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Influence of hydrodynamics on the water pathway and spatial distribution of pesticide and metabolite concentrations in constructed wetlands

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25 **Nomenclature**

26

27 σ_{θ}^2 RTD variance

28 θ dimensionless time

29 λ hydraulic efficiency

30 e_v effective volume ratio

31 HRT hydraulic residence time

32 N number of serial mixing tanks

33 Pe Peclet number

34 RTD residence time distribution

35 t_n theoretical residence time

36 t_{mean} mean residence time

37 t_{10}/t_n time to recover 10 % of the injected tracer

38 t_{90}/t_n time to recover 90 % of the injected tracer

39 t_{90}/t_{10} Morrill index

40

41

42 **Abstract**

43 Constructed wetlands (CWs) are likely to reduce pesticide levels reaching surface water.
44 However, the distribution of the water flow path between the main channel and isolated areas
45 may influence global pesticide mitigation. Little information is known about the influence of
46 water pathways on pesticide mitigation. Thus, we performed tracer experiments at low and
47 high flow rates (0.5 L/s and 4-7 L/s) in a pond CW and ditch CW to determine the localization
48 of various hydraulic zones and to understand their implication on pesticide mitigation. The
49 hydraulic performance reflecting the fraction of water transported from inlet to outlet passing
50 through the whole of CW, was greater for the pond CW than for the ditch CW regardless of
51 the flow rate, and greater at mean flow rates (MF) than at low flow rates (LF) due to a lower
52 proportion of isolated areas at a MF (11 % - 68 %) than at LF (38 % - 89 %). Dispersion
53 governed the water transport inside the isolated areas and the water convection inside the
54 main channel. Consequently, dissolved pesticide concentrations are heterogeneously
55 distributed in the CWs, i.e., in the main channel and isolated area, for both flow rates.
56 However, one month after a no-flow period, this heterogeneity disappears, and dissolved
57 pesticide concentrations become similar in the water of the whole CW due to dispersion.
58 Furthermore, sedimentation and storage in sediments were greater in the isolated area than in
59 the main channel, which is possibly due to a lower speed flow rate and a higher hydraulic
60 residence time (HRT) in the isolated area than in the main channel. Thus, isolated areas act as
61 effective's zones to mitigate pesticides from dissolved and particulate phases inside the CW
62 during a complete drainage season (i.e., succession of high/low/no-flow periods).

63

64 **Keywords:**

65 *Pond, ditch, isolated area, main channel, convection, dispersion*

66

67 **1. Introduction**

68

69 To protect or restore the surface water quality as required by the EU Water Framework
70 Directive (JOCE, 2000), constructed wetlands (CWs) have been presented as a potential
71 solution for reducing agricultural inputs such as nitrates and pesticides in surface water
72 (Alvord and Kadlec 1996; Gregoire et al. 2009; Vymazal and Březinová 2015). These CWs
73 have emerged as a cost-effective practice to reduce contaminant loading from drainage
74 (Schultz et al. 1995; Moore et al. 2001; Tournebize et al. 2012; Vallée et al. 2015) and have
75 been described as good environmental practices (JOCE, 2006). A recent review summarizes
76 32 studies related to the remediation of organophosphorus pesticides in 117 CWs during
77 2001–2017 worldwide, shown that organophosphorus pesticides were removed with
78 efficiency up to $87 \pm 16.6\%$ (Liu et al. 2019). Another study reported efficiency removal
79 $> 80\%$ for 8 pesticides in a CW with a HRT varying from 3 to 35 days (Maillard and Imfeld
80 2014). On the contrary, another study reported efficiency removal varying from -50% to 14%
81 in mean for 15 pesticides in 2 CWs, with a HRT varying from 5 h to 17 days (Vallée et al.
82 2015b). These authors have suggested that major processes are pesticide adsorption and
83 degradation. The main processes of dissolved pesticide mitigation from CW water are
84 adsorption on sediments (Matamoros et al. 2008; Stehle et al. 2011), absorption by plants
85 (Moore et al. 2013) and degradation in aqueous or sediment phases (Elsayed et al. 2014). The
86 main process of particulate pesticide removal is the sedimentation of total suspended solids
87 (TSS) on which pesticides are adsorbed (Koskiaho 2003; Maillard et al. 2011).

88 Some studies reported the important role of hydraulic parameters on pesticide
89 mitigation. For example, the hydraulic residence time (HRT), which indicates how long the
90 inflow is retained in the wetland, is considered to be one of the main factors influencing the
91 pesticide mitigation effectiveness of CWs (Elsaesser et al. 2011; Stehle et al. 2011; Vallée et

92 [al. 2015](#)). Generally, the mean HRT, determined with tracer data, is shorter than the nominal
93 HRT (corresponding to the ratio of wetland volume on the flow rate) due to the presence of
94 short-circuits, inducing a decrease in the hydraulic performance; i.e., the total CW volume is
95 not affected by water ([Martinez and Wise 2003](#)). Short-circuits have been reported as one of
96 the main drawbacks to the effectiveness of CWs because water is transported from the inlet to
97 the outlet by preferential flow, which decreases the mean HRT and the effective volume (i.e.,
98 the CW volume used for pesticide mitigation) ([Thackston et al. 1987](#)). Schematically, the
99 volume of the CW can be divided into three hydraulic zones ([Kadlec 1994](#); [Werner and](#)
100 [Kadlec 2000](#); [Martinez and Wise 2003](#)): (1) a main channel with preferential flow; (2) a
101 temporary storage zone (mixing zone) showing exchanges with the main channel; and (3) a
102 dead zone, which is more isolated from the main channel than the mixing zone. The mixing
103 and dead zones are considered isolated areas ([Martinez and Wise 2003](#)) and are differentiated
104 by their exchange rate with the main channel, such as a lower water speed and solute
105 dispersion in the case of dead zones than in mixing zones. The distribution of these three
106 hydraulic zones could be spatially and temporally influenced by (i) CW morphology: the
107 length-to-width ratio, the inlet/outlet configurations and the presence of obstructions ([Su et al.](#)
108 [2009](#)), and by (ii) hydraulic parameters such as HRT, flow rate and water depth ([Liu et al.](#)
109 [2016](#); [Shih et al. 2017](#)).

110 Thus, considering that at a local scale inside the CW, the HRT occurring in the
111 isolated areas could be longer than in the main channel, we can hypothesize that pesticide
112 mitigation processes such as adsorption, absorption, and degradation would be enhanced in
113 these areas. In addition, these hydraulic zones might move inside the CW depending of the
114 flow rate changes in the field. To our knowledge, there is no study regarding the role of these
115 hydraulic zones such as the main channel and isolated zones on pesticide and metabolite
116 mitigation.

117 Thereby, we investigated the influence of the flow rate on the water pathway
118 distribution (main channel, isolated areas) in two CWs (a succession of three ponds and a
119 ditch with lateral enlargement) and subsequently on the mitigation of pesticides and
120 metabolites in dissolved and particulate phases. Bromide-tracing experiments were carried out
121 at 3 flow rates in the pond and at 2 flow rates in the ditch. In addition, the spatial distribution
122 of pesticide and metabolite concentrations in aqueous (dissolved and particulate) and
123 sediment phases was evaluated to determine the contribution of the main channel and isolated
124 areas to pesticide and metabolite mitigation.

125

126 **2. Materials and methods**

127

128 *2.1. Constructed wetlands*

129

130 The two CWs are located under temperate climate, with mean precipitation varying from 1.9
131 to 3.5 mm/day and mean water volume drained varied from 0.3 to 4.5 mm/day. The dominant
132 cultures on crop fields are wheat, barley, maize and rapeseed (Table 1). More details about
133 climatological, hydraulic and agricultural context of these two CWs are given in Table 1.

134 The two studied CWs were built in autumn 2010 in a regulatory grass strip, and
135 spontaneous vegetation recovered the entire CW in two years. Thus, during our experiments,
136 the vegetation was present throughout the year, and its influence on the hydrodynamic
137 dispersion as reported by [Jenkins and Greenway \(2005\)](#) could be considered similar under all
138 seasons. The first CW located at Ville-sur-Illon (75 km at the South of Nancy, France)
139 consisted roughly of a succession of three ponds of 47.8 m length and 4 to 6.5 m width, with a
140 surface of 215 m² and an island at the beginning of the second pond (Fig. 1). It received the
141 drainage water from an 8 ha plot (cambisol, FAO 2006) by a drain collector located at inlet of

142 the CW. The CW was entirely vegetated and dominated by *Juncus effusus*, *Juncus inflexus*,
143 and *Juncus articulatus* on the edge of the CW, with *Typha latifolia*, *Typha angustifolia*,
144 *Epilobium hirsutum* and *Veronica becabunga* inside the CW. The second CW located at
145 Manoncourt-sur-Seille (30 km in the North of Nancy, France) consisted roughly of a ditch of
146 80 m length and 0.9 m width, and it expanded over 12 m long by 4 m wide, with a surface of
147 100 m² (Fig. 1). It received the drainage water from a 10 ha plot (gleyic cambisol, FAO
148 2006). The CW was entirely vegetated and dominated by *Juncus effusus*, *Juncus*
149 *conglomerates* and grasses. Substrates of both CWs were clayed, which allowed their
150 imperviousness. Both CWs have been precisely topographically levelled allowing the
151 determination of water volume.

152

153 2.2. Tracer experiment

154

155 The inlet and outlet flow rates were measured continuously using a pollubac (1515 DA,
156 POLLUBAC®) and an ultra-sound flow meter (950-US 50 Hz, SIGMA); a mean flow rate
157 was recorded every 30 min of measurement. Three experiments were conducted in the pond
158 CW (at high flow = HF, mean flow = MF and low flow = LF), and two were conducted in the
159 ditch CW (MF and LF) (Table 2). All tracer tests were conducted in dry weather conditions,
160 so no precipitation must be considered. However, despite no rainfall, flow rates varied
161 between the beginning and the end of the tracer experiments. Of the five tracer experiments,
162 flow rates varied from 3 % (pond-HF) to 30 % (pond-LF) (Table 2). The estimation of the
163 water transport parameters was done considering a constant flow rate, which was chosen as
164 the mean flow rate (Table 2). The CW's water volume was monitored manually thanks to
165 limnimetric scales (one limnimetric scale is localised in each of the 3 pond and in each of the
166 3 parts of the ditch). Besides, CW's geometries were determined by topographic

167 measurements. For each tracer experiment, the volume of water was calculated with
168 Autocad® and ADTOPO® softwares based on water level observed in the field.

169 For each experiment, an instantaneous pulse of 5 to 15 L of 200 g.L⁻¹ bromide (in the
170 form of KBr) was injected inside the pollubac at the CW inlet at a flow rate of 4 L.min⁻¹ using
171 the pump of an automatic sampler (SD-900 SIGMA) (Table 2).

172 Water was collected at the outlet of both wetlands in two steps: (i) manually sampling
173 approximately every 5 min (from 4 to 9 h, which was chosen according to the nominal HRT,
174 Table 2 and Table A1), and (ii) automatic sampling every 2 h during the subsequent 2 to 5
175 days, until the bromide concentration was believed to be under the limit of quantification
176 (LOQ). These two steps constitute the total sampling period (Table 2). Additionally, spatial
177 water sampling was manually performed by using a telescopic surface water sampler (except
178 for the experiment pond-HF) to determine water pathways (blue numbered circles on Fig. 1),
179 with variable frequencies between 2 min and 30 min (during 4 to 9 h) according to the
180 localization. All samples were collected in a 20 mL clean PE bottle, transported under
181 refrigeration (almost 10°C) to the laboratory and then stored at 4°C prior to analysis.

182 Samples were filtered through a 0.22 µm cellulose acetate filter, and then 1 mL
183 aliquots were transferred to polypropylene vials for analysis with a Dionex ICS-3000 ion
184 chromatographic instrument (Sunnyvale, CA, USA) using Chromeleon® software (version
185 6.80). Concentrations of Br⁻ were analysed using an AS20 guard column (4 x 50 mm) with a
186 polymeric AS20 analytical column (4 mm x 250 mm). The LOQ was 50 µg.L⁻¹. Certified
187 standard solutions from Inorganic Ventures (Washington, USA) were used for calibration.

188

189 2.3. *Water transport parameters*

190

191 To estimate the hydraulic performance of the CWs, water transport parameters were derived
 192 from Residence Time Distribution (RTD - corresponding to the bromide restitution curves):
 193 the normalized retention time (t_{θ}), the effective volume (e_v), the number of cells (N), the
 194 hydraulic efficiency (λ), the short-circuiting index (t_{10}/t_n) and the mixing index (t_{90}/t_{10}), were
 195 determined. The hydraulic performance is considered good when all of these parameters are
 196 optimized, such as when the water is transported from the inlet to outlet circulating in the
 197 whole of volume system, which limits the short-circuit.

198 The normalized hydraulic retention time t_{θ} , i.e., the ratio between the mean HRT
 199 (t_{mean}) and the nominal HRT (t_n), allows the comparison of RTDs of our 5 tracer experiments.
 200 In addition, it corresponds to the effective volume used by water (e_v , characterizing the main
 201 channel) (dimensionless) (Fan et al. 2008) allowing to assess the percentage of isolated areas
 202 as follows: $(1 - e_v) \times 100$. The nominal HRT (t_n) (h) was calculated as the ratio between the
 203 CW volume (m^3) and the flow rate through the CW ($m^3 \cdot h^{-1}$); t_{mean} , the mean HRT (h),
 204 depicted the average time that the water spent in the system (Eq. (1)):

$$205 \quad t_{mean} = \frac{\int_0^{\infty} t E(t) dt}{\int_0^{\infty} E(t) dt} \quad (1)$$

206 where $E(t)$ is the RTD function and is defined by Eq. (2) in the case of pulse injection:

$$207 \quad E(t) = \frac{C(t) \times Q}{\int C(t) \times Q \times dt} \quad (2)$$

208 where $C(t)$ is the bromide concentration ($mg \cdot L^{-1}$) at time t , Q is the flow rate ($L \cdot s^{-1}$) at time t
 209 and d_i is the interval between two consecutive measurements.

210

211 The plug flow conditions could be evaluated with the number of cells (N) used in a
 212 tank-in-series model (Eq. (3)). Generally, in CWs, the plug flow never occurs, inducing a
 213 deviation of the mean HRT (t_{mean}) compared to the nominal HRT (t_n). The higher the N is, the
 214 more that the flow is a plug-flow.

215
$$N = \frac{t_n^2}{\sigma^2} \quad (3)$$

216

217 where σ^2 is a measure of the spread of the RTD and was defined by Eq. (4):

218
$$\sigma^2 = \frac{\int_0^\infty (t_{mean} - t)^2 E(t) dt}{\int_0^\infty E(t) dt} \quad (4)$$

219

220 The hydraulic efficiency (λ) can be classified as follows: good hydraulic efficiency
221 ($\lambda > 0.75$), satisfactory hydraulic efficiency ($0.5 < \lambda < 0.75$) and poor hydraulic efficiency ($\lambda < 0.5$)
222 (Chang et al. 2016).

223
$$\lambda = t_\theta \left(1 - \frac{1}{N} \right) \quad (5)$$

224

225 Then, short-circuiting and mixing indexes were calculated. Thus, the short-circuiting
226 flow is the situation in which water passes through the CW in less than nominal residence
227 time due to convection process or velocity heterogeneity (Teixeira and Siqueira, 2008). The
228 t_{10}/t_n , defined as the required time to recover 10 % of bromide at the outlet normalized to the
229 nominal HRT t_n , is considered as the value of short-circuit, i.e., the lower the value is, the
230 higher the short-circuit (Guo et al. 2017). The mixing is due to turbulent diffusion and can
231 also be due to recirculation zones and dead zones (Teixeira and Siqueira, 2008). The t_{90}/t_{10}
232 ratio is considered as the value of the mixing index; the larger the value is, the more the
233 mixing flow (Guo et al. 2017), i.e. the t_{90}/t_n was defined as the required time to recover 90 %
234 of bromide at the outlet, normalized to the nominal HRT t_n .

235 Finally, the Peclet number (Pe) allows distinguishing between the different mixing
236 regimes: convective or dispersive flow; i.e., the lower the Pe value is, the higher the water
237 dispersion (Eq. (6)) (Nameche and Vasel 1998).

238

239
$$Pe = \frac{Q \times L}{W \times Z \times D} \quad (6)$$

240 where Q is the flow rate ($m^3 \cdot h^{-1}$), L is the length of CW (m), W is the width of CW (m), Z is
241 the height of water (m) and D is the dispersion coefficient ($m^2 \cdot h^{-1}$) defined by Eq. (7).

242

243
$$D = \alpha \times V_{mean} \quad (7)$$

244

245 with α the water dispersivity (m) and V_{mean} ($m \cdot h^{-1}$) the mean water velocity inside the CW
246 (i.e. CW length divided by t_{mean}).

247 The water dispersivity α was calculated as the mean of two dispersion parameters
248 (dimensionless) which characterized the asymmetrical tracer curve. Those parameters were
249 determined using model.

250

251 2.4. *TSS measurements and pesticide analysis in water samples*

252

253 Raw water (water + TSS) was manually sampled during the 2016/2017 hydrological
254 season. For the pond CW, the samples were collected every two weeks from 21/11/16 to
255 22/05/17 (i.e., 12 samples, 7 under drainage and 5 under no-flow periods). For the ditch CW,
256 samples were collected from 13/02/17 to 13/03/17, due to short drainage season (i.e., 3
257 samples: 2 under drainage and 1 under a no-flow period).

258 Water samples were collected at the inlet, at the outlet, in the main channel inside the
259 CW (point MC) and in an isolated area (point IA). Points MC and IA were identified by
260 bromide concentration analysis (MC and IA correspond to points 10 and 9 for the pond CW
261 and 6 and 3 for the ditch CW, respectively) (Fig. 1). Under no-flow, the inlet and outlet
262 sampling was performed in stagnant water close to the inlet and outlet, respectively. All
263 samples were collected in 250 mL PE bottles, which were transported under refrigeration to

264 the laboratory where they were homogenized and centrifuged at 7000xg and then stored at -
265 20°C until analysis. The electrical conductivity was measured *in situ* for all samples with an
266 electrical probe (HQ40D, HACH-LANGE, France). The analysis of pesticides was performed
267 on an Acquity Ultra-Performance Liquid Chromatography system (UPLC, Waters) interfaced
268 to a triple quadrupole mass spectrometer (Quattro Premier XE, Waters) according to 2
269 methods: (i) method A was performed to analyse 14 pesticides and 4 metabolites, and (ii)
270 method B was performed to analyse 14 metabolites, as detailed in Table A2. Briefly, for
271 method A, the sample was flushed onto the online SPE cartridge (Oasis HLB 25 µm, 2.1 x 20
272 mm, Waters) with water (neutral pH). Elution was realized using a gradient of acidified water
273 and acidified acetonitrile (0.05 % formic acid - FA) in the Kinetex 1.7 µm C18 100A (100 x
274 2.1 mm), Phenomenex. For method B, the sample was flushed onto the online SPE cartouche
275 (Oasis HLB 25 µm, 2.1 x 20 mm, Waters) with acidified water (pH of 3.4). Elution was
276 realized using a gradient of acidified water and acidified acetonitrile (0.007 % FA) in the
277 Kinetex PFP 1.7 µm (100 x 2.1 mm), Phenomenex. The analytical standards were purchased
278 from Cluzeau (Sainte-Foy-La-Grande, France), Restek (Lisses, France), Sigma (Lyon,
279 France), Neochema (Bodenheim, Germany) and Techlab (Metz, France). The limit of
280 quantification ranged from 0.01 to 0.05 µg.L⁻¹ according to the molecules.

281 The analyzed pesticides were chosen because of their frequent application in the agricultural
282 plots due to dominant cultures (i.e. winter wheat, rapeseed and maize), and because of their
283 frequent detection in drainage water according to a previous study (Vallée et al. 2015b).
284 Moreover, the diversity of the physico-chemical properties of these molecules (Table A2),
285 allow study the potential contrasted behavior. The metabolites were chosen on the one hand
286 because they are metabolites of widely used pesticides, but rarely studied worldwide; and on
287 the other hand, for their high polarity.

288 To quantify the TSS, 2 L water samples were also manually collected in a 2 L PE
289 bottle. The sampling was performed exclusively at the inlet and outlet due to difficulties in
290 sampling in the MC and IA zones without resuspending the TSS. Then, 250 to 1000 mL of
291 water (depending on particle laden flow) was filtered through 0.7 μm fiber glass filters to
292 separate the largest TSS from the aqueous phase. Before their use, fiber glass filters were
293 cleaned with distilled water, dried at 70°C for 24 h, weighed, and then stored in a glass
294 container. After filtration, filters with the TSS were dried at 70°C for 24 h and then weighed.

295

296 2.5. *Sediment deposition measurement and pesticide concentrations in sediment*

297

298 Sediment deposition was spatially estimated in the pond and ditch CWs (coloured squares on
299 Fig. 1) using PVC cylindrical sediment traps (25 cm high x 5 cm width, H/W ratio of 5) for
300 the 2015/2016 and 2016/2017 hydrological seasons. The sediment traps used in this study
301 allowed for the trapping of the total primary flux of new particles (allochthonously and
302 autochthonously produced) and particles resuspended from the bottom of the wetland, which
303 form the secondary flux (Evans and Håkanson, 1992). Some trap locations were switched
304 from one studied season to another due to the identification of interesting areas based on
305 tracer experiments during the first season (i.e., 2015/2016). Sediment traps were placed in the
306 two CWs before the initiation of drainage in autumn and removed after the drainage season.
307 In the pond CW, sediments were collected during 227 days in 2015/2016 (from 20/11/15 to
308 03/07/2016) and 143 days in 2016/2017 (from 05/11/16 to 27/03/17). In the ditch CW,
309 sediments were collected during 156 days in 2015/2016 (from 04/01/16 to 07/06/16) and 117
310 days in 2016/2017 (from 18/11/16 to 14/03/17).

311 At the laboratory, sediments were recovered from the trap and stored in a pre-weighed
312 250 mL PE bottle. An aliquot of 10 mL was taken after homogenization of the sediment for

313 each sample for particle size estimation. Then, the bottles were stored at -20°C for freeze-
314 drying, and the bottles were weighed. The quantification of sediment in each trap
315 corresponded to the weight difference between the empty and full bottles. The sedimentation
316 rate, i.e., the mass of sediment collected per square centimetre of trap opening per unit of
317 time, was then calculated for each trap (Gardner 1980) for the duration of the drainage season.
318 The particle sizes were measured within 48 h following the sampling using a laser diffraction
319 technique (Helos, Sympatec GmbH), which can measure particle sizes from 0.2 to 90 µm or
320 from 2.4 to 875 µm, according to the chosen lens. In this study, a range from 0.2 to 90 µm
321 was selected due to the fine particle size distribution determined previously. Aliquots of
322 suspended particles of sediment were introduced in the bath-type sonicator integrated with the
323 granulometer and sonicated for 1 min before measurement. Two consecutive measurements of
324 10 seconds, each spaced by 5 seconds, were executed to avoid extreme measurements (i.e.
325 one plant debris measurement was made in the length, biasing the results).

326 Finally, to evaluate the spatial distribution of pesticide concentrations in sediment, a
327 representative sample of each zone (inlet MC, middle MC and outlet MC, and the isolated
328 area) was obtained by mixing four sub-samples. All sub-samples were manually collected in
329 the first upper centimetre of sediment, and in different locations, inside the CW (not in the
330 sediment traps) at the end of each drainage season: in July 2016 for the 2015/2016 season and
331 in April 2017 for the 2016/2017 season. Taking into account the sedimentation rate and its
332 variability, the first centimetre collected can represent one or two years of sedimentation
333 depending on its location in the CW and on the CW. In 2017, a total of four composite
334 samples were collected per CW: 3 samples in the MC zone from inlet to outlet and 1 in the IA
335 zone (point 9 for the pond CW and point 3 for the ditch CW, Fig. 1), whereas only 3 samples
336 in MC were collected in 2016. Indeed, there was no IA zone identified at the beginning of the
337 study in 2016. After sampling, sediments were freeze-dried and then extracted by a modified

338 QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method detailed in the SM.
339 Then, they were analysed using one multi-method based on liquid chromatography-
340 electrospray ionization-tandem mass spectrometry (LCeESI-MS/MS) with multiple reaction
341 monitoring described in [Vallée et al. \(2015\)](#). This method allowed the analysis of 67
342 pesticides and 3 metabolites listed in Table A3.

343

344 **3. Results and discussion**

345

346 *3.1. Hydrodynamic of the CWs*

347

348 After the intense sampling time (step 1), the bromide recovery was 77 %, 111 % and
349 23 % for HF, MF and LF, respectively, in the pond CW and 47 % and 30 % for MF and LF,
350 respectively, in the ditch CW (Table 2). The total sampling period (from 2 to 5 days, step 1 +
351 step 2) allowed a tracer recovery of 104 % for pond-LF and 97 % for ditch-MF. Only 72 %
352 was recovered for the ditch-LF, possibly due to the total sampling period being too short (i.e.,
353 bromide was measured up to 0.2 µg/L in the last sample, 5 days after the beginning of the
354 tracer experiment). Finally, the tracer recoveries were always higher than 70 % after the total
355 sampling period (Table 2), so tracer test data can be processed ([Lin et al. 2003](#)).

356 Tracer concentrations as a function of time are shown in Fig. 2, and water transport
357 parameters calculated from RTD data are detailed in Table 3. The nominal HRT (t_n) was
358 longer than the mean HRT (t_m) regardless of the flow rates for the ditch CW and at LF for the
359 pond CW, which suggests short-circuiting for these conditions ([Wahl et al. 2010](#)). This is
360 confirmed by the values of short-circuiting (t_{10}/t_n) and mixing indexes (t_{90}/t_{10}) (Table 2). For
361 both CWs, at LF, t_{10}/t_n is lower than at MF and HF, indicating more short-circuiting, and
362 t_{90}/t_{10} is higher than at MF and HF, indicating more water mixing due to higher water

363 dispersion promoted by low flow rates (Guo et al. 2017). Naturally, these results were
364 consistent with the analysis of the number of serial mixing tanks (N), which are lower at LF,
365 indicating that a lower volume of wetland is affected at LF and the hydraulic regime is
366 considered a mixing flow. In addition, the hydraulic efficiency value (λ) was satisfactory at
367 HF and MF in the pond CW (Table 3), whereas it was poor at LF in the pond CW as well as
368 in the ditch CW regardless of the flow rate (Chang et al. 2016). Furthermore, taking all these
369 hydraulic parameters (e_v , N , λ , t_{10}) into account, the hydraulic performance is (i) higher at HF
370 and MF than at LF in the pond CW and (ii) weaker regardless of the flow rate in the ditch
371 CW. Indeed, the flow velocity at the field scale, which is higher for the ditch CW (v_{mean}
372 values from 0.87 to 1.55 m/min) than for the pond CW (v_{mean} values from 0.03 to 0.53
373 m/min), could promote the short-circuiting in the ditch CW, thus decreasing its hydraulic
374 performance. This larger short-circuiting value may be explained by a higher length-to-width
375 ratio for the ditch (80) than for the pond (7), as previously reported by Su et al. (2009). Thus,
376 a linear CW such as our ditch, despite the added enlargement, does not appear to be suitable
377 for retaining water for a long time.

378 Concerning the bromide concentration time series (Fig. 2), for the pond CW, two
379 outlet peaks are identified at LF and MF, indicating two flow paths, while only one peak is
380 visible at HF. This seems to be due to the circulation in pond 3, since only one outlet peak
381 was identified at the outlet of pond 2 (Fig. 3). Indeed, the greater depth of pond 3 (1.2 m
382 compared to 0.5 m in pond 2) could promote deeper water recirculation, inducing two distinct
383 outlet peaks due to a portion of the water being retained and recirculated in this pond. For the
384 ditch CW, only one outlet peak is visible for both flow rates (LF and MF), suggesting that
385 only one major flow path occurred. For both CWs, the outlet peaks appeared slower at LF
386 than at MF or HF (Fig. 2), and this is in agreement with a higher mean HRT at LF (Table 3).
387 In addition, the outlet peaks at LF for the ditch CW and pond CW are wider than those at MF,

388 suggesting more dispersion here. The presence of isolated areas might contribute to the
389 postponed bromide arrival at the outlet (Fig. 2). The cumulative normalized concentration
390 curves (Fig. 2) provide complementary indications of the water transport processes: the steep
391 slope at the first part of the curve corresponds to convection transport, and the flat part of the
392 curve corresponds to dispersion transport. For the pond CW, the flat part began more rapidly
393 at LF($t_{\theta} = 0.7$) than at HF and MF ($t_{\theta} = 1$), indicating more water dispersion at LF, which is
394 in agreement with the t_{90}/t_{10} values (Table 3) and the lower values of the Peclet number (Pe).
395 The lower the Pe value is, the higher the dispersion of water due to low velocity and internal
396 recirculation (Nuel et al. 2017). For the ditch CW, regardless of the flow rate, the flat part
397 begins before $t_{\theta} = 0.5$, indicating more dispersion here than in the pond regardless of the flow
398 rate. Moreover, for both CWs, the equilibrium was reached faster at LF than at MF and HF.
399 Thus, for the two CWs, the water transport was dominated by convection at HF and MF and
400 by dispersion at LF (Nuel et al. 2017; Gaullier et al. 2019). Thus, the bromide analysis
401 showed that flow rate influences the water pathways, with a higher proportion of isolated
402 areas at LF (38 % and 89 % for the pond and the ditch, respectively) than at HF or MF (11 %
403 and 68 % for the pond and the ditch, respectively). This corresponds to a volume of isolated
404 areas at LF of 21 m³ and 20 m³ for the pond and the ditch, respectively, and at HF or MF of 7-
405 11 m³ and 26 m³ for the pond and the ditch, respectively. Thus, the volume of isolated areas
406 inside the ditch CW is quite similar regardless of the flow rate (± 25 %), whereas it is 2 or 3
407 times higher at LF than at MF/HF in the pond.

408

409 *3.2. Influence of hydrodynamics on water pathways*

410

411 To locate the isolated areas, the spatial distribution of the bromide concentration inside
412 both CWs was monitored over time (Fig. 3). To maintain the readability of Fig. 3, only the

413 sampling points in the second pond and the sampling points in the enlargement of the ditch
414 CW were drawn. The supplementary sampling points for the first and the third pond are given
415 in Fig. A1 (Supplementary Material).

416 Focusing on pond 2, at MF, the peak concentration at the outlet (point 12) is lower and
417 more spread out than that at the inlet (point 5), indicating that bromide has circulated from
418 points 5 to 12 by convection and dispersion, corresponding to the main channel. The lower
419 peak concentrations for points 6, 7, 8, 10 and 11 compared to the outlet (point 12) may be
420 explained by a greater transfer of water and tracer by dispersion than by convection from
421 point 5 (Fig. 3). At LF, the concentration peak of bromide was gradually reduced from the
422 inlet (point 5), passing by points 6, 7, 8 and 10, to the outlet (point 12), by convection and
423 dispersion. In addition, all peaks are wider and smaller at LF than at MF, highlighting a
424 greater dispersion due to a water velocity that is ten times slower at LF (Table 3). Point 9 may
425 be considered an isolated area for both flow rates. More precisely, at MF, it was considered a
426 mixing zone due to (i) a more delayed peak time than at the outlet (240 min against 60 min)
427 and (ii) a larger peak than at the outlet, whereas at LF, it was considered a dead zone due to
428 the absence of bromide detection during the tracer experiment. The existence of different
429 hydraulic zones was confirmed by the electrical conductivity distribution measured under
430 seven flow rates inside the pond CW (Fig.4), allowing to generalize the conclusions obtained
431 with the 3 tracer experiments i.e. heterogeneity within the CWs varying according to flow
432 rates. Indeed, regardless of the flow rate, the electrical conductivity measured in the isolated
433 area (point 9, IA zone) is different than that measured in the inlet, main channel (point 10,
434 MC zone) and outlet. Similarly, the electrical conductivity measured in the main channel (MC
435 zone) was almost equal to those measured in the inlet and outlet under drainage. Under the
436 no-flow period, the electrical conductivity measured in the isolated area (point 9, IA zone) is
437 different from that of the main channel (point 10, MC zone) during the first month of no-flow

438 (I, J). Then, beyond this month (K, L), the electrical conductivity becomes similar in the MC
439 and IA zones, which is possibly due to a very slow dispersion during the no-flow period.

440 Concerning the ditch, at MF, peak times of points 2-5-6 and 7 were missed due to the
441 fast flow rate. The main channel path at MF corresponds to the middle of enlargement (points
442 1-5-2-6-7-4). Bromide later reached the border of enlargement (points 8-9-10), and point 3
443 located behind a tuft of *Juncus* (Fig. 3). At LF, the bromide concentration decreased from the
444 inlet to the outlet due to convection and dispersion. The peak times for points 2, 3, 7 and 10
445 are longer than the peak times at the outlet of enlargement (point 4), indicating that these
446 points are clearly affected only by dispersion. Thus, at LF, the main channel was located in
447 the middle of the enlargement and in a part of its left border (5-8-6-9-4). Point 3 could be
448 considered as an isolated area, but not especially a dead zone, as confirmed by the measured
449 electrical conductivity always different at point 3 (corresponding to IA zone, Fig.4) than in
450 the main channel, inlet and outlet (Fig. 4). Finally, points 7 and 10 could be isolated because
451 of their position in the upper corner of the enlargement, as previously suggested by
452 Sabokrouhiyeh et al. (2017). For the pond, all peaks are wider at LF than at MF, highlighting
453 the greater dispersion occurring at LF. The slow water velocity at LF (v_{mean} , Table 3) allowed
454 for the dispersion of water and solutes in the enlargement, increasing the proportion of the
455 isolated area affected by dispersion compared to MF. Otherwise, at MF, the fast water
456 velocity limited the isolated areas (point 3 and the border area, points 8-9-10) affected by
457 dispersion, whereas water was transported by convection in the middle of enlargement.

458 Thus, regardless of the CW, the flow rate influences the water pathways and their
459 geometry. For both CWs, the main channel is globally larger at MF or HF than at LF, and
460 subsequently, the isolated areas are more spread out at LF than at MF or HF.

461

462 *3.3. Influence of hydrodynamics on dissolved pesticide transport*

463

464 In the pond CW, among the 32 analysed molecules in the dissolved phase, chlortoluron
465 (CLT), two metabolites of metazachlor (OXA metazachlor, ESA metazachlor) and one
466 metabolite of dimetachlor (CGA 369873) were quantified in the four hydraulic zones (inlet,
467 outlet, MC zone and IA zone) during the 12 sampling campaigns (Table A4, Fig. 5). In the
468 ditch CW, two metabolites of metazachlor (OXA metazachlor, ESA metazachlor) and two
469 metabolites of dimetachlor (OXA dimetachlor, ESA dimetachlor) were quantified in the four
470 hydraulic zones (inlet, outlet, MC zone and IA zone) during the three sampling campaigns
471 (Table A4, Fig. 5).

472 Under the drainage period, for both CWs, the molecule concentrations are different
473 inside the four zones at a given time, as previously shown with the bromide concentration and
474 electrical conductivity values (Fig.4). No pattern can be highlighted; indeed, pesticide
475 concentrations are sometimes higher in the MC zone and sometimes higher in the IA zone,
476 except for cases G and H in the pond CW. For these two cases, where LF is preceded by MF,
477 the molecule concentrations measured in the IA zone (point 9) are always lower than those in
478 the MC zone (point 10). These results may be explained by a higher mitigation in IA
479 (adsorption in sediments and degradation) and/or a limited water dispersion inside IA. It
480 should also be kept in mind that water entering the CW has a time-dependent composition. In
481 contrast, the concentrations for all MC points (MC + inlet + outlet) are always quite similar
482 for a given sampling campaign, indicating limited pesticide removal from the inlet to outlet.
483 The few data collected in the ditch (3 samples) limit the ability to draw conclusions for this
484 CW. In conclusion, pesticide concentrations are heterogeneous in the CW during drainage,
485 regardless of whether there are high or low flow rates.

486 Under the no-flow period, the concentrations of pesticides in the pond (cases I to L),
487 measured in the MC and IA zones, are close, especially after one month of no-flow (Fig. 5).

488 This observation is consistent with the electrical conductivity values previously described as
489 homogeneous during this no-flow period (Fig. 4). Dispersion is the dominant transport under
490 the no-flow period and slowly leads to a uniform contaminant distribution inside the CW. The
491 distance travelled by diffusion is only approximately 1 cm per day for a molecule (Gaulhier et
492 al. 2018). Thus, considering a distance of 2 m from MC to IA, more than 200 days would be
493 necessary for a whole homogenization of the water volume by diffusion. Nevertheless, the
494 homogenization took place in less than one month, which suggests that other processes than
495 diffusion take place, such as wind mixing, vegetation patterns, and bioturbation, as previously
496 observed by Werner and Kadlec (2000) and Zounemat-Kermani et al. (2015).

497 In conclusion, the dissolved pesticide concentrations show spatial heterogeneity during the
498 drainage phases (LF or MF) (in agreement with the bromide monitoring and conductivity) and
499 during homogenization of the concentrations in the constructed wetland after one month of no
500 flow. On the other hand, no link could be highlighted between the pesticide concentrations
501 and the flow rate or the water pathways.

502

503 *3.4. Influence of hydrodynamics on the sedimentation rate*

504

505 In addition to being transported by the dissolved phase, pesticides can be transported by the
506 particulate phase via the suspended solids entering the CW via tile drains. The TSS
507 transported by drainage entering the pond CW was 1500 kg in 2016 ($75 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$ or 7.8
508 $\text{kg}\cdot\text{day}^{-1}$) and 400 kg in 2017 ($20 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$ or $4.8 \text{ kg}\cdot\text{day}^{-1}$). In the ditch CW, the TSS
509 entering was 780 kg in 2016 ($78 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$ or $8.3 \text{ kg}\cdot\text{day}^{-1}$) and 300 kg in 2017 ($30 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$
510 or $8.8 \text{ kg}\cdot\text{day}^{-1}$) (Fig. A2). The lower exportation in 2017 than in 2016 may be due in part to a
511 smaller total drained volume in 2017 (23920 m^3 and 2960 m^3 in the pond and the ditch,
512 respectively) than in 2016 (83530 m^3 and 10475 m^3 in the pond and the ditch, respectively).

513 To understand the transport and fate of solid-bound pesticides inside the CW, we focused on
514 the spatial repartition of pesticide concentrations in sediments, whereas sedimentation is the
515 main process of mitigation for solid-bound pesticides inside the CW, as previously shown by
516 [Koskiaho \(2003\)](#).

517 The spatial distribution of the sedimentation rate is shown in Fig. 6. The annual
518 sediment accumulation in the pond varied from 1.4 to 8 kg.m⁻².y⁻¹ (0.2 to 1 cm.yr⁻¹) in the
519 main channel (T1 to T4), varied from 0.47 to 2.9 kg.m⁻².y⁻¹ (0.1 to 0.4 cm.yr⁻¹) in the border
520 area (T5 to T8), and was 4.2 kg.m⁻².y⁻¹ (0.5 cm.yr⁻¹) in the isolated area (T9). For the ditch, the
521 sediment accumulation varied from 2 to 12.7 kg.m⁻².y⁻¹ (0.5 to 1.6 cm.yr⁻¹) in the main
522 channel (T1 to T3), from 1 to 2.5 kg.m⁻².y⁻¹ (0.1 to 0.3 cm.yr⁻¹) in the border area (T4 to T6),
523 and between 4.6 and 5.4 kg.m⁻².y⁻¹ (0.6 and 0.7 cm.yr⁻¹) in the two isolated areas (T7 and T8,
524 respectively) (Fig. 6). These sedimentation rates are in accordance with those of [Fennessy et](#)
525 [al. \(1994\)](#) who reported rates from 5.9 to 12.8 kg.m⁻².y⁻¹. For both CWs, the lower
526 sedimentation rates in the border areas than in the MC may be due to an emergence of border
527 traps during low flow rates (T5 to T8 in the pond CW and T4 to T6 in the ditch CW). In
528 addition, the sedimentation rate in MC and IA is almost equal despite a possible greater water
529 volume passing through the MC than through the IA. This result may be explained by a higher
530 resuspension of sediment in the MC than in the IA due to a faster water velocity. This process
531 of resuspension was highlighted (i) by a relatively uniform spatial distribution of sediment
532 particle size inside the CW (Fig. A3) and (ii) by the greater amount of particles settled in both
533 CW traps than the amount of particles reaching the inlet (Fig. A2).

534 Dimetachlor (DMT) was the single quantified pesticide reaching the CWs by
535 particulate phase only (data not shown) and was also quantified in sediments (Fig. 7). For
536 both CWs, the DMT concentrations in sediment were similar regardless of the sampling zone
537 (Fig. 7), which corroborates the uniform sedimentation inside the CW and even in the isolated

538 area. Thus, the isolated areas can also mitigate solid-bound pesticides by sedimentation.
539 Otherwise, the resuspension of sediments from the main channel could induce a release of
540 solid-bound pesticides towards the CW outlet, which could lead to a negative mitigation rate
541 of solid-bound pesticides.

542

543 *3.5. Influence of hydrodynamics on the spatial distribution of the pesticide levels in* 544 *sediments*

545 Concerning the pesticides reaching the CW by dissolved phase only (data not shown),
546 their quantification onto the sediments indicated their adsorption from the dissolved phase,
547 which is the case for epoxyconazole (EPX) in the pond and cyproconazole (CYP) and
548 metconazole (MCZ) in the ditch (Fig. 7). No metabolites were quantified in the sediments,
549 possibly due to their high polarity properties.

550 For the pond sediment, the EPX concentration is higher in the IA (point 9) than in the
551 MC (ponds 1, 2 and 3). This higher pesticides storage in sediments in IA than MC could be
552 due to: (i) adsorption process of EPX favoured by the dispersion transport in IA, (ii) or/and
553 due to desorption process which could be favoured in MC due to convection transport as
554 previously shown in [Gaulhier et al. \(2018\)](#); (iii) or/and due to degradation process, favoured in
555 MC. In the same manner, [Schuetz et al. \(2012\)](#) also showed that adsorption was higher in IA
556 (dead zones in their study) compared to zones where convection was dominant, such as the
557 MC in our study.

558 In the ditch sediment, the CYP and MCZ concentrations were lower in the IA (point 3)
559 than in the MC (inlet, outlet and enlargement) (Fig. 7). This contradictory observation when
560 compared with the pond could be due to the location of the IA. Indeed, the IA was located in
561 the border area of the ditch and sometimes emerged during low flow rates, whereas in the
562 pond, the IA never emerged.

563 Finally, favourable hydraulic conditions, as shown in isolated areas (slow water
564 velocity, long HRT), could increase the mitigation of dissolved pesticides inside the CW by
565 adsorption on sediment, as demonstrated in the results.

566

567 **Conclusion**

568 Bromide tracing and electrical conductivity monitoring allowed us to identify and delineate
569 two water pathways (or hydraulic zones) inside the CWs: the main channel with water
570 transported mainly by convection and the isolated areas with water transported by dispersion.
571 The area and the location of these hydraulic zones fluctuate according to the flow rate. For the
572 ditch and pond, the proportion of isolated areas is greater at low flow rates (0.5 L/s,
573 representing 50 % of annual flow rates) than at medium or high flow rates (4-7 L/s,
574 representing 10 % of annual flow rates). During drainage, these different water pathways led
575 to a heterogeneous distribution of dissolved pesticide concentrations inside the CW, as
576 illustrated for the aqueous phase and the adsorbed pesticide concentrations on sediment. This
577 heterogeneity between the main channel and the isolated areas is more notable at low flow
578 than at high flow in the short term, since isolated areas are affected later by dispersion at LF
579 than at HF. In the long term, this heterogeneity disappears during the no-flow phase due to the
580 dispersion of pesticides and metabolites inside the CWs. Pesticides entering the CW that are
581 adsorbed on TSS are mitigated by sedimentation. The sedimentation rates are quite similar
582 between the main channel and the isolated areas, whereas the isolated areas are (i) less
583 affected by water than the main channel, (ii) less impacted by resuspension of sediments than
584 the main channel and (iii) sometimes emerged (for the ditch). In addition, analyses of
585 pesticides reaching the CW inlet in the dissolved phase only showed that storage in the
586 sediments seems favoured in the isolated areas compared to the main channel. These isolated
587 areas appear effective for dissolved and particulate pesticide mitigation, especially

588 considering a complete drainage season. Finally, fine-time field monitoring is needed to
589 determine the pesticide mitigation effectiveness of CWs at different temporal scales.

590

591

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593

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604

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Figure captions

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Figure 1. Location of the sampling points in photographs taken by a drone (5 November 2018) of the two-constructed wetlands: a succession of three ponds (A) and a ditch (B)

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Figure 3. Spatial distribution of bromide concentration versus time under various flow rates (LF: low flow, MF: mean flow) in the second pond and ditch

Figure 4. Electrical conductivity ($\mu\text{S}/\text{cm}$) in the inlet, outlet, main channel (MC) and isolated area (IA) zones under distinct flow rates (HF: high flow, LF: low flow, MF: mean flow and no flow) for the pond and ditch

Figure 5. Pesticide concentrations ($\mu\text{g}/\text{L}$) in the inlet, outlet, main channel (MC) and isolated area (IA) zones under distinct flow rates (HF: high flow, LF: low flow, MF: mean flow and no flow) for the pond and ditch

Figure 6. Spatial distribution of sedimentation rate within the pond and the ditch (MC: main channel, border, IA: isolated area) for the different sediment traps (numbered T1 to T9)

747 **Figure 7.** Pesticide concentrations ($\mu\text{g}/\text{kg}$) in sediments collected at the end of the 2016/2017
748 drainage season for pesticide entering CW by dissolved phase (EPX: epoxyconazole, CYP:
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Table captions

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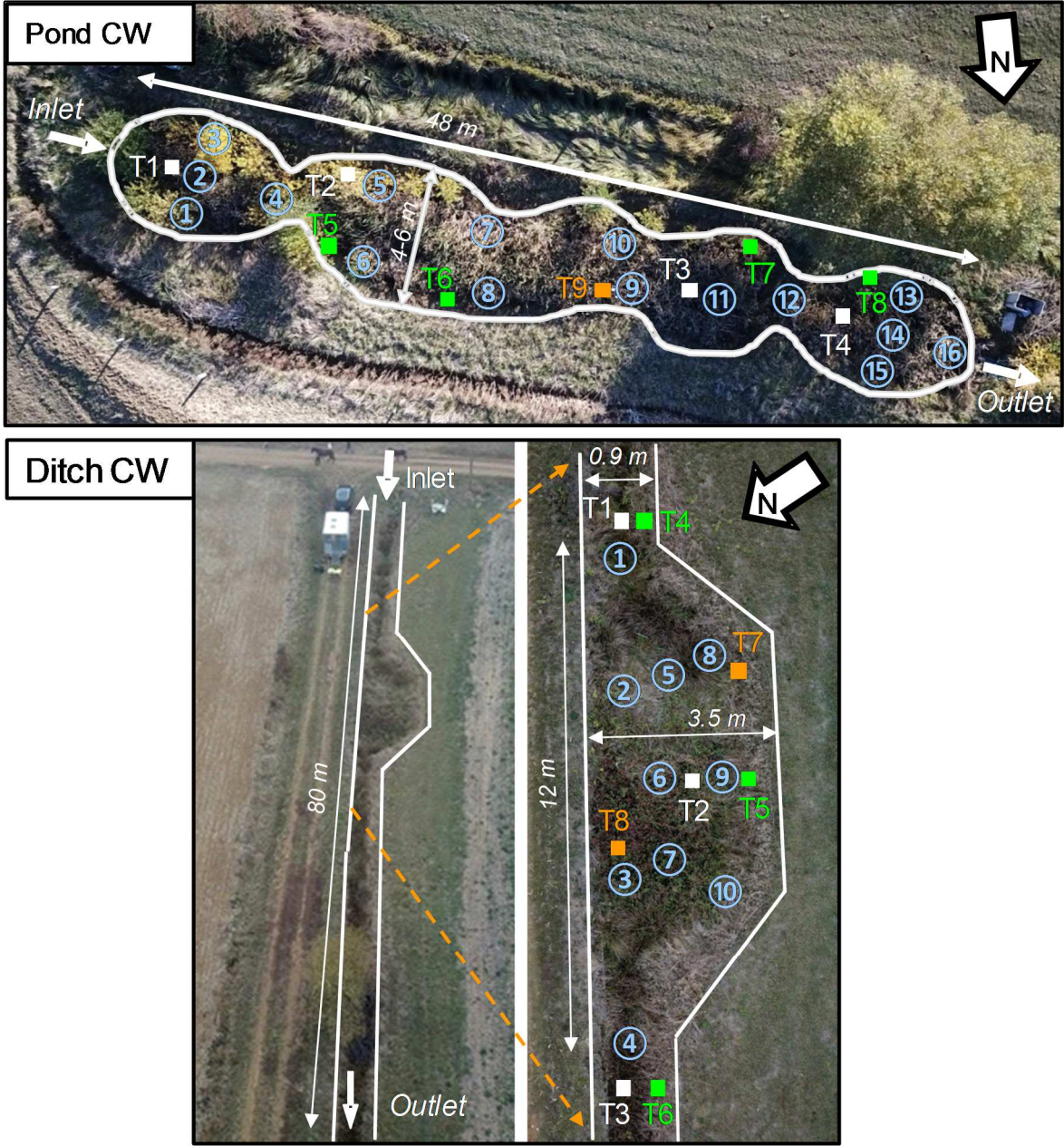
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Blue numbered circles correspond to the manual water sampling during the bromide tracing.

Coloured squares correspond to the location of sediment traps: white for the main channel, green for the borders and orange for isolated areas.

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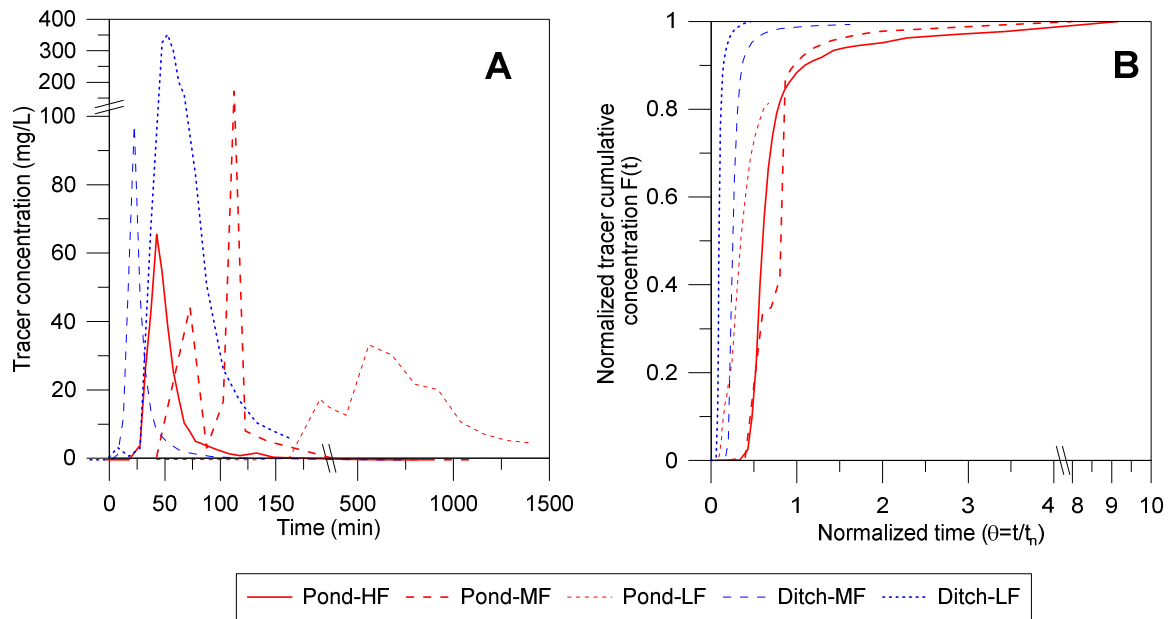
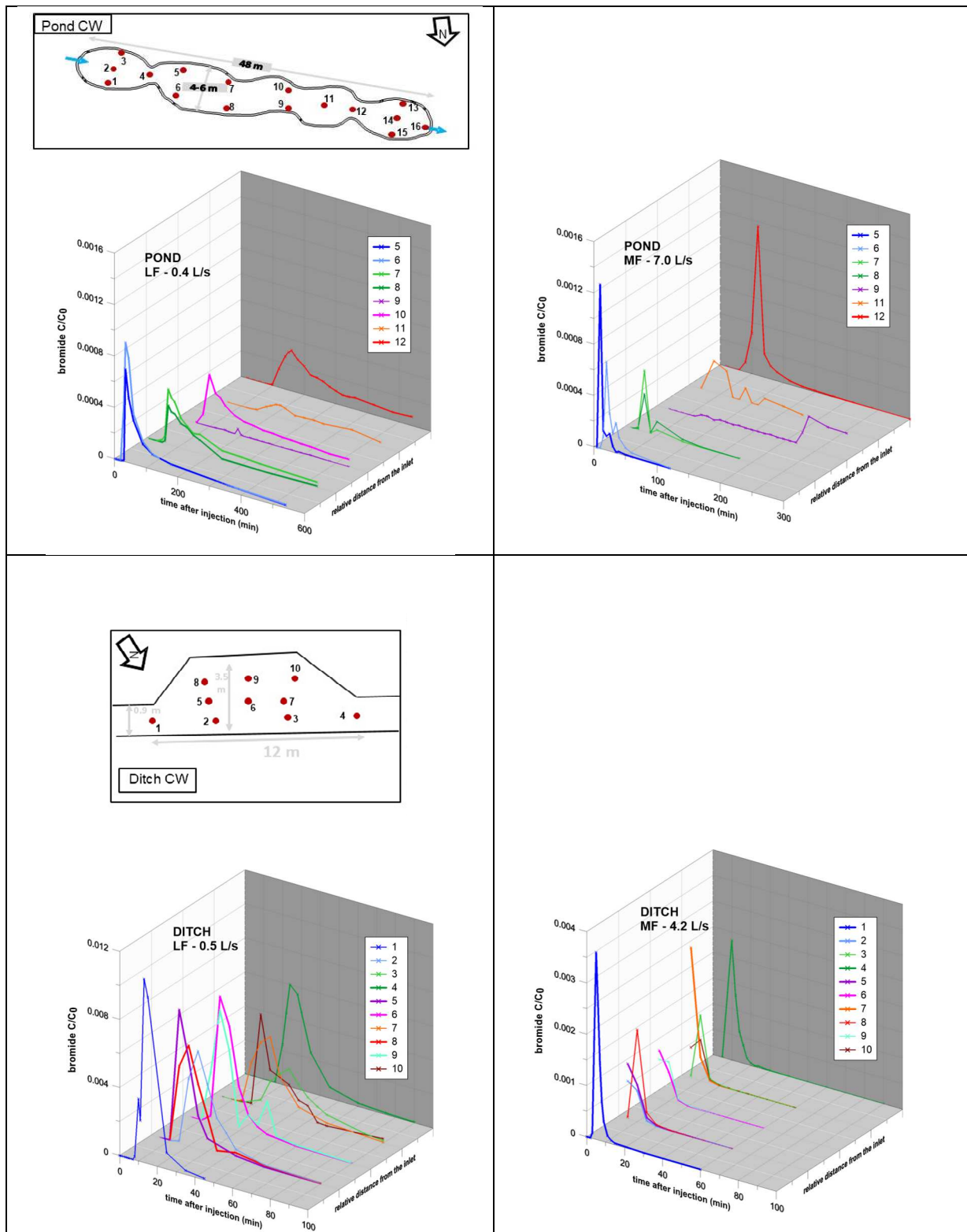


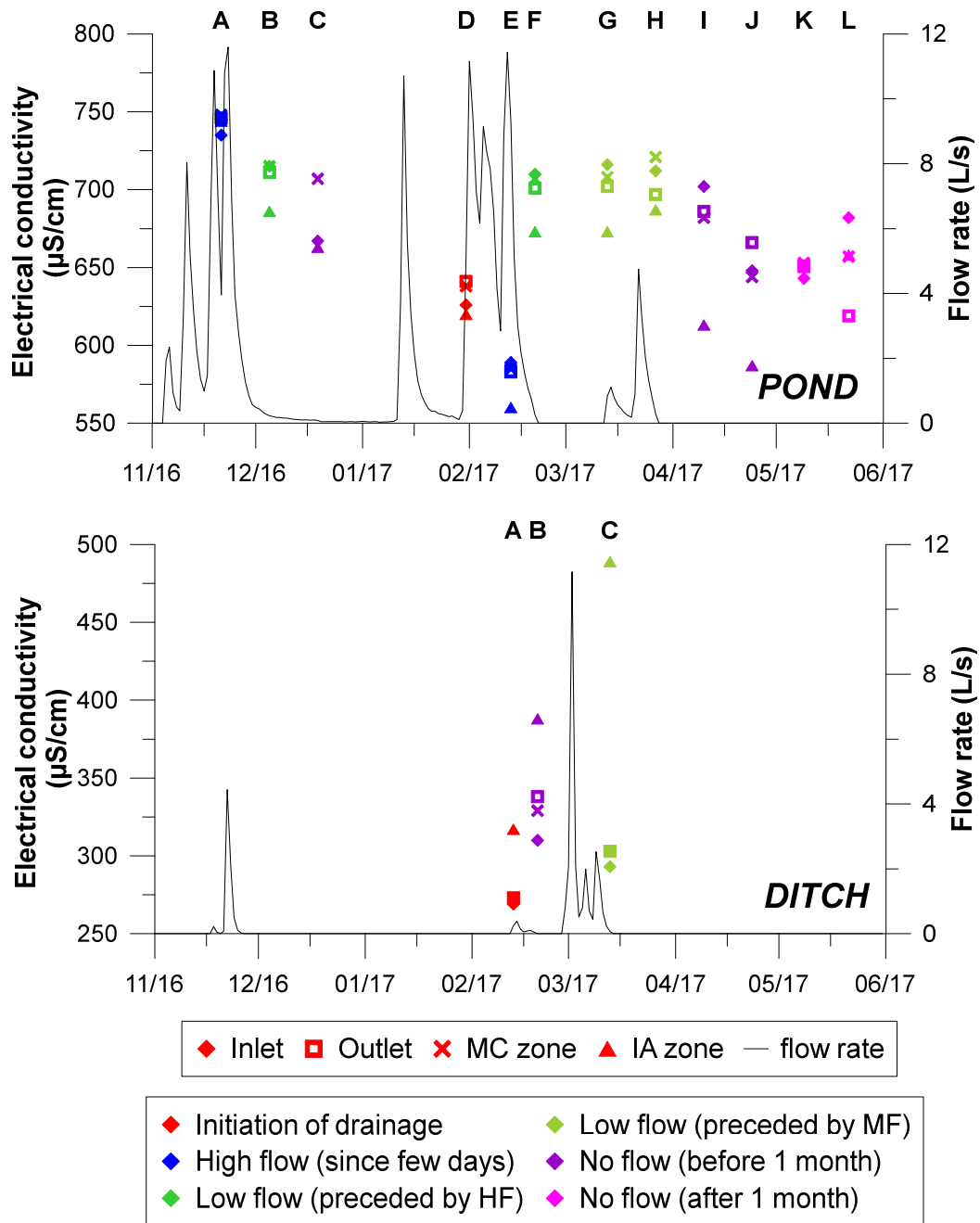
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In the pond, point 10 was not sampled at MF (7 L/s), and there is no associated curve on the graph.

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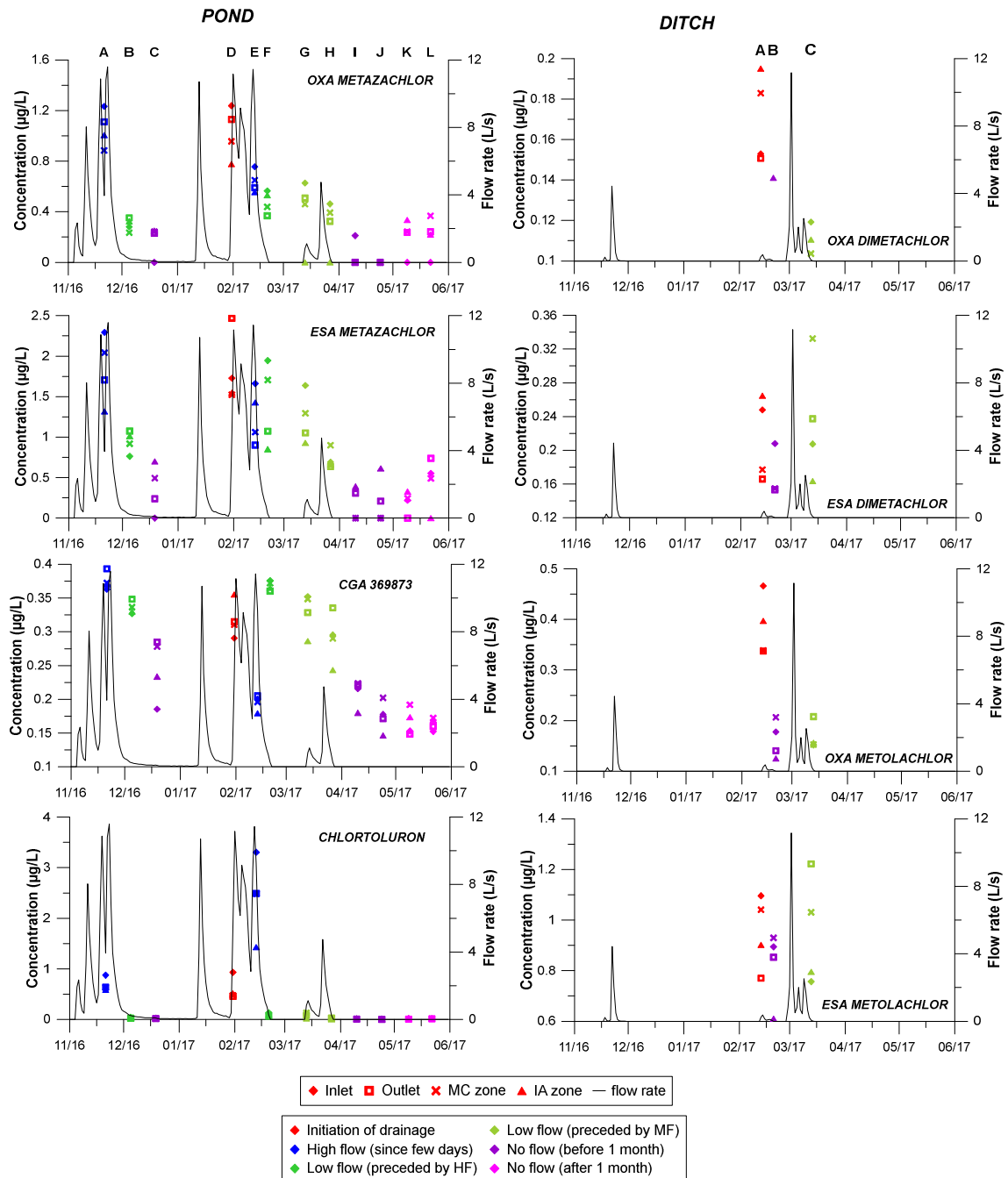
Each letter (from A to L) corresponds to one sampling date.



For the pond, the MC zone was collected in point 10, and the IA zone was collected in point 9. For the ditch, the MC zone was collected in point 6, and the IA zone was collected in point 3 (Figure 3).

Figure 5. Pesticide concentrations ($\mu\text{g/L}$) in the inlet, outlet, main channel (MC) and isolated area (IA) zones under distinct flow rates (HF: high flow, LF: low flow, MF: mean flow and no flow) for the pond and ditch

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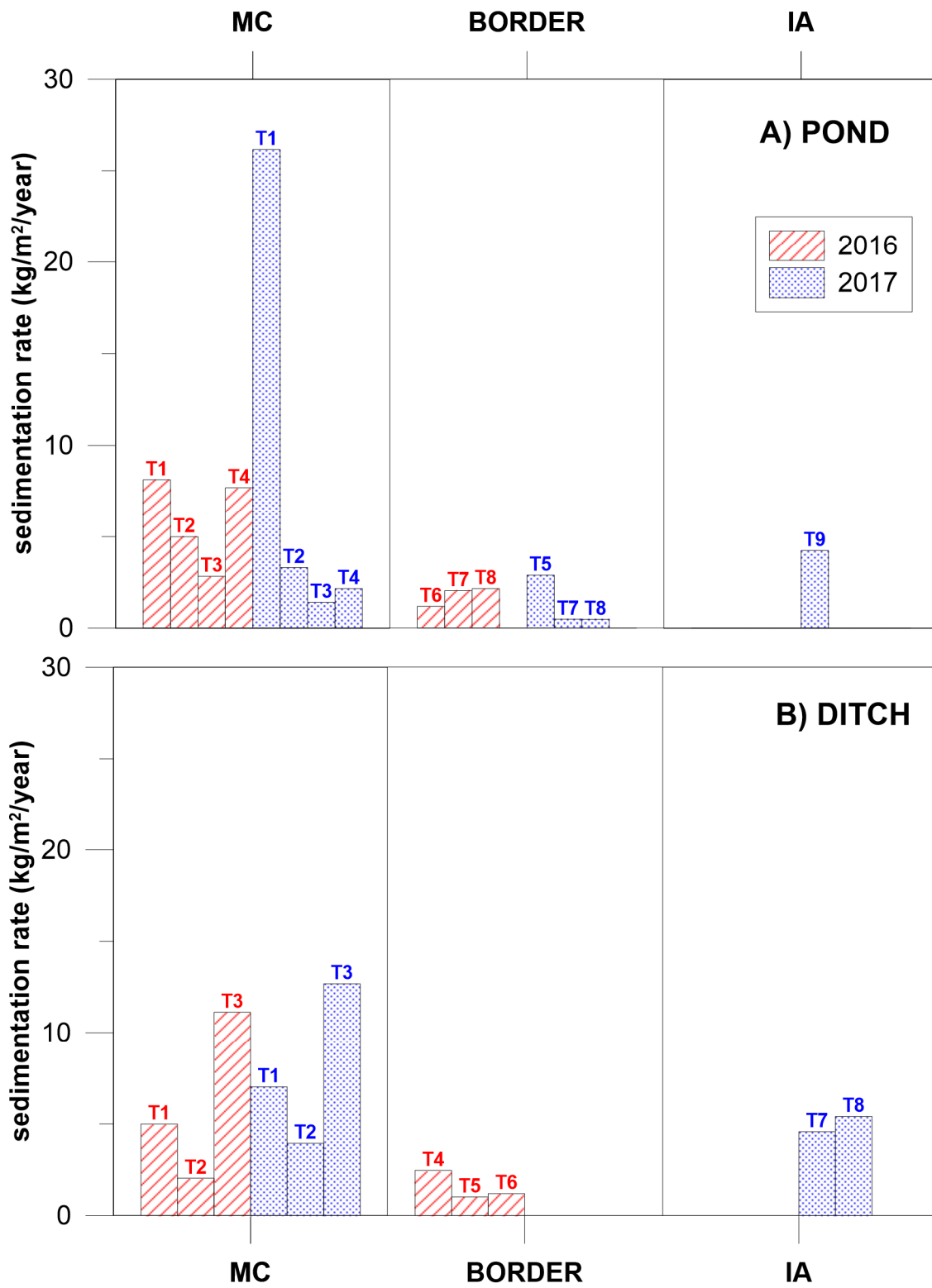


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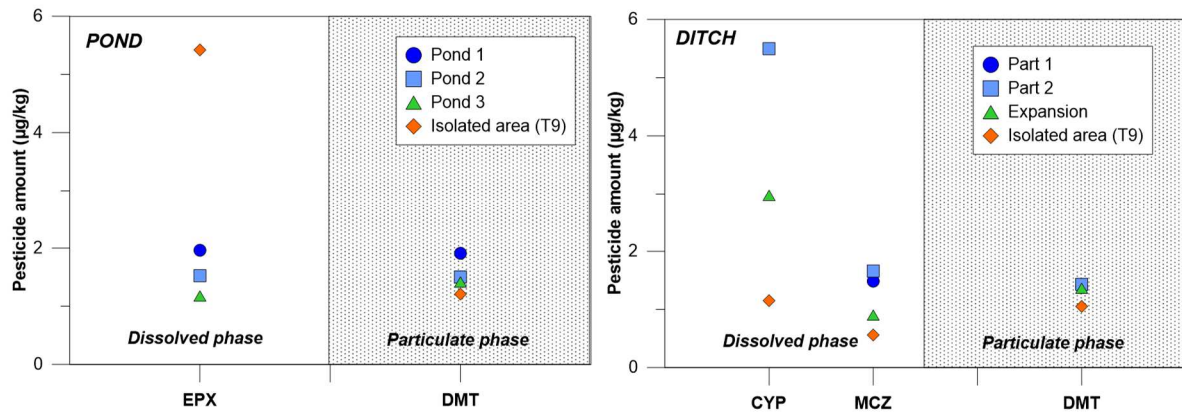


Table 1. Meteorological, hydrological and agricultural data characterizing the two studied constructed wetlands.

Crop rotation	Rainfall* (mm/d)	30-yr average rainfall* (mm/d)	Inlet volume* (mm/d)	Flow rate variation* (L/s)	Flow distribution	HRT* (h)	Drainage period* (d)	Dry period* (d)
POND								
barley/rape/ winter wheat	1.9 - 3.2	2.7	2 - 4.5**	0.2 - 21.5	<2 L/s : 50% 2-7 L/s : 25% >7 L/s : 25%	1 - 40	7 - 43	2 - 37
DITCH								
rape/winter wheat/maize/ winter wheat	1.9 - 3.5	2.3	0.3 - 0.7	0.01 - 11	<0.2 L/s : 50% 0.2-1 L/s : 25% 1-4 L/s : 21% >4 L/s : 4%	1 - 181	4 - 54	2 - 75

* From the beginning (November) to the end of drainage (March-April) during 3 drainage seasons (2014-2017).

**The drained volume higher than total rainfall might be due to runoff from an adjacent plot.

Table 2. Tracer experiment parameters and hydraulic characteristics of the pond and ditch under various flow rates for the pond and ditch

Tracer test name*	Pond-HF	Pond-MF	Pond-LF	Ditch-MF	Ditch-LF
Injection date	15/02/2016	13/06/2016	15/03/2017	01/04/2016	08/03/2017
Injected volume (L)	15	10	10	5	5
Sampling time** (step 1) (h)	7	5	9	4	6
Total sampling period*** (step 1 + step 2) (h)	48	48	96	48	120
Restitution after sampling time (%)	77	111	23	47	30
Restitution after total sampling period (%)	77	111	104	97	72
Mean flow rate (L/s)	13.0 ± 0.4	8.0 ± 0.3	0.6 ± 0.2	4.0 ± 0.9	0.34 ± 0.02
Water depth (m)****	0.18/0.34/0.48	0.08/0.25/0.35	0.05/0.20/0.31	0.15/0.10/0.35	0.10/0.05/0.21
Volume of wetland (m ³)	83	63	55	38	23
Water temperature (°C)	8	12	9	8	6
Electrical conductivity (μS/cm)	530	625	700	210	295
pH(μS/cm)	6.2	7.0	7.7	6.0	7.0

* HF=High Flow; MF = Mean Flow; LF = Low Flow

** Water was manually sampled every 5 min.

*** The outlet water was sampled every 2 hours until the bromide concentration was lower than the limit of quantification (50 μg/L)

**** Three water depths were measured inside the CWs: in the 1st/2nd/3rd ponds and in the inlet/expansion/outlet of the ditch.

Table 3. Transport parameters derived from the Residence Time Distribution analysis for the pond and ditch under distinct flow rates

	t_n (h)	t_{mean} (h)	$t_{\theta=0.5}$	N	λ	t_{10}/t_n	t_{90}/t_{10}	Pe	V_{mean} (m/min)
Pond-HF	1.7	1.5	0.87	2.3	0.50	0.48	2.3	62	0.53
Pond-MF	2.5	2.2	0.89	2.5	0.53	0.46	2.1	1697	0.36
Pond-LF	37.2	23.0	0.62	1.4	0.18	0.14	10.7	11	0.03
Ditch-MF	2.5	0.8	0.32	1.3	0.07	0.20	1.7	28	1.55
Ditch-LF	13.0	1.4	0.11	1.1	0.01	0.07	2.1	16	0.87

