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

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Abstract

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 non-technical 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.

Keywords

Catchment hydrology; Water quality; Hydrological model; Conceptual model; Transit times; HRU; SAS

Introduction

Climate change and population growth, together with agricultural intensification and economic pressures pose considerable challenges to meet the increasing demand for clean water[1-4]. These challenges span the supply and distribution of water[5,6] and water quality[7-9]. Pollutants such as nitrate[10-13], phosphorous[14-16], heavy metals[17-19] or pesticides[20] in soil-, ground- and river waters mainly originate from agricultural (diffuse) and industrial and sewage effluent (point) sources[21], and there is global concern about the impacts of eutrophication and the associated aquatic hypoxia that can put ecosystem stability at risk[22,23]. There is thus an urgent need for the implementation of sustainable strategies to manage nutrients and other contaminants in the water environment[24-27]. 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[28-35] 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[36-39]. Briefly, it was observed that many catchments world-wide 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[40]. This is true for solutes of both, atmospheric or geogenic origin[40]. 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[13,41-43]. One example of such a case is the agriculturally managed Kerrien catchment in France (Figure 1; http://www6.inra.fr/ore_agrhys)[43]. Several years after the end of fertilizer application, which was the major source of chloride (Cl^-) in that catchment, the stream water Cl^- concentration remains rather stable. The 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 Fig.1), an observation that is frequently and loosely referred to as "biogeochemical stationarity" in many catchments world-wide[41]. In addition, the higher perceived degree of attenuation between 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 Cl^- concentrations in the stream water. This does certainly not suggest that the relatively conservative 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 […]"[39]. 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 travelled 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[44], depending on the flow regime. In regimes characterized by a large influence of advective processes (e.g. preferential flow in soil pipes) [45,46] and thus by the elevation head, celerity and velocity somewhat converge. Whereas in systems controlled by diffusive flow components (e.g. groundwater) [45,46], 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 2a. In spite of being in principle well understood[38,43,47-56], 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, inter-annual 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 the system as a whole in more complete and consistent model formulations[57], 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 towards closing the gap between the hydrology and the water quality community, this non-technical 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, bedrock) and channels. Solutes, homogeneously and instantaneously applied over a catchment (i.e. non-point source pollution) will experience dispersion on their trajectory to the catchment outlet[58]. 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")[59], (2) distinct flow path lengths ("geomorphologic dispersion")[60], 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[51,55].

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[61]. 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[62] and have since been exhaustively described and further developed in a vast body of literature[63-79].

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 non-conservative solutes through the system is characterized by different spatio-temporal dynamics than those of water. These different dynamics are the result of several different process types that can exert influence on solutes. Physico-chemical 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[80-84]. 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[82,85-91]. 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 micro-organisms should be mentioned[92-99,]. Solutes 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[100]. 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[95,101-104], at the substrate-stream interface as hyporheic exchange[105-111], or as in-stream processes[112-117]. They thereby set the physico-chemical environment and control the quantity of non-conservative solutes in the system. However, the fate of solutes may, in many river systems, also be considerably affected by transport processes[40,118-123]. 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[56,124,125]. 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[126,127]. 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[21,38,128-149]. 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[150].

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[41]. 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[56].

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.[151]. 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 modelling 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[152,153], but also allow to resolve catchment-scale processes in a physically consistent and distributed way. Over the recent years, much progress was achieved[154] in particular with respect to accounting for the importance of macropore flow[155-157] in subsurface features such as root canals, animal burrows or cracks. A key advance here was the representation of the flow domain as a multi-continuum (or multi-domain).

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[158,159]. Some of the most important model developments include MACRO[160], MIKE-SHE[161,162], CATFLOW[163], FRAC3DVS[164], Hydrogeosphere[165-167], HYDRUS 3-D[168], PARFLOW[169], CATHY[170,171] and a range of other approaches[172-174]. Implicitly based on hydrological transport these models can be readily extended to cater for biogeochemical processes. In spite of frequently relying on over-simplistic assumptions in such applications, for example 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[175] 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[176]. The problem has been exhaustively discussed in a wide range of papers[176-188]. Briefly, the spatial heterogeneity of the system forcing (e.g. precipitation) and boundary conditions (e.g. topology of preferential flow features, soil hydraulic properties) cannot be sufficiently characterized with the available observations[187,188]. 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 modelling scale. Given the generally ill-posed nature of such an inverse parameter determination problem[189], parameter equifinality and the related uncertainty may adversely affect the model's predictive skill[190,191]. 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[192], 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 world-wide. Recent developments helped to considerably increase these models' hydrological consistency and predictive power. They include, for example, the flexible model adaption to catchment function[193-195], the use of hydrological response units based on landscape characteristics[196-202] and more efficient parameter selection techniques[203,204]. 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[184,185,205]. 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[206]. 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.[207]. 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[208,209]. While implicit in physically-based 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 Figs.2b,c[210]: 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[47,52]. In hydrological models such a passive storage component is typically not accounted for as this storage effect cannot be distinguished from hydrometeorological observations alone[211] but rather requires hydrochemical data to adequately parameterize this process[43,212]. 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[43,52,57,213-221]. An alternative type of model is based on the multiple interacting pathways concept and relies on a combination of particle tracking and velocity distributions[222]. 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[151,223]. However, the challenges posed to the modeller 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 characterise transport and reaction rates. In contrast, a more conceptual approach relies on some form of appropriate judgement to simplify the system into a model structure where useful results may be obtained[224]. In many cases it is a simple question of having appropriate data to characterise the response of the catchment system in question[225,226].

The choice of approach for individual case studies is often dictated by particular research or practical questions, for example: a model to estimate the extent of a contaminant plume or diffuse pollution and its likely movement in an aquifer or towards a well[227,228]; a model to understand the effect of mineral weathering on hillslope or wetland flow characteristics[229]; 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[228,230]. In the second case, a geochemical model with extensive representation of mineralogy, such as PHREEQC or WITCH[229,231-233], to identify key reactions and transformations, may be suitable. Finally, in the third case, operational tools such as SWAT[234,235], INCA[236], Wetland-DNDC[237] or HYPE[238], which feature modular descriptions of chemical and biological processes affecting water quality dynamics on the catchment scale could be feasible options for the modeller. However, the emphasis of all these models being the biogeochemical processes the formulation of transport, is kept rather simplistic and could be considerably improved[151,239].

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 modellers, 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[13,224]. 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")[240] 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 [57,241] 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 non-linearities and their heterogeneity over different source areas in the hydrological response (e.g. "fill-and-spill" hypothesis)[242,243], more flexibility in the mixing processes (e.g. "partial mixing")[47,244], quantification of catchment-scale solute stores[212], 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" (TT) and the associated "transit time 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[243], these concepts are frequently used to characterize bulk hydrological transport[244]. While many early studies focused on interpreting merely mean transit times[244], 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[245,247-249] and surface water modelling studies[78,150,250,251].

Many approaches that quantify transport by the use of the transit time 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.[252], in catchment hydrology, where transport volumes can be readily defined by observations of inputs to and outputs from the system, the general concept of transit times 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)[252,253].

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 transit time distribution* (also: transit time distribution conditional on the sampling time or the age distribution of water in flux; $p_{T,B}$). In addition, the *forward transit time distribution* (also: transit time 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 transit time 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[51]. 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[50,51,55]. 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)[50,51,55]. While a uniform distribution samples from the individual water parcels of different age stored in the system with equal probabilities (Figs.4a,5a) other distributions (e.g. gamma or beta distributions) allow more flexibility to sample preferably young or old water (Fig.4b,5a). 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; Fig.5b). 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 behaviour, for example described by a beta distribution with high values of a (Fig.5b).

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, groundwater fluctuations are frequently characterized by limited non-linearities 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[254], 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 non-linear 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[255]. The first and arguably most important of which is the temporal variability in the size of input and output signals[51,256]. 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[48,257,258]. 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 relatively high proportions of young water reaching the stream. In contrast, during drier periods, flows are often, albeit not always[259], 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[52,260,261]. 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 transit times in these layers while substances stored for example in the deeper groundwater are typically associated with longer transit times. 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[47,53,262,263]. 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 6a. 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; Figs.6b), 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").

Transit time based models

Convolution integral models

A wide variety of transport models of different complexity, explicitly based on the concept of transit times, was in the past developed for and applied at the catchment-scale. Directly adapted from groundwater studies[247], the simplest models rely on a convolution integral approach, in which input signals are routed through the system according to TTDs of pre-defined functional shapes[246]. This approach is equivalent to hydrological models based on the instantaneous unit hydrograph[264]. 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[256,265]. In addition, most of these studies merely considered mean transit times, which are a rather uninformative metric[246]. Notwithstanding the considerable inaccuracies and interpretative biases resulting from these assumptions, as demonstrated by several studies[266-268,], 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[269-276]. In stepwise improvements studies increasingly moved away from the assumptions of completely mixed systems, in favour of more flexible representations that better reflect the non-linear character of hydrological systems and the importance of long-tails in the water quality response[208,218,266,267,274,277]. Similarly, the importance of the effect of variable flow conditions on transport dynamics, as already emphasized early on[278], has eventually been somewhat embraced by allowing for some weighting according to the volumes of input signals[208,218,279-281]. In spite of such advances and the insights gained, the actual TTDs in these model types remained, with some rare exceptions[209,282,283], 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[194], 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[43,284-287].

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[288], in spite of frequently providing adequate model fits to observed data. This is can be attributed to implausible model-internal dynamics[191,289], 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 modelling domain, based on hydrologically distinct functional units (i.e. hydrological response units; HRU)[197] have, when adequately constrained[204,290], been demonstrated to be hydrologically more consistent representations of catchments, allowing more robust reproductions of observed system dynamics[204]. Even in data-spare environments, such HRUs can be readily derived from, amongst others, topography[201,202], land use[197], geology[291] 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 Fig.7b. The model consists of three parallel components. As it is well understood that for example wetlands exhibit different hydrological dynamics than hillslopes[292], 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. Cl^-, ^{18}O, ^{2}H) using multi-objective 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[293,294] 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 (Fig.7a)[208]. A further advantage of integrated conceptual models is that the transport processes are described by the choice of mixing coefficients *C* or storage age selection functions (SAS; see above) that control TTDs, rather than by the choice of TTDs themselves[50,52,221,295]. 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)[47] and thus on the temporal variability of transport processes[43,52]. 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[55]. 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[43]. It cannot only be seen that the modelled 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[43] 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 (Fig.8g,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 (Fig.8f). 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[43,52,212,219,221,285,286]. 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[43,55,296-298]. 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[54]. 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 (Fig.8d,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[47,244,299]. Irrespective of the uncertainties associated with this modelling 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.

The value of such transit time based, relatively simple, often lumped, conceptual models based was in the past mainly shown for conservative, environmental tracers (e.g. Cl^-, ^{18}O, ^{2}H). These applications contributed to improve the internal consistency of hydrological models[295,300] or, in other words, to get the right answers for the right reasons[191]. However, applications of semi-distributed, HRU-based conceptual transit time models[43] with reactive solutes are still rare[100,301] and their utility for real-world water quality issue remains to be tested.

Features, advantages and limitations of transit time based models

Avoiding the major limitations of both, physically-based (equifinality, computational cost) and lumped conceptual models (lack of physical basis, 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 rigours definition of HRUs for example due to geology, topography and land cover[197-202], together with efficient methods for constraining the feasible model space[204,206] would introduce a certain level of spatial heterogeneity in the modelling 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 transit times of water and solutes released from different parts of catchments (see Fig.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”[145,240,302,303] 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[204,287,304], 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[43,217,305] 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[306-311] and theoretically relatively well understood[255,296,312,313] temporal variability in stream water concentrations of conservative solutes, which are exclusively controlled by advective movement of water and the connectivity of source areas (Fig.8)[314-319].

It is, however, clear that although the above discussed transit time 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 modelling domain, can serve as a *basis for* and an *interface with* detailed models that account for detailed physico-chemical, 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 modelling period. For example, one such process that has previously been successfully incorporated in conceptual transport models is the first order kinetics towards 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[301]. 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[52,55,100]. 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[84,100] that can vary between different storage components, linear decay can be modelled by using decay constants[100,320,321]. The HRU-based conceptual modelling 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 transit time 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 multi-tracer 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 towards a more complete systems approach.

Box 1: Transit times, age and life expectancy

The temporal composition of water volumes in a system can be described with different metrics[64,322] that are intimately interlinked[51] but often falsely used interchangeably. By considering water of a given age composition as water "population", analogies with demographic terminology[323,324] 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 transit time 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 transit times 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[252,253].

Conclusion

Due to 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 transit times. Integrating robust formulations of transport and biogeochemical processes into one modelling framework may be an important building block of more robust water quality models and potentially a step towards the development of fully integrated models of terrestrial ecosystems.

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References

[1] Verburg, P. H., & Bouma, J. (1999). Land use change under conditions of high population pressure: the case of Java. Global environmental change, 9(4), 303-312.

[2] Alcamo, J., Flörke, M., & Märker, M. (2007). Future long-term changes in global water resources driven by socio-economic and climatic changes. Hydrological Sciences Journal, 52(2), 247-275.

[3] DeFries, R. S., Rudel, T., Uriarte, M., & Hansen, M. (2010). Deforestation driven by urban population growth and agricultural trade in the twenty-first century. Nature Geoscience, 3(3), 178-181.

[4] Parolari, A.J., Katul, G.G. & Porporato, A. (2015). The Doomsday Equation and 50 years beyond: new perspectives on the human-water system. Wiley Interdisciplinary Reviews: Water 2(4): 407-414.

[5] Seager, R., Ting, M., Held, I., Kushnir, Y., Lu, J., Vecchi, G., ... & Naik, N. (2007). Model projections of an imminent transition to a more arid climate in southwestern North America. Science, 316(5828), 1181-1184.

[6] Berghuijs, W. R., Woods, R. A., & Hrachowitz, M. (2014). A precipitation shift from snow towards rain leads to a decrease in streamflow. Nature Climate Change, 4(7), 583-586.

[7] Whitehead, P. G., Wilby, R. L., Battarbee, R. W., Kernan, M., & Wade, A. J. (2009). A review of the potential impacts of climate change on surface water quality. Hydrological Sciences Journal, 54(1), 101-123.

[8] Crossman, J., Whitehead, P. G., Futter, M. N., Jin, L., Shahgedanova, M., Castellazzi, M., & Wade, A. J. (2013). The interactive responses of water quality and hydrology to changes in multiple stressors, and implications for the long-term effective management of phosphorus. Science of the Total Environment, 454, 230-244.

[9] Laudon, H., Tetzlaff, D., Soulsby, C., Carey, S., Seibert, J., Buttle, J., ... & McGuire, K. (2013). Change in winter climate will affect dissolved organic carbon and water fluxes in mid-to-high latitude catchments. Hydrological Processes, 27(5), 700-709.

[10] Martin, C., Aquilina, L., Gascuel-Odoux, C., Molenat, J., Faucheux, M., & Ruiz, L. (2004). Seasonal and interannual variations of nitrate and chloride in stream waters related to spatial and temporal patterns of groundwater concentrations in agricultural catchments. Hydrological Processes, 18(7), 1237-1254.

[11] Burt, T. P., & Worrall, F. (2009). Stream nitrate levels in a small catchment in south west England over a period of 35 years (1970–2005). Hydrological processes, 23(14), 2056-2068.

[12] Howden, N. J. K., Burt, T. P., Worrall, F., Whelan, M. J., & Bieroza, M. (2010). Nitrate concentrations and fluxes in the River Thames over 140 years (1868–2008): are increases irreversible?. Hydrological Processes, 24(18), 2657-2662.

[13] Howden, N. J., Burt, T. P., Worrall, F., Mathias, S., & Whelan, M. J. (2011). Nitrate pollution in intensively farmed regions: What are the prospects for sustaining high-quality groundwater?. Water Resources Research, 47(6).

[14] Heckrath, G., Brookes, P. C., Poulton, P. R., & Goulding, K. W. T. (1995). Phosphorus leaching from soils containing different phosphorus concentrations in the Broadbalk experiment. Journal of environmental quality, 24(5), 904-910.

[15] Carpenter, S. R., Caraco, N. F., Correll, D. L., Howarth, R. W., Sharpley, A. N., & Smith, V. H. (1998). Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecological applications, 8(3), 559-568.

[16] Ringeval, B., Nowak, B., Nesme, T., Delmas, M., & Pellerin, S. (2014). Contribution of anthropogenic phosphorus to agricultural soil fertility and food production. Global Biogeochemical Cycles, 28(7), 743-756.

[17] Audry, S., Schäfer, J., Blanc, G., & Jouanneau, J. M. (2004). Fifty-year sedimentary record of heavy metal pollution (Cd, Zn, Cu, Pb) in the Lot River reservoirs (France). Environmental Pollution, 132(3), 413-426.

[18] Schelker, J., Burns, D. A., Weiler, M., & Laudon, H. (2011). Hydrological mobilization of mercury and dissolved organic carbon in a snow-dominated, forested watershed: Conceptualization and modeling. Journal of Geophysical Research: Biogeosciences (2005–2012), 116(G1).

[19] Shanley, J. B., & Bishop, K. (2012). Mercury cycling in terrestrial watersheds. Mercury in the environment: pattern and process, 119-142.

[20] Holvoet, K. M., Seuntjens, P., & Vanrolleghem, P. A. (2007). Monitoring and modeling pesticide fate in surface waters at the catchment scale. Ecological modelling, 209(1), 53-64.

[21] Neal, C., Jarvie, H. P., Love, A., Neal, M., Wickham, H., & Harman, S. (2008). Water quality along a river continuum subject to point and diffuse sources. Journal of Hydrology, 350(3), 154-165.

[22] Rockström, J., Steffen, W., Noone, K., Persson, Å., Chapin, F. S., Lambin, E. F., et al. (2009). A safe operating space for humanity. Nature, 461(7263), 472-475.

[23] Hughes, B. B., Levey, M. D., Fountain, M. C., Carlisle, A. B., Chavez, F. P., & Gleason, M. G. (2015). Climate mediates hypoxic stress on fish diversity and nursery function at the land–sea interface. Proceedings of the National Academy of Sciences, 112(26), 8025-8030.

[24] Verhoeven, J. T., Arheimer, B., Yin, C., & Hefting, M. M. (2006). Regional and global concerns over wetlands and water quality. Trends in ecology & evolution, 21(2), 96-103.

[25] Conley, D. J., Paerl, H. W., Howarth, R. W., Boesch, D. F., Seitzinger, S. P., Havens, K. E., et al. (2009). Controlling eutrophication: nitrogen and phosphorus. Science, 323(5917), 1014-1015.

[26] Burt, T. P., Howden, N. J. K., Worrall, F., Whelan, M. J., & Bieroza, M. (2010). Nitrate in United Kingdom Rivers: Policy and Its Outcomes Since 1970. Environmental science & technology, 45(1), 175-181.

[27] Jeppesen, E., Kronvang, B., Olesen, J. E., Audet, J., Søndergaard, M., Hoffmann, C. C., et al. (2011). Climate change effects on nitrogen loading from cultivated catchments in Europe: implications for nitrogen retention, ecological state of lakes and adaptation. Hydrobiologia, 663(1), 1-21.

[28] Ruiz, L., Abiven, S., Martin, C., Durand, P., Beaujouan, V., & Molénat, J. (2002). Effect on nitrate concentration in stream water of agricultural practices in small catchments in Brittany: II. Temporal variations and mixing processes. Hydrology and Earth System Sciences, 6(3), 507-513.

[29] Soulsby, C., Gibbins, C., Wade, A. J., Smart, R., & Helliwell, R. (2002). Water quality in the Scottish uplands: a hydrological perspective on catchment hydrochemistry. Science of the total environment, 294(1), 73-94.

[30] Worrall, F., Burt, T., & Adamson, J. (2003). Controls on the chemistry of runoff from an upland peat catchment. Hydrological Processes, 17(10), 2063-2083.

[31] Temnerud, J., & Bishop, K. (2005). Spatial variation of streamwater chemistry in two Swedish boreal catchments: Implications for environmental assessment. Environmental science & technology, 39(6), 1463-1469.

[32] Tetzlaff, D., Malcolm, I. A., & Soulsby, C. (2007). Influence of forestry, environmental change and climatic variability on the hydrology, hydrochemistry and residence times of upland catchments. Journal of Hydrology, 346(3), 93-111.

[33] Dawson, J. J. C., Soulsby, C., Tetzlaff, D., Hrachowitz, M., Dunn, S. M., & Malcolm, I. A. (2008). Influence of hydrology and seasonality on DOC exports from three contrasting upland catchments. Biogeochemistry, 90(1), 93-113.

[34] Demers, J. D., Driscoll, C. T., & Shanley, J. B. (2010). Mercury mobilization and episodic stream acidification during snowmelt: Role of hydrologic flow paths, source areas, and supply of dissolved organic carbon. Water Resources Research, 46(1).

[35] Laudon, H., Berggren, M., Ågren, A., Buffam, I., Bishop, K., Grabs, T., et al. (2011). Patterns and dynamics of dissolved organic carbon (DOC) in boreal streams: the role of processes, connectivity, and scaling. Ecosystems, 14(6), 880-893.

[36] Neal, C., & Rosier, P. T. (1990). Chemical studies of chloride and stable oxygen isotopes in two conifer afforested and moorland sites in the British uplands. Journal of Hydrology, 115(1), 269-283.

[37] Buttle, J. M. (1994). Isotope hydrograph separations and rapid delivery of pre-event water from drainage basins. Progress in Physical Geography, 18(1), 16-41.

[38] Bishop, K., Seibert, J., Köhler, S., & Laudon, H. (2004). Resolving the double paradox of rapidly mobilized old water with highly variable responses in runoff chemistry. Hydrological Processes, 18(1), 185-189.

[39] Kirchner, J. W. (2003). A double paradox in catchment hydrology and geochemistry. Hydrological Processes, 17(4), 871-874.

[40] Godsey, S. E., Kirchner, J. W., & Clow, D. W. (2009). Concentration–discharge relationships reflect chemostatic characteristics of US catchments. Hydrological Processes, 23(13), 1844-1864.

[41] Basu, N. B., Destouni, G., Jawitz, J. W., Thompson, S. E., Loukinova, N. V., Darracq, A., et al. (2010). Nutrient loads exported from managed catchments reveal emergent biogeochemical stationarity. Geophysical Research Letters, 37(23).

[42] Darracq, A., Lindgren, G., & Destouni, G. (2008). Long-term development of Phosphorus and Nitrogen loads through the subsurface and surface water systems of drainage basins. Global Biogeochemical Cycles, 22(3).

[43] Hrachowitz, M., Fovet, O., Ruiz, L., & Savenije, H. (2015). Transit time distributions, legacy contamination and variability in biogeochemical $1/f^{\alpha}$ scaling: How are hydrological response dynamics linked to water quality at the catchment scale?. Hydrological Processes.

[44] McDonnell, J. J., & Beven, K. (2014). Debates—The future of hydrological sciences: A (common) path forward? A call to action aimed at understanding velocities, celerities and residence time distributions of the headwater hydrograph. Water Resources Research, 50(6), 5342-5350.

[45] Berne, A., Uijlenhoet, R., & Troch, P. A. (2005). Similarity analysis of subsurface flow response of hillslopes with complex geometry. Water Resources Research, 41(9).

[46] Harman, C., & Sivapalan, M. (2009). A similarity framework to assess controls on shallow subsurface flow dynamics in hillslopes. Water Resources Research, 45(1).

[47] Brooks, J. R., Barnard, H. R., Coulombe, R., & McDonnell, J. J. (2010). Ecohydrologic separation of water between trees and streams in a Mediterranean climate. Nature Geoscience, 3(2), 100-104.

[48] Stumpp, C., & Maloszewski, P. (2010). Quantification of preferential flow and flow heterogeneities in an unsaturated soil planted with different crops using the environmental isotope δ18O. Journal of hydrology, 394(3), 407-415.

[49] Van der Velde, Y., De Rooij, G. H., Rozemeijer, J. C., Van Geer, F. C., & Broers, H. P. (2010). Nitrate response of a lowland catchment: On the relation between stream concentration and travel time distribution dynamics. Water Resources Research, 46(11).

[50] Van der Velde, Y., Torfs, P. J., Zee, S. E., & Uijlenhoet, R. (2012). Quantifying catchment-scale mixing and its effect on time-varying travel time distributions. Water Resources Research, 48(6).

[51] Botter, G., Bertuzzo, E., & Rinaldo, A. (2011). Catchment residence and travel time distributions: The master equation. Geophysical Research Letters, 38(11).

[52] Hrachowitz, M., Savenije, H., Bogaard, T. A., Tetzlaff, D., & Soulsby, C. (2013). What can flux tracking teach us about water age distribution patterns and their temporal dynamics?. Hydrology and Earth System Sciences, 17 (2), 2013.

[53] Klaus, J., Zehe, E., Elsner, M., Külls, C., & McDonnell, J. J. (2013). Macropore flow of old water revisited: experimental insights from a tile-drained hillslope. Hydrology and Earth System Sciences, 17(1), 103-118.

[54] Ali, M., Fiori, A., & Russo, D. (2014). A comparison of travel-time based catchment transport models, with application to numerical experiments. Journal of Hydrology, 511, 605-618.

[55] Harman, C. J. (2015). Time-variable transit time distributions and transport: Theory and application to storage-dependent transport of chloride in a watershed. Water Resources Research, 51(1), 1-30.

[56] Rinaldo, A., Benettin, P., Harman, C. J., Hrachowitz, M., McGuire, K. J., Van der Velde, Y., Bertuzzo, E., & Botter, G. (2015). Storage selection functions: A coherent framework for quantifying how catchments store and release water and solutes. Water Resources Research, 51(6), 4840-4847.

[57] Medici, C., Wade, A.J., & Frances, F. (2012). Does increased hydrochemical models complexity decrease robustness? Journal of Hydrology, 440-441, 1-13.

[58] Robinson, J. S., Sivapalan, M., & Snell, J. D. (1995). On the relative roles of hillslope processes, channel routing, and network geomorphology in the hydrologic response. Water Resources Research, 31(12), 3089-3101.

[59] Botter, G., & Rinaldo, A. (2003). Scale effect on geomorphologic and kinematic dispersion. Water Resources Research, 39(10).

[60] Rinaldo, A., Marani, A., & Rigon, R. (1991). Geomorphological dispersion. Water Resources Research, 27(4), 513-525.

[61] Kirchner, J. W., Tetzlaff, D., & Soulsby, C. (2010). Comparing chloride and water isotopes as hydrological tracers in two Scottish catchments. Hydrological Processes, 24(12), 1631-1645.

[62] Taylor, G. (1953). Dispersion of soluble matter in solvent flowing slowly through a tube. In Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences 219, pp. 186-203. The Royal Society.

[63] Bear, J., 1972. Dynamics of Fluids in Porous Media. American Elsevier, New York, NY, 764 pp.

[64] Kreft, A., & Zuber, A. (1978). On the physical meaning of the dispersion equation and its solutions for different initial and boundary conditions. Chemical Engineering Science, 33(11), 1471-1480.

[65] Dullien, F. A. L. (1979), Porous Media: Fluid Transport and Pore Structure, Academic, San Diego, Calif.

[66] Gelhar, L. W., & Axness, C. L. (1983). Three-dimensional stochastic analysis of macrodispersion in aquifers. Water Resources Research, 19(1), 161-180.

[67] Dagan, G. (1984). Solute transport in heterogeneous porous formations. Journal of Fluid Mechanics, 145, 151-177.

[68] Rinaldo, A., & Marani, A. (1987). Basin scale model of solute transport. Water Resources Research, 23(11), 2107-2118.

[69] Dagan, G., Cvetkovic, V., & Shapiro, A. (1992). A solute flux approach to transport in heterogeneous formations: 1. The general framework. Water resources research, 28(5), 1369-1376.

[70] Destouni, G. (1993). Stochastic modelling of solute flux in the unsaturated zone at the field scale. Journal of hydrology, 143(1), 45-61.

[71] Russo, D. (1993). Stochastic modeling of macrodispersion for solute transport in a heterogeneous unsaturated porous formation. Water Resources Research, 29(2), 383-397.

[72] Destouni, G., & Graham, W. (1995). Solute transport through an integrated heterogeneous soil-groundwater system. Water resources research, 31(8), 1935-1944.

[73] Dagan, G., & Fiori, A. (1997). The influence of pore-scale dispersion on concentration statistical moments in transport through heterogeneous aquifers. Water Resources Research, 33(7), 1595-1605.

[74] Cirpka, O. A., & Kitanidis, P. K. (2000). Characterization of mixing and dilution in heterogeneous aquifers by means of local temporal moments. Water Resources Research, 36(5), 1221-1236.

[75] Fiori, A., & Dagan, G. (2000). Concentration fluctuations in aquifer transport: A rigorous first-order solution and applications. Journal of Contaminant Hydrology, 45(1), 139-163.

[76] Gupta, A., & Cvetkovic, V. (2002). Material transport from different sources in a network of streams through a catchment. Water resources research, 38(7), 3-1.

[77] Lindgren, G. A., Destouni, G., & Miller, A. V. (2004). Solute transport through the integrated groundwater-stream system of a catchment. Water Resources Research, 40(3).

[78] Rinaldo, A., Botter, G., Bertuzzo, E., Uccelli, A., Settin, T., & Marani, M. (2006). Transport at basin scales: 1. Theoretical framework. Hydrology and Earth System Sciences, 10(1), 19-29.

[79] Benettin, P., Rinaldo, A., & Botter, G. (2013). Kinematics of age mixing in advection-dispersion models. Water Resources Research, 49(12), 8539-8551.

[80] Freeze, R. A., & Cherry, J. A. (1979). Groundwater, 604 pp.

[81] Bouwer, H. (1991). Simple derivation of the retardation equation and application to preferential flow and macrodispersion. Groundwater, 29(1), 41-46.

[82] Brusseau, M. L. (1994). Transport of reactive contaminants in heterogeneous porous media. Reviews of Geophysics, 32(3), 285-313.

[83] Cvetkovic, V., & Dagan, G. (1994). Transport of kinetically sorbing solute by steady random velocity in heterogeneous porous formations. Journal of Fluid Mechanics, 265, 189-215.

[84] Feng, X., Kirchner, J. W., & Neal, C. (2004). Measuring catchment-scale chemical retardation using spectral analysis of reactive and passive chemical tracer time series. Journal of Hydrology, 292(1), 296-307.

[85] Srinivasan, P., & Mercer, J. W. (1988). Simulation of biodegradation and sorption processes in ground water. Groundwater, 26(4), 475-487.

[86] Squillace, P. J., & Thurman, E. M. (1992). Herbicide transport in rivers: importance of hydrology and geochemistry in nonpoint-source contamination. Environmental science & technology, 26(3), 538-545.

[87] Hill, A. R. (1996). Nitrate removal in stream riparian zones. Journal of environmental quality, 25(4), 743-755.

[88] Galloway, J. N., Aber, J. D., Erisman, J. W., Seitzinger, S. P., Howarth, R. W., Cowling, E. B., & Cosby, B. J. (2003). The nitrogen cascade. Bioscience, 53(4), 341-356.

[89] Steefel, C. I., DePaolo, D. J., & Lichtner, P. C. (2005). Reactive transport modeling: An essential tool and a new research approach for the Earth sciences. Earth and Planetary Science Letters, 240(3), 539-558.

[90] Lutz, S. R., van Meerveld, H. J., Waterloo, M. J., Broers, H. P., & van Breukelen, B. M. (2013). A model-based assessment of the potential use of compound-specific stable isotope analysis in river monitoring of diffuse pesticide pollution. Hydrology and Earth System Sciences, 17(11), 4505-4524.

[91] Wexler, S. K., Goodale, C. L., McGuire, K. J., Bailey, S. W., & Groffman, P. M. (2014). Isotopic signals of summer denitrification in a northern hardwood forested catchment. Proceedings of the National Academy of Sciences, 111(46), 16413-16418.

[92] Jungk, A. O., Waisel, Y., Eshel, A., & Kafkafi, U. (2002). Dynamics of nutrient movement at the soil-root interface. Plant roots: The hidden half, Waisel, Y., Eshel, A., Kafkafi, U (Eds.), 587-616.

[93] Vetterlein, D., & Jahn, R. (2004). Gradients in soil solution composition between bulk soil and rhizosphere–In situ measurement with changing soil water content. Plant and soil, 258(1), 307-327.

[94] Lovett, G. M., Likens, G. E., Buso, D. C., Driscoll, C. T., & Bailey, S. W. (2005). The biogeochemistry of chlorine at Hubbard Brook, New Hampshire, USA. Biogeochemistry, 72(2), 191-232.

[95] Hinsinger, P., Plassard, C., & Jaillard, B. (2006). Rhizosphere: a new frontier for soil biogeochemistry. Journal of Geochemical Exploration, 88(1), 210-213.

[96] Turpault, M. P., Gobran, G. R., & Bonnaud, P. (2007). Temporal variations of rhizosphere and bulk soil chemistry in a Douglas fir stand. Geoderma, 137(3), 490-496.

[97] Hinsinger, P., Bengough, A. G., Vetterlein, D., & Young, I. M. (2009). Rhizosphere: biophysics, biogeochemistry and ecological relevance. Plant and soil, 321(1-2), 117-152.

[98] Svensson, T., Lovett, G. M., & Likens, G. E. (2012). Is chloride a conservative ion in forest ecosystems?. Biogeochemistry, 107(1-3), 125-134.

[99] Fatichi, S., Pappas, C., & Ivanov, V. Y. (2015). Modeling plant–water interactions: an ecohydrological overview from the cell to the global scale. Wiley Interdisciplinary Reviews: Water.

[100] Bertuzzo, E., Thomet, M., Botter, G., & Rinaldo, A. (2013). Catchment-scale herbicides transport: Theory and application. Advances in Water Resources, 52, 232-242.

[101] Fenn, M.E., Poth, M.A., Aber, J.D., Baron, J.S., Bormann, B.T., Johnson, D.W., Lemly, A.D., McNulty, S.G., Ryan, D.F. & Stottlemyer, R. (1998). Nitrogen excess in North American ecosystems: predisposing factors, ecosystem responses, and management strategies. Ecological Applications, 8(3), 706-733.

[102] Davidson, E.A., Trumbore, S.E., & Amundson, R. (2000). Biogeochemistry: soil warming and organic carbon content. Nature, 408(6814), 789-790.

[103] Binkley, D., & Fisher, R. (2012). Ecology and management of forest soils. John Wiley & Sons.

[104] Paul, E. A. (2015). Soil microbiology, ecology and biochemistry. Academic press.

[105] Findlay, S. (1995). Importance of surface-subsurface exchange in stream ecosystems: The hyporheic zone. Limnology and oceanography, 40(1), 159-164.

[106] Jones, J. B., & Mulholland, P. J. (1999). Streams and ground waters. Academic Press.

[107] Gooseff, M. N., McKnight, D. M., Lyons, W. B., & Blum, A. E. (2002). Weathering reactions and hyporheic exchange controls on stream water chemistry in a glacial meltwater stream in the McMurdo Dry Valleys. Water Resources Research, 38(12).

[108] Boano, F., Demaria, A., Revelli, R., & Ridolfi, L. (2010). Biogeochemical zonation due to intrameander hyporheic flow. Water resources research, 46(2).

[109] Krause, S., Hannah, D. M., Fleckenstein, J. H., Heppell, C. M., Kaeser, D., Pickup, R., Pinay, G., Robertson, A.L. & Wood, P. J. (2011). Inter-disciplinary perspectives on processes in the hyporheic zone. Ecohydrology, 4(4), 481-499.

[110] Trimmer, M., Grey, J., Heppell, C. M., Hildrew, A. G., Lansdown, K., Stahl, H., & Yvon-Durocher, G. (2012). River bed carbon and nitrogen cycling: state of play and some new directions. Science of the Total Environment, 434, 143-158.

[111] Cardenas, M. B. (2015). Hyporheic zone hydrologic science: A historical account of its emergence and a prospectus. Water Resources Research, 51(5), 3601-3616.

[112] McKnight, D. M., & Bencala, K. E. (1990). The Chemistry of Iron, Aluminum, and Dissolved Organic Material in Three Acidic, Metal-Enriched, Mountain Streams, as Controlled by Watershed and in-Stream Processes. Water Resources Research, 26(12), 3087-3100.

[113] Mulholland, P. J., & Hill, W. R. (1997). Seasonal patterns in streamwater nutrient and dissolved organic carbon concentrations: separating catchment flow path and in-stream effects. Water Resources Research, 33(6), 1297-1306.

[114] House, W. A., & Warwick, M. S. (1998). A mass-balance approach to quantifying the importance of in-stream processes during nutrient transport in a large river catchment. Science of the total environment, 210, 139-152.

[115] Dawson, J. J. C., Bakewell, C., & Billett, M. F. (2001). Is in-stream processing an important control on spatial changes in carbon fluxes in headwater catchments?. Science of the Total Environment, 265(1), 153-167.

[116] Dawson, J. J., Soulsby, C., Hrachowitz, M., Speed, M., & Tetzlaff, D. (2009). Seasonality of epCO2 at different scales along an integrated river continuum within the Dee Basin, NE Scotland. Hydrological processes, 23(20), 2929-2942.

[117] Ranalli, A. J., & Macalady, D. L. (2010). The importance of the riparian zone and in-stream processes in nitrate attenuation in undisturbed and agricultural watersheds–A review of the scientific literature. Journal of Hydrology, 389(3), 406-415.

[118] Dawson, J. J., Tetzlaff, D., Speed, M., Hrachowitz, M., & Soulsby, C. (2011). Seasonal controls on DOC dynamics in nested upland catchments in NE Scotland. Hydrological Processes, 25(10), 1647-1658.

[119] Thompson, S. E., Basu, N. B., Lascurain, J., Aubeneau, A., & Rao, P. S. C. (2011). Relative dominance of hydrologic versus biogeochemical factors on solute export across impact gradients. Water Resources Research, 47(10).

[120] Gall, H. E., Park, J., Harman, C. J., Jawitz, J. W., & Rao, P. S. C. (2013). Landscape filtering of hydrologic and biogeochemical responses in managed catchments. Landscape ecology, 28(4), 651-664.

[121] Kirchner, J. W., & Neal, C. (2013). Universal fractal scaling in stream chemistry and its implications for solute transport and water quality trend detection. Proceedings of the National Academy of Sciences, 110(30), 12213-12218.

[122] Aubert, A. H., Kirchner, J. W., Gascuel-Odoux, C., Faucheux, M., Gruau, G., & Mérot, P. (2014). Fractal water quality fluctuations spanning the periodic table in an intensively farmed watershed. Environmental science & technology, 48(2), 930-937.

[123] Wade, A. J., Palmer-Felgate, E. J., Halliday, S. J., Skeffington, R. A., Loewenthal, M., Jarvie, H. P., ... & Newman, J. R. (2012). Hydrochemical processes in lowland rivers: insights from in situ, high-resolution monitoring. Hydrology and Earth System Sciences, 16(11), 4323-4342.

[124] Maher, K., & Chamberlain, C. P. (2014). Hydrologic regulation of chemical weathering and the geologic carbon cycle. science, 343(6178), 1502-1504.

[125] Oldham, C. E., Farrow, D. E., & Peiffer, S. (2013). A generalized Damköhler number for classifying material processing in hydrological systems. Hydrology and Earth System Sciences, (17), 1133-1148.

[126] Martin, C., Molenat, J., Gascuel-Odoux, C., Vouillamoz, J. M., Robain, H., Ruiz, L., Faucheux, M. & Aquilina, L. (2006). Modelling the effect of physical and chemical characteristics of shallow aquifers on water and nitrate transport in small agricultural catchments. Journal of Hydrology, 326(1), 25-42.

[127] Caissie, D. (2006). The thermal regime of rivers: a review. Freshwater Biology, 51(8), 1389-1406.

[128] Haygarth, P. M., & Sharpley, A. N. (2000). Terminology for phosphorus transfer. Journal of environmental quality, 29(1), 10-15.

[129] Heathwaite, A. L., & Dils, R. M. (2000). Characterising phosphorus loss in surface and subsurface hydrological pathways. Science of the Total Environment, 251, 523-538.

[130] Hill, A. R., Devito, K. J., Campagnolo, S., & Sanmugadas, K. (2000). Subsurface denitrification in a forest riparian zone: interactions between hydrology and supplies of nitrate and organic carbon. Biogeochemistry, 51(2), 193-223.

[131] Stieglitz, M., Shaman, J., McNamara, J., Engel, V., Shanley, J., & Kling, G. W. (2003). An approach to understanding hydrologic connectivity on the hillslope and the implications for nutrient transport. Global Biogeochemical Cycles, 17(4).

[132] Laudon, H., Seibert, J., Köhler, S., & Bishop, K. (2004). Hydrological flow paths during snowmelt: Congruence between hydrometric measurements and oxygen 18 in meltwater, soil water, and runoff. Water Resources Research, 40(3).

[133] Haygarth, P. M., Condron, L. M., Heathwaite, A. L., Turner, B. L., & Harris, G. P. (2005). The phosphorus transfer continuum: linking source to impact with an interdisciplinary and multi-scaled approach. Science of the total environment, 344(1), 5-14.

[134] Johnson, M. S., Lehmann, J., Couto, E. G., Novaes Filho, J. P., & Riha, S. J. (2006). DOC and DIC in flowpaths of Amazonian headwater catchments with hydrologically contrasting soils. Biogeochemistry, 81(1), 45-57.

[135] Alexander, R. B., Boyer, E. W., Smith, R. A., Schwarz, G. E., & Moore, R. B. (2007). The role of headwater streams in downstream water quality. JAWRA Journal of the American Water Resources Association, 43(1), 41-59.

[136] Arnscheidt, J., Jordan, P., Li, S., McCormick, S., McFaul, R., McGrogan, H. J., Neal, M., & Sims, J. T. (2007). Defining the sources of low-flow phosphorus transfers in complex catchments. Science of the Total Environment, 382(1), 1-13.

[137] Edwards, A. C., & Withers, P. J. A. (2008). Transport and delivery of suspended solids, nitrogen and phosphorus from various sources to freshwaters in the UK. Journal of Hydrology, 350(3), 144-153.

[138] Holman, I. P., Whelan, M. J., Howden, N. J. K., Bellamy, P. H., Willby, N. J., Rivas-Casado, M., & McConvey, P. (2008). Phosphorus in groundwater—an overlooked contributor to eutrophication?. Hydrological Processes, 22(26), 5121-5127.

[139] Jarvie, H. P., Haygarth, P. M., Neal, C., Butler, P., Smith, B., Naden, P. S., ... & Palmer-Felgate, E. J. (2008). Stream water chemistry and quality along an upland–lowland rural land-use continuum, south west England. Journal of Hydrology, 350(3), 215-231.

[140] Kim, Y. J., Steenhuis, T. S., & Nam, K. (2008). Movement of heavy metals in soil through preferential flow paths under different rainfall intensities. CLEAN–Soil, Air, Water, 36(12), 984-989.

[141] Molenat, J., Gascuel-Odoux, C., Ruiz, L., & Gruau, G. (2008). Role of water table dynamics on stream nitrate export and concentration in agricultural headwater catchment (France). Journal of Hydrology, 348(3), 363-378.

[142] Sebestyen, S. D., Boyer, E. W., Shanley, J. B., Kendall, C., Doctor, D. H., Aiken, G. R., & Ohte, N. (2008). Sources, transformations, and hydrological processes that control stream nitrate and dissolved organic matter concentrations during snowmelt in an upland forest. Water Resources Research, 44(12).

[143] Withers, P. J. A., & Jarvie, H. P. (2008). Delivery and cycling of phosphorus in rivers: A review. Science of the total environment, 400(1), 379-395.

[144] Köhler, S. J., Buffam, I., Seibert, J., Bishop, K. H., & Laudon, H. (2009). Dynamics of stream water TOC concentrations in a boreal headwater catchment: Controlling factors and implications for climate scenarios. Journal of Hydrology, 373(1), 44-56.

[145] Vidon, P., Allan, C., Burns, D., Duval, T. P., Gurwick, N., Inamdar, S., Lowrance, R., Okay, J., Scott, D., & Sebestyen, S. (2010). Hot spots and hot moments in riparian zones: Potential for improved water quality management. Journal of the American Water Resources Association, 46(2), 278-298.

[146] Laudon, H., Berggren, M., Ågren, A., Buffam, I., Bishop, K., Grabs, T., Jansson, M., & Köhler, S. (2011). Patterns and dynamics of dissolved organic carbon (DOC) in boreal streams: the role of processes, connectivity, and scaling. Ecosystems, 14(6), 880-893.

[147] Dupas, R., Gruau, G., Gu, S., Humbert, G., Jaffrézic, A., & Gascuel-Odoux, C. (2015). Groundwater control of biogeochemical processes causing phosphorus release from riparian wetlands. Water research, 84, 307-314.

[148] Dupas, R., Gascuel-Odoux, C., Gilliet, N., Grimaldi, C., & Gruau, G. (2015). Distinct export dynamics for dissolved and particulate phosphorus reveal independent transport mechanisms in an arable headwater catchment. Hydrological Processes.

[149] Bowes, M. J., Jarvie, H. P., Halliday, S. J., Skeffington, R. A., Wade, A. J., Loewenthal, M., Gozzard, E., Newman, J.R., & Palmer-Felgate, E. J. (2015). Characterising phosphorus and nitrate inputs to a rural river using high-frequency concentration–flow relationships. Science of the Total Environment, 511, 608-620.

[150] Rinaldo, A., & Rodriguez-Iturbe, I. (1996). Geomorphological theory of the hydrological response. Hydrological Processes, 10(6), 803-829.

[151] Wellen, C., Kamran-Disfani, A. R., & Arhonditsis, G. B. (2015). Evaluation of the Current State of Distributed Watershed Nutrient Water Quality Modeling. Environmental science & technology, 49(6), 3278-3290.

[152] Fiori, A. & Russo, D. (2007). Numerical analyses of subsurface flow in a steep hillslope under rainfall: the role of the spatial heterogeneity of the formation hydraulic properties. Water Resources Research 43, W07445.

[153] Russo, D., Laufer, A., Gerstl, Z., Ronen, D., Weisbrod, N., & Zentner, E. (2014). On the mechanism of field-scale solute transport: Insights from numerical simulations and field observations. Water Resources Research, 50(9), 7484-7504.

[154] Paniconi, C., & Putti, M. (2015). Physically based modeling in catchment hydrology at 50: Survey and outlook. Water Resources Research, 51(9), 7090-7129.

[155] Beven, K., & Germann, P. (1982). Macropores and water flow in soils. Water resources research, 18(5), 1311-1325.

[156] Beven, K., & Germann, P. (2013). Macropores and water flow in soils revisited. Water Resources Research, 49(6), 3071-3092.

[157] Jarvis, N., Larsbo, M., Roulier, S., Lindahl, A., & Persson, L. (2007). The role of soil properties in regulating non-equilibrium macropore flow and solute transport in agricultural topsoils. European Journal of Soil Science, 58(1), 282-292.

[158] Šimůnek, J., Jarvis, N. J., Van Genuchten, M. T., & Gärdenäs, A. (2003). Review and comparison of models for describing non-equilibrium and preferential flow and transport in the vadose zone. Journal of Hydrology, 272(1), 14-35.

[159] Köhne, J. M., Köhne, S., & Šimůnek, J. (2009). A review of model applications for structured soils: a) Water flow and tracer transport. Journal of Contaminant Hydrology, 104(1), 4-35.

[160] Jarvis, N.J., 1994. The MACRO Model (Version 3.1). Technical Description and Sample Simulations. Reports and Dissertations 19. Department of Soil Science, Swedish University of Agricultural Science, Uppsala, Sweden, p. 51.

[161] Refsgaard, J.C., & Storm, B. (1995). MIKE SHE. In: V.P. Singh, ed. Computer models of watershed hydrology. Littleton, CO: Water Resources Publications, 809–846.

[162] Christiansen, J. S., Thorsen, M., Clausen, T., Hansen, S., & Refsgaard, J. C. (2004). Modelling of macropore flow and transport processes at catchment scale. Journal of Hydrology, 299(1), 136-158.

[163] Zehe, E., Maurer, T., Ihringer, J., & Plate, E. (2001). Modeling water flow and mass transport in a loess catchment. Physics and Chemistry of the Earth, Part B: Hydrology, Oceans and Atmosphere, 26(7), 487-507.

[164] Van der Hoven, S. J., Solomon, D. K., & Moline, G. R. (2002). Numerical simulation of unsaturated flow along preferential pathways: implications for the use of mass balance calculations for isotope storm hydrograph separation. Journal of Hydrology, 268(1), 214-233.

[165] Sudicky, E. A., Jones, J. P., Park, Y. J., Brookfield, A. E., & Colautti, D. (2008). Simulating complex flow and transport dynamics in an integrated surface-subsurface modeling framework. Geosciences Journal, 12(2), 107-122.

[166] Therrien, R., McLaren, R. G., Sudicky, E. A., & Panday, S. M. (2010). HydroGeoSphere: a three-dimensional numerical model describing fully-integrated subsurface and surface flow and solute transport. Groundwater Simulations Group, University of Waterloo, Waterloo, ON.

[167] Park, Y. J., Sudicky, E. A., Brookfield, A. E., & Jones, J. P. (2011). Hydrologic response of catchments to precipitation: Quantification of mechanical carriers and origins of water. Water Resources Research, 47(12).

[168] Šimůnek, J., van Genuchten, M. T., & Šejna, M. (2008). Development and applications of the HYDRUS and STANMOD software packages and related codes. Vadose Zone Journal, 7(2), 587-600.

[169] Kollet, S. J., & Maxwell, R. M. (2006). Integrated surface–groundwater flow modeling: A free-surface overland flow boundary condition in a parallel groundwater flow model. Advances in Water Resources, 29(7), 945-958.

[170] Camporese, M., Paniconi, C., Putti, M., & Orlandini, S. (2010). Surface-subsurface flow modeling with path-based runoff routing, boundary condition-based coupling, and assimilation of multisource observation data. Water Resources Research, 46(2).

[171] Weill, S., Mazzia, A., Putti, M., & Paniconi, C. (2011). Coupling water flow and solute transport into a physically-based surface–subsurface hydrological model. Advances in Water Resources, 34(1), 128-136.

[172] Engdahl, N. B., & Maxwell, R. M. (2014). Approximating groundwater age distributions using simple streamtube models and multiple tracers. Advances in Water Resources, 66, 19-31.

[173] Maxwell, R. M., Putti, M., Meyerhoff, S., Delfs, J. O., Ferguson, I. M., Ivanov, V., Kim, J., Kolditz, O., Kollet, S., Kumar, M., Lopez, S., Niu, J., Paniconi, C., Park, Y.J., Phanikumar, M.S., Shen, C., Sudicky, E.A. & Sulis, M. (2014). Surface-subsurface model intercomparison: A first set of benchmark results to diagnose integrated hydrology and feedbacks. Water resources research, 50(2), 1531-1549.

[174] Niu, J., & Phanikumar, M. S. (2015). Modeling watershed-scale solute transport using an integrated, process-based hydrologic model with applications to bacterial fate and transport. Journal of Hydrology, 529, 35-48.

[175] Dooge, J. C. (1986). Looking for hydrologic laws. Water Resources Research, 22(9S).

[176] Zehe, E., Ehret, U., Pfister, L., Blume, T., Schröder, B., Westhoff, M., Jackisch, C., Schymanski, S., Weiler, M., Schulz, K., Allroggen, N., Tronikce, J., van Schaik, L., Dietrich, P., Scherer, U., Eccard, J., Wulfmeyer, V. & Kleidon, A. (2014). HESS Opinions: From response units to functional units: a thermodynamic reinterpretation of the HRU concept to link spatial organization and functioning of intermediate scale catchments. Hydrology and Earth System Sciences, 18(11), 4635-4655.

[177] Beven, K. (1989). Changing ideas in hydrology—the case of physically-based models. Journal of hydrology, 105(1), 157-172.

[178] Beven, K. J. (2001). Dalton medal lecture: How far can we go in distributed hydrological modelling? Hydrology and Earth System Sciences, 5(1), 1-12.

[179] Grayson, R. B., Moore, I. D., & McMahon, T. A. (1992). Physically based hydrologic modeling: 2. Is the concept realistic?. Water resources research, 28(10), 2659-2666.

[180] O'Connell, P. E., & Todini, E. (1996). Modelling of rainfall, flow and mass transport in hydrological systems: an overview. Journal of Hydrology, 175(1), 3-16.

[181] Beven, K. J. (2000). Uniqueness of place and process representations in hydrological modelling. Hydrology and Earth System Sciences Discussions, 4(2), 203-213.

[182] Blöschl, G. (2001). Scaling in hydrology. Hydrological Processes, 15(4), 709-711.

[183] Sivapalan, M. (2005). Pattern, process and function: elements of a unified theory of hydrology at the catchment scale. Encyclopedia of hydrological sciences.

[184] McDonnell, J. J., Sivapalan, M., Vaché, K., Dunn, S., Grant, G., Haggerty, R., et al. (2007). Moving beyond heterogeneity and process complexity: A new vision for watershed hydrology. Water Resources Research, 43(7).

[185] Hrachowitz, M., Savenije, H. H. G., Blöschl, G., McDonnell, J. J., Sivapalan, M., Pomeroy, J. W., et al. (2013). A decade of Predictions in Ungauged Basins (PUB)—a review. Hydrological Sciences Journal, 58(6), 1198-1255.

[186] Gupta, H. V., Clark, M. P., Vrugt, J. A., Abramowitz, G., & Ye, M. (2012). Towards a comprehensive assessment of model structural adequacy. Water Resources Research, 48(8).

[187] Beven, K. (2006). Searching for the Holy Grail of scientific hydrology: Q t=(S, R,? t) A as closure. Hydrology and Earth System Sciences 10, 609-618.

[188] Zehe, E., Elsenbeer, H., Lindenmaier, F., Schulz, K., & Blöschl, G. (2007). Patterns of predictability in hydrological threshold systems. Water Resources Research, 43(7).

[189] Yeh, W. W. G. (1986). Review of parameter identification procedures in groundwater hydrology: The inverse problem. Water Resources Research, 22(2), 95-108.

[190] Beven, K. (2006). A manifesto for the equifinality thesis. Journal of hydrology, 320(1), 18-36.

[191] Kirchner, J. W. (2006). Getting the right answers for the right reasons: Linking measurements, analyses, and models to advance the science of hydrology. Water Resources Research, 42(3).

[192] Bergström, S., 1976. Development and application of a conceptual runoff model for Scandinavian catchments. Norrköping: SMHI Reports RHO, no. 7.

[193] Clark, M. P., Slater, A. G., Rupp, D. E., Woods, R. A., Vrugt, J. A., Gupta, H. V., et al. (2008). Framework for Understanding Structural Errors (FUSE): A modular framework to diagnose differences between hydrological models. Water Resources Research, 44(12).

[194] Fenicia, F., Kavetski, D., & Savenije, H. H. (2011). Elements of a flexible approach for conceptual hydrological modeling: 1. Motivation and theoretical development. Water Resources Research, 47(11).

[195] Fenicia, F., Kavetski, D., Savenije, H. H., Clark, M. P., Schoups, G., Pfister, L., & Freer, J. (2014). Catchment properties, function, and conceptual model representation: is there a correspondence?. Hydrological Processes, 28(4), 2451-2467.

[196] Knudsen, J., Thomsen, A., & Refsgaard, J. C. (1986). WATBAL. Hydrology Research, 17(4-5), 347-362.

[197] Flügel, W. A. (1995). Delineating Hydrological Response Units (HRU's) by GIS analysis for regional hydrological modelling using PRMS/MMS in the drainage basin of the River Bröl, Germany. Hydrological Processes, 9, 423-436.

[198] Beven, K., & Freer, J. (2001). A dynamic topmodel. Hydrological processes, 15(10), 1993-2011.

[199] Winter, T. C. (2001). The Concept of Hydrologic Landscapes. Journal of the American Water Resources Association, 37, 335-349.

[200] Schmocker-Fackel, P., Naef, F., & Scherrer, S. (2007). Identifying runoff processes on the plot and catchment scale. Hydrology and Earth System Sciences, 11(2), 891-906.

[201] Gao, H., Hrachowitz, M., Fenicia, F. F., Gharari, S., & Savenije, H. H. G. (2014). Testing the realism of a topography-driven model (FLEX-Topo) in the nested catchments of the Upper Heihe, China. Hydrology and Earth System Sciences, 18, 2014.

[202] Gharari, S., Hrachowitz, M., Fenicia, F., Gao, H., & Savenije, H. H. G. (2014). Using expert knowledge to increase realism in environmental system models can dramatically reduce the need for calibration. Hydrology and Earth System Sciences, 18(12), 4839-4859.

[203] Samaniego, L., Kumar, R., & Attinger, S. (2010). Multiscale parameter regionalization of a grid-based hydrologic model at the mesoscale. Water Resources Research, 46(5).

[204] Hrachowitz, M., Fovet, O., Ruiz, L., Euser, T., Gharari, S., Nijzink, R., Freer, J., Savenije, H.H.G., & Gascuel-Odoux, C. (2014). Process consistency in models: The importance of system signatures, expert knowledge, and process complexity. Water Resources Research, 50(9), 7445-7469.

[205] Sivapalan, M. (2005). Pattern, process and function: elements of a unified theory of hydrology at the catchment scale. Encyclopedia of hydrological sciences.

[206] Gupta, H. V., Wagener, T., & Liu, Y. (2008). Reconciling theory with observations: elements of a diagnostic approach to model evaluation. Hydrological Processes, 22(18), 3802-3813.

[207] Fenicia, F., McDonnell, J. J., & Savenije, H. H. (2008). Learning from model improvement: On the contribution of complementary data to process understanding. Water Resources Research, 44(6).

[208] Weiler, M., McGlynn, B. L., McGuire, K. J., & McDonnell, J. J. (2003). How does rainfall become runoff? A combined tracer and runoff transfer function approach. Water Resources Research, 39(11).

[209] Heidbüchel, I., Troch, P. A., Lyon, S. W., & Weiler, M. (2012). The master transit time distribution of variable flow systems. Water Resources Research, 48(6).

[210] Zuber, A. (1986). On the interpretation of tracer data in variable flow systems. Journal of Hydrology, 86(1), 45-57.

[211] Kirchner, J. W. (2009). Catchments as simple dynamical systems: Catchment characterization, rainfall-runoff modeling, and doing hydrology backward. Water Resources Research, 45(2).

[212] Birkel, C., Soulsby, C., & Tetzlaff, D. (2015). Conceptual modelling to assess how the interplay of hydrological connectivity, catchment storage and tracer dynamics controls nonstationary water age estimates. Hydrological Processes.

[213] Barnes, C. J., & Bonell, M. (1996). Application of unit hydrograph techniques to solute transport in catchments. Hydrological Processes, 10(6), 793-802.

[214] Dunn, S. M., McDonnell, J. J., & Vaché, K. B. (2007). Factors influencing the residence time of catchment waters: A virtual experiment approach. Water Resources Research, 43(6).

[215] Shaw, S. B., Harpold, A. A., Taylor, J. C., & Walter, M. T. (2008). Investigating a high resolution, stream chloride time series from the Biscuit Brook catchment, Catskills, NY. Journal of Hydrology, 348(3), 245-256.

[216] Birkel, C., Tetzlaff, D., Dunn, S. M., & Soulsby, C. (2010). Towards a simple dynamic process conceptualization in rainfall–runoff models using multi-criteria calibration and tracers in temperate, upland catchments. Hydrological Processes, 24(3), 260-275.

[217] Birkel, C., Soulsby, C., & Tetzlaff, D. (2011). Modelling catchment-scale water storage dynamics: reconciling dynamic storage with tracer-inferred passive storage. Hydrological Processes, 25(25), 3924-3936.

[218] Capell, R., Tetzlaff, D., & Soulsby, C. (2012). Can time domain and source area tracers reduce uncertainty in rainfall-runoff models in larger heterogeneous catchments?. Water Resources Research, 48(9).

[219] McMillan, H., Tetzlaff, D., Clark, M., & Soulsby, C. (2012). Do time-variable tracers aid the evaluation of hydrological model structure? A multimodel approach. Water Resources Research, 48(5).

[220] Benettin, P., Velde, Y., Zee, S. E., Rinaldo, A., & Botter, G. (2013). Chloride circulation in a lowland catchment and the formulation of transport by travel time distributions. Water Resources Research, 49(8), 4619-4632.

[221] Benettin, P., Kirchner, J. W., Rinaldo, A., & Botter, G. (2015). Modeling chloride transport using travel time distributions at Plynlimon, Wales. Water Resources Research.

[222] Davies, J., Beven, K., Rodhe, A., Nyberg, L., & Bishop, K. (2013). Integrated modeling of flow and residence times at the catchment scale with multiple interacting pathways. Water resources research, 49(8), 4738-4750.

[223] Gassman, P. W., Reyes, M. R., Green, C. H., & Arnold, J. G. (2007). The soil and water assessment tool: historical development, applications, and future research directions. Trans. ASAE, 50(4), 1211–1250.

[224] Howden, N. J. K., Burt, T. P., Mathias, S. A., Worrall, F., & Whelan, M. J. (2011). Modelling long-term diffuse nitrate pollution at the catchment-scale: Data, parameter and epistemic uncertainty. Journal of Hydrology, 403(3-4), 337–351.

[225] Burt, T. P., Howden, N. J. K., Worrall, F., & McDonnell, J. J. (2011). On the value of long-term, low-frequency water quality sampling: avoiding throwing the baby out with the bathwater. Hydrological Processes, 25(5), 828–830.

[226] Burt, T. P., Howden, N. J. K., & Worrall, F. (2013). On the importance of very long-term water quality records. Wiley Interdisciplinary Reviews: Water, 1(1), 41–48.

[227] Whitehead, P. G., Costigan, P. A., Bridges, E. M., Powlson, D. S., Goss, M. J., & Goulding, K. (1990). Modelling Nitrate from Agriculture into Public Water Supplies. Philosophical Transactions of the Royal Society of London B: Biological Sciences, 329(1255), 403-410.

[228] Green, C. T., Böhlke, J. K., Bekins, B. A., & Phillips, S. P. (2010). Mixing effects on apparent reaction rates and isotope fractionation during denitrification in a heterogeneous aquifer. Water Resources Research, 46(8).

[229] Dontsova, K., Steefel, C. I., Desilets, S., Thompson, A., & Chorover, J. (2009). Solid phase evolution in the Biosphere 2 hillslope experiment as predicted by modeling of hydrologic and geochemical fluxes. Hydrology and Earth System Sciences, 13(12), 2273-2286.

[230] Robertson, W. D. (1995). Development of steady-state phosphate concentrations in septic system plumes. Journal of Contaminant Hydrology, 19(4), 289–305.

[231] Parkhurst, D.L., and Appelo, C.A.J., 2013, Description of input and examples for PHREEQC version 3—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Techniques and Methods, book 6, chap. A43, 497 p.

[232] Frei, S., Knorr, K. H., Peiffer, S., & Fleckenstein, J. H. (2012). Surface micro-topography causes hot spots of biogeochemical activity in wetland systems: A virtual modeling experiment. Journal of Geophysical Research: Biogeosciences (2005–2012), 117(G4).

[233] Goddéris, Y., François, L. M., Probst, A., Schott, J., Moncoulon, D., Labat, D., & Viville, D. (2006). Modelling weathering processes at the catchment scale: The WITCH numerical model. Geochimica et Cosmochimica Acta, 70(5), 1128-1147.

[234] Arnold, J. G., Srinivasan, R., Muttiah, R. S., & Williams, J. R. (1998). Large area hydrologic modeling and assessment part I: Model development1.

[235] Neitsch, S. L., Arnold, J. G., Kiniry, J. R., & Williams, J. R. (2011). Soil and water assessment tool theoretical documentation version 2009. Texas Water Resources Institute.

[236] Wade, A. J., Durand, P., Beaujouan, V., Wessel, W. W., Raat, K. J., Whitehead, P. G., et al. (2002). A nitrogen model for European catchments: INCA, new model structure and equations. Hydrology and Earth System Sciences, 6(3), 559-582.

[237] Zhang, Y., Li, C., Trettin, C. C., Li, H., & Sun, G. (2002). An integrated model of soil, hydrology, and vegetation for carbon dynamics in wetland ecosystems. Global Biogeochemical Cycles, 16(4).

[238] Lindström, G., Pers, C., Rosberg, J., Strömqvist, J., & Arheimer, B. (2010). Development and testing of the HYPE (Hydrological Predictions for the Environment) water quality model for different spatial scales. Hydrology Research, 41, 295-319.

[239] Krysanova, V., & Arnold, J. G. (2008). Advances in ecohydrological modelling with SWAT—a review. Hydrological Sciences Journal, 53(5), 939-947.

[240] McClain, M. E., Boyer, E. W., Dent, C. L., Gergel, S. E., Grimm, N. B., Groffman, P. M., et al. (2003). Biogeochemical hot spots and hot moments at the interface of terrestrial and aquatic ecosystems. Ecosystems, 6(4), 301-312.

[241] Medici, C., Bernal, S., Butturini, A., Sabater, F., Martin, M., Wade, A. J., & Frances, F. (2010). Modelling the inorganic nitrogen behaviour in a small Mediterranean forested catchment, Fuirosos (Catalonia). Hydrology and Earth System Sciences, 14(2), 223-237.

[242] Spence, C., & Woo, M. K. (2003). Hydrology of subarctic Canadian shield: soil-filled valleys. Journal of Hydrology, 279(1), 151-166.

[243] Tromp-van Meerveld, H. J., & McDonnell, J. J. (2006). Threshold relations in subsurface stormflow: 1. A 147-storm analysis of the Panola hillslope. Water Resources Research, 42(2).

[244] McDonnell, J. J. (2014). The two water worlds hypothesis: ecohydrological separation of water between streams and trees?. Wiley Interdisciplinary Reviews: Water, 1(4), 323-329.

[245] Suckow, A. (2014). The age of groundwater–Definitions, models and why we do not need this term. Applied Geochemistry, 50, 222-230.

[246] McGuire, K. J., & McDonnell, J. J. (2006). A review and evaluation of catchment transit time modeling. Journal of Hydrology, 330(3), 543-563.

[247] Małoszewski, P., & Zuber, A. (1982). Determining the turnover time of groundwater systems with the aid of environmental tracers: 1. Models and their applicability. Journal of hydrology, 57(3), 207-231.

[248] Shapiro, A. M., & Cvetkovic, V. D. (1988). Stochastic analysis of solute arrival time in heterogeneous porous media. Water Resources Research, 24(10), 1711-1718.

[249] Cvetkovic, V. D., & Shapiro, A. M. (1990). Mass arrival of sorptive solute in heterogeneous porous media. Water Resources Research, 26(9), 2057-2067.

[250] Rodriguez-Iturbe, I., & Valdes, J. B. (1979). The geomorphologic structure of hydrologic response. Water Resources Research, 15(6), 1409-1420.

[251] Gupta, V. K., Waymire, E., & Wang, C. T. (1980). A representation of an instantaneous unit hydrograph from geomorphology. Water Resources Research, 16(5), 855-862.

[252] Benettin, P., Rinaldo, A., & Botter, G. (2015). Tracking residence times in hydrological systems: forward and backward formulations. Hydrological Processes.

[253] Calabrese, S., & Porporato, A. (2015). Linking age, survival and transit time distributions. arXiv preprint arXiv:1507.00366.

[254] Frisbee, M. D., Phillips, F. M., Weissmann, G. S., Brooks, P. D., Wilson, J. L., Campbell, A. R., & Liu, F. (2012). Unraveling the mysteries of the large watershed black box: Implications for the streamflow response to climate and landscape perturbations. Geophysical Research Letters, 39(1).

[255] Duffy, C.J. (2010). Dynamic modelling of concentration-age-discharge in watersheds. Hydrological Processes, 24, 1711-1718.

[256] Rinaldo, A., Beven, K. J., Bertuzzo, E., Nicotina, L., Davies, J., Fiori, A., Russo, D., & Botter, G. (2011). Catchment travel time distributions and water flow in soils. Water Resources Research, 47(7).

[257] Vogel, T., Sanda, M., Dusek, J., Dohnal, M., & Votrubova, J. (2010). Using oxygen-18 to study the role of preferential flow in the formation of hillslope runoff. Vadose Zone Journal, 9(2), 252-259.

[258] Legout, A., Legout, C., Nys, C., & Dambrine, E. (2009). Preferential flow and slow convective chloride transport through the soil of a forested landscape (Fougères, France). Geoderma, 151(3), 179-190.

[259] Klaus, J., & McDonnell, J. J. (2013). Hydrograph separation using stable isotopes: Review and evaluation. Journal of Hydrology, 505, 47-64.

[260] Harman, C. J., & Kim, M. (2014). An efficient tracer test for time-variable transit time distributions in periodic hydrodynamic systems. Geophysical Research Letters, 41(5), 1567-1575.

[261] Peters, N. E., Burns, D. A., & Aulenbach, B. T. (2014). Evaluation of high-frequency mean stream water transit-time estimates using groundwater age and dissolved silica concentrations in a small forested watershed. Aquatic geochemistry, 20(2-3), 183-202.

[262] Weiler, M., & Naef, F. (2003). An experimental tracer study of the role of macropores in infiltration in grassland soils. Hydrological Processes, 17(2), 477-493.

[263] Legout, C., Molenat, J., Aquilina, L., Gascuel-Odoux, C., Faucheux, M., Fauvel, Y., & Bariac, T. (2007). Solute transfer in the unsaturated zone-groundwater continuum of a headwater catchment. Journal of Hydrology, 332(3), 427-441.

[264] Diskin, M. H., & Boneh, A. (1975). Determination of an optimal IUH for linear, time invariant systems from multi-storm records. Journal of Hydrology, 24(1), 57-76.

[265] Beven, K. J. (2010). Preferential flows and travel time distributions: defining adequate hypothesis tests for hydrological process models. Hydrological Processes, 24(12), 1537-1547.

[266] Kirchner, J. W., Feng, X., & Neal, C. (2000). Fractal stream chemistry and its implications for contaminant transport in catchments. Nature, 403(6769), 524-527.Kirchner et al. (2000)

[267] Stewart, M. K., Morgenstern, U., & McDonnell, J. J. (2010). Truncation of stream residence time: how the use of stable isotopes has skewed our concept of streamwater age and origin. Hydrological Processes, 24(12), 1646-1659.

[268] Frisbee, M. D., Wilson, J. L., Gomez-Velez, J. D., Phillips, F. M., & Campbell, A. R. (2013). Are we missing the tail (and the tale) of residence time distributions in watersheds?. Geophysical Research Letters, 40(17), 4633-4637.

[269] Maloszewski, P., Rauert, W., Trimborn, P., Herrmann, A., & Rau, R. (1992). Isotope hydrological study of mean transit times in an alpine basin (Wimbachtal, Germany). Journal of Hydrology, 140(1), 343-360.

[270] Vitvar, T., & Balderer, W. (1997). Estimation of mean water residence times and runoff generation by ^{18}O measurements in a Pre-Alpine catchment (Rietholzbach, Eastern Switzerland). Applied Geochemistry, 12(6), 787-796.

[271] McGlynn, B., McDonnell, J., Stewart, M., & Seibert, J. (2003). On the relationships between catchment scale and streamwater mean residence time. Hydrological Processes, 17(1), 175-181.

[272] McGuire, K. J., McDonnell, J. J., Weiler, M., Kendall, C., McGlynn, B. L., Welker, J. M., & Seibert, J. (2005). The role of topography on catchment-scale water residence time. Water Resources Research, 41(5).

[273] Broxton, P. D., Troch, P. A., & Lyon, S. W. (2009). On the role of aspect to quantify water transit times in small mountainous catchments. Water Resources Research, 45(8).

[274] Hrachowitz, M., Soulsby, C., Tetzlaff, D., Dawson, J. J. C., & Malcolm, I. A. (2009). Regionalization of transit time estimates in montane catchments by integrating landscape controls. Water Resources Research, 45(5).

[275] Tetzlaff, D., Seibert, J., & Soulsby, C. (2009). Inter-catchment comparison to assess the influence of topography and soils on catchment transit times in a geomorphic province; the Cairngorm mountains, Scotland. Hydrological Processes, 23(13), 1874-1886.

[276] Kim, S., & Jung, S. (2014). Estimation of mean water transit time on a steep hillslope in South Korea using soil moisture measurements and deuterium excess. Hydrological Processes, 28(4), 1844-1857.

[277] Timbe, E., Windhorst, D., Crespo, P., Frede, H. G., Feyen, J., & Breuer, L. (2014). Understanding uncertainties when inferring mean transit times of water trough tracer-based lumped-parameter models in Andean tropical montane cloud forest catchments. Hydrol. Earth Syst. Sci, 18, 1503-1523.

[278] Niemi, A. J. (1977). Residence time distributions of variable flow processes. The International Journal of Applied Radiation and Isotopes, 28(10), 855-860.

[279] Roa-García, M. C., & Weiler, M. (2010). Integrated response and transit time distributions of watersheds by combining hydrograph separation and long-term transit time modeling. Hydrology and Earth System Sciences, 14(8), 1537-1549.

[280] Seeger, S., & Weiler, M. (2014). Lumped convolution integral models revisited: on the meaningfulness of inter catchment comparisons. Hydrology and Earth System Sciences Discussions, 11(6), 6753-6803.

[281] Stockinger, M. P., Bogena, H. R., Lücke, A., Diekkrüger, B., Weiler, M., & Vereecken, H. (2014). Seasonal soil moisture patterns: Controlling transit time distributions in a forested headwater catchment. Water resources research, 50(6), 5270-5289.

[282] Heidbüchel, I., Troch, P. A., & Lyon, S. W. (2013). Separating physical and meteorological controls of variable transit times in zero-order catchments. Water Resources Research, 49(11), 7644-7657.

[283] Hrachowitz, M., Soulsby, C., Tetzlaff, D., Malcolm, I. A., & Schoups, G. (2010). Gamma distribution models for transit time estimation in catchments: Physical interpretation of parameters and implications for time-variant transit time assessment. Water Resources Research, 46(10).

[284] Birkel, C., Tetzlaff, D., Dunn, S. M., & Soulsby, C. (2011). Using lumped conceptual rainfall–runoff models to simulate daily isotope variability with fractionation in a nested mesoscale catchment. Advances in Water Resources, 34(3), 383-394.

[285] Birkel, C., Soulsby, C., & Tetzlaff, D. (2014). Developing a consistent process-based conceptualization of catchment functioning using measurements of internal state variables. Water Resources Research, 50(4), 3481-3501.

[286] Soulsby, C., Birkel, C., Geris, J., Dick, J., Tunaley, C., & Tetzlaff, D. (2015). Stream water age distributions controlled by storage dynamics and nonlinear hydrologic connectivity: Modeling with high-resolution isotope data. Water Resources Research.

[287] Birkel, C., & Soulsby, C. (2015). Advancing tracer-aided rainfall–runoff modelling: a review of progress, problems and unrealised potential. Hydrological Processes.

[288] Abbott, M. B., Bathurst, J. C., Cunge, J. A., O'Connell, P. E., & Rasmussen, J. (1986). An introduction to the European Hydrological System—Systeme Hydrologique Europeen,“SHE”, 1: History and philosophy of a physically-based, distributed modelling system. Journal of hydrology, 87(1), 45-59.

[289] Andréassian, V., Le Moine, N., Perrin, C., Ramos, M. H., Oudin, L., Mathevet, T., Lerat, J., & Berthet, L. (2012). All that glitters is not gold: the case of calibrating hydrological models. Hydrological Processes, 26(14), 2206-2210.

[290] Gharari, S., Shafiei, M., Hrachowitz, M., Fenicia, F., Gupta, H. V., & Savenije, H. H. G. (2014). A strategy for “constraint-based” parameter specification for environmental models. Hydrology and Earth System Sciences, 18, 4861-4870.

[291] Uhlenbrook, S., Roser, S., & Tilch, N. (2004). Hydrological process representation at the meso-scale: the potential of a distributed, conceptual catchment model. Journal of Hydrology, 291(3), 278-296.

[292] Detty, J., and K. McGuire (2010), Topographic controls on shallow groundwater dynamics: implications of hydrologic connectivity between hillslopes and riparian zones in a till mantled catchment, Hydrological Processes, 24(16), 2222-2236.

[293] Bowen, G. J., & Good, S. P. (2015). Incorporating water isoscapes in hydrological and water resource investigations. Wiley Interdisciplinary Reviews: Water, 2(2), 107-119.

[294] Stewart, M. K., & Morgenstern, U. (2016). Importance of tritium-based transit times in hydrological systems. Wiley Interdisciplinary Reviews: Water, 3(2), 145-154.

[295] Fenicia, F., Wrede, S., Kavetski, D., Pfister, L., Hoffmann, L., Savenije, H. H., & McDonnell, J. J. (2010). Assessing the impact of mixing assumptions on the estimation of streamwater mean residence time. Hydrological Processes, 24(12), 1730-1741.

[296] Botter, G., Bertuzzo, E., & Rinaldo, A. (2010). Transport in the hydrologic response: Travel time distributions, soil moisture dynamics, and the old water paradox. Water Resources Research, 46(3).

[297] Velde, Y., Heidbüchel, I., Lyon, S. W., Nyberg, L., Rodhe, A., Bishop, K., & Troch, P. A. (2014). Consequences of mixing assumptions for time-variable travel time distributions. Hydrological Processes.

[298] Soulsby, C., Birkel, C., & Tetzlaff, D. (2015). Characterising the age distribution of catchment evaporative losses. Hydrological Processes (in print).

[299] Evaristo, J., Jasechko, S., & McDonnell, J. J. (2015). Global separation of plant transpiration from groundwater and streamflow. Nature, 525(7567), 91-94.

[300] Birkel, C., Dunn, S. M., Tetzlaff, D., & Soulsby, C. (2010). Assessing the value of high-resolution isotope tracer data in the stepwise development of a lumped conceptual rainfall–runoff model. Hydrological Processes, 24(16), 2335-2348.

[301] Benettin, P., Bailey, S.W., Campbell, J.L., Green, M.B., Rinaldo, A., Likens, G.E., McGuire, K.J., & Botter, G. (2016). Linking water age and solute dynamics in streamflow at the Hubbard Brook Experimental Forest, NH, USA. Water Resources Research (in print).

[302] Groffman, P. M., Butterbach-Bahl, K., Fulweiler, R. W., Gold, A. J., Morse, J. L., Stander, E. K., ... & Vidon, P. (2009). Challenges to incorporating spatially and temporally explicit phenomena (hotspots and hot moments) in denitrification models. Biogeochemistry, 93(1-2), 49-77.

[303] Pinay, G., Peiffer, S., De Dreuzy, J. R., Krause, S., Hannah, D. M., Fleckenstein, J. H., Sebilo, M., Bishop, K. & Hubert-Moy, L. (2015). Upscaling nitrogen removal capacity from local hotspots to low stream orders' drainage basins. Ecosystems, 18(6), 1101-1120.

[304] Gupta, H. V., Clark, M. P., Vrugt, J. A., Abramowitz, G., & Ye, M. (2012). Towards a comprehensive assessment of model structural adequacy. Water Resources Research, 48(8).

[305] White, E. D., Easton, Z. M., Fuka, D. R., Collick, A. S., Adgo, E., McCartney, M., ... & Steenhuis, T. S. (2011). Development and application of a physically based landscape water balance in the SWAT model. Hydrological Processes, 25(6), 915-925.

[306] McGuire, K. J., Weiler, M., & McDonnell, J. J. (2007). Integrating tracer experiments with modeling to assess runoff processes and water transit times. Advances in Water Resources, 30(4), 824-837.

[307] McGuire, K. J., & McDonnell, J. J. (2010). Hydrological connectivity of hillslopes and streams: Characteristic time scales and nonlinearities. Water Resources Research, 46(10).

[308] Aubert, A. H., Gascuel-Odoux, C., Gruau, G., Akkal, N., Faucheux, M., Fauvel, Y., et al. (2013). Solute transport dynamics in small, shallow groundwater-dominated agricultural catchments: insights from a high-frequency, multisolute 10 yr-long monitoring study. Hydrology and Earth System Sciences, 17(4), 1379-1391.

[309] Aubert, A. H., Gascuel-Odoux, C., & Merot, P. (2013). Annual hysteresis of water quality: A method to analyse the effect of intra-and inter-annual climatic conditions. Journal of Hydrology, 478, 29-39.

[310] Klaus, J., Chun, K. P., McGuire, K. J., & McDonnell, J. J. (2015). Temporal dynamics of catchment transit times from stable isotope data. Water Resources Research.

[311] Selle, B., Lange, H., Lischeid, G., & Hauhs, M. (2015). Transit times of water under steady stormflow conditions in the Gårdsjön G1 catchment. Hydrological Processes.

[312] Cvetkovic, V., Carstens, C., Selroos, J. O., & Destouni, G. (2012). Water and solute transport along hydrological pathways. Water Resources Research, 48(6).

[313] Soltani, S. S., & Cvetkovic, V. (2013). On the distribution of water age along hydrological pathways with transient flow. Water Resources Research, 49(9), 5238-5245.

[314] Destouni, G., & Cvetkovic, V. (1989). The effect of heterogeneity on large scale solute transport in the unsaturated zone. Nordic hydrology, 20(1), 43-52.

[315] Fiori, A., & Russo, D. (2008). Travel time distribution in a hillslope: Insight from numerical simulations. Water Resources Research, 44(12).

[316] Fiori, A., Russo, D., & Di Lazzaro, M. (2009). Stochastic analysis of transport in hillslopes: Travel time distribution and source zone dispersion. Water Resources Research, 45(8).

[317] Heathwaite, A. L., Quinn, P. F., & Hewett, C. J. M. (2005). Modelling and managing critical source areas of diffuse pollution from agricultural land using flow connectivity simulation. Journal of Hydrology, 304(1), 446-461.

[318] Poor, C. J., & McDonnell, J. J. (2007). The effects of land use on stream nitrate dynamics. Journal of Hydrology, 332(1), 54-68.

[319] Kirchner, J. W., Feng, X., & Neal, C. (2001). Catchment-scale advection and dispersion as a mechanism for fractal scaling in stream tracer concentrations. Journal of hydrology, 254(1), 82-101.

[320] Botter, G., Bertuzzo, E., Bellin, A., & Rinaldo, A. (2005). On the Lagrangian formulations of reactive solute transport in the hydrologic response. Water resources research, 41(4).

[321] Fovet, O., Ruiz, L., Faucheux, M., Molénat, J., Sekhar, M., Vertes, F., Aqilina, L., Gascuel-Odoux, C., & Durand, P. (2015). Using long time series of agricultural-derived nitrates for estimating catchment transit times. Journal of Hydrology, 522, 603-617.

[322] McDonnell, J. J., McGuire, K., Aggarwal, P., Beven, K. J., Biondi, D., Destouni, G., et al. (2010). How old is streamwater? Open questions in catchment transit time conceptualization, modelling and analysis. Hydrological Processes, 24(12), 1745-1754.

[323] M'Kendrick, A. G. (1925). Applications of mathematics to medical problems. Proceedings of the Edinburgh Mathematical Society, 44, 98-130.

[324] Foerster, H. V. (1959). Some remarks on changing populations. The kinetics of cellular proliferation, 382-407.

Figure captions

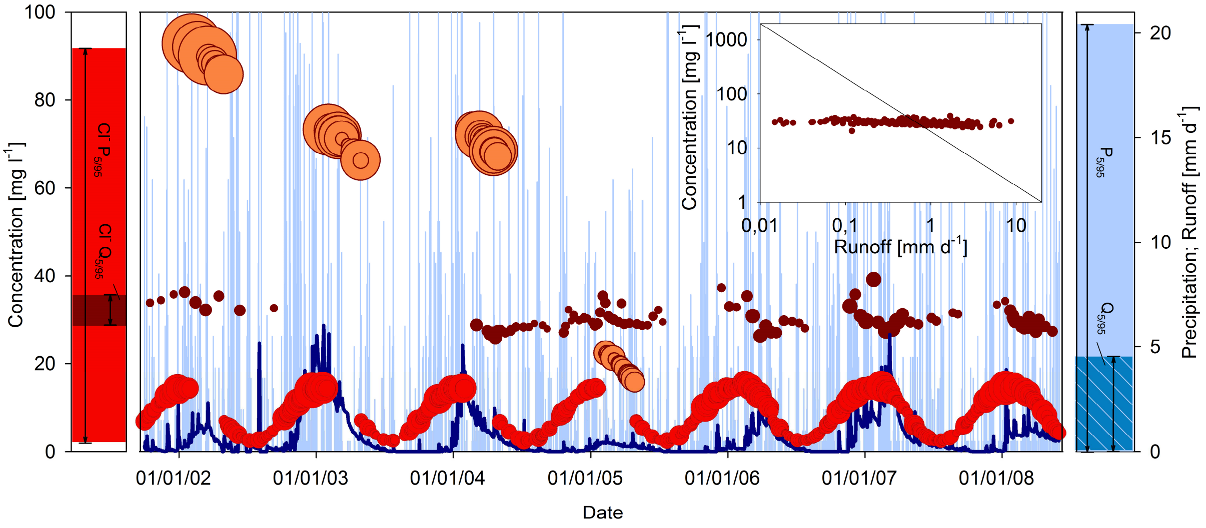


Figure 1: Daily precipitation (light blue), runoff (dark blue), observed fertilizer-derived Cl^- (orange circles) and precipitation-derived Cl^- input concentrations (red circles), as well as Cl^- concentrations in runoff (dark red circles) for the small, agriculturally managed Kerrien catchment in France (see Ref.43). Note that the circles sizes indicate the Cl^- mass flux relative to the largest mass flux during the observation period. The bars on the sides indicate the 5/95th interquantile range for Cl^- input concentrations (red), Cl^- concentrations in runoff (dark red), precipitation (light blue) and runoff (blue). The inset shows the runoff-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 α 1/Q), which would be the case if a catchment was a completely-mixed, homogeneous entity.

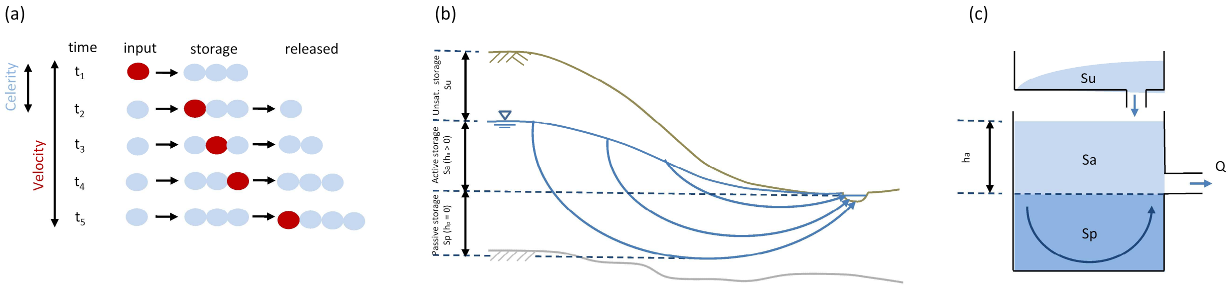
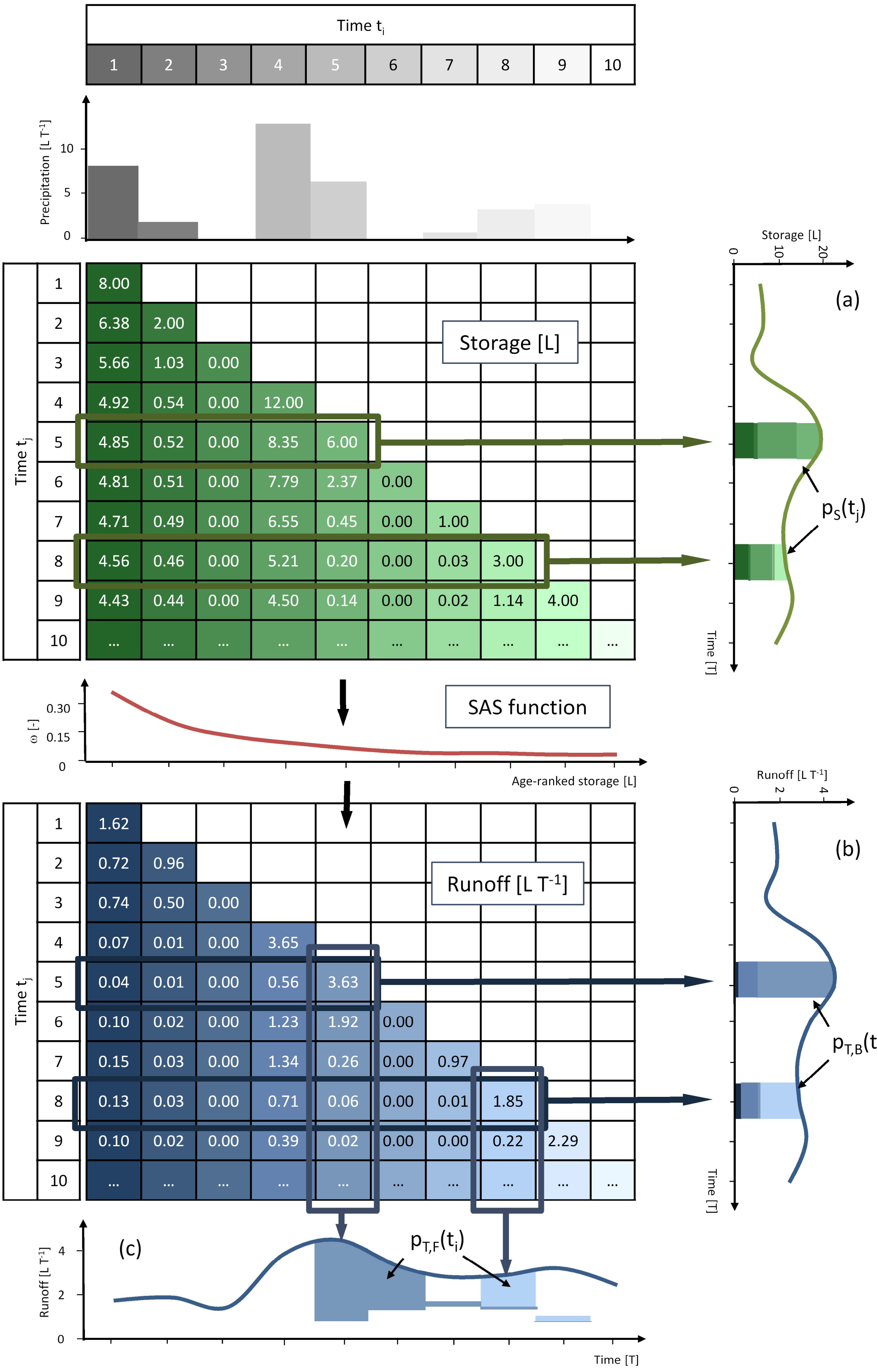


Figure 2: (a) Conceptualization of the difference between celerity-driven hydrological response and velocity-driven transport processes using the analogy of a game of billiards. A new input at t_1 (red ball) causes a disturbance of the system that propagates with a celerity and that generates a response (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.210), which (c) can be conceptualized in a model with a mixing volume below a given storage threshold. S_U represents the unsaturated zone whose non-linear behaviour is indicated by the curved line.



Storage [L]

Time t_j	1	2	3	4	5	6	7	8	9	10
1	8.00									
2	6.38	2.00								
3	5.66	1.03	0.00							
4	4.92	0.54	0.00	12.00						
5	4.85	0.52	0.00	8.35	6.00					
6	4.81	0.51	0.00	7.79	2.37	0.00				
7	4.71	0.49	0.00	6.55	0.45	0.00	1.00			
8	4.56	0.46	0.00	5.21	0.20	0.00	0.03	3.00		
9	4.43	0.44	0.00	4.50	0.14	0.00	0.02	1.14	4.00	
10	…	…	…	…	…	…	…	…	…	…

Runoff [L T⁻¹]

Time t_j	1	2	3	4	5	6	7	8	9	10
1	1.62									
2	0.72	0.96								
3	0.74	0.50	0.00							
4	0.07	0.01	0.00	3.65						
5	0.04	0.01	0.00	0.56	3.63					
6	0.10	0.02	0.00	1.23	1.92	0.00				
7	0.15	0.03	0.00	1.34	0.26	0.00	0.97			
8	0.13	0.03	0.00	0.71	0.06	0.00	0.01	1.85		
9	0.10	0.02	0.00	0.39	0.02	0.00	0.00	0.22	2.29	
10	…	…	…	…	…	…	…	…	…	…

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.52).

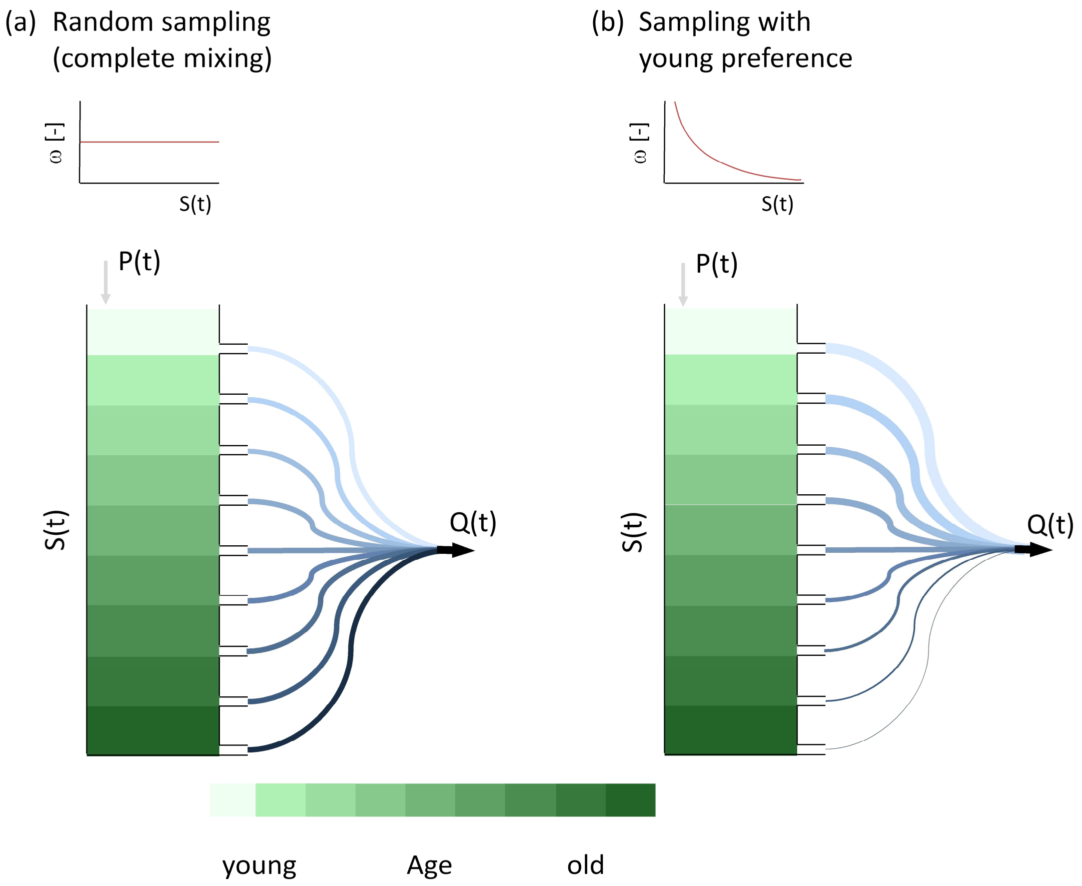


Figure 4: Illustrations of different conceptualized and simplified sampling (or mixing) processes. (a) a system characterized by a uniform storage age selection (SAS) function, sampling water with different ages from storage with equal probabilities (equivalent to the concept of a well- or completely mixed reservoir). (b) a system that releases water with preference for younger ages in storage (after ref.55). The symbol S indicates age-ranked storage, P represents the input into the storage (e.g. precipitation), 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.

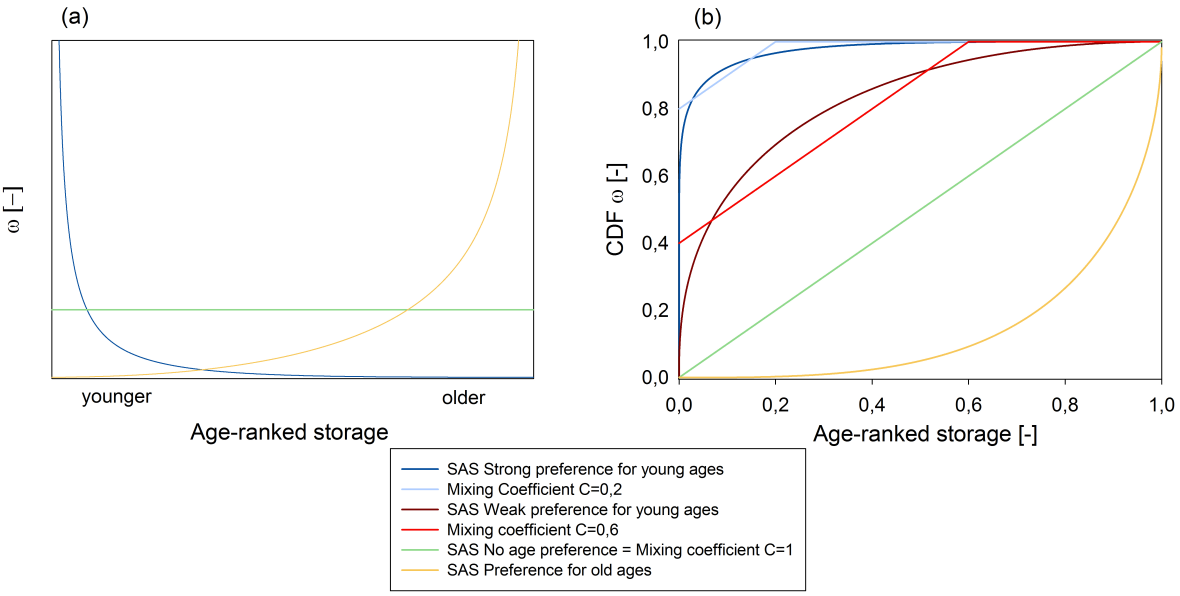


Figure 5: (a) Examples for SAS functions with no age preference (uniform distribution), as well as with preferences for young and old water, respectively. (b) Comparison of cumulative SAS functions (CDF) with the functionality of using the concept of mixing coefficients. Mixing coefficients C=0.2, 0.6 and 1 indicate examples for 20% and 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.

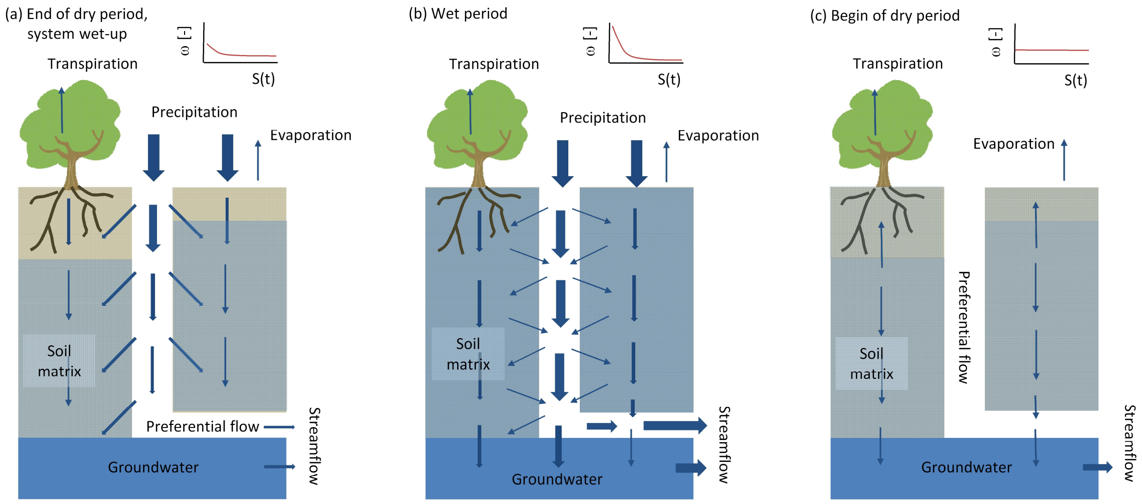


Figure 6: Schematic of changing mixing processes in the soil profile under different wetness conditions with likely shapes of SAS functions associated with these conditions. (a) at the end of dry periods, the moisture content in the soil matrix is depleted. Incoming precipitation is, due to the elevated 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.

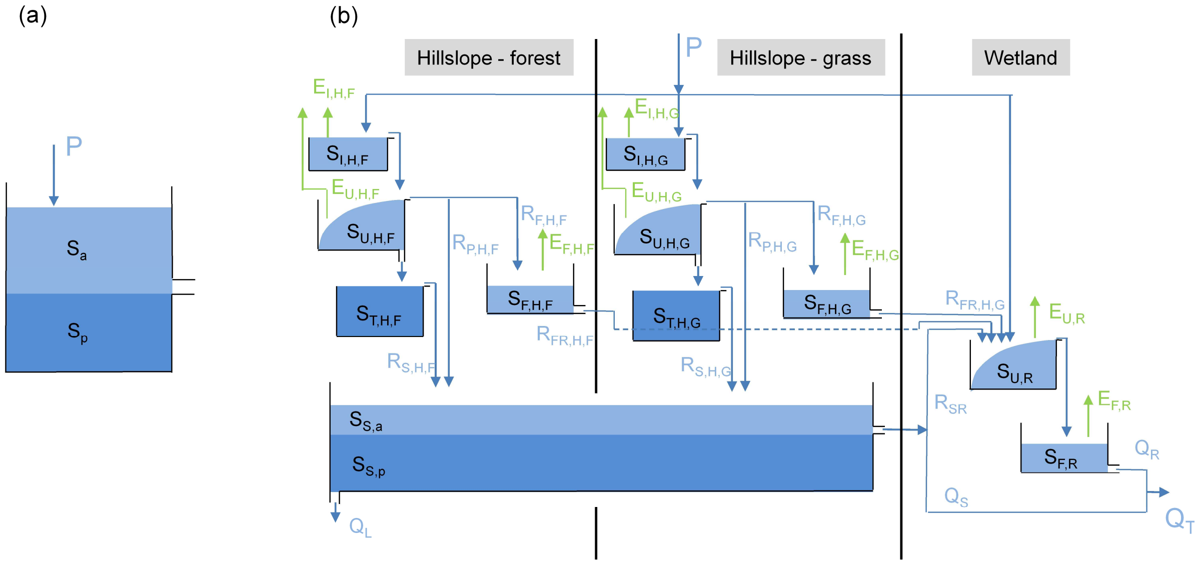


Figure 7: (a) Representation of a catchment as a lumped, completely mixed system, where P is precipitation and solute input, S_a is the hydrologically active storage that is controlled by the pressure head, S_p is a hydrologically passive mixing storage with constant water content. Evaporation is omitted 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 (p_S) for water stored in and transit time distributions (p_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, 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, 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, dark blue shades indicate hydrologically passive storage components.

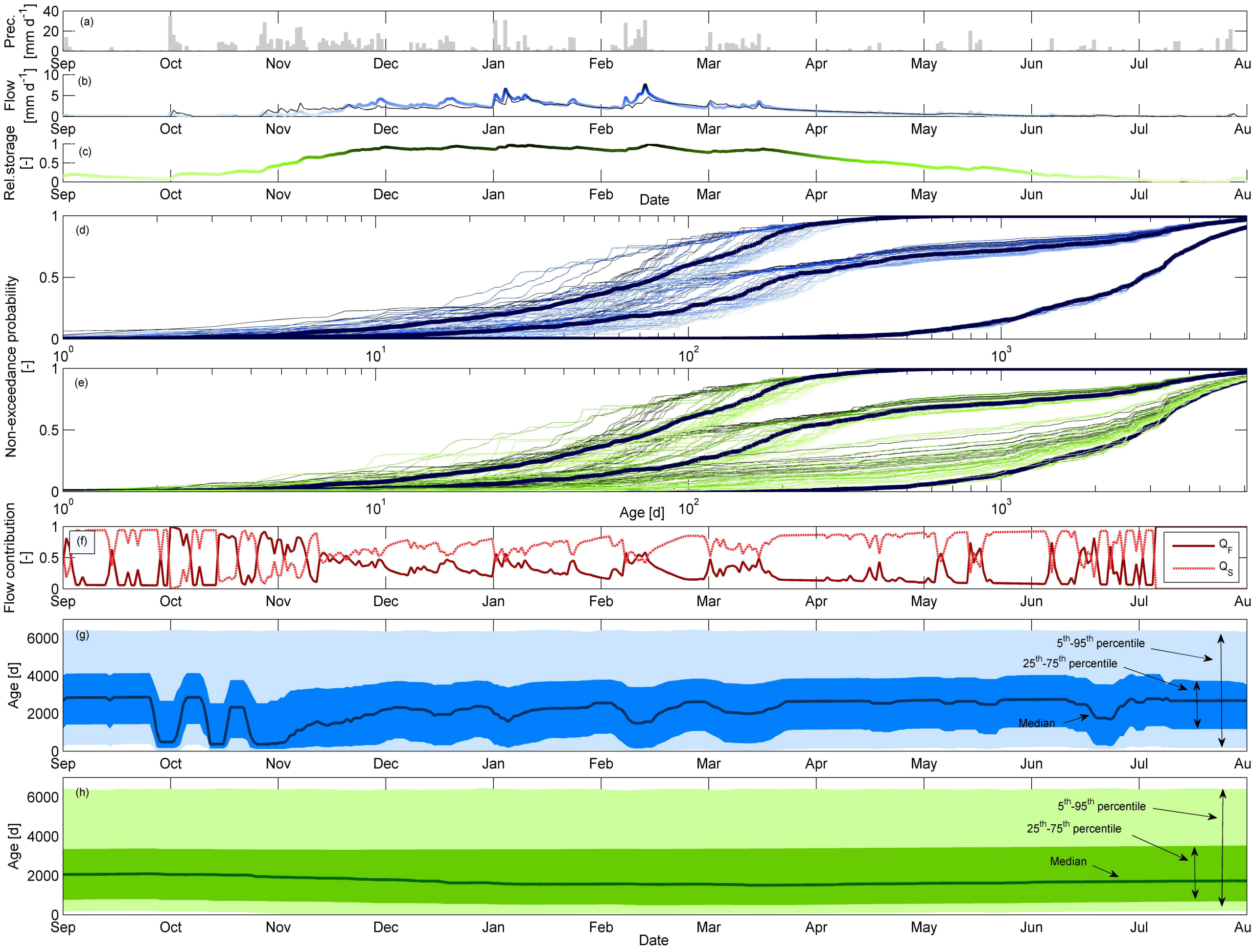


Figure 8: The upper three panels show the time series of (a) observed daily precipitation as well as of (a) observed (black) and modelled flow (blue) and (c) modelled storage in the Kerrien catchment in France. The fourth panel (d) shows the flow weighted average (bold, dark blue lines) and the daily (thin lines, shades from light to dark indicate increasing flow) age distributions $p_{T,B}$ of three selected modelled 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 modelled storage components. The sixth panel (f) shows the modelled 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.