

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

Celine Gaullier, Sylvie Dousset, Nicole Baran, Geraldine Kitzinger, Charlotte

Coureau

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3	distribution of pesticide and metabolite concentrations in constructed
4	wetlands
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6	Céline Gaullier <sup>(1, 2, 3)</sup> , Sylvie Dousset <sup>(1, 3)*</sup> , Nicole Baran <sup>(2)</sup> , Géraldine Kitzinger <sup>(1)</sup> , Charlotte
7	Coureau <sup>(2)</sup>
8	
9	
10	<sup>(1)</sup> Laboratoire Interdisciplinaire des Environnements Continentaux, Université de Lorraine -
11	CNRS, 54506 Vandœuvre-lès-Nancy
12	<sup>(2)</sup> BRGM, 45060 Orléans CEDEX 02, France
13	<sup>(3)</sup> LTSER France, Zone Atelier du Bassin de la Moselle, 54506 Vandœuvre-lès-Nancy, France
14	
15	*Corresponding author
16	sylvie.dousset@univ-lorraine.fr
17	Sylvie DOUSSET
18	Laboratoire Interdisciplinaire des Environnements Continentaux
19	Université de Lorraine - CNRS,
20	BP 70239 - Bd des Aiguillettes
21	54506 Vandœuvre-lès-Nancy
22	Tel.: +33 (0)3 72 74 52 12
23	

# 25 Nomenclature 26 27 $\sigma_{\theta}^2$ RTD variance

- 28  $\theta$  dimensionless time
- 29  $\lambda$  hydraulic efficiency
- $30 e_v$  effective volume ratio
- 31 HRT hydraulic residence time
- 32 N number of serial mixing tanks
- 33PePeclet 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

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

63

#### 64 Keywords:

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

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

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

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

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

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

125

#### 126 **2.** Materials and methods

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- 128 2.1. Constructed wetlands
- 129

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

The two studied CWs were built in autumn 2010 in a regulatory grass strip, and 134 spontaneous vegetation recovered the entire CW in two years. Thus, during our experiments, 135 the vegetation was present throughout the year, and its influence on the hydrodynamic 136 dispersion as reported by Jenkins and Greenway (2005) could be considered similar under all 137 seasons. The first CW located at Ville-sur-Illon (75 km at the South of Nancy, France) 138 consisted roughly of a succession of three ponds of 47.8 m length and 4 to 6.5 m width, with a 139 surface of 215 m<sup>2</sup> and an island at the beginning of the second pond (Fig. 1). It received the 140 drainage water from an 8 ha plot (cambisol, FAO 2006) by a drain collector located at inlet of 141

the CW. The CW was entirely vegetated and dominated by Juncus effusus, Juncus inflexus, 142 and Juncus articulatus on the edge of the CW, with Typha latifolia, Typha angustifolia, 143 Epilobium hirsutum and Veronica becabunga inside the CW. The second CW located at 144 Manoncourt-sur-Seille (30 km in the North of Nancy, France) consisted roughly of a ditch of 145 80 m length and 0.9 m width, and it expanded over 12 m long by 4 m wide, with a surface of 146 100 m<sup>2</sup> (Fig. 1). It received the drainage water from a 10 ha plot (glevic cambisol, FAO 147 2006). The CW was entirely vegetated and dominated by Juncus effusus, Juncus 148 conglomerates and grasses. Substrates of both CWs were clayed, which allowed their 149 imperviousness. Both CWs have been precisely topographically levelled allowing the 150 determination of water volume. 151

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153	2.2.	Tracer	experiment
122	<i>∠.</i> ∠.	Tracer	experiment

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

167 measurements. For each tracer experiment, the volume of water was calculated with168 Autocad® and ADTOPO® softwares based on water level observed in the field.

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

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

Samples were filtered through a 0.22  $\mu$ m cellulose acetate filter, and then 1 mL aliquots were transferred to polypropylene vials for analysis with a Dionex ICS-3000 ion chromatographic instrument (Sunnyvale, CA, USA) using Chromeleon® software (version 6.80). Concentrations of Br<sup>-</sup> were analysed using an AS20 guard column (4 x 50 mm) with a polymeric AS20 analytical column (4 mm x 250 mm). The LOQ was 50  $\mu$ g.L<sup>-1</sup>. Certified standard solutions from Inorganic Ventures (Washington, USA) were used for calibration.

188

189 2.3. Water transport parameters

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

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

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

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

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

where C(t) is the bromide concentration (mg.L<sup>-1</sup>) at time t, Q is the flow rate (L.s<sup>-1</sup>) at time t and  $d_t$  is the interval between two consecutive measurements.

210

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

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

216

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

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

219

220 The hydraulic efficiency ( $\lambda$ ) 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  $\lambda = t_{\theta} \left( 1 \frac{1}{N} \right) \tag{5}$
- 224

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

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

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

where Q is the flow rate  $(m^3.h^{-1})$ , L is the length of CW (m), W is the width of CW (m), Z is 240 the height of water (m) and D is the dispersion coefficient  $(m^2.h^{-1})$  defined by Eq. (7). 241 242  $D = \alpha \times V_{mean}(7)$ 243 244 with  $\alpha$  the water dispersivity (m) and V<sub>mean</sub> (m.h<sup>-1</sup>) the mean water velocity inside the CW 245 246 (i.e. CW length divided by t<sub>mean</sub>). The water dispersivity  $\alpha$  was calculated as the mean of two dispersion parameters 247 (dimensionless) which characterized the asymmetrical tracer curve. Those parameters were 248 249 determined using model. 250 TSS measurements and pesticide analysis in water samples 251 2.4. 252 Raw water (water + TSS) was manually sampled during the 2016/2017 hydrological 253 season. For the pond CW, the samples were collected every two weeks from 21/11/16 to 254 22/05/17 (i.e., 12 samples, 7 under drainage and 5 under no-flow periods). For the ditch CW, 255 samples were collected from 13/02/17 to 13/03/17, due to short drainage season (i.e., 3 256 257 samples: 2 under drainage and 1 under a no-flow period). Water samples were collected at the inlet, at the outlet, in the main channel inside the 258 CW (point MC) and in an isolated area (point IA). Points MC and IA were identified by 259 260 bromide concentration analysis (MC and IA correspond to points 10 and 9 for the pond CW and 6 and 3 for the ditch CW, respectively) (Fig. 1). Under no-flow, the inlet and outlet 261 sampling was performed in stagnant water close to the inlet and outlet, respectively. All 262 samples were collected in 250 mL PE bottles, which were transported under refrigeration to 263

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

The analyzed pesticides were chosen because of their frequent application in the agricultural plots due to dominant cultures (i.e. winter wheat, rapeseed and maize), and because of their frequent detection in drainage water according to a previous study (Vallée et al. 2015b). Moreover, the diversity of the physico-chemical properties of these molecules (Table A2), allow study the potential contrasted behavior. The metabolites were chosen on the one hand because they are metabolites of widely used pesticides, but rarely studied worldwide; and on the other hand, for their high polarity. To quantify the TSS, 2 L water samples were also manually collected in a 2 L PE bottle. The sampling was performed exclusively at the inlet and outlet due to difficulties in sampling in the MC and IA zones without resuspending the TSS. Then, 250 to 1000 mL of water (depending on particle laden flow) was filtered through 0.7  $\mu$ m fiber glass filters to separate the largest TSS from the aqueous phase. Before their use, fiber glass filters were cleaned with distilled water, dried at 70°C for 24 h, weighed, and then stored in a glass container. After filtration, filters with the TSS were dried at 70°C for 24 h and then weighed.

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

297

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

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

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

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

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

- 343
- **3**44 **3**.
- 345

346 3.1. Hydrodynamic of the CWs

**Results and discussion** 

347

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

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

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

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

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

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#### *3.2. Influence of hydrodynamics on water pathways*

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

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

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

438 (I, J). Then, beyond this month (K, L), the electrical conductivity becomes similar in the MC439 and IA zones, which is possibly due to a very slow dispersion during the no-flow period.

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

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

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#### 3.3.Influence of hydrodynamics on dissolved pesticide transport

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

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

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).

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

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

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#### 3.4. Influence of hydrodynamics on the sedimentation rate

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

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

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

Dimetachlor (DMT) was the single quantified pesticide reaching the CWs by particulate phase only (data not shown) and was also quantified in sediments (Fig. 7). For both CWs, the DMT concentrations in sediment were similar regardless of the sampling zone (Fig. 7), which corroborates the uniform sedimentation inside the CW and even in the isolated area. Thus, the isolated areas can also mitigate solid-bound pesticides by sedimentation.
Otherwise, the resuspension of sediments from the main channel could induce a release of
solid-bound pesticides towards the CW outlet, which could lead to a negative mitigation rate
of solid-bound pesticides.

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3.5. Influence of hydrodynamics on the spatial distribution of the pesticide levels in 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.

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

In the ditch sediment, the CYP and MCZ concentrations were lower in the IA (point 3) than in the MC (inlet, outlet and enlargement) (Fig. 7). This contradictory observation when compared with the pond could be due to the location of the IA. Indeed, the IA was located in the border area of the ditch and sometimes emerged during low flow rates, whereas in the pond, the IA never emerged. Finally, favourable hydraulic conditions, as shown in isolated areas (slow water velocity, long HRT), could increase the mitigation of dissolved pesticides inside the CW by adsorption on sediment, as demonstrated in the results.

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#### 567 Conclusion

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

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

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593

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#### 605 **References**

607	Alvord, H., Kadlec, R.,	, 1996. Atra	zine fate and	l transport i	n the Des	Plaines	Wetlands.	Ecol.
608	Model. 90, 97–1	07.						

- Chang, T-J., Chang, Y-S., Lee, W-T., Shih, S-S., 2016. Flow uniformity and hydraulic
  efficiency improvement of deep-water constructed wetlands. Ecol. Eng. 92, 28–36.
- Elsaesser, D., Blankenberg, A-G.B., Geist, A., Mæhlum, T., Schulz, R., 2011. Assessing the
  influence of vegetation on reduction of pesticide concentration in experimental surface
- flow constructed wetlands: Application of the toxic units approach. Ecol. Eng. 37,955-962.
- Elsayed, O.F., Maillard, E., Vuilleumier, S., Imfeld, G., 2014. Bacterial communities in batch
  and continuous-flow wetlands treating the herbicide S-metolachlor. Sci. Total
  Environ. 499, 327-335.
- Evans, R.D., Håkanson, L., 1992. Measurement and prediction of sedimentation in small
  Swedish lakes. Hydrobiologia 235-236, 143–152.
- Fan, L., Reti, H., Wang, W., Lu, Z., Yang, Z., 2008. Application of computational fluid
  dynamic to model the hydraulic performance of subsurface flow wetlands. J. Environ.
  Sci. 20, 1415-1422.
- Fennessy, M., Brueske, C.C., Mitsch, W.J., 1994. Sediment deposition patterns in restored
  freshwater wetlands using sediment traps. Ecol. Eng. 3, 409-428.
- Gardner, W., 1980. Sediment trap dynamics and calibration: a laboratory evaluation. J. Mar.
  Res. 38, 17-39

- Gaullier, C., Dousset, S., Billet, D., Baran, N., 2018. Is pesticide sorption by constructed
  wetland sediments governed by water level and water dynamics? Environ. Sci. Pollut.
  Res. 25, 14324-14335.
- Gaullier, C., Baran, N., Dousset, S., Devau, N., Billet, D., Kitzinger, G., Coisy, E., 2019.
  Wetland hydrodynamics and mitigation of pesticides and their metabolites at pilotscale. Ecol. Eng. 136, 185-192.
- Gregoire, C., Elsaesser, D., Huguenot, D., Lange, J., Lebeau, T., Merli, A., Mose, R.,
  Passeport, E., Payraudeau, S., Schütz, T., Schulz, R., Tapia-Padilla, G., Tournebize, J.,
  Trevisan, M., Wanko, A., 2009. Mitigation of agricultural nonpoint-source pesticide
  pollution in artificial wetland ecosystems. Environ. Chem. Lett. 7, 205-231.
- Guo, C., Cui Y., Dong B., Luo, Y., Liu, F., Zhao, S., Wu, H., 2017. Test study of the optimal
  design for hydraulic performance and treatment performance of free water surface
  flow constructed wetland. Bioresource Technol. 238, 461-471.
- Jenkins, G.A., Greenway, M., 2005. The hydraulic efficiency of fringing versus banded
  vegetation in constructed wetlands. Ecol. Eng. 25, 61-72.
- JOCE, 2000. Directive 2000/60/EC of the European Parliament and of the Council of 23
  October 2000 Establishing a Framework for Community Action in the field of Water
  Policy, L337.
- JOCE, 2006. Directive 2006/118/EC of the European Parliament and the Council of 12
  December 2006 on the Protection of Groundwater against Pollution and Deterioration,
  L372.
- Kadlec, R.H., 1994. Detention and mixing in free water wetlands. Ecol. Eng. 3, 345-380.
- Koskiaho, J., 2003. Flow velocity retardation and sediment retention in two constructed
  wetland–ponds. Ecol. Eng. 19, 325–337.

- Lewis, K.A., Tzilivakis, J., Warner, D., Green, A.,2016. An international database for
  pesticide risk assessments and management. Human and Ecological Risk Assessment:
  Internat. J. 22, 1050-1064.
- Lin, A.Y-C., Debroux, J-F., Cunningham, J.A., Reinhard, M., 2003. Comparison of rhodamine WT and bromide in the determination of hydraulic characteristics of constructed wetlands. Ecol. Eng. 20, 75-88.
- Liu, J.J., Dong, B., Guo, C.Q., Liu, F.P., Brown, L., Li, Q., 2016. Variations of effective
  volume and removal rate under different water levels of constructed wetland. Ecol.
  Eng. 95, 652-664.
- Liu T, Xu S, Lu S, Qin P, Bi B, Ding H, Liu Y, Guo X, Liu X 2019. A review on removal of
  organophosphorus pesticides in constructed wetland: Performance, mechanism and
  influencing factors.Sci. Total Environ. 651, 2247-2268.
- Maillard, E., Payraudeau, S., Ortiz, F., Imfeld, G., 2011. Removal of dissolved pesticide
  mixtures by a stormwater wetland receiving runoff from a vineyard catchment: An

665 inter-annual comparison.Int. J. Environ. An. Chem. 92, 1-16.

- Maillard E, Imfeld G (2014) Pesticide Mass Budget in a Stormwater Wetland. Environmental
  Science & Technology 48:8603–8611.
- Martinez, C.J., Wise, W.R., 2003. Hydraulic analysis of Orlando easterly wetland. J. Environ.
  Eng. 129, 553-560.
- Matamoros, V., García, J., Bayona, J.M., 2008. Organic micropollutant removal in a full-scale
  surface flow constructed wetland fed with secondary effluent. Water Res. 42, 653-660.
- Moore, M.T., Bennett, E.R., Cooper, C.M., Smith, S., Shields, F.D., Milam, C.D., Farris, J.L.,
- 673 2001. Transport and fate of atrazine and lambda-cyhalothrin in an agricultural
  674 drainage ditch in the Mississippi Delta, USA. Agric. Ecosyst. Environ. 87, 309-314.

- Moore, M.T., Tyler, H.L., Locke, M.A., 2013. Aqueous pesticide mitigation efficiency of *Typha latifolia (L.), Leersia oryzoides (L.) Sw., and Sparganium americanum Nutt.*Chemosphere 92, 1307-1313.
- Nameche, T.H, Vasel, J.L., 1998. Hydrodynamic studies and modelization for aerated lagoons
  and waste stabilization ponds. Water res. 32, 3039-3045.
- Nuel, M., Laurent, J., Bois, P., Heintz, D., Mosé, R., Wanko, A., 2017. Seasonal and ageing
  effects on SFTW hydrodynamics study by full-scale tracer experiments and dynamic
  time warping algorithms. Chem. Eng. J. 321, 86-96.
- Sabokrouhiyeh, N., Bottacin-Busolin, A., Savickis, J., Nepf, H., Marion, A., 2017. A
  numerical study of the effect of wetland shape and inlet-outlet configuration on
  wetland performance. Ecol. Eng. 105, 170-179.
- Schuetz, T., Weiler, M., Lange, J., 2012., Multitracer assessment of wetland succession:
  Effects on conservative and non-conservative transport processes. Water Resour. Res.
  48, 1-15.
- Schultz, R.C., Collettil, J.P., Isenhart, T.M., Simpkins, W.W., Mize, C.W., Thompson, M.L.,
  1995. Design and placement of a multi-species riparian buffer strip system.
  Agroforest. Syst. 29, 201-226.
- Shih, S., Zeng, Y., Lee, H., Otte, M., Fang, W., 2017. Tracer Experiments and Hydraulic
  Performance Improvements in a Treatment Pond. Water 9, 137.
- 694 Stehle, S., Elsaesser, D., Gregoire, C., Imfeld, G., Niehaus, E., Passeport, E., Payraudeau, S.,
- 695 Schäfer, R.B., Tournebize, J., Schulz, R., 2011. Pesticide Risk Mitigation by
  696 Vegetated Treatment Systems: A Meta-Analysis. J. Environ. Qual. 40, 1068-1080.
- 697 Su, T-M., Yang, S-C., Shih, S-S., Lee, H-Y., 2009. Optimal design for hydraulic efficiency
- 698 performance of free-water-surface constructed wetlands. Ecol. Eng. 35, 1200-1207.

- Thackston, E.L., Shields, D. Jr., Schroeder P.R., 1987. Residence time distributions of
  shallow basins. J. Environ. Eng. 113, 1319-1332.
- Teixeira, E.C., Siqueira, R.D.N., 2008. Performance assessment of hydraulic efficiency
  indexes. J. Environ. Eng. 134, 851–859
- Tournebize, J., Gramaglia, C., Birmant, F., Bouarfa, S., Chaumont, C., Vincent, B., 2012. Codesign of constructed wetlands to mitigate pesticide pollution in a drained catch-basin:
  a solution to improve groundwater quality. Irrig. Drain. 61, 75-86.
- Vallée R, Dousset S, Billet D (2015a). Water residence time and pesticide removal in pilotscale wetlands. Ecological Engineering 85:76–84.
- Vallée, R., Dousset, S., Schott, F.-X., Pallez, C., Ortar, A., Cherrier, R., Munoz, J.-F., Benoît,
- M., 2015b. Do constructed wetlands in grass strips reduce water contamination from
  drained fields? Environ. Pollut. 207, 365-373.
- 711 Vymazal, J., Březinová, T., 2015. The use of constructed wetlands for removal of pesticides
  712 from agricultural runoff and drainage: A review. Environ. Int. 75, 11-20.
- Wahl, M.D., Brown, L.C., Soboyejo, A.O., Martin, J., Dong, B., 2010. Quantifying the
  hydraulic performance of treatment wetlands using the moment index. Ecol. Eng. 36,
  1691-1699.
- Werner, T.M., Kadlec, R.H., 2000. Wetland residence time distribution modeling. Ecol. Eng.
  15, 77-90.
- Zounemat-Kermani, M., Scholz, M., Tondar, M-M., 2015. Hydrodynamic modelling of free
  water-surface constructed storm water wetlands using a finite volume technique.
  Environ. Technol. 36, 2532-2547.

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723	Figure captions
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725	
726	Figure 1. Location of the sampling points in photographs taken by a drone (5 November
727	2018) of the two-constructed wetlands: a succession of three ponds (A) and a ditch (B)
728	
729	Figure 2. Tracer breakthrough curves and cumulative normalized tracer concentrations
730	$(F(t) = \sum E(t) x dt)$ under various flow rates (HF: high flow, MF: mean flow, LF : low flow)
731	for both wetlands (pond and ditch)
732	
733	Figure 3. Spatial distribution of bromide concentration versus time under various flow rates
734	(LF: low flow, MF: mean flow) in the second pond and ditch
735	
736	Figure 4. Electrical conductivity ( $\mu$ S/cm) in the inlet, outlet, main channel (MC) and isolated
737	area (IA) zones under distinct flow rates (HF: high flow, LF: low flow, MF: mean flow and no
738	flow) for the pond and ditch
739	
740	<b>Figure 5.</b> Pesticide concentrations ( $\mu$ g/L) in the inlet, outlet, main channel (MC) and isolated
741	area (IA) zones under distinct flow rates (HF: high flow, LF: low flow, MF: mean flow and no
742	flow) for the pond and ditch
743	
744	Figure 6. Spatial distribution of sedimentation rate within the pond and the ditch (MC: main
745	channel, border, IA: isolated area) for the different sediment traps (numbered T1 to T9)
746	

- **Figure 7.** Pesticide concentrations ( $\mu$ g/kg) in sediments collected at the end of the 2016/2017
- 748 drainage season for pesticide entering CW by dissolved phase (EPX: epoxyconazole, CYP:
- cyproconazole, MCZ: metconazole) and by particulate phase (DMT: dimetachlor)

750	Table captions
751	
752	Table 1. Meteorological, hydrological and agricultural datas characterizing the two studied
753	constructed wetlands
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756	under various flow rates for the pond and ditch
757	
758	<b>Table 3.</b> Transport parameters derived from the Residence Time Distribution analysis for the
759	pond and ditch under distinct flow rates
760	

#### **Figure captions**

**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)

**Figure 2.** Tracer breakthrough curves and cumulative normalized tracer concentrations  $(F(t) = \sum E(t) x dt)$  under various flow rates (HF: high flow, MF: mean flow, LF : low flow) for both wetlands (pond and ditch)

**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 ( $\mu$ S/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

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## **Table captions**

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

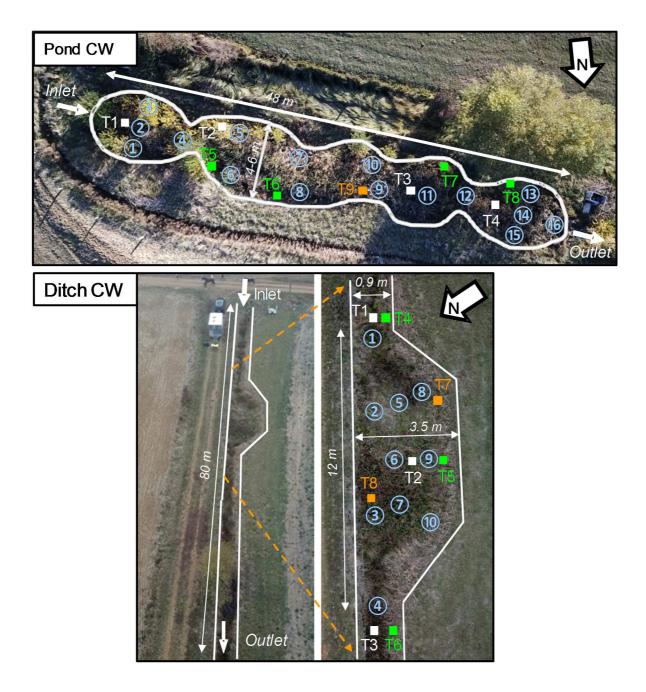
**Table 2.** Tracer experiment parameters and hydraulic characteristics of the pond and ditch

 under various flow rates for the pond and ditch

**Table 3.** Transport parameters derived from the Residence Time Distribution analysis for the

 pond and ditch under distinct flow rates

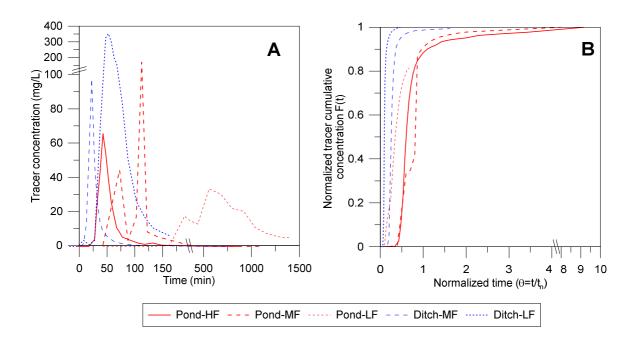
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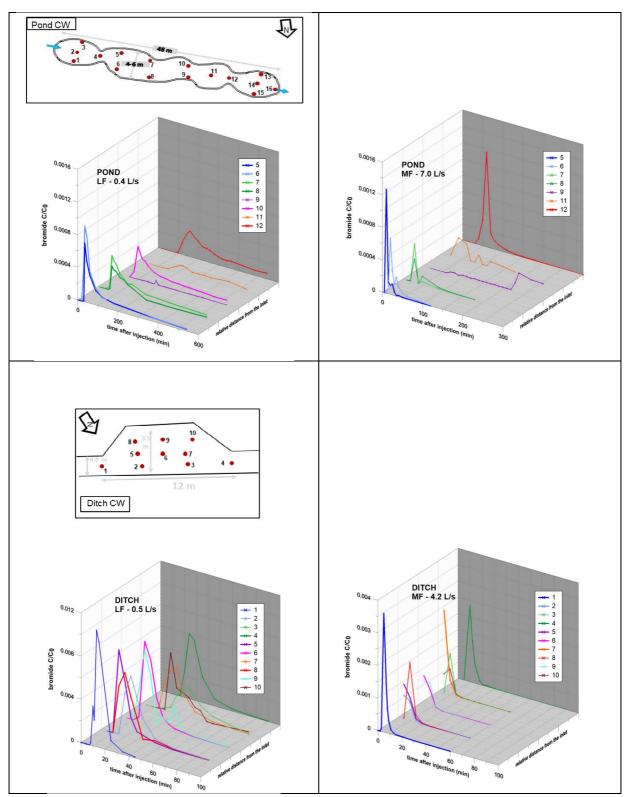
Blue numbered circles correspond to the manual water sampling during the bromide tracing.

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

**Figure 2.** Tracer breakthrough curves and cumulative normalized tracer concentrations  $(F(t) = \sum E(t) x dt)$  under various flow rates (HF: high flow, MF: mean flow, LF : low flow) for both wetlands (pond and ditch)

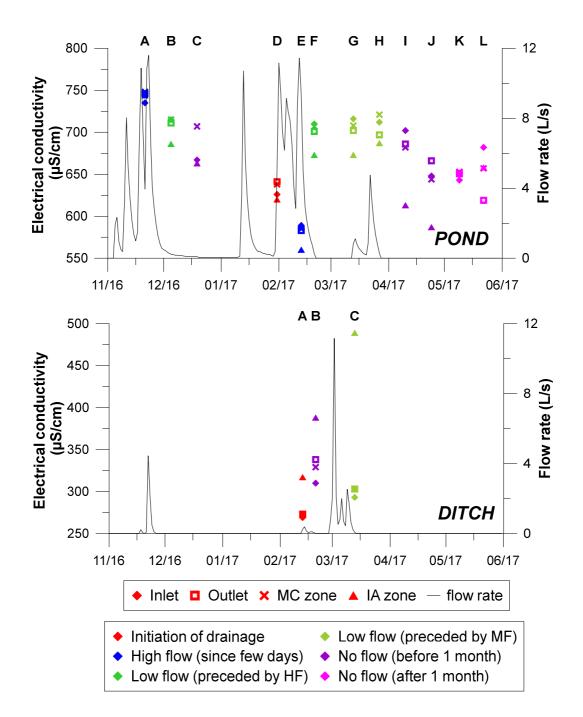


**Figure 3.** Spatial distribution of bromide concentration versus time under various flow rates (LF: low flow, MF: mean flow) in the second pond and ditch



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

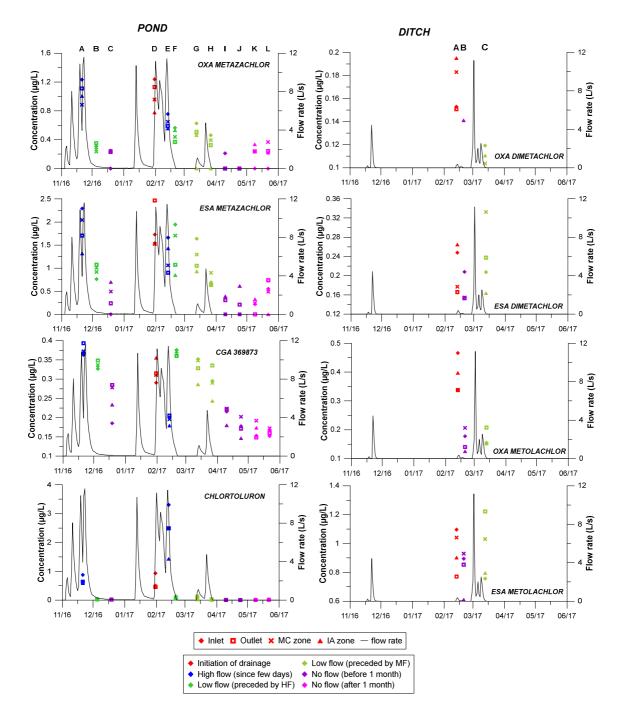
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Each letter (from A to L) corresponds to one sampling date.

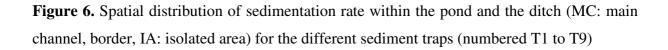
For the pond, the MC zone was collected in point 10, and the IA zone was collected in point 9. For the ditch, the MC zone was collected in point 6, and the IA zone was collected in point 3 (Figure 3).

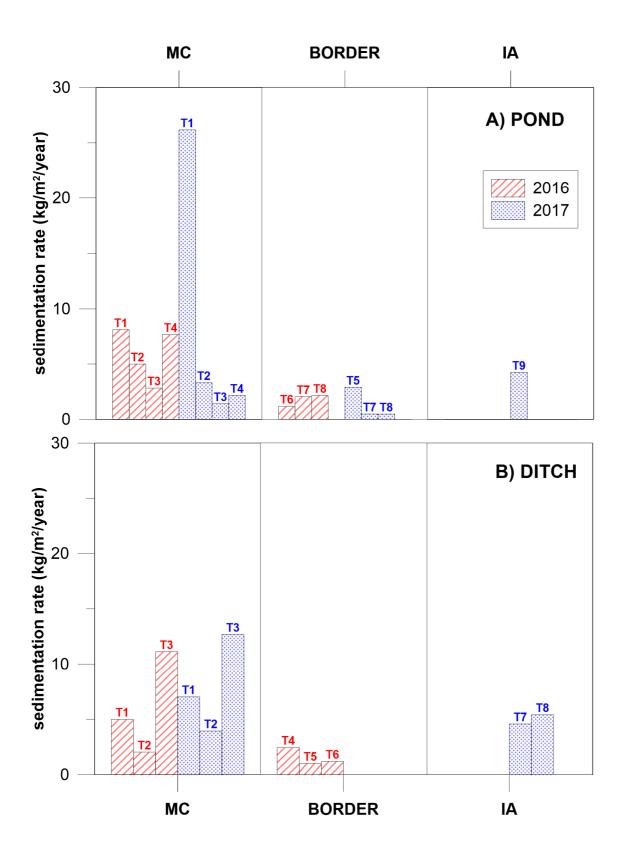
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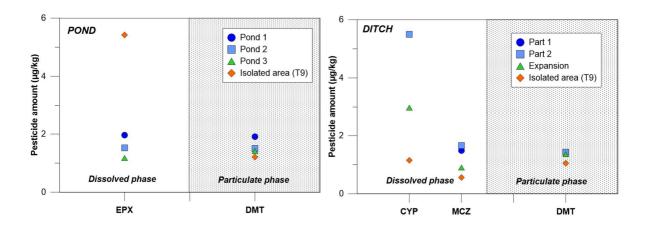
Each letter (from A to L) corresponds to one sampling date.

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 7.** Pesticide concentrations ( $\mu$ g/kg) in sediments collected at the end of the 2016/2017 drainage season for pesticide entering CW by dissolved phase (EPX: epoxyconazole, CYP: cyproconazole, MCZ: metconazole) and by particulate phase (DMT: dimetachlor)



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

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

\* 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) Sampling time**	15 7	10 5	10 9	5 4	5
(step 1) (h) Total sampling period*** (step 1 + step 2) (h)	48	48	96	48	8 120
Restitution after sampling time (%)	77	111	23	47	30
Restitution after total sampling period (%)	77	111	104	97	72
Mean flow rate (L/s) Water depth (m)**** Volume of wetland (m <sup>3</sup> )	13.0 ± 0.4 0.18/0.34/0.48 83	8.0 ± 0.3 0.08/0.25/0.35 63	0.6 ± 0.2 0.05/0.20/0.31 55	4.0 ± 0.9 0.15/0.10/0.35 38	0.34 ± 0.02 0.10/0.05/0.21 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  $\mu$ g/L)

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

	t <sub>n</sub> (h)	t <sub>mean</sub> (h)	$t_{\theta}=e_v$	Ν	λ	t <sub>10</sub> /t <sub>n</sub>	t90/t10	Pe	V <sub>mean</sub> (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

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



