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► **To cite this version:**

Myriam Dedewanou, Stéphane Binet, Jean-Louis Rouet, Yves Coquet, Ary Bruand, et al.. Groundwater Vulnerability and Risk Mapping Based on Residence Time Distributions: Spatial Analysis for the Estimation of Lumped Parameters. *Water Resources Management*, 2015, 29 (15), pp.5489-5504. 10.1007/s11269-015-1130-8 . insu-01237105

**HAL Id: insu-01237105**

**<https://insu.hal.science/insu-01237105v1>**

Submitted on 20 Jan 2016

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# Groundwater vulnerability and risk mapping based on Residence Time Distributions: Spatial analysis for the estimation of lumped parameters

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## Abstract

Specific vulnerability estimations for groundwater resources are usually geographic information system-based (GIS) methods that establish spatial qualitative indexes which determine the sensitivity to infiltration of surface contaminants, but with little validation of the working hypothesis. On the other hand, lumped parameter models, such as the Residence Time Distribution (RTD), are used to predict temporal water quality changes in drinking water supply, but the lumped parameters do not incorporate the spatial variability of the land cover and use. At the interface between these two approaches, a GIS tool was developed to estimate the lumped parameters from the vulnerability mapping dataset. In this method the temporal evolution of groundwater quality is linked to the vulnerability concept on the basis of equivalent lumped parameters that account for the spatially distributed hydrodynamic characteristics of the overall unsaturated and saturated flow nets feeding the drinking water supply. This vulnerability mapping method can be validated by field observations of water concentrations. A test for atrazine specific vulnerability of the Val d'Orléans karstic aquifer demonstrates the reliability of this approach for groundwater contamination assessment.

27 *Keywords:* Specific vulnerability, advection / dispersion, residence time distribution, equivalent  
28 parameters.

## 29 **1. Introduction**

30 The main tools for the management and the conservation of groundwater resources consist in  
31 characterizing the vulnerability of the aquifer used for drinking water. Intrinsic vulnerability uses  
32 physical characteristics as criteria to determine the sensitivity of groundwater to surface  
33 pollution. Most intrinsic vulnerability maps are multi-criteria, weighted and index-based,  
34 developed by Aller et al., (1987), Doerfliger et al., (1999), Petelet-Giraud et al., (2001) and  
35 Civita and De Maio (2004). The specific vulnerability of groundwater incorporates the physico-  
36 chemical properties and their relationship with the natural environment as supplementary  
37 criteria in the vulnerability index estimation (Vrba and Zaporozec, 1994). These tools enable  
38 policies for the development of codes of practice for groundwater protection to be proposed  
39 (Escolero et al. 2002) and open up significant opportunities to enhance the efficacy of water  
40 vulnerability assessment tools by incorporating indicators and operational measures for social  
41 considerations (Plummer et al., 2012). While the area of use is huge, the index calculation  
42 method is limited because the weighting is usually arbitrarily chosen. These approaches are  
43 qualitative and highly subject to the hydrogeologist's interpretation (Panagopoulos et al.,  
44 2006).

45 Borehole vulnerability analysis was developed for drinking water supplying watersheds. This  
46 method completes the vulnerability index with the notions of distance, horizontal flow rate and  
47 transport to the target (borehole or spring) (Goldscheider and Popescu, 2003). In this  
48 framework, two types of vulnerability can be defined: a resource vulnerability which only takes  
49 vertical transfer into account, and a borehole vulnerability which incorporates the horizontal  
50 transfer into the borehole. The key parameters for the evaluation of specific vulnerability are  
51 the residence time of contaminants, their capacity of migration underground and the

52 attenuation process. Some authors (Neukum et al., 2008; Anderson and Gosk 1987; Sadek  
53 and Abd El-Samie, 2001; Bakalowicz, 2005) suggested that a high vulnerability is related to a  
54 short residence time of the main part of the recharge. From these concepts, Brouyère (2001)  
55 relate a potential contamination to the transfer time, concentration level and duration of the  
56 phenomenon, plotted along the three axes of the cube. Jeannin et al. (2001) developed a  
57 program that relates field observations to concentration level, transfer time and duration. The  
58 model assumes an instantaneous release of a conservative contaminant at a given point on  
59 the land surface and simulates the resulting breakthrough curves at the outlet of each sub-  
60 system by means of the advection - dispersion equation, disregarding retardation and  
61 degradation processes (Zwahlen, 2003).

62 By linking the vulnerability index to physical parameters, the working hypothesis used in  
63 vulnerability mapping can be tested. Goldscheider et al. (2001) released different tracers at  
64 the land surface and observed the breakthrough at a target (spring), the travel time, the  
65 concentration and the tracer recovery rate to validate a vulnerability map. Holman et al. (2005)  
66 validated an intrinsic groundwater vulnerability method using a national nitrate database and  
67 some co-variance and variance analyses. Neukum et al. (2008) worked on the validation of a  
68 vulnerability map based on field investigation and column tracer experiments conducted on  
69 soil materials. The authors modelled tracer displacements using the advection – dispersion  
70 model and proposed a transit time distribution function of the tracer that depends on the  
71 geometric and hydraulic boundary conditions of the aquifer. Lasserre et al. (1999) developed  
72 a simple GIS-linked model to describe the groundwater transport of nitrates. For all these  
73 methods, developed to validate vulnerability criteria, the aim was to link surface land use with  
74 watershed hydrodynamic properties and water quality at the boreholes.

75 For time series analysis, several studies have applied an impulse response at the watershed  
76 scale for solute transport modeling purposes (Jury, 1982; Beltman et al., 1994; Barry and  
77 Parker, 1987; Molénat et al., 1999; Schwientek et al., 2009). The method consists in  
78 establishing a residence time distribution (RTD) to link pollutants at the surface of the

79 watershed to the contaminant concentrations measured in the borehole. Related to the  
80 geometry of the aquifer, Jurgens et al., (2012) proposed six theoretical models, (derived from  
81 analytical solutions of the advection - dispersion reaction equation) to fit the impulse response  
82 with three lumped parameters. These parameters vary from one study to another, but the ones  
83 most widely used are the average residence time, the Peclet number and the rate of  
84 degradation. To evaluate groundwater quality trends, Visser et al. (2009) after a comparison  
85 between statistical, groundwater dating and deterministic modeling, showed that impulse  
86 response methods require little information about the physical system, but rather rely on the  
87 available data, which makes them suitable for application to a wide variety of systems.

88 Linking the spatial properties that determine the vulnerability and the temporal evolution of the  
89 water quality is a key point for water resource management. At the watershed scale, some  
90 semi-distributed models incorporate the soil surface properties to model water quality with a  
91 GIS dataset based on an impulse response, such as the SWAT model (Srinivasan and Arnold,  
92 1994) or on a flow model such as Drainmod (Fernandez *et al.* 2006) MACRO (Larsbo and  
93 Jarvis, 2003) and STICS (Ledoux, 2003). For groundwater quality purposes, the flow paths  
94 must be analyzed in 3 dimensions but few tools are available to compute an impulse response  
95 from the spatially distributed 3D groundwater properties.

96 This paper proposes a method to calculate a RTD impulse response in aquifers based on  
97 spatial datasets used for specific vulnerability assessments. The spatial GIS vulnerability  
98 dataset corresponds to the thickness and hydrodynamic parameters of the geological  
99 formations found along the groundwater flow nets.

100 Based on the impulse response, which is characteristic of the watershed, the vulnerability  
101 index is defined as the mass ratio between the contaminants that exceeds a fixed threshold at  
102 the borehole and the injected mass. This makes it possible to map the relative vulnerability of  
103 each infiltration surface where contaminant application occurs. This approach includes  
104 residence times, dispersion and attenuation. Spatial vulnerability mapping is validated with GIS  
105 using the temporal evolution of the groundwater quality.

106

## 107 2. The Residence Time Distribution (RTD)

108 The Residence Time Distribution (RTD) is a probability distribution function that describes the  
 109 amount of time a fluid element can spend inside the column. After a pulse of mass  $M$ , its RTD  
 110 is defined as :

$$111 E(t) = \frac{Q C(t)}{M} = \frac{M'(t)}{M} \text{ (Equation 1)}$$

112 Here  $Q$  [ $L^3.T^{-1}$ ] is the discharge flowing through the column.

113 The concentration  $C(t)$  [ $M.L^{-3}$ ] can be obtained by solving the transport equation along a  
 114 column open at both ends (Kreft and Zuber, 1978). For the transport of a pulse of mass  $M$  in  
 115 a porous one-dimensional column (the transversal section is  $A$  [ $L^2$ ], the length  $x$  and the column  
 116 water content is  $\theta$ ), where water flow with a velocity ( $u$ ) there is many analytical solutions, most  
 117 of them use the non-dimensional Peclet number ( $Pe$ ), the average residence time ( $\bar{t}$ ) and the  
 118 rate of degradation  $\lambda$  [ $T^{-1}$ ] of the contaminant during transport.

119 To assume that the column is open at both ends (Levenspiel 1962, Maloszewski and Zuber,  
 120 1982) enables to express the RTD as follow:

$$121 E(t) = \sqrt{\frac{Pe}{4\pi\bar{t}}} \exp\left[-\frac{Pe(\bar{t}-t)^2}{4\bar{t}}\right] \exp[-\lambda t] \text{ (Equation 2)}$$

122 The contaminant transport through the column is described with only three parameters and no  
 123 assumption is made on the laminar, turbulent, unsaturated or saturated nature of the flows.  
 124 Degradation and delay are taken into account with  $\lambda$  and  $\bar{t}$ . If no reaction occurs,  $\bar{t}$  is the same  
 125 as the average residence time of the water in the column.

### 126 2.1. RTD for a column with multi layers.

127

128 For the transport of a pulse, the mean residence time  $\bar{t}$  [T] of the contaminant in the column  
 129 can be defined either with the  $C(t)$  curve or as the ratio between the water flux ( $u$ ) and the  
 130 stored water ( $\theta L$ ):

$$131 \quad \bar{t} = \frac{\int_0^{\infty} t C(t) dt}{\int_0^{\infty} C(t) dt} = \frac{u}{\theta L} \quad (\text{Equation 3})$$

132 Another important descriptor of the  $C(t)$  curve is its variance:

$$133 \quad \sigma^2 = \frac{\int_0^{\infty} (t-\bar{t})^2 C(t) dt}{\int_0^{\infty} C(t) dt} \quad (\text{Equation 4})$$

134 In decomposing the borehole watershed into  $n$  parallel flow nets. This reduces the non-linear  
 135 three-dimensional problem to a linear one-dimensional one. The water and the contaminant  
 136 mass which infiltrate the ground enter through the various  $i$  layers of the aquifer where the  
 137 hydro-dispersive properties can vary. They flow through the  $i$  layers until the borehole,  
 138 following the flow nets. For every  $n$  flow net, the  $i$  layers are considered to be independent  
 139 columns characterized by the average residence time  $\bar{t}_{n,i}$  and the Peclet number  $Pe_{n,i}$ .

140 For  $i$  serial layers, equivalent properties can be calculated. The mean residence time for the  
 141  $n^{\text{th}}$  flow net, where contaminant flows through  $i$  serial columns, is:

$$142 \quad \langle \bar{t}_n \rangle = \sum_1^i \bar{t}_{n,i} \quad (\text{Equation 5})$$

143 In 1959, Aris showed that, in the case of an infinite column, the change in the variance  
 144 (equation 4) between two points can be described as:

$$145 \quad \frac{\Delta \sigma^2}{\bar{t}^2} = \frac{2}{Pe} \quad (\text{Equation 6})$$

146 Thus, if this relation is extended to  $i$  serial columns, the equivalent Peclet number  $\langle Pe_n \rangle$  for  
 147 the  $n^{\text{th}}$  flow net, can be defined as:

$$148 \quad \frac{\langle Pe_n \rangle}{2} = \frac{\langle \bar{t}_n^2 \rangle}{\Delta \sigma_{n,i}^2 \dots - \Delta \sigma_{n,1}^2} = \frac{\langle \bar{t}_n^2 \rangle}{\sum_1^i \left( \frac{2 \bar{t}_{n,i}^2}{Pe_{n,i}} \right)} \quad (\text{Equation 7})$$

149 This formulation enables the residence time distribution  $E_{n(t)}$  at the output of the  $n^{\text{th}}$  flow net to  
 150 be described, using an equivalent average residence time and an equivalent Peclet number.

151 The mass of contaminant at the borehole is the sum of the mass arriving through the  $n$  flow  
 152 nets. The RTD becomes:

$$153 \quad E(t) = \frac{\sum_1^n [E_{n(t)} M_n]}{\sum_1^n M_n} \text{ (Equation 8)}$$

154

## 155 2.2. Computation of the equivalent lumped parameters using GIS

156

### 157 2.2.1. Water and contaminant fluxes at the upper boundary

158 The mass of contaminants entering the aquifer is considered to be the mass  $M$  [M] flowing  
 159 under the organic soil zone. Published data on the rate of contaminant seeping under the soil  
 160 ( $a$ ) [l] compared to the initial pulverized mass  $M_0$  can be used:

$$161 \quad M = M_0 * a \text{ (Equation 9)}$$

162 The delay between pulverization and exportation under the roots in the soil is considered to  
 163 be very small with respect to the average residence time used to describe groundwater flows.

### 164 2.2.2. Calculation of average residence times and Peclet numbers

165 First, the surface watershed of the borehole is discretized into unitary surfaces. The aquifer  
 166 volume is divided into an unsaturated zone with vertical flows, and a saturated zone with  
 167 horizontal flows. The contaminants flow first vertically toward the unsaturated zone, and then  
 168 horizontally towards the borehole. Based on the groundwater head maps, the flow direction  
 169 and the flow length ( $L$ ) was defined for each of the  $n$  flow nets of the system. The calculation  
 170 was carried out with the GIS ARCGIS® toolbox. For the unsaturated zone, the flow length  $L$  is  
 171 simply calculated by the difference between the topographic and water head level.

172 Along each flow net,  $i$  columns can be discretized based on the 3D geological dataset. For  
 173 each flow net  $n$  and  $i$  column, the equivalent Peclet number and the average residence time  
 174 can be computed from with the hydrogeological dataset  $u$ ,  $D$ ,  $\theta$ .

175 The equivalent parameters can be estimated using the GIS tool before being injected into the  
 176 RTD equation (Equation 8).



177

178 **2.3. Simulation of water quality by convolution**179 If we consider the various periods of infiltration as a sum of brief injections of mass  $M$  entering180 the column at time  $t'$ , the concentration in the borehole  $C(t)$  can be deduced from the RTD:

181 
$$C(t) = \frac{1}{Q} \int_{-\infty}^t M_{t'} E_{(t-t')} e^{-\lambda(t-t')} dt' \text{ (Equation 10)}$$

182 The history of the dissolved masses injected in the watershed ( $M$ ) and the steady state average183 discharge of water across the borehole ( $Q$ ) must be implemented. The Nash-Sutcliffe184 coefficient  $E$  (Nash and Sutcliffe, 1970) was used to assess the efficiency of the RTD model

185 using equivalent parameters.

186 **2.4. Analogy between RTD, vulnerability and risk indexes**

187 The equivalent RTD for each flow net represents the mass arriving at the borehole for an

188 injected mass equal to 1. Depending on the value of the equivalent parameters, and on the

189 discharge  $Q_n$  for the  $n^{\text{th}}$  flow net, the concentrations obtained make it possible to identify flow

190 nets showing concentrations higher than a threshold (LR) represented by the dashed line in

191 Fig. 1 while other flow nets present concentrations below the threshold. The spatialized grid of

192 equivalent parameters locates the surfaces which contribute to the over-concentration

193 measured at the groundwater borehole, making it possible to prioritize the various surfaces in

194 terms of borehole vulnerability and/or risk.

195 Using datasets of  $M$  values, the specific risk index ( $I$ ) is defined as the rate between the mass196 above the threshold  $M_d$  (Fig. 1) and the mass flowing under the roots  $M$ . (equation 16).

197 
$$I = \frac{M_d}{M} = \frac{\int_a^b \left[ \frac{E(t) M}{Q_n} - LR \right] dt}{M} \text{ (Equation 11)}$$

198 The boundaries  $a$  and  $b$  are defined in Fig 1 as the intercepts between the  $C(t)$  curve and the199 fixed threshold. So, the specific risk index  $I$  is defined as the percentage of the applied200 contaminant mass which will reach the borehole above a given threshold. If  $M=1$  for the entire

201 watershed and the threshold has a low value, then equation 11 becomes an intrinsic

202 vulnerability index.

203

## 204 **3. Study site and data**

205 The proposed model was tested on the Val d'Orléans karstic system, which has a wide range  
206 of flow velocities. This section presents the dataset required to apply the proposed  
207 methodology, and the various existing ways to compile this database.

208

### 209 **3.1. The Val d'Orléans**

210 The Val d'Orléans is located southeast of Orléans city, in the alluvial plain of the Loire river  
211 which corresponds to a depression of the main river bed. The length of this alluvial plain is  
212 about 40 km and its maximum width reaches 7 km in its central part (Fig. 2).

#### 213 **3.1.1. Pedology**

214 Inside the protection zone (Fig.2A), clays in soil represent about 0 to 250 g/kg. The sand  
215 contents in silt (100 to 250 g/kg) and organic carbon (0 to 10 g/kg) are quite homogeneous  
216 (BDAT-GISSOL-INRA, 2014). This database shows a low content of clays and sands in the  
217 center and east of the perimeter and higher contents in the west zone. The values range  
218 respectively from 0 to 100 g/kg and from 100 to 250 g/kg.

219

#### 220 **3.1.2. Geology**

221 The geology in this sector results from a major and regular marine sedimentation  
222 (transgression and regression phenomena), that started during the Trias and lasted until the  
223 beginning of the Tertiary (Eocene). White chalk with flint and detrital formations constitute  
224 the base of the geological formations of the Val d'Orléans. In the middle of the Tertiary  
225 (Oligocene, Aquitanien), a sedimentation of lacustrine origin formed the limestones of Beauce,  
226 interrupted with marly formations. In the second part of the Tertiary (Burdigalien), marls and  
227 sands were deposited, before being covered by fluvial (Quaternary) alluviums of the Loire  
228 (Auterives et al. 2014). For this study, only the sedimentary formations of lacustrine origin

229 which began during the Oligocene were of interest because it is the main aquifer. A karstic  
230 network developed in the Beauce limestones, generally captive, either under the alluvial  
231 formation or under the Burdigalien marls. A probability map of the karstic network was  
232 proposed by Auterives et al., 2014.

233 This karstic network is supplied by surface water coming from the Loire river which infiltrates  
234 at point sources (Albéric, 2004) in the area of Jargeau (Fig.2A) and by diffuse infiltration  
235 through the alluvial plain located mainly in the river bed. Some of these karstic conduits outflow  
236 downstream the Val d'Orléans where springs contribute to the establishment of the Loiret river  
237 (Lepiller, 2006). Three drinking water boreholes are located within or close to the karstic  
238 network (Fig. 2A). Based on the water quality data (isotopes and major elements) of the Loire  
239 water, the local surface waters and the Loiret spring waters, Joigneaux (2011) revealed that  
240 80% of the Loiret spring waters are composed of Loire water, the remainder being local surface  
241 waters. Mixing is controlled by the hydrological conditions of the Loire river.

242 The groundwater vulnerability to diffuse agricultural pollution was estimated in the protection  
243 zone of the three boreholes (Fig.2A).

244

### 245 **3.1.3. Water flux and contaminants below the root zone**

246 The discharge values  $Q$  arise from the hydrological balance. This assessment was made by  
247 various authors such as Chéry (1983), Livrozet (1984), Lepiller (2006), Lelong and Jozja  
248 (2008), Gutierrez and Binet (2010). Three different flow values were considered according to  
249 three hydrological scenarios. These three scenarios represent the minimal, maximal and  
250 average flows that transit through the system. The minimal flow can be estimated from the  
251 lowest contribution of the flow from the Loire river and the lowest contribution of impluvium in  
252 the total hydrological balance assessment. The minimal value of the contribution of the river  
253 Loire loss was estimated at 5 m<sup>3</sup>/s (Martin and Noyer, 2003; Gutierrez and Binet, 2010),  
254 whereas the lowest flow from the impluvium calculated by MACRO (Larsbo and Jarvis, 2003)

255 and calibrated for the Val d'Orleans is 0.100 m/year (Footways/Geo-Hyd, 2013). Thus, the  
256 minimal contribution in water supplied to the system was estimated at  $186.10^6$  m<sup>3</sup>/year. 15%  
257 of the water comes from diffuse infiltration.

258 Concerning the average flow, the volume of the Loire loss to the Val d'Orléans aquifer, for an  
259 average year, was estimated by hydrological balance at  $363.10^6$  m<sup>3</sup>/year. The results of  
260 models that estimate the effective rain, stemming from the impluvium, suggested a flow of  
261 0.191 m/year (Joigneaux et al., 2011). The average flow transiting through the system is  
262 estimated to be  $423.10^6$  m<sup>3</sup>/year. Here again, 15% of the water comes from diffuse infiltration.

263 The proposed RTD model was tested and calibrated for the application of atrazine, which was  
264 sprayed between 1960 and 2003 on the maize crops. The reason for this choice is the  
265 quantitative availability of analyses done on the three Val d'Orléans boreholes, which revealed  
266 the presence of atrazine from the 1990s to 2004, showing, with a quarterly sampling frequency,  
267 an erratic response with values ranging from 0 to 0.3 µg/L. Atrazine concentration in the Loire  
268 river has been below the detection limit since the beginning of the century. In the 1990s,  
269 concentrations reached 0.3 µg/L (Joigneaux, 2011). It is considered that the totality of the  
270 atrazine concentration analysed at the three Val d'Orléans boreholes comes from diffuse  
271 infiltration through the alluvial plain. The Loire river dilutes the fluxes.

272 The localization of the maize crops was mapped in 2010 and was assumed to be constant  
273 through time (Fig. 2A). The atrazine masses injected during more than 40 years were  
274 estimated from the history of agricultural practices recorded in various ways, such as  
275 questionnaires collected by agricultural associations. Atrazine was applied by spraying,  
276 generally made once a year, in April. The quantities of atrazine applied decreased over time,  
277 (2.5 kg/ha/year in the 70<sup>th</sup>, 1.5 in the 80<sup>th</sup>, 1 between 1991 to 1998, 0.75 in 1999 and 2000 and  
278 0.5 between 2000 to 2003) due to increasing constraints on the use of this herbicide, until it  
279 was banned in 2003. Some studies show that pesticides such as atrazine can have an export  
280 percentage up to 4 to 207 5% (Flury, 1996). Naturally, these ranges of values vary according

281 to the geo-hydro- morphological context of the site, but are mostly between 0.1 to 3%  
282 (Wauchope, 1978; Flury, 1996; Voltz and Louchart, 2001).

283

### 284 3.2. Field data for RTD estimation

285 Establishing the RTD requires data concerning the hydrodynamic characteristics of the aquifer  
286 (Table 1). Each hydrodynamic parameter is attributed to each surface of the grid area (250 m  
287 by 250 m, Fig. 2A).

288 The hydrodynamic characteristics of the unsaturated zone (UZ) were attributed according to  
289 the lithology of the four profiles already defined (sand (SD), sand and limestone (SD/LM), sand  
290 and clay (SD/CL) and clay and sand (CL/SD)). The length of flows are known from the  
291 topographic elevation minus the aquifer water head (Desprez in 1967).

292 In the saturated zone (Table 1), 2000 borehole logs were analysed. Alluvium, limestone and  
293 karstified limestones were observed in the area (Auterives et al. 2014). In a saturated context,  
294 the water content is equal to the porosity.

### 295 3.2.3. Atrazine in groundwater

296 Estimating the specific vulnerability requires knowledge of the specific behaviour of the studied  
297 contaminants. For atrazine, a 10-year database is available, with more than 110  
298 measurements. The atrazine degradation rate is known to be 0.4 [month<sup>-1</sup>] (IUPAC, 2013) and  
299 rate of infiltration ( $\alpha$ ) was estimated at about 0.05 (Kladivko et al., 1991).

300

### 301 3.3. Parametric tests on the “Val d’orléans” dataset

302 Uncertainty on the parameterization was explored by calculating various RTDs to assess the  
303 impact of parameterization on the results. Before estimating the vulnerability mapping with the  
304 RTD model, various parameter values were tested to observe the variability of the RTD. Here,  
305 three tests concerning the unsaturated zone (UZ) are presented, as this uncertainty accounts  
306 for the strongest error source in the calculation. The parametric tests presented will focus on  
307 the UZ profiles spatialisation. Three models are presented in the Results section:

- 308 1. RTD\_T1: For this scenario, it was considered that the UZ consisted of only one filtering  
309 facies of sand (Profile SD) and no vertical karstic conduits.
- 310 2. RTD\_T2: This configuration corresponds to the results of the spatial analysis of the  
311 UZ profiles (best fit).
- 312 3. RTD\_T3: This scenario uses the same hydrodynamic characteristics as T1 but adds  
313 34 vertical karstic conduits, positioned according to the karstic network and a database  
314 cavity, assuming that not all the vertical conduits are necessarily known.

## 315 4. Results

### 316 4.1. Equivalent Peclet numbers and average residence times

317 The spatial distributions of the hydrodynamic parameters used for the calculation of the  
318 equivalent parameters and the intermediate calculations for RTD are presented in Fig. 2B. The  
319 data concern the four types of profiles (Table1) and the limestone karst aquifer layer in the  
320 saturated zone. The alluvium aquifer located above the limestone aquifer is not shown in Fig.  
321 2B but was nevertheless taken into account in the calculation of the equivalent parameters.  
322 The Fig. 2B and C shows the spatialized values ( $V_d$ ,  $L$ ,  $\theta$ ,  $n_e$  and  $\alpha$ ) from the UZ and SZ layers.  
323 The second column gives the equivalent parameters (average residence times and equivalent  
324 Peclet numbers) for the  $n$  flow nets starting from the  $n$  grid cells and determined by equations  
325 10 and 12.

### 326 4.2. RTD Calculations

327 The time discretization unit selected for contaminant transport was one month. This is  
328 consistent with the assumption of steady-state conditions for the hydrology.

329 Fig. 2D shows the residence time distribution calculated from equation 13. The three scenarios  
330 illustrate the variability of the results when parameters are varied in the unsaturated zone. The  
331 parameters described in Table 1 correspond to the RTD\_2 scenario. In this highly karstified  
332 area, the residence times are short, less than 12 months, and the average residence time is

333 about 2 - 4 months. The two extreme cases (Fig. 3) show that the intensity of the concentration  
334 peak can be twice as high in a karstic system compared to sand.

#### 335 4.3. Concentration calculated at the water borehole by the RTD model 336

337 Figure 4 shows the concentration at the water borehole calculated by the RTD model. The  
338 average flow reproduces the maximum groundwater concentrations in atrazine at the borehole.  
339 The Nash-Sutcliffe coefficient was determined for the period 1990 to 2005. The value reaches  
340 0.70.

341

#### 342 4.4. Vulnerability and risk mapping

343 A vulnerability map can be computed, considering that each flow net receives a contaminant  
344 mass  $M=1$ . The vulnerability can be estimated by prioritizing all the calculated RTDs (equation  
345 16). Combining the vulnerability map with a hazard map (Fig. 2E) gives a risk map for atrazine  
346 in the watershed. The results obtained are scaled on a range from 0 to 100.

347 Compared to traditional vulnerability mapping, this approach adds the notion of hydraulic  
348 distance to from the borehole. Surfaces with a high index (in red) are not spatially the closest  
349 to the borehole.

350

## 351 5. Discussion

352

353 The Nash-Sutcliffe coefficient suggests that the implementation of the equations, the  
354 parameterization and the strong hypothesis proposed in the RTD model seem acceptable  
355 for a risk assessment approach.

356 Concerning the mass of Atrazine applied on the field, the survey and the coefficient  
357 used to evaluate the loss in organic soil give results in terms of water concentration at the

358 borehole in the same order of magnitude as the concentrations observed. The range of  
359 uncertainty on the discharge (Q) and on Atrazine input (M) means that one can  
360 compensate the other, and with the given data, it is difficult to determine where the  
361 greatest source of error in our calculation lies. The uncertainty on the vertical conduit  
362 location is a key parameter for a relevant vulnerability assessment.

363 The range of equivalent Peclet numbers and average residence times found for this  
364 aquifer is wide. That is why a karst system was chosen to test this model.

365 The hydrology was assumed to be steady state. Although many authors point out that  
366 water exchange between conduits and the surrounding rock drives the water quality at the  
367 karstic outlet (Charmoille et al., 2009), this strong hypothesis was made for large time  
368 steps, such as months or years. In these conditions, it is preferable to describe the average  
369 behaviour of the system, which is easier to use for risk assessment. High or low water  
370 stages can be estimated from the extreme discharge values (Fig.3).

371 Concerning the contaminant transport, the progressive decrease in atrazine concentration  
372 observed at the borehole is correctly described by the model and corresponds to the decrease  
373 in the quantities of atrazine applied to the maize crops (Table 1). The apparently erratic  
374 distribution of the atrazine concentrations observed is explained by the pulses of atrazine  
375 occurring 2 or 3 months after the injection periods. These results help to rationalize sampling  
376 campaigns and to ensure a better management of water resources.

377 No storage was observed and advective flow control was observed in this highly transitive  
378 system. However, a temporal shift of a few weeks (X axis) can be observed. The calculated  
379 concentrations appear before the observed ones. We hypothesize that the origin of this  
380 phenomenon is the uncertainty concerning the exact period of application. In our case,  
381 atrazine application was considered to occur once a year, in April, but in reality applications  
382 may have varied depending on the weather conditions.



383 The RTD model, based on literature datasets, made it possible to estimate a specific  
384 vulnerability, which can then be validated by field data. Fig. 2E can be validated by time  
385 series of contaminants observed in the water supply. There is no single solution that can fit  
386 the concentration time series at the borehole. While many spatial distributions can lead to  
387 the same lumped parameters, the advantage of the proposed approach is that it can test  
388 whether the working hypotheses are sustainable. This is an improvement over the usual  
389 method of vulnerability and risk assessment, and avoids the use of numerical groundwater  
390 flow models that are generally over-parametrized.

391

## 392 **6. Conclusions**

393 The specific vulnerability index locates the potential source of groundwater quality  
394 deterioration, but most assessment methods are qualitative. The Residence Time Distribution  
395 model can address temporal and transient aspects of contaminant spreading and represent  
396 them in a semi-quantitative manner. Such an approach makes it possible to establish a spatial  
397 risk or vulnerability indexes validated by water quality changes at the borehole. The dataset  
398 used in this method is commonly found in vulnerability studies. By using equivalent parameters  
399 to take the characteristics of each layer into consideration, the spatial complexity of the  
400 watershed can be reduced to an impulse response. The method based on the probability  
401 distribution of residence times is a semi-objective method that can help groundwater managers  
402 and decision-makers based on a physical approach to vulnerability assessment. The risk  
403 mapped with this methodology gives the opportunity to test the efficiency of land practice  
404 scenarios on the quality of the groundwater catchments.

405

### 406 **Acknowledgements**

407 This work is part of the PhD project supported by GEO-HYD (Antea members) and a national  
408 grant from the National Research and Technology Association (ANRT – CIFRE).

409 The database used was made available by the INSU/CNRS national observatory of karstic  
410 aquifers, SNO KARST.  
411

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558 **TABLE CAPTIONS**

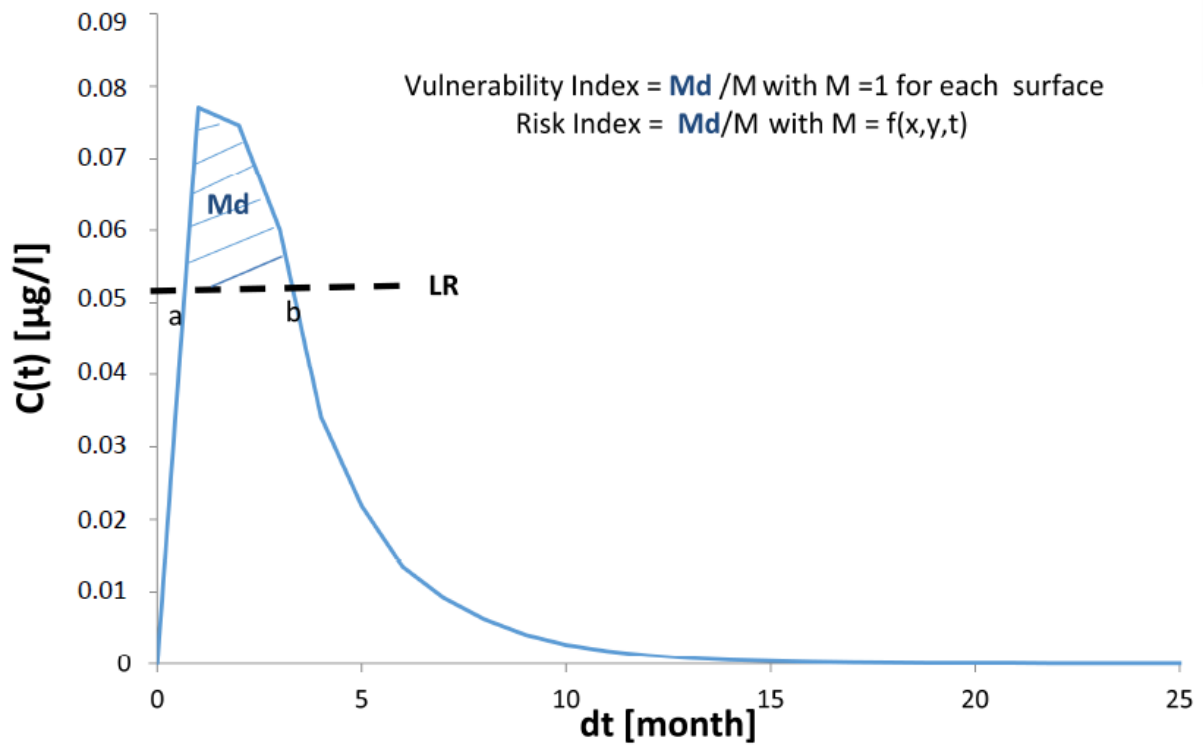
	<b>Velocity (Vd)</b>	<b>Water content (q)</b>	<b>Longitudinal dispersivity coefficient (<math>\alpha_L</math>)</b>	<b>Length of flow (L)</b>
Units	[m/s]	[-]	[m]	[m]
Unsaturated profiles SD	$2.31 \cdot 10^{-7}$	0.33	0.4	1.49 to 16.49
Unsaturated profiles SD/LM	$1.00 \cdot 10^{-8}$	0.4	0.4	4.22 to 9.39
Unsaturated profiles SD/CL	$3.50 \cdot 10^{-9}$	0.5	0.5	1.99 to 13.5
Unsaturated profiles CL/SD	$3.50 \cdot 10^{-9}$	0.6	0.5	2.05 to 10.37
Saturated alluvium	$9 \cdot 10^{-8}$ to $6 \cdot 10^{-4}$	0.15	20	1 to 14467
Saturated limestone	$8 \cdot 10^{-8}$ to $2 \cdot 10^{-2}$	0.3	2.5	1 to 10139
Saturated karstic conduit	$8 \cdot 10^{-8}$ to $2 \cdot 10^{-2}$	1	38	1 to 10139
References	Li and Ren (2011), Joodi et al (2009)	Simunek et al. (2008)	Simunek et al. (2008) and Gelhar (1992), Binet et al. (2014)	Desprez, 1967

559

560 Table1: Hydrodynamic characteristics of the zone

561

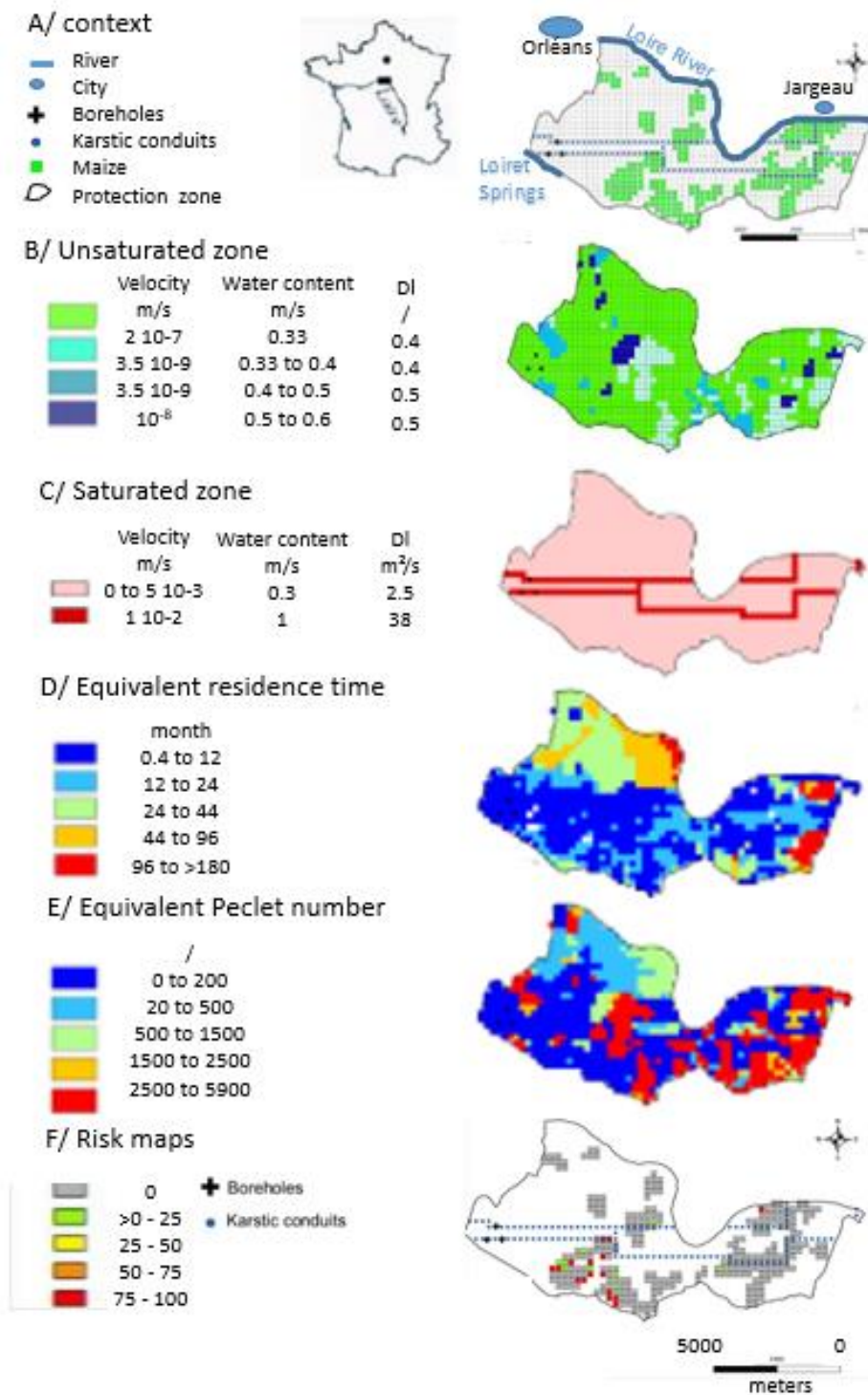
562

563 **FIGURE CAPTIONS**

564

565 Fig. 1: Contaminant concentration versus time at the borehole, following a  $M=1$  input for the  
 566  $n^{\text{th}}$  flow net. Illustration of the relationship between the concept of vulnerability and the  
 567 R.T.D. curve: the vulnerability index can be defined as the “area under the curve” higher  
 568 than the fixed threshold (LR)

569



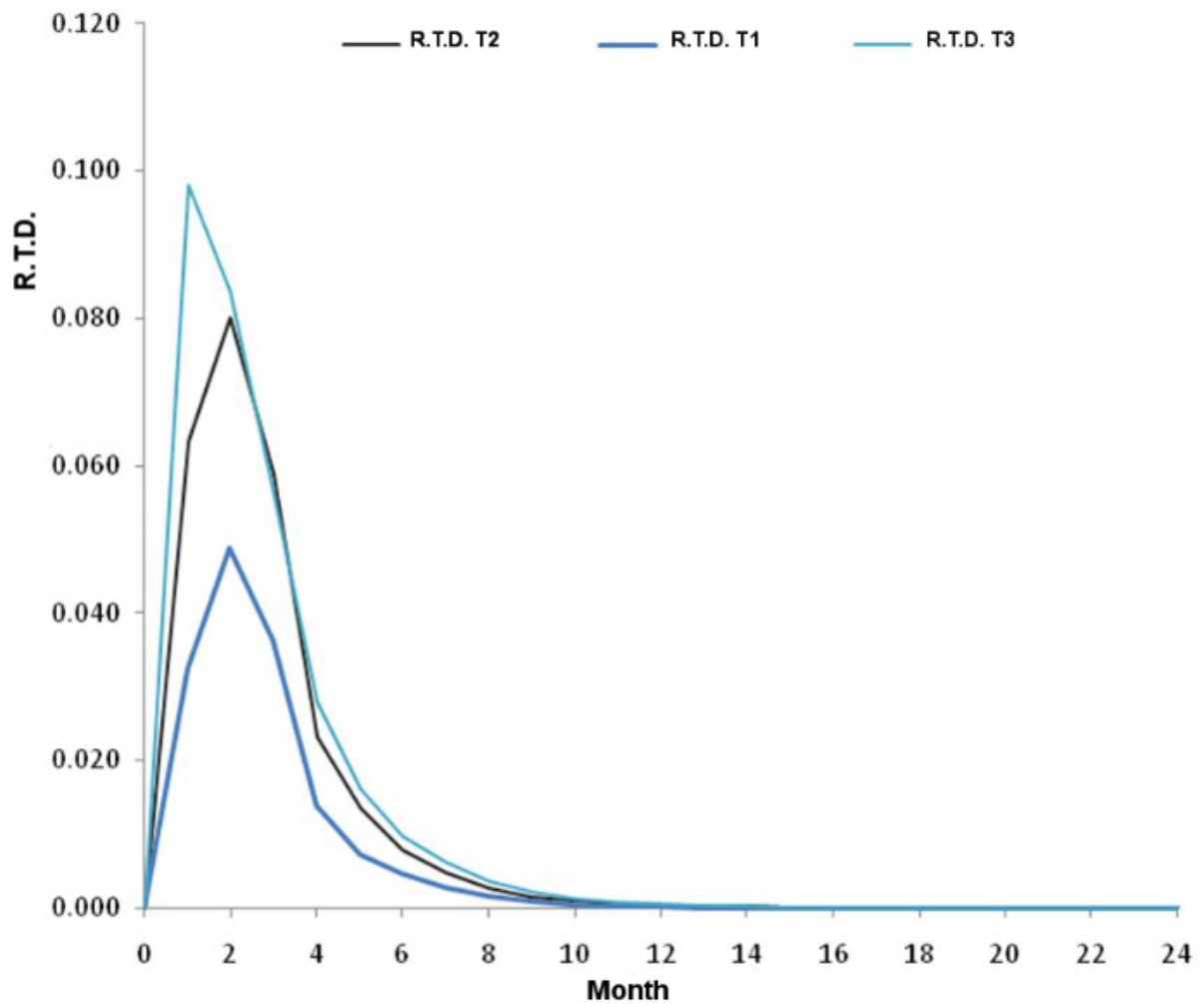
570

571 Fig. 2: The Val d'Orléans karstic aquifer, A/ grid discretization of the borehole watershed,

572 location of the 2010 maize crop. Spatial distribution of the parameters in B/ the

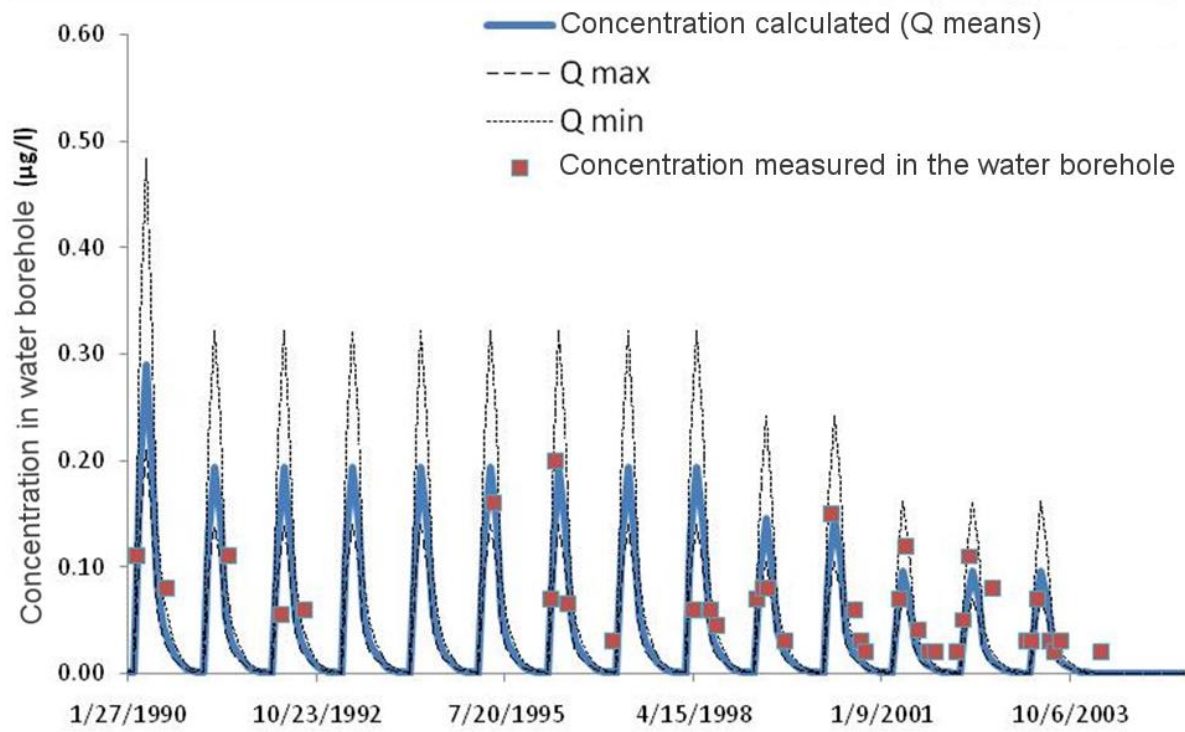
573 unsaturated and C/ saturated zones. D/ Equivalent residence time and E/ Peclet

574 number, F/ Specific risk map for Atrazine application in the borehole watershed.



575

576 Fig. 3: R.T.D. variability for the Val d'Orléans borehole related to the properties of the  
 577 unsaturated zone. RTD T1: UZ profile is made of sand (SD), RTD T2 of sand (SD),  
 578 limestone (LM) and clay (CL), RTD T3 with sand (SD) and 34 karstic point recharges



579

580 Fig. 4: Observed (crosses) and modeled (lines) atrazine concentrations versus time for high,

581

medium and low discharge values at the borehole

582