

# *Transit times – the link between hydrology and water quality at the catchment scale*

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# Transit times—the link between hydrology and water quality at the catchment scale

Markus Hrachowitz,<sup>1\*</sup> Paolo Benettin,<sup>2</sup> Boris M. van Breukelen,<sup>1</sup> Ophelie Fovet,<sup>3</sup> Nicholas J.K. Howden,<sup>4</sup> Laurent Ruiz,<sup>3</sup> Ype van der Velde<sup>5</sup> and Andrew J. Wade<sup>6</sup>

In spite of trying to understand processes in the same spatial domain, the catchment hydrology and water quality scientific communities are relatively disconnected and so are their respective models. This is emphasized by an inadequate representation of transport processes, in both catchment-scale hydrological and water quality models. While many hydrological models at the catchment scale only account for pressure propagation and not for mass transfer, catchment scale water quality models are typically limited by overly simplistic representations of flow processes. With the objective of raising awareness for this issue and outlining potential ways forward we provide a nontechnical overview of (1) the importance of hydrology-controlled transport through catchment systems as the link between hydrology and water quality; (2) the limitations of current generation catchment-scale hydrological and water quality models; (3) the concept of transit times as tools to quantify transport; and (4) the benefits of transit time based formulations of solute transport for catchment-scale hydrological and water quality models. There is emerging evidence that an explicit formulation of transport processes, based on the concept of transit times has the potential to improve the understanding of the integrated system dynamics of catchments and to provide a stronger link between catchment-scale hydrological and water quality models. © 2016 The Authors. *WIREs Water* published by Wiley Periodicals, Inc.

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\*Correspondence to: m.hrachowitz@tudelft.nl

<sup>1</sup>Faculty of Civil Engineering and Geosciences, Delft University of Technology, Delft, Netherlands

<sup>2</sup>Laboratory of Ecohydrology, Institute of Environmental Engineering, EPFL, Lausanne, Switzerland

<sup>3</sup>Agrocampus Ouest, UMR1069 SAS, INRA, Rennes, France

<sup>4</sup>Queen's School of Engineering, University of Bristol, Bristol, UK

<sup>5</sup>Department of Earth Sciences, Faculty of Earth and Life Sciences, VU University Amsterdam, Amsterdam, Netherlands

<sup>6</sup>Department of Geography and Environmental Science, University of Reading, Reading, UK

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## INTRODUCTION

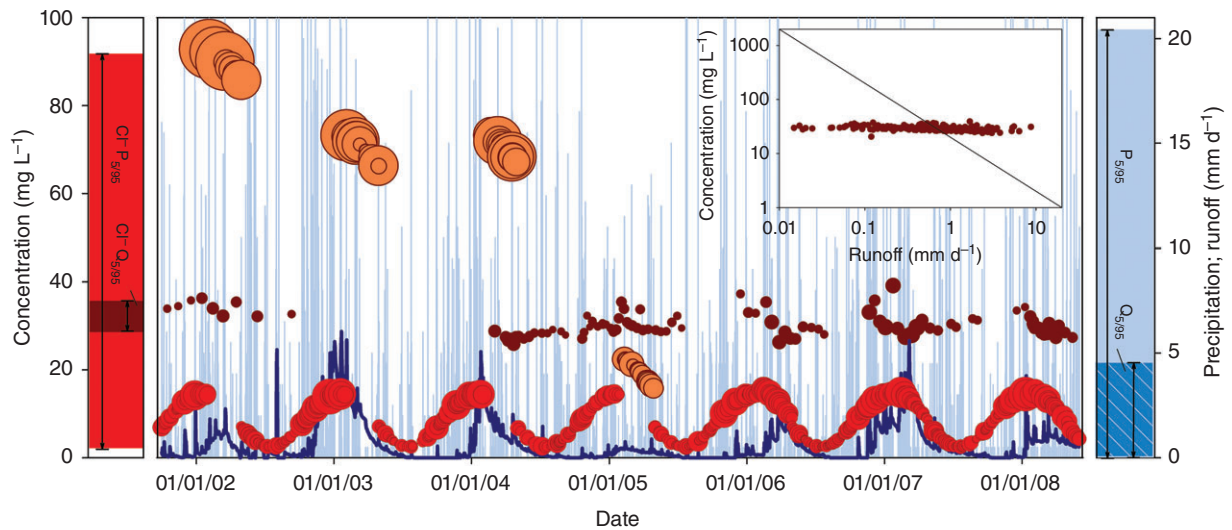
Climate change and population growth, together with agricultural intensification and economic pressures pose considerable challenges to meet the increasing demand for clean water.<sup>1–4</sup> These challenges span the supply and distribution of water<sup>5,6</sup> and water quality.<sup>7–9</sup> Pollutants such as nitrate,<sup>10–13</sup> phosphorous,<sup>14–16</sup> heavy metals,<sup>17–19</sup> or pesticides<sup>20</sup> in soil-, ground-, and river waters mainly originate from agricultural (diffuse) and industrial and sewage effluent (point) sources,<sup>21</sup> and there is global concern about the impacts of eutrophication and the associated aquatic hypoxia that can put ecosystem stability at risk.<sup>22,23</sup> There is thus an urgent need for the implementation of sustainable strategies to manage

nutrients and other contaminants in the water environment.<sup>24–27</sup> To be effective, however, the development of such strategies has to rely on robust predictions. These, in turn, require comprehensive models that are based on a solid and holistic scientific understanding of the system and adequate data to describe water and solute inputs and processing.

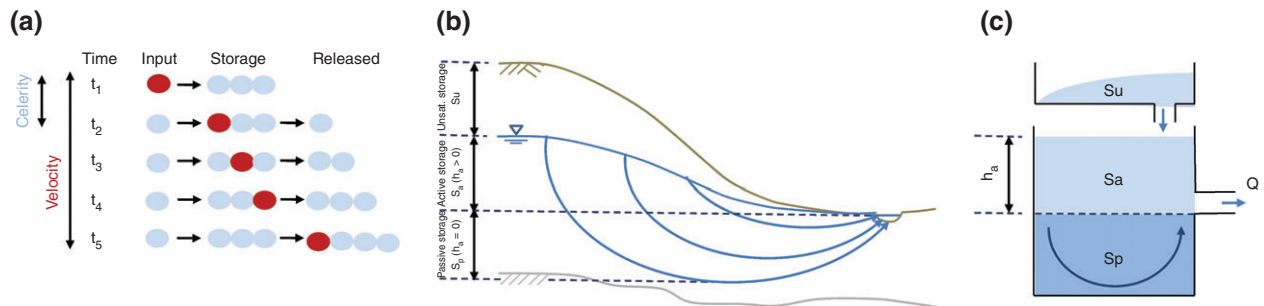
Although emphasizing different endpoints of the overall system response, both hydrology and water quality scientific communities, aim to develop an improved understanding of the same spatial domain that consists of the land surface, the subsurface and channels. Yet, in spite of the relatively well-acknowledged and understood interactions between hydrology and water quality<sup>28–35</sup> at the catchment scale, the two communities have yet to formulate an adequate and exhaustive way to quantify these interactions in their respective models. This has resulted in a considerable disconnection between many catchment-scale hydrological and water quality models. One example for such a disconnection was the widespread perception of the presence of a somewhat mysterious ‘old water paradox’ inferred from observations of conservative tracers.<sup>36–39</sup> Briefly, it was observed that many catchments worldwide are characterized by a rapid hydrological response to rainfall inputs yet by only limited fluctuations in many stream water solute concentrations. While stream water solute concentrations vary in many cases only by factors of up to approximately 10–20, stream flow can vary by several orders of magnitude.<sup>40</sup> This is true for solutes of both, atmospheric or geogenic origin.<sup>40</sup> It, however, may have the strongest effect in agriculturally managed catchments, where only small changes in stream chemistry have been observed even decades after significant reduction of fertilizer application due to legacy effects of solutes stored in groundwater and stream bed sediments.<sup>13,41–43</sup> One example of such a case is the agriculturally managed Kerrien catchment in France (Figure 1; [http://www6.inra.fr/ore\\_agrhys](http://www6.inra.fr/ore_agrhys)).<sup>43</sup> Several years after the end of fertilizer application, which was the major source of chloride ( $\text{Cl}^-$ ) in that catchment, the stream water  $\text{Cl}^-$  concentration remains rather stable. The  $\text{Cl}^-$  concentrations fluctuate only with a factor <5 compared to stream flow that varies by a factor of about 1000, thereby spanning three orders of magnitude (see inset Figure 1), an observation that is frequently and loosely referred to as ‘biogeochemical stationarity’ in many catchments worldwide.<sup>41</sup> In addition, the higher perceived degree of attenuation between  $\text{Cl}^-$  input and output signals than between water input and output signals, as indicated by the difference between their respective 5/95th interquantile ranges

in Figure 1, suggests that runoff responds faster to inputs than  $\text{Cl}^-$  concentrations in the stream water. This does certainly not suggest that the relatively conservative  $\text{Cl}^-$  is subject to significantly stronger retention than water in the flow domain but it rather indicates that ‘[...] catchments store old water for long periods but then release it rapidly during storm events [...]’.<sup>39</sup> As observed input signals of water volumes (i.e., precipitation) do not carry any further information for disambiguation, a rapid flow response to a precipitation input may be mistaken (as conceptualized in the vast majority of catchment-scale conceptual hydrological models) as the actual input signal already reaching the stream, while in reality it is the remainder of past input signals that slowly traveled through the system. The observable stream flow response is in fact largely a manifestation of the propagation of a pressure wave through the system. The movement of solutes, in contrast, is largely characterized by advective movement. While these solutes move with actual *velocities*, pressure waves propagate at *celerities* that can be orders of magnitude higher,<sup>44</sup> depending on the flow regime. In regimes characterized by a large influence of advective processes (e.g., preferential flow in soil pipes)<sup>45,46</sup> and thus by the elevation head, celerity and velocity somewhat converge. Whereas in systems controlled by diffusive flow components (e.g., groundwater),<sup>45,46</sup> which are dependent on the pressure head, the difference between celerity and flow velocity is more pronounced. A simplified analogy is that of a game of billiards, in which the red ball moves slower than the observed response of white balls as illustrated in Figure 2(a). In spite of being in principle well understood,<sup>38,43,48–57</sup> this is an example of how the omission of such processes in catchment-scale conceptual hydrological models lead in the past to wide ranging interpretative pitfalls.

Arguably, much of the disconnection between the catchment hydrology and water quality disciplines may be explained by a lack of communication and the absence of a common language, but also by the different time- and spatial scales of interest. In many cases, hydrological studies focus on short-term flow dynamics, e.g., flow peaks, in small- to meso-scale catchments. In contrast, water quality models are, depending on the solute of interest, frequently used for predicting water chemistry over a range of time-scales. While, for example, nitrate studies often focus on longer time-scales (e.g., seasonal, interannual, or decadal) in larger basins that represent actual water management units, studies of phosphorous or pesticide dynamics are characterized by a stronger focus on storm dynamics. The focus on discipline-specific, individual response variables, rather than on



**FIGURE 1** | Daily precipitation (light blue), runoff (dark blue), observed fertilizer-derived  $\text{Cl}^-$  (orange circles), and precipitation-derived  $\text{Cl}^-$  input concentrations (red circles), as well as  $\text{Cl}^-$  concentrations in runoff (dark red circles) for the small, agriculturally managed Kerrien catchment in France (see Ref 43). Note that the circles sizes indicate the  $\text{Cl}^-$  mass flux relative to the largest mass flux during the observation period. The bars on the sides indicate the 5/95th interquartile range for  $\text{Cl}^-$  input concentrations (red),  $\text{Cl}^-$  concentrations in runoff (dark red), precipitation (light blue), and runoff (blue). The inset shows the runoff– $\text{Cl}^-$  concentration relationship, with the black line indicating the log-log slope of  $-1$  that would be expected from the theoretical case of pure dilution (i.e.,  $c \propto 1/Q$ ), which would be the case if a catchment was a completely mixed, homogeneous entity.



**FIGURE 2** | (a) Conceptualization of the difference between celerity-driven hydrological response and velocity-driven transport processes using the analogy of a game of billiards. A new input at  $t_1$  (red ball) causes a disturbance of the system that propagates with a celerity and that generates a response (blue ball) at  $t_2$ . The red ball itself, however, is released from the system only at  $t_5$  as it travels at a velocity that is much smaller than the celerity. (b) For a groundwater-dominated system, the propagation of the pressure wave to the stream is controlled by the wave celerity and the active storage  $S_a$  (i.e., the pressure head  $h_a$ ) while the movement of the actual particles is controlled by the flow velocity and the length of the flow trajectory through a hydrologically passive storage volume  $S_p$  (after Ref 47), which (c) can be conceptualized in a model with a mixing volume below a given storage threshold.  $S_u$  represents the unsaturated zone whose nonlinear behavior is indicated by the curved line.

the system as a whole in more complete and consistent model formulations,<sup>58</sup> hinders our ability to develop the necessary holistic systems approaches. This is underlined by the shortage of interdisciplinary research groups or project teams in which a good balance between hydrological and water quality expertise is available. In an attempt to provide a step toward closing the gap between the hydrology and the water quality community, this nontechnical overview paper is intended to (1) discuss the importance of hydrology-controlled transport through the system

as an explicit but underexploited link between hydrological and water quality dynamics; (2) identify limitations of current generation catchment-scale hydrological and water quality models; (3) highlight the concept of transit and residence time distributions as tools to quantify catchment-scale transport that links hydrology and water quality; and (4) review the potential benefits and limitations of more detailed formulations of hydrologic transport for semi-distributed, catchment-scale conceptual hydrological and water quality models.

## THE IMPORTANCE OF HYDROLOGICAL TRANSPORT

In catchment hydrology, the term hydrological transport encompasses the movement of water, solutes, and particulate matter, for brevity thereafter collectively referred to as solutes, through the flow domain, consisting of the soil surface, the porous, heterogeneous, and fractured subsurface (e.g., soil and bedrock) and channels. Solute, homogeneously and instantaneously applied over a catchment (i.e., nonpoint source pollution) will experience dispersion on their trajectory to the catchment outlet.<sup>59</sup> In other words, they are subject to distinct lags in arrival times at the outlet. These lags are, for chemically conservative substances, caused by (1) differential flow velocity fields that partially reflect the pore structure of the flow media ('kinematic dispersion'),<sup>60</sup> (2) distinct flow path lengths ('geomorphologic dispersion'),<sup>61</sup> that depend on the location of entry to a catchment and on the depth of flow along individual trajectories, and (3) molecular diffusion, although the latter is of less importance at the catchment scale. The distribution of lags that solute input signals experience along their trajectory defines the breakthrough curve of solute arrival at the catchment outlet, which represent the catchment integrated signature of flow path distributions in a particular system. These breakthrough curves not only describe transport, but are also fundamental building blocks of the hydrological response as flow dynamics at the catchment outlet directly emerge from the history of combined water breakthrough curves from all past inputs.<sup>52,56</sup>

In a thought experiment, it therefore follows that when a perfectly conservative solute is subject to the same physical interactions in the flow domain as the water itself then this conservative solute moves with the water.<sup>62</sup> The above-described transport dynamics of water and solutes from individual input signals, characterized by the history of breakthrough curves, therefore also control the response dynamics of such conservative solutes at the catchment outlet. These fundamental descriptions of transport are well known, at least since the formulation of the dispersion equation<sup>63</sup> and have since been exhaustively described and further developed in a vast body of literature.<sup>64–80</sup>

However, most solutes cannot be considered conservative in the sense described above. Although water still acts as an agent of transport for them, the movement of such nonconservative solutes through the system is characterized by different spatiotemporal dynamics than those of water. These different dynamics are the result of several different process

types that can exert influence on solutes. Physicochemical processes, which do not chemically alter the solutes, may play an important role. For example, according to their sorption characteristics, solutes may be temporally immobilized to the surface of the porous flow medium, which result in retardation effects, i.e., reduced average transport velocities compared to water.<sup>81–85</sup> Alternatively, many solutes are reactive, being subject to chemical and biological processes, i.e., (bio-)degradation or radioactive decay. Thus, such solutes entering a catchment may never reach the stream, as they may be broken down and transformed into another set of chemical substances along their trajectory.<sup>83,86–92</sup> In addition, solute movement can also be influenced by bio-physical processes. Here in particular the distinct susceptibility of different solutes to uptake by plants and/or microorganisms should be mentioned.<sup>93–100</sup> Solute that are less prone to be taken up by plants than water do experience enrichment in the flow medium, follow different trajectories through the system, and do finally exhibit different dynamics in the stream compared to water.<sup>101</sup> In contrast, solutes that are preferentially taken up by plants can be largely removed from the flow domain, with only minor parts reaching the stream.

These biogeochemical reactions can occur in any part of the flow domain: in soils on hillslopes,<sup>96,102–105</sup> at the substrate–stream interface as hyporheic exchange,<sup>106–112</sup> or as in-stream processes.<sup>113–118</sup> They thereby set the physicochemical environment and control the quantity of nonconservative solutes in the system. However, the fate of solutes may, in many river systems, also be considerably affected by transport processes.<sup>40,119–124</sup> The underlying reason is that the temporal dynamics in hydrological connectivity between solute source areas and different flow pathways inherently determine the basis for contact times between mobile and fixed phases, which in turn influences many biogeochemical reactions.<sup>57,125,126</sup> An example for the combined influences of biogeochemical processes and transport is the interplay of oxic and anoxic conditions in the flow medium. Determining the oxygen availability and thus the redox potential, important for the denitrification process, it is strongly influenced by temperature and water movement.<sup>127,128</sup> In addition, a wealth of studies illustrates that transport processes establish, through remobilization of solutes along a variety of flow pathways, a crucial link between catchment-scale water quality dynamics and the heterogeneity of source areas and pathways.<sup>21,35,38,129–149</sup> In spite of the frequently complex pattern of (physico-)chemical and biological processes in space and time, streams integrate water (and

thus solutes) from different sources and pathways. As the contributions from these different sources and pathways can considerably vary over time, the chemistry of stream water may vary over time as well which is a consequence of the mixing of these contributions in streams.<sup>150</sup>

As water is the principal carrier of most solutes in the flow domain, the water flow inevitably influences the dynamics of solute storage in a catchment and its further release.<sup>41</sup> If we want to improve our knowledge of catchment-scale water quality dynamics, it is therefore key to develop a robust understanding and meaningful formulations of transport, to underpin detailed biogeochemical process models, as transport influences many other physical, chemical and biological processes involved.<sup>57</sup>

## CATCHMENT-SCALE MODELS AND THEIR LIMITATIONS

Common catchment-scale models typically struggle to simultaneously resolve the observed hydrological response and the dynamics of one or more water quality variables as they, depending on the model type, provide insufficiently adequate representations of different individual processes, as recently pointed out by Wellen et al.<sup>151</sup> Note that in the following, we refer to models that focus only on water as hydrological models and to models that use flow as a forcing variable but focus on chemical variables as water quality models.

### Physically Based Catchment-Scale Hydrological Models

Hydrologic bottom-up modeling approaches based on detailed process descriptions, such as the Richards and Laplace equations, provide a comprehensive representation of the hydrologic system at the small scale. Such mechanistic formulations of flow and transport do not only considerably contribute to improve our process understanding on the hillslope scale,<sup>152,153</sup> but also allow to resolve catchment-scale processes in a physically consistent and distributed way. Over the recent years, much progress was achieved<sup>154</sup> in particular with respect to accounting for the importance of macropore flow<sup>155–157</sup> in subsurface features such as root canals, animal burrows, or cracks. A key advance here was the representation of the flow domain as a multicontinuum (or multidomain). Allowing for a certain diversity of flow paths, accounting for micro-, meso- and macro-porosity, such models can, to some extent, characterize the dichotomy of matrix and preferential flow.<sup>158,159</sup> Some of the most important

model developments include MACRO,<sup>160</sup> MIKE-SHE,<sup>161,162</sup> CATFLOW,<sup>163</sup> FRAC3DVS,<sup>164</sup> Hydrogeosphere,<sup>165–167</sup> HYDRUS 3-D,<sup>168</sup> PARFLOW,<sup>169</sup> CATHY,<sup>170,171</sup> and a range of other approaches.<sup>172–174</sup> Implicitly based on hydrological transport these models can be readily extended to cater for biogeochemical processes. In spite of frequently relying on oversimplistic assumptions in such applications, e.g., by making use of a sorption isotherm, they have, in principle, considerable potential to meaningfully represent the dynamics of reactive substances. However, the application of such models is problematic at the catchment-scale. Dooge<sup>175</sup> argued that catchments belong to the realm of organized complexity. As such they are characterized by a certain level of both, stochastic heterogeneity and spatial organization. Yet, they are too small for a stochastic representation while being too large for a fully mechanistic description.<sup>176</sup> The problem has been exhaustively discussed in a wide range of papers.<sup>176–188</sup> Briefly, the spatial heterogeneity of the system forcing (e.g., precipitation) and boundary conditions (e.g., topology of preferential flow features and soil hydraulic properties) cannot be sufficiently characterized with the available observations.<sup>187,188</sup> These models thus typically require some degree of calibration to obtain effective parameters, suitable for the spatial and temporal scale of a given application, integrating the process heterogeneity occurring at scales smaller than the modeling scale. Given the generally ill-posed nature of such an inverse parameter determination problem,<sup>189</sup> parameter equifinality and the related uncertainty may adversely affect the model's predictive skill.<sup>190,191</sup> A further factor that at the present point still limits real-world applications and wide-spread use of these models is the elevated computational cost, which makes standard operational use inconvenient and frequently unfeasible.

### Conceptual Catchment-Scale Hydrological Models

A wide variety of relatively simple conceptual models, such as HBV,<sup>192</sup> has been developed in the past. In spite of their simplicity they have proven to be valuable tools for reproducing the hydrological response pattern in many catchments worldwide. Recent developments helped to considerably increase these models' hydrological consistency and predictive power. They include, e.g., the flexible model adaptation to catchment function,<sup>193–195</sup> the use of hydrological response units (HRU) based on landscape characteristics,<sup>196–202</sup> and more efficient parameter selection techniques.<sup>203,204</sup> In spite of their skill to

mimic the hydrological response dynamics, the physical basis of conceptual models is not well understood. It is hypothesized that they in general work reasonably well as they manage to mimic processes emerging at the catchment scale, such as the activation- and deactivation dynamics of preferential flow networks.<sup>183–185</sup> A problem of conceptual models is that they lack detail to resolve the small scale physics of the flow domain and as such exclusively rely on calibration.<sup>205</sup> Independent ways to scrutinize the obtained effective parameters remain largely elusive, which frequently results in implausible model internal dynamics. In addition, such traditional model formulations typically fail to reproduce the dynamics of stream chemistry, as for example highlighted by Fenicia et al.<sup>206</sup> The main reason for this is that the observable hydrological response acts at different time scales than the water quality response (celerity vs velocity) and thus requires significantly different response functions.<sup>207,208</sup> While implicit in physically based models, the difference between celerity and velocity needs in conceptual models to be accounted for by introducing a calibration parameter that represents hydrologically ‘passive’ (or ‘residual’) mixing volume  $S_p$  with a pressure head  $h_p = 0$ . This is schematically illustrated by the simplified case of a groundwater reservoir in Figure 2(b) and (c)<sup>47</sup>: the flow response depends on the pressure head of the active (or ‘dynamic’) storage volume  $S_a$  ( $h_a \geq 0$ ) above the stream level and the flow resistance in the flow domain (i.e., hydraulic conductivity). In contrast, the time of arrival in the stream for conservative solutes also depends on the size of the passive storage component they are routed through by advective transport and the temporal variability in the mixing processes.<sup>48,53</sup> In hydrological models such a passive storage component is typically not accounted for as this storage effect cannot be distinguished from hydrometeorological observations alone<sup>209</sup> but rather requires hydrochemical data to adequately parameterize this process.<sup>43,210</sup> Only a limited number of studies provide a successful implementation of mixing volumes to explicitly account for hydrological transport in detailed conceptual hydrological models to simultaneously reproduce hydrological and patterns of conservative solutes.<sup>43,53,58,211–219</sup> An alternative type of model is based on the multiple interacting pathways concept and relies on a combination of particle tracking and velocity distributions.<sup>220</sup> Although the models in these aforementioned studies do explicitly account for conservative transport, they usually do not accommodate additional physical, chemical, or biological processes reactive solutes may be subject to.

## Water Quality Models

In the same way that catchment-scale hydrological models are separated into either physically based or conceptual structures, so are water quality models. A wide variety of catchment-scale water quality models have been developed in the past for use at a wide range of temporal and spatial scales. Their importance is underlined by the sheer number of publications using them.<sup>151,221</sup> However, the challenges posed to the modeler are multiplied if we are to consider simulations to represent both the passage of water, and a number of solutes, through the catchment system. In the case of a physically based model, this requires ever increasing numbers of parameters to characterize transport and reaction rates. In contrast, a more conceptual approach relies on some form of appropriate judgment to simplify the system into a model structure where useful results may be obtained.<sup>222</sup> In many cases, it is a simple question of having appropriate data to characterize the response of the catchment system in question.<sup>223,224</sup>

The choice of approach for individual case studies is often dictated by particular research or practical questions, e.g.: a model to estimate the extent of a contaminant plume or diffuse pollution and its likely movement in an aquifer or toward a well<sup>225,226</sup>; a model to understand the effect of mineral weathering on hillslope or wetland flow characteristics<sup>227</sup>; or, a model to estimate the impacts of point- and diffuse nutrient discharges on the eutrophication status of rivers and wetlands. In the first case, we might expect a fully coupled 3D physically based groundwater model with particle tracking to represent contaminant plumes.<sup>226,228</sup> In the second case, a geochemical model with extensive representation of mineralogy, such as PHREEQC or WITCH,<sup>227,229–231</sup> to identify key reactions and transformations, may be suitable. Finally, in the third case, operational tools such as SWAT,<sup>232,233</sup> INCA,<sup>234</sup> Wetland-DNDC,<sup>235</sup> or HYPE,<sup>236</sup> which feature modular descriptions of chemical and biological processes affecting water quality dynamics on the catchment scale could be feasible options for the modeler. However, the emphasis of all these models being the biogeochemical processes the formulation of transport, is kept rather simplistic and could be considerably improved.<sup>151,237</sup>

A key feature of hydrological models is their reliance upon the principle of conservation of mass, i.e., the water balance. This is often the simplest form of hydrological model, and the means by which we determine whether the majority of system inputs and outputs have been identified and, if not, what proportion remains unaccounted for. This is also a key



challenge for water quality modelers, but one that does not receive a great deal of attention: what are the chemical inputs to the catchment system, and how do they vary in space and time? This is particularly important, because emerging research indicates that catchment responses integrate and transport inputs across both space and time to the point of observation in such a way that may be equivocal as to whether observed breakthrough curves are characteristic of the transport pathway, the shape of the time- and space-averaged inputs, or a combination of both.<sup>13,222</sup> It is therefore essential that the influence of both input forcing and transport pathways are adequately understood in order to correctly interpret observations. This will allow more detailed representations of source areas and process heterogeneity with a more adequate resolution of distinct flow pathways, including for example, overland or drain flow. Flow generation and solute export from different source areas at different times can then be characterized by differences in hydrologic connectivity between these different source areas (e.g., ‘hot spots’),<sup>238</sup> on the one hand. On the other hand, accounting for different transport processes in parts of a catchment with different hydrological function (e.g., hillslopes vs, wetlands or pastures vs forests), as for example demonstrated in the LU4-N model for nitrogen<sup>58,239</sup> may add further detail. This is in addition to further key issues that need to be addressed to provide a more detailed representation of how catchments store and release water (and thereby effect solute movement). Examples include a more adequate representation of nonlinearities and their heterogeneity over different source areas in the hydrological response (e.g., ‘fill-and-spill’ hypothesis),<sup>240,241</sup> more flexibility in the mixing processes (e.g., ‘partial mixing’),<sup>48,242</sup> quantification of catchment-scale solute stores,<sup>210</sup> and a clearer separation between hillslope processes from hyporheic exchange and physical and chemical in-stream processes, which become in particular important for reactive solutes at larger spatial scales.

## THE CONCEPT OF TRANSIT TIMES

### Definition, Disambiguation, and Characteristics

In catchment hydrology, the generic terms ‘transit times’ (TTs) and the associated ‘TT distributions’ (TTD) describe the age structure and, for conservative solutes, the chemical composition of specific pools of water. In spite of considerable ambiguity and confusion in the terminology,<sup>241</sup> these concepts

are frequently used to characterize bulk hydrological transport.<sup>242</sup> While many early studies focused on interpreting merely mean TT,<sup>242</sup> which contain comparably little information on system internal dynamics, widening the scope to investigate the actual TTDs and their temporal dynamics proved highly valuable. The concept of TTDs is convenient as it allows an intuitive interpretation of the catchment-integrated dispersion, i.e., the distribution of time lags an input signal experiences on its way to the catchment outlet. The general concept found, through its explicit link to transport, in the past wide and successful application in both, groundwater<sup>243–246</sup> and surface water modeling studies.<sup>79,150,247,248</sup>

Many approaches that quantify transport by the use of the TT concept rely on a detailed formulation of catchment-internal gradients and velocity fields with a wide range of assumptions involved to derive descriptions of individual flow paths. However, as pointed out by Benettin et al.,<sup>249</sup> in catchment hydrology, where transport volumes can be readily defined by observations of inputs to and outputs from the system, the general concept of TT provides a convenient tool to *integrate* the natural complexity of a system into a set of three distinct but mutually depended age distributions describing how catchments overall store and release water and which provide analogies to demographic models (see Box 1).<sup>249,250</sup>

### BOX 1

#### TT, AGE, AND LIFE EXPECTANCY

The temporal composition of water volumes in a system can be described with different metrics<sup>65,251</sup> that are intimately interlinked<sup>52</sup> but often falsely used interchangeably. By considering water of a given age composition as water ‘population,’ analogies with demographic terminology<sup>252,253</sup> can be drawn to facilitate a more intuitive distinction between the composition of water in flux and resident water. On the one hand, residence time distributions describe the distribution of water volumes that entered the system in the past and that are still stored in the system at a given moment. This is equivalent to the distribution of ages of all individuals of a population born in the past and still alive at a given moment. On the other hand, backward TT distributions describe the age distribution of water that entered the system in the

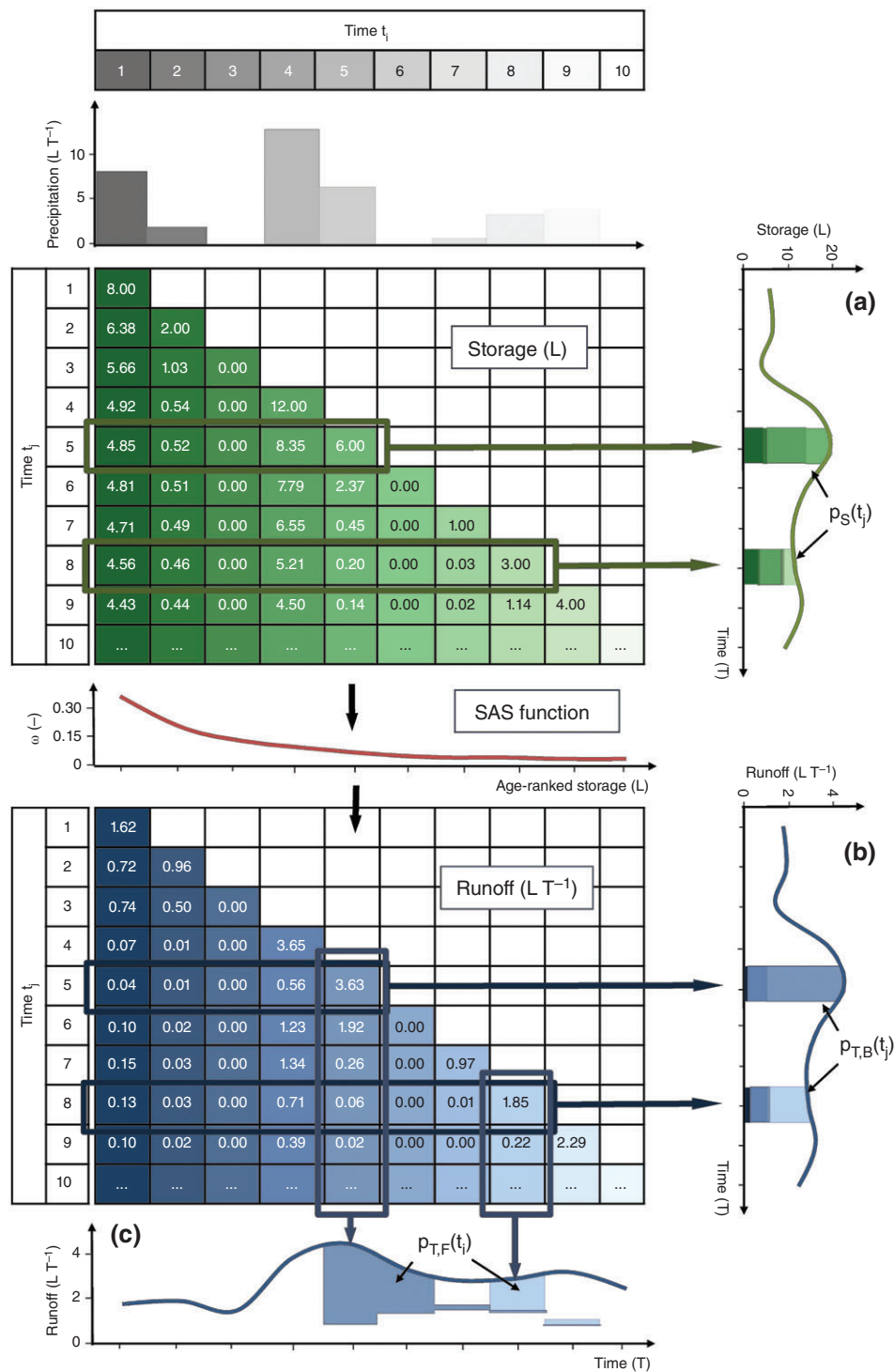
past and that is leaving the system at a given moment (e.g., the age distribution of stream flow). This is equivalent to the age distribution of individuals born in the past, passing away at a given moment, i.e., the age distribution at death. In contrast, the forward TT distribution describes how a water volume entering the system at a given moment (i.e., a precipitation signal) is routed to the system outlet, or, in other words, which proportions of this volume will remain in the system for how long. This is equivalent to the distribution of life expectancies at birth of all individuals of a population born at a given moment. Recent papers provide clear and comprehensive overviews and theoretical derivations of these different aspects of water age composition.<sup>249,250</sup>

Briefly, as shown in a simplified, illustrative example in Figure 3, precipitation (or solute) signals entering a system at time  $t_i$  are, at least transiently, stored in the system. The total volume of water stored in a catchment at a given point in time  $t_j$  is therefore characterized by a specific distribution of volumes with different ages, the *residence time distribution* ( $p_S$ ). Similarly, the water leaving the system at  $t_j$  via a specific exit route, such as stream flow or evaporation, is also characterized by a distribution of water volumes of different ages, which are a subset of the water volumes of the same ages stored in the system at  $t_j$  and which constitute the *backward TT distribution* (also: TT distribution conditional on the sampling time or the age distribution of water in flux;  $p_{T,B}$ ). In addition, the *forward TT distribution* (also: TT distribution conditional on injection time or breakthrough curve;  $p_{T,F}$ ) is the distribution of time lags (or ages) an instantaneous signal entering the system at a given time  $t_i$  will have experienced once it has been completely routed through the system. Both TT distributions,  $p_{T,B}$  and  $p_{T,F}$ , are critically dependent on how water stored in the system is released at any time  $t_j$  and can thus be directly constructed from the residence time distribution  $p_S$  by invoking the notion of water (and solutes) somehow ‘mixing’ in the system.<sup>52</sup> However, as ‘mixing’ is frequently associated with a turbulent process in a system, which can be considered negligible in catchments, the use of the term may be misleading. Rather, the output from a catchment is typically composed by a ‘combination’ of water parcels of different age reaching the catchment outlet at the same time. Thus,  $p_{T,B}$  reflects the water volumes of different ages present in a

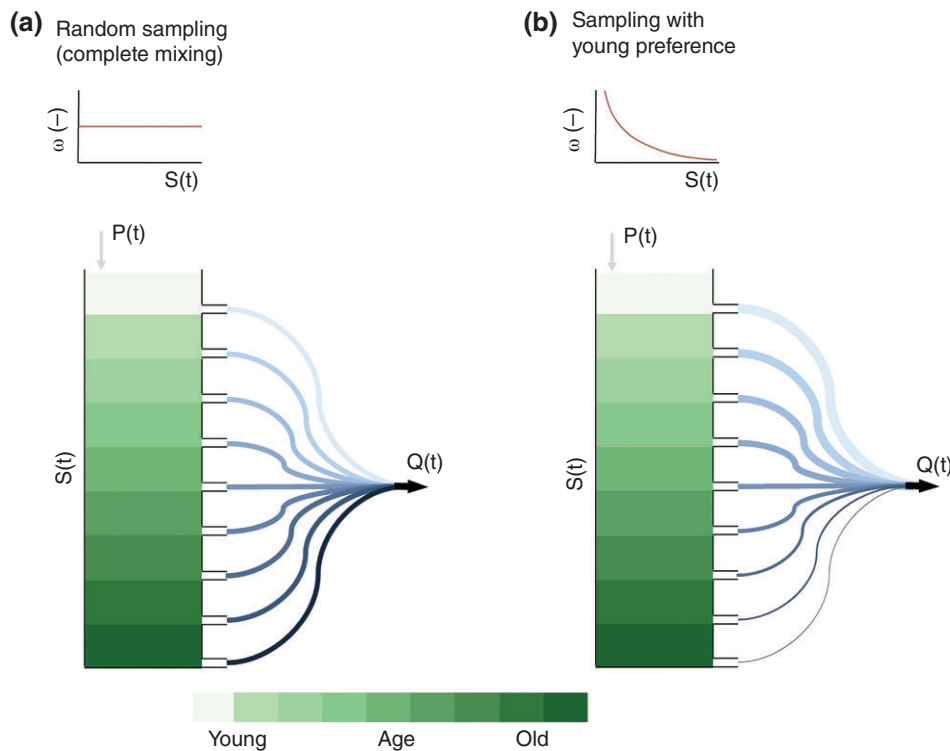
catchment that are being released from the storage at a given point in time  $t_j$ . Similarly,  $p_{T,F}$  represents the proportions of water from a given input signal that are released from storage over time.

At the catchment-scale, the ‘mixing’ or ‘combination’ process integrates two major effects. Firstly, it describes the combination of water of different ages that originate from different input locations in the catchment but that reach the outlet at the same time  $t$ , describing the distribution of flow path lengths (i.e., geomorphological dispersion). Secondly, it accounts for different effective flow velocities of particles having entered the system at the same location (i.e., kinematic dispersion). Thus, describing the combination process as a sampling of water of different ages stored in the system, offers a less ambiguous conceptualization than mixing.<sup>51,52,56</sup> If conceptualized as mixing, the process is typically defined by a dimensionless mixing coefficient  $C$  between 0 (i.e., ‘no mixing’) and 1 (i.e., ‘complete mixing,’ ‘Continuously stirred tank reactor’), which determines the proportion of mobile water, i.e., water that exceeds the storage capacity, that experiences exchange with resident water. When referring to the process as a sampling process, a sampling distribution is required, hereafter referred to as Storage Age Selection function (SAS).<sup>51,52,56</sup> While a uniform distribution samples from the individual water parcels of different age stored in the system with equal probabilities (Figures 4(a) and 5(a)) other distributions (e.g., gamma or beta distributions) allow more flexibility to sample preferably young or old water (Figures 4(b) and 5(a)). Note that the mixing and the sampling approaches are in principle functionally equivalent. A mixing coefficient  $C = 1$  exactly corresponds to a beta distribution with parameters  $a = 1$  and  $b = 1$  (i.e., a uniform distribution) used as a SAS, while a beta distribution with  $a$  converging to 0 closely approaches the functionality of  $C = 0$  (no mixing, only the youngest water is released from the system; Figure 5(b)). Complementary to these equivalences and in contrast to the use of mixing coefficients, the use of SAS functions also allows for a preferred sampling of older water, approaching piston flow behavior, for example described by a beta distribution with high values of  $a$  (Figure 5(b)).

Tightly related to the mixing mechanisms in a catchment is the temporal variability of TTDs. Although known early, the importance of the time-varying nature of transport processes was for a long time considered negligible. The reason for that can be traced back to the traditional focus of transport studies on groundwater systems. Compared to catchment-scale surface water response dynamics,



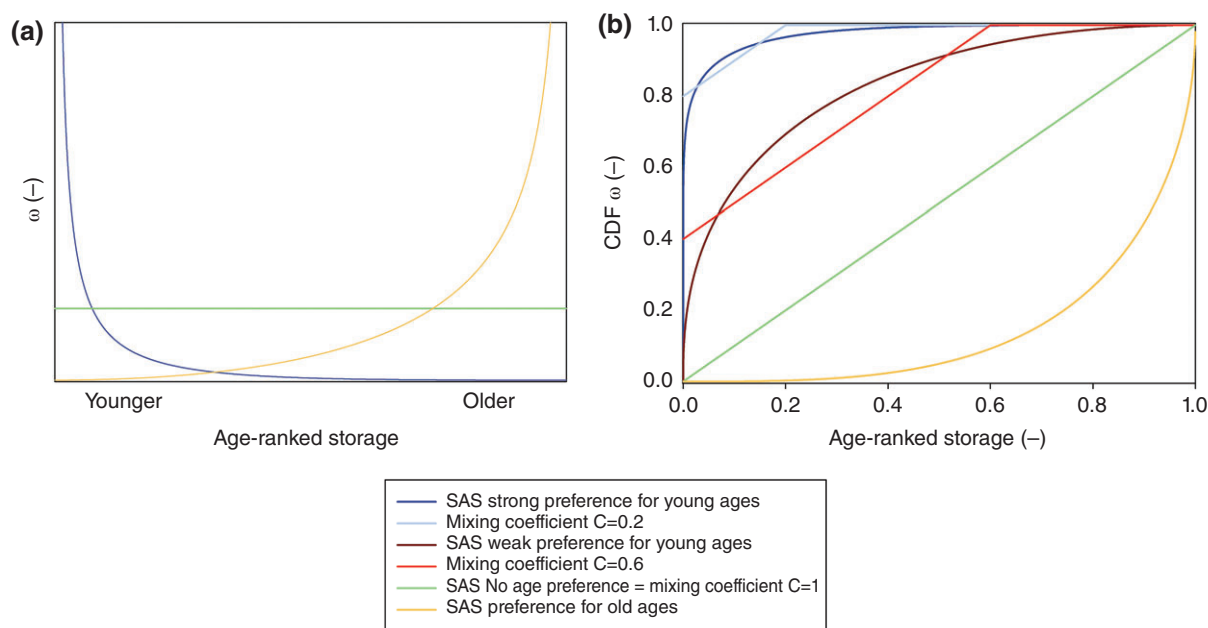
**FIGURE 3** | Conceptual and simplified illustration of the difference between residence time ( $p_S$ ), backward ( $p_{T,B}$ ), and forward ( $p_{T,F}$ ) transit time distributions. A precipitation signal enters the system at  $t_i$  and is transiently stored. The volumes of all water parcels from the past still stored in the system at  $t_j$  define  $p_S$ . Water is released from storage according to specific mixing or storage age selection (SAS) mechanisms, which sample the runoff water from the distribution of water ages in storage at  $t_j$ , resulting in the  $p_{T,B}$  and  $p_{T,F}$  (after Ref 53).



**FIGURE 4** | Illustrations of different conceptualized and simplified sampling (or mixing) processes. (a) A system characterized by a uniform storage age selection (SAS) function, sampling water with different ages from storage with equal probabilities (equivalent to the concept of a well- or completely mixed reservoir). (b) A system that releases water with preference for younger ages in storage (after Ref 56). The symbol  $S$  indicates age-ranked storage,  $P$  represents the input into the storage (e.g., precipitation), and  $Q$  a flux released from storage (e.g., stream flow). Green shades indicate water in storage, blue shades indicate water in fluxes, i.e., released from storage component.

groundwater fluctuations are frequently characterized by limited nonlinearities and moderate variability. Thus, based on the simplifying premises of steady state conditions and a homogeneous, completely mixed flow domain, time-invariant TTDs were previously shown to allow adequate representations of transport in groundwater systems. Although these assumptions may be suitable for these systems they do not hold for many surface water systems as the response of catchments is frequently characterized by highly variable flow. Switches between different runoff regimes, i.e., runoff generating processes, that act at significantly different temporal and spatial scales,<sup>254</sup> such as overland flow or groundwater flow, as well as mutual feedback between these processes can introduce complex dynamics and flow variations of several orders of magnitude. Similarly, the changing importance of geographically different source areas under changing hydrological conditions can contribute to the often observed nonlinear response patterns of catchments. As TTDs are representations of transport processes, which are, in turn, controlled by the hydrological response, they need to reflect the temporal variability of water flow.

The temporal variability of TTDs is influenced by several factors.<sup>255</sup> The first and arguably most important of which is the temporal variability in the size of input and output signals.<sup>52,256</sup> At first, consider the theoretical example of a catchment with little seasonality in precipitation input, approaching steady-state conditions (i.e., same amount of precipitation every day). The relative proportions of water of different ages stored in and released from the catchment will experience little change, resulting in similar TTDs. However, in a more realistic setting and a climate with more pronounced seasonality, the input is characterized by considerable temporal variability. This then leads to the associated temporal variations in the relative proportions of water of different ages in a catchment, which implies significant changes in TTD. The second relevant factor affecting the temporal evolution of TTDs are the different flow and transport properties of different flow paths in the system.<sup>49,257,258</sup> For example, the high connectivity of hillslopes during relatively wet conditions, characterized by the importance of shallow subsurface and/or preferential flows, fast turnover rates, and limited storage capacities, results in



**FIGURE 5** | (a) Examples for SAS functions with no age preference (uniform distribution), as well as with preferences for young and old water, respectively. (b) Comparison of cumulative SAS functions (CDF) with the functionality of using the concept of mixing coefficients. Mixing coefficients  $C = 0.2, 0.6,$  and  $1$  indicate examples for 20, 60, and 100% of an incoming signal, respectively, are stored and mix with the resident water, while 80, 40, and 0% of the incoming water, respectively, bypass the storage and are directly released again without further interaction with resident water.

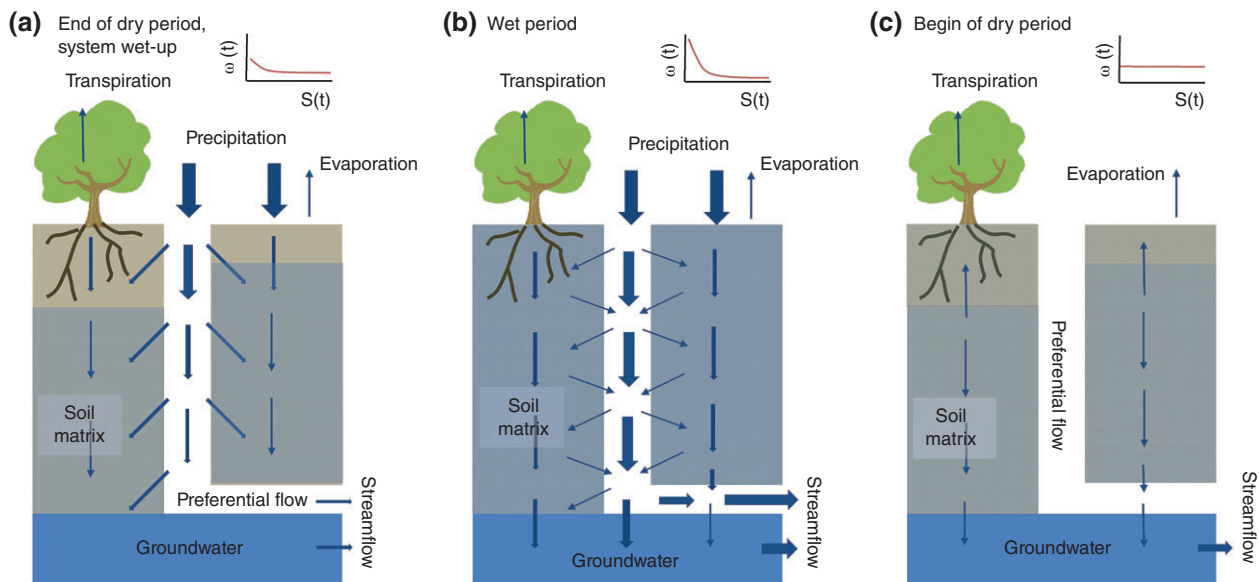
relatively high proportions of young water reaching the stream. In contrast, during drier periods, flows are often, albeit not always,<sup>2,59</sup> composed of much higher proportions of water originating from groundwater bodies. Providing considerably more storage capacity with longer flow paths and slower flow velocities, aquifers typically act as buffers, characterized by high proportions of water that is considerably older. The dynamic changes of flow proportions generated via fast (e.g., shallow subsurface) and slow processes (e.g., deep groundwater), depending on the wetness conditions of a catchment and its history of inputs therefore also introduce temporal variability in TTDs.<sup>53,260,261</sup> This is, in turn, fundamental for the understanding the dynamics of different solutes and particulates. Substances which tend to be stored on the surface or in shallow subsurface layers, such as phosphorous or DOC, will be controlled by the shorter TT in these layers while substances stored for example in the deeper groundwater are typically associated with longer TT. In addition, there is growing evidence from both, catchment and laboratory-scale experiments, that the mixing properties of the flow domain may be subject temporal heterogeneity as well.<sup>48,54,262,263</sup> Briefly, under relatively dry conditions a high proportion of incoming precipitation can be transiently stored in the porous flow media and interact with resident water of varying age, as

schematically shown in Figure 6(a). However, under wetter conditions, i.e., the lower the storage deficit, the more water is likely to bypass the matrix at relatively high velocities through preferential flow paths. This leaves little opportunity for exchange with the resident water. Higher proportions of younger water are thus being directly routed to the stream than under drier conditions ('first-in-last-out' mechanism; Figure 6(b)), which again contributes to temporally changing TTDs. Note, that the overall concept of SAS and the resulting TTDs can be applied irrespective of the spatial scale of interest, as it invokes the generally valid principle that all water (or solutes) stored in a catchment at a given time  $t$  is characterized by a distribution of ages and that the flow (or the solutes) integrated in the stream and released from the catchment at  $t$  is a sample of the stored water (or solutes). A TTD is therefore depending on the age distribution of stored water ( $p_R$ ) and the distribution according to which water (or solutes) is sampled from that storage (i.e., 'mixing').

## TT-Based Models

### *Convolution Integral Models*

A wide variety of transport models of different complexity, explicitly based on the concept of TT, was in



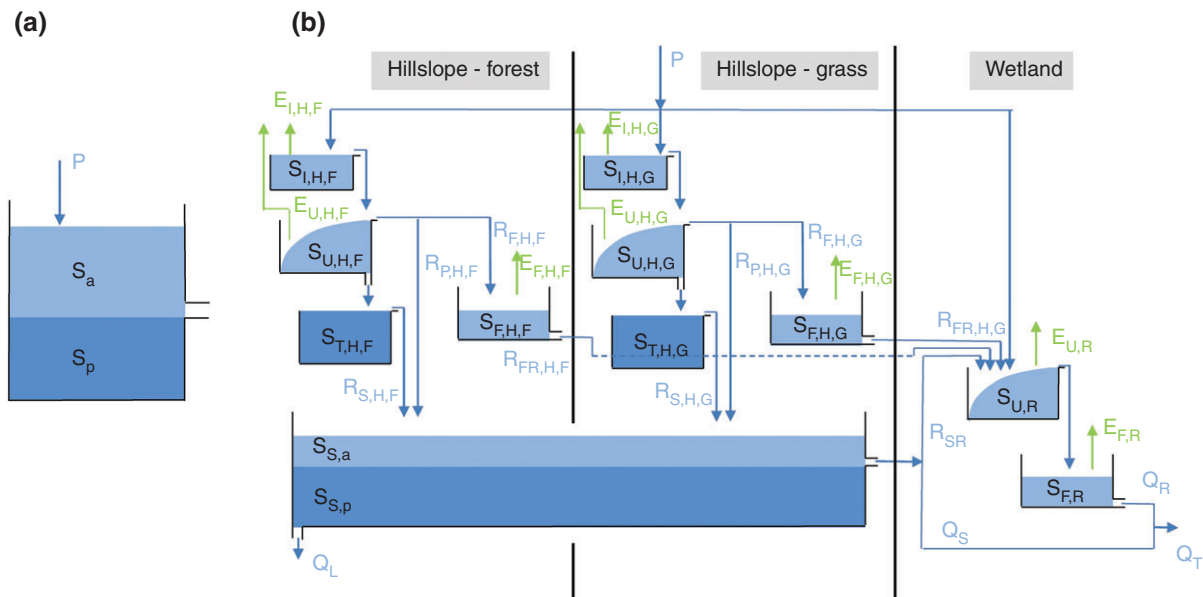
**FIGURE 6** | Schematic of changing mixing processes in the soil profile under different wetness conditions with likely shapes of SAS functions associated with these conditions. (a) At the end of dry periods, the moisture content in the soil matrix is depleted. Incoming precipitation is, due to the elevated suction forces relatively quickly adsorbed and stored in the matrix and flow is mainly sustained by relatively old groundwater. (b) As the system wets up, the soil moisture deficits are reduced and less precipitation water enters the matrix, bypassing it, and interacting less with the water stored, through preferential flow paths (e.g., root canals, cracks, animal burrows, etc.). Flows are now mainly generated relatively young water reaching the stream for example as preferential flow. (c) At the beginning of a dry period, water stored in the matrix continues to recharge groundwater, further mixing with resident water. Flow is now mainly generated by groundwater, which however, has a higher proportion of younger water than at the end of the dry period.

the past developed for and applied at the catchment-scale. Directly adapted from groundwater studies,<sup>244</sup> the simplest models rely on a convolution integral approach, in which input signals are routed through the system according to TTDs of predefined functional shapes.<sup>264</sup> This approach is equivalent to hydrological models based on the instantaneous unit hydrograph.<sup>265</sup> However, the assumptions applied in these models were frequently overly simplistic, including time-invariant TTDs, the representation of catchments as lumped, completely mixed entities (i.e., using exponential distributions as TTD) and inadequate consideration of evaporation.<sup>256,266</sup> In addition, most of these studies merely considered mean TT, which are a rather uninformative metric.<sup>264</sup> Notwithstanding the considerable inaccuracies and interpretative biases resulting from these assumptions, as demonstrated by several studies,<sup>267–269</sup> the widespread use of this simple method allowed for the development of a sense of which factors do influence the general transport characteristics of catchments.<sup>270–277</sup> In stepwise improvements, studies increasingly moved away from the assumptions of completely mixed systems, in favor of more flexible representations that better reflect the nonlinear character of hydrological systems and the importance of long-tails in the water quality

response.<sup>207,216,267,268,275,278</sup> Similarly, the importance of the effect of variable flow conditions on transport dynamics, as already emphasized early on,<sup>279</sup> has eventually been somewhat embraced by allowing for some weighting according to the volumes of input signals.<sup>207,216,280–282</sup> In spite of such advances and the insights gained, the actual TTDs in these model types remained, with some rare exceptions,<sup>208,283,284</sup> time-invariant and thus implausible representations of real-world systems.

### Conceptual Models

An alternative, avoiding the most problematic assumptions from the convolution integral method, is the use of conceptual hydrological models that are coupled with mixing volumes in their storage components. Conceptualizing the system as a suite of storage components linked by fluxes that represent the perceived dominant processes of a catchment,<sup>194</sup> provides a certain degree of flexibility. The possibility to customize these models to the environmental conditions in a given catchment can ensure an adequate level of process heterogeneity to reproduce hydrological and water quality response patterns of varying complexity.<sup>43,285–288</sup>



**FIGURE 7** | (a) Representation of a catchment as a lumped, completely mixed system, where  $P$  is precipitation and solute input,  $S_a$  is the hydrologically active storage that is controlled by the pressure head,  $S_p$  is a hydrologically passive mixing storage with constant water content. Evaporation is omitted here as it is rarely accounted for in convolution integral models for which this structure is an analogy. (b) Example of a possible semi-distributed, topography and vegetation guided model set-up in a catchment that is characterized by forest and grassland hillslopes as well as wetlands/riparian zones. The three different landscape classes are represented by three models that run in parallel. The hillslope classes are here distinguished by different parameter sets, while the wetland class reflects the distinct hydrological function of wetlands by a different model architecture. For each storage component suitable mixing/sampling mechanisms can be assumed that together with the different timescales of the storages result in different transport dynamics and thus different residence time distributions ( $\rho_r$ ) for water stored in and transit time distributions ( $\rho_t$ ) for water released from these components. This allows an improved resolution of the temporal dynamics in the system caused by changing contributions from the individual source areas and flow paths.  $S$  denotes storage components,  $R$  are recharge fluxes between storage components,  $Q$  are liquid fluxes release from the system, and  $E$  are evaporative fluxes released from the system. The subscripts  $I$  indicate interception storages, subscripts  $U$  represent unsaturated root zones, subscripts  $T$  denote hydrologically passive, unsaturated transition zones, subscripts  $F$  are fast responding components (e.g., preferential flow and overland flow), subscripts  $S$  denote slow responding components (e.g., deep groundwater), subscript  $L$  represents deep infiltration losses, subscripts  $H,F$  and  $H,G$  indicate hillslopes that are forest and grass covered, respectively, while subscript  $R$  represents riparian zones/wetlands. Light blue shades are hydrologically active storage components and dark blue shades indicate hydrologically passive storage components.

More specifically, an increasing understanding developed that the lumped representation of catchments in hydrological models, in particular with increasing spatial scale, may be insufficient to understand the ensemble of underlying processes,<sup>289</sup> in spite of frequently providing adequate model fits to observed data. This can be attributed to implausible model-internal dynamics,<sup>191,290</sup> which lump together distinct processes that in reality operate simultaneously and that are characterized by distinct dynamics. Semi-distributed representations of catchments, separating distinct process dynamics in different parts of the modeling domain, based on hydrologically distinct functional units (i.e., HRU)<sup>197</sup> have, when adequately constrained,<sup>204,291</sup> been demonstrated to be hydrologically more consistent representations of catchments, allowing more robust reproductions of observed system dynamics.<sup>204</sup> Even in data-sparse environments, such HRUs can be readily derived

from, amongst others, topography,<sup>201,202</sup> land use,<sup>197</sup> geology,<sup>292</sup> or a combination thereof.

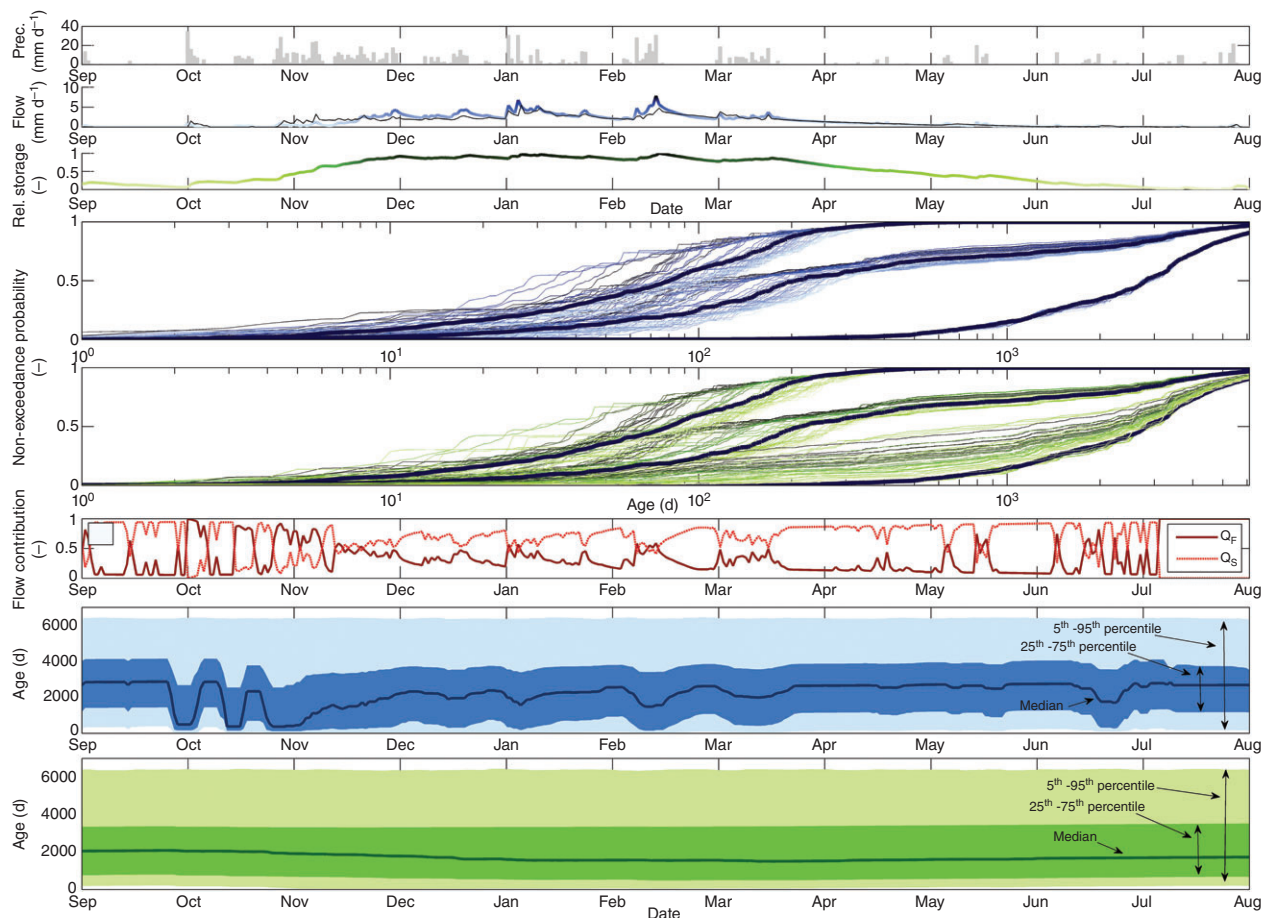
In a model, HRUs can then be represented by model structures that run in parallel and that are characterized by different architectures and/or parameter values. An illustrative example of such a, albeit simple, semi-distributed model, based on HRUs derived from topography and land use is shown in Figure 7(b). The model consists of three parallel components. As it is well understood that for example wetlands exhibit different hydrological dynamics than hillslopes,<sup>293</sup> these two HRUs are characterized by different model architectures, reflecting their dominant processes. In addition, the hillslope landscape class is further separated into forest and grassland, which differ only by the parameter values used (e.g., interception capacity). Instead of assuming one mixing volume representing transport processes in the entire catchment, the transport

dynamics in any of these model storage components can then be individually represented by suitable mixing/sampling processes thereby allowing for more variability in the transport processes.

These models are then typically calibrated to simultaneously reproduce observed dynamics of hydrologic variables (e.g., runoff, groundwater fluctuations, etc.) and dynamics of conservative tracers in the stream (e.g.,  $\text{Cl}^-$ ,  $^{18}\text{O}$ , and  $^2\text{H}$ ) using multiobjective calibration strategies. At each time step then not only the mass of water and solutes stored in and released from each model storage component is known, but also their respective distribution of ages (i.e., TTD), reflecting hydrologic transport, as defined by the parameterized and calibrated mixing process. Note that the TTDs of the individual model storage and flux components are inferred from the model and that they can therefore be subject to considerable uncertainty. However, a model constrained by multiple objective functions and a range of different tracer data<sup>294,295</sup> has the potential to efficiently limit equifinality and associated misrepresentations of the system. As a result, these models frequently permit much better simultaneous descriptions of related response mechanisms, i.e., water volume and concentrations of conservative solutes, than the much simpler and more rigid convolution integral models, which can be interpreted as equivalent to linear reservoirs consisting of one single storage component with one outflow, characterized by individual time invariant TTDs for flow and stream solute concentrations (Figure 7(a)).<sup>207</sup> A further advantage of integrated conceptual models is that the transport processes are described by the choice of mixing coefficients  $C$  or SAS functions (SAS; see above) that control TTDs, rather than by the choice of TTDs themselves.<sup>51,53,219,296</sup> Explicitly accounting for temporally variable mass fluxes, the use of  $C$  or SAS functions in this model type generates time dynamic and thus more plausible TTDs, even if  $C$  or the SAS function are time-invariant. Making use of time dynamic formulations of  $C$  or SAS functions in conceptual models does, in addition, allow to account for the influence of wetness conditions on the mixing mechanism (i.e., ‘first-in-last-out’; see above)<sup>48</sup> and thus on the temporal variability of transport processes.<sup>43,53</sup> Note, that in the absence of suitable data, typically either complete mixing is assumed for the individual system components, or the related parameters are obtained from calibration. It has recently also been shown that the slope of the power spectrum of observed stream water chemistry may potentially be used to guide the choice parameterization of the mixing process.<sup>56</sup> Another critical aspect of

conceptual models is that the availability of multiple storage components and fluxes permits an explicit representation of different storage and release characteristics (i.e., different ‘mixing’) in these different parts of the system, which can all be characterized by different TTDs. These aspects are illustrated in an example in Figure 8, showing results from a calibrated model of the Kerrien catchment in France.<sup>43</sup> It cannot only be seen that the modeled  $p_S$  and  $p_{T,B}$  are different from each other but also that the individual storage components of the conceptual model used in that catchment<sup>43</sup> generate considerable differences in the age distributions of the water stored and released from them. In addition, the dependence of the age distributions on the wetness state is clearly visible, with much younger water characterizing the system response under wet conditions than under dry conditions. It can also be seen that the age composition of water in the stream is considerably more variable than the age composition of water stored in the system (Figure 8(g) and (h)) and that stream flow is characterized by a high proportion of young water at instances when the relative contribution of the groundwater is low and the relative contribution of fast flows (e.g., preferential flow) to stream flow is high (Figure 8(f)). By doing so, these models, similarly as physically based models, can account for the changing importance of the individual system components under different wetness conditions, manifest in the frequently observed conservative solute concentration—discharge hysteresis patterns.<sup>43,53,210,217,219,286,287</sup> Finally, the explicit formulation of different individual fluxes generated from different storage components in conceptual models also allows an explicit treatment of evaporative fluxes and their influence on TTDs and the water quality response.<sup>43,56,297–299</sup> This is of crucial importance for a meaningful interpretation of TTDs and for a deeper understanding of the dichotomy between the movement of water and transport of chemically inert solutes.<sup>55</sup> For example, it was shown that the TTD of plant transpiration more closely reflects the residence time distribution of water stored in the root zone than the TTD of preferential/shallow subsurface flow released from the root zone (Figure 8(d) and (e)), highlighting that transpiration and runoff can have considerably different water compositions. This in turn suggests that these processes may draw water from different pools.<sup>48,242,300</sup> Irrespective of the uncertainties associated with this modeling approach, all these aspects together can thus give a very detailed sense of TTDs and thus transport characteristics under different wetness conditions in individual parts of the system.





**FIGURE 8** | The upper three panels show the time series of (a) observed daily precipitation as well as of (b) observed (black) and modeled flow (blue), and (c) modeled storage in the Kerrien catchment in France. The fourth panel (d) shows the flow weighted average (bold, dark blue lines) and the daily (thin lines, shades from light to dark indicate increasing flow) age distributions  $p_{T,B}$  of three selected modeled fluxes. The fifth panel (e) shows the volume weighted average (bold, dark green lines) and the daily (thin lines, shades from light to dark indicate increasing storage) age distributions  $p_S$  of three selected modeled storage components. The sixth panel (f) shows the modeled relative contribution of fast (i.e., preferential) flows  $Q_F$  and groundwater flows  $Q_S$ . The two bottom panels show the time dynamic development of (g)  $p_{T,B}$  and (h)  $p_S$ , as indicated by their 5/25/50/75/95th percentiles. Note that more detailed information about the catchment and the model are available in Ref 43.

The value of such TT-based, relatively simple, often lumped, conceptual models based was in the past mainly shown for conservative, environmental tracers (e.g.,  $\text{Cl}^-$ ,  $^{18}\text{O}$ , and  $^2\text{H}$ ). These applications contributed to improve the internal consistency of hydrological models<sup>296,301</sup> or, in other words, to get the right answers for the right reasons.<sup>191</sup> However, applications of semi-distributed, HRU-based conceptual TT models<sup>43</sup> with reactive solutes are still rare<sup>101,302</sup> and their utility for real-world water quality issue remains to be tested.

## Features, Advantages, and Limitations of TT-Based Models

Avoiding the major limitations of both, physically based (equifinality and computational cost) and

lumped conceptual models (lack of physical basis and insufficient detail), semi-distributed, HRU-based conceptual models on basis of SAS functions could potentially provide a feasible alternative for a variety of reasons. A rigorous definition of HRUs for example due to geology, topography and land cover,<sup>197–202</sup> together with efficient methods for constraining the feasible model space<sup>204,205</sup> would introduce a certain level of spatial heterogeneity in the modeling domain. Most importantly, the definition of distinct storage and flux mechanisms, according to HRUs, then facilitates a clearer distinction between the residence times of water and solutes stored in and the TT of water and solutes released from different parts of catchments (see Figure 8). By acknowledging their contrasting dynamics, interpretative pitfalls can more easily be avoided. The flexibility of such models to

adequately represent the required process heterogeneity in catchments then may bear the potential to plausibly and simultaneously mimic hydrological and hydrochemical response dynamics arising from what is frequently referred to as 'hot spots' and 'hot moments'<sup>146,238,303,304</sup> if the individual HRUs provide a sufficiently detailed spatial resolution. The reason for this is that these models, if reflecting well the hydrological functioning of a catchment,<sup>186,204,288</sup> can reproduce the dynamics of how different parts of the system establish connectivity to the stream, depending on the prevailing wetness conditions, similar to fully distributed, physically based models. In other words, explicitly accounting for a range of different processes, flow paths and source areas (as represented by different storage components in parallel model structures, as defined by HRUs), these models have the ability to mimic the contrasting dynamics of the hydrological connectivity in different parts of a catchment. This in turn may allow a more detailed and time-dynamic differentiation of the trajectories water and solutes followed through the system before reaching the stream. As a consequence, such a more detailed HRU-based representation of spatial hydrological process heterogeneity<sup>43,215,305</sup> and the associated transport processes, as reflected by TTDs, has the potential to not only adequately reproduce hydrological response dynamics (e.g., runoff) but also the frequently observed<sup>306–311</sup> and theoretically relatively well understood<sup>1255,297,312,313</sup> temporal variability in stream water concentrations of conservative solutes, which are exclusively controlled by advective movement of water and the connectivity of source areas (Figure 8).<sup>314–319</sup>

It is, however, clear that although the above discussed TT-based conceptual models may hold value for characterizing transport processes they cannot serve as standalone tools for capturing dynamics of reactive substances. Rather, these formulations of transport, by providing plausible descriptions of water fluxes in the modeling domain, can serve as a *basis for* and an *interface with* detailed models that account for detailed physicochemical, chemical, and/or biological processes. These additional processes can then be readily coupled with the transport model, which provides the boundary condition of physical movement of water and solutes at the spatial resolution of the individual HRUs for any time  $t$  in the modeling period. For example, one such process that has previously been successfully incorporated in conceptual transport models is the first order kinetics toward equilibrium concentrations. This allows to represent the chemical exchange between solutions to

quantify effects such as mineral weathering (i.e., concentration differences between precipitation and water stored in the flow domain) by making use of effective, catchment-scale kinetic constants as demonstrated for silica and sodium dynamics, respectively.<sup>302</sup> A further example is differential plant uptake of water and solutes. As demonstrated in several studies, a simple splitter operation can distinguish the proportion of a specific solute of a given age that follows water into the plant, while the rest remains stored in the flow domain.<sup>53,56,101</sup> Similarly, these models also offer the possibility to account for some aspects of reactive transport, including sorption and first-order decay, with relatively simple but effective process formulations. While sorption can be accounted for by lumped retardation factors, defined by an equilibrium partition coefficient between adsorbed and aqueous phases of the substance<sup>85,101</sup> that can vary between different storage components, linear decay can be modeled by using decay constants.<sup>101,320,321</sup> The HRU-based conceptual modeling approach also offers the possibility, in spite of the uncertainties involved, to add hydrologically passive storage volumes whose water content remains constant over time, i.e., water input volume at time  $t$  equals the water output volume at  $t$ , but which allow to increase the contact times between immobile and aqueous phases, thereby introducing a time lag for solute transport. All these examples can be applied in the hillslope flow domain of the model but can also be implemented as in-stream processes, depending on the position of the storage component in the model.

Irrespective of the potential value of catchment-scale transport formulations based on the TT concept, the approach has also limitations that need to be addressed in future studies. Although promising to some extent, it can at this point not be ruled out that the level of detail provided by semi-distributed, conceptual models that are coupled with biogeochemical process descriptions at the spatial scale of individual HRUs is insufficient for real world water quality issues such as nitrate, phosphorous, or heavy metals. In addition, it has to be noted that there can be considerable uncertainties involved in the assumptions surrounding the choice of mixing/sampling mechanism and the related parameters. The source of these uncertainties is that no systematic direct observations of dispersion pattern at the catchment scale are available so far to experimentally support the theory and assumptions behind the mixing/sampling mechanism, as these require expensive, time-consuming and complex hillslope and catchment-

scale multitracer studies, which funding agencies are typically hesitant to support. In comparison to physically based models, which are implicitly based on transport, conceptual models also necessarily have to rely on tracer data and the calibration of mixing mechanisms to be able to reproduce transport dynamics to a certain degree. Furthermore, even in the case of a plausible process characterization in a model, the lack of a sufficient spatial and temporal resolution of the available data may severely hinder a meaningful interpretation of model results.

In general, a robust integrated description of water and solute movement in a system needs to be sought and flexible, semi-distributed, conceptual models, coupled with biogeochemical process descriptions at the scale of individual HRUs may be one option for doing so. By treating the system in a more holistic way, i.e., by forcing models to adequately reproduce various response variables, they bear considerable potential to improve the predictive power of models. Eventually, such models could serve as building blocks of a unified theory of how catchments store and release water and solutes. Offering detailed descriptions of transport processes they can ultimately prove highly beneficial for replacing the current relatively simple transport descriptions in present generation catchment-scale water quality models as a step toward a more complete systems approach.

## CONCLUSION

Because of the considerable disconnection between the catchment hydrology and water quality scientific communities, catchment-scale models developed from either side do typically have considerable skill to reproduce the variables of interest to either community. Yet, while most standard catchment-scale hydrological models cannot reproduce the dynamics of even conservative solutes, widely used water quality models are characterized by overly simplistic representations of the hydrology in a system. We therefore argue that establishing a more robust connection between catchment-scale hydrological and water quality models by explicit formulations of hydrological transport may be highly beneficial for either community. It can be expected that such a more complete representation of the underlying processes will contribute to form an improved, more holistic understanding of how systems respond. Both, catchment-scale mechanistic models of transport processes and semi-distributed, transport-based conceptual hydrological models can be readily linked to detailed descriptions of biogeochemical processes by using the concept of TT. Integrating robust formulations of transport and biogeochemical processes into one modeling framework may be an important building block of more robust water quality models and potentially a step toward the development of fully integrated models of terrestrial ecosystems.

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