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## Tracing water perturbation using NO<sub>3</sub><sup>-</sup>, doc, particles size determination, and bacteria: A method development for karst aquifer water quality hazard assessment

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### ► To cite this version:

Guillaume Lorette, Nicolas Peyraube, Roland Lastennet, Alain Denis, Jonathan Sabidussi, et al.. Tracing water perturbation using NO<sub>3</sub><sup>-</sup>, doc, particles size determination, and bacteria: A method development for karst aquifer water quality hazard assessment. *Science of the Total Environment*, 2020, 725, pp.138512. 10.1016/j.scitotenv.2020.138512 . hal-03167080

**HAL Id: hal-03167080**

**<https://hal.science/hal-03167080v1>**

Submitted on 20 May 2022

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1 TRACING WATER PERTURBATION USING  $\text{NO}_3^-$ , DOC,  
2 PARTICLES SIZE DETERMINATION, AND BACTERIA: A  
3 METHOD DEVELOPMENT FOR KARST AQUIFER WATER  
4 QUALITY HAZARD ASSESSMENT

5  
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17

18 **Abstract**

19 Karst systems, as well as springs, are vulnerable to water perturbation brought by  
20 infiltration. In this research, sources of water perturbations were examined. The first  
21 objective is to provide a method that can determine the origin of the water flowing in the  
22 karst outlet. The second objective is to identify the associated water quality hazards caused  
23 by the infiltration source. The method relies on these parameters: turbidity, DOC,  $\text{NO}_3^-$ ,  
24 particle size, and bacteria (*E. coli*, enterococcus and total coliforms). As the method was  
25 applied during flood events, measurement of the water flow is also needed to have a basic  
26 knowledge on the hydrodynamic of the water resource.

27 The proposed method is based on a high resolution monitoring of physico chemical  
28 parameters of the water flowing during flood events. Using this proposed method, (1) the  
29 origin of the water can be identified, (2) the type and nature of water perturbation can be  
30 described, and (3) the type of water perturbation that accompanies contaminants such as the  
31 one with anthropogenic source (e.g.  $\text{NO}_3^-$ ) and bacterial nature can be determined. In  
32 identifying the water origin, this proposed method employed  $\text{NO}_3^-$  and DOC data  
33 normalization. Values are projected in the  $\text{NO}_3^-_{\text{norm}}=f(\text{DOC}_{\text{norm}})$  reference frame. These

34 are aligned to the slope. Depending on the obtained slope ( $\alpha$ ), water origin can be disclosed.  
35 If  $\alpha > 1$ , the increase of concentration of DOC weighs more, characterizing water from surface  
36 runoff. Whereas, if  $\alpha < 1$ , the consideration is more on the increase of  $\text{NO}_3^-$  concentration,  
37 characterizing water from unsaturated zone. However if  $\alpha$  cannot be calculated because there  
38 is no evident slope, this characterizes the water already present in the system.

39 Water originating from the surface runoff is prone to inorganic and bacterial  
40 contamination adsorbed by the particles. Identifying the type of water perturbation needing  
41 water treatment is important in managing the water resource. Hence, the evolution through  
42 time of  $\text{NO}_3^-$  and DOC with the particle size distribution, anthropogenic nature type of  
43 contaminant (*i.e.* in this study  $\text{NO}_3^-$ ), and presence or absence of bacteria were examined.

44 This method was applied in the springs of the Toulon, an important drinking water  
45 source of the city of Périgueux in France. This site was chosen considering the following  
46 factors: (1) its karst nature being vulnerable to infiltrations, having fractures and sinkholes;  
47 (2) its land use being influenced by the anthropogenic activities such as agriculture; and (3)  
48 its observed pronounced turbidity incidence. The first flood events of two hydrological cycles  
49 were assessed.

50 Three water origins of the spring water and the respective water quality hazards were  
51 identified: (i) water from saturated zone with minerals, (ii) water from unsaturated zone with  
52 nitrate, and (iii) water from surface runoff with the presence of bacteria. The second and third  
53 types of water perturbation gave evidence that the Toulon springs can be contaminated.  
54 Hence, in terms of resource management, the information obtained can be used as a basis in  
55 forecasting and planning the management actions or water quality treatments needed.

56

57 *Keywords:* karst aquifer, high resolution monitoring, nitrate, bacteria, particle, water quality  
58 hazard, water resource management

59

## 60 I. Introduction

61

62 Karst aquifers are major water resources, supplying approximately 25% of the world's  
63 population (Ford and Williams, 2007). Karst landscapes, associated with anthropogenic  
64 activities, are foremost concerns in determining karst water quality hazards specifically in  
65 terms of contamination. Since the beginning of the year 2000, researches on the issue of karst  
66 aquifers being vulnerable to water quality deterioration has increased. These are presented in  
67 the surface mapping studies (Andreo *et al.*, 2009; Kavouri *et al.*, 2011; Kazakis *et al.*, 2015;  
68 Marin *et al.*, 2015; Kazakis *et al.*, 2018; Ollivier *et al.*, 2019) and on the results of the  
69 analyses of the water temporal evolution at the outlets of karst systems (Pronk *et al.*, 2006;  
70 Goldscheider *et al.*, 2010; Jung *et al.*, 2014; Schiperski *et al.*, 2015; Doummar and Aoun,  
71 2018; Yang *et al.*, 2019).

72 Exokarstic landforms such as sinkholes or sinking stream allow punctual infiltration of  
73 pollutants (Fournier *et al.*, 2007; Kavouri *et al.*, 2011; Huneau *et al.*, 2013; Sivelle and Labat,  
74 2019). Fast infiltration and rapid transport of water can occur through fissure and conduits.  
75 This is characteristic of karst aquifers, and contribute to having incidences of contamination  
76 (Vesper and White, 2004; Geyer *et al.*, 2007; Hillebrand *et al.*, 2012; He *et al.*, 2010; Bauer  
77 *et al.*, 2013).

78 Identifying water resource hazards implies understanding the movement of water from  
79 different origins which can be done through the analysis of spring's natural and artificial  
80 responses (Massei *et al.*, 2002; Pronk *et al.*, 2006; Heinz *et al.*, 2009; Goldscheider *et al.*,  
81 2010; Ender *et al.*, 2018; Sivelle and Labat, 2019; Goepfert and Goldscheider, 2019).

82 Firstly, in infiltrations, identifying water origins are important. DOC and NO<sub>3</sub><sup>-</sup> can be  
83 used as infiltration markers. These tracers can be used in assessing the flow of water from  
84 soil or unsaturated zone (Celle-Jeanton *et al.*, 2003; Mahler and Garner, 2009; Mudarra and

85 [Andreo 2011; Mudarra et al., 2011](#)). Specifically, DOC in groundwater is used to assess a  
86 water origin ([Batiot et al., 2003; Charlier et al., 2011](#)) and as a complementary marker of  
87 turbidity in identifying fecal contamination ([Pronk et al., 2007](#)). In a rural context, the input  
88 of nitrogen, organic or inorganic matter, can lead to an accumulation of  $\text{NO}_3^-$  in soils and  
89 unsaturated zone ([Thomas et al., 2016](#)). Leaching of these may result to a nitrate increase at  
90 the outlet of karst systems ([Rowden et al., 2001; Stueber and Criss 2005; Pronk et al., 2008;](#)  
91 [Pu et al., 2011](#)).

92 The common use of  $\text{NO}_3^-$  and DOC at the outlet of a karst system with high resolution  
93 monitoring will not only help in identifying the water origins but also facilitates in evaluating  
94 the identified water quality hazards (punctual infiltration and diffuse infiltration). This  
95 brought to the second and third concerns: (2) which type of water perturbation needs water  
96 quality treatment and particularly, (3) which type hosts bacteria? In these lines, particles and  
97 bacteria were used as supplementary parameters.

98 As for the particles, these can be resuspended due to a pressure wave induced by  
99 percolating storm water reaching the phreatic water level (pulse-through turbidity). These can  
100 also be introduced into the aquifer from the Earth surface (flushthrough turbidity) as a result  
101 of either slow percolation or a more rapid point recharge such as from sinking streams. The  
102 nature of turbidity can be determined looking at the particles if these are of autochthonous  
103 (originating from the weathering of material) or allochthonous (originating from the Earth's  
104 surface) origin ([Massei et al., 2002, 2003; Valdes et al., 2005; Fournier et al., 2007;](#)  
105 [Schipperski et al., 2015](#)).

106 Particle is an important subject matter as it can induce environmental problems due to  
107 its ability to sorb bacteria. There are studies which have demonstrated the increased survival  
108 of microorganisms when they are associated with particles ([Pommepuy et al., 1992;](#)  
109 [Palmateer et al., 1993](#)). Some research results suggest that turbidity indicates microbial

110 pathogen presence such as *E. coli*, enterococcus or total coliforms (Ryan and Meiman, 1996;  
111 Nebbache *et al.*, 1997; Pronk *et al.*, 2006, 2009; Goldscheider *et al.*, 2010). However, others  
112 did not observed the same findings stating that turbidity is not always accompanied by  
113 surface contaminants (Dussart-Baptista *et al.*, 2003; Pronk *et al.*, 2007, 2009; Heinz *et al.*,  
114 2009). In these lines, this study proposed a tool that can determine the type of turbidity that is  
115 accompanied by contaminants (*e.g.* NO<sub>3</sub><sup>-</sup> and microbial pathogens).

116 The proposed method was applied to the Toulon springs in Périgueux, France. The  
117 Toulon springs, as several karst springs, are a water resource being influenced by diffuse  
118 pollution and punctual infiltration (Lastennet *et al.*, 2004; Lorette *et al.*, 2018). The  
119 hydrogeological catchment is mainly rural (agriculture). There is no livestock and few  
120 residential areas (less than 3 000 houses). The Toulon springs are experiencing an increase of  
121 nitrate for over 60 years. This is a foremost concern as it serves as a major source of drinking  
122 water for approximately 55 000 people.

123 The main objective of this research is to develop a method using high-resolution  
124 monitoring that will facilitate in determining origins of water flowing at the outlet of karst  
125 system during floods like in the Toulon. These origins are associated with water quality  
126 hazards. Specifically, this study would like to: (i) identify the types water quality hazards that  
127 springs like in the Toulon are facing brought about by the movement of water from different  
128 origins (proposing a conceptual model of transfer of contaminants) and (ii) propose a  
129 conceptual model/framework explaining the relationships between NO<sub>3</sub><sup>-</sup> and DOC in this  
130 karst environment.

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## 135 2. Site description

136

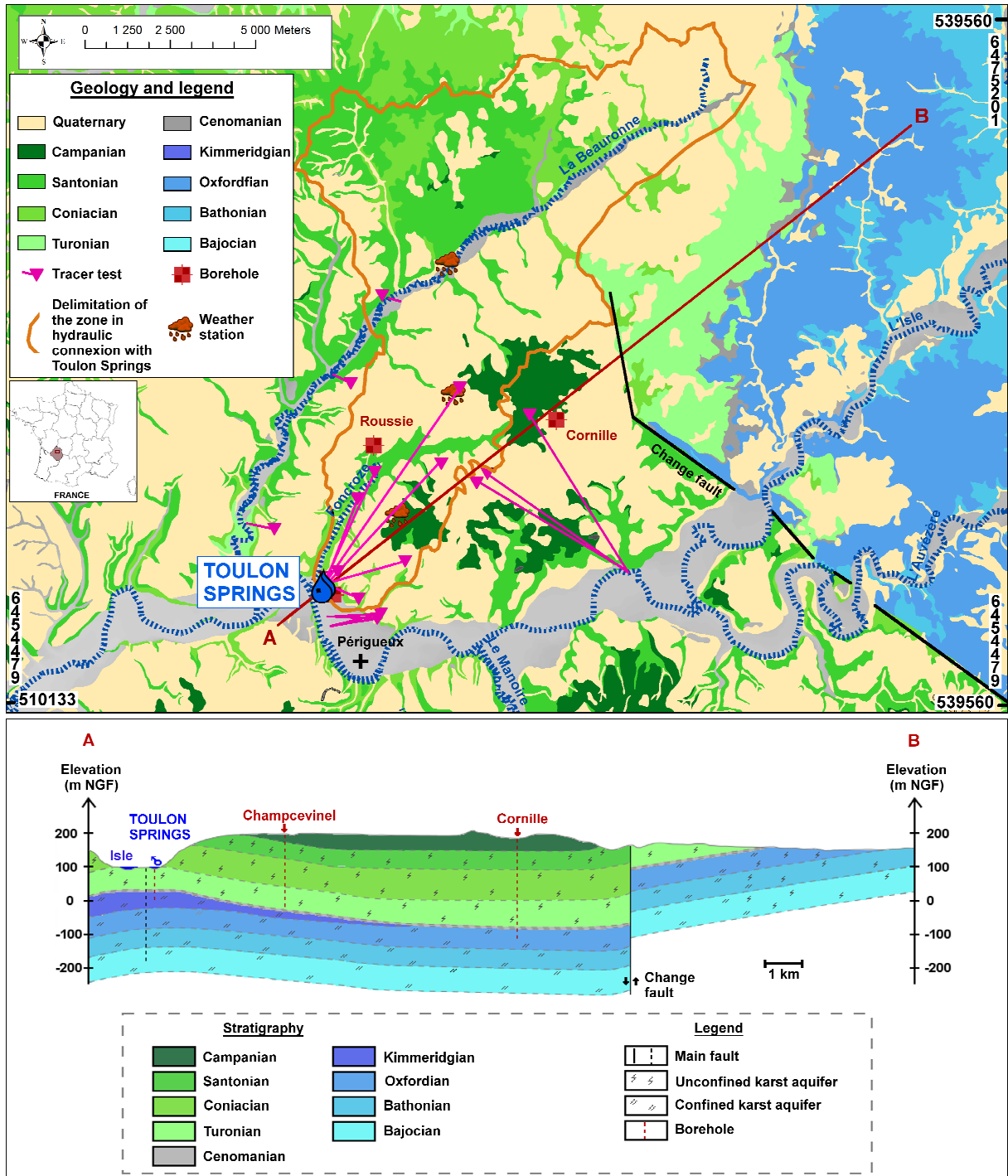
### 137 2.1 Local geology and hydrogeology

138

139 The Toulon springs supply drinking water to the city of Périgueux (France) since 1832.  
140 These consist of the Abîme Spring and the Cluzeau Spring, originating from the same karst  
141 conduit. The average discharge is  $450 \text{ L s}^{-1}$ , making it as one of the most important water  
142 resources in the Dordogne County. The springs are vauclosian type, water reaches the surface  
143 through localized faults at the extrados of an anticline fold oriented at  $\text{N}145^\circ$  ([Lastennet et](#)  
144 [al., 2004](#)).

145 Geology of the area is composed of carbonated rocks from upper Jurassic and upper  
146 Cretaceous ([Von Stempel, 1972](#); [Lorette, 2019](#)). At the bottom, the upper Jurassic formations  
147 (Oxfordian and Kimmeridgian) consist of dolomitic limestone with a thickness varying from  
148 100 m to 150 m. At the top, the upper Cretaceous formations (Turonian, Coniacian and  
149 Santonian) is made up of limestone with a thickness varying from 200 m to 250 m. At the top  
150 of the carbonate rocks is an epikarst, surmounted by a soil layer of few meters. The Toulon  
151 karst system also presents fold and faults with a principal direction NW-SE ([Fig. 1](#)).

152 Hydrogeological context, on the other hand, considers two main multilayered aquifers:  
153 (i) unconfined karstic upper Cretaceous aquifer: Turonian, Coniacian and Santonian aquifers  
154 and (ii) confined karstic upper Jurassic aquifer: Oxfordian and Kimmeridgian aquifers. The  
155 two main aquifers are separated by Cenomanian marls, considered impermeable. Spatial  
156 thickness (4-20 meters) and facies variations (marls-sand) over the study area induced an  
157 additional difficulty in understanding the relationship of the two main aquifers.



158

159  
160  
161

Fig. 1: Hydrogeological map of the Toulon karst system (Adapted from Lorette *et al.*, 2018). AB: simplified SW-NE geological cross-section. The Cenomanian is considered as not an aquifer.

162

Functioning of the Toulon springs was explained by Lorette *et al.*, (2016, 2018) and

163

Lorette (2019). The system is an example of springs originating from confined Jurassic

164

aquifer and unconfined Cretaceous aquifer according to the hydrogeological conditions.



165 During low-water period, there is a large water input coming from confined Jurassic aquifer  
166 and saturated part of the unconfined Cretaceous aquifer (Turonian). Thus, implying that the  
167 Jurassic aquifer has a reservoir function. In a high-water period, infiltration water activates  
168 the drainage network in the formation above the Turonian (*i.e.* Coniacian and Santonian).  
169 Hence, this infers that the Cretaceous aquifer has a transmission function. The Cretaceous  
170 aquifer is responsible for the hydrodynamic and hydrochemical variations. This enables the  
171 rapid transmission of the elements from the surface and subsurface. In terms of surface  
172 infiltration (*e.g.* NO<sub>3</sub><sup>-</sup>, DOC, bacteria, and turbidity), the Cretaceous aquifer contributes to the  
173 Toulon springs' water quality hazards.

174

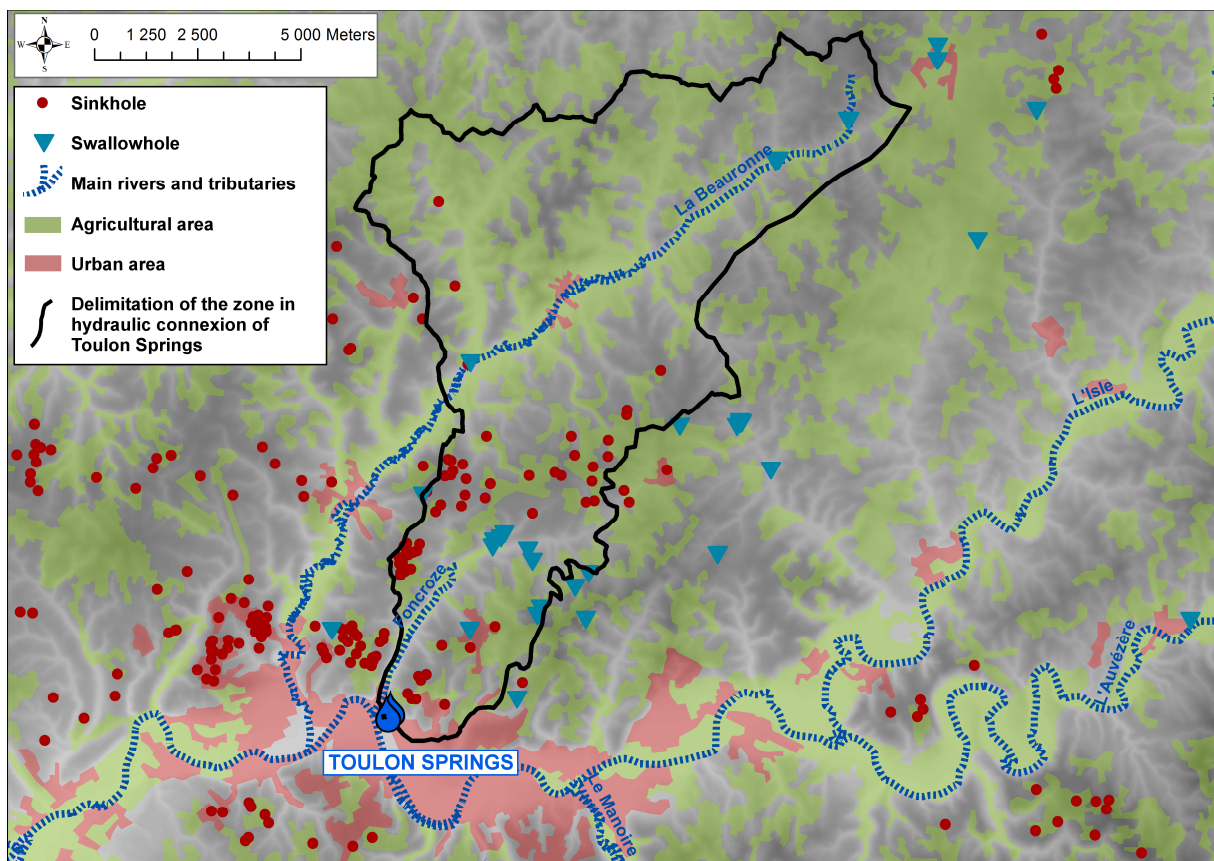
## 175 **2.2 Local geomorphology**

176

177 The surface area presents typical karstic landforms. Several exokarstic forms such as  
178 sinkholes and surface water (*e.g.* stream river) loss (Fig. 2) are noticed on the plateau above  
179 the Toulon springs. Most of the losses are temporary and activated only after heavy rainfall.  
180 Sinkholes are mostly located on the plateau, in thin soil layer area. Tracer test is an efficient  
181 tool to show relationships between the surface water losses and springs. In the area, several  
182 dye tracers were performed. Some of the results showed a rapid transit, from 5 m.h<sup>-1</sup> to 130  
183 m.h<sup>-1</sup>. This underlines the karstic behavior of the aquifer and the nature of the water quality  
184 hazard that can be brought to the system. Surface water losses are considered as major source  
185 of water quality hazard in terms of contamination due to the surface runoff (Pronk *et al.*,  
186 2006; Goldscheider *et al.*, 2010).

187 The area, localized in the north of the city of Périgueux, is considered as a rural area.  
188 Land use is mainly forest (50%) and agricultural (40%) (Fig. 2). Urban land use is only 10%.  
189 Agriculture lands mostly consist of wheat, corn, sunflower, and colza. Some livestock

190 farming is present, raising cows and ducks. The use of nitrogen synthetic fertilizer and  
191 manure increased for the last decades, leading to the augmentation of nitrate concentration in  
192 the groundwater (Lorette 2019). The local hydrochemical background was  $\sim 1 \text{ mg L}^{-1}$  in 1960  
193 at low-flow conditions and is now close to  $\sim 12 \text{ mg L}^{-1}$  on the average with a maximum peak  
194 concentration of  $\sim 20 \text{ mg L}^{-1}$  during floods. Data from 1960 to 2014 are provided by  
195 administration of Dordogne, in addition, we measure it since 2014 (Lorette 2019). For the  
196 year scale, about 40 TN/year are exported at the Toulon springs. Nitrate stored in the  
197 unsaturated zone of the aquifer may be transported to the saturated zone after some rainfall  
198 events.  
199



201  
202

Fig. 2: Geomorphological situation and land use of the Toulon karst springs.

203        **2.3 Climate**

204

205        Since January 2016, 3 rainfall stations and one meteorological station (recording  
206 temperature, humidity, wind, and the rate of sunshine) are installed at the plateau above the  
207 Toulon springs (Fig. 1). Périgueux climate is tempered, with an average of 13°C (since  
208 2016). In summer, average temperature ranges from 20°C to 21°C. In winter, average  
209 temperature ranges from 5°C to 6°C. Annual average rainfall is close to 800 mm. Real  
210 evapotranspiration is calculated between 200 mm and 350 mm per year (using Penman-  
211 Monteith equation).

212

213        **3. Material and methods**

214

215        **3.1 Hydrological Approach**

216

217        The sampling strategy aims to identify the water quality hazards of the Toulon springs  
218 in relation to the movement of water from different origins. High resolution monitoring of  
219 hydrochemical parameters combined with particle sampling measurement and bacteriology  
220 sampling were performed during the first flood events of each cycles: (i) February 2017 for  
221 the 2016-2017 cycle and (ii) December 2017 for the 2017-2018 cycle. The first floods are  
222 identifiable as these were associated with important rainfall after a long low–water period.  
223 Nitrate, turbidity, and DOC were monitored in the Toulon springs. These parameters show  
224 similar trends at each first flood of the cycle. The flood of February 2017 was chosen to  
225 establish the links between the bacterial contamination and other monitored parameters. Once  
226 relationships are established, an innovative method was developed to identify the origin of

227 the water flowing in the karst outlet during flood events. Once the  $\text{NO}_3^-$  and DOC trend is  
228 known, this can be applied for the first flood of every hydrological cycles (for example  
229 December 2017).

230

### 231 **3.2 Continuous data monitoring and discrete sampling**

232

233 Since March 2016, turbidity,  $\text{NO}_3^-$ , and DOC are measured at the Toulon springs.  
234 Turbidity is measured using an optical sensor (Solitax sc TLine, HACH) every 10 minutes,  
235 with a relative precision of 1%, and a range of measurement of 0.001 NTU to 4 000 NTU.  
236 Nitrate and DOC are measured every 6 minutes using a UV-visible scanning  
237 spectrophotometer (Spectro::lyser, S::CAN), with a precision of  $0.1 \text{ mg L}^{-1}$  and  $0.05 \text{ mg L}^{-1}$ ,  
238 respectively, and a range of measurement of 0 to  $46 \text{ mg L}^{-1}$  and 0 to  $133 \text{ mg L}^{-1}$ , respectively.  
239 To avoid measurement errors due to matrix interferences when turbidity increases, a manual  
240 calibration of the spectro::lyser was made with laboratory measurements (Lorette, 2019).

241 Simultaneously, hydrodynamic data (rainfall and discharge) were also monitored.  
242 Rainfall was measured at the Toulon springs hydrogeological catchment every 15 minutes.  
243 Only accumulated rainfall over a day for the central station is presented in this article.  
244 Finally, discharge was measured in a gauging station every 10 minutes at the Toulon springs,  
245 with an accuracy of 0.5%.

246 From 08/02/17 to 24/02/17, 12 sampling campaigns were performed to analyze the  
247 bacteriology water samples (*Escherichia coli*, total coliforms, and enterococcus) and particles  
248 (particle size distribution, observation, and chemistry) in the water. Bacteriology water  
249 samples were taken using HDPE 500 mL bottles with thiosulfate and kept at  $4^\circ\text{C}$  before the  
250 analysis on the same day of sampling. To sample particle, an HDPE bottle of 2 L is

251 immersed and filled up in the Toulon spring. These bottles were kept in darkness until the  
252 analysis is performed.

253

### 254 **3.3 Analytical methods**

255

256 Bacteriological analyses were done at the Laboratory of Dordogne Departmental  
257 Research (LDAR24). Measured parameters are: (i) *Escherichia coli* (*E. coli*), (ii) total  
258 coliforms (both using French norm NF EN ISO 9308-1), and (iii) enterococcus (using French  
259 norm NF EN ISO 7899-2).

260 Analyses on particles were done at the University of Rouen, in coastal and Continental  
261 Morpho-dynamic Laboratory. Particle counting for sizes from 0.04  $\mu\text{m}$  to 2000  $\mu\text{m}$  was done  
262 using a laser granulometer Beckman coulter LS 13 320. Observation of particles and particle  
263 chemistry characterization was done using a Scanning Electron Microscope Ziss EVO 40 Ep  
264 and a Brucker microprobe for each sample.

265

### 266 **3.4 Normalized data analysis**

267

268 Normalized data enables studying the relative variations of a parameter free from units.  
269 Comparing normalized data of river flow and sediment concentration during a flood event  
270 [Williams \(1989\)](#) described several possibilities of solid and dissolved phases transport.  
271 [Valdes et al., \(2005\)](#), [Fournier et al., \(2007\)](#) and [Schiperski et al., \(2015\)](#) used normalized  
272 data on turbidity and electrical conductivity measurements to highlight the sedimentary  
273 process.

274 In this paper, application of the method using data normalization of nitrate and DOC  
275 data is proposed as water origin markers. Using these infiltration markers will help in  
276 describing the process occurring in an anthropogenically influenced alimentation area of the  
277 Toulon springs. DOC can be used to identify water originating from soil or punctual  
278 infiltration.  $NO_3^-$  can be used as a tracer of diffuse infiltration through soil and unsaturated  
279 zone.

280 Normalization was made using the maximum and minimum values during the flood  
281 events (equation 1 and 2):

282

$$NO_3^-_{norm} = \frac{(NO_3^- - NO_3^-_{min})}{(NO_3^-_{max} - NO_3^-_{min})}$$

283 (1)

284

$$DOC_{norm} = \frac{(DOC - DOC_{min})}{(DOC_{max} - DOC_{min})}$$

285 (2)

286

## 287 4. Results

288

### 289 4.1 Geochemical variability

290

291 During February 2017 and December 2017 flood event, high-resolution monitoring of  
292 hydrodynamic (discharge and rainfall) and hydrochemical parameters (turbidity, nitrate, and  
293 dissolved organic carbon) were obtained at the outlet of the Toulon karst system. [Table 1](#)  
294 summarizes data of the Toulon springs. [Fig. 3](#) illustrates the temporal evolution of discharge  
295 and hydrochemical parameters from the Toulon springs.

296

297 **4.1.1 First cycle: February 2017**

298

299 From February 1<sup>st</sup> to February 8<sup>th</sup>, a rainfall event of 51.4 mm led to an increase of  
300 water discharge of the Toulon springs (Fig. 3A). The previous water discharge was about  
301 300 L s<sup>-1</sup> which is characterized as the regular flow level the Toulon springs (Lorette *et al.*,  
302 2018). The weak rainfall intensity (5 mm.d<sup>-1</sup> on the average) implied slow flow, taking 6 days  
303 to increase water discharge in the Toulon springs.

304 The maximum water discharge is recorded on 08/02/2017 having 511 L s<sup>-1</sup>. This high  
305 water flow influenced the hydrochemical parameters as well as the particles. The turbidity  
306 presented an inconsequential variation with minimum and maximum values of 0.70 NTU and  
307 3.95 NTU, respectively. Four increases are recorded during this water flow: three during high  
308 water flow and one when there was low water flow.

309 NO<sub>3</sub><sup>-</sup> and DOC increased during the high water flow (Fig. 3A). The average  
310 concentrations of NO<sub>3</sub><sup>-</sup> and DOC were 14.9 mg L<sup>-1</sup> and 0.7 mg L<sup>-1</sup>, respectively, with  
311 corresponding minimum values of 12.0 mg L<sup>-1</sup> and 0.20 mg L<sup>-1</sup>. The maximum values of  
312 NO<sub>3</sub><sup>-</sup> and DOC are 20.0 mg L<sup>-1</sup> and 1.30 mg L<sup>-1</sup>, respectively. These parameters did not show  
313 the same dynamic evolution during this flood event.

314 DOC appeared to have three stages: (i) a slow increase from 04/02/2017 to 10/02/2017  
315 then (ii) rapid increase from 10/02/2017 to 14/02/2017, finally, (iii) another slow increase  
316 during 14/02/2017 until 20/02/2017.

317

318

319

320        **4.1.2    Second cycle: December 2017**

321

322        From December 7 to December 15, two rainfall events for 6 days brought to an  
323 increase of the discharge at the outlet of the Toulon karst system (Fig. 3B). The first peak  
324 accounted 50.4 mm of rainfall for 2 days. Water discharge increased from 315 L s<sup>-1</sup>  
325 (10/12/2017) to 590 L s<sup>-1</sup> (12/12/2017). The second increase in water discharge is, however,  
326 associated with less intensive rainfall, accumulating with a total of 30.2 mm in 4 days. This  
327 gave an augmentation of 90 L s<sup>-1</sup> (14/12/2017 to 15/12/2017) reaching a maximum water  
328 flow of 615 L s<sup>-1</sup>.

329        Having the increase of the water flow, the turbidity increased as well identifying 2 large  
330 peaks. The first peak is recorded during the augmentation of the water flow. Turbidity was  
331 accounted from 0.36 NTU (10/12/2017) to 3.88 NTU (11/12/2017). The second is recorded  
332 from 13/12/2017 to 16/12/2017 with values of 2.58 NTU and 8.37 NTU, respectively (Fig.  
333 3B).

334        The average concentrations of NO<sub>3</sub><sup>-</sup> and DOC were 14.58 mg L<sup>-1</sup> and 1.66 mg L<sup>-1</sup>,  
335 respectively, with corresponding minimum values of 10.84 mg L<sup>-1</sup> and 0.17 mg L<sup>-1</sup>. The  
336 maximum value of NO<sub>3</sub><sup>-</sup> was 19.12 mg L<sup>-1</sup>, while, DOC was 2.30 mg L<sup>-1</sup>. The same as the  
337 water flow during February 2017, DOC had three distinct peaks (Fig. 3B): (i) a slow increase  
338 from 11/12/2017 to 15/12/2017; (ii) a rapid increase from 15/12/2017 to 17/12/2017; and  
339 then (iii) going back to a slow increase from 17/12/2017 to 22/12/2017. For NO<sub>3</sub><sup>-</sup>, three  
340 peaks were identified as well (Fig. 3B): (i) a rapid increase from 11/12/2017 to 15/12/2017;  
341 (ii) a quasi-stabilized concentrations in between 15/12/2017 to 22/12/2017; and (iii) a rapid  
342 increase from 22/12/2017 to 27/12/2017.

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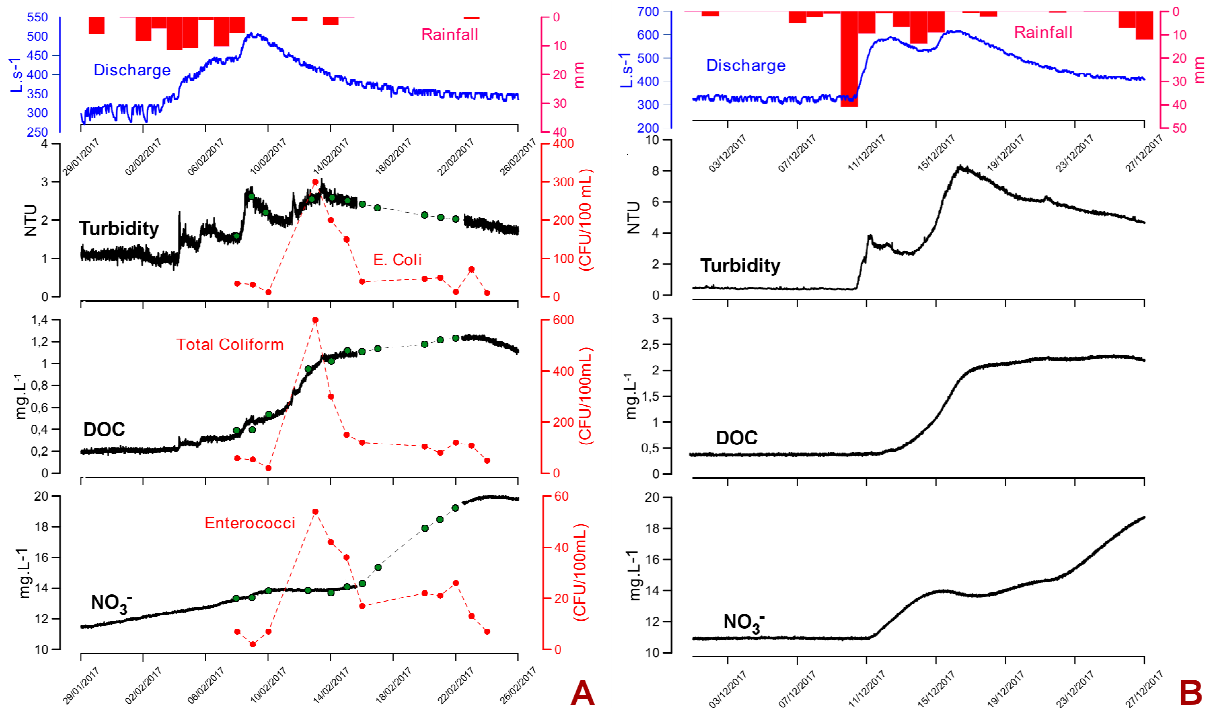


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345

**Table 1: Statistical parameters of the hydrodynamic and hydrochemical parameters, and bacteria during February 2017 and December 2017 flood events. (n) number of samples, ( $\sigma$ ) standard deviation, (CV) coefficient of variation.**

Flood event		Discharge (L.s <sup>-1</sup> )	Turbidity (NTU)	NO <sub>3</sub> <sup>-</sup> (mg.L <sup>-1</sup> )	COD (mg.L <sup>-1</sup> )	Total		
						E.coli (CFU / 100 mL)	coliforms (CFU / 100 mL)	Enterococcus (CFU / 100 mL)
February 2017	n	3600	2592	4388	4388	12	12	12
	Mean	386	1.89	14.93	0.70	80	147	21
	Min	277	0.70	12.06	0.18	10	20	2
	Max	511	3.95	20.03	1.30	300	600	54
	$\sigma$	51	0.51	2.88	0.39	88	155	16
	CV (%)	13	27	19	55	110	105	73
December 2017	n	2592	2592	4320	4320	-	-	-
	Mean	496	5.15	14.58	1.66	-	-	-
	Min	317	0.36	10.84	0.17	-	-	-
	Max	617	8.37	19.12	2.30	-	-	-
	$\sigma$	73	1.78	2.19	0.74	-	-	-
	CV (%)	15	35	15	45	-	-	-

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**Fig. 3: Temporal evolution of the water discharge and hydrochemical parameters from the Toulon springs with respect to the two flood events. (A) February 2017, (B) December 2017. Green items refers to manual sampling during February 2017 flood event.**

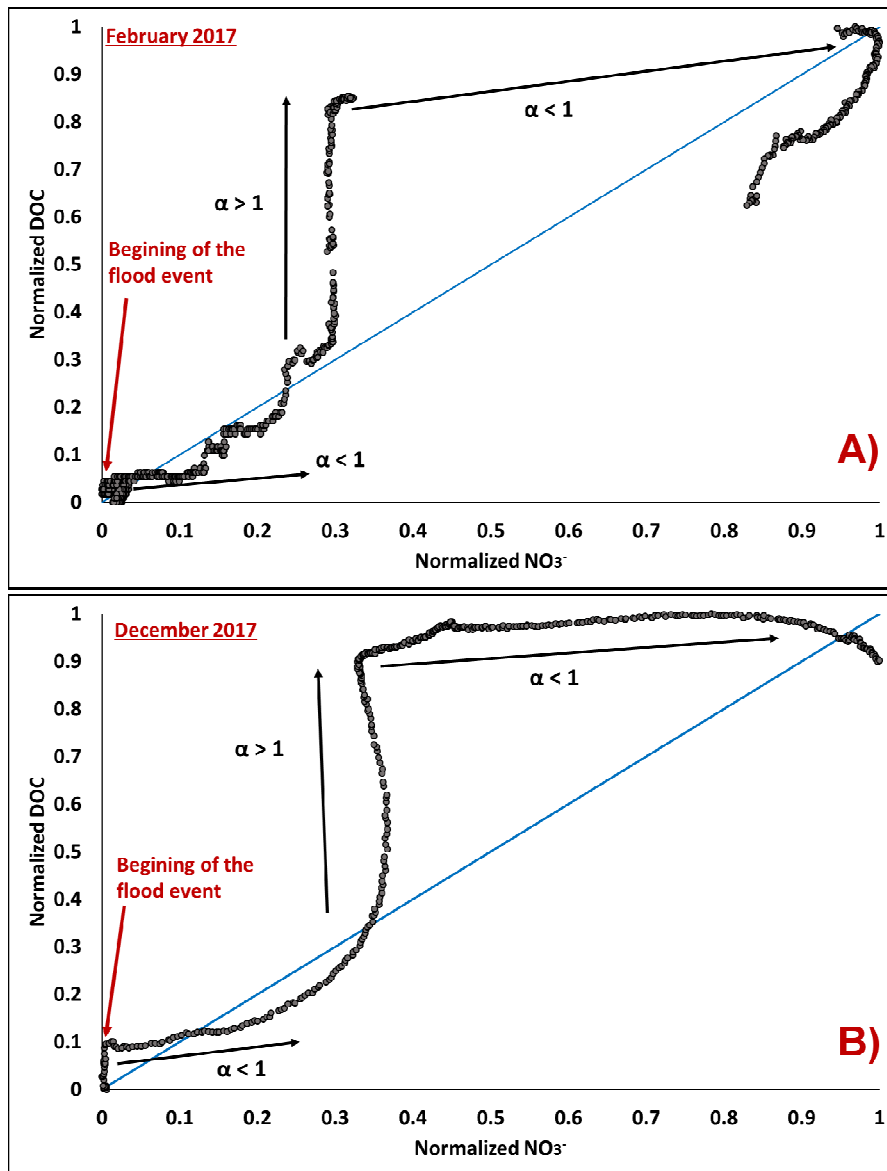
## 352 **4.2 DOC<sub>norm</sub> over NO<sub>3</sub><sup>-</sup><sub>norm</sub>: Normalized data analysis**

353

354 Normalized data were performed using the maximum and minimum values during the  
355 flood events to determine the relative variations of a parameter free from units. Normalized  
356 data analysis from DOC<sub>norm</sub> vs NO<sub>3</sub><sup>-</sup><sub>norm</sub> was performed on the two flood events previously  
357 presented.

358 February 2017 (Fig. 3A) and December 2017 (Fig. 3B) flood events presented the same  
359 trend as the DOC<sub>norm</sub> vs NO<sub>3</sub><sup>-</sup><sub>norm</sub>. In Fig. 4, the start of the high water flow is characterized  
360 by a slope inferior to 1 ( $\alpha < 1$ ). This means that the increase of NO<sub>3</sub><sup>-</sup> is higher compared to the  
361 increase of DOC. It is followed by a change of slope going to the right, having  $\alpha > 1$ . This  
362 signifies that the increase of DOC is more pronounced at this time than NO<sub>3</sub><sup>-</sup>. Then, the slope  
363 went back to  $\alpha < 1$ .

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Fig. 4: Normalized NO<sub>3</sub><sup>-</sup> - DOC during two flood events from the Toulon springs. (A) February 2017, (B) December 2017. The blue line illustrates the slope  $\alpha=1$ .

374 **4.3 Particles and bacteria**

375

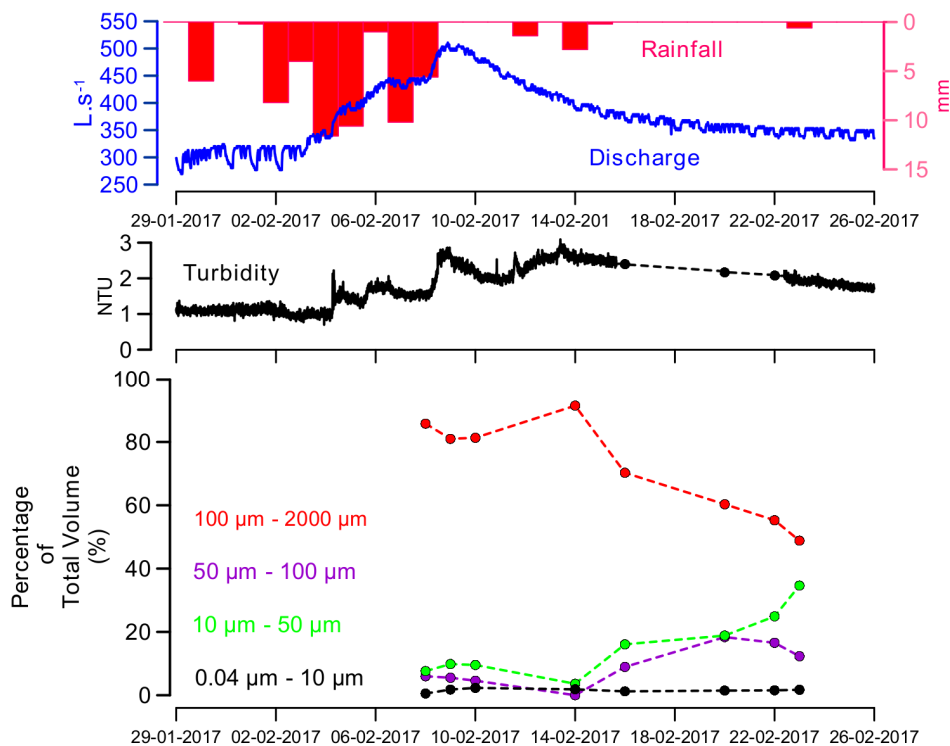
376 **4.3.1 Particle size distribution**

377

378 The particle with size more than 100  $\mu\text{m}$  dominates the whole flooding event with 91%  
379 during the 14/02/2017 to 48% during the 23/02/2017). After the peaks, the particles of this  
380 size decreased in terms of percentage with respect to other smaller sizes.

381 In Fig. 5, the sample of February 14<sup>th</sup> shows the transfer of a new water mass. This  
382 water mass is characterized by an increase of the small size particles (10-50  $\mu\text{m}$ ) and a  
383 decrease of the large size particles (100-2000  $\mu\text{m}$ ). The flowing of this new water mass is  
384 confirmed by a stagnation of nitrate and an increase of DOC (Fig. 3A).

385



386

387 **Fig. 5: Temporal evolution of the water discharge, turbidity and particles during the February 2017 flood event.**

388

389        **4.3.2 Particle Characterization using Scanning Electron Microscope (SEM)**

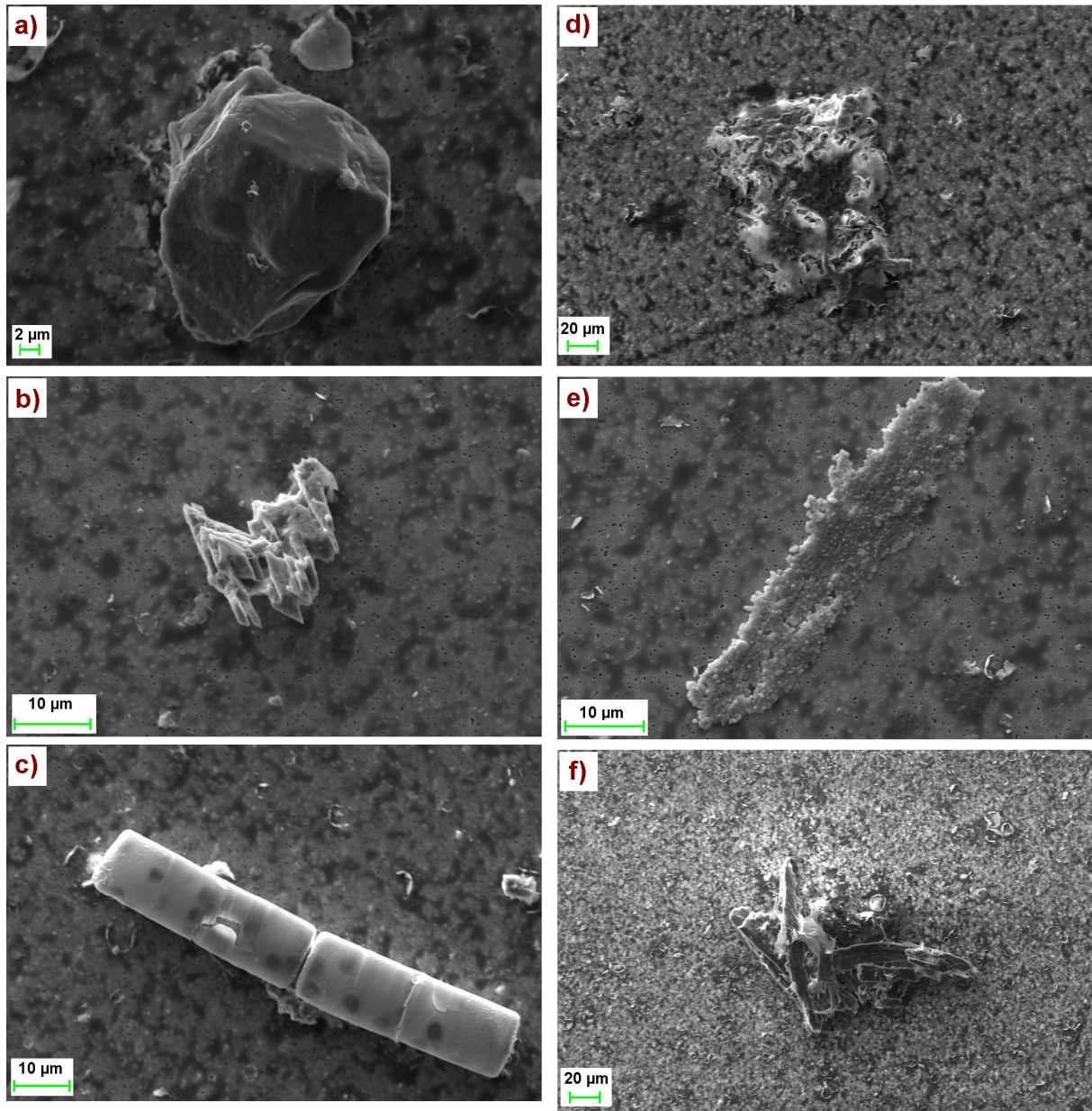
390

391        Characterization of the chemistry of the particle helps in distinguishing allochthonous  
392 and autochthonous particles. Microprobe and Scanning electron microscope were used.  
393 Analysis of particle nature and size distribution during the flood of February 2017 showed  
394 variations of the particle type along the flood event.

395        During the flood happened last February 2017, particles flowing throughout the rising  
396 of the flood were bigger than 100  $\mu\text{m}$  (we call it large particles given the range of particles  
397 size at the Toulon springs) and mainly composed by minerals like quartz (Fig. 6a) or calcite  
398 (Fig. 6b and Fig. 6c). This corresponds to the composition of the rock and implies  
399 autochthonous origin of the particles.

400        During the lowering of the flood, another nature of particle appeared, associated with  
401 an increase of the turbidity. These particles are smaller than 100  $\mu\text{m}$  (we call it small  
402 particles) and mainly organics: organic-mineral flocs (Fig. 6d) and vegetal debris (Fig. 6f).  
403 Bacterial colonies were adsorbed on vegetal debris (Fig. 6e). Also, there was an increase of  
404 fecal contaminants showing a surface origin of the water. This denotes allochthonous origin  
405 of these particles.

406



407

408 **Fig. 6:** Nature of the particles found in the Toulon springs during the 2017 flood event observed by scanning electron  
 409 microscope. a) quartz. b and c) calcite. d) organic-mineral flocs. e) bacterial colonies adsorbed on vegetal debris. f)  
 410 vegetals debris.  
 411

412 **4.3.3 Fecal bacteria**

413

414 The maximum value of *E. coli* detected is 300 CFU/100 mL with a minimum value of  
 415 10 CFU/100 mL and an average of 80 CFU/100 mL (Fig. 3A). This maximum value was

416 observed during 13/02/2017 (high flow), 4 days after the maximum of discharge. The  
417 minimum value, however, was observed during 24/02/2017, at the end of the low-flow.

418 The number of total coliforms is higher than *E. coli*. It has a maximum value of  
419 600 CFU/100 mL with a minimum value of 20 CFU/100 mL and an average of  
420 146 CFU/100 mL (Fig. 3A). This maximum value was observed during 13/02/2017, high  
421 flow, 4 days after the maximum water discharge. The minimum value, however, was  
422 observed during 10/02/2017, also within the high flow event, 1 day after the maximum of  
423 water discharge.

424 Enterococcus has the least number of detected bacterial species compared to *E. coli* and  
425 total coliforms (Fig. 3A). The maximum value identified is 54 CFU/100 mL with a minimum  
426 value of 2 CFU/100 mL and an average of 21 CFU/100 mL. This maximum value was  
427 observed during 13/02/2017, high-flow, 4 days after the maximum water discharge. The  
428 minimum value, however, was observed during 09/02/2017, still high flow, at the date of the  
429 maximum water discharge.

430

## 431 5. Discussion

432

### 433 5.1 Bacterial contamination

434

435 The concentration of *E. coli* that can be found in some karst springs are as follows: 183  
436 CFU/100 mL from Cossaux Spring (Pronk *et al.*, 2009), 648 CFU /100 mL from Moulinet  
437 Spring (Pronk *et al.*, 2009), 1088 from Moulinet Spring (Pronk *et al.*, 2007). The Toulon  
438 springs has non-negligible *E. coli* concentration having the maximum recorded during the

439 sampling campaign as 300 CFU/100 mL. The highest concentration of *E. coli* recorded in the  
440 Toulon springs is 700 CFU/100 mL during 2017 (Lorette 2019).

441 For the total coliforms, high values were found in the karst springs: 794 CFU/100 mL  
442 from AB Spring (Bucci *et al.*, 2009), 2420 CFU /100 mL from Lez Spring (Bicalho *et al.*,  
443 2012), 8680 CFU /100 mL from Moulinet Spring (Pronk *et al.*, 2009). These values are  
444 higher than the maximum concentration found in the Toulon springs during the sampling  
445 campaign. However, a higher value was recorded during 2003 with a concentration of 2000  
446 CFU/mL (Lorette 2019). Therefore, the concentrations measured in the Toulon springs are  
447 somehow in between the measured values of AB Spring and Lez Spring (Table 2).

448 The maximum concentration of enterococcus measured during the sampling campaign  
449 is lesser than other karst springs. Cossaux Spring for example has a concentration of 123  
450 CFU/mL (Pronk *et al.*, 2009). Moulinet Spring and AB Spring recorded 430 CFU/mL and  
451 1216 CFU/mL, respectively. Nonetheless, vigilance should be applied in terms of water  
452 monitoring as the concentration of enterococcus in the Toulon springs can reach up to 250  
453 CFU/mL as recorded last 2004 (Lorette 2019).

454 In terms of drinking water, the international regulation (WHO, 2006) requires 0  
455 CFU/100 mL of *E. coli*, total coliforms, and enterococcus. Hence, even the minimum  
456 concentrations 10 CFU/100 mL, 20 CFU/100 mL, and 2 CFU/100 mL of the *E. coli*, total  
457 coliforms, and enterococcus, respectively, should be addressed. As a normal standard  
458 procedure, water is treated before distributing it to the community. What is important to  
459 retain is the probable event that the bacteria can enter, facilitating in anticipating the  
460 necessary actions.

461

462



**Table 2: Minimum and maximum values of *E.coli*, total coliforms and enterococcus from several karst springs**

Source	E. Coli (CFU / 100 mL)		Total coliforms (CFU / 100 mL)		Enterococcus (CFU / 100 mL)		Reference
	Min	Max	Min	Max	Min	Max	
	AB spring	-	-	0	794	0	
PB spring	-	-	0	895	0	740	Bucci <i>et al.</i> , (2015)
FC spring	-	-	0	280	0	1 456	Bucci <i>et al.</i> , (2015)
Moulinet spring	0	1 088	14	8 680	0	480	Pronk <i>et al.</i> , (2007, 2009)
Cossaux spring	0	183	2	2 150	0	123	Pronk <i>et al.</i> , (2009)
Lez spring	-	-	26.2	2 420	-	-	Bicalho <i>et al.</i> , (2012)
Lirou spring	-	-	13.5	2 420	-	-	Bicalho <i>et al.</i> , (2012)
Fleurette spring	-	-	60.2	2 420	-	-	Bicalho <i>et al.</i> , (2012)
Gallusquelle spring	0	7 000	0	35 000	-	-	Heinz <i>et al.</i> , (2006)
CSP1 spring	0	30	-	-	-	-	Ender <i>et al.</i> , (2018)
KS2 spring	250	> 2 420	-	-	-	-	Ender <i>et al.</i> , (2018)
<b>The Toulon Springs</b>	<b>0</b>	<b>930</b>	<b>0</b>	<b>2 000</b>	<b>0</b>	<b>250</b>	<b>Lorette (2019)</b>
<b>The Toulon Springs</b>							
- February 2017	10	300	20	600	2	54	

464

## 465 5.2 Conceptual model exhibited by the Toulon springs during flood events (using the

### 466 parameters: DOC, NO<sub>3</sub><sup>-</sup>, particles, and bacterial transfer)

467

468 Previous analyses can describe several parameters considered as degrading water  
469 quality: (i) particles, (ii) dissolved organic carbon, (iii) microbial pathogens, and (iv) nitrate.

470 The flood event of February 2017 is used to evaluate the relationships between the  
471 particles and contaminant. A synopsis of this method is described in Fig. 7, leading to a  
472 conceptual model (Fig. 8). This identifies several types of water at the Toulon springs,  
473 pointing out several sources of water quality hazards:

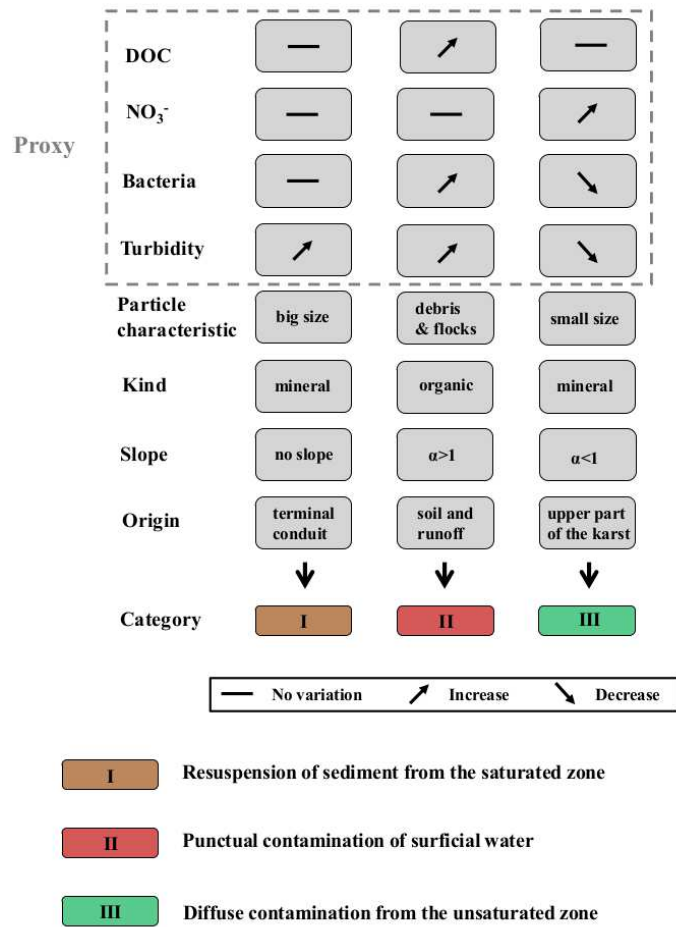
474

- 475 (i) The first one is the resuspension of particles deposited in the saturated zone of  
476 the karst system. This first water perturbation (Category I in Fig. 7) is  
477 associated with an increase of turbidity signal without hydrochemical evolution.  
478 Particles measured are inorganic and considered as big ( $> 100 \mu\text{m}$ ). These  
479 particles are associated with an autochthonous origin and are not correlated with  
480 microbial pathogens. Stability of  $\text{NO}_3^-$  and DOC concentration during this  
481 perturbation confirms the saturated zone origin of this water type.
- 482
- 483 (ii) The second (Category II in Fig. 7) is the punctual contamination of surficial  
484 water. It is characterized by a joint increase in DOC, turbidity, and bacteria.  
485 Despite a decrease in energy within the karst system (recession), an increase in  
486 the turbidity signal was recorded showing the mass transfer. The analyzed  
487 particles correspond to organic particles (algae debris, organo-mineral flocs, and  
488 colonies of bacteria adsorbed on plant debris), and sizes are between 50 and 100  
489 microns. This type of particles, of allochthonous origin, confirms the surface  
490 origin of the new water mass identified. In the diagram  $\text{DOC}_{\text{norm}}$  vs.  $\text{NO}_3^-_{\text{norm}}$ ,  
491 the arrival of this mass of water is identified by a slope  $\alpha > 1$ .
- 492
- 493 (iii) The third (Category III in Fig. 7) is the diffuse infiltration of water through the  
494 soil and the unsaturated zone. It is characterized during the recession by a single  
495 increase of  $\text{NO}_3^-$ , without increased DOC, bacteria, and turbidity. Particles  
496 associated with this water type are minerals and of size essentially between 50  
497  $\mu\text{m}$  and 100  $\mu\text{m}$ . It is of autochthonous origin to the karstic system. In the  
498  $\text{DOC}_{\text{norm}}$  vs.  $\text{NO}_3^-_{\text{norm}}$  diagram, the arrival of this new water type is identified  
499 by a slope  $\alpha < 1$ .

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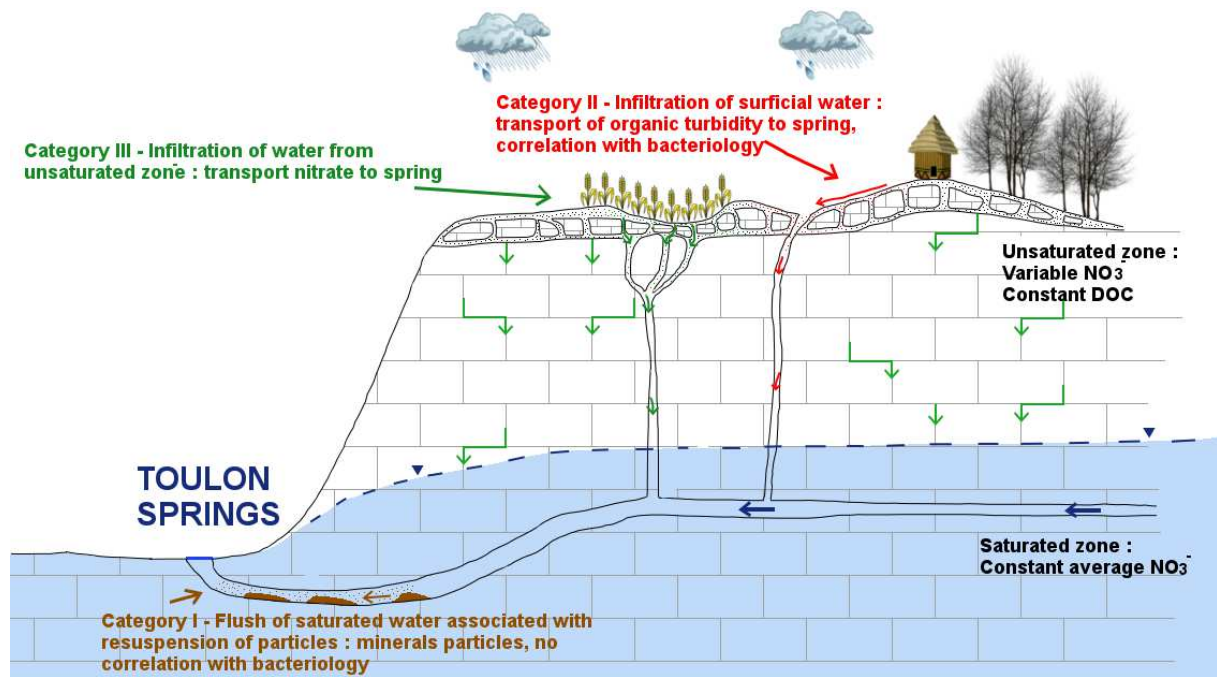


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Fig. 7: Synoptic for tracing water origins associated with hydrochemical parameters, particles and bacteria.



506

507 **Fig. 8: Conceptual model of water quality hazards associated with the identified water perturbations in the the Toulon**  
 508 **karst system. Categories are the same as showed in Fig. 7.**  
 509

510 **5.3 NO<sub>3</sub><sup>-</sup> and DOC relationship in karst environments and contribution in terms of resource**  
 511 **management and protection**

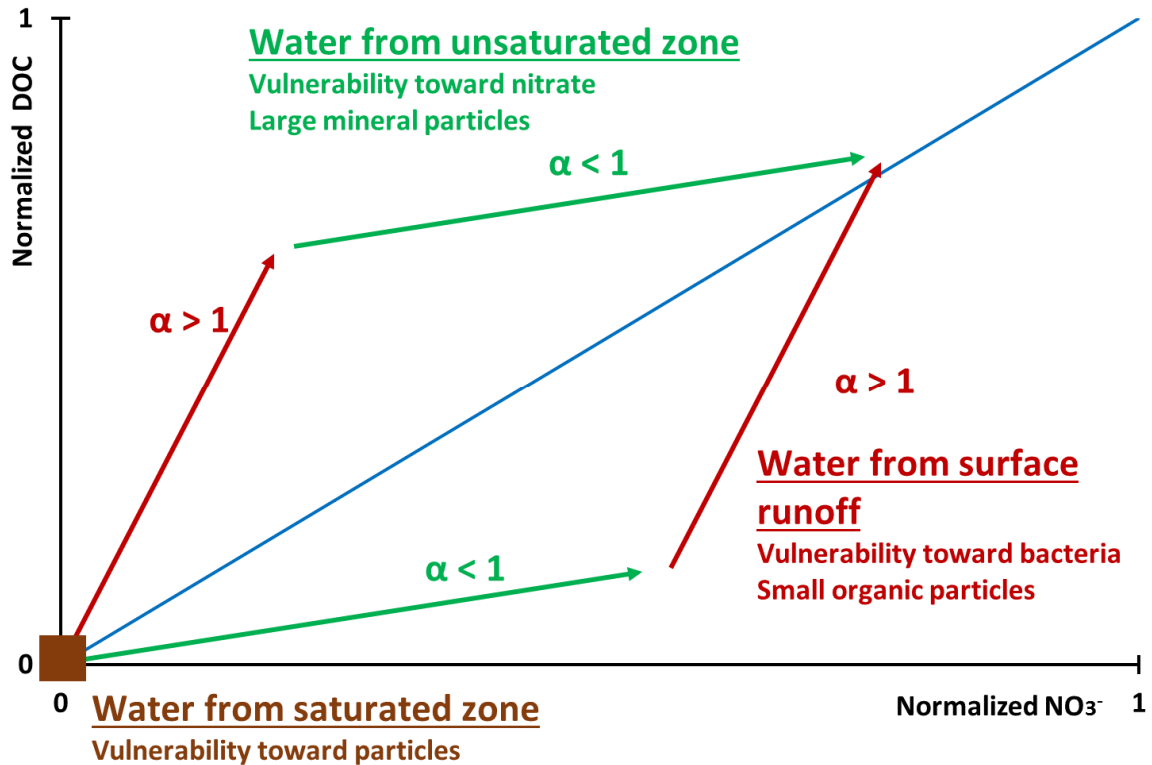
512

513 Analyses performed in this study showed complex evolution of NO<sub>3</sub><sup>-</sup> and DOC at the  
 514 Toulon springs. Coming from a same theoretical origin (soil), the evolution of these  
 515 parameters can be associated with anthropogenic nitrate input in the hydrogeological  
 516 catchment.

517 **Fig. 9** presents the implication of the result of the performed Normalized Data Analysis  
 518 of NO<sub>3</sub><sup>-</sup> and DOC. This enables to identify the infiltration process (using the slope  $\alpha$  from  
 519 DOC<sub>norm</sub> vs. NO<sub>3</sub><sup>-</sup><sub>norm</sub>) and its respective progression (with particle suspension and bacterial  
 520 input). Data presented in the DOC<sub>norm</sub> vs. NO<sub>3</sub><sup>-</sup><sub>norm</sub> diagram corresponds to the increase of  
 521 NO<sub>3</sub><sup>-</sup> and DOC during the high flow event. Through time, NO<sub>3</sub><sup>-</sup> and DOC are increasing at a  
 522 different phase. When NO<sub>3</sub><sup>-</sup> increases more than DOC, a linear regression will present a slope

523  $\alpha$  lower than 1 ( $\alpha < 1$ ). On the contrary, when  $\text{NO}_3^-$  increases less than DOC, a linear  
 524 regression will present a slope  $\alpha$  higher than 1 ( $\alpha > 1$ ).

525



526

527 **Fig. 9: Conceptual use of the  $\text{NO}_3^-_{\text{norm}}$  -  $\text{DOC}_{\text{norm}}$  diagram**  
 528

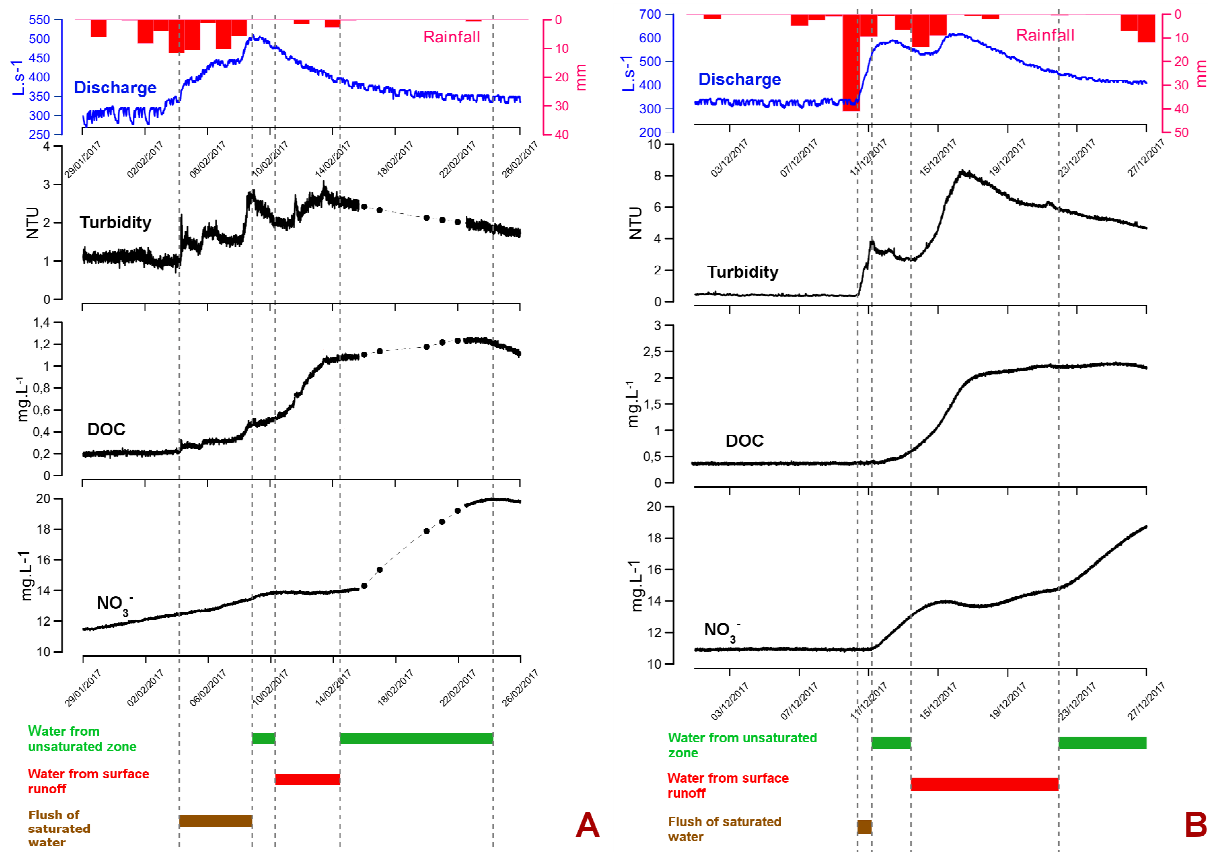
529 The common use of the  $\text{DOC}_{\text{norm}}$ - $\text{NO}_3^-_{\text{norm}}$  diagram, and especially the analysis of the  
 530 evolution of the slope with continuous data allowed distinguishing punctual infiltration from  
 531 diffuse infiltration through time. This analysis was applied in both February 2017 flood and  
 532 December 2017 flood events, leading to: (i) describing the precision of hydrogeological  
 533 functioning of the karst system and (ii) identifying water quality hazards and the period  
 534 associated with microbial pathogens.

535 According to this analysis of high-resolution monitoring of  $\text{NO}_3^-$  and DOC, the two  
 536 flood events studied have a similar functioning with:

537

- 538 (i) A flush of water close from the saturated zone, bringing particles deposited  
539 during low water period (Fig. 10). This water type is associated with the  
540 pressure transfer in the karst system and is not correlated with bacteriology.  
541 This result confirms those of Dussart-Baptista *et al.*, (2003) and Heinz *et al.*,  
542 (2009);
- 543 (ii) There is also a contribution of water coming from the unsaturated zone (Fig.  
544 10). This water type is associated to the mass transfer in the karst aquifer. It  
545 enables leaching of dissolved tracers. Inorganic nitrogen, as  $\text{NO}_3^-$  is the main  
546 tracer this research study, it is also possible to use other tracers coming from the  
547 same origin, such as pesticides, to identify this water type;
- 548 (iii) A contribution of punctual infiltration coming from the surface run-off (Fig. 10)  
549 appears with hydrological condition enabling infiltration through swallow holes.  
550 This supposition is correlated with allochthonous particles and is associated  
551 with sharp increase of DOC and microbial pathogens. This poses the highest  
552 risk to the human health. In the Toulon springs, bacteria are recorded 4 to 6  
553 days after the beginning of the flood.
- 554 (iv) Another contribution of water coming from the unsaturated zone (Fig. 10) is  
555 recorded again when hydrological conditions are not enough to generate  
556 infiltration through swallow holes. As a consequence, nitrate contamination  
557 increases.

558



559

560 **Fig. 10: Continuous application of  $\text{NO}_3^-$ norm -  $\text{DOC}_{\text{norm}}$  to differentiate concentrated recharge to diffuse recharge. A) February 2017. B) December 2017.**  
 561  
 562

563 This study showed that turbidity alone is not always a reliable indicator of the presence  
 564 of bacteria in the Toulon springs. Previous studies from [Dussart-Baptista et al. \(2003\)](#), [Pronk](#)  
 565 [et al. \(2006\)](#), [Heinz et al., \(2009\)](#) and [Ender et al. \(2018\)](#) also noticed this result in different  
 566 region such as France, Switzerland, Germany, and Vietnam, respectively. In this study also, it  
 567 is showed that the increase of DOC concentration does not mean that there will be increase  
 568 on bacterial concentration. The contribution of high resolution monitoring of  $\text{NO}_3^-$   
 569 concentration highlights the relationships of these parameters and their association with water  
 570 origins. As for the  $\text{NO}_3^-$ , concentrations increased during the first flood of the hydrological  
 571 cycle. It can be associated to the mobilization of nitrate over the soil and unsaturated zone  
 572 ([Rowden et al., 2001](#); [Stueber and Criss 2005](#); [Pronk et al., 2008](#); [Pu et al., 2011](#)). The high  
 573 level of  $\text{NO}_3^-$  in the Toulon springs is non-natural. This directly links to the agricultural land

574 use over the hydrogeological catchment (Lorette, 2019).  $\text{NO}_3^-$  can be used as a tracer of a  
 575 specific water oriin such as water from unsaturated zone. Hence, this study presented that the  
 576 comparison of relative evolution of DOC and  $\text{NO}_3^-$  can help in distinguishing sources of  
 577 water either from unsaturated zone or water from surface runoff. Table 3 is provided to give  
 578 an overview of the application of the method used to water resource management and  
 579 protection.

580 Table 3. Water quality hazards, indicators, causes, and suggested action for water resource  
 581 management and protection

<b>Water perturbation/ Water Origin</b>	<b>Indicator</b>	<b>Cause</b>	<b>Action for water resource management and protection</b>
Water Flush/ Saturated Zone	Turbidity (autochthonous particles)	Pressure transfer	Check if the indicator is more than the treatment possibility threshold:  - If more than the threshold, then stop pumping for a while.  - If less than the threshold, monitor and use classical treatment.
Change in chemistry/ Unsaturated Zone	Anthropogenic contaminant, in this study $\text{NO}_3^-$	Mass transfer Leaching	Check if the indicator is more than the required water quality threshold  -If more than the threshold, then recommendations in managing and controlling this specific contaminant are necessary  -If less than the threshold, then monitoring and recommendations to control the concentration are necessary
Punctual infiltration/	COD Turbidity (allochthones	Infiltration through swallow holes	Check the presence of bacteria, if there is, water treatment such as



Surface runoff	particles) Bacteria		chlorination is necessary.
Change in chemistry/ Unsaturated Zone	Anthropogenic contaminant, in this study NO <sub>3</sub> <sup>-</sup>	Mass transfer Leaching	Check if the indicator is more than the required water quality threshold:  -If more than, then recommendations in managing and controlling this specific contaminant are necessary.  -If less than then monitoring and recommendations to control the concentration are necessary.

582  
583

584 In order to assure good spring water quality, recommendations on hydrogeological  
585 catchment management can be provided. The recommendations are as follows: (i) improve  
586 the protection zone in the surface catchment of swallow holes; (ii) install a monitoring device  
587 on the main swallow hole as an alert system of potential contamination; and (iii) restrict the  
588 agriculture land use to avoid further increase of NO<sub>3</sub><sup>-</sup> concentration that can reach the  
589 groundwater.

590

## 591 6. Conclusion

592

593 In water resource management, it is important to know the water quality hazards. In  
594 this study, a tool that can be used in tracing water perturbation in a karst aquifer is proposed.  
595 First, method involves high-resolution monitoring of NO<sub>3</sub><sup>-</sup> and DOC. Second relies on the  
596 normalization of the data with NO<sub>3</sub><sup>-</sup>\_norm=f(DOC\_norm) reference frame. From these two  
597 steps, the infiltration process can be assessed based from the obtained slope. Applied on the

598 data acquired during a flood event, the slope ( $\alpha$ ) showed that (i) if  $\alpha > 1$ , DOC increase is more  
599 pronounced while (ii) if  $\alpha < 1$ , contaminant of anthropogenic origin, e.g.  $\text{NO}_3^-$ , is more  
600 distinct.

601 Third and fourth steps,  $\text{NO}_3^-$  and DOC parameters were complemented by (a)  
602 determining and characterizing particle size and chemistry and (b) detecting bacterial  
603 contamination (e.g. *E. coli*, total coliforms, and enterococcus). Employing the particle size  
604 and determining the presence of the bacteria, kinds of infiltration can be further examined.  
605 When  $\alpha > 1$ , it is observed that organic particles and bacteria are present. Whereas, when  $\alpha < 1$ ,  
606 it has larger range of particle size without the bacterial incidence. The slope  $\alpha > 1$  involves  
607 bacterial growth that can pose problem in terms of water quality. While, with the slope  $\alpha < 1$ ,  
608  $\text{NO}_3^-$  is a contamination concern.

609 This tool was applied on an important karst system the Toulon springs. Results showed  
610 that autochthonous and allochthonous type of turbidity can be identified at the Toulon  
611 springs. Autochthonous type of turbidity mostly consists of mineral particles. Allochthonous  
612 type, however, means that important contribution of recently infiltrated water occurs.  
613 Furthermore, three sources of water quality hazard were classified: (i) water from saturated  
614 zone, (ii) water from unsaturated zone, and (iii) water from surface runoff. Flushing of  
615 saturated water results to autochthonous type of turbidity. The punctual infiltration from  
616 surface runoff generates allochthonous type of turbidity with associated organic particles and  
617 bacteria. DOC is also a source of distress in this type. The infiltration from unsaturated zone  
618 engenders mineral type of particles associated with  $\text{NO}_3^-$  increase.

619 As the only drinking water for more than 50 000 people, management, monitoring, and  
620 protection of the Toulon springs are keys for a sustainable water resource. Hence, the  
621 identification of the sources of the water quality hazards is an important step in managing the  
622 hydrogeological catchment better. In this study, the use of high-resolution monitoring of

623 hydrochemical parameters (turbidity, DOC, and  $\text{NO}_3^-$ ) helped in determining the water  
624 quality hazards in the Toulon springs. Even if the trend of  $\text{NO}_3^-$  concentration is of  
625 anthropogenic source, it is still below the French potability threshold ( $50 \text{ mg L}^{-1}$ ). The main  
626 concern, then, for the water quality of the Toulon springs is the presence of bacteria coming  
627 from the surface runoff during flood. The presence of exokarstic forms such as swallow holes  
628 over the hydrogeological catchment is probably responsible of this contribution. The type of  
629 water perturbation associated with bacterial contamination is now identified. This is  
630 important to know as water with bacterial contamination needs treatment. This latter can help  
631 the water managers and providers in preparing necessary actions or water quality treatment  
632 before water will be supplied to the households.

633 This proposed method can be applied on any karst system hosting features like  
634 sinkholes and swallow hole in their catchment area. This is as these system are vulnerable to  
635 infiltration of runoff water. The monitoring mostly relies on high resolution monitoring for  
636  $\text{NO}_3^-$  and DOC. Particle size and chemistry characterization and bacterial detection can be  
637 done just on few events, as they are mainly used to interpret the variations of  $\text{NO}_3^-$  and DOC  
638 better. Employing this proposed method is rather simple. It can make used of in situ tools  
639 already existing in the markets. Furthermore, sampling of water does not need any new  
640 specific method. Personnel of the water providers and managers can be trained using this  
641 method straightforwardly. The future step is to characterize the  $\text{NO}_3^-$  hazard by differentiating  
642 the fertilizer and organic inputs of  $\text{NO}_3^-$  better. This would help in managing the land use of  
643 catchment area. The information gathered using the proposed method, will control the impact  
644 of allochthonous water during flood events

645

646

647 **Acknowledgements**

648

649         This work was supported by the Région Nouvelle Aquitaine, the city of Périgueux,  
650 Suez, the Conseil Départemental de la Dordogne, and the Adour-Garonne Water Agency.  
651 The authors would like to thank Jean-Christophe Studer, Jerome Donnette, Julien Frant,  
652 Pierre Pinet, Emilien Castaing and Philippe Savy for their technical and field assistance  
653 contributed.

654         This work benefited from fruitful discussion within the KARST national observatory  
655 network (SNO KARST) initiative from the INSU/CNRS.

656

657

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**Category III - Infiltration of water from unsaturated zone : transport nitrate to spring**



**Category II - Infiltration of surficial water: transport of organic turbidity to spring, correlation with bacteriology**

