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A review and evaluation of catchment transit time modeling

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Summary Transit time is a fundamental catchment descriptor that reveals information about storage, flow pathways and source of water in a single characteristic. Given the importance of transit time, little guidance exists for the application of transit time modeling in complex catchment systems. This paper presents an evaluation and review of the transit time literature in the context of catchments and water transit time estimation. It is motivated by new and emerging interests in transit time estimation in catchment hydrology and the need to distinguish approaches and assumptions in groundwater applications from catchment applications. The review is focused on lumped parameter transit time modeling for water draining catchments and provides a critical analysis of unresolved issues when applied at the catchment-scale. These issues include: (1) input characterization, (2) recharge estimation, (3) data record length problems, (4) stream sampling issues, (5) selection of transit time distributions, and (6) model evaluation. The intent is to promote new advances in catchment hydrology by clarifying and formalizing the assumptions, limitations, and methodologies in applying transit time models to catchments.

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Introduction

The time water spends traveling subsurface through a catchment to the stream network (i.e., the subsurface transit time) is a fundamental catchment descriptor that reveals

information about the storage, flow pathways and source of water in a single characteristic. Transit time is a physical measure that integrates flow path heterogeneity, is easily scaleable (Sivapalan, 2003), and is directly related to internal catchment processes (Stewart and McDonnell, 1991). The distribution of transit times describes how catchments retain and release water and solutes that in turn control geochemical and biogeochemical cycling and contamination persistence. Longer transit times indicate greater contact

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time and subsurface storage implying more time for biogeochemical reactions to occur as rainfall inputs are transported through catchments toward the stream channel (Burns et al., 2003; Scanlon et al., 2001). Thus, quantifying the mean transit time and, more importantly the transit time distribution, provides a primary description of the hydrobiogeochemical system (Wolock et al., 1997) and catchment sensitivity to anthropogenic inputs (Nyström, 1985; Landon et al., 2000; Turner et al., 2006) and land-use change (e.g., Buttle et al., 2001; Burns et al., 2005). Despite the importance of transit time and its distribution, it is impractical to determine experimentally except in rare manipulative experiments where catchment inputs can be adequately controlled (cf. Rodhe et al., 1996). Thus, transit time distributions are usually inferred using lumped parameter models that describe integrated transport of tracer through a catchment. These models do not require detailed hydrological characterization of the physical system and, consequently, are often used for characterizing catchments where data are limited (e.g., less developed countries and ungauged basins).

There has been considerable interest recently in transit time estimation as new river monitoring programs develop (e.g., Gibson et al., 2002; Aggarwal, 2002; Band et al., 2002; Hooper, 2004) to quantify stores and fluxes of water in large catchment systems (up to 10,000 km²). There are readily available computer codes that are used to interpret environmental tracer data to estimate transit time distributions using the standard lumped parameter models (Richter et al., 1993; Maloszewski and Zuber, 1998; Bayari, 2002; Ozyurt and Bayari, 2003, 2005a). However, there is little guidance on the assumptions and limitations of different modeling approaches applied to catchment systems. Even more problematic is the lack of guidance on how to quantify model uncertainty of mean transit time estimates and identifiability of other parameters used in the models. We would argue that while there have been numerous recent publications (references provided herein and Table 1) using tracers to estimate transit times, relatively little advancement in transit time estimation methodology has been made at the catchment-scale. Most methods are based on early adaptations from the chemical engineering and groundwater fields (e.g., Danckwerts, 1953; Eriksson, 1958; Maloszewski and Zuber, 1982; Haas et al., 1997; Levenspiel, 1999) and may not apply in catchments where there are complex and important controlling processes like variable flow in space and time, spatially variable transmissivity, coupled vertical and lateral flow, immobile zones, and preferential flow, to name a few. Very little guidance exists for catchment hydrologists on the use and interpretation of transit time modeling approaches for complex catchment systems.

The catchment-scale lumped parameter models that exist for the interpretation of tracer input (i.e., precipitation) and output (i.e., streamflow) data assume that the hydrologic system is at steady-state and that representative inputs can be determined (Maloszewski and Zuber, 1996). In catchments, these assumptions are almost always violated. Techniques have been developed to estimate transit time for non-steady (variable flow) systems (Lewis and Nir, 1978; Niemi, 1978; Zuber, 1986b; Rodhe et al., 1996; Ozyurt and Bayari, 2005a,b); however, they are rarely used in the published literature owing to their complexity and the diffi-

culty in interpreting results. Characterizing representative inputs for catchments can be problematic considering that precipitation is highly variable in space and time for tracer composition and precipitation amount. Catchments receive inputs that are distributed over all or part of their area. Some of these inputs are then transported along diverse flow pathways to the stream network and while others remain in storage or in less mobile phases of flow. This complex three-dimensional problem is typically simplified so that parameters that describe the flow system can be estimated. These simplifications include one-dimensional transport, time-invariant transit time distributions, uniform recharge, linear and steady-state input and output relations, and contribution from the entire catchment area (Turner and Barnes, 1998). These simplifications may lead to uncertainty in transit time characterization; nevertheless, this has not been critically evaluated in the literature, especially in the context of catchments.

While some of these problems have been recently addressed in benchmark reviews by Maloszewski and Zuber (1993, 1996), Zuber and Maloszewski (2000), and Bethke and Johnson (2002), their work has focused on using environmental tracers to estimate the transit time of groundwater systems. The treatment of stable isotope techniques has been absent in several reviews concerning transit time (e.g., Plummer et al., 1993; Cook and Böhlke, 2000) even though stable isotopes are the main tracers available for determining transit times of catchment systems and young groundwater (i.e., <5 years old) (Moser, 1980; Coplen, 1993; Clark and Fritz, 1997; Turner and Barnes, 1998; Coplen et al., 2000). We contend that problems, limitations, assumptions, and methods have not been clearly evaluated and synthesized for transit time model applications in catchments. In this review, we provide an overview of the methods available to estimate catchment-scale water transit time and present a formal listing of the sampling, modeling, and interpretation issues concerning transit time estimation in catchments. We begin with an overview of the basic concepts and modeling theory, and then introduce and address six assumptions and problems that arise from estimating transit time using lumped parameter models.

Basic concepts

We focus our discussion of catchment transit time estimation on the use of environmental tracers of the water molecule itself, ¹⁸O, ²H, and ³H. These ideal tracers are applied by precipitation and are generally distinct isotopically, which makes them reliable tracers of subsurface flow processes (Kendall and Caldwell, 1998). While groundwater transit times can be estimated using dissolved gas environmental tracers (namely chlorofluorocarbons (CFCs), tritium/helium-3 (³H/³He), sulfur hexafluoride (SF₆), and krypton-85 (⁸⁵Kr) (Ekwurzel et al., 1994; Cook and Solomon, 1997; Solomon et al., 1998)), these tracers are not applicable to surface waters because of contamination by exchange with atmospheric and vadoze zone gases (Cook and Solomon, 1995; Plummer et al., 2001).

Stream water is an integrated mixture of water sources with an age (or residence time) that reflects the ages of all precipitation that contributes to streamflow generation,

Table 1 Summary of published field studies in which transit time was estimated for streamwater^a

Reference and Site	Basin area [km ²]	Tracer	Time series length		Models ^b		Parameters ^c		
			Input [year]	Output [year]	Method	Type	τ_m [year]	D_p [-]	η [year]
Asano et al. (2002), Fudoji	0.001	² H	1	1	SW	EM	>1		
Rachdani	0.002	² H	1	1	SW	EM	1		1.37
						EPM	1.1		
Begemann and Libby (1957), Upper Mississippi (Rock Island)	n.a.	³ H	n.a.	n.a.	WB	EM	15		
Behrens et al. (1979), Rofenache	96.2	³ H	8	7.5	C	EM	4		
Bergmann et al. (1986), Pöllau	58.3	¹⁸ O	4	4			1.9		
Burgman et al. (1987), Torne Älv	6000	¹⁸ O	10	10	SW	EM	1.1		
Rickleån	1800	¹⁸ O	10	10	SW	EM	2		
Öre Älv	2880	¹⁸ O	10	10	SW	EM	1		
Ammerån	2500	¹⁸ O	10	10	SW	EM	1		
Norrstöm	22,600	¹⁸ O	10	10	SW	EM	2.25		
Botorpsstr.	1000	¹⁸ O	10	10	SW	EM	0.67		
Ljungbyån	800	¹⁸ O	10	10	SW	EM	0.33		
Lyckebyån	1100	¹⁸ O	10	10	SW	EM	0.17		
Mörrumsån	3400	¹⁸ O	10	10	SW	EM	0.6		
Tolångaån	440	¹⁸ O	10	10	SW	EM	0.83		
Nissan	2800	¹⁸ O	10	10	SW	EM	0.6		
Burns and McDonnell (1998), Woods Lake WO2	0.413	¹⁸ O	1.5	1.3	SW	EM	0.28		
Woods Lake WO4	0.612	¹⁸ O	1.5	1.3	SW	EM	0.28		
Burns et al. (1998), Winnisook	2	¹⁸ O	1	1	sw	EM	0.90		
Winnisook	2	³⁵ S	n.a.	n.a.	MM	n.a.	0.68–0.87		
Shelter Creek	1.6	¹⁸ O	1	1	SW	EM	1.03		
Shelter Creek	1.6	³⁵ S	n.a.	n.a.	MM	n.a.	0.51–0.83		
Buzek et al. (1995), Lysina	0.273	¹⁸ O	3	3	SW	EM	1.1–1.5		
Cui (1997), Rippach	1.2	¹⁸ O	1	1	C	EPM	2.33		1.2
Rippach	1.2	¹⁸ O	1	1	C	DM	1.6	0.25	
Loechnbach	1.7	¹⁸ O	1	1	C	EPM	2.29		1.35
Loechnbach	1.7	¹⁸ O	1	1	C	DM	1.46	0.09	
DeWalle et al. (1997), Benner Run	11.34	¹⁸ O	1	1	SW	EM	>5		
Fernow WS3	0.34	¹⁸ O	1	1	SW	EM	1.6		
Fernow WS4	0.39	¹⁸ O	1	1	SW	EM	1.4		
Diñçer et al. (1970), Modry Dul	2.65	³ H	8	2.5	C, $\alpha = 0$	BM	2.5		
Eden et al. (1982), Kreidenbach	1.85	¹⁸ O	2	2	SW, ml	EM	0.7		
					SW, m2	EM	1.4		
Eriksson (1958), Upper Mississippi, (Rock Island)	n.a.	³ H	n.a.	n.a.	WB	EM	8		
Frederickson and Criss (1999), Meramec River	10,300	¹⁸ O	3	3	ExpAve	—	0.3		
Herrmann et al. (1999), VAHMPIRE ^d	n.a.	³ H	24	n.a.	C	EM	7–15	0.15	
						DM	8–13		
Holko (1995), Jalovecky Creck	23	² H	3	2.5	C	DM	1.3	2.2	
Kirchner et al. (2001), Hafren Tanllwyth	3.47	Cl ⁻	14	14	PS	Gamma	0.82		

Continued on next page

Table 1 (Continued)

Reference and Site	Basin area [km ²]	Tracer	Time series length		Models ^b		Parameters ^c		
			Input [year]	Output [year]	Method	Type	τ_m [year]	D_p [-]	η [year]
Tanllwyth	0.51	Cl ⁻	14	14	PS	Gamma	0.36		
Leopoldo et al. (1992), Búfalos	1.58	¹⁸ O	4	4	SW	EM	0.34		
Paraiso	3.27	¹⁸ O	4	4	SW	EM	0.62		
Maloszewski and Zuber (1982), Modry Dul	2.65	³ H	10	4	C, $\alpha = 1$	DM	5.5	1.6	
	2.65	³ H	10	4	C, $\alpha = 0$	DM	3.6	0.25	
Maloszewski et al. (1983), Lainbach	18.7	² H	3	3	SW, m1	EM	1.1		
		² H	3	3	SW, m2	EM	2.1		
		³ H	9	7	C, m1	EM	1.8		
		³ H	9	7	C, m1	DM	1.6	0.15	
		³ H	9	7	C, m2	EM	2.2		
		³ H	9	7	C, m2	DM	2.4	0.15	
Maloszewski et al. (1992), Wimbactal	33.4	³ H	40	3	C	EM	4.3		
	33.4	³ H	40	3	C	DM	4.2	0.60	
	33.4	¹⁸ O	9	3	C	EM	4.5		
Martinec et al. (1974), Dischma		³ H			C	EM	4.0		
						DM	4.8		
Matsutani et al. (1993), Kawakami	0.14	³ H	6	4	MM/C	BN	2.5		
McGlynn et al. (2003), M15	0.026	³ H	60	n.a.	C	PF	1.1		
						EPM	1.5		n.a.
						DM	1.3	n.a.	
						PF	2.4		
K	0.17	³ H	60	n.a.	C	EPM	2.4		n.a.
						DM	2.1	n.a.	
						PF	2		
PL14	0.8	³ H	60	n.a.	C	EPM	2		n.a.
						DM	1.7	n.a.	
						PF	2		
Bedload	2.8	³ H	60	n.a.	C	EPM	2		n.a.
						DM	1.7	n.a.	
McGuire et al. (2002), Brown LR1	0.14	¹⁸ O	3	1.3	C	EPM	0.8		1.28
	1.23	¹⁸ O	3	1.3	C	EPM	0.4		1.1
McGuire et al. (2005), WS02	0.601	¹⁸ O	3	2.3	C	EM	2.2		
WS03	1.011	¹⁸ O	3	2.3	C	EM	1.3		
WS08	0.214	¹⁸ O	3	2.3	C	EM	3.3		
WS09	0.085	¹⁸ O	3	2.3	C	EM	0.8		
WS10	0.102	¹⁸ O	3	2	C	EM	1.2		
MACK	5.81	¹⁸ O	3	2.3	C	EM	2		
LOOK	62.42	¹⁸ O	3	1.5	C	EM	2		

Michel (1992), Colorado above Cisco, UT	75,000	³ H	30	22	MM	EM	14.3		
Kissimmee above L. Okeechobee	4500	³ H	30		MM	EM	2.5		
Mississippi at Anoka, MN	53,000	³ H	30	22	MM	EM	10		
Neuse at Vanceboro, NC	11,000	³ H	30		MM	EM	11.1		
Potomac at Rockes MD	27,000	³ H	30	22	MM	EM	20		
Sacramento at Sacramento	67,000	³ H	30	7	MM	EM	10		
Susquchanna above Harrisburg	70,000	³ H	30	19	MM	EM	10		
Michel (2004), Ohio River	215,400	³ H	33	23	MM	n.a.	10		
Missouri River	1073,300	³ H	44	34	MM	n.a.	4		
Pearce et al. (1986), M8	0.038	¹⁸ O	3	3	SW	EM	0.33		
Rodgers et al. (2005a,b), Feshie Bridge	230.7	¹⁸ O	1	1	SW	EM	0.3–0.55		
Allt Chomraig	44.9	¹⁸ O	1	1	SW	EM	0.5–0.84		
Feshie Lodge	114.6	¹⁸ O	1	1	SW	EM	0.18–0.37		
Upstream Braids	88.1	¹⁸ O	1	1	SW	EM	0.13–0.30		
Eidart	29.9	¹⁸ O	1	1	SW	EM	0.13–0.31		
Upper Feshie	32.3	¹⁸ O	1	1	SW	EM	0.1–0.26		
Allt a' Mharcaidh	10	¹⁸ O	1	1	SW	EM	0.72–1.22		
Rodhe et al. (1996), Gårdsjön	6300 m ²	¹⁸ O	4	4	C ^e	EM ^e	0.18 ^e		
Soulsby et al. (2000),									
Allt a' Mharcaidh, G1	10	¹⁸ O	3	3	SW	EM	>5		
Allt a' Mharcaidh, G2	1.69	¹⁸ O	3	3	SW	EM	3.6		
Allt a' Mharcaidh, G3	2.96	¹⁸ O	3	3	SW	EM	>5		
Vitvar and Balderer (1997), Rietholzbach	3.18	¹⁸ O	18	2	C	DM	1.04	0.7	
Rietholzbach	3.18	¹⁸ O	18	2	C	EPM	1.04		1.05
Oberer Rietholzbach	0.9	¹⁸ O	18	2	C	EM	2		
Vitvar et al. (2002), Winnisook	2	¹⁸ O	6	3	C	EPM	0.74		1.2
						DM	0.74	0.4	
Zuber et al. (1986), Lange Bramke	0.76	³ H	5	5	C	EM	2.2		

^a Information summarized/inferred from original reference and streamwater was typically taken as baseflow. For details on specific studies, see original reference, n.a. is not applicable or available.

^b Methods: C is convolution (m1 = model 1, m2 = model 2, usually related to direct vs. indirect streamflow [see reference; α = recharge weighting factors [see reference]]), SW is sine-wave, WB is water balance, MM is mixing model, PS is power spectra, ExpAve is exponential averaging model. Model; EM is exponential, EPM is exponential–piston flow, DM is dispersion, PF is piston flow, Gamma is the gamma distribution and BN is the binominal distribution, n.a. is not applicable or available.

^c τ_m , is mean transit time, D_p is the dispersion parameter ($1/\text{Peclet}$), and η is the piston flow parameter.

^d Validating hydrological models using process studies Internal data from research basins. Vallcebre study basins. Pvrenees.

which fell on the catchment in the past. At any point along a flow path in a catchment, the residence time would be defined as the time that has passed since a water molecule entered the catchment (Maloszewski and Zuber, 1982). More specifically, the definition of residence time is the time (since entry) that water molecules have spent *inside* a flow system, whereas the transit time is defined as the elapsed time when the molecules *exit* a flow system (Bolin and Rodhe, 1973; Etcheverry and Perrochet, 2000; Rueda et al., 2006). The distinction between residence time and transit (or travel) time is often overlooked in the literature (including in the authors own works); however, a distinction can clearly be made. For example, consider a flow system in which the flow path lengths are all equal (i.e., piston flow), the mean residence time of this system would be half of the mean transit time. The catchment transit time of water arriving at the outlet of a basin also includes surface processes such as overland flow and channel transport (Lindgren et al., 2004). Also, tracers used to estimate residence or transit times are assumed to be conservative, measured in flux mode (see Kreft and Zuber, 1978), and enter/exit the system only once.

First, if we consider a simple water balance, the hydraulic turnover time, T , is defined as

$$T = S/Q, \quad (1)$$

where S is the mobile catchment storage (L^3) and Q is the volumetric flow rate ($L^3 T^{-1}$) that is assumed to be constant or an average value. From Darcy's law, T can be expressed along a flowline as (Mazor and Nativ, 1992):

$$T = n_e(\Delta l)^2/K\Delta h, \quad (2)$$

where Δl is the distance from recharge to discharge (L), Δh is the difference in hydraulic head over the distance Δl (L), n_e is the average effective porosity ($L^3 L^{-3}$), and K is the average hydraulic conductivity over the distance Δl ($L T^{-1}$). This T is often the point of reference for mean transit times, since it defines the turnover timescale based on our best understanding or assumption of the catchment subsurface volume and mobile storage if the unsaturated zone transit time is small compared to the total transit time of the system.

Conceptually, the transit time distribution (TTD) can be represented as the response or breakthrough of an instantaneous, conservative tracer addition over the entire catchment area (assuming zero background concentration of the tracer) (Maloszewski and Zuber, 1982):

$$g(t) = \frac{C(t)}{\int_0^\infty C(t) dt} = C(t)Q/M, \quad (3)$$

where $C(t)$ is the instantaneous concentration of tracer caused by an injection at $t = 0$ ($M L^{-3}$), and M is the injected mass (M) that also appears in the discharge (Q) (i.e., all tracer mass is recovered in the outflow). The TTD (or $g(t)$) describes the fractional weighting of when mass (i.e., tracer) exits the catchment, which is equivalent to the probability density of tracer leaving the catchment resulting from the tracer applied instantaneously to the entire surface of a catchment (Zuber, 1986a). The TTD must sum to unity in order to conserve mass and it represents all possible flow pathways in a hydrological system. Other common terms

for the TTD are the travel time distribution, system response function, and weighting function. The mean transit time of the tracer (τ_m) is simply the first normalized moment or the average arrival time of $C(t)$ at the catchment outlet:

$$\tau_m = \int_0^\infty tC(t) dt / \int_0^\infty C(t) dt = \int_0^\infty tg(t) dt. \quad (4)$$

It has become common to estimate the mean transit time, since it can be compared to the hydraulic turnover of a catchment (Eq. (1)). However, TTDs are typically skewed distributions with long tails (e.g., Kirchner et al., 2001); thus, other moments (variance, skewness, etc.) and central tendency values (i.e., median and mode) are often more suitable to describe the shape and scale of the distribution.

Although these definitions (Eqs. (3) and (4)) seem highly theoretical, given that these experiments are difficult to accomplish at the catchment scale, $g(t)$ conceptually represents the response of the catchment to a unit tracer input and is analogous to a unit hydrograph for tracer. It is therefore useful to predict the tracer composition of stream flow assuming that the function $g(t)$ is known or approximately characterizes the flow system.

Mazor and Nativ (1992) claim that comparing the mean transit time and turnover time is often more instructive than estimating only one or the other, since they can describe different aspects of the subsurface system. For example, the mean transit time describes the entire volume of subsurface water accessible to tracer, whereas the turnover time describes the dynamic volume of the system (Zuber et al., 1986; Zuber, 1986b). If the tracer is conservative and there are no stagnant zones in the catchment, then the mean transit time of the tracer will equal the mean transit time of the water ($\tau_m = T$). Mazor and Nativ (1992) discuss other examples that yield differences between τ_m and T in aquifer systems, which mainly relate to poor characterization of the extent and nature of the subsurface flow system. Essentially, the volume of the subsurface that tracer can access is typically larger than that determined based on hydraulic relationships alone (e.g., Bergmann et al., 1986; Melhorn and Leibundgut, 1999; Vitvar et al., 2002), since it is difficult to characterize hydraulic discontinuities or subsurface entrapment in immobile volumes (Mazor and Nativ, 1992).

Transit time modeling theory

Water transit time distributions for catchments can be determined experimentally from temporal variations of stable isotopes (2H and ^{18}O), tritium (3H), and other conservative tracers (e.g., chloride) (Dinçer et al., 1970; Maloszewski and Zuber, 1982; Pearce et al., 1986; Kirchner et al., 2000). Fig. 1 illustrates the lumped parameter model concept for determining the transit time of water draining a catchment. Environmental tracers are applied naturally during precipitation (e.g., ^{18}O) and are transported to the stream network along diverse surface and subsurface flow paths within the catchment. In most undisturbed catchments, however, flow paths are predominantly subsurface (Dunne and Leopold, 1978). The transit time through the stream network (e.g., hyporheic and channel) is generally

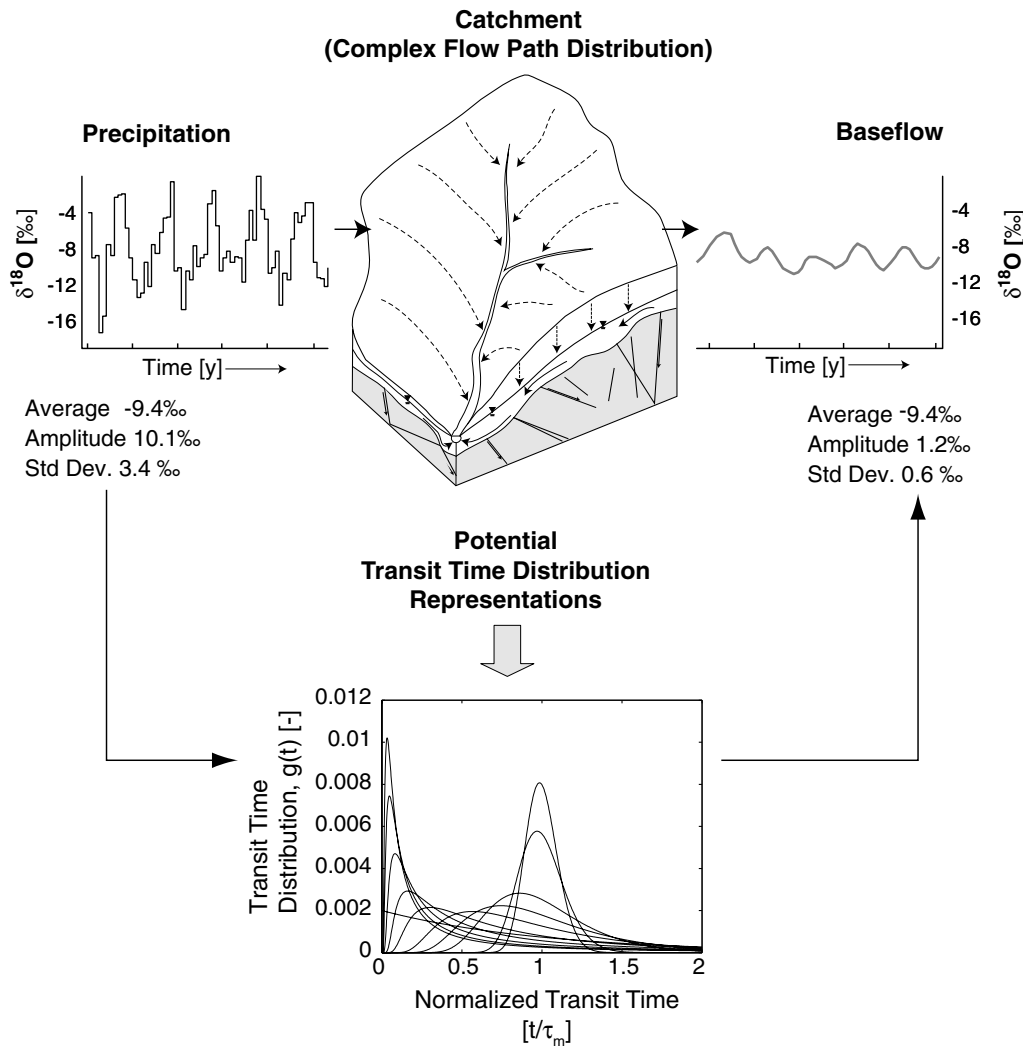


Figure 1 Conceptual diagram of the lumped parameter transit time modeling approach. Catchments receive temporal tracer (e.g., $\delta^{18}\text{O}$) inputs that are transported along diverse flow paths in the unsaturated and saturated zones as tracers migrate through the subsurface toward the stream network. The result of differential transport within the catchment is a tracer output signal (baseflow) that is damped (i.e., decrease in standard deviation and amplitude) and lagged compared to the input signal. The complex distribution of catchment flow paths is represented by a distribution of transit times, $g(\tau)$, that describe the integrated behavior of tracer transport through the catchment (modified after Plummer et al. (2001)).

much shorter than transport through the catchment's subsurface and thus has generally been ignored in catchment transit time distributions (see Kirchner et al., 2001; Lindgren et al., 2004), although it may be important in larger catchment systems (i.e., where channel storage and transport become significant). The transport process along subsurface flow paths causes delay (due to advection) and spreading (dispersion) of tracer arrival in the stream network, which is a direct reflection of the catchment's flow path distribution, runoff processes, and subsurface hydrologic characteristics. The integrated response of tracer arrival at the catchment outlet from all locations in the catchment is described by the TTD.

Mathematically, the transport of conservative tracer through a catchment can be expressed by the convolution integral, which states that the stream outflow composition at any time, $\delta_{\text{out}}(t)$, consists of tracer, $\delta_{\text{in}}(t - \tau)$, that fell uniformly on the catchment in the past ($t - \tau$), which be-

comes lagged according to its transit time distribution, $g(\tau)$ (Barnes and Bonell, 1996; Kirchner et al., 2000):

$$\delta_{\text{out}}(t) = \int_0^{\infty} g(\tau) \delta_{\text{in}}(t - \tau) d\tau = g(t) * \delta_{\text{in}}(t), \quad (5)$$

where τ are the lag times between input and output tracer composition, and the asterisk represents the short-hand of the convolution operation. Eq. (5) is similar to the linear systems approach used in catchment unit hydrograph models (e.g., Overton, 1970; Dooge, 1973), where precipitation impulses are converted to an output response by linear superposition of a system response function (i.e., $g(t)$) (for an overview see McCuen, 2005). The unit hydrograph model predicts the response of an addition of potential energy (i.e., from effective precipitation) whereas Eq. (5) predicts the tracer composition response in the stream to tracers applied during rainfall. Thus, the timescale of the runoff response (i.e., the dissipation of potential energy)

is different than the water transit time because fluctuations in hydraulic head can propagate much faster through the catchment than the transport of conservative tracer or individual water molecules (Horton and Hawkins, 1965; Kirchner et al., 2000; Torres, 2002).

The lumped parameter approach (Eq. (5)) is only valid for constant Q (i.e., steady-state) and when the mean subsurface flow pattern does not change significantly in time (Zuber, 1986b). It can be re-expressed with both t and τ replaced by accumulated flow (Nyström, 1985) or corrected as flow-time (Rodhe et al., 1996):

$$t_c = \int_0^t Q(t) dt / \bar{Q}, \quad (6)$$

where t_c is flow-corrected time and \bar{Q} is the mean annual flow. Accordingly, the assumption of time invariance holds, since t_c is proportional to the flow rate relative to the mean annual flow. For example, 1 day would be equivalent to 1 mm of discharge volume if $\bar{Q} = 365 \text{ mm year}^{-1}$. During dry periods, time effectively becomes compressed, whereas during wet periods, time is expanded. More realistically, mass flux (i.e., $C_{in}(t) \times I(t)$ and $C_{out}(t) \times Q(t)$, where C is concentration and I is input water flux) can be convolved instead of concentration (Niemi, 1978; Zuber, 1986b), although the system is still constrained by spatially uniform inputs (Barnes and Bonell, 1996). Eq. (5) without flow-corrected time and using only the concentration of tracer is suitable for catchments where flow parameters (e.g., velocity) do not deviate significantly from the long-term mean values or where the variable portion of the flow system is small compared to the total subsurface volume (e.g., Zuber et al., 1986). A more general lumped model (spatially uniform inputs) can be written as

$$\delta_{out}(t) = \int_0^\infty g(t, \tau) \delta_{in}(t - \tau) d\tau, \quad (7)$$

where the transit time distribution, $g(t, \tau)$, is permitted to be time varying, e.g., during non-steady conditions. Although Eq. (7) is more realistic in a catchment context, the transit time distribution is inherently more complex and therefore difficult to quantify. Turner et al. (1987) treated the catchment transit time distribution stochastically, which enabled them to estimate the time-variable mean transit time of water draining the catchment. One might also consider the transit time to vary depending on antecedent wetness or some other description of the catchment state. For example, the transit time may decrease as the wetness and, thereby, the hydraulic conductivity decrease and more transmissive flowpaths become activated under wetter catchment conditions.

Transit time distributions

TTDs used in Eq. (5) are time-invariant, spatially lumped characteristics of the catchment and thus describe the average catchment behavior of all factors that affect flow and tracer transport. The convolution approach implicitly assumes transport mechanisms, since parameters of the TTD are determined by solving the inverse problem based on tracer data (i.e., parameters for the TTD are estimated from known input/output tracer records). A catchment's TTD could have various shapes depending on the exact nature

of its flow path distribution and flow system assumptions. Thus, TTDs are assumed or selected from many possible distributions (as shown in Fig. 1), since the true distribution is unknown and only in exceptional cases, can be determined directly by experiment (cf. Rodhe et al., 1996). Common model types (i.e., TTDs) used in hydrologic systems include: piston flow, exponential, exponential–piston flow, and dispersion models (Maloszewski and Zuber, 1982; Cook and Böhle, 2000).

Fig. 2 shows the form of these common TTDs. The piston-flow model, which is the most straightforward, implies that all flow pathways have the same velocity and path length, which is never true in catchments. The exponential model, simply describes a catchment with flow times that are distributed exponentially, including pathways with very short transit times, whereas the exponential–piston flow model describes a system that is exponentially distributed, but is delayed in time (i.e., a portion of the flow system is piston flow). The dispersion model (from the one-dimensional solution of the advection–dispersion equation) can accommodate a range of TTDs with the addition of a second parameter, D/vx (where D/vx is inverse of the Peclet number and describes the ratio of the longitudinal dispersivity $[D/v]$ to the length $[x]$ of the flow system or the ratio of the dispersive to advective timescales), including formulations with short and dispersed (e.g., Fig. 2, DM with $D/vx = 0.6$) or near uniform (similar to the piston-flow model) (e.g., Fig. 2, DM with $D/vx = 0.01$) transit times. The example TTDs shown in Fig. 2 illustrate that the choice and parameterization of different TTDs will affect the outflow tracer composition and interpretation of catchment response. Even though these models were developed for

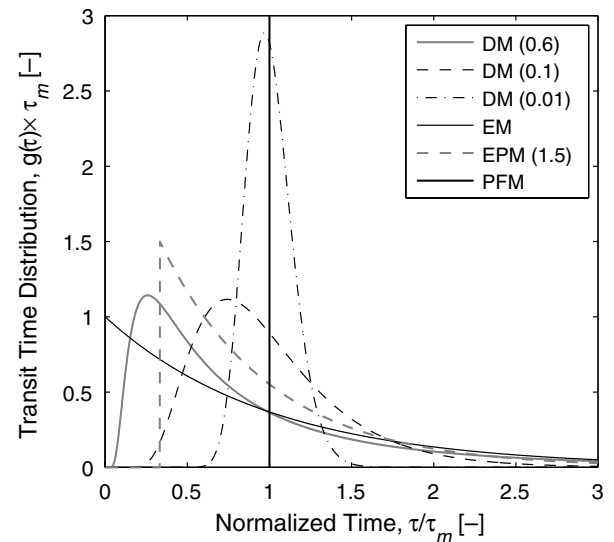


Figure 2 Examples of common transit time distributions, where DM is the dispersion model (dispersion parameter), EM is the exponential model, EPM is the exponential–piston flow model (piston flow parameter), and PFM is the piston flow model. τ_m is the mean transit time and other parameters are shown in parentheses (i.e., the dispersion parameter, D/vx , and the piston flow parameter, η , for the dispersion and exponential–piston flow model, respectively).

chemical engineering or groundwater applications, they have been used frequently in catchment systems (Stewart and McDonnell, 1991; Vitvar and Balderer, 1997; DeWalle et al., 1997; Soulsby et al., 2000; McGuire et al., 2002, 2005; McGlynn et al., 2003; Rodgers et al., 2005b). A detailed discussion of models that have been used as TTDs is beyond the scope of this review; however, discussions of the main model types (Fig. 2) can be found in Maloszewski and Zuber (1982, 1996) and Turner and Barnes (1998).

Recently, new models have been proposed such as the model of Amin and Campana (1996) that is capable of reproducing most of the aforementioned distributions (i.e., depending on the parameterization of their model). The Amin and Campana model has one or two additional fitting parameters compared to the distributions given by Maloszewski and Zuber (1982), but it is more flexible since it can represent many mixing possibilities (i.e., from no-mixing, to partial mixing, to perfect-mixing). Maloszewski and Zuber (1998) caution users of the lumped parameter approach by stating that even models with a low number of fitting parameters seldom yield unambiguous results. Additionally, they suggest that the terminology ‘‘mixing’’ is not adequate to describe subsurface flow systems, since significant mixing occurs only at the outlets of systems (e.g., streams, springs, and wells). Kirchner et al. (2001) developed a new model that is intended primarily for catchment systems. They derived an analytical expression for a spatially weighted advection–dispersion model for some common catchment geometries. They found that the shape of the spatially weighted advection–dispersion model approximated their previous empirical findings (see Kirchner et al., 2000) by yielding fractal tracer behavior if the advective and dispersive timescales were similar (i.e., Peclet number ≈ 1) (see also Scher et al., 2002).

A combination of transit time distributions and flow systems may also be used to approximate the integrated transit time distribution of a multi-component flow system (Maloszewski et al., 1983; Uhlenbrook et al., 2002). For example, in some catchments, a two- or three-component model is used to separate the rapid runoff components (e.g., Horton overland flow) from more delayed components (e.g., shallow subsurface flow or deep aquifer flow) to estimate catchment transit time based on the contribution from each component (Uhlenbrook et al., 2002). However, additional flow components should not be assumed on the basis of a poor fitting single component model, but according to a reasonable hydrological conceptual model that can be validated with other data (e.g., hydrometrics and geochemistry).

Modeling methods

There are many modeling approaches to estimate transit times such as particle tracking (e.g., Molénat and Gascuel-Odoux, 2002), direct simulation (Goode, 1996), compartment models (Campana and Simpson, 1984; Yurtsever and Payne, 1986), conceptual hydrologic models (Lindström and Rodhe, 1986), and stochastic–mechanistic methods (Destouni and Graham, 1995; Simic and Destouni, 1999). Often, these approaches require hydrological characterization of the catchment to develop models to approximate transit

times. Many catchments lack data to benefit from these techniques, and thus, the lumped parameter approach is used to infer transit times from tracer data (natural or applied).

Lumped parameter methods provide estimates of catchment-scale hydrological parameters (i.e., mean transit time, transport velocities, storage) through an inverse procedure where the parameters of a TTD are estimated by calibrating simulations to fit measured tracer output composition (Maloszewski and Zuber, 1993). This is typically accomplished by numerically integrating the convolution integral (Eq. (5)) in the time domain. Several computer codes are available to perform this procedure (Maloszewski and Zuber, 1996; Bayari, 2002; Ozyurt and Bayari, 2003); nevertheless, it is easily implemented with practically any technical computing software. The fitting can be manual (i.e., trial and error) or automated using a variety of search algorithms that minimize one or several objective functions (e.g., Legates and McCabe, 1999). Ultimately, other supporting hydrological evidence and intuition should be used to validate the selected model.

In the following two sections, we provide additional detail on methods that are absent or generally not well described in previous reviews of lumped parameter transit time modeling (e.g., Maloszewski and Zuber, 1996; Turner and Barnes, 1998; Cook and Böhlke, 2000), but are important approaches in catchment transit time modeling.

The frequency domain

While the convolution (Eq. (5)) is generally carried out in the time domain, it can be extended to the Fourier (i.e., frequency) or Laplace domain by using the respective transformations (Dooge, 1973). Then, convolution is simply the product of the transforms of $g(t)$ and $i(t)$ (input time series) according to the convolution theorem. The power spectra of $g(t)$ and $i(t)$, which describe how much information is contained in a signal at a particular frequency determined by the square of the Fourier amplitudes (Koopmans, 1995; Fleming et al., 2002), can also be convolved by multiplication:

$$o(t) = g(t) * i(t) \text{ and } |O(\omega)|^2 = |G(\omega)|^2 |I(\omega)|^2 \quad (8)$$

then the power spectrum of the transit time distribution is

$$|G(\omega)|^2 = |O(\omega)|^2 / |I(\omega)|^2, \quad (9)$$

where ω is frequency ($\omega = 1/\lambda$, where λ is wavelength), $|I(\omega)|^2$, $|O(\omega)|^2$, and $|G(\omega)|^2$ are the power spectra of the input, output, and transit time distribution, respectively. $|G(\omega)|^2$ will give the degree of damping or attenuation of input frequencies according to its shape, resembling a band-pass filter. However, the resulting the power spectra $|G(\omega)|^2$ cannot be inverted to retrieve the time domain TTD because the phase information has been lost. Spectral methods may also allow for better discrimination between potential TTDs compared to time domain methods because flow systems often have unique frequency response characteristics (Duffy and Gelhar, 1985).

Lumped parameter models computed in the frequency domain have been described in detail by Eriksson (1971) and Duffy and Gelhar (1985) and subsequently used by Kirchner et al. (2000) to examine transit time distributions of

catchments that have 1/frequency scaling. Not only is convolution simplified in the frequency domain by multiplication, but deconvolution is sometimes possible using the Fourier transforms (i.e., the complex frequency transformation) (Viitanen, 1997). While deconvolution is possible, high-frequency components and aliasing of the input/output signals (see Kirchner, 2005) can obscure the identification of the true transit time distribution (Viitanen, 1997). Recent approaches have been developed to constrain or stabilize deconvolution solutions in the time domain; however, care must be taken when deconvolving noisy signals, since the problem is considered ill-posed (Dietrich and Chapman, 1993; Skaggs and Kabala, 1994; Skaggs et al., 1998).

The sine-wave approach

A common simplification used to estimate transit time using the lumped parameter model takes advantage of the strong seasonal changes in the composition of stable isotopes in precipitation at temperate latitudes (Fritz, 1981; Stichler and Herrmann, 1983; Pearce et al., 1986; Leopoldo et al., 1992; Buzek et al., 1995; DeWalle et al., 1997; Burns and McDonnell, 1998; Burns et al., 1998; Soulsby et al., 1999; Rodgers et al., 2005a). The stable isotope composition of precipitation tends to reflect the seasonally varying tropospheric temperature variations (with relatively uniform precipitation) (see Dinçer and Davis, 1984; Herrmann and Stichler, 1980), which in some cases, can be approximated with a sine-wave function (Eden et al., 1982; Maloszewski et al., 1983; DeWalle et al., 1997):

$$\delta = \beta_0 + A[\cos(ct - \phi)], \quad (10)$$

where δ is the predicted isotopic composition, β_0 is the estimated mean annual $\delta^{18}\text{O}$, A is the annual amplitude of δ , ϕ is the phase lag of δ in units of radians, c is the angular frequency constant ($2\pi/365$) in rad d^{-1} , and t is the time in days after an arbitrary date. Eq. (10) can be evaluated statistically using sine and cosine terms (i.e., the first harmonic) as independent variables in a standard multiple regression model (Bliss, 1970):

$$\delta = \beta_0 + \beta_{\cos} \cos(ct) + \beta_{\sin} \sin(ct). \quad (11)$$

The estimated regression coefficients, β_{\cos} and β_{\sin} , are used to compute $A = \sqrt{\beta_{\cos}^2 + \beta_{\sin}^2}$ and $\tan \phi = |\beta_{\sin}/\beta_{\cos}|$.

Therefore, using Eq. (11) to predict the input and output tracer signals, all terms in the model (Eq. (5)) are known except for the parameters of an assumed TTD. Analytical solutions for the mean transit time parameter for the exponential (EM), exponential–piston flow (EPM), and dispersive (DM) models can be derived by combining Eq. (5) with sinusoidal representations of the input and output signals:

$$\tau_m = c^{-1} \sqrt{f^{-2} - 1} \quad (\text{EM}), \quad (12)$$

$$\tau_m = \frac{\eta \sqrt{f^{-2} - 1}}{c} \quad (\text{EPM}), \quad (13)$$

$$\tau_m = c^{-1} \sqrt{-(\ln f)Pe} \quad (\text{DM}), \quad (14)$$

where f is the damping coefficient, B_n/A_n ; A_n and B_n are the annual amplitudes of the input and output signals, respectively; η is a parameter that describes the piston flow portion of the model; and Pe is the Peclet number. The

parameter η is equal to the total volume of water in the system divided by the volume with an exponential distribution of transit times. For $\eta = 1$, the model is equivalent to the exponential model, whereas when $\eta \rightarrow \infty$, the model approaches pure piston flow (Maloszewski and Zuber, 1982). The derivation of Eqs. (12) and (14) are given by Kubota (2000), since they were not included in the original work of Maloszewski et al. (1983). Rather than assuming values for η (i.e., using Eq. (13)), Asano et al. (2002) calibrated Eq. (10) with observed data by finding solutions for B_n and ϕ using the exponential–piston flow model:

$$B_n = A_n \left(1 + \frac{c^2 \tau_m^2}{\eta^2} \right)^{-1/2}, \quad (15)$$

$$\phi = c\tau_m \left(1 - \frac{1}{\eta} \right) - \arccos \left[\left(1 + \frac{c^2 \tau_m^2}{\eta^2} \right)^{-1/2} \right]. \quad (16)$$

This approach allows for interpretation of the tracer signal using both the exponential and exponential–piston models.

Application of the sine-wave analysis is limited to conditions where Eq. (10) (or (11)) adequately fits the observed data. Therefore, regression statistics (e.g., coefficient of determination, root mean square error, etc.) should be provided to indicate potential uncertainty in the estimates of the mean transit time using Eqs. (12)–(14). Flux-weighted (i.e., using recharge or precipitation, see below) inputs should be used in the sine-wave analysis in order to better characterize the tracer mass that contributes to outflow (e.g., see Soulsby et al., 2000). In a comparison of three different methods used to estimate mean transit times, Stewart and McDonnell (1991) found that the convolution approach provided better results than the sine-wave method. Likewise, if sine-wave mean transit times were computed from the periodic regression data provided by McGuire et al. (2002) in Table 1, one would obtain different mean transit time results compared to what they estimated based on their models that included recharge weighting. For example, the Leading Ridge precipitation $\delta^{18}\text{O}$ amplitude was 1.84‰ and the output for the stream was 0.21‰, yielding mean transit times of 16.6 or 21.3 months for the EM and EPM models (Eqs. (12) and (13)), respectively, compared to 9.5 months based on their reported results. This highlights the importance of weighting procedures in catchment studies where precipitation or recharge may not be uniform, which is often assumed in application of the sine-wave method.

Since the sine-wave method is computationally simple, it is often used to estimate mean transit times. Nonetheless, it does not allow for discriminating between different model types, since the mean transit time is computed directly from the signal amplitudes given an a priori model selection. Also, the sine-wave technique does not take advantage of more subtle variations at frequencies other than the annual frequency, which are common in stable isotope datasets. Thus, either the power spectrum or time domain convolution approach is preferred to more accurately estimate the TTD and evaluate the potential of different models. However, the sine-wave method can be used to approximate the maximum potential catchment mean transit time that the models are capable of estimating with stable isotope data. For instance, DeWalle et al. (1997)

calculated the maximum potential mean transit time of an exponential model using the minimum analytical reproducibility of laboratory isotope determinations as the output amplitude and the observed input amplitude. The observed input precipitation amplitude in their study was 3.41‰, which yielded a maximum mean transit time of 5 years for a given $\delta^{18}\text{O}$ error of 0.1‰. Therefore, depending upon the amplitude of the input (and of course the noise/signal relationship), one can approximate, as a "back of the envelope calculation," the maximum mean transit time estimate possible based on the observed annual amplitudes of the stable isotope data series (sine-waves are assumed to be stationary and representative of long-term averages).

Assumptions and unresolved issues of catchment transit time models

Water transit times have been estimated for catchments at a variety of scales in diverse environments around the world (e.g., Burgman et al., 1987; Maloszewski et al., 1992; Vitvar and Balderer, 1997; Frederickson and Criss, 1999; Kirchner et al., 2000; Soulsby et al., 2000; Asano et al., 2002; Michel, 2004; Rodgers et al., 2005a; McGuire et al., 2005). Table 1 summarizes the findings from these and other studies that have evaluated catchment transit time using lumped parameter methods. Most studies have shown that mean transit times range from approximately <1 to 5 years and that assumed distributions vary depending upon various factors

including hydrogeological attributes, suitability of fit to data, and data limitations. Often the assumptions and problems associated with the methods presented above are not clearly stated in the literature. We argue that there are assumptions and unresolved issues that need to be synthesized in order to advance transit time estimation and modeling at the catchment-scale. The application of lumped parameter tracer models to catchments is predicated on: (1) the input characterization, (2) the recharge estimation, (3) the data record length, (4) the stream sampling methods, (5), the selection of the transit time distribution, and (6) the model evaluation process. Each of these issues is discussed below by the evaluation and review of past transit time modeling approaches and through the use of examples that illustrate outstanding problems for transit time estimation in catchments.

The input characterization issue

Measured inputs are assumed to represent the spatial and temporal inputs for the entire catchment. In practice, the isotopic composition of precipitation is usually sampled at one location and as volume-weighted, bulk samples for weekly or monthly time intervals. At the catchment scale, elevation, rainfall intensity, air temperature, and rain shadow effects may cause considerable variation in the isotopic composition of precipitation over short distances, particularly in mountainous areas (Ingraham, 1998).

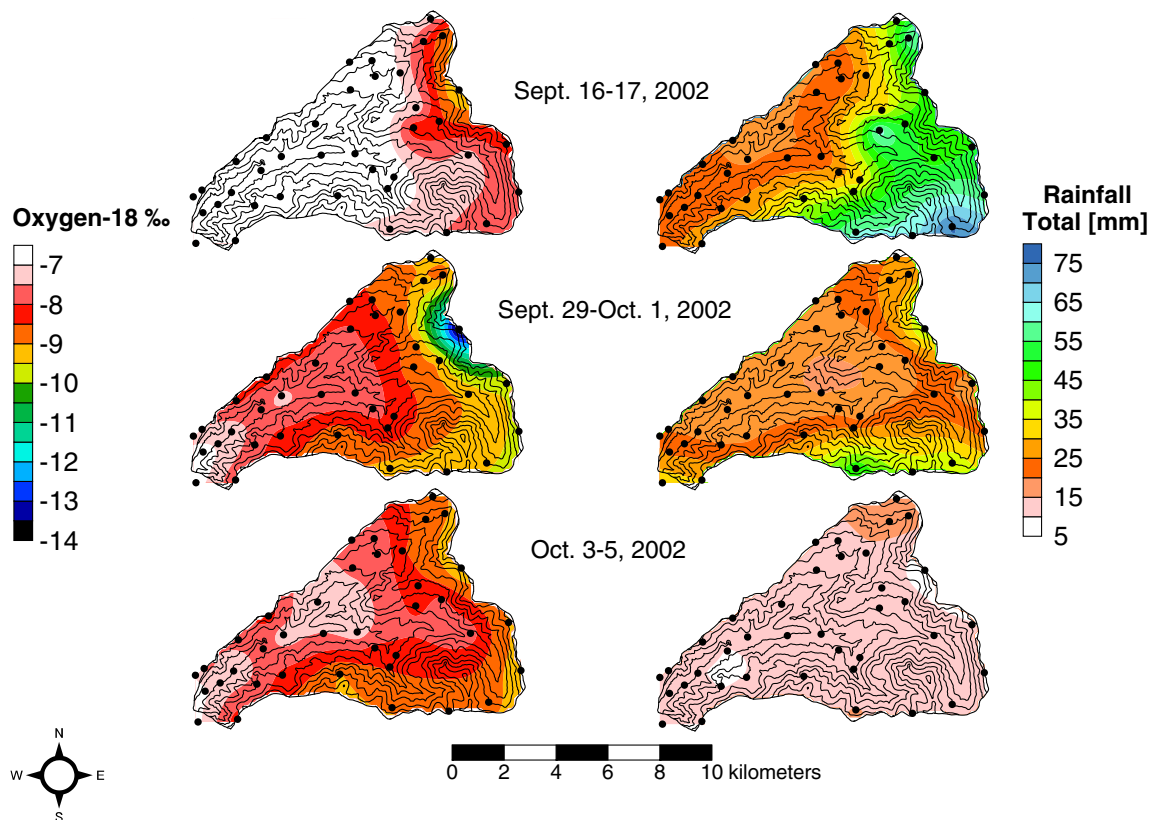


Figure 3 An illustration of rainfall $\delta^{18}\text{O}$ (per mil) and rainfall depth (mm) variation of three consecutive storms in the Lookout Creek (62.4 km²) basin within the western, central Cascades of Oregon, USA. Elevations range from 430 to 1620 m. Rainfall samples were collected as bulk storm samples (Modified after McGuire et al., 2005).

Fig. 3 shows the ^{18}O composition and rainfall amount over a 62 km² catchment in the western Cascades of Oregon, USA. There is a general persistence in the pattern of $\delta^{18}\text{O}$ between each storm that is related to the basin topography and storm track or air mass origin. $\delta^{18}\text{O}$ tends to be more depleted in high elevation areas, specifically along the southern and eastern ridges of the basin. The elevation effect (Dansgaard, 1964) was -0.26‰ per 100 m of elevation ($r^2 = 0.45$) for these three consecutive storms, which is similar to results found by other investigators (Clark and Fritz, 1997). Rainfall amounts do not explain significantly more variance ($r^2 = 0.49$) than elevation alone for the data in Fig. 3; however, including a variable to identify each storm (e.g., storm 1, storm 2, storm 3) in the regression model increases the r^2 to 0.61, suggesting that storm track is also an important variable describing the $\delta^{18}\text{O}$ patterns (see also Pionke and DeWalle, 1992). Since the majority of catchment studies are located within upland (and sometimes mountainous) terrain, this example illustrates the need to properly characterize potential catchment input variations in space and time.

Snowmelt inputs can also be problematic, particularly in areas where it is the predominant form of soil water and groundwater recharge. Isotopically light snowmelt signatures can enhance the seasonality of the input and applicability of the sine-wave method for estimating mean transit time (e.g., Maloszewski et al., 1983). Fractionation processes often cause the early snowmelt composition to be isotopically light and subsequent melt progresses toward heavier isotopic composition (Herrmann et al., 1981; Taylor et al., 2001; Unnikrishna et al., 2002). Therefore, in the presence of snowcover, the input should be estimated from the snowmelt discharge (e.g., using snow lysimeters) and not from the snowcover or bulk precipitation (Herrmann et al., 1981; Stichler and Herrmann, 1983; Taylor et al., 2001, 2002; Laudon et al., 2002).

Overall, there has been little research on how to obtain representative snowmelt composition in a catchment from spatial melt patterns for transit time estimates. Characterizing catchment isotopic input composition in general can be particularly challenging and poor characterization can potentially lead to uncertainty or error in the transit time modeling parameter estimates.

The recharge assumption

Transit time models assume that the composition of inputs (i.e., δ_{in} in Eq. (5)) equals the composition of recharge that contributes to catchment turnover. The recharge timeseries, also called the input function by Maloszewski and Zuber (1982), is not directly obtainable, even if the isotopic composition of precipitation is well known. Recharge represents the mass flux of water (i.e., volumetrically weighted isotopic composition) that infiltrates below the rooting zone and participates in runoff generation. Theoretically, if all precipitation inputs were measured and the recharge rates were known, then the weighted mean input determined from those two terms over a long period (e.g., several years) would balance the mean streamflow isotopic composition. This assumes no fractionation from either soil evaporation or canopy interception. Detailed discussion of fractionation processes that might affect recharge, can be

found in Gat and Tzur (1967) and DeWalle and Swistock (1994). Transpiration is not thought to fractionate water at the soil–root interface (Wershaw et al., 1966; Dawson and Ehleringer, 1991).

Early methods approximated the recharge function by simply weighting the tracer composition by precipitation or by assuming that summer periods did not contribute to recharge (e.g., Dinçer et al., 1970). Martinec et al. (1974) developed a more sophisticated approach to estimate a monthly tritium recharge function in which a ratio of summer to winter precipitation was used as a fitting parameter in their model. Grabczak et al. (1984) found that the additional fitting parameter caused poor identifiability of the TTD parameters, and thus, developed an isotope mass balance approach to determine summer/winter infiltration coefficients. Assuming that groundwater is derived meteorically and that its isotopic composition is relatively constant in time, it can be calculated from the isotopic compositions (δ) of summer precipitation (P_s , where s corresponds to growing season months), and winter precipitation (P_w , where w corresponds to non-growing season months) (Grabczak et al., 1984; Maloszewski et al., 1992):

$$\delta_G = \left(\alpha \sum \delta_s P_s + \sum \delta_w P_w \right) / \left(\alpha \sum P_s + \sum P_w \right), \quad (17)$$

where δ_G is the isotopic composition of groundwater and α is the infiltration coefficient equal to ratio of summer to winter infiltration, which is then

$$\alpha = \left(\sum \delta_w P_w - \delta_G \sum P_w \right) / \left(\delta_G \sum P_s + \sum \delta_s P_s \right). \quad (18)$$

The infiltration coefficients (α) can be used to determine an input function (δ_{in}) for Eq. (5) (Bergmann et al., 1986; Maloszewski et al., 1992):

$$\delta_{\text{in}}(t) = \frac{N \alpha_i P_i}{\sum_{i=1}^N \alpha_i P_i} (\delta_i - \delta_G) + \delta_G \quad (19)$$

where α_i are the individual infiltration coefficients corresponding to the i th time period, and N is the number of time periods (e.g., months) for which precipitation is collected. Usually, α_i is determined for the summer months by Eq. (19) and α_i for the winter months is equal to 1 (Maloszewski and Zuber, 1996). Maloszewski et al. (1992) claim that α computed from Eq. (19) more realistically represents tracer mass compared to α computed from hydrological data (i.e., $\alpha = (Q_s P_w) / (Q_w P_s)$), since it likely includes elevation effects and delayed isotopic input from snowpack storage.

A more flexible approach, which was introduced by Martinec et al. (1974) and later adopted by Stewart and McDonnell (1991) and Weiler et al. (2003), directly incorporates the recharge weighting, $w(t)$, into a modified convolution equation so that the streamflow composition reflects the mass flux of tracer leaving the catchment:

$$\delta_{\text{out}}(t) = \frac{\int_0^\infty g(\tau) w(t-\tau) \delta_{\text{in}}(t-\tau) d\tau}{\int_0^\infty g(\tau) w(t-\tau) d\tau}. \quad (20)$$

The weighting term, $w(t)$, can include any appropriate factor such as rainfall rates, throughfall rates, or partially weighted rainfall rates (e.g., effective rainfall). Also, Eq. (20) can be combined with simple rainfall-runoff models based on unit hydrograph or transfer function approaches (Jakeman and Hornberger, 1993; Young and Beven, 1994)

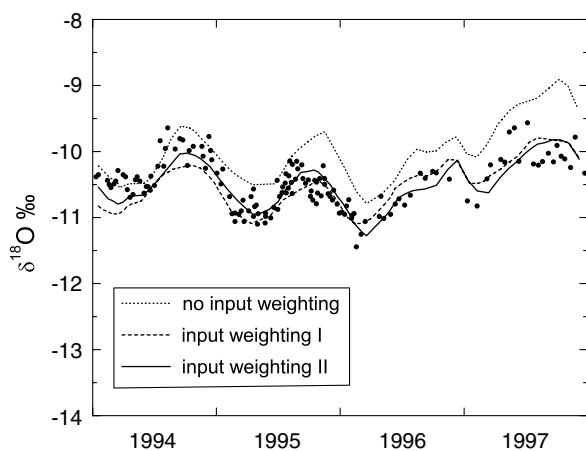


Figure 4 Simulated Mosnang baseflow $\delta^{18}\text{O}$ in the Rietholtzbach catchment (Switzerland) using inputs weighted by lysimeter outflow (input weighting I) and groundwater recharge estimated from a soil water balance model, PREVAH-ETH (input weighting II) (Modified after Vitvar et al., 1999).

that allow for the identification of effective precipitation from a non-linear soil moisture routine. In other words, a coupled hydrologic-tracer model can be constructed to describe the tracer and runoff behavior, in addition to identifying TTD parameters (cf. Weiler et al., 2003). Generally, transfer function models contain a minimal number of parameters that are often dictated by the information content in the data, and thus, are considered to be among the most parsimonious models for simulating runoff (Young, 2003).

Soil water routines in conceptual hydrological models have recently been used to weight the isotopic composition of precipitation to represent recharge (Vitvar et al., 1999; Uhlenbrook et al., 2002). Vitvar et al. (1999) compared weighting methods based on lysimeter outflow (cf. Vitvar and Balderer, 1997) and groundwater recharge calculated from the model PREVAH-ETH (Gurtz et al., 1999) and found that modeled groundwater recharge, which was calibrated independently using runoff data, gave the best fit to the observed isotopic data (Fig. 4). They suggested that modeled recharge more accurately reflected the portion of precipitation that reached the aquifer, whereas the lysimeter outflow accounted for only shallow vertical flow processes. Fig. 4 shows clearly that the input weighting based on the modeled groundwater recharge better fits the observed baseflow $\delta^{18}\text{O}$ compared to the lysimeter outflow weighting. While soil water balance models may provide better fits to data, they require additional parameters to describe soil properties and evapotranspiration, and thus, introduce potential uncertainty from the increased overall model complexity.

The data record length problem

A common problem with the lumped parameter approach is the length of tracer record, in terms of both inputs and outputs. A short input can lead to poorly estimated parameters and tracer mass imbalance if the timescale of the TTD is sufficiently longer than the input record. This problem is most

frequently encountered when stable isotopes are used as tracers. Tritium composition in precipitation is relatively well known over several decades (e.g., Michel, 1989) and therefore presents less of a problem regarding input record length. Many investigators have extended stable isotope inputs using temperature records (Burns and McDonnell, 1998; Uhlenbrook et al., 2002), sine-wave approximations (McGuire et al., 2002), and data from nearby long-term stations (Maloszewski et al., 1992; Vitvar and Balderer, 1997). In such cases, uncertainty is introduced into the estimation of the TTD parameters; thus, it is recommended to obtain the longest possible measured record. As a thought exercise, consider Fig. 5 where a measured input record length (e.g., 1 year) is equal to the catchment mean transit time (τ_m) for an exponential TTD. The mass recovery for that system is 63% (i.e., $1 - e^{-1}$) at the time equivalent to the length of the input record, which is the amount of input water leaving the system with an age less than or equal to τ_m (Fig. 5). In other words, a 1-year mean transit time requires about 5 years of input record to pass nearly all of those inputs through the basin. If the mean transit time was 25% of the input record length (e.g., 3 months instead of 1 year), then most of the inputs could pass through the catchment in a period of time approximately equal to the time in which inputs were collected (e.g., 1 year) (Fig. 5).

The convolution is essentially a frequency filter (cf. Duffy and Gelhar, 1985), which means that more repetitive frequencies at all wavelengths will allow for better identification of the TTD. Thus, if one is interested in long timescales of the catchment TTD (i.e., annual to multi-year), then several of those cycles should be “sampled” by the input time series. In practice, we deal typically with records on the order of several years; however, Kirchner et al.

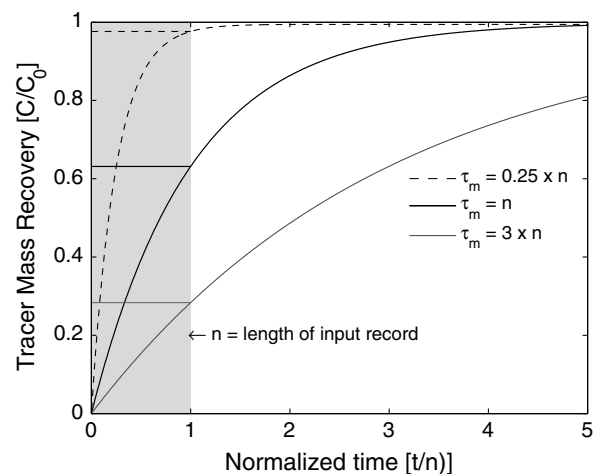


Figure 5 Exponential transit time distributions expressed as tracer mass recovery (cumulative TTDs). The gray shaded area hypothetically represents the length of time that inputs were measured, n , which is also the mean transit time, τ_m , of the solid black line. The dashed line has a mean transit time equal to 25% of the input record length and the gray line has a mean transit time equal to three times the input record length. The mass recovery of each system that occurs after an elapsed time equal to the input record length is shown by the horizontal lines in the gray shaded area.

(2000) demonstrate that long-term (and high frequency) measurements allow for the evaluation of catchment TTDs that span several orders frequency magnitude (i.e., from timescales of days to multi-year). In some cases, a short time series can be used if there are pronounced tracer variations in both the input and output data over the timescales of interest. For example, Stewart and McDonnell (1991) were able to model soil water ^2H fluctuations using a 14-week dataset because the observed isotopic composition had a consistent, strong variation with an approximate 5-week period and the expected mean transit times were on the order 2–20 weeks.

In a re-interpretation of a tritium record, Zuber et al. (1992) extended a previously published data record (cf. Grabczak et al., 1984) with new tritium observations and found, as in the original work, similar TTD parameters for a two-component dispersion model. However, better results were achieved by selecting single component models using the updated observations, which reduced the number of fitting parameters and yielded a more reliable model (Maloszewski and Zuber, 1993). In a similar effort, Vitvar et al. (1999) reanalyzed ^{18}O data from several sites presented in Vitvar and Balderer (1997) that were extended with observations an additional year and found relatively similar parameters for the TTDs. Uhlenbrook and Scissek (2003) also found that results from a reanalysis with additional observations produced similar mean transit time estimates for the Brugga catchment in Germany as in the original study (Uhlenbrook et al., 2002). Even though they were able to confirm previous results, the longer observation record (i.e., 2 additional years) did not reduce the uncertainty interval of the parameter estimates (± 0.5 year). Considering the limited number of examples in the literature, it is difficult to recommend the record length needed to reliably estimate TTDs. In most published studies (Table 1), outflow records lengths are approximately 2–4 years, while input records are typically longer (e.g., 2–10 years), often containing estimated or extrapolated values for inputs prior to the time of outflow observations. In general, longer input and output data records produce more reliable estimates of the transit time distribution.

The stream sampling issue

In most studies, the inputs are sampled as bulk weekly (or monthly) measurements due to economic constraints; thus, the models cannot be expected to resolve stream composition for timescales finer than weekly (or monthly). Typically during sample collection, storm periods are excluded so that inputs that immediately affect the stream tracer composition are removed from the analysis (e.g., DeWalle et al., 1997; Vitvar and Balderer, 1997; McGuire et al., 2002). This practice essentially aliases the time series, since the “true” signal contains higher frequencies and creates bias toward older water in the transit time estimates, which effectively excludes high flow behavior from the TTD (Kirchner et al., 2004). The stream sampling protocol will thus determine what transit time is estimated in the study, e.g., reflecting baseflow or the entire flow regime. Studies that estimate baseflow transit time do not truly represent the *catchment* transit time, but in effect, estimate the *groundwater* transit time.

Alternatively, Maloszewski et al. (1983) and Buzek et al. (1995) used a simple two-component mixing model to separate the direct influence of the rapid runoff component from the slower subsurface component (i.e., groundwater) for which they were interested in determining the TTD. In a new hydrograph separation approach, Weiler et al. (2003) show examples of event-water transit time distributions (i.e., the rapid component) that persist longer than 15–20 h after the storm event in an extremely responsive, steep humid basin. Therefore, conservatively, a lag time of 1 or 2 days after a storm or even a week after a snowmelt event may be necessary to avoid the rapid contribution of event water if estimates of groundwater mean transit time are of interest (e.g., Maloszewski et al., 1983). If inputs are sampled at finer time intervals (e.g., daily) and estimating the catchment TTD is the objective, then this issue becomes moot and the timescales that can be resolved decrease. Kirchner et al. (2000, 2001, 2004) have demonstrated based on spectral analysis that high temporal resolution observations can lead to new insights into the structure and function of catchments and better estimates of the early time portion of the TTD. Essentially, the stream tracer time series must match the temporal resolution of the input record and the TTD timescale of interest.

The TTD selection problem

A common issue in transit time modeling is selecting an appropriate transit time distribution (TTD) that describes the actual flow conditions of the catchment. The lumped parameter approach has been applied predominantly to groundwater systems and as such, many of the aforementioned TTDs (Fig. 2) have been used to represent groundwater flow conditions. Consequently, the selection of model types is often based on simplified assumptions regarding aquifer geometries (e.g., see Cook and Böhlke, 2000; Maloszewski and Zuber, 1982) and not specific catchment attributes. For instance, an exponential TTD, by far the most popular TTD used to date (see Table 1), would result from an unconfined aquifer with uniform hydraulic conductivity and porosity provided that transit times through the unsaturated zone are negligible (see Maloszewski and Zuber, 1982). Eriksson (1958) has suggested that the exponential model could also approximate the case of decreasing hydraulic conductivity with depth in an aquifer. This hydraulic conductivity decrease with depth is a defining feature of catchment hydrologic response (Beven, 1982) and fundamental to our catchment models in use today (Ambrose et al., 1996). In another example, a partially confined aquifer could be considered to delay or effectively eliminate contribution from short transit times, thus producing a TTD such as the exponential–piston flow model. In general, the TTD simply describes the integrated effect of all flow pathways expressed at the discharge location of a flow system or in the case of catchments, at the basin outlet. The assumption that we can match a TTD with functional catchment behavior is one of the biggest challenges in the application of transit time models to catchment hydrology.

There has been little theoretical work on determining the form of the TTD for catchments. One might expect a catchment TTD to conform to examples from groundwater

flow systems. In a theoretical analysis on idealized subsurface flow systems in catchments, [Haitjema \(1995\)](#) demonstrated that the TTD of any basin shape, size, and hydraulic conductivity is exponential given that the flow system is steady, locally homogeneous (not stratified), and receives uniform recharge. [Haitjema \(1995\)](#) and [Luther and Haitjema \(1998\)](#) proposed that the exponential TTD could successfully approximate TTDs for some non-steady cases or when some of the idealized assumptions presented by [Haitjema \(1995\)](#) are relaxed. Some experimental results support [Haitjema's \(1995\)](#) findings of exponential TTDs for catchments; such as the covered catchment study at Gårdsjön by [Rodhe et al. \(1996\)](#). In a later study, [Simic and Destouni \(1999\)](#) derived the TTD produced in [Rodhe et al. \(1996\)](#) with little calibration. They used a stochastic–mechanistic model that described non-uniform flow velocity resulting from groundwater recharge through the unsaturated zone. The model also incorporated preferential flow, diffusional mass transfer between mobile and relatively immobile water, and random heterogeneity resulting from spatially variable transmissivity. These features would violate the idealized conditions of [Haitjema \(1995\)](#).

In other experimental work, spectral analysis of daily chloride concentrations in rainfall and runoff at several sites around the world contest the use of exponential TTDs as the standard TTD in catchments. [Kirchner et al. \(2000\)](#) found that conventional catchment transport models (e.g., exponential and dispersive) could not reproduce the spectral characteristics (i.e., 1/frequency scaling) that were observed in stream chloride concentrations. They suggested instead that a gamma function, parameterized with a shape parameter of about 0.5, was the most appropriate TTD for the catchments in their study. [Kirchner et al. \(2001\)](#) demonstrate that advection and dispersion of spatially distributed rainfall inputs can produce the same fractal scaling behavior observed in [Kirchner et al. \(2000\)](#) when the dispersivity length scale approaches the length of the hillslope (i.e., Peclet ≈ 1). Even though such low Peclet numbers seem unrealistic (i.e., the dispersivity length approaches the length of the flow field (see [Gelhar et al., 1992](#))), [Kirchner et al. \(2001\)](#) claim that it accounts for the large conductivity contrasts in hillslopes. In using the same model as [Simic and Destouni \(1999\)](#), [Lindgren et al. \(2004\)](#) also found that the advective and dispersive transport timescales were nearly equivalent. Even when the ratio of advective to dispersive timescales was increased by one order of magnitude, they were still able to reproduce a fractal tracer behavior as observed by [Kirchner et al. \(2000\)](#).

Notwithstanding, the potential effects of hillslope topography and catchment geometry were not specifically addressed by [Lindgren et al. \(2004\)](#) and have recently been shown to control catchment-scale mean transit time of baseflow ([McGuire et al., 2005](#); [Rodgers et al., 2005a](#)). Both [Lindgren et al. \(2004\)](#) and [Kirchner et al. \(2001\)](#) used artificial catchment spatial representations (i.e., rectangular and other simple geometries); however, the complexity of the topography and other catchment features such as soil cover also likely influence catchment-scale transport ([McGlynn et al., 2003](#); [McGuire et al., 2005](#); [Rodgers et al., 2005a](#)).

Identifying plausible TTDs for use in catchments will require both experimental and theoretical developments for

a more comprehensive understanding of transport at the catchment-scale. For example, [Lindgren et al. \(2004\)](#) were able to show from a theoretical process perspective that the results of [Kirchner et al. \(2000\)](#) are explainable by considering variable groundwater advection, including preferential flow, and mass transfer between mobile and immobile zone in the subsurface system. In general, there appears to be no consensus on a functional representation of the TTD for catchments. However, with continued development of new techniques that describe first-order process controls on transit time (e.g., immobile/mobile zones, soil depth, hydraulic conductivity), long-term datasets sampled at high frequency, and approaches that utilize information contained within DEMs (digital elevation models) such as catchment geometry and topography, we will gain new insights into the TTD representation at the catchment-scale.

The model evaluation process

In current practice, TTDs are selected based either on an assumed flow system as we described for aquifers or by the best fitting results from various model simulations (i.e., through calibration). Selecting a model through calibration, which is usually based on objective measures such as the sum of squared residuals or Nash–Sutcliffe efficiency ([Nash and Sutcliffe, 1970](#)), can be problematic since parameters are often not identifiable and different models types can equally fit observations ([Beven and Freer, 2001](#)). The evaluation of parameter sensitivity and uncertainty has not been included customarily in the application of transit time models, even though it has received significant attention in the rainfall-runoff modeling ([Bergström, 1991](#); [Seibert, 1997](#); [Uhlenbrook et al., 1999](#); [Beven and Freer, 2001](#)) and the tracer-based hydrograph separation modeling ([Bazemore et al., 1994](#); [Genereux, 1998](#); [Joerin et al., 2002](#)) literature. Only a few studies have approximated uncertainties on parameter estimates of the TTD ([Kirchner et al., 2000, 2001](#); [McGuire et al., 2005](#); [Rodgers et al., 2005b](#)). Since the lumped parameter approach is focused on parameter estimation, we do ourselves disservice by not quantitatively addressing the reliability of our results. In some cases, more than one model may equally describe the system ([Vitvar and Balderer, 1997](#); [McGuire et al., 2002](#)). Thus, it can be argued that given the errors in our measured signals and the complexity of catchments, there will be many acceptable representations of the system ([Beven and Freer, 2001](#)). Additionally, some methods (e.g., forward convolution) or data may not be sufficiently sensitive to distinguish between various TTDs (see [McGuire et al., 2005](#)) and other methods (e.g., spectral techniques) may provide a more clear distinction between possible TTDs (see [Kirchner et al., 2000](#)).

Therefore, when evaluating possible TTDs through calibration it is recommended to also evaluate parameter identifiability and sensitivity. [Fig. 6](#) demonstrates schematically an example model evaluation process. In this example, two seemingly similar transit time model results are compared based on time domain convolution: the gamma model and the exponential model. The exponential model is essentially a special case of the gamma model with the shape factor parameter, α , fixed at 1. The simulations of the two TTD

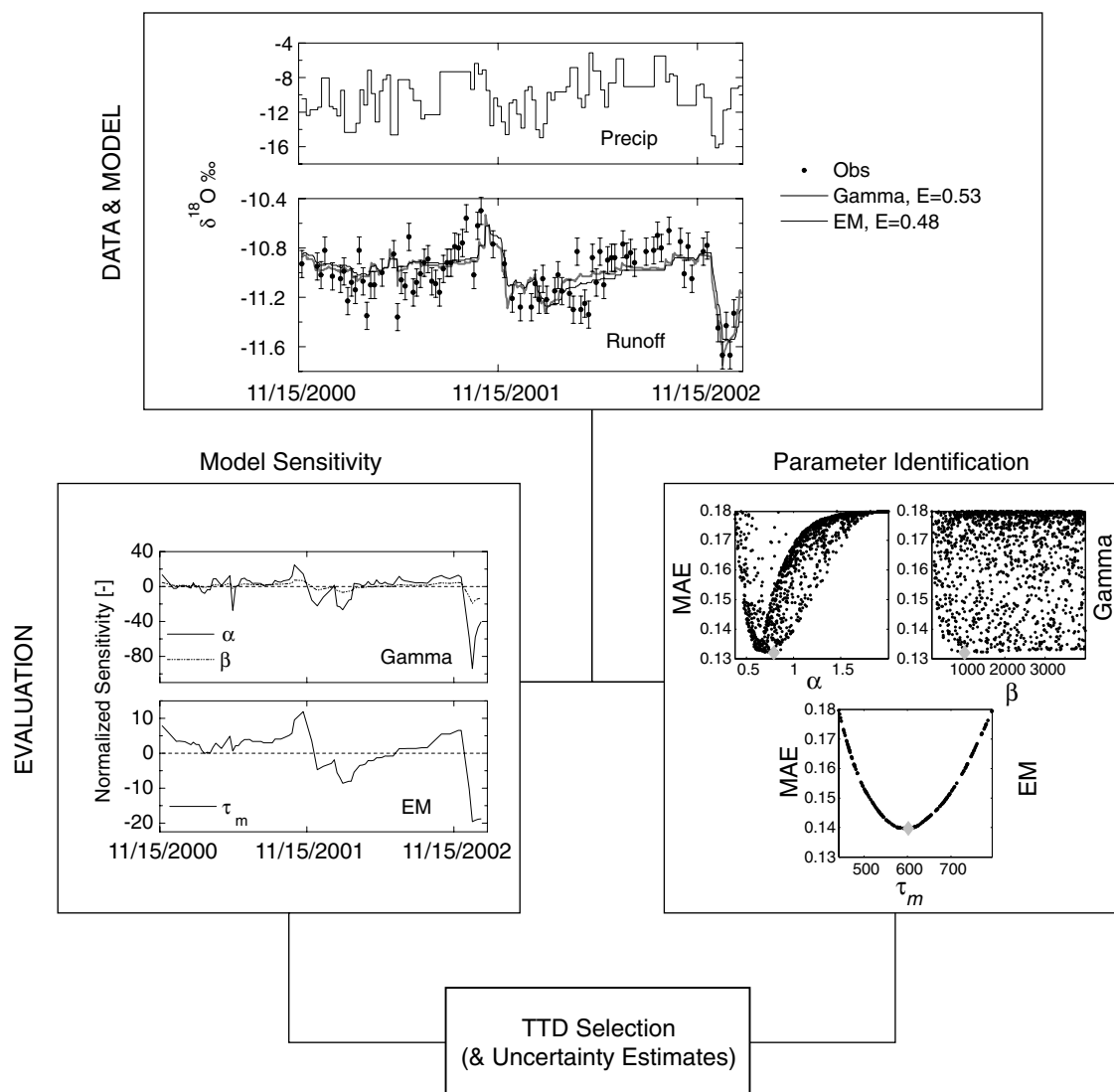


Figure 6 A diagram of the model evaluation and transit time distribution (TTD) selection process. The upper box contains observed data and model simulations for two TTDs (gamma and exponential). The two lower boxes illustrate the evaluation phase by examination of model sensitivity (in this case, temporal sensitivity (Knopman and Voss, 1987)) and parameter identification through scattergrams of mean absolute errors (MAE) computed from 1000 realizations of each model. The gray diamond indicates the parameter set with the lowest MAE. The final step is the selection of the best TTD given the observed data and the calculation of uncertainty estimates based on the evaluation step (e.g., confidence limits).

models have approximately the same goodness-of-fit to observations (Nash–Sutcliffe $E = 0.53$ for the gamma model, and $E = 0.48$ for the exponential model). However, the scale parameter for the gamma model (β) cannot be estimated using this particular modeling approach with any confidence as noted by the absent minima in the scattergram of Monte Carlo results shown in the parameter identification box in Fig. 6. The scattergram also shows that an α of 1 does not fit the data well, suggesting that an exponential model is also not a good description of TTD. In this example case, the extremely damped output $\delta^{18}\text{O}$ signal and relatively short time series (i.e., compared to the estimated mean transit times) may not allow for rigorous discrimination between models; however, the evaluation approach is useful for examining model error and parameter identifiability. The sensitivity plot for the gamma model shows that the

scale parameter (β) does not deviate significantly from zero, indicating that it is insensitive across the entire time series. The alpha parameter, on the other hand, shows some sensitivity to portions of the time series. Alternatively, the exponential model, which only has one parameter, becomes sensitive mainly during the winter periods of 2001 and 2002. A temporal sensitivity analysis may be used to evaluate parameter cross-correlation or suggest critical sampling periods for future monitoring efforts. For example, in Fig. 6, summer $\delta^{18}\text{O}$ composition does not appear to significantly influence the parameter estimates, which might suggest that intensive sample collection should focus on late fall and winter periods. The principal reason for a temporal sensitivity analysis, however, is to evaluate model performance and discriminate between potential TTDs. Several techniques that are available include dynamic identifiability

analysis (Wagener et al., 2003) and the use of the parameter covariance matrices (Knopman and Voss, 1987). Many of these techniques also allow for the computation of confidence limits on parameter estimates and simulations; however, consideration of input uncertainty should be included for a comprehensive uncertainty analysis of catchment transit time distributions. Model testing and evaluation should be included in any modeling exercise.

Summary and outlook

We have attempted to evaluate and review the transit time literature in the context of catchment water transit time estimation. Our motivation for this work relates to the new and emerging interest in transit time estimation in catchment hydrology and the need to distinguish between approaches and assumptions originating in the groundwater literature from catchment applications. Our intent has been to provide a formal clarification on the assumptions, limitations, and methodologies in applying transit time models to catchments, while highlighting new developments in research. Our review has focused on lumped parameter approaches of estimating transit times for streams and catchments, since it provides a quantitative approach to fundamentally describing the catchment flow system. The approach relies primarily on tracer data, and thus, is useful in gauged and ungauged basins and as a complement to other types of hydrological investigations. We have provided a critical analysis of unresolved issues that should be evaluated in future research through the application of lumped parameter transit time modeling at the catchment-scale. These issues included: (1) the input characterization issue, (2) the recharge assumption, (3) the data record length problem, (4) the stream sampling issue, (5) the transit time distribution selection problem, and (6) the model evaluation process. Despite the fact that many of the approaches discussed in this review are in their infancy (e.g., the spectral analysis of tracer data and theoretical, mechanistic and spatially derived models of transit time distributions), it is clear that transit time modeling will provide significant advances in catchment hydrology and improvement in understanding physical runoff generation processes and solute transport through catchments.

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