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1 Wetland hydrodynamics and mitigation of pesticides and their metabolites at
2 pilot-scale

3

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20

21 ABSTRACT

22 Constructed wetlands (CWs) are useful for reducing pesticide transfer from drainage into
23 surface water, though little was known about the influence of hydrodynamics on their
24 mitigation. We thus assessed the influence of design parameters (aspect ratio, water depth,
25 flow rate) on hydraulic performance simultaneously to pesticide mitigation. We performed
26 our work on four pesticides with contrasted properties: boscalid (BSC), cyproconazole (CYP),
27 isoproturon (IPU) and dimethachlor (DMT), under three controlled flow-rate conditions
28 (including no-flow) by using two pilots with contrasted designs (pond and ditch) over 62
29 days. Hydraulic performance and pesticide mitigation were less effective in a pond than in the
30 ditch whatever the flow. Moreover, pesticide mitigation was more significant at low than at
31 high flow rates for both pilots. At high flow rate, water transport is mainly governed by
32 convection, but at low flow rates both water transport and mitigation are governed by
33 hydrodynamic dispersion, inducing a longer contact time between pesticides and substrate due
34 to longer hydraulic retention. Finally, BSC and CYP are better mitigated than DMT and IPU,
35 even if they are also more strongly released during low flow rates. In addition, the mitigation
36 of pesticides and some of their metabolites produced inside the pilots was almost complete
37 during stagnation.

38

39

40 *Keywords:* constructed wetland; flow rate; hydraulic performance; pesticide; remediation;

41 water tracer

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44

45 **1. Introduction**

46

47 In order to protect and improve water quality (JOCE, 2000), the use of Free Water Surface
48 Constructed Wetlands (FWS CWs) with tile drains at about 1-m depth has emerged as a cost-
49 effective way of reducing contaminant loading from drainage waters (Schultz et al., 1995;
50 Moore et al., 2001; Tournebize et al., 2012; Vallée et al., 2015b). Their effectiveness in
51 mitigating pesticide concentrations has been demonstrated in several studies (Moore et al.,
52 2001; Wilson et al., 2011; Elsaesser et al., 2011), but locally negative mitigation rates have
53 been reported as well depending on molecules and hydrological year (Passeport et al., 2013;
54 Maillard and Imfeld, 2014; Vallée et al., 2015b). A review of 47 studies covering 87 reveals
55 average removals varying from 97 to 24% according to pesticide physicochemical parameters
56 (Vymazal and Březinová, 2015). For both controlled and uncontrolled flow in CW, average
57 retention efficiencies for pesticide are similar (32-39%) but the performance is highly variable
58 dependent on hydrological conditions and seasons (Tournebize et al. 2017). Indeed, several
59 parameters are known to affect the hydraulic effectiveness of CWs, such as (i) the length-to-
60 width ratio (LWR) of the wetland, and (ii) the hydraulic residence time (HRT), flow rate and
61 water depth, but the influence of these hydraulic parameters on pesticide mitigation has rarely
62 been studied (Blankenberg et al., 2007; Boutron et al., 2011; Elsaesser et al., 2011; Haarstad
63 and Braskerud, 2005; Vallée et al., 2015a).

64 HRT is considered as one of the main factors influencing the mitigation effectiveness
65 of CWs (Stehle et al., 2011; Vyzamal and Březinová, 2015; Guo et al., 2017); it is mainly
66 controlled by the flow path through the wetland, inflow rate, and water depth. From field
67 experiments, the influence of HRT on pesticide mitigation is not very clear (Maillard and
68 Imfeld, 2014; Vallée et al., 2015b), but some studies carried out under controlled conditions
69 reported an increased effectiveness with a longer HRT (Elsaesser et al., 2011; Vallée et al.,
70 2015a). These authors tested HRTs ranging from 4 hours to 7.4 days, corresponding to inflow
71 rates ranging from $3.2 \text{ L}\cdot\text{s}^{-1}$ to $0.05 \text{ L}\cdot\text{s}^{-1}$ (Holland et al., 2004; Elsaesser et al., 2011; Vallée et

72 al., 2015a; Maillard et al., 2016), which can be assimilated to low flow rates in the field,
73 where flow rates can range from 0.01 to 20 L/s (Larson et al., 2000; Vallée et al., 2015b).
74 However, the effectiveness of high flow rates coupled with very short HRTs (a few hours)
75 was rarely studied under controlled conditions, even though they may represent about 50% of
76 drainage flow over one year in the field (Tournebize et al., 2013; Vallée et al., 2015b). In
77 addition, flow rate and water depth both affect wetland hydraulics (Holland et al., 2004) by
78 changing the effective volume that can be used for pollutant mitigation, and the length-to-
79 width ratio (LWR) seems to be a major factor in determining the effectiveness of a CW by
80 controlling flow uniformity (Thackston et al., 1987; Su et al., 2009); these authors showed
81 that the mitigation effectiveness of a CW is considered as satisfactory for a LWR between 1.8
82 and 10.

83

84 Our study is one of the first to investigate the influence of highly contrasted flow rates
85 on the flow patterns of hydraulic zones in CWs, and their impact on pesticide mitigation. For
86 that purpose, laboratory experiments were carried out on two pilot-scale wetlands with
87 different designs under variable hydrodynamic conditions, studying four pesticides—boscalid
88 (BSC), cyproconazole (CYP), isoproturon (IPU) and dimethachlor (DMT)—with contrasted
89 polarities. Such a controlled small-scale approach, compared to an *in-situ* study, is required
90 for understanding the parameters and processes controlling pesticide mitigation in CWs. The
91 experiments were conducted by associating two conservative tracers (chloride and bromide)
92 with the four pesticides during a drainage period with alternating high-, low- and zero flow.

93

94 **2. Material and Methods**

95

96 2.1. Pilot set-up

97

98 Two laboratory pilot installations, both mimicking field CWs, were constructed in
99 polyvinylchloride. Soils and sediments were sampled in field CWs, dried for one week at
100 24 °C, crushed and sieved at 2 mm, and then homogenized. Their main characteristics are
101 provided in Table A.1. The first pilot reproduced a ditch-shaped CW at Manoncourt-sur-Seille
102 (France) at 1:40 scale, using 22 kg of soil from this site deposited with a thickness of 3 cm
103 and covered with 360 g of sediment over 0.5 cm thick. It was 225 cm long and 2.5 cm wide,
104 with an enlarged section of 25 x 6.5 cm. The vegetation, grown from seeds in the soil, was
105 dominated by *Juncus effusus*, *J. bufonius* and grasses on the edges of the pilot that not
106 affected flow) (Fig. 1).

107 The second pilot simulated a CW formed by a succession of three ponds at Ville-sur-
108 Illon (France) at 1:20 scale, using 55 kg of soil from the site deposited with a thickness of
109 5 cm and covered with 2 kg of sediment over 0.5 cm thick. It was 235 cm long and 20-30 cm
110 wide, depending on the ponds, with an island (15 x 7 cm) at the beginning of the second pond,
111 as in the field. The vegetation, again developed from seeds in the soil, was dominated by
112 *Juncus effusus*, *J. inflexus* and *J. articulatus* on the pond edges (not affecting flow), and by
113 *Typha latifolia* and *Veronica becabunga* inside the ponds (Fig. 1). The detailed dimensions of
114 the pilots are given in Table A.2. Both ditch and pond CWs were chosen for their contrasted
115 design and their simplicity of laboratory implementation, in order to reproduce their use for
116 large-scale pesticide mitigation.

117 Before running the experiments over a 62-day period, both pilots were left during 8
118 months for stabilization and plant growth, and were watered by tap water. Operating
119 conditions in the phytotron room were 20±2 °C, with a day/night ratio of 14/10 h, a
120 hygrometry of 70% and a brightness of 3100 to 3800 lx.

121

122 2.2. Selected pesticides

123

124 Four pesticides were selected on the basis of their actual field application, their detection in
125 the water of existing CWs, and the diversity of their polarities (Octanol-water partition
126 coefficient from 148 to 1230) or sorption coefficient K_{OC} from 69 to 772 L.kg⁻¹). The selected
127 pesticides were the two fungicides *boscalid* (2-chloro-N-(4'-chloro[1,1'-biphenyl]-2-
128 yl)pyridine-3-carboxamide) and *cyproconazole* (α -(4-chlorophenyl)- α -(1-cyclopropylethyl)-
129 1H-1,2,4-triazole-1-ethanol), and the two herbicides *isoproturon* (*N,N*-dimethyl-*N'*-(4-(1-
130 methylethyl)phenyl)urea) and *dimethachlor* (2-chloro-*N*-(2,6-dimethylphenyl)-*N*-(2-
131 methoxyethyl)acetamide). Their main properties are given in Table A.3. The analytical
132 standards of these pesticides were purchased from Cluzeau (Sainte-Foy-La-Grande, France).
133 All four were analytical standard grade (>98 %) and are used both for spiking and
134 confirmation. The analytical standards of the IPU and DMT metabolites (see Table A.4) were
135 purchased from Restek (Lisses, France), Sigma (Lyon, France), Neochema (Bodenheim,
136 Germany) and Techlab (Metz, France).

137 2.3. Simulated drainage, stagnation and tracing

138 In order to mimic real conditions, the experimental flow rates were determined based on *in*
139 *situ* observations. In the field, flow-rate monitoring (with an ultra-sound flowmeter, 950-US
140 50 Hz, SIGMA) over one year indicated that 90% of the flow values varied from 0 to 4 L.s⁻¹
141 and 10% varied from 4 to 10 L.s⁻¹ for the ditch (D) CW. For the pond (P) CW, 70% of the
142 flow values varied from 0 to 5 L.s⁻¹, 10% varied from 5 to 10 L.s⁻¹ and 20% varied from 10 to
143 18 L.s⁻¹. In addition, a stagnation period (zero flow) also occurred after a drainage event.

144 Based on these field observations, we applied two distinct inflow rates to each pilot,
145 calculated according to the pilot scales of 1:40 and 1:20. The high inflow rates were

146 7.0 mL.min⁻¹ for the ditch pilot (D-HF) and 55.5 mL.min⁻¹ for the pond pilot (P-HF),
147 corresponding to field scales of 7.5 and 7.4 L.s⁻¹. These values are representative of the high
148 and medium inflow rates defined for ditch CW and pond CW, respectively. Thus, for the high
149 flow rate, the nominal HRTs (i.e. the wetland-volume/flow-rate ratio) were 4.0 and 2.8 h for
150 ditch pilot and pond pilot, respectively. This agrees with the HRTs measured in the field at
151 high flow (about 30 min to 6 h). The low inflow rates were 1.8 and 8.0 mL.min⁻¹ for ditch
152 pilot (D-LF) and pond pilot (P-LF), respectively, corresponding to field values of 1.9 and
153 1.1 L.s⁻¹, respectively. The nominal HRTs were 11.0 and 9.8 h for the ditch and pond pilots,
154 respectively; these values have the same order of magnitude as the HRTs measured in the
155 field at low flow (about 8 to 60 h). A drainage event was simulated during 12 h for a high
156 inflow rate and during 36 h for a low inflow one, corresponding for each flow rate condition
157 to at least three nominal HRTs in the pilot. Subsequently, a stagnation period (no-flow) was
158 simulated for 50 days to represent a long *in-situ* period of stagnation (i.e. almost three months
159 in summer). During this step, to balance evapotranspiration, the water depth was maintained
160 at 1 cm and 1.5 cm, respectively for the ditch and the pond pilots, by adding distilled water
161 twice a day.

162 Drainage inflow was injected continuously through Teflon tubing (AJD00017, Saint
163 Gobain, France) using a peristaltic pump (Ismatec IPS-16). The water inlet and outlet were
164 located in the middle of each pilot. The simulated drainage was divided into eight consecutive
165 charge and discharge steps (S1 to S8) (Table 1). BSC, CYP, IPU and DMT were injected with
166 a concentration of 200 µg.L⁻¹ at the same time as water-tracer ions at 11.5±1.5 mg.L⁻¹ during
167 the S1 and S3 charge steps, and distilled water was injected during the S2, S4, S5 and S8
168 discharge steps. The tracers used were chloride (CaCl₂) during the S1 step (high flow) and
169 bromide (KBr) during the S3 step (low flow), for determining the mean (real) HRT and for
170 measuring the hydraulic efficiency. No loss of ions and pesticides was observed in the inlet

171 solution. Moreover, the first high inflow charge (S1) was done in a half-full pilot, i.e. in the
172 field the CW was not dry when drainage started.

173 In addition, a brilliant blue (BB) dye tracer at 0.05 mg.L^{-1} was continuously injected
174 after discharge S8. Pictures were automatically taking each minute for D-LF, and each 30 sec
175 for D-HF, P-HF and P-LF, to monitor the water pathways.

176

177 2.4. *Sampling strategy*

178

179 During the drainage periods (S1 to S5 and S8), outlet effluents were continuously collected
180 through a Teflon tube (AJD00017, Saint Gobain, France) with a peristaltic pump (Ismatec
181 IPS-16); they were stored in polyethylene flasks using a fraction collector (Foxy 200TM). At
182 high flow (S1-S2-S4), automatic samples were taken every 15 min during the first 3 h and
183 then every hour for the following 9 h. At low flow (S3-S5-S8), automatic samples were taken
184 every 30 min during the first 6 h and then every 3 h for the following 30 h, and over the next
185 6 days for the S8 steps. All samples were stored less than 12 h in the polyethylene flasks
186 (pesticide loss from 1 to 5% in the flasks, determined in triplicate at $200 \mu\text{g.L}^{-1}$) and then
187 stored in glass tubes. Moreover, all samples were individually analysed within 24 hours.

188 In addition, 5 mL water samples were collected manually inside the pilots in two
189 specific zones (SZ) (Fig. 1), every 3 h at high flow (S1-S2-S4), and every 9 h at low flow (S3-
190 S5-S8) for the two pilots (4 samples). During the S7 stagnation period, composite (6 x 1 mL)
191 samples representative for the pilot were taken in the same place, daily for the first 10 days,
192 and then after 12, 14, 16, 18, 20, 26, 32, 38, 44, 50 days of stagnation.

193 Finally, at the end of the experiment, after emptying the pilots, soil and plants were
194 freeze-dried, manually crushed and homogenized, before bromide and pesticide extraction
195 and analysis.

196

197 2.5. *Pesticide analyses*

198

199 For each water sample, 2 mL was placed in a PP 2 mL centrifuge tube and then centrifuged at
200 16,873 g for 5 min to eliminate any suspended particles (i.e. to investigate the mitigation on
201 the dissolved phase only). Then, a 1 mL aliquot was transferred to an amber glass vial for
202 pesticide analysis within 24 h after sampling (Method A). Finally, part of the centrifuged
203 sample was frozen at -20 °C to analyse for IPU and DMT metabolites (methods B and C) and
204 analysis within 2 months.

205 Method A was performed by liquid chromatography (LC) using an Ultimate 3000
206 RSLC system and a Diode Array Detector (Gaulhier et al., 2018), analysing BSC, CYP, IPU
207 and DMT. Methods B and C were done in an Acquity Ultra-Performance LC system (UPLC,
208 Waters), interfaced to a triple quadrupole mass spectrometer (Quattro Premier XE, Waters).
209 Method B analysed for mono-desmethyl-IPU (MD-IPU), di-desmethyl IPU (DD-IPU), and
210 the DMT metabolites CGA 39981 and CGA 42443. Method C analysed for the DMT
211 metabolites CGA 42443 (DMT-OA), CGA 354742 (DMT-ESA), CGA 369873, CGA
212 373464, SYN 530561 and SYN 528702. The three analytical methods are described in further
213 detail in the Appendices.

214 The pesticides were only extracted from the sediments (not from plants) by a modified
215 QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method described in the
216 Appendices (Fernandes et al., 2013) before analysing them with Method B, the LOQ being
217 0.0005 µg.g⁻¹ for BSC, 0.0002 µg.g⁻¹ for CYP and DMT, and 0.0001 µg.g⁻¹ for IPU. The
218 values were corrected by the extraction yield of the QuEChERS method: 88.3 ± 0.7%, 70.2 ±
219 3.8%, 74.0 ± 4.4% and 106.8 ± 1.9% for BSC, CYP, DMT and IPU, respectively.

220

221 2.6. *Ionic tracer analysis*

222

223 Each water sample was filtered through a 0.22 μm cellulose acetate filter and then a 1 mL
224 aliquot was transferred to a polypropylene vial for analysis with a Dionex ICS-3000 ion-
225 chromatographic instrument (Sunnyvale, CA, USA), using Chromeleon® software (Version
226 6.80) to determine Cl^- and Br^- concentrations. The analytical method is described in the
227 Appendices. In addition, at the end of the experiment the bromide tracer was extracted from
228 10 g of sediment with a CaCl_2 solution (10 mL – 10^{-4} M) and from 0.8 g of plant material
229 with distilled water (80 mL), by stirring for 40 min, and then analysed.

230

231 2.7. *Data analysis*

232

233 2.7.1. *Water transport parameters*

234 The residence time distribution (RTD) function, $E(t)$, is defined mathematically such that
235 $E(t) \times dt$ is the fraction, at the outlet, of fluid that has spent between t and $t+dt$ time in the flow
236 system (Adeosun and Lawal, 2009). In order to compare the RTDs for our four studied
237 conditions (D-HF, D-LF, P-HF and P-LF), each RTD must be normalized. The normalized
238 hydraulic retention time (HRT) (t_θ), was defined as the ratio between the mean HRT (t_{mean})
239 and the nominal HRT (t_n) (Fan et al., 2008). In order to estimate the hydraulic performance of
240 the pilots, the normalized HRT (t_θ), the normalized variance (σ_θ), the number of cells (N) and
241 the hydraulic efficiency (λ) were determined. The detailed calculation is given in the
242 Appendices. The hydraulic performance is considered as good when all these parameters are
243 optimized, such as when the water is transported from inlet to outlet throughout the entire
244 volume system, limiting short-circuits.

245

246 *2.7.2. Restitution of tracer ion and pesticide mitigation rate*

247 The restitution percentage of each tracer was calculated according to Equation (1):

248
$$restitution = \frac{Q_{out}}{Q_{in}} \times 100 \quad (1)$$

249 where Q_{in} is the total amount injected (mg) and Q_{out} is the total amount outlet (mg) defined by
250 Equation (2).

251
$$Q_{out} = \sum_0^{\infty} C(t) V(t) \quad (2)$$

252 where $C(t)$ (mg.L⁻¹) is the outlet concentration at each time step and $V(t)$ (L) is the outlet
253 volume at each time step.

254 The effectiveness (%) of the pilots to mitigate pesticides was also calculated with Eq.
255 (1) and (2), replacing the ion tracer by pesticides mass.

256

257 *2.7.3. Dissipation and degradation of pesticides*

258 Pesticide dissipation kinetics in water during the stagnation period were described using a
259 second-order model before calculating the associated half-live DT_{50} was calculated (see
260 Appendices).

261 The dissipation of pesticides can partly be due to their degradation. The rate of
262 degradation (ratio between the molar concentrations of metabolites and parent molecule) was
263 estimated for each metabolite during (i) the drainage period and ii) the stagnation period.

264

265 *2.8. Statistical analysis*

266

267 First, the hydraulic variables used for defining the drainage period in the two pilot systems
268 were converted into categorical (discrete) variables. The semi-quantitative values measured
269 for the volume- and hydraulic-efficiency- variables were divided into four ranks; another

270 three ranks were defined for the flow-rate variable, and HRT and the LTW values were
271 aggregated into two more ranks (Table A.5). The ranking groups were defined beforehand.

272 Of the variables used for describing the pesticide properties (DT_{50} water, K_d , P_{max} ,
273 discharge) except the T_{eq} variable, the quantitative values were also transformed into
274 categorical (discrete) variables. To this end, a unimodal distribution was calculated for each
275 variable after centring and scaling all data. After that, first and third quartiles as well as the
276 median were defined. Based on these values, four ranks were defined for each variable. The
277 first corresponds to values below the first quartile, the second is for values ranging between
278 the first quartile and the median, the third rank consists of values ranging between the median
279 and the third quartile, and the fourth rank aggregates the values above the third quartile. For
280 the T_{eq} variable, five ranks are considered.

281 Multiple correspondence analysis (MCA) then ordered the 16 observations according
282 to the hydraulic and pesticide variables used for their definition. The Φ^2 distance-based matrix
283 was calculated from re-organized data according to a Burt table. The results were displayed as
284 a symmetric plot showing both variables and observations along the first two principal axes.
285 Based on the Φ^2 distance-based matrix associated with Ward's method for aggregating data,
286 an agglomerative hierarchical principal-component clustering (HCPC) was calculated and the
287 first four principal components then were used for constructing the associated dendrogram.
288 The dendrogram tree was then cut into several groups based on the higher relative loss of
289 inertia criteria, allowing the aggregation of observations into classes.

290 Finally, a partial least squares discriminant analysis (PLS-DA) discriminated
291 observations among the groups defined from the HCPC analysis. To this end, multivariate
292 analysis computed the best discriminant functions for differentiating objects in groups while
293 maximizing variance between treatments, though minimizing intra-variance for which the
294 first four main axes from the MCA calculations were used. This analysis is based on a partial

295 least squares regression algorithm that searches for latent variables with maximum covariance
296 and represents the relevant sources of data variability with linear combinations of the original
297 variables (Ballabio and Consonni, 2013). The results were presented as a correlation circle of
298 variables, distributing the sixteen observations along the two discriminant axes. A confusion
299 matrix, comparing the *a priori* (real) and *a posteriori* (calculated) classification of the
300 observations, was calculated as well with the cross-validation technique. All statistical tests
301 were carried out using FactoMineR and ade4 R-software.

302

303 **3. Results and discussion**

304

305 *3.1 Influence of pilot design parameters and flow rate on hydrodynamic*

306

307 Table 2 shows the water-transport parameters derived from RTD data. For high flow (HF) or
308 low flow (LF), both ditch and pond have quite similar t_{mean} and v_{mean} values, indicating that
309 water-residence time and water velocity were roughly the same for both pilots. However, σ^2_{θ}
310 was lower for ditch than pond and N was higher, indicating that the ditch behaved more like a
311 plug-flow, whereas the pond behaved as a mixing system (Fan et al., 2008). In addition, σ was
312 greater for pond than ditch, indicating a greater dispersion of water in the pond compared to
313 the ditch, probably toward the borders, due to its larger width. Moreover, the hydraulic
314 efficiency (λ) was higher for the ditch than for the pond. Thus, all parameters indicated that
315 the hydraulic performance was higher for ditch than pond, regardless of flow rate. This could
316 be due to the morphology and dimensions of both pilots: as the length-to-width ratio for ditch
317 is five times higher than for pond, an optimal water-flow path is induced in the ditch pilot as
318 suggested by other authors (Thackston et al., 1987; Haarstad and Braskerud, 2005; Su et al.,
319 2009).

320 For both pilots, the t_{mean} at LF (22 h) is higher than that at HF (4-5 h), indicating that the
321 water spends a longer time in the pilot when the flow rate is lower (Table 2). In addition, for
322 both pilots, the hydraulic efficiency λ and the effective volume (e_v) were higher at LF than at
323 HF. Moreover, e_v was >1 , probably indicating a storage zone in both pilots, especially at LF
324 and probably due to greater dispersion of water. This assumption was confirmed by (i) a
325 greater σ at LF than at HF, (ii) a more dispersed progression front of the BB dye at LF than at
326 HF, and (iii) similar ionic-tracer concentrations at the outlets and in specific zones at HF,
327 which are different at LF (Fig. A.1). Thus, water-transport parameters indicated that the
328 hydraulic performance was higher at LF than at HF for both pilots, which might be due to
329 distinct water-transport mechanisms inside the pilot, depending on flow rate. At HF, the
330 transport was dominated by convection in the main channel, while at LF the transport was
331 also governed by hydrodynamic water dispersion (including molecular diffusion and
332 kinematic dispersion) from the main channel into the whole pilot volume, convection still
333 occurring in the main channel (Gaullier et al., 2018; Holland et al., 2004).

334

335 *3.2 Influence of hydrodynamics on pesticide mitigation*

336 Tracer recoveries were over 90% at the end of the experiments (Fig. 2). Regardless of the
337 studied flow rate and pesticides, the pesticide-export rate at the outlet (charge + discharge)
338 was lower for the ditch (49.1 to 86.9%) than for the pond (78.8 to 99.4%) (Fig. 2), indicating
339 a better mitigation through the ditch. Its higher mitigation could be due to the lower water
340 depth (at LF 1 cm and 1.5 cm in ditch and pond, respectively, and at HF 1.5 cm and 3 cm in
341 the same pilots), which enhances the surface contact with sediments and increase the
342 adsorption (Gaullier et al., 2018). Regardless of the studied pilots and pesticides, the exported
343 rates at the outlet (charge + discharge) for the four pesticides were lower at LF (49.1 to
344 87.1%) than at HF (66.2 to 99.4%) (Fig. 2). This result agrees with those reported under

345 controlled conditions by other authors (Boutron et al., 2011; Moore et al., 2013; Vallée et al.,
346 2015a). Thus, pesticide mitigation is higher at LF than at HF, probably associated with a
347 longer residence time as well as with water-transport mechanisms governed by hydrodynamic
348 dispersion and convection at LF, whereas at HF only convection is the main process of water
349 transport.

350 For both flow rates, during charge phases (S1 and S3), the exported rate of pesticides
351 was lower than that of ionic tracers in the ditch, indicating pesticide retention and/or
352 degradation inside the pilots. According to their mitigation, pesticides can be classified as
353 $BSC > CYP > DMT \geq IPU$, which is consistent with their adsorption coefficient and suggests
354 that retention could be a major process (Gaullier et al., 2018; Vymazal and Březinová, 2015,
355 Tournebize et al. 2017). Note, however, that the mitigation we observed is lower than those
356 mentioned by Tounebize et al. (2017). According to their classification IPU and DMT belong
357 to group I (average of 25% of removal efficiency, BSC to group II – 49% and CYP to group
358 III -51 %). In the pond, however, the exported rate of pesticides was almost similar to that of
359 ionic tracers, indicating that pesticides travelled freely in the water with few interactions with
360 substrates except for BSC having the highest adsorption coefficient.. Taking into account the
361 discharge phases (S2 and S4+S5), the exported rate was similar for all pesticides and both
362 pilots during HF conditions. During LF, however, it was higher for pond than for ditch.
363 Moreover, BSC and CYP had higher exported rates than DMT and IPU, especially during LF
364 discharge (S5), as previously shown in a pilot-scale experiment by Vallée et al. (2015a). Thus,
365 for HF, the pesticides not adsorbed on sediment during charge step (S1) are released during
366 the following discharge step (S2) due to convective flux. At LF, however, the rate of exported
367 pesticides could be due to both convective and dispersive flux and pesticide desorption from
368 sediment and vegetation, especially for BSC and CYP. Indeed, the amount of released ionic
369 tracer (i.e. not adsorbed) was lower than that of released BSC and CYP, especially for the

370 ditch pilot, indicating that desorption reactions may occur. In addition, a higher percentage of
371 metabolites was recovered at LF (0.5-1.4% of initial IPU and 0.4-0.9% of initial DMT) than
372 at HF (0.2-0.6% of initial IPU and 0.03-0.13% of initial DMT) (Fig. A.2). A low flow-rate
373 highlights differences that are related to molecular properties, probably due to the longer
374 retention time that also promotes slower processes, such as degradation or desorption.

375 Finally, the HCPC test aggregated the sixteen observations in four groups
376 corresponding to the four studied conditions: pond-HF (obs. 1-4), pond-LF (obs. 5-8), ditch-
377 HF (obs. 9-12) and ditch-LF (obs.13-16) (Figs 3). The PLS-DA statistical test (fig 3D)
378 highlights the important factors in pesticide mitigation. The first (F1=57.27%) and second
379 (F2=35.18%) discriminant axes describe with a high degree of confidence (F1+F2 represent
380 90% of variance) the distribution of the four classes determined from the sixteen observations
381 (Fig. 3). The four groups determined from HCPC analysis are all separated by discriminant
382 axis 1, which was mainly based on the first principal axis calculated from the MCA that is
383 itself based on the four hydraulic parameters of flow rate, water depth, pilot volume and
384 hydraulic efficiency. In addition, the groups are separated by the second discriminant axis,
385 calculated based on the third principal MCA-derived axes. This third principal component is
386 mainly related to pilot volume and hydraulic efficiency. Observations 1 to 4 and 13 to 16 are
387 located in the upper part of the scatter plot and are discriminated from observations 5 to 12
388 according to the second discriminant (Fig. 3). These results show that the observations with
389 higher pilot volume and hydraulic efficiency (observations 1-4 and 13-16) are clearly
390 discriminated from the others. The MCA results show that hydraulic variables contributed
391 more strongly to the principal axes than the pesticide-related variables, indicating that the
392 classes calculated from HCPC are strongly dependent upon the hydraulic variables. The high
393 variance associated with the PLS-DA confirms that hydraulic variables (flow rate, water
394 depth, volume and hydraulic efficiency) are suitable for group observations. The group

395 showing higher pesticide mitigation is associated with lower flow rates, water depth and
396 volume. These results agree with observations by others authors (Holland et al., 2004;
397 Boutron et al., 2011; Moore et al., 2013), even if the results were contradictory for flow rates
398 (Holland et al., 2004; Moore et al., 2013). Flow rate and volume conditions were different for
399 a similar HRT (due to pilot morphology), indicating that hydraulic parameters have a stronger
400 influence on pesticide mitigation than the HRT. Combining MCA and PLS-DA analyses
401 shows that pesticide-related variables (K_d , $DT_{50\text{-water}}$) contribute mainly to intragroup
402 variance. In addition, the small size of the data set implies that one observation is associated
403 with only one pesticide. Therefore, the difference of pesticide mitigation according to their
404 physico-chemical properties could not be correctly determined from our dataset. One way to
405 overcome this limit would be to repeat part of the experiments, especially the LF experiments
406 where mitigation is higher, several times to obtain multiple observations associated with each
407 tested pesticides.

408

409 *3.3 Mitigation of pesticides during a no-drainage period followed by discharge*

410

411 Regardless of pilot and molecules, the water DT_{50} values, ranging from 0.5 to 1.2 days
412 showed fast dissipation of pesticides from the aqueous phase, as earlier shown for IPU and
413 BSC (Vallée et al., 2015a) (fig. 4). The DT_{50} values are generally lower or equivalent in the
414 pond than in the ditch (0.5 vs. 0.8 for BSC, 0.6 vs. 1.1 for CYP, 0.8 vs. 1.2 for IPU and 0.7 vs.
415 0.7 for DMT). Consequently, after 50 days of stagnation, less than 1% and 0.5% of the four
416 pesticides remained in the ditch and pond waters, respectively. The decrease in IPU and DMT
417 concentrations was accompanied by a simultaneous increase in metabolite concentrations
418 (Fig. 4B and 4C) during the first ten days of stagnation, testifying to a degradation of these
419 molecules during the experiment.

420 After 50 days of stagnation, the two IPU-metabolite concentrations in water were less
421 than LOQ, whereas a small amount of DMT metabolites remained in water notably DMT-
422 OA. For the two pilots, at least 5% of the IPU was degraded into metabolites after 50 days, in
423 accordance with IPU degradation rates determined elsewhere in water: 1.6-2.2% (160-200
424 days) (Rönnefahrt et al., 1997) and 3.5-35% (50 days) (Vandermeeren et al., 2016). The
425 concentration peak of the metabolite MD-IPU was 9 and 4.5 times higher than that of DD-
426 IPU (for ditch and pond, respectively), indicating that IPU is preferentially degraded into
427 MD-IPU as earlier shown (Rönnefahrt et al., 1997). Regarding the degradation of DMT in the
428 ditch, about 17.5% was degraded into DMT-OA, CGA 42443, DMT-ESA, CGA 39981 or
429 CGA 373464, and in the pond about 35% was degraded into DMT-OA, CGA 39981 (higher
430 amount), CGA 42443, DMT-ESA or SYN 528702 (Fig. 4C). We noticed that the ratios
431 between DMT metabolites are pilot-dependant with a prevalence of DMT-OA and CGA
432 39981 vs. DMT-ESA in the pond during the first days while the three metabolites are similar
433 concentrations in the ditch. As our study is the first to provide information on DMT
434 metabolites, we could not compare our results to previous data.

435 During the last 7-day step with low-flow discharge (S8) following the stagnation period,
436 the four pesticides were quantified at higher concentrations than at the end of stagnation step
437 (S7), indicating that they may have been desorbed from sediment and/or plants. As observed
438 during drainage and in both pilots, BSC and CYP are more released into water (0.9–1.8% of
439 the initial injected amount in S6) than IPU and DMT (0.2–0.3% of the initial injected amount
440 in S6) due to their higher desorption. Compared to the previous steps, the pesticide-
441 exportation rate measured during the S8 step may be considered as negligible, even though
442 the four pesticides are present in exported water. This could indicate that renewed flow after a
443 long period of stagnation (i.e. between two drainage seasons in the field) causes a small
444 release of these four pesticides.

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3.4 Global pesticide mitigation

In the field, a drainage season is composed of successive periods of high-, low- and zero flow. In order to determine the global pesticide mitigation during a complete drainage season, a mass balance considered the amounts of pesticides injected during the charge steps (S1, S3 and S6), and the amount of pesticides and metabolites exported in water during drainage periods (from S1 to S5 and S8) and adsorbed onto sediment (Fig. 2). Over the 62 days of the experiment, the mitigation ranged from 35.2 to 45.3% for the ditch, and from 7.9 to 14.8% for the pond, with earlier reported mitigation values of 24% for IPU and of 38-67% for BSC (Vallée et al., 2015a). The pesticides from the aqueous phase were exported at outlet mainly during the first steps of HF and LF (S1 to S5, vs. 1.8% for S8). In addition, less than 1% of IPU and DMT metabolites were exported in water at the outlets of both pilots from S1 to S8 (BSC and CYP metabolites were not analysed). From 0.01 to 4.6% of pesticide residues were extracted from sediments; in terms of concentrations, the most recovered was BSC, IPU and DMT were least recovered, and CYP had an intermediate recovery, agreeing with their adsorption coefficients (Gaullier et al., 2018; Vallée et al., 2015a, 2014). We can thus conclude that pesticide mitigation may result from: (i) adsorption onto sediment as previously shown by other authors for BSC (Papaevangelou et al., 2017) and IPU (Durst et al., 2013) (no data for CYP and DMT); (ii) degradation as previously shown for IPU and DMT, (Durst et al., 2013); and (iii) other processes such as plant or biofilm absorption, hydrolysis, photolysis or volatilization, not evaluated in this study but mentioned by (Rönnefahrt et al., 1997; Rose et al., 2008).

4. Conclusions

Our mesocosm experiments demonstrated that pesticide mitigation in CWs is linked to: i) hydrodynamics and in particular flow rates; ii) CW morphology, in this case a ditch and a succession of ponds; and iii) the physico-chemical properties of the pesticide. For the studied flow rates involving similar hydraulic residence times in the two pilots, i.e. high flow and low flow of about 5 h and 24 h, respectively, the ditch seems more effective for mitigating pesticides than the ponds. This is probably due to a lower water depth in the ditch. For both pilots, the mitigation was higher at low flow than at high flow, regardless of the pesticides. In addition to the kinetic aspects of adsorption, again the difference in water depth in each pilot, depending on the flow regime, can be another factor affecting mitigation. At low flow, a higher production of metabolites indicates enhanced degradation, leading to even better mitigation. Finally, no-flow periods led to (almost) total mitigation of both pesticides and their metabolites produced in the water phase.

These laboratory results obtained in controlled conditions highlight how the hydraulic regime that will exist *in situ* and the characteristics of the different drainage episodes will have an impact on the rate of mitigation. The time scale, i.e. long term vs. specific episodes of drainage considered to evaluate the effectiveness of the CWs could thus lead to contrasting results.

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620

621 **Tables and Figures captions**

622

623

624 **Table 1:** Simulated hydraulic parameters and characteristics of each step (S0 to S8)

625

626 **Table 2:** Water transport parameters of the pilots

627

628 **Figure 1:** Experimental ditch pilot (A) and pond pilot (B) and location of specific zones (SZ)
629 inside the pilots

630

631 **Figure 2:**

632 Exported rate of dissolved pesticides at outlet during drainage periods, at high flow rate (HF –
633 S1, S2, S4) and low flow rate (LF – S3, S5) and mass balance at the end of experiment (62
634 days) corresponding of alternating phases of high-, low- and no-flow) for the ditch and the
635 pond

636

637 **Figure 3:**

638 Distributions of the 16 observations (A) and contributions of the variables (B) obtained from
639 MCA analysis applied on results listed in Table A.5. Based on MCA results, a classification
640 tree (C) obtained with the ascending hierarchical principal component clustering. Groups
641 issued (pond-HF, 1-4; pond-LF, 5-8; ditch-HF, 9-12; ditch-LF, 13-16) from classification tree
642 are used to develop a PLS-DA model (D). These groups correspond also to the intensity
643 migration rate: low (0.6–9%), middle (12.6–20.8%), high (13–33.7%), very high (43.3–
644 50.8%).

645

646 **Figure 4:**
647 Dissipation of dimethachlor (DMT) and isoproturon (IPU) for the pond and the ditch during
648 the 50-day no flow phase (A) and appearance of their metabolites mono-
649 desmethylisoproturon (MM-IPU) and di-desmethylisoproturon (DD-IPU) (B) and CGA
650 39981, CGA 42443 and CGA 373464 (C). (*one replicat per pilot, concentrations expressed in*
651 *mol/L*)

652

Table 1: Simulated hydraulic parameters and characteristics of each step (S0 to S8)

	Initial State	Charge	Discharge	Charge	Discharge	Discharge	Charge	Stagnation	Discharge
STEP	S0	S1	S2	S3	S4	S5	S6	S7	S8
C_{in} pesticides ($\mu\text{g}\cdot\text{L}^{-1}$)	0	200	0	200	0	0	200	0	0
Duration step	-	12 h	12 h	36 h	12 h	36 h	12 h	50 d	7 d
Injected ion	-	Cl^-	-	Br^-	-	-	-	-	-
Ditch		D-HF		D-LF					
Flow rate ($\text{mL}\cdot\text{min}^{-1}$)	-	6.7 ± 0.2	7.0 ± 0.1	1.8 ± 0.3	6.8 ± 0.1	1.8 ± 0.1	1.8 ± 0.1	-	1.4 ± 0.4
Water level (cm)	0.8	1.5	1.5	1	1.5	1	1	1	1
Volume (L)	0.9	1.7	1.7	1.2	1.7	1.2	1.2	1.2	1.2
HRT_n (h)	-	4.3	4.0	11.0	4.2	10.7	11.1	-	14.3
Pesticide/sediment surface contact ($\mu\text{g}\cdot\text{cm}^{-2}$)	-	0.47	-	0.33	-	-	0.33	-	-
Pond		P-HF		P-LF					
Flow rate ($\text{mL}\cdot\text{min}^{-1}$)	-	55.5 ± 1.5	55.1 ± 4.9	8.0 ± 0.2	56.0 ± 0.4	7.9 ± 0.1	8.0 ± 0.3	-	7.4 ± 0.2
Water level (cm)	1.5	3	3	1.5	3	1.5	1.5	1.5	1.5
Volume (L)	4.7	9.4	9.4	4.7	9.4	4.7	4.7	4.7	4.7
HRT_n (h)	-	2.8	2.8	9.8	2.8	10.0	9.8	-	10.6
Pesticide/sediment surface contact ($\mu\text{g}\cdot\text{cm}^{-2}$)	-	0.44	-	0.22	-	-	0.22	-	-

Table 2: Water transport parameters of the pilots

Modality*	t_n (h)	t_{mean} (h)	v_{mean} (cm.h ⁻¹)	σ	$t_{\theta} = e_v$	σ^2_{θ}	N	λ
D-HF	4.3	4.7	43	2.96	1.1	0.48	2.09	0.57
D-LF	10.9	22.3	9	8.23	2.0	0.57	1.77	0.89
P-HF	2.9	3.9	49	3.63	1.3	1.56	0.64	- 0.74
P-LF	9.8	21.7	10	9.58	2.2	0.96	1.04	0.09

*D-HF, D-LF are the ditch CW with high and low inflow rates, respectively; and P-HF, P-LF are the pond CW with high and low inflow rates, respectively.

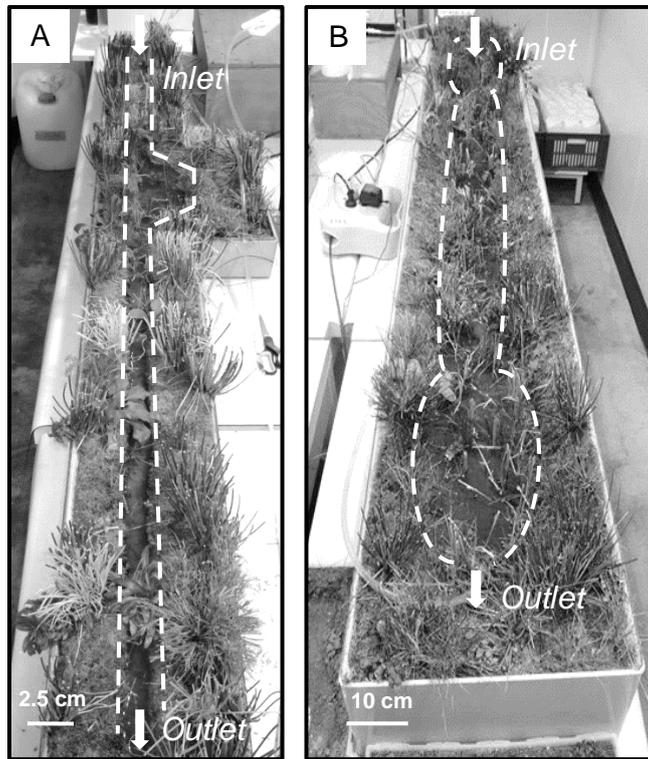


Figure 1

Experimental ditch pilot (A) and pond pilot (B)

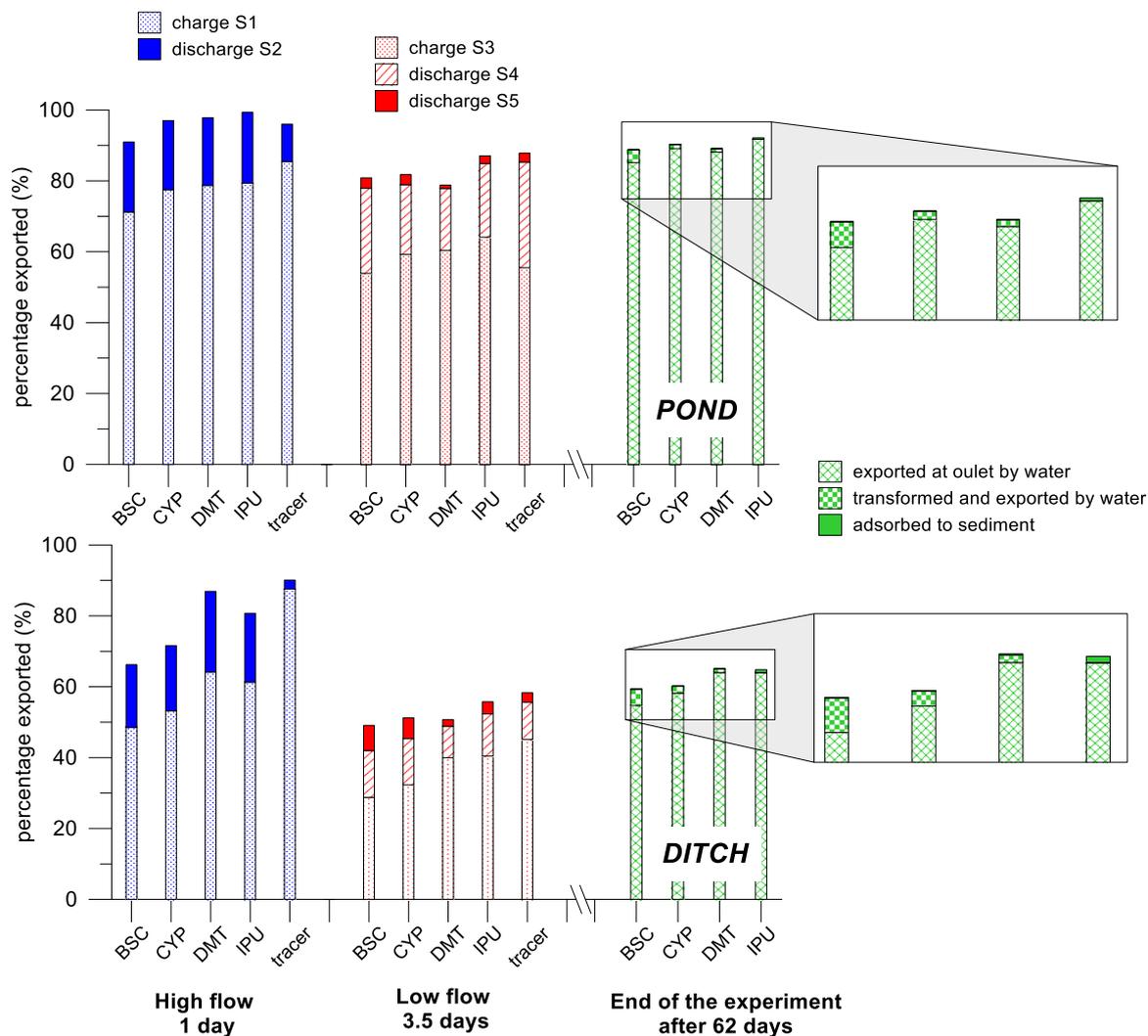


Figure 2

Exported rate of dissolved pesticides at outlet during drainage periods, at high flow rate (HF – S1, S2, S4) and low flow rate (LF – S3, S5) and mass balance at the end of experiment (62 days) corresponding of alternating phases of high-, low- and no-flow) for the ditch and the pond

*The total bromide yield was 102% in the ditch and 98% in the pond, after extraction from plants at the end of the experiment; 44% bromide was recovered from ditch plants and 9% bromide was recovered from pond plants.

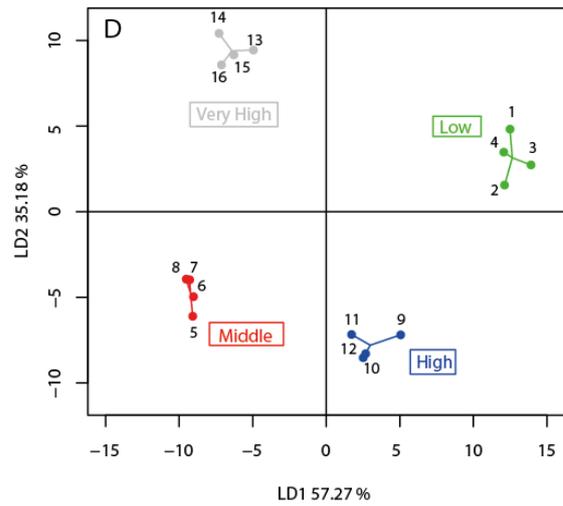
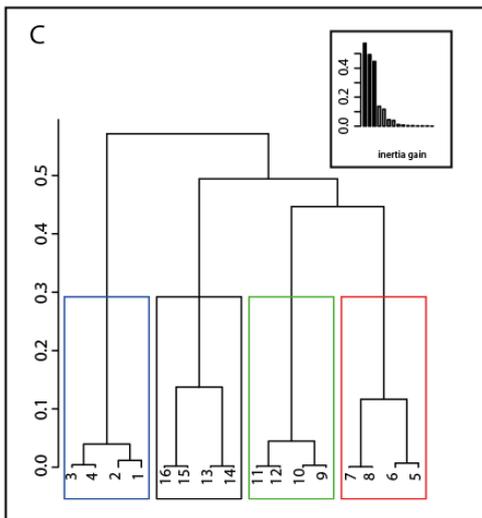
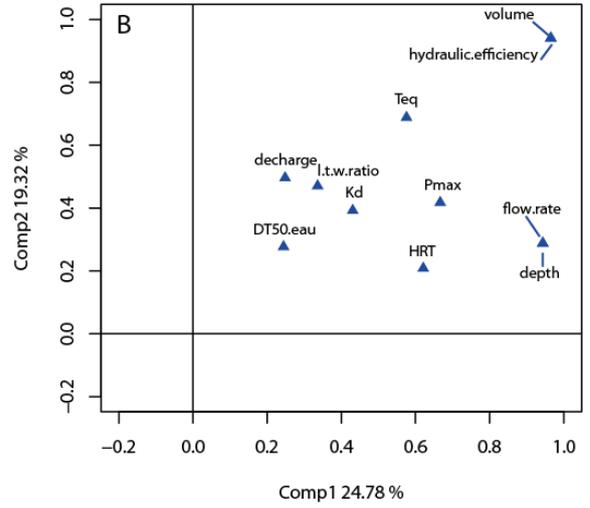
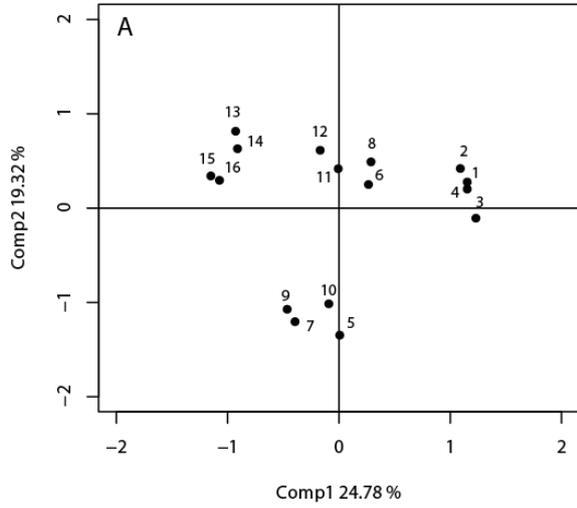


Figure 3

Distributions of the 16 observations (A) and contributions of the variables (B) obtained from MCA analysis applied on results listed in Table A.5. Based on MCA results, a classification tree (C) obtained with the ascending hierarchical principal component clustering. Groups issued (pond-HF, 1-4; pond-LF, 5-8; ditch-HF, 9-12; ditch-LF, 13-16) from classification tree are used to develop a PLS-DA model (D). These groups correspond also to the intensity migration rate: low (0.6–9%), middle (12.6–20.8%), high (13–33.7%), very high (43.3–50.8%).

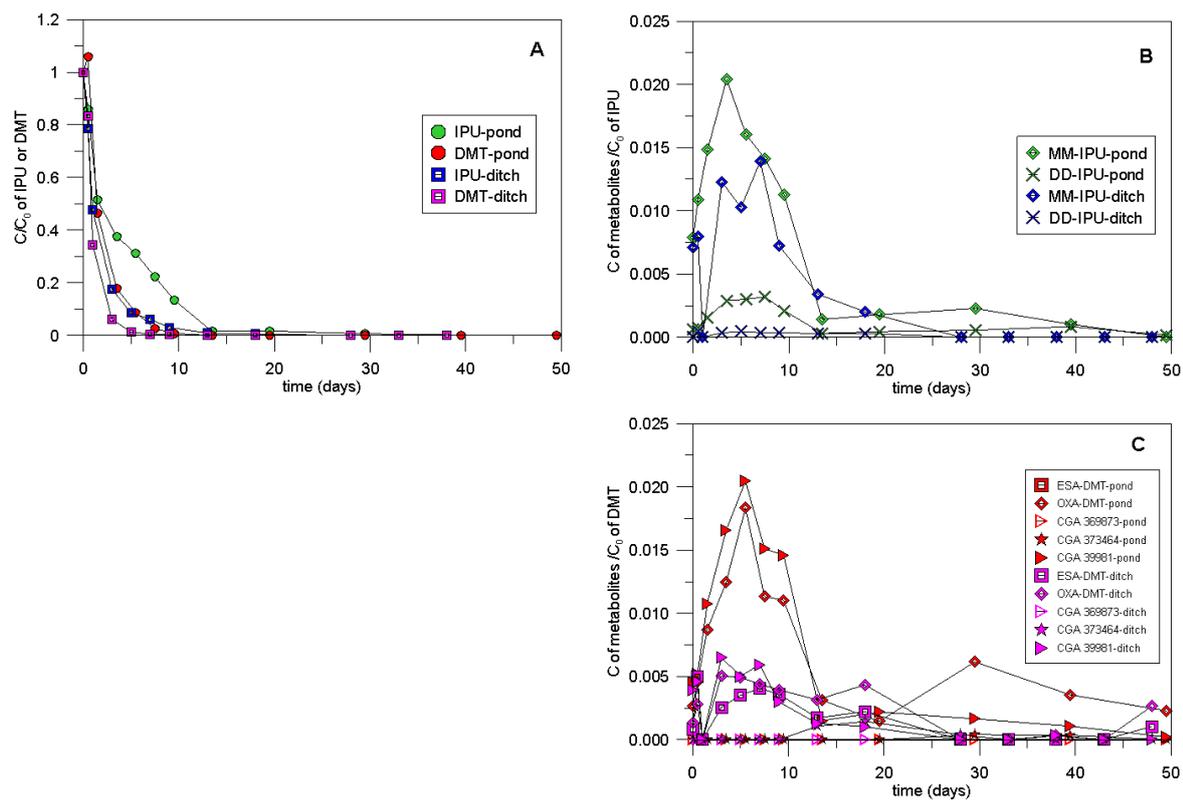
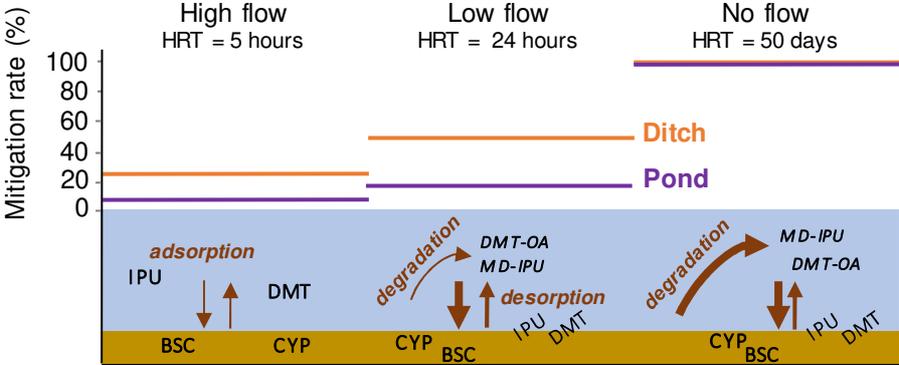


Figure 4

Dissipation of dimethachlor (DMT) and isoproturon (IPU) for the pond and the ditch during the 50-day no flow phase (A) and appearance of their metabolites mono-desmethylisoproturon (MM-IPU) and di-desmethylisoproturon (DD-IPU) (B) and CGA 39981, CGA 42443 and CGA 373464 (C). (*one replicat per pilot, concentrations expressed in mol/L*)

Graphical abstract



The thicker the arrow, the more important the process