Karst Water Resources in a Changing World: Review of Solute Transport Modelling Approaches

K. Ö. Çallı[1], G. Chiogna[2,3], D. Bittner[4,1], V. Sivelle[5] , D. Labat[6], B. Richieri[2], S.S. Çallı[7], A. Hartmann[1]

[1]Institute for Groundwater Management, Dresden University of Technology, Dresden, Germany

[2] Faculty of Civil, Geo, and Environmental Engineering, Technical University of Munich, Munich, Germany

[3] Institute of Geography, University of Innsbruck, Innsbruck, Austria

[4] Erftverband, Department of River Basin Management, Bergheim, Germany

[5] National Research Council, Research Institute for Geo-Hydrological Protection, Perugia, Italy

[6] Géosciences Environment Toulouse (GET), Université Toulouse 3-Géosciences Environment Toulouse-CNRS-UPS-IRD, Toulouse, France

[7] Faculty of Engineering, Geological Engineering Department, Ankara University, Ankara, Turkey

Corresponding author: Andreas Hartmann (andreas.hartmann@tu-dresden.de)

Key Points:

- Anthropogenic factors and global changes pose a serious threat on karst water quality
- We review solute transport process and modelling approaches in karst water resources
- Fundamental challenges afront a successful transport modelling practice are provided
- We address knowledge gaps and research directions in karst transport modelling

Abstract

Karst water resources are valuable freshwater sources for around 10 % of the world population. Nonetheless, anthropogenic factors and global changes have been seriously deteriorating the karst water quality and dependent ecosystems. Solute transport models are powerful tools to monitor, control, and manage the water quality and dependent ecosystem functioning. By representing and predicting the spatiotemporal behavior of solute migration in karst systems, the transport models enhance our understanding about the karst transport processes, thus enabling us to explore contamination risks and potential outcomes. This paper reviews the current state of knowledge on the modelling of solute transport processes in karst aquifers, thereby unveiling the fundamental challenges underlying a successful karst transport modelling. We discuss to what extent and in what ways we can handle these challenges and derive the key challenges and directions for reliable modelling of transport processes in karst systems in the present context of global changes.

Plain Language Summary

Karst aquifers are valuable freshwater sources. Nonetheless, anthropogenic factors and global changes have been seriously deteriorating the karst water quality and dependent ecosystems. Therefore, understanding, characterizing, and predicting the impacts of such changes are essential for effectively managing and sustainably protecting the karst water quality and dependent ecosystem functioning. Solute transport models are valuable decision-support tools to explore the contamination risks and the potential outcomes of deteriorated water quality. Furthermore, model predictions can be used for introducing the efficient adaptation strategies and regulatory decisions for the contamination-related problems in karst systems. In this review, we provide the current state of knowledge on modelling of solute transport in karst aquifers. By synthesizing the existing body of knowledge, we unveil the fundamental modelling challenges for successful karst transport modelling practice.

1 Introduction

A safe and clean groundwater supply is necessary for our society and water-dependent ecosystems (Hartmann et al., 2021). Karst groundwater is a valuable freshwater source that provides the potable water for nearly 10 % of the total world's population (Stevanović, 2019). However, contamination issues have been seriously threatening karst water quality (Henry & Suk, 2018; Reberski et al., 2022; Savio et al., 2018) and karst groundwater-dependent ecosystems (Goldscheider, 2019; Siegel et al., 2023). For this reason, a reliable risk assessment for the contamination-related problems in karst water resources is essential to effectively manage and sustainably protect the karst water quality and dependent ecosystems.

Deterioration of karst water quality and ecosystem functioning can be linked to two main factors including anthropogenic factors and global changes. While the anthropogenic factors represent the direct human intervention that modifies the physical, chemical, and biogeochemical characteristics of karst systems, such as water management alterations (i.e., groundwater abstractions, reservoir, and dam buildings), the global changes are indirectly influencing the water quality. Urbanization, climate change, soil degradation, land use, and land cover changes are such serious factors that predominantly impact the water quality and ecosystem services (i.e., springs, caves, groundwater-fed wetlands) (e.g., Gutiérrez et al., 2014; Hartmann et al., 2014; Katz, 2019; Vilhar et al., 2022).

Karst aquifers are particularly vulnerable to contamination risks due to the substantial heterogeneity manifested by the preferential flow paths (i.e., fractures, conduits, cave streams) at differing spatial scales (e.g., Bakalowicz, 2005; Ford & Williams, 2007; Goldscheider & Drew, 2014; Padilla & Vesper, 2018; Stevanović, 2018; Quinn et al., 2006, among many others). Besides these (multiple) discrete flow paths that cause the rapid spreading of the contaminants throughout the karst systems (Field, 2018; Hartmann et al., 2014, 2021; White, 2018), the close interaction with the surface waters (i.e., rivers, lakes) and thin soil characteristics limit the attenuation of the contaminants released into the karst aquifers (Goldscheider, 2005; Sinreich, 2014; White, 2019).

Solute transport models with differing complexity have been used for solving complex environmental issues by various scientific communities (e.g., fractured rock, geothermal energy, mining, and soil sciences). However, as the multiscale karstic heterogeneity — referring to the spatial variations of the aquifer's physical and chemical characteristics at varying scales — shapes the karst system's physical, chemical, and biogeochemical characteristics, the successful application of the solute transport model in karst systems is a challenging task, particularly due to the (significant) lack of knowledge on the karst system's physical and (biogeo)chemical characteristics that govern karst transport dynamics. While this impedes our proper understanding about contaminant mixing and transport problems in karst systems, finding a tradeoff between the proper representation of the karstic heterogeneity in the karst models and the model prediction's reliability also remains a difficult task. Besides that, predicting the impacts of anthropogenic factors and global changes on the karst water quality is still a scientific and operational challenge.

This paper reviews the current state of knowledge on the modelling of transport processes in karst water resources by synthesizing the existing body of knowledge in the literature. We initially introduce the principle of the solute transport processes in karst aquifers. We then present the state-of-the-art for karst transport modelling approaches by providing the governing

transport equations that describe the process of interest with differing complexity. We discuss the methodological concerns about a solute transport modelling practice in karst water resources, and hence report the fundamental challenges afront the successful modelling practice. To move forward, we give a broader perspective on the transport modelling in karst water resources, thereby providing emerging directions with potential drawbacks for the karst community.

2 Principles of solute transport processes in karst water resources

Heterogeneity in karst water resources manifests itself at multiple spatial scales i.e., the regional scale, aquifer scale, local scale, and single fracture scale (Figure 1). This multiscale karstic heterogeneity governs both flow and solute transport processes (i.e., advection, diffusion, mechanical and turbulent dispersion, and chemical reactions) (Figure 1). As the flow velocity field in karst systems is often extremely variable (in the order of meters per day in the matrix and of meters per second in the conduits), advection is often the most influenced process by the flow variations in the karst systems. By comparison, the diffusive processes result from the random motion of the solute molecules, and they are not significantly affected by the heterogeneity in the system's hydraulic properties. The (biogeo)chemical reactions (i.e., sorption, chemical transformation) are mostly affected by the heterogeneity in the hydrogeochemical conditions both in fractured/fissured carbonate rock (hereinafter referred to as karst matrix) and preferential flow paths within dissolution enlarged fractures and conduits of the karst systems (hereinafter referred to as karst conduits).

As compared to porous or fractured groundwater systems, the most peculiar characteristic of karst aquifers is the complex interaction between the fractured/fissured carbonate matrix and karst conduit, which leads to the duality in the flow and transport processes (Massei et al., 2003; Joodi et al., 2010; Kavousi et al., 2020). This duality is attributed to the marked difference in the water flow velocities — typically described by the laminar flow in the matrix and turbulent flow in the karst conduits (Kiraly, 1998; Hauns et al., 2001). The duality in the karst flow characteristics is therefore expressed by the definition of different characteristic spatial and temporal scales in karst transport processes over the matrix and karst conduits.

In the following, we describe the main transport processes occurring separately in matrix and conduit components, as well as karst-specific transport dynamics based on the system duality. We then briefly define the concepts of spreading, dilution, and mixing, as there is not a general agreement in the use of this terminology in the karst literature. Furthermore, we provide information on tracers as diagnostic tools to describe and/or quantify the karst transport processes, thereby only touching upon the concept of groundwater age and its primary role in identifying solute mixing and transport characteristics in karst systems.

2.1 Transport in the matrix

There is vast literature describing transport processes in the karst matrix. Recently, several review papers covered the topic by emphasizing the different characteristic aspects. Dentz et al. (2023) review concepts and approaches for the quantification of passive, non-reactive solute mixing in steady uniform porous media flows across scales. Rolle & Le Borgne (2019) focus both on the description of reactive mixing, on displacement scenarios and continuously released plumes approaching the transport problem from the pore scale to the aquifer scale. Valocchi et al. (2018) describe mixing-limited reactions and upscaling processes from the pore to the continuum scale. Berkowitz et al. (2016) emphasize the complex interplay

between reactive mixing and spreading, as well as the differences among the models to describe it. In our review, despite the undoubtful relevance of the pore-scale transport processes, we will describe transport mechanisms starting from the continuum scale (generally known as the Darcy-scale). Therefore, we refer the interested reader to the aforementioned review papers for the upscaling from the pore scale to the continuum scale.

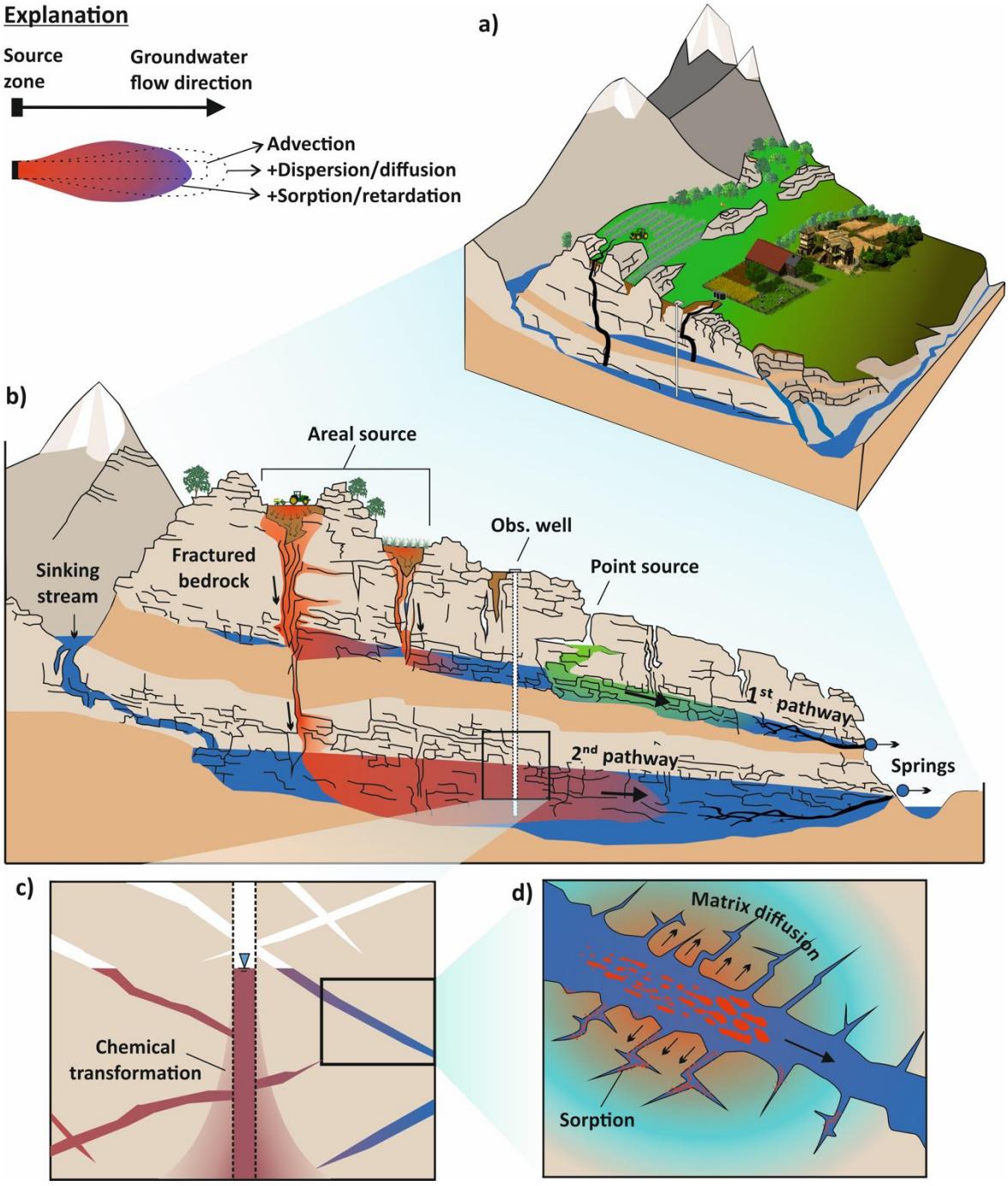

Figure 1. Conceptual representations of solute transport processes in karst water resources at differing spatial scales. **(a)** regional scale, **(b)** aquifer scale, **(c)** borehole scale, and **(d)** single-

fracture scale. Here, the solute attenuation process is described by the chemical transformation process influenced by physical, chemical, and (biogeo)chemical processes. In the figure, anthropogenic contamination source is described only while geogenic contamination is not depicted. The figure also indicates the diffuse (areal) sources whereas the point source is depicted by the intentional problem in the site.

2.1.1 Darcy scale: Pore diffusion and mechanical dispersion

Aqueous diffusion results from the random motion of the molecules of a solute in water at microscopic scale and controls the occurrence of complete mixing at the pore scale (Rolle et al., 2012). When aqueous diffusion occurs in a porous material, it is often called pore diffusion (Bear, 1972). Aqueous diffusion coefficients are compound specific and range from 10^{-7} to 10^{-9} m^2/s. In the matrix, since the solute is not free to move in all directions due to the presence of the solid material, pore diffusion is slower than aqueous diffusion. At the Darcy scale, by comparison, a pore diffusion coefficient is described as the product between aqueous diffusion and a coefficient whose value ranges between 0 and 1, and it is parametrized by the tortuous nature of the pore space (Ghanbarian et al., 2013). Therefore, pore diffusion coefficients are typically between one half and one tenth of the aqueous diffusion coefficients. When the grain Pèclet number — the ratio between the product of the groundwater flow velocity and the grain size over the aqueous diffusion coefficient — is smaller than 1, pore diffusion is the dominant transport process in the karst matrix.

Mechanical dispersion also contributes to the displacement of the solute of interest, and hence it reflects the effect of random velocity variations at the pore scale during advective transport (Bear, 1972). Generally, the advective velocity is laminar and the Reynolds number characteristic of the system is small (typically below one). If aqueous diffusion eliminates concentration gradients occurring in pore channels, mechanical dispersion at the Darcy scale is parameterized as the product of the velocity and a constant property of the porous material defined as dispersivity (Scheidegger, 1961). While dispersivity values differ in the longitudinal and transverse directions, their values are proportional to the grain diameter. If concentration gradients at the pore scale still exist, then mechanical dispersion is compound specific and depends non-linearly on the grain Pèclet number (Bear, 1972; Chiogna et al., 2010).

The sum of pore diffusion and mechanical dispersion is called hydrodynamic dispersion.

2.1.2 Field scale: Effective and macro dispersion

Correctly characterizing pore diffusion and mechanical dispersion is fundamental to reproduce transport processes at the Darcy scale. Since the heterogeneity in the matrix hydraulic conductivity is hardly measurable, we are not able to assign spatially distributed values for the pore diffusion and mechanical dispersion to the karst systems. For this reason, to move from the Darcy scale to the field scale, the concepts of effective dispersion and macro dispersion are introduced as an additional upscaling mechanism. Here, the macro dispersion is a concept for explaining “the scale effect observed in experimental data of dispersion coefficients measured in the heterogeneous porous media at different spatial scales” by Dentz et al. (2023). However, we can distinguish between the definitions of ensemble dispersion coefficients and effective dispersion coefficients. While the ensemble dispersion defines the solute distribution due to the advective spreading, effective dispersion characterizes the width of the solute plume originating from a point-like injection (Dentz et al., 2023). As a typical characteristic of both parameters,

they are all scale-dependent, which means that the larger the area of interest, the larger the coefficients. Furthermore, their values are often orders of magnitude larger than the hydrodynamic dispersion coefficients.

2.2 Transport in the conduits

Transport in karst conduits shows similarities with the transport in rivers and/or pipes. But depending on the saturation of the karst system, karst conduits can behave as a free surface flow or a (saturated) pipe flow under pressurized conditions (Liedl et al., 2003; Loop & White, 2001; Reimann et al., 2014). While solute transport in conduits is mainly controlled by advection and aqueous diffusion, typical flow velocities encountered in karst conduits are orders of magnitude larger than the ones presented in the matrix. This leads typically to turbulent flow conditions in the conduits, thus making aqueous diffusion a dominant process along the conduit, although it is generally neglected (Hauns et al., 2001). At the field scale, however, the advective flow field is often not known due to the multiscale karstic heterogeneity, as well as due to the lack of knowledge about the distribution and shape of conduits.

2.2.1 Aqueous diffusion

Aqueous diffusion in conduits is the same process as in the matrix. However, we can highlight three main differences here. First, in karst conduits we do not have to reduce the aqueous diffusion coefficient by the presence of the porous medium and its tortuosity. Second, as we often move from laminar to turbulent flow conditions, the magnitude of the aqueous diffusion coefficients is much smaller than the turbulent dispersion coefficient. Third, incomplete mixing is generally not controlled by aqueous diffusion along the conduit system, but it is mainly controlled by the conduit network topology and the turbulence occurring in the conduits.

2.2.2 Turbulent dispersion

The distinguishing characteristics of turbulent flow are the rapid changes in flow velocity over time and space, and the randomness of the velocity and pressure fields (Fischer et al., 1979). Therefore, the rapid irregular and chaotic fluctuations in flow velocity and pressure lead to the formation of swirling vortices, eddies (random complex patterns), and turbulent structures that interact with each other. Because of these random motions, turbulent flows occur at several characteristic scales. At large Reynolds number (typically larger than 500 in karst conduits), the strong nonlinearity of the equation of fluid motion results in the spreading of the kinetic energy over a range of eddy sizes, and thus causes the interaction between the large and small scales of motion (Fischer et al., 1979). These varying flow velocity fields result in the spreading and dispersion each of which is quantified by the turbulent dispersion coefficients. Therefore, being process scale-dependent, the definition of the dispersion coefficient needs to be done considering the specific spatial scale (Kinzelbach,1986).

The turbulent dispersion coefficient is commonly assumed to be proportional to the flow velocity, where the proportionality constant is called dispersivity. Taylor (1953, 1954) developed a more process-based approach by correlating dispersion to the differences in flow velocity within the flow cross-section and the consequent mass transfer processes. Under turbulent flow conditions, however, the dispersion coefficient for a pipe is proportional to the pipe radius and friction velocity (Taylor, 1954). In the field scale where the karst conduits exist, the dispersivity

is often required to adjust by the karst transport modelling during the model parametrization (see Sections 3 and 4).

2.3 Sorption, retardation, and chemical reactions in karst systems

Solutes that are neither affected by sorption nor undergo chemical reactions are defined as conservative. In our review, for the sake of simplicity, we only review the single-phase flow and transport processes in karst aquifers which are much relevant to assessing natural attenuation processes (e.g., Geyer et al., 2007; Einsiedl et al., 2009; Flynn & Sinreich, 2010; Schiperski et al., 2016; Valiente et al., 2020).

Sorption refers to the process that transfers the solute concentration from the dissolved aqueous phase into an immobile phase attached to the solid geological matrix. It is particularly relevant for solute transport in the karst matrix and at the interface between the matrix and karst conduit because it requires direct contact between the solute and the porous material. Sorption can also occur on suspended particles (Lan et al., 2018; Massei et al., 2002; Schwarz et al., 2011), thus leading to the so-called particle-facilitated transport. In general, sorption has two main effects on the solute concentration. First, the solute concentration in the water is reduced due to the mass transfer towards the immobile sorbed phase. Second, the advective velocity of the solute of interest is reduced, and hence the mass exchange between the dissolved and the sorbed phase leads to an effective retardation in the solute.

Retardation is described as the delay of the solute transport relative to the groundwater flow. In karst systems, retardation is often assumed to be negligible due to the rapid transport in the karst conduits (Kresic & Stevanovic, 2009) whereas sorption reactions (adsorption or absorption) and ion-exchanges (combined sorption-desorption processes) can occur at the conduit walls/surfaces and within the surrounding carbonate matrix (Field & Pinsky, 2000; Geyer et al., 2007; Morales et al., 2010). However, both processes are generally relevant to local-scale transport problems (Hauns et al., 2001; Jeannin & Maréchal, 1997). To account for sorption and retardation processes in karst systems, sorption isotherms (i.e., linear, Langmuir, Freundlich isotherms) that ignore the complex sorption kinetics are often preferred (e.g., Frank et al., 2021; Hillebrand et al., 2015; Luhmann et al., 2015; Morales et al., 2010; Schiperski et al., 2016; Tinet et al., 2019, among others).

Chemical reactions can lead to the production and/or degradation of the solute of interest. A prerequisite for a reaction to occur is that all reaction partners are present in the same location at the same time while diffusive and dispersive processes are mainly responsible for this. As the diffusive and dispersive processes are slow in the karst matrix, chemical reactions are limited by transport mechanisms. On the contrary, reactive transport in the karst conduit systems is often limited by the reaction rate constant of the chemical reaction due to the high turbulent dispersion coefficient. Besides, the timescales of (biogeo)chemical reactions (i.e., degradation, nitrification, dissolution, mineralization, weathering) are relatively slow in the matrix (i.e., seasonal, decadal, or multidecadal) as compared to advective transport in karst conduit (i.e., days, months). For these reasons, the (biogeo)chemical reactions are generally overlooked in karst systems. But when they are considered, a (biogeo)chemical interaction term is often coupled with the advective-dispersive transport processes (Dvory et al., 2018a, 2018b; Pastore et al., 2021).

Overall, due to the multiscale variabilities in (hydro)geochemical conditions modified both by the karst matrix and by the composition of mobile water, the proper description of the

complex reactions is hardly possible in karst systems. For this reason, sorption and (biogeo)chemical processes are crudely represented in the karst literature while there is a general lack of knowledge of the hydrogeochemical compositions of karst systems.

2.4 Dynamics of solute transport processes in karst systems

The spatiotemporal dynamics of solute transport in karst aquifers are controlled by the relative contributions of the rapid (i.e., conduits, fractures) and slow (i.e., matrix, storage zones due to the vortices and eddies in conduit systems) flow components (Ewers et al., 2012; Field, 2002, 2018; Geyer et al., 2007; Hauns et al., 2001) (Figure 2). Solute transport in karst systems is often characterized by non-ideal transport phenomena — also referred to as non-Fickian or anomalous transport — controlled both by the preferential flow paths (mostly by karst conduits and conduit networks) and by the rate-limited mass transfer between the slow and fast flow components. Overall, the key transport mechanisms in karst systems are defined as (*i*) physical transport along the main flow direction controlled both by advection and dispersion processes, (*ii*) matrix diffusion and mechanical dispersion along the conduit surfaces in and out of the (fractured) carbonate matrix, and (*iii*) mass exchange between mobile water in karst conduit and matrix components via such as sorption, ion exchange, radioactive decay, and (biogeo)chemical reactions (Figure 2) (e.g., Field & Liej, 2014; Field & Pinsky, 2000; Sinreich, 2011; Sinreich et al., 2007).

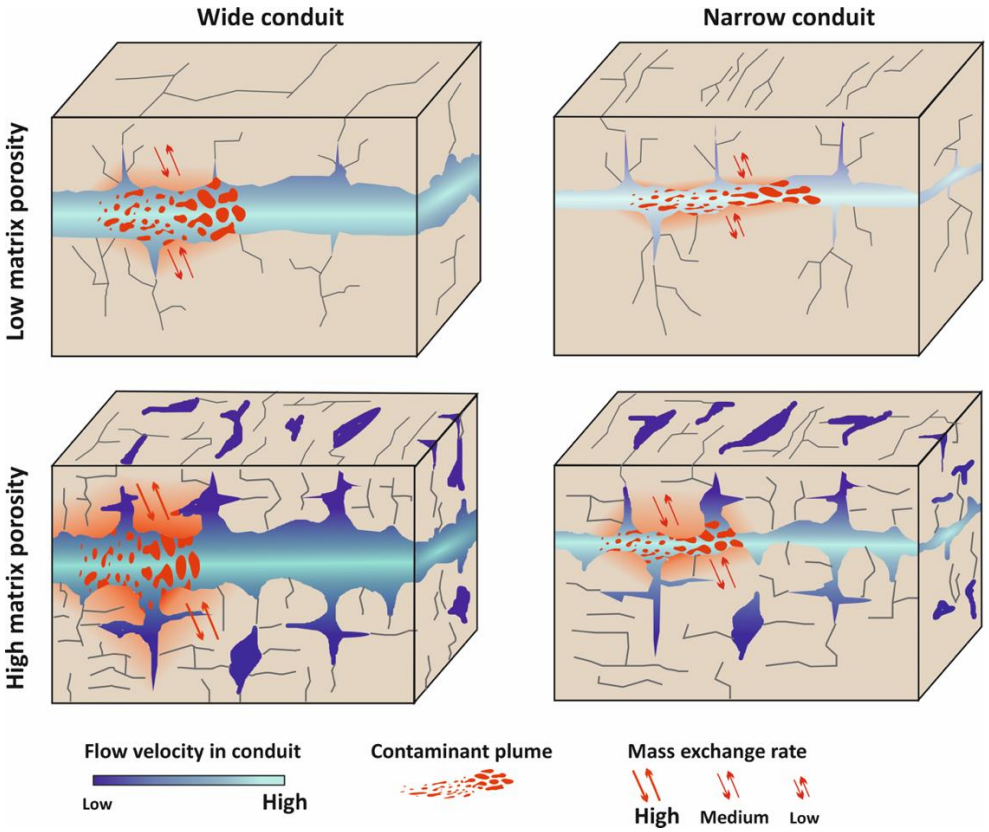

Figure 2. Schematic representations of the anomalous transport in karst systems demonstrated with the mass exchange mechanism between the (saturated) karst conduit and surrounding fractured/fissured carbonate matrix. Here, the variability of mass transfer rate is controlled by the karst system's hydraulic properties (i.e., the matrix porosity and conduit diameter). Due to the

greater hydraulic conductivity of the karst conduits, advection and dispersion processes dominate the physical transport along the conduit whilst the (fractured/fissured) carbonate matrix acts as a sink and/or source, mainly depending on the hydraulic head and concentration gradient at the domain of interest.

In karst aquifers, conduits represent the region where contaminants can be rapidly transferred (e.g., Ghasemizadeh et al., 2012; Goeppert et al., 2020; Pronk et al., 2009; Vesper et al., 2001, among many others). Along the conduit, the nature of the transport is strongly dependent on the flow regimes that range from laminar to turbulent flows (Field, 2002; Green et al., 2006; White, 2002). The conduit flow velocity is particularly important because it shapes the movement of the solute plume. Here, the (mean) flow velocity defines the rate of mass transfer between the karst conduit and matrix (Bajracharya & Barry, 1997; Lehmann et al., 2022) while the magnitude and direction of the mass exchange widely vary depending on the karst system's hydrological and antecedent conditions (i.e., soil and/or epikarst wetness). For instance, the high velocity reduces the contact time of the contaminant with the (fractured/fissured) carbonate matrix and thus limits the mass exchange between the conduit and matrix (Figure 2). In contrast, when the flow is laminar — typically characterized by lower flow and recharge conditions —, the mass exchange is generally favorable (Faulkner et al., 2009; Martin et al., 1999, 2012). While the advective transport in the karst conduit are mainly influenced by the conduit's structural properties (i.e., conduit size, morphology, sinuosity) and conduit networks (Aliouache et al., 2019; Field & Pinksy, 2000; Ronayne, 2013), the local and/or regional recharge characteristics adjust the flow magnitude and direction of the mass transfer between the conduit and matrix (Figure 2) (Doummar et al., 2018; Göppert & Goldscheider, 2008; Ji et al., 2022).

The karst matrix is characterized as the region where solutes can be stored for a long period and are slowly released into the conduit network (e.g., Berglund et al., 2020; Ji et al., 2022; Nativ et al., 1999; Padilla & Vesper, 2018; White & White, 2005; Worthington, 2011, among many others). As the mass transfer from the karst conduit to matrix is often controlled by the (matrix) pore diffusion and mechanical dispersion, these processes can be particularly important during the storage of solute of interest within the matrix, especially in the low permeable karst media, such as chalk (Zuber et al., 2011; Polak et al., 2002; Worthington, 2015). Therefore, the rate of the solute transfer in and out of the matrix is regulated by several other factors including matrix permeability, conduit flow velocity, irregularities of conduit surface, solute retardation factor, as well as the (solute) matrix pore diffusion and mechanical dispersion coefficients (Field, 2002, Joodi et al., 2010; Kresic & Stevanovic, 2009; Mosthaf et al., 2018; Luo et al., 2024) (Figure 2).

2.5 Spreading, Dilution, and Reactive Mixing

A large amount of literature deals with the proper distinction among three different concepts to quantify transport processes: spreading, dilution, and mixing (e.g., Dentz et al., 2023; Kitanidis, 1994).

Spreading refers to a change of the solute plume shape due to the spatially varying velocity, and thus to an increase in the average distance of the particles. This process is quantified by computing the second spatial moments of the solute present in the system. If we neglect aqueous diffusion, mechanical and turbulent dispersion, then spreading, if only caused by advective transport, is a reversible process and does not lead to a change in the concentration of the solute, but only to a different spatial distribution of the solute concentration.

Dilution, on the contrary, quantifies the increase in volume of the fluid occupied by the solute. Due to dilution, the solute plume tends to occupy a larger volume leading to a decrease in the solute concentration (Kitanidis, 1994). This process is irreversible and is controlled both by diffusive and dispersive processes. Dilution is typically used to characterize conservative solute transport. However, we can often find the term mixing to refer to dilution in the literature. Since the term 'mixing' is widely established for the description of conservative transport, we will use this term as a synonym for dilution in our review.

Reactive mixing is the process that brings two different chemical species together as the result of molecular diffusion, mechanical dispersion, and turbulent dispersion (Neupauer et al., 2014), which allows a chemical reaction to occur. Here, it is important to notice that dilution (mixing) is not necessarily affected by incomplete mixing at the pore scale whereas reactive mixing is significantly controlled by incomplete mixing (Berkowitz et al., 2016), particularly in the karst matrix. Therefore, the presence of incomplete mixing very often leads to the need for case study-specific reaction rate constants to match the experimental observations.

2.6 Tracers as diagnostic tool in describing transport processes in karst systems

Describing flow and transport processes in karst systems is difficult mainly due to the unknown configuration and geometry of the conduit network (Borghi et al., 2012; Fandel et al., 2022). Tracers are frequently used to define the karst system's flow and transport dynamics (Geyer et al., 2007; Goldscheider et al., 2008; Martín-Rodríguez et al., 2023; Mudarra et al., 2014). Various substances (i.e., solutes, particles, solids, and gasses) and physical quantities (i.e., temperature or heat) can be used for quantifying flow and transport parameters (i.e., porosity, dispersivity, flow velocity) at the spatiotemporal scales of interest (Benischke, 2021; Field, 2020; Massei et al., 2006). Additionally, tracers are frequently utilized as additional information sources to confirm and/or invalidate for karst simulation models (e.g., Hartmann et al., 2014, 2017; Mudarra et al., 2019; Rusjan et al., 2019; Zhang et al., 2021; Çallı et al., 2023a).

Environmental tracers and artificial tracers are two main groups commonly used for the description of the karst transport processes. While the environmental tracers such as stable isotopes, radionuclides, dissolved gasses (i.e., chlorofluorocarbons and Sulphur hexafluoride), hydro-chemicals, and sediments already exist in the karst groundwater, artificial tracers (i.e., fluorescent dyes, salts, and bacteria) are introduced into the karst system under pre-defined experimental conditions where the substance is supposed to be nonexistent under natural conditions (Benischke, 2021; Goldscheider et al., 2008).

Among environmental tracers, water isotopes such as Oxygen-18 and Deuterium are frequently used for defining hydrological system's water age and (water) age distributions (i.e., travel time distributions (TTDs) and residence time distributions (RTDs) (Jasechko et al., 2017; Musgrove et al., 2023). As a terminology, water 'age' refers to the time elapsed since the meteoric water entered the system (Bethke & Johnson, 2008; Long & Putnam, 2009; Suckow, 2014). In groundwater studies, water age is often denoted as residence time which indicates the time between the water entrance and leave (Aquilina et al., 2003; Maloszewski et al., 1992; Małoszewski & Zuber, 1993; Plummer et al., 1998a, 1998b) whereas travel time is defined as the time required for a volume of water moving across the specified flow paths. The knowledge of water age and/or its distributions — distributions of the different water ages — is particularly useful for revealing the vulnerability of karst aquifers to the contamination risks (Malík et al., 2016; Musgrove et al., 2023; Çallı et al., 2023a) as it provides valuable insight into the karst

system's underlying mixing, storage, and transport characteristics (i.e., piston flow, complete mixing) (Figure 3). For instance, the karst aquifers characterized by (relatively) younger water age (i.e., shorter travel time) are often at the risk of contamination problem due to the system's rapid response whilst the karst systems represented with older groundwater ages (i.e., longer residence time) is often an indication of the sufficient time for the contaminant attenuation processes (Figure 3).

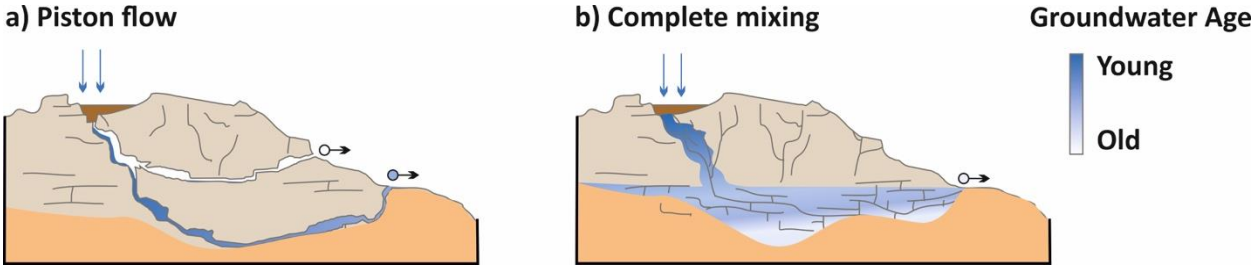

Figure 3. Sketch for idealized groundwater age distribution in two different karst systems. **a)** Conduit-dominated karst system resembling advection-dominated transport dynamics — characterized by relatively younger water age (i.e., shorter travel time), **b)** Matrix-dominated transport dynamics, which reflects diffusive-dispersive dominant transport characteristics — characterized by older groundwater age (i.e., longer residence time).

Artificial tracer test is powerful tool to estimate the karst system's hydraulic properties (i.e., porosity, hydraulic conductivity, conduit volumes) and transport parameters (i.e., dispersion, mass exchange rate, sorption) (Aquilanti et al., 2003; Mudarra et al., 2019; Lauber et al., 2014; Peely et al., 2021; Perrin & Luetscher, 2008). In these tests, the investigation scale is very often a key factor in characterizing and quantifying the karst system's flow and transport characteristics. For this reason, the observations/data obtained by the tracer tests are rather site-specific, and hence the estimated parameters are frequently dependent on the initial and boundary conditions of the experimental works (i.e., climatic, hydrological conditions) (Duran et al., 2016; Sivelle & Labat, 2019; Stevanović & Stevanović, 2021) (see discussion in Section 4.1).

The solute breakthrough curve (BTC) is the primary production of artificial tracer tests (Figure 4), which reflects solute transport behaviour at the scales of interest. BTC is often used as a karst system's (characteristic) response obtained at the given spatial and/or temporal scales (e.g., Field, 2002; Labat & Mangin, 2015). However, due to the multiscale karstic heterogeneity, BTC is often described by the various anomalous characteristics such as power-law tailing, high skewness (positive or negative), and multi-modality in BTC (Figure 4) while each of which can resemble the karst system's flow and transport dynamics. In general, the tailing effects in BTC are associated with the dispersion and (matrix) diffusion processes, as well as with the presence of conduit pools where the eddies and vortices form the (transient) storage zones to retain the solute of interest (Bodin et al., 2022; Hauns et al., 2001; Li & Loper, 2011; Morales et al., 2010). The multi-peaked BTC is considered as a resemble of anastomoses (or channeled) of the conduits and/or conduit networks (i.e., auxiliary conduits) along which advective transport is often the dominant mechanism (Figure 4) (e.g., Cen et al., 2021; Goldscheider et al., 2008; Deleu et al., 2023; Dewaide et al., 2018).

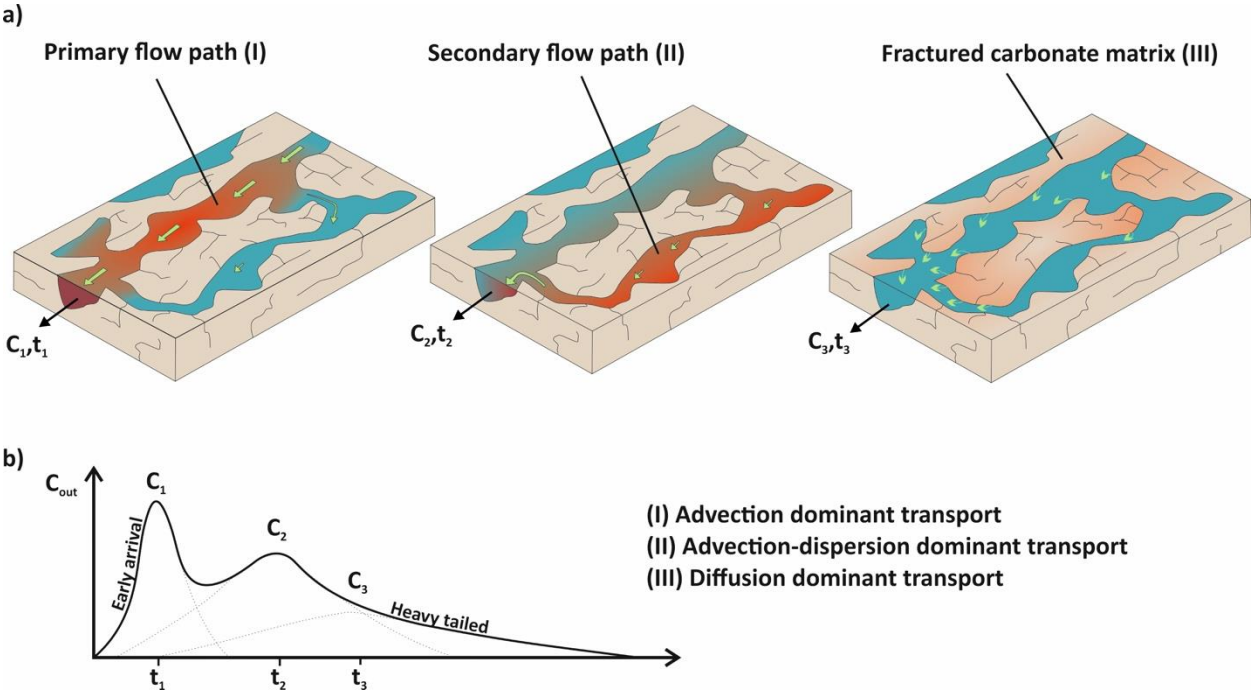

Figure 4. A conceptual description of the (typical) anomalous behaviours of the (saturated) karst systems. **a)** Contaminant plume migration along the different karst compartments under changing time. **b)** Solute Breakthrough Curve (BTC) characterized by the dominant transport characteristics at the domain of interest within the selected time-periods given in Panel-a.

3 The current status of solute transport modelling in karst water resources

3.1 A generic framework for a successful transport modelling in karst systems

To present the current status of solute transport modelling in karst water resources, we first define a workflow for a successful transport modelling application. A successful transport modelling practice starts with the definition of the karst transport problem for which some critical information about the properties of the source of nutrient or contaminant (i.e., source type such as point or areal sources, source locations) and the karst system's physical and chemical boundaries are mainly gathered. Similar to the development of a flow model (Beven, 2002, 2011; Wagener et al., 2001, 2021), a successful implementation of a transport model in karst systems is a strategy that contain three main successive stages including (*i*) system conceptualization, (*ii*) development of mathematical model and model parametrization, and (*iii*) model evaluation (Figure 5). Here, each stage feeds one another with the multiple feedback loops to retrieve more robust and reliable results for the successful karst transport model. The overall success in this modelling practice, therefore, reflects the level of accumulated knowledge and observational inputs for the proper descriptions of the complex physical, chemical, and (biogeo)chemical processes in karst systems. A successful transport model application usually requires an a priori definition of a flow model that solves the water mass balance equations based on the changes of the variable of interest (i.e., hydraulic head, drawdown, or water pressure) within the flow domain where the dominant hydrodynamic conditions (i.e., regional and/or local flow directions and magnitudes) govern the karst transport processes, which has been extensively discussed in previous reviews (e.g. Hartmann et al., 2014).

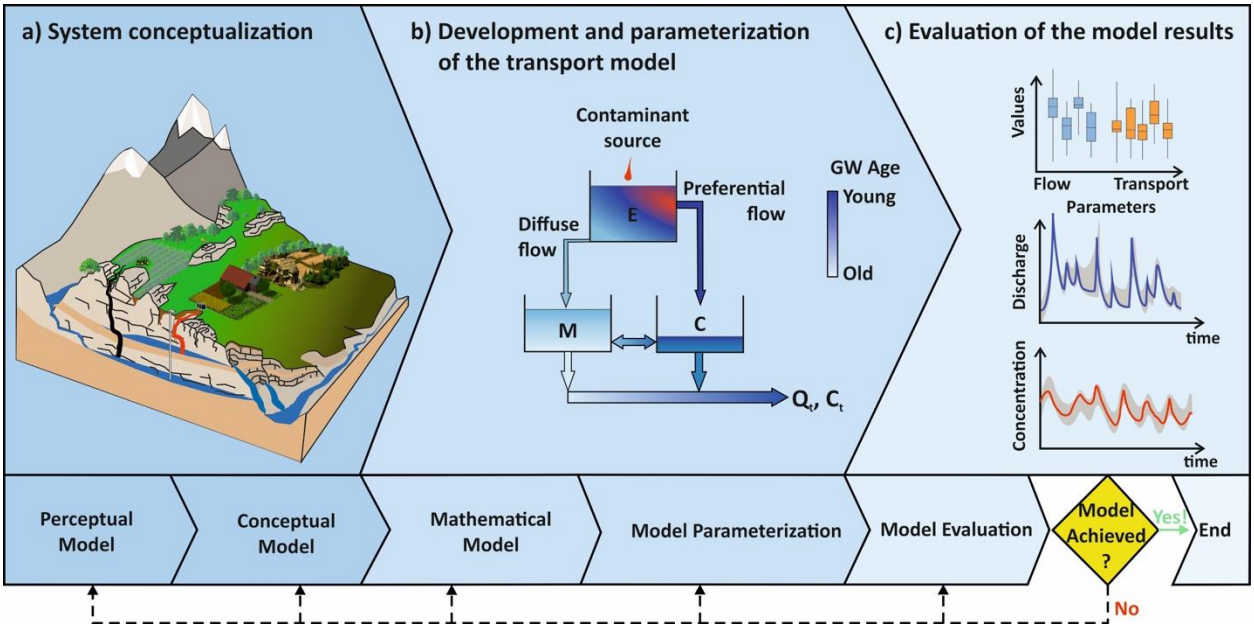

Figure 5. Schematic representations of knowledge transfer starting from the karst system conceptualization to the assessments of the model results including model parameters and predictions. **(a)** System conceptualization, **(b)** Development and parametrization of the solute transport model, **(c)** Evaluation of the transport model results. Here, the dashed black line indicates the feedback mechanisms across the different stages of the successful transport modelling practice to ensure the (robust) model outcomes (i.e., model parameters and simulations). Here, the acronyms are E (Epikarst), M (Matrix), C (Conduit), Q (spring discharge), C (solute concentration).

3.1.1 Model conceptualization for karst transport processes

Perceptual understanding of transport processes is a key stage of successful transport modeling practice. A perceptual model is a qualitative description of the karst system's physical, chemical, and (biogeo)chemical transport characteristics, each of which forms the definition of the dominant physicochemical processes at the domain of interest (e.g., Hartmann et al., 2012a, 2013a, 2018). At this stage, the understanding of a dominant process is critical as it mainly conditions the concept of the karst transport mechanism (i.e., advection-dominated transport, diffusion-dominated transport) for the conceptual model development. Since the perceptual model is just a mental model amongst the multiple other possibilities, it is more likely to be updated by the accumulated scientific knowledge and collected data (Beven & Chappell, 2021; Wagener et al., 2021) before evolving into a conceptual model (Enemark et al., 2019; Gupta et al., 2012).

The development of a conceptual model for representing transport processes in karst systems is a critical stage of the successful transport modelling practice (Figure 5). This model is structured based on generic scientific knowledge and a set of decisions on how the karst system functions and/or it might function over the changing time and space (Chang et al., 2017, 2019; Hartmann et al., 2014). Model conceptualization helps to determine and/or select a suitable mathematical formulization (hereinafter referred to mathematical model) for karst transport processes, thereby refining the governing equations within the given range of spatiotemporal scales. While these equations represent the dominant (physicochemical) processes, the

mathematical formulation can be adjusted by which type of contaminant is of interest (i.e., reactive, conservative transport). In most cases, the formulation for the conservative solute transport is expanded by coupling reactive and/or chemical processes (i.e., such as by the organic chemicals that are sorbed onto the carbonate matrix and/or fracture filling) where these processes can play a role for karst transport dynamics. In such a process-coupling, system conceptualization can be extended by the development of a karst "hydrochemical conceptual model". Here, a hydrochemical conceptual model refers to the spatial variations of different hydrochemical facies — or water type — in which similar geochemical characteristics are grouped (e.g., Güler & Thyne, 2004; Kresic & Stevanovic, 2009; Thyne et al., 2008). In this manner, building hydrochemical conceptual model is a complementary stage for a successful transport modeling practice because it provides valuable information on modelling chemical and/or reactive transport processes, particularly during the representation of the (different) origins of contaminant sources and their mixing characteristics at the domain of interest (i.e., borehole scale, aquifer scale).

3.1.2 Model parameterization in karst transport models

Mathematical models translate the system conceptualization into a set of governing equations that are formulated based on the karst system's physical and (biogeo)chemical properties under (specified) boundary and initial conditions (Figure 5). The mathematical models (or numerical codes) solve solute mass balance to define the spatiotemporal dimension of the process of interest. In general, the structure of the mathematical model (or model structure) is formed and/or chosen by the modeler himself/herself depending on the adequate representation of the system and process of interest. But the selection of an appropriate model structure often depends on data availability and information collected. For this reason, different models with differing complexity can be successful for solving (different) karst transport problems at various spatial and/or temporal scales. To solve the solute mass balance, the mathematical models attribute specific values to the coefficients of the governing equations. These coefficients are called as model parameters (i.e., hydraulic conductivity, dispersivity, sorption constant). While the parameters are the main integrators of available data and/or information content, they are often formulated based on the karst system's physical and chemical properties (see further discussion in Section 4.3).

Model parametrization is the stage for the (realistic) estimation of the parameter values to capture the spatial and/or temporal dimensions of the karst transport dynamics. The parameter values can be obtained by three common ways: (*i*) direct measurements (field and/or lab-scale measurements), (*ii*) model calibration (i.e., inverse solution, history matching), and (*iii*) the combination of thereof. Since the direct field measurements and/or laboratory scale experiments often resemble the spatial and temporal variabilities of the process of interest at the domain of interest, they are favorable for the improved model parameterization due to the well-defined parameter values. Nonetheless, the characterization methods for the data acquisition and/or interpretation techniques in karst aquifers is rather appropriate for the continuum (Darcy) scale applications where the effective parameters can be readily used for the entire model domain (e.g., Faulkner et al., 2009; Huntoon, 1995; Kresic & Stevanovic, 2009; Reimann et al., 2011a; Zhang et al., 2021). For this reason, when the direct measurements of transport parameters (i.e., dispersivity, mass transfer coefficient) are not practical and/or their values might not be representative in resembling the process of interest, model parameters are frequently estimated

via model calibration (e.g., Bittner et al., 2020; Cinkus et al., 2023; Dewaide et al., 2016; Sivelle et al., 2023; Çallı et al., 2023a).

Model calibration refers to model tuning during which the parameter values are frequently adjusted to reduce the misfit the observations. In a successful model calibration, the measured variables (i.e., solute concentrations for the transport models, discharge and/or groundwater heads for the flow models) are required to reasonably meet the simulated counterparts (Dietrich & Uniyal, 2020; Neven & Sorab, 2021; Oehlmann et al., 2015; Sullivan et al., 2019). Such a model parameterization requires a calibration metric (i.e., objective function, performance criteria or likelihood) to indicate how well and to what degree the transport model represents the system‘s reality (Hartmann et al., 2018; Gharari et al., 2021; Çallı et al., 2023a). For the calibration of karst simulations models, a single variable (i.e., spring discharge, groundwater level) is often used to quantify the misfit between the simulated and observed variables. But when it is possible, introducing multiple sources of information (i.e., isotope concentrations, water age information) and/or soft data (i.e., knowledge and experience on the modelled area) into the model calibration phase is rather preferable, particularly for the improvement of model robustness and parameter reliability (e.g., Banusch et al., 2022; Hartmann et al., 2013a, 2013b; Çallı et al., 2022; Çallı et 2023b).

The number of parameters required for modelling of transport processes is typically greater than the flow models (Konikow, 1996, 2010; Reilly, 1987). For this reason, multiple parameters (i.e., degrees of freedom or parameter space) are often necessary to represent the system’s physical and chemical behaviors in karst solute transport models. Besides, the number of parameters can be increased when the multispecies and/or multiphase (air and water phases) transport is considered in the modelling framework (e.g., Faulkner et al., 2009; Dewaide et al., 2016; Loop & White, 2001; Zhang et al., 2017). The model calibration for solute transport models is often framed by how the transport model is coupled with the flow model. Here, this coupling can be done at two different levels, either fully or partly/loosely. Mainly depending on the model coupling, two approaches are frequently applied for the parametrization of karst transport models: (*i*) sequential calibration and (*ii*) simultaneous calibration (Schilling et al., 2019). In sequential calibration, the (calibrated) parameters of the karst flow model is served for the parametrization of the transport model (e.g., Husic et al., 2021; Sullivan et al., 2019; Çallı et al., 2023a) whereas the simultaneous calibration is performed for a fully coupled model (flow model coupled by transport model) and hence whole parameter set is considered against the available observations (e.g., both karst spring discharge and $\delta^{18}O$ composition of spring discharge) (e.g., Hartmann et al., 2017, 2012a, Kavousi et al., 2022; Zhang et al., 2020a, 2020b).

3.1.3 Evaluation of karst transport model results

The successful application of a karst transport model requires a robust model evaluation to ensure the reliability of the model predictions (Hartmann et al., 2013b; Çallı et al., 2023a) (Figure 5). In general, the tools used for the model evaluation are (*i*) model performance assessment (similarity of the observed variable), (*ii*) model plausibility (alignment with the conceptual model), and (*iii*) uncertainty estimation (Dietrich & Uniyal, 2020; Hartmann, 2018; Jeannin et al., 2021; Jukić & Denić-Jukić, 2009). The model predictions might be greatly varied during the modelling practice depending on the modeler’s target, system conceptualization, model selection, and applied calibration scheme (i.e., selection of objective function, calibration-validation periods, multi-objective, and/or multivariable calibration) (e.g., Bittner et al., 2020; Mai, 2023; Mazzilli et al., 2012; Zhang et al., 2020b; Çallı et al., 2023a). However, as the karst

transport model often relies on the accuracy of a karst flow model, the transport model's predictions are generally less reliable as compared to flow models (e.g., Konikow, 1996, 2011; Scanlon et al., 2003). Therefore, the predictions of transport models are always uncertain to some degree, which thus requires diagnosing and quantifying sources of uncertainty in the model results.

Nonetheless, uncertainty propagates and amplifies throughout the modelling practice (Figure 5). For that reason, the exploration of the principal sources of uncertainty is strictly limited (Beven, 2005; Hartmann, 2018). Similarly, the translation of each uncertainty source into a quantitative form — refers to the attribution of a numerical value for each uncertainty source — might change from one modeler to another and is mostly dependent on the progressive decisions and choices over the modelling practice. Therefore, different sources of uncertainty in model results (i.e., data uncertainty, model structure, and parameter uncertainties) could be reduced to a certain degree, only if a systematic model assessment in the model results is carried out. This assessment can identify what we need for the reduction of model uncertainty, and how much we shall put effort to reduce the different sources of uncertainty. Although this is not an easy task, some techniques such as Generalized Likelihood Uncertainty Estimation (GLUE) (Beven & Binley, 1992), Bayesian model averaging (BMA) (Hoeting et al., 1999; Neuman, 2003), and multi-model ensemble method (MME) can be useful for the systematic and robust uncertainty assessment.

3.2 Description and classification of solute transport models in karst water resources

3.2.1 Generic classification of karst simulation models

To deal with a wide variety of flow and transport problems in karst water resources, two fundamental approaches have been using for representing the physical heterogeneities of karst systems: (*i*) spatially lumped karst simulation models and (*ii*) spatially distributed karst simulation models (Hartmann et al., 2014) (Figure 6) while various forms of models in between (called semi-distributed or hybrid models) are available for the simulations of the karst systems (Kovács & Sauter, 2014; Hartmann et al., 2013a, Gill et al., 2013, 2021). Since the distributed models represent the physical processes more explicitly based on the physical laws by discretizing the karst systems into several grid cells, data requirement is often too high to adequately represent the karst flow and transport processes at varying spatial scales (Hartmann et al., 2014). By comparison, the spatially lumped karst simulation models do not explicitly consider the karst system's spatial variabilities (i.e., geometric boundaries, flow pathways) (Hartmann et al., 2014), thereby implicitly representing the physical processes across the domain of interest.

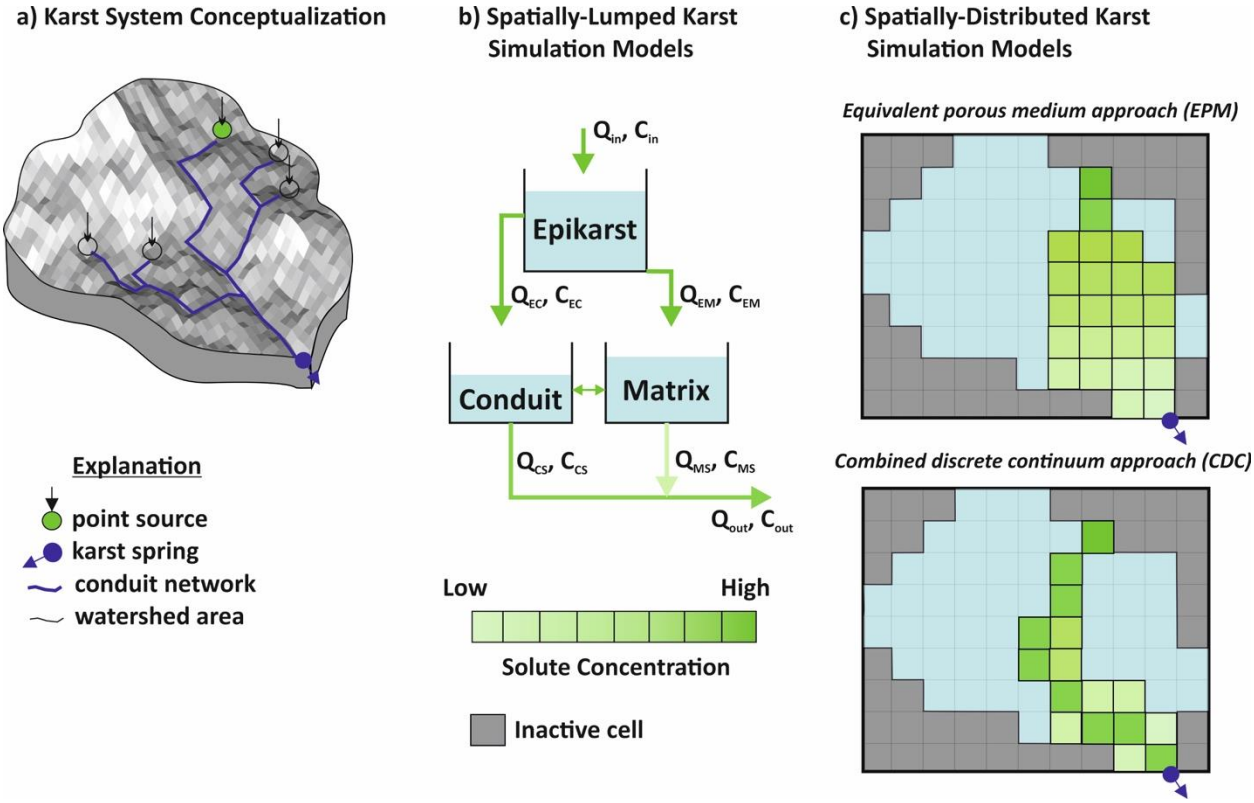

Figure 6. Generic classification of karst simulation models based on the model parametrization considering process complexity and data requirement. **(a)** Conceptualization of the karst aquifer physical boundaries depicted by the gray-shaded area with a blue-indicated karst conduit network (the blank-circles also describe the swallets/sinkholes along the conduit network), **(b)** Spatially lumped karst simulation models depicted based on the solute concentration distribution over different karst compartments, **(c)** Spatially distributed karst simulation models described considering the spatial distribution of the solute concentration. The classification is adapted from Hartmann et al., 2014 (see the further details in Hartmann et al., 2014). Herein, an artificial tracer test is described for demonstrating only the spatial distributions of contamination plume across two main karst simulation approaches.

For karst systems, spatially distributed karst simulation models are classified as (*i*) Equivalent Porous Medium Approach (EPM), (*ii*) Double Continuum Approach (DC), and (*iii*) Combined Discrete-Continuum approach (CDC) (Ghasemizadeh et al., 2012; Hartmann et al., 2014). EPM is a continuum-based modelling approach that considers the Representative Elementary Volume (REV) and groundwater flow equations (Hartmann et al., 2014; Scanlon et al., 2003) (Figure 6c). REV is defined as the smallest volume over which the averaged flow and transport parameters can be represented by the spatial scale where we can still apply the Darcy law based on the laminar flow conditions. REV represents a threshold volume in which the hydrological properties are assumed to be invariant after then (Medici & West, 2021). Nonetheless, due to the presence of the karst conduit and/or conduit networks, the flow in karst conduits is often characterized by turbulent flow characteristics, and hence representing the whole karst system with a single REV is not necessarily possible (Geyer et al., 2013; Kiraly, 2002). For that, EPM is often (more) suitable for simulating larger scale model applications where the karst flow and transport processes can be described by a single REV (Anderson et al.,

2015; Scanlon et al., 2003). In DC approach, the karst system consists of (at least) two overlapping continua (i.e., karst conduit and matrix) where the physical and/or chemical interaction between these two continua is addressed by an exchange rate (i.e., flow and/or mass exchange) (Cherubini, 2008; Kiraly,1998; Maréchal et al., 2008, Robineau et al., 2018; Teutsch & Sauter, 1998). Here, the rate of exchange is proportional to the differences of hydraulic head and/or concentration gradient between the karst conduit and matrix continua (Kavousi et al., 2020; Oehlmann et al., 2015; Reimann, 2011a, 2011b, 2014).

By comparison, CDC treats the karst conduits as the main flow and transport regions while an additional parameter set (i.e., mass exchange parameter) is defined for the matrix component. According to the CDC approach, karst conduits can be either treated as high permeable regions or characterized as drain (or pipe) (Figure 6c). This approach considers the discrete conduit and/or conduit networks, it is often more reasonable choice for the well-defined sites and/or small-scale karst modelling applications due to extensive data need and high computational effort for representing karst conduits and its topology (i.e., conduit networks, fracture intersection) (e.g., Kovács, 2003, Ravbar et al., 2011; Xanke et al., 2016). Here, the turbulent flow characteristics in karst conduit and/or discrete conduits is often simulated by Conduit Flow Process (CFP) (developed by Shoemaker et al., 2008 and later extended by Reimann et al., 2013, 2018, 2023). CFP has been successfully applied for well-characterized karst systems to simulate conduit flow and transport characteristics (Chang et al., 2019; Spieesl et al., 2017; Shirafkan et al., 2023; Sullivan et al., 2019; Xu et al., 2015, among many others). Therefore, CFP can consider both laminar and turbulent flow regimes by coupling solute and/or heat transport processes (Kavousi et al., 2020; Reimann et al., 2018).

Spatially lumped karst simulation models (i.e., bucket-type models, cascading reservoirs) conceptualize the entire karst systems based on the karst system's compartments (i.e., matrix, conduit, epikarst) in which average physical properties of the system are represented (e.g., Charlier et al., 2012; Geyer et al., 2008; Jukić & Denić-Jukić, 2009; Mazzilli et al., 2019; Orban et al., 2010; Tritz et al., 2011, among many others) (Figure 6b). By quantifying the vertical and/or horizontal water exchange between these compartments, the lumped models are often coupled with the 'mixing' concept to describe the transport dynamics in karst systems (see following subsection).

3.2.2 Classification of solute transport models in karst systems

As there is not a generic classification for the solute transport models in karst water resources, we suggest the following classification for modelling approaches of solute transport processes in karst systems. This proposed classification is categorized based on the complexity of karst system conceptualization, (model) data requirement, and (model) numerical formulation. Therefore, the solute transport models are divided into two main classes: Lumped transport models (LTMs) and Advanced transport models (ATMs) (Figure 7).

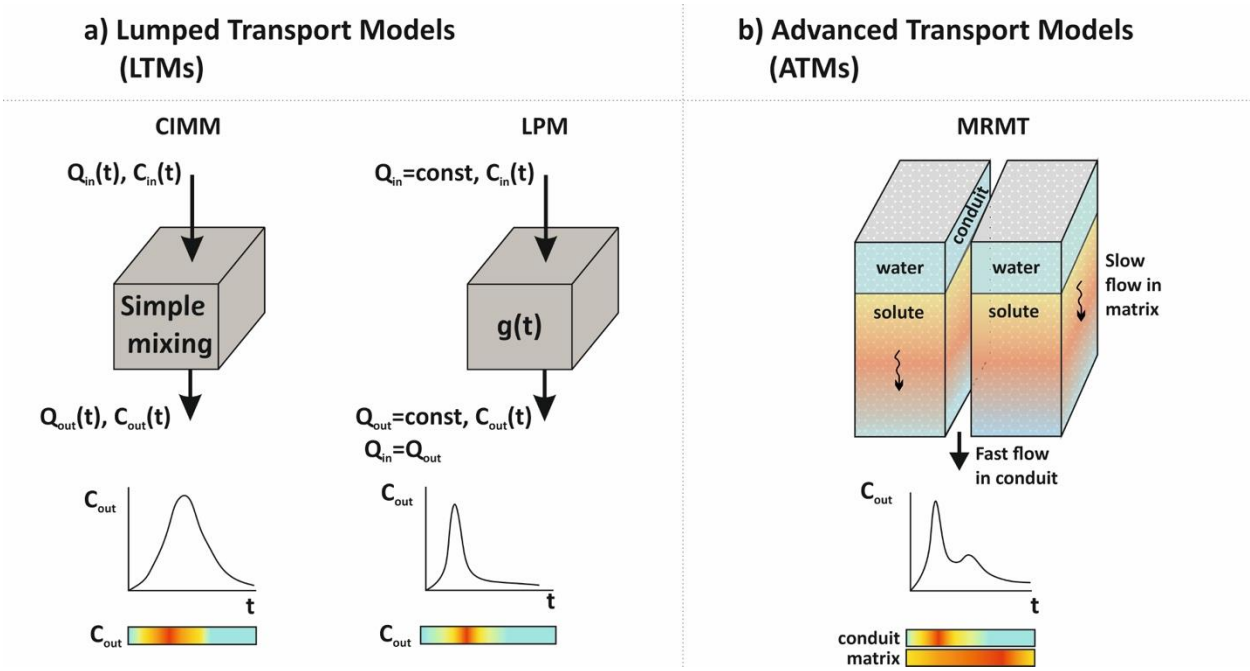

Figure 7. The conceptual descriptions of the solute transport models often used in karst systems. **(a)** Lumped transport models (LTMs) including complete instantaneous mixing model (CIMM) and lumped parameter model (LPM), **(b)** Advanced transport models (ATM) such as Multi-rate Mass-transfer Model (MRMT).

Overall, LTMs consider the karst flow field as a single non-distributed black box by assuming the karst flow is constant at the domain of interest (Bayari, 2002; Ozyurt & Bayari, 2005, 2008). Since LTMs do not require specific knowledge about the various transport processes (i.e., advection, dispersion, mass exchange) within the flow domain, they are often preferable for karst modelling applications particularly at aquifer scale and/or regional scale (Małoszewski & Zuber, 1996; Toth & Katz, 2006). ATMs, by comparison, explicitly consider the impact of the karstic heterogeneities both on the flow velocity field and on the anomalous transport (i.e., late-time and/or early arrivals in BTC). Therefore, the underlying assumptions of ATMs are physically better than LTMs whereas the mathematical solutions are more complex and rather prone to the numerical errors.

Lumped transport models (LTMs)

Lumped transport models (LTMs) comprise the compartmental mixing models — often referred as complete and instantaneous mixing models (CIMMs) — and lumped parameter models (LPMs) (Figure 7).

CIMM is a compartmental model approach, in which a solute of interest is mixed in a model compartment (usually the bucket of a lumped model) based on an assumption of instantaneous and complete mixing. The mixing can be applied to each of the model's compartments (i.e., epikarst, matrix, and conduits as depicted in Figure 6b) or to the entire simulated dynamic water storage. Also, partial mixing within the same storage has been applied in some studies (e.g., McMillan et al. 2012). In CIMMs, while the structure of the lumped karst flow model specifies the flow paths between the compartments, solute mass balance between those compartments is solved by the solute mixing ratios. Although simple, this approach brings

683 the advantage of requiring no (complete mixing, Hartmann et al. 2012b, 2013a, 2016a) or few
684 (partial mixing, Zhang et al., 2020a) transport modeling parameters. However, CIMMs ignore
685 advection and time-variant mixing transport characteristics of the karst systems. Therefore, their
686 application for karst transport modeling is often limited.

687 LPMs were a common modelling approach in karst aquifers mainly due to its simplicity
688 (significant simplifications with fewer parameters) and suitability for the data-rare sites (e.g.,
689 Bayari, 2002; Małoszewski et al., 1992, 2002; Zuber, 1986; Zuber & Małoszewski, 2001, among
690 many others). LPM was first introduced by Małoszewski & Zuber (1982) to solve the transport
691 problems in karst systems.

692 LPM is a groundwater age-based modelling approach that solves age distributions (i.e.,
693 TTDs, RTDs) of the solute of interest at the karst system outlet (i.e., karst spring, observation
694 well). In doing so, LPM converts the input solute concentrations (i.e., $\delta^{18}O$ concentrations of
695 atmospheric precipitation) to the output solute concentrations (i.e., $\delta^{18}O$ concentration of karst
696 spring) using a convolution integral in Eq. 1.

697 $$C_{out}(t) = \int_0^\infty C_{in}(t-\tau)g(\tau)exp(-\eta\tau)d\tau \quad (1)$$

698 where C_{out} [ML^{-3}] and C_{in} [ML^{-3}] are the input and output tracer concentrations,
699 respectively. τ [T] is the travel time (or residence time is often used in groundwater studies).
700 $g(\tau)$ is the impulse response function (or transfer function) that is characterized by the system's
701 TTDs. Here, t refers to the calendar (or current) time and η is a decay constant accounting for the
702 non-conservative transport mechanisms. In Eq.1, when a conservative tracer is considered for the
703 model application, the decay term is then set to zero (Małoszewski & Zuber, 1982; Zuber &
704 Małoszewski, 2001). But the critical parameter for karst transport modelling studies in Eq.1 is
705 the mean transit time of the solute of interest, referred to as mean transit time (MTT) for the
706 time-invariant hydrological conditions (Eq. 2);

707 $$MTT = \int_0^\infty tg(\tau)d\tau \quad (2)$$

708 In LPMs, the response function plays an important role in quantifying the physical
709 spreading of solutes of interest at the transport domain. It describes how different (groundwater)
710 ages in the convolution integral contribute to the age distributions at the karst system's outlet
711 (i.e., springs, observation well). Consequently, a proper definition and/or selection of a suitable
712 response function for the LTMs is a critical step in representing the underlying flow and
713 transport processes (Małoszewski & Zuber, 1993; Zuber, 1986). This functional form can either
714 be defined by a priori understanding or by comparing the simulations of different response
715 functions to historical records of the solute concentrations at a particular sampling location (i.e.,
716 springs, observation wells). For instance, the simplistic LPMs resemble the individual flow and
717 transport paths with no mixing in karst systems (i.e., for the conduit-dominated karst aquifers) or
718 well-mixed (or perfect mixing) karst systems (i.e., for the matrix-dominated karst aquifers).
719 While the former would be represented by the Piston Flow Model (PFM) response function, the
720 latter one would be represented by the Exponential Model (EM) (e.g., Małoszewski & Zuber,
721 1982, 1993; Zuber, 1986). There are also different combinations of the response functions that
722 are used to represent the transport dynamics of karst systems such as the combined exponential
723 piston models (EPM) and dispersion models (DM) which resembles the solute mixing between
724 perfect mixing and no mixing (Maloszewski et al., 2002; Małoszewski & Zuber, 1982, 2002;
725 Zuber & Maloszewski, 2001).

Furthermore, as the response function in Eq.1 defines groundwater age distributions in the karst system (i.e., TTDs or RTDs), it also enables us to link between LPMs and groundwater age models — known as Direct Age Models (DAMs) — (e.g., Cornaton & Perrochet, 2006a, 2006b; Ginn, 1999, 2009; Goode, 1996; Sanford, 2011; Suckow, 2014).These models predict the water age distributions by solving ADE in which the 'solute mass' concentration is replaced by a groundwater 'age term' (see more details in Ginn, 1999, 2009; Goode, 1996).

Single-fissure dispersion model (SFDM) and Multi-dispersion model (MDM) — known also as the multi-flow dispersion model are two common types used for estimating karst flow and transport parameters (Figure 8) by including more process understanding compared to simple LPMs. These models differ from LTMs in that the additional parameters (i.e., dispersion parameter) are required for solving dispersive-diffusive processes in karst matrix. In general, as both SDFM and MDM analytically solve the karst transport problems, they are more suitable for the well-defined aquifer conditions where the initial and boundary conditions are known (e.g., Göppert & Goldscheider, 2008; Frank et al., 2021; Kübeck et al., 2013; Vincenzi et al., 2009). They are derived from the earliest analytical solutions of one-dimensional ADE by Lenda & Zuber (1970) and Kreft & Zuber (1978). The general form of the advection-dispersion model (ADM) is as followed by;

$$C_f(x,t) = \frac{M}{Q.t_0.\sqrt{4\pi.Pe^{-1}.\left(\frac{t}{t_0}\right)^3}} exp\left[\frac{\left(1-\frac{t}{t_0}\right)^2}{4.Pe^{-1}.\frac{t}{t_0}}\right] \quad (3a)$$

$$P_e = \frac{D_L}{\vartheta.x};\ D_L = \alpha_L.x \quad (3b)$$

where $C_f(x,t)$ [ML^{-3}] is solute concentration, Q [M^3T^{-1}] is discharge, and t_0 [T] is the time of mean flow (or refers also to the mean residence time) [T]. D_L [L^2T^{-1}] is the longitudinal dispersion, and α_L [L] is the longitudinal dispersivity.

In Eq. 3, P_e is the (dimensionless) Pèclet number which is the characteristic flow length multiplied by the mean flow velocity (ϑ) and divided by the diffusivity (Labat & Mangin, 2015) and it represents the ratio of the advective transport rate to the diffusive transport rate. Along this characteristic length, P_e is assumed to be constant and homogeneous. However, this rarely holds the reality in karst aquifers. For a (karst) aquifer scale, when P_e is below 0.4 [-], diffusion controls the solute transport while P_e > 6.0 [-] indicates the advection-dominated transport characteristics. 0.4 < P_e < 6.0 demonstrates the (transition) transport characteristics varying between the diffusion-dominated and advection-dominated transport (Field & Nash, 1997). In Eq. 3a, $1/P_e$ is called as a dispersion parameter for describing the (matrix) diffusion effect on the solute transport behaviour (e.g., Małoszewski & Zuber, 1982, 1992; Zuber, 1986).

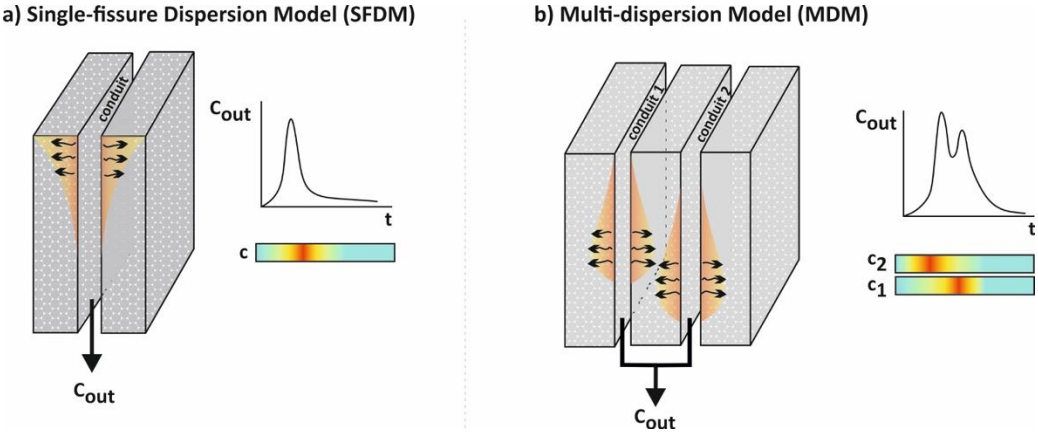

Figure 8. The conceptual descriptions of **a)** Single-fissure dispersion model (SFDM), **b)** Multi-dispersion model (MDM). Here, c refers to a single conduit while c_1 and c_2 are denoted as Conduit-1 and Conduit-2.

SFDM or Parallel fissure dispersion model (PFDM) by Małoszewski & Zuber (1985) is based on the theory of the parallel-plate modelling approach introduced by Sudicky & Frind (1982). This approach considers the solute transport along the parallel fissure plates and into the matrix coupled by the matrix diffusion (Małoszewski & Zuber, 1985). For karst aquifers, SFDM is first applied into the fissured chalk aquifers by Małoszewski & Zuber (1990) and modified later by Witthüser et al. (2003) to simulate transversal dispersion in chalk aquifers. To solve the karst transport problem, SFDM requires three parameters including dispersion parameter, diffusion parameter, and mean transit time (Małoszewski & Zuber, 1985; Małoszewski et al., 1994; Witthüser et al., 2003).

MDM is an extension of ADM, and it considers the multiple discrete flow and transport pathways. While MDM solves ADM in each flow path based on the specified parameters (i.e., flow rate, transit time, and dispersivity) (Małoszewski et al., 1992, 1994), it is often used for the (a large-scale) multi-peaked BTC analysis in karst systems (e.g., Goldscheider et al., 2008; Richter et al., 2022).

Advanced transport models (ATMs)

The anomalous behaviour in karst transport is frequently characterized by the rapid spread of the font of the contaminant plume due to existence of preferential paths, as well as by the slow diffusion owing to the mass exchange between the karst conduit and surrounding carbonate matrix (e.g., Berkowitz et al., 2006; Goeppert et al., 2020; Ewers et al., 2012; Wang et al., 2022). Diffusion and retardation processes often result in the late-time heavy tailing in BTC, and thus refers to time-nonlocality in karst transport behaviour. By comparison, highly skewed and/or multi-peaked BTC characteristics is defined by the space-nonlocality in solute transport behaviour (see also Figure 4) (e.g., Haggerty & Gorelick, 1995; Haggerty et al., 2000; Zhang et al., 2020; Zhang et al., 2009). In this context, ATMs intend to capture the spatiotemporal dynamics of the anomalous karst transport.

In this review, ATMs is divided into three main modelling concepts: (*i*) Continuous-time Random Walk (CTRW) that discretizes the solute concentration into the particles to describe the spatiotemporal evolution of each particle, (*ii*) Fractional Advection-Dispersion Equation (FADE) wherein the solute movement obeys the non-Gaussian distribution, and (*iii*) Multi-rate mass

transfer (MRMT) models that divide flow and transport domain into (at least) matrix and conduits. Broadly speaking, MRMT and FADE represent the Eulerian-type (Continuum) modelling approaches while CTRW is the Lagrangian-based transport modelling approaches. Here, the Eulerian-type models consider the volume-based flow and transport by discretizing the problem domain into the different volumes while the Lagrangian-based approaches, such as Particle Tracking (PT), Random Walk Particle Tracking (RWPT) discretize the solute concentration into the particles, thereby considering the solute particles as a discrete phase without an explicit need for a flow field definition. CTRWs and FADEs are the robust transport modeling approaches, especially for capturing the time-nonlocalities in solute transport behaviors in heterogeneous groundwater systems (e.g., Benson et al., 2000; Meerschaert et al., 1999; Metzler & Klafter, 2000; Schumer et al., 2009) although the applications of both modelling approaches in solving karst transport problems are rather new. In the following, we will provide fundamental knowledge about these advanced karst transport models and their primer applications in modelling of karst solute transport processes.

CTRW considers the solute (particle) transport as a random walk in spatial and temporal scales (Berkowitz et al., 2006; Dentz & Berkowitz, 2003). It is a generalization of the Random walk methods in that the spatial displacement and temporal resolution (or time-step) are counted as random variables (Dentz et al., 2004). In fact, the formalism of CTRW originates from Einstein's Brownian motion approach that considers the random motions of the solute particles. While CTRW has been extensively applied for the fractured rocks and aquifers (e.g., Berkowitz et al., 2001, 2006; Hansen & Berkowitz, 2020), the first application of CTRW in karst systems was done by Goeppert et al. (2020) for the simulation of the flow and transport processes in an alpine karstic aquifer. The CTRW approach is particularly useful for simulating the late-time and heavy-tailed characteristics of the solute transport behaviour (e.g., Berkowitz et al., 2006; Berkowitz & Scher, 1995; Dentz & Berkowitz, 2003). For this reason, it better resembles the dispersion and diffusion processes as compared to the particle tracking techniques (Tsang & Tsang, 2001). In general, the applications of the Particle-tracking based methods in karst aquifers are preferable for the delineation of capture zone characteristics in the well-head protection studies (e.g., Klaas et al., 2017; Rayne et al., 2001; Qiao et al., 2015).

FADE uses an additional "fractional" term in the classical ADE given in Eq. 4 for non-sorbing (immiscible, single dissolved) solute transport without a source term,

$$R\frac{\partial C}{\partial t} = -\vartheta\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2} \quad (4)$$

in which ϑ [LT^{-1}] is the flow velocity and x [L] is the transport distance in the main flow direction. C [ML^{-3}] is the solute concentration in time (t) [T]. D [L^2T^{-1}] is the (longitudinal) dispersion coefficient in the main flow direction. Here, R is denoted as a retardation factor and estimated by the following formula,

$$R = 1 + \rho_s K_d \quad (5)$$

where K_d [L^3M^{-1}] is denoted as the distribution (or partition) coefficient that is described as a ratio of the sorbed concentration into (geological) material and the dissolved concentration in groundwater at (thermodynamically) equilibrium conditions. In karst aquifers, K_d is often used to describe the sorption degree of any species in karst groundwater based on the distribution of solute between solid matrix and groundwater (e.g., Pastore et al., 2021). Therefore, as for the

833 estimation of retardation given in Eq.5, when K_d is equivalent to 0, it equals 1, which means that
834 the retardation is negligible during the karst transport mechanism.

835 The "fractional" term in FADE refers to the fractional derivatives of dispersion that are
836 incorporated by time and/or space for solving time and/or space non-localities in BTC (see for
837 latest discussions on FADEs by Sun et al. (2020)). For one-dimensional solute transport form of
838 FADE is followed by Meerschaert et al. (1999) and Kelly & Meerschaert (2019);

839 $$\frac{\partial C}{\partial t} = -\vartheta \frac{\partial C}{\partial x} + D_\rho \frac{\partial^\alpha C}{\partial x^\alpha} + D(1-\rho)\frac{\partial^\alpha C}{\partial(-x)^\alpha} \qquad (6)$$

840 where C [ML^{-3}] is the solute concentration in time (t) [T] and the transport distance (x)
841 [L] in the direction of main flow. ϑ [LT^{-1}] is the mean flow velocity, and D [L^2T^{-1}] is a dispersion
842 coefficient in the main flow direction. Here, $0 \leq \rho \leq 1$ describes the skewness of the transport
843 processes while α [-] is the order of fractional derivatives.

844 Depending on which nonlocality problem (time or space nonlocalities) is being solved,
845 FADE is either called the time-in-fractional advection-dispersion equation or the space-in-
846 fractional advection-dispersion equation. While the time-nonlocality is typically related with the
847 diffusion and retardation processes resulting in late-time heavy tailing in breakthrough curve
848 (BTC), the space-nonlocality leads to highly skewed and/or multi-modality on the BTC (e.g.,
849 Feehley et al., 2000; Haggerty & Gorelick, 1995; Haggerty et al., 2000; Zhang et al., 2020,
850 among many others). For solving karst transport problems, Yin et al. (2022) proposed the
851 efficient fractional-in-time transient storage model for simulating the multi-peaked BTC in karst
852 aquifers which considers the karst solute transport in two domains by solving the tailing effects
853 in BTC due to the mass exchange between these regions while Zang et al. (2024) introduced an
854 improved version of the FADE to solve the late-time behaviors of BTC characterized by the
855 multiple-conduit flow within an intermediate-scale karst aquifer, named as the impulsive
856 tempered FADE approach.

857 MRMT models are the generalization of the mobile-immobile model (MIM) concept —
858 known also as the classical dual domain approach — (Carrera et al., 1998; Coats & Smith, 1964;
859 Gerke & Van Genuchten, 1993; Haggerty & Gorelick, 1995). MIM simulates the flow and solute
860 transport processes based on two distinct flow and transport regions: mobile zone (e.g., conduit,
861 fracture, fissure) and immobile zone (e.g., matrix, voids, vugs, dead-end passages along conduits
862 and/or cave streams). Here, MRMT differs from the MIM approach in that it considers the (one)
863 mobile domain with the multiple immobile regions (Figure 9). For this reason, MRMT considers
864 the multi-rate mass transfer exchange terms for each interaction zone to solve the solute transport
865 characteristics that are frequently characterized by heavy-tailing and multi-modality in BTC
866 (Figure 9).

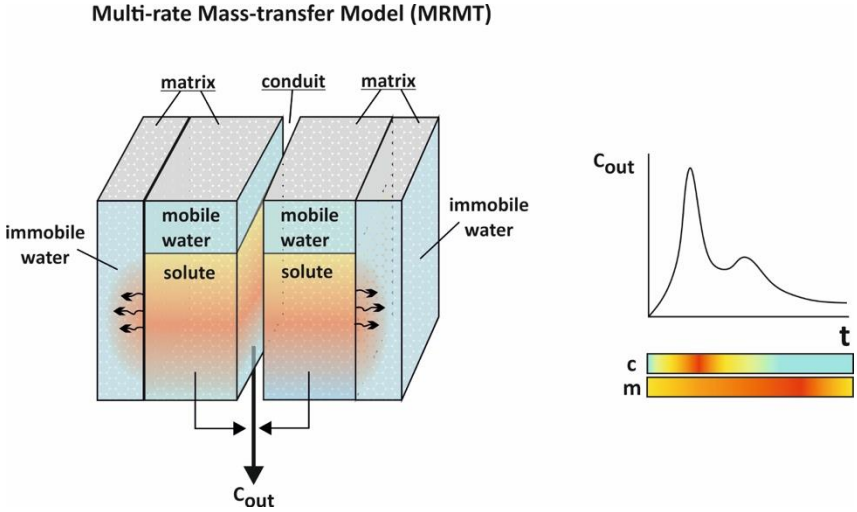

Figure 9. The schematic description of the Multi-Rate Mass-Transfer (MRMT) model. Here, *c* and *m* are denoted as karst conduit and matrix components, respectively.

In karst aquifers, adaptations of the MIM approach have been extensively used to simulate transport processes. In the MIM approach, the dominant transport is described by the advective-dispersive processes along the mobile zone while the mass transfer between the mobile and immobile regions is only controlled by the (matrix) diffusion without any fluid exchange (Becker & Bellin, 2013; Małoszewski & Zuber, 1990; Toride et al., 1995). Therefore, solute transport is set by the classical ADE with an additional term that describes the mass transfer gradient. For one dimensional solute transport with MIM approach is then written as follows:

$$\beta \frac{\partial C_m}{\partial t} + (1-\beta)\frac{\partial C_{im}}{\partial t} = D_m \frac{\partial^2 C_m}{\partial x^2} - \vartheta_m \frac{\partial C_m}{\partial x} \quad (7a)$$

$$\frac{\partial C_{im}}{\partial t} = \omega(C_m - C_{im}) \quad (7b)$$

where C_m [ML^{-3}] and C_{im} [ML^{-3}] refer to the solute concentrations in mobile and immobile regions, respectively. D_m [L^2T^{-1}] refers to the (longitudinal) dispersion in the mobile region while ϑ_m [LT^{-1}] is the mean flow velocity in the mobile region. Here, β [-] is the partition coefficient that describes the proportion of water in the mobile region. Higher values of β indicate that the substantial amount of water influences the solute transport ($0 \leq \beta \leq 1$). When β is equal to 0, however, the MIM model turns out to be the classical ADE (see Eq. 3). ω [T^{-1}] is the first-order mass transfer coefficient that characterizes the mass exchange rate between the mobile and immobile regions. For instance, increasing values for ω [T^{-1}] implies that the intensive (mass) transfer takes place between the mobile and immobile regions. In case multiple-rate mass transfer exchanges is considered, the term $\frac{\partial C_{im}}{\partial t}$ can be defined based on the memory function that defines the (particle) travel time distributions over the immobile region.

To simulate karst transport, the two-region non-equilibrium (2RNE) approach is frequently used for simulating transport dynamics in karst aquifers (e.g., Assunção et al., 2023; Barberá et al., 2018; Birk et al., 2005; Ender et al., 2018; Geyer et al., 2007; Goeppert et al., 2020; Göppert & Goldscheider, 2008, among many others). Here, 2RNE only considers the flow along the karst conduit in which flow velocity is assumed to be constant whilst no water

exchanges are considered in between the matrix and conduit components (Field & Li, 2011; Li & Liu, 2014). For the simulation of reactive processes in karst aquifers, 2RNE was extended by the inclusion of the retardation factor by Geyer et al. (2007). Furthermore, similar approaches such as the physical non-equilibrium transport (PNE), the chemical non-equilibrium transport (CNE), and the physical and chemical non-equilibrium transport (PCNE) models by Field & Leij (2014) are also available. For more detailed representation of transport dynamics, the dual-domain based models (frequently dual-porosity models over the dual-permeability models) has also been extended by a triple porosity concept where the conduit flow is formulated based on the turbulent flow properties (Faulkner et al., 2009; Reimann et al., 2011a, 2014).

Other adaptations of the MRMT approach for karstic transport comprise the Dual-advection dispersion (DADE) model and the Transient storage model (TSM). Developed by Field & Leij (2012), DADE considers the solute transport characteristics between physically interacting two conduits (named for *i* and *j* in Eq. 8) whilst the mass exchange is (again) approximated by a first-order mass exchange between the main and auxiliary conduits (Bodin, 2020; Dewaide et al., 2016, 2018; Zhao et al., 2017; 2021) formulated by;

$$\theta_i \frac{\partial C_i}{\partial x} = \theta_i D_i \frac{\partial C_i}{\partial x} - \theta_i \vartheta_i \frac{\partial C_i}{\partial x} + \omega(C_j - C_i) \tag{8}$$

where θ_i [L^3L^{-3}] is the volumetric water content in *Conduit-i* while C_i is the solute concentration in *Conduit-j*. D_i [L^2T^{-1}] is the (longitudinal) dispersion coefficient while ϑ_i [LT^{-1}] is the mean flow velocity in the *Conduit-i*. ω [T^{-1}] is an effective first-order rate coefficient for the mass exchange between the *Conduit-i* and *Conduit-j*. Here, $\theta_i = \frac{A_i}{A}$ and $A_i = A - A_j$ while A_i represents the water-filled area for the *Conduit-i* (see more explanations by Field & Leij (2012)).

As for TSM, it is built upon the dual-domain model concept in which the preferential flow paths are considered the main flow and transport regions. Originally developed for solving transport problems in streams, TSM has been adapted to simulate karst transport problems (e.g., Morales et al., 2010; Hensley & Cohen, 2012). TSM was then reformulated by Dewaide et al. (2016) for the karst aquifers such that the karst conduits are counted as the main flow and transport regions whereas the (transient) storage zones are represented either by the pools in which eddies and vortices frequently occur (Figure 10) or by cave sediments and carbonate matrix (e.g., Deleu et al., 2023; Dewaide et al., 2018; Tinet et al., 2019; Zhao et al., 2017, 2019, 2021). TSM is formulated as followed by,

$$\frac{\partial C}{\partial t} = -\frac{Q}{A}\frac{\partial C}{\partial x} + \frac{1}{A}\frac{\partial}{\partial x}\left(AD_L\frac{\partial C}{\partial x}\right) + \alpha(C_s - C) \tag{9a}$$

$$\frac{\partial C_s}{\partial x} = \alpha\frac{A}{A_s}(C - C_s) \tag{9b}$$

where Q [L^3T^{-1}] is the volumetric flow rate and D_L [L^2T^{-1}] is the (longitudinal) dispersion coefficient. C and C_s [ML^{-3}] represent the solute concentrations in the main flow channel and in the storage zone, respectively. While A [L^2] and A_s [L^2] are the cross-sectional areas of the main flow channel and storage zones, the term $\frac{Q}{A}$ [LT^{-1}] refers to the mean flow velocity along the main flow channel (i.e., karst conduit, cave stream). α [T^{-1}] is the (first order) mass exchange term (described also as a storage zone exchange coefficient, see Figure 10)

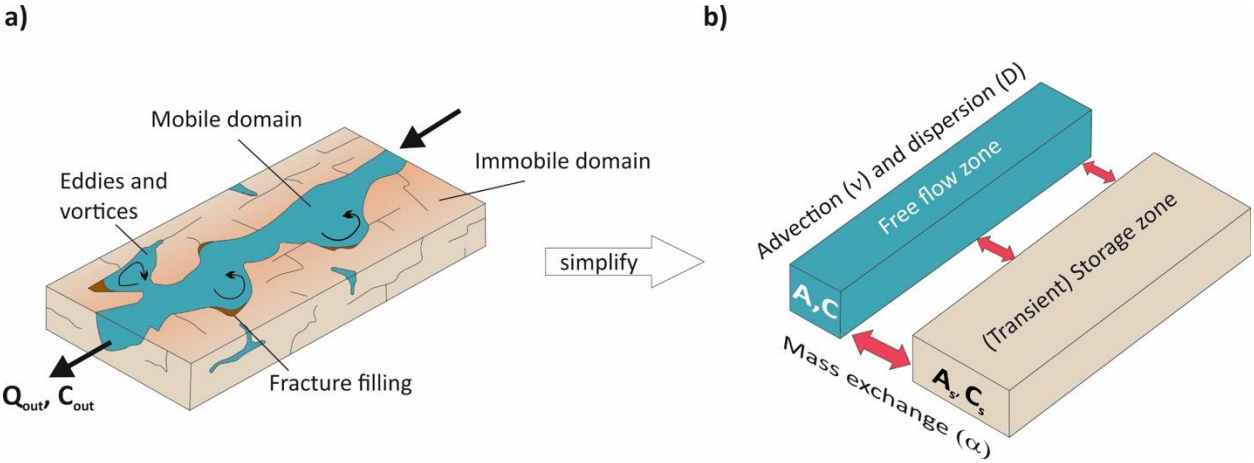

Figure 10. a) A perceptual schematic of the dual transport domain along the (reach) of karst conduit and an overlapping (fractured/fissured) carbonate matrix. **b)** The transformation of the conceptual model in Panel-a into the mathematical concept of the Transient Storage model (TSM). Here, the lateral inflow and outflow rates are not considered along the reach of karst conduit.

Overall, the MIM-based modelling approaches have strong limitations by representing the physical transport region in karst systems, particularly by representing the eddy mixing and inertial flow (Anwar & Sukop, 2009). There are newly proposed advanced transport models to solve the anomalous transport such as late-time, early arrivals, and/or multi-peaked BTC in karst systems while some of them were originally developed for the heterogeneous porous media and fractured aquifers. The fundamental concept of these advanced modelling approaches is (again) the consideration of two-region transport. But they require more sophisticated parameters in describing the mass exchange between the karst conduit and matrix. For instance, the dual heterogeneous domain model (DHDM) developed by Yin et al. (2022) solves the large-scale anomalous transport in karst systems that are characterized by the multiple peaks and strong tailing in BTC (Ji et al., 2022; Yin et al., 2022). DHDM considers the combination of MRMT and DADE (Leij et al., 2012) based on the memory function and fractional derivatives (see further details in Yin et al., 2022 and Ji et al., 2022). That way, two main parameter sets in DHDM describe the individual flow velocity (advection) and (hydrodynamic) dispersion for each mobile region. Similarly, the multi-region advection dispersion (MRAD) and Dual Region Advection Dispersion (DRAD) models proposed by Majdalani et al. (2018) consider the karst flow and transport process for (at least) two mobile regions in parallel and the mass exchange resulted from the concentration gradient (Majdalani et al., 2018).

4 Lessons learned: Challenges in the successful transport modelling practice

Considerable efforts have been devoted to representing transport processes in karst flow models over the last couple of decades (see Section 3). However, great challenges remain to successfully model solute transport dynamics in karst systems and to provide robust transport predictions. The challenges spread over all parts of the karst transport modeling practice (subsection 3.1, Figure 5) and will be elaborated in the following.

4.1 System conceptualization considering data collection and system understanding

System conceptualization for modelling of karst transport processes requires a proper understanding of the system's physical, chemical, and bio(geo)chemical characteristics. This requires extensive data sets (Huntoon, 1995; Jeannin et al., 2013; Parise et al., 2015; Perrin et al., 2003a). However, given that the availability of such a massive data is very limited, a proper conceptualization of the spatiotemporal variabilities of karst transport processes (i.e., advection, dispersion, sorption and/or chemical transformations) is limited, too (e.g., Covington et al., 2011; Field & Pinsky, 2000; Hartmann et al., 2014; Quinlan et al., 1996).

Knowledge accumulation by the compiled data feeds the perceptual understanding of the karst system's characteristics, and thus allows the modelers to map the system's conceptual definition out. For this reason, the required level of details for the karst transport problem often shapes our data collection strategy, and hence designs the monitoring networks (e.g., Hunkeler & Mudry, 2014; Nativ et al., 1999; Panno et al., 2019; Stevanović & Stevanović, 2021; Vucinic et al., 2022, among many others). In practice, however, there are certain difficulties during the karst system conceptualization including the (*i*) right definition of spatial scale for the transport problem, (*ii*) right definition of the temporal scale of karst transport dynamics with their temporal variabilities, (*iii*) realistic definitions of parameter values, and (*iv*) process dependency to the complex karst flow. Each of which will be pointed out in the following.

The right definition of the scale of karst transport problem is vital for the system conceptualization. However, due to the karstic heterogeneity at multiple scales, the investigated/modelled domain might substantially differ from the actual transport domain in which physical and (biogeo)chemical processes predominantly occur. This is often the case in karst systems in that both physical and chemical parameters controlling flow and transport processes rely on the scale being investigated (e.g., Göppert & Goldscheider, 2008; Medici & West, 2021). The spatial extent for the transport problem is generally defined by the field experts and/or modelers themselves. As an implicit rule, the scale of interest should not be less or greater than the scale of method (i.e., artificial tracer tests, pumping tests) applied for the characterization of that particular process (Bakalowicz, 2005; Geyer, 2008; Ghasemizadeh et al., 2016; Maréchal et al., 2008). Nonetheless, the methods for data acquisition and/or interpretation techniques are often (more) appropriate for the continuum (Darcy) scale applications where the effective parameters can often be used for the entire domain (Faulkner et al., 2009; Huntoon, 1995; Reimann et al., 2011; Zhang et al., 2021). For this reason, more sophisticated equipment and research techniques might be required for the descriptions of the karst transport dynamics. For instance, the characterization of nitrate or (dissolved) organic carbon migrations in karst systems are rather challenging due to the (contaminant) input variability (e.g., Husic et al., 2019; Orban et al., 2010; Opsahl et al., 2017; Yue et al., 2019, 2020) and less-known source history (e.g., Liu et al., 2021; Lu et al., 2023; Ren et al., 2022; Sullivan et al., 2019). Therefore, it might also be difficult to successfully capture the spatiotemporal dynamics of the contaminant migration depending on the contaminant of interest with the regular measurement devices and/or monitoring systems (e.g., Finsterle et al., 2012; Zhu et al., 2007).

The right identification of the transport timescale with its temporal resolution is crucial for the proper representation of the karst transport dynamics (e.g., Bailly-Comte et al., 2011; Covington et al., 2012; Zhang et al., 2019). However, given that karst conduit and matrix might have order-of-magnitude differences in their hydraulic and physicochemical properties (i.e., porosity, hydraulic conductivity, reactivity constants), a wide range of timescales can be

identified for the karst transport (e.g., Robinson & Hasenmueller, 2017; Sivelle et al., 2019). But in the context of experimental characterization, the (karst) transport timescale is related to the process-timescale along the karst conduits (i.e., hours, days), for which shorter-timescale observations with higher sampling resolution (i.e., in minute, hourly, daily) are usually enough for capturing the karst transport dynamics (Figure 11). Without a long-term monitoring and (further) data collection strategy, however, the chemical and (biogeo)chemical processes occurring at (rather) larger timescales (i.e., annual, seasonal, decadal) might be underestimated and/or overlooked in such a data collection (e.g., Mathias et al., 2005; Tran et al., 2020; Wynn et al., 2013; Zhang et al., 2020b). Therefore, proper understanding of the (actual) mass transfers between the karst conduit and matrix is strictly limited (Brettmann et al., 1993; Cherubini et al., 2013; Zhao et al., 2017).

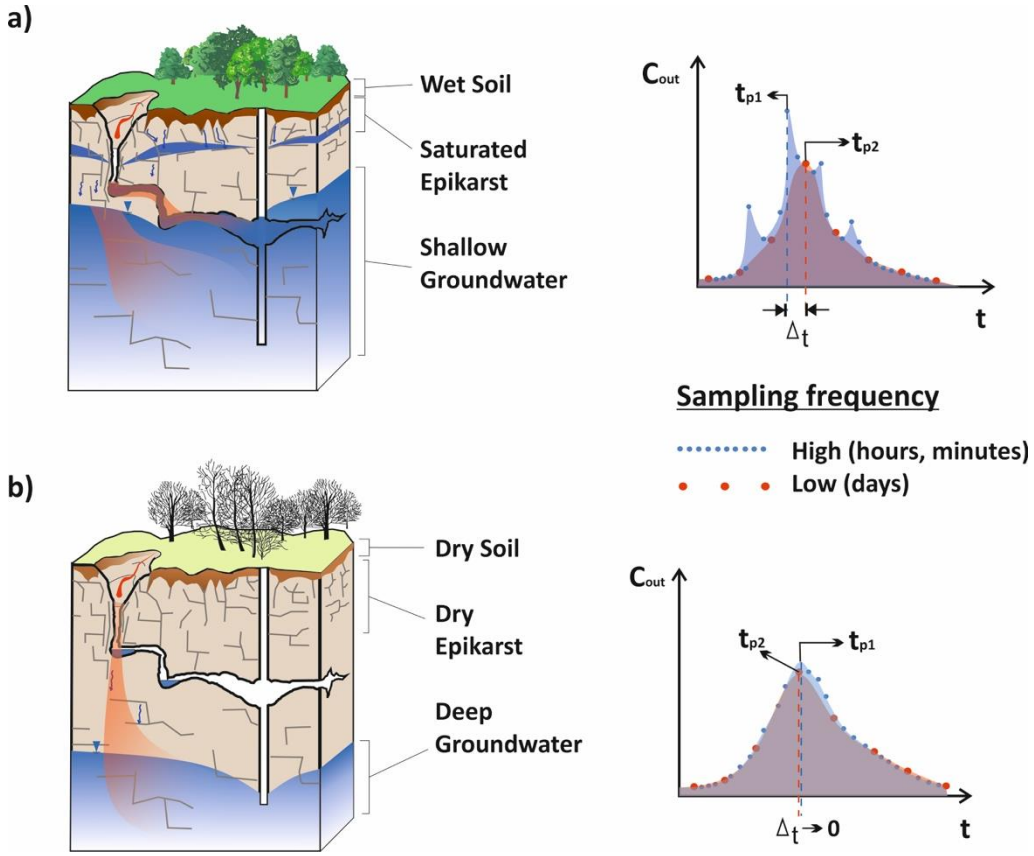

Figure 11. Schematic representations of the model conceptualization for solute transport dynamics in karst system considering the spatial extent and temporal scale of the karst transport. The schematic also demonstrates what affects the temporal variability of the transport processes under different hydrological conditions. **a)** Contaminant plume migration under the high-water flow conditions, **b)** Contaminant plume migration under the low-water flow conditions. Here, t_p depicts the time to the peak solute concentrations with respect to the hydrological variability and sampling frequency. t_{p1} (high resolution) and t_{p2} (low resolution) describe the time of the peak concentrations depending on sampling frequency.

The temporal variability of the data is another complement of the successful conceptualization because the karst transport dynamics are often controlled by the hydrological conditions being investigated (Figure 11). For instance, BTC resembles one of the solute

transport behaviours under certain flow conditions at certain time periods (Figure 11). However, actual transport can be broadly varied by the different timescales ranging from an event to seasonal and/or inter-annual timescales (e.g., Doummar et al., 2018; Luo et al., 2024; Remondi et al., 2018, 2019; Sivelle & Labat, 2019; Zhang et al., 2020a). As a matter of fact, the same shape for BTC might not actually be reproduced again if those particular conditions (both hydrological and physicochemical) at that particular timescale are not meet (e.g., Aydin et al., 2014; Chu et al., 2021; Kogovsek & Petric, 2014; Morales et al., 2007, 2018; Ravbar et al., 2012, among others). Therefore, the system conceptualization is restricted to the certain timescales and might not properly represent the overall karst transport dynamics especially when the hydrological or (biogeo)chemical conditions change or vary temporarily.

Another limitation in the system conceptualization is the identification of the realistic values for the system's parameters since both hydraulic and transport parameters can vary by orders of magnitude at differing spatial scales — from a few centimeters to hundreds of meters or more — (Berkowitz, 2002; Giese et al., 2018; Medici et al., 2019; Medici & West, 2021). Hydraulic conductivity and dispersivity are such parameters very sensitive to the scale variations, thus causing substantial variations in the spreading of the contamination plume in the karst aquifer. Likewise, chemical parameters (i.e., sorption parameters) obtained under the laboratory conditions might largely differ from those measured at the field scale (Faulkner et al., 2009; Witthüse et al., 2003). For instance, the partition coefficient (K_d) and mass transfer coefficient (i.e., first-order mass transfer coefficient) could not be generalized (e.g., Stockmann et al., 2017; Swami et al., 2018) because their values are extremely varied (often by order of magnitudes) at the field-scale measurements depending both on the matrix hydraulic properties (e.g., surface area, matrix porosity, permeability) and on the fracture/conduit characteristics (Howroyd & Novakowski, 2021; Lehmann et al., 2022; Maloszewski & Zuber, 1993; Zhou et al., 2007). Similarly, the values for reactive transport parameters could also be misleading particularly when they are scaled up or extrapolated, because of the oversimplification of the multifaceted processes that are varied both by chemical heterogeneities in the matrix and local/global groundwater chemistry (e.g., Howroyd & Novakowski, 2021; Jiang et al., 2023; Katz et al.,1998; Kaufmann et al., 2014; Mohammadi et al., 2021; Maqueda et al., 2023, among many others). For this reason, a realistic definition of the reactive transport parameters is strictly limited by the well-defined karstic sites or site-specific applications (i.e., single-well push-pull test) (e.g., Hillebrand et al., 2012a, 2012b, 2015; Priebe et al., 2022; Schiperski et al., 2016; Tran et al., 2020, 2021).

Field-scale experiments, particularly artificial tracer tests, are frequently performed under highly vulnerable aquifer conditions in which sinkholes and/or swallets are frequently utilized as tracer injection points (e.g., Jones, 2019; Li et al., 2008; Morales et al., 2007; Sinreich, 2011). For such experimental designs, as the preferential flow paths predominantly shape the spatiotemporal behaviour of the contamination plume, karst transport dynamics are often characterized by the advection-dominated transport between the injection and sampling points (i.e., between sinkhole and observation well, Figure 11). As a result, the role of matrix diffusion and mass exchange processes between the karst conduit and surrounding matrix might be underestimated. Furthermore, due to the randomly varying flow velocities in karst conduits, physical parameters such as hydraulic conductivity, velocity, dispersivity, solute travel time (Kavousi et al., 2020; Rehrl & Birk, 2010; Zhao et al., 2017) and chemical parameters including sorption and mass exchange parameters are rarely understood (Barberá et al., 2018; Field & Pinsky, 2000; Haggerty et al., 2004). Consequently, the observed data might not provide a

complete picture about the karst system's (overall) hydrochemical functioning and transport characteristics due to the limited transport distance and (certain) flow conditions under specific experimental conditions.

All these difficulties explain why a robust conceptualization for the karst transport dynamics is inherently limited, and why there are only few real-world applications of the karst transport models that solves the classical ADE (see Section 3.4). In this matter, the limitations in system conceptualization for karst transport point out the need for in-depth discussions on how to better align the investigated (transport) domain and the model domain in karst systems, as well as for finding better ways to collect physical and (biogeo)chemical data across the scales.

4.2 Selection and parameterization of the karst transport model

4.2.1 Model selection based on the (right) choice of dominant process

Model selection with a detailed understanding of its assumptions and limitations is one of the key steps for the successful transport modelling in karst systems. However, such a choice from a model plethora is not an easy task (Horton et al., 2022; Masciopinto et al., 2021) as each model has its own features (i.e., numerical formulations, parameters) that may be appropriate for a specific application and/or specified conditions (Figure 12). Certainly, the modeler's perceptual understanding on the karst flow and transport processes can also be judicious in selecting a candidate model structure (e.g., Cousquer & Jourde, 2022; Hartmann et al., 2013b, 2014). Of the numerous criteria, however, the objective of the study, data availability, and model structural adequacy generally define our most-suitable choice in simulating karst transport dynamics (see Section 3).

In general, an (accurate) representation of the flow and transport processes in the model structure can be seen as a crux of the robust model selection (Figure 12). But, as we have often poor understanding about the complicated physical, chemical, and (biogeo)chemical processes, a special care is required for the representation of the karst transport dynamics in the (selected) model structure with the adequate numerical formulation and parameters. From a modelling point of view, however, the representations of multiple processes at differing spatiotemporal scales under a broad range of karstic environments — in which different transport problems might be encountered — with the similar model structures is neither possible nor enough to realistically simulate the karst transport dynamics (e.g., Chang et al., 2017, 2021; Cen et al., 2021; Hublart et al., 2015; Makropoulos et al., 2008; Massmann et al., 2005, among many others). For this reason, the overall success in the robust model selection is attributed to the 'right' choice of the key process that predominantly controls the karst system's hydrological and/or physicochemical behaviors by the available data (Hartmann et al., 2013a, 2018).

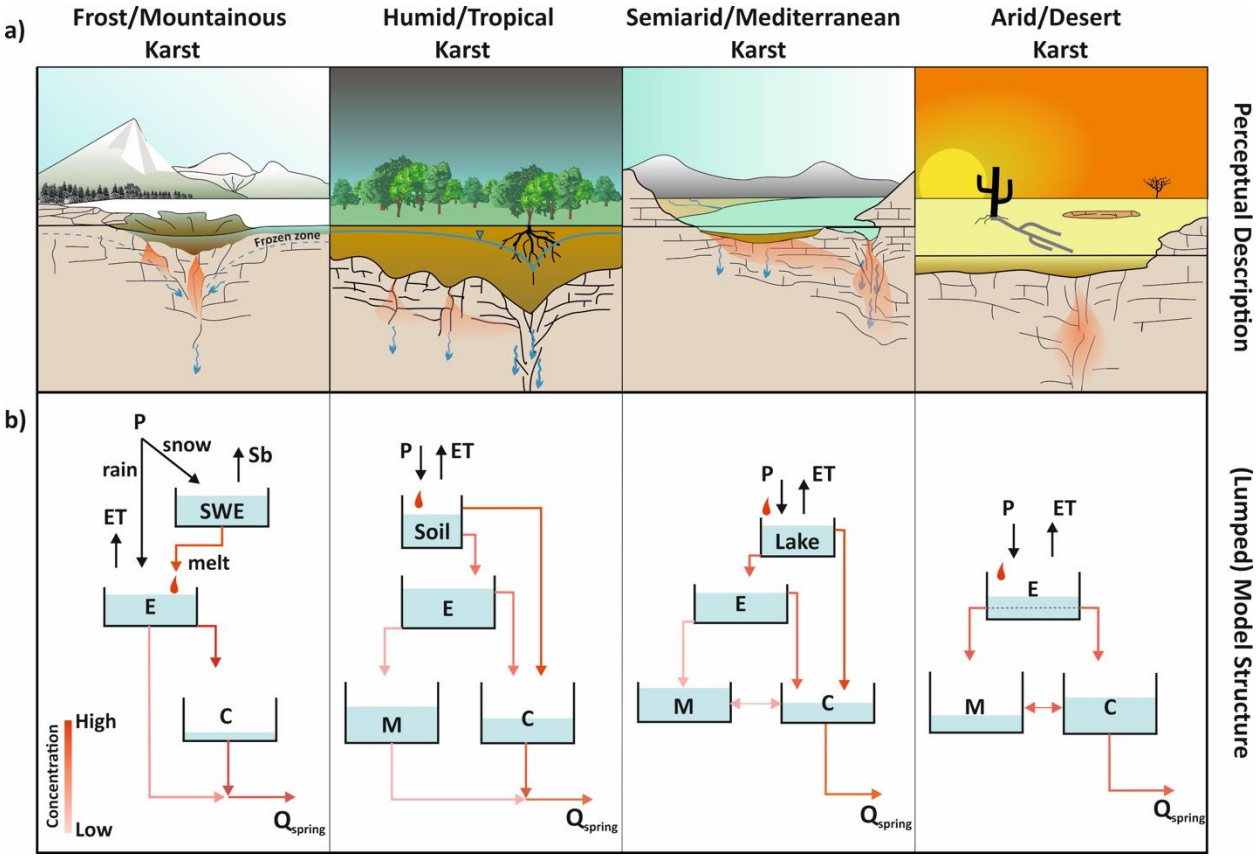

Figure 12. Model selection based on the dominant processes across the different karstic environments. **(a)** (Generic) perceptual descriptions of the broad range of karstic environments under differing climatological, hydrological, and hydrogeochemical conditions, and (potential) karst transport dynamics, **(b)** The selected (conceptual) model structures depending on the right choice of the dominant process associated with corresponding karstic environments. Here, only lumped simulation models with its (possible) structures are depicted to emphasize that a wide range of the (parsimonious) model structure can also be possible depending on the proper definition of the dominant processes and the transport problem of interest. Here, the acronyms indicate the different components of karst systems such as E (Epikarst), C (Conduit), and M (Matrix), as well as the model state variables including P (Precipitation or Rainfall), ET (Evaporation/Evapotranspiration), S_b (Sublimation), and SWE (Snow Water Equivalent).

In karst systems, since the (accurate) process description is restricted by data availability, the principle of parsimony — the minimum level of the model complexity — (Schoups et al., 2008; Wagener et al., 2001, 2003) has been recommended to ensure the adequate model complexity in terms of process representation with the data we have (e.g., Hartmann et al., 2014, 2018; Labat & Mangin, 2015; Kavousi et al., 2023). In general, based on the data/knowledge on the spatial variabilities of the dominant processes, the model structure can be implemented as the lumped (parsimonious), distributed (more process-based), and semi-distributed way. Amongst them, the spatially lumped karst simulation models (i.e., CIMMs) are often preferable to simulate the karst transport dynamics in data-scarce karst regions (Barrett, 1996; Barrett & Charbeneau, 1997; Hartmann et al., 2014, 2016a; Scanlon et al., 2003) while spatially distributed process-based models (i.e., ATMs) require a large type of observations to resemble varying physical and chemical processes with a high dimensional of parameter sets (e.g., Assari & Mohammadi, 2017;

Chang et al., 2019; Kavousi et al., 2020; Xu et al., 2015). For instance, mass transfer between the karst conduit and matrix need to be considered with an additional parameter sets that resemble the mass exchange in such models i.e., 2RNE, TSM, DHDM (Assunção et al., 2023; Ender et al., 2018; Schiperski et al., 2022; Yin et al., 2022) (see subsection 3.2.2). As consequence, the successful applications of the advanced transport models are strictly limited by the well-defined sites, small-scale field and/or lab-scale investigations where the rather site-specific parameters (i.e., mass transfer rate, sorption constants) are obtained (e.g., Lehmann et al., 2022; Shu et al., 2020; Schiperski et al., 2022; Wang et al., 2022). Because of this limitation, the semi-distributed karst simulations models, like Varkarst (Hartmann et al., 2013a) and TCD-Dublin (Gill et al., 2013), are frequently served as the optimal model structures to ensure the balance between the process representation and data availability (Borghi et al., 2016; Hartmann et al., 2014). The complexity of such models is often enough to represent karst transport dynamics as compared to the parsimonious lumped models, as well as better choice with the lower/adapted data need than that of distributed counterparts (e.g., Hartmann, 2016b; Teixeira Parente et al., 2019; Zoghbi & Basha, 2020, among many others). But despite the semi-distributed, physically oriented flow path simulation of these models, a big gap remains in their presentation of transport dynamics which has been relying on simple CIMM approaches.

Overall, finding the most adequate transport model structure and degree of complexity is a particular challenge for karst transport modelling. But the optimal structure should be as simple as possible and as complex enough to better represent the karst system's underlying key physical and chemical phenomena in accordance with the available data. In principle, the complexity of selected model structure can only be increased when data amount (i.e., multiple observations) and its quality ensure the proper representations of the multiple processes in the model structure (Milanović & Vasić, 2015; Hartmann et al., 2013a, 2014a, 2018), thereby increasing the model realism in terms of process representation. Nonetheless, seeking a trade-off between the (robust) representation of karst transport processes and their proper transcriptions in the model structures based on the principle of parsimony has not yet been fully explored yet. Therefore, which type of model we could use, and how complex it would be are those questions still open to discussion.

4.2.2 Model parametrization: Parameter non-uniqueness and transferability

A successful transport model parametrization must ensure robust parameter estimation with reliable model predictions (e.g., Chang et al., 2017; Hartmann et al., 2017; Sivelle et al., 2022; Çallı et al., 2023a). Yet, a common tenet in karst modelling studies is to obtain physically reasonable parameters in comparison with the actual site characteristics. For that, a successful model parametrization is required. However, due to the limited system knowledge with the insufficient field estimates, a robust parameterization in karst transport models is a challenging task particularly in two ways. First, how to better translate the karst transport dynamics into the model structure with sufficient parameters is a serious matter because additional parameters are involved in the karst transport model (i.e., dispersivity, mass transfer coefficient) as compared to the flow models. Second, since most parameter values cannot be assessed from the direct measurements, inverse modelling (i.e., model calibration) is necessary to describe the key physical and (biogeo)chemical processes (Figure 13). The former task could be handled by sticking to the principle of parsimony where the minimum number of parameters meet with observational datasets (Hartmann et al., 2018; Kavousi et al., 2020, 2023), the later one is often rather difficult because it will possibly go along with overparameterization. This limits the physical interpretation of the parameter values, thus reducing the model reliability with a certain

degree of uncertainty (Figure 13) (Hartmann, 2016b; Teixeira Parente et al., 2019; Zhang et al., 2020b; Zoghbi & Basha, 2020; Çallı et al., 2023a).

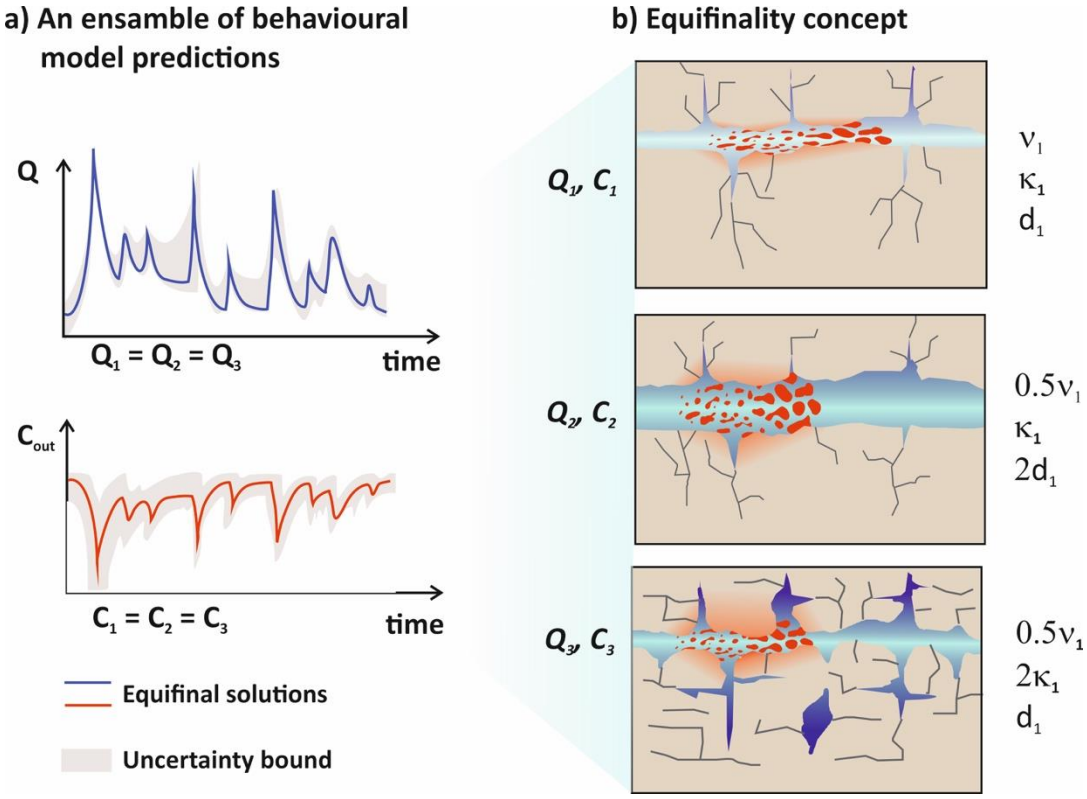

Figure 13. Description of the model calibration results for karst transport model based on the concept of model equifinality, both in model solutions and in parameters. **(a)** Calibration of a karst transport model ended up with the equifinal simulations within a certain range of uncertainty (depicted as an ensemble of the behavioral model simulations with the shaded area), **(b)** The (hypothetical) description of the equifinality concept in the transport model parameters resulting from the equifinal solutions in Panel a (In the figure, the acronyms are v_1 (*flow velocity*), K_1 (*hydraulic conductivity*), and d_1 (*cross-sectional area*). Here, multiple feasible parameter-sets provide equally-well hydrological (i.e., spring discharge, Q) and physicochemical (solute concentration, C_{out}) responses with respect to the (selected) calibration metric. In equifinal model results, finding the "best" or "most acceptable" solution is not necessarily possible, and the results might be misleading.

The direct field measurements and/or lab-scale experiments are favorable for the improved parameterization of the karst transport models in that the spatial and temporal variabilities of the transport processes could be defined by the well-defined parameter values. In principle, since the (more) physically based models (i.e., ATMs) consider the parameter heterogeneities along the domain of interest, they are often built upon the experimental data that describes the physical/chemical significance of the processes of interest with the effective values (e.g., Dentz, 2011; Li et al., 2008; Orban et al., 2010; Pérotin et al., 2021; Zhang et al., 2021). Nevertheless, it might not be still not possible to define the specified values for some of parameters, especially for the regional scale transport modelling such as conduit/fracture geometry (i.e., orientation, spacing, aperture) and conduit/fracture networks (i.e., distributions,

intersections, tortuosity factor). Consequently, such parameters are frequently unknown and required to be calibrated (e.g., Barberá et al., 2018; Dreybrodt, 2012; Faulkner et al., 2009; Florea &Wicks, 2001; Geyer et al., 2013; Robineau et al., 2018, among many others). For instance, to parametrize Transient Storage Model (TSM) where transport distance is divided into several smaller reaches needs several effective parameter-sets to represent the transport processes along the karst conduit. Here, the length of each reach is defined by the (extensive) field works whereas dispersion and cross-sectional areas for the main flow channel and transient storage are still obtained by the model calibration (e.g., Cholet et al., 2017; Deleu et al., 2023; Dewaide et al., 2016; Tinet et al., 2019; Zhao et al., 2021). Likewise, the mass transfer coefficient is often considered as a calibration parameter, especially for the dual-domain transport models (i.e., MIM, 2RNE, TSM). Considering all, the model calibration is an inevitable part of the successful model applications, both for the lumped and advanced karst transport models.

As an inverse solution of the karst system's transport dynamics, a successful calibration seeks to infer a (unique) parameter set which resembles the process of interest at the spatiotemporal domain of interest. Yet, as there is not a unique solution for an inverse problem (Hartmann, 2018; Sivelle et al., 2020; Valota et al., 2002), it is often difficult to link the karst transport parameters with the actual transport dynamics. For that reason, karst transport models are more prone to suffering from the issue of non-uniqueness as compared to the flow models, particularly in describing and (physically) interpreting transport parameters (i.e., flow velocity, dispersivity) (e.g., Adinehvand et al., 2017; Chang et al., 2017; Johnston et al., 2009; Field & Li, 2011; Massmann et al., 2005, among many others). This often results in overparameterization and equifinality as exemplified in Figure 13. While the overparameterization is often a serious problem for the advanced/distributed models where the multiple parameters are represented in the model structure despite the less information available (Fischer et al., 2024; Kavousi et al., 2020, 2023), it might be rather less of a problem for the lumped transport models (i.e., CIMMs, LPMs) where the direct observations are not possible due to the aggregation of the karst flow and transport processes along the domain of interest (e.g., Hartmann et al., 2014; Sivelle et al., 2022).

Model overparameterization or equifinality manifests itself larger uncertainties in the model predictions and parameters (Figure 13). For this reason, finding the "best" or "most acceptable" solution is not necessarily possible. Therefore, model predictions (or equifinal solutions) can be strongly misleading (e.g., Beven, 2006; Husic et al., 2020; Zhang et al. 2019, 2020b; Wang et al., 2020). In theory, parameter identifiability tests can quantify the equifinality and help to reduce it with additional information or model structure simplifications. However, these improvements may be limited because the physical and (biogeo)chemical parameters that control the migration of the contamination plume are highly sensitive to the karst system's physical and (biogeo)chemical heterogeneities (Bonanno et al., 2022; Jia et al., 2018; Zhang et al., 2020b; Zoghbi & Basha, 2020). For instance, the interpretation of mass exchange rate, spatially varying sorption properties, reactive kinetic surface areas for the dual-domain transport models (e.g., 2RNE, MIM, TSM) are often problematic and less reliable for predicting the karst transport dynamics due to the lack of exhaustive information. Therefore, the non-identifiability problem in such transport parameters might be inherent.

A (successful) application of the karst transport model is often unique in solving (particular) flow and transport conditions at the domain of interest. For this reason, the transferability of the (model-specific) calibrated parameters for the (rather) larger and/or smaller

transport domains, for various karstic environments, and for different models under different concepts is strictly limited, too. As a result, using the literature values for some of the transport parameters might not be entirely possible since the karst transport parameters and their values are mostly unique in place and time.

Overall, it is particularly important to emphasize that the substantial limitations behind the successful model parametrization of karst transport models reside especially in the governing solutions (i.e., ADE) that are particularly developed for the porous aquifer-specific transport problems (e.g., Bear et al., 2012; Faulkner et al., 2009; Field & Pinsky, 2000; Zoghbi & Basha, 2020). For that reason, the targeted solutions cannot be easily transferred for the highly heterogeneous karst aquifers in which the additional mathematical complexities (e.g., inclusion of mass transfer coefficients, sorption parameters in classical ADE) are not easily incorporated and overparameterization is likely to arise.

4.3 Uncertainty of the model simulations

Characterization and reduction of the uncertainty is one of the priorities for the evaluation of transport model applications as it ensures the robustness and reliability of the model predictions (e.g., Chang et al. 2021; Hartmann et al., 2013b, 2018; Çallı et al., 2023a). For this reason, treating uncertainty with its (potential) sources requires a special care throughout the karst transport modelling practice, especially for identifying the ways for the model improvements.

Taxonomically, the larger source of uncertainty in the model predictions is attributed to the epistemistic uncertainty due to the lack of system knowledge and/or ignorance of some key processes in the formal model structure, rather than the stochastic uncertainty arising from the natural variability of the hydro(geo)logical systems (e.g., Beven et al., 2011; Beven, 2023; Reichert et al., 2021). This uncertainty type is particularly relevant for the karst flow and transport models because they are mostly built upon insufficient and site-specific information, while often shaped by the expert elicitations on the complex physical and chemical properties of the karst systems (Hartmann et al., 2014; Padilla & Vesper, 2018; Zhang et al., 2017). In general, uncertainty in karst transport modeling is raised from the different stages of the karst transport modelling practice but the main sources of uncertainty in the model predictions can be attributed to following sources: (*i*) data uncertainty, (*ii*) model structural uncertainty (both conceptual and numerical), (*iii*) parameter uncertainty, (*iv*) uncertainty associated with the unknown future behavior of the karst system.

Despite clear evidence that the uncertainties in groups (*i*)-(*iii*) are substantial (see previous subsections), only few karst transport studies with LTMs have quantified the uncertainty of their transport simulations (Chang et al. 2021; Mudarra et al., 2019; Çallı et al., 2023a). Amongst them, Chang et al. (2021) was the only one trying to reveal structural uncertainty by comparing different model structures. For ATMs, different modelling approaches (i.e., ADE, MIM, PCNE) were also tested for the simulations of the shape characteristics of BTCs (e.g., multi-modality and heavy tailing) obtained from different karst conduits by Field & Leij (2014). This model comparison research provided a better understanding about the suitable model structure and parameterization of the karst transport process (Massmann et al., 2005; Zhao et al., 2019). Therefore, the disagreements in the model predictions with differing complexity for the same applications might provide a complete understanding about the suitable model structure and improved parameterization (Assunção et al., 2023; Dong et al., 2023; Massmann et al., 2005;

Zhao et al., 2019) as well as indicate the scale dependency of the model parameters and process interactions (Goeppert et al., 2020; Kaufmann, 2003; Liu et al., 2021).

Concerning the uncertainty associated with the unknown future behavior of the karst system, realistic representations of a karst the system's current and historical transport conditions may not guarantee that future conditions (e.g., unknown future state variables) will successfully met by the chosen model structure (Beven & Chappell, 2021; Oreskes et al., 1994; Wagener, 2022). Regarding this, one of the critical tasks for the karst modelers is to assess the model results by seeking (more) reasonable answers for to what extent the model simulates the process behaviour under (globally) changing hydrological and physiochemical conditions. Improving our physical understanding of karst systems and implementing it into new and better model structure is an ongoing challenge for the successful modelling practice.

5 Ways ahead of modelling karst transport dynamics and future perspectives

Studies on modelling of karst flow and transport processes have considerably increased over the last decades. Several factors can play a role in such a progress including the variety of collected data (i.e., multiple observations), its accuracy, and increments in computational power and capacity (both accuracy and efficiency). But the driving force is the need for solving transport problems in karst water resources across the world. Nonetheless, as a community, we are still at the stage of model improvements for the successful real-world applications of the karst transport models by confronting the main challenges (i.e., system conceptualization, model parametrization, uncertainty quantification) to ensure model robustness and reliability (see Section 4). Along with these (long-lasting) challenges, however, new challenges and ways are ahead of us, especially considering the deterioration of karst water quality in a changing world due to climate change impact on karst water quality and ecosystem services. For that, we highlight four key directions that could be addressed for better representing and predicting the solute transport behaviour in karst systems, as well as for exploring karst water quality risks and potential outcomes.

5.1 Collect and provide more data for improved karst transport understanding

To reasonably predict karst transport dynamics, the solute transport models often require spatially and temporally continuous and consistent datasets. However, the collection of chemical and (biogeo)chemical data (i.e., nitrate, arsenic, biological and microbial contaminants, microplastics) is still sparse, and mostly inconsistent with the temporal coverage of the physical data (i.e., spring discharge, groundwater head, water pressure). As a result, our proper understanding about the karst system-specific contaminant mixing and transport characteristics, as well as the knowledge on reactive transport processes and (biogeo)chemical transformations are substantially limited. Nonetheless, taking long-term precautions to protect karst water quality from anthropogenic factors and global changes (i.e., climate, land cover and land use changes, soil degradation) often rely on better understanding of chemical and biogeochemical processes. For this reason, a particular attention is required for improved understanding of the (multiple) physicochemical interactions between the preferential flow paths (i.e., fractures, conduits) and overlapping (fractured) carbonate matrix, thereby developing more integrated karst modelling approaches that simultaneously consider flow, transport, and (bio)geochemical reactions in karst systems.

Karst scientists and water authorities are collecting more data than ever before. However, the collected data are rarely published and shared with the community, especially those used for flow and transport modelling studies (i.e., karst spring $\delta^{18}O$ isotope ratios). Some working groups under specified goals, for instance SISAL (Speleothem Isotope Synthesis and Analysis), provide a readily available global database for the speleothem isotopes collected from individual speleothems and grouped them by the cave locations across the world (Atsawawaranunt et al., 2018; Comas-Bru et al., 2020; Kaushal et al., 2023). There is, therefore, a need for the common database in which we can gather the original data on karst transport dynamics from different experimental and modelling works (i.e., tracer tests, hydrochemical studies, hydraulic tests, cave isotopic and hydrochemical experiments) similar to the few and valuable attempts to collect and provide karst data by Jourde et al. (2018), Petrič et al. (2020), Olarinoye et al. (2020).

5.2 Fill the gap between oversimplified LTMs and data-demanding ATMs

The critical discussion on how to find a tradeoff between the model complexity and the choice of a right process controlling the system's physicochemical behavior (with a reasonable number of parameters) with respect to the data availability is a requirement for a completion of the successful transport modelling practice in karst systems. Due to suitability in data-rare sites, mathematically simpler LTMs have outpaced their sophisticated ATM fellows that are represented by more variables with multiple parameters. But although the LTMs are often served as valuable heuristic tools for modelling karst transport processes, they are still the most simplistic approach in representing rather complicated karst transport dynamics. By comparison, due to the (substantial) data need, ATMs are often inapplicable for resembling the karst transport dynamics, especially for the larger scale field applications. Therefore, we see a particular need for representing karst transport processes with more-process oriented and well-constrained models that can be used for alternative modeling approaches to better resemble the spatiotemporal dynamics of contaminant migration in karst systems.

In this direction, this review reveals that there is an emerging modelling concept that is coming outside of the karst. StorAge Selection (SAS) Function Approach (hereinafter referred to the SAS model) can be an alternative approach to simulate the karst transport dynamics (Figure 14). The SAS theory was built by Botter (2011), Harman (2015), and Van der Valde et al. (2012) for the catchment scale flow and transport modelling applications while the successful applications were also extended to simulate the karst transport processes by Zhang et al. (2021) and Çallı et al. (2023a). The SAS model defines the relationship between the distribution of water ages in the reservoir storage (i.e., soil, groundwater) and the ages exiting as system's outflux (either discharge or evapotranspiration, or both) (Figure 14). Compared to LTMs, the SAS model considers the time-variant characteristics of TTDs by revealing the time-dependent mixing, storage, and discharge characteristics (e.g., Benettin & Bertuzzo, 2018; Botter et al., 2011; Botter, 2012; Harman, 2015; Rinaldo et al., 2015; Schwemmle & Weiler, 2024, among many others). Therefore, the SAS model is structured by rather less parameters as compared to ATMs, and it thus allows better identification of the model parameters while reducing overparameterization and equifinality issues.

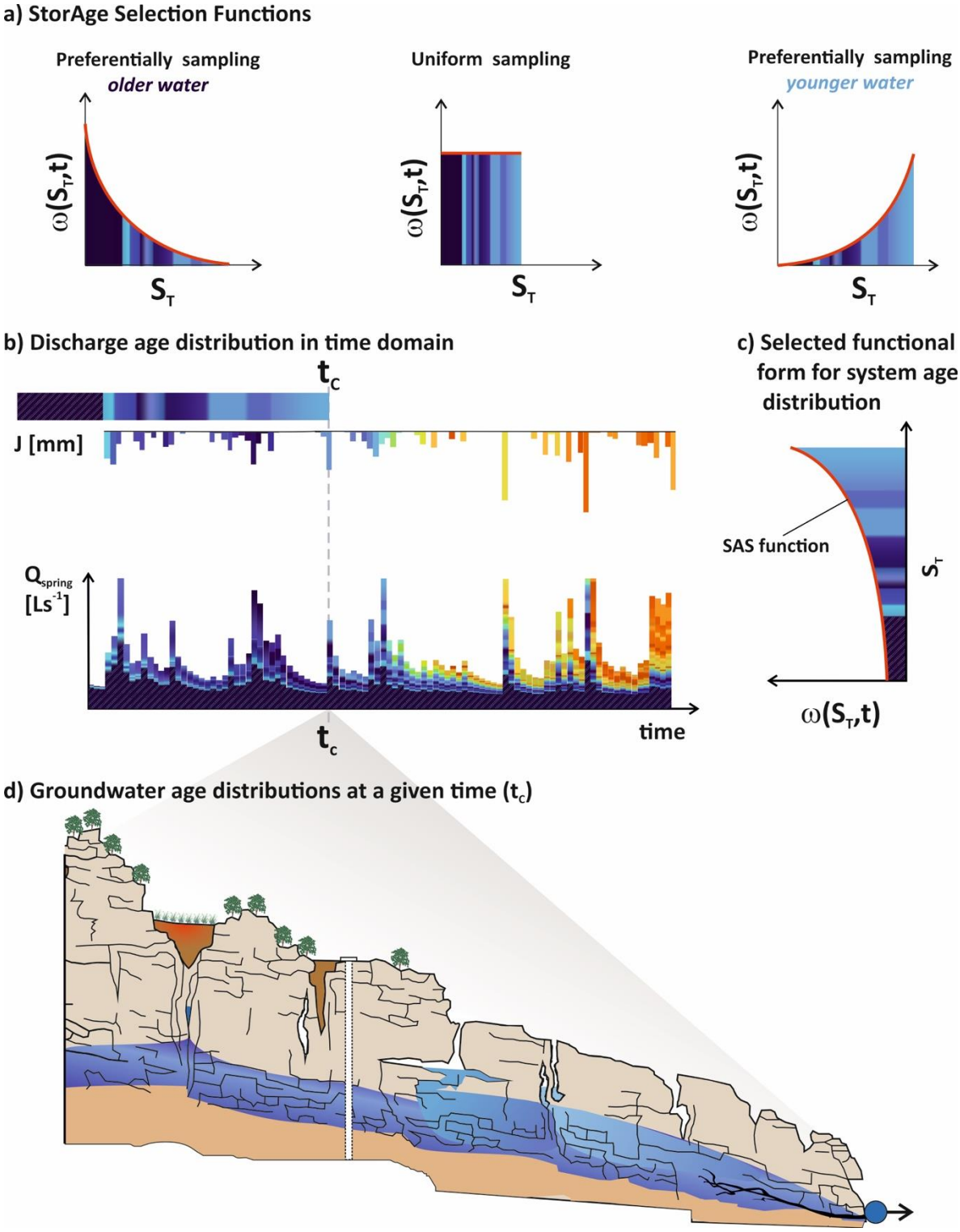

Figure 14. Schematic representations of **a)** StorAge Selection functions, **b)** Precipitation and discharge age distributions in the SAS model conceptualization, **c)** Selected functional form for the description of age distributions in the SAS model (here, younger water age preference is described, often known as the power-law distribution), **d)** Hypothetical demonstration of karst groundwater age distributions at a given time period, t_c (Here, the figures (a), (b), and (c) were

adapted for the karst systems based on the SAS model descriptions in Benettin et al. (2022), Harman et al. (2015) and Harman (2019). In the depicted figures, S_T refers to the age ranked storage that describes the amount of water in storage whose age is younger than (or equal to) certain age T at current time t_c. $\omega(S_T, t)$ is the probability density function of the travel time expressing each water age (T) removed from the storage (for further the details see Benettin & Bertuzzo (2018)).

5.3 Develop adequate approaches for sediment transport in karst systems

Karst transport model is frequently applied for the predictions of solute transport dynamics in karst systems. However, some agents such as vapor, heat, (suspended) sediments (i.e., particles and colloids) can also play a role in defining solute transport behaviours. Suspended sediments are such agents that are often induced by the turbulent flow along the karst conduits and cave streams (Mueller et al., 2023; Jukić et al., 2022; Richter et al., 2022). In this respect, understanding the (suspended) sediment transport is particularly important for karst transport processes in two ways. First, since (suspended) sediments can adsorb a wide range of contaminant types (i.e., organic substance, hydrocarbons, heavy, and trace metals, biological contaminants), they often act as storage and/or transformation regions for the contaminants (Herman et al., 2012; Mahler et al., 1999, 2000; Mueller et al., 2023). Second, they can attenuate the contaminant of interest as a zone of remobilization (Bettel et al., 2022; Nerantzaki et al., 2015). Furthermore, while the origin of the sediments provides the evidence of transport conditions during the contaminant events taking place (Bosch & White, 2018; Çelik et al., 2022), microbial transport in karst aquifers is frequently approximated by the suspended sediment transport (e.g., Goldscheider et al., 2010; Göppert & Goldscheider, 2008). But the transportation and transformation of the contaminants with the suspended materials are not directly measurable and observable. For these reasons, their characterizations require high-resolution monitoring and suitable technologies. Therefore, future research is recommended to address contaminant fate and transport processes due to the (suspended) sediment and/or particles at high temporal resolution.

5.4 Estimate the impact of climate and land use changes on karst water quality

Karst water resources are highly regulated, stressed, and managed by the human dimension, especially by the operational water management (i.e., dam and reservoir capacity) and increased water consumption (i.e., pumping rate, water needs). For this reason, a greater uncertainty is available for the karst system's (natural) hydrological and hydrochemical functioning. In this matter, the impacts of the human-induced factors (i.e., pumping rate, sectoral water needs) on karst flow and transport dynamics need to be considered. But up until now, the human dimension on karst transport dynamics is overlooked and/or underestimated in the real-world applications of karst transport models while the focus is often more on naturalized aquifer conditions. Therefore, coupling the knowledge of human-induced factors with the (naturalized) system dynamics at differing scales under different scenarios (i.e., the impact of groundwater abstraction rates on karst water quality) is one of the key research areas to provide more realistic predictions, as well as to support decision-makers for sustainable water management in karst systems.

Contaminant mixing and transport problems in karst water resources are frequently denoted as (saturated) groundwater zone specific issues, and the role of epikarst in karst transport dynamics is significantly simplified or completely ignored from the (formal) model structures.

Nonetheless, epikarst is a karst critical zone whereby contaminant mixing, storage, and transport characteristics are largely controlled (e.g., Dal Soglio et al., 2020; Flynn & Sinreich, 2010; Li et al., 2017; Perrin et al., 2003b; Zhang et al., 2017, among many others). Furthermore, as the epikarst forms the reactive and biogeochemical processes (i.e., sorption, microbial activities, and oxidation), it significantly modifies the (initial) composition of the contaminants released from the ground surface before reaching the saturated groundwater table (Druhan et al., 2021; Dubois et al., 2014; Oster et al., 2021; Zeqiraj, 2022) while predominantly controlling the karst system's (biogeo)chemical functioning (Anna-Neva et al., 2021; Laincz & Hays, 2014; Panno et al., 2001). For these reasons, better understanding of epikarst transport dynamics is a fundamental need to protect and manage karst water quality and dependent ecosystem functioning. Nevertheless, due to the unbearable complexity and substantial heterogeneity of epikarst, scientific attempts to develop epikarst-dedicated transport models are quite rare.

Degradation of karst water quality is not only a local scale issue in which we can only apply a site-specific solute transport model to predict the spatiotemporal behaviour of contaminant migration, but it is also a global phenomenon that we shall further consider global changes and their potential impacts on the karst water quality and dependent ecosystems. However, to the best of our knowledge, the effects of the global changes on the karst water quality in the context of the transport modelling are not adequately addressed at local/global scales. For that, the impact of local/global changes on the karst water quality brings us fundamental responsibility to make robust predictions under a changing world, despite the substantial uncertainty. Therefore, future works call attention to what extent (and how) karst transport dynamics can (could be) linked to the altered boundary conditions due to anthropogenic factors and global changes such as climate change, land-use and/or land-type changes, soil degradation, water management alterations, and groundwater depletion.

6 Conclusions

The threat of contamination in karst water resources has come to light over the last couple of decades. Nonetheless, the multiscale physical and (biogeo)chemical heterogeneities still pose an enormous challenge for properly characterizing, understanding, and modelling flow and transport dynamics in karst water resources. In this manner, we still have substantial limitations in providing more reasonable and reliable transport model predictions, thus handling the modelling issues such as parameter scaling, model non-uniqueness, and uncertainty. But beyond that, both anthropogenic factors and global changes (i.e., climate change, land use-land cover changes, soil degradation, urbanisation, agricultural practices, and water management alterations) have been seriously deteriorating the quality of karst water resources and dependent ecosystem functioning. As the karst system's functioning both hydrodynamically and biogeochemically is controlled by such global changes in a way that they can shape the karst flow and transport characteristics, understanding karst transport dynamics is critical to successfully predict the impacts of such factors on the water quality and dependent ecosystems. With this review, we hope to provide the necessary overview of available methods, challenges and directions to support and improve the present and future management of water quality in different karst regions across the globe.

Acknowledgments

Kübra Özdemir Çallı, Daniel Bittner, and Andreas Hartmann are supported by the German Research Foundation (DFG, grant number: HA 8113/6–1, project "Robust Conceptualisation of KArst Transport (ROCKAT)"). Gabriel Chiogna and Beatrice Richteri are supported by the German Research Foundation (DFG, grant number: CH 981/6–1, project "Robust Conceptualisation of KArst Transport (ROCKAT)"). Süleyman Selim Çallı was financially supported by the Scientific and Technological Research Council of Türkiye (TÜBİTAK, grant number: 1059B142000592).

Open Research

No original/new data were collected and/or developed for this review. The paper is a synthesis of the published works.

References

Adinehvand, R., Raeisi, E., & Hartmann, A. (2017), A step-wise semi-distributed simulation approach to characterize a karst aquifer and to support dam construction in a data-scarce environment. *Journal of Hydrology*, *554*, 470-481.

Allwright, A., & Atangana, A. (2018b), Fractal advection-dispersion equation for groundwater transport in fractured aquifers with self-similarities. *The European Physical Journal Plus*, 133, 1-20.

Anderson, M. P., Woessner, W. W., & Hunt, R. J. (2015), Applied groundwater modeling: simulation of flow and advective transport. Academic press.

Anna-Neva, V., Lehmann, M. F., Hermann, R., Grathwohl, P., Nia, B., Kappler, A., & Karsten, O. (2021), Fate of nitrate during groundwater recharge in a fractured karst aquifer in Southwest Germany. *Hydrogeology Journal*, 29(3), 1153-1171.

Anwar, S., & Sukop, M. C. (2009), Lattice Boltzmann models for flow and transport in saturated karst. *Groundwater*, 47(3), 401-413.

Aquilanti, L., Clementi, F., Nanni, T., Palpacelli, S., Tazioli, A., & Vivalda, P. M. (2016), DNA and fluorescein tracer tests to study the recharge, groundwater flowpath and hydraulic contact of aquifers in the Umbria-Marche limestone ridge (central Apennines, Italy). *Environmental Earth Sciences*, 75, 1-17.

Aquilina, L., Ladouche, B., Dörfliger, N., & Bakalowicz, M. (2003), Deep water circulation, residence time, and chemistry in a karst complex. *Groundwater*, *41*(6), 790-805.

Assari, A., & Mohammadi, Z. (2017), Assessing flow paths in a karst aquifer based on multiple dye tracing tests using stochastic simulation and the MODFLOW-CFP code. *Hydrogeology Journal*, *25*(6), 1679.

Assunção, P., Galvão, P., Lucon, T., Doi, B., Fleming, P. M., Marques, T., & Costa, F. (2023), Hydrodynamic and hydrodispersive behavior of a highly karstified neoproterozoic hydrosystem indicated by tracer tests and modeling approach. *Journal of Hydrology*, 619, 129300.

Atsawawaranunt, K., Comas-Bru, L., Amirnezhad Mozhdehi, S., Deininger, M., Harrison, S. P., Baker, A., ... & Scroxton, N. (2018), The SISAL database: a global resource to document oxygen and carbon isotope records from speleothems. *Earth System Science Data*, 10(3), 1687-1713.

Aydin, H., Ekmekçi, M., & Soylu, M. E. (2014), Effects of sinuosity factor on hydrodynamic parameters estimation in karst systems: a dye tracer experiment from the Beyyayla sinkhole (Eskişehir, Turkey). *Environmental Earth Sciences*, 71, 3921-3933.

Bailly-Comte, V., Martin, J. B., & Screaton, E. J. (2011), Time variant cross correlation to assess residence time of water and implication for hydraulics of a sink-rise karst system. *Water Resources Research*, *47*(5).

Bajracharya, K., & Barry, D. A. (1997), Nonequilibrium solute transport parameters and their physical significance: Numerical and experimental results. *Journal of Contaminant Hydrology*, 24(3-4), 185-204.

Bakalowicz, M. (2005), Karst groundwater: a challenge for new resources. *Hydrogeology Journal*, 13, 148-160.

Banusch, S., Somogyvári, M., Sauter, M., Renard, P., & Engelhardt, I. (2022), Stochastic modeling approach to identify uncertainties of karst conduit networks in carbonate aquifers. *Water Resources Research*, 58(8), e2021WR031710.

Barberá, J. A., Mudarra, M., Andreo, B., & De la Torre, B. (2018), Regional-scale analysis of karst underground flow deduced from tracing experiments: examples from carbonate aquifers in Malaga province, southern Spain. *Hydrogeology journal*, 26(1), 23-40.

Barrett, M. E. (1996), A parsimonious model for simulation of flow and transport in a karst aquifer. The University of Texas at Austin.

Barrett, M. E., & Charbeneau, R. J. (1997), A parsimonious model for simulating flow in a karst aquifer. *Journal of Hydrology*, 196(1-4), 47-65.

Bayari, S. (2002), TRACER: an EXCEL workbook to calculate mean residence time in groundwater by use of tracers CFC-11, CFC-12 and tritium. *Computers & Geosciences*, 28(5), 621-630.

Bear, J. (1972), Dynamics of fluids in porous media. Courier Corporation.

Becker, M., & Bellin, A. (2013), A reservoir model of tracer transport for karstic flow systems. *Hydrogeology Journal*, 21(5), 1011.

Benettin, P., & Bertuzzo, E. (2018), tran-SAS v1. 0: a numerical model to compute catchment-scale hydrologic transport using StorAge Selection functions. *Geoscientific Model Development*, 11(4), 1627-1639.

Benettin, P., Rodriguez, N. B., Sprenger, M., Kim, M., Klaus, J., Harman, C. J., ... & McDonnell, J. J. (2022), Transit time estimation in catchments: Recent developments and future directions. *Water Resources Research*, 58(11), e2022WR033096.

Benischke, R. (2021), Advances in the methodology and application of tracing in karst aquifers. *Hydrogeology Journal*, 29(1).

Benson, D. A., Wheatcraft, S. W., & Meerschaert, M. M. (2000), Application of a fractional advection-dispersion equation. *Water Resources Research*, 36(6), 1403-1412.

Berglund, J. L., Toran, L., & Herman, E. K. (2020), Can karst conduit models be calibrated? A dual approach using dye tracing and temperature. *Groundwater*, 58(6), 924-937.

Berkowitz, B. (2002), Characterizing flow and transport in fractured geological media: A review. *Advances in Water Resources*, 25(8-12), 861-884.

Berkowitz, B., Cortis, A., Dentz, M., & Scher, H. (2006), Modeling non-Fickian transport in geological formations as a continuous time random walk. *Reviews of Geophysics*, 44(2).

Berkowitz, B., Dror, I., Hansen, S. K., & Scher, H. (2016), Measurements and models of reactive transport in geological media. *Reviews of Geophysics*, 54(4), 930-986.

Berkowitz, B., Kosakowski, G., Margolin, G., & Scher, H. (2001), Application of continuous time random walk theory to tracer test measurements in fractured and heterogeneous porous media. *Groundwater*, 39(4), 593-604.

Berkowitz, B., & Scher, H. (1995), On characterization of anomalous dispersion in porous and fractured media. *Water Resources Research*, 31(6), 1461-1466.

Bethke, C. M., & Johnson, T. M. (2008), Groundwater age and groundwater age dating. *Annual Review of Earth and Planetary Science*, 36, 121-152.

Bettel, L., Fox, J., Husic, A., Zhu, J., Al Aamery, N., Mahoney, T., & Gold-McCoy, A. (2022), Sediment transport investigation in a karst aquifer hypothesizes controls on internal versus external sediment origin and saturation impact on hysteresis. *Journal of Hydrology*, 613, 128391.

Beven, K. (2002), Towards a coherent philosophy for modelling the environment. Proceedings of the royal society of London. Series A: mathematical, *Physical and Engineering Sciences*, 458(2026), 2465-2484.

Beven, K. (2005), On the concept of model structural error. *Water Science and Technology*, 52(6), 167-175.

Beven, K. (2006), A manifesto for the equifinality thesis. *Journal of Hydrology*, *320*(1-2), 18-36.

Beven, K. (2023), Benchmarking hydrological models for an uncertain future. *Hydrological Processes*, e14882.

Beven, K., & Binley, A. (1992), The future of distributed models: model calibration and uncertainty prediction. *Hydrological Processes*, 6(3), 279-298.

Beven, K. J. (2011), *Rainfall-runoff modelling: the primer*. John Wiley & Sons.

Beven, K. J., & Chappell, N. A. (2021), Perceptual perplexity and parameter parsimony. *Wiley Interdisciplinary Reviews: Water*, 8(4), e1530.

Beven, K., Smith, P. J., & Wood, A. (2011), On the colour and spin of epistemic error (and what we might do about it). *Hydrology and Earth System Sciences*, 15(10), 3123-3133.

Birk, S., Geyer, T., Liedl, R., & Sauter, M. (2005), Process-based interpretation of tracer tests in carbonate aquifers. *Groundwater*, 43(3), 381-388.

Bittner, D., Parente, M. T., Mattis, S., Wohlmuth, B., & Chiogna, G. (2020), Identifying relevant hydrological and catchment properties in active subspaces: An inference study of a lumped karst aquifer model. *Advances in Water Resources*, 135, 103472.

Bodin, J. (2020), MFIT 1.0. 0: Multi-Flow Inversion of Tracer breakthrough curves in fractured and karst aquifers. *Geoscientific Model Development*, 13(6), 2905-2924.

Bodin, J., Porel, G., Nauleau, B., & Paquet, D. (2022), Delineation of discrete conduit networks in karst aquifers via combined analysis of tracer tests and geophysical data. *Hydrology and Earth System Sciences*, 26(6), 1713-1726.

Bonanno, E., Blöschl, G., & Klaus, J. (2022), Exploring tracer information in a small stream to improve parameter identifiability and enhance the process interpretation in transient storage models. *Hydrology and Earth System Sciences*, 26(23), 6003-6028.

Borghi, A., Renard, P., & Cornaton, F. (2016), Can one identify karst conduit networks geometry and properties from hydraulic and tracer test data?. *Advances in Water Resources*, 90, 99-115.

1588 Borghi, A., Renard, P., & Jenni, S. (2012), A pseudo-genetic stochastic model to generate karstic
1589 networks. *Journal of Hydrology*, *414*, 516-529.

1590 Bosch, R. F., & White, W. B. (2018), Lithofacies and transport for clastic sediments in karst conduits.
1591 In Karst Groundwater Contamination and Public Health: Beyond Case Studies (pp. 277-281). Springer
1592 International Publishing.

1593 Botter, G. (2012), Catchment mixing processes and travel time distributions. *Water Resources*
1594 *Research*, 48(5).

1595 Botter, G., Bertuzzo, E., & Rinaldo, A. (2011), Catchment residence and travel time distributions: The
1596 master equation. *Geophysical Research Letters*, 38(11).

1597 Brettmann, K. L., Jensen, K. H., & Jakobsen, R. (1993), Tracer Test in Fractured Chalk: 2. Numerical
1598 Analysis. *Hydrology Research*, 24(4), 275-296.

1599 Carrera, J., Sánchez-Vila, X., Benet, I., Medina, A., Galarza, G., & Guimerà, J. (1998), On matrix
1600 diffusion: formulations, solution methods and qualitative effects. *Hydrogeology Journal*, 6, 178-190.

1601 Cen, X., Xu, M., Qi, J., Zhang, Q., & Shi, H. (2021), Characterization of karst conduits by tracer tests for
1602 an artificial recharge scheme. *Hydrogeology Journal*, 29(7), 2381-2396.

1603 Chang, Y., Hartmann, A., Liu, L., Jiang, G., & Wu, J. (2021), Identifying more realistic model structures
1604 by electrical conductivity observations of the karst spring. *Water Resources Research*, 57(4),
1605 e2020WR028587.

1606 Chang, Y., Wu, J., Jiang, G., & Kang, Z. (2017), Identification of the dominant hydrological process and
1607 appropriate model structure of a karst catchment through stepwise simplification of a complex conceptual
1608 model. *Journal of Hydrology*, 548, 75-87.

1609 Chang, Y., Wu, J., Jiang, G., Liu, L., Reimann, T., & Sauter, M. (2019), Modelling spring discharge and
1610 solute transport in conduits by coupling CFPv2 to an epikarst reservoir for a karst aquifer. *Journal of*
1611 *Hydrology*, 569, 587-599.

1612 Charlier, J. B., Bertrand, C., & Mudry, J. (2012), Conceptual hydrogeological model of flow and transport
1613 of dissolved organic carbon in a small Jura karst system. *Journal of Hydrology*, 460, 52-64.

1614 Cherubini, C. (2008), A modeling approach for the study of contamination in a fractured
1615 aquifer. *Geotechnical and Geological Engineering*, 26, 519-533.

1616 Cherubini, C., Giasi, C. I., & Pastore, N. (2013), Evidence of non-Darcy flow and non-Fickian transport
1617 in fractured media at laboratory scale. *Hydrology and Earth System Sciences*, 17(7), 2599-2611.

1618 Chiogna, G., Eberhardt, C., Grathwohl, P., Cirpka, O. A., & Rolle, M. (2010), Evidence of compound-
1619 dependent hydrodynamic and mechanical transverse dispersion by multitracer laboratory
1620 experiments. *Environmental Science & Technology*, *44*(2), 688-693.

1621 Cholet, C., Charlier, J. B., Moussa, R., Steinmann, M., & Denimal, S. (2017), Assessing lateral flows and
1622 solute transport during floods in a conduit-flow-dominated karst system using the inverse problem for the
1623 advection–diffusion equation. *Hydrology and Earth System Sciences*, 21(7), 3635-3653.

1624 Chu, X., Ding, H., & Zhang, X. (2021), Simulation of solute transport behaviors in saturated karst aquifer
1625 system. *Scientific Reports*, 11(1), 1-17.

1626 Cinkus, G., Wunsch, A., Mazzilli, N., Liesch, T., Chen, Z., Ravbar, N., ... & Jourde, H. (2023),
1627 Comparison of artificial neural networks and reservoir models for simulating karst spring discharge on
1628 five test sites in the Alpine and Mediterranean regions. *Hydrology and Earth System Sciences*, 27(10),
1629 1961-1985.

Coats, K. H., & Smith, B. D. (1964), Dead-end pore volume and dispersion in porous media. *Society of Petroleum Engineers Journal*, 4(01), 73-84.

Comas-Bru, L., Rehfeld, K., Roesch, C., Amirnezhad-Mozhdehi, S., Harrison, S. P., Atsawawaranunt, K., ... & SISAL Working Group members. (2020), SISALv2: a comprehensive speleothem isotope database with multiple age–depth models. *Earth System Science Data*, 12(4), 2579-2606.

Cornaton, F., & Perrochet, P. (2006a), Groundwater age, life expectancy and transit time distributions in advective–dispersive systems: 1. Generalized reservoir theory. *Advances in Water resources*, *29*(9), 1267-1291.

Cornaton, F., & Perrochet, P. (2006b), Groundwater age, life expectancy and transit time distributions in advective–dispersive systems; 2. Reservoir theory for sub-drainage basins. *Advances in Water Resources*, *29*(9), 1292-1305.

Cousquer, Y., & Jourde, H. (2022), Reducing uncertainty of karst aquifer modeling with complementary hydrological observations for the sustainable management of groundwater resources. *Journal of Hydrology*, 612, 128130.

Covington, M. D., Doctor, D. H., King, J. N., & Wicks, C. M. (2011), Research in karst: a model for future directions in hydrologic science?. From the section President 18.

Covington, M. D., Luhmann, A. J., Wicks, C. M., & Saar, M. O. (2012), Process length scales and longitudinal damping in karst conduits. *Journal of Geophysical Research: Earth Surface*, *117*(F1).

Dal Soglio, L., Danquigny, C., Mazzilli, N., Emblanch, C., & Massonnat, G. (2020), Modeling the matrix-conduit exchanges in both the epikarst and the transmission zone of karst systems. *Water*, 12(11), 3219.

Deleu, R., Poulain, A., Rochez, G., Soares-Frazao, S., Van Rentergem, G., De Poorter, E., & Hallet, V. (2023), Multipeaked breakthrough curves in karstic rivers: effects of a diffluence-confluence system. *Hydrogeology Journal*, 1-19.

Dentz, M., & Berkowitz, B. (2003), Transport behavior of a passive solute in continuous time random walks and multirate mass transfer. *Water Resources Research*, 39(5).

Dentz, M., Cortis, A., Scher, H., & Berkowitz, B. (2004), Time behavior of solute transport in heterogeneous media: transition from anomalous to normal transport. *Advances in Water Resources*, 27(2), 155-173.

Dentz, M., Hidalgo, J. J., & Lester, D. (2023), Mixing in porous media: concepts and approaches across scales. *Transport in Porous Media*, 146(1-2), 5-53.

Dentz, M., Le Borgne, T., Englert, A., & Bijeljic, B. (2011), Mixing, spreading and reaction in heterogeneous media: A brief review. *Journal of Contaminant Hydrology*, 120, 1-17.

Dewaide, L., Bonniver, I., Rochez, G., & Hallet, V. (2016), Solute transport in heterogeneous karst systems: dimensioning and estimation of the transport parameters via multi-sampling tracer-tests modelling using the OTIS (One-dimensional Transport with Inflow and Storage) program. *Journal of Hydrology*, 534, 567-578.

Dewaide, L., Collon, P., Poulain, A., Rochez, G., & Hallet, V. (2018), Double-peaked breakthrough curves as a consequence of solute transport through underground lakes: a case study of the Furfooz karst system, Belgium. *Hydrogeology Journal*, 26(2), 641-650.

Dietrich, J., & Uniyal, B. (2020), Modeling interbasin groundwater flow in karst areas: Model development, application, and calibration strategy. *Environmental Modelling & Software*, 124, 104606.

1672 Dong, P., Yin, M., Zhang, Y., Chen, K., Finkel, M., Grathwohl, P., & Zheng, C. (2023), A Fractional-
1673 order dual-continuum model to capture non-Fickian solute transport in a regional-scale fractured
1674 aquifer. *Journal of Contaminant Hydrology*, 258, 104231.

1675 Doummar, J., Margane, A., Geyer, T., & Sauter, M. (2018), Assessment of key transport parameters in a
1676 karst system under different dynamic conditions based on tracer experiments: the Jeita karst system,
1677 Lebanon. *Hydrogeology Journal*, 26(7), 2283-2295.

1678 Dreybrodt, W. (2012), Processes in karst systems: physics, chemistry, and geology (Vol. 4). Springer
1679 Science & Business Media.

1680 Druhan, J. L., Lawrence, C. R., Covey, A. K., Giannetta, M. G., & Oster, J. L. (2021), A reactive
1681 transport approach to modeling cave seepage water chemistry I: Carbon isotope
1682 transformations. *Geochimica et Cosmochimica Acta*, 311, 374-400.

1683 Dubois, C., Quinif, Y., Baele, J. M., Barriquand, L., Bini, A., Bruxelles, L., ... & Vergari, A. (2014), The
1684 process of ghost-rock karstification and its role in the formation of cave systems. *Earth-Science*
1685 *Reviews*, 131, 116-148.

1686 Duran, L., Fournier, M., Massei, N., & Dupont, J. P. (2016), Assessing the nonlinearity of karst response
1687 function under variable boundary conditions. *Groundwater*, 54(1), 46-54.

1688 Dvory, N. Z., Kuznetsov, M., Livshitz, Y., Gasser, G., Pankratov, I., Lev, O., ... & Yakirevich, A.
1689 (2018a), Modeling sewage leakage and transport in carbonate aquifer using carbamazepine as an
1690 indicator. *Water Research*, 128, 157-170.

1691 Dvory, N. Z., Livshitz, Y., Kuznetsov, M., Adar, E., Gasser, G., Pankratov, I., ... & Yakirevich, A.
1692 (2018b), Caffeine vs. carbamazepine as indicators of wastewater pollution in a karst aquifer. *Hydrology*
1693 *and Earth System Sciences*, 22(12), 6371-6381.

1694 Einsiedl, F., Maloszewski, P., & Stichler, W. (2009), Multiple isotope approach to the determination of
1695 the natural attenuation potential of a high-alpine karst system. *Journal of Hydrology*, 365(1-2), 113-121.

1696 Ender, A., Goeppert, N., & Goldscheider, N. (2018), Spatial resolution of transport parameters in a
1697 subtropical karst conduit system during dry and wet seasons. *Hydrogeology Journal*, 26(7).

1698 Enemark, T., Peeters, L. J., Mallants, D., & Batelaan, O. (2019), Hydrogeological conceptual model
1699 building and testing: A review. *Journal of Hydrology*, 569, 310-329.

1700 Ewers, R. O., White, K. A., & Fuller, J. F. (2012), Contaminant plumes and pseudoplumes in karst
1701 aquifers. *Carbonates and Evaporites*, 27, 153-159.

1702 Fan, X., Sun, S., Wei, W., & Kou, J. (2011), Numerical simulation of pollutant transport in fractured
1703 vuggy porous karstic aquifers. *Journal of Applied Mathematics*, 2011.

1704 Fandel, C., Miville, F., Ferré, T., Goldscheider, N., & Renard, P. (2022), The stochastic simulation of
1705 karst conduit network structure using anisotropic fast marching, and its application to a geologically
1706 complex alpine karst system. *Hydrogeology Journal*, *30*(3), 927-946.

1707 Faulkner, J., Hu, B. X., Kish, S., & Hua, F. (2009), Laboratory analog and numerical study of
1708 groundwater flow and solute transport in a karst aquifer with conduit and matrix domains. *Journal of*
1709 *Contaminant Hydrology*, 110(1-2), 34-44.

1710 Feehley, C. E., Zheng, C., & Molz, F. J. (2000), A dual-domain mass transfer approach for modeling
1711 solute transport in heterogeneous aquifers: Application to the Macrodispersion Experiment (MADE)
1712 site. *Water Resources Research*, *36*(9), 2501-2515.

Field, M. S. (2002), The QTRACER2 program for tracer-breakthrough curve analysis for tracer tests in karstic aquifers and other hydrologic systems. National Center for Environmental Assessment--Washington Office, Office of Research and Development, US Environmental Protection Agency.

Field, M. S. (2018), Investigating and remediating contaminated karst aquifers. In Karst groundwater contamination and public health: beyond case studies (pp. 101-115). Springer International Publishing.

Field, M. S. (2020), Groundwater sampling in karst terranes: passive sampling in comparison to event-driven sampling strategy. *Hydrogeology Journal*, 29.

Field, M. S., & Li, G. (2011), Inversion for the input history of a dye tracing experiment. *Journal of Cave and Karst Studies*, 73(1), 16-20.

Field, M. S., & Leij, F. J. (2012), Solute transport in solution conduits exhibiting multi-peaked breakthrough curves. *Journal of Hydrology*, 440, 26-35.

Field, M. S., & Leij, F. J. (2014), Combined physical and chemical nonequilibrium transport model for solution conduits. *Journal of Contaminant Hydrology*, 157, 37-46.

Field, M. S., & Nash, S. G. (1997), Risk assessment methodology for karst aquifers:(1) Estimating karst conduit-flow parameters. *Environmental Monitoring and Assessment*, *47*, 1-21.

Field, M. S., & Pinsky, P. F. (2000), A two-region nonequilibrium model for solute transport in solution conduits in karstic aquifers. *Journal of Contaminant Hydrology*, 44(3-4), 329-351.

Finsterle, S., Kowalsky, M. B., & Pruess, K. (2012), TOUGH: Model use, calibration, and validation. *Transactions of the ASABE*, 55(4), 1275-1290.

Fischer, H. B. (1979), Mixing in inland and coastal waters. Academic press.

Fischer, P., Jourde, H., Brunet, P., & Leonardi, V. (2024), Large-scale spatial reconstitution of groundwater fluxes in a karst aquifer on the basis of hydrodynamic and hydrodispersive measurements. *Journal of Hydrology*, 130866.

Florea, L. J., & Wicks, C. M. (2001), Solute transport through laboratory-scale karstic aquifers. *Journal of Cave and Karst Studies*, 63(2), 59-66.

Flynn, R. M., & Sinreich, M. (2010), Characterisation of virus transport and attenuation in epikarst using short pulse and prolonged injection multi-tracer testing. *Water Research*, 44(4), 1138-1149.

Ford, D., & Williams, P. D. (2007). Karst hydrogeology and geomorphology. John Wiley & Sons

Frank, S., Goeppert, N., & Goldscheider, N. (2021), Field tracer tests to evaluate transport properties of tryptophan and humic acid in karst. *Groundwater*, 59(1), 59-70.

Gerke, H. H., & Van Genuchten, M. T. (1993), A dual-porosity model for simulating the preferential movement of water and solutes in structured porous media. *Water Resources Research*, 29(2), 305-319.

Geyer, T. (2008), Process-based characterisation of flow and transport in karst aquifers at catchment scale. (Doctoral dissertation). Retrieved from [https://ediss.uni-goettingen.de/handle/11858/00-1735-0000-0006-B276-E?locale-attribute=de]. (21/03/2024). Göttingen: Georg-August-Universität.

Geyer, T., Birk, S., Licha, T., Liedl, R., & Sauter, M. (2007), Multitracer test approach to characterize reactive transport in karst aquifers. *Groundwater*, 45(1), 36-45.

Geyer, T., Birk, S., Liedl, R., & Sauter, M. (2008), Quantification of temporal distribution of recharge in karst systems from spring hydrographs. *Journal of Hydrology*, *348*(3-4), 452-463.

Geyer, T., Birk, S., Reimann, T., Dörfliger, N., & Sauter, M. (2013), Differentiated characterization of karst aquifers: some contributions. *Carbonates and Evaporites*, 28, 41-46

Ghanbarian, B., Hunt, A. G., Ewing, R. P., & Sahimi, M. (2013), Tortuosity in porous media: a critical review. *Soil Science Society of America Journal*, 77(5), 1461-1477.

Gharari, S., Gupta, H. V., Clark, M. P., Hrachowitz, M., Fenicia, F., Matgen, P., & Savenije, H. H. (2021), Understanding the information content in the hierarchy of model development decisions: Learning from data. *Water Resources Research*, 57(6), e2020WR027948.

Ghasemizadeh, R., Hellweger, F., Butscher, C., Padilla, I., Vesper, D., Field, M., & Alshawabkeh, A. (2012), Groundwater flow and transport modeling of karst aquifers, with particular reference to the North Coast Limestone aquifer system of Puerto Rico. *Hydrogeology Journal*, 20(8), 1441.

Ghasemizadeh, R., Yu, X., Butscher, C., Padilla, I. Y., & Alshawabkeh, A. (2016), Improved regional groundwater flow modeling using drainage features: a case study of the central northern karst aquifer system of Puerto Rico (USA). *Hydrogeology Journal*, 24(6), 1463.

Giese, M., Reimann, T., Bailly-Comte, V., Maréchal, J. C., Sauter, M., & Geyer, T. (2018), Turbulent and laminar flow in karst conduits under unsteady flow conditions: Interpretation of pumping tests by discrete conduit-continuum modeling. *Water Resources Research*, 54(3), 1918-1933.

Gill, L. W., Naughton, O., & Johnston, P. M. (2013), Modeling a network of turloughs in lowland karst. *Water Resources Research*, 49(6), 3487-3503.

Gill, L. W., Schuler, P., Duran, L., Morrissey, P., & Johnston, P. M. (2021), An evaluation of semidistributed-pipe-network and distributed-finite-difference models to simulate karst systems. *Hydrogeology Journal*, 29(1), 259.

Ginn, T. R. (1999), On the distribution of multicomponent mixtures over generalized exposure time in subsurface flow and reactive transport: Foundations, and formulations for groundwater age, chemical heterogeneity, and biodegradation. *Water Resources Research*, *35*(5), 1395-1407.

Ginn, T. R., Haeri, H., Massoudieh, A., & Foglia, L. (2009), Notes on groundwater age in forward and inverse modeling. *Transport in Porous Media*, *79*, 117-134.

Goldscheider, N. (2005), Karst groundwater vulnerability mapping: application of a new method in the Swabian Alb, Germany. *Hydrogeology Journal*, 13, 555-564.

Goldscheider, N. (2019), A holistic approach to groundwater protection and ecosystem services in karst terrains. *Carbonates and Evaporites*, 34(4), 1241-1249.

Goldscheider, N., & Drew, D. (Eds.). (2014), Methods in karst hydrogeology: IAH: International Contributions to Hydrogeology, 26. Crc Press.

Goldscheider, N., Meiman, J., Pronk, M., & Smart, C. (2008), Tracer tests in karst hydrogeology and speleology. International *Journal of Speleology*, 37(1), 27-40.

Goldscheider, N., Pronk, M., & Zopfi, J. (2010), New insights into the transport of sediments and microorganisms in karst groundwater by continuous monitoring of particle-size distribution. *Geologia Croatica*, 63(2), 137-142.

Goeppert, N., Goldscheider, N., & Berkowitz, B. (2020), Experimental and modeling evidence of kilometer-scale anomalous tracer transport in an alpine karst aquifer. *Water Research*, 178, 115755.

Goode, D. J. (1996), Direct simulation of groundwater age. *Water Resources Research*, *32*(2), 289-296.

1792 Göppert, N., & Goldscheider, N. (2008), Solute and colloid transport in karst conduits under low-and
1793 high-flow conditions. *Groundwater*, 46(1), 61-68.

1794 Green, R. T., Painter, S. L., Sun, A., & Worthington, S. R. (2006), Groundwater contamination in karst
1795 terranes. *Water, Air, & Soil Pollution*: Focus, 6, 157-170.

1796 Gupta, H. V., Clark, M. P., Vrugt, J. A., Abramowitz, G., & Ye, M. (2012), Towards a comprehensive
1797 assessment of model structural adequacy. *Water Resources Research*, 48(8).

1798 Gutiérrez, F., Parise, M., De Waele, J., & Jourde, H. (2014), A review on natural and human-induced
1799 geohazards and impacts in karst. *Earth-Science Reviews*, 138, 61-88.

1800 Güler, C., & Thyne, G. D. (2004), Delineation of hydrochemical facies distribution in a regional
1801 groundwater system by means of fuzzy c-means clustering. *Water Resources Research*, 40(12).

1802 Haggerty, R., & Gorelick, S. M. (1995), Multiple-rate mass transfer for modeling diffusion and surface
1803 reactions in media with pore-scale heterogeneity. *Water Resources Research*, 31(10), 2383-2400.

1804 Haggerty, R., Harvey, C. F., Freiherr von Schwerin, C., & Meigs, L. C. (2004), What controls the
1805 apparent timescale of solute mass transfer in aquifers and soils? A comparison of experimental
1806 results. *Water Resources Research*, 40(1).

1807 Haggerty, R., McKenna, S. A., & Meigs, L. C. (2000), On the late-time behavior of tracer test
1808 breakthrough curves. *Water Resources Research*, 36(12), 3467-3479.

1809 Hansen, S. K., & Berkowitz, B. (2020), Modeling non-Fickian solute transport due to mass transfer and
1810 physical heterogeneity on arbitrary groundwater velocity fields. *Water Resources Research*, *56*(10),
1811 e2019WR026868.

1812 Harman, C. J. (2015), Time-variable transit time distributions and transport: Theory and application to
1813 storage-dependent transport of chloride in a watershed. *Water Resources Research*, 51(1), 1-30.

1814 Harman, C. J. (2019), Age-ranked storage-discharge relations: A unified description of spatially lumped
1815 flow and water age in hydrologic systems. *Water Resources Research*, 55(8), 7143-7165.

1816 Hartmann, A. (2018), Experiences in calibrating and evaluating lumped karst hydrological
1817 models. *Geological Society, London, Special Publications*, 466(1), 331-340.

1818 Hartmann, A., Kralik, M., Humer, F., Lange, J., & Weiler, M. (2012a), Identification of a karst system's
1819 intrinsic hydrodynamic parameters: upscaling from single springs to the whole aquifer. *Environmental*
1820 *Earth Sciences*, 65, 2377-2389.

1821 Hartmann, A., Lange, J., Weiler, M., Arbel, Y., & Greenbaum, N. (2012b). A new approach to model the
1822 spatial and temporal variability of recharge to karst aquifers. *Hydrology and Earth System*
1823 *Sciences*, 16(7), 2219-2231.

1824 Hartmann, A., Barberá, J. A., Lange, J., Andreo, B., & Weiler, M. (2013a), Progress in the hydrologic
1825 simulation of time variant recharge areas of karst systems–Exemplified at a karst spring in Southern
1826 Spain. *Advances in Water Resources*, 54, 149-160.

1827 Hartmann, A., Wagener, T., Rimmer, A., Lange, J., Brielmann, H., & Weiler, M. (2013b), Testing the
1828 realism of model structures to identify karst system processes using water quality and quantity
1829 signatures. *Water Resources Research*, 49(6), 3345-3358.

1830 Hartmann, A., Goldscheider, N., Wagener, T., Lange, J., & Weiler, M. (2014), Karst water resources in a
1831 changing world: Review of hydrological modeling approaches. *Reviews of Geophysics*, 52(3), 218-242.

Hartmann, A. (2016b), Putting the cat in the box: why our models should consider subsurface heterogeneity at all scales. *Wiley Interdisciplinary Reviews: Water*, 3(4), 478-486.

Hartmann, A., Kobler, J., Kralik, M., Dirnböck, T., Humer, F., & Weiler, M. (2016a), Model-aided quantification of dissolved carbon and nitrogen release after windthrow disturbance in an Austrian karst system. *Biogeosciences*, 13(1), 159-174.

Hartmann, A., Barberá, J. A., & Andreo, B. (2017), On the value of water quality data and informative flow states in karst modelling. *Hydrology and Earth System Sciences*, 21(12), 5971-5985.

Hartmann, A., Jasechko, S., Gleeson, T., Wada, Y., Andreo, B., Barberá, J. A., ... & Wagener, T. (2021), Risk of groundwater contamination widely underestimated because of fast flow into aquifers. *Proceedings of the National Academy of Sciences*, 118(20), e2024492118.

Hauns, M., Jeannin, P. Y., & Atteia, O. (2001), Dispersion, retardation and scale effect in tracer breakthrough curves in karst conduits. *Journal of Hydrology*, 241(3-4), 177-193.

Henry, H. F., & Suk, W. A. (2018), Public health and karst groundwater contamination: from multidisciplinary research to exposure prevention. In Karst Groundwater Contamination and Public Health (pp. 7-14). Springer, Cham.

Hensley, R. T., & Cohen, M. J. (2012), Controls on solute transport in large spring-fed karst rivers. *Limnology and Oceanography*, 57(4), 912-924.

Herman, E. K., Toran, L., & White, W. B. (2012), Clastic sediment transport and storage in fluviokarst aquifers: an essential component of karst hydrogeology. *Carbonates and Evaporites*, 27, 211-241.

Hillebrand, O., Nödler, K., Licha, T., Sauter, M., & Geyer, T. (2012a), Identification of the attenuation potential of a karst aquifer by an artificial dual tracer experiment with caffeine. *Water Research*, 46(16), 5381-5388.

Hillebrand, O., Nödler, K., Licha, T., Sauter, M., & Geyer, T. (2012b), Caffeine as an indicator for the quantification of untreated wastewater in karst systems. Water Research, 46(2), 395-402.

Hillebrand, O., Nödler, K., Sauter, M., & Licha, T. (2015), Multitracer experiment to evaluate the attenuation of selected organic micropollutants in a karst aquifer. *Science of the Total Environment*, 506, 338-343.

Hoeting, J. A., Madigan, D., Raftery, A. E., & Volinsky, C. T. (1999), Bayesian model averaging: a tutorial (with comments by M. Clyde, David Draper and EI George, and a rejoinder by the authors. *Statistical Science*, 14(4), 382-417.

Howroyd, M., & Novakowski, K. S. (2021), The use of scaling parameters and the impact of non-uniqueness in the simulation of a large-scale solute transport experiment conducted in discrete fractures. *Journal of Contaminant Hydrology*, 243, 103890.

Hublart, P., Ruelland, D., Dezetter, A., & Jourde, H. (2015), Reducing structural uncertainty in conceptual hydrological modelling in the semi-arid Andes. *Hydrology and Earth System Sciences*, 19(5), 2295-2314.

Hunkeler, D., & Mudry, J. (2014), Hydrochemical methods. In Methods in karst hydrogeology (pp. 93-121). CRC Press.

Huntoon, P. W. (1995), Is it appropriate to apply porous media groundwater circulation models to karstic aquifers. Groundwater models for resources analysis and management, 339-358.

Husic, A., Fox, J., Adams, E., Ford, W., Agouridis, C., Currens, J., & Backus, J. (2019), Nitrate pathways, processes, and timing in an agricultural karst system: Development and application of a numerical model. *Water Resources Research*, 55(3), 2079-2103.

Husic, A., Fox, J., Mahoney, T., Gerlitz, M., Pollock, E., & Backus, J. (2020), Optimal transport for assessing nitrate source-pathway connectivity. *Water Resources Research*, 56(10), e2020WR027446.

Husic, A., Fox, J., Al Aamery, N., Ford, W., Pollock, E., & Backus, J. (2021), Seasonality of recharge drives spatial and temporal nitrate removal in a karst conduit as evidenced by nitrogen isotope modeling. Journal of Geophysical Research: *Biogeosciences*, 126(10), e2021JG006454.

Jamal, M. S., & Awotunde, A. A. (2020), Darcy's model with optimized permeability distribution for the simulation of Stokes flow and contaminant transport in karst aquifers. *Hydrogeology Journal*, 28(4), 1249-1267.

Jasechko, S., Perrone, D., Befus, K. M., Bayani Cardenas, M., Ferguson, G., Gleeson, T., ... & Kirchner, J. W. (2017), Global aquifers dominated by fossil groundwaters but wells vulnerable to modern contamination. *Nature Geoscience*, 10(6), 425-429.

Jeannin, P. Y., Artigue, G., Butscher, C., Chang, Y., Charlier, J. B., Duran, L., ... & Wunsch, A. (2021), Karst modelling challenge 1: Results of hydrological modelling. *Journal of Hydrology*, 600, 126508.

Jeannin, P. Y., Eichenberger, U., Sinreich, M., Vouillamoz, J., Malard, A., & Weber, E. (2013), KARSYS: a pragmatic approach to karst hydrogeological system conceptualisation. Assessment of groundwater reserves and resources in Switzerland. *Environmental Earth Sciences*, 69, 999-1013.

Jeannin, P. Y., & Maréchal, J. C. (1997), Dispersion and tailing of tracer plumes in a karstic system (Milandre, JU, Switzerland). *Sciences & Techniques de l'Environnement, université de Franche-Comté. Mémoire hors-série*, 149-152.

Ji, H., Luo, M., Yin, M., Li, C., Wan, L., & Huang, K. (2022), Storage and release of conservative solute between karst conduit and fissures using a laboratory analog. *Journal of Hydrology*, 612, 128228.

Jia, H., Xu, T., Liang, S., Zhao, P., & Xu, C. (2018), Bayesian framework of parameter sensitivity, uncertainty, and identifiability analysis in complex water quality models. *Environmental Modelling & Software*, 104, 13-26.

Jiang, C., Jourde, H., Aliouache, M., & Wang, X. (2023), The effect of seasonal variation of precipitation/recharge on karst genesis behaviors in different climatic contexts. *Journal of Hydrology*, 130385.

Johnston, P. B., Atkinson, T., Barker, J., & Odling, N. (2009), Constraining the uncertainty in fracture geometry using tracer tests. *Hydrogeology journal*, *17*(3), 527.

Jones, W. K. (2019). Water tracing in karst aquifers. In Encyclopedia of caves (pp. 1144-1155). Academic Press.

Joodi, A. S., Sizaret, S., Binet, S., Bruand, A., Alberic, P., & Lepiller, M. (2010), Development of a Darcy-Brinkman model to simulate water flow and tracer transport in a heterogeneous karstic aquifer (Val d'Orléans, France). *Hydrogeology Journal*, 18(2), 295.

Jourde, H., Massei, N., Mazzilli, N., Binet, S., Batiot-Guilhe, C., Labat, D., ... & Wang, X. (2018), SNO KARST: A French network of observatories for the multidisciplinary study of critical zone processes in karst watersheds and aquifers. *Vadose Zone Journal*, *17*(1), 1-18.

Jourde, H., & Wang, X. (2023), Advances, challenges and perspective in modelling the functioning of karst systems: a review. *Environmental Earth Sciences*, 82(17), 396.

Jukić, D., & Denić-Jukić, V. (2009), Groundwater balance estimation in karst by using a conceptual rainfall–runoff model. *Journal of Hydrology*, 373(3-4), 302-315.

Jukić, D., Denić-Jukić, V., & Kadić, A. (2022), Temporal and spatial characterization of sediment transport through a karst aquifer by means of time series analysis. *Journal of Hydrology*, 609, 127753.

Katz, B. G., Catches, J. S., Bullen, T. D., & Michel, R. L. (1998), Changes in the isotopic and chemical composition of ground water resulting from a recharge pulse from a sinking stream. *Journal of Hydrology*, 211(1-4), 178-207.

Katz, B. G. (2019), Nitrate contamination in karst groundwater. In Encyclopedia of caves (pp. 756-760). Academic Press.

Kaufmann, G. (2003), A model comparison of karst aquifer evolution for different matrix-flow formulations. *Journal of Hydrology*, 283(1-4), 281-289.

Kaufmann, G., Gabrovšek, F., & Romanov, D. (2014), Deep conduit flow in karst aquifers revisited. *Water Resources Research*, 50(6), 4821-4836.

Kaushal, N., Lechleitner, F. A., & Wilhelm, M. (2023), SISALv3: Speleothem Isotopes Synthesis and AnaLysis database version 3.0.

Kavousi, A., Reimann, T., Liedl, R., & Raeisi, E. (2020), Karst aquifer characterization by inverse application of MODFLOW-2005 CFPv2 discrete-continuum flow and transport model. *Journal of Hydrology*, 587, 124922.

Kavousi, A., Reimann, T., Wöhling, T., Birk, S., Luhmann, A. J., Kordilla, J., ... & Liedl, R. (2023), Joint inversion of groundwater flow, heat, and solute state variables: a multipurpose approach for characterization and forecast of karst systems. *Hydrogeology Journal*, 1-26.

Kelly, J. F., & Meerschaert, M. M. (2019), The fractional advection-dispersion equation for contaminant transport. In Application in physics, part B (pp. 129-150). Boston: De Gruyter, Berlin.

Kinzelbach, W. (1986), Groundwater modelling: An introduction with sample programs in BASIC. Elsevier.

Kiraly, L. (1998), Modelling karst aquifers by the combined discrete channel and continuum approach. *Bulletin du Centre d'hydrogéologie*, 16, 77-98.

Kiraly, L. (2002), Karstification and groundwater flow. In Proceedings of the conference on evolution of karst: from Prekarst to Cessation. Postojna-Ljubljana (pp. 155-190).

Kitanidis, P. K. (1994), The concept of the dilution index. *Water Resources Research*, 30(7), 2011-2026.

Klaas, D. K., Imteaz, M. A., & Arulrajah, A. (2017), Development of groundwater vulnerability zones in a data-scarce eogenetic karst area using Head-Guided Zonation and particle-tracking simulation methods. *Water Research*, 122, 17-26.

Kogovsek, J., & Petric, M. (2014), Solute transport processes in a karst vadose zone characterized by long-term tracer tests (the cave system of Postojnska Jama, Slovenia). *Journal of Hydrology*, 519, 1205-1213.

Konikow, L. F. (1996), Use of numerical models to simulate groundwater flow and transport. US Geological Survey.

Konikow, L. F. (2010), Applying dispersive changes to Lagrangian particles in groundwater transport models. *Transport in Porous Media*, 85, 437-449.

Konikow, L. F. (2011), The secret to successful solute-transport modeling. *Groundwater*, 49(2), 144-159.

Kovács, A. (2003), Geometry and hydraulic parameters of karst aquifers: a hydrodynamic modeling approach (Doctoral dissertation). Retrieved from [Université de Neuchâtel], 21/03/2023, Switzerland, Université de Neuchâtel.

Kovács, A., & Sauter, M. (2014), Modelling karst hydrodynamics. In *Methods in karst hydrogeology* (pp. 201-222). CRC Press.

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.

Kresic, N., & Stevanovic, Z. (Eds.). (2009), Groundwater hydrology of springs: engineering, theory, management and sustainability. Butterworth-heinemann.

Kübeck, C., Maloszewski, P. J., & Benischke, R. (2013), Determination of the conduit structure in a karst aquifer based on tracer data—Lurbach system, Austria. *Hydrological Processes*, 27(2), 225-235.

Labat, D., & Mangin, A. (2015), Transfer function approach for artificial tracer test interpretation in karstic systems. *Journal of Hydrology*, 529, 866-871.

Laincz, J., & Hays, P. D. (2014), Geochemical Evidence for Denitrification in the Epikarst at the Savoy Experimental Watershed, Northwest Arkansas. US Geological Survey Karst Interest Group Proceedings, Carlsbad, New Mexico, April 29–May 2, 2014, 109.

Lan, J., Sun, Y., & Yuan, D. (2018), Transport of polycyclic aromatic hydrocarbons in a highly vulnerable karst underground river system of southwest China. *Environmental Science and Pollution Research*, *25*, 34519-34530.

Lauber, U., & Goldscheider, N. (2014), Use of artificial and natural tracers to assess groundwater transit-time distribution and flow systems in a high-alpine karst system (Wetterstein Mountains, Germany). *Hydrogeology Journal*, 22(8), 1807.

Lehmann, F., Rajabi, M. M., Belfort, B., Delay, F., Fahs, M., Ackerer, P., & Younes, A. (2022), Bayesian inversion of laboratory experiments of transport through limestone fractures. *Journal of Contaminant Hydrology*, 249, 104045.

Lenda, A., & Zuber, A. (1970), Tracer dispersion in groundwater experiments. Isotope hydrology, 1970, 619-641.

Liedl, R., Sauter, M., Hückinghaus, D., Clemens, T., & Teutsch, G. (2003), Simulation of the development of karst aquifers using a coupled continuum pipe flow model. *Water Resources Research*, 39(3).

Leij, F. J., Toride, N., Field, M. S., & Sciortino, A. (2012), Solute transport in dual-permeability porous media. *Water Resources Research*, 48(4).

Li, G., & Liu, H. (2014), An advection–dilution model to estimate conduit geometry and flow. *Acta Carsologica*, 43(1).

Li, G., & Loper, D. E. (2011), Transport, dilution, and dispersion of contaminant in a leaky karst conduit. *Transport in Porous Media*, 88, 31-43.

Li, G., Loper, D. E., & Kung, R. (2008), Contaminant sequestration in karstic aquifers: Experiments and quantification. *Water Resources Research*, 44(2).

Li, L., Maher, K., Navarre-Sitchler, A., Druhan, J., Meile, C., Lawrence, C., ... & Beisman, J. (2017), Expanding the role of reactive transport models in critical zone processes. *Earth-Science Reviews*, 165, 280-301.

Liu, X. L., Han, G., Zeng, J., Liu, M., Li, X. Q., & Boeckx, P. (2021), Identifying the sources of nitrate contamination using a combined dual isotope, chemical and Bayesian model approach in a tropical agricultural river: Case study in the Mun River, Thailand. *Science of the Total Environment*, 760, 143938.

Long, A. J., & Putnam, L. D. (2009), Age-distribution estimation for karst groundwater: Issues of parameterization and complexity in inverse modeling by convolution. *Journal of Hydrology*, 376(3-4), 579-588.

Loop, C. M., & White, W. B. (2001), A conceptual model for DNAPL transport in karst ground water basins. *Groundwater*, 39(1), 119-127.

Lu, M., Yue, F. J., Wang, X. D., Liu, Z. H., Shi, Z. Y., & Zhang, P. (2023), Identify nitrogen transport paths and sources contribution in karst valley depression area using isotopic approach. *Journal of Environmental Management*, 337, 117751.

Luhmann, A. J., Covington, M. D., Myre, J. M., Perne, M., Jones, S. W., Alexander Jr, E. C., & Saar, M. O. (2015), Thermal damping and retardation in karst conduits. *Hydrology and Earth System Sciences*, 19(1), 137-157.

Luo, M., Chen, J., Xu, Y., Zhou, Z., & Zhou, H. (2024), Recharge dynamic and flow-path geometry controls of solute transport in karst aquifer. *Journal of Hydrology*, 628, 130554.

Mahler, B. J., Lynch, L., & Bennett, P. C. (1999), Mobile sediment in an urbanizing karst aquifer: implications for contaminant transport. *Environmental Geology*, 39(1), 25-38.

Mahler, B. J., Personné, J. C., Lods, G. F., & Drogue, C. (2000), Transport of free and particulate-associated bacteria in karst. *Journal of Hydrology*, 238(3-4), 179-193.

Mai, J. (2023), Ten strategies towards successful calibration of environmental models. *Journal of Hydrology*, 620, 129414.

Majdalani, S., Guinot, V., Delenne, C., & Gebran, H. (2018), Modelling solute dispersion in periodic heterogeneous porous media: model benchmarking against intermediate scale experiments. *Journal of Hydrology*, 561, 427-443.

Makropoulos, C., Koutsoyiannis, D., Stanić, M., Djordjević, S., Prodanović, D., Dašić, T., ... & Wheater, H. (2008), A multi-model approach to the simulation of large scale karst flows. *Journal of Hydrology*, 348(3-4), 412-424.

Malík, P., Švasta, J., Michalko, J., & Gregor, M. (2016), Indicative mean transit time estimation from δ 18 O values as groundwater vulnerability indicator in karst-fissure aquifers. *Environmental Earth Sciences*, 75, 1-12.

Malozewski, P., & Zuber, A. (1982), Determining the turnover time of groundwater systems with the aid of environmental tracers. *Journal of Hydrology*, 57, 207-231.

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(1-4), 343-360.

Maloszewski, P., Stichler, W., Zuber, A., & Rank, D. (2002), Identifying the flow systems in a karstic-fissured-porous aquifer, the Schneealpe, Austria, by modelling of environmental 18O and 3H isotopes. *Journal of Hydrology*, 256(1-2), 48-59.

2035 Maloszewski, P., & Zuber, A. (1993), Tracer experiments in fractured rocks: Matrix diffusion and the
2036 validity of models. *Water Resources Research*, 29(8), 2723-2735.

2037 Maloszewski, P., & Zuber, A. (1996), Lumped parameter models for the interpretation of environmental
2038 tracer data.

2039 Maloszewski, P., & Zuber, A. (2002), Manual on lumped parameter models used for the interpretation of
2040 environmental tracer data in groundwaters.

2041 Maqueda, A., Renard, P., & Filipponi, M. (2023), Karst conduit size distribution evolution using
2042 speleogenesis modelling. *Environmental Earth Sciences*, 82(14), 360.

2043 Maréchal, J. C., Ladouche, B., Dörfliger, N., & Lachassagne, P. (2008), Interpretation of pumping tests in
2044 a mixed flow karst system. *Water Resources Research*, 44(5).

2045 Martin, J. B., & Dean, R. W. (1999), Temperature as a natural tracer of short residence times for
2046 groundwater in karst aquifers. Karst Modeling. *Karst Waters Institute Special Publication*, 5, 236-242.

2047 Martin, J. B., Gulley, J., & Spellman, P. (2012), Tidal pumping of water between Bahamian blue holes,
2048 aquifers, and the ocean. *Journal of Hydrology*, 416, 28-38.

2049 Martín-Rodríguez, J. F., Mudarra, M., De la Torre, B., & Andreo, B. (2023), Towards a better
2050 understanding of time-lags in karst aquifers by combining hydrological analysis tools and dye tracer tests.
2051 Application to a binary karst aquifer in Southern Spain. *Journal of Hydrology*, 129643.

2052 Masciopinto, C., Passarella, G., Caputo, M. C., Masciale, R., & De Carlo, L. (2021), Hydrogeological
2053 Models of Water Flow and Pollutant Transport in Karstic and Fractured Reservoirs. *Water Resources*
2054 *Research*, 57(8), e2021WR029969.

2055 Massei, N., Lacroix, M., Wang, H. Q., Mahler, B. J., & Dupont, J. P. (2002), Transport of suspended
2056 solids from a karstic to an alluvial aquifer: the role of the karst/alluvium interface. *Journal of*
2057 *Hydrology*, *260*(1-4), 88-101.

2058 Massei, N., Wang, H. Q., Field, M. S., Dupont, J. P., & Rodet, J. (2003), Dual-flow phenomena and
2059 longitudinal dispersivity interpretation in a karstic aquifer. In *Sinkholes and the Engineering and*
2060 *Environmental Impacts of Karst* (pp. 232-240).

2061 Massei, N., Wang, H. Q., Field, M. S., Dupont, J. P., Bakalowicz, M., & Rodet, J. (2006), Interpreting
2062 tracer breakthrough tailing in a conduit-dominated karstic aquifer. *Hydrogeology Journal*, 14(6), 849-858.

2063 Massmann, C., Birk, S., Liedl, R., & Geyer, T. (2005), Identification of hydrogeological models:
2064 Application to tracer test analysis in a karst aquifer. Calibration and Reliability in Groundwater
2065 Modelling: From Uncertainty to Decision Making, Proceedings of ModelCARE, 59-64.

2066 Mathias, S. A., Butler, A. P., McIntyre, N., & Wheater, H. S. (2005), The significance of flow in the
2067 matrix of the Chalk unsaturated zone. *Journal of Hydrology*, 310(1-4), 62-77.

2068 Mazzilli, N., Guinot, V., & Jourde, H. (2012), Sensitivity analysis of conceptual model calibration to
2069 initialisation bias. Application to karst spring discharge models. *Advances in Water Resources*, 42, 1-16.

2070 Mazzilli, N., Guinot, V., Jourde, H., Lecoq, N., Labat, D., Arfib, B., ... & Bertin, D. (2019), KarstMod: a
2071 modelling platform for rainfall-discharge analysis and modelling dedicated to karst
2072 systems. *Environmental Modelling & Software*, 122, 103927.

2073 McMillan, H., Tetzlaff, D., Clark, M., & Soulsby, C. (2012), Do time-variable tracers aid the evaluation
2074 of hydrological model structure? A multimodel approach. *Water Resources Research*, *48*(5).

Medici, G.,West, L. J., & Banwart, S. A. (2019), Groundwater flow velocities in a fractured carbonate aquifer-type: implications for contaminant transport. *Journal of Contaminant Hydrology*, 222, 1-16.

Medici, G., & West, L. J. (2021), Groundwater flow velocities in karst aquifers; importance of spatial observation scale and hydraulic testing for contaminant transport prediction. *Environmental Science and Pollution Research*, 28(32), 43050-43063.

Meerschaert, M. M., Benson, D. A., & Bäumer, B. (1999), Multidimensional advection and fractional dispersion. *Physical Review E*, 59(5), 5026.

Metzler, R., & Klafter, J. (2000), The random walk's guide to anomalous diffusion: a fractional dynamics approach. *Physics Reports*, 339(1), 1-77.

Milanović, S., & Vasić, L. (2015), Monitoring of karst groundwater. Karst Aquifers—Characterization and Engineering, 335-359.

Mohammadi, Z., Illman, W. A., & Field, M. (2021), Review of laboratory scale models of karst aquifers: approaches, similitude, and requirements. *Groundwater*, 59(2), 163-174.

Morales, T., de Valderrama, I. F., Uriarte, J. A., Antigüedad, I., & Olazar, M. (2007), Predicting travel times and transport characterization in karst conduits by analyzing tracer-breakthrough curves. *Journal of Hydrology*, 334(1-2), 183-198.

Morales, T., Uriarte, J. A., Angulo, B., Olazar, M., Arandes, J. M., & Antigüedad, I. (2018), Characterization of flow and transport dynamics in karst aquifers by analyzing tracer test results in conduits and recharge areas (the Egino Massif, Basque Country, Spain): environmental and management implications. *Environmental Earth Sciences*, 77, 1-16.

Morales, T., Uriarte, J. A., Olazar, M., Antigüedad, I., & Angulo, B. (2010), Solute transport modelling in karst conduits with slow zones during different hydrologic conditions. *Journal of Hydrology*, 390(3-4), 182-189.

Mosthaf, K., Brauns, B., Fjordbøge, A. S., Rohde, M. M., Kerrn-Jespersen, H., Bjerg, P. L., ... & Broholm, M. M. (2018), Conceptualization of flow and transport in a limestone aquifer by multiple dedicated hydraulic and tracer tests. *Journal of Hydrology*, 561, 532-546.

Mudarra, M., Andreo, B., Marín, A. I., Vadillo, I., & Barberá, J. A. (2014), Combined use of natural and artificial tracers to determine the hydrogeological functioning of a karst aquifer: the Villanueva del Rosario system (Andalusia, southern Spain). *Hydrogeology Journal*, 22(5), 1027.

Mudarra, M., Hartmann, A., & Andreo, B. (2019), Combining experimental methods and modeling to quantify the complex recharge behavior of karst aquifers. *Water Resources Research*, 55(2), 1384-1404.

Mueller, Y. K., Goldscheider, N., Eiche, E., Emberger, H., & Goeppert, N. (2023), From cave to spring: Understanding transport of suspended sediment particles in a fully phreatic karst conduit using particle analysis and geochemical methods. *Hydrological Processes*, 37(10), e14979.

Musgrove, M., Jurgens, B. C., & Opsahl, S. P. (2023), Karst groundwater vulnerability determined by modeled age and residence time tracers. *Geophysical Research Letters*, 50(18), e2023GL102853.

Nativ, R., Günay, G., Hötzl, H., Reichert, B., Solomon, D. K., & Tezcan, L. (1999), Separation of groundwater-flow components in a karstified aquifer using environmental tracers. *Applied Geochemistry*, 14(8), 1001-1014.

Nerantzaki, S. D., Giannakis, G. V., Efstathiou, D., Nikolaidis, N. P., Sibetheros, I. A., Karatzas, G. P., & Zacharias, I. (2015), Modeling suspended sediment transport and assessing the impacts of climate change in a karstic Mediterranean watershed. *Science of the Total Environment*, 538, 288-297.

Neuman, S. P. (2003), Maximum likelihood Bayesian averaging of uncertain model predictions. *Stochastic Environmental Research and Risk Assessment*, 17(5), 291-305.

Neupauer, R. M., Meiss, J. D., & Mays, D. C. (2014), Chaotic advection and reaction during engineered injection and extraction in heterogeneous porous media. *Water Resources Research*, 50(2), 1433-1447.

Neven, K., & Sorab, P. (2021), Modeling of groundwater flow and transport in coastal karst aquifers. *Hydrogeology Journal*, 29(1), 249-258.

Olarinoye, T., Gleeson, T., Marx, V., Seeger, S., Adinehvand, R., Allocca, V., ... & Hartmann, A. (2020), Global karst springs hydrograph dataset for research and management of the world's fastest-flowing groundwater. *Scientific Data*, 7(1), 59.

Oreskes, N., Shrader-Frechette, K., & Belitz, K. (1994), Verification, validation, and confirmation of numerical models in the earth sciences. *Science*, 263(5147), 641-646.

Opsahl, S. P., Musgrove, M., & Slattery, R. N. (2017), New insights into nitrate dynamics in a karst groundwater system gained from in situ high-frequency optical sensor measurements. *Journal of Hydrology*, 546, 179-188.

Orban, P., Brouyère, S., Batlle-Aguilar, J., Couturier, J., Goderniaux, P., Leroy, M., ... & Dassargues, A. (2010), Regional transport modelling for nitrate trend assessment and forecasting in a chalk aquifer. *Journal of Contaminant Hydrology*, 118(1-2), 79-93.

Oster, J. L., Covey, A. K., Lawrence, C. R., Giannetta, M. G., & Druhan, J. L. (2021), A reactive transport approach to modeling cave seepage water chemistry II: Elemental signatures. *Geochimica et Cosmochimica Acta*, 311, 353-373.

Ozyurt, N. N., & Bayari, C. S. (2005), Steady-and unsteady-state lumped parameter modelling of tritium and chlorofluorocarbons transport: Hypothetical analyses and application to an alpine karst aquifer. *Hydrological Processes: An International Journal*, 19(17), 3269-3284.

Ozyurt, N. N., & Bayari, C. S. (2008), Temporal variation of chemical and isotopic signals in major discharges of an alpine karst aquifer in Turkey: implications with respect to response of karst aquifers to recharge. *Hydrogeology Journal*, 16, 297-309.

Padilla, I. Y., & Vesper, D. J. (2018), Fate, transport, and exposure of emerging and legacy contaminants in karst systems: state of knowledge and uncertainty. Karst groundwater contamination and public health: beyond case studies, 33-49.

Panno, S. V., Hackley, K. C., Hwang, H. H., & Kelly, W. R. (2001), Determination of the sources of nitrate contamination in karst springs using isotopic and chemical indicators. *Chemical Geology*, 179(1-4), 113-128.

Panno, S. V., Kelly, W. R., Scott, J., Zheng, W., McNeish, R. E., Holm, N., ... & Baranski, E. L. (2019), Microplastic contamination in karst groundwater systems. *Groundwater*, 57(2), 189-196.

Parise, M., Ravbar, N., Živanović, V., Mikszewski, A., Kresic, N., Mádl-Szőnyi, J., ... & Kukurić, N. (2015), Hazards in karst and managing water resources quality. In Karst aquifers—Characterization and engineering (pp. 601-687). Cham: Springer International Publishing.

Pastore, N., Cherubini, C., Giasi, C. I., & Dimitra, R. (2021), Numerical model of the behavior of chlorinated ethenes in a fractured, karstic limestone aquifer. *Hydrogeology Journal*, 29(2), 667-686.

Peely, A. B., Mohammadi, Z., & Raeisi, E. (2021), Breakthrough curves of dye tracing tests in karst aquifers: Review of effective parameters based on synthetic modeling and field data. *Journal of Hydrology*, 602, 126604.

Perrin, J., Jeannin, P. Y., & Zwahlen, F. (2003a), Implications of the spatial variability of infiltration-water chemistry for the investigation of a karst aquifer: a field study at Milandre test site, Swiss Jura. *Hydrogeology Journal*, 11, 673-686.

Perrin, J., Jeannin, P. Y., & Zwahlen, F. (2003b), Epikarst storage in a karst aquifer: a conceptual model based on isotopic data, Milandre test site, Switzerland. *Journal of Hydrology*, 279(1-4), 106-124.

Perrin, J., & Luetscher, M. (2008), Inference of the structure of karst conduits using quantitative tracer tests and geological information: example of the Swiss Jura. *Hydrogeology Journal*, 16, 951-967.

Petrič, M., Ravbar, N., Gostinčar, P., Krsnik, P., & Gacin, M. (2020), GIS database of groundwater flow characteristics in carbonate aquifers: Tracer test inventory from Slovenian karst. *Applied Geography*, 118, 102191.

Polak, A., Nativ, R., & Wallach, R. (2002), Matrix diffusion in northern Negev fractured chalk and its correlation to porosity. *Journal of Hydrology*, 268(1-4), 203-213.

Priebe, E. H., Amos, R. T., Jackson, R. E., & Rudolph, D. L. (2022), Regional-scale reactive transport modelling of hydrogeochemical evolution in a karstic carbonate aquifer. *Hydrogeology Journal*, 1-18.

Pronk, M., Goldscheider, N., Zopfi, J., & Zwahlen, F. (2009), Percolation and particle transport in the unsaturated zone of a karst aquifer. *Groundwater*, 47(3), 361-369.

Pérotin, L., de Montety, V., Ladouche, B., Bailly-Comte, V., Labasque, T., Vergnaud, V., ... & Seidel, J. L. (2021), Transfer of dissolved gases through a thick karstic vadose zone–Implications for recharge characterisation and groundwater age dating in karstic aquifers. *Journal of Hydrology*, 601, 126576.

Oehlmann, S., Geyer, T., Licha, T., & Sauter, M. (2015), Reducing the ambiguity of karst aquifer models by pattern matching of flow and transport on catchment scale. *Hydrology and Earth System Sciences*, 19(2), 893-912.

Qiao, X., Li, G., Li, Y., & Liu, K. (2015), Influences of heterogeneity on three-dimensional groundwater flow simulation and wellhead protection area delineation in karst groundwater system, Taiyuan City, Northern China. *Environmental Earth Sciences*, 73, 6705-6717.

Quinlan, J. F., Davies, G. J., Jones, S. W., & Huntoon, P. W. (1996), The applicability of numerical models to adequately characterize ground-water flow in karstic and other triple-porosity aquifers. Subsurface fluid-flow (ground-water and vadose zone) modeling, ASTM STP, 1288, 114-133.

Quinn, J. J., Tomasko, D., & Kuiper, J. A. (2006), Modeling complex flow in a karst aquifer. *Sedimentary Geology*, 184(3-4), 343-351.

Ravbar, N., Engelhardt, I., & Goldscheider, N. (2011), Anomalous behaviour of specific electrical conductivity at a karst spring induced by variable catchment boundaries: the case of the Podstenjšek spring, Slovenia. *Hydrological Processes*, 25(13), 2130-2140.

Ravbar, N., Barberá, J. A., Petrič, M., Kogovšek, J., & Andreo, B. (2012), The study of hydrodynamic behaviour of a complex karst system under low-flow conditions using natural and artificial tracers (the catchment of the Unica River, SW Slovenia). *Environmental Earth Sciences*, 65, 2259-2272.

Rayne, T. W., Bradbury, K. R., & Muldoon, M. A. (2001), Delineation of capture zones for municipal wells in fractured dolomite, Sturgeon Bay, Wisconsin, USA. *Hydrogeology Journal*, 9, 432-450.

Reberski, J. L., Terzić, J., Maurice, L. D., & Lapworth, D. J. (2022), Emerging organic contaminants in karst groundwater: A global level assessment. *Journal of Hydrology*, 604, 127242.

Rehrl, C., & Birk, S. (2010), Hydrogeological characterisation and modelling of spring catchments in a changing environment. *Austrian Journal of Earth Sciences*, 103(2).

Reichert, P., Ammann, L., & Fenicia, F. (2021), Potential and challenges of investigating intrinsic uncertainty of hydrological models with stochastic, time-dependent parameters. *Water Resources Research, 57(3)*, e2020WR028400.

Reimann, T., Rehrl, C., Shoemaker, W. B., Geyer, T., & Birk, S. (2011a), The significance of turbulent flow representation in single-continuum models. *Water Resources Research*, 47(9).

Reimann, T., Geyer, T., Shoemaker, W.B., Liedl, R. and Sauter, M., (2011b), Effects of dynamically variable saturation and matrix-conduit coupling of flow in karst aquifers. *Water Resources Research*, 47(11).

Reimann, T., Liedl, R., Birk, S., & Bauer, S. (2013), MODFLOW-CFPV2. Dresden Technical University: Dresden, Germany.

Reimann T., Liedl R., Birk S., Bauer S., (2018), Modifications and enhancements to CFPM1 flow subroutines and addition of transport subroutines. — Accessible at:http://tu-dresden.de/die_tu_dresden/fakultaeten/fakultaet_forst_geo_und_hydrowissenschaften/fachrichtung_wasserwesen/igw/forschung/downloads/cfpv2.

Reimann, T., Rehrl, C., Shoemaker, W. B., Geyer, T., & Birk, S. (2011a), The significance of turbulent flow representation in single-continuum models. *Water Resources Research*, 47(9).

Reimann, T., Rudolph, M. G., Grabow, L., & Noffz, T. (2023), CFPy—A Python Package for Pre-and Postprocessing of the Conduit Flow Process of MODFLOW. *Groundwater*, 61(6), 887-894.

Reilly, T. E. (1987), A conceptual framework for ground-water solute-transport studies with emphasis on physical mechanisms of solute movement (Vol. 87, No. 4191). Department of the Interior, US Geological Survey.

Ren, K., Pan, X., Yuan, D., Zeng, J., Liang, J., & Peng, C. (2022), Nitrate sources and nitrogen dynamics in a karst aquifer with mixed nitrogen inputs (Southwest China): Revealed by multiple stable isotopic and hydro-chemical proxies. *Water Research*, 210, 118000.

Remondi, F., Kirchner, J. W., Burlando, P., & Fatichi, S. (2018), Water flux tracking with a distributed hydrological model to quantify controls on the spatio-temporal variability of transit time distributions. *Water Resources Research*, 54(4), 3081-3099.

Remondi, F., Botter, M., Burlando, P., & Fatichi, S. (2019), Variability of transit time distributions with climate and topography: A modelling approach. *Journal of Hydrology*, 569, 37-50.

Richter, D., Goeppert, N., & Goldscheider, N. (2022), New insights into particle transport in karst conduits using comparative tracer tests with natural sediments and solutes during low-flow and high-flow conditions. *Hydrological Processes*, 36(1), e14472.

Rinaldo, A., Benettin, P., Harman, C. J., Hrachowitz, M., McGuire, K. J., Van Der Velde, Y., ... & 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.

Robineau, T., Tognelli, A., Goblet, P., Renard, F., & Schaper, L. (2018), A double medium approach to simulate groundwater level variations in a fissured karst aquifer. *Journal of Hydrology*, 565, 861-875.

Robinson, H. K., & Hasenmueller, E. A. (2017), Transport of road salt contamination in karst aquifers and soils over multiple timescales. *Science of the Total Environment*, *603*, 94-108.

Rolle, M., Hochstetler, D., Chiogna, G., Kitanidis, P. K., & Grathwohl, P. (2012), Experimental investigation and pore-scale modeling interpretation of compound-specific transverse dispersion in porous media. *Transport in Porous Media*, *93*, 347-362.

Rolle, M., & Le Borgne, T. (2019), Mixing and reactive fronts in the subsurface. *Reviews in Mineralogy and Geochemistry*, 85(1), 111-142.

Ronayne, M. J. (2013), Influence of conduit network geometry on solute transport in karst aquifers with a permeable matrix. *Advances in Water Resources*, 56, 27-34.

Rusjan, S., Sapač, K., Petrič, M., Lojen, S., & Bezak, N. (2019), Identifying the hydrological behavior of a complex karst system using stable isotopes. *Journal of Hydrology*, 577, 123956.

Sanford, W. (2011), Calibration of models using groundwater age. *Hydrogeology Journal*, 19(1), 13-16.

Savio, D., Stadler, P., Reischer, G. H., Kirschner, A. K., Demeter, K., Linke, R., ... & Farnleitner, A. H. (2018), Opening the black box of spring water microbiology from alpine karst aquifers to support proactive drinking water resource management. *Wiley Interdisciplinary Reviews: Water*, 5(3), e1282.

Scanlon, B. R., Mace, R. E., Barrett, M. E., & Smith, B. (2003), Can we simulate regional groundwater flow in a karst system using equivalent porous media models? Case study, Barton Springs Edwards aquifer, USA. *Journal of Hydrology*, 276(1-4), 137-158.

Schwarz, K., Gocht, T., & Grathwohl, P. (2011), Transport of polycyclic aromatic hydrocarbons in highly vulnerable karst systems. *Environmental Pollution*, *159*(1), 133-139.

Scheidegger, A. E. (1961), General theory of dispersion in porous media. *Journal of Geophysical Research*, *66*(10), 3273-3278.

Schilling, O. S., Cook, P. G., & Brunner, P. (2019), Beyond classical observations in hydrogeology: The advantages of including exchange flux, temperature, tracer concentration, residence time, and soil moisture observations in groundwater model calibration. *Reviews of Geophysics*, 57(1), 146-182.

Schiperski, F., Zirlewagen, J., & Scheytt, T. (2016), Transport and attenuation of particles of different density and surface charge: a karst aquifer field study. *Environmental Science & Technology*, 50(15), 8028-8035.

Schiperski, F., Zirlewagen, J., Stange, C., Tiehm, A., Licha, T., & Scheytt, T. (2022), Transport-based source tracking of contaminants in a karst aquifer: Model implementation, proof of concept, and application to event-based field data. *Water Research*, 213, 118145.

Schwemmle, R., & Weiler, M. (2024), Consistent modeling of transport processes and travel times—coupling soil hydrologic processes with StorAge Selection functions. *Water Resources Research*, *60*(1), e2023WR034441.

Schoups, G., Van de Giesen, N. C., & Savenije, H. H. G. (2008), Model complexity control for hydrologic prediction. *Water Resources Research*, 44(12).

Schumer, R., Meerschaert, M. M., & Baeumer, B. (2009), Fractional advection-dispersion equations for modeling transport at the Earth surface. *Journal of Geophysical Research: Earth Surface*, 114(F4).

Shirafkan, M., Mohammadi, Z., Kavousi, A., Sivelle, V., Labat, D., & Reimann, T. (2023), Toward the estimation of the transfer coefficient in karst systems: Using baseflow recession coefficient under matrix-restrained flow regime. *Journal of Hydrology*, 620, 129441.

Shoemaker, W. B., Kuniansky, E. L., Birk, S., Bauer, S., & Swain, E. D. (2008), Documentation of a conduit flow process (CFP) for MODFLOW-2005 (Vol. 6). Reston, Va: US Department of the Interior, US Geological Survey.

Shu, L., Zou, Z., Li, F., Wu, P., Chen, H., & Xu, Z. (2020), Laboratory and numerical simulations of spatio-temporal variability of water exchange between the fissures and conduits in a karstic aquifer. *Journal of Hydrology*, 590, 125219.

Siegel, L., Goldscheider, N., Petitta, M., Xanke, J., Andreo, B., Bakalowicz, M., ... & Stevanović, Z. (2023), Distribution, threats and protection of selected karst groundwater-dependent ecosystems in the Mediterranean region. *Hydrogeology Journal*, 31(8), 2231-2249.

Sinreich, M., (2011), Towards developing conceptual models for reactive contaminant transport in karst. IAHS Publ, 342, 473-476.

Sinreich, M. (2014), Contaminant attenuation in karst aquifers: a paradigm shift. H2Karst research in limestone hydrogeology, 175-184.

Sinreich, M., Cornaton, F., & Zwahlen, F. (2007), Evaluation of reactive transport parameters to assess specific vulnerability in karst systems. IAH-SP, 11, 21-31.

Sivelle, V., Cinkus, G., Mazzilli, N., Labat, D., Arfib, B., Massei, N., ... & Jourde, H. (2023), Improvement of the KarstMod modeling platform for a better assessment of karst groundwater resources. *Hydrology and Earth System Sciences Discussions*, 1-26.

Sivelle, V., & Labat, D. (2019), Short-term variations in tracer tests responses in a highly karstified watershed. *Hydrogeology Journal*, 27(6), 2061-2075.

Sivelle, V., Labat, D., Mazzilli, N., Massei, N., & Jourde, H. (2019), Dynamics of the flow exchanges between matrix and conduits in karstified watersheds at multiple temporal scales. *Water*, *11*(3), 569

Sivelle, V., Pérotin, L., Ladouche, B., de Montety, V., Bailly-Comte, V., Champollion, C., & Jourde, H. (2022), A lumped parameter model to evaluate the relevance of excess air as a tracer of exchanged flows between transmissive and capacitive compartments of karst systems. *Frontiers in Water*, 4, 930115.

Sivelle, V., Renard, P., & Labat, D. (2020), Coupling SKS and SWMM to solve the inverse problem based on artificial tracer tests in karstic aquifers. *Water*, 12(4), 1139.

Stevanović, Z. (2018), Global distribution and use of water from karst aquifers. *Geological Society, London, Special Publications*, *466*(1), 217-236.

Stevanović, Z. (2019), Karst waters in potable water supply: a global scale overview. *Environmental Earth Sciences*, 78(23), 662.

Stevanović, Z., & Stevanović, A. M. (2021), Monitoring as the Key Factor for Sustainable Use and Protection of Groundwater in Karst Environments—An Overview. Sustainability, 13(10), 5468.

Stockmann, M., Schikora, J., Becker, D. A., Flügge, J., Noseck, U., & Brendler, V. (2017), Smart Kd-values, their uncertainties and sensitivities-Applying a new approach for realistic distribution coefficients in geochemical modeling of complex systems. *Chemosphere*, 187, 277-285.

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

Sudicky, E. A., & Frind, E. O. (1982), Contaminant transport in fractured porous media: Analytical solutions for a system of parallel fractures. *Water Resources Research*, 18(6), 1634-1642.

Sun, L., Qiu, H., Wu, C., Niu, J., & Hu, B. X. (2020), A review of applications of fractional advection–dispersion equations for anomalous solute transport in surface and subsurface water. *Wiley Interdisciplinary Reviews: Water*, 7(4), e1448.

Sullivan, T. P., Gao, Y., & Reimann, T. (2019), Nitrate transport in a karst aquifer: numerical model development and source evaluation. *Journal of Hydrology*, 573, 432-448.

Swami, D., Sharma, P. K., Ojha, C. S. P., Guleria, A., & Sharma, A. (2018), Asymptotic behavior of mass transfer for solute transport through stratified porous medium. *Transport in Porous Media*, 124, 699-721.

Taylor, G. I. (1953), Dispersion of soluble matter in solvent flowing slowly through a tube. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, 219(1137), 186-203.

Taylor, G. I. (1954), The dispersion of matter in turbulent flow through a pipe. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, 223(1155), 446-468.

Teixeira Parente, M., Bittner, D., Mattis, S. A., Chiogna, G., & Wohlmuth, B. (2019), Bayesian calibration and sensitivity analysis for a karst aquifer model using active subspaces. *Water Resources Research*, 55(8), 7086-7107.

Teutsch, G., & Sauter, M. (1998), Distributed parameter modelling approaches in karst-hydrological investigations. *Bulletin d'hydrogéologie*, (16), 99-109.

Thyne, G., Güler, C., & Poeter, E. (2004), Sequential analysis of hydrochemical data for watershed characterization. *Groundwater*, 42(5), 711-723.

Tinet, A. J., Collon, P., Philippe, C., Dewaide, L., & Hallet, V. (2019), OM-MADE: An open-source program to simulate one-dimensional solute transport in multiple exchanging conduits and storage zones. *Computers & Geosciences*, 127, 23-35.

Toride, N., Leij, F. J., & Van Genuchten, M. T. (1995), The CXTFIT code for estimating transport parameters from laboratory or filed tracer experiments (Vol. 2). Riverside, CA: US Salinity Laboratory.

Toth, D. J., & Katz, B. G. (2006), Mixing of shallow and deep groundwater as indicated by the chemistry and age of karstic springs. *Hydrogeology Journal*, 14, 1060-1080.

Tran, E. L., Reimus, P., Klein-BenDavid, O., Teutsch, N., Zavarin, M., Kersting, A. B., & Weisbrod, N. (2020), Mobility of radionuclides in fractured carbonate rocks: lessons from a field-scale transport experiment. *Environmental Science & Technology*, 54(18), 11249-11257.

Tran, E., Zavrin, M., Kersting, A. B., Klein-BenDavid, O., Teutsch, N., & Weisbrod, N. (2021), Colloid-facilitated transport of 238Pu, 233U and 137Cs through fractured chalk: Laboratory experiments, modelling, and implications for nuclear waste disposal. *Science of The Total Environment*, 757, 143818.

Tritz, S., Guinot, V., & Jourde, H. (2011), Modelling the behaviour of a karst system catchment using non-linear hysteretic conceptual model. *Journal of Hydrology*, 397(3-4), 250-262.

Tsang, Y. W., & Tsang, C. F. (2001), A particle-tracking method for advective transport in fractures with diffusion into finite matrix blocks (Vol. 37, No. 3, pp. 831-835).

Van Der Velde, Y., Torfs, P. J. J. F., Van Der Zee, S. E. A. T. M., & Uijlenhoet, R. (2012), Quantifying catchment-scale mixing and its effect on time-varying travel time distributions. *Water Resources Research*, 48(6).

Valiente, N., Gil-Márquez, J. M., Gómez-Alday, J. J., & Andreo, B. (2020), Unraveling groundwater functioning and nitrate attenuation in evaporitic karst systems from southern Spain: An isotopic approach. *Applied Geochemistry*, 123, 104820.

Valocchi, A. J., Bolster, D., & Werth, C. J. (2019), Mixing-limited reactions in porous media. *Transport in Porous Media*, 130, 157-182.

Valota, G., Giudici, M., Parravicini, G., Ponzini, G., & Romano, E. (2002), Is the forward problem of ground water hydrology always well posed?. *Groundwater*, 40(5), 500-508.

Vesper, D. J., Loop, C. M., & White, W. B. (2001), Contaminant transport in karst aquifers. *Theoretical and Applied Karstology*, 13(14), 101-111.

Vilhar, U., Kermavnar, J., Kozamernik, E., Petrič, M., & Ravbar, N. (2022), The effects of large-scale forest disturbances on hydrology–An overview with special emphasis on karst aquifer systems. *Earth-Science Reviews*, 104243.

Vincenzi, V., Gargini, A., & Goldscheider, N. (2009), Using tracer tests and hydrological observations to evaluate effects of tunnel drainage on groundwater and surface waters in the Northern Apennines (Italy). *Hydrogeology Journal*, 17(1), 135-150.

Vucinic, L., O'Connell, D., Teixeira, R., Coxon, C., & Gill, L. (2022), Flow cytometry and fecal indicator bacteria analyses for fingerprinting microbial pollution in karst aquifer systems. *Water Resources Research*, 58(5), e2021WR029840.

Wagener, T. (2022), On the evaluation of climate change impact models for adaptation decisions. In *Climate Adaptation Modelling* (pp. 33-40). Cham: Springer International Publishing.

Wagener, T., Boyle, D. P., Lees, M. J., Wheater, H. S., Gupta, H. V., & Sorooshian, S. (2001), A framework for development and application of hydrological models, *Hydrology and Earth System Sciences*, 5(1), 13-26.

Wagener, T., Gleeson, T., Coxon, G., Hartmann, A., Howden, N., Pianosi, F., ... & Woods, R. (2021), On doing hydrology with dragons: Realizing the value of perceptual models and knowledge accumulation. *Wiley Interdisciplinary Reviews: Water*, 8(6), e1550.

Wagener, T., Wheater, H. S., & Gupta, H. V. (2003), Identification and evaluation of watershed models. Calibration of watershed models, 6, 29-47.

Wang, C., Majdalani, S., Guinot, V., & Jourde, H. (2022), Solute transport in dual conduit structure: Effects of aperture and flow rate. *Journal of Hydrology*, 613, 128315.

Wang, C., Wang, X., Majdalani, S., Guinot, V., & Jourde, H. (2020), Influence of dual conduit structure on solute transport in karst tracer tests: An experimental laboratory study. *Journal of Hydrology*, *590*, 125255.

White, W. B. (2002), Karst hydrology: recent developments and open questions. *Engineering Geology*, 65(2-3), 85-105.

White, W. B. (2018), Contaminant transport in karst aquifers: systematics and mechanisms. In Karst groundwater contamination and public health: beyond case studies (pp. 55-81). Springer International Publishing.

White, W. B. (2019), Hydrogeology of karst aquifers. In Encyclopedia of caves (pp. 537-545). Academic Press.

White, W. B., & White, E. L. (2005), Ground water flux distribution between matrix, fractures, and conduits: constraints on modeling. Speleogenesis and evolution of Karst aquifers, 3(2), 1-6.

Witthüser, K., Reichert, B., & Hotzl, H. (2003), Contaminant transport in fractured chalk: Laboratory and field experiments. Groundwater, 41(6), 806-815.

Worthington, S. R. (2011), Management of carbonate aquifers. In Karst management (pp. 243-261). Dordrecht: Springer Netherlands.

Worthington, S. R. (2015), Diagnostic tests for conceptualizing transport in bedrock aquifers. *Journal of Hydrology*, 529, 365-372.

Wynn, P. M., Borsato, A., Baker, A., Frisia, S., Miorandi, R., & Fairchild, I. J. (2013), Biogeochemical cycling of sulphur in karst and transfer into speleothem archives at Grotta di Ernesto, Italy. *Biogeochemistry*, 114, 255-267.

Xanke, J., Jourde, H., Liesch, T., & Goldscheider, N. (2016), Numerical long-term assessment of managed aquifer recharge from a reservoir into a karst aquifer in Jordan. *Journal of Hydrology*, 540, 603-614.

Xu, Z., Hu, B. X., Davis, H., & Cao, J. (2015), Simulating long term nitrate-N contamination processes in the Woodville Karst Plain using CFPv2 with UMT3D. *Journal of Hydrology*, 524, 72-88.

Yin, M., Ma, R., Zhang, Y., Chen, K., Guo, Z., & Zheng, C. (2022), A Dual Heterogeneous Domain Model for Upscaling Anomalous Transport With Multi-Peaks in Heterogeneous Aquifers. *Water Resources Research*, 58(4), e2021WR031128.

Yue, F. J., Li, S. L., Waldron, S., Wang, Z. J., Oliver, D. M., Chen, X., & Liu, C. Q. (2020), Rainfall and conduit drainage combine to accelerate nitrate loss from a karst agroecosystem: Insights from stable isotope tracing and high-frequency nitrate sensing. *Water Research*, 186, 116388.

Yue, F. J., Waldron, S., Li, S. L., Wang, Z. J., Zeng, J., Xu, S., ... & Oliver, D. M. (2019), Land use interacts with changes in catchment hydrology to generate chronic nitrate pollution in karst waters and strong seasonality in excess nitrate export. *Science of the Total Environment*, 696, 134062.

Zeqiraj, D. (2022), 3D stochastic modeling of flow and solute transport in karst vadose zone. Case Studies in Chemical and Environmental Engineering, 6, 100217.

Zhang, Y., Benson, D. A., & Reeves, D. M. (2009), Time and space nonlocalities underlying fractional-derivative models: Distinction and literature review of field applications. *Advances in Water Resources*, 32(4), 561-581.

Zhang, Y., Liu, X., Lei, D., Yin, M., Sun, H., Guo, Z., & Zhan, H. (2024), Modeling hydrologically mediated hot moments of transient anomalous diffusion in aquifers using an impulsive fractional-derivative equation. *Water Resources Research*, 60(3), e2023WR036089.

Zhang, Y., Zhou, D., Yin, M., Sun, H., Wei, W., Li, S., & Zheng, C. (2020), Nonlocal transport models for capturing solute transport in one-dimensional sand columns: Model review, applicability, limitations and improvement. *Hydrological Processes*, 34(25), 5104-5122.

Zhang, Z., Chen, X., & Soulsby, C. (2017), Catchment-scale conceptual modelling of water and solute transport in the dual flow system of the karst critical zone. *Hydrological Processes*, 31(19), 3421-3436.

Zhang, Z., Chen, X., Cheng, Q., & Soulsby, C. (2019), Storage dynamics, hydrological connectivity and flux ages in a karst catchment: conceptual modelling using stable isotopes. *Hydrology and Earth System Sciences*, 23(1), 51-71.

Zhang, Z., Chen, X., Cheng, Q., Li, S., Yue, F., Peng, T., ... & Soulsby, C. (2020b), Coupled hydrological and biogeochemical modelling of nitrogen transport in the karst critical zone. *Science of The Total Environment*, 732, 138902.

Zhang, Z., Chen, X., Cheng, Q., & Soulsby, C. (2020a), Characterizing the variability of transit time distributions and young water fractions in karst catchments using flux tracking. *Hydrological Processes*, 34(15), 3156-3174.

Zhang, Z., Chen, X., Cheng, Q., & Soulsby, C. (2021), Using StorAge selection (SAS) functions to understand flow paths and age distributions in contrasting karst groundwater systems. *Journal of Hydrology*, 602, 126785.

Zhao, X., Chang, Y., Wu, J., & Fu, P. (2017), Laboratory investigation and simulation of breakthrough curves in karst conduits with pools. *Hydrogeology Journal*, 25(8), 2235-2250.

Zhao, X., Chang, Y., Wu, J., Li, Q., & Cao, Z. (2021), Investigating the relationships between parameters in the transient storage model and the pool volume in karst conduits through tracer experiments. *Journal of Hydrology*, 593, 125825.

Zhao, X., Chang, Y., Wu, J., & Xue, X. (2019), Effects of flow rate variation on solute transport in a karst conduit with a pool. *Environmental Earth Sciences*, 78, 1-18.

Zhou, Q., Liu, H. H., Molz, F. J., Zhang, Y., & Bodvarsson, G. S. (2007), Field-scale effective matrix diffusion coefficient for fractured rock: Results from literature survey. *Journal of Contaminant Hydrology*, 93(1-4), 161-187.

Zhu, W. C., Liu, J., Elsworth, D., Polak, A., Grader, A., Sheng, J. C., & Liu, J. X. (2007), Tracer transport in a fractured chalk: X-ray CT characterization and digital-image-based (DIB) simulation. *Transport in Porous Media*, 70, 25-42.

Zoghbi, C., & Basha, H. (2020), Simple transport models for karst systems. *Journal of Hydrology*, 588, 125046.

Zuber, A. (1986), Mathematical models for the interpretation of environmental radioisotopes in groundwater systems. Handbook of environmental isotope geochemistry, 2, 1-59.

Zuber, A., Maloszewski, P., (2001), Lumped-parameter models. In: Environmental Isotopes in the Hydrological Cycle – Principles and Applications Technical Documents in Hydrology. UNESCO, Paris, pp. 5–36.

Zuber, A., Różański, K., Kania, J., & Purtschert, R. (2011), On some methodological problems in the use of environmental tracers to estimate hydrogeologic parameters and to calibrate flow and transport models. *Hydrogeology Journal*, 19(1), 53-69.

Çallı, K. Ö., Bittner, D., Liu, Y., Çallı, S. S., Melsen, L. A., Bense, V., & Hartmann, A. (2023a), Revealing the positive influence of young water fractions derived from stable isotopes on the robustness of karst water resources predictions. *Journal of Hydrology*, 621, 129549.

Çallı, K. Ö., Bittner, D., & Hartmann, A. (2023b), On the Choice of a Performance Metric for Model Calibration Scheme Using Discharge-Age Information. In EuroKarst 2022, Málaga: Advances in the Hydrogeology of Karst and Carbonate Reservoirs (pp. 123-129). Cham: Springer International Publishing.

Çallı, S. S., Çallı, K. Ö., Yılmaz, M. T., & Çelik, M. (2022), Contribution of the satellite-data driven snow routine to a karst hydrological model. *Journal of Hydrology*, 607, 127511.

Çelik, M., Çallı, S. S., & Karakaş, Z. S. (2022), The role of mineralogical studies in delineating the recharge area and groundwater circulation of Susuz springs, Central Taurus Belt, Turkey. *Hydrogeology Journal*, 30(8), 2399-2415.