# A method of estimating in-stream residence time of water in rivers

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## Abstract

This study develops a method for estimating the average in-stream residence time of water in a river channel and across large catchments, i.e. the time between water entering a river and reaching a downstream monitoring point. The methodology uses river flow gauging data to integrate Manning's equation along a length of channel for different percentile flows. The method was developed and tested for the River Tees in northern England and then applied across the United Kingdom (UK).

i) The study developed methods to predict channel width and main channel length from catchment area.
ii) For an 818 km$^2$ catchment with a channel length of 79 km, the in-stream residence time at the 50% exceedence flow was 13.8 hours.
iii) The method was applied to nine UK river basins and the results showed that in-stream residence time was related to the average slope of a basin and its average annual rainfall.
iv) For the UK as a whole, the discharge-weighted in-stream residence time was 26.7 hours for the median flow. At median flow, 50% of the discharge-

weighted in-stream residence time was due to only 6 out of the 323 catchments considered.

v) Since only a few large rivers dominate the in-stream residence time, these rivers will dominate key biogeochemical processes controlling export at the national scale.

vi) The implications of the results for biogeochemistry, especially the turnover of carbon in rivers, are discussed.

**Keywords:** transit time; reaction kinetics; DOC; BOD

## 1. Introduction

The time water spends travelling through a catchment is an important control of biogeochemical cycling and contaminant persistence. Water spends most time moving through subsurface storage before it enters the river channel (McGuire and McDonnell, 2006). Nevertheless, for a number of reasons it is important to understand how long water spends in a river channel, this can be called the in-stream residence time. This is not the same as the residence time or age of the water in the catchment since that encompasses the entire time between water entering the catchment as precipitation and leaving at the river mouth (McGuire and McDonnell, 2006; Heidbüchel et al., 2012). Here we are only concerned with the time between water entering the river channel and it passing a point of interest. In-stream residence time will be important if, for example, we wish to predict: how much of a pollutant will be lost in-stream; the in-stream turnover of a nutrient (eg. Honti et al., 2010); the emissions of greenhouse gases from riverwater to the atmosphere (eg. Battin et al., 2009); or, the in-stream algal abundance (Talling and Rzoska, 1967). It is often possible to know the kinetics of in-stream processes (eg. Köhler et al., 2002) but knowing the rate of a process is only part of the solution as we need to know the amount of time over which the process will work, thus the in-stream residence time is critical. For example, soil and groundwaters are often highly concentrated in dissolved $CO_2$ with respect to the atmosphere (Worrall and Lancaster, 2005): when soil water containing excess dissolved $CO_2$ enters a river it will begin to degas $CO_2$ to the atmosphere (Billett and Moore, 2008). At the same time organic matter in the river water will be mineralised to produce dissolved $CO_2$ (Wickland et al., 2007). Rates of $CO_2$ degassing are known (Liss and Slater, 1974) and rates of DOC turnover in-stream are known (eg. del Georgio and Pace, 2008), but it is only possible to estimate the amount of $CO_2$ entering the atmosphere if the in-stream residence time over which rates of processes are to be integrated is also known.

In-stream residence time ($t_r$) can be defined as:

$$t_r = \int_{x_e}^{x_m} \frac{x}{v} dx \quad \text{(i)}$$

where: v = the mean cross-sectional velocity at point x; x = the downstream distance along the river channel; $x_m$ = the downstream monitoring point; and $x_e$ = the point along the river length where the water enters the river. For example, $x_m$ could be the river mouth and $x_e$ would be the point at which, on average, water enters the river. The distance $x_m$ – $x_e$ represents the length of the river travelled by water and henceforward we refer to this as the expected length of the river. Equation (i) therefore shows that, if we are able to estimate the change in mean river velocity along a river length, we can also estimate the in-stream residence time.

Mean cross-sectional velocity is commonly estimated as part of the consideration of hydraulic geometry. Leopold and Maddock (1953) proposed a series of power law equations that relate channel depth and mean velocity to stream discharge. This approach has the advantage that continuity constrains the constant and exponent terms. The power law approach has been popular and several studies have published the empirical fit of these equations for many rivers worldwide (e.g. Griffiths, 2003) and related the form of these equations to flow resistance (e.g. Ferguson, 2007). In some early studies, discharge was related to depth and to a residence time (Leopold et al., 1964). However, these equations do not tend to consider independent variables other than discharge, if this the focus were changed to consider in-stream residence time, then this would view downstream river length as the key independent variable (Equation (i)).

There have been a number of approaches to estimate the distribution of in-stream residence times using transient storage models (Bencala and Walters, 1983), but these approaches have a number of limitations. Firstly, they tend to rely on tracer studies and these have their own limitations - for example, irreversible adsorption of rhodamine dye (Lin et al., 2003). Secondly, the studies are based on solute transit times, i.e. they consider distribution of travel times from one point to another and, as observed by Gomez et al. (2012), these distances are typically short (of the order of 1000m) rather <10 to >100 km which maybe the scale of interest for large-scale biogeochemcial processes. Thirdly, not only have studies not considered scales of interest, they have not used these results to scale up to larger catchment areas or indeed to a wider range of flows. Wondzell (2011) has shown that transit storage becomes negligible when considering catchments greater than approximately 1 $km^2$

and so either if they were or could be applied at larger catchments that would not be of much benefit.

Alternatively, some studies have considered transit times for water in whole catchments. Boning (1974) developed an empirical model of water transit times based on measured solute transit times from dye tracer tests. Soballe and Kimmel (1987) estimated annual average transit time ($t_w$) for a series of east-coast US rivers based on the following empirical formula from Leopold et al. (1964):

$$t_w = 0.08A^{0.6}Q_{ave}^{-0.1} \quad \text{(ii)}$$

where: A = catchment area (km$^2$); and $Q_{ave}$ = arithmetic mean annual discharge (m$^3$/s).

A similar approach to calculate a transit time for flood peaks was proposed by Pilgrim (1987) and used by Robinson and Sivapalan (1997) and Sivapalan et al. (2002) where the mean channel response time ($t_n$ - hours) is:

$$t_n = \tau A^{\omega} \qquad \text{(iii)}$$

where: A = catchment area (km$^2$); and $\tau, \omega$ = constants which for the case of Sivapalan et al. (2002) were 0.28 and 0.5 respectively.

Van Nieuwenhuyse (2005) proposed a method to calculate the transit time of surface water from its source as the water enters the river channel. Van Nieuwenhuyse (2005) showed there was a significant relationship with transit time based on dye tracer studies or average velocity at gauged sites based on discharge characteristics and catchment area. However, this empirical approach to the calculation of transit time has some limitations. Firstly, the method had to consider average conditions where “average” was defined as arithmetic mean rather than the expected value of the true distribution of the river discharge. Thus, an estimate of average transit time could not be used to consider actual (expected) in-stream residence time or its distribution as is also the case for the methods illustrated in Equations (ii) and (iii) above. Understanding the distribution of transit times is important because it is often the extreme values that represent the greatest risk. At low values of transit time there is a risk of causing excess pollution: a risk of exceedence causing excess release of, for example, greenhouse gases; or conversely, underestimating pollutant retention as short-term storage is ignored (Drummond et al., 2012). Second, Van Nieuwenhuyse (2005) admits that the proposed approach estimated transit time and not in-stream residence time. While transit time is useful for predicting the flushing time of a pollutant along a given reach, it is not the in-stream age of the water passing any point, as transit time can only consider one point to one point, whereas water enters the river along a continuum at an infinite number of locations stretching back along the length of river to the channel. Indeed, Equation (i) could be used to estimate a transit time if $x_e$ is a fixed point rather than the length of the river experienced by the water flowing past the point of interest. What is needed is a means of predicting the point at which the “average” water enters the river. The point at which the “average” water can be taken to enter the river could be understood in terms of the expected value of the downstream discharge profile of the river, i.e. it is the discharge weighted “average” river length. By using a discharge weighted approach, the “average” length is assessed on the basis of river length experienced by the volume of water passing down the channel.

Therefore, there is gap between the application of the transient storage models (eg. Gooseff et al., 2005) and the empirical models used to predict in-stream residence time (eg. Van Nieuwenhuyse (2005). The purpose of this study was to develop a method for estimating in-stream residence time of water in river channels where the method should work across a range of flows and across the full length of the river but rely on readily available information. The method developed needs to be applicable in different catchments and here it is applied across the United Kingdom (which includes the countries of England, Scotland, Wales and Northern Ireland – UK).

## 2. Approach & Methodology

The approach of this study is (i) to develop a method for calculating in-stream residence time; (ii) apply this method to a UK river where there is sufficient high-frequency flow data to test the method; and (iii) apply the method to other UK rivers.

### *2.1. In-stream residence time*

The in-stream residence time can be defined as in Equation (i). The mean velocity of a river at any point can be estimated from the Manning equation (Manning, 1891):

$$v = \left(\frac{1}{n}\right)\left(\frac{a_{cross}}{p}\right)^{\frac{2}{3}} s^{\frac{1}{2}} \quad \text{(iv)}$$

where: $a_{cross}$ = cross-sectional area of the river at point x; p = the wetted perimeter; s = the water surface slope; and n = the Manning coefficient. If Equation (iv) is expressed in terms of x, i.e. the down-channel distance along the river, then Equation (i) can be used to estimate velocity as a function of down-channel distance. This assumes that the river is not impacted in any substantial way by impoundment.

It is common for the longitudinal slope profile of a river to be expressed as an exponential function of river length (Putzinger 1919):

$$S_x = S_0 e^{-\varphi x} \quad \text{(v)}$$

where $S_x$ = the bed slope at point x; $S_0$ = the bed slope at source; φ = a constant. At the scale of the entire river length and at steady state, then it can be assumed that bed slope is a good approximation of the water surface slope in Equation (iv) (Wilson, 1994). Equation (v) can be readily calibrated for any catchment; here this was done by reference to altitudes of gauging stations on studied rivers.

If it is assumed that the river has a rectangular cross-sectional area then:

$$\frac{a_{cross}}{p} = \frac{dw}{(2d+w)} \qquad \text{(vi)}$$

where d = river channel depth and w = river channel width. For a rectangular cross-section, the width of the river does not vary with discharge and so it is only necessary to find an expression for river width change with river length. The assumption of a rectangular section is the simplest possible formulation but could be readily replaced if more complex formulations of the river cross-section were required. A possible alternative formulation for equation (vi) is to consider a v-shapped, or triangular cross-section: :

$$\frac{a_{cross}}{p} = \frac{dw}{\sqrt{w^2 + 4d^2}} \qquad \text{(vii)}$$

Other formulations of the channel-section, eg. trapezoidal, would mean that additional paramters would be required to calculate cross-sectional area, eg. the angle of the river bank. Since the angle of channel banks could not readily be known for any individual catchment, this cannot be a general approach.

The further advantage of using the formulation in equation (vi) is that river width does not vary with river depth. To calibrate equation (vi) with respect to width, we used data collected by Dangerfield (1997) to create an empirical equation for river width variation with catchment area. Dangerfield (1997) lists the bankfull width of 124 UK rivers and these data were augmented with data from the River Tees (Figure 1) to give the following equation (Figure 2):

$$w = 0.061C + 9.0 \qquad r^2 = 0.73, n = 129 \qquad \text{(viii)}$$

where C = catchment area ($km^2$); and $w_0$ = river channel width at source (m).

River channel depth, the other component of equation (vi), will vary with flow and we propose the following form of equation:

$$^{f}d_x = {}^{f}d_m - \beta e^{\left(\frac{x}{\gamma}\right)^{\delta}} \qquad \text{(ix)}$$

where: $^{f}d_x$= depth at exceedence flow f (eg. 10% exceedence) at river length x (m); $^{f}d_m$ = depth of the river at the monitoring point m for exceedence flow f; and $\beta, \gamma, \delta$ = constants where $\beta$ approximates to $^{f}d_m - {}^{f}d_0$ . Equation (ix) can be calibrated against of observations of river depths at a given point for a given exceedence flow; furthermore, a Weibull function has a physical interpretation where a simple power law approach does not. For example, a Weibull function can represent a range of shapes of response, including sigmoidal, and the paramters in the equation can have physical meaning and be read directly from observations, eg. the minimum and maxium values observed are explicitly included in the equation.

One problem remains: relative to the monitoring point (at distance $x_m$) at what point, on average, does the water enter the river system? In other words what is the average length travelled, what is the value of $x_e$? We propose that average length travelled is the expected value of the function of discharge with river length: this is a discharge weighted length of the river. The form of the equation was taken as a Weibull function:

$$^{f}Q_x = {}^{f}Q_m - \varepsilon e^{\left(\frac{x}{\theta}\right)^{\mu}} \qquad \text{(x)}$$

Therefore the expected value is:

$$l_e = {}^{f}Q_m log_e(2)^{\frac{1}{\mu}} \qquad \text{(xi)}$$

where: $^{f}Q_x$ = discharge at river length x at exceedence discharge f; $^{f}Q_m$ = discharge of the river at the monitoring point m for the exceedence discharge f; and $\varepsilon, \theta, \mu$ = constants. Again, equation (x) could be calibrated against records from river gauging stations.

### 2.2. Testing

The above approach was calibrated for the River Tees given data readily available for gauging stations in the UK as reported within the National River Flow Archive (www.nrfa.ac.uk) and the Flood Studies Report (NERC, 1975 - Table 1). The data required were: mainstream river length to the gauge; altitude of the gauging station; flow duration curve (values for $Q_{10}$, $Q_{50}$, $Q_{95}$ and $Q_{bf}$ are routinely reported for river flow gauging stations in the UK); and the bankfull width and depth.

It is not possible to validate the above approach directly because there is no direct method of measuring in-stream residence time. However, it is possible to estimate the travel time of a storm hydrograph peak between two gauging stations if flow records of sufficient detail are available for stations at sufficient distance apart. Of course, the peak travel time is not the same as the in-stream residence time and so this cannot be strictly considered a validation, but it can at least be used to test whether the proposed method produces results of the correct order of magnitude. On the River Tees 15-minute flow records are available from 1982 for 3 gauging stations. Using the 2 stations that were furthest apart on the River (Broken Scar and Middleton-in-Teesdale – Figure 1, Table 1), the 15-minute flow record was examined for almost 5 years (1982-87) and each peak in flow at the upstream site was examined to see at what time it occurred at the lower stream site. The time of travel for each peak between the upper and lower gauging site was calculated and compared to the percentile flow at the upper and lower sites. This time of travel was then compared to the calculated in-stream residence time.

### 2.3. Application to UK rivers

The UK's National River Flow Archive (NRFA) was examined and all rivers where there were 5 or more gauging stations along the main stream length were considered; for each of these gauging stations the same data as for the River Tees were collected. For those rivers where it was possible to apply the above method, other catchment characteristics were recorded, including: catchment area to the lowest gauging station; maximum altitude within the catchment; and average annual rainfall (1961-1991) – these are all catchment characteristics reported as standard within the National River Flow Archive. The main stream river length to each gauging station from the start of the river was available from the Flood Studies Report (NERC, 1975); using its definition of a river start and by combining these data, the average slope of the river was calculated. The in-stream residence time ($t_r$) was estimated at each of the flow exceedences ($Q_{10}$, $Q_{50}$, $Q_{95}$, and $Q_{bf}$) for each of the selected rivers and compared to the selected catchment characteristics to develop a linear model of in-stream residence time that may be applied more broadly, particularly to rivers where the necessary catchment characteristics were available but where there were insufficient gauging stations for a separate calculation of the in-stream residence time. If an understanding of what controls in-stream residence time can be achieved, then it can be applied across regions. The catchments identified were amongst the largest in the UK and henceforward will be referred to as basins.

Linear equations developed for predicting in-stream residence time were applied across the UK. Since the aim of this study was to assess how long it takes water to travel through the river channel network across large catchments, it was the gauging stations furthest downstream that were examined. There are 323 "downstream" gauging stations across the UK. Results from individual catchments were both discharge- and area-weighted in order to give an average value of in-stream residence time for the UK.It should be noted that no river flow data were available for Northern Ireland and so strictly all data were for Great Britain and not the UK.

## 3. Results

### *3.1. Calibration for the River Tees*

The method was applied to the River Tees (Table 1). Equation (v) was fitted to the available slope data (Figure 3):

$$S_x = 0.033e^{-0.022\,x} \quad r^2 = 0.93,\ n = 6. \qquad \text{(xii)}$$

Dangerfield (1997) did not include data from the River Tees and so data from the 5 gauging stations on the Tees were used to augment Dangerfield's dataset. The smallest catchment area included by Dangerfield (1997) was 13 km$^2$; this could only be marginally improved with data from the Tees to 11.4 km$^2$ (Table 1). Equation (vii) shows a significant linear relationship between catchment area and river width for catchments to 11.4 km$^2$ (5 km river length) but this equation suggest that rivers would be over 9 m wide at source. In order to correct for this overestimation in small catchments, it was assumed that Equation (v) applied for catchments larger than 11.4 km$^2$ but for smaller catchments a second function (Equation xiii) was assumed to give a more suitable value of width at river sources:

$$w = 0.68C + w_0 \qquad \text{(xiii)}$$

Equation (vii) can be calibrated against measurements for the Tees gauging stations (Figure 4):

$$^{bf}d_x = 2.43 - 2.33e^{\left(\frac{x}{16.6}\right)^{1.47}} \quad \text{rmse} = 0.02 \quad \text{(xiv)}$$

where rmse is the root mean square error. For the range of flows, Equation (ix) can be fitted against the available flow duration curves for the gauging sites along the Tees, for example for the 50% exceedence flows:

$$Q_{50} = Q_{50m} - 8.1e^{\left(\frac{x}{40.1}\right)^{4.8}} \quad \text{rmse} = 0.11 \quad \text{(xv)}$$

The good fit of the calibrated equations (equations xiv and xv) helps justify using the Weibull function. Given the fit of Equation (x) to the range of flows, the expected length and the depth correction are given in Table 2. As the expected length is a discharge-weighted length, it is not surprising that it will vary with the flow, in this case as measured by the % exceedence flow. The surprising result here is that the expected length of the river is relatively insensitive to changes in flow with only a decline in the expected length as bankfull discharge is approached, i.e. the average point at which water enters the river relative to the monitoring point moves closer to the source at maximum flows. For the River Tees the in-stream residence time varied from 46 hours for the 95% exceedence flows to 4 hours at bankfull. For each exceedence flow, Equation (ii) can be solved, in this case by numerical integration, to get the longitudinal velocity profile of the River Tees to the monitoring point at Broken Scar (Figure 5). It is notable that there is a maximum in the velocity for this river which is more pronounced with decreasing percentile exceedence flow.

For the period from the start of 15-minute flow records (February 1982) until December 1987, there were 531 events for which a transit time could be estimated. These 531 events covered percentile exceedence flows from 0 to 100% based upon all daily flows measured from 1961 to 2011. The measured peak transit times show a limiting curve from a peak transit time of 16.5 hours at 97.1% exceedence flow to a peak transit time of between 2.75 and 5.75 hours at 0.2% exceedence flow (Figure 6). The calculated in-stream residence times for the same distance varied from 4 hours at 1% exceedence flow to 36 hours at 95% exceedence flow. The estimated in-stream residence times match well to the measured peak transit times for flows greater than, approximately, the 50% exceedence flow but there is divergence between the measured transit times and the estimated in-stream residence time with in-stream residence time estimates curving upwards while transit time varies approximately linearly with flow. As noted previously, this comparison is not a true validation of the method as transit time represents the kinematic wave travel time while the in-stream residence time is the solute or particle travel time. Firstly, the data clearly show very short transit times occurred for flows that would have been different by orders of magnitude; this can easily be explained if the geometry of the catchment is considered. The assessment of transit time assumes that the flood wave enters from the river reach of interest through the upstream site but, depending upon the nature of the storm causing the increase in flow, this assumption may not be valid. The River Tees is predominantly a west-to-east flowing river and so any rainstorm which has a resolved component east to west will mean that a proportion of rain will enter the system below the upstream monitoring point causing a short circuit in the river reach between monitoring points, and would thus invalidate the assumption of the transit time calculation. Secondly, as noted by Van Nieuwenhuyse

(2005), a transit time is not an in-stream residence time. Transit time is a peak to peak comparison whereas in-stream residence time is the amount of time the average water spends in the river. If the method of Soballe and Kimmel (1987) (Equation (ii)) is applied to the Tees, a transit time of 3.5 hours would be predicted while observations from this study would suggest values between 4.25 and 9.25 hours. Equally, Equation (iii) would suggest a value of 8 hours but it is not known for what percentile flow this is a prediction for. Although this was not a strict validation, the comparisons do provide some evidence that the method is capable of producing sensible results.

### ***3.2. Application to the UK***

There are 9 rivers in Great Britain where the main stream has 5 or more gauging stations upon it and, fortuitously, they cover much of the UK from north to south and thus span the range of land uses, hydroclimatic conditions and geomorphological settings found in the UK (Table 3 - Figure 7). The 9 selected catchments include the 5 longest rivers in the UK and 8 of the 11 longest rivers with only the Tees being outside the top 20. The chosen catchments cover 43,000 $km^2$ out of a total UK area of 244000 $km^2$. The catchments cover altitude ranges up to 1303 m above sea level while the extreme altitude range in the UK is 1343 m above sea level. The 9 catchments include sub-catchments that are in top 25 wettest gauged catchments in the UK and the 25 driest gauged catchments in the UK out of 1453 gauged catchments. The method was applied to each of these basins and the results show a broad variation in estimated residence times (Table 3). The longest in-stream residence times was calculated for the largest basin considered (River Thames) which is also the largest catchment in the UK with a predicted in-stream residence time of 151 hours (6.3 days) at median flow.

Using the readily-available catchment characteristics it was possible to produce significant relationships predicting in-stream residence times at different exceedence flows:

$ln(t_{r95}) = 6.8 - 1.5\ln(slope)$ $r^2$ = 90%, n=9 (xv)

(0.3) (0.19)

$ln(t_{r50}) = 16.4 - 0.86\ln(slope) - 1.7\ln(rain)$ $r^2$ = 96.1%, n=9 (xvi)

(4.4) (0.22) (0.68)

$ln(t_{r10}) = 24.5 - 3.2\ln(slope)$ $r^2$ = 78%, n=9 (xvii)

(4.3) (0.6)

$ln\left(t_{rbf}\right) = 3.3 - 0.94\ln(slope)$ $r^2$ = 65%, n=9 (xviii)

(0.4) (0.26)

where: slope = the average slope of the catchment to the downstream gauging station (m/km); rain = the annual average rainfall 1961 – 1990 (mm). Only those variables found to be significant at least at the 95% probability of being greater than zero were included and the numbers in the brackets are the standard errors in the regression coefficients and y-intercept. Equations (xv – xviii) all show a significant effect due to slope, in-stream residence time decreasing with increasing slope. It is possible to recalculate Equation (xvi) so as to include slope only and therefore Equations (xv – xviii) can all plotted together (Figure 8). It is not clear to the authors why a rainfall term should be significant only for the 50% exceedence flows but it may be that rainfall is collinear with slope at the national scale.

Equations (xv - xviii) were applied to 323 rivers across the UK to sites on those rivers that represent the most downstream gauging station in their respective catchments. The catchments cover an area of 149,000 km$^2$ out of possible 244,000 km$^2$ (65% of total area); catchment areas range from 1 to 9,948 km$^2$ with a geometric mean of 147 km$^2$. The unsampled catchments are most likely to be small and close to the coast and, for most of the gauging stations being considered, the most downstream gauging station is not precisely at the tidal limit. For 222 catchments no mean stream length was reported; for the 111 catchments where a mainstream length was known, the best fit equation with catchment area was found to be:

$$l = \frac{\alpha C_{1/2max} C}{(\alpha C + C_{1/2max})} \qquad r^2=0.90,\ n=111 \quad \text{(xix)}$$

where: $\alpha$ = a constant (km/km$^2$); and $C_{1/2}$ = the area constant (km$^2$ – the catchment area at which half the maximum rate of length increase is achieved) (km$^2$). When expressed in this manner, the constant represents the initial rate of change of river length with catchment and for the best-fit equation $\alpha$= 0.142 km/km$^2$. The best-fit value of $C_{1/2}$ for the UK was 226 km$^2$.

Equations (xv - xviii) were applied to all 323 catchments and their calculated in-stream residence time was calculated at the 50% exceedence flow. The discharge-weighted average in-stream residence time for the UK at 50% exceedence flow was 26.7 hours (Table 4). The cumulative distribution of the flow weighted in-stream residence time at 50% exceedence flow shows that 50% of discharge-weighted average in-stream residence time for the country was accounted for by only 6 out of the 323 catchments considered (Thames, Ely Ouse, Severn, Trent, Tweed, Wye – Figure 7 and 9a). The distribution of in-stream residence time at 50% exceedence flow shows that the UK almost divides exactly east-west with all the long-residence time rivers in the east (Figure 9b); this distribution represents the topography of the UK with eastward-flowing rivers being longer and coming from lower altitudes regions compared to shorter, steeper west-flowing rivers. It should be noted that none of these rivers are in Scotland where high slopes and high rainfall may give rise to high discharges but also short in-stream residence times. The Thames accounts for 14% of the discharge weighted in-stream residence time for the entire country at median flows. The longest in-stream residence time calculated was for the River Glen which is a 37 km stream but has a mean slope of only 0.34 m/km; however, when discharge weighted, the in-stream residence time of the River Glen represents only 0.7% of the national in-stream residence time. At 10% exceedence flow the in-stream residence time decreases to 2 hours; and is 67 hours at 95% exceedence flow. At the lowest flows 32% of the discharge weighted in-stream residence time is contributed by only two rivers (Thames and Ely Ouse – Figure 7 and 9).

When area-weighted, the UK in-stream residence time at 50% exceedence flow is 56 hours (Table 4) with 50% of the area-weighted in-stream residence time accounted for by only 5 catchments. At 10% exceedence flow the area-weighted in-stream residence time is 2.5 hours with only 12 catchments accounting for 50% of the area-weighted in-stream residence time of the entire country. At 95% exceedence flow the area-weighted in-stream residence time is 156 hours with 50% of this value contributed by only 3 rivers

## 4. Discussion

The method presented in this study includes changing flows across large-scale (10,000 km$^2$) basins but does so using information often readily-available in developed countries, i.e. multiple rated sections along the course of the river, and thus the approach can be considered as a clear advance on the empirical methods as represented by Equation (ii). The question is: how good is the approach relative to the more physically-based approaches used in transient storage models? Firstly, this approach does work across large catchments and basins even scalable to the size of the UK which has not been done for transient storage approaches. Secondly, the approach did not require tracer studies but could use river flow and topographic data. The expected effect of transient storage within a stream would be to increase the in-stream residence time with the increased time being spent in dead-zones, pools and the hyporheic zone. The importance of time spent in the hyporheic zone is the great potential for biogeochemical processing (e.g. Pinay et al., 2009). However, studies have struggled to show a relationship between exchange with transient storage and, for example, in-stream nutrient cycling (e.g. Hall et al., 2002). The role of transient storage is then either highly variable across time and space, or not as important as first thought. Wondzell (2011) compared exchange of water with the hyporheic zone ($Q_{hz}$) with down-channel discharge (Q) and found that the ratio of $Q_{hz}/Q$ was maximum for the lowest order stream but even then it was 1.9%: at 60 km$^2$ the $Q_{hz}/Q$ was as low as 0.002%, i.e. negligible. The study showed that $Q_{hz}$ was essentially constant with changing Q and so its importance decreased with increasing Q. Furthermore, potential hyporheic exchange would be lowest where the stream bed was composed of fine-grained sediments as opposed to gravels with the exchange being limited by the effective hydraulic conductivity of the stream-bed. Given the catchment scale used in this study, the result of Wondzell (2011) suggests that transient storage has a near negligible effect on a method that was discharged-weighted. The result of Wondzell (2011) mirrors that of Robinson et al. (1995) who showed that transport properties in catchments greater than 10 $km^2$ were network-dominated as distinct from being hillslope-dominated. This is not to say that transient storage areas are not important for biogeochemical processing, because their ability to cycle nutrients or remove pollutants might be disproportionate to the volumes of water exchange, but the inclusion of biogeochemical rates would be a separate study. Equally, no method for estimating transit time in rivers, be it the method proposed here or other methods discussed, can allow for the presence of lakes and reservoirs. It is known that lakes and reservoirs act as large stores of biogeochemically important components and can have water residence times of years (e.g. Syvitski et al., 2005). Fortunately, the UK is relatively unimpounded and has few large lakes. The method proposed here is limited by its need for calibration data; in this study a minimum of 5 gauging stations per river was set as a minimum number so that the fit of equations such as equation (viii) is based only on a very small number of data points. However, the results from calibrated catchments could be used to generalise across flows and catchments and other approaches also require calibration often with more parameters to fit than required here.

Our motivation for modelling in-stream residence is to understand the time over which biogeochemical reactions can occur. For example, the measurement of BOD in the UK is based upon a 5-day measurement yet the in-stream residence time even at 95% exceedence flow is less than 3 days. When a 5-day in-stream residence time is considered, then even at 95% exceedence flow there are only 26 out of 323 catchments that showed a in-stream residence time greater than 5 days: these catchments represent 18% of the land area, but represent only 2% of the discharge. Therefore, for UK conditions a 5-day BOD measurement represents an extreme worse case and, in most cases, would represent impacts on estuaries and not on the river.

An improved method to estimate the in-stream residence time would be to use a tracer which starts changing the moment it enters the stream. One possibility is the excess dissolved $CO_2$ concentration: this is the concentration of $CO_2$ that is present in excess over and above that would be in equilibrium with the atmosphere. Soil- and ground-waters have dissolved $CO_2$ concentrations well in excess of that which would be present in equilibrium with the atmosphere. Worrall and Lancaster (2005) considered the excess dissolved $CO_2$ concentrations throughout the River Thames catchment over a 29-year period and showed the mean concentration of excess dissolved $CO_2$ in groundwater was 4.99 mg C/l, for clay soil catchment at source the mean was 4.46 mg C/l, while for surface water at the catchment outlet the average concentration was 0.79 mg C/l, i.e. groundwater and soil water had degassed on emergence at the surface. Jones and Mulholland (1998) suggested that excess dissolved $CO_2$ concentration at a catchment outlet was:

$$pCO_{2stream} = pCO_{2gw} - pCO_{2evasion} + pCO_{2metabol} \qquad (xx)$$

where: $pCO_{2stream}$ = dissolved $CO_2$ in stream at the catchment monitoring point; $pCO_{2gw}$ = the dissolved $CO_2$ from the soil-groundwater of the catchment; $pCO_{2evasion}$ = the dissolved $CO_2$ lost to the atmosphere between groundwater emergence and the catchment monitoring point; and, $pCO_{2metabol}$ = the dissolved $CO_2$ produced by in-stream metabolism between the discharge of groundwater into the channel and the catchment monitoring point. It should be possible to reverse this equation, if the concentration at source and outlet are known and the rates of evasion and metabolic production are known, then the in-stream residence time can be calculated. Neal et al. (1998) give a range of methods for calculating excess dissolved $CO_2$ from a range of often readily available monitoring data (combinations of pH, alkalinity, Ca and stream temperature). The evasion rate of $CO_2$ from the stream water can be estimated from the stagnant two-film model (Liss and Slater, 1974). The problem is the estimation of the metabolic production of $CO_2$ in stream from the turnover of organic matter. River flow gauging stations and catchment characteristics are widely available in many developed countries, but measures of organic matter turnover are rare and perhaps the only widespread measure of organic turnover is BOD and such a measure has already been criticised above.

Zarnetske et al. (2012) proposed that a bulk Damköhler number could be used for stream channels once a residence time is known. A bulk Damköhler number can be defined as:

$$D_{river} = \frac{kl}{v} C^{n-1} = kt_r \qquad \text{(xxi)}$$

where: k = the first order removal rate ($[M][L]^{-3}[T]^{-1}$)l = the river length ([L]); v = water velocity ($[L][T]^{-1}$); C = initial concentration ($[M][L]^{-3}$); and n = reaction order. Worrall et al. (2013) have measured zero-order rate constants for DOC loss in the River Tees as between (0.19 and 2.15 mg C/l/hr). Moody et al. (2013) gave the average initial concentration of the DOC in the headwaters of the River Tees between 1993 and 2008 as 17.6 ± 6 mg C/l, where n= 896 and the variation is difference between the $25^{th}$ and $75^{th}$ percentiles. Applying the above method for in-stream residence time to the DOC sources of the River Tees over the period for which initial concentrations were known gives values of 50.3 ± 22 hours. Applying these ranges to Equation (xxi) gives a median Damköhler number of 2.9 with an inter-quartile range of 1.8 to 4.2, i.e. this would approach would suggest that for DOC in the River Tees the dominant process is removal of DOC over advection.

For wider application, the in-stream residence time to a point of interest could help target management intervention to relieve problems of water quality For any water quality component (e.g. dissolved organic carbon, DOC; nitrate) that is turned over and removed in stream water, then knowing the in-stream residence time can then target land management options in a catchment. If the rate of turnover is known and this compared to the in-stream residence time, then it would be possible to identify the region within which the river has not had time to reduce the concentration. For example, Moody et al. (2013) has shown that on average over a 12-month period DOC concentrations decreased by an average of 70% in UK river water over a 24 hour period and within this time reached a new equilibrium concentration. Therefore, for areas of a catchment outside 24 hours travel time of a water treatment works, there is little point investing in land management as the river has sufficient time to process and limit the concentration; however, within a 24 hour travel time then the river will not have sufficient time to process the inputs and source control would be more effective.

## 5. Conclusions

The study has developed a method for calculating in-stream residence time applicable to catchments where there are 5 or more gauging stations. The method was applied to 323 catchments across the UK by comparison to catchment characteristics in order to give regional estimates of in-stream residence time. When estimates of in-stream residence time were compared between catchments, it is shown that, for UK rivers as a whole, the in-stream residence is dominated by a small number of large, low-gradient rivers.

## Acknowledgements

The authors would like to thank two anonymous reviewers for their constructive comments on the context of this work.

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Figure 1. Location of gauging stations within the River Tees, northern England.

Figure 2. The bankfull width compared to catchment are for 124 catchments from Dangerfield (1997) and from 5 gauging stations on the River Tees.

Figure 3. The change in slope along the length of the River Tees from its source at the channel head with Putzinger equation fitted (Equation (v)).

Figure 4. The fit of equation (xiii) to the observed river depth at bankfull discharge for 5 gauging stations on the River Tees.

Figure 5. The downstream velocity profile (from channel head of the main channel) of the River Tees for varying exceedence flows as predicted by this study.

Figure 6. Observed transit times with varying exceedence flow for the River Tees between Middleton-in-Teesdale and Broken Scar in comparison to predicted in-stream residence times.

Figure 7. The location of the rivers and gauging stations used in the calculation of in-stream residence time for the UK. Where: 1 = Tees; 2 = Thames; 3 = Severn; 4 = Trent; 5 = Bedford Ouse; 6 = Tweed; 7 = Clyde; 8 = Spey; 9 = Wye; and 10 = Ely Ouse.

Figure 8. The variation of mainstream channel length with catchment area.

Figure 9. a) The percentage of the national in-stream residence time at 50% exceedence flow represented by each river in the study. b) The the instream residence time at 50% exceedence flow for each river catchment studied.