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Title page
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ii.   Title
Using isotopes to understand the evolution of water ages in disturbed mixed land-use catchments
iii. Running head

EVOLUTION OF WATER AGES IN DISTURBED MIXED LAND-USE CATCHMENTS

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Using isotopes to understand the evolution of water ages in disturbed mixed land-use catchments

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Abstract

Tracer studies have been key to unravelling catchment hydrological processes, yet most insights have been gained in environments with relatively low human impact. We investigated the spatial variability of stream isotopes and water ages to infer dominant flow paths in a ~10 km^2 nested catchment in a disturbed, predominantly agricultural environment in Scotland. We collected long-term (>5 years) stable isotope data of precipitation, artificial drainage, and four streams with varying soil and land use types in their catchment areas. Using a gamma model, Mean Transit Times (MTTs) were then estimated in order to understand the spatial variability of controls on water ages. Despite contrasting catchment characteristics, we found that MTTs in the streams were generally very similar and short (<1 year). MTTs of water in artificial drains were even shorter, ranging between 1 to 10 months for a typical field drain and <0.5 to 1 month for a country road drain. At the catchment scale, lack of heterogeneity in the response could be explained by the extensive artificial surface and subsurface drainage, "short-circuiting" younger water to the streams during storms. Under such conditions, additional intense disturbance associated with highway construction during the study period had no major effect on the stream isotope dynamics. Supplementary short term (~ 14 months) sampling of mobile soil water in dominant soil-land use units also revealed that agricultural practices (ploughing of poorly draining soils and soil compaction due to grazing on freely draining soils) resulted in subtle MTT variations in soil water in the upper profile. Overall, the isotope dynamics and inferred MTTs suggest that the evolution of stream water ages in such a complex human-influenced environment are largely related to near-surface soil processes and the dominant soil management practices. This has direct implications for understanding and managing flood risk and contaminant transport in such environments.

1. Introduction

Catchment storage dynamics and flow path activation exert important controls on the transport of water and solutes to rivers (Rinaldo et al., 2015). Transit time distributions (TTDs) characterise the range of times that water molecules spend travelling through a catchment from entry as precipitation, and provide useful metrics that can capture these transport dynamics and lump catchment heterogeneities into a single function (Botter et al., 2010; Sprenger et al., 2019). The mean transit time (MTT) integrates this into a single index (Asano & Uchida, 2012; Klaus et al., 2015; McGuire et al., 2015) that has been used extensively to infer flow path characteristics and catchment mixing processes. Isotope time-series in rainfall – runoff transformations are routinely used to determine water age distributions and such studies have significantly improved the understanding of flow paths and helped quantify fluxes between surface and subsurface stores (Klaus & McDonnell, 2013). As such, this can help provide insights into potential impact of human activities on water partitioning in the landscape (Banks et al., 2011). Previous studies have shown that controls on water ages are complex and can depend on the internal structure of the catchment, and can be variously dominated by physiographical characteristics, including drainage density (Hrachowitz et al., 2010), topography (McGuire et al., 2005; Mosquera et al., 2016), soil cover (Hrachowitz et al., 2009), soil hydraulic properties (Heidbüchel et al., 2013; Muñoz-Villers et al., 2016), land cover (Ma & Yamanaka, 2016), and their spatial variation. However, several of these characteristics can be affected by land management (e.g. Soulsby et al., 2015), which makes MTT a useful indicator to evaluate land use impacts on hydrological processes (Jacobs et al., 2018).

However, so far, most catchment studies exploring water age have been conducted in relatively small (<10 km^2), long term observatories with limited human impact: far fewer are in catchments that have been disturbed though agricultural intensification and urban development (e.g. Brauer et al., 2018; Soulsby et al., 2014a). Nevertheless, as the human population continues to rise, increasing proportions of catchments are indeed being subject to more intensive disturbance and are undergoing major land use change (Mirus et al., 2017). In such landscapes, understanding the evolution of water age and the changing hydrological behaviour of the system can be challenging (Yu et al., 2019), as land management has the potential to induce complex scale-dependent change (Thompson et al., 2013). Therefore, it is important to consider disturbed catchments in water age studies, as the resulting insights into the effects on water and contaminant transport can have important implications for management decisions in an era of unprecedented environmental change. (Hrachowitz et al., 2016; Savenije et al., 2014).

Land management can vary widely across catchments and can affect water fluxes in multiple ways e.g. affecting recharge and streamflow, sediment and nutrient export (Bai et al., 2019; Russell et al. , 2017; Scanlon et al., 2007). Intensive agriculture for food production covers approximately 40% of the Earth's land surface (Foley et al., 2005) and has been shown to be a major driver of many alterations in catchment hydrological function. These include land degradation and soil compaction (Alaoui et al., 2018) which accelerates the delivery of water (O'Connell et al., 2007), solutes and sediments (Russell et al., 2017) to streams, having direct implications for flooding and water quality issues. In addition, artificial drainage, has been shown to have a large impact on runoff, water storage and water quality by "short-circuiting" hydrological flow paths to take younger water to stream courses (Hallett et al., 2016). Artificial drainage affects one third of the globe's land surface where natural drainage limits agricultural production (Blann et al., 2009) and 34% of NW Europe's farmland (Gramlich et al., 2018). A further major land use with profound effects on the way water is stored and flows through landscapes is urbanization and road infra-structure which increases impermeable surface cover. This typically increases runoff and shortens hydrological travel times (Soulsby et al., 2015; Soulsby et al., 2014a; Yu et al., 2019).

Key hydrological processes that partition water into "green fluxes" that sustain plant growth (evaporation and transpiration) and "blue fluxes" that control groundwater recharge and runoff generation, occur mostly in the upper portions of the soil (Geris et al., 2015a; Rinderer & Seibert, 2012; Vereecken et al., 2015). Therefore, to understand the hydrological functioning of complex landscapes where modern land use practices overlay historic management, the upper soil is an obvious focus for study (Ebel & Mirus, 2014; Falkenmark et al., 2019). While agricultural impacts on soil properties and water movement have been extensively reported (Babin et al., 2019; Keller et al., 2019; Pulido et al., 2018; Xie et al., 2019), much less is known about how this propagates to impacting water ages (Wang et al., 2012; Yang et al., 2018).

Here, we carried out an extensive isotope study in an agricultural catchment in NE Scotland to explore how water age evolved in a heavily disturbed landscape. In addition to natural variability in soil cover, the catchment includes a wide range of farming practices, as well as significant recent development through construction of a highway, termed in the UK as a dual carriage way. We adopted a nested catchment approach to isotope sampling, combined with detailed soil water experiments in key agricultural soil-land use units. This allowed us to assess the integrated effect of spatially distributed landscape heterogeneities and hydroclimatic conditions on isotope dynamics. We used these data to

derive TTDs using simple convolution integral models (Hrachowitz et al., 2009a). Despite the relatively simplistic assumption of stationarity and potential issues with parameter identifiability (Stewart et al., 2010), recent studies (e.g. Stockinger et al., 2016) have shown that in responsive catchments, they can be applied to long-term data sets to provide insights into TTDs that are equivalent to those derived from more complex non-stationary approaches (Birkel et al., 2016). Whilst the main aim of the study was to better understand the evolution of water ages in a disturbed agricultural catchment, our specific objectives were to: (i) assess the spatial distribution of water ages in the drainage network using relatively long term (>5 year) stable water isotope records, (ii) examine additional short-term impacts of recent land use change related to the road construction of a highway as a new city bypass; and (iii) identify the catchment sources of younger water in the main soil-land use units.

2. Methodology

2.1 Study site description

The study site was the Elsick Burn catchment (~ 10 km^2), in NE Scotland, UK (Figure 1; Table 1). The stream drains a gently sloping landscape (90 to 165 m.a.s.l.) mainly covered by arable crops and grazed grassland. The stream network comprises the Elsick Burn (MAIN; 7.1 km^2) and its major tributary (TRIB; 2.8 km^2) (Figure 1, Table 1), both of which are subjected to agricultural drainage. Mean annual precipitation is ~ 800 mm and potential evapotranspiration PET ~ 350 mm (Met Office, 2019b), calculated as the average of the monthly Thornthwaite PET of the two nearest (<25 km away) weather stations with long-term records (1981-2010); Dyce Aberdeen Airport and Inverbervie. Precipitation lacks strong seasonality, though the winter months are generally wettest. In contrast, PET ranges between 4 mm d^{-1} in summer and well below 1 mm d^{-1} in winter.

The metamorphic bedrock is overlain by glacial drift and relatively thin soils (0-1 m) (British Geological Survey, 2019) (Figure 1d). The Soil Survey of Scotland (1970-1987) have identified the main soil types as poorly drained gleys (Gleysols, IUSS, 2015), which cover approximately 68% of catchment mainly in lower areas fringing the stream network (Figure 1 b). The gleys have been systematically and intensively drained, with tile drains below the plough layer where rotational crops, such as wheat, barley and rape seed are cultivated (Lilly et al., 2012). More freely draining podzols (covering 17% of the catchment) are found in the headwaters of the MAIN catchment and predominantly in the SE section near the outlet. The podzols typically support either grazed grassland or rotational crops. In the NE headwaters of the catchment there are less intensely managed peats and peaty podzols (Histosols and histic Podzols, IUSS, 2015), associated with more natural woodland and moorland

cover. These are characterised by an organic rich topsoil and are typically not artificially drained (Table 1). The nature of agricultural management results in year-to-year changes in cropped and grazed land; though the proportions described in Table 1 are relevant for the duration of the study period and based on the Land cover 2015 map of the region (Rowland et al., 2017), satellite images and field observations. The suburban cover in Elsick Burn is relatively low, 4% in MAIN and 2% in TRIB, although 3% of it in MAIN is associated with new highway development which started in 2015. The 26m wide highway, consisting of a dual carriageway, runs for ~2.5km in the west of the catchment. The disturbance corridor was around 50m wide for construction. During construction and following completion, surface runoff from the highway was managed via a series of constructed wetlands and soakaways, with no managed diversion of water directly into the stream channel network.

2.2 Data collection and analyses

2.2.1. Long term monitoring

Drainage network isotope data (since January 2014) and hydrometric variables (locally since 2015) were collected until March 2019, so that the total long-term monitoring period is up to 5 years and 3 months. Precipitation was measured using an *Environmental Measurements* tipping bucket rain gauge (ARG100 gauge) in the MAIN catchment (Figure 1; latitude 57°02'25.58''N, longitude 2°11'18.84''W, elevation= 95 m.a.s.l.). At the same location, meteorological variables were measured every 30 minutes to calculate potential evapotranspiration (PET) using the Penman - Monteith method. We deployed a bespoke automatic weather station built by *EML* containing an anemometer and a net radiometer connected to a CR200 logger. Temperature, barometric pressure and relative humidity were recorded by the coupled Cosmic Ray Sensor (CRS) station (CRS-1000/B, Hydroinnova, New Mexico). Occasional precipitation data gaps were filled using distance weighted interpolation from 14 neighbouring gauges in the national monitoring network (Centre for Environmental Data Analysis, Met Office, 2019b) within a 3 to 35 km radius of the Elsick catchment. Site corrected data from Dyce Aberdeen Airport were used to fill gaps in PET estimates (Met Office, 2019b). Water levels (TD-Diver, Van Essen Instruments) were recorded at 15 min intervals at the outlets of the MAIN and TRIB catchments. Stream discharge for both sites was calculated using field-derived rating curves fitted for each stream (R^2=0.98 for MAIN and R^2=0.96 for TRIB, respectively). For the purpose of catchment water balance calculations, discharge for the Elsick Burn outlet is presented as the sum of observations at MAIN and TRIB. Also, at the site of the meteorological station, daily field-average soil water content SWC (Figure 2) was obtained since November 2015 using the CRS sensor (Figure 1 A, B), calibrated for site-specific conditions following Evans et al. (2016). The CRS footprint (approximately 7 ha and with

an average sensing depth of 13 cm) covers three fields representative for the most common soil-land use units found in the catchment: Gley-Wheat and Gley-Barley (75% of footprint) and Podzols-Pasture (25%). All precipitation, PET and SWC data were aggregated or averaged to daily timeseries for the purpose of the current study, where they mainly provide the context of hydroclimatological conditions during the isotope sampling campaigns.

Regular weekly to fortnightly sampling of precipitation and streams for stable water isotopes was carried out for the full duration (~ 5 years) of the monitoring period. Where possible, we also targeted the major rainfall events and extreme dry periods to ensure sampling captured the full range of hydroclimatological conditions. Bulk precipitation was sampled at the CRS – meteorological - station. The rationale for the stream network sampling design included coverage of the spatial variability in soil, land use and management found within the catchment (see Figure 1 and Table 1). In addition to the four nested streamflow sites, we also sampled the piped outflow of a typical agricultural field drain, close to site MAIN, as well as an existing minor country road drain near site TRIBa (Figure 1). The drains only flowed in wetter conditions, and so were sampled on approximately 35% of field visits.

2.2.2. Short-term monitoring

To understand the age distribution of younger waters in the main soil-land use units of the catchment (Gley-Wheat, Gley-Barley and Podzol-Pasture), we monitored isotope dynamics weekly in soil water in the three most representative fields (Figure 1 B) between January 2018 and March 2019. During this more intense sampling period, the resolution of bulk precipitation was increased to daily sampling using an automatic sampler (ISCO 3700, Teledyne ISCO, Lincoln, USA). Mobile soil pore water, held at relatively low tensions (0 to - 50 kPa), was collected at 0.1, 0.3 and 0.5 m depth using MacroRhizon samplers (Rhizosphere Research products, (Di Bonito et al., 2008)) in each of these units. The means of duplicate samples are presented for each soil water sampling point. As a result of exceptionally dry conditions during the summer of 2018, samples of mobile soil water and drains occasionally could not be obtained. In addition to the CRS SWC estimates, topsoil (upper 6 cm) volumetric SWC spot measurements (ML2 soil moisture sensor, Delta T Devices Ltd.) were taken on each sampling day for comparison and to explore any variability between fields. Topsoil SWC was estimated by an average of ten replicate measurements randomly distributed within each field on each sampling day.

2.2.3. Laboratory and data analyses of stable water isotopes

All water samples were analysed for their stable water isotope ratios (δ^2H and $\delta^{18}O$) using a Los Gatos IWA 45E laser spectrometer (Los Gatos Research, Inc., San Jose, USA) following standard protocols, by analysing a reference sample every three water samples. The data are provided in the δ-notation [‰]

relative to the Vienna Standard Mean Ocean Water (VMOW). The precision of the measurements is ± 0.6‰ for δ^2H and ± 0.2‰ for δ^{18}O. The local meteoric water line (LMWL) was calculated using bulk and daily precipitation samples collected during the full study period. Precipitation amount-weighted mean δ^2H for the study period was also calculated for comparison. For all stream, drain and soil water samples, we calculated deuterium excess (d-excess) following (Dansgaards, 1964) to identify possible effects of evaporative fractionation. To explore short-term impacts of recent land use change related to the highway development, we compared the deuterium isotope dynamics and d-excess data before (~ 2 years) and after (~3.5 years) construction was initiated during September 2015. The construction took place upstream of sites MAIN and MAINa; detection of any impacts of the construction, not associated with the natural variability in hydroclimatological conditions, would rely on before vs after differences in isotopic signatures at these sites as compared to sites TRIB and TRIBa for the same periods.

2.2.4. Transit time modelling and young water fraction estimation

To assess the relative differences between water age evolutions at different sites we estimated mean transit times (MTT) based on the widely used two-parameter gamma distribution model as described by Kirchner et al. (2000). The model relates variations in weighted precipitation tracer inputs (i.e. in δ^2H or δ^{18}O) to those observed in output waters (e.g. in streams, drains or soils) using a time-invariant transfer function. Despite its simplicity, the gamma model gives a suitable representation of advection-dispersion processes and has consistently been shown to perform as well as other, more complex TTDs when long time series are available (Birkel et al., 2012; Hrachowitz, et al., 2009a; Hrachowitz et al., 2010; Seeger & Weiler, 2014; Tetzlaff et al., 2014). However, given the potential relevance of fast flow paths in this heterogeneous disturbed environment, MTT analyses were complemented with estimates of young water fractions (F_{yw}) (Kirchner, 2016a) for the stream and artificial drains for the long-term period. By quantifying the contribution of young water (i.e. ~<60 days in age) to the outputs gives an alternative metric that overcomes the potential problem of MTTs being uncertain due to the influence of the heavy tailing of older water in a gamma distribution (von Freyberg et al., 2018).

MTTs were calculated as the product of the shape parameter α (-) and scale parameter β (days) of the gamma function (MTT= α*β). For the initial parameter range, we used an upper limit of 2000 days for β, as the application of stable water isotopes for detecting travel times is limited to ~5 years (Stewart et al., 2010).   The upper limit for α was set to 1, whereby α=1 is equivalent to an exponential

distribution. Previous studies in a range of catchments have shown that α remains close to 0.5 for advective-dispersive systems (Berghuijs & Kirchner, 2017; Heidbüchel et al., 2012; Hrachowitz et al., 2010), which reflects a pronounced initial tracer breakthrough peak but long tail in the TTD.

For precipitation input, we created a ~7.5-year daily isotope precipitation timeseries (period 1 October 2011 to 11 March 2019). Precipitation data for the "warm-up" period (prior to the monitoring start date at Elsick) were based on daily rainfall isotope data from two nearby catchments (Burn of Bennie (Soulsby et al., 2015) and the Bruntland Burn (Benettin et al., 2017), 20 and 70 km west of Elsick, respectively). Distance corrections were made based on relationships between data from these sites with the Elsick ~4-year bulk weekly and ~1-year daily isotope data. These relationships were also used to infer daily timeseries from the bulk Elsick precipitation samples for the period prior to December 2017. Daily precipitation δ^2H data from Burn of Bennie for the period 1 October 2011 to 10 March 2016 was directly used as modelling input. We investigated the relationship between bulk precipitation samples from Elsick and Burn of Bennie for the period 6 June 2014 to 20 October 2016, expressed as the proportion between δ^2H precipitation Burn of Bennie / δ^2H precipitation Elsick. This was on average 1.1 ± 0.5 (R^2=0.43), being 1 a perfect match of the δ^2H precipitation at both sites. We used this relationship to derive the daily precipitation input for Elsick. The same procedure was applied for the period 10 March 2016 – 10 January 2018 (22 months) where we used precipitation δ^2H data from long-term observatory Bruntland Burn in the Scottish Highlands (70 km away) (R^2=0.54).

We ran the model using a Monte Carlo approach, whereby 10,000 parameter sets were randomly chosen within the initially defined parameter ranges (Table 3). For the long-term dataset, we accounted for parameter uncertainty by choosing the best 500 parameter sets for each subcatchment and artificial drain using the Kling-Gupta efficiency [-] (KGE), (Gupta et al., 2009). For the shorter but more intense sampling period, we used a one-year "warm-up" period and selected the best 100 runs. To further evaluate model performance, we also provided the root-mean-square error (RMSE) as an alternative measure of goodness of fit. As the relative results of the transit time analysis between sites were correlated i.e. no different using either δ^2H or δ^{18}O, here we only report the outcomes of the analyses using δ^2H due its greater analytical precision. The uncertainty in the young water fraction estimates are expressed as standard error, using iteratively re-weighted least squares (von Freyberg et al., 2018).

3. Results

3.1 Long term hydro-climatological conditions and isotope dynamics

The study period spanned a wide range of hydrometeorological conditions, including two extreme precipitation events (a prolonged intense >100 year return period rainfall starting in December 2015 and rain on snow in March 2018) and an unusually dry summer in 2018. Overall, the first three complete hydrological years (October-September) were wetter (precipitation 908, 925, 947 mm y^{-1} for 2014-15, 2015-16, 2016-17, respectively) and the last drier than average (707 mm y^{-1} for 2017-18). PET was fairly similar across the years (502, 456, 471 and 458 mm y^{-1}, respectively), although the actual evapotranspiration for 2017-18 was likely much lower than for the other years due to diminished soil water availability during the prolonged dry conditions. Estimated stream discharge at the catchment outlet was greatest for hydrological year 2015-16 (625 mm y^{-1}) which related to the large flood events that winter. It was followed by a year of relatively lower stream output (435 mm y^{-1}). For hydrological year 2017-2018, annual discharge was lowest at 403 mm y^{-1}. Volumetric SWC, monitored at the CRS-met. station across the three agricultural fields, was on average 0.37 m^3 m^{-3} (median 0.38) during the period November 2015- March 2019, ranging from 0.14 during the dry period in 2018 to saturated conditions at 0.59 during the extreme rainfall events (Figure 2).

Isotopic values for precipitation plotted slightly below the global meteoric water line (GMWL), resulting in a local meteoric water line (LMWL) with a slope of 7.07 and an intercept of 2.85 (Figure 3). The δ^2H values of precipitation samples (n=279) ranged from -120‰ in winter to -11.4 ‰ in the summer months (mean -47.9 ‰, weighted mean -55.8‰; Table 2). Compared to precipitation, the isotopic variability in the streams was strongly damped, except during bigger events, particularly noticeable during those associated with more depleted winter precipitation inputs (Figures 2&4). Stream isotope data revealed that all means reflect that of precipitation, and all d-excess data were close to 10, indicating little evaporative fractionation effects. Although differences between streams were subtle (Table 2), MAINa displayed most variability (CV = 0.13) and TRIBa the least (CV = 0.08). The drains were on average more enriched than the streams. The isotopic variations in the field drain and especially the country road drain were more similar to precipitation (Table 2), which is consistent with their function to rapidly route unmixed water to streams during high precipitation events and particularly during periods of high soil wetness. Nevertheless, of the water sources sampled, the country road drain showed most evidence of evaporative fractionation effects, albeit limited, as indicated by the flatter evaporation water line slope (Figure 3) and lowest d-excess mean value (Table 2).

3.2 Water age evolution across the drainage network

The gamma model results showed a good fit in simulating isotope variations in both the streams and the drains (KGE ranging between 0.77 to 0.99; Table 3). RMSE of the long-term simulations were modest relative to the variability and fairly similar for the streams and the field drain. The lowest RMSE was obtained in the TRIBa and the highest in the country road drain, being 4 ‰ and 11.4 ‰ on average, respectively. The simulations captured the variability of the δ^2H signatures in the streams during the study period including the major precipitation events, e.g. during December 2015-January 2016, which were characterised by a large isotopic depletion (Figure 4). During drier periods, the model generally over-estimated more enriched values than observed. Posterior parameter ranges were reasonably well constrained. For example, the mean alpha parameter of the 500 best simulations was always <0.5 and the beta parameter was identifiable.

Overall, all sites had relatively short MTTs (< 1 year), indicating a predominance of younger water in the streams. Additionally, the MTT results between stream water sites varied relatively little, having the same order of magnitude. Nevertheless, while the median and range of modelled MTTs in the MAIN and TRIB streams were similar, larger differences were found between their respective tributaries; the MTT of TRIBa (~ one year) was around twice as long as that of MAINa (< 6 months) (Table 3). These observations were further supported by the catchments F_{yw} estimates. The MTT of MAIN increased and that of TRIB decreased with catchment scale. The drain features exhibited even shorter travel times than the streams, with MTTs ranging between 1 month and less than 1 year (mean < 6 months) for the field drain and in the order of few days to <1 month (mean ~2 weeks) for the country road drain. The F_{yw} in Elsick were strongly related to the MTTs (R^2=0.91), being therefore comparable for MAIN and TRIB, 0.12 and 0.10, respectively. Lowest F_{yw} were obtained in TRIBa (0.07 on average) and doubling in MAINa (0.15). The field and country road drain displayed the largest values of F_{yw} in Elsick, 0.20 and 0.34 respectively (Table 3). The F_{yw} in Elsick were strongly related to the MTTs (R^2=0.91), being comparable for MAIN and TRIB at 0.12 and 0.10, respectively. Lowest F_{yw} were obtained in TRIBa (0.07 on average) and twice as much in MAINa (0.15). The field and country road drain displayed the largest values of F_{yw}, in Elsick, 0.20 and 0.34 respectively (Table 3). Given the weekly sampling, these are likely to be conservative estimates of the F_{yw}.

We found no clear, or statistically significant, change in the isotopic signals that could be related to impacts of the highway construction (Figure 5). If any, differences between 'before' and 'after' periods were more similar for catchments that were affected (MAINa and MAIN) and those that were not (TRIB and TRIBa).

3.3 Soil and management controls on water age evolutions

The shorter, more intense sampling period between January 2018 and March 2019 experienced some of the most extreme hydrometeorological conditions observed, including the large rain on snowmelt event in March 2018, followed by a prolonged dry summer which were reflected in both discharge amount and mean SWC (Fig 2 and 6). Topsoil SWC across all individual land use-soil units were close to saturation in the winter months (maximum values for gleys 0.49-0.50 m^3 m^{-3} and 0.56 m^3 m^{-3} for the podzols). Minimum values were measured over the summer (down to 0.08-0.11 m^3 m^{-3} in the Gley units and 0.13 m^3 m^{-3} in the Podzol - Pasture) with consequent rewetting from September onwards (Fig 6 b). While similar SWC values were observed in the topsoil of the Gley units, the Podzol - Pasture was consistently wetter. SWC differences between land use-soil units were generally larger during the drier months.

The spread of precipitation deuterium values in this shorter period was largely comparable with the long-term record (Table 4), but average isotopic values were enriched by a few per mille (mean -46.6‰ and weighted mean -51.5‰) compared with the long-term and variations in the streams generally lower (cf. Figure 4). Correspondingly, the estimated MTTs for streams and drains over this shorter period were considerably longer than over 5 years (Table 5). Nevertheless, the same relative differences between the four stream sites were still evident, with MAINa showing the most variability and shortest median MTT (<6 months) and TRIBa exhibiting the least variability and longest median MTT (>3 years). The simulated MTT for MAIN and TRIB was approximately 1.5-2 years.

Compared to the precipitation input, the isotopic signal in all soil units was again damped, but less so than for the streams (Table 4). Figure 3 shows that there is no evidence for strong evaporative fractionation in the sampled mobile soil water (slope of 6.27 for soil water as opposed to 7.07 for precipitation). Although inter-site differences between soil isotopes were generally small, the dynamics in isotopes for the two Gley - units (Wheat and Barley) were most similar and both distinctly different to those observed for the Podzol-Pasture unit. Across all depths, soil water in the podzol was more depleted. Variability in isotopic values was highest in the Gley-Barley unit for the topsoil (at 0.1 m depth) and in the podzol at greater depth (0.5 m depth) (Table 4; Figure 6). These temporal changes were fairly similar for all soil units and depths. During the dry period soil water gradually became more enriched and the lack of fractionation implied that this was due to inputs of enriched summer precipitation. Isotopic depletion of soil water was evident from the late autumn onwards, as rainfall composition changed (Figure 6). However, there appeared to be a delay in the pattern of depletion

for the podzol at 0.5 m depth. This layer also exhibited the most extreme response to the large rain on snowmelt event in March 2018, which could indicate differences in the governing soil hydrological flow paths from the other soil units and depths.

The isotope dynamics during this period were used to estimate the MTT in the different soil units, to compare to stream and artificial drainage waters using the gamma model approach. The MTT and posterior parameter ranges for the best 100 runs for soils, streams and drains are summarised in Table 5. The gamma model was able to simulate MTT in most soil units and layers, however the model was not as well-constrained as for the long-term stream and drain water analysis. The KGE for the soil ranged between 0.68 and 0.99, except for Podzol - Pasture 0.3 m (median KGE=-0.16), largely reflecting the extremely flat deuterium signal in that layer, compounded by the relatively low sample size.

MTT analyses in the soils again, indicated short travel times and relatively quick flow pathways. In the gleys, the topsoil exhibited the shortest MTTs (<2 months on average for gley-wheat and ~1 month for Gley-Barley), indicating that water in topsoil moves rapidly, via macropores to deeper layers. Longer MTTs in the layers below the root-zone, (at 0.3 and 0.5 m depth) ranged between 87 and 212 days which would be consistent with gleying and reduced permeability below the plough layer slowing percolation and facilitating more mixing with stored pre-event water. In contrast, the Podzol-Pasture unit revealed decreasing MTTs with depth (Table 5). The MTT values of the central (0.3 m depth) layer were highest in the gleys profiles and for the podzol the lowest, though the model performance was poorer here too. Apart from the topsoil (~3 months), MTTs in the deepest layers (at 0.5 m depth) were much shorter (< 1 month) for the podzols than for the gleys (3 to 5 months).

4. Discussion

4.1 Water age evolution in managed landscapes

In this study we evaluated the evolution of MTTs in an intensely managed agricultural landscape using long-term water isotope data in a nested stream network with varying proportions of contrasting soil-land use units. Although many factors are known to control the evolution of water ages (McGuire & McDonnell, 2006; Sprenger et al., 2019), previous work across Scotland has shown that there is a strong correlation with the coverage of soils that are associated with fast hydrological responses (e.g. Hrachowitz et al., 2009b). To some extent, this might explain the subtle differences we found between the different subcatchments and soil types (schematically represented in Figure 7). For example, the catchment with the high percentage of unmanaged soils (TRIBa) also revealed the longest MTT. Similarly, simulated MTTs for the soil units showed much shorter time scales for more freely draining

podzols (~1 month) than poorly draining gleys (~6 months) in the deeper subsurface. Again this is consistent with results from across a natural soil catena found elsewhere in Scotland (Tetzlaff et al., 2014) and from shallow depths at different soil types in Luxembourg (Sprenger et al., 2016).

Nevertheless, the main finding of our study is that the estimated MTTs across the stream network were similar and short. When compared to what may be expected based on the proportion of soil type alone, the MTT results we found here are fairly similar to catchments predominantly covered by soils with responsive hydrological properties (e.g. 0.5 to 1.2 times the MTT found in gley-dominated Loch Ard catchment), whilst catchments dominated by freely-draining podzols are 4-8 times longer, as reported in Hrachowitz et al., 2009a. Additionally, no relationship was observed between MTT and catchment size, suggesting that effects other than scale are important for MTT differences. The most obvious explanation for the lack of heterogeneity in MTT is the effect of the well-maintained network of artificial drains in Elsick Burn. Drainage density, usually related to natural factors including soil type, geology and precipitation (Kaandorp et al., 2018), reflects the degree of connectivity between the landscape and the channel network. Previous studies in more natural environments have related more dense channel networks to shorter travel times (Klaus et al., 2015b). In an intensively managed landscape like Elsick, connectivity is additionally enhanced during wet conditions via the activation of artificial subsurface drains (Brauer et al., 2018; Orlowski et al., 2014). The short MTT results of the sampled drains in Elsick support this. Additionally, these short MTTs are probably a reflection of the small drainage areas and short flow paths these drainage features are engineered to facilitate. Moreover, the greater similarity between the isotopic characteristics and ranges of estimated F_{yw} of the agricultural field drain and the more intensely farmed catchments (e.g. MAINa) strongly indicate that artificial drains represent a dominant source of storm runoff in Elsick. Conversely, where soils have less artificial subsurface drainage, such as in TRIBa, the lowest drainage density is consistent with the longer MTT.

A second explanation for the short overall MTTs is that the soils in the Elsick catchment are relatively shallow and underlain by relatively impermeable glacial drift. These conditions have been previously shown to result naturally in short travel times (Pfister et al., 2017). Other reasons may include different aspects of agricultural management. For example, soil compaction and land degradation are typically associated with increased overland flow and faster delivery of water to the streams (Hallett et al., 2016; O'Connell et al., 2007), thus shortening travel times. Within the upper part of the soil itself, we found that the podzol, which was relatively compacted due to grazing (Singleton et al., 2000) and as a consequence with increased water holding capacity (Hansson et al., 2019), had a longer MTT (~ 3

months) than the gley soils (~1 month), which were regularly ploughed. In agreement, the measured topsoil SWC in the cropped fields (with gleys) was always lower than in the pasture (with podzols). On the contrary, the effects of compaction were not obvious in deeper soil layers in the podzols. This points to more subtle impacts of land management on MTTs.

Given the complexity of how agricultural landscapes vary in space and time, the controls on MTTs are multi-faceted, though increased sub-surface drainage is likely dominant. However, the role of the artificial drainage is non-stationary and is most effective in wet conditions. The more intense sampling campaign of soil waters in 2018 coincided with an unusually prolonged, dry period. In such conditions, the effect of the artificial drains on travel times would be expected to decrease, as they activated less regularly so that the delivery of younger water to the streams decreases. This is consistent with the longer MTT estimates for the drains and streams during this period, which also reflects the less frequent and intense rainfall events (Wilusz et al., 2017). Moreover, the use of a shorter observation period as an input which also coincides with less hydrometeorological variability captured also explains the relatively shorter MTTs for streams and drains. This increased the influences of soil properties and vegetation characteristics on water flow paths and ages (Geris et al., 2015b); such prolonged dry periods are likely to become more common in the future with dry summers forecast under climate change (Chan et al., 2018).

However, climate change scenarios for the region also suggest wetter, more intense winter rainfall leading to greater drainflow and accelerated pollutant transport (Capell et al., 2014; Lowe et al., 2018). Greater variability in the isotopic signatures in both field and country road drains reflects the fact that these features rapidly evacuate water laterally from relatively small areas *i.e.* a single field or a road segment, and thus reduce the opportunity for sub-surface mixing which would dampen the isotope signal. The more enriched δ^2H signals observed in the field drain compared to the stream waters (*e.g.* MAIN catchment) likely reflects processes taking place within the upper soil profile, including lower mixing volumes for incoming summer precipitation, preferential water uptake from plants and evaporative fractionation in the topsoil (Oerter & Bowen, 2017; Sprenger et al., 2016). Also, drain water has limited groundwater influence; as deeper groundwater is preferentially recharged by depleted winter precipitation, the lack of mixing with deeper groundwater sources would also result in more enriched drain water (Scheliga et al., 2017). The country road drain showed a greater effect of evaporative fractionation compared to other water sources in the catchment, though the effect was limited. These drainage features at this location have traditional drain design, where overland flow on the roads is directed straight into road-side ditches and the stream network. While the short

MTTs reveal that this involves mostly recent rainfall, in a wetter environment, surface ponding and slow drainage of excess precipitation occurs. It is therefore likely that at these times waters sources are subject to open water evaporation allowing fractionation signals to develop (Cappa et al., 2003).

In general, the effect of drainage management in homogenising the responses of the nested catchments is summarised in Figure 7. As a result of the impact of the drainage network, together with local mitigation measures (e.g. soakaways and retention ponds), any hydrological effect of the major disturbance of the highway construction was not obvious from the hydrometric or isotope data. Although the new highway might be expected to accelerate water fluxes through the landscape and increase runoff coefficients (Nardi et al., 2018) or affect stream water ages, there was no evidence that it did so. Using a similar isotope-based modelling approach, Soulsby et al. (2014b) reported parameter ranges and MTTs of the same order of magnitude in a network of urbanised catchments in Scotland ~20km from Elsick, where urban storm drains facilitated rapid transport of storm runoff, giving similarly low MTTs and alpha parameter values <0.5. The urban catchments have broadly similar soil characteristics (of gleys and podzols) suggesting that drainage of the farmland-dominated catchments at Elsick produced a similar effect on isotope dynamics and catchment TTDs to that caused by urban development. Consequently, despite the obvious disturbance of the new highway, the existing effects of drainage, together with small area of the catchment affected, and – probably most importantly – storm control measures implemented appear to have mitigated detectable impacts on water ages.

4.2 Limitations

We used a relatively long (> 5 years) isotopic time series in this study, albeit at a relatively coarse (~weekly) resolution to characterise water ages. It is well known that travel time distributions are non-stationary, and vary with hydroclimatological conditions, whereby wetter conditions (e.g. annually, seasonally or even on an event-basis) are typically associated with shorter MTTs and more younger water (Harman, 2015; Peralta-Tapia et al., 2016; Segura et al., 2012) and larger young water fractions (Remondi et al., 2018; Bansah & Ali, 2019). Moreover, despite our efforts to sample higher flows, the relatively coarse sampling resolution could be under-representing some important short term processes (Aubert & Breuer, 2016; Birkel et al., 2012; Cayuela et al., 2018), especially as MTTs are short (Timbe et al., 2015). For the same reason, any short-term perturbations related to the highway construction at the scale of individual storm events may be under-represented. The non-stationary nature of the MTTs was shown during the more intensive sampling during in the drier latter part of the study, where MTT predictions of streams were longer than for the five-year period, though

the relative differences were similar. Nevertheless, whilst the time-invariant approach used can be viewed as simplistic compared to non-stationary approaches (e.g. Benettin et al., 2015; Davies et al., 2013; Heidbüchel et al., 2012; Kirchner, 2016b; Rinaldo et al., 2015) over the 5 year period, the fitted models likely give a constrained average TTD for each site that compares to what would be derived by non-stationary approaches (van der Velde et al., 2015), especially given the relatively short MTTs (Birkel et al., 2016). Prolonged daily to hourly sampling resolutions are currently becoming more widely available (*e.g.* von Freyberg et al. 2017), but these are usually still limited to shorter periods of time (i.e. weeks or months). Hence there is still a trade-off between sampling frequency and length (Penna et al., 2018). However, it is clear that event sampling will be an important next step in the Elsick catchment to better constrain the younger water fraction, which is likely under-estimated here.

Finally, caution is advised when comparing the MTTs of mobile soil waters, drains and the stream waters given the different sampling periods, and the fact that the drains only flowed for ~35% of the time during the wetter periods. Drain activation is wetness threshold-dependent, while our sampling campaign involved a regular regime to include all hydroclimatological conditions. Despite this, there is a strong linkage between drain and stream water ages, highlighting the connectivity between surface and subsurface waterways in these intensively managed agricultural landscapes which is key to understanding its hydrological functioning (Klaus et al., 2015b). Similarly, the mobile soil water isotope data set has only a relatively short length and low number of samples. Mobile soil water can represent key water source for streamflow generation (Staudinger et al., 2017), and the relative differences we found between dominant soil-land use units were informative for understanding the local impact of land management practices as well as differences between MTTs of catchments with varying proportions of these units. However, the mobile soil water also interacts with soil water stored under greater tensions, and future work in the catchment would benefit from investigating the isotope dynamics of "bulk" soil water (*i.e.* both mobile and less mobile water) to understand water partitioning in the soils in a more complete way (Sprenger et al., 2018).

4.3 Implications

Tracer data have been successfully used to constrain hydrological models in relatively natural catchments to improve understanding of water ages and flow paths (Ala-aho et al., 2017; Klaus et al., 2015a; McGuire et al., 2007; van Huijgevoort et al., 2016). So far, such applications have been rare in more disturbed catchments (Orlowski et al., 2016; Soulsby et al., 2015), where predicting hydrological behaviour is a complex challenge (Thompson et al., 2013), yet pressing need (Tetzlaff et al., 2015). Human interference with the water cycle occurs at multiple spatio-temporal scales around the globe

(Falkenmark et al., 2019), affecting nearly every water store and flux, yet this is often underrepresented in our understanding and depiction of water cycles (Abbott et al., 2019). Here we have shown that artificial drainage and other land management practices that increase the connectivity of surface and subsurface waters to the streams (Boardman et al., 2019; Shuster et al., 2005), can have a profound effect on the evolution of water ages. The extensive "short-circuiting" of hydrological pathways that we found in the catchment can radically change storage – flux interactions, diminishing a natural catchment buffering capacity, especially under extreme conditions (Remondi et al., 2018). Artificial drains are typically installed to reduce soil moisture content and enable crop growth. However, during precipitation events in wet conditions their activation and routing of water can exacerbate flood problems and water quality issues by making streamflow responses flashier and "short-circuiting" the delivery of water and a range of contaminants to the streams (Gramlich et al., 2018; Marsh et al., 2016). In Scotland, and many other northern environments, the impacts on floods and water quality can be greater in winter and autumn due to generally greater precipitation inputs, saturated soils and, in some cases, high groundwater levels i.e. very little available storage (Banks et al., 2011; Hallett et al., 2016; Oliver et al., 2005; Soulsby et al., 2017) which usually routes young water and contaminants faster to the streams. Further quantification of water ages in other drained landscapes would contribute to a better understanding of the trade-offs between maintaining drains for food production and the exacerbation of flooding and contaminant transport. This would contribute to an evidence base for adaptive management decisions in historically managed catchments to ultimately secure landscape and community resilience to hydrological extremes at a time of rapid environmental change (Bridgewater, 2018).

5. Conclusions

We investigated the evolution of water ages and flow paths in a complex mixed agricultural landscape in Scotland. Our study combined relatively long-term (> 5years) records of isotope tracers in precipitation and along a nested stream network with transit time modelling to explore the natural and artificial controls on water ages. We explored MTTs for catchments draining a varying proportion of characteristic soil-land units. Overall, we found that stream water ages were short and management practices, in particular artificial drainage, made the distributed catchment responses homogeneous, despite the variations in sub-catchment physical characteristics. Consequently, any short-term impacts from an intense, localised disturbance in the form of a new highway development was not detectable using isotope-based approaches, as extensive "short-circuiting" of water was already facilitated by pre-existing drainage. Dynamics of mobile soil water in dominant soil-land use units were also assessed to better understand the role of soils on the evolution of water ages. Again, subtle

differences between soil-land use units could be related to land management such as the effect of compaction or ploughing. This study is one of the few which, to date, provides insights into water ages and flow paths in a disturbed and intensively managed landscape. Given the potential relevance to managing hydrological extremes of floods and droughts, in addition to contaminant transport, there is a pressing need to better understand how catchments water ages are affected by past and current disturbances to build resilience of catchment ecosystem services in the rapidly changing Anthropocene.

Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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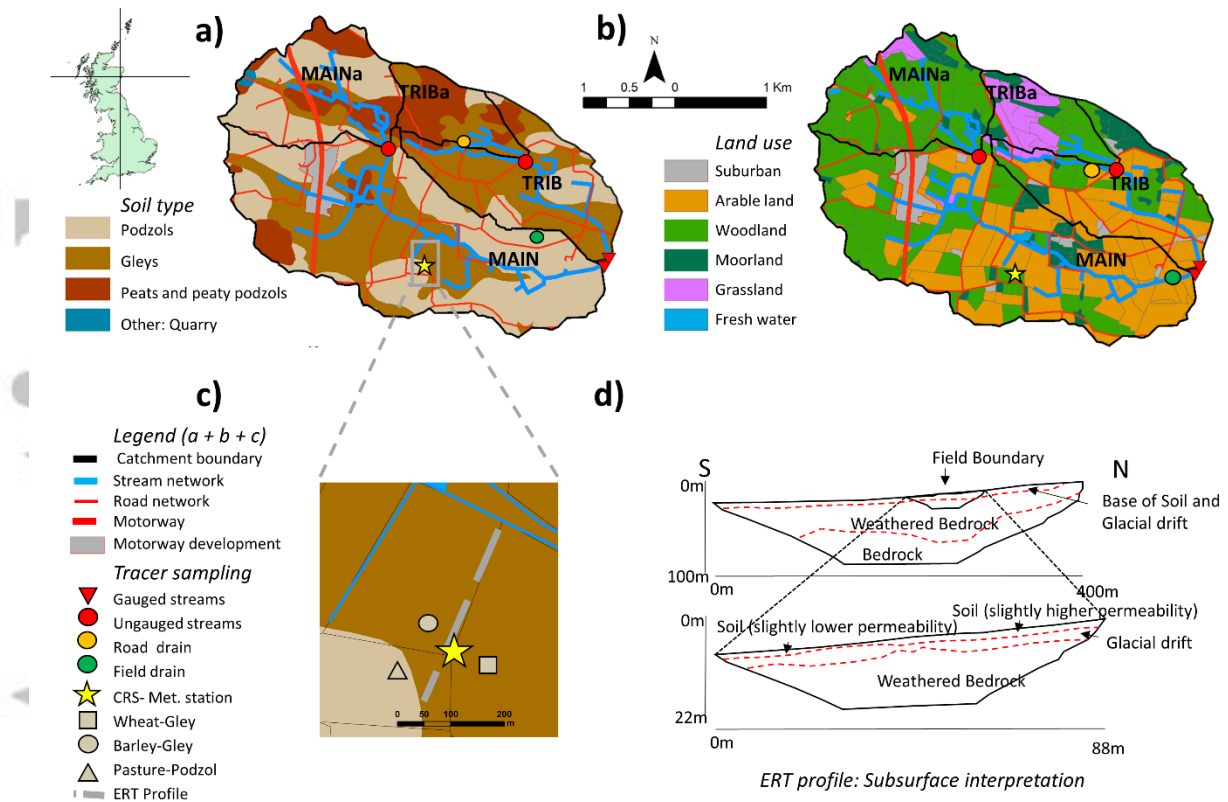
Figure 1. The Elsick Burn study site, showing (a) the soil type distribution and locations of a meteorological and Cosmic Ray Sensor (CRS) monitoring station and sampling points for discharge and isotope sampling; (b) Land use classes; (c) a zoom of the location of soil water experiment and transect of Electrical resistivity tomography (ERT) survey; and (d) the interpretation of subsurface physical characteristics based on the ERT. Map data 1:25 000 Soil Map, The James Hutton Institute/Land Cover Map 2015, NERC Environmental Information Data Centre.
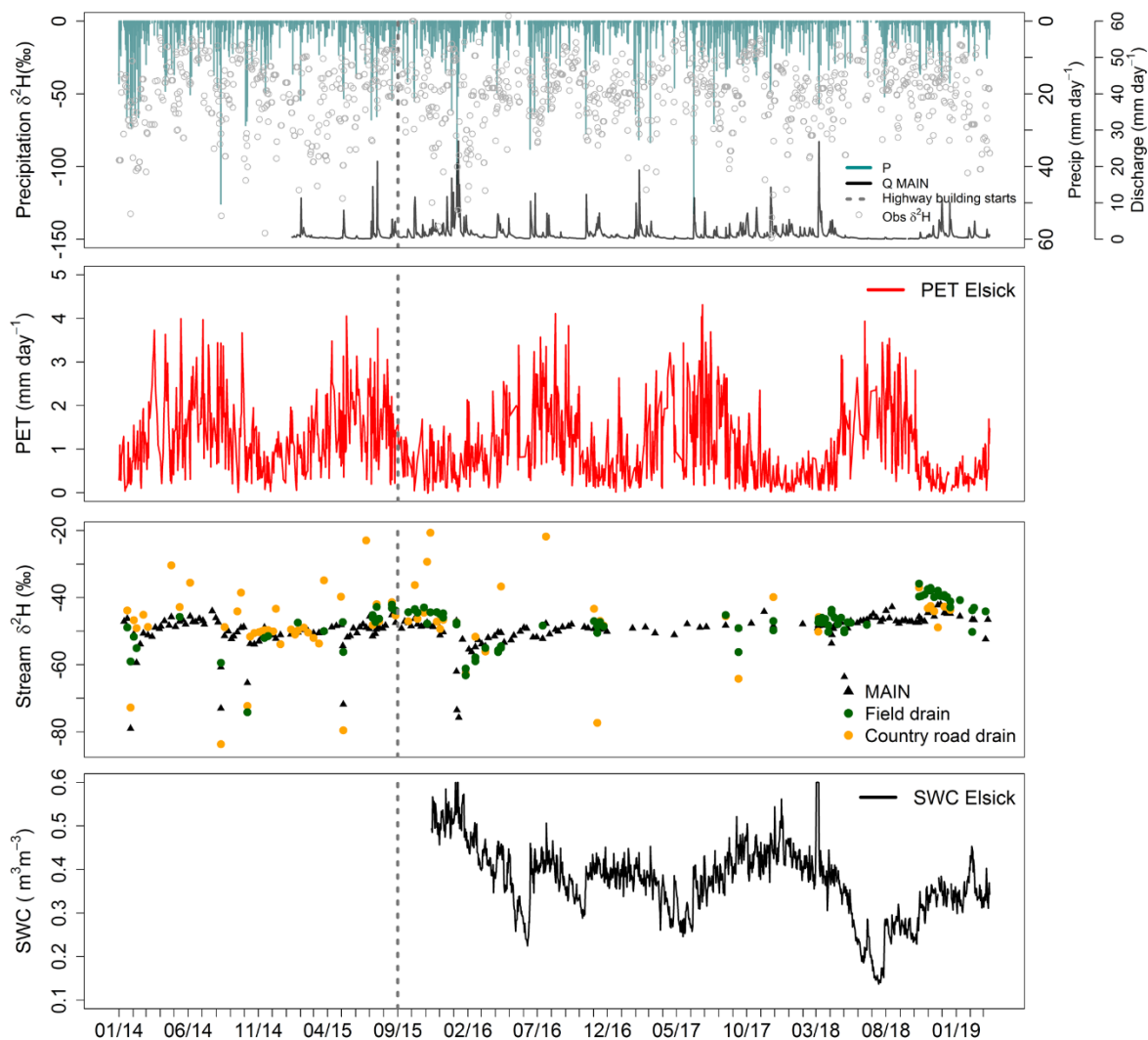
Figure 2. Temporal variability of water balance components for the period January 2014 – March 2019. (a) Daily precipitation and discharge in the MAIN stream (mm day-1) as well as daily precipitation δ2H (‰) dynamics; (b) Daily potential evapotranspiration (PET in mm day-1) for Elsick; (c) Weekly deuterium δ2H (‰) dynamics for the MAIN stream and artificial field and country road drains as well as (d) field-average volumetric soil water content (SWC in m3 m-3) within the CRS-met. station footprint. The grey dotted line indicates the start of highway construction.
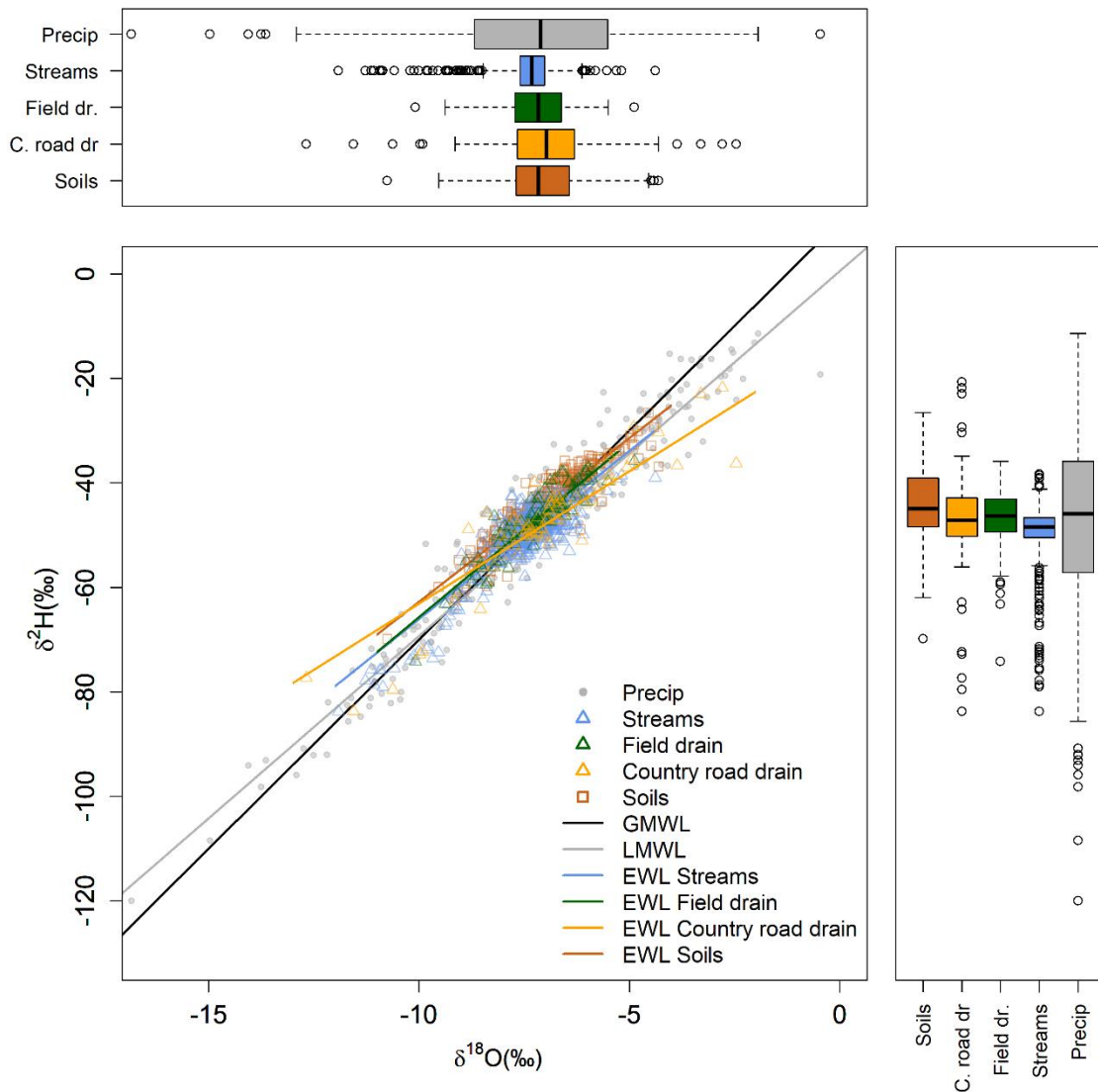
Figure 3. Dual isotope plot grouping data per source i.e. precipitation, streams, field and country road drains and soils in Elsick Burn with different colours per water source and showing distributions as boxplots on side as side and top panels. Data is plotted along the Global (black) and Local (grey) Meteoric Water Lines (GMWL and LMWL, respectively). Evaporation water lines (EWL) are fitted through the data to show their difference with the precipitation input.
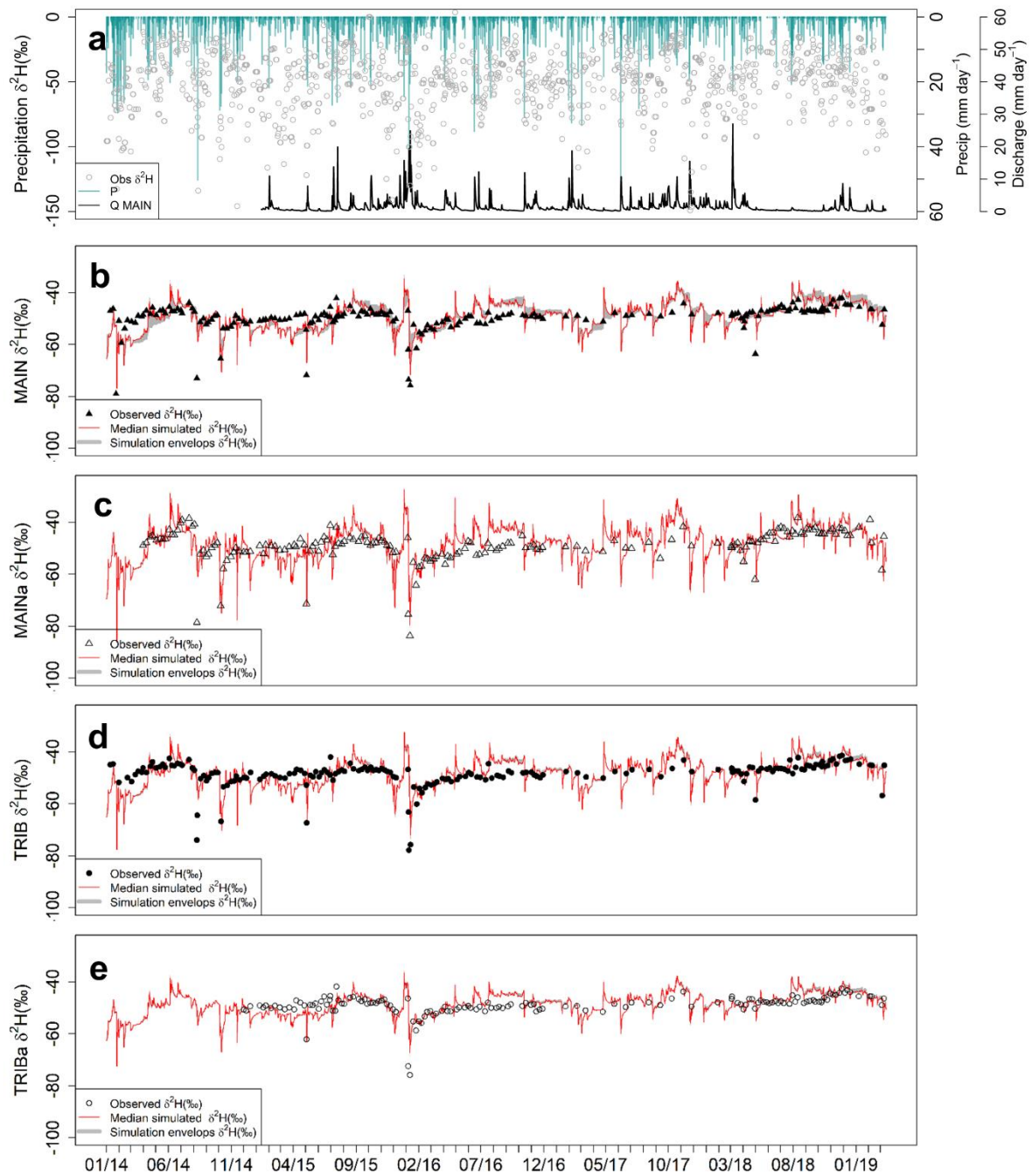
Figure 4. (a) Input of daily precipitation (mm day-1) and its deuterium signature δ2H (‰), used for gamma model transit time simulations, together with stream discharge in MAIN (mm day-1); and observed and simulated stream δ2H (‰) dynamics for (b) MAIN; (c) its upstream site MAINa; (d) TRIB; and (e) its upstream site TRIBa, showing weekly observations (as points), median (in red) and uncertainty bands (grey) of best 500 simulations using a Monte-Carlo approach. Period January 2014 – March 2019.
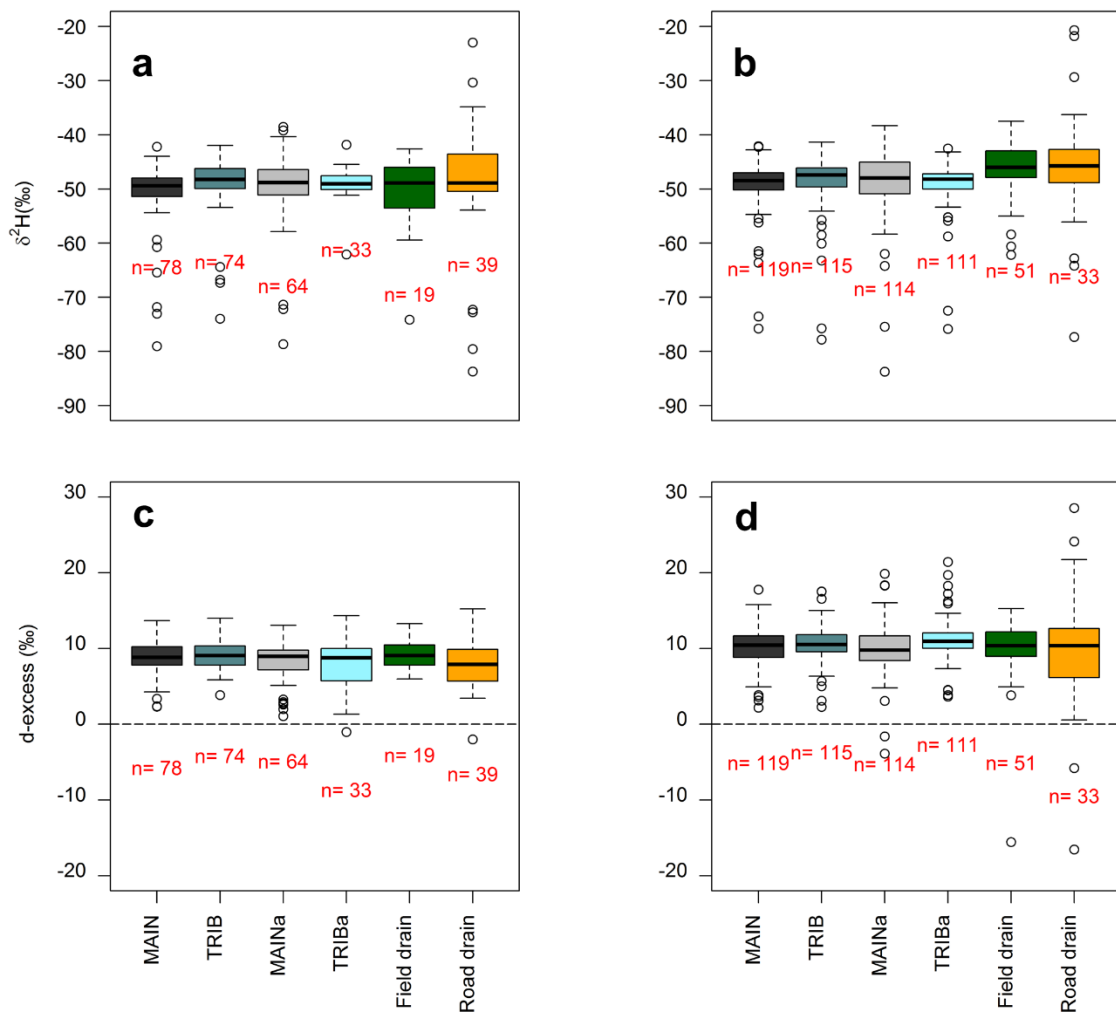
Figure 5. Stream and artificial drains (field and country road) δ2H (‰) (top row) and d-excess (‰) (bottom row) results before (left) and after (right) the start of the construction of the highway crossing Elsick Burn. The approximate start date of construction is September 2015. Number of samples for each of the periods are indicated in red.
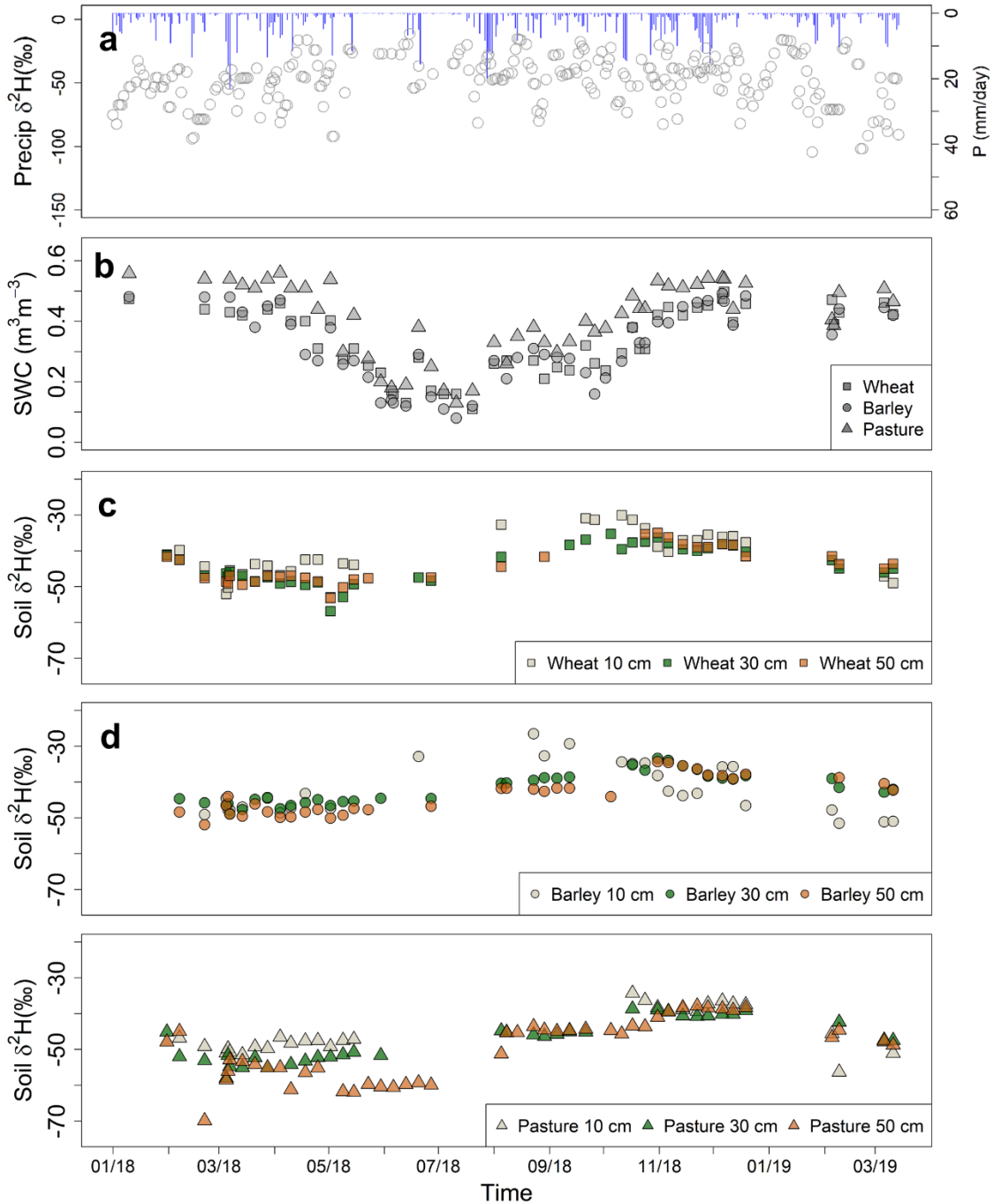
Figure 6. (a) Temporal dynamics of daily precipitation and its deuterium δ2H signature; (b) weekly values of near surface soil water content (SWC) (m3 m-3) in each of the three monitored soil-land use units ; and deuterium δ2H dynamics at three selected depths (10 cm, 30 cm, 50 cm) of each of the soil-land use units, namely, (c) Gleys Wheat, (d) Gleys Barley and (e) Podzols Pasture.
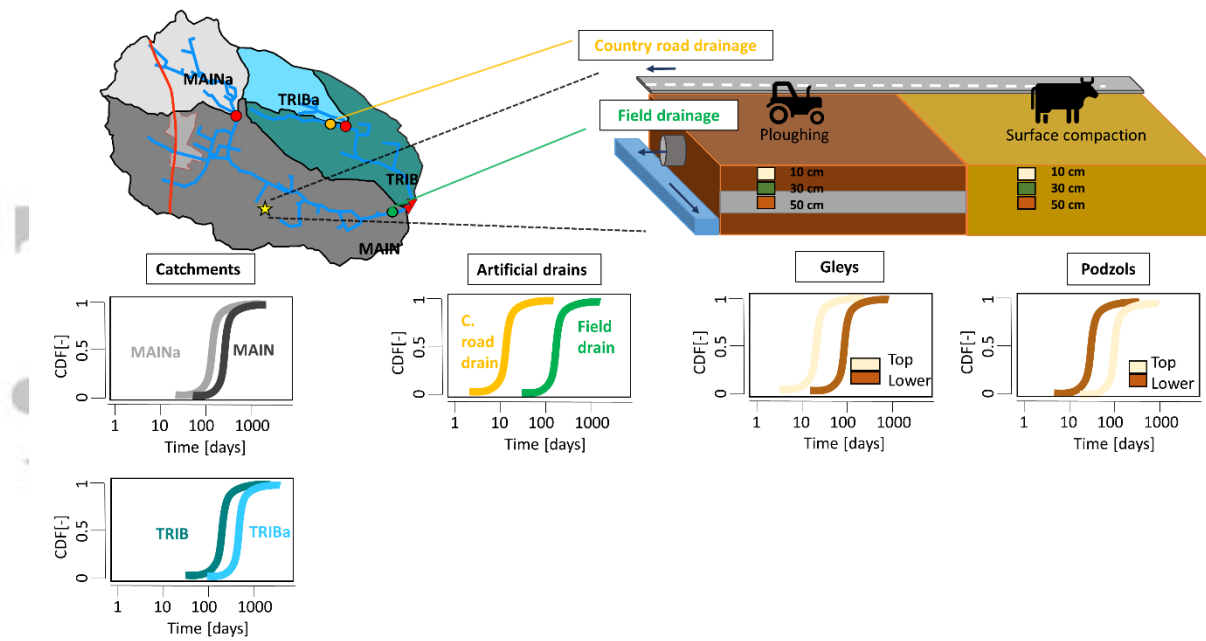
Figure 7. Conceptual summary diagram of travel time distributions (TTDs) from the catchment scale to soil profile including TTDs of artificial drainage features. TTDs are expressed as cumulative distribution function (CDF) over time. Median of best 100 runs is shown. TTDs differences between catchments are subtle, resulting from the interplay of soil type - land use history. Land management may affect TTDs, either enhancing (artificial drainage, ploughing) or delaying (compaction) them. Yellow star indicates location of the soil water sampling and CRS-meteorological station.

Table 1: Summary of catchment physical characteristics for the four stream network monitoring sites.

	Catchment ID			
	MAIN	MAINa	TRIB	TRIBa
Area [km^2]	7.1	1.9	2.8	0.8
Drainage density [km/km^{-2}]	1.91	1.99	1.99	1.42
Mean elevation [m.a.s.l.]	117	144	94	111
Elevation range [m]	105	50	75	40
Land use [proportion of catchment area][1]				
Suburban	0.04	0	0.02	0
Arable agriculture	0.41	0.03	0.37	0.01
Grassland	0.46	0.82	0.31	0.39
Woodland	0.07	0.09	0.14	0.13
Moorland	0.02	0.05	0.16	0.47
Soil groups based on HOST [2] classification [proportion of catchment area]				
Podzols (HOST 17)	0.17	0.12	0.18	0.05
Peats and peaty podzols (HOST 12 and 15)	0.11	0.28	0.21	0.55
Gleys (HOST 10, 14 and 18)	0.71	0.58	0.61	0.40
Baseflow index (BFI) [3]	0.46	0.43	0.47	0.43

[1] Land use classes following the UK LCM2015 map (Rowland et al., 2017).

[2] Soil classification following UK Hydrology of Soil Types (HOST) (Boorman et al., 1995).

[3] Area weighted BFI based on proportions of different HOST soil classes in each subcatchment (Gagkas and Lilly, 2019).

Table 2: Deuterium and d-excess summary statistics for precipitation, stream water and artificial drains for January 2014 to March 2019.

| | Precipitation | Catchments | | | | Artificial drains | |
		MAIN	MAINa	TRIB	TRIBa	Field	Country road
		δ^2H [‰]					
n	279	197	178	189	144	99	72
Min	-120.0	-79.04	-83.73	-77.82	-75.83	-74.15	-83.69
Mean	-47.87[1]	-49.86	-48.99	-48.70	-49.04	-46.94	-47.41
Max	-11.40	-42.07	-38.32	-41.36	-41.82	-35.83	-20.66
CV	0.39	0.11	0.13	0.11	0.08	0.14	0.24
		d-excess [‰]					
Min	-15.48	2.17	-3.87	2.29	-1.02	2.31	-36.95
Mean	9.51	9.63	9.40	9.99	10.36	10.36	7.8
Max	27.08	17.78	19.87	17.53	21.42	15.25	24.12
Stdev	5.67	2.57	3.15	2.34	3.14	2.58	7.75

[1] Weighted mean is -55.8

Table 3: Summary of median [min max] of the posterior parameter distribution and resulting mean transit times (MTT) for the 500 best simulations of gamma-model in the sub-catchments and artificial drains for the period 12 January 2014 to 11 March 2019. KGE was used as best fit performance criterion while RMSE is shown for comparison. Initial parameter ranges [min-max] for α and β were [0-1] and [0-2000] respectively. Summary of mean [min max] fraction of young water (F_{yw}) estimated for the same period is also reported.

	Catchments				Artificial drains	
	MAIN	**MAINa**	**TRIB**	**TRIBa**	**Field**	**Country road**
α [-]	0.33 [0.26 - 0.99]	0.17 [0.11 - 0.99]	0.38 [0.22 - 0.99]	0.43 [0.3 - 0.99]	0.17 [0.1 - 0.7]	0.1 [0.0001 - 0.96]
β [days]	709 [95 - 2000]	997 [64 - 1997]	875 [100 - 2000]	939 [150 - 1997]	916 [56 - 1999]	159 [7 - 1101]
MTT [days]	231 [94 - 524]	167 [61 - 286]	260 [97 - 509]	368 [148 - 667]	148 [40 - 282]	12 [0.004 - 32]
KGE [-]	0.97 [0.94 - 0.99]	0.97 [0.95 - 0.98]	0.97 [0.95 - 0.99]	0.97 [0.95 - 0.99]	0.98 [0.95- 0.99]	0.83 [0.77 - 0.97]
RMSE [‰]	5.3 [5.1 - 6.2]	5.6 [5.8 - 6.6]	5.4 [5 - 6.2]	4 [3.8 - 4.7]	5.5 [4.9- 5.9]	11.4 [11 - 14.5]
F_{yw} [-]	0.12 [0.06 - 0.14]	0.15 [0.10 – 0.18]	0.10 [0.05 – 0.14]	0.07 [0.04 – 0.10]	0.20 [0.13 – 0.23]	0.34 [0.21 – 0.38]

Table 4: Summary statistics of deuterium δ²H [‰] dynamics of precipitation, soils, streams and artificial drains, for the intense monitoring period 31 January 2018 – 11 March 2019.

|	Precip	Gley (Wheat)			Gley (Barley)			Podzol (Pasture)			Catchments				Artificial drains	
		10 cm	30 cm	50 cm	10 cm	30 cm	50 cm	10 cm	30 cm	50 cm	MAIN	MAINa	TRIB	TRIBa	Field	Country Road
n	189	33	37	33	29	37	25	30	35	45	54	50	50	47	28	10
Min	-104.43	-52.94	-56.87	-53.22	-51.51	-48.88	-51.91	-56.3	-57.99	-69.85	-63.62	-61.99	-58.5	-50.58	-50.01	-50.13
Mean	-46.59 (1)	-41.02	-43.77	-44.21	-41.99	-41.83	-43.75	-45.16	-47.33	-49.86	-47.28	-45.79	-46.19	-46.88	-43.48	-44.17
Max	-11.4	-30.07	-35.26	-34.98	-26.54	-33.38	-34.31	-34.28	-38.67	-37.86	-42.07	-38.32	-41.36	-42.54	-37.5	-37.95
CV	0.40	0.15	0.12	0.11	0.17	0.1	0.11	0.13	0.12	0.17	0.07	0.09	0.07	0.04	0.09	0.07

(1) Weighted mean is -51.52

Table 5: Summary of median [min max] of the posterior parameter distribution (α and β) and resulting mean transit times (MTT) for the 100 best simulations of gamma-model for the intense monitoring period 31 January 2018 – 11 March 2019 for soils, streams and drains. KGE was used as best fit performance criterion while median RMSE is shown for comparison. Initial parameter ranges [min-max] for α and β were [0-1] and [0-2000] respectively.

| | MTT analysis | | | | |
	α [-]	β [days]	MTT [days]	KGE [-]	RMSE [‰]
Soil-land units					
Gley (Wheat)					
10 cm	0.43 [0.22 - 0.99]	103 [42 - 271]	43 [35 - 59]	0.97 [0.95 - 0.99]	4.2
30 cm	0.19 [0.16 - 0.97]	1128 [76 - 1998]	212 [70 - 342]	0.98 [0.98 - 0.98]	4.8
50 cm	0.23 [0.18 - 0.97]	664 [80 - 989]	151 [71 - 364]	0.99 [0.99 - 0.99]	4.2
Gley (Barley)					
10 cm	0.19 [0.0002 - 0.99]	110 [33 - 344]	21 [0.04 - 37]	0.98 [0.97 - 0.99]	5.0
30 cm	0.87 [0.68 - 0.99]	165 [107 - 283]	144 [101 - 194]	0.77 [0.7 - 0.95]	2.2
50 cm	0.59 [0.36 - 0.99]	146 [87 - 385]	87 [72 - 138]	0.96 [0.93 - 0.98]	4.0
Podzol (Pasture)					
10 cm	0.82 [0.52 - 0.995]	89 [19 - 229]	84 [18 - 118]	0.77 [0.69 - 0.97]	3.3
30 cm	0.63 [0.006 - 0.99]	18 [0.13 - 39]	5 [0.01 - 35]	-0.16 [-0.67 - 0.55]	11.7
50 cm	0.19 [0.0001 - 0.99]	152 [33 - 941]	29 [0.1 - 38]	0.96 [0.95 - 0.97]	4.5
Catchments					
MAIN	0.51 [0.47 - 0.72]	1164 [322 - 1986]	587 [233 - 955]	0.99 [0.98 - 0.99]	3.1
MAINa	0.82 [0.66 - 0.99]	227 [132 - 390]	190 [131 - 260]	0.72 [0.68 - 0.87]	3.8
TRIB	0.46 [0.43 - 0.54]	1340 [606 -1984]	613 [329 - 871]	0.98 [0.98 - 0.98]	3.3
TRIBa	0.81 [0.78 - 0.87]	1455 [1022 - 1994]	1172 [884 - 1570]	0.99 [0.98 - 0.99]	1.5
Artificial drains					
Field	0.17 [0.14 - 0.57]	1005 [159 - 1967]	165 [87 - 282]	0.98 [0.98 - 0.98]	3.4
Country road	0.11 [0.09 - 0.13]	1564 [892 - 1978]	161 [118 - 207]	0.93 [0.93 - 0.93]	5.8

Title: Using isotopes to understand the evolution of water ages in disturbed mixed land-use catchments

Authors: Katya Dimitrova-Petrova *; Josie Geris; Mark, E. Wilkinson; Allan Lilly; Chris Soulsby.

Graphical abstract
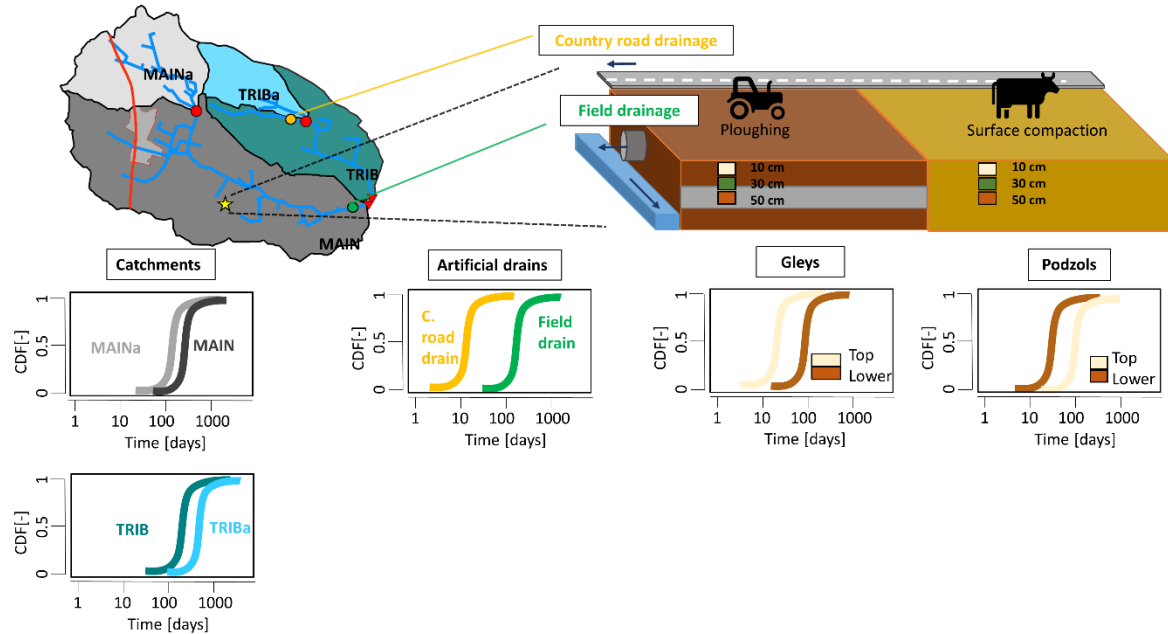
Key findings:

Mean transit times (MTT) in a disturbed mixed land-use catchment were short and spatially homogeneous, explained by extensive artificial drainage, "short-circuiting" water to the streams during storms.

Subtle MTT variations in mobile soil water in the upper soil of key soil-land use units related to dominant agricultural practices.

Evolution of stream water ages in a complex human-influenced environment were mainly related to near-surface soil processes and dominant soil management practices with minimal effect of additional disturbance of highway construction.