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# Karst water resources in a changing world: Review of solute transport modelling approaches

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## 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.

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

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16 **Key Points:**

- 17 ● Anthropogenic factors and global changes pose a serious threat on karst water quality  
18 ● We review solute transport process and modelling approaches in karst water resources  
19 ● Fundamental challenges afront a successful transport modelling practice are provided  
20 ● We address knowledge gaps and research directions in karst transport modelling  
21

22 **Abstract**

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

35 **Plain Language Summary**

36 Karst aquifers are valuable freshwater sources. Nonetheless, anthropogenic factors and global  
37 changes have been seriously deteriorating the karst water quality and dependent ecosystems.  
38 Therefore, understanding, characterizing, and predicting the impacts of such changes are  
39 essential for effectively managing and sustainably protecting the karst water quality and  
40 dependent ecosystem functioning. Solute transport models are valuable decision-support tools to  
41 explore the contamination risks and the potential outcomes of deteriorated water quality.  
42 Furthermore, model predictions can be used for introducing the efficient adaptation strategies  
43 and regulatory decisions for the contamination-related problems in karst systems. In this review,  
44 we provide the current state of knowledge on modelling of solute transport in karst aquifers. By  
45 synthesizing the existing body of knowledge, we unveil the fundamental modelling challenges  
46 for successful karst transport modelling practice.  
47

## 48 **1 Introduction**

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

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

66 Karst aquifers are particularly vulnerable to contamination risks due to the substantial  
67 heterogeneity manifested by the preferential flow paths (i.e., fractures, conduits, cave streams) at  
68 differing spatial scales (e.g., Bakalowicz, 2005; Ford & Williams, 2007; Goldscheider & Drew,  
69 2014; Padilla & Vesper, 2018; Stevanović, 2018; Quinn et al., 2006, among many others).  
70 Besides these (multiple) discrete flow paths that cause the rapid spreading of the contaminants  
71 throughout the karst systems (Field, 2018; Hartmann et al., 2014, 2021; White, 2018), the close  
72 interaction with the surface waters (i.e., rivers, lakes) and thin soil characteristics limit the  
73 attenuation of the contaminants released into the karst aquifers (Goldscheider, 2005; Sinreich,  
74 2014; White, 2019).

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

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

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

## 97 **2 Principles of solute transport processes in karst water resources**

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

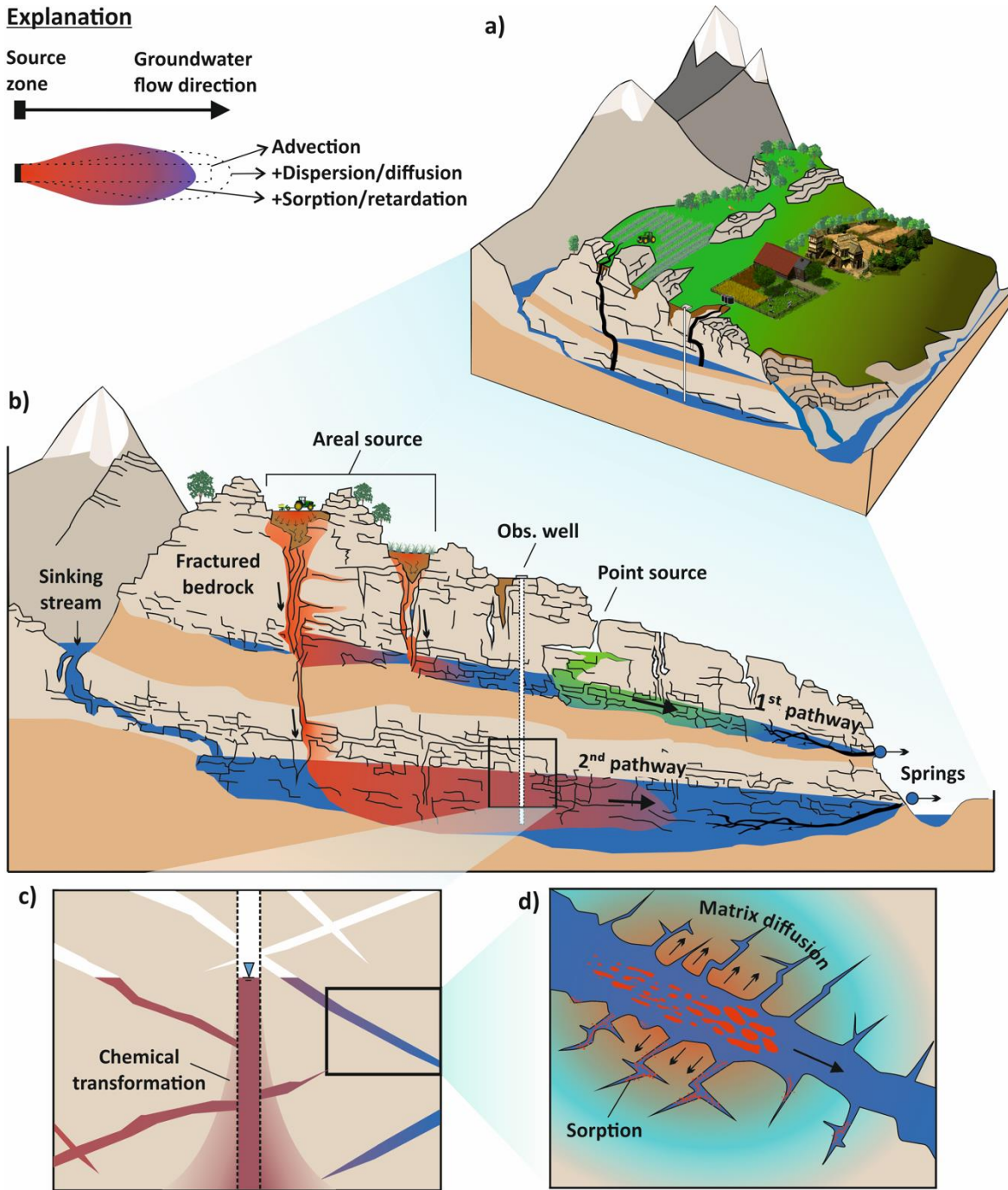
111 As compared to porous or fractured groundwater systems, the most peculiar characteristic  
 112 of karst aquifers is the complex interaction between the fractured/fissured carbonate matrix and  
 113 karst conduit, which leads to the duality in the flow and transport processes (Massei et al., 2003;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

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

### 126 **2.1 Transport in the matrix**

127 There is vast literature describing transport processes in the karst matrix. Recently,  
 128 several review papers covered the topic by emphasizing the different characteristic aspects.  
 129 Dentz et al. (2023) review concepts and approaches for the quantification of passive, non-  
 130 reactive solute mixing in steady uniform porous media flows across scales. Rolle & Le Borgne  
 131 (2019) focus both on the description of reactive mixing, on displacement scenarios and  
 132 continuously released plumes approaching the transport problem from the pore scale to the  
 133 aquifer scale. Valocchi et al. (2018) describe mixing-limited reactions and upscaling processes  
 134 from the pore to the continuum scale. Berkowitz et al. (2016) emphasize the complex interplay

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



140

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

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

#### 148 2.1.1 Darcy scale: Pore diffusion and mechanical dispersion

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

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

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

#### 173 2.1.2 Field scale: Effective and macro dispersion

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



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

## 189 2.2 Transport in the conduits

190 Transport in karst conduits shows similarities with the transport in rivers and/or pipes.  
191 But depending on the saturation of the karst system, karst conduits can behave as a free surface  
192 flow or a (saturated) pipe flow under pressurized conditions (Liedl et al., 2003; Loop & White,  
193 2001; Reimann et al., 2014). While solute transport in conduits is mainly controlled by advection  
194 and aqueous diffusion, typical flow velocities encountered in karst conduits are orders of  
195 magnitude larger than the ones presented in the matrix. This leads typically to turbulent flow  
196 conditions in the conduits, thus making aqueous diffusion a dominant process along the conduit,  
197 although it is generally neglected (Hauns et al., 2001). At the field scale, however, the advective  
198 flow field is often not known due to the multiscale karstic heterogeneity, as well as due to the  
199 lack of knowledge about the distribution and shape of conduits.

### 200 2.2.1 Aqueous diffusion

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

### 208 2.2.2 Turbulent dispersion

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

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

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

### 229 2.3 Sorption, retardation, and chemical reactions in karst systems

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

235 Sorption refers to the process that transfers the solute concentration from the dissolved  
236 aqueous phase into an immobile phase attached to the solid geological matrix. It is particularly  
237 relevant for solute transport in the karst matrix and at the interface between the matrix and karst  
238 conduit because it requires direct contact between the solute and the porous material. Sorption  
239 can also occur on suspended particles (Lan et al., 2018; Massei et al., 2002; Schwarz et al.,  
240 2011), thus leading to the so-called particle-facilitated transport. In general, sorption has two  
241 main effects on the solute concentration. First, the solute concentration in the water is reduced  
242 due to the mass transfer towards the immobile sorbed phase. Second, the advective velocity of  
243 the solute of interest is reduced, and hence the mass exchange between the dissolved and the  
244 sorbed phase leads to an effective retardation in the solute.

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

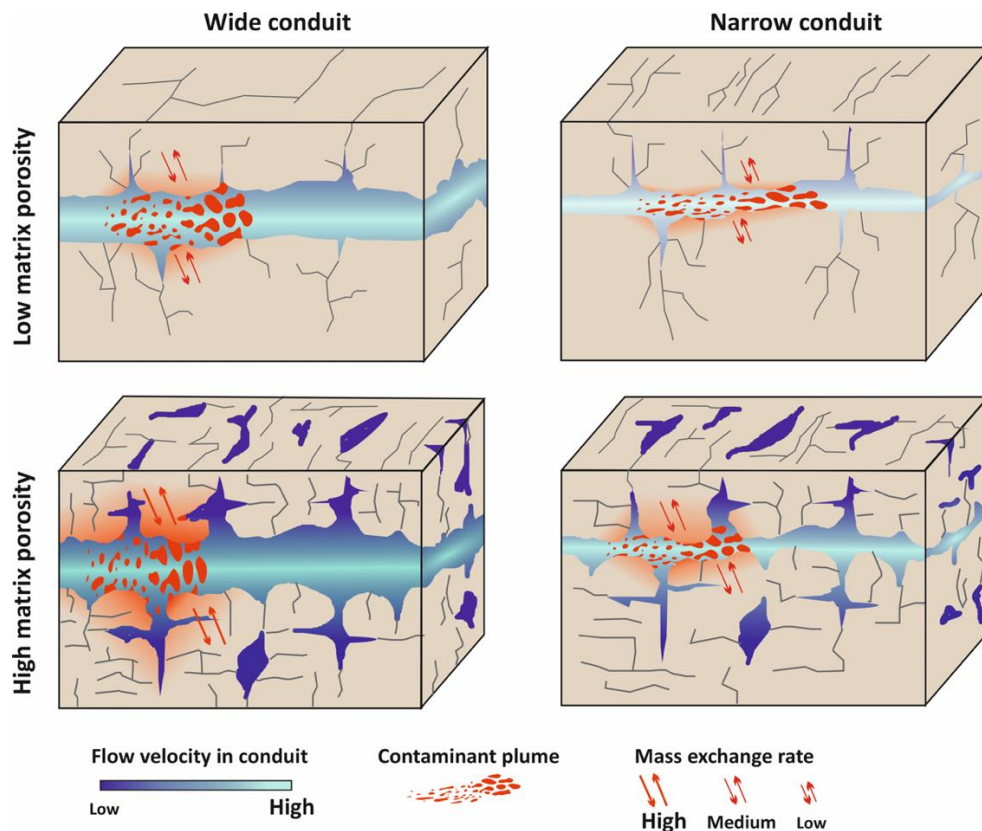
256 Chemical reactions can lead to the production and/or degradation of the solute of interest.  
257 A prerequisite for a reaction to occur is that all reaction partners are present in the same location  
258 at the same time while diffusive and dispersive processes are mainly responsible for this.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

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

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

#### 273 2.4 Dynamics of solute transport processes in karst systems

274 The spatiotemporal dynamics of solute transport in karst aquifers are controlled by the  
 275 relative contributions of the rapid (i.e., conduits, fractures) and slow (i.e., matrix, storage zones  
 276 due to the vortices and eddies in conduit systems) flow components (Ewers et al., 2012; Field,  
 277 2002, 2018; Geyer et al., 2007; Hauns et al., 2001) (Figure 2). Solute transport in karst systems is  
 278 often characterized by non-ideal transport phenomena — also referred to as non-Fickian or  
 279 anomalous transport — controlled both by the preferential flow paths (mostly by karst conduits  
 280 and conduit networks) and by the rate-limited mass transfer between the slow and fast flow  
 281 components. Overall, the key transport mechanisms in karst systems are defined as (i) physical  
 282 transport along the main flow direction controlled both by advection and dispersion processes,  
 283 (ii) matrix diffusion and mechanical dispersion along the conduit surfaces in and out of the  
 284 (fractured) carbonate matrix, and (iii) mass exchange between mobile water in karst conduit and  
 285 matrix components via such as sorption, ion exchange, radioactive decay, and (biogeo)chemical  
 286 reactions (Figure 2) (e.g., Field & Liej, 2014; Field & Pinsky, 2000; Sinreich, 2011; Sinreich et  
 287 al., 2007).



288

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

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

297 In karst aquifers, conduits represent the region where contaminants can be rapidly  
298 transferred (e.g., Ghasemizadeh et al., 2012; Goepfert et al., 2020; Pronk et al., 2009; Vesper et  
299 al., 2001, among many others). Along the conduit, the nature of the transport is strongly  
300 dependent on the flow regimes that range from laminar to turbulent flows (Field, 2002; Green et  
301 al., 2006; White, 2002). The conduit flow velocity is particularly important because it shapes the  
302 movement of the solute plume. Here, the (mean) flow velocity defines the rate of mass transfer  
303 between the karst conduit and matrix (Bajracharya & Barry, 1997; Lehmann et al., 2022) while  
304 the magnitude and direction of the mass exchange widely vary depending on the karst system's  
305 hydrological and antecedent conditions (i.e., soil and/or epikarst wetness). For instance, the high  
306 velocity reduces the contact time of the contaminant with the (fractured/fissured) carbonate  
307 matrix and thus limits the mass exchange between the conduit and matrix (Figure 2). In contrast,  
308 when the flow is laminar — typically characterized by lower flow and recharge conditions —,  
309 the mass exchange is generally favorable (Faulkner et al., 2009; Martin et al., 1999, 2012). While  
310 the advective transport in the karst conduit are mainly influenced by the conduit's structural  
311 properties (i.e., conduit size, morphology, sinuosity) and conduit networks (Aliouache et al.,  
312 2019; Field & Pinsky, 2000; Ronayne, 2013), the local and/or regional recharge characteristics  
313 adjust the flow magnitude and direction of the mass transfer between the conduit and matrix  
314 (Figure 2) (Doummar et al., 2018; Göppert & Goldscheider, 2008; Ji et al., 2022).

315 The karst matrix is characterized as the region where solutes can be stored for a long  
316 period and are slowly released into the conduit network (e.g., Berglund et al., 2020; Ji et al.,  
317 2022; Nativ et al., 1999; Padilla & Vesper, 2018; White & White, 2005; Worthington, 2011,  
318 among many others). As the mass transfer from the karst conduit to matrix is often controlled by  
319 the (matrix) pore diffusion and mechanical dispersion, these processes can be particularly  
320 important during the storage of solute of interest within the matrix, especially in the low  
321 permeable karst media, such as chalk (Zuber et al., 2011; Polak et al., 2002; Worthington, 2015).  
322 Therefore, the rate of the solute transfer in and out of the matrix is regulated by several other  
323 factors including matrix permeability, conduit flow velocity, irregularities of conduit surface,  
324 solute retardation factor, as well as the (solute) matrix pore diffusion and mechanical dispersion  
325 coefficients (Field, 2002, Joodi et al., 2010; Kresic & Stevanovic, 2009; Mosthaf et al., 2018;  
326 Luo et al., 2024) (Figure 2).

## 327 2.5 Spreading, Dilution, and Reactive Mixing

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

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

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

344 Reactive mixing is the process that brings two different chemical species together as the  
345 result of molecular diffusion, mechanical dispersion, and turbulent dispersion (Neupauer et al.,  
346 2014), which allows a chemical reaction to occur. Here, it is important to notice that dilution  
347 (mixing) is not necessarily affected by incomplete mixing at the pore scale whereas reactive  
348 mixing is significantly controlled by incomplete mixing (Berkowitz et al., 2016), particularly in  
349 the karst matrix. Therefore, the presence of incomplete mixing very often leads to the need for  
350 case study-specific reaction rate constants to match the experimental observations.

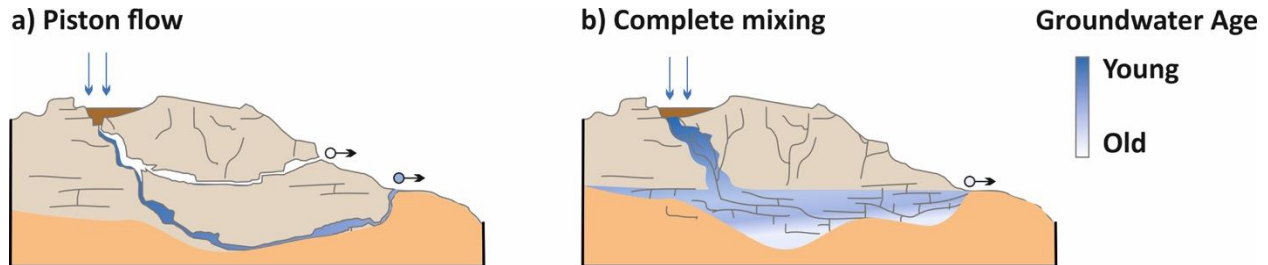
## 351 2.6 Tracers as diagnostic tool in describing transport processes in karst systems

352 Describing flow and transport processes in karst systems is difficult mainly due to the  
353 unknown configuration and geometry of the conduit network (Borghi et al., 2012; Fandel et al.,  
354 2022). Tracers are frequently used to define the karst system's flow and transport dynamics  
355 (Geyer et al., 2007; Goldscheider et al., 2008; Martín-Rodríguez et al., 2023; Mudarra et al.,  
356 2014). Various substances (i.e., solutes, particles, solids, and gasses) and physical quantities (i.e.,  
357 temperature or heat) can be used for quantifying flow and transport parameters (i.e., porosity,  
358 dispersivity, flow velocity) at the spatiotemporal scales of interest (Benischke, 2021; Field, 2020;  
359 Massei et al., 2006). Additionally, tracers are frequently utilized as additional information  
360 sources to confirm and/or invalidate for karst simulation models (e.g., Hartmann et al., 2014,  
361 2017; Mudarra et al., 2019; Rusjan et al., 2019; Zhang et al., 2021; Çallı et al., 2023a).

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

369 Among environmental tracers, water isotopes such as Oxygen-18 and Deuterium are  
370 frequently used for defining hydrological system's water age and (water) age distributions (i.e.,  
371 travel time distributions (TTDs) and residence time distributions (RTDs) (Jasechko et al., 2017;  
372 Musgrove et al., 2023). As a terminology, water 'age' refers to the time elapsed since the  
373 meteoric water entered the system (Bethke & Johnson, 2008; Long & Putnam, 2009; Suckow,  
374 2014). In groundwater studies, water age is often denoted as residence time which indicates the  
375 time between the water entrance and leave (Aquilina et al., 2003; Maloszewski et al., 1992;  
376 Maloszewski & Zuber, 1993; Plummer et al., 1998a, 1998b) whereas travel time is defined as the  
377 time required for a volume of water moving across the specified flow paths. The knowledge of  
378 water age and/or its distributions — distributions of the different water ages — is particularly  
379 useful for revealing the vulnerability of karst aquifers to the contamination risks (Malík et al.,  
380 2016; Musgrove et al., 2023; Çallı et al., 2023a) as it provides valuable insight into the karst

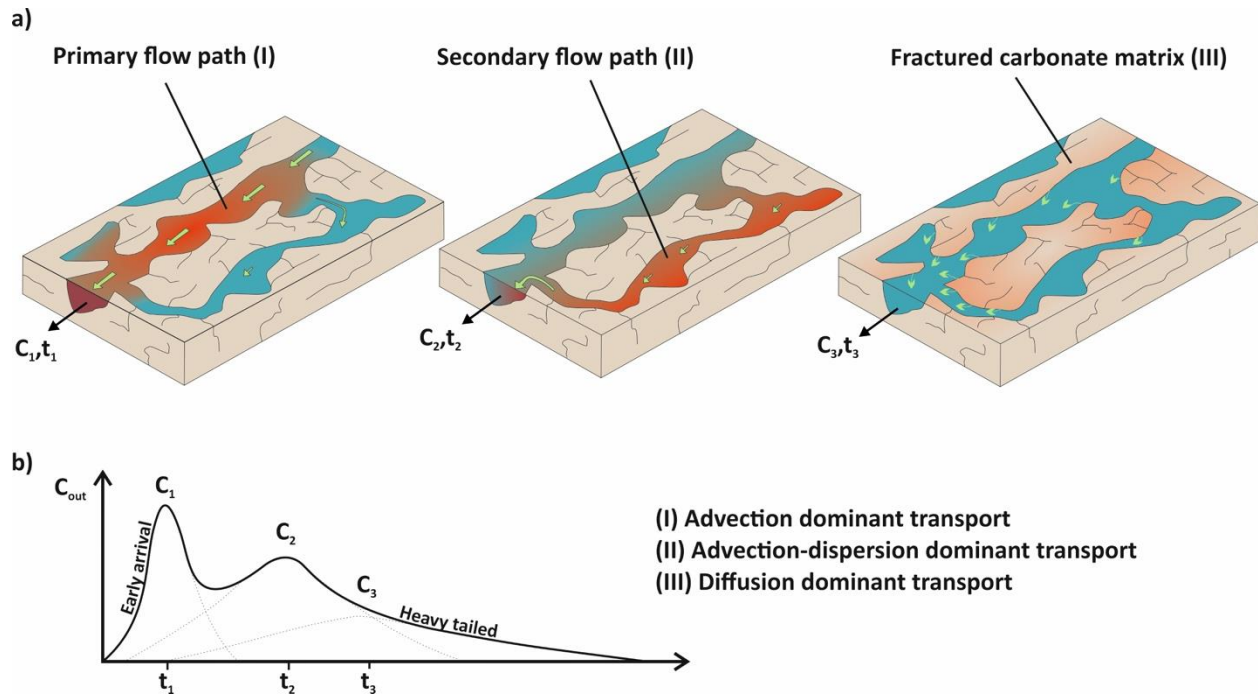
381 system's underlying mixing, storage, and transport characteristics (i.e., piston flow, complete  
 382 mixing) (Figure 3). For instance, the karst aquifers characterized by (relatively) younger water  
 383 age (i.e., shorter travel time) are often at the risk of contamination problem due to the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



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

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

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



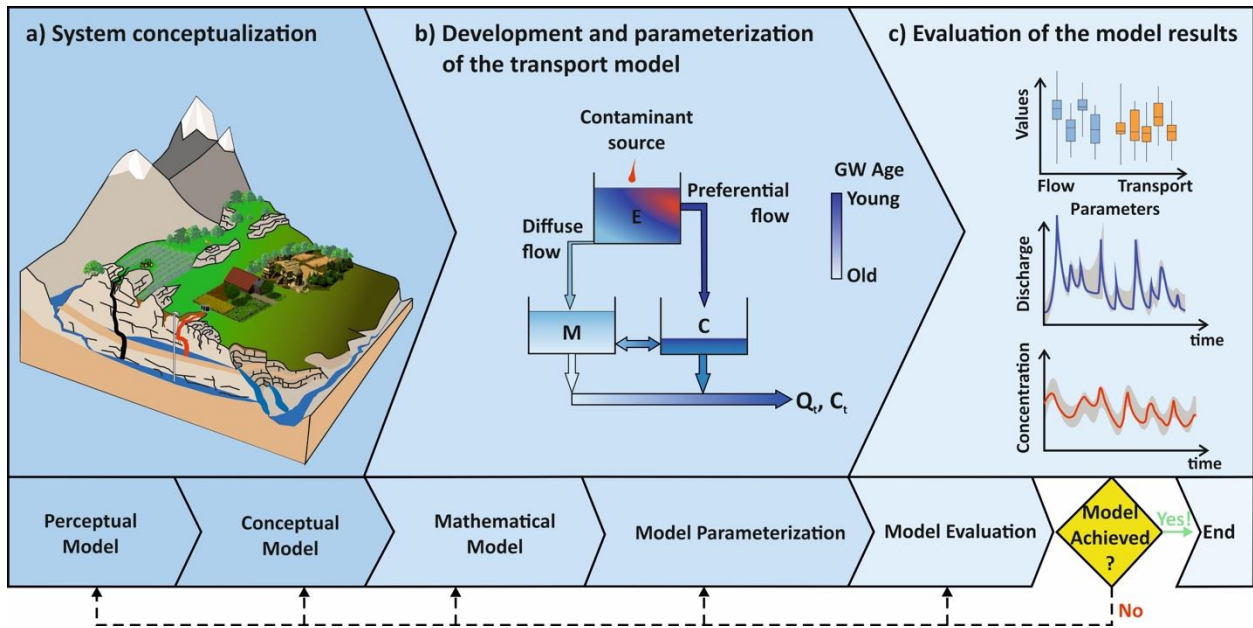
416

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

### 421 3 The current status of solute transport modelling in karst water resources

#### 422 3.1 A generic framework for a successful transport modelling in karst systems

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



442

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

451

### 3.1.1 Model conceptualization for karst transport processes

452

453 Perceptual understanding of transport processes is a key stage of successful transport  
 454 modeling practice. A perceptual model is a qualitative description of the karst system's physical,  
 455 chemical, and (biogeo)chemical transport characteristics, each of which forms the definition of  
 456 the dominant physicochemical processes at the domain of interest (e.g., Hartmann et al., 2012a,  
 457 2013a, 2018). At this stage, the understanding of a dominant process is critical as it mainly  
 458 conditions the concept of the karst transport mechanism (i.e., advection-dominated transport,  
 459 diffusion-dominated transport) for the conceptual model development. Since the perceptual  
 460 model is just a mental model amongst the multiple other possibilities, it is more likely to be  
 461 updated by the accumulated scientific knowledge and collected data (Beven & Chappell, 2021;  
 462 Wagener et al., 2021) before evolving into a conceptual model (Enemark et al., 2019; Gupta et  
 al., 2012).

463

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



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

### 485 3.1.2 Model parameterization in karst transport models

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

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

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

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

532 The number of parameters required for modelling of transport processes is typically  
533 greater than the flow models (Konikow, 1996, 2010; Reilly, 1987). For this reason, multiple  
534 parameters (i.e., degrees of freedom or parameter space) are often necessary to represent the  
535 system's physical and chemical behaviors in karst solute transport models. Besides, the number  
536 of parameters can be increased when the multispecies and/or multiphase (air and water phases)  
537 transport is considered in the modelling framework (e.g., Faulkner et al., 2009; Dewaide et al.,  
538 2016; Loop & White, 2001; Zhang et al., 2017). The model calibration for solute transport  
539 models is often framed by how the transport model is coupled with the flow model. Here, this  
540 coupling can be done at two different levels, either fully or partly/loosely. Mainly depending on  
541 the model coupling, two approaches are frequently applied for the parametrization of karst  
542 transport models: (i) sequential calibration and (ii) simultaneous calibration (Schilling et al.,  
543 2019). In sequential calibration, the (calibrated) parameters of the karst flow model is served for  
544 the parametrization of the transport model (e.g., Husic et al., 2021; Sullivan et al., 2019; Çallı et  
545 al., 2023a) whereas the simultaneous calibration is performed for a fully coupled model (flow  
546 model coupled by transport model) and hence whole parameter set is considered against the  
547 available observations (e.g., both karst spring discharge and  $\delta^{18}\text{O}$  composition of spring  
548 discharge) (e.g., Hartmann et al., 2017, 2012a, Kavousi et al., 2022; Zhang et al., 2020a, 2020b).

### 549 3.1.3 Evaluation of karst transport model results

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

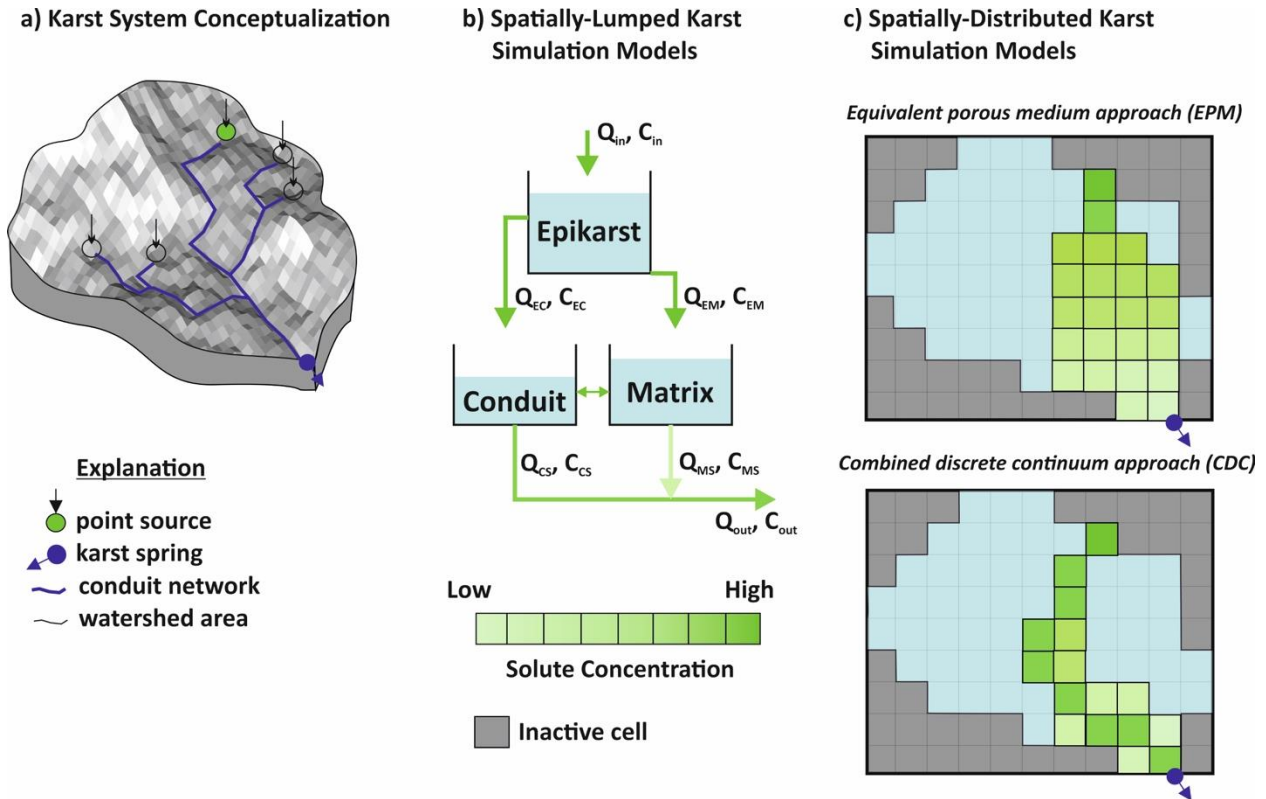
560 transport model often relies on the accuracy of a karst flow model, the transport model's  
561 predictions are generally less reliable as compared to flow models (e.g., Konikow, 1996, 2011;  
562 Scanlon et al., 2003). Therefore, the predictions of transport models are always uncertain to some 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

565 Nonetheless, uncertainty propagates and amplifies throughout the modelling practice  
566 (Figure 5). For that reason, the exploration of the principal sources of uncertainty is strictly  
567 limited (Beven, 2005; Hartmann, 2018). Similarly, the translation of each uncertainty source into  
568 a quantitative form — refers to the attribution of a numerical value for each uncertainty source  
569 — might change from one modeler to another and is mostly dependent on the progressive  
570 decisions and choices over the modelling practice. Therefore, different sources of uncertainty in  
571 model results (i.e., data uncertainty, model structure, and parameter uncertainties) could be  
572 reduced to a certain degree, only if a systematic model assessment in the model results is carried  
573 out. This assessment can identify what we need for the reduction of model uncertainty, and how  
574 much we shall put effort to reduce the different sources of uncertainty. Although this is not an  
575 easy task, some techniques such as Generalized Likelihood Uncertainty Estimation (GLUE)  
576 (Beven & Binley, 1992), Bayesian model averaging (BMA) (Hoeting et al., 1999; Neuman,  
577 2003), and multi-model ensemble method (MME) can be useful for the systematic and robust  
578 uncertainty assessment.

### 579 3.2 Description and classification of solute transport models in karst water resources

#### 580 3.2.1 Generic classification of karst simulation models

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



594

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

605 For karst systems, spatially distributed karst simulation models are classified as (i)  
 606 Equivalent Porous Medium Approach (EPM), (ii) Double Continuum Approach (DC), and (iii)  
 607 Combined Discrete-Continuum approach (CDC) (Ghasemizadeh et al., 2012; Hartmann et al.,  
 608 2014). EPM is a continuum-based modelling approach that considers the Representative  
 609 Elementary Volume (REV) and groundwater flow equations (Hartmann et al., 2014; Scanlon et  
 610 al., 2003) (Figure 6c). REV is defined as the smallest volume over which the averaged flow and  
 611 transport parameters can be represented by the spatial scale where we can still apply the Darcy  
 612 law based on the laminar flow conditions. REV represents a threshold volume in which the  
 613 hydrological properties are assumed to be invariant after then (Medici & West, 2021).  
 614 Nonetheless, due to the presence of the karst conduit and/or conduit networks, the flow in karst  
 615 conduits is often characterized by turbulent flow characteristics, and hence representing the  
 616 whole karst system with a single REV is not necessarily possible (Geyer et al., 2013; Kiraly,  
 617 2002). For that, EPM is often (more) suitable for simulating larger scale model applications  
 618 where the karst flow and transport processes can be described by a single REV (Anderson et al.,

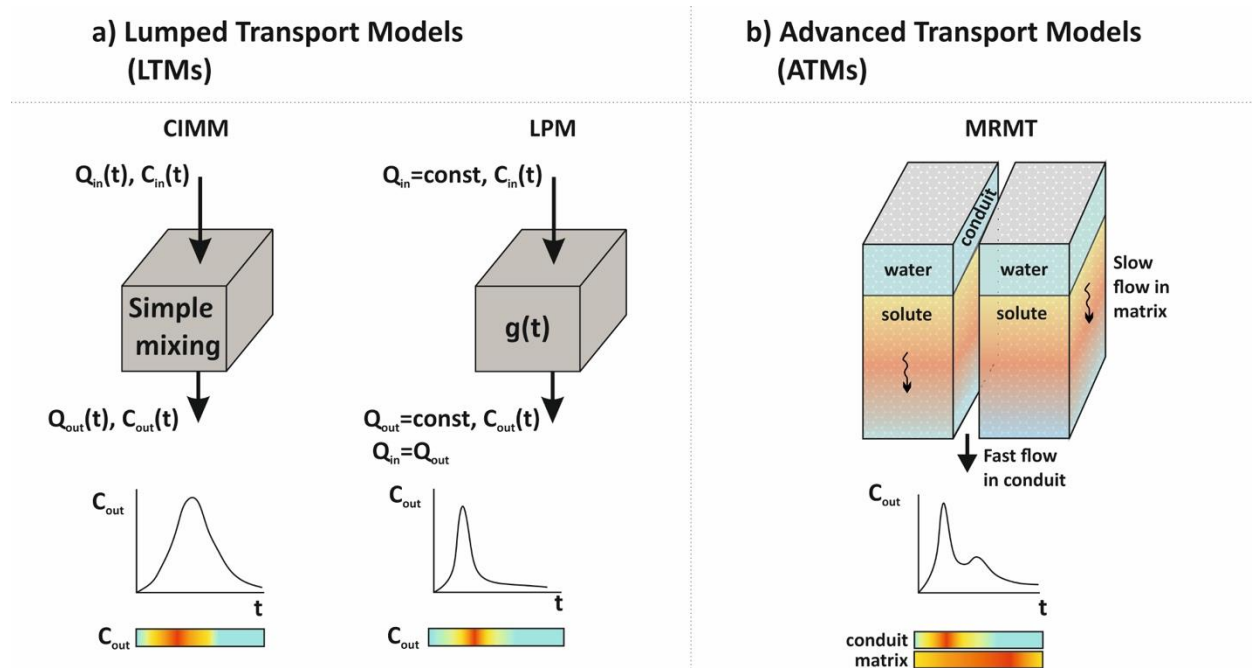
619 2015; Scanlon et al., 2003). In DC approach, the karst system consists of (at least) two  
620 overlapping continua (i.e., karst conduit and matrix) where the physical and/or chemical  
621 interaction between these two continua is addressed by an exchange rate (i.e., flow and/or mass  
622 exchange) (Cherubini, 2008; Kiraly, 1998; Maréchal et al., 2008, Robineau et al., 2018; Teutsch  
623 & Sauter, 1998). Here, the rate of exchange is proportional to the differences of hydraulic head  
624 and/or concentration gradient between the karst conduit and matrix continua (Kavousi et al.,  
625 2020; Oehlmann et al., 2015; Reimann, 2011a, 2011b, 2014).

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

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

### 649 3.2.2 Classification of solute transport models in karst systems

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



656

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

661 Overall, LTMs consider the karst flow field as a single non-distributed black box by  
 662 assuming the karst flow is constant at the domain of interest (Bayari, 2002; Ozyurt & Bayari,  
 663 2005, 2008). Since LTMs do not require specific knowledge about the various transport  
 664 processes (i.e., advection, dispersion, mass exchange) within the flow domain, they are often  
 665 preferable for karst modelling applications particularly at aquifer scale and/or regional scale  
 666 (Małozzewski & Zuber, 1996; Toth & Katz, 2006). ATMs, by comparison, explicitly consider  
 667 the impact of the karstic heterogeneities both on the flow velocity field and on the anomalous  
 668 transport (i.e., late-time and/or early arrivals in BTC). Therefore, the underlying assumptions of  
 669 ATMs are physically better than LTMs whereas the mathematical solutions are more complex  
 670 and rather prone to the numerical errors.

#### 671 *Lumped transport models (LTMs)*

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

675 CIMM is a compartmental model approach, in which a solute of interest is mixed in a  
 676 model compartment (usually the bucket of a lumped model) based on an assumption of  
 677 instantaneous and complete mixing. The mixing can be applied to each of the model's  
 678 compartments (i.e., epikarst, matrix, and conduits as depicted in Figure 6b) or to the entire  
 679 simulated dynamic water storage. Also, partial mixing within the same storage has been applied  
 680 in some studies (e.g., McMillan et al. 2012). In CIMMs, while the structure of the lumped karst  
 681 flow model specifies the flow paths between the compartments, solute mass balance between  
 682 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.,  $\delta^{18}\text{O}$  concentrations of  
 695 atmospheric precipitation) to the output solute concentrations (i.e.,  $\delta^{18}\text{O}$  concentration of karst  
 696 spring) using a convolution integral in Eq. 1.

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

698 where  $C_{out}$  [ $\text{ML}^{-3}$ ] and  $C_{in}$  [ $\text{ML}^{-3}$ ] are the input and output tracer concentrations,  
 699 respectively.  $\tau$  [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  $\eta$  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);

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

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 LPMs 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 (Małoszewski et al., 2002; Małoszewski & Zuber, 1982, 2002;  
 725 Zuber & Małoszewski, 2001).

726 Furthermore, as the response function in Eq.1 defines groundwater age distributions in  
 727 the karst system (i.e., TTDs or RTDs), it also enables us to link between LPMs and groundwater  
 728 age models — known as Direct Age Models (DAMs) — (e.g., Cornaton & Perrochet, 2006a,  
 729 2006b; Ginn, 1999, 2009; Goode, 1996; Sanford, 2011; Suckow, 2014). These models predict the  
 730 water age distributions by solving ADE in which the ‘solute mass’ concentration is replaced by a  
 731 groundwater ‘age term’ (see more details in Ginn, 1999, 2009; Goode, 1996).

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

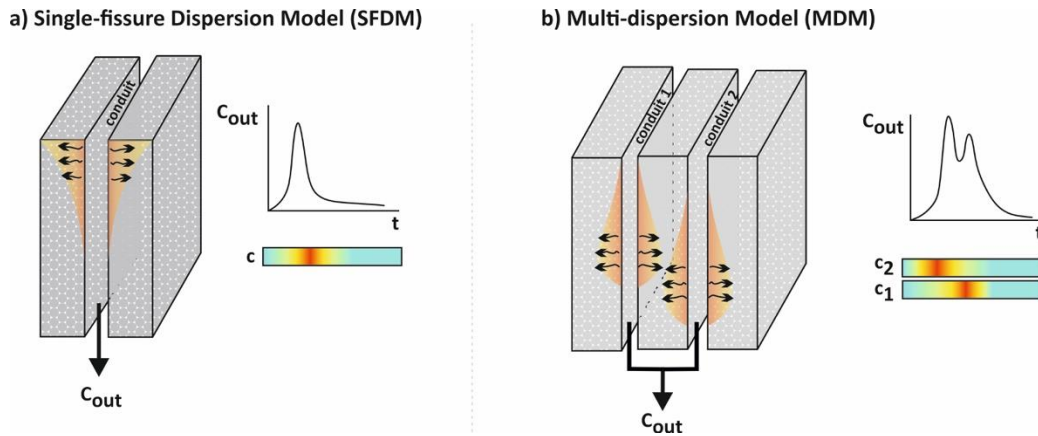
$$743 \quad C_f(x, t) = \frac{M}{Q \cdot t_0 \cdot \sqrt{4\pi \cdot P_e^{-1} \cdot \left(\frac{t}{t_0}\right)^3}} \exp\left[\frac{\left(1 - \frac{t}{t_0}\right)^2}{4 \cdot P_e^{-1} \cdot \frac{t}{t_0}}\right] \quad (3a)$$

$$744 \quad P_e = \frac{D_L}{\vartheta \cdot x}; \quad D_L = \alpha_L \cdot x \quad (3b)$$

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

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





758

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

762 SFDM or Parallel fissure dispersion model (PFDM) by Małozzewski & Zuber (1985) is  
 763 based on the theory of the parallel-plate modelling approach introduced by Sudicky & Frind  
 764 (1982). This approach considers the solute transport along the parallel fissure plates and into the  
 765 matrix coupled by the matrix diffusion (Małozzewski & Zuber, 1985). For karst aquifers, SFDM  
 766 is first applied into the fissured chalk aquifers by Małozzewski & Zuber (1990) and modified  
 767 later by Witthüser et al. (2003) to simulate transversal dispersion in chalk aquifers. To solve the  
 768 karst transport problem, SFDM requires three parameters including dispersion parameter,  
 769 diffusion parameter, and mean transit time (Małozzewski & Zuber, 1985; Małozzewski et al.,  
 770 1994; Witthüser et al., 2003).

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

#### 776 *Advanced transport models (ATMs)*

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

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

791 transfer (MRMT) models that divide flow and transport domain into (at least) matrix and  
 792 conduits. Broadly speaking, MRMT and FADE represent the Eulerian-type (Continuum)  
 793 modelling approaches while CTRW is the Lagrangian-based transport modelling approaches.  
 794 Here, the Eulerian-type models consider the volume-based flow and transport by discretizing the  
 795 problem domain into the different volumes while the Lagrangian-based approaches, such as  
 796 Particle Tracking (PT), Random Walk Particle Tracking (RWPT) discretize the solute  
 797 concentration into the particles, thereby considering the solute particles as a discrete phase  
 798 without an explicit need for a flow field definition. CTRWs and FADEs are the robust transport  
 799 modeling approaches, especially for capturing the time-nonlocalities in solute transport  
 800 behaviors in heterogeneous groundwater systems (e.g., Benson et al., 2000; Meerschaert et al.,  
 801 1999; Metzler & Klafter, 2000; Schumer et al., 2009) although the applications of both  
 802 modelling approaches in solving karst transport problems are rather new. In the following, we  
 803 will provide fundamental knowledge about these advanced karst transport models and their  
 804 primer applications in modelling of karst solute transport processes.

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

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

$$822 \quad R \frac{\partial C}{\partial t} = -\vartheta \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2} \quad (4)$$

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

$$827 \quad R = 1 + \rho_s K_d \quad (5)$$

828 where  $K_d$  [ $\text{L}^3\text{M}^{-1}$ ] is denoted as the distribution (or partition) coefficient that is described  
 829 as a ratio of the sorbed concentration into (geological) material and the dissolved concentration  
 830 in groundwater at (thermodynamically) equilibrium conditions. In karst aquifers,  $K_d$  is often  
 831 used to describe the sorption degree of any species in karst groundwater based on the distribution  
 832 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.

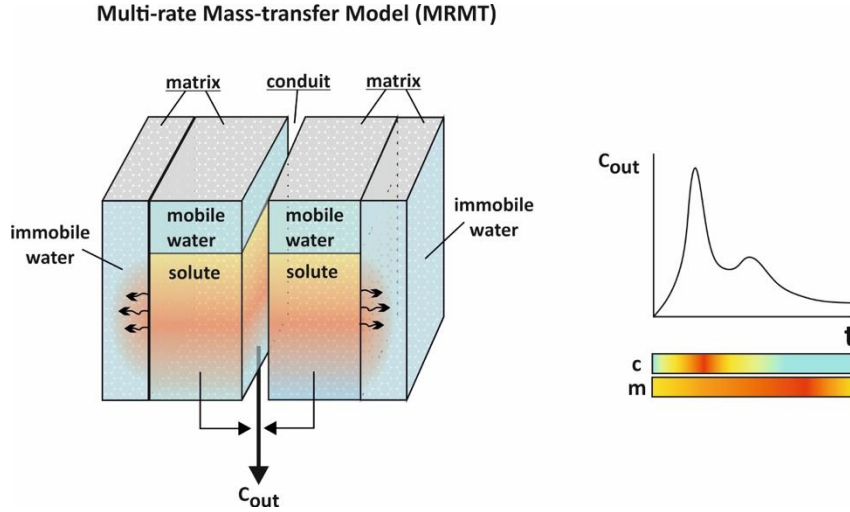
835 The “fractional” term in FADE refers to the fractional derivatives of dispersion that are  
 836 incorporated by time and/or space for solving time and/or space non-localities in BTC (see for  
 837 latest discussions on FADEs by Sun et al. (2020)). For one-dimensional solute transport form of  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

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

840 where  $C$  [ $\text{ML}^{-3}$ ] is the solute concentration in time ( $t$ ) [T] and the transport distance ( $x$ )  
 841 [L] in the direction of main flow.  $\vartheta$  [ $\text{LT}^{-1}$ ] is the mean flow velocity, and  $D$  [ $\text{L}^2\text{T}^{-1}$ ] 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  $\alpha$  [-] 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).



867

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

870

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

$$878 \quad \beta \frac{\partial C_m}{\partial t} + (1 - \beta) \frac{\partial C_{im}}{\partial t} = D_m \frac{\partial^2 C_m}{\partial x^2} - \vartheta_m \frac{\partial C_m}{\partial x} \quad (7a)$$

$$879 \quad \frac{\partial C_{im}}{\partial t} = \omega (C_m - C_{im}) \quad (7b)$$

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

891 To simulate karst transport, the two-region non-equilibrium (2RNE) approach is  
 892 frequently used for simulating transport dynamics in karst aquifers (e.g., Assunção et al., 2023;  
 893 Barberá et al., 2018; Birk et al., 2005; Ender et al., 2018; Geyer et al., 2007; Göppert et al.,  
 894 2020; Göppert & Goldscheider, 2008, among many others). Here, 2RNE only considers the flow  
 895 along the karst conduit in which flow velocity is assumed to be constant whilst no water

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

905 Other adaptations of the MRMT approach for karstic transport comprise the Dual-  
 906 advection dispersion (DADE) model and the Transient storage model (TSM). Developed by  
 907 Field & Leij (2012), DADE considers the solute transport characteristics between physically  
 908 interacting two conduits (named for  $i$  and  $j$  in Eq. 8) whilst the mass exchange is (again)  
 909 approximated by a first-order mass exchange between the main and auxiliary conduits (Bodin,  
 910 2020; Dewaide et al., 2016, 2018; Zhao et al., 2017; 2021) formulated by;

$$911 \quad \theta_i \frac{\partial C_i}{\partial x} = \theta_i D_i \frac{\partial C_i}{\partial x} - \theta_i v_i \frac{\partial C_i}{\partial x} + \omega(C_j - C_i) \quad (8)$$

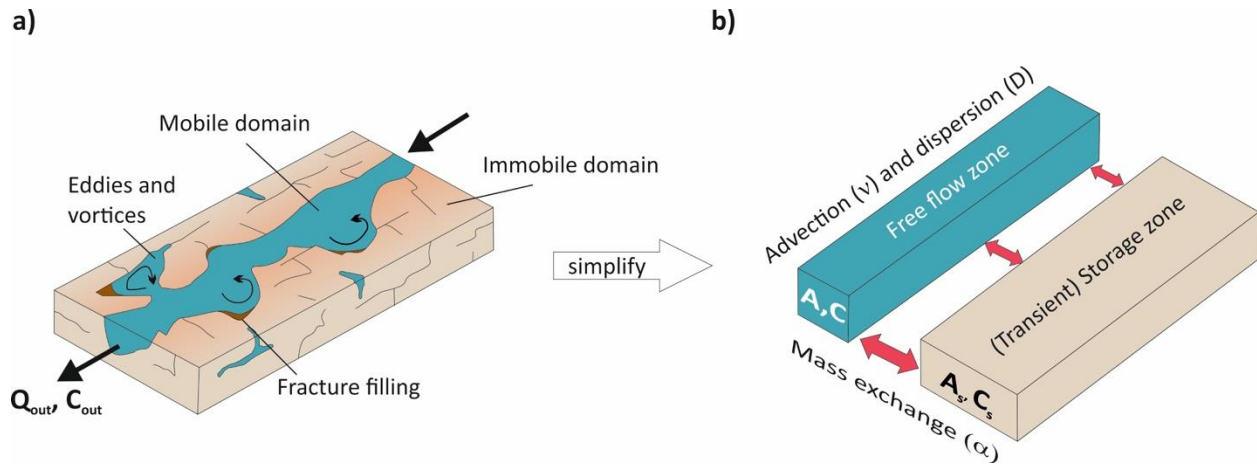
912 where  $\theta_i$  [ $L^3 L^{-3}$ ] is the volumetric water content in *Conduit-i* while  $C_i$  is the solute  
 913 concentration in *Conduit-j*.  $D_i$  [ $L^2 T^{-1}$ ] is the (longitudinal) dispersion coefficient while  $v_i$  [ $LT^{-1}$ ]  
 914 is the mean flow velocity in the *Conduit-i*.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

917 As for TSM, it is built upon the dual-domain model concept in which the preferential  
 918 flow paths are considered the main flow and transport regions. Originally developed for solving  
 919 transport problems in streams, TSM has been adapted to simulate karst transport problems (e.g.,  
 920 Morales et al., 2010; Hensley & Cohen, 2012). TSM was then reformulated by Dewaide et al.  
 921 (2016) for the karst aquifers such that the karst conduits are counted as the main flow and  
 922 transport regions whereas the (transient) storage zones are represented either by the pools in  
 923 which eddies and vortices frequently occur (Figure 10) or by cave sediments and carbonate  
 924 matrix (e.g., Deleu et al., 2023; Dewaide et al., 2018; Tinetti et al., 2019; Zhao et al., 2017, 2019,  
 925 2021). TSM is formulated as followed by,

$$926 \quad \frac{\partial C}{\partial t} = -\frac{Q}{A} \frac{\partial C}{\partial x} + \frac{1}{A} \frac{\partial}{\partial x} \left( A D_L \frac{\partial C}{\partial x} \right) + \alpha(C_s - C) \quad (9a)$$

$$927 \quad \frac{\partial C_s}{\partial x} = \alpha \frac{A}{A_s} (C - C_s) \quad (9b)$$

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



934

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

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

#### 958 **4 Lessons learned: Challenges in the successful transport modelling practice**

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

## 964 4.1 System conceptualization considering data collection and system understanding

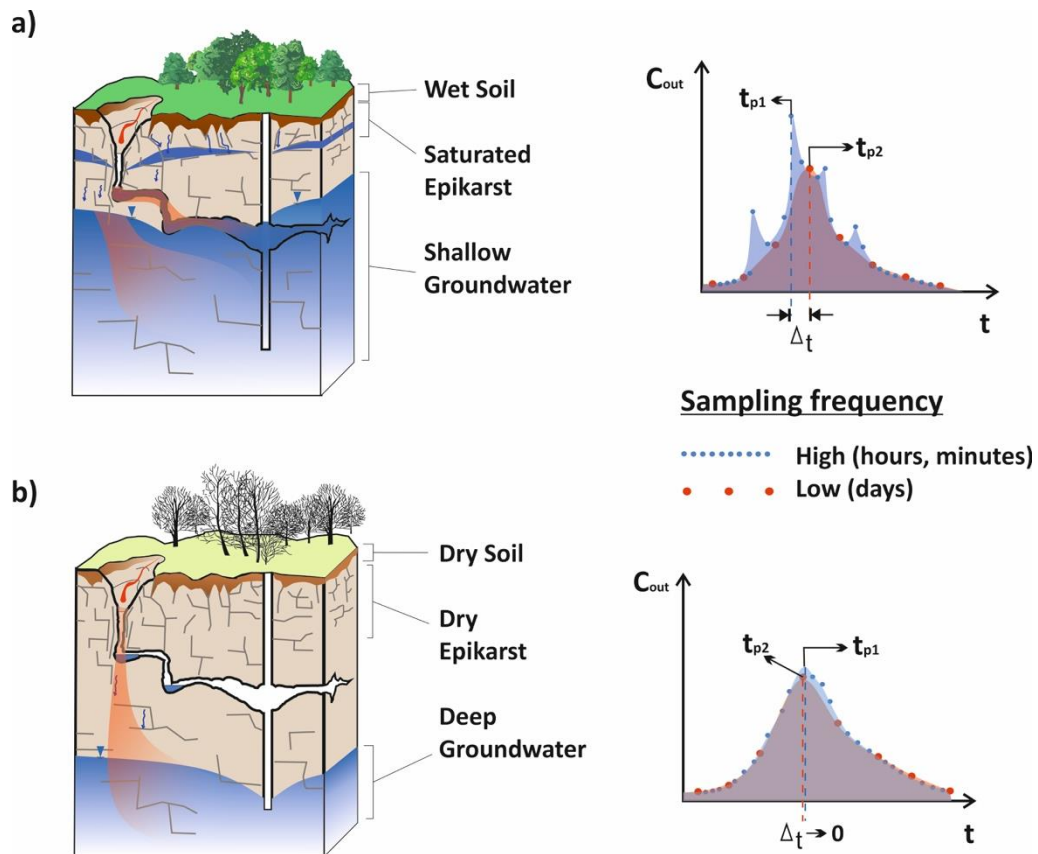
965 System conceptualization for modelling of karst transport processes requires a proper  
966 understanding of the system's physical, chemical, and bio(geo)chemical characteristics. This  
967 requires extensive data sets (Huntoon, 1995; Jeannin et al., 2013; Parise et al., 2015; Perrin et al.,  
968 2003a). However, given that the availability of such a massive data is very limited, a proper  
969 conceptualization of the spatiotemporal variabilities of karst transport processes (i.e., advection,  
970 dispersion, sorption and/or chemical transformations) is limited, too (e.g., Covington et al., 2011;  
971 Field & Pinsky, 2000; Hartmann et al., 2014; Quinlan et al., 1996).

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

982 The right definition of the scale of karst transport problem is vital for the system  
983 conceptualization. However, due to the karstic heterogeneity at multiple scales, the  
984 investigated/modelled domain might substantially differ from the actual transport domain in  
985 which physical and (biogeo)chemical processes predominantly occur. This is often the case in  
986 karst systems in that both physical and chemical parameters controlling flow and transport  
987 processes rely on the scale being investigated (e.g., Göppert & Goldscheider, 2008; Medici &  
988 West, 2021). The spatial extent for the transport problem is generally defined by the field experts  
989 and/or modelers themselves. As an implicit rule, the scale of interest should not be less or greater  
990 than the scale of method (i.e., artificial tracer tests, pumping tests) applied for the  
991 characterization of that particular process (Bakalowicz, 2005; Geyer, 2008; Ghasemizadeh et al.,  
992 2016; Maréchal et al., 2008). Nonetheless, the methods for data acquisition and/or interpretation  
993 techniques are often (more) appropriate for the continuum (Darcy) scale applications where the  
994 effective parameters can often be used for the entire domain (Faulkner et al., 2009; Huntoon,  
995 1995; Reimann et al., 2011; Zhang et al., 2021). For this reason, more sophisticated equipment  
996 and research techniques might be required for the descriptions of the karst transport dynamics.  
997 For instance, the characterization of nitrate or (dissolved) organic carbon migrations in karst  
998 systems are rather challenging due to the (contaminant) input variability (e.g., Husic et al., 2019;  
999 Orban et al., 2010; Opsahl et al., 2017; Yue et al., 2019, 2020) and less-known source history  
1000 (e.g., Liu et al., 2021; Lu et al., 2023; Ren et al., 2022; Sullivan et al., 2019). Therefore, it might  
1001 also be difficult to successfully capture the spatiotemporal dynamics of the contaminant  
1002 migration depending on the contaminant of interest with the regular measurement devices and/or  
1003 monitoring systems (e.g., Finsterle et al., 2012; Zhu et al., 2007).

1004 The right identification of the transport timescale with its temporal resolution is crucial  
1005 for the proper representation of the karst transport dynamics (e.g., Bailly-Comte et al., 2011;  
1006 Covington et al., 2012; Zhang et al., 2019). However, given that karst conduit and matrix might  
1007 have order-of-magnitude differences in their hydraulic and physicochemical properties (i.e.,  
1008 porosity, hydraulic conductivity, reactivity constants), a wide range of timescales can be

1009 identified for the karst transport (e.g., Robinson & Hasenmueller, 2017; Siville et al., 2019). But  
 1010 in the context of experimental characterization, the (karst) transport timescale is related to the  
 1011 process-timescale along the karst conduits (i.e., hours, days), for which shorter-timescale  
 1012 observations with higher sampling resolution (i.e., in minute, hourly, daily) are usually enough  
 1013 for capturing the karst transport dynamics (Figure 11). Without a long-term monitoring and  
 1014 (further) data collection strategy, however, the chemical and (biogeo)chemical processes  
 1015 occurring at (rather) larger timescales (i.e., annual, seasonal, decadal) might be underestimated  
 1016 and/or overlooked in such a data collection (e.g., Mathias et al., 2005; Tran et al., 2020; Wynn et  
 1017 al., 2013; Zhang et al., 2020b). Therefore, proper understanding of the (actual) mass transfers  
 1018 between the karst conduit and matrix is strictly limited (Brettmann et al., 1993; Cherubini et al.,  
 1019 2013; Zhao et al., 2017).



1020

1021 **Figure 11.** Schematic representations of the model conceptualization for solute transport  
 1022 dynamics in karst system considering the spatial extent and temporal scale of the karst transport.  
 1023 The schematic also demonstrates what affects the temporal variability of the transport processes  
 1024 under different hydrological conditions. **a)** Contaminant plume migration under the high-water  
 1025 flow conditions, **b)** Contaminant plume migration under the low-water flow conditions. Here,  $t_p$   
 1026 depicts the time to the peak solute concentrations with respect to the hydrological variability and  
 1027 sampling frequency.  $t_{p1}$  (high resolution) and  $t_{p2}$  (low resolution) describe the time of the peak  
 1028 concentrations depending on sampling frequency.

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1030 The temporal variability of the data is another complement of the successful  
 1031 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



1032 transport behaviours under certain flow conditions at certain time periods (Figure 11). However,  
1033 actual transport can be broadly varied by the different timescales ranging from an event to  
1034 seasonal and/or inter-annual timescales (e.g., Doummar et al., 2018; Luo et al., 2024; Remondi et  
1035 al., 2018, 2019; Sivelle & Labat, 2019; Zhang et al., 2020a). As a matter of fact, the same shape  
1036 for BTC might not actually be reproduced again if those particular conditions (both hydrological  
1037 and physicochemical) at that particular timescale are not met (e.g., Aydin et al., 2014; Chu et  
1038 al., 2021; Kogovsek & Petric, 2014; Morales et al., 2007, 2018; Ravbar et al., 2012, among  
1039 others). Therefore, the system conceptualization is restricted to the certain timescales and might  
1040 not properly represent the overall karst transport dynamics especially when the hydrological or  
1041 (biogeo)chemical conditions change or vary temporarily.

1042 Another limitation in the system conceptualization is the identification of the realistic  
1043 values for the system's parameters since both hydraulic and transport parameters can vary by  
1044 orders of magnitude at differing spatial scales — from a few centimeters to hundreds of meters  
1045 or more — (Berkowitz, 2002; Giese et al., 2018; Medici et al., 2019; Medici & West, 2021).  
1046 Hydraulic conductivity and dispersivity are such parameters very sensitive to the scale  
1047 variations, thus causing substantial variations in the spreading of the contamination plume in the  
1048 karst aquifer. Likewise, chemical parameters (i.e., sorption parameters) obtained under the  
1049 laboratory conditions might largely differ from those measured at the field scale (Faulkner et al.,  
1050 2009; Witthüse et al., 2003). For instance, the partition coefficient ( $K_d$ ) and mass transfer  
1051 coefficient (i.e., first-order mass transfer coefficient) could not be generalized (e.g., Stockmann  
1052 et al., 2017; Swami et al., 2018) because their values are extremely varied (often by order of  
1053 magnitudes) at the field-scale measurements depending both on the matrix hydraulic properties  
1054 (e.g., surface area, matrix porosity, permeability) and on the fracture/conduit characteristics  
1055 (Howroyd & Novakowski, 2021; Lehmann et al., 2022; Maloszewski & Zuber, 1993; Zhou et al.,  
1056 2007). Similarly, the values for reactive transport parameters could also be misleading  
1057 particularly when they are scaled up or extrapolated, because of the oversimplification of the  
1058 multifaceted processes that are varied both by chemical heterogeneities in the matrix and  
1059 local/global groundwater chemistry (e.g., Howroyd & Novakowski, 2021; Jiang et al., 2023;  
1060 Katz et al., 1998; Kaufmann et al., 2014; Mohammadi et al., 2021; Maqueda et al., 2023, among  
1061 many others). For this reason, a realistic definition of the reactive transport parameters is strictly  
1062 limited by the well-defined karstic sites or site-specific applications (i.e., single-well push-pull  
1063 test) (e.g., Hillebrand et al., 2012a, 2012b, 2015; Priebe et al., 2022; Schiperski et al., 2016; Tran  
1064 et al., 2020, 2021).

1065 Field-scale experiments, particularly artificial tracer tests, are frequently performed under  
1066 highly vulnerable aquifer conditions in which sinkholes and/or swallets are frequently utilized as  
1067 tracer injection points (e.g., Jones, 2019; Li et al., 2008; Morales et al., 2007; Sinreich, 2011).  
1068 For such experimental designs, as the preferential flow paths predominantly shape the  
1069 spatiotemporal behaviour of the contamination plume, karst transport dynamics are often  
1070 characterized by the advection-dominated transport between the injection and sampling points  
1071 (i.e., between sinkhole and observation well, Figure 11). As a result, the role of matrix diffusion  
1072 and mass exchange processes between the karst conduit and surrounding matrix might be  
1073 underestimated. Furthermore, due to the randomly varying flow velocities in karst conduits,  
1074 physical parameters such as hydraulic conductivity, velocity, dispersivity, solute travel time  
1075 (Kavousi et al., 2020; Rehrl & Birk, 2010; Zhao et al., 2017) and chemical parameters including  
1076 sorption and mass exchange parameters are rarely understood (Barberá et al., 2018; Field &  
1077 Pinsky, 2000; Haggerty et al., 2004). Consequently, the observed data might not provide a

1078 complete picture about the karst system's (overall) hydrochemical functioning and transport  
1079 characteristics due to the limited transport distance and (certain) flow conditions under specific  
1080 experimental conditions.

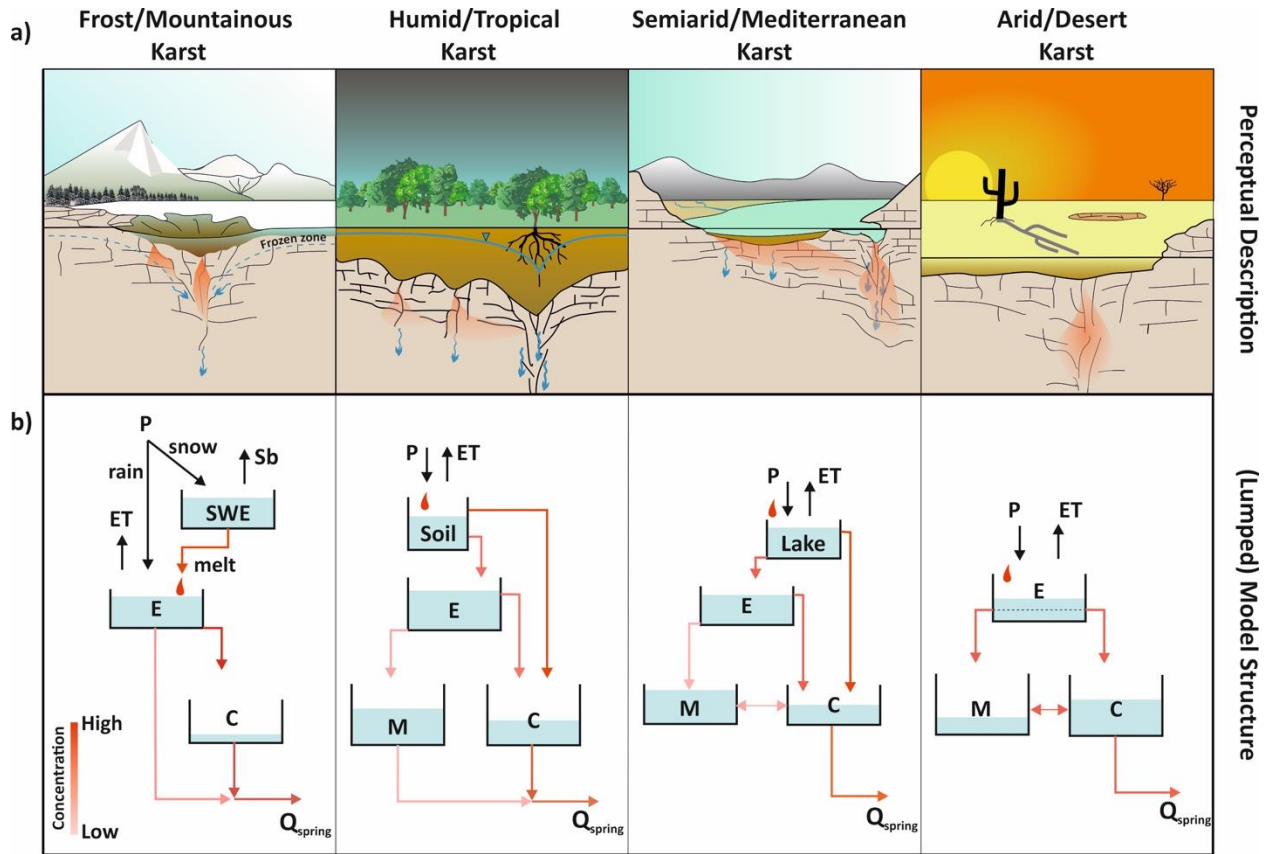
1081 All these difficulties explain why a robust conceptualization for the karst transport  
1082 dynamics is inherently limited, and why there are only few real-world applications of the karst  
1083 transport models that solves the classical ADE (see Section 3.4). In this matter, the limitations in  
1084 system conceptualization for karst transport point out the need for in-depth discussions on how to  
1085 better align the investigated (transport) domain and the model domain in karst systems, as well as  
1086 for finding better ways to collect physical and (biogeo)chemical data across the scales.

## 1087 4.2 Selection and parameterization of the karst transport model

### 1088 4.2.1 Model selection based on the (right) choice of dominant process

1089 Model selection with a detailed understanding of its assumptions and limitations is one of  
1090 the key steps for the successful transport modelling in karst systems. However, such a choice  
1091 from a model plethora is not an easy task (Horton et al., 2022; Masciopinto et al., 2021) as each  
1092 model has its own features (i.e., numerical formulations, parameters) that may be appropriate for  
1093 a specific application and/or specified conditions (Figure 12). Certainly, the modeler's perceptual  
1094 understanding on the karst flow and transport processes can also be judicious in selecting a  
1095 candidate model structure (e.g., Cousquer & Jourde, 2022; Hartmann et al., 2013b, 2014). Of the  
1096 numerous criteria, however, the objective of the study, data availability, and model structural  
1097 adequacy generally define our most-suitable choice in simulating karst transport dynamics (see  
1098 Section 3).

1099 In general, an (accurate) representation of the flow and transport processes in the model  
1100 structure can be seen as a crux of the robust model selection (Figure 12). But, as we have often  
1101 poor understanding about the complicated physical, chemical, and (biogeo)chemical processes, a  
1102 special care is required for the representation of the karst transport dynamics in the (selected)  
1103 model structure with the adequate numerical formulation and parameters. From a modelling  
1104 point of view, however, the representations of multiple processes at differing spatiotemporal  
1105 scales under a broad range of karstic environments — in which different transport problems  
1106 might be encountered — with the similar model structures is neither possible nor enough to  
1107 realistically simulate the karst transport dynamics (e.g., Chang et al., 2017, 2021; Cen et al.,  
1108 2021; Hublart et al., 2015; Makropoulos et al., 2008; Massmann et al., 2005, among many  
1109 others). For this reason, the overall success in the robust model selection is attributed to the  
1110 'right' choice of the key process that predominantly controls the karst system's hydrological  
1111 and/or physicochemical behaviors by the available data (Hartmann et al., 2013a, 2018).



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**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).

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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;

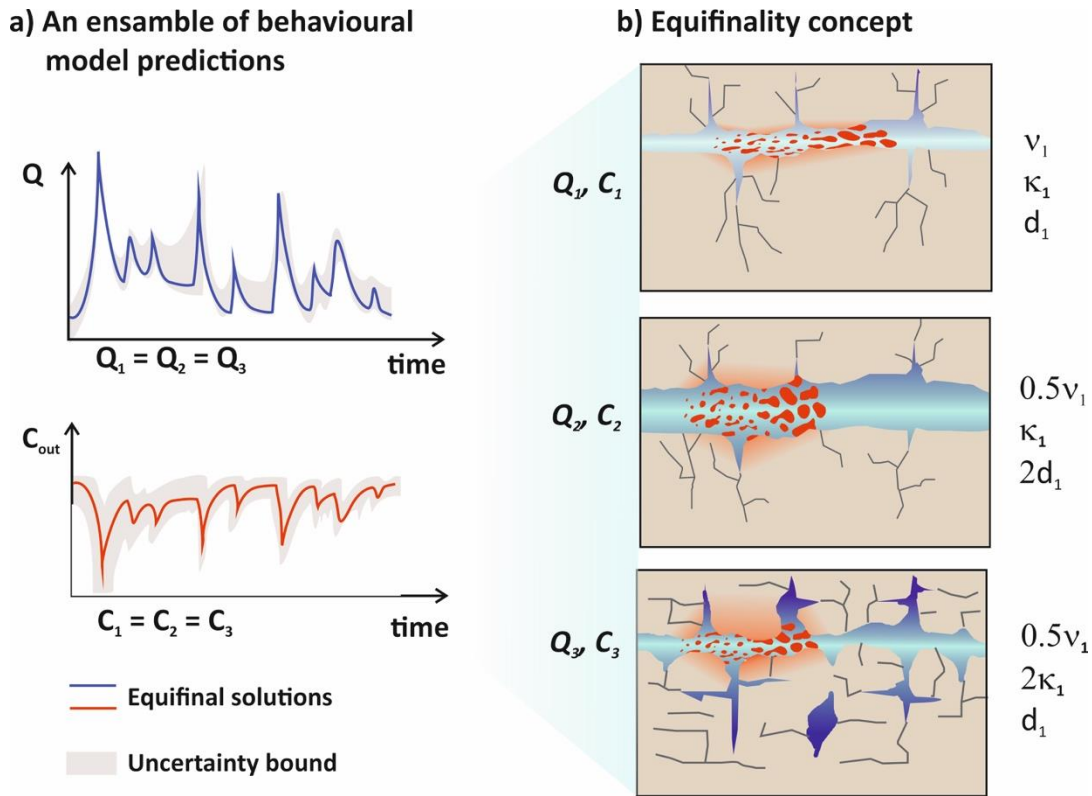
1136 Chang et al., 2019; Kavousi et al., 2020; Xu et al., 2015). For instance, mass transfer between the  
1137 karst conduit and matrix need to be considered with an additional parameter sets that resemble  
1138 the mass exchange in such models i.e., 2RNE, TSM, DHDM (Assunção et al., 2023; Ender et al.,  
1139 2018; Schiperski et al., 2022; Yin et al., 2022) (see subsection 3.2.2). As consequence, the  
1140 successful applications of the advanced transport models are strictly limited by the well-defined  
1141 sites, small-scale field and/or lab-scale investigations where the rather site-specific parameters  
1142 (i.e., mass transfer rate, sorption constants) are obtained (e.g., Lehmann et al., 2022; Shu et al.,  
1143 2020; Schiperski et al., 2022; Wang et al., 2022). Because of this limitation, the semi-distributed  
1144 karst simulations models, like Varkarst (Hartmann et al., 2013a) and TCD-Dublin (Gill et al.,  
1145 2013), are frequently served as the optimal model structures to ensure the balance between the  
1146 process representation and data availability (Borghi et al., 2016; Hartmann et al., 2014). The  
1147 complexity of such models is often enough to represent karst transport dynamics as compared to  
1148 the parsimonious lumped models, as well as better choice with the lower/adapted data need than  
1149 that of distributed counterparts (e.g., Hartmann, 2016b; Teixeira Parente et al., 2019; Zoghbi &  
1150 Basha, 2020, among many others). But despite the semi-distributed, physically oriented flow  
1151 path simulation of these models, a big gap remains in their presentation of transport dynamics  
1152 which has been relying on simple CIMM approaches.

1153 Overall, finding the most adequate transport model structure and degree of complexity is  
1154 a particular challenge for karst transport modelling. But the optimal structure should be as simple  
1155 as possible and as complex enough to better represent the karst system's underlying key physical  
1156 and chemical phenomena in accordance with the available data. In principle, the complexity of  
1157 selected model structure can only be increased when data amount (i.e., multiple observations)  
1158 and its quality ensure the proper representations of the multiple processes in the model structure  
1159 (Milanović & Vasić, 2015; Hartmann et al., 2013a, 2014a, 2018), thereby increasing the model  
1160 realism in terms of process representation. Nonetheless, seeking a trade-off between the (robust)  
1161 representation of karst transport processes and their proper transcriptions in the model structures  
1162 based on the principle of parsimony has not yet been fully explored yet. Therefore, which type of  
1163 model we could use, and how complex it would be are those questions still open to discussion.

#### 1164 4.2.2 Model parametrization: Parameter non-uniqueness and transferability

1165 A successful transport model parametrization must ensure robust parameter estimation  
1166 with reliable model predictions (e.g., Chang et al., 2017; Hartmann et al., 2017; Sivelles et al.,  
1167 2022; Çalı et al., 2023a). Yet, a common tenet in karst modelling studies is to obtain physically  
1168 reasonable parameters in comparison with the actual site characteristics. For that, a successful  
1169 model parametrization is required. However, due to the limited system knowledge with the  
1170 insufficient field estimates, a robust parameterization in karst transport models is a challenging  
1171 task particularly in two ways. First, how to better translate the karst transport dynamics into the  
1172 model structure with sufficient parameters is a serious matter because additional parameters are  
1173 involved in the karst transport model (i.e., dispersivity, mass transfer coefficient) as compared to  
1174 the flow models. Second, since most parameter values cannot be assessed from the direct  
1175 measurements, inverse modelling (i.e., model calibration) is necessary to describe the key  
1176 physical and (biogeo)chemical processes (Figure 13). The former task could be handled by  
1177 sticking to the principle of parsimony where the minimum number of parameters meet with  
1178 observational datasets (Hartmann et al., 2018; Kavousi et al., 2020, 2023), the later one is often  
1179 rather difficult because it will possibly go along with overparameterization. This limits the  
1180 physical interpretation of the parameter values, thus reducing the model reliability with a certain

1181 degree of uncertainty (Figure 13) (Hartmann, 2016b; Teixeira Parente et al., 2019; Zhang et al.,  
 1182 2020b; Zoghbi & Basha, 2020; Çallı et al., 2023a).



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1184 **Figure 13.** Description of the model calibration results for karst transport model based on the  
 1185 concept of model equifinality, both in model solutions and in parameters. **(a)** Calibration of a  
 1186 karst transport model ended up with the equifinal simulations within a certain range of  
 1187 uncertainty (depicted as an ensemble of the behavioral model simulations with the shaded area),  
 1188 **(b)** The (hypothetical) description of the equifinality concept in the transport model parameters  
 1189 resulting from the equifinal solutions in Panel a (In the figure, the acronyms are  $v_1$  (*flow*  
 1190 *velocity*),  $\kappa_1$  (*hydraulic conductivity*), and  $d_1$  (*cross-sectional area*). Here, multiple feasible  
 1191 parameter-sets provide equally-well hydrological (i.e., spring discharge,  $Q$ ) and physicochemical  
 1192 (solute concentration,  $C_{out}$ ) responses with respect to the (selected) calibration metric. In  
 1193 equifinal model results, finding the “best” or “most acceptable” solution is not necessarily  
 1194 possible, and the results might be misleading.

1195 The direct field measurements and/or lab-scale experiments are favorable for the  
 1196 improved parameterization of the karst transport models in that the spatial and temporal  
 1197 variabilities of the transport processes could be defined by the well-defined parameter values. In  
 1198 principle, since the (more) physically based models (i.e., ATMs) consider the parameter  
 1199 heterogeneities along the domain of interest, they are often built upon the experimental data that  
 1200 describes the physical/chemical significance of the processes of interest with the effective values  
 1201 (e.g., Dentz, 2011; Li et al., 2008; Orban et al., 2010; Pérotin et al., 2021; Zhang et al., 2021).  
 1202 Nevertheless, it might not be still not possible to define the specified values for some of  
 1203 parameters, especially for the regional scale transport modelling such as conduit/fracture  
 1204 geometry (i.e., orientation, spacing, aperture) and conduit/fracture networks (i.e., distributions,

1205 intersections, tortuosity factor). Consequently, such parameters are frequently unknown and  
1206 required to be calibrated (e.g., Barberá et al., 2018; Dreybrodt, 2012; Faulkner et al., 2009;  
1207 Florea & Wicks, 2001; Geyer et al., 2013; Robineau et al., 2018, among many others). For  
1208 instance, to parametrize Transient Storage Model (TSM) where transport distance is divided into  
1209 several smaller reaches needs several effective parameter-sets to represent the transport  
1210 processes along the karst conduit. Here, the length of each reach is defined by the (extensive)  
1211 field works whereas dispersion and cross-sectional areas for the main flow channel and transient  
1212 storage are still obtained by the model calibration (e.g., Cholet et al., 2017; Deleu et al., 2023;  
1213 Dewaide et al., 2016; Tinot et al., 2019; Zhao et al., 2021). Likewise, the mass transfer  
1214 coefficient is often considered as a calibration parameter, especially for the dual-domain  
1215 transport models (i.e., MIM, 2RNE, TSM). Considering all, the model calibration is an inevitable  
1216 part of the successful model applications, both for the lumped and advanced karst transport  
1217 models.

1218 As an inverse solution of the karst system's transport dynamics, a successful calibration  
1219 seeks to infer a (unique) parameter set which resembles the process of interest at the  
1220 spatiotemporal domain of interest. Yet, as there is not a unique solution for an inverse problem  
1221 (Hartmann, 2018; Sivelles et al., 2020; Valota et al., 2002), it is often difficult to link the karst  
1222 transport parameters with the actual transport dynamics. For that reason, karst transport models  
1223 are more prone to suffering from the issue of non-uniqueness as compared to the flow models,  
1224 particularly in describing and (physically) interpreting transport parameters (i.e., flow velocity,  
1225 dispersivity) (e.g., Adinehvand et al., 2017; Chang et al., 2017; Johnston et al., 2009; Field & Li,  
1226 2011; Massmann et al., 2005, among many others). This often results in overparameterization  
1227 and equifinality as exemplified in Figure 13. While the overparameterization is often a serious  
1228 problem for the advanced/distributed models where the multiple parameters are represented in  
1229 the model structure despite the less information available (Fischer et al., 2024; Kavousi et al.,  
1230 2020, 2023), it might be rather less of a problem for the lumped transport models (i.e., CIMMs,  
1231 LPMs) where the direct observations are not possible due to the aggregation of the karst flow and  
1232 transport processes along the domain of interest (e.g., Hartmann et al., 2014; Sivelles et al., 2022).

1233 Model overparameterization or equifinality manifests itself larger uncertainties in the  
1234 model predictions and parameters (Figure 13). For this reason, finding the "best" or "most  
1235 acceptable" solution is not necessarily possible. Therefore, model predictions (or equifinal  
1236 solutions) can be strongly misleading (e.g., Beven, 2006; Husic et al., 2020; Zhang et al. 2019,  
1237 2020b; Wang et al., 2020). In theory, parameter identifiability tests can quantify the equifinality  
1238 and help to reduce it with additional information or model structure simplifications. However,  
1239 these improvements may be limited because the physical and (biogeo)chemical parameters that  
1240 control the migration of the contamination plume are highly sensitive to the karst system's  
1241 physical and (biogeo)chemical heterogeneities (Bonanno et al., 2022; Jia et al., 2018; Zhang et  
1242 al., 2020b; Zoghbi & Basha, 2020). For instance, the interpretation of mass exchange rate,  
1243 spatially varying sorption properties, reactive kinetic surface areas for the dual-domain transport  
1244 models (e.g., 2RNE, MIM, TSM) are often problematic and less reliable for predicting the karst  
1245 transport dynamics due to the lack of exhaustive information. Therefore, the non-identifiability  
1246 problem in such transport parameters might be inherent.

1247 A (successful) application of the karst transport model is often unique in solving  
1248 (particular) flow and transport conditions at the domain of interest. For this reason, the  
1249 transferability of the (model-specific) calibrated parameters for the (rather) larger and/or smaller

1250 transport domains, for various karstic environments, and for different models under different  
1251 concepts is strictly limited, too. As a result, using the literature values for some of the transport  
1252 parameters might not be entirely possible since the karst transport parameters and their values are  
1253 mostly unique in place and time.

1254 Overall, it is particularly important to emphasize that the substantial limitations behind  
1255 the successful model parametrization of karst transport models reside especially in the governing  
1256 solutions (i.e., ADE) that are particularly developed for the porous aquifer-specific transport  
1257 problems (e.g., Bear et al., 2012; Faulkner et al., 2009; Field & Pinsky, 2000; Zoghbi & Basha,  
1258 2020). For that reason, the targeted solutions cannot be easily transferred for the highly  
1259 heterogeneous karst aquifers in which the additional mathematical complexities (e.g., inclusion  
1260 of mass transfer coefficients, sorption parameters in classical ADE) are not easily incorporated  
1261 and overparameterization is likely to arise.

#### 1262 4.3 Uncertainty of the model simulations

1263 Characterization and reduction of the uncertainty is one of the priorities for the evaluation  
1264 of transport model applications as it ensures the robustness and reliability of the model  
1265 predictions (e.g., Chang et al. 2021; Hartmann et al., 2013b, 2018; Çallı et al., 2023a). For this  
1266 reason, treating uncertainty with its (potential) sources requires a special care throughout the  
1267 karst transport modelling practice, especially for identifying the ways for the model  
1268 improvements.

1269 Taxonomically, the larger source of uncertainty in the model predictions is attributed to  
1270 the epistemistic uncertainty due to the lack of system knowledge and/or ignorance of some key  
1271 processes in the formal model structure, rather than the stochastic uncertainty arising from the  
1272 natural variability of the hydro(geo)logical systems (e.g., Beven et al., 2011; Beven, 2023;  
1273 Reichert et al., 2021). This uncertainty type is particularly relevant for the karst flow and  
1274 transport models because they are mostly built upon insufficient and site-specific information,  
1275 while often shaped by the expert elicitations on the complex physical and chemical properties of  
1276 the karst systems (Hartmann et al., 2014; Padilla & Vesper, 2018; Zhang et al., 2017). In general,  
1277 uncertainty in karst transport modeling is raised from the different stages of the karst transport  
1278 modelling practice but the main sources of uncertainty in the model predictions can be attributed  
1279 to following sources: (i) data uncertainty, (ii) model structural uncertainty (both conceptual and  
1280 numerical), (iii) parameter uncertainty, (iv) uncertainty associated with the unknown future  
1281 behavior of the karst system.

1282 Despite clear evidence that the uncertainties in groups (i)-(iii) are substantial (see  
1283 previous subsections), only few karst transport studies with LTMs have quantified the  
1284 uncertainty of their transport simulations (Chang et al. 2021; Mudarra et al., 2019; Çallı et al.,  
1285 2023a). Amongst them, Chang et al. (2021) was the only one trying to reveal structural  
1286 uncertainty by comparing different model structures. For ATMs, different modelling approaches  
1287 (i.e., ADE, MIM, PCNE) were also tested for the simulations of the shape characteristics of  
1288 BTCs (e.g., multi-modality and heavy tailing) obtained from different karst conduits by Field &  
1289 Leij (2014). This model comparison research provided a better understanding about the suitable  
1290 model structure and parameterization of the karst transport process (Massmann et al., 2005; Zhao  
1291 et al., 2019). Therefore, the disagreements in the model predictions with differing complexity for  
1292 the same applications might provide a complete understanding about the suitable model structure  
1293 and improved parameterization (Assunção et al., 2023; Dong et al., 2023; Massmann et al., 2005;

1294 Zhao et al., 2019) as well as indicate the scale dependency of the model parameters and process  
1295 interactions (Goeppert et al., 2020; Kaufmann, 2003; Liu et al., 2021).

1296 Concerning the uncertainty associated with the unknown future behavior of the karst  
1297 system, realistic representations of a karst the system's current and historical transport conditions  
1298 may not guarantee that future conditions (e.g., unknown future state variables) will successfully  
1299 met by the chosen model structure (Beven & Chappell, 2021; Oreskes et al., 1994; Wagener,  
1300 2022). Regarding this, one of the critical tasks for the karst modelers is to assess the model  
1301 results by seeking (more) reasonable answers for to what extent the model simulates the process  
1302 behaviour under (globally) changing hydrological and physiochemical conditions. Improving our  
1303 physical understanding of karst systems and implementing it into new and better model structure  
1304 is an ongoing challenge for the successful modelling practice.

## 1305 **5 Ways ahead of modelling karst transport dynamics and future perspectives**

1306 Studies on modelling of karst flow and transport processes have considerably increased  
1307 over the last decades. Several factors can play a role in such a progress including the variety of  
1308 collected data (i.e., multiple observations), its accuracy, and increments in computational power  
1309 and capacity (both accuracy and efficiency). But the driving force is the need for solving  
1310 transport problems in karst water resources across the world. Nonetheless, as a community, we  
1311 are still at the stage of model improvements for the successful real-world applications of the  
1312 karst transport models by confronting the main challenges (i.e., system conceptualization, model  
1313 parametrization, uncertainty quantification) to ensure model robustness and reliability (see  
1314 Section 4). Along with these (long-lasting) challenges, however, new challenges and ways are  
1315 ahead of us, especially considering the deterioration of karst water quality in a changing world  
1316 due to climate change impact on karst water quality and ecosystem services. For that, we  
1317 highlight four key directions that could be addressed for better representing and predicting the  
1318 solute transport behaviour in karst systems, as well as for exploring karst water quality risks and  
1319 potential outcomes.

### 1320 **5.1 Collect and provide more data for improved karst transport understanding**

1321 To reasonably predict karst transport dynamics, the solute transport models often require  
1322 spatially and temporally continuous and consistent datasets. However, the collection of chemical  
1323 and (biogeo)chemical data (i.e., nitrate, arsenic, biological and microbial contaminants,  
1324 microplastics) is still sparse, and mostly inconsistent with the temporal coverage of the physical  
1325 data (i.e., spring discharge, groundwater head, water pressure). As a result, our proper  
1326 understanding about the karst system-specific contaminant mixing and transport characteristics,  
1327 as well as the knowledge on reactive transport processes and (biogeo)chemical transformations  
1328 are substantially limited. Nonetheless, taking long-term precautions to protect karst water quality  
1329 from anthropogenic factors and global changes (i.e., climate, land cover and land use changes,  
1330 soil degradation) often rely on better understanding of chemical and biogeochemical processes.  
1331 For this reason, a particular attention is required for improved understanding of the (multiple)  
1332 physicochemical interactions between the preferential flow paths (i.e., fractures, conduits) and  
1333 overlapping (fractured) carbonate matrix, thereby developing more integrated karst modelling  
1334 approaches that simultaneously consider flow, transport, and (bio)geochemical reactions in karst  
1335 systems.



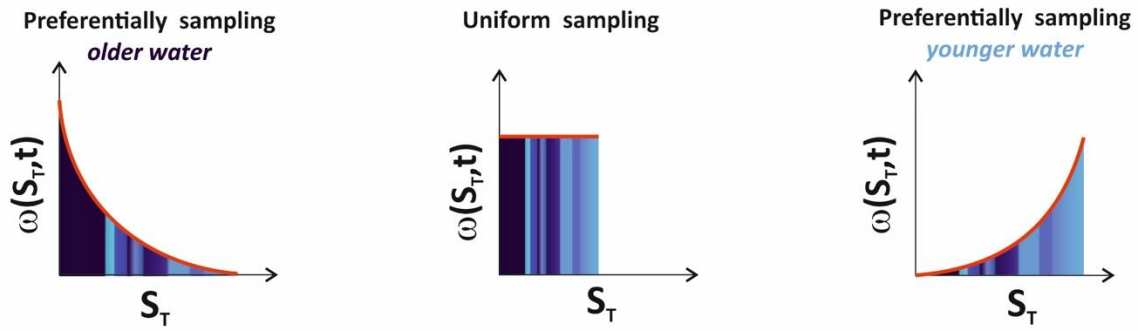
1336 Karst scientists and water authorities are collecting more data than ever before. However,  
1337 the collected data are rarely published and shared with the community, especially those used for  
1338 flow and transport modelling studies (i.e., karst spring  $\delta^{18}\text{O}$  isotope ratios). Some working  
1339 groups under specified goals, for instance SISAL (Speleothem Isotope Synthesis and Analysis),  
1340 provide a readily available global database for the speleothem isotopes collected from individual  
1341 speleothems and grouped them by the cave locations across the world (Atsawawaranunt et al.,  
1342 2018; Comas-Bru et al., 2020; Kaushal et al., 2023). There is, therefore, a need for the common  
1343 database in which we can gather the original data on karst transport dynamics from different  
1344 experimental and modelling works (i.e., tracer tests, hydrochemical studies, hydraulic tests, cave  
1345 isotopic and hydrochemical experiments) similar to the few and valuable attempts to collect and  
1346 provide karst data by Jourde et al. (2018), Petrič et al. (2020), Olarinoye et al. (2020).

#### 1347 5.2 Fill the gap between oversimplified LTMs and data-demanding ATMs

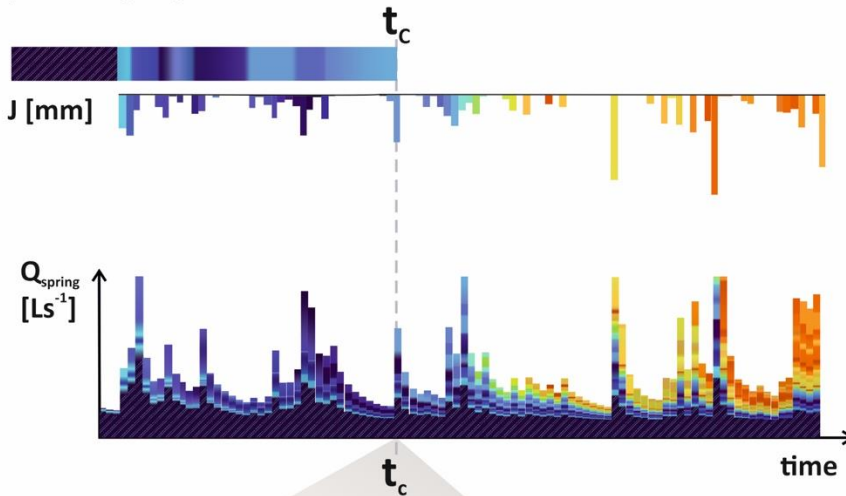
1348 The critical discussion on how to find a tradeoff between the model complexity and the  
1349 choice of a right process controlling the system's physicochemical behavior (with a reasonable  
1350 number of parameters) with respect to the data availability is a requirement for a completion of  
1351 the successful transport modelling practice in karst systems. Due to suitability in data-rare sites,  
1352 mathematically simpler LTMs have outpaced their sophisticated ATM fellows that are  
1353 represented by more variables with multiple parameters. But although the LTMs are often served  
1354 as valuable heuristic tools for modelling karst transport processes, they are still the most  
1355 simplistic approach in representing rather complicated karst transport dynamics. By comparison,  
1356 due to the (substantial) data need, ATMs are often inapplicable for resembling the karst transport  
1357 dynamics, especially for the larger scale field applications. Therefore, we see a particular need  
1358 for representing karst transport processes with more-process oriented and well-constrained  
1359 models that can be used for alternative modeling approaches to better resemble the  
1360 spatiotemporal dynamics of contaminant migration in karst systems.

1361 In this direction, this review reveals that there is an emerging modelling concept that is  
1362 coming outside of the karst. StorAge Selection (SAS) Function Approach (hereinafter referred to  
1363 the SAS model) can be an alternative approach to simulate the karst transport dynamics (Figure  
1364 14). The SAS theory was built by Botter (2011), Harman (2015), and Van der Valde et al. (2012)  
1365 for the catchment scale flow and transport modelling applications while the successful  
1366 applications were also extended to simulate the karst transport processes by Zhang et al. (2021)  
1367 and Çallı et al. (2023a). The SAS model defines the relationship between the distribution of  
1368 water ages in the reservoir storage (i.e., soil, groundwater) and the ages exiting as system's  
1369 outflux (either discharge or evapotranspiration, or both) (Figure 14). Compared to LTMs, the  
1370 SAS model considers the time-variant characteristics of TTDs by revealing the time-dependent  
1371 mixing, storage, and discharge characteristics (e.g., Benettin & Bertuzzo, 2018; Botter et al.,  
1372 2011; Botter, 2012; Harman, 2015; Rinaldo et al., 2015; Schwemmler & Weiler, 2024, among  
1373 many others). Therefore, the SAS model is structured by rather less parameters as compared to  
1374 ATMs, and it thus allows better identification of the model parameters while reducing  
1375 overparameterization and equifinality issues.

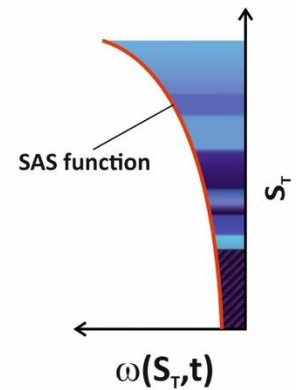
a) StorAge Selection Functions



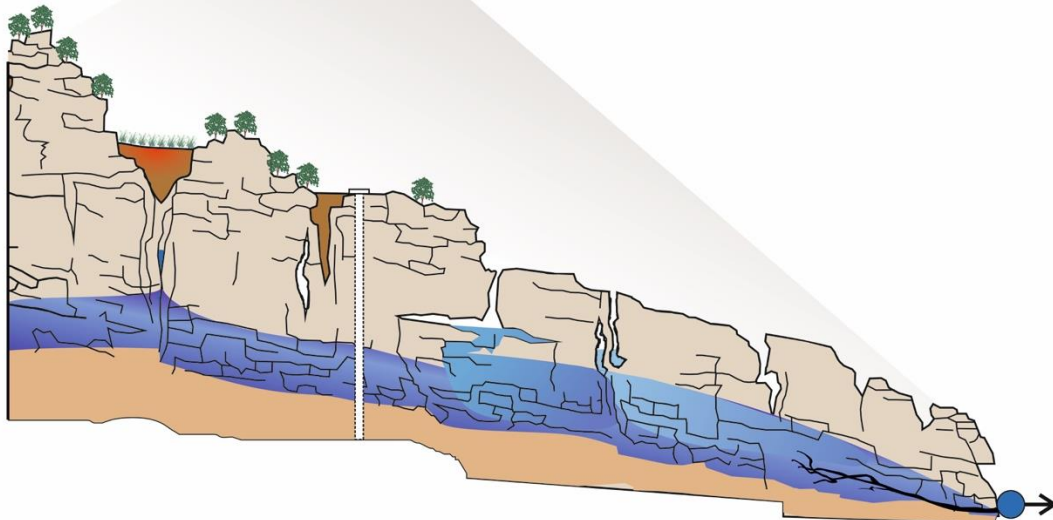
b) Discharge age distribution in time domain



c) Selected functional form for system age distribution



d) Groundwater age distributions at a given time ( $t_c$ )



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**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

1382 adapted for the karst systems based on the SAS model descriptions in Benettin et al. (2022),  
 1383 Harman et al. (2015) and Harman (2019). In the depicted figures,  $S_T$  refers to the age ranked  
 1384 storage that describes the amount of water in storage whose age is younger than (or equal to)  
 1385 certain age  $T$  at current time  $t_c$ .  $\omega(S_T, t)$  is the probability density function of the travel time  
 1386 expressing each water age ( $T$ ) removed from the storage (for further the details see Benettin &  
 1387 Bertuzzo (2018)).

### 1388 5.3 Develop adequate approaches for sediment transport in karst systems

1389 Karst transport model is frequently applied for the predictions of solute transport  
 1390 dynamics in karst systems. However, some agents such as vapor, heat, (suspended) sediments  
 1391 (i.e., particles and colloids) can also play a role in defining solute transport behaviours.  
 1392 Suspended sediments are such agents that are often induced by the turbulent flow along the karst  
 1393 conduits and cave streams (Mueller et al., 2023; Jukić et al., 2022; Richter et al., 2022). In this  
 1394 respect, understanding the (suspended) sediment transport is particularly important for karst  
 1395 transport processes in two ways. First, since (suspended) sediments can adsorb a wide range of  
 1396 contaminant types (i.e., organic substance, hydrocarbons, heavy, and trace metals, biological  
 1397 contaminants), they often act as storage and/or transformation regions for the contaminants  
 1398 (Herman et al., 2012; Mahler et al., 1999, 2000; Mueller et al., 2023). Second, they can attenuate  
 1399 the contaminant of interest as a zone of remobilization (Bettel et al., 2022; Nerantzaki et al.,  
 1400 2015). Furthermore, while the origin of the sediments provides the evidence of transport  
 1401 conditions during the contaminant events taking place (Bosch & White, 2018; Çelik et al., 2022),  
 1402 microbial transport in karst aquifers is frequently approximated by the suspended sediment  
 1403 transport (e.g., Goldscheider et al., 2010; Göppert & Goldscheider, 2008). But the transportation  
 1404 and transformation of the contaminants with the suspended materials are not directly measurable  
 1405 and observable. For these reasons, their characterizations require high-resolution monitoring and  
 1406 suitable technologies. Therefore, future research is recommended to address contaminant fate  
 1407 and transport processes due to the (suspended) sediment and/or particles at high temporal  
 1408 resolution.

### 1409 5.4 Estimate the impact of climate and land use changes on karst water quality

1410 Karst water resources are highly regulated, stressed, and managed by the human  
 1411 dimension, especially by the operational water management (i.e., dam and reservoir capacity)  
 1412 and increased water consumption (i.e., pumping rate, water needs). For this reason, a greater  
 1413 uncertainty is available for the karst system's (natural) hydrological and hydrochemical  
 1414 functioning. In this matter, the impacts of the human-induced factors (i.e., pumping rate, sectoral  
 1415 water needs) on karst flow and transport dynamics need to be considered. But up until now, the  
 1416 human dimension on karst transport dynamics is overlooked and/or underestimated in the real-  
 1417 world applications of karst transport models while the focus is often more on naturalized aquifer  
 1418 conditions. Therefore, coupling the knowledge of human-induced factors with the (naturalized)  
 1419 system dynamics at differing scales under different scenarios (i.e., the impact of groundwater  
 1420 abstraction rates on karst water quality) is one of the key research areas to provide more realistic  
 1421 predictions, as well as to support decision-makers for sustainable water management in karst  
 1422 systems.

1423 Contaminant mixing and transport problems in karst water resources are frequently  
 1424 denoted as (saturated) groundwater zone specific issues, and the role of epikarst in karst transport  
 1425 dynamics is significantly simplified or completely ignored from the (formal) model structures.

1426 Nonetheless, epikarst is a karst critical zone whereby contaminant mixing, storage, and transport  
1427 characteristics are largely controlled (e.g., Dal Soglio et al., 2020; Flynn & Sinreich, 2010; Li et  
1428 al., 2017; Perrin et al., 2003b; Zhang et al., 2017, among many others). Furthermore, as the  
1429 epikarst forms the reactive and biogeochemical processes (i.e., sorption, microbial activities, and  
1430 oxidation), it significantly modifies the (initial) composition of the contaminants released from  
1431 the ground surface before reaching the saturated groundwater table (Druhan et al., 2021; Dubois  
1432 et al., 2014; Oster et al., 2021; Zeqiraj, 2022) while predominantly controlling the karst system's  
1433 (biogeo)chemical functioning (Anna-Neva et al., 2021; Laincz & Hays, 2014; Panno et al.,  
1434 2001). For these reasons, better understanding of epikarst transport dynamics is a fundamental  
1435 need to protect and manage karst water quality and dependent ecosystem functioning.  
1436 Nevertheless, due to the unbearable complexity and substantial heterogeneity of epikarst,  
1437 scientific attempts to develop epikarst-dedicated transport models are quite rare.

1438 Degradation of karst water quality is not only a local scale issue in which we can only  
1439 apply a site-specific solute transport model to predict the spatiotemporal behaviour of  
1440 contaminant migration, but it is also a global phenomenon that we shall further consider global  
1441 changes and their potential impacts on the karst water quality and dependent ecosystems.  
1442 However, to the best of our knowledge, the effects of the global changes on the karst water  
1443 quality in the context of the transport modelling are not adequately addressed at local/global  
1444 scales. For that, the impact of local/global changes on the karst water quality brings us  
1445 fundamental responsibility to make robust predictions under a changing world, despite the  
1446 substantial uncertainty. Therefore, future works call attention to what extent (and how) karst  
1447 transport dynamics can (could be) linked to the altered boundary conditions due to anthropogenic  
1448 factors and global changes such as climate change, land-use and/or land-type changes, soil  
1449 degradation, water management alterations, and groundwater depletion.

## 1450 **6 Conclusions**

1451 The threat of contamination in karst water resources has come to light over the last  
1452 couple of decades. Nonetheless, the multiscale physical and (biogeo)chemical heterogeneities  
1453 still pose an enormous challenge for properly characterizing, understanding, and modelling flow  
1454 and transport dynamics in karst water resources. In this manner, we still have substantial  
1455 limitations in providing more reasonable and reliable transport model predictions, thus handling  
1456 the modelling issues such as parameter scaling, model non-uniqueness, and uncertainty. But  
1457 beyond that, both anthropogenic factors and global changes (i.e., climate change, land use-land  
1458 cover changes, soil degradation, urbanisation, agricultural practices, and water management  
1459 alterations) have been seriously deteriorating the quality of karst water resources and dependent  
1460 ecosystem functioning. As the karst system's functioning both hydrodynamically and  
1461 biogeochemically is controlled by such global changes in a way that they can shape the karst  
1462 flow and transport characteristics, understanding karst transport dynamics is critical to  
1463 successfully predict the impacts of such factors on the water quality and dependent ecosystems.  
1464 With this review, we hope to provide the necessary overview of available methods, challenges  
1465 and directions to support and improve the present and future management of water quality in  
1466 different karst regions across the globe.

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1475 **Open Research**

1476 No original/new data were collected and/or developed for this review. The paper is a synthesis of  
 1477 the published works.

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