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1 **Short-term variations in tracer tests**
2 **responses in a highly karstified watershed**

3 Vianney SIVELLE ^(a), David LABAT ^(a)

4 ^(a) Géosciences Environnement Toulouse, Université Toulouse 3 (Paul Sabatier)

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17 **Corresponding author:**

18 Vianney SIVELLE

19 Géosciences Environnement Toulouse, Université Toulouse 3 (Paul Sabatier)

20 14, avenue Edouard Belin, 31400 Toulouse

21 (+33) 5.61.33.46.04

22 vianney.sivelle@get.omp.eu

23 **Abstract**

24 Modelling non-reactive solute transport based on artificial tracer tests have been widely used
25 in the past decades. The dependence of solute transport from boundary conditions have
26 been investigated across different hydrological conditions (low and high-water level) but still
27 not investigated on short-term scale (i.e. hourly and daily scale). In this study, a campaign of
28 several tracer tests is performed on a few days to investigate the short-term variations of
29 tracer tests responses in a conduit dominated karst system during a recession without the
30 influence of rainfall. Also, an improved artificial tracer test interpretation using a process
31 engineering tool is introduced. It consists of a Laplace-transform transfer function approach
32 of the residence time distribution curve. Considering the karstic system as a chemical
33 reactor, the introduction of a transfer function approach appears to be an efficient way to
34 describe the solute transport. Moreover, the transfer function is parametrized depending on
35 the spring discharge. Finally, the model is extended to deal with source pollution scenario
36 testing.

37 **Keywords:** artificial tracer test, karstic system, transfer function, pollution scenario

38 **1 Introduction**

39 Karstic systems consist of calcareous formations (carbonate rocks) in which the karstification
40 process takes place. Three types of energy must be dispelled (Quinif, 1999): (1) mechanical
41 actions create fissures and fractures that constitute a preferential underground pathway for
42 water; (2) water-dissolved CO₂ reacts with carbonate rocks, and CO₂ partial pressure
43 governs the rock dissolution potential (Dreybrodt, 1988); (3) water flows due to a hydraulic
44 gradient between the inlet and outlet of the system (Mangin, 1975). This gradient controls
45 water flow and dynamics in karstic systems (Delannoy, 1997; Jeannin, 1998; Mangin, 1984).
46 Then, the process of karstification generates a subterranean network of cavities and drifts.
47 This also leads to typical surface landscapes with geomorphological features such as dolines
48 and karrens.

49 Artificial tracer tests is one of the most powerfull tools to study the conduit flow dynamics and
50 have been widely used to study the solute transport in conduit dominated karst aquifers (Birk
51 et al., 2005; Duran et al., 2016; Ender et al., 2018; Field and Pinsky, 2000; Goldscheider et
52 al., 2008; Göppert and Goldscheider, 2007; Labat and Mangin, 2015; Massei et al., 2006;
53 Morales et al., 2010). Solute transport is investigated under various hydrological conditions
54 (i.e. low and high-water level, following “dry” or “rainy” periods). Then, modelling the solute
55 transport includes knowledge about boundary conditions and their influence on the transport
56 parameters (Cholet, 2017; Duran et al., 2016; Ender et al., 2018). This has been investigated
57 over the hydrological cycle but remains not investigated on a short-term scale (i.e. hourly and
58 daily scale).

59 To improve the understanding of the effect of short-term variations in boundary conditions,
60 11 tracer tests were performed over two weeks without significant influence of rainfall. These
61 operations were performed with a certain temporal repartition to investigate the hourly and
62 daily change in tracer tests response. We assume to summarize variations in boundary
63 conditions through variations in the spring discharge. Also, as the tracer tests were
64 performed in close hydrological conditions, we attempt to discriminate the effect of short-term

65 variation in tracer test response. Therefore, the following items are examined: (1) a transfer
66 function approach is introduced to simulate non-reactive solute transport in a highly karstified
67 watershed; (2) assessment of short-term (from hourly to daily scale) variations in tracer tests
68 responses and (3) a new method is proposed to predict the solute transport between a
69 preferential infiltration point in the watershed (typically a loss) and the outlet of the
70 watershed.

71 **2 Materials and methods**

72 **2.1 Artificial tracer tests in karstic systems**

73 Artificial tracer tests enable analysis of the time of transit of a tracer in a karstic system.
74 Basically, it consists of an injection of a known quantity of tracer, and the careful analysis of
75 the curve for tracer restitution at the outlet, often called a tracer breakthrough curve (BTC). If
76 a mass of tracer denoted M is added to the system at time $t = 0$, then the concentration at
77 the outlet will be a function of time, denoted $C_{out}(t)$. After an infinite time, because of mass
78 conservation, the recovered mass of tracer is given by Eqn (1).

$$79 \quad M = \int_{t=0}^{t=\infty} C_{out}(t) \cdot Q(t) \cdot dt$$

80 **(1)**

81 where $Q(t)$ is the spring flow as a function of time (m^3/s) and $C_{out}(t)$ is the concentration
82 measured at the outlet of the system as a function of time (g/m^3). Because of natural
83 heterogeneities and experimental approach, the mass conservation is rarely observed.
84 Artificial tracer tests in karstic media often show a recovery of about 80% in high water level
85 and around 20% in low water level. The reason of the discrepancy in recovery rate is still
86 subject to investigation.

87 Fig. 1 shows a conceptual scheme for artificial tracer tests operated over a karstic system.
88 The tracer response is formulated as an unsteady material balance, in terms of a linear
89 differential equation with a constant coefficient that relates an input function $C_{in}(t)$ to a
90 response function $C_{out}(t)$. The general form of the material balance is:

91 **Inputs + Sources = Outputs + Sinks + Accumulations**
 92 **(2)**

93 where inputs are the mass of tracer added by an operator, sources are the mass naturally
 94 present in the environment, outputs are the mass recovered at the measurement station,
 95 sinks are the mass reaching one or several non-monitored outlets of the drainage system
 96 and accumulations are the mass temporally stored in the drainage system. Sinks and
 97 accumulations can both be non-negligible in karstic systems. Considering multiple
 98 underground water pathways, part of the tracer could flow to several outputs (Luhmann et al.,
 99 2012) or could be temporally stored in immobile fluid regions (Dewaide et al., 2017;
 100 Goldscheider, 2008; Morales et al., 2010). Also, multiple peaked RTD curves could give
 101 evidence of multiple flow dynamics in the tracing system or multiple flow path (Field and Leij,
 102 2012; Filippini et al., 2018; Vincenzi et al., 2011).

103 The residence time distribution (RTD), denoted $E(t)$ (s^{-1}), is derived from the concentration
 104 curve, denoted $C_{out}(t)$. It measures how long a tracer particle stays in the system and
 105 represents the probability density function for a water molecule to stay in the system during a
 106 period t (Jury and Roth, 1990). The $E(t)$ curve corresponds to normalization of the C curve to
 107 unity. Thus, in the case of a tracer system without dead space, the concentration can simply
 108 be divided:

109
$$E(t) = \frac{C_{out}(t)}{M/v} = \frac{C_{out}(t).Q(t)}{\int_{t=0}^{t=\infty} C_{out}(t).Q(t)dt}$$
 where $\int_{t=0}^{t=\infty} E(t)dt = 1$

110 **(3)**

111 where $C_{out}(t)$ (t) is the concentration as a function of time (g/m^3), M is the mass of tracer
 112 injected (g) and v is the mean flow rate (m^3/s). If the tracer is injected on period sufficiently
 113 short to be considered as instantaneous (i.e. the injection is close to a Dirac function) the
 114 observed RTD corresponds to the impulse response of the system.

115 One of the most frequently used methods for artificial tracer test interpretation is based on
 116 the advection-dispersion equation (ADE) introduced by Wang et al. (1987), and then

117 implemented in CXTFIT (Toride et al., 1995), QTRACER (Field, 2002; Field and Pinsky,
118 2000) and STANDMOD (Van Genuchten et al., 2012). The model is based on a
119 dimensionless Peclet's numbers. It corresponds to the product of the length of flow and the
120 mean velocity divided by the diffusivity and so roughly correspond to the Reynolds number
121 but in term of porous media. ADE models allow determining the dispersivity coefficient which
122 is dependent from boundary conditions (Duran et al., 2016; Massei et al., 2006) and from
123 flow pathway (Ender et al., 2018; Lauber et al., 2014). The physical signification of
124 parameters such as flow velocity and dispersivity can be questionable when it represents
125 flow processes in karstic areas over several kilometres. Applications of ADE models assume
126 that both the flow velocity and the dispersivity are constant in the system, but this is a
127 condition rarely observed in karstic media. Because of high structural heterogeneities, the
128 water flow velocity may present a spatial variation. This may influence the solute transport in
129 the different compartment of the system (Ender et al., 2018). Nonetheless the physical
130 signification of transport parameters in ADE models can be improved when the flow is
131 segmented into sections, widely called "reach", where the flow conditions can be
132 homogenous (Dewaide et al., 2017, 2016; Ender et al., 2018; Lauber et al., 2014). Here, as
133 the underground drainage structure is not well constrained, a transfer function approach is
134 chosen. It provides a framework including all processes (advection, diffusion, dispersion and
135 mixing) in an assembly of conceptual reservoirs.

136 **2.2 Tracer tests interpretation: a comparison with chemical engineering**

137 Chemical engineering consists of all activities concerned with the exploitation of chemical
138 reactions on an industrial scale (Levenspiel, 1999). These industrial processes are based on
139 the concept of elementary reactors assembly to run material transformations. The flow
140 behaviour of such reactors can be described based on a lumped model (Amin and Campana,
141 1996). This has been applied to the natural system, where the transit time can be estimated
142 through the probability density function (PDF) of time residency (Bolin and Rodhe, 1973;
143 Cornaton and Perrochet, 2006; Małoszewski and Zuber, 1982).

144 There may be several analogies between the structure present in karst aquifers and
145 chemical reactor. An empty tubular reactor can be simulated as a plug flow reactor, often
146 denoted as PFR (Walas, 2005). In karstic media, it corresponds to a piston effect (Bovolin et
147 al., 2017; Milanović, 2014). A stirred tank can be modelled by considering bypass zones,
148 stagnant zones and other parameters associated with the geometry of the vessels. In karstic
149 media, structures such as drains play the role of bypass zones, and annexe systems
150 constitute stagnant zones that could be connected to the main drainage system (Mangin,
151 1984; Marsaud, 1997). In the case of non-ideal reactors the flow conditions could be derived
152 from tracer test operations. The experimental RTD shape gives information about the main
153 flow and transport processes (Levenspiel, 2012; Walas, 2005).

154 As suggested by Becker and Bellin (2013), "*water moves through a series of different*
155 *elements that can be conceptualized as reservoirs or conduits, such as the epikarst,*
156 *fractures, open joints, pipes, solution conduits, pools, etc*". By analogy with process
157 engineering, a karstic system can be assimilated to a reservoir or an assembly of elementary
158 reservoirs. In this way, a karstic system could be studied as if it was a chemical reactor.
159 Nonetheless, in the case of a fluorescent dye tracer test, there is no material transformation
160 along water flow. Here, we focus on an approach widely used in chemical engineering to
161 study flow dynamics in chemical reactors from tracer tests. We do not consider any material
162 transformation but only mixing and transport.

163 **Otherwise, this approach suffers from certain limitations. In industrial process engineering,**
164 **the chemical reactors characteristics are known. So, the chemical reactors are designed to**
165 **meet clearly-defined expectations. Then, tracer tests allow checking that reactors respond to**
166 **these expectations. On the contrary, in the karstic system study, it is difficult to understand**
167 **the geometrical arrangement of subterranean water flow. So, here it is proposed to use a**
168 **process engineering approach for interpretation of artificial tracer tests in a conduit**
169 **dominated karstic aquifer.**

170 **2.3 Proposal for a reservoir model for solute transport in conduit dominated**
171 **flow**

172 As shown in the previous part, karstic systems can be considered as an assembly of
173 elementary reservoirs: water mixing takes place in a different compartment of the karstic
174 system, leading to transformations between input and output signals. In this study, only the
175 mixing between water and fluorescent dyes is considered. The input signal is a Dirac
176 function, i.e. the injection period is extremely short compared to the mean residence time of
177 the tracer in the system. The output signal is the experimental RTD derived from the
178 concentration curve (BTC). The ratio between the input signal and the output signal in the
179 Laplacian concept is called the transfer function, denoted $H(p)$ (Walas, 2005):

180 $\mathbf{H(p) = C_{out}(p)/C_{in}(p)}$

181 **(4)**

182 $\mathbf{H(p) = \mathcal{L}\{H(t)\} = \int_0^{\infty} e^{-p \cdot t} \cdot H(t) \cdot dt}$

183 **(5)**

184 where $C_{in}(p)$ is the Laplace transform of the entrance, $C_{out}(p)$ is the Laplace transform of the
185 outlet, p is the Laplace complex variable and $\mathcal{L}\{H(t)\}$ is the Laplace transform of the $H(t)$
186 function. Also, $E(t)$ and $C_{out}(t)$ differ only by a constant, and the Laplace transform of a Dirac
187 function is equal to 1. The a synthetic RTD, denoted $E^*(t)$, can be calculated from the inverse
188 Laplace transform of the transfer function with the Mellin's inverse formula:

189 $\mathbf{E^*(t) = \mathcal{L}^{-1}\{H(p)\} = \frac{1}{2\pi i} \lim_{T \rightarrow \infty} \int_{\gamma - iT}^{\gamma + iT} e^{p \cdot t} \cdot C_{out}(p) \cdot dp}$

190 **(6)**

191 where $E^*(t)$ is the simulated RTD in response to a Dirac function input for a system whose
192 transfer function is $H(p)$, and $\mathcal{L}^{-1}\{H(p)\}$ is the inverse Laplace transform of the $H(p)$ transfer
193 function. $H(p)$ is also called the impulse response of the system.

194 The transfer function formalism has been little used for artificial tracer test interpretation in
 195 karstic area. Only a few studies proposed this approach. Leibundgut (1998) proposed a
 196 dimensionless transfer function linking the peak of concentrations, the time of tracer peak
 197 and the standard deviation of the mean residence times to the discharge. Then, a synthetic
 198 tracer BTC can be proposed. Becker and Bellin (2013) proposed a conceptual model based
 199 on an assembly of several reservoirs in series, partitioning mass transfer between mobile
 200 and immobile zones. It consists of the transfer function approach of the Mobile-Immobile
 201 Model (Toride et al., 1993). Labat and Mangin (2015) split mass-transfer between fast and
 202 slow component. Nonetheless, their transfer function does not include a piston effect
 203 allowing to model the delay between slow and fast component. If tracer particles are
 204 transported by different flow dynamics, why do both slow and fast component restitutions
 205 start at the same time?

206 In this study, two perfect reactor models are considered: the plug flow reactor (PFR) and the
 207 mixed flow reactor (MFR). The corresponding transfer function is given in Eqn (7) and Eqn
 208 (8) (Levenspiel, 2012; Walas, 2005).

- 209 • mixed flow reactor (MFR):

$$210 \quad \mathbf{H}(\mathbf{p}) = \frac{1}{1 + \bar{t} * \mathbf{p}}$$

211 **(7)**

- 212 • plug flow reactor (PFR):

$$213 \quad \mathbf{H}(\mathbf{p}) = \exp(-\bar{t} * \mathbf{p}) \tag{8}$$

214 where \bar{t} is the mean residence time.

215 Here, we propose a composite transfer function corresponding to an assembly of MFR and
 216 PFR:

$$217 \quad \mathbf{H}(\mathbf{p}) = \sum_{i=1}^k \left[\alpha_i * \left(\frac{1}{1 + A_i * \mathbf{p}} \right)^N * \exp(-\tau_i * \mathbf{p}) \right] \tag{9}$$

218 where:

- 219 - k is an integer value corresponding to the number of flow components used in the
 220 model. So, it allows an extension of the model in case of complex RTD curves,
 221 with multiple parallel flow components due to friction effects (Massei et al., 2006)
 222 or flow partition between fast and slow flow (Labat and Mangin, 2015).
- 223 - α_i consists in the contribution of the flow component in the total tracer recovery
 224 and by construction $\sum \alpha_i = \int_{t=0}^{t=\infty} E(t) dt = 1$
- 225 - A is the mixing coefficient. In case of a perfect mixed flow reactor, it is equal to the
 226 mean time of residence of the tracer in the system. The corresponding transfer
 227 function is given in Eqn (7) (Levenspiel, 2012).
- 228 - N corresponds, from a conceptual point of view, to several reservoirs in cascade.
 229 In case of N is an integer value, it corresponds to a Nash cascade (Nash, 1957).
 230 Here, the Laplace framework allows to easily handle cases with non-integer N
 231 values belonging to R^+ .
- 232 - τ is the time of transit for each of the sub-function. That is the time between the
 233 injection of the tracer into the system and its detection at the outlet. This is a delay
 234 which is classically expressed by an exponential function with a negative
 235 coefficient in the Laplace plane. When τ is equal to the mean time of residence, it
 236 corresponds to a PFR whose transfer function given in Eqn (8).

237 As the inverse Laplace transform cannot be operated analytically, we use the algorithm
 238 described by De Hoog et al. (1982) and implemented in MATLAB by Hollenbeck (1998).
 239 Then, an optimization procedure allows the definition of the best parameters for the model.
 240 This consists of the application of a particle swarm optimization (PSO) procedure (Kennedy
 241 and Eberhart, 1995) implemented in MATLAB (Global Optimization Toolbox). The cost
 242 function to reduce between observed and simulated RTD curves is based on a normalized
 243 root mean square error (NRMSE).

244
$$\mathbf{RMSE} = \sqrt{\frac{\sum_{i=1}^n (y_{obs}(i) - y_{sim}(i))^2}{n}} \quad (10)$$

245
$$\mathbf{NRMSE} = \frac{\mathbf{RMSE}}{\max(y_{obs}) - \min(y_{obs})} \quad (11)$$

246 where $y_{sim}(i)$ is the simulated discretized time series, $y_{obs}(i)$ is the observed discretized
 247 time series and n is the number of data.

248 At this stage, it is important to insist that ‘tracing systems’ should not be confused with
 249 ‘karstic systems’ as already mentioned in Fig. 1. Then, in term of transfer function approach,
 250 this implies that one transfer function runs for one tracing system whereas one karstic
 251 system can contain several tracing systems, and so must be described by several transfer
 252 functions that can be in series or in derivation.

253 **3 Studied area and tracer test campaign**

254 We applied the transfer function approach to several artificial tracer tests over the Baget
 255 karstic watershed (Fig. 2), part of the SNO Karst consortium (INSU-CNRS). This basin,
 256 located in the Pyrenees Mountains (Ariège, France), is characterized by a median altitude of
 257 about 940 m and an area of around 13 km². It belongs to the carbonated belt bordering the
 258 north of the French Pyrenees. The area is affected by the Alas fault: Jurassic to Cretaceous
 259 metamorphic limestone dips 45° to 75° under slaty flysch on the southern border. Jurassic
 260 and Palaeozoic metamorphic dolomite and flysch constitute the northern border of the
 261 watershed (Debroas, 2009). The valley is oriented in a west-east direction, following the
 262 contact between karstified calcareous formations and impervious flysch. In the upper part of
 263 the watershed, the Lachein river flows during periods of the high-water level. As mentioned
 264 by Mangin (1975) and Marsaud (1997), the Baget karstic system is composed of so-called
 265 “main drainage” and “annexe drainage” systems. The main drainage system consists of the
 266 most transmissive part with short residence time, whereas the annexe drainage system
 267 (ADS) would physically correspond to voids and caves connected to the main drainage
 268 systems characterized by a much longer residence time.

269 The Baget watershed has already been studied based on artificial tracer tests interpretation
270 (Labat and Mangin, 2015). The study was based on classical artificial tracer tests with
271 separated instantaneous injections. Here, a new field campaign is carried out with 11 tracer
272 tests performed in April 2018 using fluorescein. Tracer tests were performed during a period
273 without an important influence of rainfall, so there was not a high degree of fluctuation on the
274 outlet discharge during the tracer recovery. During the tracer tests campaign the discharge
275 rate varies from $0.9 \text{ m}^3/\text{s}$ at the beginning of the first injection (used as calibration tracer test)
276 down to around $0.45 \text{ m}^3/\text{s}$ at the beginning of the second injection campaign. Then the
277 discharge rate has gradually decreased down to $0.3 \text{ m}^3/\text{s}$ at the end of the campaign.
278 Therefore, the discharge rate has decreased by 33% during the 7 days long tracer tests
279 campaign. A field fluorimeter GGUN-FL30 (Schneegg, 2002) was installed in station B1 on the
280 12th of April 2018 and programmed to measure on a 15 minutes sampling rate until the 21st
281 of April 2018. During the same period, the time interval for water sampling was adjusted for
282 60 minutes. Fluorescence measurement and water sampling were done near the station B1,
283 where the discharge is measured since the late 1970s (Mangin, 1975). Water samples were
284 analysed by the CETRAHE laboratory (Orléans, France) using spectrofluorimeter Hitachi
285 F2500 and F7000. The characteristics of tracer tests are summarized in Table 1, and the
286 injection-recovery (RTD) time series are placed in the rainfall-runoff time series in Fig. 3.

287 The injection point, called P2 Loss, was chosen so the tracer reached the subterranean
288 drainage system rapidly. This led us to approach instantaneous injection (Dirac function)
289 which is the basic hypothesis for artificial tracer tests interpretation. Both injection site, called
290 P2 Loss, and recovery site, called B1, are in the downstream part of the watershed (Fig. 2). It
291 is characterized by the presence of losses and of temporary or permanent resurgences in a
292 spatially limited area of about 2 km^2 . We should note that, during periods with high water
293 levels, P2 Loss could run as a temporary resurgence. During tracer tests it was running as a
294 loss, allowing quick tracer infiltration in the drainage system.

295 The tracer tests were performed on a period overlapping two states of the watershed: (1)
296 from the 8 April 2018 to the 17 April 2018 the temporary resurgence of Moulo de Jaur is
297 activated (Figure 2 - b) and (2) as the water level dropped, the temporary resurgence is
298 deactivated until the end of the tracer tests. As the tracer tests were performed during a
299 period overlapping the transition between these two states of the watershed, we try to assess
300 if this change in the global hydrodynamic behaviour has an impact on the solute transport
301 through artificial tracer tests responses.

302 **4 Results**

303 **4.1 Calibration of the transfer function parameters**

304 The first tracer test was performed on the 12 April 2018 as a classical artificial tracer test
305 operation. This tracer test has two goals: (1) it gives preliminary information about flow
306 dynamics to prepare the tracer tests campaign and (2) it is used to calibrate the transfer
307 function model. The injection of 500 g of fluorescein is made in P2 Loss on a short period to
308 get close from a Dirac function. Then, any other injection was performed before tracer
309 concentration back to zero. The BTC shows a maximum concentration value of 23.7 $\mu\text{g/L}$
310 and a strong asymmetry with a rapid climb lasting about 3 hours and an important tailing
311 effect lasting about 65 hours long. This can be interpreted as the coexistence of multiple flow
312 processes: (1) a fast flow component with rapid transit time dominated by a plug flow effects
313 leading to a high tracer concentration on a short period and (2) a slow flow component
314 dominated by mixing and diffusivity leading to less important concentration on longer period
315 (Labat and Mangin, 2015; Massei et al., 2006). Also, tailing effects can be associated with
316 the existence of immobile water zone, corresponding to dead spaces were part of the tracer
317 mass could be temporarily stored (Becker and Bellin, 2013; Field and Leij, 2012;
318 Goldscheider, 2008; Zhao et al., 2017).

319 The first tracer test is used to calibrate the transfer function parameters using PSO
320 procedure (Fig. 4). The simulated RTD is composed of three sub-functions. These sub-
321 functions, noted from component 1 to component 3, represent respectively 40%, 32% and

322 28% of the total mass transport. These successive sub-functions show a different time of
323 transit in the studied tracing system, namely the volume of the drainage system sought
324 during mass transport between the injection site and recovery site. The transit time of the first
325 component is 75 min whereas the transit time for the two following sub-functions are
326 respectively about 92 min and 110 min. Then, considering an apparent distance of 850 m
327 between injection and recovery sites, the apparent flow velocity is respectively of 11.3 m/min,
328 9.2 m/min and 7.8 m/min. Also, the mixing coefficient A is equal to 47.8 and N is equal to
329 3.88. These coefficients are in the same order of magnitude as for the Norville chalk aquifer
330 when the spring discharge is high (Sivelle et al., 2018).

331 Following this first tracer test, ten other tracer injections were performed at various time
332 interval constituting a complex input signal. Each of these injections is made on a short
333 period to get close from a Dirac function, in the same way as for the calibration tracer test. As
334 the time between each injection is low, there is overlapping of BTC at the outlet. Also, as
335 there is no rainfall during tracer tests, the temporal variation in boundary conditions might be
336 summarized through outlet discharge decrease because of the watershed emptying. This
337 has been observed on the field through the deactivation of the temporary resurgence called
338 Moulo de Jaur (Fig 2 - b). Then, the output signal is deconvoluted using transfer function
339 approach to identify the RTD associated to each tracer injection and to highlight potential
340 non-stationarity or non-linearity.

341 **4.2 Running deconvolution of the RTD**

342 To estimate the outlet recovery signal, one needs to run a convolution with the transfer
343 function model. Here, we cannot run a classical convolution operator as the signal is
344 composed of a succession of so-called Dirac function. As for each injection all frequency is
345 sought this could not be described with a Fourier transform. Here, the simulated output signal
346 is considered as a summation of the contribution of the RTD corresponding to each tracer
347 injection shifted in time on the total signal measured at the outlet.

348 In case of a linear system, with steady-state conditions, the transfer function of a system
349 must be efficient regardless of time and of boundary conditions. Dealing with a natural flow in
350 karstic aquifers is a complex task because temporal and spatial variations in boundary
351 conditions may have a strong effect on the solute transport. Several studies have shown the
352 effect of boundary conditions variations on solute transport based on artificial tracer tests
353 performed in contrasted hydrological conditions. The variability of solute transport between
354 high and low water level is well documented in the literature (Doummar et al., 2018; Duran et
355 al., 2016, 2015; Ender et al., 2018). Also, these studies deal with solute transport variability
356 at the hydrological cycle. In this study, artificial tracer tests were carried out in a few days
357 period, without the influence of rainfall. Otherwise, the Baget watershed is not subject to tidal
358 influence that can influence flow transport on the half-daily scale (Duran et al., 2016). So, as
359 the hydrological conditions appear to be quite similar for each tracer tests, it could be
360 possible to analyse more precisely the effect of conduit flow dynamics on the solute transport
361 in the karstic conduit at hourly scale.

362 To investigate if solute transport can be influenced at a flood scale, the hypothesis of the
363 linearity and stationarity of the system has been tested (Fig. 5 - A). If solute transport is
364 considered not to be influenced by short-term variations in boundary conditions, at a daily
365 scale, initial calibration of the transfer function appears not to be enough to model the outlet
366 signal. Also, the variation in travel time might be considered in the transfer function (Fig. 5 –
367 B). So, one needs to find the relation between transit time and discharge rate. Here, as all
368 tracer tests were performed in close hydrological conditions, the relation between outlet
369 discharge rate and transit time might be quite simple. As there is no important variation of the
370 spring discharge, we could consider that the discharge measured at the outlet can be
371 enough to correctly describe tracer transit time between input and output of the studied
372 tracing system. Transit time is determined from the BTC curve for tracer tests 1, 2, 3, 8 and
373 9. These tests were performed such the tracer concentration at the outlet is sufficiently low to
374 allow discrimination of a new arrival of the tracer. Transit time for tracer tests 4, 5, 6, 7, 10

375 and 11 could not be classically determined because of important interference of tracer
376 restitution of each tracer injections. So, they have been determined from the experimental
377 relationship between time of transit for tracer tests 1, 2, 3, 8 and 9 and corresponding outlet
378 discharge. The relation is given by the Eqn (12) (Fig. 6).

$$379 \quad \tau \text{ (hour)} = \begin{cases} -33.72 * Q + 15.94, & Q_{inj} < 0.36 \text{ m}^3/\text{s} \\ -4.02 * Q + 4.98, & Q_{inj} \geq 0.36 \text{ m}^3/\text{s} \end{cases} \quad (12)$$

380 Where τ is the transit time (hour) and Q (m^3/s) is the discharge measured at the outlet when
381 the tracer is added to the system. We have shown previously that the tracer tests were
382 performed during a period overlapping a change in the global hydrodynamic watershed
383 behaviour with deactivation of a temporary resurgence when the outlet discharge drops
384 under $0.440 \text{ m}^3/\text{s}$. This is also observed in the apparent transport velocity of the tracer. So,
385 the model is naturally composed of a linear relation with a different coefficient, depending if
386 the temporary resurgence Moulo de Jaur is activated or not.

387 Also, it appears that the mixing coefficient shows variability depending on the outlet
388 discharge rate. The previous study has shown that the mixing coefficient could be linked to
389 the outlet discharge in case of a conduit dominated flow (Sivelle et al., 2018). As the
390 discharge rate has decreased by 33% during the tracer tests campaign, the variation is
391 considered sufficient to impact the solute transport. Here, the relation between the mixing
392 coefficient A and the outlet discharge is considered as an *a priori* for the transfer function
393 parametrization. Several regression equations have been tested and linear regression
394 appears to be the more suitable solution. The parameters of the regression are part of the
395 optimization procedure. Also, it allows reducing the number of parameters to optimize.
396 Basically, the model needs an A value for each tracer injection, in this case 11. Here, it is
397 reduced to 2 parameters and allow to expand the model for source pollution scenario testing
398 for different outlet discharge rate. Then, the relation between the mixing coefficient and outlet
399 discharge is given by Eqn (13) (Fig. 6).

$$400 \quad A = 48.06 * Q + 14.89 \quad (13)$$

401 Where A is the mixing coefficient in the transfer function and Q (m³/s) is the discharge
402 measured at the outlet when the tracer is added to the system.

403 So, the transfer function now includes parameters variations directly linked to the boundary
404 conditions, described through the outlet discharge. The transfer function is now expressed by
405 Eqn (14).

$$406 \quad \mathbf{H}(\mathbf{p}) = \sum_{i=1}^k \left[\alpha_i * \left(\frac{1}{1 + A(\mathbf{q})^i * \mathbf{p}} \right)^N * \exp(-\tau(\mathbf{q})_i * \mathbf{p}) \right] \quad (14)$$

407 As a result, considering the effects of changes in discharge rate allows a better simulation of
408 the outlet signal (Fig. 5 - C). It appears that the transfer function might include part of the
409 temporal variations of the boundary conditions, even at a recession scale. In this case it
410 occurs on a few days without the influence of rainfall. It has been possible to find a relation
411 between transfer function parameters and outlet discharge to improve the description of the
412 solute transport in karst conduit. The output signal has been deconvoluted using a transfer
413 function approach to identify each impulse response from a complex input signal. The signal
414 has been simulated with an acceptable confidence level (NRMSE = 0.03 and NSE = 0.97)
415 between observed and simulated data. Results of the parametrization are summarized in
416 table 2 and corresponding normalized simulated RTD are shown in Fig. 7. Also,
417 deconvolution of the global outlet signal allows discriminating the mixing effect of three
418 different flow dynamics depending on the apparent velocity (Fig. 8). This differentiation in
419 solute transport can be explained by friction effects (Massei et al., 2006) or by the spatial
420 arrangement of the water flow throughout the transport between inlet and outlet (Field and
421 Leij, 2012; Hauns et al., 2001)

422 **4.3 Testing a pollution scenario**

423 Considering the non-linear and non-stationary hydrodynamic behaviour in karst conduit, an
424 efficient scenario testing should include these special features, and their influence on solute
425 transport. Also, several questions must be answered in vulnerability assessment: (1) when
426 the contamination will arrive at the target, (2) at what concentration level and (3) how long

427 the contaminant will last (Goldscheider, 2004; Iván and Mádl-Szőnyi, 2017). The VULK
428 method (Jeannin et al., 2001) was the first process based on vulnerability mapping. The main
429 idea of the method consists in modelling the breakthrough curve of a conservative
430 contaminant along the water pathway, separated in the sub-system. Nonetheless, the
431 possibility to consider a concentrated infiltration is not implemented into the original model. In
432 this study, a transfer function approach is used to model the solute transport in a karstic
433 area, based on artificial tracer tests performed from a loss, allowing quick infiltration in the
434 main drainage system. The model allows to correctly describe the residence time distribution
435 of a non-reactive tracer, and by extension of a potential contaminant with the same
436 behaviour. The model proposed here remains valid for solute transport occurring between
437 injection and recovery sites in a specific range of hydrological conditions. So, in term of
438 vulnerability assessment, the model proposed here may be classified as source vulnerability
439 and could help to prevent accidental pollution (Kavouri et al., 2011). As the model include a
440 dependence from the outlet discharge it is possible to investigate pollution scenario across
441 various hydrological conditions. The source vulnerability evolves across time depending on
442 the boundary conditions. These have an influence on a multi-temporal scale range, from the
443 daily scale (recessional following a rainfall event) to annual scale (between high and low
444 water level).

445 A primary approach in modelling RTD curves for various flood event consists in applying
446 transfer function approach to an input signal different from classical Dirac function
447 considering the discharge variation while tracer (or contaminant) is supposed to be added in
448 the system. Here, the solute transport transfer function proposed have been calibrated in a
449 specific range of spring discharge, during a recession where spring discharge decreases
450 from 0.9 m³/s down to 0.3 m³/s. The pollution scenario is tested on recession events with
451 spring discharge in the same order of magnitude. To do so, 17 recessions close to the one
452 observed during tracer tests have been identified (Fig. 9). These recessions checked the
453 following conditions: (1) the recession last more than four days, (2) the initial discharge is

454 about $0.9 \text{ m}^3/\text{s}$ and (3) the final discharge is above $0.3 \text{ m}^3/\text{s}$. Thus, the scenario of pollution is
455 tested in conditions close to the one investigated though artificial tracer tests. The scenario
456 consists of infiltration at a constant concentration lasting 6 hours. As the recession coefficient
457 varies between all the recession event, the effects of discharge decrease during contaminant
458 infiltration and transport may be different. To asses these effects we ran the model on the 17
459 flood recessions and show some results in Fig. 10. The first scenario (Fig. 10 - a), with a
460 mean discharge rate of around $0.7 \text{ m}^3/\text{s}$, shows that neglecting the discharge variation can
461 lead to underestimating the peak of concentration. Nonetheless, in this scenario the time of
462 transit and the duration of restitution appears to be quite good. Two other scenarios (Fig. 10
463 – b and c), with mean discharge rate of around $0.4 \text{ m}^3/\text{s}$, show that neglecting discharge
464 variations can lead to significative errors in transit time estimation. This is a consequence of
465 the ceiling effect present in Eqn 12 (Fig. 6) and highlights the effect of non-linearity in karstic
466 media on solute transport.

467 **5 Discussion**

468 **5.1 Model application**

469 The model proposed here is based on a transfer function approach. The parametrization is
470 derived from artificial tracer tests performed in close hydrological conditions. The main
471 objective was to assess the effect of short-term variations in boundary condition on artificial
472 tracer test response. One should keep in mind several limitations of the model.

473 The model remains valid as the hydrological conditions are closed to the one investigated
474 during the field campaign. An extrapolation of the linear regression between transfer function
475 parameters and spring discharge appears not to be relevant. Indeed, the Eqn (14) gives a
476 negative transit time in case of the spring discharge is above $1.240 \text{ m}^3/\text{s}$, which is physically
477 non-acceptable. So, an extension of the model to a lager range of hydrological conditions
478 needs more field data to find a suitable model. The model consists of both the transfer
479 function and the regression equation between transfer function parameters and the
480 environmental variables. Here, only the influence of spring discharge has been investigated

481 but the model may be extended by integration of other variables such as piezometric level or
482 tidal coefficient in case of coastal aquifers submitted to tidal influence.

483 The model offers a new way to deal with pollution scenario testing including a short-term
484 variation of boundary condition on the solute transport. Users should keep in mind the range
485 of hydrological conditions where the model has been calibrated. The validity domain of the
486 model is strongly dependent on the range of hydrological condition investigated through
487 artificial tracer tests. Also, the model is calibrated depending on the objective in term of
488 source vulnerability characterization and depending on available data on the area.

489 **6 Conclusion**

490 In this paper, several problems with solute transport in karstic areas have been addressed:
491 (1) solute transport modelling in karst conduit using a transfer function approach, (2)
492 assessment of the short-term variations in tracer test responses and (3) testing accidental
493 pollution scenario including discharge variations along the infiltration and restitution of the
494 contaminant.

495 A transfer function approach is used for the RTD curves modelling from fluorescent dye
496 tracer tests. It consists of a systemic approach, allowing inclusion of all processes in a
497 conceptual reservoir model. The model introduced here is composed of 3 delayed sub-
498 functions. The delay in solute transport can be explained by the existence of complex
499 structure acting like dead zones (Becker and Bellin, 2013; Field and Pinsky, 2000;
500 Goldscheider, 2008), by friction effects (Massei et al., 2006) or by partition in flow dynamics
501 (Labat and Mangin, 2015). Flow dynamics in karst aquifers shows strong non-linearity: it may
502 exist cell effects depending on the activation or deactivation of flow path depending on the
503 water table level. In this study, artificial tracer tests were performed during a period when one
504 temporary resurgence (called Moulo de Jaur) has been deactivated. As a result, the
505 regression equation between spring discharge and time of transit show different coefficient
506 from either side of the spring discharge cell, corresponding to the activation/deactivation of
507 this temporary loss.

508 The main result of the study highlights the influence of short term variation in boundary
509 condition on artificial tracer test response.. It constitutes a new way to deal with source
510 pollution scenario. Considering one accidental pollution scenario lasting 6 hours over several
511 quite similar recession event, it appears that the shape of the recession has an influence on
512 solute transport. So, the model allows to include discharge fluctuation during solute transport
513 (and by extension contaminant) and gives a better description of the recovery at the outlet.
514 Omit the effects of short-term variations in boundary condition can lead to under-estimate the
515 peak of concentration. Also, the time of transit and the time for maximal concentration
516 reaching outlet can be badly estimated considering a constant discharge rate. Users should
517 keep in mind the range of hydrological conditions where the model have been calibrated to
518 ensure the model prevision is sufficiently reliable.

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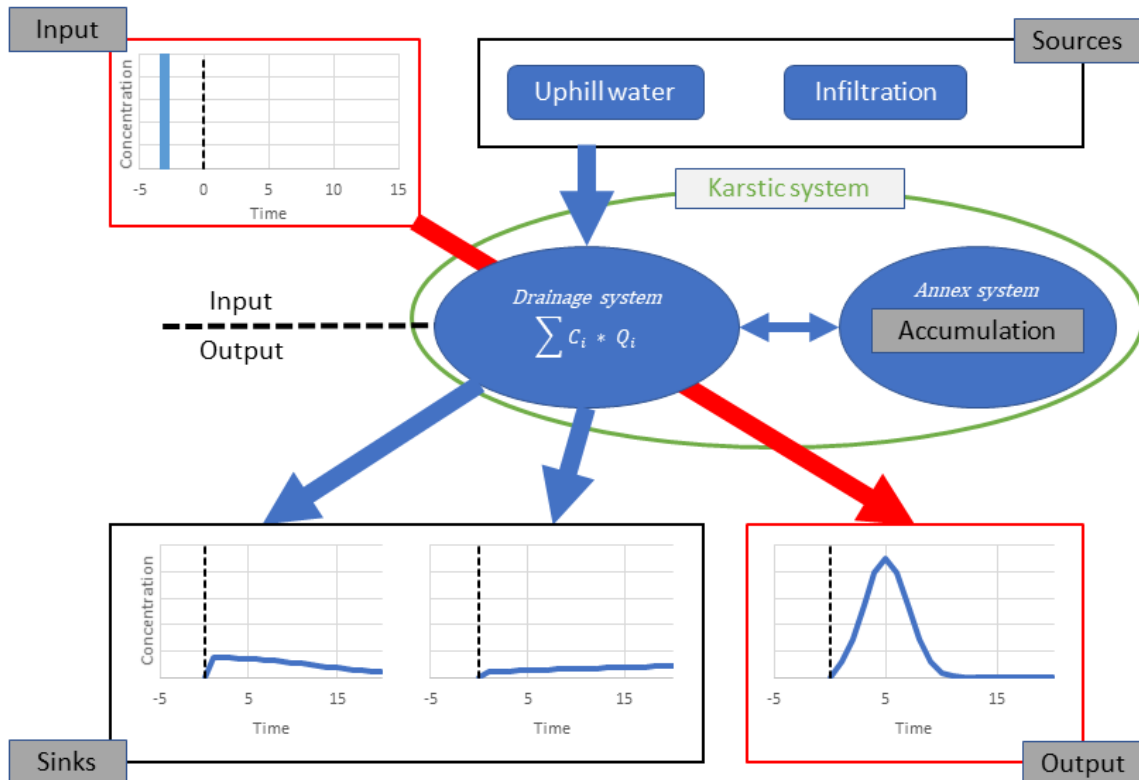
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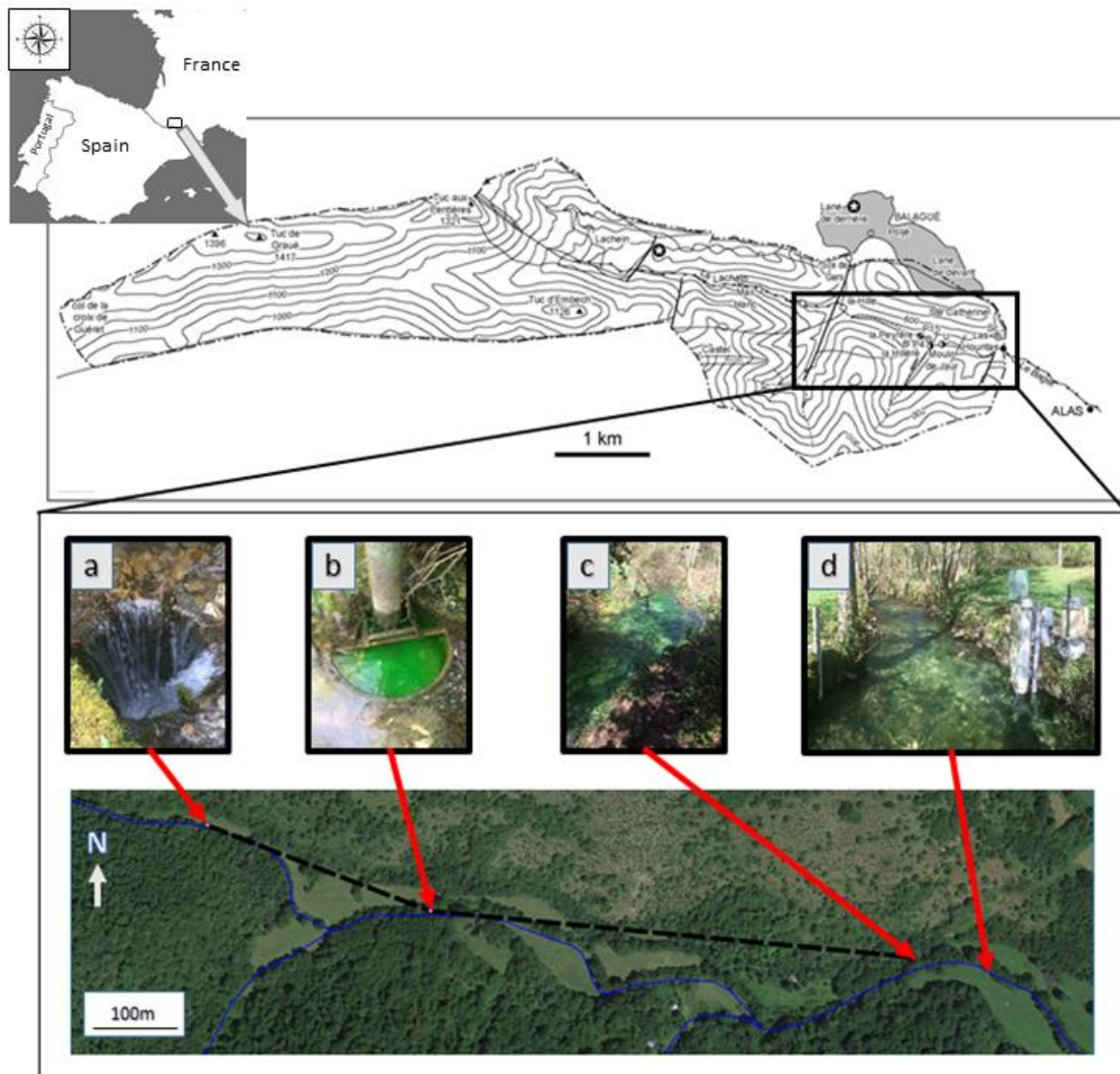
711



712

713 Fig. 1:

714 A conceptual model for artificial tracer tests interpretation using a transfer function approach.
 715 The transfer function is used to model de solute transport in a tracing system, which
 716 represents only a limited part of the karstic system, by considering the input/output relation
 717 (systemic approach). The tracing system corresponds to the red arrow linking the input to the
 718 output. Input consists of an instantaneous injection of a tracer mass injected by an operator.
 719 Sources are equal to 0 for artificial tracer tests. It consists of the injection of fluorescent dyes,
 720 normally nonexistent in natural conditions. By this way, the only mass of tracer present in the
 721 system corresponds to the one introduced by the operator. The output is the tracer
 722 breakthrough tracer curve measured at the monitored outlet of the karstic system.

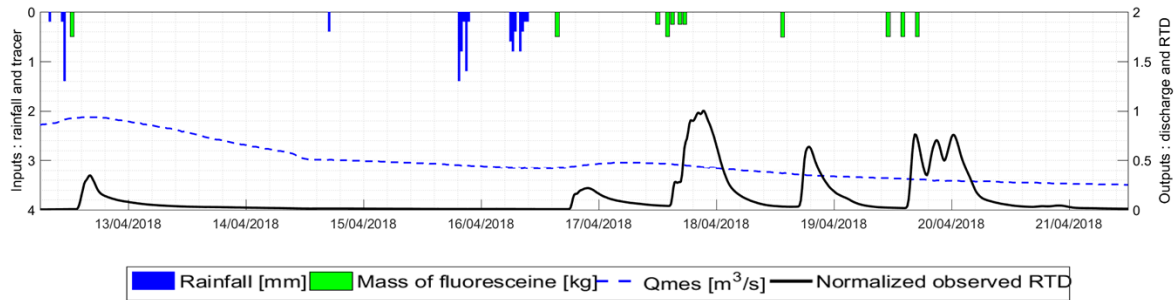


723

724 Fig. 2:

725 Top: localization of the Baget karstic system and description of the watershed which limits
 726 are represented by the *black dashed line*. The inlet and outlet tracer injection/recovery are in
 727 the upstream part of the basin (*black rectangle*).

728 Bottom: pictures of injection/recovery point over the area: a) P2 Loss is the point of injection,
 729 b) Moulo de Jaur is an intermediate observation point of the tracer transfer, c) Las Hountas is
 730 the recovery point and d) is the monitored station, denoted B1 (discharge, water sampling
 731 and fluorimeter).



732

733 Fig. 3:

734 Rainfall-runoff time series on the Baget karstic watershed from 12 April to 22 April 2018.

735 Rainfall is measured by Meteo France at the Antichan station. Gauging station and

736 fluorimeter are located downstream Las Hountas. The successive injection of fluorescein and

737 residence time distribution are also reported in the same input-output format. Tracer tests

738 were performed in periods without the influence of rainfall. During the tracer tests campaign

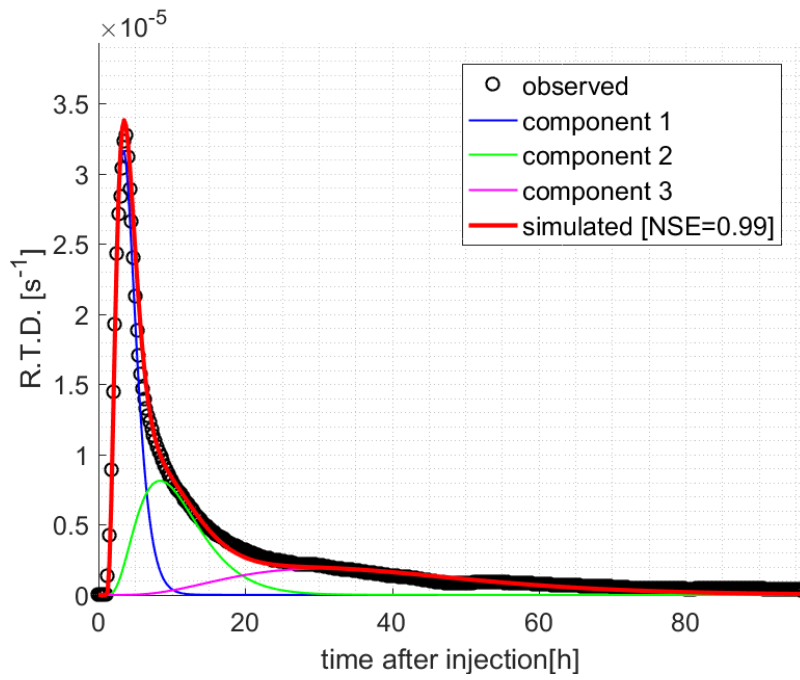
739 the discharge rate varies from 0.9 m³/s at the beginning of the first injection down to around

740 0.45 m³/s at the beginning of the second injection campaign. Then the discharge rate has

741 gradually decreased down to 0.3 m³/s at the end of the campaign. Therefore, the discharge

742 rate has decreased by 33% during the 7 days long tracer tests campaign.

743



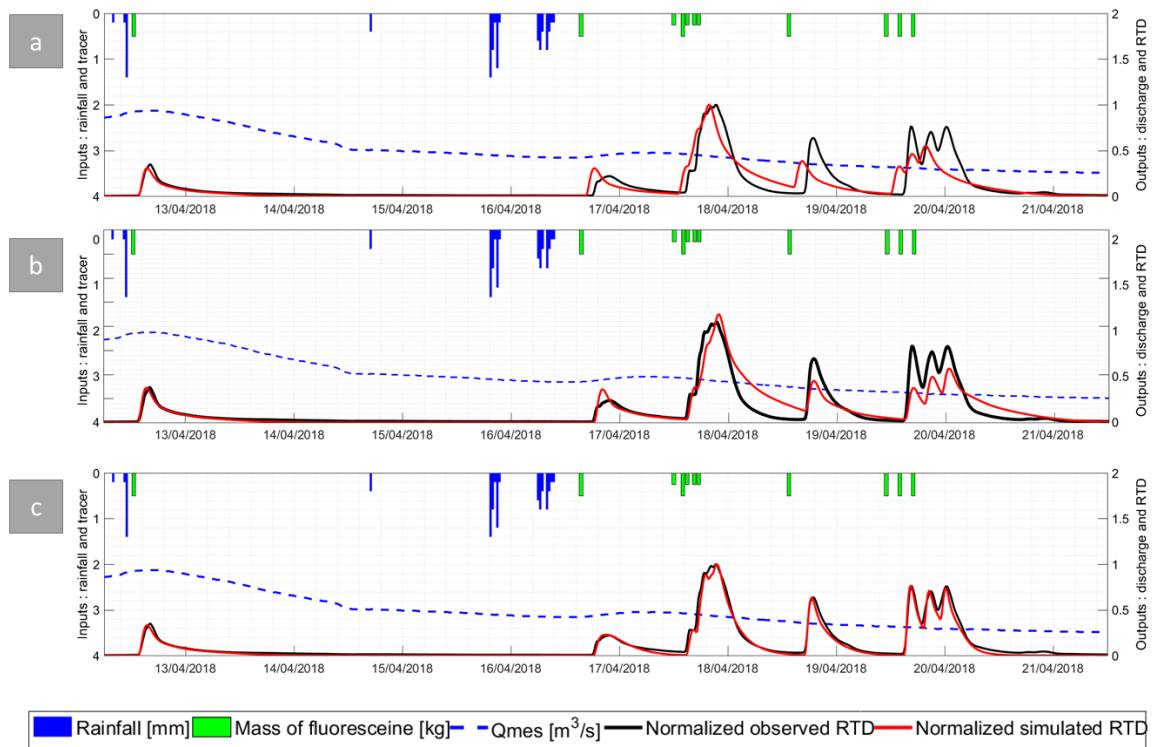
744

745 Fig. 4:

746 Experimental RTD and simulated RTD curves. The simulated curve is composed of 3 sub-

747 functions, called from component 1 to component 3, corresponding respectively to 40%, 32%

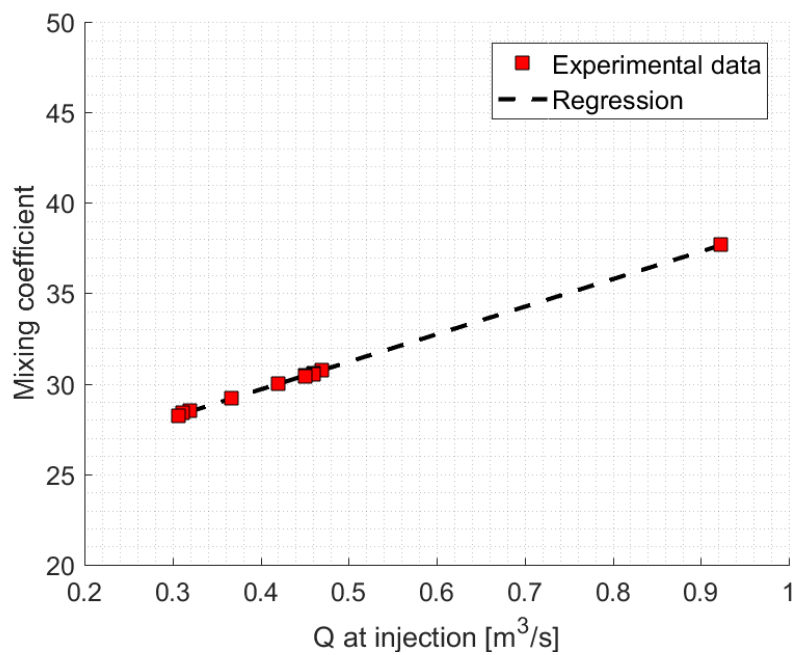
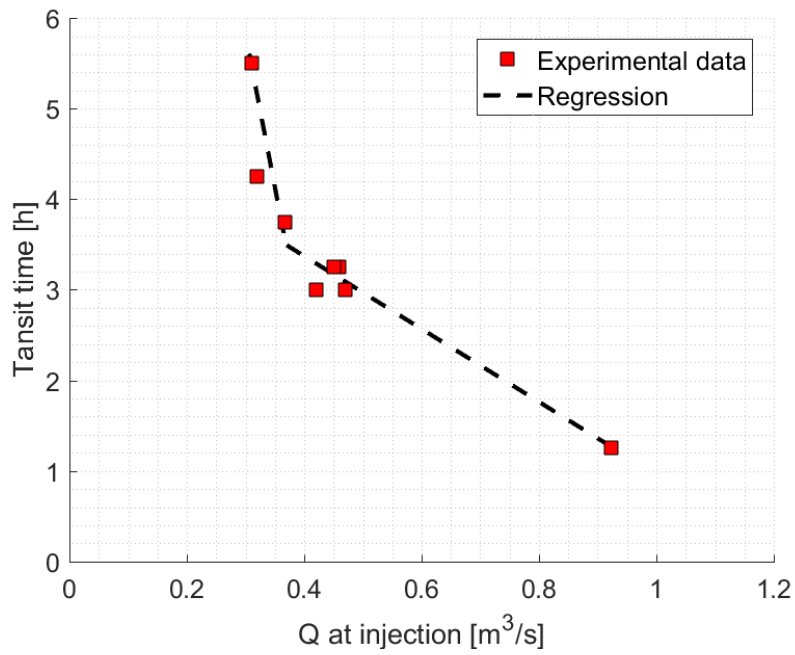
748 and 28% of the total solute transport.



749

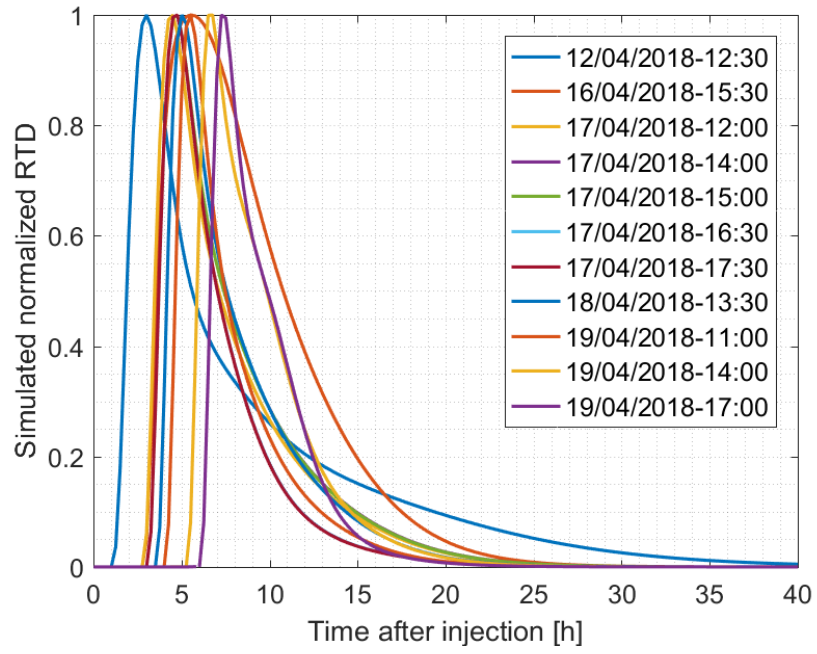
750 Fig. 5:

751 Experimental RTD and simulated RTD curves: a) hypothesis: the system is linear and transit
 752 time is independent of discharge rate, b) hypothesis: the system is linear and transit time is
 753 dependent on discharge rate and c) hypothesis: the system is non-linear, both transit time
 754 and mixing coefficient are dependents from discharge rate.



755 Fig. 6:

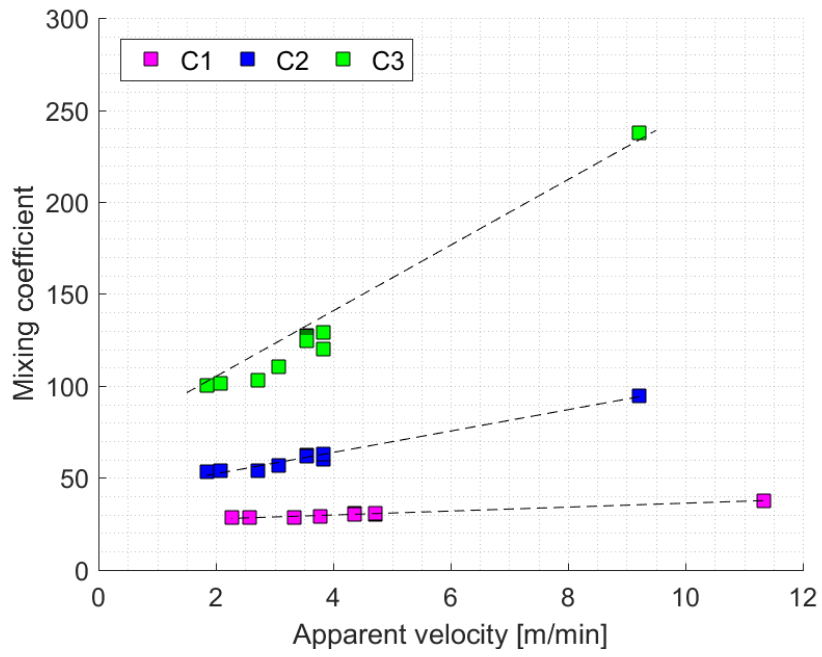
756 Regression between boundary conditions dependent parameters of the transfer function and
 757 the outlet discharge rate at the time of injection of the tracer in P2 loss. As all tracer tests
 758 were performed in close hydrological conditions and as there was no important influence of
 759 rainfall, the outlet discharge is assumed to be representative of the boundary conditions.



760

761 Fig. 7:

762 Simulated RTD for each of the 11 tracer tests and the corresponding date of injection.

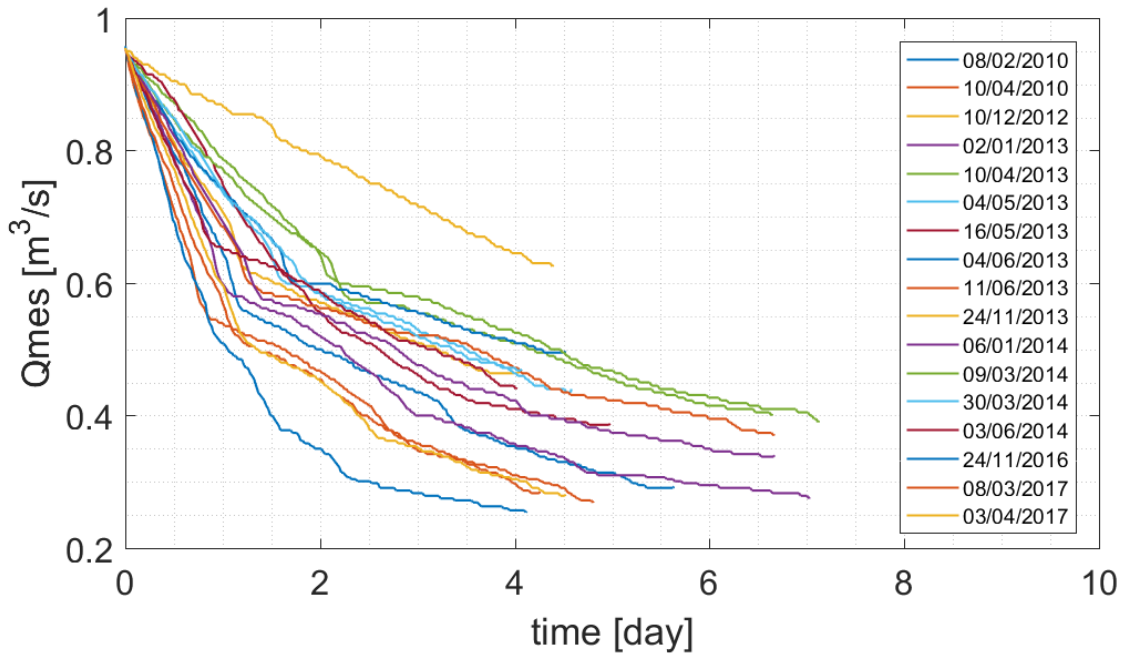


763

764 Fig. 8:

765 Regression between mixing coefficient, noted A in the transfer function, and the apparent

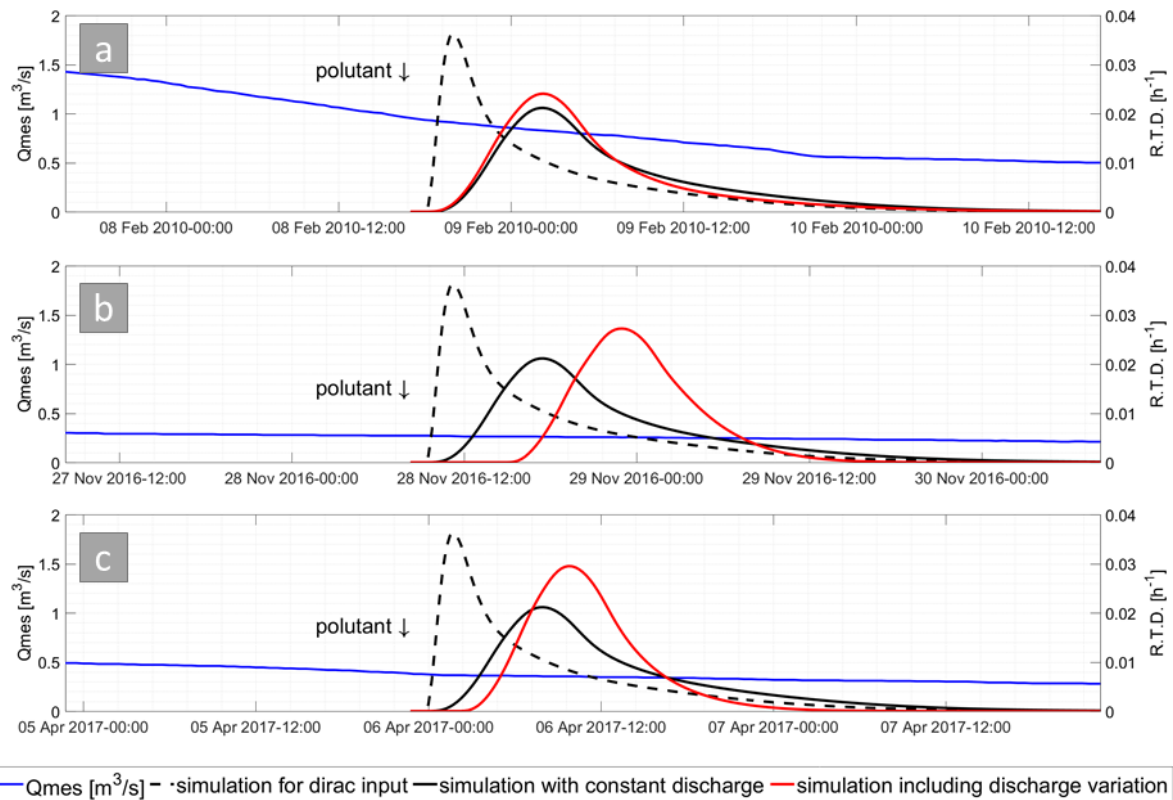
766 velocity.



767

768 Fig. 9:

769 Recessions like the one studied through tracer tests observed over the Baget karstic
 770 watershed between January 2009 and April 2018: the recession last more than 4 days, the
 771 initial discharge is about $0.900 \text{ m}^3/\text{s}$ and final discharge is above $0.300 \text{ m}^3/\text{s}$. So, the scenario
 772 of pollution is tested in conditions close to the one investigated field campaign.



773
774

775 Fig. 10:

776 Residence time distribution estimated from the model for a constant injection lasting 6 hours.
 777 The black arrow corresponds to the beginning of the simulated injection, the black dashed
 778 lines represent the impulse response derived from the calibration tracer test, black lines
 779 represent the response to a six hours long continuous injection using transfer function
 780 regardless discharge variations and red lines represent response including dependence from
 781 the outlet discharge.

Test	Date	Mass injected (g)	Q (m³/s)	Sampling rate (min)
01	12/04/2018 12h30	500	0.923	15
02	16/04/2018 16h30	500	0.421	15
03	17/04/2018 12h00	250	0.470	15
04	17/04/2018 14h00	500	0.460	15
05	17/04/2018 15h00	250	0.460	15
06	17/04/2018 16h30	250	0.450	15
07	17/04/2018 17h30	250	0.450	15
08	18/04/2018 13h30	500	0.367	15
09	19/04/2018 11h00	500	0.320	15
10	19/04/2018 14h00	500	0.311	15
11	19/04/2018 17h00	500	0.306	15

782

783 Table 1:

784 Mass injected and hydrological conditions for each tracer injections.

$\alpha 1$ (%)	A1	$\tau 1$ (H)	$\alpha 2$ (%)	A2	$\tau 2$ (H)	$\alpha 3$ (%)	A3	$\tau 3$ (H)
36	2.51	1.25	30	6.31	1.54	34	15.85	1.83
20	2.00	3.00	38	4.00	3.69	42	8.00	4.38
40	2.05	3.00	32	4.20	3.69	27	8.60	4.38
40	2.04	3.25	32	4.16	4.00	27	8.49	4.75
40	2.04	3.25	32	4.15	4.00	27	8.45	4.75
49	2.03	3.25	39	4.12	4.00	12	8.37	4.75
49	2.03	3.25	39	4.10	4.00	12	8.31	4.75
43	1.95	3.75	31	3.79	4.61	26	7.38	5.48
52	1.90	4.25	30	3.61	5.23	18	6.86	6.21
46	1.89	5.50	40	3.58	6.82	14	6.77	8.15
55	1.88	6.25	40	3.55	7.69	5	6.68	9.13

785

786 Table 2:

787 Parameters of the transfer function for all tracer tests. The simulated RTD is obtained by
788 summation of the contribution of 3 sub-functions where α [%] is the contribution of the total
789 mass transport, A is the mixing coefficient – dependent from outlet discharge – and τ [h] is
790 transit time between input and outlet of the tracing system.