event (21 November 2016) the tubing became blocked with wind-blown debris. In this case the isotopic signature of the adjacent bulk sample was compared with the volume-weighted mean of the sequential samples at the eastern site. Given similarities in the event rainfall pattern and the volume-weighted mean isotopic signature, the bulk sample values were distributed throughout the event at the same time step in order to carry out hydrograph separation for the western catchments.



Figure 4.2: The internal structure of the two sequential rainfall samplers following the July 2016 event.

For one event (December 2015) 10 bulk rainfall samplers (in addition to the two at the event sampling sites in the east and west of the catchment) were also distributed across the catchment to estimate catchment-wide variation in isotopic composition (Appendix C, Figure C.1). These were homemade from identical 2 L plastic drinks bottles attached to a wooden post and set up in open locations, far from trees and fences, with the aperture 0.4 m above the ground. While the data from these could not be directly compared with the Met Office standard gauges, given the different

design, it provided a useful relative insight for a single event. It showed little variation in isotopic composition across the catchment during the event ($\delta^{18}\text{O}$ ranged from -6.32 to -5.41 ‰). While this was only one event, any systematic differences between the east and the west of the catchment should be accounted for by sampling rainfall in both locations.

One event (February 2017) involved some snowfall (~ 5 cm depth) and rain on snow on ground above ~ 350 m altitude. Four samples of snow for isotopic analysis were collected by taking a profile of fresh snow from an approx. 0.3 m x 0.3 m area at two locations in the eastern catchment and two locations in the western catchments. These were bottled at each location and allowed to melt in the bottle, providing ~500 mL of water from which two 15 mL samples were taken for isotopic analysis.

River sampling for the first event (December 2015) used two automatic water samplers (ISCO 6712, Teledyne ISCO, Nebraska, USA) programmed for a 2-hourly sampling frequency and manual sampling in the third catchment (Middle Burn) at lower frequency, as an automatic sampler was not available. All subsequent events used three automatic samplers programmed at a 2-hourly sampling frequency. All samplers were left on site during the study but were programmed and primed with clean, dry bottles prior to the event, timed to start a few hours before forecast rainfall and programmed to purge the inlet tubing with river water prior to collecting each sample. The samples from the automatic samplers were collected within 12 hours of their programmes finishing. Samples for isotopic analysis were transferred into two 15 mL HDPE bottles in the field directly from the automatic sampler bottles and were filled completely to exclude air. The remainder of each automatic sampler bottle was capped for transport to the laboratory, where they were refrigerated at 4 °C prior to alkalinity analysis and analysed within 48 hours of the event ending.

Automatic water samplers failed during two events. During the July 2016 event, a blockage in the sampling tube in Shiplaw (EGS06) meant that only the first sample was collected and this catchment had to be removed from the analysis of that event. An electronic failure in the Middle Burn automatic sampler during the February 2017 event resulted in some missing data for the first part of the event. Manually collected samples prior to the event and before the onset of the main flow peak enabled estimation of the event fraction using interpolation and linear regression based on

the neighbouring Shiplaw catchment data (as explained in Appendix C, Tables C.1 and C.2).

In total 60 event rainfall samples, 4 event snow samples and 395 stream samples were collected across the seven events. Given resource constraints, some smaller than forecast events and sampler failure in some events, isotopic analyses were conducted on water samples for five events, of which only four had rainfall of sufficiently different isotopic composition compared to rivers to allow for hydrograph separation. The final event dataset for isotopic and ANC analysis therefore included four events (Table 4.2).

In addition to event samples, grab stream water samples for isotopic and geochemical analysis were also collected on at least a 2-weekly basis for the three sub-catchments, the catchment outlet (Kidston (EGS02)), as well as at three storage rain gauges in the wider catchment for the duration of the event sampling campaign in order to contextualise the results. Two-weekly sampling commenced on 21 May 2015, increased to weekly sampling from 2 September 2015 to 26 August 2016 for the experiment discussed in Chapter 3 and returned to two-weekly sampling until 3 May 2017. The methods used were the same as those described in Chapter 2, Section 2.3.4 for routine sampling procedures.

Laboratory analysis methods used to determine the isotopic composition, ANC, conductivity and pH of all samples are described in Chapter 2, Section 2.4.

Table 4.2: Summary of event samples collected in the study. Isotopic analysis was not conducted for the samples shown in italics. All precipitation samples are rainfall unless indicated. Note that 10 additional event precipitation samples were collected across the wider catchment during the 29 December 2015 event.

Event	Catchment	Precipitation samples (Sequential)	Precipitation samples (Bulk)	Stream water samples	Analysis
29-Dec-15	Shiplaw (EGS06)	0	1	21	ANC and isotope analysis
	Middle Burn (EGS07)			5	
	Longcote (EGS12)	0	1	23	
16-Feb-16	<i>Shiplaw (EGS06)</i>	2	1	11	<i>Event data not used as rainfall lower than predicted</i>
	<i>Middle Burn (EGS07)</i>			0	
	<i>Longcote (EGS12)</i>	2	1	12	
20-Jul-16	Shiplaw (EGS06)	4	1	0	ANC and isotope analysis
	Middle Burn (EGS07)			18	
	Longcote (EGS12)	4	1	19	
16-Nov-16	<i>Shiplaw (EGS06)</i>	4	1	22	<i>Event data not used as rainfall lower than predicted</i>
	<i>Middle Burn (EGS07)</i>			22	
	<i>Longcote (EGS12)</i>	4	1	24	
21-Nov-16	Shiplaw (EGS06)	2	1	18	ANC and isotope analysis
	Middle Burn (EGS07)			23	
	Longcote (EGS12)	4	1	18	
23-Dec-16	<i>Shiplaw (EGS06)</i>	0	0	24	<i>Event data not used as rainfall very variable</i>
	<i>Middle Burn (EGS07)</i>			24	
	<i>Longcote (EGS12)</i>	0	0	0	
23-Feb-17	Shiplaw (EGS06)	4 (22-24 Feb); 4 (24-27 Feb)	1 (22-24 Feb); 2 snow	43	ANC and isotope analysis
	Middle Burn (EGS07)			26	
	Longcote (EGS12)	4 (22-24 Feb); 4 (24-27 Feb)	1 (22-24 Feb); 1 (24-27 Feb); 1 (22-27 Feb); 2 snow	42	

4.2.4 Data analysis methods

Hydrometric data

Hydrometric data were initially analysed for the three catchments using the whole time series from 2011 to 2017 to generate the following summary statistics relevant to high flows analysis: mean annual maximum runoff (MAPR), Richards-Baker Flashiness Index (RB) (Baker et al., 2004), the gradient of the flow duration curve at high flows (taken as the mean gradient between Q1 and Q5) (FDC_Q1_5) and the

overall runoff ratio (RR - event runoff as proportion of even rainfall) using a low pass digital filter based on the EcoHydrology package (version 0.4.12) in R.

A dataset of events was also created for the whole time series in order to analyse the response of catchments under different event conditions. Events were selected based on total event rainfall depth and an intensity metric that selected only events with minimal interruptions in rainfall. The specific event definition chosen was: >15 mm total rain for the event and no period of 'no rain' greater than 1 hour. Based on catchment field experience, such events were deemed to have a noticeable impact on runoff, particularly when antecedent conditions (previous 28 day total rainfall) were wet. 63 events matched these criteria in Shiplaw and Middle Burn and 60 events matched the criteria in Longcote.

Event hydrographs in the discharge time series were selected automatically with the start of the event defined as the point with greatest change in slope of the stream hydrograph within a window following the event rainfall centroid and before the event peak. The procedure was applied to smoothed data (3-hour moving average) to avoid problems of noise that can result in high gradients that are not associated with actual increases in discharge. This procedure worked well for 95% of events, but failed on some of the most complex events that had one or more of the following characteristics: extremely long and low rainfall, considerable variability in the rising limb of the hydrograph, multiple hydrograph peaks. These events were removed manually from the analysis across all catchments in order to maintain consistency.

Lag time (LT) was calculated as the time lag between the rainfall centroid and the peak stream flow for the event. Time to peak (TTP) was calculated as the time between the start of the event and the peak flow of the event. Three different methods were used to separate event hydrographs into 'quickflow' and 'baseflow' (constant slope, sliding interval and digital filter), for calculating runoff ratios for the whole time series. All three methods yielded similar relative results and the digital filter results are reported here as they gave intermediate values. All three methods use somewhat arbitrary definitions of baseflow and quickflow, but they have been widely applied for catchment comparison and other hydrograph separation methods are subject to similar challenges (Mei and Anagnostou, 2015).

The same suite of methods was used to analyse the hydrometric data for the events during which water sampling was conducted for isotopic and geochemical analysis.

However, whilst most of these met the 15 mm-total rainfall depth threshold, most did not meet the intensity threshold, so this was relaxed in order to account for all rainfall associated with the event. The end of the event window was also defined by the end of isotopic / ANC sampling for the event to ensure comparability with the chemically based separations for the sampled events.

Isotopic and geochemical dynamics

Prior to the use of ^2H and ^{18}O data in subsequent analysis, the event and routine data were first checked on dual isotope plots for evidence of any significant deviation from the local meteoric water line in the three catchments (Appendix C Figure C.2). Given that no deviation was found, it was assumed that the two isotopes behave in a similar way. The same data analyses methods applied to both isotopes yielded similar findings so only the ^2H data are presented here. This is in line with many similar studies that use only one isotope (e.g. Birkel et al., 2018).

Isotopic and geochemical dynamics were initially assessed using the weekly / 2-weekly routine sampling data to determine general information about the geochemistry of the three streams, including median and interquartile ranges for ANC, conductivity, pH, and isotopic composition.

Isotopic and geochemical dynamics were then analysed in more detail for each of the events. While the focus of the event analysis was on hydrograph separation (outlined below), temporal dynamics were also analysed, including hysteresis during events.

Isotope-based hydrograph separation

Isotope-based hydrograph separation (IHS) was used to determine the fraction of event and pre-event water in each stream during each event. This approach relies on a number of assumptions and has limitations that have been extensively reviewed elsewhere (Klaus and McDonnell, 2013), including:

1. The isotopic content of the event and the pre-event water are significantly different.
2. The event water maintains a constant isotopic signature in space and time, or any variations can be accounted for.
3. The isotopic signature of the pre-event water is constant in space and time, or any variations can be accounted for.

4. Contributions from the vadose zone must be negligible, or the isotopic signature of the soil water must be similar to that of groundwater.
5. Surface storage contributes minimally to the streamflow.

Despite the limitations of the method, IHS is arguably 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 isotopic composition of stream water prior to the event was used as the pre-event water endmember and the isotopic composition of event rainfall was used as the event water endmember. Each of these endmembers is expressed as a ratio of either $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$, where:

$$\delta^{18}\text{O} \text{ or } \delta^2\text{H} = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000 \quad (\text{Eq. 4.1})$$

and R_{sample} is $^{18}\text{O}/^{16}\text{O}$ or $^2\text{H}/^1\text{H}$ and R_{standard} is the Vienna Standard Mean Ocean Water (VSMOW). The absolute VSMOW ratio is $^2\text{H}/^1\text{H} = 155.76 \pm 0.05 \times 10^{-6}$ and $^{18}\text{O}/^{16}\text{O} = 2005.2 \pm 0.45 \times 10^{-6}$ (Klaus and McDonnell, 2013).

Calculation of the fraction of pre-event water uses a mass balance approach, assuming that the two endmembers have significantly different compositions, as follows:

$$Q_t = Q_p + Q_e \quad (\text{Eq. 4.2})$$

$$C_t Q_t = C_p Q_p + C_e Q_e \quad (\text{Eq. 4.3})$$

$$F_p = \frac{C_t - C_e}{C_p - C_e} \quad (\text{Eq. 4.4})$$

$$F_e = 1 - F_p \quad (\text{Eq. 4.5})$$

where Q_t is the streamflow, Q_p the flow contribution from pre-event water, Q_e the flow contribution of event water, C_t , C_p and C_e are the δ values of streamflow, pre-event water and event water, and F_p and F_e are the fractions of pre-event and event water in the stream (Klaus and McDonnell 2006).

To define the pre-event endmember for each stream, we used the mean of the high frequency pre-event stream water samples, as in other studies (Klaus and McDonnell, 2013). For the event endmember, we used both the sequential rainfall samples for each event (except December 2015 when sequential samples were not available) and bulk rainfall samples in order to cross-check the results. As already explained in Section 4.2.3, for the November 2016 event, the sequential rainfall sampler for the western catchments (Middle Burn and Shiplaw) was blocked, so $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values for sequential samples were estimated using the sequential samples from the EGS12 catchment normalised to the bulk sample collected from the west.

We also carried out two sensitivity tests. Firstly, we checked for the influence of throughfall on separation results for the Middle Burn by running the hydrograph separations with bulk event water endmembers increased by 0.4 ‰ and 0.28 ‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ respectively, based on findings from Kubota and Tsuboyama (2003). Secondly, we checked for the influence of snow during the February event by recalculating the volume weighted mean values for the event endmember for the eastern and western areas of the catchment using the snow sample isotopic data. We assumed that the density of snow is 1/10 the density of water and that approximately half (ground above ~350 m) the area of each catchment was covered in snow 50 mm deep, which melted equating to ~ 2.5 mm of additional runoff.

The results of the sensitivity analysis for throughfall are discussed in Section 4.3.2 as they relate to all events and a key theme of this research. The sensitivity analysis for the influence of snow during the February 2017 event indicated that there was a 7.1 – 9.5% decrease in the fraction of event water at peak discharge ($F_e Q_{\max}$) and a 7.9 – 9.3% decrease in the fraction of event water based on total runoff ($F_e Q_{\text{tot}}$). However, there was no change in relative differences between catchments, between events or in the significance of any relationships discussed. While the effects could be substantial in events with greater snowfall, they were small for this event and the results presented in this chapter are based on separations using only the rainfall data.

Uncertainty in the pre-event water fraction was estimated using the Gaussian error propagation approach of Genereaux et al. (1998), based on 70% confidence intervals which were considered appropriate for analysis of this size of dataset and

given the uncertainties involved in hydrograph separation (Bazemore et al., 1994). The input parameters for uncertainty analysis were as follows: 1) the uncertainty in the pre-event water endmember was calculated using the standard deviation of routine samples collected in the month prior to the storm (given that in some storms there were only one or two high frequency pre-event samples); 2) the uncertainty in the event endmember was based on the standard deviation of the spatially distributed samples taken in the West (n = 7) and East (n = 5) of the catchment during the December 2015 storm event (we assumed that the sequential sampling helped to account for uncertainty in temporal variation). 3) The uncertainty in the isotopic composition measurement of each stream water sample was estimated based on the mean standard deviation of the seven sample duplicates analysed (see Section 2.4.1).

ANC-based hydrograph separation

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

$$F_{gw} = \frac{A_r - A_s}{A_r - A_{gw}} = \frac{Q_{gw}}{Q_t} \quad (\text{Eq. 4.6})$$

$$F_{sw} = 1 - F_{gw} \quad (\text{Eq. 4.7})$$

Where F_{gw} is groundwater fraction, Q_t is stream discharge, Q_{gw} is groundwater discharge, A_s is ANC of stream water, A_r is ANC of surface runoff endmember, and A_{gw} is ANC of groundwater endmember. F_{sw} is the fraction surface water, calculated by difference from F_{gw} .

The selection of endmembers to represent groundwater and surface runoff was based on previous studies in similar catchments and on assumptions about runoff mechanisms in the catchment. At small catchment scales surface water samples give better-integrated measures of endmember chemistry than point-based measurements (Neal, 1997). The groundwater endmember 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 as discussed in Chapter 3). The surface water endmember was defined as zero, as this approximates the ANC of rainfall. Other endmember definitions for surface runoff were explored, resulting in large (up to 25%) variations in groundwater fraction estimates, but all gave similar relative estimates. The stream water endmember was taken as the ANC at the time of sampling.

Uncertainty in the groundwater fraction was also estimated using Genereaux et al. (1998) based on 70% confidence intervals. The uncertainty in the groundwater endmember was estimated from the standard deviation of ANC values of the five lowest flows in the routine sampling dataset (see Chapter 3). The standard deviation of the ANC values of the five highest flows in the Middle Burn catchment (EGS07) was used to estimate the uncertainty in the surface runoff endmember as these were the lowest measured ANC values in all catchments and the catchment is dominated by hydrologically-responsive soils, so these values are assumed to approximate rapid runoff. The uncertainty for each stream water sample was estimated from the mean standard deviation of all stream water sample replicates collected across all three sub-catchments that were the focus of event water sampling in this chapter.

Beyond the assumptions associated with hydrograph separation (Klaus and McDonnell 2013) a number of further assumptions and corrections were made to ensure comparability between storms and catchments. These included using an event window with the start defined as the start of the rising limb of the hydrograph (change in slope) and the end defined by time at which the earliest final sample across all catchments was taken. This helped to correct for differences in the length of sampling for some storms and was used as the basis for calculating key event statistics. These included: the fraction event water (F_e) and fraction of groundwater (F_{gw}) based on either the ratio of the total event water discharge for the whole event to the total discharge (Q_{tot}), or the ratio of event water discharge at the maximum discharge (Q_{max}); time to peak (TTP) from the start of the rising limb to the peak discharge (with subscripts p, e and gw denoting pre-event, event and groundwater components respectively); and runoff ratio (RR) based on event water fraction calculated from isotope data. Further minor adjustments were made to isotopic and ANC data for individual storms prior to hydrograph separation to ensure

comparability between catchments and storms, as outlined in Appendix C, Tables C.1 and C.2.

Three component hydrograph separation

Three component hydrograph separation was also conducted to estimate the soil water fraction in stream runoff for each catchment. This used the two-step approach (Klaus and McDonnell 2013) to approximate soil water based on the difference between the pre-event water and groundwater fractions. In summary, the three main components used in the analysis were:

- **Pre-event water:** all runoff that is not event water. It was estimated by subtracting event water from the total runoff. Event water is all water that has the same isotopic signature as the event rainfall and is assumed to be all rain falling directly on the stream surface and rapid surface runoff.
- **Soil water:** all pre-event water that is not groundwater, as defined below. This would likely include all water stored in catchment soils, surface water features (e.g. stream channels, ponds) and potentially in shallow superficial geology. It was obtained as the difference between the pre-event water and groundwater fractions.
- **Groundwater:** pre-event water present in the stream at the lowest flows, assumed to be fed by deeper groundwater sources. Surface water is all runoff that is not groundwater (i.e. containing both pre-event soil water and event water).

4.3 Results

4.3.1 Overview of sub-catchment hydrology and chemistry

Stream hydrology

There were differences between the catchments in their discharge characteristics calculated from six years of available discharge data (October 2011-September 2017). Longcote had a low MAPR, RB, and RR, which is typical of a more groundwater dominated catchment (Table 4.3). However, the short lag time indicates that it was still relatively responsive to rainfall events, potentially due to steeper slopes in the catchment. Shiplaw was the flashiest catchment, with high MAPR, RB and RR. It also responded quickly during events, with the lowest LT and TTP of all the catchments. Middle Burn had similarities to Shiplaw, although it

appeared to be slightly less responsive, with intermediate values across most of the indicators. However, it is notable that Middle Burn had considerably longer lag times than the other catchments.

Table 4.3: High discharge statistics for the three catchments based on daily discharge data for October 2011-September 2017; MAPR: mean annual maximum runoff; RB: Richards-Baker flashiness index (Baker et al., 2004); Lag time (LT) is between rainfall centroid and discharge peak for ~60 events (n differs by catchment) selected based on rainfall depth threshold of 15 mm and intensity threshold limiting gaps in rainfall to a minimum of 1 hour for any event. Time to peak (TTP) and runoff ratio (RR) are based on the same events dataset.

<i>Variable</i>	<i>M. Burn (EGS07)</i>	<i>Shiplaw (EGS06)</i>	<i>Longcote (EGS12)</i>
MAPR (mm hr ⁻¹)	0.84	1.10	0.78
RB	0.43	0.59	0.18
FDC_Q1_5	28	32	22
LT (hours)	8.6	5.9	6.3
TTP (hours)	10.7	9.0	10.1
RR	0.8	0.6	0.2

Stream water geochemistry and isotopic composition from routine sampling

There were differences between the three catchments in the long-term absolute values of the three chemical components analysed in routine stream water samples collected over two years (Figure 4.3). The forested Middle Burn catchment was most acidic (median pH of 6.5), and had lower ANC and conductivity compared to the other catchments. Shiplaw had intermediate values and a larger range for ANC and conductivity, whilst Longcote had the highest values. These patterns are probably associated with both land cover (particularly the acidifying impact of the forest and the higher percentage of peat in the forested Middle Burn catchment) and depth of flow paths as outlined in Chapter 3.

The median values and range in isotopic composition were similar for the two western catchments (Middle Burn and Shiplaw), but notably different for Longcote. The lower absolute value in Longcote is probably an artefact because the data presented in Figure 4.3 are not flow-weighted. As a comparison, flow-weighted data discussed in Chapter 3, Section 3.3.1 suggest little absolute difference in mean isotopic composition for the three streams for the one-year routine sampled data. The lower IQR in Longcote is perhaps more instructive and may be linked to the operation of deeper flow paths and greater storage, as discussed in Chapter 3, Section 3.3.1.

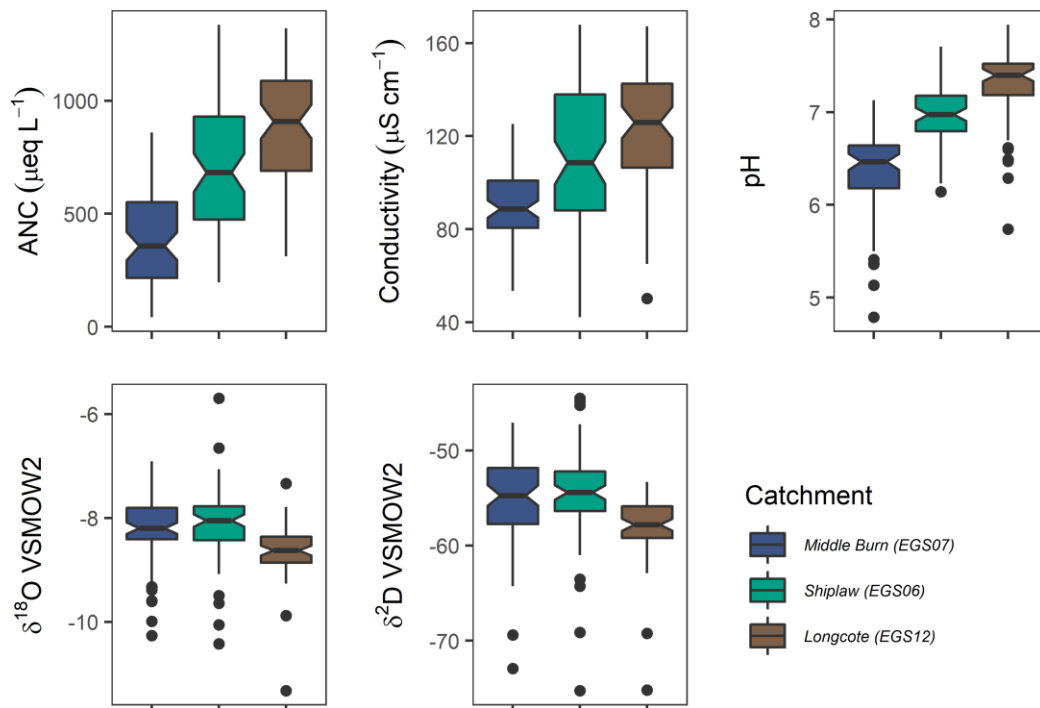


Figure 4.3: Boxplots of the composition of stream water samples collected during the study period, based on weekly routine sampling (May 2015-Aug 2016) and two-weekly routine sampling (September 2016-April 2017). The horizontal line represents the median and the lower and upper hinges correspond to the first and third quartiles (the 25th and 75th percentiles). The upper and lower whiskers extend from the hinge to the largest value no further than $1.5 \times$ the interquartile range (IQR) from the hinge. The notches extend $1.58 \times \text{IQR} / \sqrt{n}$. This gives a roughly 95% confidence interval for comparing medians. Black circles are outliers. ANC: acid neutralising capacity.

Temporal variation in isotopic composition was seasonal and was dominated by the wet 2015/2016 winter with depleted rainfall having a delayed effect on the composition of all streams (Figure 4.4). There was a much less clear seasonal signal during the 2016/2017 winter and the lack of variability in stream composition reflects this (although masks much shorter term variation that is observed during single events). There is some indication that the wet 2015/2016 winter had a lasting impact on the isotopic composition of water in the catchment, with values remaining lower throughout the following year – evidence for the ‘memory’ of the catchment.

The results from the routine sampling indicate that stream chemistry (in terms of ANC, conductivity and pH) varied in a similar way through time in each of the catchments (Figure 4.4), with clear concentration-discharge relationships. The wet winter of 2015/2016 was associated with a large decline in all three chemical components, followed by a steady increase through the drier summer and autumn. The drier winter of 2016/2017 had a smaller impact on stream flow and chemistry.

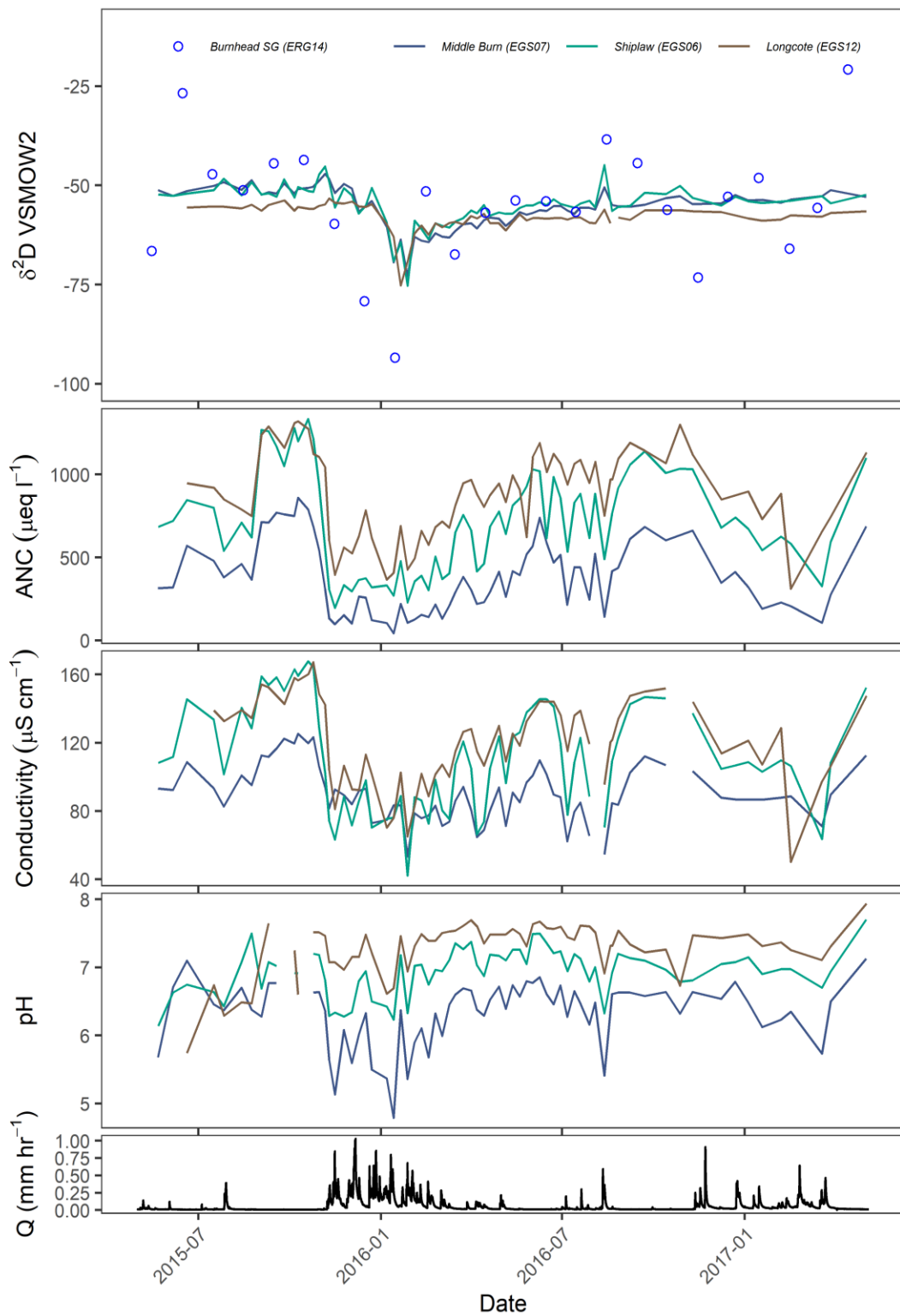


Figure 4.4: Time series of the composition of stream water samples collected during the study period, based on weekly routine sampling (May 2015-Aug 2016) and two-weekly routine sampling (September 2016-April 2017). Blue dots in topmost figure represent the monthly volume-weighted isotopic composition from the rain gauge at Burnhead in the east of the catchment. Q: stream discharge at the catchment outlet (Kidston Mill (EGS02)); ANC: acid neutralising capacity. Small gaps in some datasets are due to some measurements not being made.

4.3.2 Responses during sampled events

Event characteristics

The events during which isotopic and geochemical sampling were carried out represent some of the larger peaks in the six years of record. Peak flows across all of the catchments for the winter events were within the first percentile of the complete flow time series for the period 2011-2017 (below the 0.07 percentile for the largest event and below the 1.0 percentile for the smallest winter event). The summer event (July 2016) was below the tenth percentile. The events were also varied in terms of total rainfall depth, intensity, antecedent conditions and flow characteristics (Figure 4.5). Detailed sampling of isotopes and stream water chemistry occurred in only two catchments in the summer event sampled. While this event was small in terms of peak discharge, it occurred after intense rainfall. The other events were all in autumn/winter with much lower rainfall intensities, but with some variation in total rainfall depth and antecedent rainfall. While the December 2015 event (storm 'Frank') was small in terms of total rainfall, it occurred during a sequence of depressions crossing the UK that resulted in very wet antecedent conditions and the storm itself caused significant flooding in the wider Tweed river catchment (Met Office, 2015).

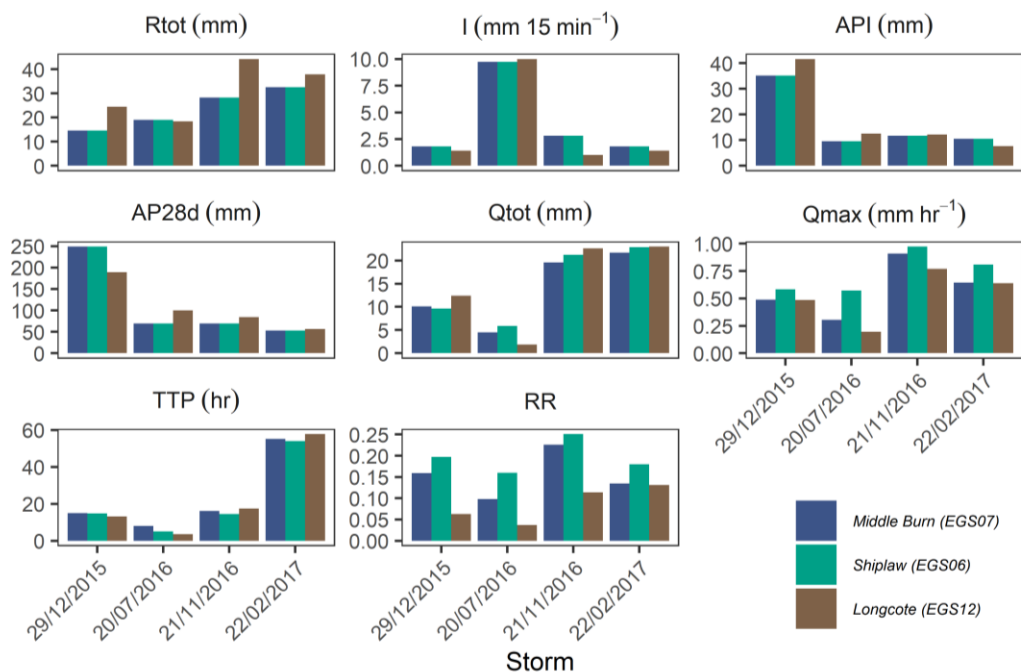


Figure 4.5: Summary hydrological characteristics for four events sampled at high frequency in sub-catchments of the Eddleston Water. Rain: total event rainfall; Max I: maximum rainfall intensity; API: 5 day Antecedent Precipitation Index; API28d: 28-day pre-event rainfall; Qtot: total event discharge; Qmax: max event discharge; TTP: time to peak; RR: runoff ratio.

Isotopic and ANC responses during events

Large and rapid changes in stream water isotopic composition and ANC in all catchments during the events sampled (as illustrated in Figure 4.6 for the November 2016 event and Appendix C, Figures C.3-C.5), demonstrate that all catchments were hydrologically responsive to rainfall inputs. However, there were differences between the catchments in terms of how rapidly they responded, the magnitude of shift in stream water composition and the rate of recovery towards pre-event values following the event.

The eastern Longcote catchment responded most rapidly to event rainfall with a rapid rise in the hydrograph, but an extended and slow recession. This suggests that the catchment has some relatively rapid event runoff pathways but these are dominated by pre-event flow paths that dampen the peak and result in faster recovery of stream chemistry and pre-event isotopic composition on the falling limb.

Shiplaw catchment also responded rapidly to event rainfall, had the largest peak shift in isotopic composition, but also a relatively quick recovery of ANC and isotopic composition towards pre-event values on the falling limb of the hydrograph. This suggests that it has some relatively quick runoff pathways resulting in a responsive hydrograph but also important slower pathways.

The adjacent Middle Burn catchment had a shallower rising limb, lower peak shift and slower recovery in stream water isotopic composition, suggesting greater damping of runoff pathways. The slower recovery compared to the other catchments suggests that the damping may be related to longer or more attenuated (e.g. through surface roughness) surface flow paths rather than the dominance of deep flow paths as seen in the other catchments.

The initial stream water isotopic compositions also support this interpretation for the slow recovery Middle Burn tracer responses. For example, the pre-event endmember for the December 2015 event was significantly different for the adjacent Shiplaw and Middle Burn catchments, despite their similar long-term median stream water isotopic compositions (Middle Burn was negatively shifted compared to Shiplaw). This may have been due to wet antecedent conditions, with surface event runoff still flowing through the Middle Burn catchment from events in the preceding days (that had very depleted rainfall) (see Appendix C, Figure C.3). Patterns in ANC response to events were similar to isotopic responses. Particularly noticeable is the

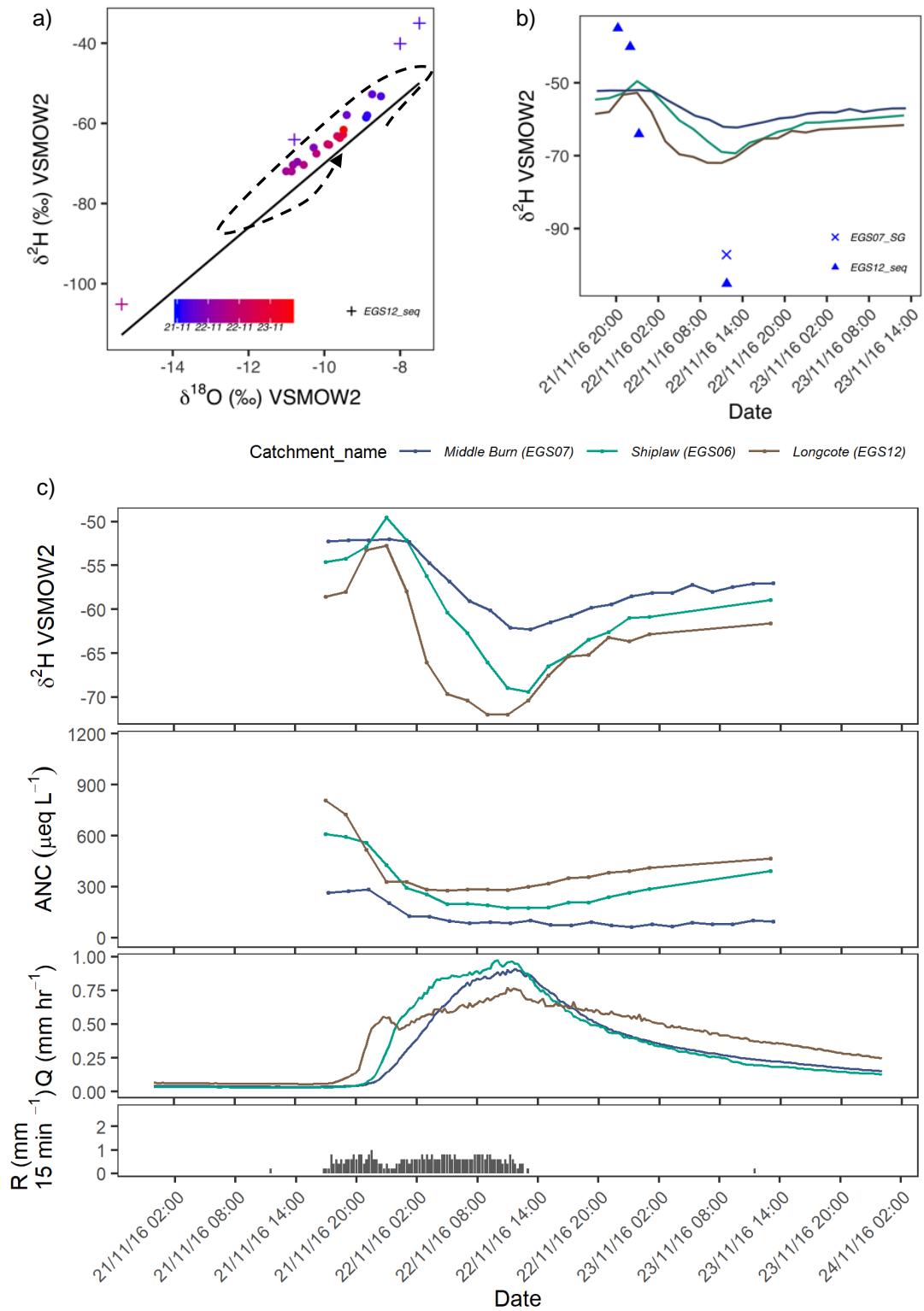


Figure 4.6: Rainfall isotopic and stream water isotopic and ANC dynamics during the November 2016 event. a) Dual-isotope plot showing changes in isotopic composition through time (indicated by blue-red colours) for one catchment (Longcote – EGS12) and the sequential rain sampler in the catchment (shown by +). Dotted arrow shows direction of hysteresis; b) $\delta^2\text{H}$ dynamics in all catchments plotted with data from one sequential rainfall sampler (EGS12_seq) and one bulk sampler (EGS07_SG); c) time series of stream water isotopic and ANC composition, rainfall and discharge for all catchments.

slow recovery of ANC in Middle Burn following all of the events. The differences between catchments and during events with different antecedent conditions are clearly apparent in hysteresis plots (Figure 4.7). In Shiplaw and Middle Burn, ANC was higher at similar discharges on the rising limb compared to the falling limb, although in Shiplaw ANC rebounded more quickly following the event peak. In Longcote, ANC on the falling limb rebounded more rapidly towards pre-event values than either of the western catchments. The direction of hysteresis is consistent across all events in the western catchments, but reverses in Longcote catchments for the higher discharge events.

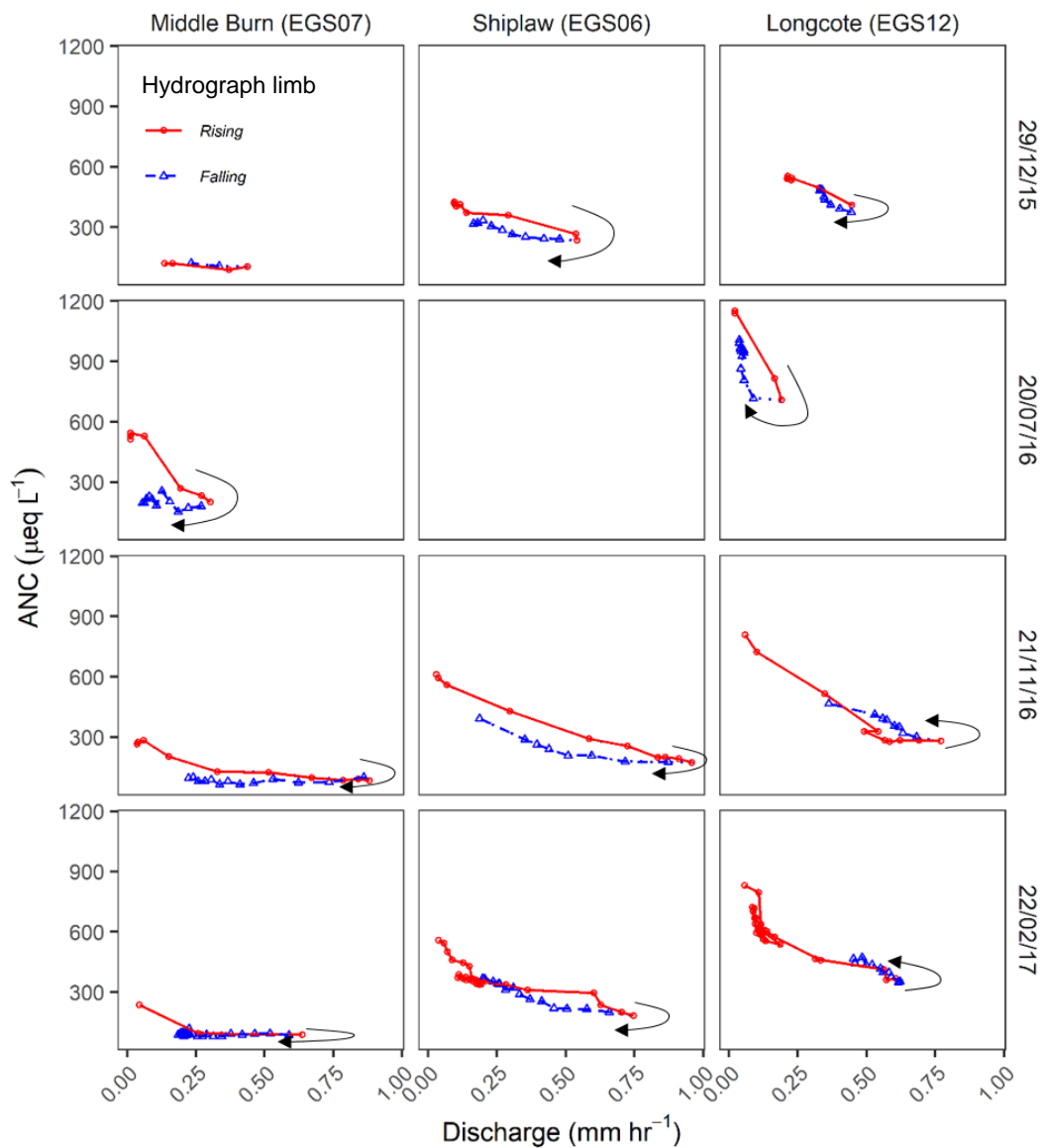


Figure 4.7: ANC-discharge plots for four events sampled at a 2-hourly intervals in the three sub-catchments. Black arrows show direction of hysteresis.

Temporal and spatial differences in runoff sources

The results from isotope and ANC-based hydrograph separation give insights into the runoff mechanisms operating in the three catchments and their temporal variation. The total event water fraction ($F_e(Q_{tot})$) was low (< 0.36) for all events and catchments, although with large uncertainties for some events (Table 4.4, Figure 4.8c). However, there were differences between catchments in terms of total event water fractions and these were consistent between catchments and events. When spatial differences in total event rainfall were taken into account, Shiplaw had the highest total event water runoff ratio, followed by Middle Burn, and Longcote had the lowest runoff ratio (Table 4.4). There is good consistency between the relative order of runoff ratios for each catchment and those calculated using the hydrometric data for the events (cf. Figure 4.5 and Table 4.4).

The fraction of event water at peak discharge ($F_e(Q_{max})$) shows the same relative responses between events as the values based on storm totals, though with lower uncertainty for the largest event (Figure 4.8a and Table 4.4). There were significant differences between the $F_e(Q_{max})$ for the two larger autumn/winter storms in the adjacent Shiplaw and more heavily forested Middle Burn catchments. $F_e(Q_{max})$ was 0.54 ± 0.14 in Shiplaw catchment during the event with largest peak discharge (November 2016). By contrast the fraction of event water at peak discharge was lower (0.37 ± 0.04) for the same event in Middle Burn catchment. In the eastern Longcote catchment, the fraction was also close to 0.50 ± 0.09 but peak discharge was lower than in the western catchments.

The sensitivity analysis for the influence of throughfall on the isotopic composition of the rainfall endmember in Middle Burn indicated that this did not alter the relative order of catchments in terms of their event water runoff fractions. The event fraction at peak discharge varied from 10 and 12% lower for the December 2015 and July 2016 events respectively, to 7 and 17% higher for the November 2016 and February 2017 events respectively. These values increase the contrast between catchments for the first two events. For the second two events they reduce the magnitude of the contrast between Middle Burn and Shiplaw for the November 2016 event (at a 70% confidence interval) but have no impact on the February 2017 event.

Table 4.4: Summary of hydrograph separations for four events across the three catchments. Note that stream water in the summer event was sampled at Middle Burn and Longcote only as explained in the text. F_e : fraction event water. F_{sw} : fraction surface water. F_{soil} : fraction soil water. F_{gw} : fraction groundwater. ' Q_{tot} ' is fraction based on summing event water fraction over whole event (event window is defined in the text) and ' Q_{max} ' is fraction at the maximum Q . ' δ^2H ' denotes fraction calculation based on δ^2H data. ' ANC ' denotes fraction calculation based on ANC data. TTP: Time to peak with subscripts p, e and gw denoting pre-event, event and groundwater components respectively. RR: runoff ratio based on separation with δ^2H data.

Event	Catchment	Q_{max} (mm hr ⁻¹)	F_e (Q_{tot}) (δ^2H)	F_{sw} (Q_{tot}) (δ^2H)	F_e (Q_{max}) (δ^2H)	F_{sw} (Q_{max}) (ANC)	F_{soil} (Q_{max}) (δ^2H & ANC)	TTP (hrs)	TTP _p (hrs)	TTP _e (hrs)	TTP _{gw} (hrs)	RR (δ^2H)
29/12/2015	M. Burn (EGS07)	0.49	0.02	0.88	0.04	0.89	0.85	15.0	15.0	11.8	15.0	0.02
	Shiplaw (EGS06)	0.58	0.04	0.78	0.12	0.82	0.70	14.8	14.8	13.0	13.8	0.03
	Longcote (EGS12)	0.49	0.02	0.65	0.10	0.70	0.60	13.2	13.2	13.2	13.3	0.01
20/07/2016	M. Burn (EGS07)	0.30	0.25	0.75	0.34	0.77	0.43	8.0	8.0	7.3	6.0	0.06
	Longcote (EGS12)	0.20	0.20	0.35	0.32	0.45	0.13	3.5	1.5	3.8	1.5	0.02
	M. Burn (EGS07)	0.90	0.25	0.89	0.37	0.90	0.53	16.2	11.5	16.2	17.8	0.18
21/11/2016	Shiplaw (EGS06)	0.97	0.36	0.82	0.54	0.86	0.32	14.5	7.8	16.0	7.8	0.27
	Longcote (EGS12)	0.77	0.28	0.73	0.48	0.79	0.31	17.5	24.0	17.5	24.0	0.14
	M. Burn (EGS07)	0.64	0.12	0.87	0.16	0.90	0.74	55.2	56.2	55.2	55.3	0.08
22/02/2017	Shiplaw (EGS06)	0.80	0.22	0.78	0.34	0.86	0.52	54.0	54.0	55.0	49.0	0.15
	Longcote (EGS12)	0.64	0.09	0.65	0.10	0.73	0.63	57.8	61.8	54.2	53.5	0.05

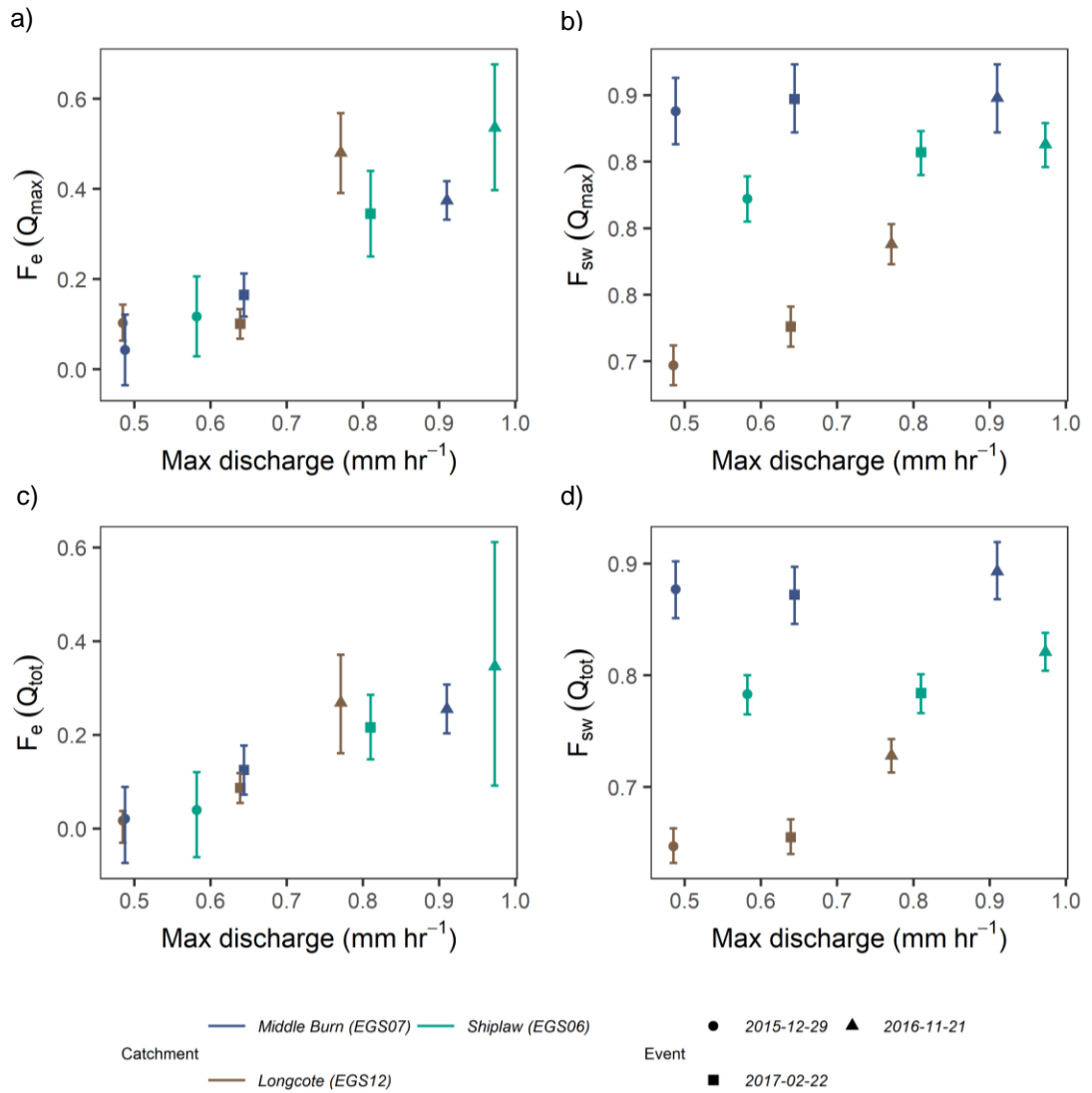


Figure 4.8: Exploring relationships between the event size and event water (F_e) or surface water (F_{sw}) fractions, in plots of (a, b) maximum event water (or surface water) discharge to maximum discharge (Q_{max}) and (c, d) total event water (or surface water) discharge to to maximum discharge (Q_{max}). Error bars represent 70% confidence intervals calculated using the method outlined in the text. Only the three autumn/winter events are plotted.

Estimated total surface water fractions ($F_{sw} (Q_{tot})$) were high for all winter events ($0.65 \pm 0.02 - 0.89 \pm 0.03$ of total runoff), though much lower in the summer event in the two catchments sampled ($0.35 \pm 0.02 - 0.75 \pm 0.03$ of total runoff). However, there were systematic and significant differences in surface water/groundwater discharge between catchments and events (Figure 4.8d and Table 4.4). Longcote was the most groundwater-dominated catchment in all events, though surface water still contributed 0.73 ± 0.02 of total runoff during the event with largest peak discharge and 0.35 ± 0.02 of runoff during the intense summer event. Shiplaw had intermediate levels of surface water discharge compared to the other catchments,

and Middle Burn had the highest, with 0.89 ± 0.03 of total runoff from surface water in the largest event and 0.75 ± 0.03 for the summer event. Estimated surface water fractions at peak discharge ($F_{sw}(Q_{max})$) showed a similar pattern between catchments and events, but were slightly higher (1 – 10%) than fractions based on totals (Figure 4.8b and Table 4.4).

Event water fractions increased approximately linearly with event size in the autumn/winter events in all catchments (Figure 4.8a,c). The exception was Longcote (EGS12), which had a more non-linear response, particularly in the $F_{sw}(Q_{max})$ values, which may be due to the higher recorded rainfall on the eastern side of the catchment for this event or to threshold behaviour. While the data suggest that event water and surface water fractions scale with event discharge, it is not possible with this dataset to determine the main meteorological drivers due to the limited number of events. Correlations with event total rainfall depth, rainfall intensity and antecedent rainfall were explored, with some possible relationships but it was hard to account for co-linearity without more data.

The dynamics of pre-event / event water and groundwater fractions within events are also useful for understanding runoff processes. For example, during the event with largest peak discharge all three catchments responded differently in terms of their discharge components (Figure 4.9). Longcote had a 'double peak' hydrograph (also observed in some other events that were not sampled) with an initial rapid discharge of pre-event / groundwater and a pulse of event water during the first peak, followed by a slower increase in event water during the second peak that is quickly overwhelmed by pre-event / groundwater on the falling limb. It was the only catchment with significant increases in pre-event / groundwater fraction following the hydrograph peak, which is indicative of deeper subsurface flow paths and a more groundwater dominated catchment.

The adjacent Shiplaw and Middle Burn catchments in the west also show contrasting responses. The response of Shiplaw was more similar to Longcote, in that the initially high pre-event water / groundwater inputs appear to have been rapidly overwhelmed by event water runoff that dominated the peak of the hydrograph, but decreased rapidly on the falling limb. In Middle Burn, the response was generally more damped with more coincident peaks in event water, pre-event water and groundwater, and a greater fraction of event water on the falling limb.

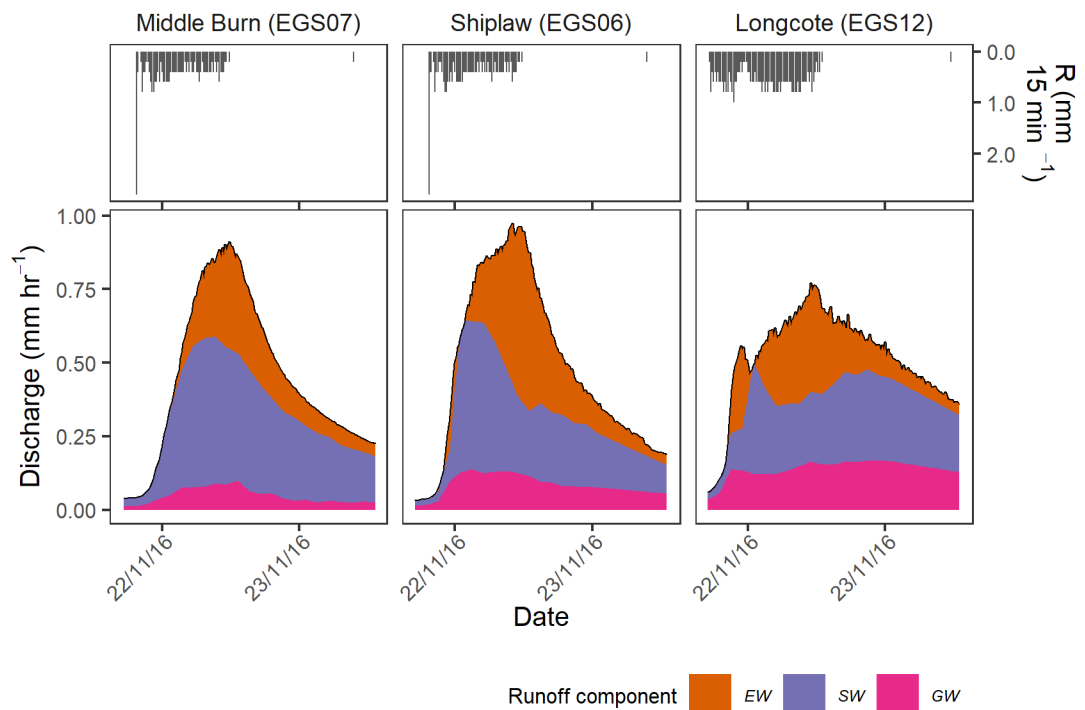


Figure 4.9: Three-component hydrograph separation based on $\delta^2\text{H}$ measurements in 2-hourly stream water samples and sequential rainfall samples in the November 2016 event. EW: event water; SW: soil water; GW: Groundwater.

4.4 Discussion

4.4.1 Temporal and spatial sources of runoff during events

The results suggest that pre-event water is an important fraction of stream discharge in all sampled events and sub-catchments, constituting a significant fraction of total runoff. During the largest event, pre-event water was 0.64 of total runoff and 0.46 of runoff at peak discharge in the most responsive catchment. This finding is consistent with many other IHS studies that have demonstrated the importance of pre-event water in event hydrographs (Bonell et al., 1990; McDonnell, 1990; Pearce et al., 1986; Sklash and Farvolden, 1979). Such findings imply more limited event runoff than might have been assumed under a conceptual model of infiltration or saturation excess overland flow.

The groundwater contribution to stream discharge is less important under winter event conditions, although quite variable between catchments. In the eastern catchment up to 0.25 of runoff was from groundwater sources during the largest

winter event monitored. The low groundwater fraction implies that soil water is an important water source; estimated from three component hydrograph separation to contribute 0.31-0.85 of streamflow at peak discharge in the winter events. This is consistent with studies in similar temperate catchments with relatively impermeable bedrock (or impermeable superficial deposits), where surface runoff and shallow subsurface runoff in soils tend to dominate (Tetzlaff et al., 2007b). Groundwater may be more important in summer events, but testing this hypothesis would require sampling larger summer events (groundwater was 0.27 and 0.55 of runoff at peak discharge during the summer event in the forested Middle Burn (EGS07) and the eastern Longcote (EGS12) catchments respectively).

Cross-catchment comparison gives insights into the role of catchment characteristics in controlling flow paths. Discharge in the three catchments had quite distinct responses to rainfall inputs. Longcote responded rapidly, but had a damped response overall in terms of peak flows and event water fractions. It suggests that the catchment has some relatively rapid event water runoff pathways but these are dominated by pre-event flow paths that dampen the peak and result in faster recovery of stream chemistry and pre-event isotopic composition on the falling limb. It is possible that the initial event water inputs are due to the near stream influence of impermeable glacial till acting as a rapidly responding variable source area in the Longcote catchment, as has been reported in studies in similar upland landscapes (Neal et al., 1997).

Shiplaw also responded rapidly to rainfall inputs; it had the highest peak discharge and highest event water fractions at peak discharge of the three catchments, suggesting rapid event water runoff. However, stream water isotopic composition on the falling limb returned relatively rapidly towards pre-event water values, suggesting that slower pathways are also important during events. These findings may reflect the more varied catchment characteristics, which include forest cover (41%), improved grassland (28%) and wetland (27%). The relative partitioning effects of these different land uses can be complicated. For example, Roa-Garcia and Weiler (2010) showed, in a tropical environment, that even a low percentage of wetlands can prolong mean response time (a measure of the transit time distribution for unit rainfall) significantly, whilst forests also increased response time but to a lesser extent, and grasslands had the fastest response time. They suggest these differences are due to the relative role of increased water storage, interception and

soil porosity, and compaction, across wetlands, forests and grasslands respectively. Their findings are supported by a number of other studies in both temperate and tropical environments (Bonell et al., 1990; Gremillion et al., 2000; Laudon et al., 2007). However, in contrast to the results of Roa-Garcia and Weiler (2010), the fact that Shiplaw had the highest improved grassland cover and event water fractions of the three catchments suggests that compaction and drainage of the improved grassland, and the resulting increase in rapid event water runoff, may be dominant over the damping effects of the wetland and forest cover.

Middle Burn responded in an intermediate way between Shiplaw and Longcote. Comparisons with the adjacent Shiplaw catchment give insights into the role of forest cover in influencing the event water fraction. Despite similar topographic characteristics, catchment area, geology and a higher percentage of responsive soils in Middle Burn compared to Shiplaw, the event water fraction in Middle Burn was consistently lower across the sampled events, and even in the largest event it was 17% lower at peak discharge. These lower values are most likely caused by increased interception, infiltration rates and soil porosity due to forest cover, as suggested in other studies (Roa-García and Weiler, 2010). Nevertheless, the low overall groundwater fraction, in combination with a slow recovery of stream water isotopic and ANC values towards pre-event composition following events, suggests that these damping effects occur in a shallow subsurface system, presumably within the peats and gleyed soils overlying glacial till in the catchment. These results are consistent with findings from Chapter 3 that showed that storage and transit times for the Middle Burn catchment are slightly greater than for the Shiplaw catchment.

Another important question for implementing effective NFM measures concerns the relative role of soils and geology compared to forest cover in controlling the event water fraction. This study suggests that soils and geology dominate forest cover, based on comparisons between the three catchments. Longcote had the lowest event water runoff ratios and highest groundwater fractions, despite steeper slopes and low forest cover, implying that within the Eddleston Water catchment as a whole, forest cover is not a primary control on flow path partitioning.

4.4.2 Relative influence of event and catchment characteristics on runoff mechanisms

Event characteristics (in terms of total rainfall depth, intensity and API) appear to be more important controls on the amount of event water in the hydrograph than catchment characteristics, with the differences between events greater than the differences between catchments. Antecedent conditions may be particularly important, as suggested by the switch in hysteresis direction in Middle Longcote, which has been linked to the changing inputs of hillslope soil water in streams under different wetness states (Zuecco et al., 2016). Although other studies suggest that these factors are important (Fischer et al., 2017; Roa-García and Weiler, 2010), it was not possible with this dataset to identify the effects of individual event characteristics on flow partitioning.

The study findings support suggestions in recent NFM literature that climatic conditions and individual storm event characteristics dominate over catchment characteristics in influencing peak flows in the largest events (Dadson et al., 2017). Nevertheless, there are consistent differences between catchments for each event and, within the events studied here, these are maintained across events of different sizes, suggesting that catchment characteristics have a considerable influence on runoff processes. The consistency of catchment responses (in terms of event water fraction and groundwater fraction) between events and over different antecedent conditions suggests that detectable threshold behaviour does not occur in the sub-catchments for the range of event magnitudes that were sampled (with the potential exception of Longcote, where further data for larger events is required). The dataset includes some of the largest events in 7 years of continuous hydrometric monitoring, so if threshold behaviour is a feature of runoff generation in this environment it only occurs for the largest flood events. Such behaviour has been identified in other studies, for example due to 'fill and spill' occurring in subsurface bedrock topography at certain thresholds of rainfall depth and antecedent conditions (Tromp-van Meerveld and McDonnell, 2006).

4.4.3 Implications for planning NFM interventions

The study demonstrates the importance of pre-event water in runoff mechanisms in landscapes subject to NFM interventions, implying that overland flow may not be a dominant runoff mechanism even in relatively responsive catchments. The results

suggest that forests can influence the partitioning of runoff at the catchment scale, so could be used to manipulate flow paths in NFM, but that the effects might be overwhelmed by high total rainfall in the largest events and limited by soil water storage capacity (Soulsby et al., 2017; Tetzlaff et al., 2007a). In areas with compacted soils overlying relatively permeable soils or geology, forest planting may help to connect runoff to streams via the groundwater zone. In this case the location of forest cover and the type of trees become important, as discussed by Neal et al. (1997) who suggested possible long term experiments with more deeply rooting trees. To take account of these mechanisms in NFM, implementation might require greater consideration of subsurface features at the planning stage. Flood vulnerability maps focussed on surface properties may not be sufficient for determining where NFM interventions might be effective and need to consider more subsurface aspects such as soil permeability, geological substrate permeability and depth to groundwater.

The high degree of heterogeneity in runoff mechanisms across the Eddleston Water catchment suggests this needs to be well understood for NFM planning purposes. Such heterogeneity has been noted in many other studies (Fischer et al., 2017), but results from this study provide insights into areas for further investigation from an NFM perspective. For example, investigating in more detail runoff pathways from drained improved grassland under different antecedent conditions to understand whether they are acting as fast runoff pathways for event water or contributing to the storage and release of groundwater as found in some studies (Sklash et al., 1996). It would also be useful to identify whether extensive wetland areas act as sources of pre-event water or rapid runoff of event water under different conditions, as studies have suggested a range of alternative mechanisms (Bonell et al., 1990; Roa-García and Weiler, 2010). Finally, it would be useful to examine in more detail the effects of forest throughfall on the isotopic signatures of inputs and the impacts this has on estimates of flow path partitioning (Kubota and Tsuboyama, 2003).

This study highlights the potential value of tracer-based approaches in NFM planning. Whilst good consistency was found between hydrograph separations conducted using hydrometric and isotope-based methods in the current study, other studies have reported that similar hydrometric responses can be accompanied by very different tracer responses, giving insights into flow path mechanisms (Hale and McDonnell 2016). Tracers are also a powerful tool for evaluating hydrological

models as they provide an independent method to test process understanding. Given the marginal changes to flood peaks that are expected due to NFM interventions, which may be within the confidence limits of hydrometric monitoring techniques, especially at larger spatial scales (Environment Agency, 2018), tracers may help to reduce some of the uncertainties in attributing NFM impacts.

At the implementation stage of NFM, targeted tracer studies could help locate interventions. Fennell et al. (2018), for example, suggest that the efficacy of NBS (Nature-Based Solutions) will be spatially variable and highlights the “importance of obtaining an in-depth understanding of the relevant flow paths and catchment functioning as an evidence base to guide site selection for NBS.” Tracers may also be particularly useful for quantifying co-benefits of NFM, such as helping to characterise how interventions might alter flow pathways and residence times of water pollutants. Of course, there are practical challenges, given the costs associated with tracer studies. However, costs are decreasing and there are now widely available in-situ high frequency sensors for tracers such as conductivity, temperature and potentially isotopic tracers (Berman et al., 2009) that could be incorporated into NFM planning and monitoring.

4.5 Conclusions

To our knowledge this is the first study using tracers at the catchment scale to investigate runoff mechanisms in UK-based natural flood management projects. It gives insights into the diversity of runoff mechanisms operating during storm events across different upland catchments. The main conclusion is that pre-event water makes up an important fraction of stream discharge during events for the size of catchments (< 10 km²) and events (< 20% of the mean annual flood) for which there is currently some evidence that forest cover could have an impact (Dadson et al., 2017). Since many NFM measures are designed to target event water, this implies a need for careful consideration of the types and locations of NFM interventions that are put in place to ensure they are effective. The study also suggests that forest cover reduces, and improved grassland increases, the fraction of event water runoff in streams over this range of event magnitudes. However, the effects of these differences in land cover are dominated by differences in event characteristics, suggesting limited impacts for the largest events. Finally, the study demonstrates

the potential utility of using tracers in NFM for understanding runoff processes and monitoring co-benefits such as surface water and groundwater pollution.

5 The impact of across-slope forest strips on hillslope subsurface hydrological dynamics

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The candidate, as lead author, identified the field site and liaised with stakeholders, installed all monitoring equipment, organised and carried out ERT surveys, and undertook laboratory analyses. Jon Chambers and Sebastian Uhlemann processed the raw ERT data. All other data analysis and the writing of the paper were carried out by the candidate. Co-authors provided guidance on the scope and design of the project, and contributed to the editing of the manuscript.

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Abstract

Forest cover has a significant effect on hillslope hydrological processes through its influence on the water balance and flow paths. However, knowledge of how spatial patterns of forest plots control hillslope hydrological dynamics is still poor. The aim of this study was to examine the impact of an across-slope forest strip on subsurface soil moisture and groundwater dynamics, to give insights into how the structure and orientation of forest cover influences hillslope hydrology. Soil moisture and groundwater dynamics were compared on two transects spanning the same elevation on a 9° hillslope in a temperate UK upland catchment. One transect was located on improved grassland; the other was also on improved grassland but included a 14 m wide strip of 27-year-old mixed forest. Subsurface moisture dynamics were investigated upslope, underneath and downslope of the forest over 2 years at seasonal and storm event timescales. Continuous data from point-based soil moisture sensors and piezometers installed at 0.15, 0.6 and 2.5 m depth were combined with seasonal (~ bi-monthly) time-lapse electrical resistivity tomography (ERT) surveys. Significant differences were identified in subsurface moisture dynamics underneath the forest strip over seasonal timescales: drying of the forest soils was greater, and extended deeper and for longer into the autumn compared to the adjacent grassland soils. Water table levels were also persistently lower in the forest and the forest soils responded less frequently to rainfall events. Downslope of the forest, soil moisture dynamics were similar to those in other grassland areas and no significant differences were observed beyond 15 m downslope, suggesting minimal impact of the forest at shallow depths downslope. Groundwater levels were lower downslope of the forest compared to other grassland areas, but during the wettest conditions there was evidence of upslope-downslope water table connectivity beneath the forest. The results indicate that forest strips in this environment provide only limited additional subsurface storage of rainfall inputs in flood events after dry conditions in this temperate catchment setting.

5.1 Introduction

There is renewed interest in forest strips (often termed 'field boundary planting', 'shelterbelts' or 'buffer strips') as a flood management tool in wet upland environments (Dadson et al., 2017; Lane, 2017; Soulsby et al., 2017). Past work in the UK has shown that forest shelterbelts in improved grassland can control surface runoff (Wheater et al., 2008; Wheater and Evans, 2009). This work, and other studies, have reported significant increases in soil water storage capacity in shallow soils and increased infiltration rates within forest strips, and evidence of forest rain shadow effects on soil moisture in adjacent grassland (Jackson et al., 2008; Lunka and Patil, 2016; Marshall et al., 2009). Thus understanding the impacts of forest strips on subsurface hydrology appears key for controlling surface runoff and such interventions have the potential for "reducing run-off even when only present as a small proportion of the land cover" (Carroll et al., 2004, p. 357). If these findings can be generalised, there are obvious applications within a catchment management perspective for reducing flood risk. They are also important globally, given rapid changes in land use towards more mosaic landscapes and the effects this might have on hydrological processes (Haddad et al., 2015; Ziegler et al., 2004; Zimmermann et al., 2006).

While some evidence of forest strip impacts on hillslope hydrology exists, there has been limited mechanistic investigation of forest strip impacts on hillslope runoff processes. Of course, mechanistic studies on single completely forested hillslopes have been conducted for decades (Hewlett and Hibbert, 1967; Tromp- van Meerveld and McDonnell, 2006; Wenninger et al., 2004). But the 'black box' before and after treatments applied at the catchment scale (e.g. Hornbeck et al., 1970; Swank et al., 1988) have not been conducted at the hillslope scale. At best there are some hillslope intercomparisons (Bachmair and Weiler, 2012; Scherrer et al., 2007; Uchida et al., 2006, 2005) that explore hillslope response under different land covers. All of these approaches suffer from difficulties in controlling for significant heterogeneities even at the plot scale, a reliance on point-based data, and the challenges that these raise for developing transferable process understanding (Bachmair and Weiler, 2012).

Therefore, whilst plot scale studies have shown measurable impacts of forest cover on local hydrology, the use and application of these findings to assess the

effectiveness of forest strip planting at the hillslope scale is limited. Specifically, forest strip planting raises important additional questions related to the location and structure of forest cover in landscapes and its interaction with other physical hillslope properties. For example, forest strips or vegetation patches in more arid environments appear to ‘interrupt’ hydraulic connectivity across landscapes (Fu et al., 2009; Liu et al., 2018) so may have variable effects on downslope hydrological processes. However, such questions have only been looked at in a few modelling studies (Reaney et al., 2014).

Here we examine the influence of a forest strip on hillslope subsurface hydrological dynamics. We focus on a typical example of a narrow (14 m wide), mixed forest shelterbelt planted on improved grassland (land used for grazing that has been improved through management practices such as liming or drainage) - a configuration similar to that being used in some ‘natural’ flood risk management schemes in the UK (Environment Agency, 2018; Tweed Forum, 2019). We pair hillslope scale soil moisture and groundwater level measurements with time-lapse electrical resistivity tomography (ERT) to help extrapolate from point-based measurements to hillslope scale process understanding. We build on work by Cassiani et al. (2012), Garcia-Montiel et al. (2008) and Jayawickreme et al. (2008), extending the ERT technique to investigate the interaction of two vegetation types and spatial orientation on the slope. Our specific questions are:

1. How do across-slope forest strips alter soil moisture and groundwater level dynamics beneath the forest?
2. Do forest strips have downslope impacts on soil moisture and groundwater level dynamics?

We consider these questions over seasonal and storm event timescales, and also the potential implications from a flood risk management perspective.

5.2 Methods

5.2.1 Site description

The experiment was established on a hillslope in the 67 km² Eddleston Water catchment, a tributary of the River Tweed in the Scottish Borders, UK (Figure 5.1). The catchment hosts an ongoing project initiated in 2010 to investigate the impact of

natural flood management (NFM) measures aimed at controlling runoff from farmland and forest land (Werritty et al., 2010). The measures include tree-planting, establishment of holding ponds on farmland, re-meandering the Eddleston Water river, and the construction of 'leaky' dams in some sub-catchments (Tweed Forum, 2019).

Catchment characteristics are typical of much of the UK uplands. Topography is varied with elevations of 180-600 m and the climate is cool with mean annual precipitation of 1180 mm (at Eddleston village, 2011-2017), falling mainly as rainfall. Mean daily temperatures range from 3 °C in winter to 13 °C. Daily evapotranspiration ranges from 0.2 mm in winter to 2.5 mm in summer (estimated using the Granger-Gray method (Granger and Gray, 1989) using data from the weather station in the catchment at Eddleston village). Bedrock throughout most of the catchment is comprised of Silurian impermeable well-cemented, poorly sorted sandstone greywackes (Auton, 2011). Extensive glaciation has affected the superficial geology and soil types. Soils on steeper hillsides are typically freely draining brown soils overlying silty glacial till, rock head or weathered head deposits. Towards the base of the hillslopes the ground is typically wetter and soils comprise sequences of gleyed clays and peats on sub-angular head deposits or alluvial deposits closer to the river. Land cover is mainly improved or semi-improved grassland on the lower slopes and rough heathland at higher elevations. Forest cover is typically mixed coniferous and deciduous woodland, concentrated along field boundaries.

The experimental hillslope is located ~100-200 m from the Eddleston Water rising to 30 m above the river with a relatively uniform slope of ~9°. Soil pit surveys (0.7 m depth) found that soils comprise typically 0.15-0.20 m deep silty cambisols containing numerous sub-angular cobbles up to 60 mm length. Large roots (< 30 mm) were prevalent in the top 0.20 m of the forest soils, with occasional large tree roots and frequent smaller tree roots (< 5 mm) present down to the bottom of the soil pits. By contrast, small roots were prevalent in the top 0.20 m of the grassland soils, with no roots identified at the base of the soil pits (Appendix D, Figure D.1). Borehole logs (Appendix D, Figure D.1) and a grid of initial ERT surveys showed a clear layered structure to the underlying geology, with soils above a layer of silt/loam glacial till containing numerous large cobbles, which transition at 1.5-2 m depth into sub-angular head deposits or weathered rock head.

Soils on the hillslope are generally freely draining, although surface runoff was observed at the wettest times of year in the area upslope of the forest strip. Hydraulic conductivity of soils overlying head deposits has been measured as part of the wider project on a similar hillslope 2 km to the north which found median values of 21-39 mm h⁻¹ (0.50-0.94 m d⁻¹) for improved grassland and 42 mm h⁻¹ (1 m d⁻¹) for an ~50 year old plantation forest, and 119-174 mm h⁻¹ (2.86-4.18 m d⁻¹) for broadleaf forests > 180 years old (Archer et al., 2013). The hydraulic conductivity of the glacial till was estimated to range from < 0.001 to 1 m d⁻¹ based on data from other locations in Scotland (MacDonald et al., 2012). Hydraulic conductivities of the underlying head deposits could not be measured directly using falling head tests in the piezometers as values were beyond the design limit of the test methodology (40 m d⁻¹). However, elsewhere in the Eddleston catchment, the permeability of the head deposits has been measured as 500 m d⁻¹ (Ó Dochartaigh et al., 2018). Hydraulic conductivity of the bedrock was not measured, but Silurian greywacke aquifers elsewhere in southern Scotland have been shown to have low productivity (Ó Dochartaigh et al., 2015), with an estimated average transmissivity of 20 m² d⁻¹ (Graham et al., 2009).

Particle size and organic matter content were determined from soil samples taken at 0.15 m and 0.6 m depth at all 14 soil moisture monitoring sites (Appendix D, Table D.1). Particle size analysis used the sieving method for the proportion above 2 mm and a Beckmann Coulter LS230 particle size analyser for the proportion below 2 mm, according to international standards (ASTM international, 2004). The soil texture is predominately silty loam with a substantial proportion of gravel and cobbles (22-58% by mass). There is little variation between locations and transects, although the 0.6 m depth sample at the top of the grassland transect and one of the 0.15 m depth samples in the forest strip had slightly higher sand content than the other locations. Organic content was measured for the same samples using the loss on ignition method at 375 °C for 24 hours (Ball, 1964), and was 2-7%.

5.2.2 Experimental setup

The experiment consisted of two 64 m instrumented transects established at the same topographic elevation (212-195 m) on the hillslope and separated by 30 m (Figure 5.1). One transect was on improved grassland, whilst the other intersected, and was centred on, a 14 m wide strip of 27 year old fenced mixed forest containing Sitka spruce (*Picea sitchensis*), European larch (*Larix decidua*), ash (*Fraxinus*

excelsior), hawthorn (*Crataegus monogyna*), oak (*Quercus robur*) and elder (*Sambucus nigra*). Tree height ranged from 7 to 14 m and rooting depths were estimated as 0-1.5 m for Sitka spruce and 0-2.5 m for the deciduous trees, based on trees of similar age on similar soils (Crow, 2005; Fraser and Gardiner, 1967). Both land cover types are typical of the wider catchment and much of the UK uplands, with the grassland used throughout the year for grazing sheep and occasionally horses.

Fourteen soil moisture sensors (Delta-T SMT150 with GP4 loggers) were installed in pairs at 0.15 m and 0.6 m depth at upslope, midslope and downslope elevations in each transect (3 pairs on the grassland and 4 pairs on the forest transect). Nine 50 mm-diameter piezometers were installed at 2.5 m depth using a hand held rock drill at similar locations to the soil moisture sensors (3 on the grassland and 6 on the forest transect). The additional piezometers on the forest transect were installed close to the upslope and downslope boundaries of the forest. All piezometers were sealed with bentonite to 0.6 m depth and contained a 0.35 m screen at their base. All piezometers were instrumented with non-vented Rugged TROLL 100 loggers logging at 15-minute intervals and levels were checked manually every 3 months. A barometric logger (Rugged BaroTROLL 100) at the site was used to correct for atmospheric pressure. Two tipping bucket rain gauges were installed 16 m upslope and downslope of the forest to check for the influence of the prevailing wind on rainfall on either side of the forest (Figure 5.1).

The logging period was November 2016 to November 2018 inclusive. One of the soil moisture and rainfall loggers failed on the forest transect, resulting in a ~5-month data gap for the shallow soil moisture sensor at the top of the transect (F1_15), a ~3-month gap in the upslope rain gauge, and a ~1-month gap in data for the other three sensors attached to this logger. The groundwater data was also discontinuous due to large seasonal variations in groundwater level leading to water table levels below the level of the sensors. The gaps in data have been taken into account in the analysis where necessary. Additionally, one of the upper soil moisture sensors in the forest (F2b_15) did not respond for any event, perhaps because it was in an air pocket, and was removed from the analysis. Two piezometers (BH_F2b, BH_F3b) which did not respond during the study period were also removed from the analysis.

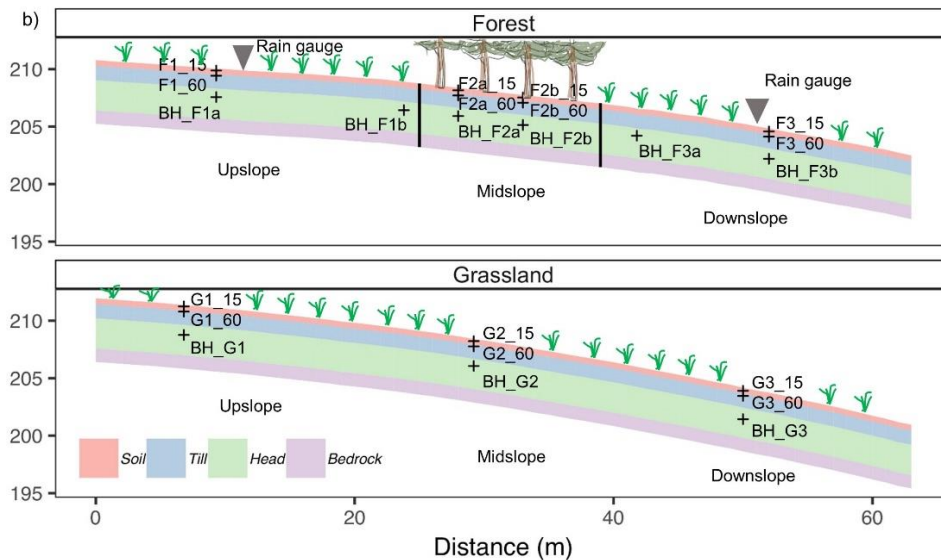
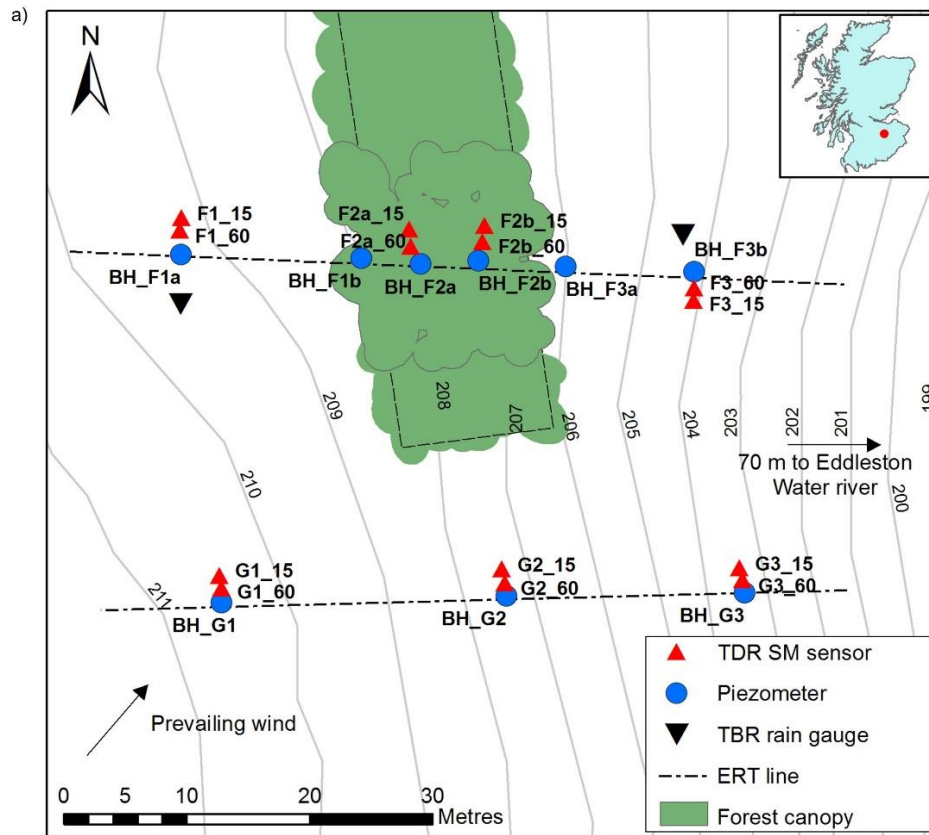


Figure 5.1: a) Site layout and location in Scotland. Soil moisture sensors at 15 cm and 60 cm depth are marked ‘_15’ and ‘_60’ respectively and prefixed with ‘F’ and ‘G’ for the forest and grassland transects. ‘BH_F’ and ‘BH_G’ are piezometers on the forest and grassland transects respectively. TDR SM sensor: Time domain reflectometry soil moisture sensor; TBR: Tipping bucket rain gauge. Grey lines are contours in masl. Grey outline in the forest indicates the extent of the surveyed canopy. Dotted boundary of forest marks the location of the fence (which continues under the mapped canopy). b) Schematic cross sections of the forest and grassland hillslope transects, showing vegetation type, geology and locations of different sensors.

Two soil temperature probes (Delta-T ST4) were installed at 0.15 m and 0.6 m depth at the top of the grassland transect, and temperature data were also collected from the pressure transducers at 2.5 m depth. Air temperature, wind speed and direction, solar radiation and rainfall data were obtained from an automated weather station 3 km north of the site at Eddleston village and a similar elevation of 200 masl. These datasets were used to estimate evapotranspiration and to infill missing rainfall data as explained in section 2.3.2. Most of the trees closest to the transect in the forest are conifers, but the deciduous trees had no leaves between mid-November and mid-April.

Initial 2D ERT surveys consisting of 6 lines at 2 m spacing were carried out in August 2016 across and down the slope to help characterise the geological structure of the site. A series of ten repeated 2D ERT surveys were then conducted between November 2016 and April 2018 along the forest and grassland transects. The surveys were undertaken using an AGI SuperSting R8 imaging system connected to arrays of 64 stainless steel pin electrodes positioned at 1 m intervals. Measurements were made using the dipole-dipole configuration with dipole sizes (a), of 1, 2, 3 and 4 m and unit dipole separations (n) of 1-8a. Time-lapse inversion of the data was performed using RES2DINV (Loke et al., 2013), which employs a regularised least-squares optimisation approach, in which the forward problem was solved using the finite-element method.

5.3 Soil moisture and groundwater data analysis

The soil moisture and groundwater data were analysed using the whole time series to understand annual changes and through the selection of specific events to understand event dynamics. The whole time series data and event data were also examined on a seasonal basis, with the following definitions: Winter ('Wi': Dec-Feb), Spring ('Sp': Mar-May), Summer ('Su': Jun-Aug) and Autumn ('Au': Sep-Nov), These periods were defined based on the soil moisture data that showed full wetting up did not occur until late Nov-early Dec, providing a better baseline for comparison.

5.3.1 Whole time series analysis

Soil moisture and groundwater level data were first analysed for the whole time series to give an indication of seasonal patterns, discontinuities in the groundwater data and logger errors. Summary statistics included median values; minimum and

maximum values; interquartile range; and graphical inspection of wetting up and recession characteristics. Given the discontinuity of the groundwater data, only the proportion of the year for which a water table was recorded and the range in levels were of interest, along with more descriptive details (e.g. recession behaviour) of the water table response to rainfall events.

5.3.2 Event analysis

Soil moisture and groundwater events were selected for analysis by first identifying rainfall events and then finding the associated event in the soil moisture/groundwater time series. The rainfall events were selected automatically from the upslope rain gauge time series based on a total event rainfall of ≥ 8 mm and an intensity criterion that an event contained no period longer than 2 hours without rainfall. This resulted in 56 events, which was reduced to 52 events as described in the following paragraph. Characteristics were calculated for each event in the final event dataset, including total rainfall (TR, ranging from 8.2 to 52.6 mm), mean hourly intensity (I , ranging from 0.5 to 2.5 mm h⁻¹), a 5-day weighted antecedent wetness index (AWI, ranging from 1.3 to 48.3 mm) (Kohler and Linsley, 1951) and the 28-day antecedent rainfall (AP28d, ranging from 13.2 to 138 mm). The gap in the upslope rainfall gauge time series from 01/09/2017 – 02/12/2017 was filled directly with data from the weather station at Eddleston village, which was considered appropriate based on the small differences in rainfall recorded across multiple sites in the catchment. A full summary of the selected events is given in Appendix D, Table D.2.

Events in the time series for the operational 13 soil moisture sensors were initially selected automatically by locating the point after the start of event rainfall where the 1-hour rolling mean smoothed soil moisture exceeded a gradient threshold of $>0.001 \text{ m}^3 \text{ m}^{-3} \text{ h}^{-1}$ and where the total change in soil moisture was $>0.012 \text{ m}^3 \text{ m}^{-3} \text{ h}^{-1}$. Events in the time series for the seven operational groundwater sensors were selected in the same way but with a gradient threshold of $>0.008 \text{ m h}^{-1}$ and where the total change in groundwater level was $>0.001 \text{ m h}^{-1}$ in the 1-hour smoothed groundwater data. These thresholds were determined iteratively by graphical inspection of several randomly selected events from each sensor. Saturation behaviour was identified in some of the soil moisture time series as a rapid rise in soil moisture to near saturation, followed by a plateauing in soil moisture and then a rapid decrease in value, which was captured in the algorithm using a combination of

the gradient of the rising limb and the maintenance of a peak within 95% of the peak level for more than 1.5 h.

Given the variety in types of response, all selected events were inspected manually. Four events were removed completely due to excessive noise, even in the smoothed soil water and groundwater time series, leading to spurious event characteristics across all locations. Further manual adjustments were made for particular locations in some events to adjust start and peak selection due to excessive noise and to correct peaks where very close consecutive events resulted in peak selection associated with the subsequent event. The final event dataset consisted of 52 events (Appendix D, Table D.2).

The following metrics were calculated for each event, including: whether response occurred in the soil moisture or groundwater data (R); time to response from the start of rainfall (TTR); time to peak from start of rainfall (TTPR); and maximum absolute rise (MR). Response was defined by the criteria above including, in the case of the piezometers, those that rose from an initially dry state.

Comparison of R, TTR, TTPR and MR between grassland and forest transects was made for a subset of nine events at the wettest points in the time series when the piezometer downslope of the forest responded (and most other sensors were also responding), to enable comparison of sensors with a more balanced design. Pairwise comparisons between sensors in the same domains (upslope, midslope and downslope) and depths on the different transects were also made for all responding sensors in the pair to enable analysis under a wider range of conditions. Tests for normality (Shapiro-Wilk) and homoscedasticity (Fligner-Killeen) were conducted prior to statistical testing. These showed that with a \log_{10} transformation the majority of sensor datasets followed a normal distribution and all of them were homoscedastic. Given some deviation from normality but relatively uniform differences in variance, the non-parametric Kruskal-Wallis test was used to compare medians and Dunn's post-hoc test to determine where any significant differences occurred.

Logistic regression was used to test the relationship between event characteristics and whether sensors responded given the binary nature of the data. Spearman's rank correlation was used to assess associations between event characteristics and TTR, TTPR and MR. Prior to the exploration of the relationship between event

characteristics and response metrics, co-linearity between the different event characteristics was checked (Appendix D, Table D.3). There was some co-linearity between event rainfall and event intensity, and also AWI and AP28d, which was considered in the interpretation of the results. All statistical analyses were conducted in R version 3.5.1 with significance defined as $p < 0.05$.

5.3.3 ERT data analysis

The ERT surveys were carried out following variable antecedent rainfall conditions (Figure 5.2). After correction of the ERT model for effects of soil temperature using data from the nested temperature probes (at 0.15 m and 0.6 m depth) and the BH_G1 pressure transducer at 2.5 m depth, temporal changes in resistivity between the surveys were assumed to be due to changes in soil moisture content, based on relationships established in other studies (Brunet et al., 2010; Cassiani et al., 2009; Chambers et al., 2014). To factor out potential differences between material properties, comparisons in each of the transects were made relative to the May 2017 survey as it was the driest survey with the highest resistivities.

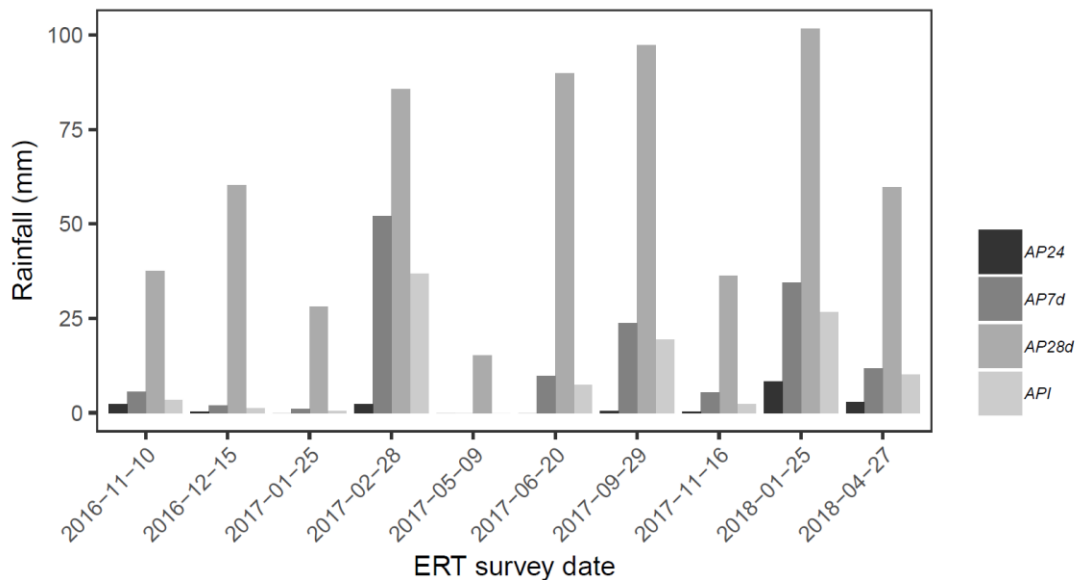


Figure 5.2: Antecedent rainfall conditions for the ten ERT surveys. API: 5 day weighted antecedent rainfall (as described in text); AP24, AP7d and AP28d are total antecedent rainfall over 24 hours, 7 days and 28 days prior to the survey.

Resistivity contrasts between depths and locations on the different transects were analysed by averaging resistivities across different lateral or vertical groups of cells in the ERT datasets from each of the transects. Given some deviation from normality in resistivity distributions within groups, median resistivities were compared using the same non-parametric tests as for the in-situ sensor data and a

bias-corrected bootstrapping procedure used to estimate confidence intervals for each group.

5.4 Results

5.4.1 Seasonal subsurface hydrological dynamics

Soil moisture content and groundwater level

Soil moisture content had a distinct seasonal pattern, with generally drier conditions in summer and wetter in winter. This was most pronounced in the shallow soil moisture sensors and lasted longer in the forest compared to the grassland (April to December and April to July, respectively) (Figure 5.3). Saturation occurred during winter in most of the soil moisture time series on grassland areas as distinct plateaued peaks that also recessed rapidly (Figure 5.3). In most instances this was due to infiltration, but occasionally at locations F1_60 and G2_60 the water table rose above the level of the soil moisture sensor. Saturated soil moisture conditions were not apparent in the forested areas (F2 sensors).

Soil moisture content in the grassland areas upslope and downslope of the forest strip (F1 and F3 sensors) displayed similar behaviour to those on the grassland transect, with the exception of the 0.6 m depth sensor upslope (F1_60), which had a higher soil moisture content throughout almost the entire time series than the paired grassland sensor (G1_60), possibly due to the location in a shallow topographic depression. The upslope rain gauge had higher daily rainfall than the downslope gauge during the study period (paired t-test, $p < 0.01$), probably due to the prevailing wind direction, but the mean difference was only 0.1 mm d^{-1} .

Over seasonal timescales there was generally more variability in soil moisture content at 0.15 m depth compared to at 0.6 m depth, apart from in the forest strip, where seasonal variability was similar in both shallow and deeper soil depths. This deeper and prolonged drying of the forest soils in summer and autumn has implications for soil water storage potential. For the whole time series, cumulative soil moisture content was 72-75% and 81-96% compared to a baseline of cumulative median winter soil moisture content for all sensors in the forest (F2 sensors) and all sensors on grassland respectively. An example of this contrast

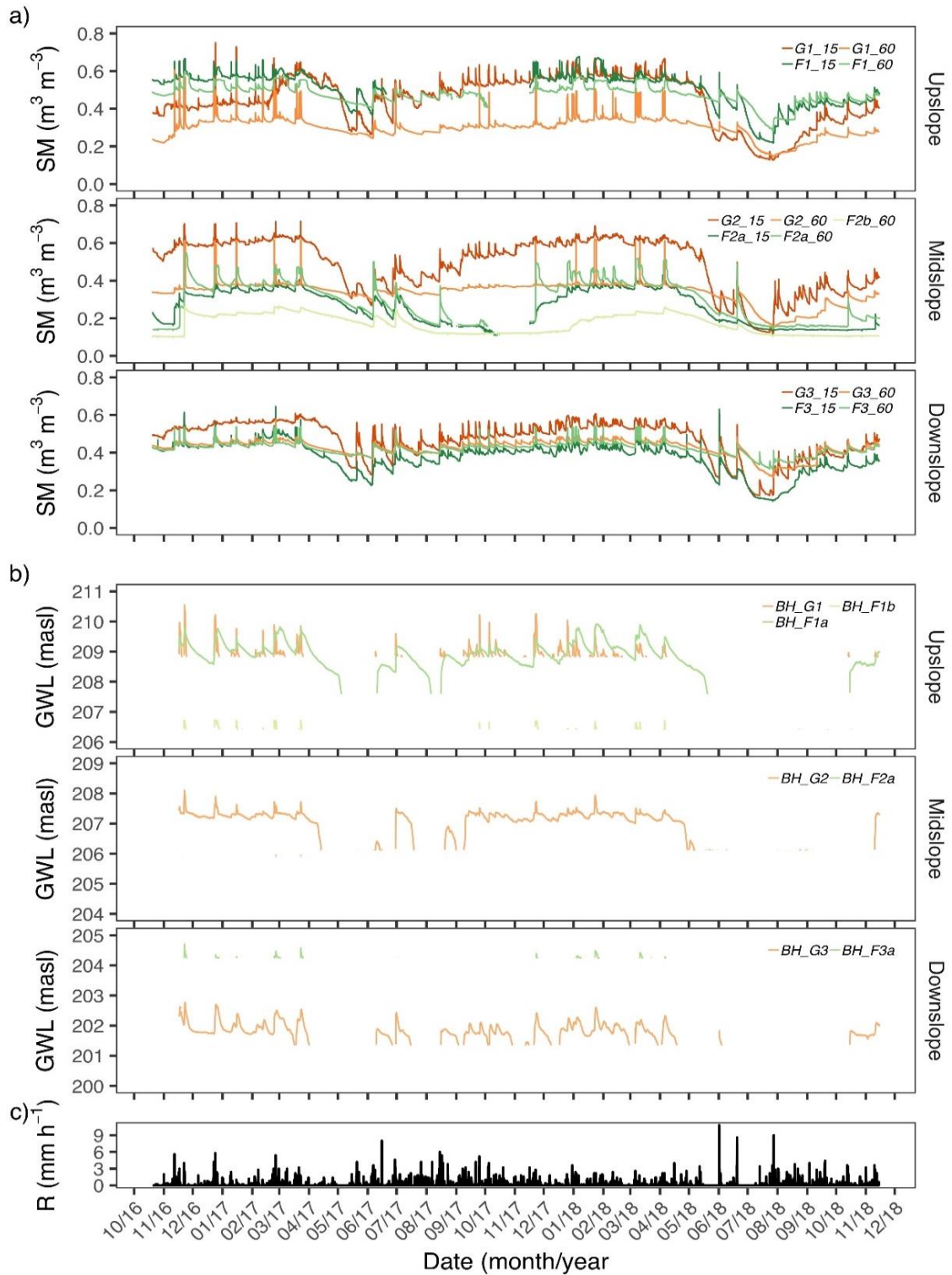


Figure 5.3: Time series of a) 15-minute soil moisture (SM) and b) 15-minute groundwater level (GWL) data from the grassland and forest strip transects for the entire study period November 2016–November 2018. Soil moisture sensor F2b_15 was poorly responsive and possibly in an air pocket so data are not shown. Note different y-axis scales for GWL data. c) Hourly rainfall data (R) from the upslope rain gauge (aggregated from 15-minute data for clarity).

between two sensors is shown in Figure 5.4. Most of the estimated 15% ‘additional’ storage capacity in the soil beneath the forest strip occurred in the three months September–November. This is likely to be an underestimate of the actual storage, or the additional storage available in winter, because saturation was not observed in the forest soils during the study period.

Groundwater data were discontinuous at the depths of all the hillslope piezometers. A water table was recorded for much of the study period on the grassland transect and in the upslope part of the forest transect. It was highest during winter but disappeared from all piezometers during mid-summer, with a range of over 2 m in some piezometers. In three of the four piezometers with the most continuous data, the water table showed bi-modal recession behaviour, with an abrupt drop in water table depth below a threshold level of 1.87 m below ground level in BH_F1a, 1.50 m in BH_G2 and 2.48 m in BH_G3 (Figure 5.3). This is indicative of layered geology with large contrasts in permeability between layers, probably representing the transition from less permeable glacial till to unconsolidated gravelly head deposits or weathered rock head.

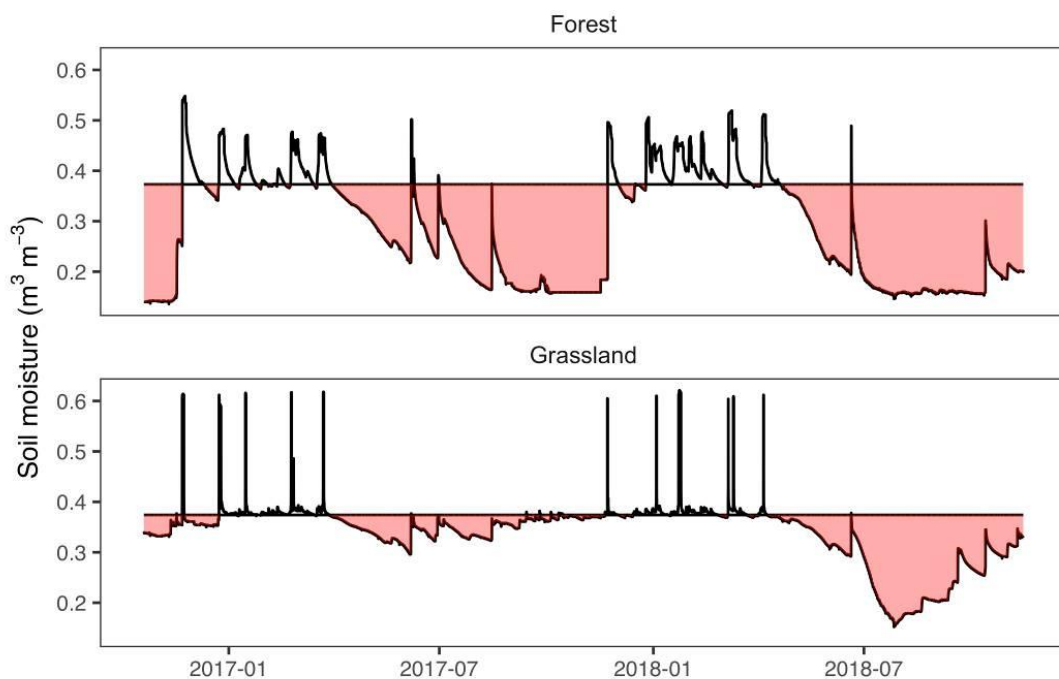


Figure 5.4: Soil moisture content at 60 cm depth under forest (F2a_60) and grassland (G2_60) and for the entire study period compared to the baseline of the median winter soil moisture content for each sensor (horizontal lines). Highlighted areas are the soil moisture deficit in summer/autumn months, indicating the potential soil moisture storage.

ERT survey data

Resistivity structure along transects

The resistivity surveys give insights into the geological structure of the hillslope, with a layered structure visible on both transects (an example is given in Figure 5.5 and the same structures are visible in Appendix D, Figure D.2). Outside the forest strip the topmost layer (0-0.5 m) on both transects had lower resistivities in winter and higher resistivities in summer. This layer corresponds with more organic rich soil according to the borehole logs and soil pits, and sits on a much higher resistivity layer (0.5- 1.7 m) that corresponds with glacial till (Appendix D, Table D.1, Figure D.1). Below 1.7 m depth, resistivities decreased again, probably due to the presence of a water table in many of the grassland areas on both transects, as the borehole logs do not indicate a significant change in geological properties at this depth. The upslope part of the grassland transect differed from other grassland areas, with higher resistivities below a depth of 0.5 m. The resistivity structure was different in the forested area, with less obvious layering and high resistivities to the bottom of the section.

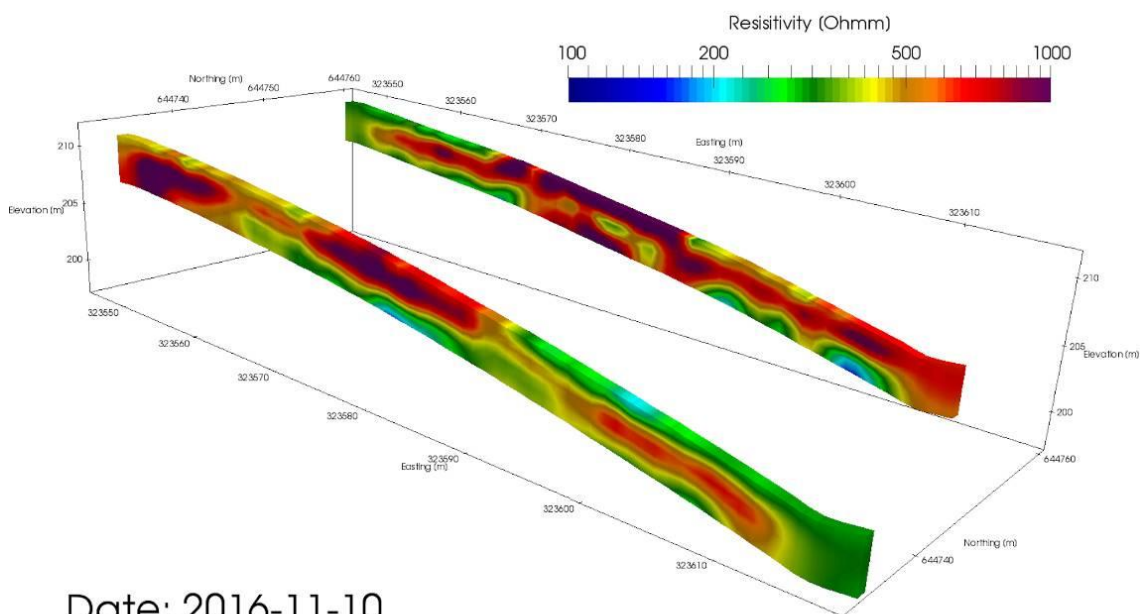


Figure 5.5: Resistivity cross section for the grassland (foreground) and forest (background) transects in November 2016.

Resistivity variation with depth and time along transects

The time-lapse ERT data indicate that the variation in resistivity across the ten surveys generally decreased with depth on both transects and at all slope locations

(Figure 5.6). However, variability was greater on the forest transect, particularly to 1.7 m depth within the midslope forest strip area. In this zone interquartile range (IQR) of the relative resistivities was 4.0-16.8 % for the forest and 2.5-6.8 % for the adjacent grassland. Within the first 12 m downslope of the forest, there was also greater variation in relative resistivities in the top 1.7 m depth compared to the adjacent grassland and compared to similar locations upslope of the forest. In this zone the IQR of the relative resistivities was 6.71-12.7 % for the forest and 1.7-10.2 % for the adjacent grassland (Figure 5.6).

The ERT time series data give further insight into the changing seasonal impact of the forest strip on hillslope subsurface hydrological dynamics along the hillslope (Figure 5.7). In the upslope domain, resistivities displayed similar seasonal patterns on both transects. They were higher in the drier summer surveys compared to the autumn, winter and spring surveys, with the amplitude of the changes decreasing with depth, and little variation below 2.5 m.

The largest differences between transects were in the midslope area. The absolute changes in resistivity between surveys were more pronounced in the midslope forest domain than in the grassland, implying more extreme wetting and drying of the subsurface below the forest strip. The forest area also remained more highly resistive later into the year (through the autumn surveys). This effect was minimal below 2.5 m and insignificant below 3.4 m.

The seasonal pattern of changes in resistivity was similar in the downslope domain to the upslope domain, with higher relative resistivities in the summer surveys and lower resistivities in the autumn, winter and spring surveys. There is no indication that the prolonged subsurface drying into the autumn beneath the forested area extended downslope of the forest strip. As in the upslope and midslope domains, the amplitude of seasonal changes decreased with depth on both transects.

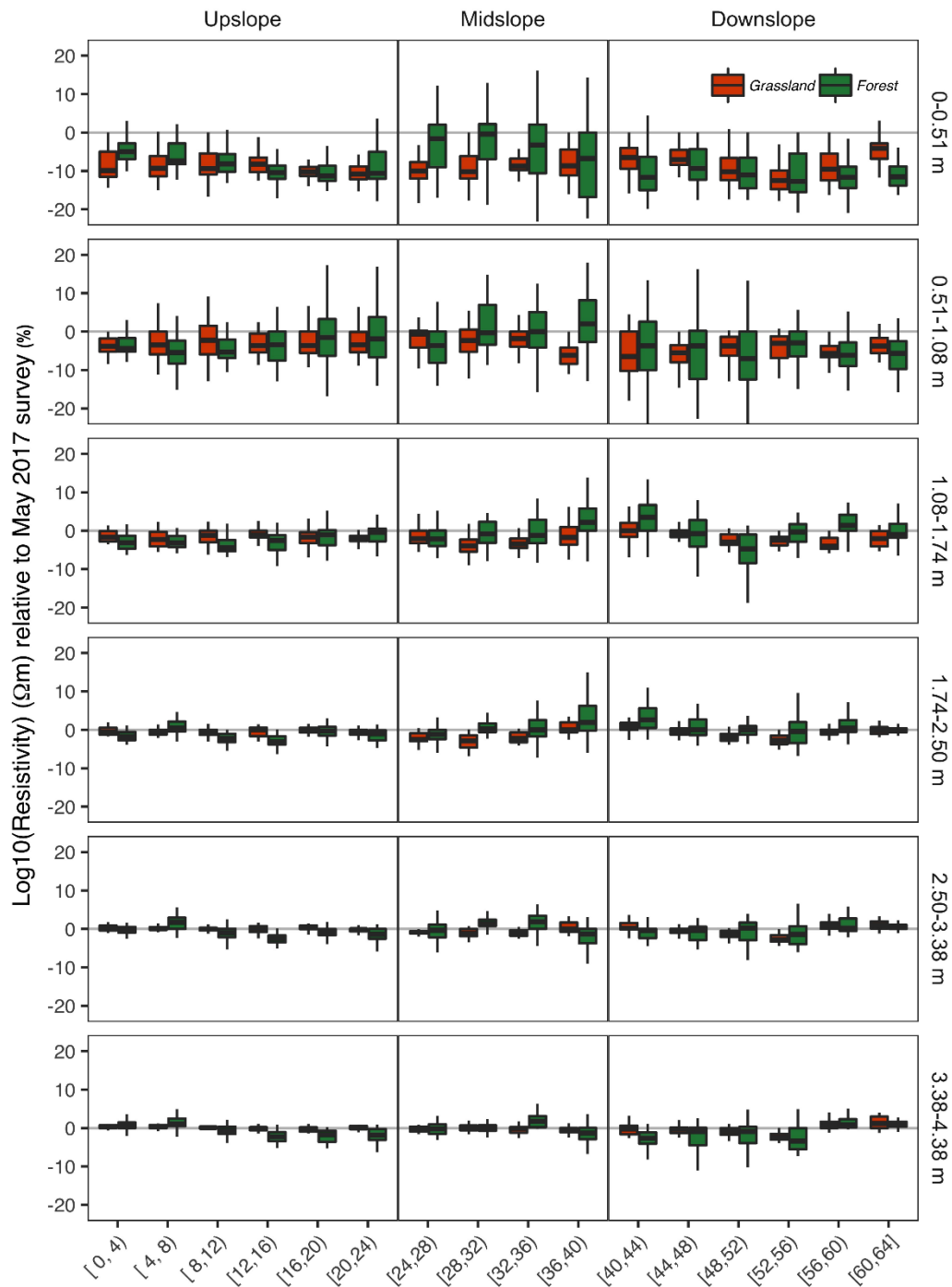


Figure 5.6: Resistivity variation at different depths along the two transects for the 10 surveys conducted between November 2016 and April 2018 relative to the May 2017 survey (horizontal line at 0). The forested area is located within the midslope domain. The horizontal line inside the box represents 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). Outliers removed for clarity. x-axis labels represent range of cells (as distance along the transect) used to calculate statistics – e.g. [0,4) indicates the first four model cells on the line between 0-1,1-2, 2-3 and 3-4 m.

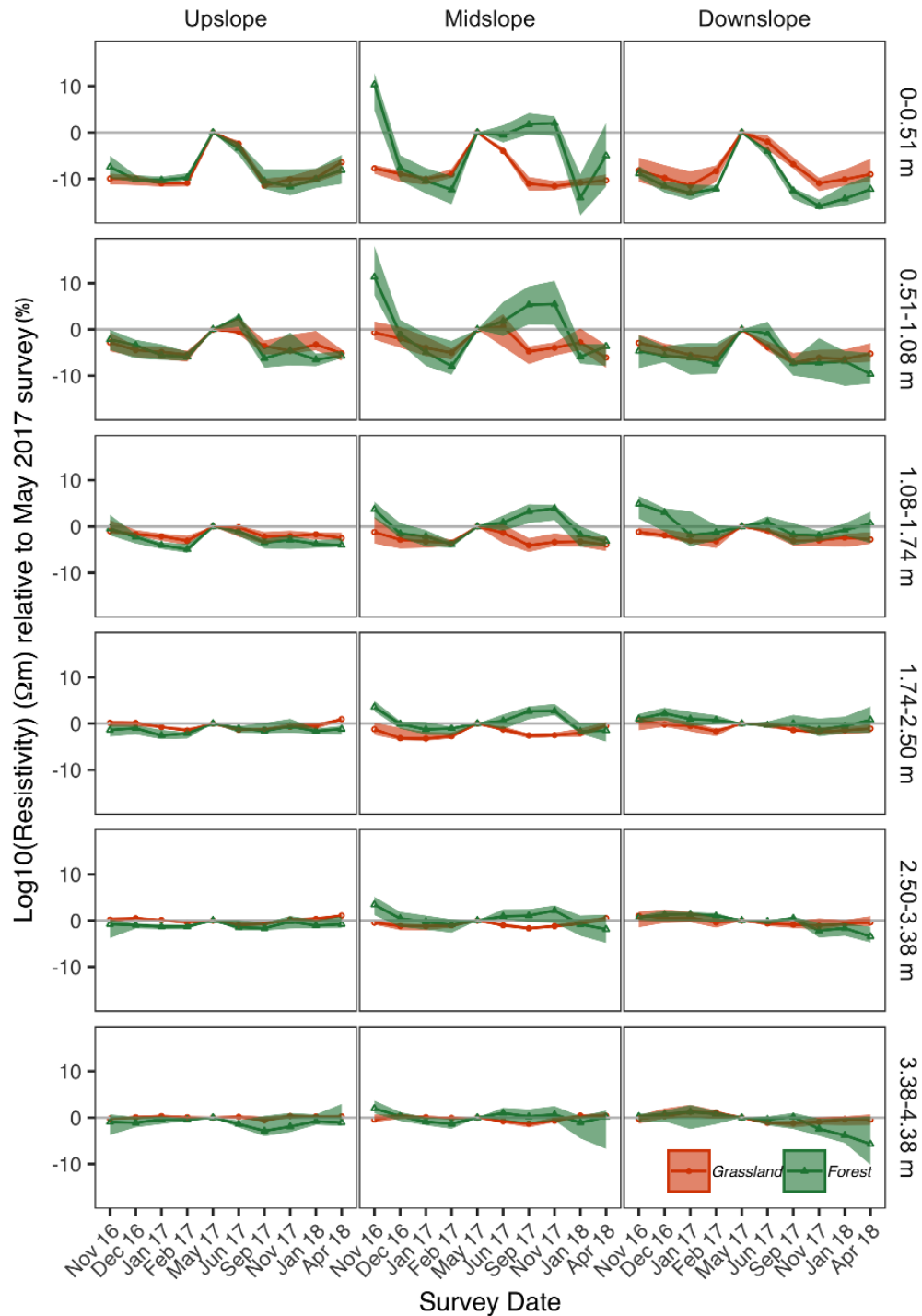


Figure 5.7: Median resistivities for each transect across different domains and depths for the 10 surveys conducted between November 2016 and April 2018 relative to the May 2017 survey (horizontal line at 0). The forested area is located within the midslope domain. Median resistivities for each survey are calculated from cells across the whole domain (i.e. 0-24 m for the upslope domain, 24-40 m for the midslope domain, and 40-64 m for the downslope domain). Shading represents 95% confidence intervals

5.4.2 Event-scale dynamics

Differences in subsurface hydrology response between hillslope locations

The number of sensors responding decreased consistently with depth in each domain from the soil moisture sensors at 0.15 and 0.6 m depths to the groundwater sensors at ~2.5 m depth (Figure 5.8). However, there were significant differences in the number responding between transects at different locations on the hillslope, when comparing sensors at all depths in each domain. The most significant difference in the number responding was in the midslope domain ($p < 0.001$). 66% of grassland sensors in the midslope domain responded over the 52 events, whilst only 31% responded in the forest strip. Much of the relative decrease in the forest domain was due to fewer of the 0.15 m (particularly in summer) and 2.5 m sensors responding (Figure 5.8). There was less difference in number responding between the transects in the upslope domain (58% and 74% responded for forest and grassland respectively) and downslope domain (62% and 69% responded for forest and grassland respectively). Some of the difference in the upslope domain can be

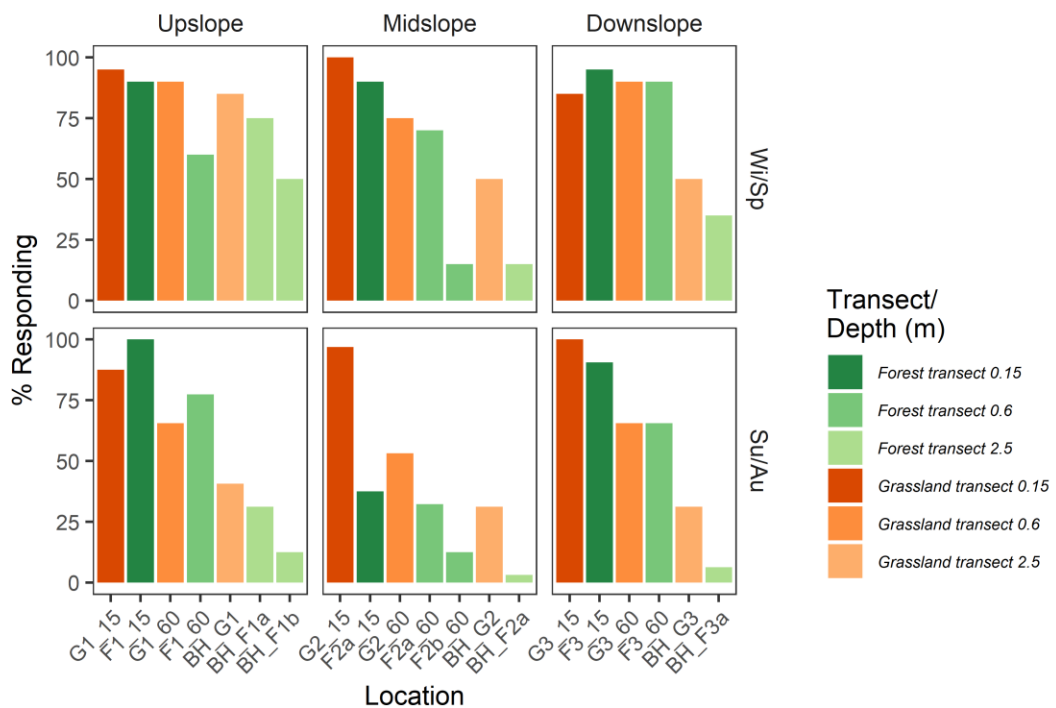


Figure 5.8: Number of sensors responding (%) across all rainfall events (n=52) for all working soil moisture and groundwater sensors at different depths and domains on the forest strip and grassland transects for Winter/Spring (Wi/Sp) and Summer/Autumn (Su/Au) seasons

explained by events not being logged as responses due to soil saturation prior to the event for three events at location F1_60 and one event at F1_15.

Comparing data from the nine events when most of the sensors responded, the time taken for sensors to respond (TTR) increased with depth in all domains and there was no significant difference in TTR between forest and grassland transects at any location or depth (Figure 5.9). However, TTR increased downslope for the piezometers, with significant differences between upslope and downslope locations ($p < 0.05$), but not for the soil moisture sensors (Figure 5.9). The pairwise comparison of all events ($n=52$) additionally indicates that there were no significant differences in TTR between summer and winter at any location, although summer TTRs were slightly more variable than winter TTRs (Appendix D, Figure D.3).

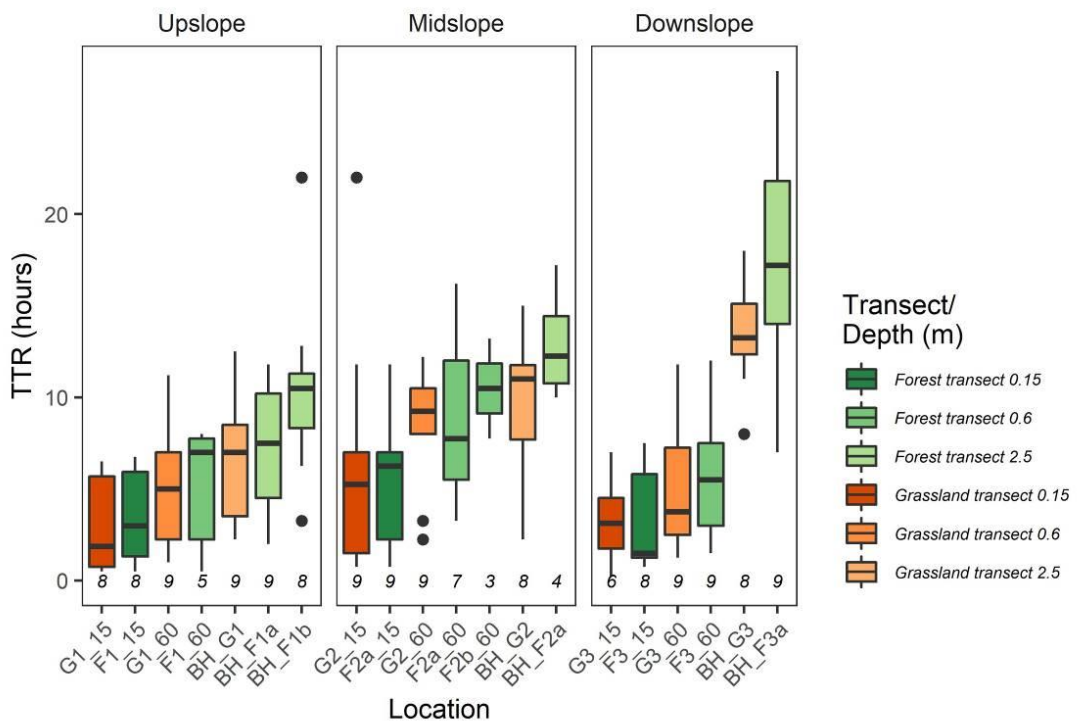


Figure 5.9: Time to response from the start of rainfall (TTR) for the different domains and depths on the forest strip and grassland transects during nine rainfall events when the borehole downslope of the forest responded and the majority of the other soil moisture and groundwater sensors responded. The 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). Numbers in italics show the number of events in which sensor responded. Dots are outliers.

The time that sensors took to reach peak soil moisture/water table from start of rainfall (TTPR) and the maximum rise (MR) were much more variable at individual sensors and between sensors, especially during the subset of nine events in wetter conditions (Appendix D, Figure D.4a). This was mainly due to the rapid occurrence of saturation in some of the 0.6 m sensors. However, there appears to be a similar pattern to that seen in the TTR data, of increasing water table TTPR downslope but no systematic increase in soil moisture TTPR. The pairwise comparison of all 52 events suggests that TTPR was seasonally variable, especially in the forested midslope domain. In summer, the TTPR interquartile range for all forest locations was 13-16 hours, compared to 6-11 hours for the adjacent grassland) (Appendix D, Figure D.4b).

Relationships between event characteristics and subsurface hydrology response metrics

Total event rainfall and the 5-day AWI are good predictors of overall number of sensors responding ($p < 0.001$). There are also significant seasonal differences, with the log odds of response much less likely in summer/autumn compared to the winter/spring ($p < 0.001$). Comparison between transects, depths and domains reveals a more complex picture. Total event rainfall and seasonal differences are significant explanatory factors for whether sensors respond to events in most locations (Figure 5.10). However, event characteristics and seasonal variation in conditions have less impact on the response of the 0.15 m soil moisture sensors, because these respond easily across the whole range of events. The 0.15 m sensor in the forest strip is an exception, where response seems to be significantly affected by total event rainfall and there are significant seasonal differences (in summer/autumn compared to winter/spring) compared to grassland areas. Total event rainfall appears to have a more significant impact on the number of the 0.6 m and 2.5 m sensors that respond in most locations, presumably because a threshold level is required for these to respond. The seasonal variation in these deeper sensors is less clear than at shallower levels, but there are similar patterns between 0.6 m sensors on the forest and grassland lines, with significant differences between summer/autumn, compared to winter/spring on the forest transect. These differences are consistent with seasonal changes in soil moisture being more marked in the forest strip, with a later onset of sensor response.

Correlation of event characteristics and response metrics at individual locations showed some significant correlations but no clear pattern could be identified between transects. Correlation coefficients calculated for data for all sensors across both transects showed more generally that total event rainfall appears to be the most important factor controlling MR for both soil moisture sensors and piezometers. Event intensity also appears to be a significant control on TTR and TTPR for both soil moisture sensors and piezometers. Finally, in winter the 5-day AWI appears to be an important factor in controlling the rate of response of the piezometers and AP28d for the maximum rise in the soil moisture sensors (Appendix D, Table D.4).

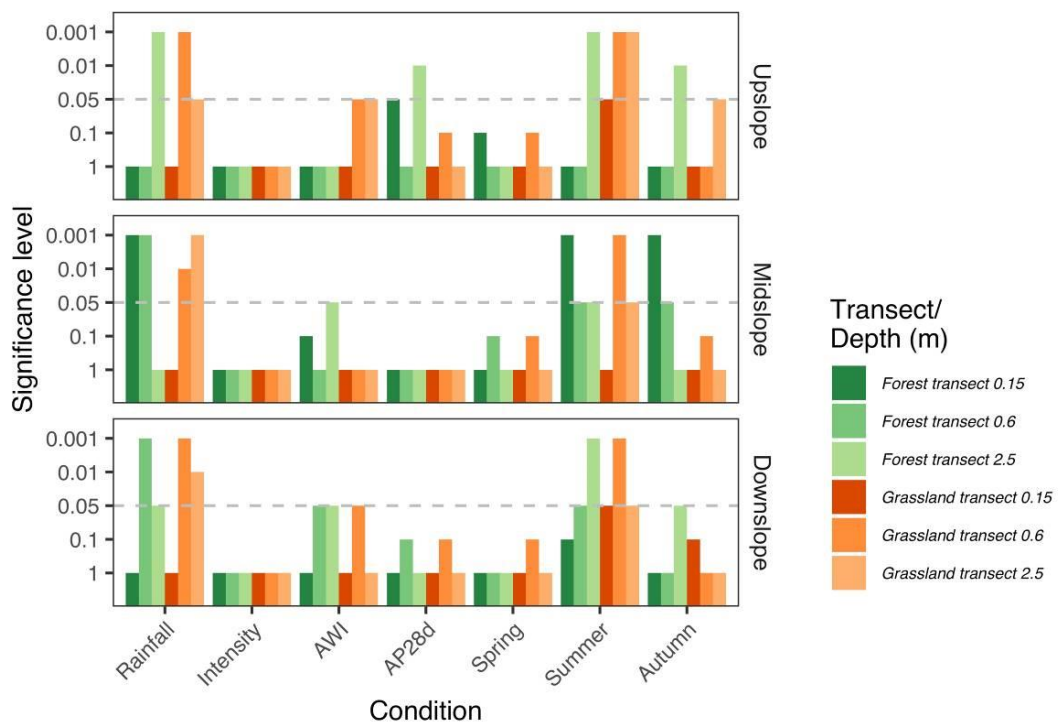


Figure 5.10: Graphical representation of significance levels from logistic regression of the number of soil moisture and groundwater sensors responding for different transects, domains and depths for different independent variables across all 52 rainfall events. Spring, Summer and Autumn are based on logistic regression comparisons to Winter. Dashed grey line highlights significance level of $p = 0.05$.

5.5 Discussion

5.5.1 Forest influence on soil moisture and groundwater dynamics beneath the forest strip

Pronounced differences in subsurface hydrology characteristics and dynamics were identified between the forest strip area and the grassland areas on both transects from the 2-year monitoring programme based on soil moisture, groundwater and time-lapse ERT measurements. These observations have been used to infer the hydrological processes operating in the hillslope and to devise the conceptual model of these described below.

The forested area had lower absolute but more variable soil moisture content, higher relative ERT resistivities, a considerably lower water table and less event-driven response of subsurface sensors. In the zone above the water table and within the rooting depth of the trees (~ 2.5 m), there were reductions in soil moisture levels and in the numbers of sensors responding during events, that extended later into the autumn compared to the grassland. The ERT data show the same seasonal effects and additionally suggest these were contained within the boundaries of the forest.

Our conceptual model to explain these findings is shown in Figure 5.11. We hypothesise that the differences between the grassland (Figure 5.11a) and the forest strip (Figure 5.11b) can be attributed to a combination of greater evapotranspiration and canopy interception by trees, and the likely increased infiltration rate of the forest soils and sub-soils due to more extensive rooting systems and their effects on hydraulic conductivity. Studies in the UK have found that interception losses can range between 25 and 50% of precipitation, with greater losses for summer events and the interception fraction decreasing with increasing rainfall (Johnson, 1995). Conifers and broadleaves can also lose an additional 300-390 mm yr⁻¹ through transpiration (Nisbet, 2005). These findings provide indirect evidence to explain the differences in response of the forest sensors between seasons, sporadic responses during larger summer rainfall events and the delayed 'wetting up' of the forest soils until the onset of larger rainfall events in the late autumn when some trees had also lost their leaves. Median soil hydraulic conductivities in the forest are likely to range from 42-174 mm h⁻¹, based on results from a study investigating similar hillslopes and land uses in the same catchment, which found that tree rooting systems played a significant role in controlling

hydraulic conductivity (Archer et al., 2013). We also found that while there were similarities in the soil matrix and horizon depths under the forest and grassland areas, there were differences in rooting systems, with larger roots and deeper rooting systems in the forest compared to the grassland. These differences in hydraulic conductivity likely contribute to the observed lower absolute soil moisture levels in the forest, higher resistivities and the lower water table.

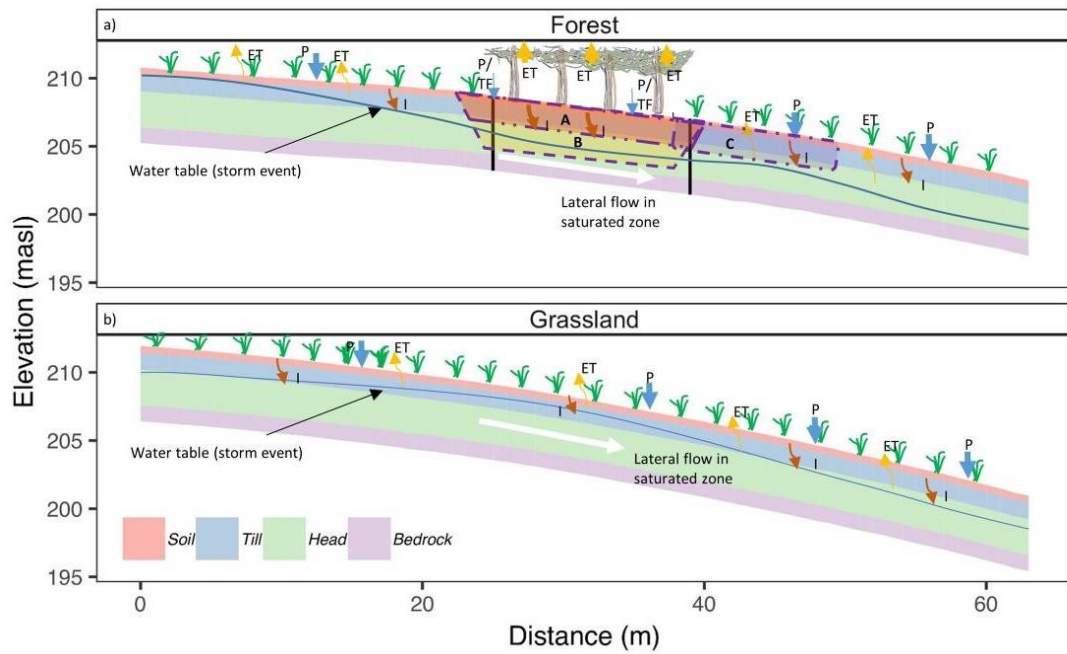


Figure 5.11: Conceptual model showing the hillslope with (a) the across-slope forest strip and (b) the grassland transects. The major hydrological fluxes are shown in relation to hillslope, land cover and geological structure, with arrow size relating to the size of the flux. ET: evapotranspiration; P: precipitation; TF: throughfall; I: infiltration. Dashed purple lines in (a) delineate zones of differing moisture dynamics in the forest transect: A) zone within rooting depth of trees (~2.5 m) with greater variability in soil moisture, extended seasonal reduction in soil moisture and reduction in event-driven response of sensors; B) zone below rooting depth of trees and with seasonal water table that attenuates seasonal variation in moisture dynamics observed at shallower depths; and C) zone with greater variation in moisture dynamics (inferred from ERT data) due potentially to deeper unsaturated zone and wind shadow effect close to trees. Depths of zones are not drawn to scale.

At depths greater than 2.5 m there were no significant observable seasonal impacts of the forest on moisture dynamics (Figure 5.11b). Piezometer data from the rainfall events indicate that the water table was within 2.5 m of the ground surface for the wettest periods in the year, probably attenuating the seasonal variations in resistivity observed at shallower depths. The zone below 2.5 m is also likely to be at the limit of the rooting depths of the trees, reducing their impacts on both evapotranspiration and hydraulic conductivity. The lower water table in the forest strip compared to the

grassland is one of the most striking differences between the transects (Figure 5.11). We suggest that this is due to enhanced hydraulic conductivity within forest soils and sub-soils, rather than 'pumping' by trees as the effect persists through the winter when evapotranspiration and interception are greatly reduced.

These results are consistent with studies at the hillslope scale on the effects of forest planting on soil moisture dynamics. Significant increases in hydraulic conductivity in forest soils have been reported (Archer et al., 2013; Carroll et al., 2004; Ghestem et al., 2011; Wheeler et al., 2008), although few studies have examined directly how variations in hydraulic conductivity due to trees affect groundwater levels across hillslopes. Others have demonstrated the seasonal depletion of soil moisture content and groundwater levels due to forest evapotranspiration (Bonell et al., 2010; Greenwood and Buttle, 2014), but there is considerable variability depending on canopy structure, climate and soil and vegetation characteristics (Guswa, 2012). Similar effects of forest planting and removal have been described at the catchment scale, with afforestation/reforestation often leading to a reduction in annual water yield (Bosch and Hewlett, 1982; Brown et al., 2005; Filoso et al., 2017). It has been suggested that subsurface storage (e.g. due to substrate porosity, permeability and unsaturated zone depth) and its relationship to forest cover plays an important role in modulating annual water yield (McDonnell, 2017).

5.5.2 Forest influence on downslope soil moisture and groundwater dynamics

While the forest strip had measurable impacts on the subsurface hydrological conditions beneath the forest, no significant effects were observed downslope in the zone above the water table (< 2.5 m depth). There were no significant differences between transects in long-term median soil moisture content or variability at the downslope soil moisture sensors at 0.15 m and 0.6 m depth. For the same sensors there was no significant difference in rainfall event metrics. In the ERT data, the more extreme seasonal variation and prolonged summer/autumn drying that was observed beneath the forest at depths of < 2.5 m was not observed in the hillslope portions downslope of the forest, even in areas very close to the forest (< 2 m from the forest boundary). As shown in Figure 5.11, we suggest that the forest has only limited seasonal influence on shallow moisture dynamics. We attribute this mainly to

the dominance of vertical processes (evapotranspiration and drainage) in the unsaturated zone as in other areas of the slope, as well as the continued infiltration and percolation of any surface and shallow subsurface flow as it moves downslope (Klaus and Jackson, 2018).

These findings notwithstanding, the forest did appear to depress groundwater depths downslope. During the wettest periods, groundwater depths were up to 1.7 m lower downslope of the forest compared to depths upslope of the forest, and up to 1.5 m lower compared to similar locations on the grassland transect. However, there is evidence that groundwater connectivity existed between the areas upslope and downslope of the forest during larger events. Time to response in the 0.15 m and 0.6 m soil moisture sensors was similar at all locations on the slope, but increased downslope for the piezometers. These longer response times downslope than upslope in the piezometers are interpreted as an indication that lateral flow processes from upslope to downslope are more important than vertical infiltration in driving groundwater dynamics in this part of the slope and in moving water down the slope through a connected shallow groundwater system. This implies that the forest does not 'interrupt' lateral downslope water table connectivity during larger events. This is consistent with findings from studies on catchment scale hydrological connectivity and threshold behaviour (Detty and McGuire, 2010a, 2010b; McNamara et al., 2005).

Lastly, the ERT data show that while median relative resistivities across all surveys were similar between transects in the downslope area, they were more variable at shallow depths (< 1.7 m) in the first 12 m downslope of the forest strip, compared to the adjacent grassland and similar locations upslope of the forest strip. This may be indicative of a seasonally variable deeper unsaturated zone in the area immediately downslope of the forest with less attenuation of resistivity due to the seasonal water table. The south-westerly prevailing wind and the north-south orientation of the forest strip means that a rain shadow effect from the forested area could also contribute to such variability. This effect has been observed to extend to ~6 m on to adjacent grassland at sites with similar height trees in the UK, particularly in winter when frontal rainfall is accompanied by stronger winds (Wheater et al., 2008).

5.5.3 Implications for flood risk management

Our study suggests that in temperate environments forest boundary strips could marginally increase catchment storage due to evapotranspirative ‘pumping’ and interception by trees that extends to deeper depths and is more prolonged than in grassland areas. However, our results show that this additional subsurface moisture storage is highly restricted in space to the area in and around the forest itself. This effect is greatest in summer and autumn, so may have a mitigating effect on summer flood events, but additional storage capacity is likely to be limited in winter and spring. Such effects are also likely to vary with forest type and age, as discussed in other studies (Archer et al., 2013; Chandler et al., 2018; Jipp et al., 1998). Given that flood events commonly have higher frequencies in summer in small catchments in Scotland (Black and Werritty, 1997) and in the immediate region of this study (Masson, 2019), additional subsurface moisture storage provided in summer by forest strips may provide some benefit depending on storm characteristics and antecedent conditions.

At the storm event timescale, our results suggest that forest strips locally decrease the responsiveness of soils and groundwater beneath the forest strip to rainfall events, especially in summer/autumn. During larger rainfall events and in winter, forest soils respond similarly to rainfall events and at similar rates as grassland, but appear to saturate less frequently, suggesting that forest strips could reduce runoff through combined effects of intra-event evaporation and more rapid drainage to the subsurface. This is aligned with reported increased hydraulic conductivity and porosity in soils below forest strips (Carroll et al., 2004; Wheater et al., 2008).

From this study, the spatial influence of forest strips appears to be slightly larger than their width, with some downslope depression observed in soil moisture content and groundwater levels. In slopes with much less permeable soils or compacted soils, the forest may act more like a ‘French drain’, channelling water into deeper layers. However, the effectiveness of such a system would be limited by the connectivity of the ‘drain’ to deeper, more permeable substrate, or to more permeable areas laterally, and to the permeability of soils/geology downslope. On its own the limited storage capacity of the strip would be quickly overwhelmed if surrounded by a less permeable system. This highlights the highly context-specific nature of the impacts of forest strips on subsurface moisture storage and on the attenuation effects of increases in hydraulic conductivity.

The role of water table connectivity and its links to threshold behaviour in catchment response is increasingly recognised in the hydrological literature (Bracken et al., 2013; Detty and McGuire, 2010a). This study suggests that the forest strip has little impact on groundwater connectivity during larger events, implying that similar upland landscapes with fragmented forest strips might have limited impact on groundwater dynamics at the event timescale and in wetter periods. There is need for further investigation to assess whether there are optimal soil and geological conditions, and extents and locations of forest cover that might have a larger influence at the catchment scale, as has been suggested in other environments (Ilstedt et al., 2016).

5.6 Conclusions

Forest strips are being used around the world for reduction of flood risk. Nevertheless, our knowledge of how forest strips impact runoff in general and local- and down-gradient hydrological conditions, is still poor. This study examined the impact of an across-slope forest strip on subsurface soil moisture and groundwater dynamics. We found that an increase in soil moisture storage potential associated with the forest strip was highly seasonal and did not extend much beyond the forest strip itself. In this temperate climate, during wetter winter periods, when widespread runoff is typically highest, isolated strips of forest like the one we studied are likely to have only a marginal impact on subsurface moisture storage. However, in specific contexts, such as lower magnitude events or intense summer storms, forest strips could locally reduce catchment responsiveness to storm events. This study only considered subsurface processes; the impacts of forest strips on surface runoff, for example through increased roughness and infiltration, could be greater.

Our study showed the utility of time-lapse ERT for extrapolating findings from point-based measurements along hillslopes and to greater depths in terrain that is difficult to instrument invasively. ERT helped to show the larger, longer and deeper seasonal changes in soil moisture in the forest compared to adjacent grassland, as well as providing insight into the lateral variability of moisture changes within the transects. Higher frequency ERT data that is now available at daily or sub-daily time-steps (Chambers et al., 2014) would be a useful extension to this study to further understanding of subsurface hydrological dynamics at the storm event scale.

6 Discussion

This chapter brings together findings from Chapters 3-5 to address the aim of this thesis set out in Section 1.6, which was to “investigate how NFM interventions using land cover change to reduce rapid runoff from hillslopes alter discharge dynamics and hydrological flow paths, with particular emphasis on partitioning between surface and sub-surface flow”. The Chapter discusses the findings in the context of relevant wider hydrological debates, identifies limitations of the research, and suggests areas for further research. An objective of the research was to investigate these questions at different spatial and temporal scales, given that spatial upscaling (beyond ~ 10 km²) remains one of the key uncertainties in NFM and also the links between short term (e.g. event) and long term (e.g. seasonal) hydrological dynamics. The chapter is structured to draw links, where possible, across these different scales. Firstly, the results are briefly summarised in a spatio-temporal framework, then links between findings related to longer term (seasonal) dynamics at catchment and hillslope scales are discussed, followed by links between findings related to event scale dynamics at the two spatial scales. Finally, the wider implications of the study in the context of future climate change and land use change are discussed.

6.1 Summary of findings across spatial and temporal scales

This study sought to investigate key controls on runoff partitioning in the Eddleston Water catchment in order to draw insights into the potential role of NFM interventions focussed on land cover change. Whilst different and independent methods were used to investigate flow pathways at the catchment and hillslope scales, there were similarities in findings at these different spatial scales (Table 6.1). This finding in itself is interesting, given that scaling relationships in catchment hydrology are often non-linear. Some of the metrics used to quantify catchment hydrological behaviour in this study, such as storage and MTT, have been suggested as useful descriptors of catchment hydrological dynamics that might be scalable. For example, as discussed by Spence (2010), concepts of storage can help describe hydrological processes occurring within soils, hillslopes and catchments.

Table 6.1: Summary of the main findings from results chapters 3-5.

Temporal scale	Spatial scale	
	Catchment	Hillslope
Seasonal	<p>(Results from Chapter 3)</p> <p>Dynamic storage and passive storage capacity were low (ranging from 16 – 200 mm and 209 – 870 mm respectively) in all sub-catchments, but particularly those in the west.</p> <p>MTT estimates varied across different sub-catchments (134 – 370 days). Correlation coefficients suggest that soil type dominates forest cover as a key control on storage/MTT.</p> <p>Groundwater fraction in streams was variable (0.20 – 0.52 of annual stream runoff) and only weakly correlated with measures of storage/MTT, suggesting more localised geographic controls on groundwater flow in different sub-catchments (e.g. forest cover, source rock type)</p>	<p>(Results from Chapter 5)</p> <p>Forest and grassland soil moisture deficits were ~27% and ~12% respectively compared to a baseline of median winter soil moisture levels (median winter levels were similar in each area) suggesting limited 'additional' water storage capacity provided by forest.</p> <p>No differences observed in downslope seasonal soil moisture dynamics between forest and grassland transects, suggesting limited spatial impacts of forest.</p>
Event	<p>(Results from Chapter 4)</p> <p>Pre-event water dominated streamflow during most events and sub-catchments (0.46 – 0.96 of runoff at peak discharge), suggesting important role of subsurface flow.</p> <p>Low groundwater fraction (0.10 – 0.30 of runoff at peak discharge) during winter events suggests water stored in soils dominates runoff in most sub-catchments.</p> <p>Hierarchy of influences: Storm characteristics > soils/geology > forest cover in terms of controls on runoff partitioning. However, forest cover appeared to reduce event water runoff when comparing (within events) sub-catchments with similar soils and geology.</p>	<p>(Results from Chapter 5)</p> <p>Forest cover reduced the number of sensors responding to events in summer/autumn, but not winter.</p> <p>Forest cover had no impact on measures of soil moisture and groundwater response relative to grassland during the largest events, suggesting little impact of the forest during such events.</p> <p>No differences observed in downslope soil moisture and groundwater responses between forest and grassland transects during events, suggesting limited spatial impacts of forest.</p>

6.2 Hydrological processes operating at seasonal timescales: Links between catchment and hillslope scales

6.2.1 Controls on storage and mixing dynamics in managed temperate upland environments

Catchment and hillslope scale storage and mixing dynamics, and the links these processes have with runoff generation mechanisms, have gained increasing prominence in hydrological research over the last decade, given the critical influence that storage can have on hydrological, chemical and biological fluxes in catchments (Tetzlaff et al., 2011). Defining and quantifying storage, and its links to mixing dynamics, may help solve fundamental questions in hydrology such as scaling relationships and finding integrated measures of catchment hydrology that can be compared across different environments (Spence, 2010).

Nevertheless, catchment storage and mixing are still rarely quantified, despite their importance in regulating hydrological processes. This is partly because of conceptual challenges, for example in defining what storage is being quantified and the associated boundary conditions. Various concepts of storage have been defined, such as 'dynamic', 'active', 'passive', and 'total' storage (Table 6.2), each with a specific physical basis. These different concepts give different insights into catchment storage and mixing dynamics (Staudinger et al., 2017), so there is a need for careful definition, particularly in more applied settings. There are also significant methodological constraints, particularly in measuring subsurface storage. Many studies still rely on (often shallow) point-based estimates (e.g. using TDR derived soil moisture data), which are difficult to upscale in heterogeneous landscapes and do not necessarily give information on deeper storage and mixing processes. Novel and multi-method approaches, for example using geophysical techniques, are likely to be crucial to better characterise the subsurface (Brooks et al., 2015). This study has demonstrated the potential utility of approaches at different scales, particularly combined hydrometric and tracer-based approaches used in Chapters 3 and 4 to investigate runoff partitioning, and the time-lapse ERT methods used in Chapter 5 to better constrain and generalise soil moisture changes at depth.

Table 6.2: Examples of different catchment scale storage definitions and their use in the literature.

Storage definition	Explanation	Example references
Dynamic	Proportion of total basin storage that is hydrologically active and contributes to stream flow. Usually estimated using water balance approaches or modelling.	Buttle (2016); McNamara et al. (2011); Sayama et al. (2011)
Active	Same as dynamic storage, but used in some papers as the corollary of passive storage.	Birkel et al., (2011); Pfister et al. (2017)
Passive	Immobile water that is available for mixing. It does not alter the hydrological response but exchange of water molecules can occur with active storage reservoir.	Birkel et al. (2011); Rodriguez et al. (2018)
Total	<p>Various definitions of total storage are used in the literature, as the concept is linked to the definition of the lower boundary of a catchment.</p> <ul style="list-style-type: none"> • Hypothetical maximum storage deficit derived using water balance and defined as the difference between maximum storage in a time series and storage during a hypothetical or observed no flow period. • Sum of active and passive storage. This approximation of total storage ignores storage components that are irrelevant to streamflow. • Multiple further definitions more commonly used in hydrogeology (e.g. depth to saline water). 	Condon et al. (2020); Hale et al. (2016); Pfister et al. (2017)

A key aim of this thesis was to use hydrometric and tracer data as a tool to investigate controls on subsurface storage and mixing at different scales in order to evaluate the potential impacts of land cover change. In a wider context, current evidence suggests that these controls vary across different landscape and climates, so patterns are difficult to generalise. As discussed in Chapter 3, studies have identified different controls in different contexts, including for example, 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). These wide-ranging findings have led to critiques that there has been a tendency for studies to look at selected metrics that may “have a strong physical rationale, [but] the reasons why some are included in or omitted from some papers are rarely mentioned, except perhaps for the obvious reason of availability.” (Ali et al., 2012b).

In temperate northern climates, such as those in the UK uplands, a number of studies have demonstrated the importance of soil type as a key control on catchment storage and mixing dynamics (Geris et al., 2015b; Hrachowitz et al., 2009a; Tetzlaff et al., 2015). The data presented in Chapter 3 suggested a similar importance of soils at the catchment scale in the study catchment. However, it also highlighted the potential role of superficial geology in influencing runoff dynamics and introducing significant heterogeneity, which may be particularly important in post-glacial upland landscapes, such as those in much of the northern UK. The importance of superficial geology has been noted in other work (Buttle, 2016; Dunn et al., 2008; Salve et al., 2012; Soulsby et al., 1999; Tetzlaff et al., 2014), but arguably deserves further investigation to help disentangle relative relationships between soil and geological controls on storage-discharge dynamics, which may not always be correlated in such landscapes (Lacoste et al., 2011). From a management perspective, soil properties are also possibly more subject to either positive or negative anthropogenic alteration, making the quantification of these relative controls important in understanding catchments' 'hydrologic resistance' (Carey et al., 2010).

6.2.2 Interaction of forest cover with catchment storage and mixing processes

In terms of the role of forest cover, the implication of the findings regarding the importance of soil properties in controlling storage and mixing dynamics (the conclusion of Chapter 3) is that even large scale changes in forest cover are unlikely to have a significant impact on catchment hydrology in such environments, at least from a storage and mixing perspective. There may be important exceptions, for example in highly responsive catchments where relative impacts may be more observable, or in catchments with highly compacted soils overlying a more permeable substrate (Neal et al., 1997). This corresponds with findings from the wider literature on forests and flooding, but also more recent research and reviews in the context of UK NFM policy. These studies suggest that forest planting may only help mitigate smaller flood events in areas close to forest and in summer, when available storage capacity in soils is higher (Dadson et al., 2017; FAO and CIFOR, 2005; Marshall et al., 2009; Soulsby et al., 2017). However, as Soulsby et al. (2017) note, despite these findings, many current NFM schemes continue to have high

expectations of the benefits of tree planting for flood mitigation through enhanced infiltration and storage.

The hillslope-scale experiment described in Chapter 5 also suggests that forest planting has limited benefits for flood risk mitigation and provides more mechanistic insights into the interaction between forests, soils and subsurface moisture dynamics. The main finding at the seasonal timescale was that there were differences in soil moisture storage capacity between the grassland and the forest, but limited inferred 'additional' storage capacity in the forest in wetter winter periods. This is similar to data comparing forest and moorland soils presented by Soulsby et al. (2017) for a large storm event in another upland area of Scotland. However, the results presented in Chapter 5 also showed the prolonged drying of the forest soils in the summer and autumn periods, suggesting potential to reduce runoff at these times. As noted in Chapter 5, this may be relevant in Scotland where flood events commonly have higher frequencies in summer in small catchments (Black and Werritty, 1997; Masson, 2019). The time-lapse ERT data enabled investigation of moisture dynamics at greater depths than in many studies and indicated that variations in moisture dynamics appear to be limited below ~ 2.5 m at the study site. It was not possible to determine whether this was due to limits on the rooting depths of the trees or homogenising effects of the seasonal water table, but it is similar to findings in other UK settings, which have found little seasonal variation in soil moisture below 5 m, though in a different (chalk) geological setting (Roberts and Rosier, 2005).

Chapter 5 also more explicitly introduced questions about the spatial location of tree planting in landscapes and the potential impacts of forest fragments in altering catchment storage, mixing and runoff processes. Such questions are increasingly important given large-scale conversion of forests to agriculture globally, and conversely, efforts to increase tree cover on farms through agroforestry, field boundary planting, and the re-introduction of hedgerows that have been systematically removed in the post-WW2 period. There are still relatively few studies investigating these questions in temperate environments (e.g. Carroll et al., 2004; Holden et al., 2019), although the interaction of vegetation structure and runoff has received more attention in arid landscapes (e.g. Ludwig et al., 2005). Whilst it is only a single example, the finding that there were limited impacts on seasonal soil

moisture dynamics outside and downslope of the forest strip studied in Chapter 5, suggests that there are also likely to be limited impacts at larger scales.

6.2.3 Limitations and areas for further seasonal scale research

The findings at different scales highlight the need for a more nuanced approach in how the impacts of tree planting on runoff mechanisms are evaluated and communicated in an NFM context. This thesis has not examined in detail other aspects of forest cover controls on runoff mechanisms, such as those linked to fluxes into catchments (through interception and evapotranspiration) and slowing the conveyance of water (through surface roughness effects). These are potentially significant factors influencing runoff processes, including responses to storm events (Jasechko et al., 2013; Thomas and Nisbet, 2007) so need to be considered in order to make a full assessment of hydrological impacts.

This study has only given initial insights and quantification of catchment and hillslope scale storage and mixing processes. One of the key limitations of the research is the short time frame of tracer data collection, which has only enabled initial insights to be drawn about catchment hydrological processes. Longer time series of tracer data would allow the application of more powerful models for fitting transit time distributions, so helping to constrain uncertainties. More crucially, there is now significant research on how such distributions vary with time, which demonstrates how, for example, fractions of young water increase and MTTs decrease substantially under wetter conditions (Harman, 2015). This can lead to large differences in absolute quantification, complicate catchment comparison, and possibly to changes in relative controls on runoff generation mechanisms between different storms, seasons or years (Geris et al., 2015a).

There would also be scope to further constrain storage estimates by pairing the more integrated measures of storage used, with estimates based, for example, on measurements in different hydrological response units. This could help to more directly link estimates at different scales and consider other forms of land use relevant to NFM (e.g. improved grassland). In particular, a more complete quantification of storage and hydrological fluxes (especially surface runoff and throughfall) surrounding the forest strip discussed in Chapter 5 would give insights into the impacts of forest fragments in upland landscapes. There has been limited work investigating how impacts might aggregate across landscapes at different

scales, or investigating impacts at different locations on hillslopes (Reaney et al., 2014; Wheeler et al., 2008), which would benefit from further empirical and modelling based research.

There are also still many unknowns about how trees use water and the controls this exerts on subsurface storage and mixing processes. For example, in the past decade, isotope-based tracer studies have helped to identify differences in the signatures of water taken up by plants and that delivered to streams, suggesting potential biophysical partitioning processes occur within the soil matrix (Berry et al., 2018). Such findings fundamentally alter our understanding of catchment mixing processes, and the interaction between land cover and physical catchment properties. While this may not make a large difference in terms of water fluxes from a flood management perspective, better process understanding will help in building models that get the “right answer for the right reasons” (Kirchner, 2006) and eventually develop a more nuanced approach to land cover-based flood management interventions.

The research has also demonstrated the need to study processes below different land cover classes at greater subsurface depths in order to quantify fluxes and the impacts of land cover change. As Roberts and Rosier (2005) note, “previous studies of water use, particularly by woodlands, may not have sampled the depth of soil adequately over which drying can occur”. Such insights would seem crucial from an applied NFM perspective in terms of where to target NFM interventions and quantifying their impacts.

Investigation of other NFM interventions focussed on ‘reducing rapid runoff’ on hillslopes (Lane, 2017), such as measures to reduce soil compaction and blocking or removing artificial field under-drainage, was beyond the scope of this study. However, they are important to mention because of their prominence in many upland landscapes and because many afforestation activities associated with NFM will occur on or close to such features. Soil compaction and field drainage are both extensive in the UK uplands and in many other areas globally. It is estimated that 60% of managed pasture in England and Wales shows signs of compaction (Wallace and Chappell, 2019) and that 61% of agricultural land in the UK is drained (Wiskow and van der Ploeg, 2003). There is still relatively little research on storage and mixing processes in such landscapes, or the impacts on flood generation,

despite the impacts being potentially highly significant (Rogger et al., 2017). For example, studies have highlighted the complex and time-variant effects of field under-drainage, which can act to increase catchment water storage (by lowering the water table and reducing soil moisture) (Dunn et al., 2008), 'homogenise' travel time distributions across differing soil types (Dimitrova-Petrova et al., 2020), and result in threshold-like behaviour by rapidly transferring runoff to streams under wet antecedent conditions. Further tracer-based studies on field compaction and drainage could help to quantify how these features affect hydrological processes under different conditions, and the relative benefits of NFM measures to address soil compaction and disconnect artificial drainage.

6.3 Hydrological processes operating at event timescales: Links between catchment and hillslope scales

6.3.1 Forest cover influence on runoff partitioning during storm events

Chapters 4 and 5 of this thesis investigated questions related to the influence of forest cover on surface/subsurface runoff partitioning at the storm event timescale. Whilst different approaches were used at the different spatial scales, the findings are generally consistent. The hillslope scale work also gave further mechanistic insights into some of the processes that may be operating at larger scales.

The main finding from both chapters was that there appeared to be a relatively limited impact of forest cover on either runoff partitioning or subsurface moisture dynamics during the events studied. Chapter 4 suggested a hierarchy of influences in which event characteristics (in terms of total rainfall depth, intensity and API) appeared to be the dominant control on the amount of event runoff, catchment soils/geology a secondary influence, and forest cover having the lowest influence. When comparing two paired catchments, with similar characteristics but large differences in forest cover, forest cover reduced the fraction of event water runoff. The hillslope experiment in Chapter 5 controlled for differences in topography, soils and geology, so it is not possible to directly compare the hierarchy of influences at the two spatial scales, but it suggested some influence of the forest at the event timescale compared to the grassland in terms of reducing the number of sensors activated at different depths. This was probably a seasonal effect related to greater summer forest canopy cover, combined with a lack of large summer storms

observed in the study. However, during larger events the soil moisture and groundwater on the forest and grassland transects responded in a similar way.

A similar hierarchy of influences has been reported in other studies, both at catchment and hillslope scales. For example, Fischer et al. (2017) found that pre-event water contributions in multiple sampled storms in 5 pre-alpine headwater catchments were controlled by rainfall amount and intensity, and varied more between events than between catchments, despite significant differences in land cover. Geris et al. (2015a), whilst not specifically examining event characteristics, found that soils, rather than vegetation type controlled mixing dynamics at the plot scale at a site in Scotland. NFM literature also suggests that forest cover, and NFM interventions more generally, may have little impact on flood peaks during larger events (e.g. Archer and Newson, 2016; Dadson et al., 2017).

Another finding from the event-scale research reported in Chapter 4 was that there appeared to be little indication of threshold behaviour at the catchment or hillslope scale. The different catchments investigated in Chapter 4 appear to have behaved approximately linearly in terms of their runoff fractions from different sources over different sizes of event, with the exception perhaps of Longcote catchment in the east. In the hillslope experiment there was no indication of significant differences in response, for example, under different antecedent wetness conditions. 'Threshold behaviour' and the associated concept of 'connectivity' have, along with the concept of storage discussed in Section 6.2.1, been suggested as representing a potential "paradigm shift" in hydrology (Tetzlaff et al., 2011). These concepts have been observed and quantified in many catchment and hillslope experiments (Detty and McGuire, 2010b; Tromp-van Meerveld and McDonnell, 2006; Zehe and Sivapalan, 2009), and fundamentally alter our understanding of catchment hydrological processes, the role of subsurface flow, scaling behaviour, and ultimately our ability to model catchment behaviour. Observing threshold behaviour in the context of the Eddleston NFM project, would therefore have changed many aspects of the approach to implementing NFM interventions. It should be noted of course, that a limitation of the research in Chapters 4 and 5 is that no large flood events occurred during the course of the fieldwork (the largest event was at the 0.07 percentile on the flow duration curve constructed using data from 2011-2017), so it is difficult to extrapolate findings to larger events.

The hillslope experiment discussed in Chapter 5 provided more detailed insights into dynamics at different depths during events on different land covers. A key finding was that water table dynamics were similar between the grassland and forest areas during the largest events, suggesting that water table dynamics are somewhat independent of forest cover at these event magnitudes. This has obvious implications in terms of the need to better quantify the impact of forests, and particularly forest fragments, on subsurface connectivity in different environments. It also links to key questions in 'critical zone research', which are calling for a more integrated approach to studying water use by trees that considers interactions with deeper hydrogeological processes and spatial variability across landscapes (Brooks et al., 2015; Fan et al., 2019).

Finally, at the hillslope scale, the event scale data highlighted the heterogeneity in responses of different sensors across the hillslope and at different depths. The use of observations from many events, comparisons with the seasonal scale datasets, and the use of complementary research methods enabled broad patterns to be interpreted at a representative hillslope. Quantifying spatial heterogeneity in hillslope and catchment hydrological research is still a major challenge. It has large implications for how to design experiments that are statistically robust and scalable, especially with the added challenge of investigating processes at greater depths (Bachmair et al., 2012). This is an ongoing concern with NFM implementation, where, for example, the impacts of different land use management systems on soil moisture heterogeneity are poorly understood. This has led to calls for larger and more systematic paired plot experiments to understand landscape scale processes (Wallace and Chappell, 2020).

6.3.2 Limitations and areas for further event scale research

There are a number of limitations to the event scale research carried out here, which suggest areas for further research. The research at the catchment scale only enabled an initial investigation of different runoff endmembers and fluxes during events. A more detailed characterisation of different water sources would enable more detailed quantification of the effects of different land covers and management systems in the catchment. Key among these would be characterising different water pools in grassland soils, forest soils, land drains, and wetlands to enable more detailed analysis of water sources in stream flow. For example, studies investigating managed grasslands have been able to quantify the transit time distributions for

different soil layers to better interpret the effects of compaction and the effects of preferential flow in forest soils (Orlowski et al., 2016). Wetland areas can also drive rapid runoff during wet periods, but act as sources of 'older' water that may have a large impact on quantified proportions of pre-event water even when present in only small areas of catchments (Bonell et al., 1990; Roa-García and Weiler, 2010; Tetzlaff et al., 2014). Roa-García and Weiler (2010), for example, found significant influence of wetlands on increasing the fraction of old water in stream flow during storm events, even though they covered only 6% of the catchment area. Better characterisation of precipitation inputs would also help further constrain the role of land cover in runoff partitioning. As noted in Chapter 4, quantifying the isotopic signature of throughfall would be a priority, given the impact this can have in forested catchments (Kubota and Tsuboyama, 2003). Spatio-temporal variations can also be important in quantifying the uncertainties in hydrograph separation (Cayuela et al. 2019).

Higher frequency sampling could also provide greater insights into runoff dynamics. The event-scale research added significant detail to process understanding in both the catchment and hillslope studies described here. At the sub-catchment scale, Chapter 4 highlighted the changing direction of ANC hysteresis in different catchments. It also helped to illustrate differences in the timing and amplitude of runoff endmembers with respect to the hydrograph peak, which are not identifiable using the weekly data. Both of these findings could be further explored using targeted higher frequency rainfall and stream water sampling in the catchments, which is now becoming more widely available (Freiin von Freyberg et al., 2017). Continuous tracer measurement studies (e.g. every 15 minutes) have already helped to uncover more detailed process understanding in some agricultural catchments (Aubert and Breuer, 2016; Kirchner et al., 2004). For example, Tweed et al. (2016) used such approaches to better quantify pre-event water at the start of storms and also the time lag between physical and chemical responses in streams. In responsive catchments, this level of detail could be particularly useful for quantifying the incremental impacts of NFM measures, which may otherwise be difficult to quantify because of measurement noise. There are obviously trade-offs with scale in terms of sampling more water sources and sampling at higher frequencies that would need to be carefully considered during experimental design, given that it would be highly resource intensive (Timbe et al., 2015).

Tracer-based studies would also be a natural extension of the work on forest strips presented in Chapter 5. Event scale sampling of different endmembers (rainfall, throughfall, surface runoff, soil water and groundwater) would help develop better process understanding of how forest strips alter hydrological fluxes during events and identify impacts on flow paths. Such investigations would link questions about the spatial location of forests in agricultural landscapes, with numerous studies that have looked at tracer dynamics in hillslopes (e.g. Wenninger et al., 2004). This could be combined with high frequency time-lapse ERT (Chambers et al., 2014) to help quantify dynamics in a more integrated way. Given the significant emphasis placed on field boundary planting as a means of controlling agricultural pollution, this would also help in quantifying one of the key 'co-benefits' of NFM (Holden et al., 2019).

6.4 Climate change and land use change impacts on runoff mechanisms – implications for tree planting as a NFM measure

The findings from this study need to be considered within the context of future climate change and land use change. From a climate change perspective, current projections based on a high emissions scenario suggest that the UK will experience rising temperatures and greater extremes in rainfall variability at both seasonal and daily timescales by 2070 (Lowe et al., 2018). Seasonal temperatures are projected to increase between 0.7 and 5.4°C by 2070. Winters are expected to be up to 35% wetter and summers up to 47% drier by 2070, with increased extremes in hourly rainfall intensity, a greater contribution of frontal rainfall in winter, and high intensity showers in summer (Lowe et al., 2018). These changes are likely to alter catchment hydrology through impacts on energy and water balances.

Increased temperatures have been shown to lengthen the growing season in the northern hemisphere, increasing potential annual evapotranspiration fluxes (Yang et al., 2015). In summer, this would increase plant water uptake and decrease catchment water storage in soils and groundwater (House et al., 2016). This would likely accentuate the reductions in soil moisture in the forest strip observed in Chapter 5, potentially fractionally enhancing catchment resilience to summer floods but also reducing resilience to drought due to increased water stress (Gosling, 2014). However, increases in winter rainfall, combined with increased rainfall intensity, would likely increase rapid event runoff and contribute to more severe

winter flood events. Conclusions from this research support this scenario, as they suggest that event characteristics (in terms of total rainfall depth, intensity and API) are a key control on the fraction of event runoff and that catchments have limited available storage during winter periods.

Greater seasonal differences in energy and water balances, as well as increased rainfall intensity, may also alter water sources and flow paths feeding stream flow at different timescales, given the time-variant nature of catchment storage and mixing. Greater seasonality (e.g. wetter winters and drier summers) might be expected to change mixing dynamics, for example, by increasing the fraction of young water in streams in winter and contributing to greater variability in transit time distributions in summer. Changes would also be expected at shorter timescales. For example, Heidbuchel et al. (2013) observed changes in relative controls on transit time distributions depending on the interaction of meteorological forcing (clustered precipitation events, evenly distributed seasonal rainfall, and low overall seasonal rainfall) and catchment properties (soil hydraulic conductivity, soil depth and planform curvature). Such findings have obvious implications in terms of evaluating the relative impacts of NFM-type interventions on flood risk. They also alter how co-benefits of NFM such as effects on water quality might be quantified, given how such changes could influence the mobilisation of different pollutants (Hrachowitz et al., 2016).

Projected changes in land use will also have effects on catchment storage, mixing and associated runoff mechanisms. Afforestation is likely to be an important aspect of land use change in many managed temperate upland environments in the next few decades. Significant woodland expansion is planned in many countries, increasingly driven by concerns about climate change and the potential for trees remove CO₂ from the atmosphere (Bastin et al., 2019). There is particular interest in tree planting given that it might be relatively cheap, is relatively well tested, and has additional environmental benefits compared to some other forms of GHG reduction/removal, although all of these are highly contested (Buis, 2019). In Scotland, for example, the Climate Change Act (2009) sets a target for net zero carbon emissions by 2045 (Scottish Government, 2009b) and, via the Land Use Strategy, targets of 100 kha of woodland expansion for 2012–2022, increasing to 15 kha yr⁻¹ from 2024 (Scottish Government, 2016).

Afforestation will likely lead to increases in interception, evapotranspiration, and infiltration (Basche and DeLonge, 2019; Carlyle-Moses and Gash, 2011; Zhang et al., 2001), although some of these effects are still debated (e.g. Thompson et al., 2010) and will depend on the type of trees, soil type, and forest management systems. These changes will combine with climate change impacts in complex and location specific ways, especially in headwater catchments, which exhibit a high degree of heterogeneity in hydrological response. A number of studies have assessed the relative role of climate change and land use change in altering catchment hydrology, with divergent conclusions depending on existing catchment properties, the nature of land use changes, and the degree of projected climate change (Wang et al., 2018). In temperate upland environments that are not moisture limited, some modelling studies have suggested that afforestation will dominate over climate change impacts in terms of reductions of water fluxes into catchments (through increased ET and reduced percolation) (Wang et al., 2018).

From an NFM perspective, increased afforestation targets provide a potential opportunity to influence catchment runoff mechanisms. However, the impacts of afforestation are likely to be highly dependent on the location of planting and the types of land use that forests are replacing. Many studies have compared afforestation with grassland, but the way grassland is managed can result in large differences in water storage potential, mixing processes at different depths, and runoff partitioning under different antecedent conditions (e.g. Orłowski et al., 2016; Wallace and Chappell, 2019). As suggested by the results of Chapters 4 and 5, afforestation in areas with highly compacted soils or which have significant under-drainage, might have greater relative impacts on flood risk during wet periods due to improved infiltration rates and reductions in rapid preferential subsurface flow. These comparative impacts on catchment runoff warrant further investigation at catchment and basin scales given the level of ambition in current land use policy, the opportunity costs with agriculture and, in the case of Scotland, the need to adhere to the principle of "the right tree, in the right place, for the right purpose" (Scottish Government, 2019).

Finally, afforestation associated with NFM may provide many ecohydrological 'co-benefits' from a climate change perspective. For example, riparian planting may help to reduce summer stream temperatures, with benefits for freshwater fish species (Dugdale et al., 2018). Such benefits have not been a focus of this research, but

they may be extensive and suggest that “alternative evidence-based justifications (for increasing tree cover) should be established and their multiple roles in the landscape considered” (Carrick et al., 2018) within the context of NFM.

7 Key findings, policy implications and further research priorities

7.1 Key findings

Soil type and underlying superficial geology appear to be dominant controls on catchment storage and mixing in the study catchment representative of many temperate upland environments

A year-long tracer and hydrological study of 9 sub-catchments of the 67 km² Eddleston Water, showed low but variable dynamic storage capacities (16 – 200 mm), mean transit times (134 – 370 days) and groundwater fractions (0.20 – 0.52 of annual stream runoff). Soil type (and soil hydraulic properties) correlated most strongly with metrics of catchment storage, mean transit time and groundwater fraction, suggesting soils (and co-linear superficial geology) are the primary control on catchment storage and mixing. Percentage forest cover was not positively correlated with increases in storage, mean transit time or groundwater fraction, suggesting that any influence of forest cover on catchment storage and mixing is dominated by soils and geology in this environment. While these findings are from a single catchment, they are similar to storage estimates and primary controls identified in other Scottish catchments, and would likely extrapolate to other previously glaciated temperate areas with poorly permeable fractured bedrock.

Afforestation in temperate upland catchments is unlikely to lead to significant reductions in peak flows during large flood events

The study of the temporal and spatial sources of runoff during four high flow events in three different sub-catchments of the Eddleston Water showed that pre-event water stored in soils dominated stream runoff, suggesting that rapid overland flow is not the primary runoff mechanism during events. It also showed that there is a hierarchy of controls on the fraction of event water in stream discharge during events, in which meteorological factors (in terms of total rainfall depth, intensity and API) dominate soils/geology, which dominate forest cover. Nevertheless, forest cover may have some mediating effects when comparing event water runoff fractions across catchments with similar soils/geology and within storms. While peak discharge was similar, the event water fraction at peak discharge was found to be

17% lower in the forested catchment during the largest event studied here compared to an adjacent catchment with lower forest cover but similar soils and geology. These findings relating to the hierarchy of controls correspond with similar studies in other settings. They also provide additional field evidence to support findings in reviews of NFM suggesting limited impacts of forest cover on reducing rapid runoff at the catchment scale. There may be exceptions to these findings as they depend on the types of land use that afforestation is replacing (e.g. there may be greater effects in landscapes which have more compacted soils).

Forest fragments on hillslopes increase and seasonally extend subsurface moisture deficits compared to improved grassland but the effects are spatially limited and do not exist in winter periods

The hillslope study comparing subsurface moisture dynamics on an improved grassland hillslope and an adjacent area of the hillslope crossed by a mature forest strip demonstrated differences in seasonal dynamics between the two land covers. Soil moisture deficits extended to greater depths below the forest (~ 2.5 m) and were prolonged by ~ 2 months into the autumn before increasing again during the winter compared to the grassland. There was little evidence of downslope impacts of the forest strip on soil moisture dynamics. These findings suggest such forest strips and other forest fragments in temperate upland environments are likely to have spatially and temporally limited impacts on hillslope subsurface water storage over seasonal timescales.

Hillslope soil moisture and groundwater dynamics are similar beneath forest fragments and improved grassland during rainfall events in wetter periods

The hillslope study demonstrated that while the water table level was persistently lower in the forest and the forest soils responded less frequently to rainfall events compared to grassland, there were no significant differences beneath or downslope of the forest strip during the largest events in the wettest periods. There was also evidence of upslope-downslope water table connectivity beneath the forest during these periods, suggesting minimal influence of the forest on the groundwater system at this timescale. These results suggest that such forest strips and other forest fragments on hillslopes are likely to have spatially and temporally limited impacts on subsurface runoff during large storms and in wetter winter periods.

The impacts of forest cover on runoff partitioning are consistent at both hillslope and small catchment scales

Similar conclusions can be drawn from the research undertaken at hillslope and meso-catchment scales. Whilst different research methods were used at different spatial scales, results at both scales suggest a similar hierarchy of influences in which soils and geology dominate over forest cover in controlling catchment storage, mixing and runoff partitioning during rainfall events.

7.2 Policy implications

7.2.1 Tree planting as an NFM strategy

The promotion of land use change as a flood risk mitigation strategy has gained renewed focus globally and in the UK, as part of broader interest among governments, NGOs and the private sector in implementing nature-based solutions (NBS) to environmental problems (Seddon et al., 2020). Increasing upland tree planting forms a key part of these approaches. The research presented here suggests that the flood mitigation benefits of tree planting are likely to be limited in many temperate upland settings, supporting findings from recent reviews (Carrick et al., 2018). This needs to be much more clearly communicated within the NFM debate to allow for a more nuanced discussion about the objectives of tree planting within NFM schemes and the potential flood mitigation benefits. This finding also implies a need to shift the balance of emphasis in NFM research and implementation towards other types of interventions that may have more impact on peak flows. Surface storage features (e.g. temporary holding ponds) may, for example, provide more scope for 'engineering' catchment storage. Alterations to under-field drainage may also provide scope for reducing rapid runoff given the extent of such drainage in many upland landscapes; it is certainly an area that is under-researched given difficulties in observing hydrological processes in such drainage systems.

While there are likely to be limitations surrounding tree planting as a method for mitigating large floods, this does not necessarily mean it should not be part of the suite of interventions promoted within NFM. There may be potentially localised or seasonally specific benefits from a flood mitigation perspective, for example in altering local flow paths on farmland or mitigating some summer or dry season flood

events. Trees may also help to control other damaging processes linked with flooding, such as soil erosion, slope stability, the transport of suspended sediment, and water pollution. There are also many other potential benefits to large scale tree planting, particularly in the UK, which has some of the lowest forest cover in Europe (FAO, 2015). The potential for forest systems to act as carbon sinks is one of the primary reasons for increased interest in tree planting and is the key driver behind many of the recent tree planting targets that have been established worldwide (Bond et al., 2019; Brown, 2020). Other co-benefits include, among others, increased biodiversity and increased connectivity of ecosystems and improved human health and wellbeing (de Bell et al., 2017). These benefits need to be carefully assessed in different landscapes and weighed against potential risks, such as soil degradation or reductions in biodiversity, which can arise through poor management systems being applied (e.g. monoculture plantations with low biodiversity value).

7.2.2 Integrating NFM tree planting into broader landscape planning

The implication is that tree planting, and other forms of land use change within NFM schemes, should be evaluated as part of much broader evidence-based frameworks to plan ‘multifunctional landscapes’ (Carrick et al., 2018; Franco et al., 2020). Currently, most NFM schemes exist as localised pilot projects often dominated by the natural sciences in the “framing and research agenda” (Wingfield et al., 2019), and with varying degrees of integration into wider land use planning policy, which raises questions about how they might be scaled up or ‘mainstreamed’. The growing application of ecosystem service valuation approaches within mainstream policy making may help to do this, although there is currently a lack of frameworks for assessing cost-effectiveness, trade-offs and function over time (Seddon et al., 2020). Such tools will also need to be accompanied by significant institutional changes at local and national levels to improve levels of sectoral coordination in rural landscapes (Waylen et al., 2017), for example through catchment or regional scale land use planning. Large scale land use planning is still relatively rare globally, but there is increasing interest in many European countries. In Scotland, for example, the national Land Use Strategy aims to promote more coordinated land use planning and management at a regional scale to address climate change risks. It also promotes the application of ecosystem-based approaches to land use decision making (Scottish Government, 2016).

7.2.3 Finding synergies between ‘green’ and ‘grey’

A broader implication of the research conducted here links to the finding that meteorological processes dominate over catchment characteristics in terms of their controls on event runoff. While land cover as an NFM intervention has only been investigated in this study, reviews of NFM suggest that meteorological factors are likely to dominate over any type of NFM intervention in terms of impacts on peak flow reduction during the largest events (Dadson et al., 2017). This suggests that there may be limits to NFM as a tool for managing flood risk. It follows that along with the need to integrate NFM approaches into wider land use strategy, there is also a need to integrate it into a continuum of approaches to flood risk management and to “find synergies among solutions instead of pitching green against grey” (Seddon et al., 2020). In practice, this means that to reduce flood risks to societally acceptable levels, NFM measures will likely have to be combined with ‘hard’ flood defences in many catchments, as well as changing planning systems that prevent building on floodplains and make housing infrastructure more resilient to floods.

7.2.4 Evaluating, communicating and reducing uncertainty in NFM

While the ‘mainstreaming’ of NFM into new and existing policy frameworks, as well as finding synergies with grey infrastructure, should help to improve the incorporation of NFM principles into landscape and flood risk management, there are still likely to be considerable barriers to NFM uptake. The large uncertainty associated with NFM effectiveness is a key challenge for all NBS, particularly where they involve multiple actions taking place over broad landscapes (Seddon et al., 2020; Waylen et al., 2017). Unless uncertainty can be reduced, it is unlikely that there will be significant uptake. Using complementary approaches to assessing impacts on runoff (e.g. hydrometric and tracer-based approaches) could in the long-run help to constrain some of these uncertainties through the development of better monitoring and models. It could also help to quantify NFM co-benefits, which as noted above, may be key to making the case for NFM-based approaches over more traditional hard engineering solutions.

7.2.5 Defining and investigating the subsurface in multifunctional landscapes

All of these policy challenges surrounding NFM suggest a key role for further research. As part of the process of developing better indicators and assessment

tools for planning and managing multifunctional landscapes, this study has highlighted the importance of subsurface hydrological processes, particularly in soils and superficial geology. Significant gaps in our conceptual understanding of the subsurface are one of the key barriers to developing better hydrological models (Beven et al., 2020). Critical zone research is also highlighting the need for greater interdisciplinary research into subsurface processes, for example to investigate where plants source their water from within the subsurface (Brooks et al., 2015). Policy processes surrounding multifunctional landscapes are mainly focussed on land use and soils, but will need to consider the limits on the 'lower boundary' to landscapes and ensure there is adequate research addressing this relatively unknown area.

7.2.6 Tree planting and NFM in a development context

While the focus of this research has been on temperate upland catchments, many of the findings and policy implications for NFM are relevant in other contexts. NFM and other NBS are now particularly promoted in developing countries by donors such as the World Bank and UN Agencies, as well as by the private sector, for example as forms of 'ecosystem-based adaptation' to climate change (e.g. Nature, 2017; World Bank, 2018). This is often on the grounds that they are a cost-effective and equitable method of both mitigating and adapting to climate change, which can benefit local communities. There are many examples of these initiatives (Browder et al., 2019; Cohen-Shacham et al., 2016). However, the costs and benefits are still poorly understood, and governance and policy coordination challenges may be accentuated in data poor environments with more poorly resourced authorities.

If these implementation challenges can be overcome, tree planting as part of NFM strategies in arid or tropical developing country contexts may have greater potential than in the temperate settings discussed in this study. These environments are less energy limited and may be more moisture limited, meaning land cover can have greater impact on seasonal and annual water balances. Tree planting may therefore help to enhance catchment storage and reduce runoff during dry season floods. Trees may also help to enhance groundwater recharge, through the effects of tree root system redistribution of water (Neumann and Cardon, 2012). However, the impacts of afforestation on low flows will also be more accentuated and need to be carefully assessed, to avoid intensifying water-scarcity in regions that are already subject to high water stress (Ellison et al., 2017). In such situations, there may be

scope for more targeted tree planting, for example on field boundaries as discussed in Chapter 5, as a method of controlling surface runoff and soil erosion on hillslopes, or lowering water tables on floodplains to enhance agricultural yields. Agroforestry systems can also help improve soil structure, increase macroporosity and increase infiltration rates (Tobella et al., 2014). These are methods which have been used successfully in many situations worldwide.

7.2.7 Summary of recommendations

- Clearer communication of the objectives of, and potential flood mitigation benefits of tree planting within NFM schemes.
- Enhance research on impacts of other forms of land use change on flood risk (particularly compaction and field drainage) as well as research aimed at building a better conceptual understanding of the subsurface 'critical zone'.
- 'Mainstream' tree planting within NFM into wider policy processes to develop multifunctional landscapes and associated planning tools such as ecosystem service based approaches.
- Ensure NFM implementation is combined with other flood risk mitigation measures – integrating 'green' and 'grey'.
- Better evaluate and communicate uncertainty within assessments of NFM to better define what change is observable and attributable, and to allow comparison with 'grey' infrastructure solutions.
- Support research on tree planting within NFM as part of overseas development assistance in order to quantify the potential opportunities and risks in arid and tropical environments.

7.3 Priorities for further research

Areas for further research have been discussed throughout Chapter 6. This section provides a brief summary of research priorities for NFM in Eddleston Water and the UK more generally, and for the wider hydrological sciences.

7.3.1 Further research priorities for NFM in Eddleston and the UK

Disaggregation of flow sources and pathways during storm events in the most responsive areas of catchments: A more detailed characterisation of different water sources would enable improved quantification of the effects of different land

covers and management systems in the catchment. Key among these would be characterising different water pools in grassland soils, forest soils, land drains, and wetlands to enable more detailed analysis of water sources in stream flow. In Eddleston Water this could be implemented as a more in-depth paired catchment study between Shiplaw and Middle Burn, extending the research presented in Chapter 4.

Quantifying storage and mixing processes associated with ‘runoff attenuation features’ (RAFs): RAFS include debris dams and temporary holding ponds. While research has been carried out in Eddleston and in other NFM pilots in the UK to investigate the effects of these features on hydraulic responses, tracers do not appear to have been used to investigate storage and mixing. Sampling these features during high flow events for stable isotope analysis would give additional insights into how they affect hydrological processes within upland headwater environments.

Hydrological impacts of field boundary planting: The research on the forest strip in Chapter 5 raised a number of further questions surrounding the impact of such features on catchment hydrology. While the overall impact appeared to be low from a catchment storage perspective, surface runoff processes were not investigated. Further research in this area is a priority given that there are still relatively few studies on the hydrological impacts of boundary planting and that such planting is likely to be a key part of reforestation in agricultural landscapes (due to lower opportunity costs). There are a number of research avenues, including: a more complete flux analysis; comparison of strips in different soil types; as well as modelling the effects of such strips in different locations on hillslopes and at larger scales.

7.3.2 Further research priorities for the hydrological sciences

Quantifying the relative role of soils and superficial geology as controls on catchment storage and mixing: The research presented here has highlighted this as a priority for a number of reasons. Firstly, whilst the evolution of soils and the underlying geology are often strongly related, a number of studies have demonstrated that this is not always the case. Quantifying where and under what conditions soils help predict the properties of underlying materials would help in interpreting the predictive power of surface mapping data (e.g. soil maps or remotely

sensed data) for investigating runoff processes. Secondly, in catchments underlain by poorly permeable bedrock, the important role of superficial geology in catchment storage and mixing processes has been highlighted but is more rarely quantified. Thirdly, understanding the relative importance of these controls is important in quantifying the potential impacts of human alterations to catchments.

Quantifying interactions among vegetation, soils, geology and terrain to greater depths: These interactions are still poorly understood, partly because of difficulties in quantifying the structure of the subsurface. As Chapter 5 highlighted the depth to which tree cover influences moisture dynamics may be much greater than is observed through typical monitoring setups. Understanding the dynamics at greater depths, and how these vary with geological substrate (Roberts and Rosier, 2005), hillslope location (Brooks et al., 2015), and over different timescales, is likely to be crucial in resolving key questions about how plants utilise and partition water between evapotranspiration and streamflow. From an applied perspective such knowledge would help in areas such as quantifying dynamic catchment storage, particularly under land use change scenarios, which has been suggested as a key research priority (Beven et al., 2020). There is scope for the application of advanced geophysical techniques, combined with tracer-based studies and more traditional soil and groundwater monitoring, within catchment observatories to address some of these questions.

Quantifying the impacts of forest fragments on connectivity in different environments and in different locations on hillslopes: Global land cover patterns are becoming more fragmented, yet much research is focussed on more simplistic comparisons such as ‘with’ and ‘without’ treatment paired catchment studies. Research on the hydrology of more fragmented ‘multifunctional’ landscapes is likely to be essential for drawing insights into the future impacts of land cover change, including those promoted within NFM-type schemes. As noted by Rogger et al. (2017) “Quantifying the effects of land use changes on connectivity, and identifying the factors controlling the importance of the location of the disturbance relative to the topography and the catchment outlet... may lead to inferential relationships of how land use changes modify the spatial organization of the flow paths.”

The research agenda outlined above is aligned with a number of the priorities identified in recent reviews and research prioritisation exercises in the hydrological sciences (Blöschl et al., 2019; Rogger et al., 2017).

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Appendix A: Methods Chapter 2

Daily rainfall data

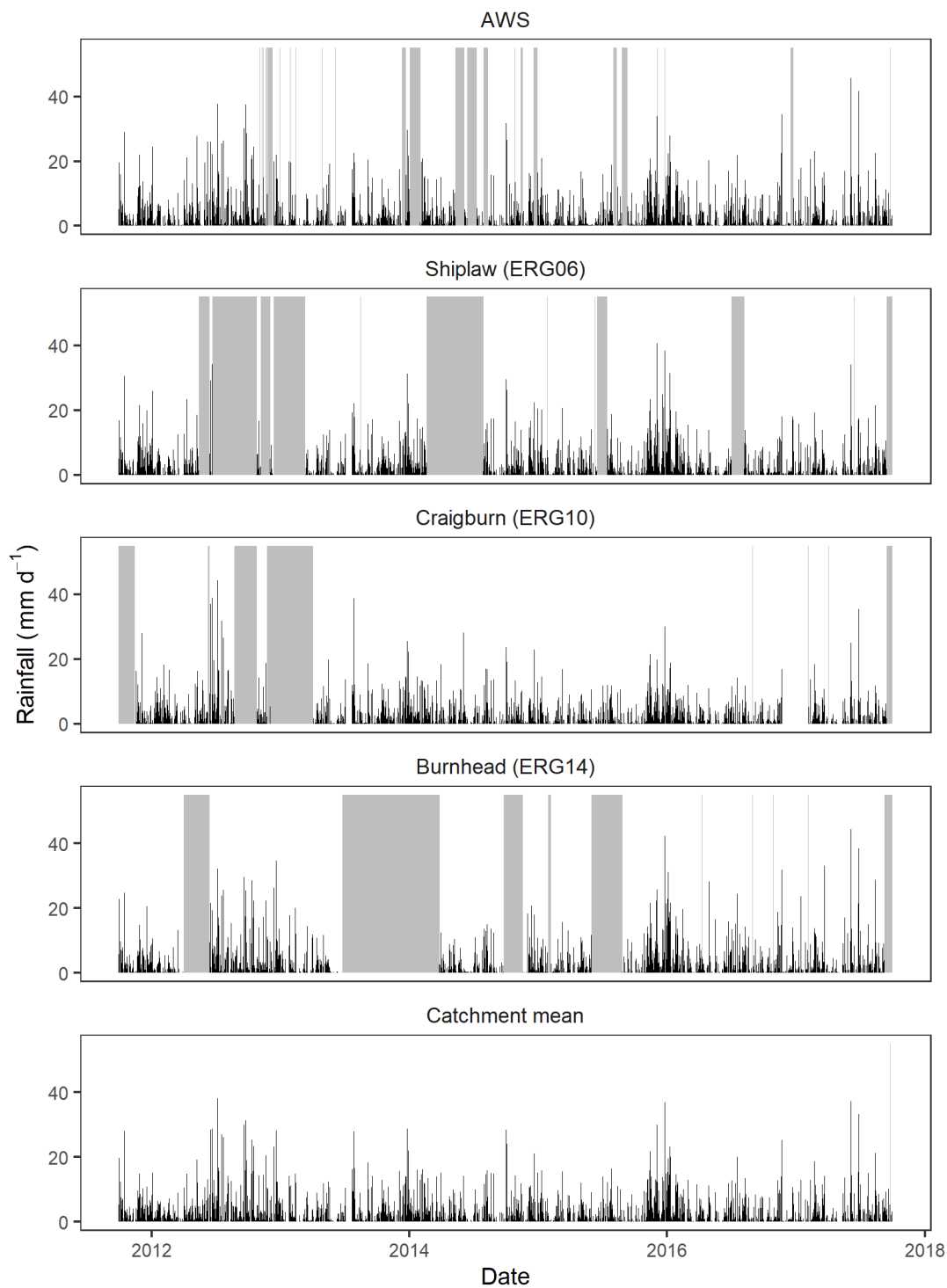


Figure A.1: Daily rainfall for the four TBR rain gauges in the Eddleston Water catchment and the catchment mean rainfall Oct 2011-Sept 2017. AWS is the Automatic Weather Station near Eddleston Village. Data gaps are highlighted in grey.

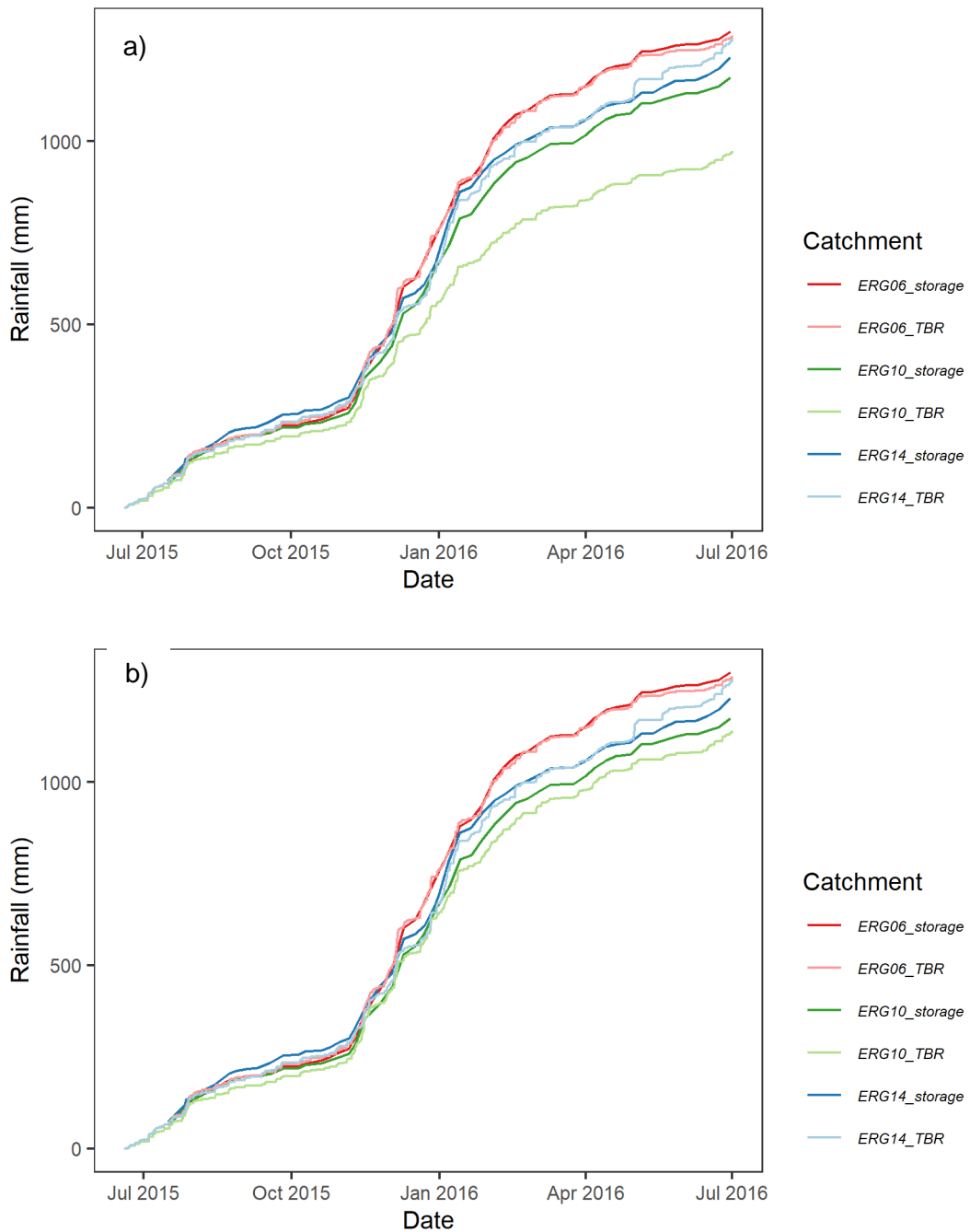


Figure A.2: a) Cumulative rainfall in storage gauges compared to cumulative rainfall in TBRs in the Eddleston Water catchment June 2015-July 2016. Darker lines represent the storage gauges, whilst the lighter lines are the TBR gauges. Both datasets are continuous without gaps for the whole period. b) Corrected cumulative plots of the storage gauges and adjacent TBRs. ERG10 was corrected by a factor of $1/0.825$ since 15/09/2015 based on an analysis of ratios between the gauges over the time series, which showed a threshold change at this date. The ratio reflects the difference in mean values of the difference between gauges before and after this date.

Daily discharge data

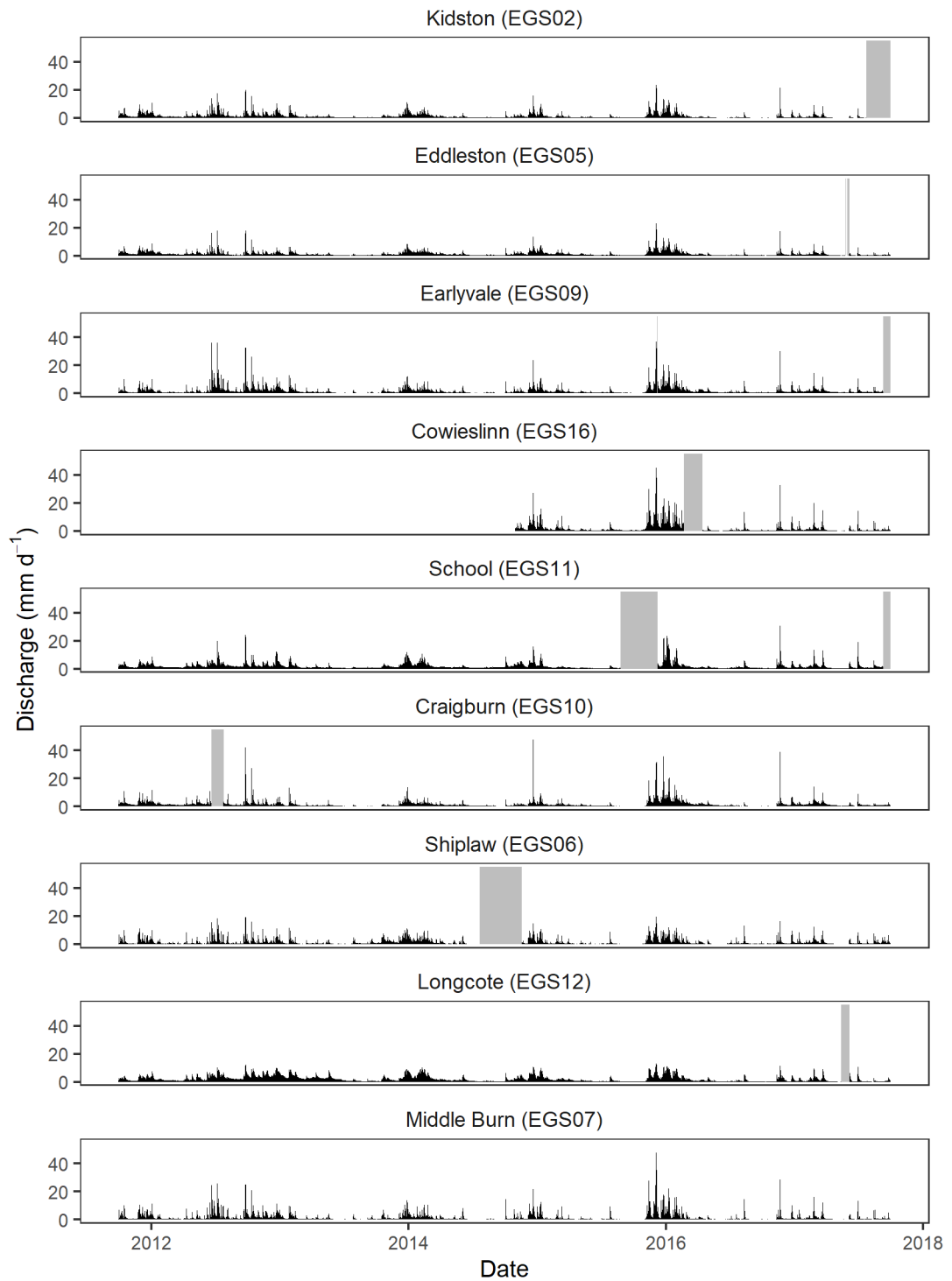


Figure A.3: Daily discharge scaled by catchment area for 9 catchments Oct 2011-Sept 2017. Grey rectangles show missing data. Note that the Cowieslinn gauging station was only established in late 2014. Catchments are ordered by decreasing catchment size, with the top three plots showing gauging stations along the main stem of the Eddleston Water river.

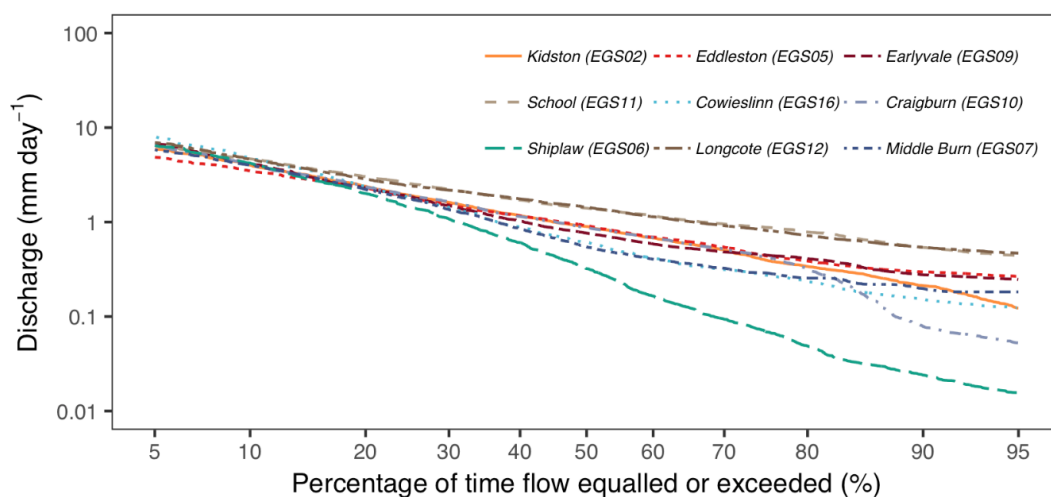


Figure A.4: Flow duration curves for each catchment based on data from October 2011-September 2016. Lognormal probability plot used to highlight patterns at the extremes of the data after Searcy (1959).

Weather data

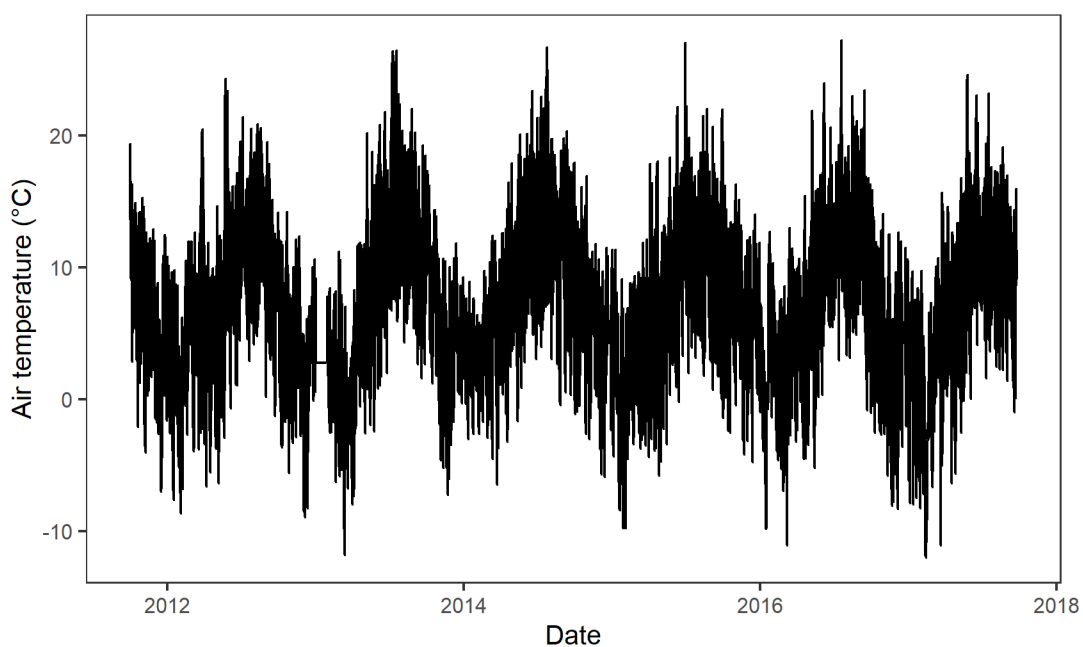


Figure A.5: Air temperature (15-minute values) for automatic weather station near Eddleston Village October 2011-September 2017. Missing data in 2013 infilled using monthly mean values from the rest of the record.

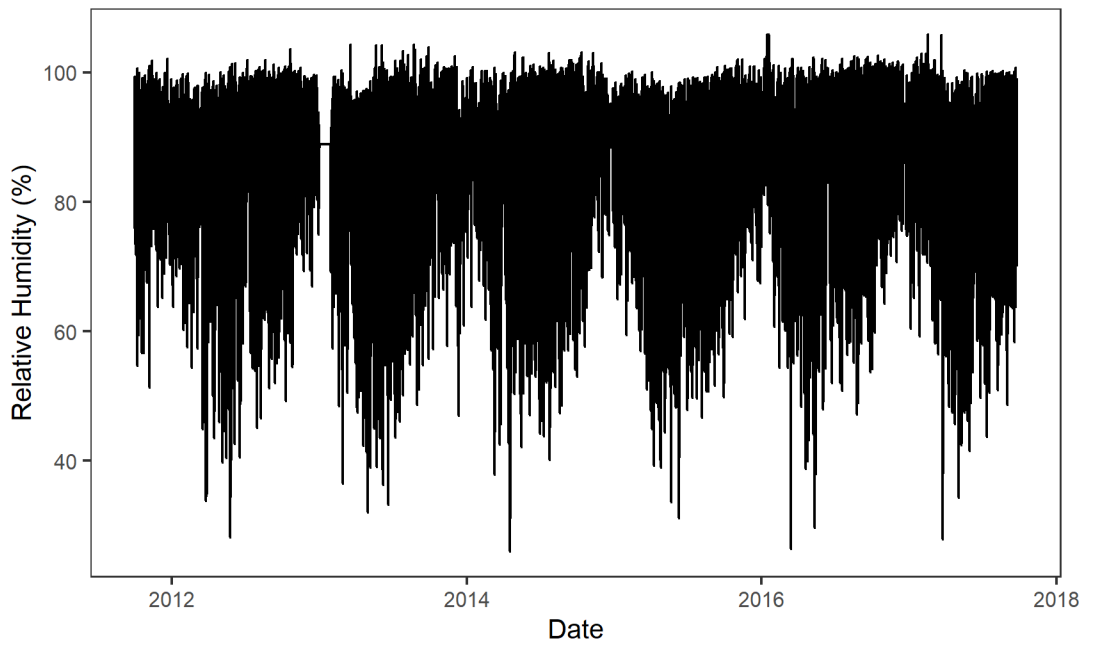


Figure A.6: Relative humidity (15-minute values) for automatic weather station near Eddleston Village October 2011-September 2017. Missing data in 2013 infilled using monthly mean values from the rest of the record.

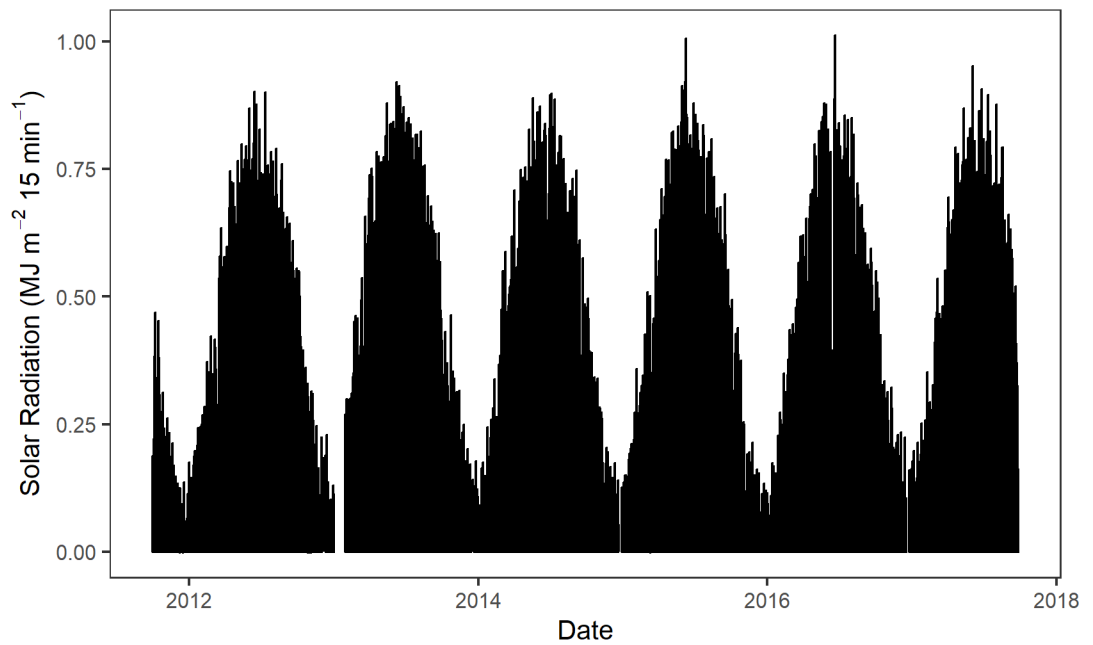


Figure A.7: Solar radiation (15-minute values) for automatic weather station near Eddleston Village October 2011-September 2017. Missing data in 2013 infilled using monthly mean values from the rest of the record.

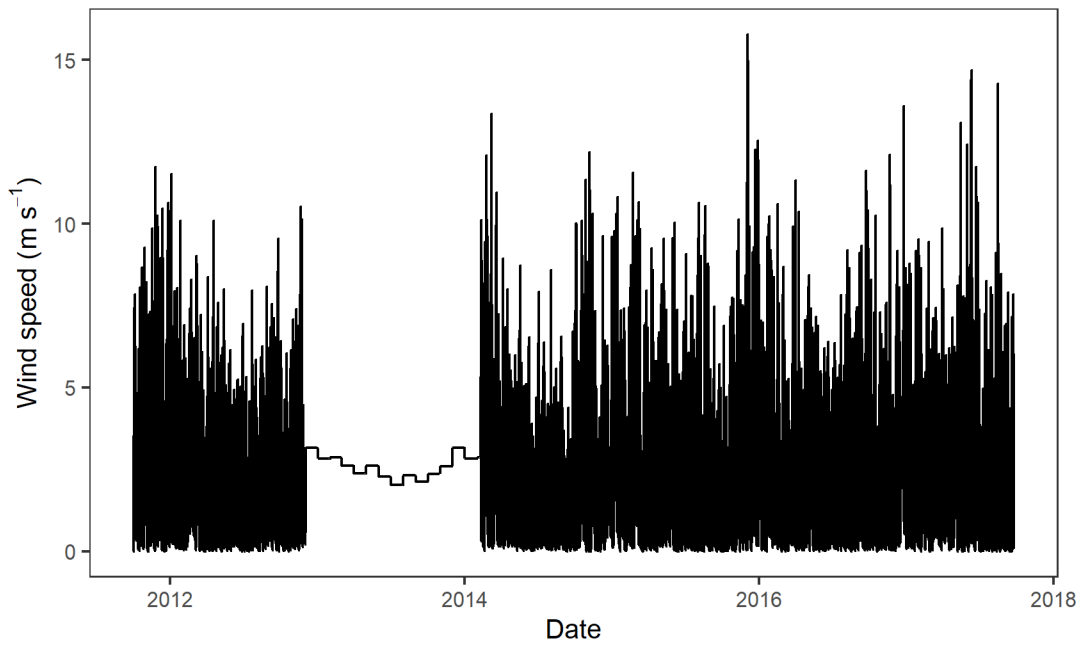


Figure A.8: Windspeed (15-minute values) for automatic weather station near Eddleston Village October 2011-September 2017. Missing data in 2013 infilled using monthly mean values from the rest of the record.

Evapotranspiration data

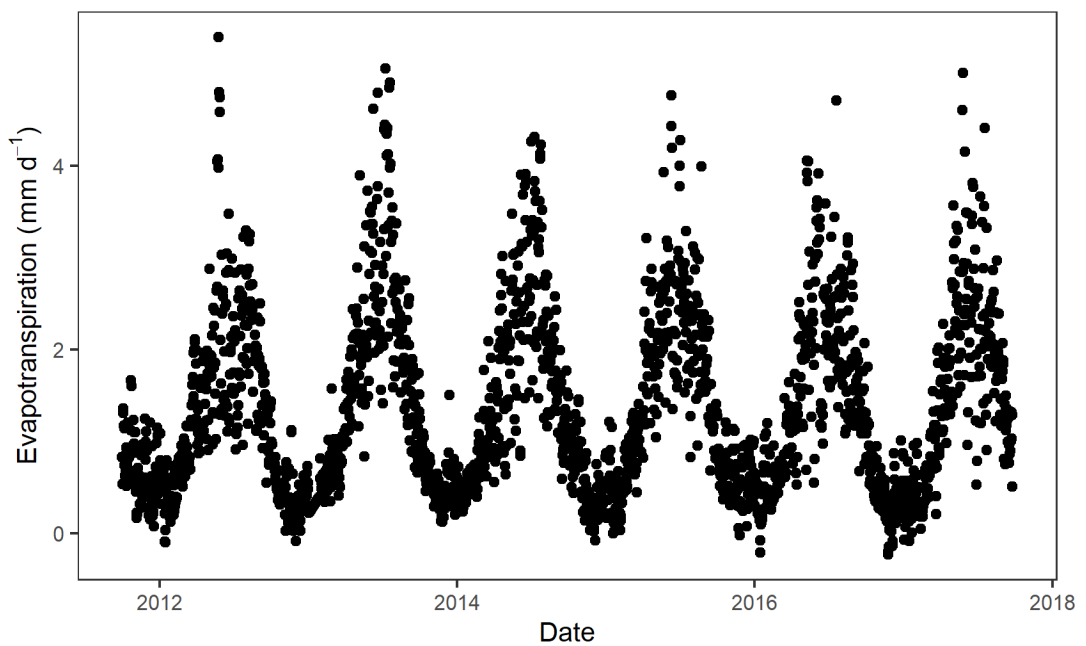


Figure A.9: Daily potential evapotranspiration calculated from the Eddleston Village automatic weather station data using the Penman-Monteith method, Oct 2011 - Sept 2017.

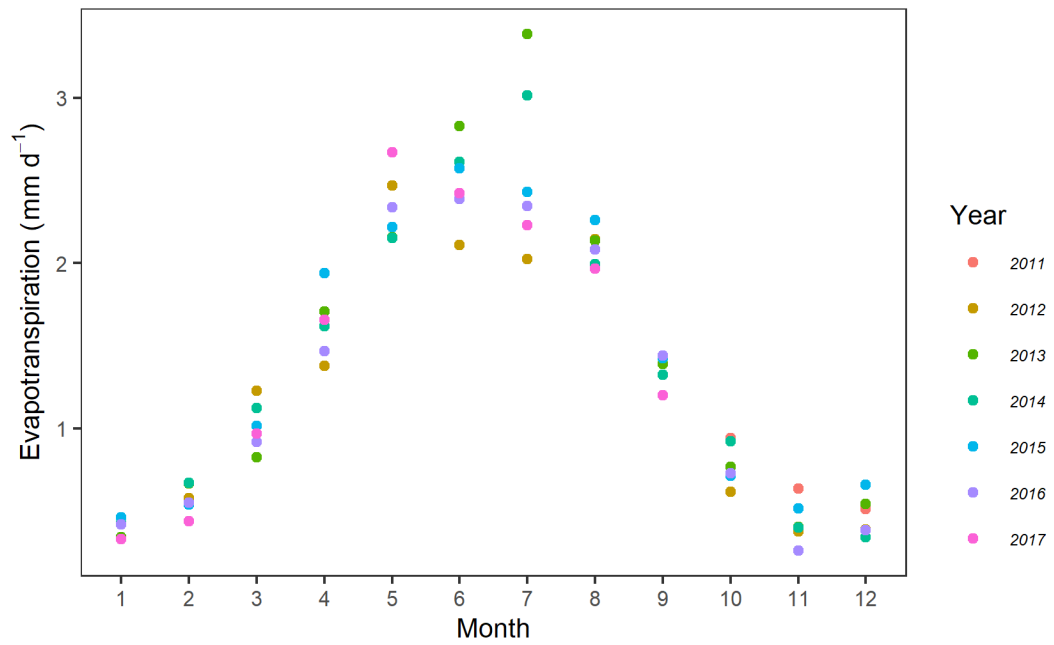


Figure A.10: Monthly mean daily potential evapotranspiration (Oct 2011- Sept 2017) calculated from the Eddleston Village automatic weather station data using the Penman-Monteith method.

Appendix B: Storage Chapter 3

Catchment characteristics

Table B.1: Cross-correlation matrix of landscape characteristics. Correlations based on Spearman Ranks. $p < .001$ ^{***}, $p < .01$ ^{**}, $p < .05$ ^{*}

	G_Br	G_Di	G_SG	HWC_1	HWC_2	HWC_3	LU_F	LU_Gi	LU_Gui	LU_M	T_A	T_DD	T_DI	T_DtS	T_E	T_EAS	T_FLG	T_GTS	T_MSC	T_S	T_TWI	
G_Br																						
G_Di	-0.96 ^{***}																					
G_SG	-0.45	0.17																				
HWC_1	0.87 ^{**}	-0.90 ^{***}	-0.19																			
HWC_2	-0.73 [*]	0.62	0.59	-0.69 [*]																		
HWC_3	-0.75 [*]	0.84 ^{**}	-0.04	-0.94 ^{***}	0.4																	
LU_F	-0.64	0.67 [*]	0.09	-0.90 ^{**}	0.43	0.93 ^{***}																
LU_Gi	-0.32	0.21	0.43	0.16	0.28	-0.33	-0.49															
LU_Gui	0.99 ^{***}	-0.95 ^{***}	-0.44	0.80 ^{**}	-0.70 [*]	-0.68 [*]	-0.54	-0.43														
LU_M	0.00	0.02	-0.07	0.29	-0.05	-0.34	-0.59	0.52	-0.09													
T_A	-0.19	-0.05	0.82 ^{**}	0.1	0.41	-0.33	-0.18	0.58	-0.23	-0.1												
T_DD	-0.54	0.51	0.25	-0.26	0.32	0.18	0.03	0.62	-0.6	0.21	0.13											
T_DI	0.96 ^{***}	-0.93 ^{***}	-0.42	0.73 [*]	-0.65	-0.62	-0.45	-0.52	0.99 ^{***}	-0.13	-0.25	-0.67 [*]										
T_DtS	-0.19	0.20	0.00	0.00	0.39	-0.19	-0.32	0.54	-0.27	0.61	0.04	0.56	-0.31									
T_E	0.77 [*]	-0.66	-0.59	0.39	-0.44	-0.29	-0.15	-0.74 [*]	0.83 ^{**}	-0.13	-0.55	-0.65	0.87 ^{**}	-0.14								
T_EAS	0.98 ^{***}	-0.93 ^{***}	-0.44	0.75 [*]	-0.66	-0.64	-0.48	-0.48	1.00 ^{***}	-0.15	-0.26	-0.6	0.99 ^{***}	-0.27	0.86 ^{**}							
T_FLG	-0.74 [*]	0.78 [*]	0.11	-0.44	0.35	0.4	0.09	0.63	-0.81 ^{**}	0.55	-0.02	0.64	-0.85 ^{**}	0.44	-0.75 [*]	-0.84 ^{**}						
T_GTS	0.97 ^{***}	-0.92 ^{***}	-0.44	0.74 [*]	-0.67 [*]	-0.61	-0.45	-0.52	0.99 ^{***}	-0.14	-0.27	-0.66	1.00 ^{***}	-0.32	0.87 ^{**}	1.00 ^{***}	-0.84 ^{**}					
T_MSC	0.73 [*]	-0.72 [*]	-0.26	0.49	-0.58	-0.35	-0.12	-0.51	0.78 [*]	-0.64	-0.08	-0.42	0.77 [*]	-0.6	0.56	0.80 [*]	-0.85 ^{**}	0.78 [*]				
T_S	0.95 ^{***}	-0.93 ^{***}	-0.36	0.71 [*]	-0.58	-0.63	-0.44	-0.51	0.98 ^{***}	-0.2	-0.2	-0.62	0.99 ^{***}	-0.29	0.86 ^{**}	0.99 ^{***}	-0.88 ^{**}	0.99 ^{***}	0.81 ^{**}			
T_TWI	-0.91 ^{***}	0.94 ^{***}	0.17	-0.73 [*]	0.58	0.65	0.42	0.47	-0.93 ^{***}	0.19	0.03	0.6	-0.94 ^{***}	0.3	-0.77 [*]	-0.93 ^{***}	-0.90 ^{***}	-0.94 ^{***}	-0.76 [*]	-0.95 ^{***}		
T_UA	0.80 [*]	-0.73 [*]	-0.45	0.42	-0.45	-0.32	-0.1	-0.75 [*]	0.86 ^{**}	-0.35	-0.38	-0.58	0.90 ^{**}	-0.24	0.95 ^{***}	0.89 ^{**}	-0.89 ^{**}	0.89 ^{**}	0.75 [*]	0.91 ^{***}	-0.86	

Table B.2: The independent variables used in correlation analyses with MTT, S and Qgw and their rationale for consideration.

<i>Variable</i>	<i>Code</i>	<i>Justification</i>
Topographic indices		
Area (km ²)	T_A	Area has been found in some studies to scale with indices such as MTT. Given the nested nature of some of the catchments, identifying a relationship with area is important for explaining the relationships between other independent variables and the dependent variables. It is also not co-linear with other topographic variables in the dataset.
Drainage density	T_DD	The greater the drainage density, the more connected the drainage networks will be with the soil. Streamwater residence time and the drainage density will likely be negatively related, and both are also linked to slope. T_DD also has low correlation coefficients with most other topographic indices.
Topographic wetness index	T_TWI	Compound index that includes information on both area and slope, with lower clustering across the different catchments compared to some other topographic variables. It is also a widely used index in catchment comparisons, modelling etc. Higher topographic index might be expected to correlate with lower MTT, S and Qgw.
Soils		
HOST wetness 1&2	HWC_1	Highly negatively co-linear with HWC_3. These more freely draining wetness classes will likely be correlated with MTT, S and Qgw.
HOST wetness 3&4	HWC_2	Has low correlation coefficients with most other indices, so kept as a variable. However, the intermediate permeability values and lower catchment coverage mean it is likely to have lower correlation with dependent variables.
Geology		
Glacial till and peat	G_Di	The percentage diamicton and peat was highly co-linear with percentage bedrock, and was included because there is more variability across the catchments compared to bedrock exposure. Higher percentage diamicton and peat might be expected to correlate with lower MTT, S and Qgw.
Sand and Gravel	G_SG	Has low correlation coefficients with most other indices, so kept as a variable. The percentage is low but significant in some catchments. Higher percentage sand and gravel might be expected to correlate with higher MTT, S and Qgw.
Land cover		
Improved and semi-improved grassland	LU_Gi	Included due to low correlation with other independent variables and it is a variable of interest. Higher percentage of improved grassland likely to have unpredictable effect on MTT, S and Qgw. E.g. compaction and drainage could reduce MTTs, but drainage could increase S and Qgw through increased water table depth.
Woodland – all	LU_F	Highly inversely co-linear with HWC_1 and weakly co-linear with G_Di_Pe. Kept as it is a variable of interest for exploring the direction of the relationship with the dependent variables. Higher percentage forest cover might be expected to correlate with higher MTT, S and Qgw.
Dry/wet modified bog and fenland	LU_M	Included due to low correlation with other independent variables. Lower percentage cover in some catchments but significant in some catchments. Higher percentage LU_M might be expected to correlate with higher MTT, S and Qgw.

Isotopic analysis

Table B.3: Summary of annual isotopic values for the different rain gauges and catchments, showing mean and standard deviation (mn, sd) and weighted mean and standard deviation (w, wsd). Values for rivers are based on one year of sampling data.

Gauge/Catchment	mn_d18 O (‰)	mn_dD (‰)	sd_d18 O (‰)	sd_dD (‰)	wm_d18 O (‰)	wm_dD (‰)	wsd_d1 8O(‰)	wsd_dD (‰)
Rain gauge								
Shiplaw SG (ERG06) (1 yr)	-7.56	-52.29	2.78	20.74	-9.20	-63.87	2.89	22.23
Shiplaw SG (ERG06) (2 yr)	-7.44	-50.34	2.61	20.13	-8.69	-59.04	2.62	20.55
Craigburn SG (ERG10) (1 yr)	-7.67	-53.81	2.64	19.59	-9.25	-65.35	3.01	22.82
Craigburn SG (ERG10) (2 yr)	-7.69	-53.16	2.47	18.86	-8.80	-61.12	2.65	20.63
Burnhead SG (ERG14) (1 yr)	-7.69	-52.74	2.56	20.68	-9.27	-65.28	2.89	23.23
Burnhead SG (ERG14) (2 yr)	-7.73	-52.19	2.52	20.43	-8.93	-61.50	2.52	20.57
River catchment								
Kidston (EGS02)	-8.33	-56.97	0.49	3.73	-8.67	-59.50	0.69	6.64
Eddleston (EGS05)	-8.24	-56.32	0.54	4.24	-8.59	-58.86	0.83	7.25
Earlyvale (EGS09)	-8.20	-55.81	0.62	4.66	-8.86	-61.11	1.02	8.81
School (EGS11)	-8.51	-57.84	0.43	2.82	-8.52	-58.11	0.52	4.46
Cowieslinn (EGS16)	-8.07	-54.99	0.77	5.51	-8.76	-59.79	1.00	8.21
Craigburn (EGS10)	-8.09	-55.53	0.76	4.70	-8.77	-60.61	0.99	8.43
Shiplaw (EGS06)	-8.19	-55.61	0.79	5.31	-8.62	-58.39	1.10	9.03
Longcote (EGS12)	-8.64	-58.33	0.57	3.70	-8.60	-58.19	0.65	4.87
Middle Burn (EGS07)	-8.34	-56.65	0.73	5.42	-8.67	-59.12	1.01	7.94
Eddleston Spring (EGW17)	-8.16	-56.25	0.33	1.85				

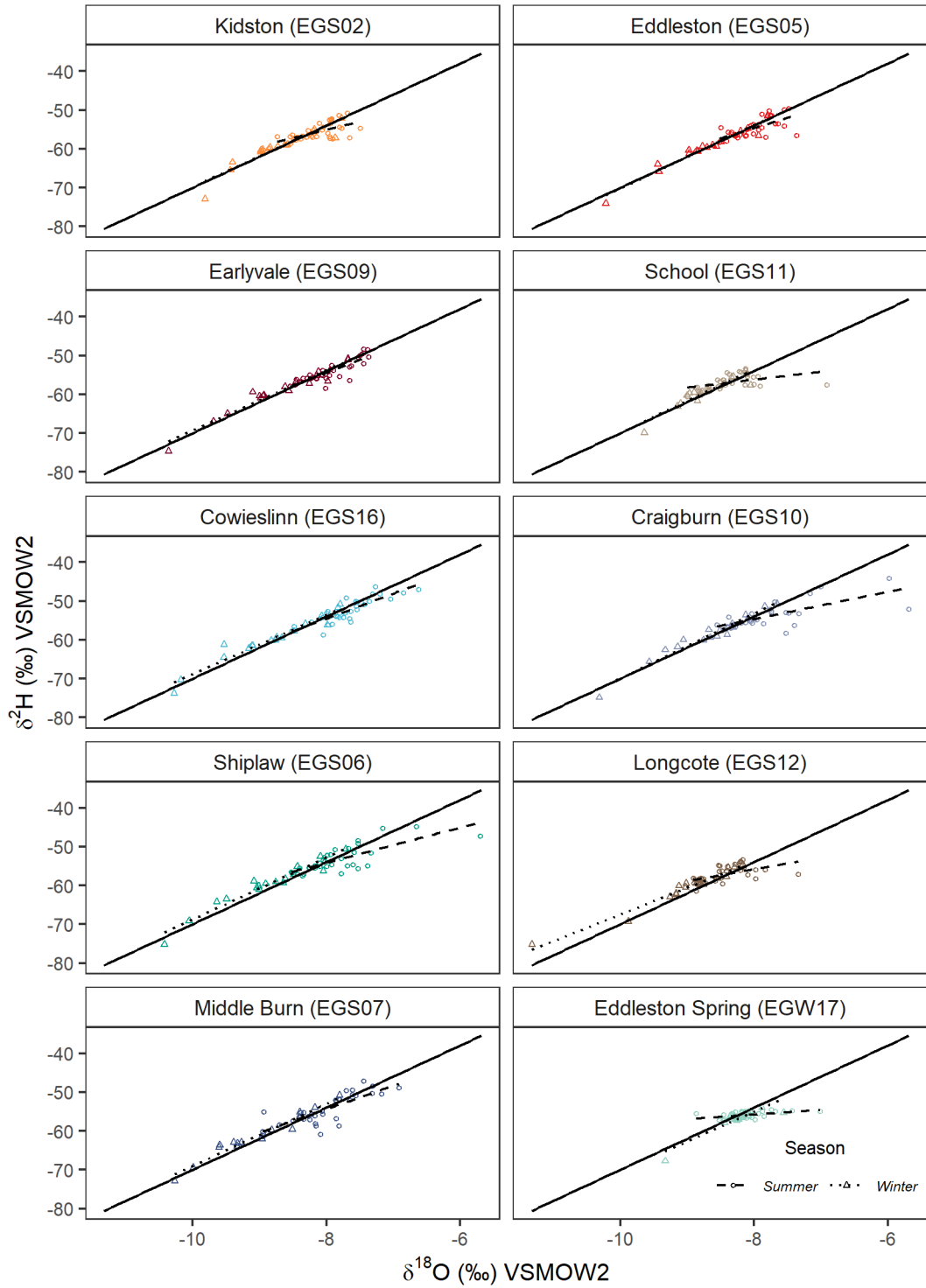


Figure B.2: Dual isotope plots for each catchment (ordered largest to smallest). Black line represents the Global Meteoric Water Line (GMWL). Summer: June-November; Winter: December-May, as defined in Chapter 5.

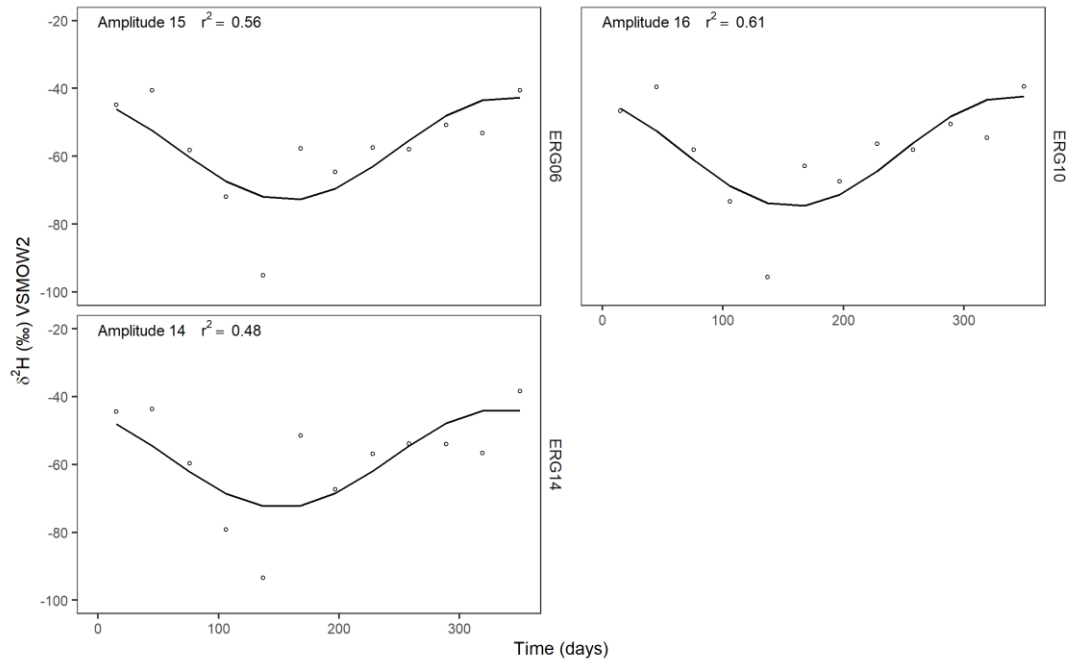


Figure B.3: Periodic regression analysis used to fit monthly volume-weighted rainfall data at rain gauges in the West, North and East of the catchment.

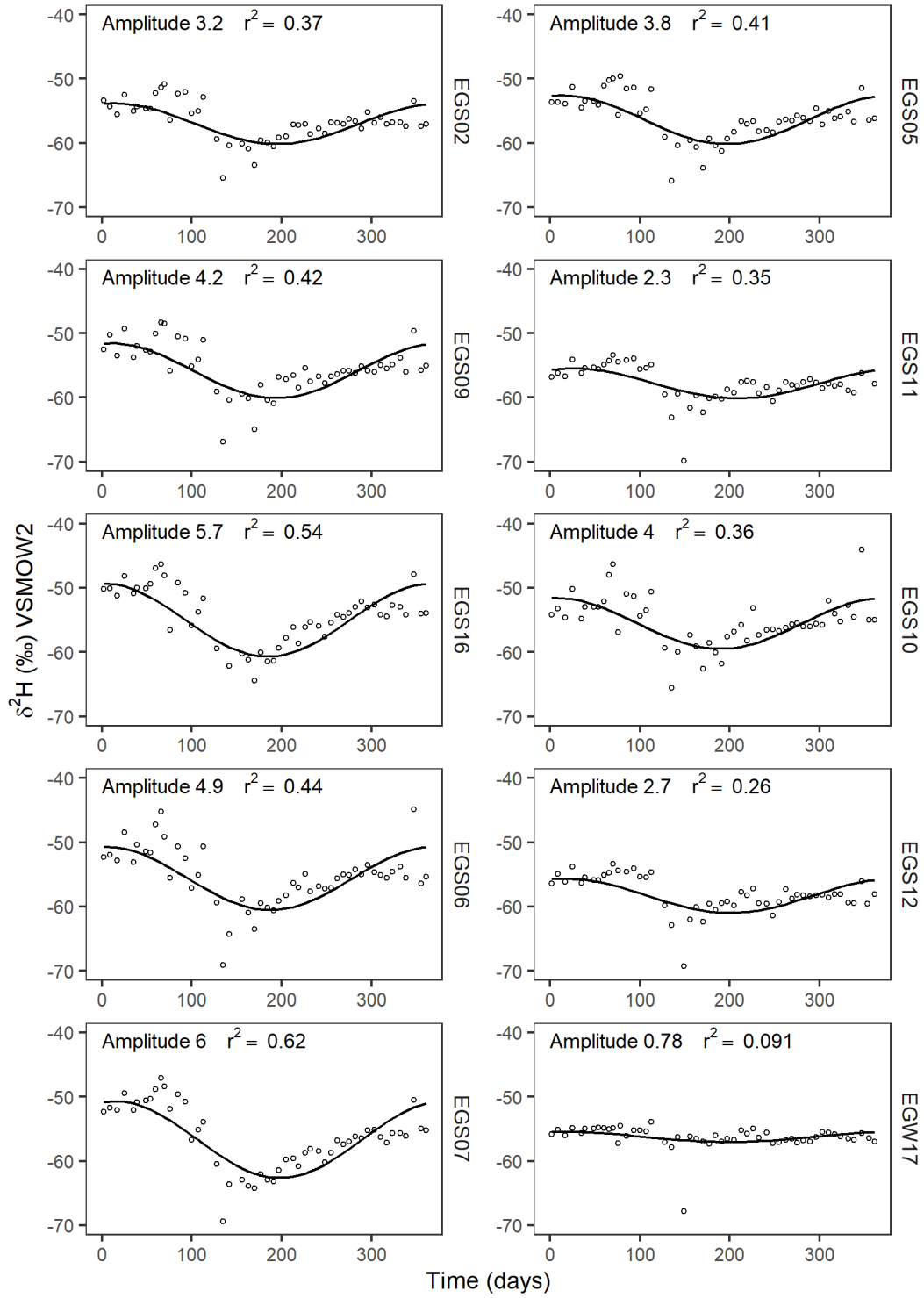


Figure B.4: Periodic regression analysis used to fit river and spring data. Catchment area decreases left to right and top to bottom.

Storage

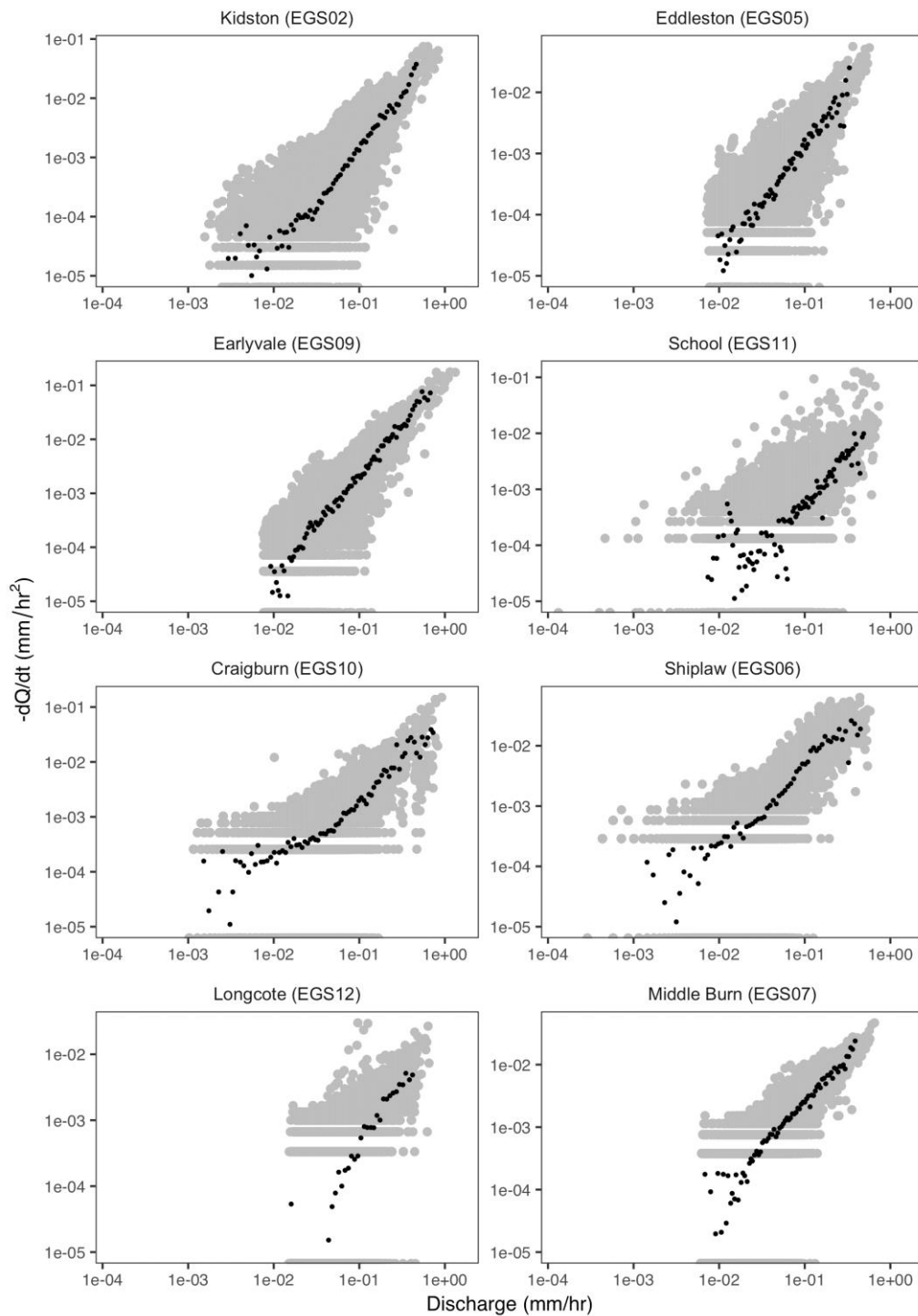


Figure B.5: Plots of discharge against the rate of change of discharge (recession rate) for eight catchments. Black dots represent the mean values of the binned data (binned according to criteria defined in the text). Note that negative recession rates and negative mean recession rates cannot be plotted on these log-log axes.

ANC analysis

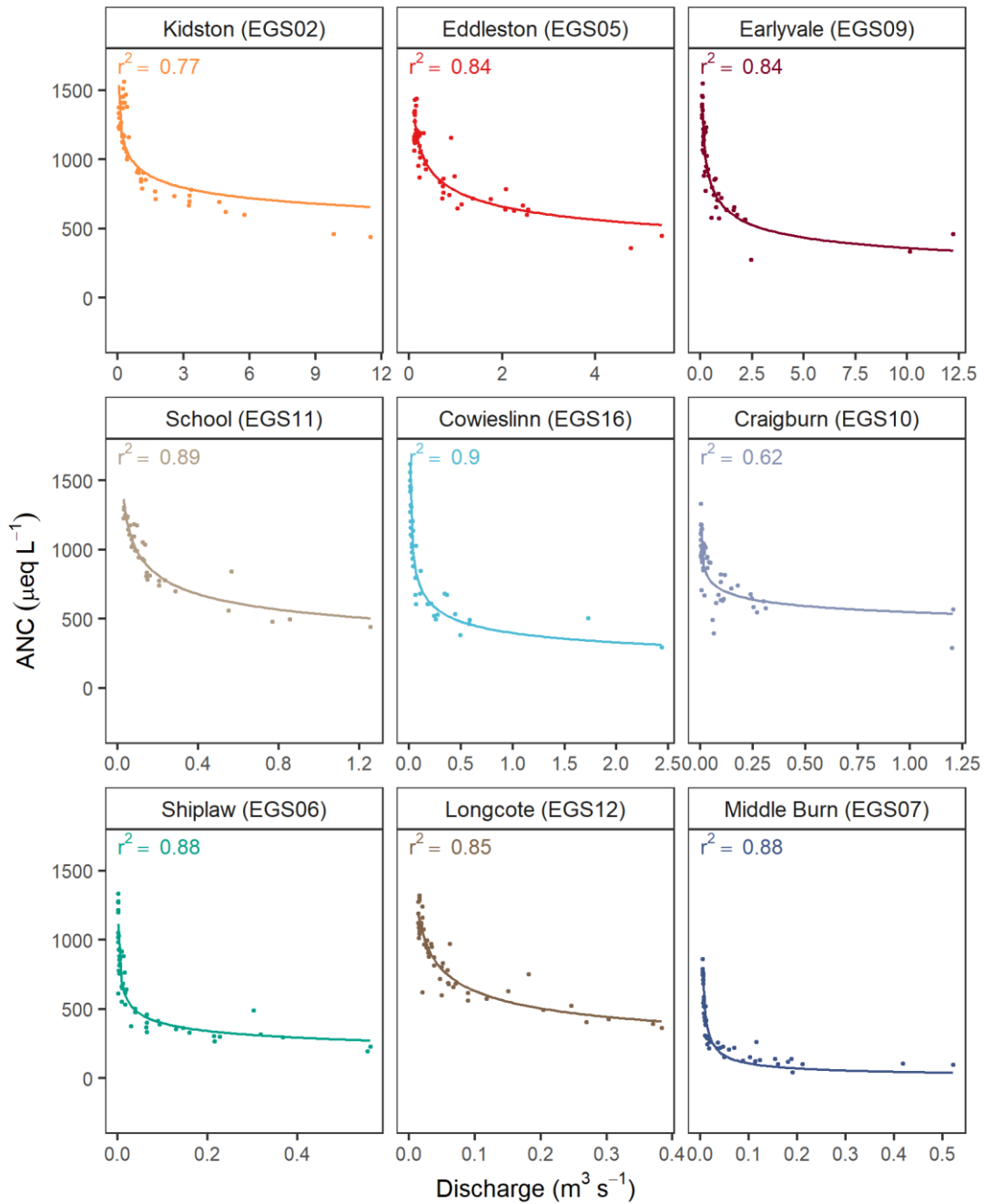


Figure B.6: ANC-discharge relationships for all catchments during the sampling period, September 2015 – August 2016.

Appendix C: Event analysis Chapter 4

Geographic variation in event rainfall

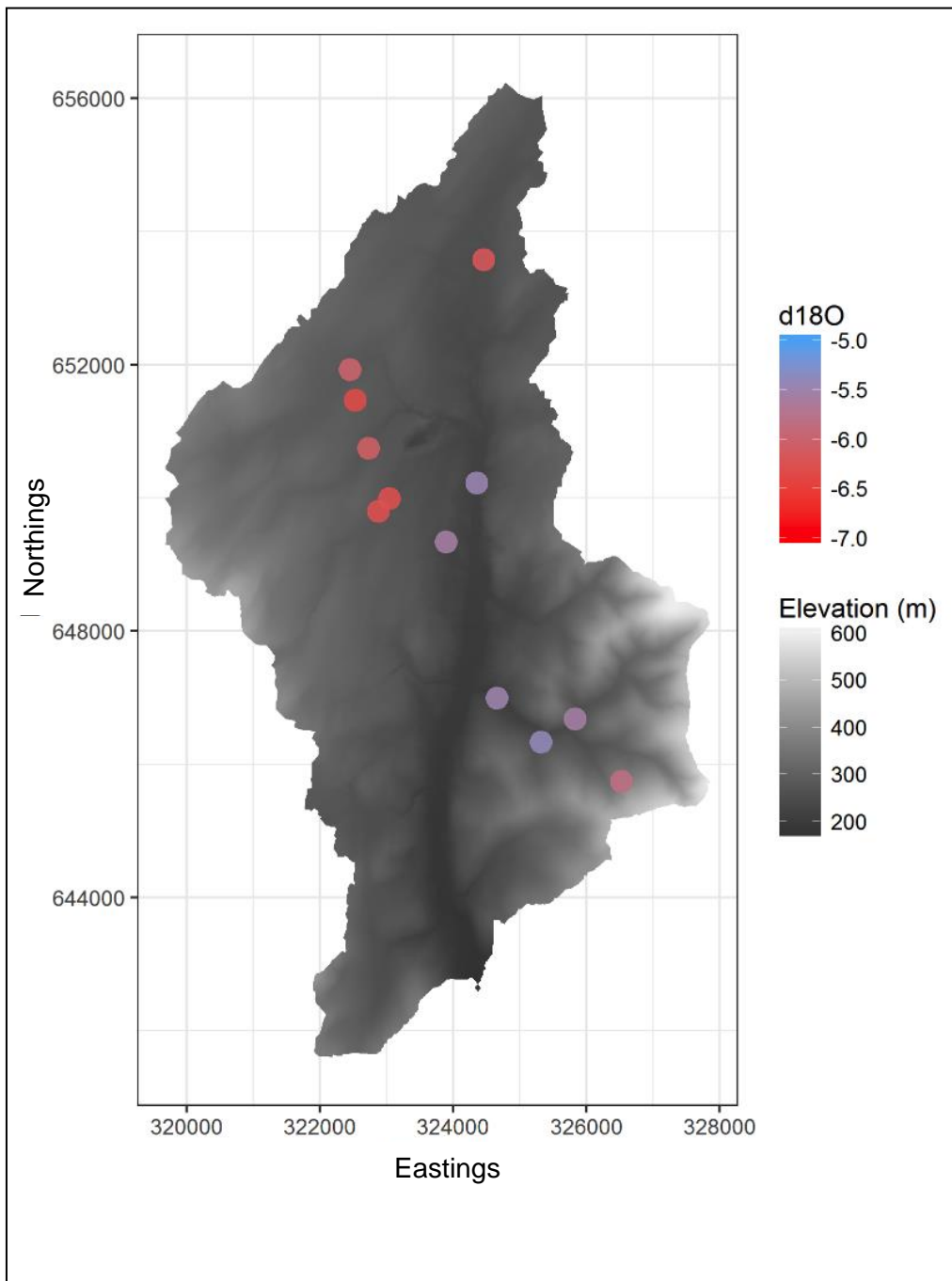


Figure C.1: Variation in $\delta^{18}\text{O}$ across the Eddleston Water catchment during storm event 29-31 December 2015

Notes on hydrograph separation

Table C.1: Notes on adjustments made to isotope data prior to hydrograph separation to ensure comparability between catchments and storms.

Event	Notes
29/12/15	<ul style="list-style-type: none"> Added in a predicted pre-storm endmember at the start of the rising limb of the hydrograph for Middle Burn based on the first stream water sample (which was a few hours before the storm) and the slope of the regression line of the isotope values for stream water samples in the adjacent Shiplaw catchment prior to the storm.
21/11/16	<ul style="list-style-type: none"> Replaced a spurious isotope value in the Middle Burn catchment data, using linear interpolation between the values for the samples collected immediately before and after. The resulting values and trend were then similar to those in the adjacent catchment.
22/02/17	<ul style="list-style-type: none"> Due to the sampler failure at the start of the event at Middle Burn, statistics were calculated for a 'long storm' and a 'short storm'. The long storm covered the complete sampling window and the short storm started at the first sample prior to the onset of the second (and greater) rise in the hydrograph. The short storm had more significant discharge than the long storm and samples were captured at the start of this part of the event as well as at the peak and on the falling limb, so separations are considered robust for this storm but do not capture well the dynamics in the lead up to this larger part of the event. In the 'long storm' a sample was also available prior to the start of the rising limb but it was assumed for all calculations that the first part of the event was pre-event water, based on the high pre-event fraction in the second sample and the high pre-event fraction in the other two catchments. Runoff ratios presented in the text are based on the fraction of event water calculated for the long storm and the total rainfall over the long storm event, to ensure they are comparable with the other catchments and with the fraction based on separation using the low pass filter. Given that a stream water sample was collected close to the peak discharge during the event, the separations at Q_{max} reported in the text are not affected by these assumptions and are considered most reliable.

Table C.2: Notes on adjustments made to ANC data prior to hydrograph separation to ensure comparability between catchments and storms.

Event	Notes
29/12/15	<ul style="list-style-type: none"> Added in a predicted pre-storm endmember for Middle Burn based on first sample point (which was a few hours before the storm) and the regression line of the sample points in the adjacent Shiplaw catchment prior to the storm.
22/02/17	<ul style="list-style-type: none"> Due to the sampler failure for the start of the event at Middle Burn, statistics were calculated for a 'long storm' and a 'short storm'. The long storm covered the complete sampling window and the short storm started at the first sample prior to the onset of the second (and greater) rise in the hydrograph. The short storm had much more significant discharge than the long storm and samples were captured at the start of this part of the event as well as at the peak and on the falling limb, so separations are considered robust for this storm but don't capture well the dynamics in the lead up to this larger part of the event. For the long storm, groundwater fraction was calculated using linear interpolation between the ANC of the stream water sample prior to the event and the sample prior to the second (larger) part of the event. This will have led to a small over estimation of groundwater fraction for the whole event but within the margin of error, given that overall discharge for the first part of the event was much lower than the second part of the event where high frequency sampling data were available. Given that a stream water sample was collected close to the event peak discharge, the separations at Qmax reported in the text are not affected by these assumptions and are considered most reliable.

Dual isotope plots

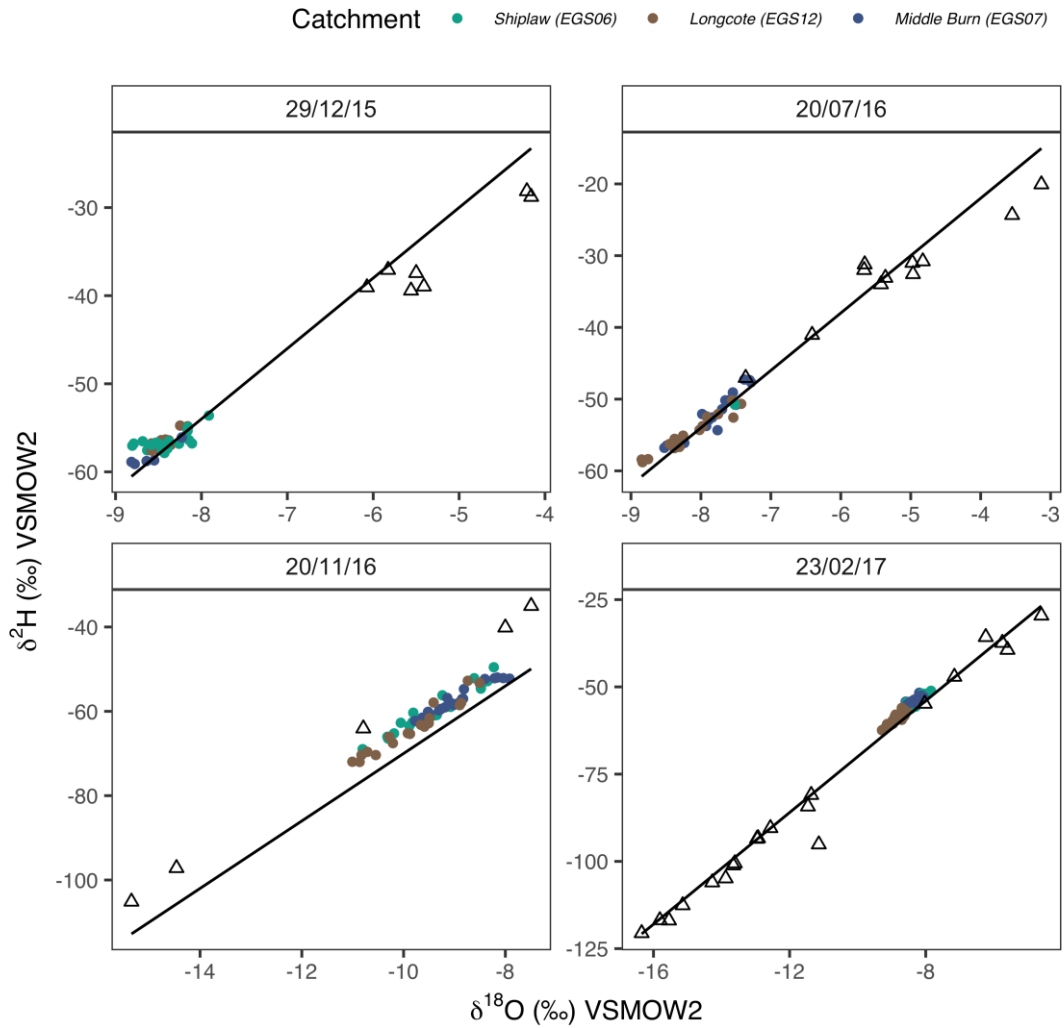


Figure C.2: Dual isotope plots for the four events discussed in the text. Open triangles are rainfall samples and coloured circles are stream water samples. Note different x- and y-axis scales.

Storm discharge, isotope and geochemical dynamics

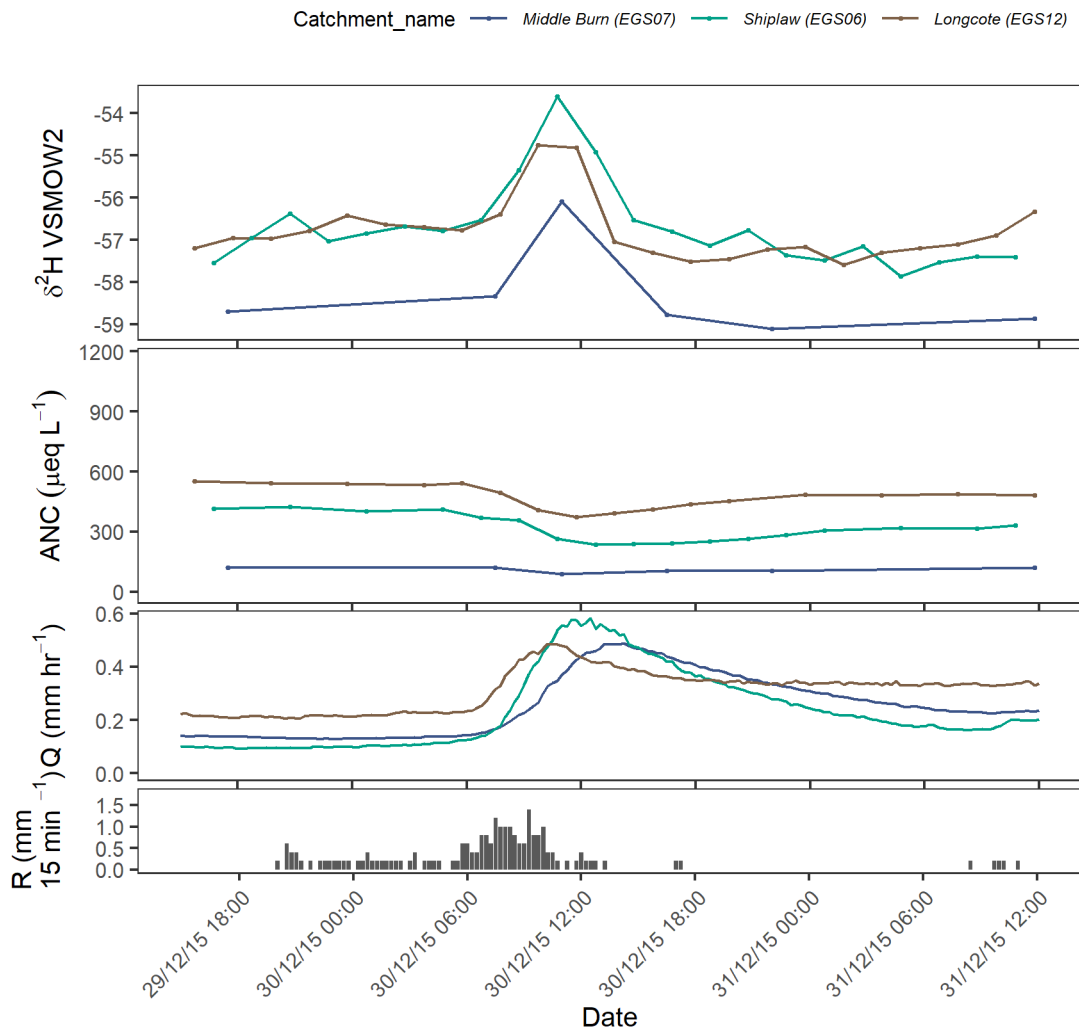


Figure C.3: Isotope, ANC, stream flow and rainfall dynamics for the December 2015 storm event.

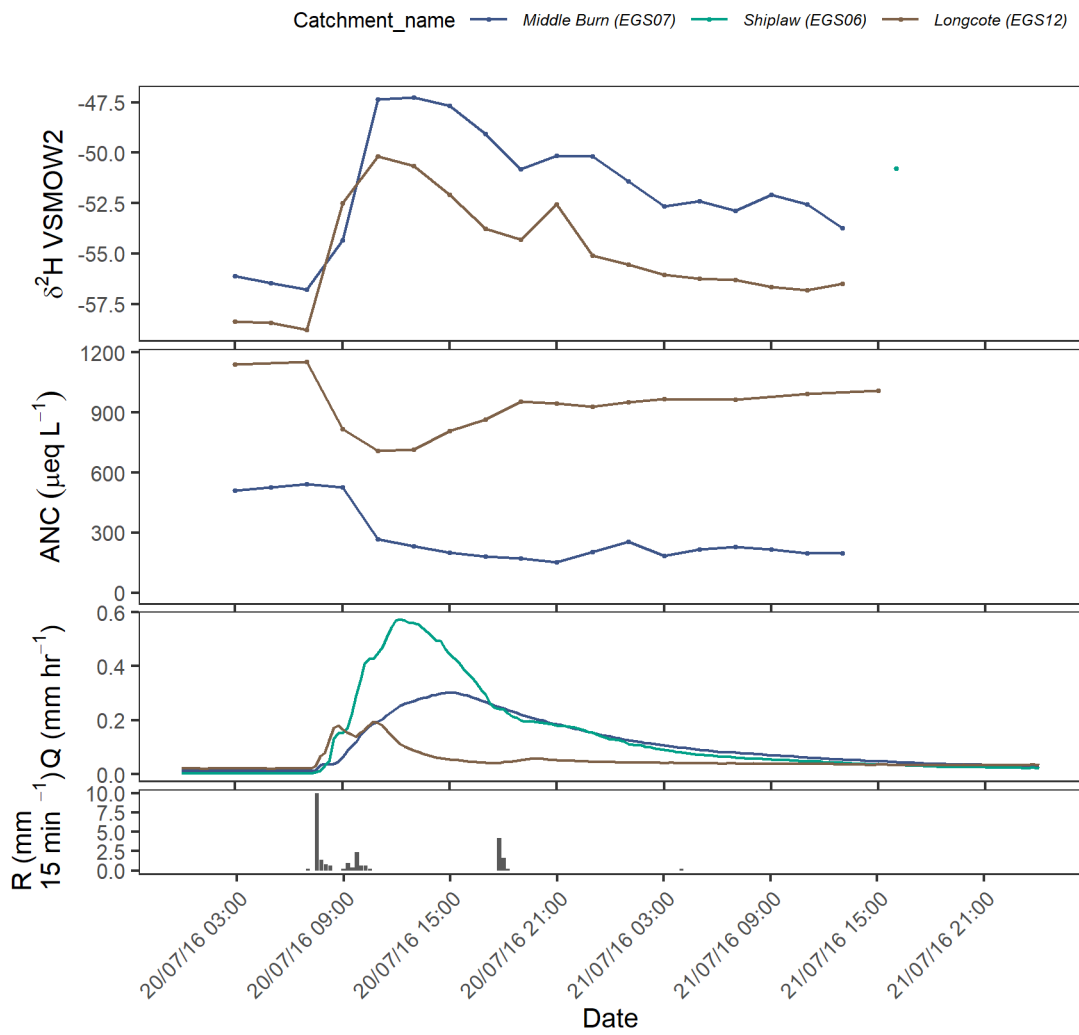


Figure C.4: Isotope, ANC, stream flow and rainfall dynamics for the July 2016 storm event.

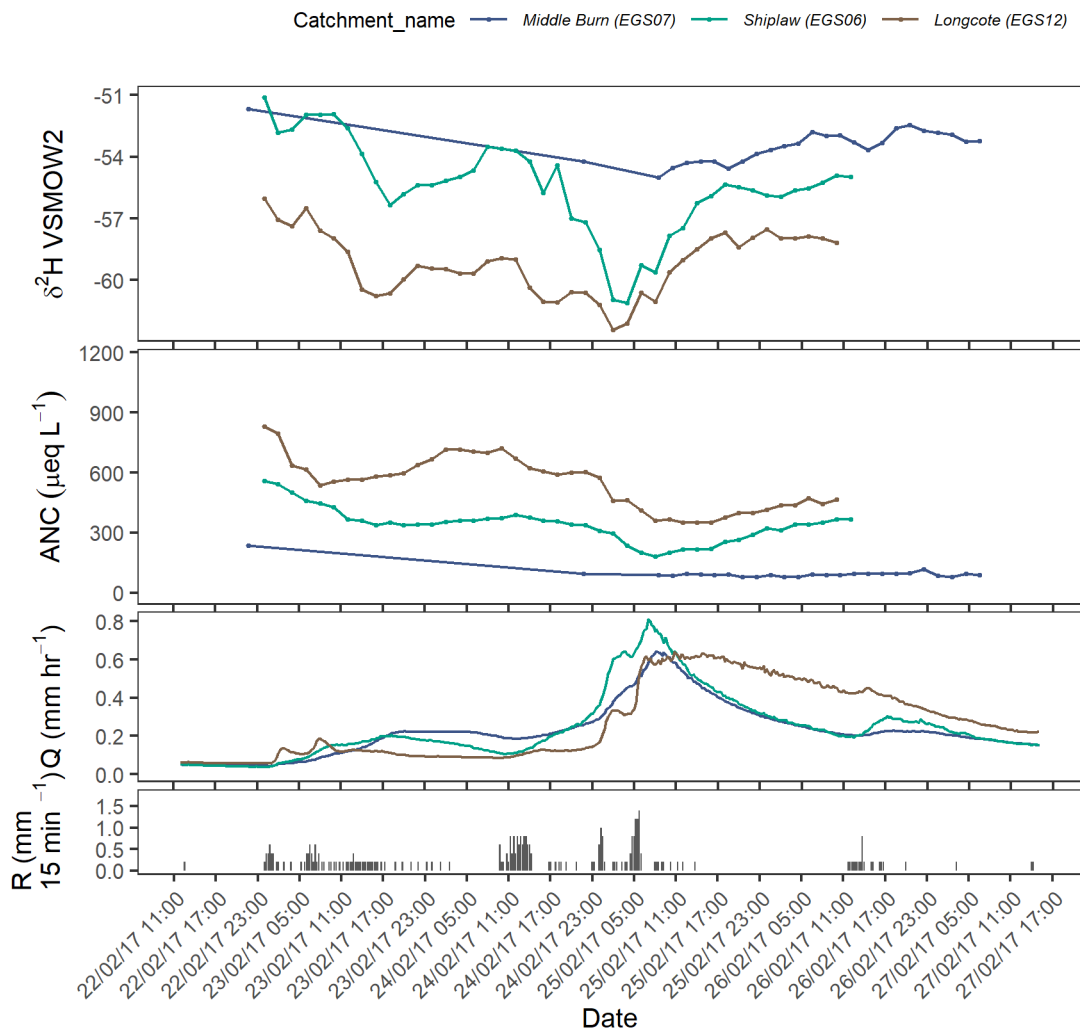


Figure C.5: Isotope, ANC, stream flow and rainfall dynamics for the February 2017 event.

Table D.1: Soil properties at each soil moisture sensor location

<i>Location</i>	<i>Depth</i>	<i>Clay</i>	<i>Silt</i>	<i>Sand</i>	<i>Gravel and cobbles</i>	<i>Organic content</i>	<i>Soil texture</i>
	(m)	(%fraction by volume)			(% of total by mass)	(% of total by mass)	
G1_15	0.15	9.83	65.4	24.8	37.0	6.95	Silty loam
F1_15	0.15	18.0	65.0	17.0	22.3	5.67	Silty loam
G1_60	0.60	12.1	48.6	39.3	55.5	2.03	Loam
F1_60	0.60	14.1	63.4	22.6	25.3	4.44	Silty loam
G2_15	0.15	15.3	63.6	21.1	53.4	4.91	Silty loam
F2a_15	0.15	10.7	53.7	35.6	49.0	1.97	Silty loam
F2b_15	0.15	11.2	64.8	24.0	26.1	5.73	Silty loam
G2_60	0.60	11.3	65.8	23.0	44.5	2.63	Silty loam
F2a_60	0.60	11.3	64.1	24.6	32.9	6.07	Silty loam
F2b_60	0.60	16.8	62.8	20.5	58.2	2.78	Silty loam
G3_15	0.15	11.5	60.0	28.6	44.6	5.19	Silty loam
F3_15	0.15	10.6	68.8	20.6	30.0	5.32	Silty loam
G3_60	0.60	13.5	67.7	18.8	40.7	4.20	Silty loam
F3_60	0.60	10.6	63.5	25.9	39.2	3.03	Silty loam

Table D.2: Summary of rainfall events selected (n=52) and key event characteristics used in the analysis. Percentage of sensors responding is based on all working soil moisture and groundwater sensors at the site (n=20).

<i>Rainfall start time</i>	<i>No. responding (%)</i>	<i>Total rainfall, TR (mm)</i>	<i>Intensity, I (mm h⁻¹)</i>	<i>AWI (mm)</i>	<i>AP28d (mm)</i>
11/11/16 20:15	50	19.8	2.4	4.8	13.2
16/11/16 11:00	68	19.0	1.1	26.8	45.2
21/11/16 19:30	91	41.0	2.5	11.6	67.0
22/12/16 15:00	64	8.6	2.0	3.8	14.2
23/12/16 08:45	77	20.2	1.7	11.6	23.2
24/12/16 00:15	77	17.4	1.3	30.5	43.0
03/02/17 18:30	50	8.2	0.8	4.3	34.6
23/02/17 00:15	82	21.8	1.3	11.0	49.4
24/02/17 17:45	77	15.2	0.8	28.4	71.4
17/03/17 02:00	68	13.2	0.7	2.0	87.6
18/03/17 20:00	59	10.2	0.7	16.7	102
21/03/17 09:30	64	9.8	1.7	28.8	114
22/03/17 21:15	73	11.2	1.0	29.8	122
20/05/17 00:15	32	11.0	0.8	6.8	15.6
05/06/17 19:30	64	48.0	1.5	6.7	40.0
08/06/17 07:30	64	14.8	2.0	48.3	87.8
15/06/17 12:15	27	9.0	1.5	3.5	100
27/06/17 00:15	24	11.2	1.0	2.0	89.8
28/06/17 23:15	76	52.6	1.5	10.7	100
04/07/17 03:45	43	10.8	0.8	38.7	138
26/07/17 06:00	24	11.6	1.6	8.5	96.8
14/08/17 03:15	24	9.8	1.4	4.9	63.4
14/08/17 20:45	67	20.8	2.2	14.0	72.8
23/08/17 05:00	24	8.2	2.2	4.6	97.0
21/09/17 03:00	38	10.2	1.9	5.7	70.4
24/09/17 22:15	62	20.8	2.0	9.9	77.6
04/10/17 14:45	62	14.6	1.3	12.3	97.6
11/10/17 00:45	58	11.4	0.9	5.0	89.8
19/11/17 19:30	59	18.8	0.5	6.5	32.8
22/11/17 02:45	82	25.2	1.0	20.2	50.0
24/12/17 23:00	68	20.0	0.9	4.8	21.8
30/12/17 02:45	55	19.6	0.7	12.0	41.6

02/01/18 20:45	68	15.2	1.0	21.4	65.4
22/01/18 05:45	73	17.2	1.3	4.4	83.6
10/02/18 18:00	68	8.6	0.9	4.8	78.4
18/02/18 16:30	41	8.2	0.6	3.1	86.8
05/03/18 20:15	82	13.0	1.0	6.0	42.8
10/03/18 05:00	77	10.2	0.7	16.1	55.6
12/05/18 23:30	23	8.8	1.1	8.7	40.2
01/06/18 12:00	32	18.2	2.5	1.4	19.2
19/06/18 18:00	59	37.2	2.5	5.5	38.4
27/07/18 21:30	23	12.0	1.5	9.3	20.6
01/08/18 14:30	18	10.8	1.4	25.1	50.4
11/08/18 23:15	14	11.4	1.0	8.1	70.2
18/08/18 22:15	32	12.2	1.2	11.4	90.4
03/09/18 04:00	27	11.4	1.2	1.3	66.2
10/09/18 14:00	41	12.4	1.1	5.0	61.0
19/09/18 07:00	46	17.4	1.8	11.3	60.6
12/10/18 12:15	32	9.6	2.1	10.0	51.2
13/10/18 04:45	55	17.6	1.3	17.9	57.6
31/10/18 22:30	46	9.4	1.4	4.1	49.8
09/11/18 17:30	59	12.2	1.0	5.7	44.6

Table D.3: Spearman rank correlation coefficients calculated to compare relationships between different rainfall event characteristics. * $p < 0.05$; * $p < 0.01$; * $p < 0.001$.**

	<i>Rainfall (mm)</i>	<i>Intensity (mm h⁻¹)</i>	<i>AWI (mm)</i>
<i>Intensity (mm h⁻¹)</i>	0.32*	1.00	
<i>AWI (mm)</i>	0.00	-0.05	1.00
<i>AP28d (mm)</i>	-0.14	-0.08	0.33*

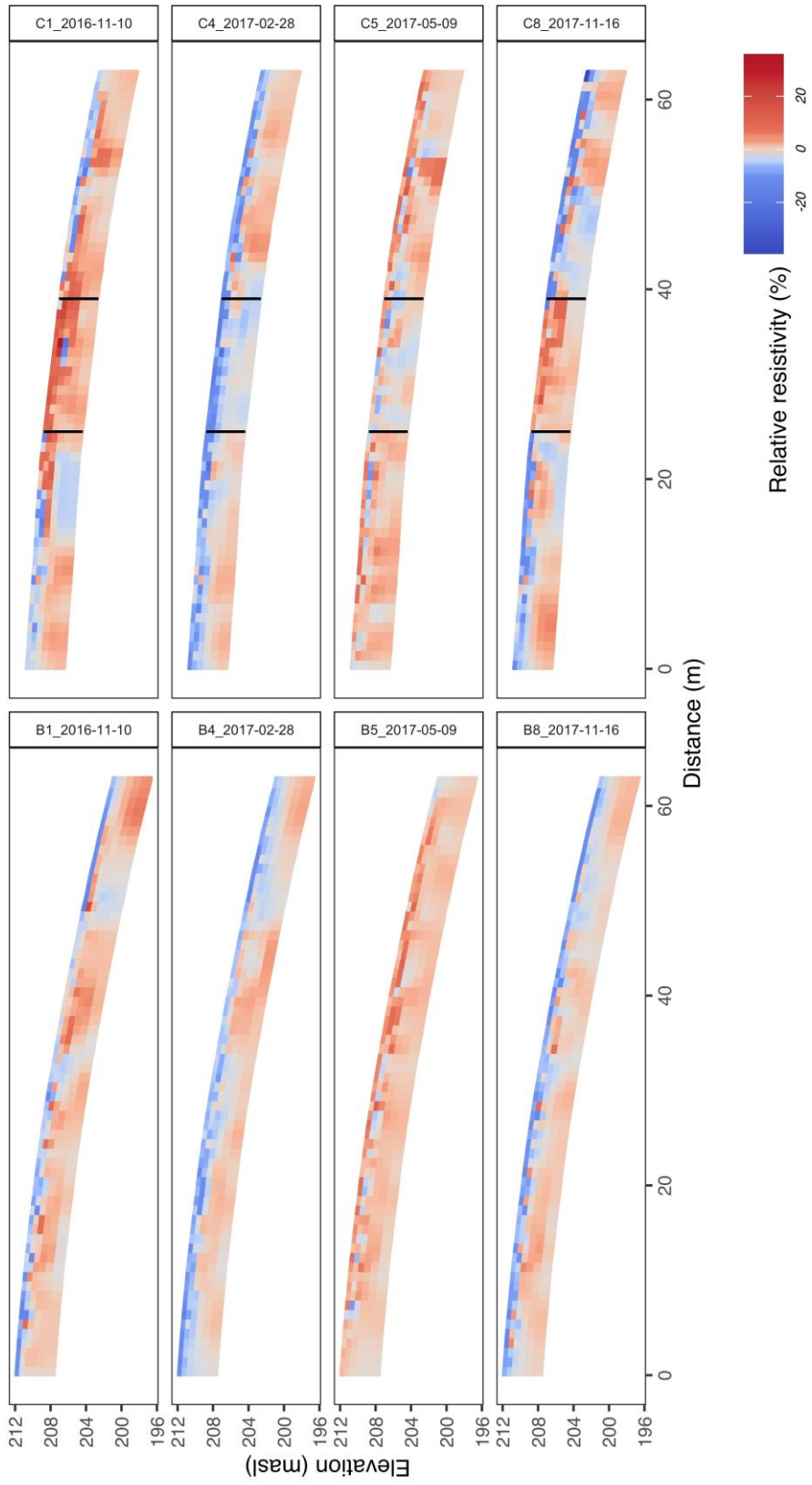


Figure D.2: Resistivity measurements in four surveys in different seasons relative to June 2017 survey. Black lines mark outside edges of forest strip.

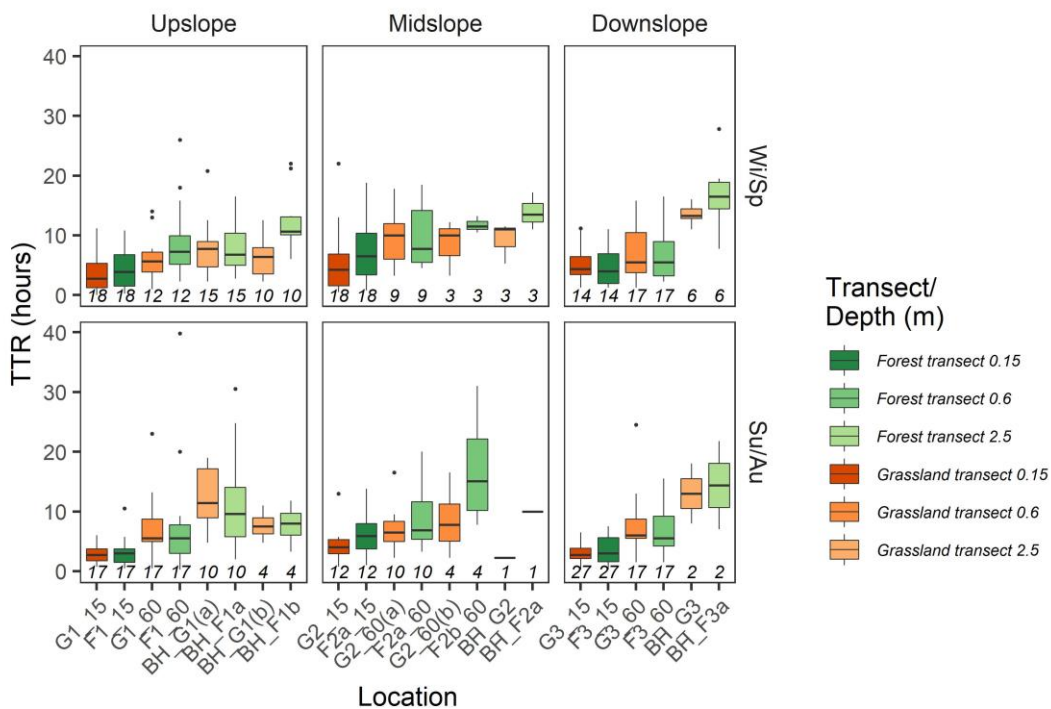


Figure D.3: Pairwise comparison of soil moisture and groundwater TTR between the two transects and between seasons for all rainfall events analysed (n=52). Pairs are filtered to contain only events when sensors on each transect responded and the event sample size for each pair is denoted in italics. The 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). Numbers in italics show the number of events in which sensor responded. Dots are outliers.

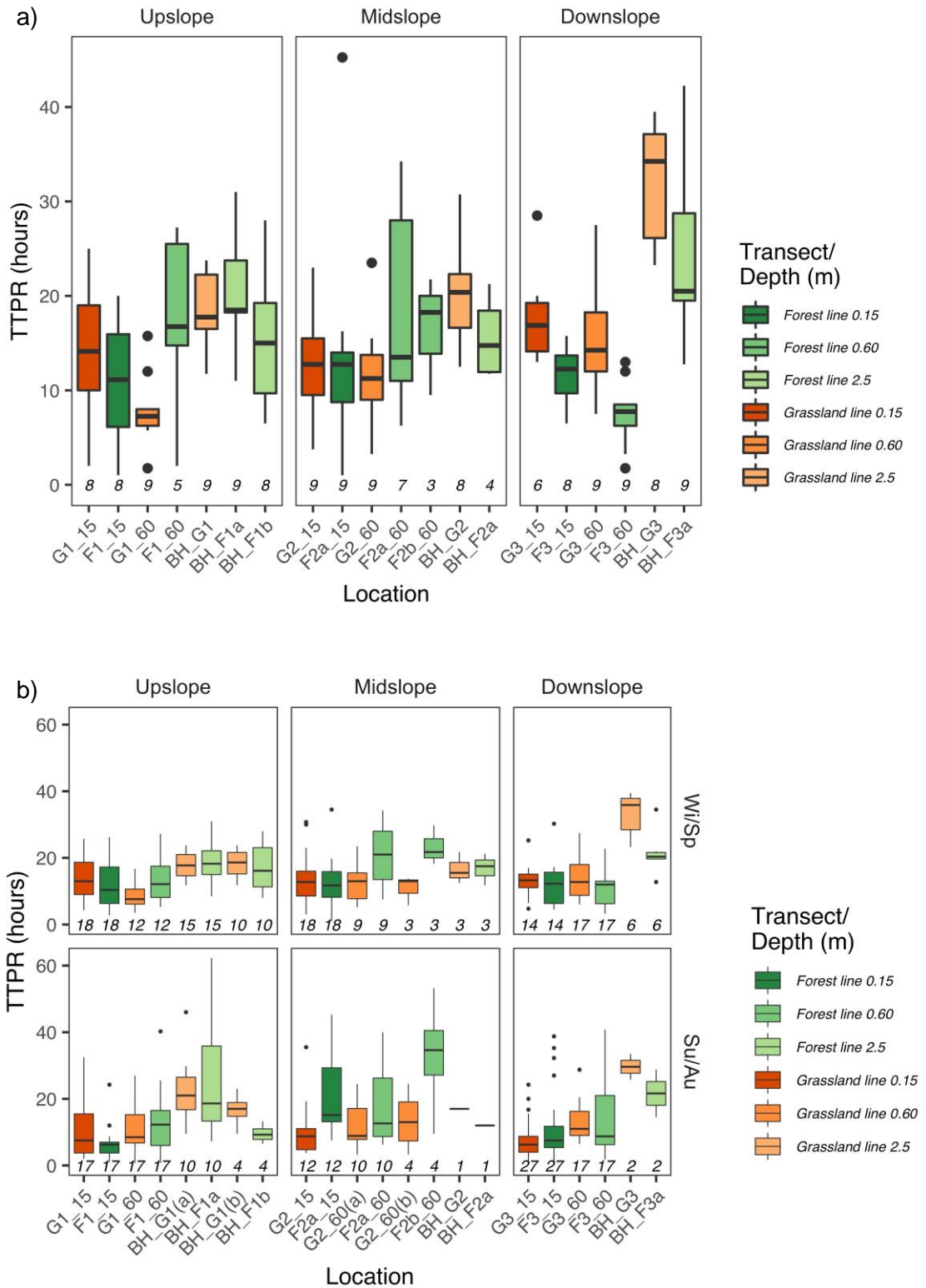


Figure D.4: a) Time to peak from the start of rainfall (TTPR) for the different domains and depths on the forest strip and grassland transects during nine rainfall events when the borehole downslope of the forest responded and the majority of the other soil moisture and groundwater sensors responded. b) Pairwise comparison of soil moisture and groundwater TTPR between the two transects and between seasons for

all events ($n=52$). Pairs are filtered to contain only events when sensors on each transect are active and the event sample size for each pair is denoted in italics. The 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 $1.5 * \text{the interquartile range (IQR)}$. Numbers in italics show the number of events in which sensor responded. Dots are outliers.

Table D.4: Spearman rank correlation coefficients between rainfall event characteristics / antecedent conditions and response metrics for all soil moisture sensors and for all piezometers across both the forest strip and grassland transects. Coefficients are shown for all events (n=52) and separately for events in Winter/Spring (Wi/Sp, n=20) and Summer/Autumn (Su/Au, n=32). * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$.

	Time to response from the start of rainfall (TTR, h)			Time to peak from start of rainfall (TTPR, h)			Maximum absolute rise (MR, m ³ m ⁻³ for soil moisture and m for groundwater level)		
	All	Wi/Sp	Su/Au	All	Wi/Sp	Su/Au	All	Wi/Sp	Su/Au
Soil moisture sensors									
Total rainfall (mm)	0.0286	-0.0043	0.136*	0.151***	0.232***	0.194**	0.295***	0.263***	0.271***
Intensity (mm h ⁻¹)	-0.375***	-0.402***	-0.375***	-0.437***	0.458***	-0.365***	0.225***	0.123	0.175**
AWI (mm)	0.0596	0.0152	0.0401	0.0121	-0.112	0.0771	0.0142	0.0768	-0.0376
AP28d (mm)	0.0306	0.081	0.0228	-0.000769	0.0627	0.0115	-0.132**	-0.225**	-0.0614
Piezometers	All	Wi/Sp	Su/Au	All	Wi/Sp	Su/Au	All	Wi/Sp	Su/Au
Total rainfall (mm)	0.0844	0.146	-0.0714	0.121	0.152	0.0501	0.325***	0.287*	0.336*
Intensity (mm h ⁻¹)	-0.262**	-0.337**	-0.396**	-0.309***	-0.294*	-0.434**	0.181*	0.241*	0.0416
AWI (mm)	0.0118	-0.0138	0.0465	-0.232*	-0.39***	-0.0314	-0.113	-0.169	0.0764
AP28d (mm)	0.00493	-0.0214	0.0614	-0.0755	-0.0677	-0.0686	0.00722	-0.141	0.250