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Using long-term data sets to understand transit times in contrasting headwater catchments

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SUMMARY

Long-term tracer data collected over an 8 year period were analyzed to explore the transit times of two small ($\sim$1 km^2), contrasting headwater catchments in the uplands of Scotland. At Loch Ard, the catchment was characterized by low permeability gleyed soils overlying metamorphic geology. At Sourhope, more freely draining podzolic soils were dominant, which mantled fractured and faulted volcanic rocks. Hydrometric data and chemically-based hydrograph separations indicated that Loch Ard was a flashy catchment dominated by runoff processes in the upper soil horizons. In contrast, around 77% of annual flow at Sourhope was sustained by well-buffered groundwater sources. Weekly Cl^- time series in precipitation and stream flow revealed similar variability in inputs at both sites, but much greater damping in outputs at Sourhope. Despite this, both catchments filtered white noise frequencies in precipitation inputs into 1/*f* outputs. These input–output relationships were modeled with a range of transit time distributions (TTD). At the responsive Loch Ard catchment, mean transit times (MTT) for the study period were estimated at 135–202 days. Models based on a gamma distribution or two parallel linear reservoirs were best able to capture the short- and long-term fluctuations in stream water in response to input variations. At Sourhope, the highly damped tracer signal in stream waters was poorly captured by all the TTDs used. Resulting MTT estimates of 1830–1970 days are based on weak model fits and poorly identifiable parameter sets, indicating that natural tracers such as Cl^- are inadequate for catchments where MTTs are greater than a few years. At both sites, estimates of MTT using moving windows over the 8 year data sets revealed sensitivity to precipitation amounts and the length of monitoring period. It is concluded that time series of around 4 years are required to adequately constrain MTT estimates.

Introduction

Small experimental catchments have been invaluable in hydrological science providing the basis for detailed process investigations and understanding of hydrological functioning (Sidle, 2006). For example, recent work has focused on how the hydrology of small catchments is composed of an integration of hill slope responses (Uchida et al., 2005). Other investigations have shown how larger catchments are composed of the integration of headwater catchment responses (Shaman et al., 2004; Soulsby et al., 2006a). Over the past two decades tracer studies have significantly contributed to such advances. This is because tracers can reflect the integrated effect of different hydrological processes and give insight into the emergent nature of catchment response. Thus, geochemical hydrograph separation has been used to identify different runoff sources (Dunn et al., 2006) and time series modeling has been used to identify transit time distributions (TTDs) and estimate mean transit times (MTT) of catchments by analyzing input–output relationships for conservative tracers in rainfall and runoff (McGuire and McDonnell, 2006).

Recent work has shown that natural tracer outputs are highly responsive to inputs in catchments that have surface and near-surface flow paths, low groundwater storage and short transit times (Tetzlaff et al., 2007a). In contrast, tracer responses are very damped in catchments dominated by sub-surface flow paths and well-mixed groundwater inputs (Dunn et al., 2008). The differences largely reflect the integrated effects of differences in catchment topography (McGuire et al., 2005), soils (Rodgers et al., 2005a,b; Soulsby et al., 2006b) and geology (Viville et al., 2006). Recent work has, however, also highlighted the importance of climatic variability and non-stationary nature of hydrological functioning (Burt and Worrall, 2007). This has demonstrated the contingent nature of many short-term (ca. 1–2 years) studies that have been used to evaluate hydrological sources and assess residence times (Tetzlaff et al., 2007b). Thus, there is a need to

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examine catchments with contrasting characteristics that have long-term tracer data to evaluate how hydrological function is affected by inter-annual climatic variability.

Chloride has utility as a natural conservative tracer in catchments dominated by maritime air-masses where marine-salts dominate the composition of precipitation. For example, Neal et al. (1988) used the damped behavior of Cl^- in stream water at Plynlimon to show how hydrological models, although able to simulate the stream hydrograph, could not simulate Cl^- input/output relations. This led to a re-conceptualization of upland hydrology which demonstrated, amongst other things, the importance of groundwater in upland catchments (Neal et al., 1997). This further sheds new light on the understanding of mixing processes in catchments, and demonstrates how they might act as fractal filters which can convert Gaussian white noise in the tracer input power spectrum to $1/f$ noise in the power spectrum of the stream response, indicating the influence of both short-term responses as well as long-time chemical memory (Kirchner et al., 2000, 2001). Recent work has incorporated such Cl^- data into hydrological models to explore the extent to which these mixing processes can be represented (Page et al., 2007; Shaw et al., 2008).

In this study we examine two of the best long-term Cl^- data sets in the uplands of northern Britain in two small catchments: Loch Ard – a catchment in the central Scottish Highlands underlain by metamorphic geology and responsive gleyed soils (Tetzlaff et al., 2007b), and Sourhope – a catchment in the Cheviots characterized by volcanic geology and freely draining podzolic soils (Miller et al., 2001). The objectives of the study were to: (1) assess the differences in hydrological sources using geochemical hydrograph separation; (2) use a range of transit time models to explore how well Cl^- input/output relationships could be simulated by various TTD in each catchment; (3) evaluate the degree of dependence of MTT estimates on variability in precipitation amounts and the length of the sampling period.

Study sites

Loch Ard

A number of streams in Loch Ard forest in the Central Scottish Highlands have been monitored as part of long-term hydrochemical studies (Harriman et al., 2001). Burn 11 (National Grid Reference NS469987) is a stream that drains a catchment of 1.44 km^2 which ranges from 99 to 282 m a.s.l. in altitude (Fig. 1a). Long-term mean annual precipitation is around 2000 mm (Harriman et al., 2001) and the mean annual air temperature for the observation period was 8.3 °C. The catchment is afforested with Sitka Spruce (*Picea sitchensis*) and is characterized by gently undulating hills with occasional steep slopes. The quartz-rich Dalradian geology is metamorphic and covered by siliceous, slowly weathering, low permeability glacial drifts (Wilson et al., 1984; Miller et al., 1990a). This fine-textured parent material, together with the high precipitation amounts and low gradients results in the dominance of poorly drained, gleyed soils (Tetzlaff et al., 2007b). These are generally characterized by a humic/peaty horizon up to 40 cm thick, overlaying Eag and B/Cg horizons down to 60 cm (Miller et al., 1990b). A flat area in the centre of the catchment is characterized by peat (Table 1). These soils remain at, or close to saturation for much of the year. As shown by Soulsby and Reynolds (1993) for a similar upland catchment in Wales, water tables can rise from the B/C horizons into the organic horizons during storm events, causing transmissivity feedback as hydraulic conductivities increase by 2–3 orders of magnitude. This results in rapid routing via shallow subsurface preferential flow paths causing a very responsive runoff pattern (Miller et al., 1990a). Mean daily stream flow (1988–1996) ranged from ~1 to 1583 l s^{-1}. The median annual flow duration curve (Fig. 2) shows the very responsive behavior of the catchment, with Q_5 exceeding Q_{95} by more than two orders of magnitude.

Sourhope

The Rowantree Burn (National Grid Reference NT860204) is part of the Sourhope Research Station, located in the Scottish Borders on the south-west slopes of the Cheviot ridge. The stream gauge is located upstream of the confluence with the Sourhope burn, with a catchment area of 0.44 km^2, and an elevation ranging from 297 to 508 m a.s.l. (Fig. 1b). Long-term mean annual precipitation is around 1000 mm (Bain et al., 1998) and the recorded mean annual air temperature for the observation period (1994–2002) was 7.5 °C. The Cheviot Hills are undulating uplands that have strong and steep slopes. Land use is grassland used for rough grazing with *Nardus stricta*, *Molinia caerulea*, *Agrostis capillaries* and *Festuca Ovinia* being the dominant species. The soils are developed on locally-derived glacial drift from underlying lavas and andesites of the Lower Old Red Sandstone age (Bain et al., 1998; Miller et al., 2001). The volcanic geology is highly fractured in places and unusual drainage patterns may indicate strong geological faulting in the region (Paul Younger, personal communications). The dominant soils at Sourhope are acidic, free-draining podzols on

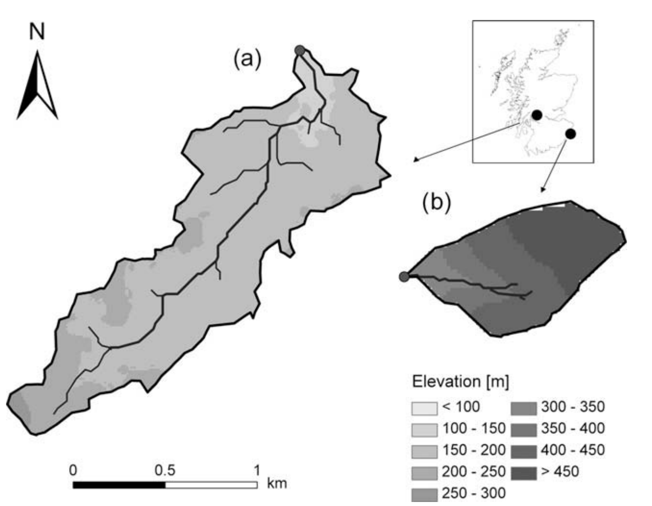

Fig. 1. Elevation maps of the study catchments at (a) Loch Ard and (b) Sourhope.

Table 1
Summaries of catchment characteristics.

	Loch Ard[a]	Sourhope[b]
Area (km^2)	1.44	0.44
Q_5 (l s^{-1} km^{-2})	224	53
Q_{50} (l s^{-1} km^{-2})	20	18
Q_{95} (l s^{-1} km^{-2})	1.5	9
Mean groundwater contribution (%)	57 ± 21	77 ± 13
Mean annual runoff (mm)	1660	501
Mean annual precipitation (mm)	1835	876
Mean annual temperature (C)	8.3	7.5
Mean elevation (m)	183	430
Min elevation (m)	99	297
Max elevation (m)	282	508
Mean slope (°)	9	12
Max slope (°)	39	32
Soils		
Mineral and humic gleys (%)	21.7	0
Podzols and peaty podzol (%)	0	100
Humic and peaty gley (%)	76.6	0
Peat (%)	1.7	0

[a] Observation period 07/01/1988–23/12/1996.
[b] Observation period 01/06/1994–31/12/2002.

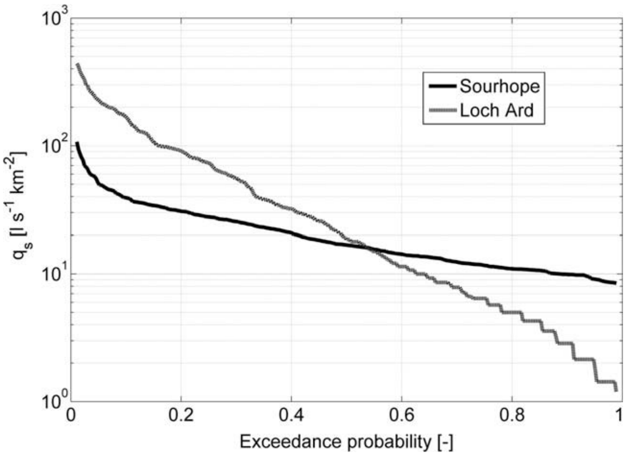

Fig. 2. Median annual flow duration curves based on the observation periods 1988–1996 (Loch Ard) and 1994–2002 (Sourhope).

the steeper slows and small patches of peat and peaty gleys on the hill tops (Miller et al., 2001; Sheppard and Lloyd, 2002). The podzols typically comprise thin (0–10 cm) organic horizons, overlying a thin Ah horizon grading into B horizon at 30–40 cm (Sheppard and Lloyd, 2002; Bruneau et al., 2005). Mean daily stream flows ranged from <1 to 336 l s^{-1} with moderate flows characterized by lengthy hydrograph recession periods apparently reflecting the interaction between well-drained soils and the fractured and permeable bedrock (Fig. 2).

Data and methods

Hydrological and hydrochemical data

Precipitation volumes at Loch Ard were recorded by a gauge located in a forest clearing at 180 m a.s.l. approximately 1 km southwest of the catchment outlet. Weekly totals were recorded for the observation period 07/01/1988–23/12/1996 (Fig. 3a). Stream flow at the outlet of Burn 11 was recorded at 15 min intervals using a concrete crump weir operated by the Scottish Environment Protection Agency (SEPA). At Sourhope precipitation is gauged using an unheated tipping bucket at ground level (resolution: ±0.1 mm). It is located about 800 m west of the catchment outlet on Fassett Hill. Weekly precipitation totals were available for the observation period 01/06/1994–31/12/2002 (Fig. 3b). Stream flow in the Rowantree Burn was recorded at 15 min intervals using a flume and a stage level recorder. Unfortunately, no flow record was available for part of 2001 during the UK "Foot and Mouth" crisis.

Precipitation samples were obtained weekly in open funnel bulk deposition samplers at both sites during the study period. Stream water dip samples were also taken at weekly sampling intervals throughout the observation period at both Loch Ard and Sourhope. All water samples were filtered through a 0.45 μm polycarbonate membrane filter. Ion chromatography (Dionex DX100) was used to determine the Cl^- concentrations. Alkalinity was measured by sequential acidimetric titration to dual end points of pH 4.5 and 4.2 according to HMSO (1981) procedures.

Geochemical hydrograph separation

Stream flow can be separated geochemically into distinct conceptual runoff components if these show distinct signatures of conservative geochemical tracers (e.g. Christophersen et al., 1990; Buttle and Peters, 1997; Wade et al., 1999; Soulsby et al., 2003) according to:

$$\frac{Q_{GW}}{Q_T} = \frac{(c_S - c_T)}{(c_S - c_{GW})} \quad (1)$$

where Q_{GW} and Q_T are the groundwater and the total stream flow and c_S, c_{GW} and c_T are the observed tracer concentrations of soil water, groundwater and stream water, respectively. For detailed discussion and assumptions of the method the reader is referred to Sklash and Farvolden (1979), Buttle (1994), Durand and Torres (1996), and Hoeg et al. (2000).

In the present study, alkalinity was used as tracer to estimate groundwater contribution to total runoff. Alkalinity is the capacity of bases to neutralize acids and it is a directly measurable approximation of the chemically conservative acid neutralizing capacity (ANC) in waters with low aluminium concentrations (Wade et al., 1999). It can be used as a conservative tracer to distinguish between acidic shallow subsurface water, termed in this study "soil water" and more alkaline deeper subsurface water, termed "groundwater" (Robson and Neal, 1990; Soulsby et al., 2003).

Due to the lack of direct measurements of alkalinity in groundwater, end members had to be estimated indirectly. The groundwater alkalinity was defined as the median alkalinity at low flow, i.e. at flows $<Q_{95}$ (Loch Ard: $c_{GW} = -12 \pm 5$ μeq l^{-1}, $n = 34$; Sourhope: $c_{GW} = 1020 \pm 79$ μeq l^{-1}, $n = 22$). A preliminary estimate of soil water alkalinity was obtained from soil water samples taken at several occasions (Loch Ard: $c_S = -65 \pm 7$ μeq l^{-1}, $n = 34$ and Sourhope: $c_S = 0 \pm 5$ μeq l^{-1}, $n = 14$). Obviously, the assumptions inherent in these suggested end member definitions and the limited number of samples are likely to result in considerable uncertainty. Hence uncertainty was quantified using the approach suggested by Genereux (1998) which is based on error propagation on the 95% confidence bounds of the individual components in the estimation of groundwater contribution.

Transit time estimation

Weekly Cl^- concentrations in precipitation and stream flow were used for estimating MTT at each site using a range of approaches. MTT can be used as a descriptor of the hydrological function of a catchment and is conceptualized as the time integrated response of a catchment to tracer inputs for a specified period of the past, assuming no zones of immobile water are present (Rodhe et al., 1996). In other words, the tracer concentration in the stream water $c_{out}(t)$ at any time t reflects the combined tracer input of the past $c_{in}(t-\tau)$ lagged and weighed by the transfer function $g(\tau)$, which represents the lumped TTD of tracers in the system (Maloszewski and Zuber, 1982):

$$c_{out}(t) = \int_0^\infty g(\tau)c_{in}(t-\tau)\mathrm{d}\tau \quad (2)$$

where τ is the transit time, t is the time of exit from the system and $(t-\tau)$ represents the time of entry into the system.

MTT estimation using Eq. (2) can be problematic for stream water: strictly speaking it is only valid for systems in a quasi-steady-state (McGuire and McDonnell, 2006) or when it is expressed in terms of cumulative flows rather than time (Niemi, 1977). However, it has been shown that "functionally equivalent" results can be obtained using the non-steady state time-based approach (Kirchner et al., 2001) assuming average, time invariant TTDs (McGuire et al., 2005), which ignore the influence of seasonal precipitation distribution. This approach was considered to be adequate particularly given that precipitation in Scotland is distributed fairly evenly throughout the year (Tetzlaff et al., 2007b).

Eq. (2) only takes into account the input concentrations of the conservative tracer. Yet, it is the actual tracer input mass flux (or input mass weighed concentration) that governs the mixing and the resulting stream flow output concentration c_{out}. Therefore,

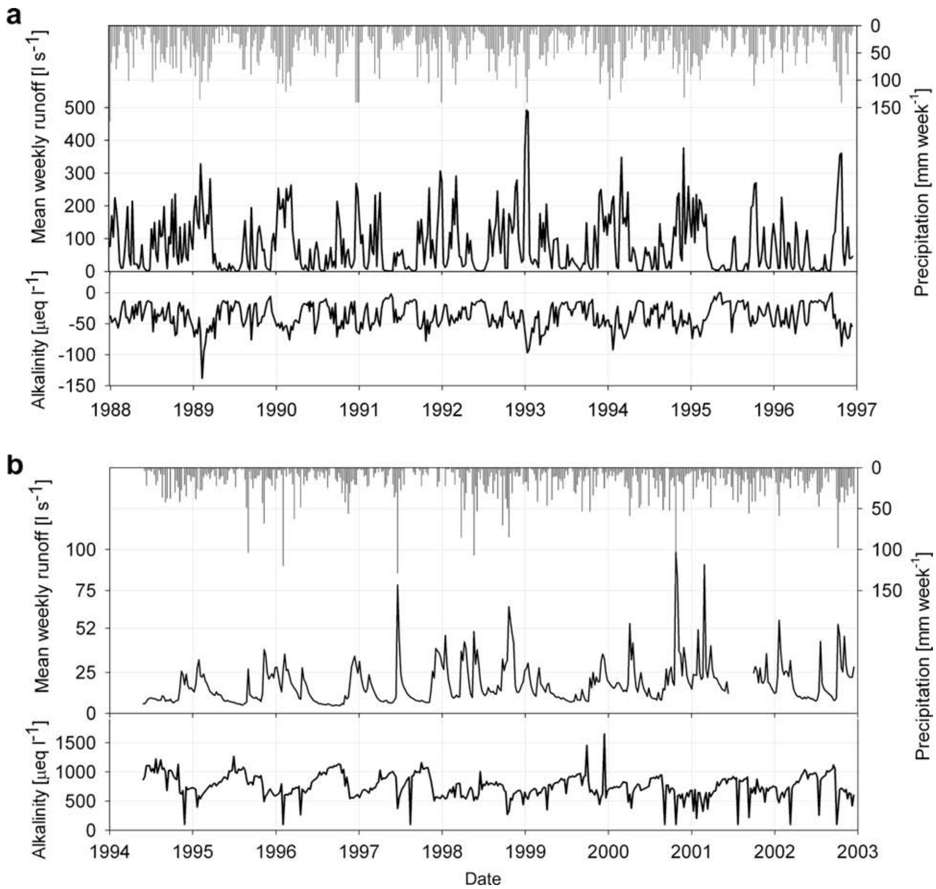

Fig. 3. Total weekly precipitation, mean weekly runoff and weekly alkalinity concentrations (dip samples) for the study catchments at (a) Loch Ard and (b) Sourhope.

the input concentration is weighed using weekly precipitation rates $p(t-\tau)$ adjusted for evapotranspiration (cf. Stewart and McDonnell, 1991; Weiler et al., 2003; McGuire and McDonnell, 2006):

$$c_{out}(t) = \frac{\int_0^\infty g(\tau)p(t-\tau)c_{in}(t-\tau)\mathrm{d}\tau}{\int_0^\infty g(\tau)p(t-\tau)\mathrm{d}\tau} \tag{3}$$

Adjusting the measured Cl^- input for evapotranspiration affects Cl^- output concentrations whilst the flux is conserved. The approximate annual actual evapotranspiration loss for each catchment (1961–1990, MORECS) was distributed over the year according to a sine wave. The enhancement of Cl^- inputs by dry and occult deposition (Page et al., 2007) required the application of an adjustment factor on the measured bulk Cl^- deposition. According to the deficit in catchment Cl^- budgets, an adjustment factor of 2.1 was used at the afforested Loch Ard catchment (cf. 2.5 reported by Shaw et al. (2008) for a forest catchment) and 1.3 at the Sourhope catchment (cf. 1.55 reported for a moorland catchment by Dunn and Bacon, 2008). This, of course, ignores temporal variability in dry and occult deposition, though such effects will be less in the wet Scottish climate than at some other sites, and represents a pragmatic approach in the absence of more detailed information.

As no a priori assumptions about the flow mechanisms were made, several different TTDs were used in this study (Table 2). The one-parameter exponential model (EM) represents a simple model, mathematically equivalent to a well mixed linear reservoir, while the exponential-piston flow model (EPM) adds a delayed piston flow component for delayed flows to the EM. Both approaches have been widely used (e.g. Maloszewski et al., 1983; Stewart and McDonnell, 1991; Vitvar and Balderer, 1997; McGuire et al., 2002; McGlynn et al., 2003; McGuire et al., 2005; Tetzlaff et al., 2007b). The two parallel linear reservoir (TPLR) approach was suggested

Table 2
Descriptions of transit time distributions (TTD).

Model	TTD $g(\tau)$	MTT	Other parameters
Exponential	$\tau_m^{-1}\exp\left(-\frac{\tau}{\tau_m}\right)$	τ_m	–
Exponential piston flow	$\frac{\eta}{\tau_m}\exp\left(-\frac{\eta\tau}{\tau_m}+\eta-1\right)$ for $\tau \geq \tau_m(1-\eta^{-1})$ 0 for $\tau < \tau_m(1-\eta^{-1})$	τ_m	η = total volume/volume with exponential TTD
Two parallel linear reservoirs	$\frac{\phi}{\tau_f}\exp(-\frac{\tau}{\tau_f})+\frac{1-\phi}{\tau_s}\exp\left(-\frac{\tau}{\tau_s}\right)$	–	τ_f = mean transit time of fast reservoir τ_s = mean transit time of slow reservoir Φ = volume of fast reservoir/total volume
Diffusion/dispersion	$\left(\frac{4\pi D_p\tau}{\tau_m}\right)^{-1/2}\tau^{-1}\exp\left[-\left(1-\frac{\tau}{\tau_m}\right)^2\left(\frac{\tau_m}{4D_p\tau}\right)\right]$	τ_m	D_p = 1/Peclet number
Gamma	$\frac{\tau^{\alpha-1}}{\beta^\alpha\Gamma(\alpha)}\exp\left(-\frac{\tau}{\beta}\right)$	$\alpha\beta$	α = shape parameter β = scale parameter

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by Weiler et al. (2003) and allows a somewhat more realistic characterization of flow path distributions by combining a fast and a slow response reservoir in the distribution function. The dispersion model (DM) is obtained as a uni-dimensional solution to the dispersion equation for a semi-infinite medium with injection and detection in flux (C_{IFF}, Kreft and Zuber, 1978). In the present lumped application of the dispersion model the dispersion parameter *Dp* is a conceptual quantity which depends on the distribution of transit times rather than describing the dispersive properties of the flow medium (Maloszewski and Zuber, 1996). Kirchner et al. (2000) showed that a gamma distribution with shape parameter $\alpha \approx 0.5$ is a mathematically appropriate representation of tracer response, which tends to show an apparent fractal pattern over some orders of magnitude. This gamma distribution (GM) can be approximated by a power law in the frequency domain demonstrating its ability to reproduce the influence of both high initial values as well as long tails to trace inputs. In addition to the models based on the convolution integral, a simple sine-wave model of input–outputs (DeWalle et al., 1997; Soulsby et al., 2000) was used for comparative reasons.

Note that due to the weekly sampling intervals, Cl^- peaks in the stream are likely to be underestimated, i.e. the part of Cl^- which left the system immediately or shortly after deposition is likely to be missed, which in turn results in an overestimate of MTTs. This is particularly true for TTDs with high values at short lag-times, i.e. TPLR with low τ_f and GM with $\alpha < 1$.

The use of the convolution integral implies that the stream response is controlled by summed inputs during past specified periods. This causes uncertainties, particularly for systems with long mean transit times, as typically no data sets are available to cover the necessary "warm-up" period. To avoid artificially generated data for the "warm-up" period the available Cl^- input time series was duplicated and used to generate initial conditions for the actual model runs with the same data set.

Uncertainty estimation

Although the transit time models have a maximum of three parameters, identifiability can be a limiting issue. This is true particularly for systems with long transit times and therefore extremely damped tracer responses (Dunn et al., 2008). The resulting uncertainty was evaluated using the Generalized Likelihood Uncertainty Estimation (GLUE) technique introduced by Beven and Binley (1992). This involves the rejection of an optimal parameter set in favor of a range of "equally" good parameter sets, with resulting upper and lower uncertainty bounds for the modeled time series (Freer et al., 1996). Within a pre-defined parameter space Monte Carlo sampling is carried out, usually assuming uniform distribution over the parameter space (Beven and Freer, 2001). Dunn et al. (2008) highlighted that streams with a damped response (i.e. catchments with long transit times) can show Cl^- signals which are attenuated to the point where they plot essentially as a straight line. Even very low absolute deviations from this damped signal can therefore result in extremely low Nash–Sutcliffe efficiencies. On the other hand, catchments with a low degree of Cl^- attenuation can show elevated RMSE even for models with high Nash–Sutcliffe efficiency. Considering the contrasting nature of the two study catchments, each Monte Carlo realization ($n = 10{,}000$) was thus evaluated using a combined Nash–Sutcliffe efficiency *E* (Nash and Sutcliffe, 1970) and a normalized 1-RMSE (cf. Weiler et al., 2003) likelihood measure, where a value of 1 would indicate a perfect fit. Due to the subdued flow pattern, very low efficiencies *E* were expected at Sourhope. Therefore models were retained as "behavioral" *only* if they showed both: RMSE < 2.5 mg l^{-1} and $E > 0.1$. The likelihood-weighted uncertainty bounds at each site were generated from realizations which were kept as "behavioral" models and whose likelihood weights *L* were rescaled to give a cumulative sum of 1:

$$P(\hat{Y}_t < y_t) = \sum_{j=1}^{j=N} L\left(\theta_i \middle| \hat{Y}_t < y_t\right) \tag{4}$$

where *P* is the prediction quantile for $\hat{Y}$ (the value of variable *Y* at time *t*, simulated by model θ_i) being less than *y* and *N* is the number of retained, behavioral models (Page et al., 2007).

Spectral analysis

Spectral analysis was used to examine any influence of contrasting catchment characteristics on the respective Cl^- power spectra (Kirchner et al., 2000). Frequency analysis of the weekly precipitation and stream water Cl^- concentrations was done using a Discrete Fourier Transform (DFT), decomposing the signal in $N/2$ wavelengths, where *N* is the number of samples in the time series and spectral power is the square of the absolute Fourier transforms of the constituting wavelengths of a time series. Due to the wet Scottish climate, gaps in rainfall Cl^- time series were rare (12 occasions at Loch Ard, 19 occasions at Sourhope); to facilitate analysis, these were interpolated as random values between the Cl^- concentrations of the preceding and subsequent weeks. The power spectrum typically plots wavelength (or frequency) against spectral power on log–log scales. The power spectra were smoothed using a Tukey-Hanning window with a window length of 128 weeks and an overlap of 50%. As highlighted by Kirchner (2005), real world data are usually not band-limited to frequencies below the Nyquist frequency and therefore subject to aliasing (i.e. overestimating of spectral power with increasing frequency) even at frequencies well below the Nyquist frequency. The spectra were therefore alias-filtered using the algorithm provided by Kirchner (2005), which estimated the filtered spectrum by fitting the originally obtained, aliased spectrum to an assumed spectral model.

Time-variant mean transit times

To assess any effects of precipitation totals and sampling period on resulting transit times a moving window approach, where windows of varying lengths (0.5, 1, 2, 3, 4, 5, 6, 7, and 8 years) are applied to the Cl^- time series. To keep the computation logistically feasible, only the EM was used. For each window, the best fit MTT is computed, thereafter the window is shifted by 1 week, and the best fit model is determined again, and then repeated until the end of the time series. As the precipitation amounts are likely to be different in the individual windows, this facilitates the evaluation of its relationship with MTT. The second aspect of this analysis is the use of moving windows of different lengths. From this, possible impacts of the length of an observed time series on MTT estimates can be identified.

4. Results and discussion

Catchment hydrology

The annual precipitation at Loch Ard ranged between 1476 mm and 2168 mm over the study period (Fig. 3a). The maximum weekly precipitation amount was 176 mm (07/01/1988). At Sourhope the annual precipitation ranged between 695 mm and 1100 mm, with the maximum weekly precipitation of 152 mm occurring in the week of 08/11/2000 (Fig. 3b). Inspection of the hydrographs reveals distinct differences in the two catchments. While the runoff response at Loch Ard shows high peak flows and very short hydrograph recession periods, the runoff at Sourhope exhibits a much more subdued pattern with extended recessions, underpinning the different flow duration curves (Fig. 2). At flows higher than Q_{50}, specific flows at Loch Ard are consistently higher than at Sourhope. The opposite is true for specific low flows which are significantly higher at Sourhope.

Hydrochemical variations and hydrograph separation

A wide range of alkalinities can be observed in both catchments. Alkalinity remains negative throughout the observation period at Loch Ard, ranging from -138 to 0 μeq l^{-1}, whilst it ranges between 150 and 1650 μeq l^{-1} at Sourhope (Fig. 3). Alkalinity is negatively correlated with flow and the indirectly proportional logarithmic stream flow–alkalinity relationships (not shown) have coefficients of determination $R^2 = 0.56$ at Loch Ard ($n = 468$) and $R^2 = 0.78$ at Sourhope ($n = 424$, both significant at $\alpha = 0.01$). Low alkalinity storm flow at both sites is consistent with near-surface sources in acidic soils being active during precipitation events. Conversely, base flow shows high alkalinity signatures due to prolonged interaction between ground water and the bedrock. Obviously the bedrock weathering in the volcanic geology of Sourhope is higher than in the more siliceous, lower permeability drifts and solid geology at Loch Ard.

The results from the hydrograph separation are presented in Fig. 4 in terms of the specific discharges of both catchments plotted against the estimated groundwater contribution. At Loch Ard, the mean groundwater contribution was estimated at around 57% of total flow over the period of record (Table 1). At Sourhope there is an estimated mean groundwater contribution of 77% and even high flows ($<Q_5$) are characterized by a mean groundwater contribution of ~40%.

Uncertainties associated with the estimated groundwater contributions were quantified using the error propagation technique of Genereux (1998). For Loch Ard a 90% confidence interval of ±21% around the mean groundwater contribution was obtained. Analysis of the individual error terms revealed that the error in the estimation of the soil water and groundwater end members accounts for 42 and 43% of the total uncertainty, respectively, while the uncertainty in stream water accounts for 15% of the total uncertainty. The confidence interval at Sourhope of (±13%) is slightly smaller. Soil water and groundwater end member definition cause 83% and almost 17% of the total uncertainty, leaving the uncertainty of stream water measurement precision as negligible. These considerable uncertainties were expected because of the approximate definition of the soil water end members, but the results still demonstrated the greater significance of groundwater contributions at Sourhope.

Chloride variations and transit time estimation

Chloride concentrations in precipitation are highly variable at both sites and tend to show a seasonal cycle (Fig. 5). Highest concentrations and highest variability occur in winter whereas summer concentrations tend to converge at low levels. Given the maritime location of each catchment, concentrations largely reflect marine derived salts which tend to dominate the ionic composition of precipitation (Neal and Kirchner, 2000). Higher storminess and wind speeds in the north Atlantic source areas of the dominant frontal systems tend to result in enhanced Cl^- concentrations during winter. Consistent with the findings of previous studies (e.g. Neal and Rosier, 1990), variations in stream Cl^- concentrations at both sites are damped compared to precipitation. However, while stream variations at Loch Ard broadly reflect those in precipitation, those at Sourhope are attenuated to the point where the seasonal signal almost disappears. As highlighted by others (Neal et al., 1988; Öberg and Sanden, 2005; Page et al., 2007), stream water Cl^- flux is frequently elevated compared to the flux in precipitation. Significant contributions to Cl^- inputs can be attributed to dry, cloud and occult deposition, and thus the timing of some inputs may therefore be decoupled from measured wet inputs, though given the high and frequent precipitation in Scotland, and the weekly sampling time frame, the effect is probably relatively modest,

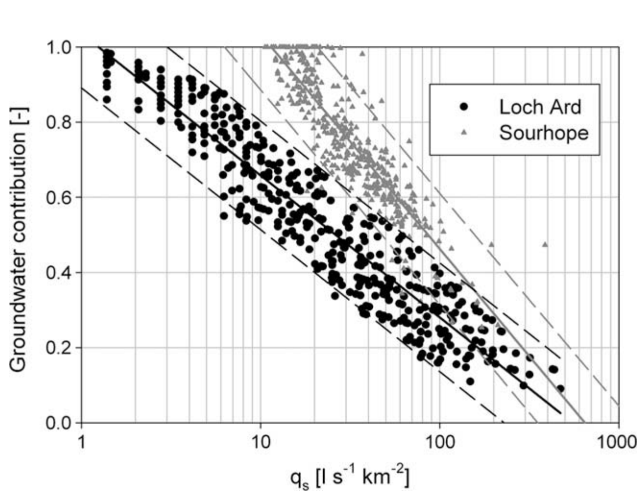

Fig. 4. Specific discharge plotted against groundwater contribution (including 95% prediction intervals) obtained from two-component geochemical hydrograph separation using alkalinity as conservative tracer for Loch Ard and Sourhope.

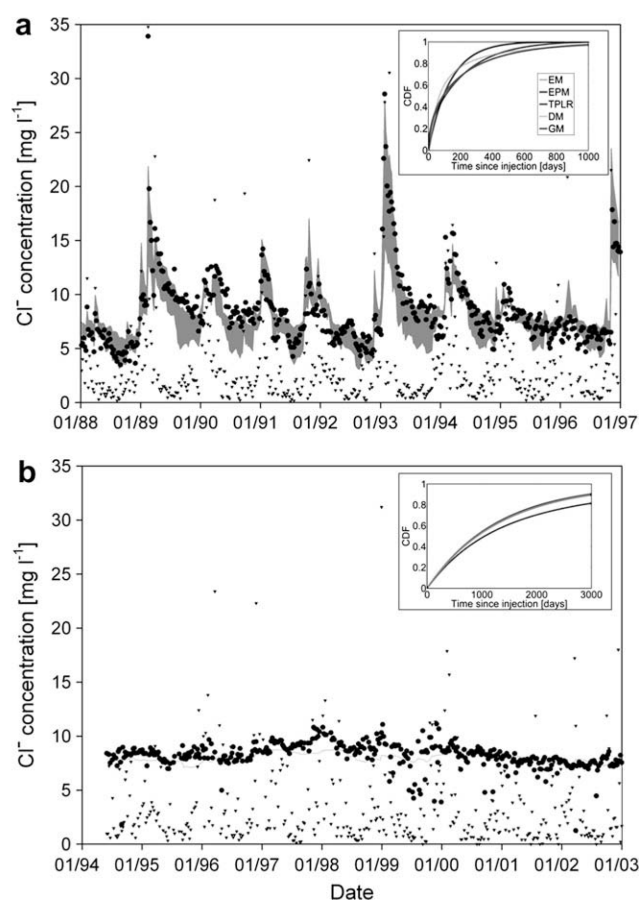

Fig. 5. Time series of Cl^- input and output concentrations at (a) Loch Ard and (b) Sourhope. (+) Symbols are observed Cl^- concentrations in precipitation, (•) symbols are observed Cl^- concentrations in the stream water, and the grey shaded area shows the GLUE uncertainty bounds. The insets show the cumulative distribution function (CDF) of the best fit parameter sets for each TTD.

though lumped adjustment factors should only be seen as first approximations especially in damped catchments such as Sourhope. It is also possible that biogeochemical cycling can affect Cl^- fluxes, contrary to its assumed conservative nature (Öberg, 2002).

Best fit MTT estimates at Loch Ard obtained from the convolution-based models fall within a relatively narrow range from 135 days (EM) to 202 days (GM). The different TTDs give model simulations with best fit Nash–Sutcliffe efficiencies ranging from 0.46 to 0.79 and RMSE ranging from approximately 1.5 to 2.5 (Table 3). Model distributions with Cl^- maxima at times later than the time of entry to the system $(t-\tau)$ either show poor fits (DM) or approximate the exponential model (EM): For example the piston flow percentage in the EPM is almost negligible. Best representations were obtained from the TPLR and GM which both allow a rapid initial response as well as long-term effects. The best fit fast reservoir transit time of the TPLR approach reaches 15 days and is reasonably well identified (Fig. 6b). The weighting parameter Φ seems to be quite identifiable too (Fig. 6c). On the other hand the slow reservoir transit time, with a best fit of 228 days, exhibits somewhat poorer identifiability (Fig. 6a). Although not outstandingly well identified, this parameterization basically corroborates the catchment conceptualization derived from the flow duration curve and the hydrograph separation: a significant portion of storm flow is routed to the stream through rapidly responding pathways, but also sustaining a certain level of base flow, which is represented by the slowly responding reservoir. Interestingly, although simple sine wave models provide a relatively poor fit, the resulting MTT estimates, although lowest of all methods, are reasonably close to the other models.

The uncertainty bounds derived from the GLUE bracket much of the unexplained variance of the best fit models (Fig. 5a). Table 3 gives details of the best fit parameter sets compared to the parameters obtained with GLUE. The predicted values obtained by GLUE tend to be non-Gaussian, i.e. highly skewed (Freer et al., 1996). Therefore, the median as measure of central tendency and the range between 5% and 95% quantiles as measure of spread were used in Table 3 to illustrate the approximate consequences of limited parameter identifiability.

The cumulative TTDs (inset Fig. 5a) can be interpreted as tracer "mass recovery from an instantaneous, uniform tracer mass addition" (McGuire et al., 2005). Given the short MTTs at Loch Ard, 100% of the tracer mass theoretically exits the system after $\sim$1000 days. The probability of such full tracer recovery in the observation period increases confidence in the feasibility of the TTDs and the validity of the initial assumptions (McGuire et al., 2005).

The power spectra for Loch Ard (Fig. 7a) show that while Cl^- concentrations in precipitation plot as approximately white noise (slope = 0.5), indicating independent random events (cf. Molenat et al., 1999), the stream chloride response (slope = 1.5) can be interpreted as $1/f$ noise, which is loosely defined with slope between 0.5 and 1.5 (Gisiger et al., 2001). This implies that the influences of both short-term and long-term variability in inputs are evident in outputs. This absence of a characteristic process time scale has been reported by several others (Kirchner et al., 2000; Page et al., 2007; Shaw et al., 2008) who have suggested that catchments may act as fractal filters on conservative tracers and water movement. The Cl^- power spectra also provide insight into the

Table 3
Model parameters for individual TTDs and the goodness of fit for the associated models expressed as Nash–Sutcliffe efficiency E and RMSE.

Model	Mean transit time (τ_m, $\alpha\beta$ for Gamma) (d)	η (–)	τ_f (d)	τ_s (d)	Φ (–)	D_p (–)	α	β	E (–)	RMSE (mg l^{-1})
Loch Ard										
Exponential	135[a] n.a.[c]	–	–	–	–	–	–	–	0.65[a]	2.00[a]
Exponential piston flow	136[a] 187 (70–373)[b]	1.01[a] 1.03 (1.00–1.09)[b]	–	–	–	–	–		0.65[a]	2.00[a]
Two parallel linear reservoirs	–	–	15[a] 45 (12–72)[b]	228[a] 327 (101–571)[b]	0.20[a] 0.26 (0.08–0.91)[b]	–	–	–	0.79[a]	1.56[a]
Diffusion/dispersion	196[a] 234 (97–455)[b]	–	–	–	–	1.98[a] 1.59 (0.92–1.98)[b]	–	–	0.46[a]	2.48[a]
Gamma	202[a] 341 (48–1067)[b]	–	–	–	–	–	0.49[a] 0.59 (0.06–1.19)[b]	411[a] 789 (103–1547)[b]	0.77[a]	1.61[a]
Sine wave	110[a]	–	15[a]	–	–	–	–	–	0.21[a]	2.34[a]
Sourhope										
Exponential	1283[a] n.a.[c]	–	–	–	–	–	–	–	0.15[a]	0.85[a]
Exponential piston flow	1287[a] 1302 (943–1994)[b]	1.00[a] 1.00 (1.00–1.01)[b]	–	–	–	–	–	–	0.15[a]	0.85[a]
Two parallel linear reservoirs	–	–	991[a] 803 (376–1054)[b]	1948[a] 1994 (1232–2968)[b]	0.56[a] 0.37 (0.05–0.86)[b]	–	–	–	0.16[a]	0.87[a]
Diffusion/dispersion	1970[a] n.a.[b,d]	–	–	–	–	0.88[a] n.a.[b,d]	–	–	0.09[a]	0.90[a]
Gamma	1332[a] 1881 (1110–2636)[b]	–	–	–	–	–	0.98[a] 0.90 (0.78–0.99)[b]	1361[a] 2141 (1172–2920)[b]	0.16[a]	0.87[a]
Sine wave	1059[a]	–	–	–	–	–	–	–	0.06[a]	0.98[a]

[a] Values for best fit.
[b] Results from GLUE showing median parameter and in brackets 5–95% interquantile parameter range.
[c] n.a.: No GLUE uncertainty bounds available as EM is a model with only one parameter.
[d] n.a.: Not available, because no model was accepted as behavioral.

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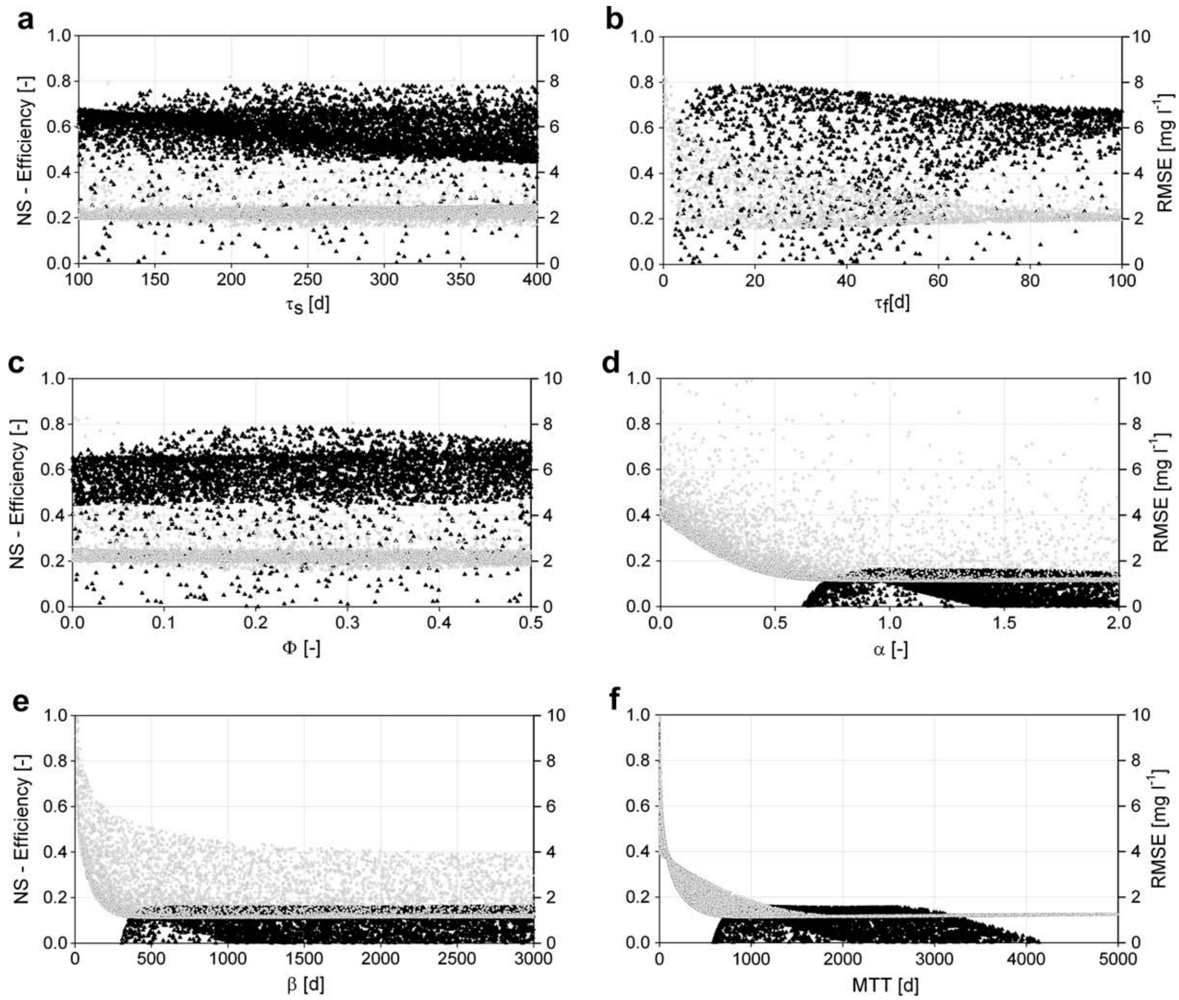

Fig. 6. Scatterplots of parameter value versus Nash–Sutcliffe efficiency E (▲) and RMSE (○) (10,000 Monte Carlo realizations) for the TPLR model at Loch Ard: (a) MTT of slow reservoir τ_s, (b) MTT of fast reservoir τ_f, (c) weighting factor Φ and for the gamma model at Sourhope: (d) shape parameter α, (e) scale parameter β, and (f) MTT ($\alpha\beta$).

ability of the applied TTD to reproduce the variability in stream water when plotted in the frequency domain. Despite having the highest efficiencies and low RMSE, the TPLR model largely fails to reproduce $1/f$ noise (slope = 1.9), whilst the power spectrum of the GM (slope = 1.8) is somewhat closer to the observed data. The other model outputs show slopes >2, which is a sign of brown noise, emphasizing processes at long time-scales. In terms of the models' abilities to describe the Cl^- signal in the stream this means that the higher the slopes of the power spectra are, the more information on short-term fluctuations is lost. The long-term trends with wavelengths >0.8 years are captured reasonably well by all models while the observed variations at shorter time scales can only be roughly approximated by the GM and partly by the TPLR which provides better estimates than the gamma model for time scales >0.15 years.

The best fit MTT estimates at Sourhope are an order of magnitude higher than at Loch Ard, ranging from 1283 (EM) to 1970 days (DM). The damped tracer response and high transit times resulted in much poorer model efficiency E than at Loch Ard. The best performing model was the GM which reached an efficiency of 0.16, while the DM was poorest with an efficiency of 0.09 (Table 3). However, RMSE for all models is about 0.9 mg l^{-1}, which is significantly lower than at Loch Ard, which suggests that in spite of low E the models do not necessarily have to be rejected. Inspection of the best fit parameter sets reveals that the models converge to a shape with immediate but moderate response maxima, which is basically represented by the EM; i.e. $\eta = 1$ for the EPM and shape parameter $\alpha \approx 1$ for the GM. Parameter identifiability is consistently lower than at Loch Ard (Fig. 6d and e): β can only be identified to be higher than about 1000. The resulting MTT can also therefore only be broadly identified to be in the range of 1000–2300 days, with a best fit at 1332 days (Fig. 6f). The best fit, though poorly identified, for the TPLR parameters suggest a "fast" mean transit time of 991 days and a "slow" transit time of 1948 days. Regardless of the weak model fits and poor parameter identifiability, the general result is consistent with the catchment conceptualization derived from the flow duration curve and the hydrograph separation. The damped stream signal is, to a certain extent, controlled by longer transit times, and it is clear that the effects of more rapid, short-term response of storm flow paths are poorly characterized. This may be as a result of the transit time models failing to capture non-linear threshold event-based behavior and the marked mixing in groundwater. Again, simple sine wave models provide a poor fit and the resulting MTT estimates are the lowest of all methods, but of the same order as those given by the other methods. The cumulative TTDs (inset Fig. 5b) indicate that only 80–90% of the tracer mass is recovered for the individual models.

The GLUE uncertainty bounds for Sourhope, shown in Fig. 5b, are too narrow to explain some of the variance in the stream signal, it is the long-term trends which are best captured. The short-term fluctuations cannot be accounted for adequately, particularly in the first years of observation. The modeled stream signal is almost

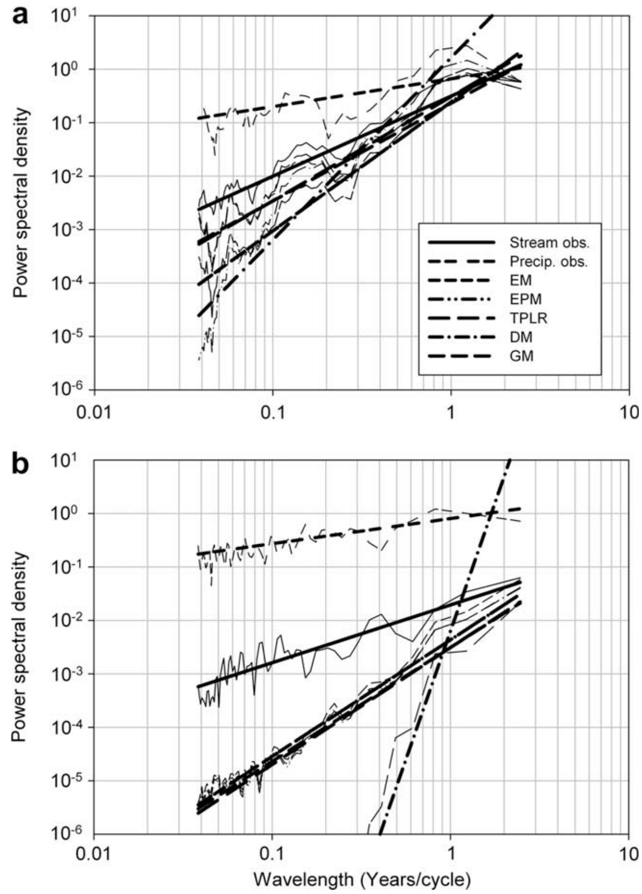

Fig. 7. Power spectra of observed Cl^- concentrations in precipitation and stream water as well as modeled Cl^- concentrations in stream water at (a) Loch Ard and (b) Sourhope. The power spectra were smoothed using Tukey-Hanning window with 50% overlap and a window length of 128 weeks.

constant for this period and fails to reproduce the observed weak seasonal pattern. Except for the peaks missed at the beginning of 1998 and 1999 the model roughly mimics the observed stream signal. Table 3 gives details of the best fit parameter sets compared to the median and 90% interquantile ranges of the parameters obtained with GLUE. These results reflect the low degree of identifiability for all models at Sourhope with MTT interquantile ranges of up to 1500 days. The narrow uncertainty intervals at Sourhope reflect equifinal model results with many parameter sets from different parts of the parameter space able to produce similar results.

The power spectra at Sourhope also revealed the general behavior of Cl^- in the catchment and some of the model limitations. The power spectrum of Cl^- in precipitation again plots approximately as white noise (slope = 0.4). As the tracer is routed through the catchment, its signature in the power spectrum is again transformed into $1/f$ noise (slope = 1.1). However, the $1/f$ scaling cannot be reproduced by any of the other models (Fig. 7b), which basically plot on top of each other (slope = 2.2), except for the DM (slope = 9.7). The high slopes of the model results imply that long-term trends at time scales >1 year (e.g. seasonal fluctuations) can be reproduced reasonably well but not the short-term fluctuations which have very low spectral power, throughout.

Influence of precipitation and sampling period on mean transit times

Calculating MTT using a "moving window", shifted by weekly time steps for time periods of 0.5–8 years showed that the resulting estimates depended on the total amount of precipitation and the length of observation period. For moving window lengths of 1 year, the MTT derived from the EM at Loch Ard is reduced from approximately 225 days for drier periods to about 125 days for the wettest (Fig. 8a). At Sourhope, the pattern is similar and the apparent MTT decreases from around 3600 days during dry spells to ~1500 days for periods with highest precipitation. Although only low R^2 values, particularly for Sourhope, could be identified, the relationships are significant at $\alpha = 0.05$, throughout. Because precipitation totals are not the only control on MTTs, the high scatter (i.e. low R^2) in the precipitation–MTT relationships is likely attributable to additional factors such as precipitation intensity and evaporation controls.

It is also apparent from Fig. 8 that the length of the observation period has an influence on the goodness of fit of the average MTT and on the rate of change with increased precipitation. Using a five year moving window, R^2 is significantly increased and it can be seen that the levels of MTT are lower than those for shorter observation periods with the influence of precipitation on the MTT estimate being reduced. Fig. 9 provides further insight into the relation between moving window length and MTT. For both catchments the residuals of the MTTs exhibit a high scatter for short observation periods which stabilizes at about 4 years. The median MTTs decrease with increasing length of the moving window ($R^2 = 0.84$ at Loch Ard and $R^2 = 0.77$ at Sourhope, both significant at $\alpha = 0.01$). The power laws which consistently describe these relationships at both catchments suggest classical fractal scaling (cf. Mandelbrot,

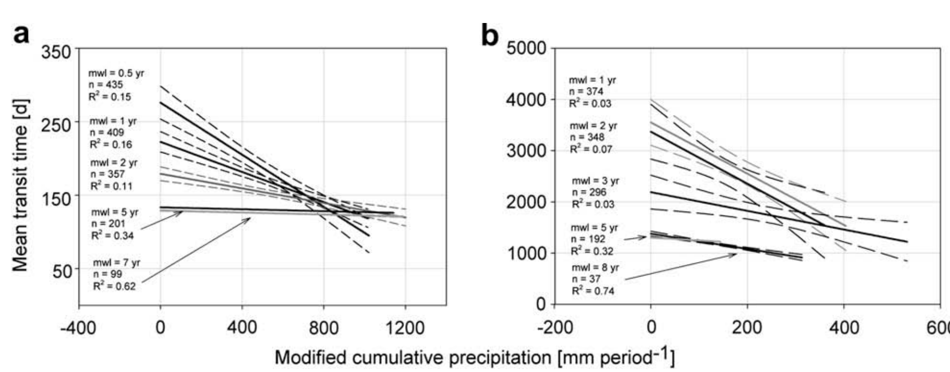

Fig. 8. Modified cumulative precipitation during the observation period plotted against MTT for the study sites at (a) Loch Ard and (b) Sourhope. The wider the respective moving window, the higher is the cumulative precipitation. It is therefore difficult to visually compare the results for different moving window lengths. To overcome this problem a modified cumulative precipitation was used in the figure. It is the cumulative precipitation for one observation period with a certain moving window length minus the lowest cumulative precipitation of all observation periods with the same moving window length (i.e. the lowest cumulative precipitation is 0 for all moving window lengths). This allows visual comparability of observation periods with different moving window lengths, as the graphs are shifted to plot on top of each other.

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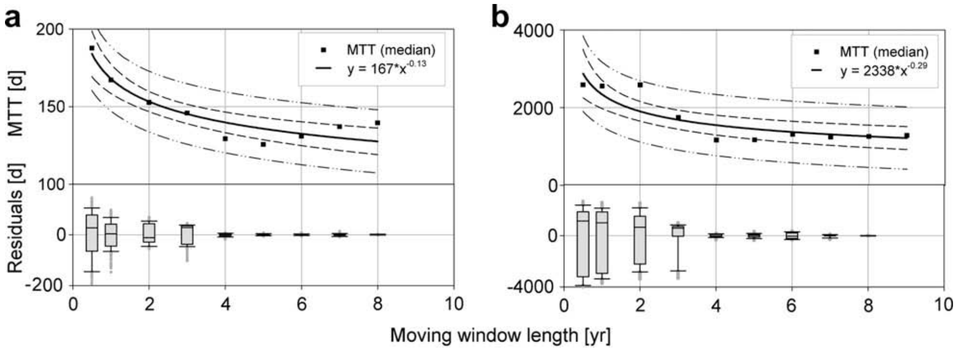

Fig. 9. Plots of moving window lengths against median MTT and its residuals for the study sites at (a) Loch Ard and (b) Sourhope.

1983). The scale invariance, inherent to power laws, also suggests the absence of a characteristic MTT. Fig. 8 also highlights the impact of moving window length on the rate of change of MTT with precipitation: the longer the observation period, the less pronounced is the relationship between precipitation and transit time, i.e. the lower the slope. Somewhat surprisingly, this relationship also plots as a power law (not shown), again indicating scale invariance on the one hand and an operational cut-off value, at which the relation approaches a constant, at about 4 years.

Wider implications

Both geochemically-based hydrograph separations and hydrometric data showed that the Sourhope catchment was dominated by groundwater sources which accounted for around 77% of annual flows. This is a large groundwater component for an upland catchment in the UK; even compared to other sites where groundwater has been shown to be important (e.g. Soulsby et al., 1998; Dunn et al., 2008). Although the concept of transit time modeling was originally developed for groundwater systems, which can usually be assumed to be at steady-state (e.g. Maloszewski and Zuber, 1986) various TTDs were relatively poor at explaining both the long-term and short-term variation in Cl^- at Sourhope. It seems likely that these low parameter transit time models failed to capture the effect of dynamic runoff processes with non-linear thresholds, in a system where so much of the response was dominated by well-mixed groundwater contributions (McGuire and McDonnell, 2006). In addition, the lumped enhancement factor may be relatively insensitive to short-term enhanced deposition which can affect short-term outputs. Despite uncertainty over the resulting estimates, MTT seem to be of the order of at least several years, which is comparable to other studies in montane catchments where geological conditions mean that groundwater contributions are high (e.g. McGuire et al., 2005; Viville et al., 2006). Nevertheless, in such catchments natural tracers such as Cl^- or stable isotopes may be insufficient to characterize transit times, and alternative approaches, such as use of CFCs or ^3H may be needed to characterize longer-residence waters.

In contrast, the dominance of a responsive hydrological regime with lower groundwater contributions observed at Loch Ard is typical of upland catchments dominated by surface and near-surface runoff processes (e.g. Soulsby et al., 2004). Although the underlying schist is a potential aquifer (cf. Haria and Shand, 2004), limited recharge from the peaty soils and drift appears to reduce the importance of groundwater contributions. The resulting relatively short MTT of a few months, corresponds to those estimated for similar upland UK catchments dominated by gleyed and peaty soils such as the Tanllwyth (Kirchner et al., 2001), Upper Feshie (Soulsby et al., 2006) and Girnock (Tetzlaff et al., 2007a). Although such catchments are highly dynamic, the wetter climates and more responsive soils may result in tracer fluxes that exhibit less marked non-linearity in response to rainfall inputs compared to drier sites with more freely draining soils that are less well-connected to the river channel network. That said, the weekly sampling deployed here will miss short-term (i.e. sub-daily) dynamics associated with individual events which are needed to accurately characterize the transit times of the most responsive hydrological components (e.g. Kirchner, 2003; Tetzlaff et al., 2007c).

It is also apparent that estimates of MTT are non-stationary and influenced by climatic variability (i.e. precipitation amount). Although MTTs at Loch Ard and Sourhope differ by one order of magnitude, they both show a very similar dependence on climatic variability. It was shown that particularly for short observation periods of 1–2 years, which are quite common in catchment studies, precipitation variability has a marked influence on the resulting MTT estimates. This can be potentially problematic for inter-comparison of studies, especially with data sets of different periods and lengths. Using only short-term data, Dunn et al. (2007) demonstrated that an important control on MTT at the Maimai catchment in New Zealand is storage in the unsaturated zone which in the longer-term may have high temporal dependence both seasonally and inter-annually (Turner et al., 1987). Obviously precipitation totals will influence antecedent soil moisture conditions and the degree of connectivity between dynamic, responsive sources of storm runoff and the river channel (Lane et al., 2004), which in turn will effect transit times.

The influence of the length of observation period length on MTT estimates is likely to be an artifact of averaging: the longer the observation period, the less the model will be reproducing extremes as a result of the least-squares fitting process. Transit time estimates should therefore be contextualized in relation to the length of the data set, especially for short observation periods <3 years, where resulting MTTs may vary by as much as 50%.

Despite the markedly contrasting characteristics of the two catchments in terms of flow regimes, groundwater contributions and tracer input–output relationships, the spectral pattern of the Cl^- signal in the stream signal showed a similar structure, transforming white noise inputs into approximately $1/f$ outputs. As shown by others (e.g. Duffy and Gelhar, 1985; Duffy and Gelhar, 1986; Molenat et al., 1999) catchments can act as "low-pass" filters, attenuating the spectral power at high frequencies and thereby the variance in the output time series, especially for white noise inputs, while preserving it at low frequencies. The $1/f$ scaling reflects this presence of both long-range and short-range dependence in time series with white noise input, which appears to be a common feature of natural systems when somewhat loosely defined as ranging from $1/f^{0.5}$ to $1/f^{1.5}$ (cf. Gisiger et al., 2001; Wagenmakers et al., 2004). The origin and interpretation of this filter or transfer function, which seem to be independent of the actual catchment structure, however, is disputed and the concept might be ill-specified (Mandelbrot, 2002) as no single underlying process is so far identifiable. Rather, different processes, leading to the same structure in the power spectrum can be identified for individual data sets. For example, some studies (e.g. Koutsoyiannis, 2002; Wagenmakers et al., 2004; Shaw et al., 2007) suggest that a filter consisting of a combination of parallel auto-regressive processes at different short time scales, which are clearly not fractal, can approximate 1/*f* scaling. However, Kirchner et al. (2001) make an elegant and convincing case for how catchment scale advection–dispersion processes along different flow path lengths can model the fractal behavior of Cl^- in stream waters at Plynlimon. The strength of this hypothesis is that it makes no *a priori* assumptions about poorly identifiable parallel processes and thus may explain the consistency of 1/*f* responses in very different catchments.

The emerging question for future research therefore is whether there is one single characteristic mechanism, such as advection–dispersion, which underlies the generation of 1/*f* scaling for chloride output in catchments, indicating long-range dependence? Or whether a generally valid pattern of parallel short-range auto-regressive processes acting as transfer function and generating 1/*f* scaling in chloride output can be identified? Indeed both mechanisms are reflected in the best fit MTT models observed in this study for the two very different small catchments. Resolution of this issue would give deeper insight in the hydrological functioning of catchments. Moreover, it is particularly important to understand how tracer responses may be used in up-scaling studies, where runoff processes and transit times in sub-catchments with different properties integrate together.

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