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Transfer and degradation of the common pesticide atrazine through the unsaturated zone of the Chalk aquifer (Northern France)

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Abstract

Groundwater in the Chalk aquifer is an important water resource whose quality has degraded due to fertilizer and pesticide use. Atrazine, classified as a priority substance, has been one of the most applied pesticides and also one of the most frequently detected pesticides in groundwater. The present study investigated the transfer and degradation of atrazine in the unsaturated zone of the Chalk aquifer in Northern France. The study was conducted in an underground quarry (Saint-Martin-le-Noeud), which provides a direct access to the water table and intercepts the unsaturated zone at different depths. The lake and the ceiling percolation of 16 sites throughout the quarry were followed. For 16 sites, the percolating flow rate and lake level were measured and the lake water was sampled for nitrate, atrazine and deethylatrazine (DEA, main degradation product of atrazine) analysis over 2.5 years. High spatial variations in hydrodynamics (percolating flow rate and lake level) and in lake water quality (atrazine between 55 ± 11 and 202 ± 40 ng L^{-1} and DEA between 269 ± 53 and 1727 ± 345 ng L^{-1}) indicate that the properties of the unsaturated zone influence the transfer and the degradation of atrazine. A counterclockwise hysteresis characterizes

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the relationship between the lake level and atrazine concentration. Temporal variation shows that the atrazine is transferred through the matrix and fractures with a delay caused by the sorption process that differs in atrazine and DEA. The layer of clay-with-flints is shown to favor the degradation of atrazine near the surface. Preferential pathways may be created below clay-with-flints, through which the transfer of atrazine is quicker.

Keywords: Chalk groundwater; Atrazine; Unsaturated zone; Clay-with-flints

1. Introduction

Chalk aquifer provides a large quantity of drinking water in Europe (Lapworth et al., 2015). The groundwater extracted from the Chalk aquifer of the Paris Basin supplies 70% of the drinking water consumed in the north of France (Lallahem, 2002). In the UK, the Chalk aquifer provides almost 60% of the total withdrawal groundwater (Azeez, 2017). It is also a substantial water resource to sustain and exchange with river flows (Grapes et al., 2005; Sear et al., 1999). Water quality of the Chalk aquifer is an important issue. Beginning in the 1970s, the impact of intensive agriculture on groundwater has been demonstrated (Headworth, 1989; Johnson et al., 2001). Numerous studies have shown degradation of groundwater quality of the Chalk aquifer due to the use of fertilizers and pesticides (Baran et al., 2008; Brouyère et al., 2004). To protect groundwater, it's crucial to better understand the transfer of pesticides from the soil to the water table, and particularly how pesticides move through the unsaturated zone (UZ), which has not been fully understood because of limited access. The Saint-Martin-le-Noeud underground quarry provides access to the UZ of the Chalk aquifer with groundwater at different depths (Barhoum et al., 2014). Chen et al. (2019) studied the transfer of water and contaminants through the matrix in the UZ of the quarry but the transfer of the pesticides to the water table remains unclear.

1.1. Pesticides - Atrazine

The World Health Organization defines pesticides as chemical organic compounds that are used to kill pests, fungi and unwanted plants (weeds). The European Drinking Water Directive sets the maximum limit of 0.1 $\mu\text{g}/\text{L}$ for each individual pesticide in drinking water and 0.5 $\mu\text{g}/\text{L}$ for total pesticides, i.e., the sum of all the substances detected in a sample. Among pesticide substances, atrazine is one of the most widely applied herbicides. It is classified as a priority substance due to its toxicity to the environment (Official Journal of the European Communities, 2001). Gammon et al. (2005) showed that life-time

30 exposure to atrazine may cause cancer. Araújo et al. (2018) demonstrated that
31 the presence of atrazine can affect the spatial distribution of fish in freshwater
32 by forming a chemical barrier isolating fish populations. Exposure to atrazine
33 can cause breaks in erythrocytes of *Carrasius auratus*, demonstrating the geno-
34 toxic potential of atrazine on fish (Cavas, 2011). In 2003, the application of
35 atrazine was banned in the European Union, although it is still widely used in
36 the United States (Mahler et al., 2017). It is still one of the most frequently
37 detected pesticides in freshwater (Vryzas et al., 2011).

38 Degradation is the process that transforms a substance into by-products.
39 The mechanisms of degradation are physical, chemical and biological (Coats,
40 1991). The main degradation products are deethylatrazine (DEA), deisopropy-
41 latrazine (DIA) and hydroxyatrazine (HA). DEA is the most frequently detected
42 degradation product of atrazine (Cahoon and Cutting, 2009). Biological pro-
43 cesses are responsible for metabolizing atrazine to DEA in soil by microorgan-
44 isms under aerobic conditions (Solomon et al., 2013). The half-life (the time
45 it takes for half of the pesticide to be degraded) of atrazine varies depending
46 on soil type, soil pH and the atrazine quantity applied. Accinelli et al. (2001)
47 showed that the average half-life of atrazine in non-sterile soils is 49 days under
48 aerobic conditions and 407 days under anaerobic conditions. The degradation of
49 atrazine mainly occurs in soil, but it may also occur in the UZ with the presence
50 of micro-organisms. Johnson et al. (2000) found no potential degradation in the
51 groundwater over a 200-day incubation. Issa and Wood (1999) showed that the
52 degradation of atrazine might occur in the UZ at a lower rate than in soil if
53 micro-organisms are present.

54 *1.2. Chalk aquifer*

55 Chalk is a marine sedimentary rock. It is a carbonate rock, made up of
56 more than 90% calcite and a variable proportion of dolomite (Fabricius, 2007).
57 The Chalk aquifer has been considered a double/triple porosity aquifer made of
58 matrix, fractures and conduits (in the most karstic areas). It is partly covered
59 by a layer of clay-with-flints (Laignel et al., 1999). The clay-with-flints is the

60 residual deposit formed from the dissolution, decalcification and cryoturbation
61 of bedrock strata of the Chalk Group (Jukes-Browne, 1906). The thickness
62 of the layer of clay-with-flints may reach several meters. Valdes et al. (2014)
63 showed that the presence of clay-with-flints on the surface may have an impact
64 on infiltration processes of water and solutes in the Chalk aquifer: it may store
65 water on the surface and also create preferential pathways.

66 The conduits are developed in some areas of the Chalk aquifer, e.g., in
67 Northern France. For the areas without conduits, the water transfer process
68 may occur through the matrix and fractures. However, most studies considered
69 that the main transfer process mainly occurs through the matrix (Cooper et al.,
70 2006; Mathias et al., 2005). The water transfer through fractures may be active
71 occasionally depending on different conditions such as rainfall intensity and
72 soil moisture (Haria et al., 2003; Ireson and Butler, 2011). Van den Daele
73 et al. (2007) showed that the solute exchange between the matrix porewater and
74 the porewater in the fractures is driven by two possible processes: advection
75 and diffusion. For an organic component such as atrazine, the sorption, i.e.,
76 adsorption - desorption, is a major process controlling their fate (Chefetz et al.,
77 2004). Adsorption of an organic component on the Chalk delays the transport
78 time, leading to a storage of the component in the Chalk UZ.

79 *1.3. Pesticide study in the Chalk aquifer*

80 For the past 30 years, most studies on pesticides have focused on soil com-
81 ponents (Gutierrez and Baran, 2009) because it is widely considered that less
82 than 1% of pesticides pass through soil components (Flury et al., 1995). Some
83 studies observing pesticides (especially atrazine) in the groundwater show that
84 the concentration can be higher than $0.1 \mu\text{g } L^{-1}$, and some even higher than
85 $0.5 \mu\text{g } L^{-1}$ (Vonberg et al., 2014; Lapworth and Gooddy, 2006). Thurman et al.
86 (1992) observed the river-groundwater interaction with the exchange of pesti-
87 cides and showed the importance of studying pesticides in groundwater because
88 it may also impact surface water. Few studies took an interest in the transfer
89 of atrazine in the UZ of the Chalk aquifer. Baran et al. (2008) studied the

90 infiltration processes of water with atrazine from 1989 to 2006, showing that
91 the pesticide concentrations remained stable during periods of low-flow and in-
92 creased episodically after rapid infiltration. Chilton et al. (2005) studied the
93 main factors controlling the fate of pesticides in order to establish a model
94 predicting pesticide behavior in the groundwater. However, these studies exam-
95 ined water samples from wells whose characteristics result from all the possible
96 transfer processes in the Chalk aquifer, in both the unsaturated and saturated
97 zones, in which it is difficult to focus on the transfer only through the UZ. Chen
98 et al. (2019) showed that the transfer of atrazine in the UZ of the Chalk aquifer
99 occurs mainly through the matrix with a velocity estimated between 0.7 and
100 2.1 m year^{-1} for the water percolating in the Saint-Martin-le-Noeud quarry
101 (Northern France).

102 *1.4. Objective of the study*

103 The aim of this study is to characterize the processes of the transfer and
104 degradation of atrazine in the UZ of the Chalk aquifer. The study was con-
105 ducted in the Saint-Martin-le-Noeud underground quarry in the Paris Basin
106 (Northern France). Chen et al. (2019) have analyzed the ceiling percolation
107 water in the same quarry. They have shown that the percolation water resulted
108 mainly from the transfer through matrix. The quarry gives also a direct ac-
109 cess to groundwater. Water table outcrops in the quarry, forming 16 lakes with
110 different characteristics of UZ. The present study focus on the 16 underground
111 lakes (water table). This study followed the spatio-temporal variation of the
112 concentration of atrazine and its main degradation product DEA in groundwa-
113 ter has been followed. Spatio-temporal variations of the pesticides and nitrate
114 are analyzed to characterize transfer processes in the unsaturated zone. Com-
115 pared to nitrate variation, the variation of atrazine and DEA highlights the
116 transfer process of pesticides including sorption effect.

117 **2. Materials and methods**

118 *2.1. Site settings*

119 Located in Saint-Martin-le-Noeud, 70 km north of Paris (Fig. 1), the under-
120 ground quarry is 1200 m long and 150 m wide at an altitude of 165 m a.s.l. The
121 coordinates of the quarry is 49.4 °N and 2.05 °E. The quarry was exploited
122 from the 12th to the 18th century for chalk as a construction material, using
123 room-and-pillar method. The quarry has been studied since 2012 (Barhoum
124 et al., 2014; Chen et al., 2019).

125 The climate data used from January 2016 to April 2018 are recorded at the
126 Beauvais station managed by Météo-France. The station is located 7 km from
127 the quarry and is nearly at the same altitude. The average annual temperature
128 is 11°C (minimum temperature in January and maximum temperature in July).
129 The annual rainfall amount is 670 mm (values from Météo-France for the 1981-
130 2010 period). An agricultural zone overlies the quarry. The landowner over
131 the quarry provided information on agricultural practices beginning in 1974:
132 cultivated fields contain corn, wheat and rapeseed. He claims that atrazine was
133 used from 1977 to 2003.

134 *2.1.1. Geology and hydrogeology*

135 The quarry has been excavated in the Upper Cretaceous chalk layer, within
136 the limit of Coniacian and Turonian. The excavation followed the dip of Chalk
137 layers. The dip is about 12° NNE. The Bray anticline is located at the western
138 side of the quarry (Fig. 1). The Chalk aquifer, where the quarry is located, is
139 considered to be an aquifer with two porosity types: matrix and fractures, since
140 no karstic conduit was discovered. The quarry is partly covered by a layer of
141 the clay-with-flints. The total porosity of the Chalk aquifer was estimated at
142 40% (Lafrance, 2016).

143 Effective rainfall infiltrates through the unsaturated zone (chalk with or
144 without clay-with-flints) before arriving into the quarry, where the water table
145 outcrops at deeper parts. The water table forms 16 underground isolated lakes

146 in the quarry (Fig. 2). The infiltrated water flows into the lakes by two path-
147 ways: percolating water dropping from the quarry ceiling and water circulating
148 through the pillars and walls of the lake. The water of the lakes (corresponding
149 to groundwater) is therefore a mixture of water coming from ceiling percolation
150 and water passing through walls and pillars.

151 2.1.2. Characterization of the unsaturated zone of the study sites

152 The UZ thickness (from the soil surface to the quarry ceiling) varies spatially
153 from 18 to 30 m. The thickness of the layer of clay-with-flints, measured with
154 an electromagnetic ground conductivity geophysical instrument (EM31), varies
155 from 30 cm to more than 5 m (Barhoum et al., 2014). Method EM31 measures
156 the electrical conductivity of soil. Soil with clay-with-flints has higher electrical
157 conductivity than soil without clay-with-flints. However, the relation between
158 thickness of clay-with-flints and electrical conductivity of soil is not a linear
159 relation. The exact thickness of clay-with-flints was measured for 3 sites: 30 cm
160 for PED (lowest electrical conductivity, 20 mS m^{-1}); 2 m for BLE (electrical
161 conductivity medial, 47.5 mS m^{-1}); more than 3 m for STA (highest electrical
162 conductivity, 72 mS m^{-1}).

163 According to Chen et al. (2019), the 16 sites (Fig.2) can be divided into
164 three groups according to the UZ thickness and thickness of the clay-with-flints
165 layer.

- 166 – Group 1 (G1): CAS, CHA, BLE, PIL, JAR and LIT. The sites have the
167 highest UZ thickness (around 30 m) with a thin layer of clay-with-flints
168 (electrical conductivity between 30 and 60 mS m^{-1}).
- 169 – Group 2 (G2): NAT, TSA, STA, LUC, VOU, NIC and PI2. The sites have
170 a high UZ thickness (around 28 m) with a thick layer of clay-with-flints
171 (electrical conductivity higher than 70 mS m^{-1}).
- 172 – Group 3 (G3): SQU, CAR and PED. The sites have the lowest UZ thick-
173 ness (around 20 m) with a thin layer of clay-with-flints electrical conduc-
174 tivity less than 30 mS m^{-1}).

175 *2.2. Data and methods*

176 *2.2.1. Sampling and measurements*

177 Groundwater was sampled in 16 underground lakes (water table outcrops
178 and porewater percolated through the UZ in quarry ceiling). From 2016 to
179 2018, 14 campaigns were conducted: 2016-04-12, 2016-06-06, 2016-06-23, 2016-
180 09-05, 2016-10-20, 2017-01-09, 2017-02-27, 2017-05-02, 2017-06-26, 2017-09-05,
181 2017-10-23, 2018-01-16, 2018-04-10, 2018-05-16. The campaigns are divided into
182 three groups. Table 1 presents the measurements and analysis done during each
183 campaign.

184 For all 16 sites, the lake level and percolating volume were measured. For
185 BLE, STA and PED, daily data of percolating flow rate and lake level were
186 recorded from 2016-01-01 to 2018-05-16. Daily time series of the percolating
187 flow rate were recorded using rain gauges. Daily time series of the lake level
188 were recorded using CTD-Diver loggers.

189 The percolating flow was calculated as the ratio of the collected water depth
190 (collected percolation volume divided by beaker area) between two field cam-
191 paigns. In case of overflow, the percolating flow was underestimated. For each
192 site, the lake level was standardized considering the lowest level as 0. Therefore,
193 the standardized lake level of each campaign is the difference between the lake
194 level measured and the lowest level.

195 *2.2.2. Chemical analysis*

196 Lake water from the 16 sites was sampled for nitrate, atrazine and DEA anal-
197 ysis. The nitrate concentration was analyzed by ion chromatography (Dionex
198 ISC 3000). The accuracy is $1 \text{ mg } L^{-1}$ with 5% uncertainty. The ionic balance
199 error was checked with other major ions (HCO_3^- , K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Cl^- ;
200 SO_4^{2-}). Atrazine, DEA, DIA and HA were analyzed using an on-line method
201 with liquid chromatography-tandem mass spectrometry (Agilent Technology)
202 with filtered samples (by $0.2 \text{ }\mu\text{m}$ filters) (Blanchoud et al., 2019). The quanti-
203 fication limit of this method is $20 \text{ ng } L^{-1}$ with 20% uncertainty.

204 *2.2.3. Atrazine degradation rate*

205 Atrazine degradation rate can be expressed by DAR. DAR, introduced by
206 Adams and Thurman (1991), is the ratio of the concentration of DEA, the main
207 degradation product of atrazine to the concentration of atrazine, the primary
208 molecule.

209 The equation to calculate DAR is: $\text{DAR} = \text{DEA} / \text{Atrazine}$.

210 This parameter is used as an indicator of atrazine degradation processes. A
211 higher DAR value means greater degradation of atrazine.

212 **3. Results**

213 *3.1. Spatial variation*

214 Figure 3 presents UZ thickness, the electrical conductivity of soil (indicator
215 of the thickness of clay-with-flints), hydrodynamics (total percolation and stan-
216 dardized lake level), quality (concentration of nitrate, atrazine and DEA) and
217 DAR of the lake for the 16 sites. In Fig. 3, the six campaigns in group A (April
218 2016 to September 2017, Table 1) were used for the boxplots, and all ten cam-
219 paigns in groups A and B (Table 1) were used to calculate the total percolation
220 between April 2016 and September 2017. Within 1200 m, high spatial variation
221 was observed in the hydrodynamics and the quality of the groundwater.

222 Among the 16 sites, the total percolation varied from 180 cm to more than
223 1500 cm during the same period covering nearly 1.5 years. The amplitude of lake
224 level varied from 11 to 134 cm. LUC and VOU (G2) behaved very differently
225 from the 14 other sites. These two sites had the highest total percolation (more
226 than 1500 cm) but the smallest lake level amplitude (11 cm for LUC and 17 cm
227 for VOU). Most of the sites had a lake level amplitude between 40 and 80 cm
228 with a total percolation less than 1000 cm.

229 High spatial variation of nitrate concentration was observed. The medians
230 of nitrate concentrations of the 16 sites varied between 23 ± 1 and 93 ± 4 mg
231 $NO_3^- L^{-1}$. The highest nitrate concentration observed was 95 ± 4 mg $NO_3^- L^{-1}$.
232 The concentrations observed in the quarry were at the upper end of what other
233 studies had found. For example, El Gaouzi et al. (2013) observed a nitrate
234 concentration between 34 and 49 mg $NO_3^- L^{-1}$ in the Paris Basin. Sorensen
235 et al. (2015) found nitrate concentrations varied between 30 and 60 mg $NO_3^- L^{-1}$
236 for the Chalk aquifer in the UK.

237 High spatial variation of atrazine and DEA concentration was observed.
238 The concentration of DIA and HA is lower than the limit of quantification, so
239 these two degradation products of atrazine are not presented in this study. The
240 medians of the atrazine concentrations at the 16 sites varied between 55 ± 11 and
241 202 ± 40 ng L^{-1} . The medians of the DEA concentrations of the 16 sites varied

242 between 269 ± 53 and 1727 ± 345 ng L^{-1} . The highest atrazine concentration was
243 501 ± 100 ng L^{-1} and the highest DEA concentration was 3941 ± 788 ng L^{-1} .
244 These atrazine and DEA concentrations were much higher than any published
245 values in other studies. For example, Baran et al. (2008) recorded that, from
246 2000 to 2006, for the Paris Basin, groundwater atrazine varied between 50 and
247 100 ng L^{-1} and DEA varied between 100 and 200 ng L^{-1} . Hakoun et al. (2017)
248 observed the maximum concentrations of atrazine and DEA less than 200 ng
249 L^{-1} concentration of atrazine and DEA for the Chalk aquifer in Belgium.

250 High spatial variation of DAR was observed. The DAR medians for the
251 16 sites varied between 2.9 and 10.3, with the highest DAR value observed for
252 the lakes in the quarry at 41.9. These DAR values partly match what other
253 studies had found, e.g., maximum DAR around 3 for the groundwater of the
254 Luxembourg's Sandstone aquifer (Farlin et al., 2017). The high DAR values may
255 mean more degradation of atrazine in the soil, or also result from the different
256 transfer processes in DEA and atrazine.

257 Spatial variations were clearly observed between the three groups. For the
258 sites with thin layers of clay-with-flints (G1 and G3) the lake level amplitude
259 was between 46 and 134 cm. The G1 sites, with 30-m UZ thickness, had a low
260 concentration in nitrate (less than 40 mg $NO_3^- L^{-1}$, atrazine (less than 150 ng
261 L^{-1}) and DEA (less than 450 ng L^{-1}). The G3 sites with a UZ thickness less
262 than 20 m showed higher concentrations in nitrate (medians up to 93 ± 4 mg
263 $NO_3^- L^{-1}$), atrazine (medians up to 202 ± 40 ng L^{-1}) and DEA (medians up to
264 1127 ± 225 ng L^{-1}). The difference of nitrate, atrazine and DEA concentrations
265 between G1 and G3 could be due to the different UZ thicknesses of the sites.

266 For G2, the sites have a thick layer of clay-with-flints and an UZ thickness
267 around 28 m (about the same depth as for G1, thicker than G3). Water had
268 a DAR higher than the G1 and G3 sites. However, high spatial variation of
269 the quality of the groundwater was observed within G2. LUC and VOU were
270 particularly different from the 14 other sites. These two sites had the highest
271 concentrations of atrazine and DEA and the highest DAR, and also nitrate
272 concentration. The hydrodynamic features and water quality at LUC and VOU

273 could indicate that the transfer processes are different for these two sites.

274 *3.2. Temporal variation*

275 The boxplots in Fig.3 show a temporal variability of the hydrodynamics and
276 quality of the lakes between the campaigns. The temporal variability differed
277 between the sites and between the parameters. For example, the nitrate boxplots
278 showed small variability between the campaigns for most of the sites. But for
279 DAR, the temporal variability between the campaigns varied greatly between
280 the sites: most of the sites showed very little variability while DAR at VOU
281 varied between 5 and 30.

282 To understand the temporal variation in nitrate, atrazine, DEA and DAR,
283 the data are presented over time (Fig.4). Four sites are presented: two sites with
284 a thin layer of clay-with-flints (BLE in G1 and PED in G3) and two sites under
285 a thick layer of clay-with-flints (STA and VOU in G2). Figure 4 presents the
286 time series of the monthly rainfall amount, percolating flow rate, standardized
287 lake level, nitrate, atrazine, DEA and DAR for the four sites (BLE, STA, VOU
288 and PED) between 1 January 2016 and 16 May 2018.

289 The annual rainfall recorded at the Beauvais station was 750 mm for 2016
290 and 600 mm for 2017. The distribution of the rainfall varied from one year
291 to the other. An intense rainfall event occurred in May 2016 with a monthly
292 rainfall more than 170 mm. January 2018 was also a wet period with monthly
293 rainfall greater than 100 mm. The temporal variation of the lake level and the
294 percolating flow were, therefore, different between the two years. The lake level
295 at VOU (Fig.4) presented little temporal variation, which is different from what
296 was observed at the three other sites. BLE, STA and PED show a high temporal
297 variation in lake level (e.g., lake level amplitude was 100 cm for BLE).

298 Temporal variation was observed for the lake level and the percolating flow
299 rate at BLE, STA and PED: in 2016, the percolation stopped from November to
300 December 2016, and percolation stopped earlier in 2017 from July to August.
301 The highest percolating flow rate in 2016 was more than twice as high as in
302 2017. The lake level variation presented the same behavior as the percolating

303 flow rate. The maximum lake level variation in 2016 was also more than twice
304 as high as in 2017. The temporal lake level and percolating flow rate variation
305 between 2016 and 2017 may result from the temporal variation of rainfall.

306 The nitrate concentration shows a low variation for BLE, STA and PED,
307 unlike hydrodynamics. Atrazine and DEA, on the other hand, show high tem-
308 poral variation and little temporal variation for DAR. The differences between
309 the temporal variation of nitrate and the temporal variation of atrazine and DEA
310 mean that the transfer processes differ for the two molecules. For BLE, STA
311 and PED, the temporal variation seems to be synchronized between atrazine
312 and DEA but not synchronized with the lake level: the highest concentration of
313 atrazine and DEA is delayed compared to the highest lake level and the lowest
314 concentration of atrazine and DEA was observed at the same time as the lowest
315 lake level (January 2018).

316 The temporal variation of the lake level and the percolating flow at VOU
317 differed from BLE, STA and PED. The VOU lake level showed a little varia-
318 tion. The percolating flow of VOU was uninterrupted but the intensity of the
319 percolation varied over time. The fact that the temporal variation was observed
320 for the percolating flow but not for the VOU lake level indicates that the VOU
321 lake may be recharged continuously by other infiltrated water (water passing
322 through walls and pillars).

323 High temporal variation was observed in atrazine, DEA and DAR for VOU.
324 However, the temporal variations of atrazine differed from that of DEA. The
325 highest concentration of atrazine was observed in January 2017 and the lowest
326 concentration of atrazine was observed in January 2018, with the highest con-
327 centration of DEA observed in April 2016. The differences between the temporal
328 variation of atrazine and DEA indicate that the transfer processes of atrazine
329 and of DEA are different for VOU. The DAR value at VOU showed a high
330 temporal variation between 3 and 30. The highest DAR value was observed in
331 January 2018 when the concentration of atrazine was at the lowest level.

332 4. Discussion

333 Since atrazine was used for the treatment of crops from 1977 to 2003, the high
334 concentrations observed in atrazine and DEA indicate that the groundwater in
335 the quarry has a residence time of one to several decades. Assuming a transfer
336 within the UZ by piston flow, the apparent residence time between 14 and 40
337 years can be calculated ($2017 - 2003 = 14$ years and $2017 - 1997 = 40$ years).
338 With an UZ thickness between 18 and 31 m, the transfer velocity of atrazine and
339 DEA for the groundwater in the quarry can be estimated between 0.45 and 2.21
340 m/year. The apparent velocities match the matrix velocities (Van den Daele
341 et al., 2007; Chen et al., 2019) but this cannot exclude the presence of transfer
342 through fractures.

343 4.1. Degradation processes

344 In this study, most of the G1 and G3 sites had a DAR value around 3.5 with a
345 very low temporal variation despite the high temporal variation observed in the
346 concentration of atrazine and DEA. Farlin et al. (2017) also found DAR values
347 around 3 for the groundwater of the Chalk aquifer. Several sites of G2, covered
348 by a thick layer of clay-with-flints, had DAR values higher than 6. Martins et al.
349 (2018) observed that atrazine could be easily adsorbed by clay-with-flints. Con-
350 sidering that the clay-with-flints may be responsible for the storage of water and
351 atrazine on the surface, atrazine at the G2 sites may stay longer on the surface,
352 leading to more degradation. Degradation of atrazine is a biological process,
353 normally under aerobic condition. The degradation of atrazine is considered
354 occurring mainly in the soil with nearly no degradation in the UZ (anaerobic
355 condition) (Johnson et al., 2000). Groundwater in the quarry is under aerobic
356 condition. Therefore, degradation of atrazine may also occur in the quarry if
357 micro-organisms are present (Issa and Wood, 1999; Solomon et al., 2013). The
358 different DAR values in the groundwater related to the different thicknesses of
359 the clay-with-flints layer indicate that the clay-with-flints on the surface may
360 favor atrazine degradation processes with potential atrazine degradation in the
361 groundwater if micro-organisms are present.

362 *4.2. Atrazine transfer process in the Chalk aquifer UZ*

363 Chen et al. (2019) showed that the transfer process of atrazine is different
364 from the transfer process of nitrate and estimated the transfer velocity of nitrate
365 and atrazine in the Chalk UZ about 1 m year^{-1} . This shows that the transfer of
366 the contaminants, nitrate and pesticide, is mainly driven by piston flow. With
367 this hypothesis, the difference of the concentration of nitrate, atrazine and DEA
368 between the sites of G1 and G3 may be due to the difference of the sites' depths.
369 Deeper the groundwater is, less contaminant is presented.

370 Baran et al. (2008) observed that pesticides can be transferred through both
371 matrix and fractures in UZ of the Chalk aquifer. A number of studies (Keim
372 et al., 2012; Smith et al., 1970) suggested that transfer of water and contami-
373 nants through fractures can account for 30% of the total recharge and, in certain
374 conditions, transfer through fractures may dominate during the recharge period.
375 Foster et al. (1991) showed that, unlike nitrate, pesticides are more likely trans-
376 ferred through fractures. In this study, nitrate shows a small temporal variation,
377 independent of water tables dynamic. This may lead to a conclusion that the
378 transfer of nitrate occurs mainly through matrix by piston flow. Atrazine and
379 DEA, on the contrary, show a high temporal variation, which seems to be linked
380 to water tables dynamic. Therefore, the transfer of atrazine and DEA is differ-
381 ent from the transfer of nitrate: other than matrix, it may occur mainly through
382 fractures. In a recent study, Chen et al. (2019), who studied percolation water in
383 the same quarry, considered percolation as water mainly passing through matrix
384 with no atrazine and no DEA (concentration lower than Quantification limit,
385 20 ng L^{-1}) found in the percolation water of the G1 sites (water before 1977).
386 In the present study, lake water at the G1 sites showed higher concentrations
387 than percolation water (Fig.3) in atrazine (medians varied between 67 ± 13.4
388 and $149 \pm 14.8 \text{ ng L}^{-1}$) and in DEA (medians varied between 257 ± 51.4 and
389 $514 \pm 102.8 \text{ ng L}^{-1}$). Therefore G1 lakes include some water infiltrated between
390 1977 and 2003, younger than percolation water. The lakes are recharged by a
391 transfer quicker than the transfer through matrix. Consequently, a significant
392 proportion of the recharge is likely transfer through fractures.

393 Since atrazine and DEA are organic components, the transfer of these sub-
394 stances in the Chalk aquifer UZ may be influenced by the sorption process
395 (Wefer-Roehl et al., 2001). Ezra et al. (2006) showed that the transfer of or-
396 ganic components in the Chalk UZ can be delayed due to adsorption. Nitrate, a
397 soluble molecule, is less influenced by sorption, compared to the pesticides. In
398 the present study, temporal variations were observed in atrazine and DEA but
399 not in nitrate. These results indicate that the transfer processes are different be-
400 tween nitrate and pesticides. Moreover, the maximum pesticide concentrations
401 in the water table occurred a few weeks later than the maximum of the lake
402 level (Fig.4). This could be explained by the sorption processes (adsorption and
403 desorption). Atrazine and DEA adsorbed in the UZ are likely desorbed after
404 the arrival of water recharging the water table. There is a 4-month delay due
405 to the time for desorption.

406 *4.3. Hysteresis (water level - pesticide concentration)*

407 To better understand the relationships between lake level and the concentra-
408 tion of atrazine and DEA over time, Fig.5 was plotted to present the hysteresis
409 between the water level and atrazine and DEA concentrations for four lakes
410 (BLE, STA, VOU and PED). Data from April 2016 to May 2018 were used.
411 Two types of hysteresis were observed (Fig.5a): i) no clear hysteresis for VOU,
412 perhaps because the lake level does not present temporal variation; ii) counter-
413 clockwise hysteresis clearly observed in atrazine and DEA for BLE, STA and
414 PED. Atrazine and DEA showed similar hysteresis, meaning that the varia-
415 tion of atrazine and the variation of DEA are synchronized. A sketch of the
416 counterclockwise hysteresis is presented into four steps (Fig.5b).

- 417 (1) Start of the recharge: the concentrations of atrazine and DEA remain
418 stable as the lake level starts to rise: not enough time for desorption.
- 419 (2) Recharge continues: concentrations of atrazine and DEA start to increase
420 as the lake level continues to rise: there is enough time for the desorption.

421 (3) Decrease of recharge: concentrations of atrazine and DEA increase to the
422 maximum value as the lake level starts to drop: desorption continues.

423 (4) End of recharge: concentrations of atrazine and DEA decrease to the
424 minimum value as the lake level drops to the minimum: there is no more
425 desorption. All desorbed pesticides have been leached out and the con-
426 centration decreases to the lowest value.

427 The sites with temporal variation observed in lake level showed synchronized
428 transfers of atrazine and DEA. The transfer of the pesticides is delayed by the
429 adsorption and desorption processes.

430 *4.4. Water table beneath clay-with-flints formation*

431 The LUC and VOU sites had a behavior different from the other 14 sites.
432 Both presented little temporal variation in terms of lake level but the highest
433 concentrations of atrazine and DEA. Valdes et al. (2014) suggested that the
434 layer of clay-with-flints may have two roles in the infiltration process: it can
435 store water near the surface and it can also accelerate the infiltration by creating
436 preferential pathways beneath it. The high concentrations of atrazine and DEA
437 observed in the LUC and VOU lakes may result from the quick transfer through
438 preferential pathways under the clay-with-flints. Below the layer of clay-with-
439 flints, a perched water table may form near the surface between the Chalk and
440 the clay-with-flints due to the contrast of hydraulic conductivity. The stored
441 water then infiltrates by the preferential pathways, recharging LUC and VOU
442 lakes continuously, explaining the low variation of lake levels and continuous
443 percolating flow of these two sites. The presence of preferential pathways may
444 allow micro-organisms entering the UZ, leading to the degradation of atrazine
445 in groundwater. LUC and VOU have higher DAR than other sites and this may
446 be because of higher degradation rate in soil or because of the degradation of
447 atrazine in the lakes with the presence of micro-organisms.

448 LUC and VOU also had the highest temporal variation of DAR. The high
449 temporal variation of DAR values may result from the differences observed be-

450 tween the atrazine concentration and the DEA concentration time series. This
451 difference between the temporal variation of atrazine concentration and DEA
452 concentration is due to the different transfer processes in atrazine and DEA.
453 Unlike other sites, VOU lake atrazine and DEA concentrations have different
454 temporal variations (Fig. 4). The VOU temporal variation of atrazine is similar
455 to other sites, so the transfer of atrazine is similar for all the sites, independent
456 of the thickness of the layer of clay-with-flints. However, the DEA of LUC and
457 VOU time series differ from the 14 other sites and no relation was observed
458 between the lake level and DEA for LUC and VOU. These results may be
459 explained by the different sorption capacities between atrazine and DEA. Sorp-
460 tion capacity depends on materials and the physico-chemical properties of the
461 organic component (Coquet, 2003). Bottoni et al. (1996) showed that atrazine
462 has lower mobility than DEA in soil with a Koc (Soil Organic Carbon-Water
463 Partitioning Coefficient) of $111 \text{ mL } g^{-1}$ for atrazine and a Koc of $38 \text{ mL } g^{-1}$ for
464 DEA (higher Koc indicates higher capacity of being adsorbed by soil). Brouwer
465 et al. (1990) and Mersie and Seybold (1996) showed that atrazine is more ad-
466 sorbed than DEA on soils, meaning that atrazine is more easily to be adsorbed
467 by the Chalk aquifer than DEA, and also more difficult to desorb than DEA.
468 Since we assumed that the transfer of atrazine and DEA for LUC and VOU
469 occurs mainly through preferential pathways, the transfer of DEA may occur
470 through fractures with very little adsorption in the Chalk aquifer. Atrazine is
471 more easily adsorbed, so its transfer is delayed by sorption. The preferential
472 pathways may result in different transfer processes of atrazine and DEA with
473 the transfer of DEA quicker because DEA desorbs more easily.

474 **5. Conclusion**

475 This study shows very high concentrations of atrazine and its degradation
476 product, DEA, in groundwater, which is the output of the UZ under an agricul-
477 tural area. The transfer velocities from soil surface towards the water table of
478 atrazine and DEA are estimated between 0.45 and 2.21 m/year. Spatial varia-

479 tions were observed in the groundwater concentration of nitrate, atrazine and
480 DEA, and also in DAR in the groundwater, which may be related to the prop-
481 erties of the UZ of the Chalk aquifer (thickness of clay-with-flints and depth).
482 Temporal variations were observed in the concentration of atrazine and DEA.
483 The spatio-temporal variation of atrazine, DEA and DAR shows that:

- 484 - The transfer of atrazine and DEA occurs through both matrix and frac-
485 tures, and the transfer is delayed by the sorption in the UZ.
- 486 - Clay-with-flints may favor the degradation of atrazine by creating a “perched
487 water table”, leading to atrazine staying near the surface for a long time.
- 488 - Clay-with-flints can create preferential pathways, through which the trans-
489 fers of atrazine and DEA are quicker. The transfers of atrazine and DEA
490 differ in their preferential pathways because DEA is more easily to be
491 desorbed.

492 The multi-sites with different UZ properties is a simple system (output of the
493 UZ), which makes it possible to study how the UZ properties (UZ thickness and
494 thickness of clay-with-flints) impact the transfer and degradation processes of
495 pesticides. It is possible to apply this study to other studies on a larger scale,
496 e.g., the study of the transfer of pesticides in the Chalk aquifer of the Paris
497 Basin.

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Table 1: The measurements and analyses made for each campaign.

Groups	Campaigns	Sites	Measurements	Analyses
A	2016-04-12, 2016-06-23, 2016-10-20, 2017-01-09, 2017-02-27, 2017-09-05	16 sites	percolating flow rate, lake level	nitrate, atrazine, DEA
B	2016-06-06, 2016-09-05, 2017-05-02, 2017-06-26	16 sites	percolating flow rate, lake level	N.A.
C	2017-10-23, 2018-01-16, 2018-04-10, 2018-05-16	BLE, STA, VOU, PED	percolating flow rate, lake level	nitrate, atrazine, DEA

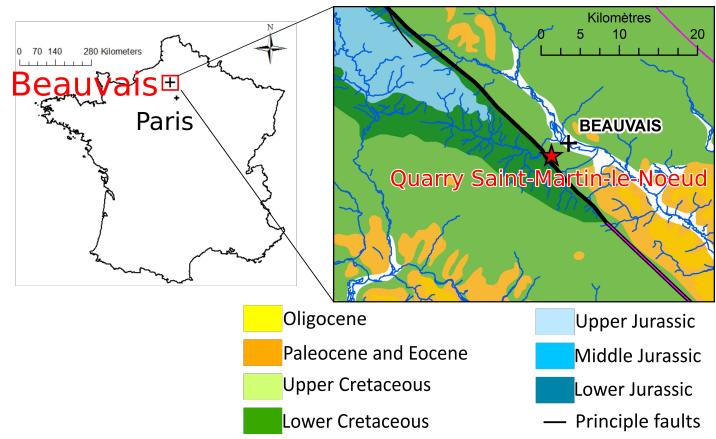


Figure 1: Location of the study site with the zoom of the geology of the study site.

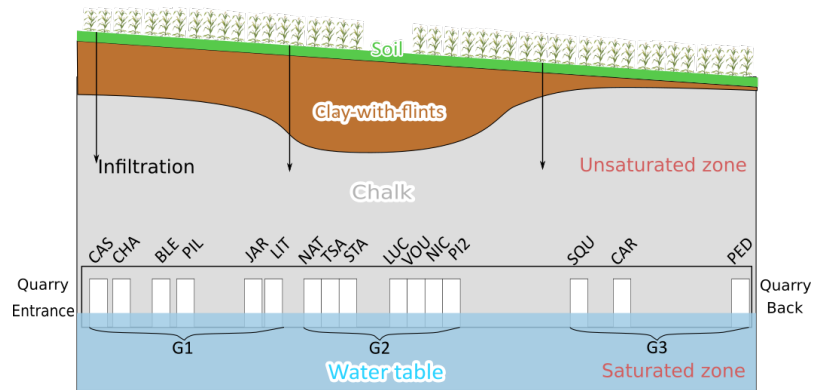


Figure 2: Schematic cross section of the Saint-Martin-le-Noeud quarry with the presentation of the 16 sites in the quarry.

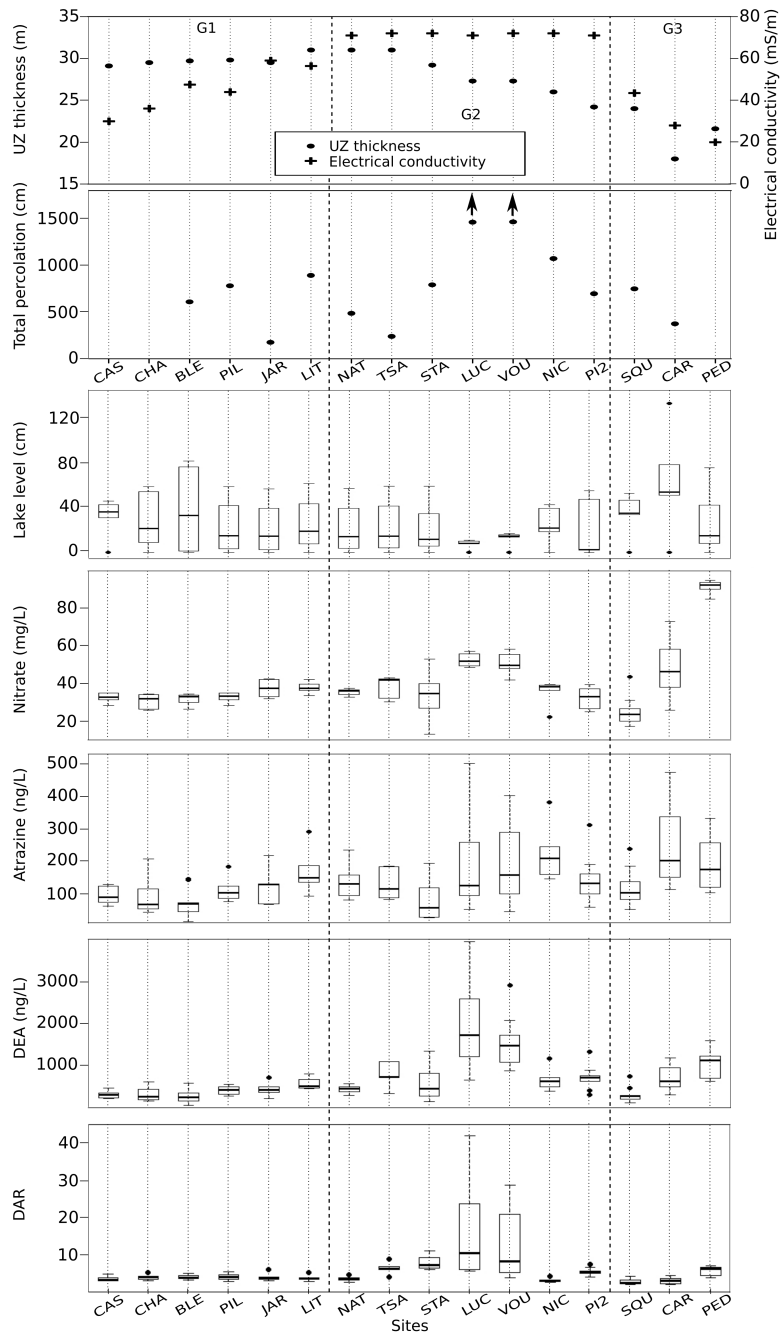


Figure 3: UZ thickness and electrical conductivity of the 16 sites. The total percolation between April 2016 and September 2017 and the boxplot of lake level variation, of concentration of nitrate, atrazine and DEA, and of DAR of the lake of the 16 sites. Campaigns used for the box are: 2016-04-12, 2016-06-23, 2016-10-20, 2017-01-09, 2017-02-27, 2017-09-05. The box range between the 25th and 75th percentiles, whiskers correspond to minimum and maximum, horizontal bars indicate the median. The 16 sites are divided into three groups: G1, G2 and G3.

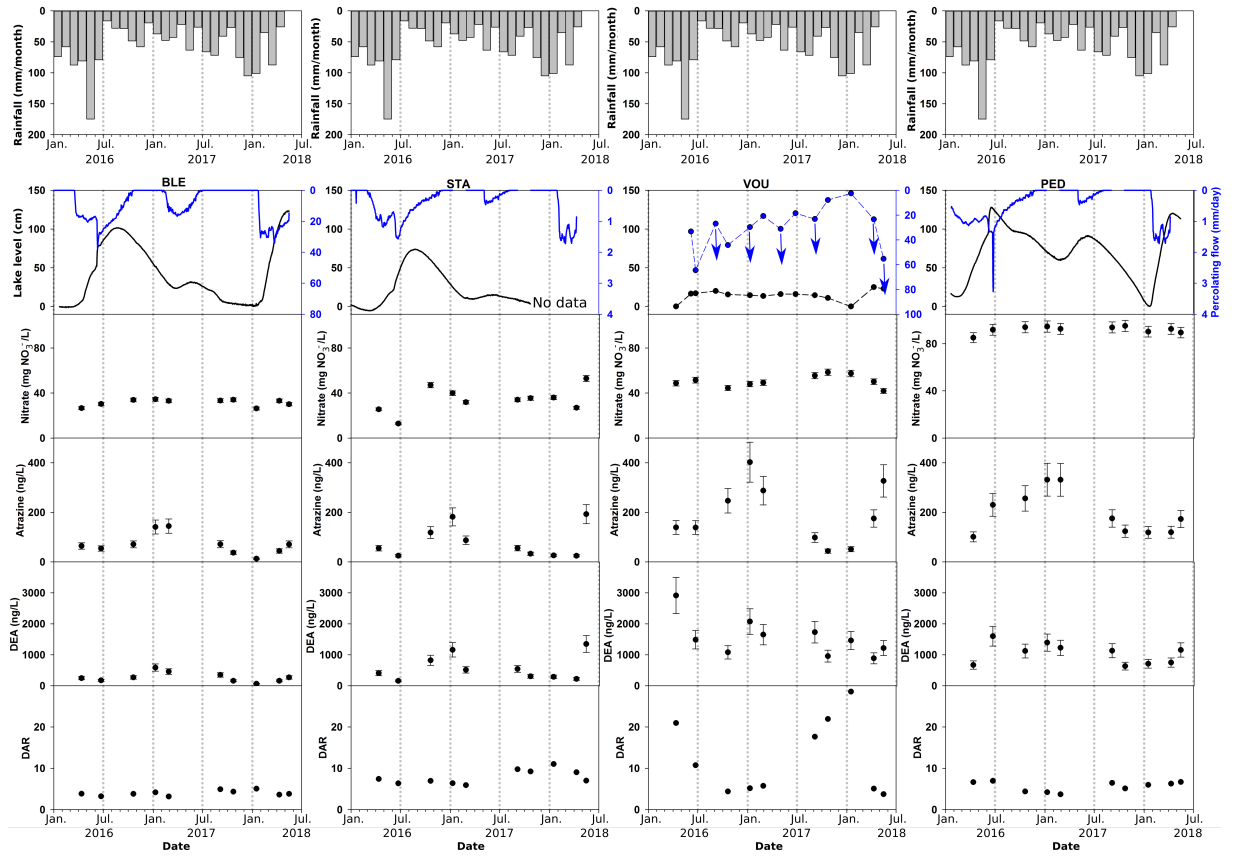


Figure 4: Time series of rainfall, lake level variation, percolating flow, nitrate, atrazine, DEA and DAR from 2016-01-01 to 2018-06-31 for BLE, STA, VOU and PED. Time series of percolating flow is presented with reversed y-axis. Arrows of the percolating flow of VOU indicate that the values are underestimated.

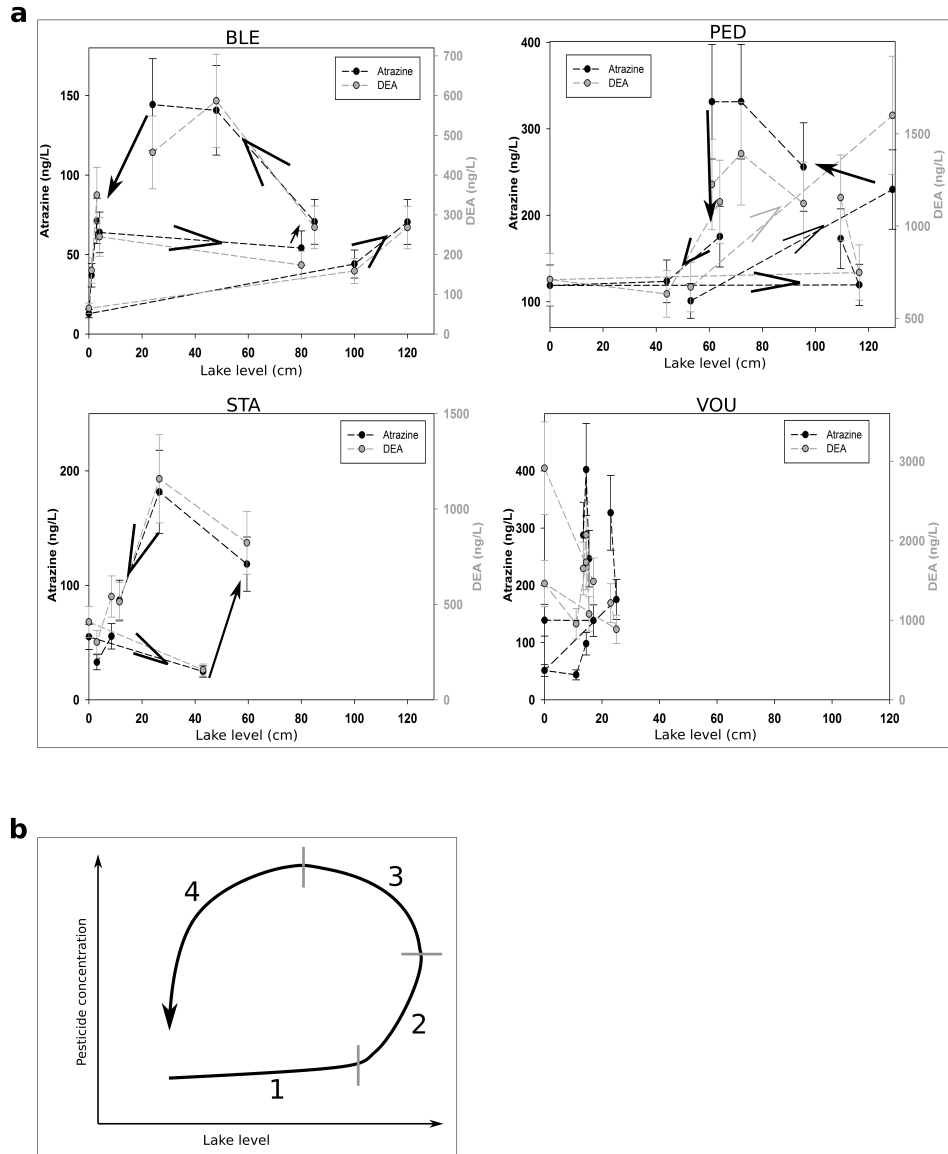


Figure 5: Hysteresis between lake level and pesticide concentration. a, hysteresis between atrazine, DEA and lake level variation for BLE, STA, Vou and PED. Campaigns used are: 2016-04-12, 2016-06-23, 2016-10-20, 2017-01-09, 2017-02-27, 2017-09-05, 2017-10-23, 2018-01-16, 2018-04-10, 2018-05-16. b, Sketch of the hysteresis observed between lake level variation and pesticide concentration.

