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USING WATER AGE TO EXPLORE HYDROLOGICAL PROCESSES IN CONTRASTING ENVIRONMENTS

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# Travel times for snowmelt-dominated headwater catchments: Influences of wetlands and forest harvesting, and linkages to stream water quality

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## Abstract

The time it takes water to travel through a catchment, from when it enters as rain and snow to when it leaves as streamflow, may influence stream water quality and catchment sensitivity to environmental change. Most studies that estimate travel times do so for only a few, often rain-dominated, catchments in a region and use relatively short data records (<10 years). A better understanding of how catchment travel times vary across a landscape may help diagnose inter-catchment differences in water quality and response to environmental change. We used comprehensive and long-term observations from the Turkey Lakes Watershed Study in central Ontario to estimate water travel times for 12 snowmelt-dominated headwater catchments, three of which were impacted by forest harvesting. Chloride, a commonly used water tracer, was measured in streams, rain, snowfall and as dry atmospheric deposition over a 31 year period. These data were used with a lumped convolution integral approach to estimate mean water travel times. We explored relationships between travel times and catchment characteristics such as catchment area, slope angle, flowpath length, runoff ratio and wetland coverage, as well as the impact of harvesting. Travel time estimates were then used to compare differences in stream water quality between catchments. Our results show that mean travel times can be variable for small geographic areas and are related to catchment characteristics, in particular flowpath length and wetland cover. In addition, forest harvesting appeared to decrease mean travel times. Estimated mean travel times had complex relationships with water quality patterns. Results suggest that biogeochemical processes, particularly those present in wetlands, may have a greater influence on water quality than catchment travel times.

KEYWORDS
catchment, chloride, forest harvesting, headwaters, transit time, wetlands

## 1 | INTRODUCTION

Forested watersheds show a wide range of hydrologic and biogeochemical responses to environmental change, such as forest harvesting and climate variability (Brown, Zhang, McMahon, Western, & Vertessy, 2005; Buttle, 2011; Jones et al., 2012; Zhang et al., 2017). We need to understand the underlying controls of this response variability to help inform effective management of forests and the water resources they supply (Creed et al., 2019). Water storage within a catchment has been proposed as a key characteristic influencing catchment sensitivity to change (McDonnell et al., 2018; Spence, 2010). Efforts have been made to quantify catchment storage and understand its influence on catchment response to environmental change (Buttle, 2016; Carey et al., 2010; McNamara et al., 2011; Nijzink et al., 2016).

One such measure of catchment storage is catchment travel time, which is the time it takes a water molecule to travel from where it enters the soil as rain or snowmelt to when it exits the catchment outlet (Soulsby, Tetzlaff, & Hrachowitz, 2009). In contrast to approaches focused on water balance calculations for understanding catchment storage, water travel times attempt to account for water velocities within a catchment in place of water celerities (McDonnell & Beven, 2014). Partly because of this distinction, it is hypothesized that water travel times may not only effectively characterize the hydrologic response of catchments, but may also be a critical control on stream water quality (Hrachowitz et al., 2016).

Different methods involving hydrologic tracers have been used to estimate catchment water travel times. The most common approach has been spatially lumped and time averaged convolution integral models (McGuire & McDonnell, 2006). These models have been employed to estimate mean travel times since the 1980s (Małoszewski & Zuber, 1982; Rodhe, Nyberg, & Bishop, 1996) and continue to be used because of their parsimony (Lane et al., 2020; Parajulee, Wania, & Mitchell, 2019), despite recognized limitations in accounting for variable flow conditions and catchment heterogeneity (Kirchner, 2016a). To tackle some of these limitations, time variant models have been developed (Benettin et al., 2017; Harman, 2015; Klaus, Chun, McGuire, & McDonnell, 2015; Rinaldo et al., 2015). Although these time variant models provide a more realistic representation of hydrologic dynamics, they can be difficult to estimate due to issues of equifinality and can be subject to considerable uncertainty (Seeger & Weiler, 2014; Hrachowitz et al., 2016). Both time averaged and time variant approaches for estimating travel times rely on the use of hydrologic tracers, such as stable water isotopes or chloride (Shaw, Harpold, Taylor, & Walter, 2008; Stewart & McDonnell, 1991). Hydrologic tracers are assumed to act conservatively within catchments although chloride has been shown to be influenced by biogeochemical cycling (Bastviken et al., 2006; Lovett, Likens, Buso, Driscoll, & Bailey, 2005) and water isotopes can be fractionated by evaporation (Kendall & McDonnell, 1998). Despite these limitations, research suggests that chloride and water isotopes can be treated as approximate conservative tracers (Kirchner, Tetzlaff, & Soulsby, 2010).

Numerous studies have documented variability in travel time estimates across catchments and how they vary in relation to catchment characteristics and meteorological conditions. Mean travel times have been related to flowpath distance, hillslope gradient, soil characteristics, catchment area and meteorological conditions such as rainfall intensity (Broxton, Troch, & Lyon, 2009; Cartwright, Irvine, Burton, & Morgenstern, 2018; Heidbüchel, Troch, & Lyon, 2013; Hrachowitz, Soulsby, Tetzlaff, Dawson, & Malcolm, 2009; Hrachowitz, Soulsby, Tetzlaff, & Speed, 2010; McGuire et al., 2005; Tetzlaff et al., 2009). Most studies are from rain-dominated systems although there has been an increase in the number of studies focused on catchments influenced by snow (Ala-Aho, Tetzlaff, McNamara, Laudon, & Soulsby, 2017; Broxton et al., 2009; Fang et al., 2019; Lane et al., 2020; Lyon et al., 2010; Parajulee et al., 2019; Peralta-Tapia et al., 2016). Concerns have been raised about comparing travel times estimates across space and time using the common time averaged models. Some of the key issues identified are that travel time estimates are sensitive to catchment heterogeneity, as well as differences between catchments in terms of water and tracer input estimates (Kirchner, 2016a, 2016b; Seeger & Weiler, 2014).

In this study, we use comprehensive and long-term chloride observations made at 12 forested headwater catchments influenced by seasonal snowfall to estimate relative mean catchment travel times. These are small headwater catchments with similar forest cover and surficial geology, which may allow us to reasonably avoid issues associated with lumped travel time models for spatially heterogeneous catchments (Kirchner, 2016a). In addition, the catchments are located in a small geographic area and we can reasonably assume they are subject to similar water and tracer inputs; therefore, we inherently account for differences in climate between catchments which can confound the ability to assess the influences of catchment characteristics on travel time estimates (Seeger & Weiler, 2014).

The main objectives of this study are to: (a) compare relative mean catchment travel times for 12 forested headwater catchments; (b) explore relations between estimated travel times and catchment characteristics, including the influence of forest harvesting; and (c) assess whether mean travel times account for differences in water chemistry patterns observed across the 12 catchments. We specifically assessed multiple working hypotheses (Chamberlin, 1890) associated with Objectives 2 and 3. For Objective 2, we expected:

- Shorter travel times associated with shorter mean flowpath lengths (McGuire et al., 2005).
- Either no relationship (McGuire et al., 2005; Rodgers, Soulsby, & Waldron, 2005) or shorter travel times associated with smaller catchment areas (Hale & McDonnell, 2016; McDonnell, Rowe, & Stewart, 1999; Soulsby, Malcolm, Helliwell, Ferrier, & Jenkins, 2000).
- Shorter travel times associated with greater catchment wetland cover due to the ability of wetlands to rapidly move water laterally (Laudon, Sjöblom, Buffam, Seibert, & Mörth, 2007; Lyon et al., 2010; Peralta-Tapia, Sponseller, Tetzlaff, Soulsby, & Laudon, 2015). Alternatively, we might expect longer travel times associated with greater catchment wetland cover due to the water storage capacity of wetlands (Lane et al., 2020).

- Shorter travel times associated with steeper slopes (McGuire et al., 2005); however, this relationship could be confounded by the influence of wetlands if they are found to be associated with shorter travel times.
- Shorter travel times associated with higher annual runoff ratios if event quickflow strongly influences annual runoff ratios. Alternatively, we might expect longer travel times associated with higher annual runoff ratios if annual runoff ratios are strongly influenced by augmented baseflows due to groundwater contributions (Hale & McDonnell, 2016).
- Shorter travel times following forest harvesting due to an increase in the quickflow proportion of total streamflow, as was previously documented for the harvested catchments used in our study (Buttle, Webster, Hazlett, & Jeffries, 2019).

Our working hypotheses for linkages between travel times and stream chemistry (Objective 3) were based on the assumption that longer travel times are associated with water flowpaths dominated by deeper flow in contact with mineral soils, whereas shorter travel times indicate water flowpaths dominated by shallow flow more in contact with soil organic layers. This appears to be a common assumption regarding the relationship between catchment travel times and dominant hillslope flowpaths (Tetzlaff et al., 2015; Tetzlaff, Seibert, & Soulsby, 2009). Therefore, we expected:

- Higher stream silica concentrations associated with longer travel times (Buttle et al., 2018; Elsenbeer, Lack, & Cassel, 1995); however, because wetlands in boreal regions can be a source of silica (Struyf, Mörth, Humborg, & Conley, 2010), silica concentrations may be higher for shorter travel times if wetland cover is negatively related to mean travel time.
- Higher stream potassium concentrations associated with shorter travel times due to high concentrations of potassium in the soil organic layers (Buttle et al., 2018).
- Higher phosphorous concentrations associated with shorter travel times due to less potential for adsorption to mineral soils (O'Brien, Eimers, Watmough, & Casson, 2013).
- Higher nitrate concentrations associated with longer travel times due to a greater potential for nitrate to leach away from root zones (Asano, Compton, & Church, 2006) or longer travel times and flowpath lengths being associated with hillslope conditions that have a greater potential for nitrate flushing (Creed & Beall, 2009).
- Higher pH associated with longer travel times due to observed increase in soil pH with soil depth (Hazlett, Curry, & Weldon, 2011).
- Higher concentrations of calcium, sodium and magnesium associated with longer travel times due to these base cations being mineral weathering products (Casson, Eimers, Watmough, & Richardson, 2019). However, redistribution within soil due to adsorption and biological activity may confound this relationship for calcium and magnesium, but not sodium since it is not an essential plant element and shows an increase in concentration with soil depth (Foster, Nicolson, & Hazlett, 1989).

## 2 | FIELD OBSERVATIONS

### 2.1 | Turkey Lakes Watershed

The study was conducted at the Turkey Lakes Watershed (TLW; 47° 03′N, 84° 25′W) situated about 65 km north of Sault Ste. Marie, Ontario (Figure 1). The 10.5 km$^2$ watershed is located in the rugged terrain of the Algoma Highlands in a leeward location 13 km from the eastern shore of Lake Superior. The outlet stream that drains TLW is called Norberg Creek and is a tributary of the Batchawana River which flows into Lake Superior. The watershed is in the Great Lakes – St. Lawrence forest region (Rowe, 1972) of the Boreal Shield Ecozone in the Algoma region of central Ontario. The elevation of the TLW ranges from 330 to 625 m above sea level. Mean daily air temperature measured at a long-term meteorological station near the site is 4.6°C based on observations from 1980 to 2010, with mean daily January and July air temperatures of −10.7 and 17.9°C, respectively (Semkin et al., 2012). Snow cover typically begins to develop in late October and melts during the March–May period.

Regional bedrock for TLW is Precambrian metamorphic basalt (silicate greenstone) with some granitic outcrops, covered by thin discontinuous two-component till: bouldery silt loam ablation till overlying compacted sandy loam basal till (Hazlett, Semkin, & Beall, 2001). Hillslope soil cover is orthic humo-ferric podzols (spodosols) with well-defined L and F (Oi and Oe) horizons with a combined average thickness of 0.05 m (Hazlett et al., 2001), while dispersed organic soils occupy depressions and riparian areas (Creed, Beall, Clair, Dillon, & Hesslein, 2008). In the headwater catchments, average depth of soil to basal till or bedrock is around 0.5 m (Buttle et al., 2019; Hazlett et al., 2011).

The TLW has a mature shade-tolerant hardwood forest cover of sugar maple (*Acer saccharum* Marsh., 90%), yellow birch (*Betula alleghaniensis* Britton; 9%) and some conifers (1%; Jeffries, Kelso, & Morrison, 1988). The TLW forest is undisturbed, with the exception of a light selective harvest in the 1950s (Beall, Semkin, & Jeffries, 2001) and an experimental harvest in late summer and fall of 1997 involving three of the catchments (Buttle et al., 2018). Catchment c31 was clearcut using a diameter limit cut in which all trees with a diameter of greater than 20 cm were harvested and all trees with a diameter between 10 and 20 cm were felled and left on site. Catchment c33 was harvested using a single-tree selection, an uneven-aged system where mature and undesirable trees were removed. The lower 70% of catchment c34 was harvested using an even-aged uniform shelterwood system where about 50% of mature trees were harvested. Selection and shelterwood harvesting left 64 and 61% of the pre-harvest overstory volume as live standing, compared to 22% for the clearcut harvest (Buttle et al., 2018).

### 2.2 | Hydrometeorologic measurements

Meteorological measurements were made at a 10 m tower situated about 1.5 km south-east of the TLW catchment boundary (Figure 1).

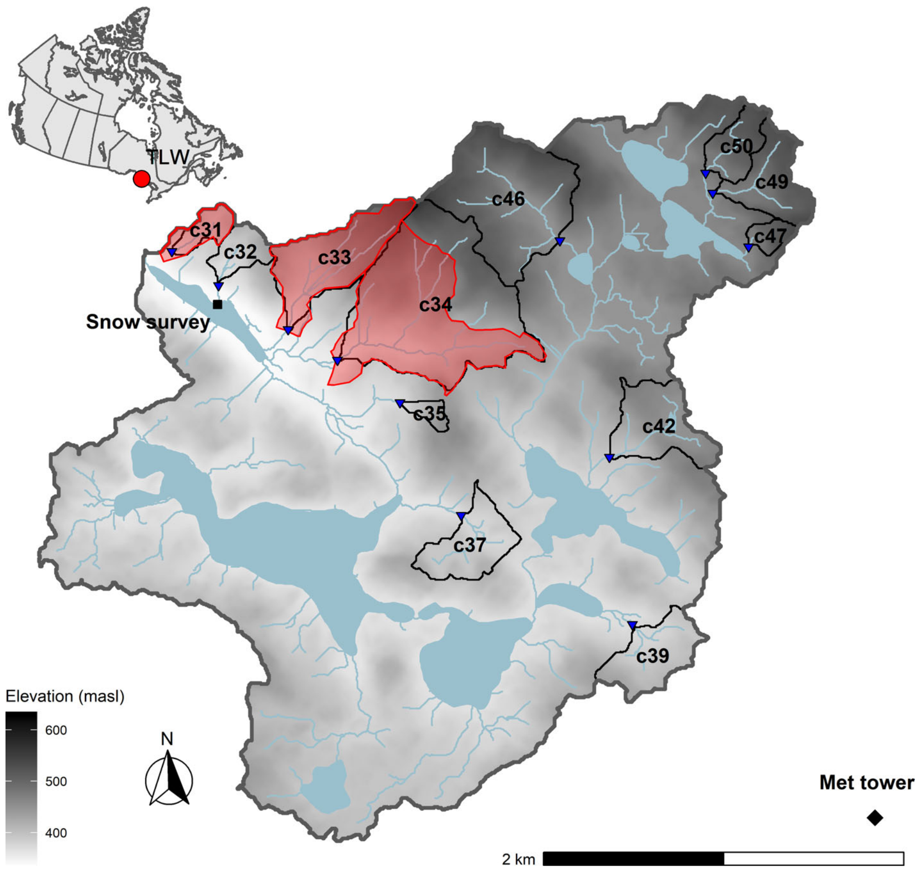


**FIGURE 1** Map of the Turkey Lakes Watershed (TLW). The 12 headwater catchments and their weir locations (blue triangles) are shown within the greater Turkey Lakes Watershed. The 1997 forest harvesting is shown in red. Inset map in top left corner situates the TLW within Canada. Elevation is shown in metres above sea level (masl)

Sensors for air temperature, wind speed and relatively humidity were logged over 10 min intervals and averaged over a 24 hr period to provide daily mean values (Semkin et al., 2012). For air temperature, daily maximum and daily minimum values were also extracted. Solar radiation and precipitation were summed over a 24 hr period to provide daily totals.

Manual snow surveys have been conducted at 11–13 locations (depending on year) within the TLW since 1980 (Semkin et al., 2012). Sampling occurred during both accumulation and ablation stages and consisted of snow depth and density measurements to calculate snow water equivalence. For the hydrologic modelling detailed below, we used the snow survey site located near catchment 32 (Figure 1) since this was the catchment used for the modelling.

Daily mean streamflow from the 12 headwater catchments (Table 1) was estimated from stage-discharge relationships developed using v-notch weirs, stilling wells and water level loggers (Beall et al., 2001; Buttle et al., 2018). Weirs were installed into the basal till in an effort to capture all flow from the catchments; however, there was the potential for some subsurface flow to bypass the weirs.

## 2.3 | Chloride and stream solute measurements

Atmospheric deposition measurements have been made at the TLW since 1981 by the Canadian Air and Precipitation Monitoring Network (Vet, 1987). Dry deposition of chloride was estimated with air concentration measurements made at 24 hr intervals combined with an inferential method to obtain monthly dry deposition fluxes (Sirois, Vet, & MacTavish, 2001). A wet-only deposition collector (Sirois et al., 2001) was used to measure chloride concentrations in precipitation at 24 hr intervals.

Manual samples for stream chloride were made by field technicians visiting the site. Each stream was sampled between 30 and 55 times per year, with daily samples taken during snowmelt periods and biweekly to monthly measurements throughout the rest of the year. Monthly sampling frequency was most common during winter and late summer when some streams no longer had surface flow. Although stream water samples have been collected since 1981, we restricted our analyses to 1985–2012 since chloride export exceeded inputs for all the catchments from 1981 to 1984.

The stream and precipitation samples were analysed for chloride concentration using ion chromatography (various Dionex instruments) at the Water Chemistry Laboratory, Natural Resources Canada, Great Lakes Forestry Centre in Sault Ste. Marie, Ontario. Ion chromatography instrumentation changed over the study period; however, whenever a change occurred extensive testing was done to ensure results were consistent within ±10%. In addition, the laboratory participates in a proficiency testing program through Environment and Climate Change Canada. We assumed a ±10% error in concentrations for the chloride mass balance analysis detailed below.

**TABLE 1** Properties of the 12 headwater catchments at the Turkey Lakes Watershed

| Catchment | Harvest | Area (ha) | Mean elevation (m) | Relief (m) | Wetland cover (%) | Mean slope (%) | Aspect | Mean flowpath length (m) |
|---|---|---|---|---|---|---|---|---|
| c31 | Clearcut | 4.9 | 405 | 47 | 2.0 | 25 | Southwest | 27 |
| c32 | Reference | 6.6 | 413 | 59 | 1.5 | 30 | Southwest | 31 |
| c33 | Selection cut | 24.1 | 470 | 114 | 0.4 | 28 | Southwest | 45 |
| c34 | Shelterwood | 68.9 | 474 | 111 | 1.2 | 30 | Southwest | 44 |
| c35 | Reference | 4.5 | 447 | 65 | 0.0 | 34 | South | 67 |
| c37 | Reference | 15.3 | 401 | 18 | 12.4 | 21 | West | 31 |
| c39 | Reference | 15.6 | 415 | 37 | 1.9 | 20 | West | 35 |
| c42 | Reference | 18.3 | 477 | 71 | 6.6 | 22 | West | 30 |
| c46 | Reference | 43.0 | 544 | 63 | 1.4 | 29 | Northwest | 42 |
| c47 | Reference | 3.5 | 553 | 49 | 0.0 | 36 | South | 36 |
| c49 | Reference | 14.9 | 554 | 56 | 2.0 | 27 | Southwest | 25 |
| c50 | Reference | 9.2 | 554 | 42 | 7.6 | 23 | Southwest | 24 |

*Note*: Catchment area, mean elevation, relief, mean slope, aspect and mean flowpath length were extracted from a lidar-derived 5 m digital elevation model. Percent wetland cover was based on field measurements outlined in Creed, Sanford, Beall, Molot, and Dillon (2003). Harvest refers to whether the catchment was harvested during the 1997 experimental harvesting (Buttle et al., 2018) or was unharvested (reference).

The manual water samples collected for chloride were also analysed for a range of other water solutes (Nicolson, 1988). For this study, we considered calcium, potassium, magnesium, nitrate, silica, total dissolved phosphorous and pH. Sampling frequency was the same as for chloride and mean and median concentrations were computed for each catchment from the spot measurements made during the pre-harvest period (1985–1996). A summary of the data used in this study is provided in Table 2.

## 3 | MODELLING AND ANALYSES

### 3.1 | Hydrologic modelling

The streamflow regimes of the headwater catchments within TLW are heavily influenced by snowmelt. Therefore, it was necessary to model snow accumulation and melt to estimate the timing of water and chloride flux into the catchment soils. In addition, the travel time models used in this study benefit from an estimate of effective precipitation (McGuire & McDonnell, 2006). The effective precipitation term has been estimated using different approaches (Hrachowitz et al., 2009; Stewart & McDonnell, 1991; Weiler, McGlynn, McGuire, & McDonnell, 2003). In this study, we define it as the precipitation and snowmelt recharging the catchment soil after accounting for canopy interception losses. To estimate snow dynamics and soil recharge, we used a version of HBV-EC (Hamilton, Hutchinson, & Moore, 2000) within the Raven modelling platform (Craig & The Raven Development Team, 2019).

The model was run at a daily time step from 1980 to 2012 using meteorological data collected at the TLW meteorological station. Although the focus of the modelling was to estimate snow dynamics and soil recharge, we calibrated the model to mean daily stream discharge since this should provide an integrated signal of both snowmelt timing and interception losses. We calibrated the model to discharge measured at the c32 catchment in part because it is a relatively small catchment whose hydrology should be dominated by vertical water fluxes, it has a long-term snow survey site in close proximity, and it has been used previously as a reference catchment (Buttle et al., 2018). We calibrated the model to the entire data record and did not hold back data for model evaluation because we were not interested in making model-based inferences.

We assumed that differences in precipitation across the catchments were negligible. This seems to be reasonable based on precipitation and snow water equivalent observations from different elevations within TLW (see Supporting Information). Mean annual precipitation totals for the period of 1983–2010 for five long-term precipitation stations at TLW (including the main meteorological station) that span a range of 350–500 m above sea level only varied up to 6% between sites (Semkin et al., 2012). Snow water equivalent measurements made within TLW highlight how the relationship between elevation and snow accumulation changes between years (see Supporting Information). In some years, a clear elevation effect is observed; however, in most years an orographic effect is minimal.

The hydrologic model was calibrated using a dynamically dimensioned search – approximation of uncertainty (DDS-AU) approach (Tolson & Shoemaker, 2008) using Ostrich (Matott, 2017). Model performance was assessed using the Nash-Sutcliffe efficiency (Nash & Sutcliffe, 1970). Parameter sets that resulted in Nash-Sutcliffe efficiencies of greater than 0.52 were deemed behavioural (Beven & Binley, 1992). Fifty search trials were run and a randomly selected behavioural parameter set from each independent trial was retained for subsequent analyses.

**TABLE 2** Summary of the field observations and modelled output used in this study

| Variable | Source | Spatial resolution | Temporal resolution | Use |
|---|---|---|---|---|
| Meteorological data (air temperature, wind speed, relative humidity, solar radiation) | Field measurements | Main meteorological tower | Daily | Forcing hydrologic model |
| Snow water equivalent | Field measurements | 11–13 survey locations | Weekly to monthly | Calibrating and evaluating snowmelt model |
| Stream discharge | Estimated from observed water levels | 12 headwater catchment outlets | Daily | Chloride outputs and calibrating hydrologic model |
| Dry chloride deposition | Estimated from air concentrations | Main meteorological tower | Monthly | Chloride inputs |
| Wet chloride deposition | Field measurements | Main meteorological tower | Daily | Chloride inputs |
| Stream chloride concentration | Field measurements | 12 headwater catchment outlets | Daily to monthly | Chloride outputs |
| Stream solute concentrations | Field measurements | 12 headwater catchment outlets | Daily to monthly | Stream water quality analysis |
| Canopy interception | Modelled | Same for all 12 catchments | Daily | Soil water and chloride inputs |
| Snow accumulation and melt | Modelled | Same for all 12 catchments | Daily | Soil water and chloride inputs |
| Chloride catchment inputs | Modelled | Same for all 12 catchments | Monthly | Chloride inputs |

*Note*: Soil water inputs, chloride inputs and chloride outputs refer to $F_{recharge}$, $C_{recharge}$ and $C_{out}$ in Equation (6), respectively.

## 3.2 | Chloride and soil water recharge

For the travel time modelling, we used time series of chloride input and output concentrations at monthly scales. This was done for three reasons: (a) for certain periods of the stream chemistry record sampling frequency was limited to once a month and on rare occasions no monthly samples were taken, often due to lack of stream flow, (b) dry chloride deposition was only available at monthly intervals and (c) aggregating snowmelt and canopy interception to monthly intervals helped resolve discrepancies in timing at event scales between daily precipitation measured at the meteorological tower and precipitation measured with the wet deposition collectors.

Due to the strong influence of snow at these sites, it was necessary to track the timing and amount of chloride storage in the snowpack in order to estimate the chloride concentration of soil recharge water. This was done by tracking the chloride and water mass balances of a storage reservoir that was assumed to be well mixed:

$$C_{reservoir,i} = M_{reservoir,i}/F_{reservoir,i} \tag{1}$$

where $C_{reservoir}$ is the chloride concentration of the reservoir, $M_{reservoir}$ is the mass of chloride in the reservoir and $F_{reservoir}$ is the total water in the reservoir for month $i$. The total water in the reservoir, $F_{reservoir}$, is computed as:

$$F_{reservoir,i} = SP_{i-1} + R_{effective,i} + SF_{effective,i} \tag{2}$$

where $SP_{i-1}$ is the snowpack remaining on the catchment from the previous month, $R_{effective}$ is the amount of rainfall minus interception during the month and $SF_{effective}$ is the amount of snowfall minus interception during the month. Total monthly soil recharge $F_{recharge}$, which is used to weight concentrations in the travel time models, is computed as:

$$F_{recharge,i} = R_{effective,i} + SM_i \tag{3}$$

where $SM_i$ is the amount of snow melt during month $i$.

The total mass of chloride in the storage reservoir, $M_{reservoir,\ i}$ is computed as:

$$M_{reservoir,i} = SP_{i-1} \cdot C_{reservoir,i-1} + M_{deposition,i} \tag{4}$$

where $M_{deposition,\ i}$ is the total deposition of chloride on the catchment:

$$M_{deposition,i} = M_{wet,i} + M_{dry,i} \tag{5}$$

where $M_{wet}$ and $M_{dry}$ are wet and dry chloride deposition, respectively, estimated from observations at the TLW meteorological station.

## 3.3 | Mean travel time modelling

We estimated mean travel times for the 12 catchments using a convolution approach (Małoszewski & Zuber, 1982; McGuire &

McDonnell, 2006). The approach assumes that tracer concentration of stream discharge at time $t$ ($C_{\text{out}}[t]$) is a function of the combined tracer input of the past ($C_{\text{recharge}}[t - \tau]$) lagged and weighted by a transfer function ($g[\tau]$), which represents the lumped travel time distribution of tracers in the system (Hrachowitz, Soulsby, Tetzlaff, & Speed, 2010; Stewart & McDonnell, 1991; Weiler et al., 2003):

$$C_{\text{out}}(t) = \frac{\int_0^t g(\tau) F_{\text{recharge}}(t-\tau) C_{\text{recharge}}(t-\tau) dt}{\int_0^t g(\tau) F_{\text{recharge}}(t-\tau) d\tau} \tag{6}$$

where $\tau$ is the travel time, $t$ is the exit time from the catchment and ($t - \tau$) represents the time of entry into the catchment. We applied five different travel time transfer functions (Table 3): exponential, exponential piston flow (Stewart & McDonnell, 1991), two parallel linear reservoirs (with fast and slow reservoirs; Weiler et al., 2003), diffusion–dispersion (Małoszewski & Zuber, 1996) and gamma (Kirchner, Feng, & Neal, 2000).

Due in part to evapoconcentration, observed stream chloride concentrations are often higher than precipitation concentrations. Therefore, we applied correction factors to account for the differences in mean concentration between chloride inputs and outputs. We followed the approach used by Tetzlaff, Malcolm, and Soulsby (2007) where chloride input concentrations were multiplied by a factor that ensured mean stream and input concentrations balanced. Correction factors ranged between 1.1 and 2.1 across the 12 catchments, similar in magnitude to those reported for other studies (Hrachowitz, Soulsby, Tetzlaff, Dawson, Dunn, & Malcolm, 2009; Hrachowitz, Soulsby, Tetzlaff, Malcolm, & Schoups, 2010; Shaw et al., 2008).

An experimental harvesting study was conducted at TLW which impacted three of the study catchments (c31, c33 and c34). In order to account for the potential impact of harvesting on the travel time estimates, we fit the travel time models to two different periods for each of the catchments: 1985–1996 (pre-harvest) and 1998–2011 (post-harvest). The pre-harvest and post-harvest periods also correspond with a change in dominant climate conditions (Buttle et al., 2018). As will be shown, the pre-harvest period was generally colder and wetter and the post-harvest period was warmer and drier.

Separating the data record into the colder and wetter pre-harvest and warmer and drier post-harvest periods maximized the number of years used to fit the travel time models; however, variability in mean travel times at finer temporal scales may be masked by this approach. Therefore, we fit the travel time models using 5- and 9-year moving windows applied to the monthly chloride input and output time series for the unharvested catchments to assess stationarity in travel time estimates (Hrachowitz, Soulsby, Tetzlaff, Dawson, Dunn, & Malcolm, 2009; Tetzlaff, Birkel, Dick, Geris, & Soulsby, 2014).

For both the pre-harvest and post-harvest and moving window analyses, the time series of chloride input and output concentrations were looped three times to remove potential artefacts from the beginning of the time series (Hrachowitz, Soulsby, Tetzlaff, & Malcolm, 2011). Models were fit using a generalized likelihood uncertainty estimation (GLUE) approach (Beven & Binley, 1992) by running the models 20,000 times using different parameter combinations sampled from uniform distributions. The parameter sets with the top 10% Nash-Sutcliffe efficiencies for each catchment and time period were deemed behavioural. From the retained behavioural sets, likelihood-weighted uncertainty bounds (5 and 95% quantiles) were also estimated (Hrachowitz, Soulsby, Tetzlaff, Dawson, Dunn, & Malcolm, 2009; Page, Beven, Freer, & Neal, 2007).

## 3.4 | Catchment characteristics and forest harvesting

We extracted catchment characteristics from a lidar-derived 5 m digital elevation model of the TLW using SAGA GIS (Conrad et al., 2015) to evaluate the multiple working hypotheses associated with Objective 2. The characteristics included: catchment area (determined using the D8 method), mean catchment slope and mean hillslope flowpath length. For the hillslope flowpath length, which requires stream channel network locations to know when a hillslope connects to a channel, we assumed a channel initiation threshold of 10,000 m$^2$ based on knowledge of the channel locations (Webster, Creed, Beall, & Bourbonnière, 2011). We also included percent wetland cover and runoff ratio. Percent wetland cover was based on field measurements

**TABLE 3** Overview of the travel time transfer functions

| Model | Transfer function | Analytical MTT | Other parameters |
|---|---|---|---|
| Exponential | $\tau_m^{-1} \exp\left(-\frac{\tau}{\tau_m}\right)$ | $\tau_m$ | None |
| Exponential piston flow | $\frac{\eta}{\tau_m} \exp\left(-\frac{\eta\tau}{\tau_m} + \eta - 1\right)$ for $\tau \geq \tau_m(1-\eta^{-1})$<br>$0$ for $\tau < \tau_m(1-\eta^{-1})$ | $\tau_m$ | $\eta$ total volume divided by volume with exponential distribution |
| Two parallel linear reservoirs | $\frac{\phi}{\tau_f} \exp\left(-\frac{\tau}{\tau_f}\right) + \frac{1-\phi}{\tau_s} \exp\left(-\frac{\tau}{\tau_s}\right)$ | $\phi\tau_f + (1 - \phi)\tau_s$ | $\phi$ = fraction of fast reservoir<br>$\tau_f$ = travel time of fast reservoir<br>$\tau_s$ = travel time of slow reservoir |
| Diffusion–dispersion | $\left(\frac{4\pi D_p \tau}{\tau_m}\right)^{-1/2} \tau^{-1} \exp\left[-\left(1-\frac{\tau}{\tau_m}\right)^2 \left(\frac{\tau_m}{4D_p\tau}\right)\right]$ | $\tau_m$ | $D_p$ = 1/Peclet number |
| Gamma | $\frac{\tau^{\alpha-1}}{\beta^\alpha \Gamma(\alpha)} \exp\left(-\frac{\tau}{\beta}\right)$ | $\alpha\beta$ | $\alpha$ = shape parameter<br>$\beta$ = scale parameter |

*Note*: Adapted from Hrachowitz, Soulsby, Tetzlaff, Dawson, Dunn, and Malcolm (2009).

reported by Creed et al. (2003). Each catchment was surveyed on foot and the perimeters of surface or near surface-saturated areas were mapped during June 2000. Runoff ratio was included to explore differences in water partitioning between runoff and evapotranspiration within each catchment.

Relationships between catchment characteristics and mean travel times for the pre-harvest and post-harvest periods were explored both visually and statistically. For the statistical approach, we used an information theoretic method (Burnham & Anderson, 2002). Linear statistical models were fit with mean travel time as the predicted variable and catchment area, mean slope, mean hillslope flowpath length and percent wetland cover as the predictor variables. The global model and all its subsets were fit and the Akaike information criterion (AICc) for small samples sizes (Sugiura, 1978) and Akaike weights were computed to compare the various models. The statistical models were fit using the MuMIn package in R (Barton, 2019; R Core Team, 2019).

In order to assess the impact of harvesting on mean travel times, we compared travel time estimates for the pre-harvest period against the post-harvest period for the three harvested catchments (c31, c33, c34). We did the same comparison for the remaining catchments and used them as references to assess potential differences in hydrometeorology between the pre-harvest and post-harvest period.

### 3.5 | Mean travel times and stream water quality

We evaluated the multiple working hypotheses associated with Objective 3 that considered how mean travel times might account for variability in observed stream water quality. We conducted graphical assessments by plotting mean solute concentrations against mean travel time estimates. We restricted this analysis to the pre-harvest period only so that we could include the three harvested catchments.

## 4 | RESULTS

### 4.1 | Hydrometeorology

The pre-harvest and post-harvest periods correspond to an overall difference in climate conditions. The pre-harvest period was generally wetter and cooler than the post-harvest period (Figure 2). Interestingly, the water year (October to September) prior to harvest (1996) was one of the wettest and coldest years on record and the water year immediately following harvesting (1998) was the driest and warmest year on record.

We provide some hydrologic context for the 12 study catchments by examining long-term runoff ratios. Median annual runoff ratios for the 12 catchments range from about 0.3 (c32) to 0.6 (c50) (Figure 3). Runoff ratios were relatively higher during the 1985–1996 period compared to the 1998–2011 period. The exceptions were c31, c33 and c47 which either show an increase or no considerable difference in runoff ratios between the pre-harvest and post-harvest periods.

### 4.2 | Hydrologic modelling

The HBV-EC hydrologic model calibrated to c32 did a reasonable job of capturing the spring freshet, but struggled to simulate low flows

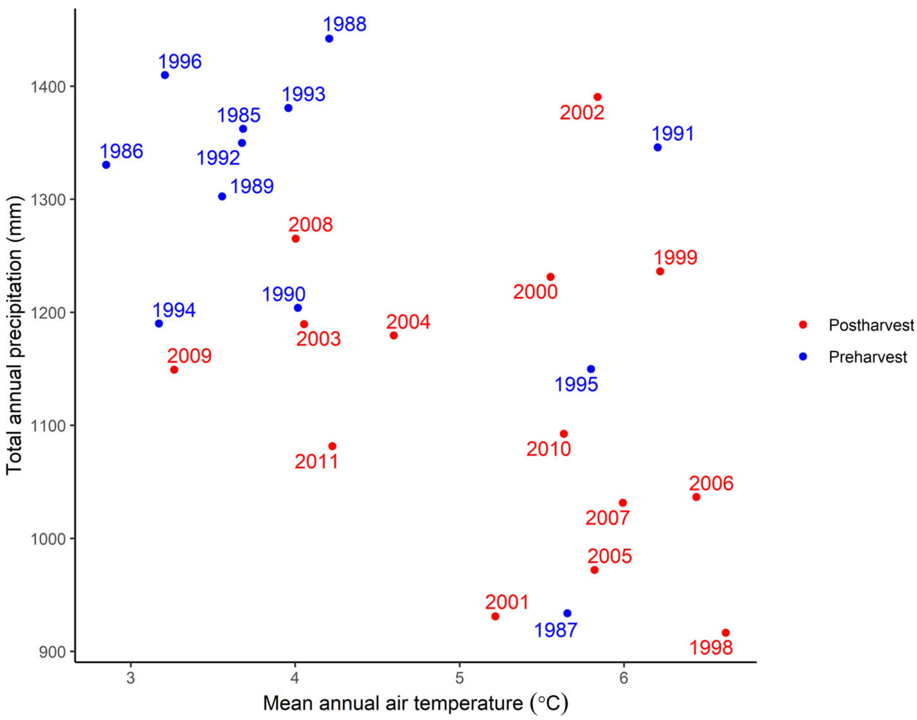


**FIGURE 2** Mean annual air temperature and total precipitation for the study period. Years are water years (October 1 to September 30)

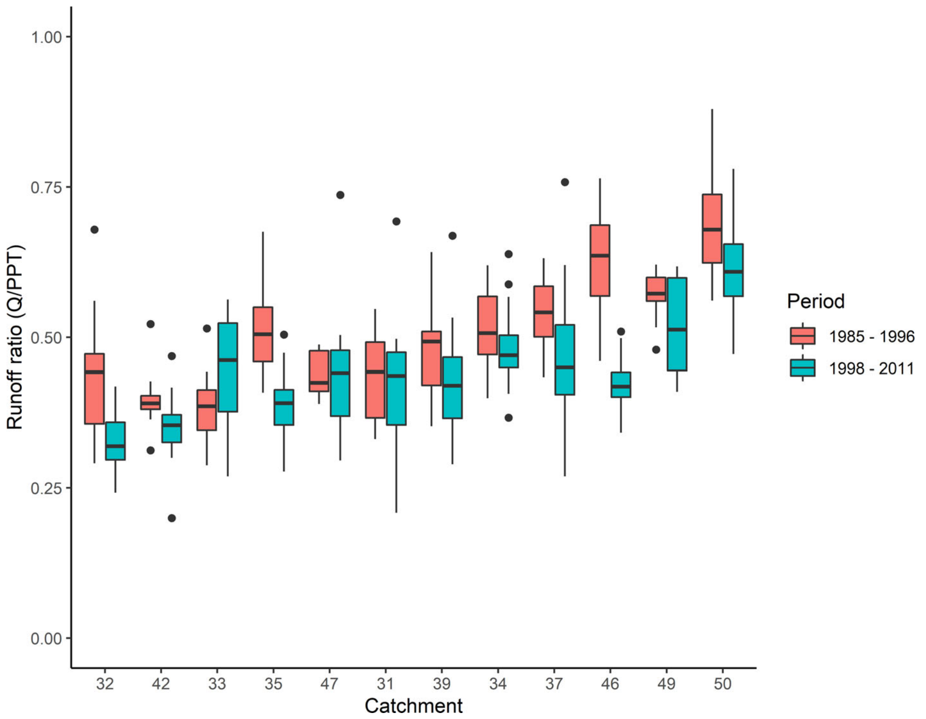


**FIGURE 3** Boxplots of annual runoff ratios (Q/PPT) for the TLW headwater catchments. Runoff ratios for each catchment are calculated based on water year (October 1 to September 30) for 1985–1996 and 1998–2011, except for c46 (1985–1996 and 1998–2007). The catchments are ranked from left to right by the overall median annual runoff ratio. The boxplots summarize the median (middle horizontal line), first and third quartiles (lower and upper hinges), 1.5 times the interquartile range (lower and upper whiskers) and outliers beyond the end of the whiskers (points)

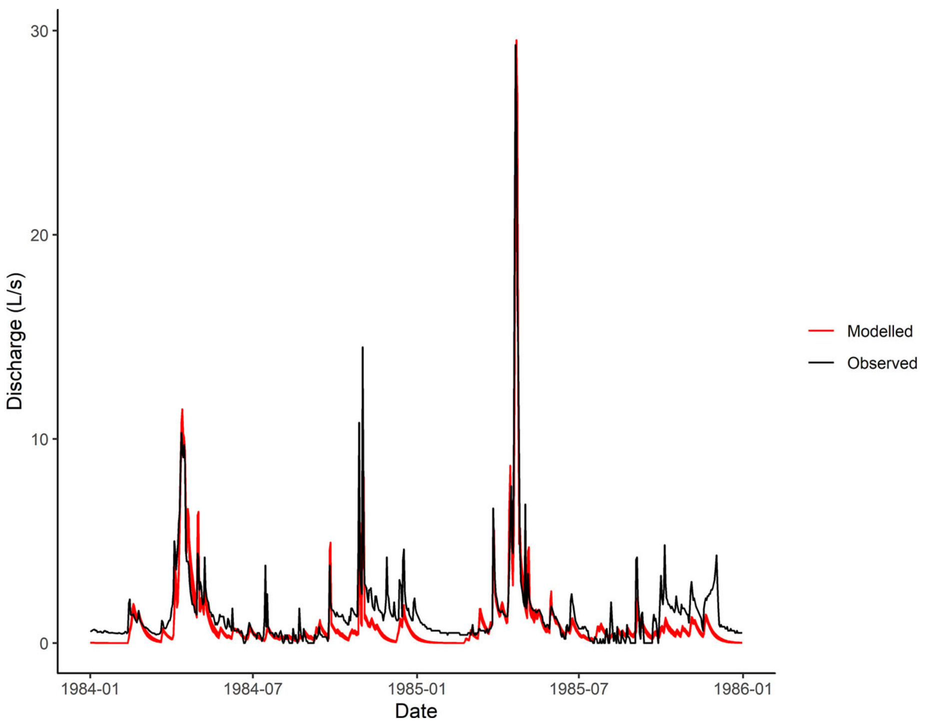


**FIGURE 4** An example hydrograph comparing observed (black) and modelled (red) daily mean stream discharge for c32. Modelled output is the simulated discharge for 50 behavioural parameter sets (Nash-Sutcliffe efficiencies greater than 0.52)

accurately during certain periods (Figure 4). Overall, the stream discharge model performance compared against observed discharge from 1980 to 2012 exhibited a root mean square error of 1.6 L/s and a percent prediction bias of −13.6%. The model generally did well at simulating the snowpack accumulation and melt (Figure 5). Overall prediction fits for snow water equivalent were root mean square error of 44 mm and percent prediction bias of −8.8%.

### 4.3 | Chloride balances and dynamics

We evaluated the chloride mass balances of the catchments as a check for assuming that chloride behaves as a conservative tracer in these catchments (Figure 6). Overall, there was general closure in the annual chloride budgets. There was a net export of chloride for some of the catchments in the first few years (1985–1990),

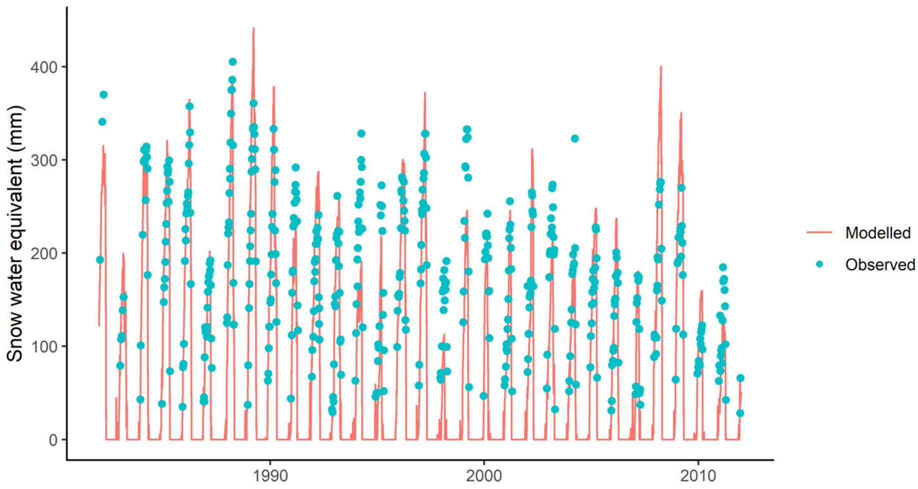


**FIGURE 5** Modelled snow water equivalent (mm; solid line) and observed snow water equivalent from the snow survey site (points)

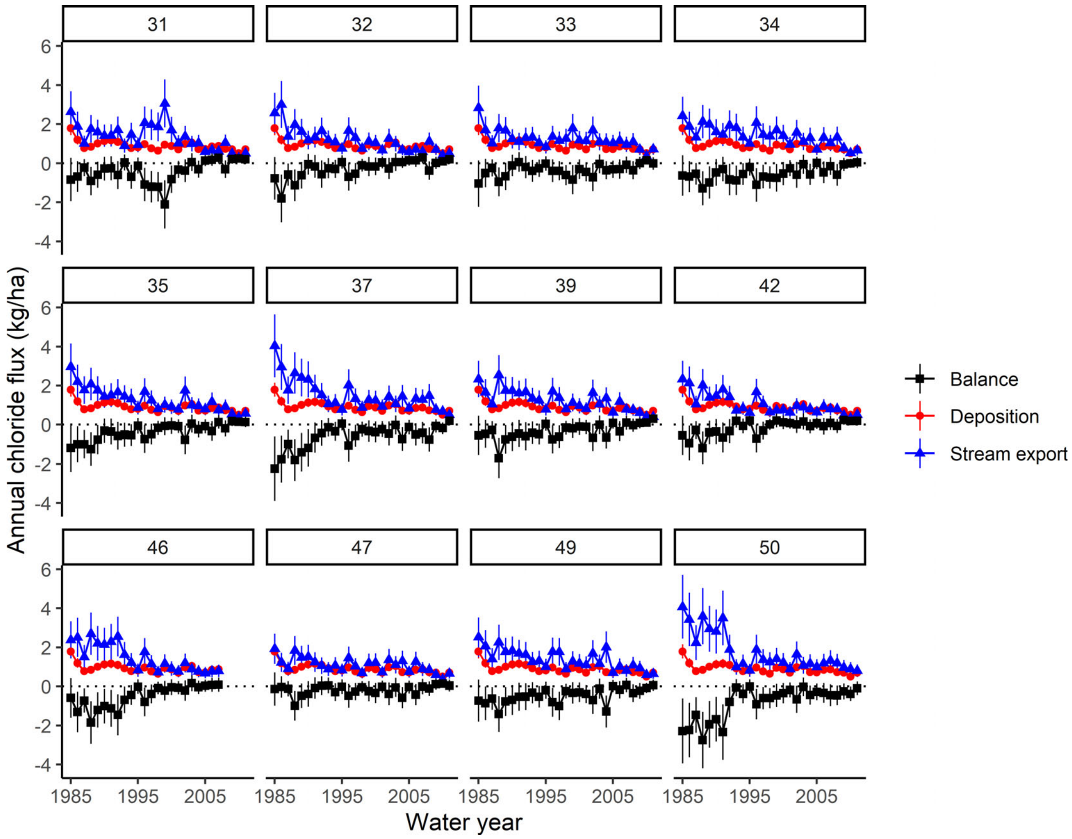


**FIGURE 6** Annual chloride mass balances for the 12 catchments. Mass balance calculated based on water year (October to September; 1985–2011). Standard error bounds account for propagated uncertainty in catchment area, discharge, chloride sample concentration and stream chloride interpolation approach

most notably c37, c50 and c46. The two with the greatest initial imbalances (c37 and c50) are also the two catchments with the largest percent wetland cover. Catchment c31 shows net export of chloride for a handful of years following the clearcut harvest in 1997.

Figure 7 shows monthly chloride concentrations for soil recharge and stream export time series used for the travel time estimations. Note that the two occurrences with values above 2 mg/L are associated with low recharge water volumes. The recharge and stream concentration

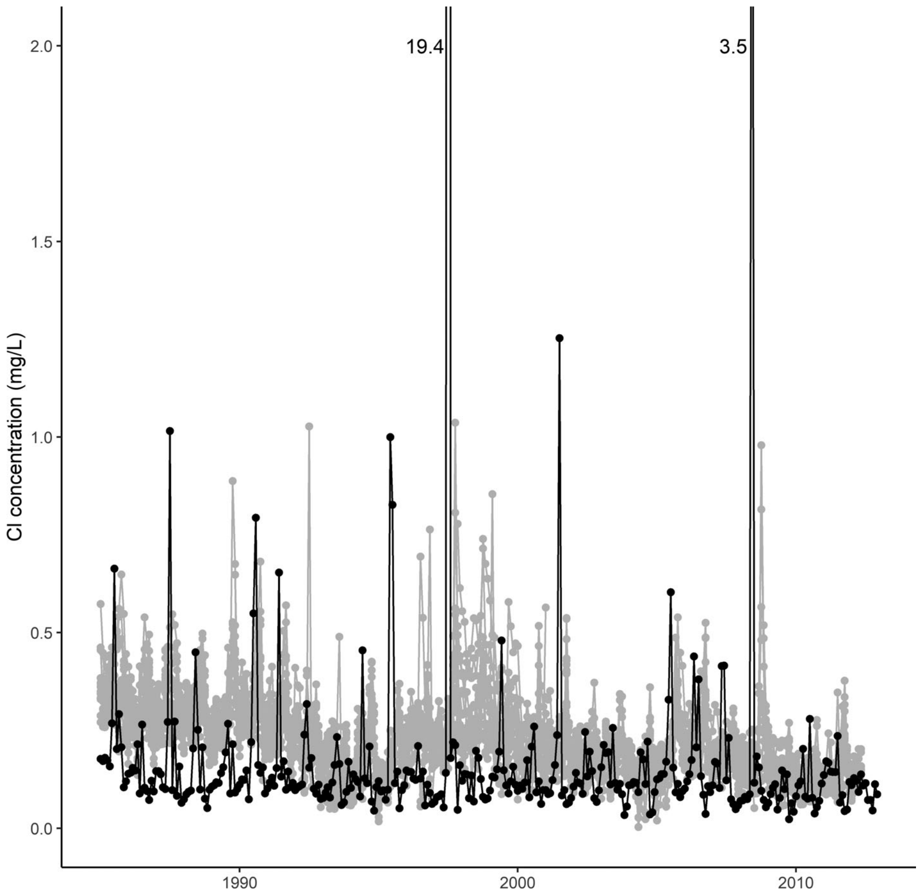


**FIGURE 7** Monthly chloride concentrations for soil recharge (water inputs to the catchment – black line) and stream export from the 12 catchments (grey lines) for 1985–2011. Note that two large recharge values above 2.0 mg/L plot off the *y*-axis scale

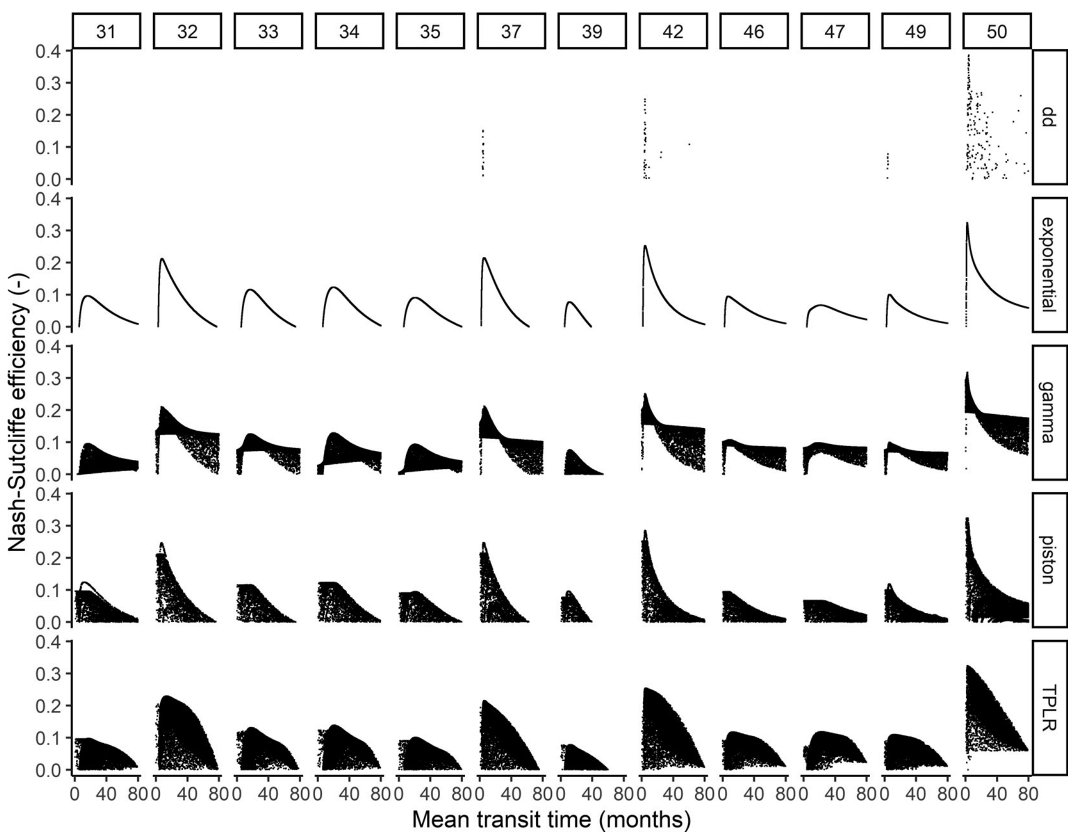


**FIGURE 8** Dotty plots of mean travel time and Nash-Sutcliffe efficiencies for five transfer functions fit to the 1985–1996 period using 20,000 simulations

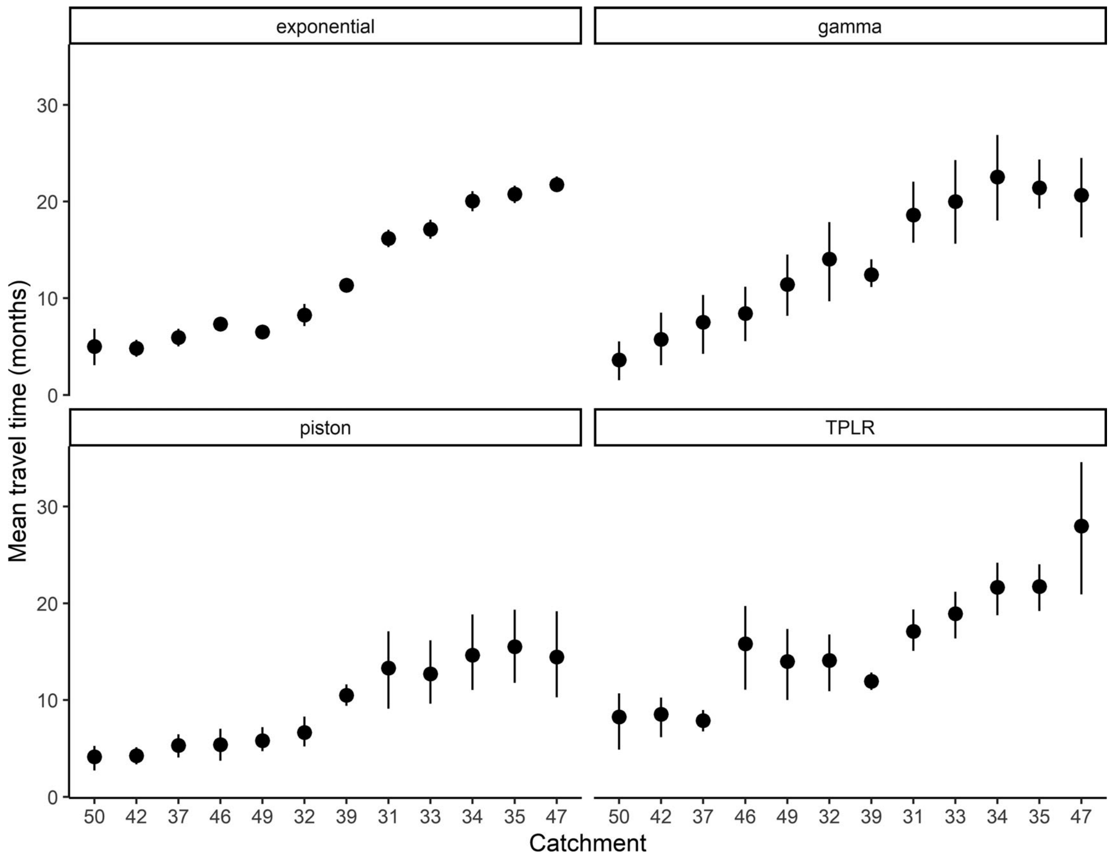


**FIGURE 9** Weighted (based on Nash-Sutcliffe efficiency) mean travel time and 5 and 95% quantiles for the behavioural model runs for four transfer function approaches using data from the pre-harvest (1985–1996) period

signals exhibit a seasonal pattern with generally lower concentrations during winter and higher concentrations during late spring and summer.

## 4.4 | Mean travel times

### 4.4.1 | Mean travel time estimates

Figure 8 shows dotty plots for the five transfer functions fit to the 1985–1996 data records for the 12 catchments using 20,000 randomly sampled parameter sets. The diffusion–dispersion transfer function did not work well with these data and was omitted from subsequent analyses. For the remaining transfer functions, the overall best fits were associated with Nash-Sutcliffe efficiencies of less than 0.4; however, for most of the catchments, the transfer functions tend to be constrained and converge to an optimum peak.

We compared and ranked the weighted mean travel time estimates from the four transfer functions for the 12 catchments during the pre-harvest period (Figure 9). There is some consistency in relative catchment rankings between the four transfer functions. Catchments c50, c42 and c37 tend to have lower mean travel time estimates than most other catchments. Catchments c31, c33, c34, c35 and c47 consistently show the longest travel times.

We estimated mean travel times for the pre-harvest and post-harvest periods using only the gamma distribution since this transfer function provided the best fits of the five considered (Figure 10). With the exception of c39, all catchments exhibited lower Nash-Sutcliffe efficiencies for the model fits during the post-harvest period than during the pre-harvest period.

We estimated travel times using 5- and 9-year moving windows for the unharvested catchments to assess their variability through time. The best model fits for estimating travel times using the 5-year moving windows frequently resulted in Nash-Sutcliffe efficiencies less than zero (results not shown). The model fits for the 9-year moving window analysis were also weaker than the models fit to the two periods (Figure 11). In general, the moving window mean travel time estimates agree with the travel times estimated using the two period groupings, with the exception of c32 and the pre-harvest period of c47. The moving window analysis appears to support the use of the pre-harvest and post-harvest grouping, since these periods show some stationarity whereas the moving windows that contain years from both the pre-harvest and post-harvest periods (1992–2002) tend to have more variable travel time estimates. The moving window analysis also highlights that model fits are generally weaker during the post-harvest period than during the pre-harvest period.

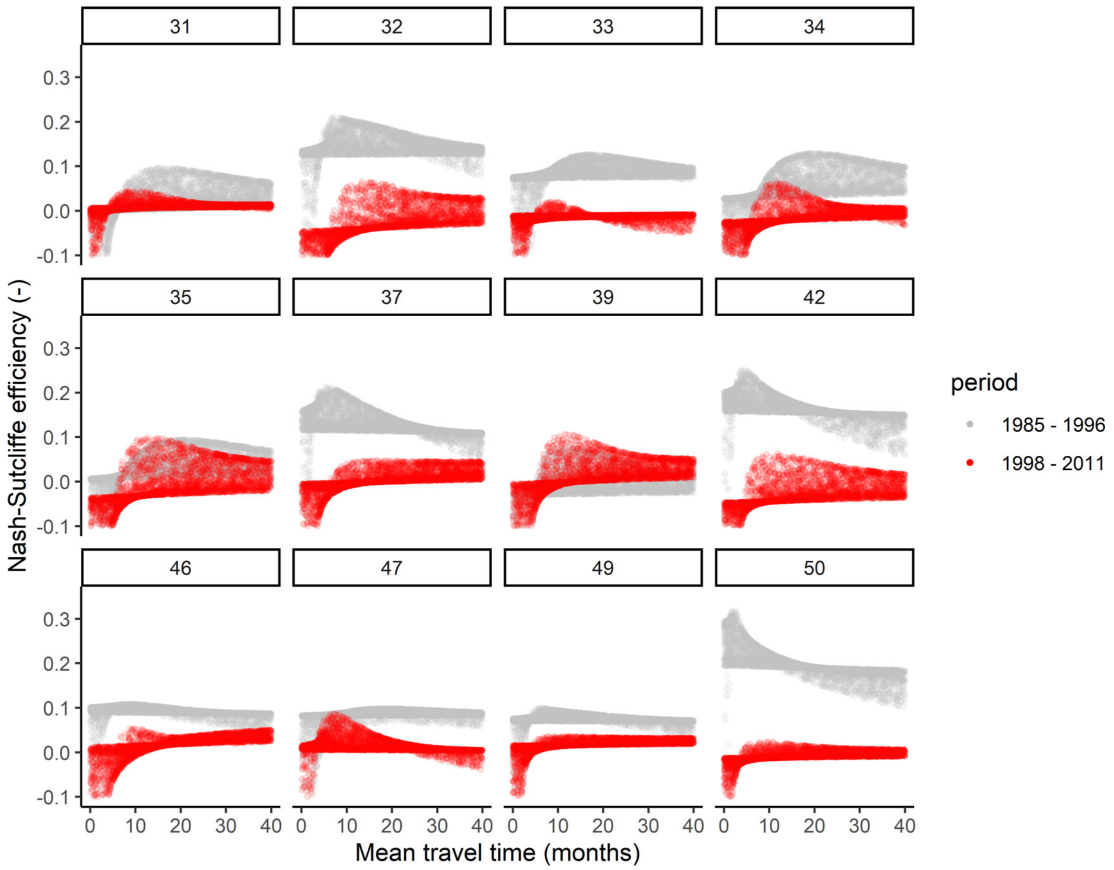


**FIGURE 10** Dotty plots of mean travel time and Nash-Sutcliffe efficiencies using the gamma distribution transfer function fit to the 1985–1996 (pre-harvest) and 1998–2011 (post-harvest) periods using 20,000 simulations

#### 4.4.2 | Catchment characteristics

We explored relationships between the pre-harvest and post-harvest estimated mean travel times and various catchment properties (Figure 12). We constrained our analyses to using the gamma distribution transfer function because it provided the best performance during the post-harvest period. During the 1985–1996 period, catchment area ($r$ = .14), hillslope flowpath length ($r$ = .63) and mean slope angle ($r$ = .62) all show positive, albeit noisy, relationships with travel times. In contrast, percent wetland cover and runoff ratio are negatively correlated with mean travel time ($r$ = –.72 and –0.47, respectively). During the 1998–2011 period, mean travel times have greater uncertainty and most show no correlation with catchment properties (catchment area $r$ = .13, flowpath length $r$ = .02, slope $r$ = –.29, runoff ratio $r$ = –.02). The exception is that percent wetland cover is positively correlated with mean travel time during the 1998–2011 period ($r$ = .47).

The statistical model comparison (Table 4) supports the graphical interpretation and suggests that a model with only wetland cover as a predictor variable is the single best model for accounting for differences in the estimated mean travel times during the pre-harvest period. Models with mean flowpath length also ranked as having explanatory power; however, the model comparison suggests less support for models that include the other catchment properties. For the post-harvest period, there was little support for including any of the considered predictor variables in a model to explain the variation in mean travel times as indicated by the intercept only model having a similar AICc to models that included predictor variables.

#### 4.4.3 | Harvesting

We compared mean travel time estimates using the gamma distribution for the pre-harvesting and post-harvesting periods (Figure 13). We estimated a post-harvest decrease in mean travel times for c31, c33 and c34 (the harvested catchments). In contrast, the other catchments either show an increase in mean travel time during the post-harvest period (c32, c37, c42, c46, c49, c50) or little change (c35 and c39), with exception of c47 which shows a decrease in mean travel time but, unlike the other catchments showing a decrease, was not harvested.

#### 4.4.4 | Stream water chemistry

We compared mean solute concentration and pH values to mean travel times for the pre-harvest period (Figure 14). Mean and

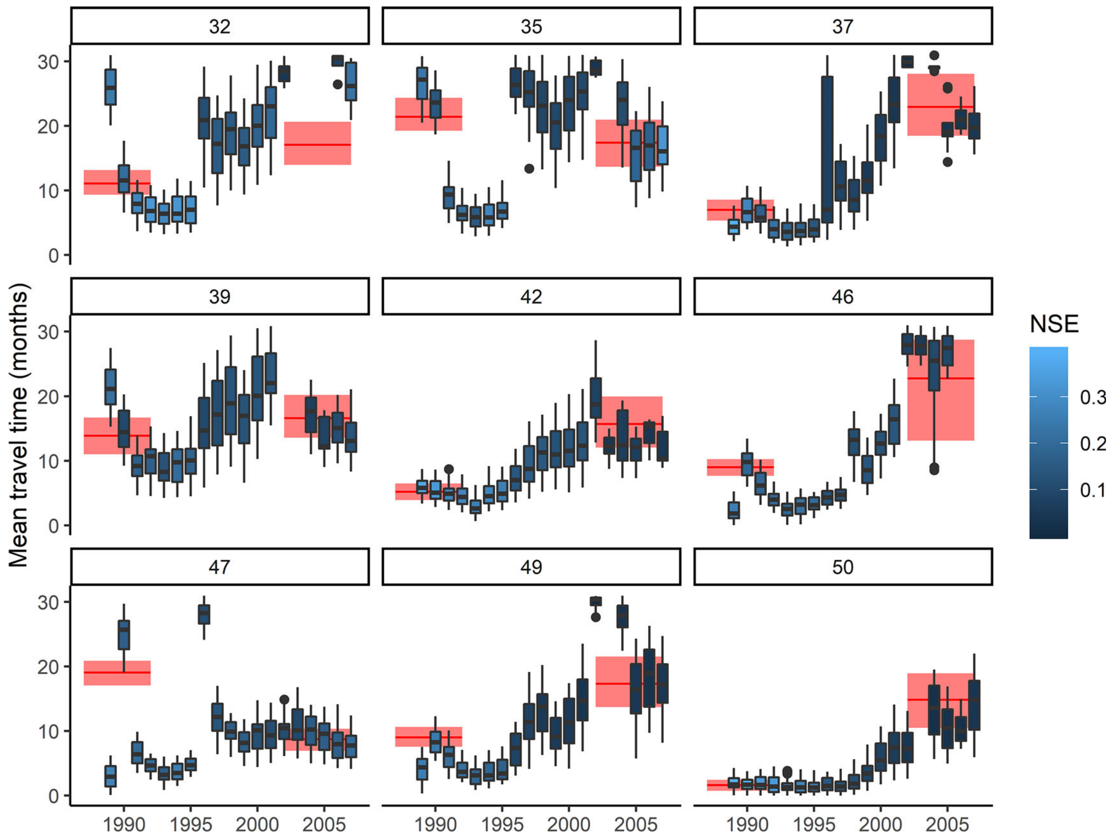


**FIGURE 11** Boxplots of the mean travel time and 5 and 95% quantiles for the behavioural model runs using a 9-year moving window to fit the gamma transfer function. The year associated with the boxplot represents the centre year of the 9 year window. Boxplots are coloured by mean Nash-Sutcliffe efficiency (NSE) of the behavioural model runs. Years without a boxplot indicate a Nash-Sutcliffe of less than zero. The horizontal red lines and rectangles represent the mean travel time and 5 and 95% quantiles, respectively, for the behavioural model runs fit using the 1985–1996 (pre-harvest) and 1998–2011 (post-harvest) periods. The horizontal extent of the red lines and rectangles are such that they only overlap years where the entire 9 year moving window is contained within either the 1985–1996 or 1998–2011 periods

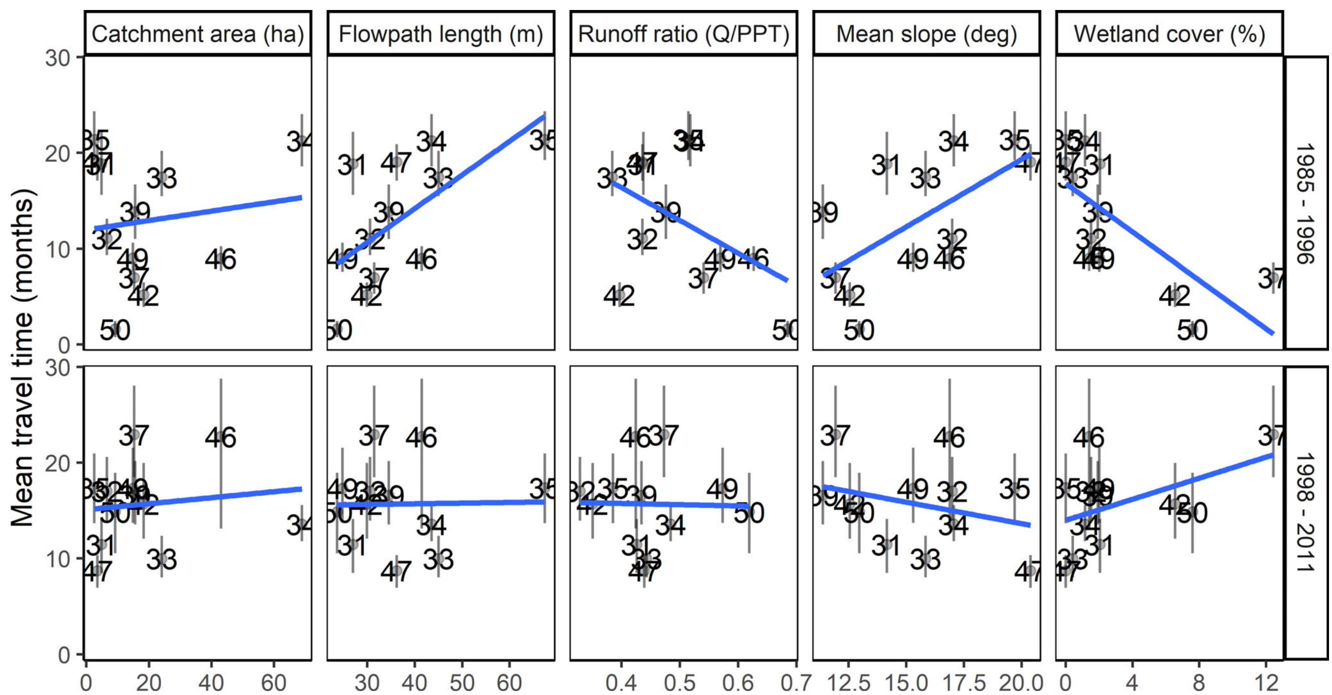


**FIGURE 12** Best pre-harvest (1985–1996) and post-harvest (1998–2011) mean travel time estimates using the gamma distribution transfer function compared to five catchment properties. Error bars represent the 5 and 95% quantiles for the behavioural model parameter sets

median solute concentration values were similar. Many of the solutes are uncorrelated or show weak correlations with mean travel times. Nitrate exhibits a positive correlation with mean travel time (*r* = .63); whereas total phosphorus exhibits a negative correlation (*r* = −.72). Omitting the wetland-dominated catchments (c37, c42 and c50) improved correlations between some solute concentrations and mean travel time. For example, silica (*r* = .38 with c37, c42 and c50 removed vs. *r* = .02 when included), potassium (*r* = .39 with c37, c42 and c50 removed vs. *r* = .04 when included) and sodium (*r* = .41 with c37, c42 and c50 removed vs. *r* = .21 when included) show weak positive correlations with travel time when the wetland dominated sites are removed.

**TABLE 4** Model comparisons using catchment characteristics as predictors of mean travel times during the pre-harvest and post-harvest periods. Only models with ΔAICc less than 4 are shown here

| Model parameters | AICc | ΔAICc | Akaike weight |
|---|---|---|---|
| *Pre-harvest period* | | | |
| Percent wetland | 79.0 | 0 | 0.50 |
| Percent wetland + flowpath length | 80.5 | 1.4 | 0.24 |
| Flowpath length | 81.5 | 2.5 | 0.14 |
| Slope | 81.9 | 2.9 | 0.12 |
| *Post-harvest period* | | | |
| Intercept only | 74.0 | 0 | 0.43 |
| Percent wetland | 74.6 | 0.6 | 0.31 |
| Slope | 76.5 | 2.5 | 0.12 |
| Catchment area | 77.4 | 3.4 | 0.08 |
| Flowpath length | 77.6 | 3.6 | 0.07 |

Abbreviation: AICc, Akaike information criterion.

## 5 | DISCUSSION

### 5.1 | Headwater travel time estimates and assumptions

Our study highlights that estimated catchment travel times can be variable over relatively small geographic areas of similar forest cover and surficial geology. Because of limitations in the simple travel time models applied in this study, our focus was primarily on comparing inter-catchment differences in mean travel time. Comparing absolute mean travel time estimates from this study with others should be done with caution due to limitations in the methodology (Hrachowitz et al., 2011; Kirchner, 2016b; Seeger & Weiler, 2014); however, the

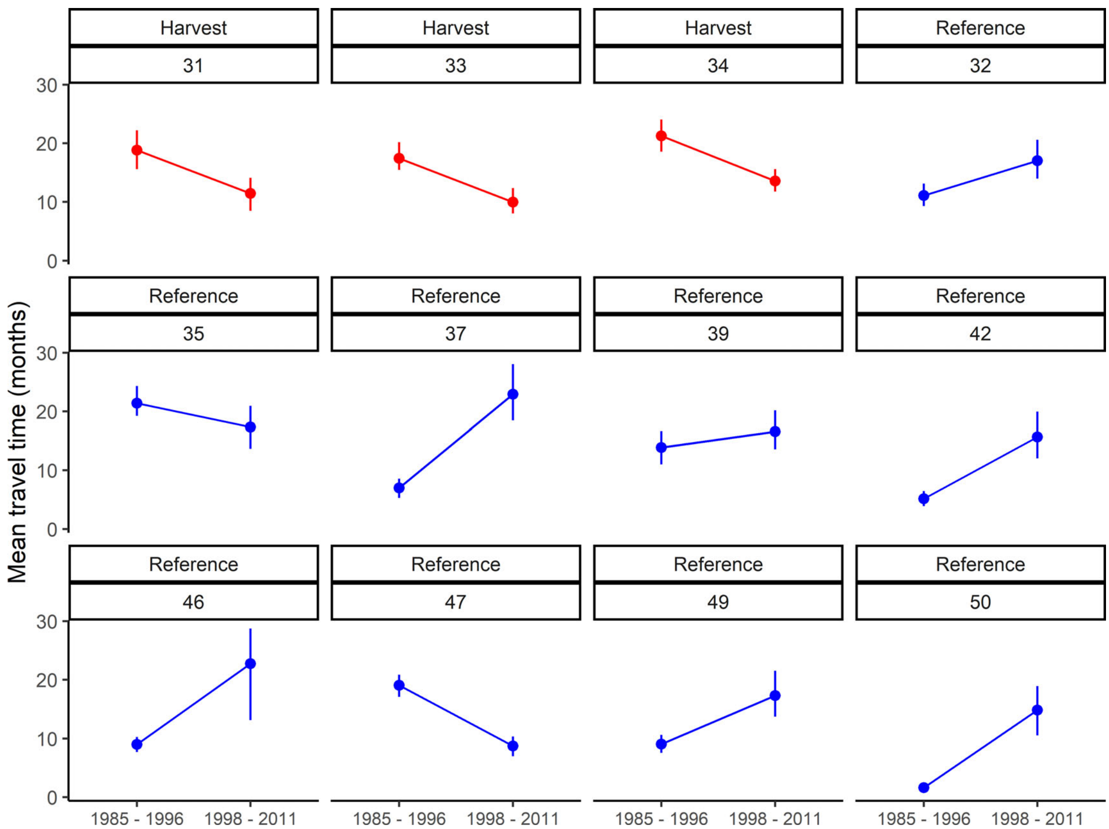


**FIGURE 13** Comparison of catchment mean travel times during pre-harvest and post-harvest periods. Error bars represent the 5 and 95% quantiles for the behavioural model parameter sets

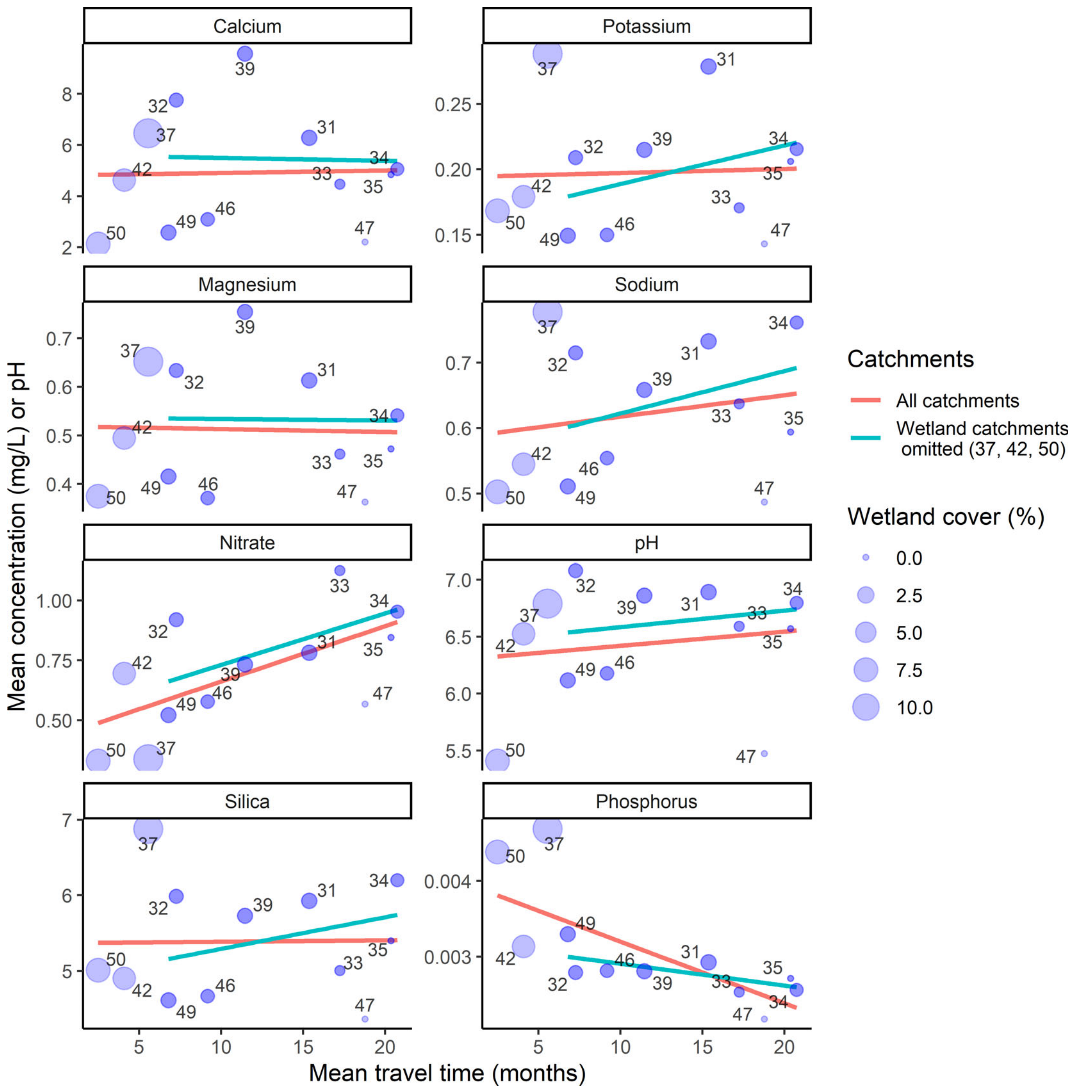


**FIGURE 14** Mean travel time estimates for the pre-harvest period compared against mean water chemistry concentrations and pH. Points are scaled by percent wetland coverage. The red lines are the lines of best fit using all catchments. The blue lines are the lines of best fit omitting the three wetland dominated catchments (c37, c42 and c50)

range of mean travel times in this study (3–25 months) is similar in magnitude to those estimated for other high relief headwater forested catchments (McGuire et al., 2005), but shorter than those from low relief, more wetland-dominated catchments (Lane et al., 2020). In addition, the Nash-Sutcliffe values for our best performing travel time models (0.1–0.4) are similar in magnitude to those reported for other studies (Hrachowitz, Soulsby, Tetzlaff, Dawson, & Malcolm, 2009; Lane et al., 2020).

There are a number of key assumptions and sources of uncertainty in this analysis. We used spatially lumped and time invariant travel time models which have well-documented limitations in accounting for catchment heterogeneity and variable flow conditions (Kirchner, 2016a, 2016b). We recognize these issues; however, our focus was on inter-catchment comparisons, not absolute mean travel time estimates. The moving window analysis highlights variability in catchment travel times through time, but does suggest estimating lumped travel time estimates for the pre-harvest and post-harvest periods may be reasonable (Figure 11). In addition, these are small catchments (<70 ha catchment area) and can reasonably be treated as homogeneous in terms of land cover type, compared to those catchments that have typically been used for mean travel time estimates (Kirchner, 2016a). The catchment estimates were all forced using the same chloride and water input data; therefore, using these simple travel time models helps focus the analysis on relative comparisons between the 12 catchments (Seeger & Weiler, 2014).

We assumed chloride was a conservative hydrologic tracer in our catchments. This may not be reasonable, particularly for the harvested catchments (Lovett et al., 2005) and given the low chloride loads experienced at TLW compared to other sites influenced by more marine-sourced chloride deposition (Neal & Kirchner, 2000; Svensson, Lovett, & Likens, 2012). However, with the exception of the clearcut catchment (c31) and two of the wetland dominated catchments (c37 and c50), the annual chloride budgets show reasonable balance after about 1985. The increase in chloride export for a few years following clearcut harvesting is consistent with post-harvest observations at Hubbard Brook, which was attributed to high decomposition rates of roots, litter and soil organic matter (Kauffman, Royer, Chang, & Berner, 2003; Lovett et al., 2005). Compared to the shelterwood and selection harvesting, the clearcut treatment resulted in greater canopy opening which is likely why there was a detectable increase in chloride export for the clearcut and not for the other two catchments. The relatively large export of chloride from the two wetland dominated catchments during the mid-1980s may be a legacy of chloride deposition associated with acid rain and how wetlands may delay stream chloride export (Lovett et al., 2005). Finally, we assumed that chloride within the snowpack was well mixed. This is a reasonable assumption, since the water and chloride inputs are simulated at monthly time steps so any preferential elution of chloride form the snowpack is likely minimal (Semkin & Jeffries, 1988).

## 5.2 | Travel times and catchment characteristics

The contrast in climatic conditions between the wetter pre-harvest and drier post-harvest periods influenced the relationships between travel time and catchment characteristics. In addition, estimated travel times during the pre-harvest period were generally more constrained in their uncertainty than those for the post-harvest period. During the pre-harvest period, we found longer travel times associated with longer mean flowpath lengths which is consistent with previous findings (Lyon et al., 2010; McGuire et al., 2005). That relationship disappeared for the post-harvest period. This could be due to more uncertainty in the travel time estimates for this period or that topographic controls have less influence on runoff processes during drier conditions (Woods & Rowe, 1996). Catchment area was not strongly related to travel times during either period, similar to findings from other studies (Lane et al., 2020; McGuire et al., 2005; Rodgers et al., 2005).

Increased presence of wetlands and peatlands in a catchment has generally corresponded with shorter mean travel times (Laudon et al., 2007; Lyon et al., 2010; Peralta-Tapia et al., 2015; Tetzlaff, Waldron, Brewer, & Soulsby, 2007). This has been attributed to wetlands and peatlands being able to rapidly move water laterally due to elevated water tables and high hydraulic conductivities in the surface layers. In contrast, Lane et al. (2020) found that greater wetland cover was associated with longer mean travel times for six catchments located in central Ontario. Although the catchments studied in Lane et al. (2020) share some similarities to those at Turkey Lakes (e.g., small headwater catchments, similar climate, post-glacial landscape with shallow soils), wetland cover for those catchments are higher (11–32% vs. 0–12% at Turkey Lakes), the wetlands tend to be deeper and have greater storage capacity potential, and are generally located closer to catchment outlets (Creed et al., 2003; Devito, Hill, & Dillon, 1999). The study by Lane et al. (2020) was conducted over 3 years characterized by below or average annual precipitation amounts for the region. They suggested that wetland cover may be associated with longer travel times during dry conditions and shorter travel times during wet conditions. Our findings, based on a longer data record encompassing prolonged wet and dry periods, appear to support this statement (Figure 12); however, support for wetland cover being positively correlated with mean travel time during the drier post-harvest period was weak (Table 4).

If we assume vegetation transpiration is similar across catchments, catchments will have higher annual runoff ratios because of a greater quickflow proportion of total streamflow or greater baseflow during low flow periods due to groundwater contributions. If the former, higher runoff ratios should be associated with shorter mean travel times. If the latter, higher runoff ratios should be associated with longer mean travel times (Hale & McDonnell, 2016). The negative relationship observed in the pre-harvest period suggests annual runoff ratios are strongly influenced by the proportion of quickflow to total streamflow, which is consistent with the flashy hydrographs for these small catchments (Buttle et al., 2019). In addition, wetland cover likely influences the relationship between runoff ratio and mean travel time. The wetland-dominated catchments, particularly c50 and c37, appear to have a strong influence on driving the negative correlation between annual runoff ratio and travel times during the pre-harvest period and the lack of correlation during the post-harvest period (Figure 12). It is also possible that variability in the runoff ratios are partly due to uncertainties in discharge, precipitation and catchment area estimates used in their calculation. Wetland cover is also negatively correlated with mean slope and it is likely the relationship between wetland cover and mean travel time that is driving the relationships between mean slope and travel time (i.e., catchments with more wetland cover generally have lower mean slopes).

The degree of hydrologic connectivity between wetlands and stream outlets may influence the relationship between wetland cover and mean travel time. The wetlands in the TLW catchments are well connected to surface water networks, being either located at stream initial points or within the stream network itself (Creed et al., 2003). Although not the case for the catchments studied at TLW, wetlands can also be geographically isolated from the stream network (Tiner, 2003). In these cases, we might expect a positive relationship between wetland cover and mean travel time even during generally wet conditions since these wetlands should be effective at storing water and prohibit or attenuate downslope flow. However, the degree of subsurface hydrologic connectivity between geographically isolated wetlands and stream networks can be complex and variable in time (Ameli & Creed, 2017, 2019). More research is needed on the hydrologic functioning of forested wetlands and their influence on water travel times in a changing environment.

## 5.3 | Travel times and forest harvesting

The harvested catchments show a post-harvest decrease in mean travel times which is consistent with an expected increase in runoff being dominated by shallow flowpaths following harvest (Buttle et al., 2018, 2019; Hewlett & Helvey, 1970; Swank, Swift, &

Douglass, 1988). There is potential for differences in climate pre-harvest and post-harvest to confound these results; however, most of the unharvested catchments show either negligible change or an increase in travel times during the post-harvest period. The one exception is that c47 also shows a decrease in mean travel time during the post-harvest period, but was not subject to harvesting. We are unsure why this is the case, but the moving window analysis (Figure 11) does highlight that travel time estimates during the pre-harvest period for c47 may be more variable than was captured by the GLUE analysis.

The estimates of mean travel time for the Turkey Lakes Watershed provide an opportunity to place the harvesting experiment (Buttle et al., 2018, 2019) within a new context. Buttle et al. (2018) documented relative increases in annual water yields following harvesting (80–300 mm), but no detectable change in peak flows. In addition, they found that the increase in water yield due to harvesting persisted at least 15 years post-harvest. Recent discussions have suggested that catchment storage capacity is a critical control on the hydrologic response to forest harvesting (McDonnell et al., 2018; Nijzink et al., 2016). If mean travel time is assumed to be a proxy for catchment storage, it follows that the differences in travel times may influence hydrologic response to harvesting. The three harvested catchments (c31, c33, c34) had some of the longest estimated travel times during the pre-harvest period of the 12 catchments. This raises the question of what if harvesting had been done in one of the catchments with shorter mean travel times (e.g., c50, c42 or c46)? Would there have been an increase, decrease or no change in the hydrologic impact of harvesting compared to what was observed at c31, c33 and c34? The answer likely depends on complex interactions between relative differences in pre-harvest vegetation transpiration, catchment storage and dominant runoff processes, and how they change following harvest. However, it may be that differences in evapotranspiration and travel time (and thus storage capacity) between these catchments are not enough to result in a substantial difference in post-harvest response between catchments, in contrast to what might be expected when comparing the shallow soil Turkey Lakes sites to catchments with deep soils and considerably larger storage capacities (Buttle, 2016; Cooke & Buttle, 2020). Clearly, more research is needed on how subsurface hydrologic processes influence catchment response to forest harvesting (McDonnell et al., 2018).

A critical element of paired-catchment studies is the choice of appropriate reference catchments. It is important that treatment and reference catchments be located in the same region in order to minimize differences in meteorological conditions, vegetation, soil and geology (Brown et al., 2005). In snowmelt dominated regions, it can also be important to account for differences in snow accumulation and melt as the result of differences in elevation and aspect. Often reference catchments are selected to best match catchment areas between the treatment and reference or selected based on operational constraints, such as site accessibility for harvesting or monitoring. The use of catchment area as a selection criterion could mask differences in mean travel times, with implications for assessing hydrologic and water quality response. For the TLW harvesting experiment, catchments c32, c35 and c46 have been used as reference catchments (Buttle et al., 2018, 2019). In terms of matching mean travel times to the harvesting catchments, c35 may be the most appropriate reference catchment despite its relatively small catchment area; therefore, we may weight conclusions using c35 more heavily than the results based on c32 or c46. As discussed, mean travel time estimates can be highly uncertain and may themselves not be the best criterion for selecting paired-catchments; however, it would be useful to develop better criteria for selecting reference catchments based on hydrologic processes controlling the responses of interest.

## 5.4 | Travel times and stream water quality

Catchment travel times have been proposed as a critical link between catchment hydrology and water quality (Hrachowitz et al., 2016). In addition, it is often assumed that travel times provide an indication of dominant hillslope flowpaths with longer travel times associated with deeper flowpaths and shorter travel times associated with shallower flowpaths (Tetzlaff et al., 2015; Tetzlaff, Seibert, & Soulsby, 2009). Indeed, a number of stream water quality studies conducted at Turkey Lakes have used topographic metrics, as proxies for hydrologic processes and flow pathways, to account for observed differences in stream solutes (Creed et al., 2008; Creed & Band, 1998a, 1998b; Creed & Beall, 2009; Mengistu, Creed, Webster, Enanga, & Beall, 2014). By testing the hypothesized relationships between mean travel time and stream water quality outlined in Objective 3, we generate questions about what mean travel times might represent in terms of flow pathways and the suitability of certain solutes as indicators of runoff processes.

Soil weathering products, such as silica, calcium, sodium and magnesium, have been used as indicators of deeper and longer flow pathways (Buttle et al., 2018; Casson et al., 2019; Elsenbeer et al., 1995). Although there is some support for these assumptions, specifically considering silica and sodium, they are confounded by the influence of wetlands, in the case of silica, and redistribution within the soil, in the cases of calcium and magnesium. Northern wetlands can store and export considerable amounts of silica (Struyf et al., 2010) and spot soil water samples taken from the wetland complex in c50 show elevated silica concentrations, thus suggesting that this may also be the case for wetlands in the TLW (data not shown). Although much of the calcium and magnesium in the soils originates from the parent materials, atmospheric deposition, plant uptake and microbial processing redistributes these solutes within the soil horizon (Foster et al., 1989; Hazlett et al., 2011), limiting their use as indicators of deeper flowpaths.

High potassium concentrations within the soil are constrained to surface organic layers (Hazlett et al., 2011) and we expected that high potassium concentrations would be associated with short travel times (Buttle et al., 2018). Soil pH generally shows an increase with soil depth (Hazlett et al., 2011); therefore, we expected longer travel times to be associated with higher pH. The results did not support either of these expectations. This may suggest that mean travel times are a weak proxy for flowpaths or that solute signatures can be influenced by near-stream flow and biogeochemical conditions regardless of their dominant hillslope flowpaths (Casson et al., 2019; Ledesma et al., 2013).

Phosphorus and nitrate were correlated with mean travel times in directions that agreed with our working hypotheses. It is reasonable to assume that higher phosphorous concentrations were associated with shorter travel times due to less potential for adsorption to mineral soils (O'Brien et al., 2013). The reason for a strong positive correlation between nitrate and mean travel time is less clear. It could be due to longer travel times having greater potential for nitrate to leach away from root zones (Asano et al., 2006). It is also possible that longer travel times are associated with longer mean flowpath lengths, which are ideal conditions for generating nitrate flushing from hillslopes (Creed et al., 1996; Creed & Beall, 2009). In addition, the presence of wetlands may be influencing the relationship, as wetlands are associated with short travel times during the pre-harvest period and are effective at removing nitrate from runoff (Spoelstra, Schiff, Semkin, Jeffries, & Elgood, 2010).

Overall, these results highlight that mean travel times are an imperfect proxy for dominant water flow pathways. Caution should be taken when interpreting the relationships shown in our study since there is uncertainty in the travel time estimates and we have only 12 data points (i.e., catchments). For the solute concentrations, we only used long-term means, in part to match temporal scales with the mean travel time estimates. It is likely that this coarse resolution misses important seasonal dynamics in solute concentrations and runoff, and thus important potential linkages between water quality and hydrology (Hrachowitz et al., 2016).

## 6 | CONCLUSION

Understanding the underlying hydrological processes controlling forested catchment response to environmental change is crucial for developing effective management strategies for forest ecosystems and their water resources. We explored differences in mean catchment travel times for 12 headwater catchments at the Turkey Lakes Watershed using long-term chloride observations from rain, snow and streams. We found that mean travel times were variable and that this variability was negatively related to wetland cover and positively related to hillslope flowpath length during generally wet periods. In contrast, the generally dry period exhibited more uncertain travel time estimates and weak or no relationships with catchment characteristics. Forest harvesting appeared to reduce mean catchment travel times, which was consistent with the documented increase in quickflow following harvesting (Buttle et al., 2019). Stream water chemistry was partly related to travel times, but also appeared to be influenced by biogeochemical processes, particularly those associated with wetlands. The importance of small wetlands for stream water quality is well documented, but our study illustrates that these wetlands also strongly influence catchment hydrology and water storage. We also highlight the need to develop hydrologic criteria for informing paired-catchment studies to better address the impacts of forest change on water resources.

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## DATA AVAILABILITY STATEMENT

Snow survey data are available from the Government of Canada: https://open.canada.ca/data/en/dataset/beda0dbe-bcd7-49d3-9473-212e550dfbc6 Other data used in this study are available from the authors upon request and will be available in a forthcoming data article.

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## SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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