

## Process formulations and controlling factors of pesticide dissipation in artificial ponds: A critical review

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## 1 List of abbreviations

Abbreviation	Description			
TSS	Total suspended solids			
DP	Dissolved pesticides			
PP	Particulate pesticides			
OM	Organic matter			
OC	Organic carbon			
HRT	Hydraulic residential time			
DOC	Dissolved organic carbon			
POC	Particulate organic carbon			
Re	Reynolds number			
vp	Vapor pressure			
FWS	Free water surface			
OECD	Organization for Economic Co-operation and Development			
PPDB	Pesticide Properties			
NER	Non-extractable residue			
SET	Settling			
RES	Resuspension			
VOL	Volatilization			
SOR	Sorption			
BIO	Biotransformation			
PHO	Photolysis			
HYD	Hydrolysis			

Process formulations and controlling factors of pesticide dissipation in artificial ponds: a critical review Aya Bahi<sup>a\*</sup>, Sabine Sauvage<sup>b</sup>, Sylvain Payraudeau<sup>c</sup>, Gwenaël Imfeld<sup>c</sup>, José-Miguel Sánchez-Pérez<sup>b</sup>, Betty Chaumet<sup>b</sup>, Julien Tournebize<sup>a\*</sup>

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### 16 Graphical abstract:



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### 19 Abstract

Pesticides are a non-point source of pollution affecting the quality of drinking water supplies 20 and aquatic environments. Many facilities are set up to reduce the transfer of pesticides from 21 agricultural parcels into the environment, preventing their input into water bodies. Artificial 22 ponds collecting runoff and erosion fluxes offer a complementary tool to mitigate pesticide 23 transfer. Ponds are free-water surface-constructed wetlands, rarely dried out and not 24 25 exceeding two meters in depth. Their main compartments include a water column, a sediment layer, living organisms, and suspended particles. The dissipation potential of ponds is due to a 26 combination of physical, chemical, and biological processes that pesticides undergo in an 27 interplay between different pond compartments. Although many studies on the dissipation 28 potential of ponds focus on nitrates and suspended sediments, very little is known about the 29 behavior of pesticides. Also, most studies evaluate a process individually without 30 emphasizing its eventual interaction with other processes. Few papers address and compare 31 mathematical formulations of pesticide transfer and transformation processes for artificial 32 pond modeling. In this review, we investigate the interactions and contribution of multiple 33 34 processes to artificial pond dissipation function by comparing their rates evaluated at different scales. We also discuss the mathematical formulations of processes and their relationship with 35 pesticide properties. Our evaluation suggests that quantifying the contribution of each process 36 to pesticide dissipation in artificial ponds is a major tool for hierarchizing dissipation 37 38 processes. We believe that quantification and hierarchization may improve the overall artificial pond efficiency estimation. We anticipate this work to be the basis for developing a 39 process-based model of pesticide fate in artificial ponds. The model will be particularly 40 helpful in setting up the dimensioning criteria to design performant and efficient ponds to 41 mitigate pesticide transfer into the environment. 42

#### 43 Keywords:

44 Artificial pond; pesticide; dissipation; process; model, review.

## 46 Highlights:

47 48	•	Identification and formalisms of dissipation processes of pesticides in artificial ponds
49 50	•	Sorption as a key process for lowly soluble and hydrophobic pesticide dissipation
51 52	•	Biotransformation enhanced in water-substrate interfaces favoring microbial activity
53 54	•	Volatilization and hydrolysis can be mostly neglected
55 56	•	Processes interplay contributes more significantly to the dissipation of pesticides
57 58 59	•	Added value of descriptive process-based model of pesticide behavior in artificial ponds
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#### 96 **1.1 Wetlands and artificial ponds**

In agriculture, various pests (e.g., weeds, insects, rodents, fungi, molds.) can significantly 97 deteriorate the quantity and quality of agricultural products. In order to protect agricultural 98 production, chemicals called "pesticides" are commonly used. Pesticides cover many 99 compounds, including insecticides, fungicides, herbicides, rodenticides, molluscicides, 100 nematicides, plant growth regulators, and others (Aktar et al., 2009). Due to their toxicity, 101 pesticides represent a non-point source of pollution for the ecosystem and affect the quality of 102 103 drinking water supplies and aquatic environments. Material solutions can be implemented as a 104 complementary tool to safeguard water resources quality and mitigate pesticide input into water bodies, such as edge-of-field and riparian buffer strips, vegetated ditches, wetlands, and 105 artificial ponds (Vymazal et al., 2015). In this paper, we will focus on constructed wetlands, 106 especially artificial ponds, since they have the advantages of needing minimal operations, i.e., 107 being inexpensive to operate and construct and providing wildlife habitat (Sudarsan et al., 108 2021). A neat definition of wetlands and ponds and a description of their different types can 109 be found in (Kadlec et al., 2008). 110

Artificial ponds are free water surface constructed wetlands, often kept wet and not exceeding 111 2m depth (Z. Zhang et al., 2021), and they serve different purposes. Artificial ponds can be 112 used as detention ponds to store water for irrigation purposes (Chaumet et al., 2022; 113 Tournebize et al., 2015) or stormwater ponds to prevent flooding (Maillard et al., 2012). 114 115 Artificial ponds are also used as complementary tools to treat contaminated agricultural water (Tournebize et al., 2017). These artificial ponds intercept agricultural water through runoff or 116 subsurface drainage from cultivated agricultural plots. Artificial ponds are constructed upon 117 118 an impermeable layer of sediments. The main artificial pond compartments are a water column, a sediment layer, living organisms (i.e., vegetation and microorganisms), and 119 suspended particles. Since the late '80s, artificial ponds have been generally applied to treat 120 various wastewaters, including agricultural water (Chouinard et al., 2014; Grinham et al., 121 2018; Wang et al., 2018; Zamora et al., 2019; Zhuang et al., 2019). It was widely reported that 122 artificial ponds are able to reduce the transfer of chemicals (pesticides, organics, and 123 inorganics pollutants), physical components (solid suspended particulates), and biological 124 elements (bacteria) to natural water resources and preserve their quality (Kasak et al., 2018; 125 Zheng et al., 2018). For example, artificial ponds had an important removal efficiency for 126 organic matter, solids, and nitrogen up to 90% (de Oliveira et al., 2020; Tournebize et al., 127 128 2015). For pesticides, artificial pond efficiency can reach 97% for the organochlorine chemical group (Matamoros et al., 2006; Rose et al., 2006), 96% for the strobilurin/strobin 129 group, and 84% for pyrethroids (Vymazal et al., 2015). 130

In that matter, significant research effort has been dedicated to understanding the fate of pesticides in artificial ponds and their link to the pond and pesticide properties (Bloomfield et al., 2006). In artificial ponds, pesticides are dissolved in water, attached to suspended particles, and sorbed on sediments and vegetation. The dissipation potential of artificial ponds results from a combination of transport, transfer, and transformation processes of pesticides. Transport processes carry pesticides following a water flow. Transfer processes allow the pesticide molecule to move from one phase to another (i.e., dissolved phase to particulate

- 138 phase or dissolved phase to gas phase), and transformation degrades and modifies the original
- 139 chemical structure of pesticides.
- 140 Most studies could not distinguish the extent of removal processes because they depend on
- 141 each other (Gregoire et al., 2009; Liu et al., 2019; Sahin et al., 2020) and thus could not model
- 142 their impact on pesticide behavior. Additionally, previous reviews and studies (Stehle et al.,
- 143 2011; Vymazal et al., 2015) focused on the efficiency of artificial ponds to remove pesticides 144 and the ecological risk assessment of pesticides (Haith, 2010). However, they did not detail 145 the processes behind pesticide dissipation, and they could not identify a direct link between 146 ponds' efficiency and the pesticides' properties. Therefore, this paper investigates the 147 relationship between dissipation processes and the main characteristics of pesticides in 148 artificial ponds. Contrarily to the studies reviewed in this paper, this survey will evaluate 149 plentiful pesticides with contrasting physicochemical properties and present the mathematical
  - 150 formulations of multiple processes evaluated from lab-scale to field-scale. These formulations
  - 151 are useful for modeling that help to estimate artificial pond efficiency and to optimize their
  - 152 implantation in agricultural areas.

#### 153 **1.2 Processes governing the fate of pesticides in artificial ponds**

The dissipation of pesticides in artificial ponds results from the synergy between biophysicochemical processes detailed thereafter. Several studies have proved the possibility of quantifying this dissipation and predicting the fate of pesticides by a black-box model (Braschi et al., 2022). However, a black box approach does not explicit the origin of pesticide dissipation and does not detail the contribution of each process since it only considers a single dissipation rate  $k_{diss}$  (d<sup>-1</sup>) (Yuan et al., 2020).

- In this review, we will describe and present different estimation methods of processes behind 160 pesticide dissipation in artificial ponds. The form under which pesticides are introduced to the 161 artificial pond depends on how agricultural water is drained into the artificial pond. If the 162 watershed is drained with significant subsurface flow, pesticides are more likely to be 163 dissolved rather than particulate (Braschi et al., 2022; Le Cor et al., 2021). In contrast, 164 pesticides can be present in dissolved and particulate phases if runoff occurs. Gramlich et al. 165 (2018) assumed that subsurface drainage reduces erosion risk, while runoff may increase it. 166 167 Dissolved Pesticides (DP) in water bodies are widely studied in the literature, whereas few studies focus on Particulate Pesticides (PP) (Climent et al., 2019). PP are transported within 168 the artificial pond along with TSS following the water flow. According to the hydraulic 169 regime of the artificial pond, PP can settle on the sediment bed or be suspended back to the 170 171 water. In contrast, DP can be bound to the solid surfaces available in the artificial pond through sorption. Sorbed DP can be released back into water through desorption. DP can also 172 be transported to the atmosphere when volatilized or uptakes by the plants growing in the 173 artificial pond. On the other hand, pesticides can be a subject of transformation processes, 174 whose prevailing drivers are microorganisms, solar radiation, and hydrolysis. 175
- Processes involved in pesticides dissipation in artificial ponds depend on many factors such as the characteristics of the soil (i.e., Organic matter (OM), organic carbon (OC), and clay content), water physicochemical properties (pH, temperature (T) and redox conditions), vegetation, and the hydraulic conditions of the artificial pond (Papaevangelou et al., 2017; Vymazal et al., 2015). The mitigation of pesticides in artificial ponds also depends on the pesticide's physicochemical properties. The main physicochemical properties of a pesticide include mobility, hydrophobicity, the solubility in water (S), and the pesticide half-life (DT<sub>50</sub>)

- the time required for the dissipation of 50% of the concerned substance (Gregoire et al., 2009).
- The properties of pesticides and the processes behind their dissipation in artificial ponds willbe detailed afterward.

#### **187 1.3 Hydraulics of artificial ponds**

- 188 The hydraulic performance is a key factor controlling the pesticide dissipation function of a
- artificial pond. The hydraulic performance of artificial ponds includes lowering peak flow and
- 190 limiting sediment export from agricultural parcels to natural water bodies (Passeport et al.,
- 2010; Tournebize et al., 2013). Artificial ponds hydraulic parameters include (i) The hydro
  period (Bojcevska et al., 2007; Convertino et al., 2013; Liu et al., 2019; Prochaska et al.,
- 2007) and (ii) The hydraulic residence time (HRT) of the water within the artificial pond (J.
  Holland et al., 2004; Kjellin et al., 2007).
- 195 The hydraulic performance of artificial ponds depends on design parameters such as depth,
- the layout of the inlet and outlet, and plant spacing. In this subsection, we will describe the impact of design parameters on the hydraulic performance of artificial ponds.
- Multi tracer experiments showed that shallow water depth was an essential factor enhancing sorption and that pesticide load reduction was more significant in shallow artificial ponds than in deep ones (Lange et al., 2011). A low water depth allows a uniform fluid distribution compared to higher depths. The uniformity of the fluid flow decreases the hydraulic dead zones and increases the effective volume, which is the artificial pond volume used for pesticides dissipation (Rayen et al., 2019).
- Globally, an artificial pond volume can be divided into three hydraulic zones (C. J. Martinez
  et al., 2003; Werner et al., 2000):
- 1. The main channel with the preferential flow.
- 207 2. The mixing zone is a temporary storage zone showing exchanges with the main208 channel.
- 3. The dead zone is more isolated from the main channel than the mixing zone.
- Tracing studies showed that water is transported mainly by convection in the main channel, 210 while it is transported by dispersion in the isolated zones (mixed and dead zones). The HRT in 211 isolated zones is longer than in the main channel. Thus, isolated zones could enhance 212 213 dissipation processes such as sorption, settling, and degradation (Gaullier et al., 2018). The main channel is where short circuits in the water flow can occur, causing the transport of 214 water from the inlet to the outlet by preferential flow, which decreases the HRT and effective 215 216 volume of the pond (Vieira et al., 2018). Another controlling parameter of the artificial pond hydraulic performance is the inlet/outlet design. Shilton et al. (2003) reported that positioning 217 the outlet in an isolated zone from the main channel avoids short-circuiting issues and 218 maintains the maximum hydraulic performance of artificial ponds. In addition, vegetation 219 density slows down water velocity and increases the HRT (Gu et al., 2017). Increasing the 220 hydraulic residence time (HRT) increases the contact time between pesticides and pond 221 substrates, giving pesticides more time to be sorbed, settled, or degraded. 222
- A good hydraulic performance also guarantees an optimistic interception of agricultural water
   by catching the highest concentrations of pesticides (during the post-application period) in
   minimum water volumes through off/on stream artificial ponds (Passeport et al., 2013;
   Passeport et al., 2010).

Usually, the risk of transfer of a pesticide is evaluated by the FOCUS models to decide 228 whether to be authorized for use or not. However, since pesticides are still transferred to the 229 230 environment after their application and their concentration in water resources than the RAC 231 (regulatory acceptable concentrations) (Gassmann et al., 2015; Halbach et al., 2021; Tang et al., 2012), this theoretical study can be improved. Therefore, this work is based on a detailed 232 bibliographic analysis to present the required knowledge to understand the behavior of 233 pesticides after being applied on agricultural plots and intercepted by artificial ponds. This 234 235 knowledge is useful for developing a simple and robust conceptual model to simulate the fate of pesticides in artificial ponds and then at the catchment scale, like the models developed for 236 nutrients (Hantush et al., 2013; Kalin et al., 2017; Walker Jr et al., 2011). Modeling can also 237 improve the understanding and hierarchization of the dissipation process and optimize its 238 implantation in agricultural areas. Therefore, the next section will describe the key processes 239 240 behind pesticide dissipation in artificial ponds and their mathematical formulations used in modeling. 241

#### 242 2. Description and modeling of dissipation processes in artificial ponds

Modeling is an efficient, comprehensive tool for assessing and setting up facilities to treat 243 contaminated environments (Warren et al., 2002). There are mainly two types of models that 244 describe pesticide fate in the environment, (i) Physical 3D and 2D models that simulate the 245 hydraulic performance of wetlands by considering water velocity profiles and the vegetation 246 impact of the flow (Carleton et al., 2010; Luo et al., 2016; Christopher J. Martinez et al., 247 2003; Tsavdaris et al., 2013). (ii) Conceptual models that simulate the biogeochemistry and 248 249 the dissipation performance of the wetland for a large-scale application (Gobas et al., 2018; Willkommen et al., 2018). The asset of this paragraph is to identify and describe processes 250 behind pesticide dissipation in artificial ponds, along with their mathematical formulations 251 252 established as part of conceptual models.

253 Our literature investigation showed that researchers had widely discussed the fate of pesticides in artificial ponds. Although, most studies are generally limited to one pesticide or 254 one specific process evaluation and are rarely supported by mathematical formulae. However, 255 we assume that mathematical formulations allow the integration of processes into a 256 257 computational model to quantify and predict the fate of contaminants in artificial ponds. The originality of this review lies in the description of the main processes influencing the behavior 258 of multiple pesticides in artificial ponds, namely transport, sorption, and transformation 259 processes. The evaluation and formulation of these processes are necessary to develop 260 261 predictive models for pesticides dissipation in artificial ponds (Papaevangelou et al., 2017; Saaristo et al., 2018). In this section, we will investigate the behavior of multiple pesticides 262 with contrasting physicochemical proprieties and describe different methods currently 263 employed to evaluate and formulate the processes controlling dissipation in artificial ponds. 264

#### 265 **2.1 Transport of pesticides**

Pesticides reaching artificial ponds can be dissolved in water or associated with dissolved organic carbon (DOC). They can also be bound to the organic fraction of suspended matter (i.e., particulate organic carbon (POC)), featuring pesticides in a particulate form. PP are carried along with suspended matter throughout the pond artificial pond due to water movements. PP can be deposited on the sediment bed due to settling and released back to water through resuspension. Settling and resuspension are transport processes that strongly depend on the particle size and the strength of the water flow in pond artificial ponds.

- 273 Pesticides can also be the subject of advection, dispersion, and diffusion processes within the
- 274 water column and pore water of the sediment layer. According to the Hjulstrom curve, the
- water velocity in the artificial pond can determine which transport process is prevailing
- 276 (Hjulstrom, 1935).

#### 277 **2.1.1 Settling**

Settling is a physical transport process through which suspended particles in water settle on
the sediment bed of artificial ponds. Settling depends on the particle size of pesticides, water
velocity and turbulence, temperature, and water column depth (Kadlec et al., 2008).

281 Settling has been efficient in the water-quality improvement function of artificial ponds, 282 especially in lower flows, since suspended particles, on which pesticides may be attached, can leave the water column while settling on the sediment bed (O'Geen et al., 2010). Settling is 283 enhanced when vegetation covers a significant surface of the artificial pond; emergent 284 macrophytes slow down water flow and amplify settling (Vymazal, 2013). In addition, stems 285 and leaves in the water column obstruct water flow and dissipate the energy required to 286 support particle suspension (Schmid et al., 2005). Rose et al. (2008) pond (0.021 h<sup>-1</sup>). A small 287 water depth was also reported that the settling rate in a vegetated artificial pond (0.042  $h^{-1}$ ) 288 was double the rate estimated in a non-vegetated artificial to promote the settling process; it 289 fosters plant growth and shortens the settling distance for particles (Lange et al., 2011). It is 290 291 valid for water depths between 20 cm and 50 cm (Braskerud, 2002). Pesticides associated with fine suspended particles may hardly be retained in ponds since fine particles (clay and 292 silts) are highly transported across preferential pathways where the HRT is low (see section 293 1.3) (Maynard, 2009). The settling of PP is more likely to occur in hydraulically isolated 294 zones with lower water flow and higher HRT (Gaullier et al., 2020; Passeport et al., 2010). 295 Ponds with the highest settling rate are the ones receiving agricultural surface runoff (Fiener 296 297 et al., 2003; Zhang et al., 2011), where the intercepted agricultural water is heavily loaded 298 with coarser (>200 µm) particles from the fields (Li et al., 2017). It is due to the higher TSS load from erosion that is less available in artificial ponds collecting subsurface drainage water 299 (Koskiaho, 2003; Maillard et al., 2011). It was also suggested that coarse particles settle 300 before the water is distributed across pond compartments, unlike fine particles requiring a 301 longer time to settle. As a result, fine particles become more concentrated downstream of the 302 pond (Gan et al., 2005) because gravity induces the settling of heavy particles (>36 µm) (i.e., 303 sand) more than lighter particles (<2 µm) (i.e., clay and OM) (Fiener et al., 2003). Several 304 studies suggested that a large proportion of highly hydrophobic organic substances in artificial 305 ponds were retained by settling pesticide-laden solids (sorbed on suspended solids) (Luo et 306 al., 2009; Matamoros et al., 2006; Rose et al., 2008). Therefore, settling may not be sufficient 307 to trap pesticides with a stronger affinity to fine suspended particles in ponds. Consequently, a 308 higher HRT and vegetation are required to increase the settling of fine PP (Budd et al., 2009, 309 310 2011; Fiener et al., 2003).

Settling was commonly integrated with an accumulation rate expressed empirically in pesticide dissipation models. The empirical formulations of settling rates can be found in Table A.1.The first formulae (i) estimates the settling rate  $v_s$  according to Stokes equation for laminar conditions (Reynolds number Re <500). Fiener et al. (2003) computed the settling rates of particles of different sizes in a vegetated wetland. It was observed that particles >63  $\mu$ m (i.e., sand) were fully sedimented, whereas particles 2  $\mu$ m< x <63  $\mu$ m (i.e., silt) were moderately sedimented (up to 26%). In contrast, only 4% of fine particles <2  $\mu$ m (i.e., clay)

settled on the sediment bed. It was also noticed that settling primarily occurred on the side-318 slopes with small Re. The second formulation (ii) suggested by Kadlec et al. (2008) allows 319 320 calculating the settling rate in both laminar and turbulent flow based on a drag coefficient  $C_{D}$ 321 that depends on Re. Formula (ii) assumes that settling results from density difference between suspended particles and water, so it expresses the rate of a single and isolated spherical 322 particle. The limit of the first (i) and second method (ii) are the required parameters since in 323 artificial ponds, neither the density nor the particle size is known. In addition, particles are not 324 325 spheres or discs and can agglomerate to a larger size. The formula (iii) estimates the settling rate of suspended particles in wetlands (Hawley et al., 2014). This formulation required more 326 parameters such as the water kinematic viscosity since it is adapted for also non-spherical 327 particles. However, it was often applied to large size particles. 328

Overall, the formula (i) could be sufficient and easy to use for a simple simulation of PP 329 settling in laminar flows. If the flow is turbulent with a known Re, formula (ii) would be more 330 331 suitable for its accuracy. For formula (ii), particle sizes are often approximated according to their nature (i.e., clay, silt, sand, and OM). Otherwise, the settling rate could be calibrated if 332 333 the required data is available. But still, the majority of settling studies are done on nutrients, 334 and little is known about pesticides (Hantush et al., 2013; Kalin et al., 2017; Walker Jr et al., 2011). Regarding behavior, settling seems to be a key process of pesticide accumulation in 335 336 pond artificial ponds alimented by surface runoff in erosive areas, especially for hydrophobic 337 pesticides and coarse PP.

#### 338 2.1.2 Resuspension

Resuspension is the opposite process of settling, through which PP are transported from the sediment bed to water. Resuspension depends mainly on the water flow and the water depth in artificial ponds.

Resuspension is likely to occur when water turbulence is important (Siobhan Fennessy et al., 342 1994), and high water flow can remobilize settled PP back to the water (Collins, 2004; 343 Jamieson et al., 2005; Vallet, 2011; Wilkes et al., 2009). It was proved that resuspension was 344 highly affected by the type and density of vegetation in artificial ponds (Liu et al., 2019; 345 Schulz et al., 2001). Braskerud (2001) presumed that an increase of 30% in a vegetative 346 347 cover, initially less than 20%, could reduce resuspension rates from 40% up to 100%. Rose et al. (2008) showed that the resuspension rate was divided in half by switching to a vegetated 348 artificial pond. Some studies suggested that deeper FWS wetlands enhanced settling and 349 burial rather than resuspension (Brueske et al., 1994; Budd et al., 2011). Resuspension is 350 likely to occur in the main channel where the water velocity is fast (see section 1.3) (Gaullier 351 et al., 2020) and is mainly driven by wave action generated by the wind (Hawley et al., 2014). 352 Other agitation factors may be responsible for particle resuspension, such as wildlife 353 movements within the artificial pond (i.e., bioturbation), although quantitative studies on this 354 topic remain scarce. Resuspension was significantly less considered in the literature than 355 settling. However, resuspension occurred with a slow rate of remobilization ( $v_r \sim 10^{-6}$  mm/s) 356 (Hawley et al., 2014; Sharifi et al., 2013), while Rijn (1984) suggested that the resuspension 357 rate  $v_r$  reached the quarter of the settling rate  $v_s$ . 358

Globally, significantly lower concentrations of PP measured at the outlet of wetlands than at the inlet suggests that the contribution of resuspension in pesticides behavior might be negligible (Budd et al., 2009; Cryder et al., 2021; Supowit et al., 2016), also resuspension is more dominant in systems with stronger water flows (i.e., rivers) rather than artificial ponds. In addition, high water flow events are usually short and have a long return period, whichdecreases the occurrence of resuspension.

#### 365 **2.1.3 Advection, dispersion and diffusion**

Among the processes behind pesticide transport within the artificial pond are advection, 366 dispersion including diffusion. Advection carries pesticides in the same direction as the water 367 flow. Dispersion results from heterogeneities in flow patterns and is a macroscopic process. In 368 369 contrast, diffusion is a microscopic movement of pesticide molecules due to a random molecular motion (i.e., Brownian motion) (Hamdi, 2007). Dispersion and diffusion processes 370 result from a concentration gradient of pesticides in artificial pond water and carry pesticides 371 from highly concentrated areas to low concentrations. Advection, dispersion, and diffusion 372 allow the homogenization of DP concentrations in the artificial pond. 373

374 Gaullier et al. (2019) showed that water transport is mainly governed by advection at a high flow rate. While at low flow rates, both water transport and pesticide mitigation are governed 375 by hydrodynamic dispersion, including molecular diffusion, resulting in a longer contact time 376 between pesticides and substrate. Without agitation, pesticide transport is only influenced by 377 diffusion, while agitation enhances advection and dispersion (Gaullier et al., 2018). Thus, 378 advection/dispersion is more important in the main channel, while diffusion is more likely to 379 occur in the dead zones (section 1.3). Moreover, diffusion is slower in the sediment layer pore 380 water because of its tortuosity and the increased length of the water pathway between pores 381 (Beulke et al., 2004). When the hydraulic regime is laminar, the diffusion is on the molecular 382 scale, with a thermal diffusion of the order  $1.4 \times 10^{-7} \text{m}^2 \text{s}^{-1}$  in pure water. In river water 383 systems, the water is always turbulent. Thus, the effective diffusion is several orders of 384 magnitude greater. Still, the given thermal diffusion is considered in wetlands, where water 385 disperses horizontally, and the flow rate is lower than in rivers (Damalas et al., 2011). For 386 pesticide molecules, the diffusion coefficients usually range from  $10^{-11}$  to  $10^{-10}$  m<sup>2</sup>/s 387 (Kipkoech, 2019). Dispersion, including diffusion, also depend on the internal structure of the 388 artificial pond. For instance, the dispersion was proved to be greater in artificial ponds with a 389 larger width (Gaullier et al., 2019), while macrophytes enhance diffusion and the hydraulic 390 performance of the artificial pond (J. F. Holland et al., 2004). 391

In a pesticide transport equation, advection is expressed by the term  $-v \frac{\partial C_w}{\partial x}$  and dispersion is expressed by  $D_L \frac{\partial^2 C_W}{\partial x^2}$ . Where v [L.T<sup>-1</sup>] is the water velocity;  $C_w$  [M.L<sup>-3</sup>] is the pesticide concentration in water;  $D_L$  [L<sup>2</sup>.T<sup>-1</sup>] is the hydrodynamic dispersion coefficient; with  $D_L=D_e+\alpha_L v$ , where  $D_e$  the effective diffusion coefficient, and  $\alpha_L$ [L] the dispersivity.

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#### 397 2.2 Transfer of pesticides

Once pesticides reach the artificial pond, they are distributed among water, sediments, TSS, and vegetation are transferred among artificial pond compartments. DP can be exchanged between the water column and the solid compartments due to "Sorption" and the atmosphere during "Volatilization". Also, DP can become PP when sorbed to TSS.

#### 402 **2.2.1 Sorption process**

Sorption was commonly reported as an important process in the fate of pesticides in artificial ponds (Cryder et al., 2021; Fernández-Pascual et al., 2020; Hand et al., 2001). In the following two subsections, we will first present the sorption theory and analyze study cases of pesticide sorption in artificial ponds. This review will focus on sorption information directly related to pesticides' fate in artificial ponds; more detailed knowledge of sorption can be found in the literature (Huang et al., 2003; M. McBride, 1994; Pignatello, 1989; Sposito, 2008)

#### 410 **2.2.1.1 Sorption theory**

Physically, *sorption* refers to all exchange processes between a dissolved substance and solid matter in a solution. Among these exchanges, adsorption and desorption remain the most studied for pesticide fate in the environment. Adsorption is a physical transfer process of retaining dissolved substances in water on solid surfaces. The dissolved substances are the "sorbate," and the solid surface to which they are bound is called "sorbent" or "substrate." *Desorption* is when the substrate releases the sorbate and returns to water (Sposito, 2008). From now on, the term "sorption" will be used to refer to adsorption plus desorption.

- Most of the sorption studies are conducted in the laboratory and adapted from OECD 106 418 guidelines for individual molecules, in which sorption experiments are performed using a 419 batch equilibration technique (OCDE, 2000). The retention and release of the sorbate on a 420 substrate at various concentrations and a constant temperature are described by a curve called 421 "adsorption isotherm" and "desorption isotherm," respectively. The isotherms represent the 422 relationship  $C_{se} = f(C_{we})$  during adsorption and desorption equilibrium, where  $C_{se} (\mu g. g^{-1})$  and 423  $C_{we}$  (µg.L<sup>-1</sup>) are the sorbate concentration in the substrate and the sorbate concentration in 424 425 the solution at the equilibrium state, respectively.
- Based on the thermodynamic equilibria theory that assumes complete reversibility of the
  chemical reactions, the adsorption and desorption isotherms should be the same (Strawn et al.,
  1999). However, sorption mechanisms are driven by different kinetically controlled reactions
  or physical phenomena with a large variability of reaction times going from seconds to years,
  emphasizing the kinetic character of sorption (Beulke et al., 2004; Caceres-Jensen et al., 2019;
  Cara et al., 2021; Kaur et al., 2018; Mamy et al., 2007; Sparks, 2000; Villaverde et al., 2009;
  Wu et al., 2017).
- A difference between adsorption and desorption kinetic rates to reach the equilibrium is 433 translated by a mismatch between the adsorption and desorption isotherms curves. This 434 mismatch is called "pseudo-hysteresis" or 'kinetic hysteresis" (Strawn et al., 1999), also 435 referred to as an "apparent irreversibility" (Bladel et al., 1967; M. B. McBride, 1994). It is 436 important to clarify that the term "irreversibility" does not mean that the sorbate will not 437 desorb after its adsorption. Still, it will take a long time to reach the equilibrium state 438 439 (Limousin et al., 2007). In other terms, hysteresis means that desorption requires a more 440 significant amount of energy than needed by adsorption (Bowman et al., 1985; Koskinen et al., 1979; Wu et al., 1988), which could be caused by experimental artifacts or transformation 441 of the sorbent (Pignatello et al., 1996). 442
- The evaluation of sorption requires the determination of its equilibrium and kinetic properties 443 (Douven et al., 2015). Sorption kinetics are studied with the most applied chemisorption 444 models: Pseudo-first-order (PFO), pseudo-second-order (PSO), and Elovich models (Azizian, 445 2004; Ho, 2006; Ho et al., 1998, 1999; Yuh-Shan, 2004), to describe the temporal evolution 446 of the sorbed amount of the sorbate. At the same time, sorption equilibrium is commonly 447 modeled by the Freundlich and Langmuir isotherm models (Azizian et al., 2018; Foo et al., 448 449 2010; Mckay, 1995). As the equilibrium of kinetic sorption is reached, isotherm models are 450 applied. The corresponding equations of kinetic and isotherm models can be found in Table 451 A.2.

#### 452 **2.2.1.2 Sorption of pesticides in artificial ponds**

In the case of artificial ponds, the sorbates are dissolved pesticides (DP), and substrates are 453 total suspended solids (TSS) with organic and inorganic compounds, sediments, and 454 vegetation (Gregoire et al., 2009; Sahin et al., 2020), which represent development support for 455 OM and biofilm. The Freundlich and the linear model are commonly used isotherm models to 456 describe pesticide sorption on artificial pond substrates (Liu et al., 2019; Takagi et al., 2012; 457 Watanabe et al., 2006; Zhang et al., 2018). Pesticide adsorption is widely described by the 458 adsorption coefficient normalized to substrate organic carbon content  $K_{\text{foc}}$  and  $K_{\text{oc}}$  for the 459 460 linear isotherm:

461 
$$K_{foc} = \frac{K_{fads}}{OC}$$
 (1)

462  $K_{oc} = K_d / OC$  (2)

463 Where OC (%) is the organic carbon content of the pond substrates,  $K_{fads}$  is the Freundlich 464 adsorption coefficient, and  $K_d$  is the distribution coefficient (Table A.2).

Vallée (2015) and Passeport et al. (2011b) studied the sorption of 12 pesticides with 465 contrasting physicochemical properties on pond substrates (i.e., sediments, vegetation, and 466 TSS). Sorption coefficients can be found in Table A.3. Based on the K<sub>fads</sub> values, 467 epoxiconazole was the highly adsorbed pesticide, followed by prochloraz. Epoxiconazole and 468 prochloraz have a  $K_{foc}$  range of 702-1962 mg<sup>1-n</sup><sub>f</sub>.L<sup>n</sup><sub>f</sub>.kg<sup>-1</sup> and 1222-8654mg<sup>1-n</sup><sub>f</sub>.L<sup>n</sup><sub>f</sub>.kg<sup>-1</sup>, 469 respectively (Lewis et al., 2016), which, according to the Soil Survey and Land Research 470 Centre (SSLRC) soil persistence classification system, means that they are lowly mobile 471 molecules (PSD, 2005). In contrast, the lowest sorption concerned isoproturon, with the 472 lowest K<sub>foc</sub> values 55-60 mg<sup>1-n</sup><sub>f</sub>.L<sup>n</sup><sub>f</sub>.kg<sup>-1</sup> (Vallée, 2015), followed by MCPA. The low 473 adsorption of MCPA could be due to its anionic form, inducing an electrostatic repulsion of 474 negatively charged particles (i.e., clay and OM), as supported by Thorstensen et al. (2001). 475 Likewise, Poissant et al. (2008) and Wu et al. (2004) reported that pesticides with higher  $K_{oc}$ 476 values ( $K_{oc} > 500 \text{ L.kg}^{-1}$ ) are most likely to be sorbed to pond solid particles, agreeing with 477 previous findings (Papp, 2009; Saripalli, 1997). The low solubility of epoxiconazole and 478 prochloraz also favored their retention on pond substrates. The literature widely reported that 479 low solubility enhances pesticide adsorption (Blachnio et al., 2020; Brusseau et al., 2019; Kah 480 et al., 2006). Sorption also depends on the hydrophobicity of the pesticide expressed by the 481 octanol-water partition coefficient Kow. Hijosa-Valsero et al. (2016) analyzed fifty-nine 482 compounds in water and sediment samples. They found that herbicides in the sediments had 483 an average S=194 mg.L<sup>-1</sup> and a log  $K_{ow} = 3.7$ , while herbicides in the water phase were highly 484 soluble  $\tilde{S} = 1395 \text{ mg.L}^{-1}$  with an average log  $K_{ow} = 2.24$ . These results support that lowly 485 soluble, and hydrophobic pesticides (log  $K_{ow} > 3$ ) are likely to be sorbed on pond sediments, 486 which agrees with O'Geen et al. (2010), that observed a 50% reduction in pesticide 487 concentration with log  $K_{ow} > 4.2$ . Likewise, Tang et al. (2017) found that adsorption rates of 488 hydrophobic pesticides were significantly higher on the artificial pond vegetation (5.52-8.84 489 g m-2 d-1) than hydrophilic pesticides (log  $K_{ow} < 3$ ). These results suggest that sorption may 490 be the primary driving process of removing hydrophobic pesticides from the artificial pond 491 water. 492

493 On the other hand, vegetation, biofilm, and the OM and clay content of the substrate have a 494 significant role in pesticide sorption in artificial ponds. Barchanska et al. (2019) observed that

the artificial pond remediation of pesticides due to adsorption on vegetation reached 30%. An

499 Olvera-Velona et al., 2008).

Passeport et al. (2011b) and Vallée (2015) observed higher K<sub>fads</sub> on vegetation than in 500 sediments (Table A.3), showing greater retention on OC-rich substrates. Moore et al. (2007) 501 502 and Sahin et al. (2020) also proved that diazinon preferentially sorbed on vegetation surfaces rather than sediments. In like manner, Rogers et al. (2009) showed that the lowly mobile 503 chlorpyrifos ( $K_{oc} = 5509 \text{ L.kg}^{-1}$  (Lewis et al., 2016)) adsorption was ten times higher on 504 vegetation than on sediments, and several other papers demonstrated that adsorption is more 505 dominant in OC-rich substrates, including vegetation (Guo et al., 2000; Mahabali et al., 2014; 506 507 Moore et al., 2007; Mugni et al., 2011). Biofilm was also proven to enhance adsorption for 508 certain pesticides (Agudelo et al., 2012; Beecraft et al., 2021).

- 509 Desorption was also evaluated and was reported to be less dominant in sediments with high
- clay and OC content, especially for lowly soluble pesticides (Gramlich et al., 2018; Olvera-
- 511 Velona et al., 2008; Passeport et al., 2011b; Song et al., 2021; Vallée, 2015). In comparison,
- 512 greater desorption was observed on some highly soluble pesticides (Olvera-Velona et al.,
- 513 2008). Hence, hysteresis was generally observed on OC and clay-rich substrates from which
- 514 hydrophobic and lowly soluble pesticides are hardly desorbed (Hand et al., 2001; Li et al.,
- 515 2003; Vagi et al., 2010).
- In addition, kinetic sorption rates showed that desorption was slower than adsorption for six 516 evaluated pesticides, except for picloram. The reviewed kinetic rates of adsorption and 517 518 desorption can be found in Table A.4. The picloram exception can be explained because its sorption was evaluated in lab conditions. Since, in the experimental sample, there was no 519 consideration of other processes that may compete with desorption (i.e., transformation). The 520 interaction between desorption and transformation was also observed by Sørensen et al. 521 522 (2006), noticing that slower desorption of MCPA (coincided with higher microbial 523 transformation. In fact, unlike laboratory-batch sorption observations, sorption and transformation processes co-occur under field conditions, favoring the occurrence of 524 hysteresis in the presence of other competitive processes like transformation and diffusion 525 into sediment layer micropores (Mamy et al., 2007; Paszko et al., 2016; Takagi et al., 2012; 526 527 Uchimiya et al., 2012). In contrast, advection/dispersion enhance sorption by facilitating the access of DP to the pond substrates (Gaullier et al., 2018). 528
- 529 Overall, we assume that both adsorption and desorption depend on the clay and OC content of 530 pond substrates and the properties of pesticides. Adsorption is more dominant for 531 hydrophobic, lowly mobile, and lowly soluble pesticides, and desorption hysteresis is more 532 accentuated in clayey and OC-rich pond substrates, especially for highly soluble pesticides.

#### 533 2.2.2 Volatilization

534 Volatilization is a process through which pesticides are transferred outside the pond, from the 535 water to the atmosphere. This non-degradative removal process strongly depends on the 536 pesticide molecule's vapor pressure.

537 There are two regimes controlling volatilization: the atmospherically controlled regime and 538 the regime controlled by water properties. Most pesticides (80-90%) belong to the 539 atmospherically controlled regime, where the gas exchange between the water and the

atmosphere is only sensitive to the parameterization of atmospheric turbulence, and the 540 majority of pesticides belong to it; therefore, we will focus on the atmospherically controlled 541 regime. In the atmospherically controlled regime, at a very low dimensionless Henry constant 542  $(<10^{-7})$  (equivalent to a vapor pressure vp  $<10^{-5}$  Pa), the volatilization rate is so slow that the 543 volatilization half-life is tens to hundreds of years. In that case, volatilization becomes 544 insignificant compared to other processes (Jacobs et al., 2012). In that respect, Höllrigl-Rosta 545 (2017) classified of volatilization according to the vapor pressure of the pesticide molecule 546 547 (Table A.5).

In modeling, volatilization is often described by a first-order kinetic equation (Barchanska et al., 2019; Comoretto et al., 2008; Gobas et al., 2018; Inao et al., 1999; Singh et al., 1991;
Watanabe et al., 2006) :

$$551 \quad \frac{dMw}{dt} = -k_v * Mw \quad (3)$$

552 Where Mw is the mass of the DP, and  $k_v (d^{-1})$  is the pesticide rate constant of volatilization to 553 the atmosphere. Volatilization can also be represented by its corresponding half-life  $DT_{50v} (d)$ :

554 
$$DT_{50\nu} = \frac{\ln(2)}{k_{\nu}}$$
 (4)

Since this transfer process depends on other factors, the volatilization rate may be expressed empirically as a function of both pesticide properties and climate conditions. Table A.6 are simplified form of the rate of volatilization  $k_v$  used in descriptive models of the fate of pesticides. In other studies, there are many complicated formulations (Bunyakan et al., 2006; Comoretto et al., 2008), in which  $k_v$  depends on diffusion coefficients, air-water side, waterair side mass transfer coefficient, and friction. However, they are usually left for volatilization-specific studies and do not model the fate of pesticides in artificial ponds.

A bibliographic review of calculated volatilization half-lives  $DT_{50v}$  (d) of certain pesticides 562 can be found in Table A.7. For most pesticides in artificial ponds, the vapor pressure is lower 563 than  $10^{-5}$  Pa, which enables to neglect the contribution of volatilization to the artificial pond 564 dissipation function according to the classification in Table A.5. However, it was 565 demonstrated that some pesticides were efficiently removed from water by volatilization 566 (Wang et al., 2014; Wang et al., 2019). In an aquatic microcosm under semi-field conditions, 567 Laabs et al. (2007) showed that volatilization was a primary reason for high pesticide losses 568 from the water shortly after application, especially for non-polar pesticides (i.e., endosulfan, 569 chlorpyrifos, and trifluralin). Similarly, Comoretto et al. (2008) reported that oxadiazon had a 570 DT<sub>50v</sub> of 23 days in a rice field, making it more vulnerable to volatilization when compared to 571 stable MPCA and pretilachlor. k<sub>v</sub> rates were either calculated using the empirical formulas in 572 Table A.6 or estimated in laboratory experiments. Empirical formulations of  $k_v$  show that 573 volatilization rates are mainly dependent on water depth, a mass water-air transfer coefficient 574 that is a function of the wind speed, the Henry constant (or vapor pressure and solubility), and 575 the molecular weight of the pesticide. Pesticides with a vp lover than  $10^{-5}$  require years to be 576 volatilized according to volatilization half-lives in Table A.7, making them virtually non-577 volatile. In contrast, other pesticides such as alphamethrin, molinate, endosulfan, and dieldrin 578 need a few days to volatilize, while oxadiazon requires more days to volatilize. With careful 579 consideration of the vp of these substances, we assume that these assumptions agree with the 580 581 classification in Table A.5. These observations showed that most pesticides are non-volatile due to their low vapor pressure. However, there are still some for which volatilization takespart in their dissipation in artificial ponds.

#### 584 **2.3 Transformation of pesticides**

In addition to the transport and transfer processes described in sections 2.1 & 2.2, pesticides 585 face other processes that transform their original chemical structure. They are also designated 586 as "degradative" processes when attempting to degrade pesticides to non-organic products 587 588 (Cessna et al., 2015; Imfeld et al., 2021). The importance of transformation processes in the artificial pond dissipation efficiency was widely proved. Pesticides can be transformed into 589 less toxic products or, in the ideal case, wholly degraded to simple mineral products under the 590 action of the chemical, photochemical, and biological processes (Tournebize et al., 2017). 591 This section describes the main biotic and abiotic transformation processes to which 592 pesticides are exposed in the different compartments of the artificial pond. 593

#### 594 2.3.1 Biotransformation

Biotransformation is a process by which organic substances are transformed by 595 microorganisms (bacteria, archaea, and fungi) into chemical substances called metabolites, 596 resulting in some cases in their complete mineralization (Garcia-Rodríguez et al., 2014). If the 597 598 microbial transformation is complete, it becomes a transformation, and pesticides are 599 mineralized to CO<sub>2</sub> and CH<sub>4</sub>. Otherwise, co-metabolism occurs, during which microorganisms degrade OM substrates, the primary source of nutrients of the bacteria, primarily to produce 600 601 enzymes that will break down sequentially the pesticide molecule, representing a secondary 602 source of nutriments of the bacteria (Arcangeli et al., 1997), resulting in a metabolite.

Recently, in a artificial pond system context, some metabolites were less toxic than their
parent pesticides (Kang et al., 2020). However, it remains unknown if other metabolites are
less or more toxic than the mother compounds. Nonetheless, biotransformation has been
extensively shown as a significant removal process for micro-organic pollutants (HijosaValsero et al., 2010; Langergraber, 2008; Llorens et al., 2011; Lyu et al., 2018; Samso et al.,
2013; Yang et al., 2017; Zhang et al., 2017).

Biotransformation occurs in both aerobic and anaerobic conditions. 609 Aerobic biotransformation occurs in oxic conditions, mainly near the plant roots or the water surface, 610 where the amount of dissolved oxygen is high enough. Biotransformation is anaerobic in deep 611 water and sediment depths with generally dissolved oxygen concentrations below 0.5 mg.L<sup>-1</sup> 612 613 (U.S.G.S, 2020). The rhizosphere can also be considered as an aerobic zone since oxygen can be transported from the plant body to the roots (Maltais-Landry et al., 2009), but researchers 614 showed that the amount of oxygen released by the plant was too little to be considered in 615 artificial pond fate models (Bezbaruah et al., 2005; Llorens et al., 2011). Artificial ponds are 616 mostly aerobic in the water column surface, with anaerobic conditions occurring at the bottom 617 sediment layer and deep water (Vymazal et al., 2015). The sediment layer was proved to be 618 characterized by a sharp decrease in oxygen (Martínez-Lavanchy et al., 2015; Stottmeister et 619 al., 2003; Thomas et al., 2011; Zhang et al., 2010). Karpuzcu et al. (2013), Paszko et al. 620 (2016) and (Mulligan et al., 2016); Paszko et al. (2016) demonstrated that anaerobic 621 conditions would result in lower biotransformation rates than under aerobic conditions. It 622 agrees with the recent study of commonly used herbicides in which Droz et al. (2021) 623 indicated that acetochlor and S-metolachlor transformation prevailed in the water phase and 624 seemed insignificant in the sediment. 625

- Microbial transformation also depends on temperature and radiation (Burrows et al., 2002), 626 pH, OM content, and microbial population (Vink et al., 1997). Sahin et al. (2020) reported 627 that humic substances increase biotransformation rates since they can carry microorganisms to 628 629 the pesticide. This effect has been widely investigated (Cai et al., 2017; Ortega-Calvo et al., 1998; Smith et al., 2009; Tejeda-Agredano et al., 2014), mainly for hydrophobic pesticides. 630 For instance, atrazine was highly biodegraded when sorbed onto clay-humic acid complexes 631 (Besse-Hoggan et al., 2009). Likewise, Rong et al. (2019) found that the interfacial reactions 632 on clay surfaces increased the biotransformation rates of methyl parathion. The exposure 633 history to pesticides of artificial ponds also influences biotransformation. Johnson et al. 634 (2004) demonstrated that sites with a higher pesticide exposure history had higher 635 biotransformation rates due to microbial acclimation and microbial community adaptation. 636
- 637 The water level is another controlling factor of biotransformation in the sediment 638 compartment of artificial ponds. Ma et al. (2018) speculated that a decline in the water level 639 enhances microbial growth and activity and would modify the structure and function of 640 microbial communities. The study also emphasized that a water volume drop-off would 641 enhance aerobic conditions, induce plant succession to the artificial pond center, and stimulate 642 OM accumulation and mineralization.
- The aging of sediments also intensifies the sequestration of PP after their settling, thus decreasing their bioavailability and hindering microbial transformation (Ahmad et al., 2004). Budd et al. (2011) proved that once pyrethroids were settled, they were stable in dry and aerobic sediments between irrigation seasons. They were moderately persistent under flooded and anaerobic conditions, with a  $DT_{50}$  between 106-353 days. This agrees with the observation of Cryder et al. (2021), showing that adsorption and subsequent settling were the dominant processes governing the fate of pyrethroids in ponds instead of biotransformation.
- Vegetation has been widely recognized as an important stimulator of biotransformation 650 (Moore et al., 2007; Rai, 2009; Stang et al., 2016; Sur et al., 2003; Wang et al., 2017). For 651 instance, chlorpyrifos removal rate reached 0.1 mg.m<sup>-1</sup>.day<sup>-1</sup> due to biotransformation in 652 vegetated mesocosms (Tang et al., 2019). Submerged stems and leaves of macrophytes are an 653 essential habitat for biofilms (Brix, 2003; C. Zhang et al., 2021). These biofilms, along with 654 those on all other immersed solid surfaces in the artificial pond system - including dead 655 macrophytes - are stimulators of microbial processing in artificial ponds (Brix, 2003; Dash et 656 657 al., 2020; Lv et al., 2017). Several kinds of phototrophic bacteria, algae, and biofilms in the water-sediment interface and on the surface of macrophytes were proved to be important 658 659 agents of pesticides transformation in artificial ponds (Katagi et al., 2016). Although, biotransformation in the biofilm can be limited sometimes due to the slow kinetics of mass 660 transfer or enzymatic reactions (Chen et al., 2015). 661
- In modeling, biotransformation is often described by a first-order kinetic model (Beringer et al., 2021; Green et al., 1990; Mamy et al., 2007; Pignatello, 1999; Scow et al., 1996; Torabi et al., 2020). Where  $k_{bio}$  (d<sup>-1</sup>) is the biotransformation kinetic constant in the compartment in question. Biotransformation can be represented either by the kinetic constant  $k_{bio}$  (d<sup>-1</sup>) or by the corresponding half-life DT<sub>50bio</sub> (d) (see Eq.(3) and Eq.(4)).
- 667 Several studies managed to estimate the biotransformation rate constants in artificial ponds in 668 laboratory conditions, through incubation manipulations. Incubation experiments aims to 669 calculate pesticide concentrations in the different compartments of a contaminated sample

670 (water and sediments). Then, the concentrations are fitted to a first-order kinetic decay model

- to estimate the rate constants  $k_{bio}$  and half-lives  $DT_{50bio}$ . Table A.8 presents a literature review
- 672 of estimated biotransformation half-lives  $DT_{50bio}$ .

The values of biotransformation half-lives (Table A.8) show that hydrophobic pesticides 673 pretilachlor and fenthion were rapidly biodegraded in sediments; we suggest that it may be 674 related to the fact that they were mainly sorbed on substrates easily accessible to 675 microorganisms. Pretilachlor was more rapidly degraded in water ( $DT_{50bio.w} = 9.8$  d). Even 676 though being hydrophobic and lowly mobile ( $K_{oc} = 5509 \text{ L.kg}^{-1}$ ), chlorpyrifos was more 677 persistent in sediments than in water columns, and was favorable to aerobic conditions 678 (O'Geen et al., 2010). Comparing the behavior of pretilachlor, fenthion, and chlorpyrifos, that 679 hydrophobicity, and low mobility may not necessarily favor biotransformation in sediments 680 rather than water. On the other hand, biotransformation in sediments seemed relatively slower 681 for more mobile pesticides (i.e., 2, 4-D, clothianidin, acetochlor, metazachlor, and S-682 metolachlor), except for the MCPA. We suggest that MCPA was not expected to sorb on TSS 683 and sediments due to its low K<sub>oc</sub>. Its transformation might be more favorable under aerobic 684 conditions (on the water surface) (PubChem, 2021), explaining its short half-life in the water 685 phase. S-metolachlor was moderately persistent in both water and sediments; this may be 686 explained by its complex chemical structure that forbids access to enzymes and prevents its 687 transformation under aerobic and anaerobic conditions (Droz et al., 2021). Finally, DT<sub>50bio</sub> 688 values showed that biotransformation was faster in oxic areas, except for acetochlor (DT<sub>50bio.w</sub> 689 = 47 d) and clothianidin ( $DT_{50bio,w}$  = 27.2 d) that were rapidly transformed under anaerobic 690 conditions. Although, it is not possible to infer any direct link between the OC content and the 691 biotransformation rate since sites were in the same range of OC. 692

693 Compared to the values of the Pesticide Properties Database (PPDB) (Lewis et al., 2016), 694 biotransformation half-lives were faster when estimated in artificial ponds, and for now, we 695 cannot make any conclusion about this difference since the conditions to estimate  $DT_{50bio}$  in 696 PPDB have not been detailed.

Overall, biotransformation is commonly expressed by a first-kinetic order model and 697 enhanced by increased vegetation within the artificial pond providing OM that supports 698 699 microbes and increases the HRT. Therefore, we suggest introducing a modulation coefficient according to vegetation cover and OC content in water and sediments of a specific site will 700 701 increase  $k_{bio}$  representability. At this time, no rule has been set up for pesticides 702 biotransformation in artificial ponds: neither a direct link with the pesticide properties has 703 been highlighted because biotransformation does not act alone, but simultaneously with other 704 processes. In the future, a more profound exam of biotransformation rates of different pesticides accounting for their interaction with other processes (i.e., adsorption and settling, 705 adsorption/desorption, and dispersion/diffusion) is needed. There is a lack of information 706 707 concerning biotransformation in vegetation/biofilm compartments. Therefore further studies should be carried out to estimate corresponding transformation rates and account for a 708 possible lag phase reflecting microbial acclimation, as shown by Passeport et al. (2011a). In 709 pesticides databases (i.e., PPDB) there is no distinction between the different compartments 710 (water, sediments, and vegetation) for biotransformation half-lives, making it hard to compare 711 and confront the rates measured as a part of artificial pond surveys with those in pesticides 712 databases. 713

Globally, biotransformation remains a highly changing phenomenon that depends on both the pesticide properties and the site conditions in which microorganisms can act. Defining

- 717 PPDB DT<sub>50bio</sub> values to estimate the contribution of biotransformation to overall dissipation in
- 718 artificial ponds.

#### 719 2.3.2 Photodegradation

- 720 Photodegradation or photolysis transforms pesticides exposed to sunlight, especially at
- wavelengths below 400 nm. The products formed by sunlight-induced transformations are known as photoproducts (Gerecke et al., 2001). Photodegradation is one of the significant
- abiotic degradation processes in artificial ponds (Lin et al., 2005; Papaevangelou et al., 2017;
- 724 Stangroom et al., 2000).
- Photolysis can be direct or indirect. During direct photolysis, pesticides absorb light energy 725 and become excited; they can be transformed depending on the availability of the activation 726 energy. In indirect photolysis, the pesticide reacts with other species produced 727 photochemically (i.e.,  $CO3^{\bullet}$ , hydroxyl radical  $OH^{\bullet}$ , singlet oxygen  $O^{1}_{2}$ , and triplet-excited 728 state dissolved OM (DOM)), causing degradation or conversion into other products (Katagi et 729 al., 2016; Miller et al., 2005; Pohlman et al., 1983; Zeng et al., 2013; Zepp et al., 1987). OH• 730 can be produced by nitrate photolysis, even at a concentration as low as 0.02 mg.L<sup>-1</sup> (Vione et 731 al., 2014). DOM generates DOM\*, the precursor of singlet molecular oxygen  $(O_{12})$  in surface 732 733 waters. DOM\* and  $O_{12}^{1}$  can react with pesticides (Drouin et al., 2021). The most reactive species is *OH*• attacking C-H bonds and mainly controls pesticide photodegradation. 734
- Because of the non-ability of solar radiation to penetrate deeper into the water, direct 735 photolysis remains efficient only in the first centimeters of the artificial pond (Frank et al., 736 2002). The effectiveness of photodegradation strongly depends on the shading capacity of the 737 738 vegetation canopy and turbidity within the water column, which may attenuate the penetration of solar radiation (MacIntyre et al., 2006; Rose et al., 2008). This transformation process was 739 also reported to be positively correlated to the artificial pond water pH (Le Person et al., 740 2016). In natural waters, DOM and inorganic compounds are essential absorbents of sunlight 741 742 and influence the photochemistry of pesticides in artificial pond (Burrows et al., 2002). In addition, particulate matter such as sediment particles and microorganisms suspended in the 743 water column may scatter incident light and prevent the light from penetrating the artificial 744 pond. This phenomenon is called the quenching effect of OM (Larson et al., 1994; Pattanayak 745 746 et al., 2018; Ruiz-Medina et al., 2018). Photochemical degradation would be more efficient in an open water artificial pond with low turbidity (O'Geen et al., 2010; Vymazal et al., 2015). In 747 DOC-rich ponds (DOC > 20 mg.L<sup>-1</sup>), photolysis is unlikely to be operative in pesticide 748 dissipation since DOC content massively attenuates UV light transmission to DP (Waiser et 749 al., 2004). Lagunas-Allué et al. (2010) observed less than an 8% decrease of boscalid caused 750 by direct photolysis, while the main removal processes were adsorption on OM and plant 751 uptake. This observation can be explained by the high OM content that prevents light 752 penetration to pesticides and limits direct photolysis. 753

On the other hand, several herbicide were efficiently removed by indirect photolysis, such as atrazine, diuron, and chlorpyrifos in a study conducted by Zeng et al. (2013). Mathon et al. (2019) evaluated the photodegradation of 23 pesticides using in-situ photo-reactors. They found that 15 pesticides were photodegraded in the summer against 12 in winter, which showed that photolysis was not directly linked to the season. However, when Mathon et al. (2019) compared each of the 23 pesticides photolysis direct and direct+indirect experimental

- half-lives, they found that indirect photolysis enhances the degradation compared to direct
  photolysis. Additionally, the contribution of direct and indirect photolysis was studied for 60
  pesticides. Direct photolysis predominated for dinitroaniline herbicides, although more than
  50% of the total photodegradation rate could be attributed to indirect photolysis for the other
  pesticides. This observation supports the relevance of indirect photolysis in artificial ponds
  when light attenuation is minimal (Katagi et al., 2016; Zeng et al., 2013).
- As with most transformation processes, photodegradation was commonly computed with a first-order kinetic model (Green et al., 1990; Lam et al., 2003; Rose et al., 2008; Watanabe et al., 2006; Zeng et al., 2013), where  $k_{photo}$  (d<sup>-1</sup>) is the photodegradation kinetic constant, assumed to be the sum of direct and indirect photolysis kinetic rates (Mathon et al., 2019), and DT<sub>50photo</sub> (d<sup>-1</sup>) is the photodegradation half-life. Photolysis half-lives that fitted a first-order kinetic model in pesticide fate models are presented in Table A.9.
- Photodegradation half-lives show that the slowest pesticides to be photodegraded were mobile and moderately mobile pesticides, according to their  $K_{oc}$  values. In contrast, while lowly mobile pesticides were rapidly photodegraded (Table A.9). Since lowly pesticides are likely to be sorbed (see section 2.2.1), we propose that they might be indirectly photodegraded once sorbed on sediments, suspended solids, or plants through chemical reactions with free radicals in the water-substrate interface.
- Overall, since the penetration of solar radiation to deeper water is limited, direct photolysis is considered only in the first centimeters of the artificial pond, depending on the DOC content. In contrast, indirect photolysis involving excited radicals may be more relevant through photochemical degradation and is well described by a first-order kinetic rate. We suggest that introducing a modulating factor taking into consideration vegetation cover and OM limit light penetration will increase the accuracy of photolysis modeling.

#### 784 **2.3.3 Hydrolysis**

- Another abiotic transformation process is the hydrolysis of DP, which depends on the pH and temperature of artificial ponds. Hydrolysis was commonly considered a minor dissipation process when compared to adsorption, microbial and photochemical degradation. However, in some cases, hydrolysis played a significant role in the dissipation function of artificial ponds, especially under alkaline conditions (Bondarenko et al., 2004; Liu et al., 2001; Papaevangelou et al., 2017; Yu et al., 2019).
- For instance, chlorpyrifos was proved sensitive to hydrolysis (Liu et al., 2001; Wu et al., 791 792 2002). Experimental studies showed that higher pH (> 8) increased the hydrolysis rate of 793 chlorpyrifos (Agudelo et al., 2010; Baskaran et al., 2003; Sardar et al., 2005), corresponding to a half-life of 50 days (Liu et al., 2019; Mackay et al., 2006). Similarly, carbaryl insecticide 794 795 was mainly degraded by photolysis and hydrolysis in a pond (Wolfe et al., 1978). Hydrolysis mainly contributed to endosulfan dissipation (Walse et al., 2002) and dichlorvos had a 796 hydrolysis half-life of 3 days (Tomlin, 2009). In contrast, hydrolysis contributed to less than 797 2% of boscalid degradation (Lagunas-Allué et al., 2010). Similarly, the hydrolysis half-life of 798 dieldrin exceeded three months (Singh et al., 1991) and reached 115 and 138 days for 799 diazinon and fenthion, respectively (Ibanez et al., 2006; Mackay et al., 2006; Sakellarides et 800 al., 2003). S-Metolachlor and butachlor were also proved to be persistent to hydrolysis with a 801 half-life of 200-1155 days at different pH (Masbou et al., 2018; Zheng et al., 2001). 802 803 Sometimes, change in diurnal pH due to photosynthesis by aquatic algae and macrophytes

- may result in photo-synthetically-driven alkaline hydrolysis of some pesticides (Katagi, 2006, 2013).
- Likewise, hydrolysis can be estimated with a first-order kinetic model (Rose et al., 2008; Wang et al., 2019), where  $k_h(d^{-1})$  is the hydrolysis kinetic constant and  $DT_{50h}$  ( $d^{-1}$ ) is the hydrolysis half-life. It was reported that the main controlling factor of hydrolysis is pH (Deer et al., 2001; Farran et al., 1988; Sereshti et al., 2021; Stangroom et al., 2000).

Overall, most pesticides that threaten water quality were considered insensitive to hydrolysis. It may be due to their chemical structure, such as the lack of methyl ester linkage for sulfosulfuron herbicide (Sabadie, 2002; Saha et al., 2002) and phosphodiester linkages for organophosphate pesticides (Sahin et al., 2020). In addition, artificial pond water might generally be beyond the range of alkaline or acidic conditions, making hydrolysis a very slow process (Rose et al., 2008). Therefore, we assume that hydrolysis could be neglected in modeling pesticide dissipation in artificial ponds.

### 818 **3. Discussion**

After reviewing various research works about pesticide dissipation in artificial ponds, it 819 appears that some studied different processes, while others only focused on one specific 820 process. Similarly, some surveys investigated the behavior of multiple pesticides while others 821 only evaluated one or multiple pesticides from the same chemical group (see section 2). 822 Papers evaluating multiple processes often studied one process. Therefore for a better 823 824 understanding of artificial pond processing, this review combines the investigation of multiple 825 pesticides behavior with contrasting physicochemical properties and evaluates transport, transfer, and transformation processes occurring in the artificial pond compartments (water, 826 sediments, and vegetation). In the following subsections, we discuss this critical review's 827 main assumptions regarding the processes' controlling factors, the estimation of parameters 828 829 required to model processes, and the hierarchization of processes.

#### 830 **3.1 Controlling factors of the processes**

As described in section 2, the surveyed processes depend on several factors:

- The environmental conditions: hydraulic parameters, temperature, sediments and TSS composition (OC, clay content), vegetation cover, solar radiation, pH, and redox conditions.
- The pesticide physicochemical properties: mobility K<sub>oc</sub>, hydrophobicity K<sub>ow</sub> and vapor pressure vp.
- The hydraulic regime is responsible for the residence time. A long HRT gives time for the pesticide to settle, sorb, desorb, or be transformed (Liu et al., 2019; Sahin et al., 2020). Another hydraulic parameter is the water column depth; a shallow water depth enhances photolysis and biotransformation by increasing the oxygen concentration in artificial ponds.
- 841 Sediments and TSS composition interfere in the sorption process. As presented in section 842 2.2.1, OC content adsorption and clay content increase the trapping of pesticides in sediments 843 by favoring desorption hysteresis. Thus, OC and clay content increase the removal of 844 pesticides from the artificial pond water. There was no direct link between biotransformation 845 half-lives  $DT_{50bio}$  in substrates and their OC content (Table A.11).  $DT_{50bio,s}$  values show that 846 the extent of the studied pesticides was not resistant to biotransformation in the sediment 847 regardless of the OC content.
- However, biotransformation half-lives in the water  $DT50_{bio,w}$ , and sediments  $DT50_{bio,s}$  varied according to pesticide properties. However, no direct link was observed between half-life ( $DT50_{bio}$ ) and pesticide hydrophobicity (Koc) (Table A.8). This observation supports our hypothesis of process synergy, and that dissipation is explained by the interaction between processes (i.e., sorption and transformation) and not a single process.
- For pesticides properties, the most affecting ones are the  $K_{oc}$  and  $K_{ow}$ , since they control the distribution, mobility, and availability of pesticides in the different artificial pond compartments. We observed that  $K_{oc}$  and  $K_{ow}$  were determining factors for sorption, biotransformation, and photodegradation.
- We have also noticed that biotransformation half-lives were faster in artificial ponds than half-lives in pesticide databases (i.e., PPDB). It should also be noticed that biotransformation half-lives are faster in artificial ponds sediments than in agricultural soils (Bolan et al., 1996; Passeport et al., 2011a), which support the efficiency and usefulness of artificial ponds.

Besides biotransformation, the  $K_{oc}$  and log  $K_{ow}$  also affect the sorption process. Once lowly mobile and hydrophobic pesticides are sorbed onto a substrate ( $K_{oc} > 1000 \text{ L.kg}^{-1}$  and log  $K_{ow}$ >3), they become harder to release back into the water. In comparison, more mobile pesticides ( $K_{oc} < 1000 \text{ L.kg}^{-1}$ ) are continuously transported within the artificial pond. However, it is unknown whether sorbed pesticides will be trapped in the sediment, suspended solid or vegetation, or desorbed afterward.

Numerous studies proved that vegetation is a determining agent in the fate of pesticides as it 867 intervenes implicitly in the removal function of artificial ponds. It provides habitat to 868 microorganisms responsible for pesticide transformation, decreases water velocity to increase 869 870 settling, increases the OC content and composition diversity to enhance adsorption, and brings oxygen to sediments to promote aerobic transformation. In rare cases, vegetation was also 871 responsible for trapping pesticides due to plant uptake. Nevertheless, it remains complex to 872 estimate and quantify the effect of plant uptake on the fate of pesticides (Jorda et al., 2021). 873 874 Another phytoremediation function of vegetation is through entophytic bacteria living in the interior tissue of plants that can potentially degrade pesticides. However, the fraction of 875 pesticides collated in plants were often insignificant (< 10%) (Butkovskyi et al., 2021; Singh 876 et al., 2021). 877

878 Temperature is a stimulator for transformation that increases the microbial activity behind
879 biotransformation, solar radiation is responsible for photodegradation and enhances
880 hydrolysis.

881

We suggest that process interactions affect their contribution to pesticide fate. The strong 882 relationship between a process and pesticide properties may explain the choice of studying a 883 specific process and pesticide. For instance, sorption is more involved in hydrophobic 884 pesticide dissipation. At the same time, volatilization contributes more to the behavior of 885 pesticides with a significant vapor pressure (Table A.7). On the other hand, PPDB half-life 886 values can be used to model the behavior of some pesticides if they are close to the half-lives 887 estimated in laboratory conditions or give satisfactory simulation results close to the 888 889 observations.

#### 890 **3.2 Parameter estimation for modeling**

- After the analysis of different formulations, we suggest that processes can be quantified and hierarchized according to:
- Kinetic rates k (d<sup>-1</sup>) for the transport and transfer processes: adsorption-desorption;
   settling-resuspension; and volatilization.
- Half-lives DT<sub>50</sub> (d) for the transformation processes: biotransformation, photolysis,
   and hydrolysis.
- The different methods used to evaluate the previously described processes and their corresponding parameters are summarized in Table 1.

#### 900 Table 1

901 Commonly established methods in the literature to quantify and parametrize a process for a pesticide dissipation902 modeling approach in artificial ponds.

Process	Method	Parameter	Units
	Transport		
Settling-Resuspension	Empirical formulas	$V_s; V_r$	m.day <sup>-1</sup>
	Transfer		
Adsorption-Desorption	Batch experiments	k <sub>ads</sub> ; k <sub>des</sub>	day <sup>-1</sup>
	+		
	Kinetic model fitting		
Volatilization	Empirical formulas	$\mathbf{k}_{\mathbf{v}}$	day <sup>-1</sup>
	Transformation		
Biotransformation	Incubation experiments	DT <sub>50bio</sub>	day <sup>-1</sup>
	+		
	Kinetic model fitting		
Photolysis	Lab experiments	DT <sub>50photo</sub>	day <sup>-1</sup>
Hydrolysis	Empirical formulas	DT <sub>50h</sub>	day <sup>-1</sup>

903

904 Most studies were conducted on a laboratory scale (batch, microcosms, and mesocosms). However, laboratory experiments are less advantageous than the rarely conducted in-situ 905 manipulations (Fig. 1). More representative; in-situ manipulations imply a better description 906 of the processes and the fate of pesticides while considering the interactions and links 907 between the different processes (i.e., between sorption and transformation, sorption and 908 dispersion/diffusion), which is not easy to bring out in laboratory conditions. In fact, in 909 laboratory experiments, only one process is emphasized and examined independently of other 910 processes that usually co-occur in field conditions. This often results in the overestimation of 911 912 dissipation in lab-scale studies.

Additionally, not all estimated half-lives are compatible with those available in the PPDB, 913 especially biotransformation (Table A.8). This incompatibility may be explained by the 914 different sites where parameters were estimated, whereas, for the accessible PPDB data, there 915 is no site specification. This observation questions the validity of parameters in the free PPDB 916 data and their applicability in a process-based model that aims to describe what is happening 917 in the field accurately. Using PPDB values in models increases the incertitude; therefore, we 918 suggest defining a DT50 specific to ponds for each process to use in models. The fact that 919 DT50 values in the PPDB are higher than those calculated in-situ shows a greater dissipation 920 in pond artificial ponds. Because certain photodegradation half-lives in the literature present 921 better compatibility with the PPDB values (Table A.8), they could be a good model fit. 922

Table 2 summarizes the studied processes for each pesticide described in this review and the equation used to describe it. We noticed a lack of studies quantifying and modeling dissipation processes in artificial ponds because studies are often limited to observing the process without a modeling approach. A considerable number of pesticides (55) were studied to evaluate their behavior according to previously described processes. However, many of

- 928 these pesticides have only been evaluated once. Hence, more studies are needed on these 929 pesticides to compare their behavior and draw more robust conclusions.
- Some pesticides (i.e., boscalid, chlorpyrifos, and pretilachlor) were evaluated according to
  multiple processes, but not necessarily with a modeling perspective (Agudelo et al., 2010;
  Laabs et al., 2007; Lagunas-Allué et al., 2010; Rogers et al., 2009; Tang et al., 2019;
  Karpuzcu et al., 2013; Mackay et al., 2006; Yu et al., 2019). Only, 57 of the 252 reviewed
  articles concern modeling.
- Little is known about the estimation of biotransformation half-life in artificial pond 935 compartments, except that macrophytes and algae enhance both adsorption and 936 biotransformation of DP (Katagi et al., 2016). Similarly, anaerobic biotransformation may 937 occur in the sediment layer yet is still under-researched (Maillard et al., 2014; Vandermaesen 938 et al., 2016). Globally, it remains challenging to determine a DT<sub>50bio</sub> in each compartment 939 with lab experiments due to the different behavior a pesticide may have in each of them. It is 940 also challenging because laboratory experiments can hardly mimic reproducibly process 941 942 interactions occurring in the field. For sorption, vegetation remains the least exploited 943 compartment since there were few surveys to estimate sorption kinetics on vegetation, its biotransformation rates, or its uptake rates. 944
- 945
- We propose that the previously mentioned controlling factors (temperature, OM, and vegetation cover) and their interactions are considered for better accuracy by integrating sitespecific modulating factors in the development of pesticide fate models. Modulating factors also highlight the temporal variation of process efficiency, such as biotransformation prevailing during the plant growth period (Vandermaesen et al., 2016). So then the question is whether it is necessary to include this temporal variation in a process-based model to improve the accuracy or if, by doing so, the complexity increases.
- 953

### 954 **3.3 Hierarchization of dissipation processes**

- This review provides a primary idea about the hierarchization of processes according to their contribution to the removal function of artificial ponds.
- As adsorption can only trap pesticides in artificial ponds, degradation (i.e., complete biotransformation, photolysis, and hydrolysis) contributes more to the artificial pond removal function since it can permanently eliminate toxic substances from the environment. Although little is known about whether sorbed pesticides will be degraded or released back into the environment over time, we assume that sorption is still a key process, as it determines the distribution and availability of pesticides in artificial pond compartments.
- Among the transformation processes, the most rapid was biotransformation compared to photodegradation for some pesticides. By comparing the different half-lives, volatilization was the slowest process, which is in line with the fact that most pesticides are non-volatile due to their low vapor pressure ( $<10^{-5}$  Pa). Lastly, hydrolysis appears negligible of most pesticides.
- Previous reviews, such as Stehle et al. (2011) and Vymazal et al. (2015), did not find a direct
  link between pesticide dissipation or accumulation in artificial ponds and pesticide properties
- 970 (i.e.,  $K_{oc}$  vs sorption). We suggest that it is because the fate of pesticides in artificial ponds 971 does not result from a single process but a combination of different transport, transfer, and

transformation processes involving multiple artificial pond compartments. This combination 972 depends on different conditions (i.e., hydrology, climate, physico-chemical factors, and 973 vegetation cover). We assume that the most dependent processes are sorption and 974 975 biotransformation. For some moderately mobile and hydrophilic pesticides, biotransformation can be the main dissipation process in a artificial pond. After 42 days, up to 86% of diuron 976  $(K_{oc} = 600 \text{ L.kg}^{-1})$ , atrazine  $(K_{oc} = 100 \text{ L.kg}^{-1})$  and terbuthylazine  $(K_{oc} = 318 \text{ L.kg}^{-1})$  were 977 degraded (Anderson et al., 2002; Gregoire et al., 2009; Hijosa-Valsero et al., 2016). Also, the 978 removal of the moderately mobile triazophos ( $K_{oc} = 308 \text{ L.kg}^{-1}$ ) was mostly achieved by 979 biotransformation rather than adsorption (Cheng et al., 2007; Imfeld et al., 2009; Meng et al., 980 2014; Rani et al., 2001). In contrast, for the highly hydrophobic butachlor (log  $K_{ow} = 4.5$ ), 981 adsorption was the main process contributing to its dissipation in microcosm experiments. 982 983 Many researchers ascertained that strong adsorption to sediments and limited desorption (also known as "aging") might decrease the bioavailability of pesticides and thus limit their 984 biotransformation (Ahmad et al., 2004; Budd et al., 2011; Chaumet et al., 2021; Lee et al., 985 2004; Mulligan et al., 2016). All of these results emphasize the dependency between sorption 986 987 and biotransformation.

988 When examining citation frequency, some processes (i.e., sorption, biotransformation) were 989 more cited than others (i.e., settling, resuspension, and volatilization). When a process is not 990 frequently cited, this could be explained by the difficulty level of its evaluation in both 991 laboratory and field conditions.

992 The previous conclusions were based on observing removal rates of different processes and 993 pesticides. The limitations of this approach are the relevance of the statements made based on 994 a single case study. Nevertheless, describing one survey means that no other case study was 995 found. The robustness of the conclusions made in this review will be stronger if the same 996 processes are tested on multiple pesticides and sites with contrasting properties to highlight 997 the link between the impact of processes and the properties of the pesticides and artificial 998 ponds.

999

1004

1000 Identifying the processes with a higher impact can be used to hierarchize processes based on 1001 their contribution to the dissipation function of artificial ponds. We believe that a 1002 hierarchization of relevant processes may improve the estimation of the overall efficiency of 1003 artificial ponds in reducing pesticide transfer into the environment.

In addition, the black box model does not consider the processes mentioned above and 1005 describes pesticide behavior with an overall dissipation rate k<sub>diss</sub>. Although easy to apply, the 1006 1007 black box approach does not provide enough information on the behavior of pesticides and the contribution of each process to the dissipative function of artificial ponds. Therefore, this 1008 paper discusses the required elements to develop a simple process-based model involving the 1009 transfer, transport, and transformation processes in an interplay of artificial pond 1010 compartments to open the black box (Fig. 3). We assume that a model with multiple process 1011 1012 rates shows the complexity of modeling the fate of pesticides in artificial ponds; however, it can describe and predict pesticide behavior more realistically. We believe this work will 1013 contribute to a better understanding of artificial pond processing and optimize pesticide fate 1014 models. 1015



Process-based dissipation model

1018 Fig. 3. Summarized elements and steps detailed in this work in order to develop a process-based model, that

- 1019 contrarily to black models, involves multiple processes in an interplay between different artificial pond1020 compartments.

### 1025 Table 2

1024

List of the surveyed processes for each cited pesticide in the reviewed papers, and the equation used to estimatethe rate of processes. NA means that the process was evaluated without a modeling approach.

				Proces	ses			-
Pesticides	SET	RES	SOR	VOL	BIO	РНО	HYD	Source
Acetochlor					Eq. (13)			(Droz et al., 2021)
Aclonifen					NA			(Passeport et al., 2013)
Alphamethrin				Eq. (11)				(Comoretto et al., 2008)
Atrazine			NA		NA			(Besse-Hoggan et al., 2009; Moore et al., 2013; Zeng et al., 2013)
Bifenthrin	NA							(Cryder et al., 2021)
Boscalid			NA		NA	NA	Eq. (17)	(Lagunas-Allué et al., 2010; Vallée, 2015)
Butachlor			NA		NA		NA	(Masbou et al., 2018; Torabi et al., 2020; Zheng et al., 2001)
Carbaryl							NA	(Wolfe et al., 1978)
Chlorothalonil					NA			(Passeport et al., 2013)
Chlorotoluron					NA			(Passeport et al., 2013)
Chlorpyrifos			NA	NA	Eq. (13)		NA	(Agudelo et al., 2010; Laabs et al., 2007; Sardar et al., 2005 ; Rogers et al., 2009; Tang et al., 2019; Wang et al., 2019 ; Karpuzcu et al., 2013; Liu et al., 2019; Mackay et al., 2006; Yu et al., 2019)
Clothianidin					Eq. (13)			(Beringer et al., 2021)
Cyfluthrin	NA							(Cryder et al., 2021)
Cyproconazole					NA			(Passeport et al., 2013)
Diazinon			NA		Eq. (13)		Eq. (17)	(Ibáñez et al., 2006; Mackay et al., 2006; Sahin et al., 2020; Sakellarides et al., 2003)
Dichlorvos					NA		Eq. (17)	(Sahin et al., 2020; Tomlin, 2009)
Dieldrin				Eq. (11)			Eq. (17)	(Singh et al., 1991)
Diuron					NA			(Zeng et al., 2013)
Endosulfan				Eq. (11)		Eq. (15)	Eq. (17)	(Rose et al., 2008; Singh et al., 1991; Walse et al., 2002)
Epoxiconazole			NA		NA			(Passeport et al., 2011; Passeport et al., 2013)
Ethofumesate					NA			(Passeport et al., 2013)
Fenitrothion						Eq. (15)		(Sakellarides et al., 2003)
Fenpropidine					Eq. (13)			(Passeport et al., 2013)
Fenthion					NA	Eq. (15)	NA	(Sahin et al., 2020; Sakellarides et al., 2003)
Fipronil	NA							(Cryder et al., 2021)
Fludioxonil			NA			Eq. (15)		(Katagi et al., 2016; Maillard et al., 2014)
Fluometuron			NA			Eq. (15)	Eq. (17)	(Hand et al., 2001; Rose et al., 2008)
Glyphosate			NA					(Maillard et al., 2014)
Imazosulfuron			Eq. (8)					(Takagi et al., 2012)
Imidacloprid			NA					(Mahabali et al., 2014)
Isoproturon			NA		NA			(Passeport et al., 2011; Passeport et al., 2013; Vallée, 2015)
Kresoxim-methyl				Eq. (11)				(Gobas et al., 2018)
Lindane			Eq. (8)					(Krishna et al., 2008)
МСРА			NA		Eq. (13)			(Comoretto et al., 2008; Sørensen et al., 2006; Thorstensen et al., 2001)
Mefenacet			Eq. (8)	Eq. (11)				(Bolan et al., 1996; Watanabe et al., 2006; Yoshida et al., 2000)
Mefenpyr-diethyl				NA				(Passeport et al., 2013)
Metazachlor			NA		Eq. (13)			(Passeport et al., 2011; Passeport et al., 2013)

				Processe	es			
Pesticides	SET	RES	SOR	VOL	BIO	рно	HYD	Source
Methyl parathion		NA	NA					(Rong et al., 2019; Schulz et al., 2003)
Molinate			Eq. (8)	Eq. (11)		Eq. (15)		(Inao et al., 1999)
Napropamide			NA		NA			(Passeport et al., 2013; Vallée, 2015)
Oxadiazon				Eq. (11)				(Comoretto et al., 2008)
Parathion-Methyl						Eq. (15)		(Sakellarides et al., 2003)
Picloram			Eq. (8)					(McCall et al., 1985)
Pretilachlor			Eq. (8)	Eq. (11)	Eq. (13)	Eq. (15)		(Vallée, 2015)
Prochloraz			NA		NA			(Passeport et al., 2013)
Prosulfocarb					NA			(Gobas et al., 2018)
Pyraclostrobin				Eq. (11)				(Maillard et al., 2014)
Pyrimethanil			NA					(Droz et al., 2021; Masbou et al., 2018; Passeport et al., 2013)
S-Metolachlor					Eq. (13)	Eq. (15)	NA	(Comoretto et al., 2008; Nakano et al., 2004; Watanabe et al., 2006; Yoshida et al., 2000)
Spiroxamine			NA					(Maillard et al., 2014)
Tebuconazole			NA		NA			(Maillard et al., 2014; Passeport et al., 2011; Passeport et al., 2013; Vallée, 2015)
Terbutylazine					NA			(Hijosa-Valsero et al., 2016)
Triazophos					NA			(Cheng et al., 2007)
Trifluralin				NA				(Laabs et al., 2007)

1030

### 1031 **4. Conclusion**

1032 The scientific community has widely proved the role and efficiency of artificial ponds in 1033 reducing pesticide transfer into the environment. However, few papers have identified the set 1034 of processes behind the behavior of pesticides in artificial ponds and opened the black box. 1035 The relationship between the dissipation potential of processes and the properties of artificial 1036 ponds and pesticides has yet to receive little attention.

When reviewing the literature, we assumed that pesticide behavior is due to multiple 1037 processes acting to degrade or trap them in artificial ponds. From this, we can conclude that 1038 the fate of pesticides results from the interaction of different processes. These processes 1039 depend on several hydraulic, climatic, and physicochemical factors and vegetation cover. 1040 Since previous studies have generally focused on a single pesticide or dissipation process, this 1041 review combines research work on pesticides with contrasting properties. This extends to 1042 pesticide behavior, reflecting several processes involved in the dissipation of pesticides in a 1043 1044 large variety of artificial ponds. We also describe and compare the methods used to quantify processes behind pesticide dissipation or accumulation in artificial ponds. 1045

Based on the bibliometric analysis, we explain the citation frequency of a process by the difficulties of evaluating its contribution in the field or the laboratory. Moreover, investigating pesticide behavior in an interplay between transfer, transport, and transformation processes can be used to hierarchize processes based on their contribution to the dissipation function of pond artificial ponds. We suggest that this hierarchization may also improve the estimation of the overall efficiency of pond artificial ponds in pesticide dissipation. 1052 This work is a detailed analysis of the literature to improve our understanding of the potential 1053 of artificial ponds to dissipate incoming pesticide loads and thus lead to better management 1054 and, therefore, water quality improvement. This work paves the way for the scientific 1055 community to develop generic process-based models that, contrary to black-box models, will 1056 predict pesticide behavior at the artificial pond scale while integrating the key dissipation 1057 processes.

### 1059 Author Contributions:

Conceptualization: A.B, J.T, S.S, S.P, G.I.; Writing - Original Draft: A.B; Writing - Review
& Editing: J.T, S.S, S.P, G.I, J.P, B.C; Supervision: J.T, S.S; Project administration: G.I;
Funding acquisition: G.I, J.T, S.S, S.P, J.P.

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### **Declaration of competing interest:**

1068 The authors declare that they have no known competing financial interests or personal 1069 relationships that could have appeared to influence the work reported in this paper.

1070

# Appendix A.

### 

#### 1074 Table A.1

1075 Formulation of settling rates of suspended particles in wetlands and associated parameters.

Settling rate v <sub>s</sub> (m.s <sup>-1</sup> )	Parameters	Conditions of application	Source
$\frac{2}{9} * \frac{r_p^2 * \left(\rho_p - \rho_w\right) * g}{\mu}  (i)$	$  eq:rescaled_rescale$	Reynolds number < 500	(Fiener et al., 2003; Marois et al., 2016; Reddy et al., 2008)
$(\frac{4}{3}*\frac{g*d}{C_D}*\frac{(\rho_s-\rho_w)}{\rho_w})^{\frac{1}{2}}$ ( <i>ii</i> )	$  \label{eq:states} \begin{array}{l} \bullet v_s \ (m.s^{-1}) \text{: Settling rate.} \\ \bullet d \ (m) \text{: Particles diameter.} \\ \bullet \rho_s \ (kg.m^{-3}) \text{ : Solid density.} \\ \bullet \rho_w \ (kg.m^{-3}) \text{ : Water density.} \\ \bullet g \ (m.j^{-2}) \text{ : Gravity.} \\ \bullet C_D = f \ (Rep) \ , \ Rep \ \text{: Reynolds} \\ number \ of \ the \ particle. \end{array} $	Spherical particles in water at 20°C	(Kadlec et al., 2008)
$ \mu * d^{-1} * ((25 + 1, 2 * d^{*2})^{0,5} - 5))^{1.5}  (iii) $ $ d^* = (d * (g * \mu^{-2} * (s - 1))^{1/3} $	• $v_s$ (m.s <sup>-1</sup> ): Settling rate. • d (m): Particles diameter. • g (m.j <sup>-2</sup> ): Gravity. • $\mu$ (kg.m <sup>-1</sup> .day <sup>-1</sup> ) : Water viscosity. • s : Relative density= $f(\rho_s, \rho_w)$	Natural sand particles	(Hawley et al., 2014)

1079 Integrated sorption kinetic and isotherm models. Kinetic models describe the temporal evolution of the sorbed
 1080 amount of a dissolved substance. Kinetic rates are estimated from fitting laboratory measurements to the kinetic
 1081 models. Isotherm models describe adsorption and desorption equilibrium. Likewise, isotherm constants are
 1082 calculated from fitting laboratory measurements to isotherm curves.

	Kinetic models						
Equations	Parameters	Source					
<u>Pseudo first order (PFO):</u> $C_s = C_{se} - e^{-k_1 * t}$	<ul> <li>C<sub>s</sub> (μg.g<sup>-1</sup>): Sorbate concentration in the substrate at instant t.</li> <li>C<sub>se</sub> (μg.g<sup>-1</sup>): Sorbate concentration in the substrate at the equilibrium.</li> <li>k<sub>1</sub> (min<sup>-1</sup>): Kinetic constant.</li> </ul>	(Lin et al., 2009)					
<u>Pseudo second order</u> (PSO): $C_{s} = \frac{k_{2} * C_{se}^{2} * t}{1 + k_{2} * C_{se} * t}$	<ul> <li>C<sub>s</sub> (μg.g<sup>-1</sup>): Sorbate concentration in the substrate at instant t.</li> <li>C<sub>se</sub> (μg.g<sup>-1</sup>): Sorbate concentration in the substrate at the equilibrium.</li> <li>k<sub>2</sub> (g.mg<sup>-1</sup>.min<sup>-1</sup>): Kinetic constant rate.</li> </ul>	(Boparai et al., 2011)					
Elovich: $C_{s} = \frac{1}{\beta} * \ln (1 + \alpha * \beta + t)$	<ul> <li>C<sub>s</sub> (μg.g<sup>-1</sup>): Sorbate concentration in the substrate at instant t.</li> <li>α (g.mg<sup>-1</sup>.min<sup>-1</sup>), β (g.mg<sup>-1</sup>): Kinetic constants.</li> </ul>	(Chien et al., 1980; Ho et al., 2002)					

	Isotherm models	
Equations	Parameters	Source
Freundlich:	• C <sub>se</sub> (µg.g <sup>-1</sup> ): Sorbate concentration in the substrate at the equilibrium.	(Mckay, 1995)
$C_{se} = K_f * C_{we}^{n_f}$	<ul> <li>C<sub>we</sub> (μg.g<sup>-1</sup>): Sorbate concentration in the water at the equilibrium.</li> <li>K<sub>f</sub> (mg<sup>1-n</sup><sub>f</sub>.L<sup>n</sup><sub>f</sub>.kg<sup>-1</sup>): Freundlich</li> </ul>	
	constant expressing the molecule- substrate affinity. During adsorption $K_{\rm f}$ is called $K_{\rm fads}$ and $K_{\rm fdes}$ during	
	desorption. • $n_f$ (unitless): Freundlich constant. When $n_f = 1$ , the kinetic model becomes linear and $K_f$ becomes the classical distribution coefficient $K_d$ .	
<u>Langmuir:</u> $C_{se} = \frac{K_L * C_{we}}{1 + n_L * C_{we}}$	<ul> <li>C<sub>se</sub> (μg.g<sup>-1</sup>): Sorbate concentration in the substrate at the equilibrium.</li> <li>C<sub>we</sub> (μg.g<sup>-1</sup>): Sorbate concentration in the water at the equilibrium.</li> <li>K<sub>L</sub> (L.g<sup>-1</sup>), n<sub>L</sub> (unitless): Langmuir constants.</li> </ul>	(Mckay, 1995)

1084

#### 1085 Table A.3

1086 Non-linear Freundlich isotherm adsorption  $K_{fads}$  (mg<sup>1-n</sup> kg<sup>-1</sup> L<sup>n</sup>) and desorption  $K_{fdes}$  (mg<sup>1-n</sup> kg<sup>-1</sup> L<sup>n</sup>) coefficients. 1087 Linear isotherm coefficient  $K_d$  (L.kg<sup>-1</sup>) for metazachlor, isoproturon, epoxiconazole, napropamide, boscalid, 1088 prochloraz, tebuconazole, glyphosate, pyrimethanil, tetraconazole, fludioxonil and spiroxamine. The sorption 1089 coefficients were measured in laboratory conditions with batch experiments on different pond substrates: 1090 Sediments, vegetation, and total suspended solids (TSS) (Maillard et al., 2014; Passeport et al., 2011b; Vallée, 1091 2015).

Pesticide	K <sub>d</sub> /K <sub>f</sub> *	Substrates	K <sub>d</sub>	<b>K</b> <sub>fads</sub>	K <sub>fdes</sub>	Source
	$K_{d} = 0.78$	Sediments	3.65	4.5	0.11	
Metazachlor	$K_f = -$	Vegetation	53	60	3,35	
	$K_d = -$	Sediments	5.85	3.5	0.1	
Isoproturon	$K_{\rm f} = 2.83$	Vegetation	34	44	26.5	
	$K_d = -$	Sediments	-	281.5	0.2	
Epoxiconazole	$K_{\rm f}{=}12.2$	Vegetation	546	902	2.34	(Passeport et al., 2011)
	$K_{d} = 21.5$	Sediments		5	4.8	
Napropamide	$K_{f} = 21,6$	Vegetation		77.4	75.2	
	$K_d = -$	Sediments		9.05	8.9	
Boscalid	$K_{\rm f}{=}12.6$	Vegetation	-	191.8	129.5	
	$K_d = -$	Sediments		63.3	10.3	
Prochloraz	$K_f = 38$	Vegetation		442.2	110	
	$K_d = -$	Sediments		12.3	9	
Tebuconazole	$K_{\rm f} = 12.69$	Vegetation		127.8	98.1	(Vallée, 2015)
	$K_d = 209.4$		Inlet: 87.06			
Glyphosate	$K_{\rm f} = 226.3$	TSS	Outlet: 18067			
	$K_d = -$		Inlet: 833.3			
Pyrimethanil	$K_{f} = 8.38$	TSS	Outlet: 414			
	$K_d = -$		Inlet: 524.8	-		
Tetraconazole	$K_{\rm f}{=}145$	TSS	Outlet: 1533			
	$K_d = -$		Inlet: 944.4			
Fludioxonil	$K_{f} = 3312$	TSS	Outlet: 977			
	$K_d = -$		Inlet: 1461			
Spiroxamine	$K_{f} = 142.3$	TSS	Outlet: 1681			(Maillard et al., 2014)



1093 (\*): Sorption coefficients (K<sub>d</sub>, K<sub>f</sub>) were extracted from the pesticide database PPDB (Lewis et al., 2016).

(-): Not measured.

1095

1098Adsorption and desorption kinetics  $(k_{ads}, k_{des})$   $(d^{-1})$  of five selected pesticides (imazosulfuron, lindane,1099mefenacet, molinate and picloram) in different ponds, along with their physicochemical properties S (mg.L<sup>-1</sup>)1100and K<sub>oc</sub>(L.kg<sup>-1</sup>) (Inao et al., 1999; Krishna et al., 2008; Mccall et al., 1985; Takagi et al., 2012; Yoshida et al.,11012000). Pesticide properties were extracted from pesticide databases (ChemSpider; Kim et al., 2021; Lewis et al.,11022016).

Pesticide	Physicochemical properties	$\begin{array}{c} Adsorption \\ k_{ads}(d^{-1}) \end{array}$	$\begin{array}{c} \text{Desorption} \\ k_{\text{des}}(d^{\text{-1}}) \end{array}$	Site	Source
Imazosulfuron	S (mg/l) = 1400 $K_{oc}(L/kg) = 754$	1.64*10 <sup>-1</sup>	7.59*10 <sup>-3</sup>	Paddy field OC = 1% OM = 1.83%	(Takagi et al., 2012)
Lindane	S (mg/l) = 8.5 $K_{oc}(L/kg) =$ 1081	$1.7*10^{-4}$	8.54*10 <sup>-6</sup>	Agricultural pond OC=2% Clay=56%	(Krishna et al., 2008)
Mefenacet	$S (mg/l) = 4$ $K_{oc}(L/kg) = 2964$	1.2	2*10 <sup>-1</sup>	Paddy field OC = 16% OM = 27%	(Yoshida et al., 2000)
Molinate	S (mg/l) = 1100 $K_{oc}(L/kg) = 190$	4.87*10 <sup>-1</sup>	2.9*10 <sup>-1</sup>	Paddy field OC = 2%, OM=3.44% Clay = 47%	(Inao et al., 1999)
Picloram	S (mg/l) = 430 $K_{oc}(L/kg) = 100$	$1.78*10^{-1}$	3.7	Agricultural pond OC= 3%	(McCall et al., 1985)
Pretilachlor	S (mg/l) = 50 $K_{oc}(L/kg) =$ 1159	1.4*10 <sup>-5</sup>	2.3*10 <sup>-6</sup>	Paddy field OC = 16% OM = 27%	(Yoshida et al., 2000)

### 1106 Table A.5

1107 Volatilization classes according to the vapor pressure values (Höllrigl-Rosta, 2017).

	Vapor pressure (Pa) at 20°C	Volatilization class
	< 10 <sup>-5</sup>	Non-volatile
	< 10 <sup>-4</sup>	Non-volatile from soil surfaces, no volatilization from greenhouses
	$10^{-5} < \_\_ < 10^{-4}$	Semi volatile
	$10^{-4} < \_ < 5.10^{-3}$	Semi volatile
	$\geq 10^{-3}$	Volatile
1108		

Empirical formulations of volatilization rate  $k_v(d^{-1})$  along with their corresponding parameters, based on a 1<sup>st</sup> order kinetic volatilization model. 

Volatilization rate $k_v$	Parameters	Source
$\frac{\frac{1}{h_w} * \frac{\frac{H}{RT}}{\frac{1}{720 * \sqrt{\frac{18}{MW}}} + \frac{1}{4.8 * \sqrt{\frac{44}{MW}}}}$	<ul> <li>H (Pa.m<sup>3</sup>.mol<sup>-1</sup>): Henry coefficient at 25°C.</li> <li>R (Pa.m<sup>3</sup>.mol<sup>-1</sup> K<sup>-1</sup>): Universal gas constant.</li> <li>T (K): Absolute temperature.</li> <li>MW (g.mol<sup>-1</sup>): Molecular Weight of the chemical compound.</li> <li>hw (m): Water depth.</li> </ul>	(Jacobs et al., 2012)
$\frac{1}{\frac{1}{36+0.01*u^{1,2}}+\frac{8.3T}{H*(3.6+5*u^{1,2})}}$	<ul> <li>u (m.s<sup>-1</sup>): Wind speed.</li> <li>H (Pa m<sup>3</sup> g<sup>-1</sup>): Henry constant.</li> <li>T(°C) : Temperature.</li> </ul>	(Rose et al., 2008)



1118 Review of the volatilization half-lives  $DT_{50v}$  (d) and the corresponding volatilization rates  $k_v(d^{-1})$  in ponds, of

according to the table A.5.

Pesticide	vp (Pa)*	Classification	DT <sub>50v</sub> (d)	$\mathbf{k}_{\mathbf{v}}\left(\mathbf{d}^{-1}\right)$	Source	
Alphamethrin	$2.3*10^{-3}$	Volatile	0.2	3.01		
Oxadiazon	$1.49*10^{-5}$	Semi volatile	24.8	0.03	(Comoretto et al., 2008)	
Kresoxim-methyl	$2.29*10^{-6}$	Non-volatile	96924	0.00		
Pyraclostrobin	$2.60*10^{-8}$	Non-volatile	6850343	0.00	(Gobas et al., 2018)	
Molinate	1.3	Volatile	2.6	0.27	(Inao et al., 1999)	
Endosulfan	$7.59*10^{-1}$	Volatile	3	0.23		
Dieldrin	3.20*10 <sup>-3</sup>	Volatile	4.4	0.16	(Singh et al., 1991)	
Pretilachlor	$1.2*10^{-4}$	Semi volatile	346.5	0.00		
Mefenacet	6.39*10 <sup>-7</sup>	Non-volatile	5941	0.00	(Watanabe et al., 2006)	

1121

\*: vp (Pa) is the vapor pressure of the pesticide at 20°C. The values were extracted from pesticides properties databases
 PPDB, PubChem and ChemSpider.

1124

1127Biotransformation half-lives in the water column  $DT_{50bio,w}$  (d) and sediment surface  $DT_{50bio,s}$  (d) of nine1128pesticides in different wetlands, along with their mobility  $K_{oc}(L.kg^{-1})$  (Beringer et al., 2021; Bondarenko et al.,11292004; Comoretto et al., 2008; Droz et al., 2021; Nakano et al., 2004; Passeport et al., 2011a; Passeport et al.,11302013; Sahin et al., 2020). These half-lives were confronted to the PPDB values.

Pesticide	K <sub>oc</sub> <sup>+</sup> (L/kg)	$DT_{50bio,w}(d)$	$DT_{50bio,s}(d)$	Site	DT <sub>50bio,w</sub> (d) PPDB	DT <sub>50bio,s</sub> (d) PPDB	Source
	156	Anaerobic: 59	Anaerobic: 47	Wetland			(Droz et al.,
Acetochlor 156		Aerobic: 31	Aerobic: 53	OC=2.3%	40.5	19.7	2021)
Chlorpyrifos 5509	5509	_	Anaerobic: 125-746	Urban stream sediment	-	36.5	(Bondarenko et al., 2004)
1.7			Aerobic: 1.8 - 4.9	OC=1.8%			
Clathianidia	102	-	Anaerobic: 27.2	Wetland		-	(Beringer et al., 2020)
Ciotnianidin	125		Aerobic: 115	OC=0.2%	-		
Diazinon	165-189	-	Aerobic: 53.32	Lake sediment	4.3	10.4	(Sahin et al.,
Fenthion	1500	-	Aerobic: 5.5	OC= 2.22%	-	92	2020)
МСРА	100	-	5.1*	Paddy field OC=0.9%, Clay=47%	-	25	(Comoretto et al., 2008)
Metazachlor 134	124	216*	20.6*	Wetland	-	-	(Passeport et al., 2013)
	134			OC = -			
Pretilachlor 1159	1150	0.0*	* 19.0*	Paddy field	-	-	(Nakano et al., 2004)
	1159	159 9.8*		OC=2.3%			
S-Metolachlor	300	Anaerobic: 199	Anaerobic: 182	Wetland	88	365	(Droz et al.,
		Aerobic: 29	Aerobic: 151	OC=2.3%			2021)
Enoviconazolo	300		170	Wetland	1000	103.6	(Passeport et al., 2011)
Epoxiconazole	300	170	170	OC=2%			

1131

1132 \*: It was not specified under which conditions (aerobic or anaerobic) biotransformation half-lives were measured.

+: The K<sub>oc</sub> values were extracted from pesticides databases (ChemSpider; Kim et al., 2021; Lewis et al., 2016; Zambonin et al., 2002).

1135 - : Not available.

1136

41

1139Photodegradation half-lives in the water column  $DT_{50photo}$  (d) of eight selected pesticides with different1140mobilities  $K_{oc}$  (L.kg<sup>-1</sup>). The  $DT_{50}$  values were estimated in (Inao et al., 1999; Katagi et al., 2016; Rose et al.,11412008; Sakellarides et al., 2003).

Pesticide	K <sub>oc</sub> * (L/kg)	DT <sub>50photo</sub> (d)	PPDB	Source
Atrazine	100	385	2.6	(Mathon et al. 2019)
Dimethoate	5.2-50	495	175	(Mathon et al. 2019)
Diuron	680	93.7	43	(Mathon et al. 2019)
Endosulfan	11500	12	-	(Rose et al., 2008)
Fenitrothion	2000	0.5	3.5	(Sakellarides et al., 2003)
Fenthion	1500	1.6	0.4	(Sakellarides et al., 2003)
Fludioxonil	145 600	9	10	(Katagi et al., 2016)
Fluometuron	202	1	stable	(Rose et al., 2008)
Isoproturon	126	41.3	48	(Mathon et al. 2019)
Molinate	190	54	stable	(Inao et al., 1999)
Parathion-Methyl	1500	25	9	(Sakellarides et al., 2003)
Simazine	130	173	1.9	(Mathon et al. 2019)

\*: The K<sub>oc</sub> values were extracted from pesticides databases (ChemSpider; Kim et al., 2021; Lewis et al., 2016; Zambonin et al., 2002).

1144

1147 Modulating factors applied to the photolysis rate  $k_{photo}$  to account for controlling factors (i.e., Temperature, 1148 depth, and radiation).

Modulating factors of $k_{\mbox{\scriptsize photo}}$	Parameters	Source
$\frac{1}{h_w} * \frac{l_0}{l_{max}} * \frac{1}{25 * TSS * e^{-25 * TSS * z}}$	• z (m): Depth. • $I_0$ (MJ m <sup>-2</sup> h <sup>-1</sup> ): Actual radiation. • $I_{max}$ (MJ m <sup>-2</sup> h <sup>-1</sup> ): Maximum radiation. • TSS (mg.g <sup>-1</sup> ): Amount of TSS.	(Rose et al., 2008)
$R_{UVB-b}$	• R <sub>UVB-b:</sub> Daily UV-B radiation that penetrates the pond.	(Watanabe et al., 2006)

1150

1152Biotransformation half-lives  $DT_{50bio,s}$  (d) of five pesticides with different mobilities  $K_{oc}$  and hydrophilicities log1153 $K_{ow}$ , measured in laboratory studies on sediment substrates with different organic carbon content OC (%) (Vallee1154et al., 2016). Along with, biotransformation half-lives at the water-sediment interface in wetlands, extracted from

the PPDB.

Pesticides	K <sub>oc</sub> (L/kg)*	log (K <sub>ow</sub> )*	OC (%)	DT <sub>50bio,s</sub> (d)	DT <sub>50bio,s</sub> (d) PPDB
Boscalid	9500	2.96	1.23	39.4	
			1.5	29.8	545
			1.7	9.4	
Isoproturon	122	2.5	1.2	100	
			1.5	61	149
			1.7	63.9	
Napropamide	885	3.3	1.23	82.7	
			1.5	80.1	316
			1.7	54	
Prochloraz	378	4.6	1.2	100	
			1.5	17.2	359
			1.7	10.2	
Tebuconazole	769	3.7	1.2	30.5	
			1.5	30.6	365
			1.7	1.4	

1156

1157(\*): The physicochemical properties  $K_{oc}$  and  $log(K_{ow})$  were extracted from the Pesticide Properties DataBase PPDB and1158PubChem.

1160

### Appendix B.

### 1161 Methodology

In this paragraph, we will present the methodology adopted to realize this critical review of process formulations and controlling factors behind pesticide dissipation in ponds. This work started with a bibliometric research. We used the listed research equations in different bibliographic research tools\*:

- 1166 (constructed wetland) AND ((wastewater OR agricultural) AND treatment)
- 1167 pesticide AND (dissipation OR mitigation) AND (wetland OR pond)
- 1168 (pesticide OR "Organic pollutant") AND wetland AND model
- 1169 (pesticide OR "Organic pollutant") AND wetland AND fate
- 1170 pesticide AND *process* AND (pond OR wetland)
- 1171 pesticide AND transfer AND (wetland OR pond)
- 1172 process AND (rate OR model OR kinetic) AND pesticide AND pond
- 1173 \*: Web of Science (1), Scopus (2), Google Scholar (3), EndNote (4), and Science direct (5).
- 1174 (1):<u>https://www.webofscience.com/wos/woscc/basic-search</u>
- 1175 (2):<u>https://www.scopus.com/search/form.uri?display=basic#basic</u>
- 1176 (3): https://scholar.google.com/schhp?hl=fr
- 1177 (4): <u>https://www.myendnoteweb.com/EndNoteWeb.html</u>

*Italic* represents the name of the processes (i.e., sorption/adsorption/desorption, biodegradation/degradation,
 settling/sedimentation/burial, resuspension, photolysis/photodegradation, volatilization, and hydrolysis).

First, we looked for general studies about the fate of pesticides in wetlands to record every 1180 potential process behind their dissipation. Afterward, we searched for each process whose 1181 effect was investigated in ponds on single or multiple pesticides. We selected theoretical 1182 papers for the descriptive part of processes and modeling papers to extract the equations for 1183 the formulation part in section 3. In each paper, we identified the pesticides targeted, 1184 1185 processes investigated, site, and the scale of their evaluation (i.e., laboratory, in-situ) by focusing more on recent work. Given this, three categories of processes in ponds can be 1186 distinguished: 1187

- 1188 1. Transport is responsible for the fate of pesticides within a compartment of the pond.
- 1189 2. Transfer controls redistribution of pesticides from a compartment to another.
- 1190 3. Transformation degrades and modifies the original chemical structure of pesticides.
- 1191









Among the set of processes, according to transformation processes, biodegradation was the 1199 most one surveyed with a total of 267 papers, followed by 91 studies of sorption (Fig. 1). 1200 Photolysis and settling were less evaluated; only 28 and 26 articles cited them, respectively. 1201 Finally, resuspension and volatilization had a minor presence in search results. As for 1202 processes formulations, it was necessary to look for modeling papers that either presented a 1203 process equation within the framework of a fate model or studied just that specific process. 1204 1205 Among the 273 reviewed papers, only 20% were about descriptive models of pesticides in

ponds, and over 80% evaluated more than one pesticide. Although, most of the studies
investigated a single process for a group of 2-6 pesticides. Most studies aiming to quantify a
process rate were conducted at a laboratory scale in controlled conditions. They were few
studies conducted in mesocosms\* and even less in the field.

- 1210 \*: Mesocosms are experimental water enclosures designed to provide a limited body of water with close to
- 1211 natural conditions, in which environmental factors can be realistically manipulated (Berger et al., 2016).
- 1212
- 1213

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