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## Research article

## Pesticide sorption and mitigation efficiency of a detention pond in a Champagne vineyard catchment

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## HIGHLIGHTS

- Pesticide sorption on various substrates of a vineyard detention pond was assessed.
- The measured equilibrium time was less than the *in situ* hydraulic residence time.
- Plant roots and rhizomes showed greater pesticide adsorption capacity than sediments.
- Sorption capacity was higher on cattail and iris than on mint and reed.
- Affinity of selected pesticides for roots and sediments was related to their  $K_{ow}$ .

## ARTICLE INFO

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Adsorption  
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Sediments  
Emergent macrophyte roots

## ABSTRACT

Detention ponds (DPs) are used to reduce the pesticide inputs from runoff to surface water. This study aimed to assess the role of the sorption process in the mitigation of a DP made up of four successive units and built at the outlet of a vineyard catchment in Champagne (France) to treat runoff waters. Sorption kinetics and isotherms were studied for four pesticides with contrasting properties, cyazofamid (CYA), fludioxonil (FLX), fluopicolide (FLP) and oryzalin (ORY), in the presence of copper in sediments and four emergent macrophyte roots and rhizomes sampled in the DP units 2 (photodegradation) and 3 (phytoremediation). The adsorption equilibrium time (from 24 to 96 h) was less than the hydraulic residence times in the two units (6 and 18 days on average) between November 2016 and November 2017. Sorption equilibrium could then be reached *in situ* in 85 % of cases. The  $K_d$  coefficients of the four pesticides were overall greater in plant roots (14–6742 L kg<sup>-1</sup>) than in sediments (6–163 L kg<sup>-1</sup>) because of their affinity for organic matter and the molecular and porous structure of the plant matrices. *Typha latifolia* and *Iris pseudacorus* exhibited greater  $K_d$  coefficients than *Mentha aquatica* and *Phragmites australis*, probably due to their greater specific surface area. The pesticide adsorption capacity in sediments and in *T. latifolia* and *I. pseudacorus* roots (ORY ≥ FLX > CYA > FLP) was linked to their  $K_{ow}$ . The estimated total annual amounts of the four pesticides adsorbed *in situ* were determined to be 1236 mg for unit 2 and 1570 mg for unit 3. The four plants improved the removal efficiency of the unit 3 by 33%. Thus, the establishment of suitable and effective plants should be promoted to optimize sorption processes and DP efficiency in reducing water pollution.

## 1. Introduction

The repeated use of pesticides in vineyards to fight vine diseases leads to elevated concentrations of Cu (e.g., Chopin et al., 2008; Chaignon et al., 2009) and pesticide residues (e.g., Bermúdez-Couso et al., 2007) in soils. The high slopes of northern vineyards (for the best

exposure of vines) favour runoff and can lead to the diffuse pollution of water bodies (Rabiet et al., 2010). From 0.5 to 3% of the pesticides applied in vineyard plots migrate to aquatic ecosystems during runoff events (Stottmeister et al., 2003; Vymazal and Březonivá 2015; Lefrancq et al., 2017), leading to deleterious effects on aquatic ecosystems (Komárek et al., 2010).

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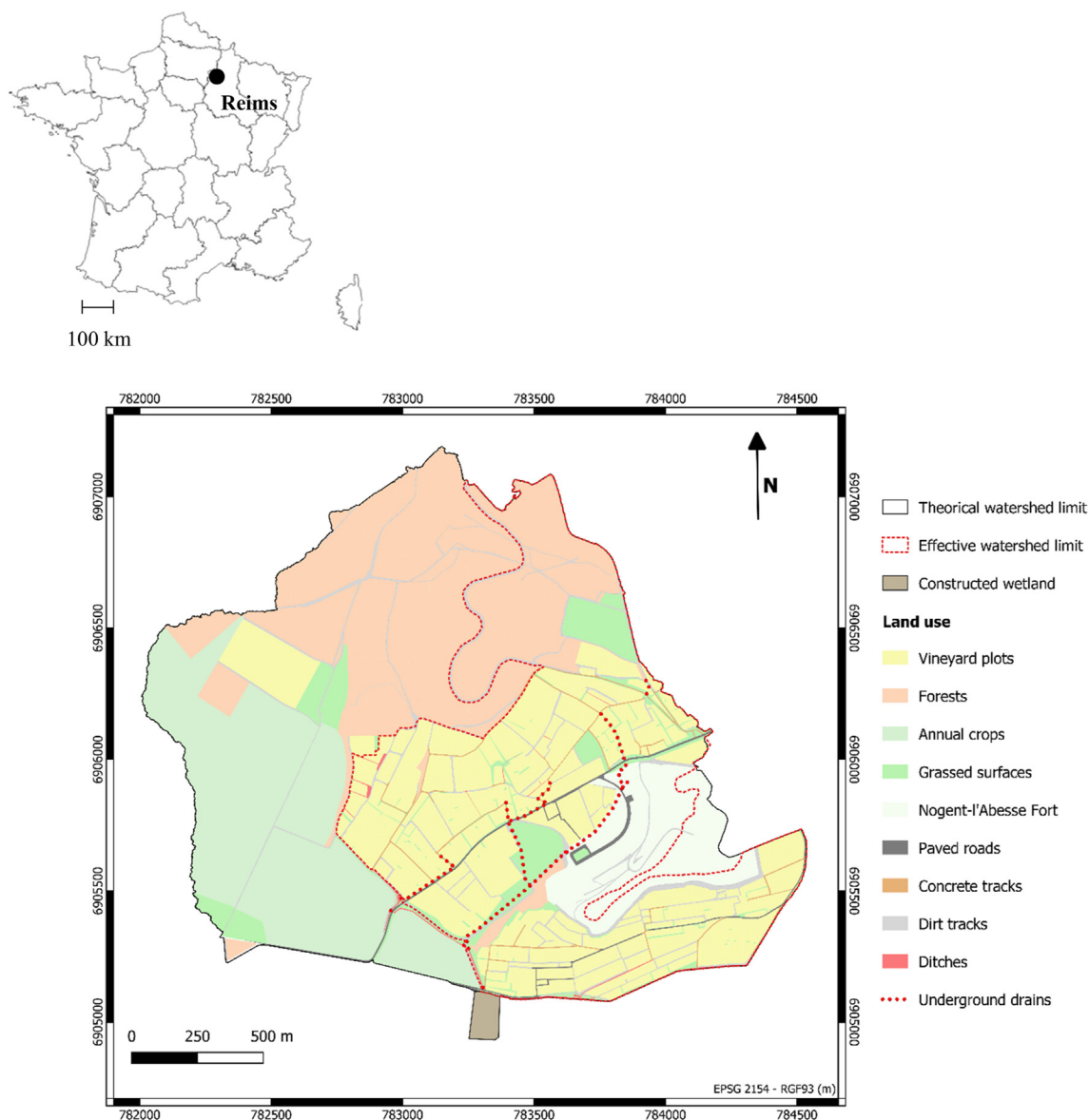
2405-8440/© 2022 Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

A solution to mitigate pesticide pollution from vineyard runoff water is detention ponds (DPs) (e.g., Maillard et al., 2011; Maillard and Imfeld 2014; Liu et al., 2019; Malyan et al., 2021). DPs are engineered systems designed to use nature-based solutions such as adsorption followed by sedimentation, physicochemical and microbial degradation and plant uptake (Vymazal 2005), depending on the hydraulic residence time (HRT) and thus water inputs. The adsorption of pesticides on solid substrates depends on the physicochemical properties of the pesticides, i.e. water solubility, octanol/water partition coefficient ( $K_{ow}$ ) and half-life (Landry et al., 2004; De Wilde et al., 2009; Komárek et al., 2010; Passeport et al., 2011). Pesticide adsorption is influenced by the HRT (Grégoire et al., 2009; Elsaesser et al., 2011; Gaullier et al. 2018, 2019), inlet pesticide load (Liu et al., 2019), and physicochemical properties of sediments and plants (Ahmad et al., 2006; Passeport et al., 2011; Mukherjee et al., 2016; Butkovskiy et al., 2021). These substrates can act as sinks or sources of pesticides in the water compartment (Maillard and Imfeld 2014).

The presence of macrophytes enhances the mitigation efficiency of DPs by reducing hydraulic flow and allowing a greater residence time for sedimentation, by increasing the contact time of water with vegetation

and sediment, and by creating habitats for organisms that enhance degradation (Grégoire et al., 2009; Elsaesser et al., 2011; Maillard et al., 2011; Guo et al., 2014; Vymazal and Březonivá 2015; De Souza et al., 2017). The removal of contaminants is 5–30 % higher in vegetated wetlands than in nonvegetated ponds (Rose et al., 2006; Lyu et al., 2018; Liu et al., 2019) depending on the season (Maillard and Imfeld, 2014) and plant species (Elsaesser et al., 2011). Many studies have been conducted on *Phragmites australis* and *Typha latifolia* (Grégoire et al., 2009; Maillard et al., 2011; Guo et al., 2014; Liu et al., 2019), the most planted emergent species in DPs, but fewer have been conducted on *Iris pseudacorus* (Malyan et al., 2021). To our knowledge, only one has been conducted in presence of *Mentha aquatica* (De Souza et al., 2017). Although it is known that the adsorption of pesticides is a key process in DPs, the assessment of sorption on emergent macrophytes, especially their roots anchored in the sediments, has been little explored.

The aim of this study was to evaluate the relative contribution of sediments and emergent macrophyte roots in the adsorption process to DP mitigation in a vineyard area. For that purpose, the adsorption of a mixture of four pesticides widely applied in a Champagne vineyard, detected in runoff water and showing contrasting physicochemical



**Figure 1.** Location of the constructed wetland of Nogent-l'Abbesse (Champagne, Northeast France), with limits and land cover of the theoretical (in black) and actual (in blue) watershed.

properties (cyazofamid, fludioxonil, fluopicolide, and oryzalin), was conducted on sediments and roots of four macrophytes. Batch experiments were carried out with horizontal gentle agitation reflecting the field conditions. The sorption experiments were also performed in the presence of copper, widely used to fight against vine diseases, and found in nonnegligible amounts in vineyard soils and consequently in DP water and sediment, which could influence pesticide adsorption.

## 2. Material and methods

### 2.1. Study site

The studied samples originated from a DP located in a vineyard catchment in Nogent-l'Abesse (Champagne area, Northeast France). After a detailed spatial study of the area with Light Detection and Ranging (LiDaR) and filed inspections, the effective surface area of the catchment was determined to be 176.3 ha with 95 ha of vineyard (54%), 19 ha of forest (11%), 17 ha of grassed surfaces (10%), 3 ha of paved roads (2%), 3 ha of concrete tracks (2%), 12 ha of dirt tracks (7%) and 1 ha of ditches (1%) (Figure 1). A fort occupies 26 ha, i.e. 15% of the effective watershed. The DP receives runoff waters coming from roads, tracks and ditches, as well as waters from underground drains, i.e. soft-engineered runoff attenuation features.

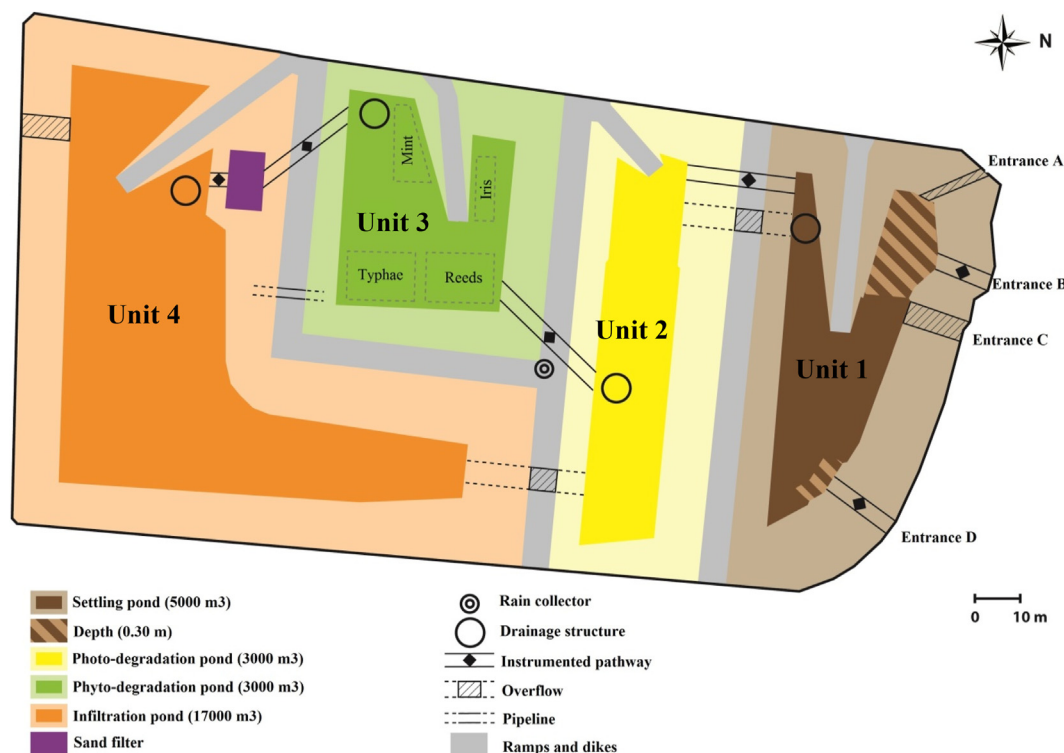
The DP was built in 1982 and renovated in 2015 to accommodate the new embankment policies, which require dikes lower than 2 m. The current hybrid DP has a surface area of 10,584 m<sup>2</sup> and a water storage capacity of 28,000 m<sup>3</sup>. It comprises four units dedicated to (1) decantation (1,870 m<sup>2</sup>; 5,000 m<sup>3</sup>), (2) additional decantation and photo-degradation (1,764 m<sup>2</sup>; 3,000 m<sup>3</sup>), (3) phytodegradation (2,310 m<sup>2</sup>; 3,000 m<sup>3</sup>) and (4) infiltration (4,640 m<sup>2</sup>; 17,000 m<sup>3</sup>; Figure 2). From November 2016 to November 2017, 52 runoff events occurred and were monitored; the water flows and volumes at the inlet and the outlet of the four units were continuously measured with an interval of 5 min. At every runoff event, waters were automatically sampled at the inlet and

the outlet of each unit, and the concentrations of numerous pesticides were measured in liquid phase by LC-MS/MS after filtration of samples. The concentrations of pesticides were also determined in detention pond waters in March and October 2017 (Table 1). The hydraulic residence times (HRT) in the first three units (calculated for 52 runoff events) varied greatly, from 0.4 to 27.5 h in unit 1 (average 5.0 h), 0.7–97 days in unit 2 (average 18.3 days) and 1.6–20.8 days in unit 3 (average 5.7 days), according to the rainfall pluviometry, intensity and frequency and the entering water fluxes (unpublished data). Four species of macrophytes naturally growing in French native wetlands were planted in unit 3: *Typha latifolia*, *Phragmites australis*, *Mentha aquatica* and *Iris pseudacorus*. The planted areas in March 2017 were 293, 258, 80 and 36 m<sup>2</sup>, respectively.

### 2.2. Sediment and plant sampling

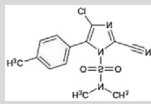
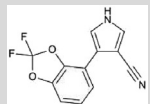
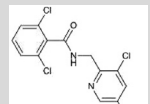
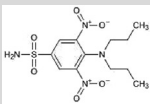
Sediment samples were collected in March 2017 from units 2 and 3. The whole sediment layers (with a total thicknesses of nearly 6.5 cm in unit 2 and 2 cm in unit 3) were sampled in five locations in the two units but in two different ways because of the different water depths in the two units (approximately 80 cm in unit 2 and 50 cm in unit 3). We used a plastic beaker in unit 2 and plastic cylinders of 4 cm diameter and 2 cm height (to mimic a core sampling), namely 25 cm<sup>3</sup> and 40 g of wet sediment at each location, in unit 3. The samples were stocked in polyvinyl chloride (PVC) trays and transported to the laboratory, where they were dried at 40 °C in an oven for 48 h, carefully crushed and sieved through a 2 mm mesh riddle. For each unit, samples were homogenized to obtain a composite sample for further experiments.

The underground parts (roots and rhizomes if present) of the four plants planted in unit 3 (*Typha latifolia*, *Phragmites australis*, *Mentha aquatica*, *Iris pseudacorus*), which are the anchorage system of plants in the sediment (Malyan et al., 2021), were collected on the same day as the sediments. Depending on each species, roots and rhizomes of 5–10 plants were sampled and pooled together. The roots and rhizomes were stocked



**Figure 2.** Scheme and instrumentation of the constructed wetland of Nogent-l'Abesse composed of four units. The instrument pathways indicate the location of flowmeters and automatic samplers.

**Table 1.** The average annual application from 2013 to 2017 ( $\text{kg ha}^{-1} \text{ year}^{-1}$ ), the means  $\pm$  standard deviations of concentrations in water entering the units 2 and 3 ( $\mu\text{g L}^{-1}$ ) between November 2016 and November 2017 and the physicochemical properties of the four selected pesticides (cyazofamid, fludioxonil, fluopicolide, oryzalin).

	Cyazofamid CYA	Fludioxonil FLX	Fluopicolide FLP	Oryzalin ORY
Average application ( $\text{kg ha}^{-1} \text{ year}^{-1}$ )*	$0.75 \pm 0.30$	$0.24 \pm 0.06$	$0.08 \pm 0.01$	$0.16 \pm 0.13$
Mean concentrations in waters entering the unit 2 ( $\mu\text{g L}^{-1}$ )**	$0.02 \pm 0.04$	$0.2 \pm 0.5$	$0.7 \pm 1.8$	$0.09 \pm 0.2$
Mean concentrations in waters of the unit 2 ( $\mu\text{g L}^{-1}$ )**	$0.01 \pm 0.01$	$0.05 \pm 0.02$	$0.24 \pm 0.23$	nd****
Mean concentrations in waters entering the unit 3 ( $\mu\text{g L}^{-1}$ )**	$0.02 \pm 0.03$	$0.2 \pm 0.4$	$0.6 \pm 1.0$	$0.07 \pm 0.1$
Mean concentrations in waters of the unit 3 ( $\mu\text{g L}^{-1}$ )**	$0.01 \pm 0.01$	$0.02 \pm 0.01$	$0.25 \pm 0.19$	nd****
Pesticide type	fungicide	fungicide	fungicide	herbicide
Structural formula***	$\text{C}_{13}\text{H}_{13}\text{ClN}_4\text{O}_2\text{S}$	$\text{C}_{12}\text{H}_6\text{F}_2\text{N}_2\text{O}_2$	$\text{C}_{14}\text{H}_8\text{Cl}_3\text{F}_3\text{N}_2\text{O}$	$\text{C}_{12}\text{H}_{18}\text{N}_4\text{O}_6\text{S}$
Structure***				
Molecular mass ( $\text{g.mol}^{-1}$ )***	324.78	248.19	383.58	346.36
Solubility in water (20 °C; $\text{mg L}^{-1}$ )***	0.107	1.8	2.8	1.13
$K_{ow}$ (pH 7, 20 °C)***	1580	13200	794	5370
Log $K_{ow}$ ***	3.2	4.12	2.9	3.73
$K_f$ *** (range)	23.0 (4.1–65.1)	3312 (290–7300)	4.20 (1.42–9.27)	4.93 (4.83–5.04)
1/n*** (range)	0.96 (0.83–1.07)	1.00 (0.81–1.19)	0.90 (0.86–0.93)	0.943 (0.926–0.943)
$K_{foc}$ in soil ( $\text{L kg}^{-1}$ )*** (range)	1338 (736–2172)	132000 (7500–210000)	321.1 (172–580)	724 (439–1008)
pKa (at 25 °C)***	Not applicable	0 (strong acid)	Not applicable	9.4 (very weak acid)
DT50 in water (days)***	6.2	2	91.4	5.9
DT50 in water-sediment (days)***	14	575	1117	32.7

\* Quantities applied on the vineyard were given by the Coopérative Viticole de Nogent l'Abbesse et Cernay-lès-Reims.

\*\* Concentrations measured by LC-MS/MS. LOQ = 10  $\mu\text{g L}^{-1}$ .

\*\*\* Pesticides Properties Database (PPDB; Lewis et al., 2016).

\*\*\*\* Non detected.

in plastic bags and transported to the laboratory. They were washed with pure water (Direct Q<sub>3</sub>, Millipore™), dried at 70 °C in an oven for 48 h, cut into pieces of approximately 2 cm and stored at −18 °C until use.

### 2.3. Physicochemical characterization of substrates

The measurement of the grain size distribution of the sediments (NF X 31-107) was performed by laser granulometry (Mastersizer 2000, Malvern Instrument). Sediment pH was measured using the French norm NFX 31-103. The contents of carbon (NF ISO 10964) and nitrogen (NF ISO 10878) in the sediments and plant roots were determined by an elemental analyzer (EuroEA, EuroVector) at the research unit INRA-FARE (UMR CNRS 0614) of the University of Reims Champagne-Ardenne. The C/N ratio, reflecting the organic matter composition and structure (Simpson and Simpson, 2012), was also calculated.

### 2.4. Selected contaminants

Four organic pesticides were chosen based on the average quantity applied in the vineyard catchment during the previous five years (from 2013 to 2017), the concentrations detected in the water entering the DP between November 2016 and November 2017 (analysis by LC-MS/MS after automatically water sampling during runoff events and filtration) and the diversity of their physicochemical properties (Table 1). The selected pesticides were three fungicides, cyazofamid (CYA; 4-chloro-2-cyano-N,N-dimethyl-5-(4-methylphenyl)-1H-imidazole-1-sulfonamide), fludioxonil (FLX; 4-(2,2-difluoro-2H-1,3-benzodioxol-4-yl)-1H-pyrrole-3-carbonitrile), and fluopicolide (FLP; 2,6-dichloro-N-((3-chloro-5-(trifluoromethyl)-2-pyridinyl)methyl)benzamide), and one herbicide, oryzalin (ORY; 4-(dipropylamino)-3,5-dinitrobenzenesulfonamide). CYA is insoluble (solubility of 0.1  $\text{mg L}^{-1}$ ), while the three others are slightly soluble (solubility between 1 and 3  $\text{mg L}^{-1}$ ; Table 1). FLX and ORY are the most hydrophobic ( $\log K_{ow} = 4.12$  and 3.73, respectively), CYA is

moderately hydrophobic ( $\log K_{ow} = 3.2$ ) and FLP is poorly hydrophobic ( $\log K_{ow} = 2.9$ ; Table 1; Lewis et al., 2016). FLX is a strong acid (pKa = 0 and 14.1) and ORY is a very weak acid (pKa = 9.4). To our knowledge, there are a few studies about the adsorption of these four pesticides in the literature, but no study has been conducted on the combined adsorption of these four pesticides. Copper is applied in large quantities in vineyards simultaneously with organic pesticides; therefore, we chose to carry out the following experiments in the presence of copper. The pesticides were purchased from Cluzeau and were of analytical standard grade (>98%). The solution of 99% Cu used in the experiments was purchased from Sigma-Aldrich in the form of  $\text{CuCl}_2$ .

### 2.5. Kinetic experiments

Before the adsorption experiments, the four pesticides were extracted from sediments and plant roots via the QuEChERS method (Fernandes et al., 2013). The cumulative concentrations were lower than 5  $\mu\text{g kg}^{-1}$ . In the kinetic experiments, 10 mL of  $10^{-2} \text{ mol L}^{-1}$   $\text{CaCl}_2$  solution (>97%, Sigma-Aldrich) with 2.5  $\text{mg L}^{-1}$  of each pesticide (the highest concentration used for adsorption experiments, see below) and 1  $\text{mg L}^{-1}$  of copper were added to a flask containing  $2 \pm 0.1 \text{ g}$  of sediment or  $0.2 \pm 0.01 \text{ g}$  of plant dry weight (corresponding to an equivalent solid volume and solid:solution volume ratio; Vallée et al., 2014) previously humidified with 1 mL of pure water. The flasks were covered with Parafilm® (Bemis, Neenah, USA) to avoid evaporation. Under these experimental conditions (substrate weight, length of cut roots, solid:solution ratio), the exchange surface areas were estimated to be 3.5–5.5  $\text{cm}^2$  for the plant roots (calculated from 0.2 g of cylindrical pieces of 2 cm length) and approximately 20  $\text{cm}^2$  for sediments (calculated from the flask diameter without agitation and hence underestimated). The concentrations of the pesticides in solution were determined after 2, 8, 24, 48, 72, 96 and 120 h of gentle horizontal agitation (160 rpm; Innova 2300, New Brunswick) at  $20 \pm 1 \text{ °C}$ . This gentle agitation speed was chosen to mimic the hydraulic

conditions in units 2 and 3 of the DP apart from water inputs. Most adsorption studies followed the OECD guidelines (2000) with end-over-end shaking (Arias et al., 2005; Bermúdez-Couso et al., 2007; De Wilde et al., 2009; Hall et al., 2015), and very few were conducted with low agitation although it is closer to field conditions (Pose-Juan et al., 2011; Gaullier et al., 2018). For each contact time, samples were prepared in triplicate. Likewise, triplicate samples without sediment or plant (blanks) underwent the same experimental conditions to verify the absence of pesticide degradation or adsorption on glass vials. In the same way, triplicate samples without contaminant solution (controls) were performed to verify the negligible release of pesticides by sediments and plant roots. After agitation, the supernatant (pH 6.8–7 for sediments and 5.6–6.5 for plant roots and rhizomes) was sampled and placed in a polycarbonate centrifuge tube and then centrifuged at 5,500 rpm for 30 min to eliminate the suspended solid particles. For the root samples, the solution was filtered through a 0.7  $\mu\text{m}$  glass fiber filter (Sigma-Aldrich) after centrifugation, agitated with 0.150 g of  $\text{MgSO}_4$  and 0.05 g of PSA (Primary Secondary Amine, Sigma-Aldrich), and then centrifuged at 3500 rpm for 5 min to purify the samples (QuEChERS extraction procedure; Fernandes et al., 2013). Finally, a 1-mL aliquot was transferred to an amber glass vial for pesticide analysis, and a 5-mL aliquot acidified with 50  $\mu\text{L}$  of  $\text{HNO}_3$  (Trace Metal analysis grade, VWR International) was transferred to polyether sulfone (PES) flasks for copper analysis.

The adsorbed percentage of the initial quantity of a given contaminant at any time  $t$ ,  $P_{\text{ads}}$  (%), was calculated using the following mass balanced equation (Eq. (1); Aljerf, 2018):

$$P_{\text{ads}} = \frac{Q_{\text{ads}}}{Q_i} \times 100 \quad (1)$$

where  $Q_{\text{ads}}$  (mg of contaminant per kg of substrate;  $\text{mg kg}^{-1}$ ) is the amount of contaminant adsorbed at any time  $t$  and  $Q_i$  ( $\text{mg kg}^{-1}$ ) is the initial contaminant concentration. Previously,  $Q_{\text{ads}}$  was calculated as follows (Eq. (2)):

$$Q_{\text{ads}} = C_{\text{ads}} \times \frac{V}{m} \quad (2)$$

where  $C_{\text{ads}}$  is the adsorbed concentration at any time ( $\text{mg L}^{-1}$ ; calculated as the difference between the initial concentration and the measured concentration in the supernatant),  $V$  is the solution volume (0.01 L) and  $m$  is the substrate weight (kg). The blank analysis revealed that pesticide removal by adsorption on the glass flasks was negligible (less than 5 %), and the control analysis revealed that any pesticide present was released by the different matrixes.

## 2.6. Adsorption experiments

Adsorption isotherms were conducted by adding 10 mL of a  $10^{-2}$  mol  $\text{L}^{-1}$   $\text{CaCl}_2$  solution with various concentrations of each pesticide (0.05–0.25–0.5–1–2.5  $\text{mg L}^{-1}$ ) and a constant concentration of copper (1  $\text{mg L}^{-1}$ ) to  $2 \pm 0.1$  g of sediment or  $0.2 \pm 0.01$  g of plant root previously humidified. The total pesticide concentrations in the runoff and DP waters were lower than 1  $\mu\text{g L}^{-1}$  for one pesticide and 2  $\mu\text{g L}^{-1}$  for the four pesticides (Table 1). The concentrations of Cu were comprised between 10 and 20  $\mu\text{g L}^{-1}$ . The selected concentrations for the adsorption experiments then were 10–1000 times more elevated for analysis purposes, as it was often the case in earlier studies (Vallée et al., 2014; Gaullier et al., 2018; Sahin and Karpuzcu, 2020). After covering with Parafilm<sup>®</sup>, the mixtures were gently agitated like above for 48 h corresponding to the pseudo-equilibrium time that was previously determined by the kinetic experiments under the experimental conditions used here. Indeed, the colloidal organic matter released from the roots (mostly from *M. aquatica* and *P. australis*) after 48 h of agitation during the kinetic experiments induced analysis difficulties. These biopolymers, which were likely proteins/protein-like substances or polysaccharides that are commonly responsible for drinking water ultrafiltration membrane

fouling (Xiao et al., 2012; Chen et al., 2014), clogged the HPLC columns despite filtration and purification via the QuEChERS method. Therefore, we had to determine an agitation time less than 72 h for the adsorption isotherm experiments. Statistical tests showed no significant differences in the  $P_{\text{ads}}$  ( $p$  value = 0.1) between 48 h and 96 h in *I. pseudacorus* and *T. latifolia*. The time of 48 h was thus used to carry out the adsorption isotherm experiments for the sediments and for all of the plant roots to be able to compare the obtained results.

After 48 h of agitation, the sediment and plant root samples were treated as described above. For each concentration, samples were prepared in triplicate. The blanks and the controls revealed negligible removal or release of pesticides (less than 5 %) for all the tested concentrations.

The adsorbed pesticide concentration ( $x/m$ , in  $\text{mg kg}^{-1}$ ) was calculated using Eq. (2) at equilibrium. The experimental results were described using the Freundlich equation (Freundlich, 1906; Eq. (3)) and the linear equation (eq. (4)):

$$x/m = K_{\text{fads}} \times C_{\text{eq}}^{1/n} \quad (3)$$

where  $K_{\text{fads}}$  ( $\text{mg L}^{-1} \text{kg}^{-1}$ ) and  $1/n$  are empirical adsorption coefficients of sorption capacity and sorption intensity, respectively,  $C_{\text{eq}}$  is the concentration at equilibrium ( $\text{mg L}^{-1}$ ) and  $x/m$  is the adsorbed concentration ( $\text{mg kg}^{-1}$ ). The coefficient  $1/n$  describes the adsorption processes.

$$x/m = K_d \times C_{\text{eq}} \quad (4)$$

where  $K_d$  ( $\text{L kg}^{-1}$ ) is the sorption coefficient and  $C_{\text{eq}}$  is the concentration at the equilibrium time ( $\text{mg L}^{-1}$ ). The  $K_d$  values of CYA, FLX and FLP in the six substrates were directly calculated from the slope of the linear adsorption isotherms. Oryzalin was almost always adsorbed at 100% ( $C_{\text{eq}} < \text{LOQ}$  of 0.01  $\text{mg L}^{-1}$ ) during the adsorption experiments, and reliable modeling was not feasible. The  $K_d$  values of ORY in the six substrates were therefore calculated from the results of the kinetic experiments when linearity was obtained (from only one available point for *T. latifolia* and *P. australis*, from a straight line with two points for *I. pseudacorus* and *M. aquatica* and from a straight line with three points for sediments of units 2 and 3).

The  $K_d$  values, obtained with the linear equation (Eq. (4)) for each substrate-pesticide interaction (except for ORY in roots of *T. latifolia* and *P. australis* for which  $K_d$  was calculated from only one available point above LOQ), were normalized to the organic carbon content of the substrate (% OC) to obtain the  $K_{\text{oc}}$  coefficient (Eq. (5)):

$$K_{\text{oc}} = \frac{K_d}{\% \text{OC}} \times 100 \quad (5)$$

## 2.7. Pesticide analysis

Chromatographic analyses were conducted using the dual RSLC (Rapid Separation Liquid Chromatography) Ultimate 3000 Dionex<sup>®</sup>. A sample volume of 500  $\mu\text{L}$  was injected and flushed onto the online solid phase extraction (SPE) column with water at a flow rate of 1  $\text{ml min}^{-1}$ . The SPE column was an Oasis HLB 25  $\mu\text{m}$ ,  $2.1 \times 20$  mm (Waters). After 1 min of flushing, a ten-port switching valve diverted the sample from the SPE system to the LC system. Retention times of cyazofamid, fludioxonil, fluopicolide and oryzalin were 5.82, 3.54, 4.32 and 4.98 min, respectively. After switching to the LC system in back flush mode, the analytical pump was used to separate the four analytes at 20 °C on the Kinetex C18 2.6  $\mu\text{m}$  column (100 mm  $\times$  4.6 mm; Phenomenex). Elution was isocratic (50 % acetonitrile, 50 % distilled water) with a flow rate of 1  $\text{mL min}^{-1}$ . The four pesticides were detected using a diode array at 215 nm. The LOQ values were 10  $\mu\text{g L}^{-1}$  in the solutions, corresponding to 0.05  $\text{mg kg}^{-1}$  in the sediments and 0.5  $\text{mg kg}^{-1}$  in the roots.

## 2.8. Copper analysis

The concentration of Cu was determined by inductive coupled plasma-atomic emission spectrometry (ICP-AES, Iris Advantage, Thermo

Sharell Ash Corp.). A sample volume of 2 mL was injected at a flow rate of 1.85 ml min<sup>-1</sup> and nebulized at 28.0 psi. The read delay per replicate was 60 s and the wavelength used was 224.7 nm. Three measurements were made, and the copper concentration was given as the mean concentration of these three measurements. The LOQ value was 5 µg L<sup>-1</sup> in the solutions, corresponding to 0.03 mg kg<sup>-1</sup> in the sediments and 0.25 mg kg<sup>-1</sup> in the roots.

2.9. Statistical analysis

Statistical analyses were conducted using R software. Concerning the sorption kinetic results, the Kruskal-Wallis test was used to determine the adsorption equilibrium time by comparing the values of adsorbed concentration of adjacent time points. The equilibrium time (*T<sub>eq</sub>*) was determined as the time beyond which the concentrations presented no significant difference (with a degree of significance of *p* = 0.05). After that, the adsorbed percentage of contaminants at equilibrium (*P<sub>ads</sub>*) was calculated with Eq. (1). Then, analysis of variance (ANOVA) was conducted using Tukey's HSD post hoc test to detect significant differences (with a degree of significance of *p* = 0.05) between *P<sub>ads</sub>* of the five contaminants for the six substrates (two sediments and four plant roots). For the adsorption isotherms, we compared the adsorbed amount at equilibrium of the six substrates (two sediments and four plant roots) using ANOVA followed by Tukey's HSD test to detect significant differences (with a degree of significance of *p* = 0.05) for each tested concentration (from 0.05 to 2.5 mg L<sup>-1</sup>) of the four pesticides.

2.10. Rough estimate of adsorbed pesticide amounts onto sediments and plant roots in the DP

The quantity of the sediments in units 2 and 3 (kg) after two and a half years working were calculated from the area of each unit, the height of sediments measured in the units themselves, the water content and the dry density estimated with laboratory measurements (weight difference before and after lyophilization; Eq. (6)):

$$Q_{\text{sediment}} = S_{\text{unit}} \times h_{\text{sediment}} \times (1 - \%_{\text{water}}) \times d_{\text{sediment}} \tag{6}$$

where *Q<sub>sediment</sub>* is the sediment quantity (kg), *S<sub>unit</sub>* is the unit area (m<sup>2</sup>), *h<sub>sediment</sub>* is the sediment height in the units (m), *%<sub>water</sub>* is the percentage of water and *d<sub>sediment</sub>* is the dry density of sediments (0.61 and 0.96 g cm<sup>-3</sup> for unit 2 and unit 3, respectively).

The quantity of the roots of the four plants (kg) was estimated from the planted areas, measured in the field, and the weight of the roots, measured in an area of approximately 0.07 m<sup>2</sup> after sampling and drying (Eq. (7)):

$$Q_{\text{roots}} = S_{\text{plants}} \times P_{\text{roots}} \tag{7}$$

where *Q<sub>roots</sub>* is the quantity of roots (kg), *S<sub>plants</sub>* is the planted area (m<sup>2</sup>) and *P<sub>roots</sub>* is the weight of roots per unit area (kg m<sup>-2</sup>).

The adsorbed quantity of pesticides in the sediments or roots was then calculated according to Eq. (8), using the average concentration of pesticides measured in the water arriving in each unit from November 2016 to November 2017 (Table 1):

$$Q_{\text{ads}} = Kd \times C_{\text{pest}} \times Q_{\text{substrate}} \tag{8}$$

where *Q<sub>ads</sub>* is the adsorbed quantity (µg), *K<sub>d</sub>* is the linear adsorption coefficient (L kg<sup>-1</sup>), *C<sub>pest</sub>* is the concentration of pesticides in arriving waters (µg L<sup>-1</sup>) and *Q<sub>substrate</sub>* is the total weight of sediments or roots (kg).

3. Results and discussion

3.1. Physico-chemical characteristics of substrates

The sediments from units 2 and 3 were alkaline (pH of approximately 7.5–8). The particle size distribution and organic carbon (OC) content were similar in the sediments of both units (Table 2). In contrast, the sediments of unit 3 contained less nitrogen (1.9 ± 0.4 g kg<sup>-1</sup>) than those of unit 2 (2.6 ± 0.2 g kg<sup>-1</sup>), leading to a greater C/N ratio in unit 3 (52.9) than in unit 2 (36.0), indicating more humified organic matter in unit 3. The plant roots were ten times richer in carbon and twenty times richer in nitrogen than the sediments. *T. latifolia*, *I. pseudacorus* and *P. australis* contained higher rates of OC (406–451 g kg<sup>-1</sup>) than *M. aquatica* (333 g kg<sup>-1</sup>; Table 2). *T. latifolia* and *M. aquatica* presented the highest rate of nitrogen at 40.6 g kg<sup>-1</sup>, while *I. pseudacorus* and *P. australis* presented concentrations of 37.6 and 32.8 g kg<sup>-1</sup>, respectively. *M. aquatica* showed the lowest C/N ratio (8.2), while *P. australis* had the highest ratio (13.8). The literature data on lignin, cellulose and hemicellulose content in macrophyte roots are scarce, and the single values obtained for roots were the lignin content in *P. australis* (21.8% from Iversen et al., 2017 in TRY Plant Trait Database, Kattge et al., 2020) and *M. aquatica* (15–20% from Mustin, 1987). The other values were measured in whole plants (He et al., 2014; Cavalaglio et al., 2016). The content of lignin in the roots of *P. australis* (21.8%; Iversen et al., 2017) is on the same order as that in the whole plant (17.7–23.0%; Cavalaglio et al., 2016; He et al., 2014). According to the literature, the content of lignin does not vary significantly from one macrophyte to another (15–23%; Mustin, 1987; He et al., 2014; Cavalaglio et al., 2016). The percent of cellulose was 32.9–38.1 % in *P. australis*, 36.9% in *I. pseudacorus* and 28.0% in *T. latifolia* (He et al., 2014; Cavalaglio et al., 2016). The percent of hemicellulose was almost 20% in *P. australis* and lower than 10% in *T. latifolia* and *I. pseudacorus*.

**Table 2.** The physicochemical characteristics (granulometry, pH, organic carbon and nitrogen content, C/N ratio) of the six studied substrates (sediments of units 2 and 3; roots of *T. latifolia*, *I. pseudacorus*, *M. aquatica* and *P. australis*). Values are expressed as the means ± standard deviations calculated from three replicates. The literature data for the lignin, cellulose and hemicellulose in the four plants (expressed as weight percent of dry matter) are also given.

	Clay (%)	Silt (%)	Sand (%)	pH	Organic Carbon (g kg <sup>-1</sup> )	Nitrogen (g kg <sup>-1</sup> )	C/N ratio	Lignin (%)	Cellulose (%)	Hemicellulose (%)
Unit 2	14.7 ± 2.2	78.4 ± 2.2	6.8 ± 2.8	7.52 ± 0.02	93.6 ± 1.3	2.6 ± 0.2	36.0 ± 2.5	–	–	–
Unit 3	14.5 ± 2.9	70.4 ± 5.0	9.0 ± 4.3	8.01 ± 0.05	100.6 ± 9.5	1.9 ± 0.4	52.9 ± 5.0	–	–	–
<i>Typha latifolia</i>	–	–	–	–	406 ± 0.5	40.6 ± 0.9	10.0 ± 0.2	15.9 <sup>1</sup>	28.0 <sup>1</sup>	9.2 <sup>1</sup>
<i>Iris pseudacorus</i>	–	–	–	–	439 ± 0.6	37.6 ± 0.9	11.7 ± 0.3	17.9 <sup>1</sup>	36.9 <sup>1</sup>	4.5 <sup>1</sup>
<i>Mentha aquatica</i>	–	–	–	–	333 ± 2.2	40.6 ± 0.4	8.2 ± 0.0	15–20 <sup>2</sup>	–	–
<i>Phragmites australis</i>	–	–	–	–	451 ± 0.9	32.8 ± 1.1	13.8 ± 0.5	17.7 <sup>1</sup>	32.9 <sup>1</sup>	19.7 <sup>1</sup>
								21.8 <sup>3</sup>	38.1 <sup>4</sup>	20.5 <sup>4</sup>
								23.0 <sup>4</sup>		

<sup>1</sup> He et al., 2014 (whole plant).

<sup>2</sup> Mustin, 1987 (roots).

<sup>3</sup> Iversen et al., (2017) (roots).

<sup>4</sup> Cavalaglio et al., 2016 (whole plant).

**Table 3.** Equilibrium time determined using the Kruskal-Wallis test ( $T_{eq}$ ,  $p < 0.05$ ) and percentage of the initial quantity adsorbed at equilibrium ( $P_{ads}$ ) for the four pesticides (CYA, FLX, FLP and ORY) in the six substrates (sediments of units 2 and 3, roots of *T. latifolia*, *I. pseudacorus*, *M. aquatica* and *P. australis*). Kinetic experiments in *M. aquatica* and *P. australis* were not carried out beyond 48 h because the presence of organic polymers in the sample solutions made analysis impossible.

		CYA	FLX	FLP	ORY	Cu
Unit 2	$T_{eq}$ (h)	96***	96**	96**	96***	72***
	$P_{ads}$ (%)	78.5 ± 1.0 <sup>a;2</sup>	98.2 ± 0.1 <sup>a;3</sup>	78.3 ± 0.6 <sup>a;2</sup>	95.6 ± 0.2 <sup>a;1</sup>	96.2 ± 1.2 <sup>a;1</sup>
Unit 3	$T_{eq}$ (h)	>120***	72***	>120***	72***	48*
	$P_{ads}$ (%)	80.7 ± 0.2 <sup>a;2</sup>	95.9 ± 8.4 <sup>a;1</sup>	77.7 ± 1.2 <sup>a;2</sup>	91.1 ± 10.0 <sup>a;1</sup>	97.6 ± 0.1 <sup>a;1</sup>
<i>Typha latifolia</i>	$T_{eq}$ (h)	>96***	>96***	72***	48***	72*
	$P_{ads}$ (%)	94.3 ± 1.5 <sup>b;2</sup>	56.7 ± 7.4 <sup>b;3</sup>	90.0 ± 1.7 <sup>b;2</sup>	99.1 ± 1.3 <sup>b;4</sup>	77.7 ± 0.9 <sup>b;1</sup>
<i>Iris pseudacorus</i>	$T_{eq}$ (h)	48**	>96**	48**	48**	72**
	$P_{ads}$ (%)	70.9 ± 2.3 <sup>c;2</sup>	65.7 ± 4.7 <sup>b;2</sup>	95.6 ± 1.9 <sup>b;3</sup>	98.9 ± 1.0 <sup>b;3</sup>	89.7 ± 0.8 <sup>c;1</sup>
<i>Mentha aquatica</i>	$T_{eq}$ (h)	24**	>48**	24**	>48**	>48**
	$P_{ads}$ (%)	78.5 ± 0.1 <sup>a;2</sup>	60.8 ± 13.8 <sup>b;2</sup>	93.9 ± 3.2 <sup>b;1</sup>	97.4 ± 1.1 <sup>b;3</sup>	92.9 ± 0.5 <sup>c;1</sup>
<i>Phragmites australis</i>	$T_{eq}$ (h)	24 <sup>ns</sup>	>48**	24**	>48**	24 <sup>ns</sup>
	$P_{ads}$ (%)	67.5 ± 3.8 <sup>c;1</sup>	45.3 ± 7.8 <sup>c;2</sup>	72.2 ± 8.1 <sup>a;1</sup>	99.7 ± 0.4 <sup>b;3</sup>	75.3 ± 1.4 <sup>b;1</sup>

\*\*\* $p < 0.01$ ; \*\* $p < 0.05$ ; \* $p < 0.1$ ; ns: non significant (n = 15).

a,b,c,d,e,f: Two different letters in the same row indicate a significant difference according to Tuskey's test (p value = 0.05).

1,2,3,4,5: Two different numbers in the same line indicate a significant difference according to Tuskey's test (p value = 0.05).

No data relative to the cellulose and hemicellulose percentages in *M. aquatica* were found in the literature.

### 3.2. Effect of substrates on pesticide adsorption

The adsorption of the four organic molecules reached equilibrium faster in plant roots (from 24 to >96 h; Table 3; Figure S1c–f) than in sediments (from 72 to >120 h; Figure S1a, b; Table 3). This faster adsorption on plant roots compared to sediments may be explained by easier access to adsorption sites on plant roots. In contrast, the equilibrium time for Cu was nearly similar in roots and sediments (between 24 and 72 h).

For the adsorption coefficient, the determination coefficient ( $R^2$ ) values were all satisfactory and were between 0.48 and 0.95 for the Freundlich equation (Table S1) and between 0.45 and 0.99 for the linear

equation (Table 4; nonsignificant values of  $R^2$  were obtained for CYA in *P. australis* and FLX in *M. aquatica*, probably due to the difficulties encountered with these substrates during the analyses). The  $K_d$  values are directly comparable, whereas the  $K_f$  coefficients are not because of the variability in  $1/n$  ( $K_d$  and  $K_f$  can be compared when  $1/n$  is close to 1). We therefore chose to focus on the linear partitioning  $K_d$ .

The values of the adsorption coefficient ( $K_d$ ) of the four pesticides were greater in plant roots (from 14.2 to 6,742 L kg<sup>-1</sup>; Figure 3b–d; Table 4) than in sediments (from 5.7 to 163 L kg<sup>-1</sup>; Figure 3a–c; Table 4), except for CYA in *P. australis* (15.2 L kg<sup>-1</sup>), FLX in *P. australis* (14.8 L kg<sup>-1</sup>) and *M. aquatica* 15.0 L kg<sup>-1</sup>), where  $K_d$  was lower than in sediments (28 L kg<sup>-1</sup> for CYA and 111–116 L kg<sup>-1</sup> for FLX). These results might be explained by the higher content of OC in plant roots than in sediments (Table 2), as previously reported. For instance, Rogers and Stringfellow (2009) showed that the sorption of chlorpyrifos in *T. latifolia*

**Table 4.** The determination coefficient  $R^2$ , adsorption coefficient  $K_d$  (L kg<sup>-1</sup>; Eq. (4)) and coefficient  $K_{oc}$  (L kg<sup>-1</sup>; Eq. (5)) for CYA, FLX and FLP in the six substrates (sediments of units 2 and 3, roots of *T. latifolia*, *I. pseudacorus*, *M. aquatica* and *P. australis*). Oryzalin was almost always adsorbed at 100% ( $C_{eq} < 0.01$  mg L<sup>-1</sup>), and reliable modeling of the experimental values was not feasible. The adsorption coefficients for ORY were directly calculated using the few values higher than the LOQ.

		CYA	FLX	FLP	ORY
Unit 2	$R^2$	0,85***	0,87***	0,80***	-
	$K_d$ (L kg <sup>-1</sup> )	27.8 ± 3.2	116 ± 12	6.0 ± 0.8	108 ± 4
	$K_{oc}$ (L kg <sup>-1</sup> )	297 ± 3	1289 ± 13	64.0 ± 0.9	1150 ± 4
Unit 3	$R^2$	0,67**	0,92***	0,95***	-
	$K_d$ (L kg <sup>-1</sup> )	27.7 ± 5.4	111 ± 9	5.7 ± 0.4	163 ± 8
	$K_{oc}$ (L kg <sup>-1</sup> )	276 ± 6	1100 ± 10	56.7 ± 1.4	1622 ± 9
<i>Typha latifolia</i>	$R^2$	0,70***	0,70***	0,74***	-
	$K_d$ (L kg <sup>-1</sup> )	389 ± 101	819 ± 147	54.1 ± 8.8	5618
	$K_{oc}$ (L kg <sup>-1</sup> )	958 ± 101	2018 ± 147	133 ± 9	13837
<i>Iris pseudacorus</i>	$R^2$	0,64**	0,77***	0,84***	-
	$K_d$ (L kg <sup>-1</sup> )	290 ± 60	798 ± 7	85.8 ± 10.3	3081
	$K_{oc}$ (L kg <sup>-1</sup> )	661 ± 60	1818 ± 7	195 ± 10	7018
<i>Mentha aquatica</i>	$R^2$	0,72***	0,16 <sup>ns</sup>	0,78***	-
	$K_d$ (L kg <sup>-1</sup> )	55.6 ± 9.5	15.0 ± 9.7	14.2 ± 2.1	1866
	$K_{oc}$ (L kg <sup>-1</sup> )	167 ± 10	45.0 ± 9.9	42.5 ± 2.3	5604
<i>Phragmites australis</i>	$R^2$	0,33 <sup>ns</sup>	0,45*	0,73***	-
	$K_d$ (L kg <sup>-1</sup> )	15.2 ± 5.9	14.8 ± 4.6	43.9 ± 7.4	6742
	$K_{oc}$ (L kg <sup>-1</sup> )	33.7 ± 6.0	32.8 ± 4.7	97.3 ± 7.5	14949

\*\*\* $p < 0.01$ ; \*\* $p < 0.05$ ; \* $p < 0.1$ ; ns: non significant (n = 15).



( $K_d = 570\text{--}1300\text{ L kg}^{-1}$ ) was greater than that in soil ( $K_d = 40\text{--}71\text{ L kg}^{-1}$ ). In the same manner, Vallée et al. (2014) reported that the  $K_f$  of six pesticides in straw ( $20.48\text{--}442.63\text{ mg}^{1-n}\text{ L}^n\text{ kg}^{-1}$ ) was 7–41 times higher than the  $K_f$  obtained in sediments ( $1.0\text{--}63.3\text{ mg}^{1-n}\text{ L}^n\text{ kg}^{-1}$ ) in an agricultural drainage ditch.

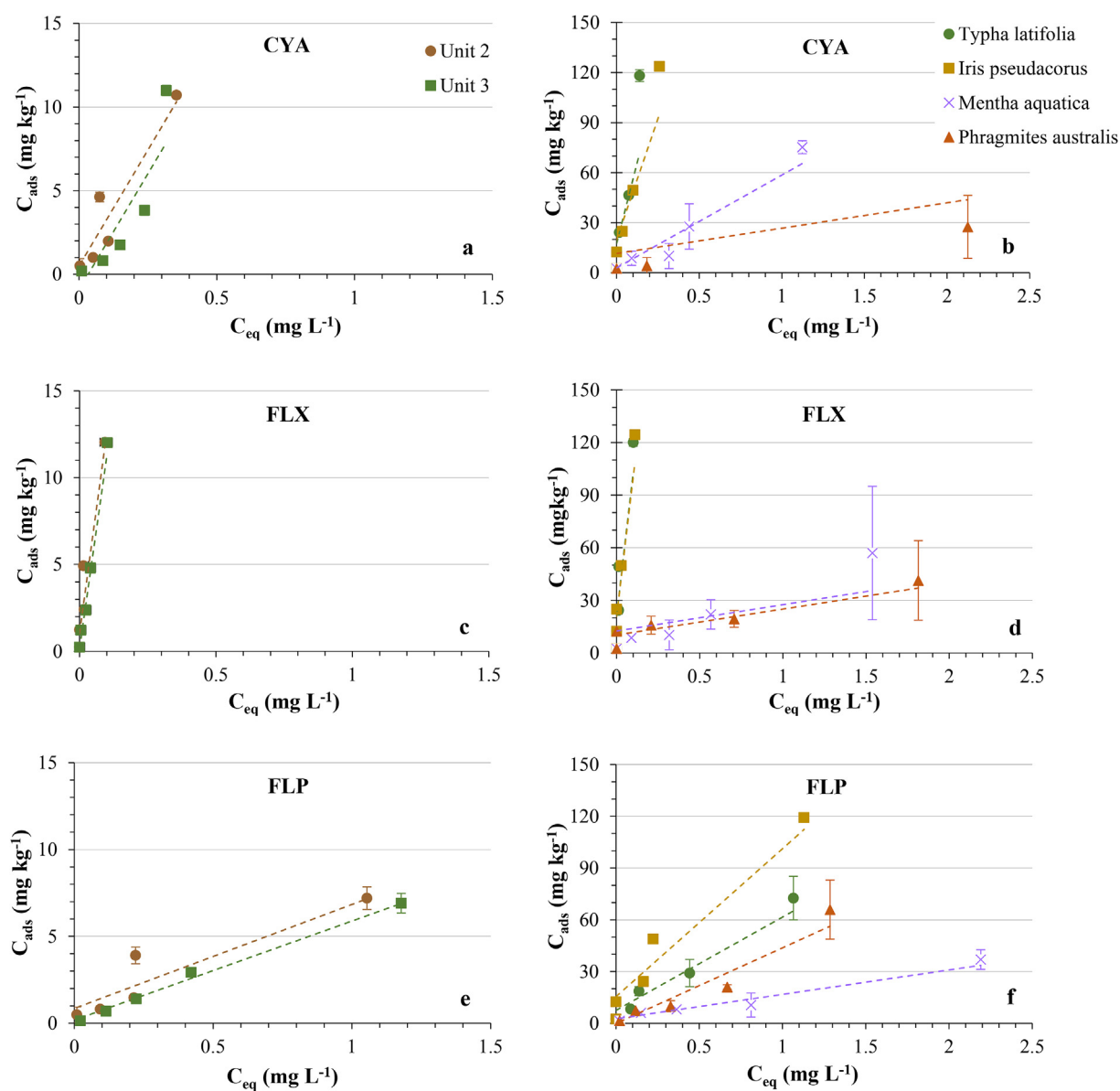
The  $K_{oc}$  coefficients were also greater in plant roots (from 42.5 to 14,949  $\text{L kg}^{-1}$ ) than in sediments (from 56.7 to 1,622  $\text{L kg}^{-1}$ ), except for the  $K_{oc}$  of CYA and FLX in *P. australis* and *M. aquatica* and FLP in *M. aquatica*, which were lower in plant roots than in sediments (Table 4). These higher  $K_{oc}$  values in plant roots indicated that not only the organic carbon content but also the nature of organic matter influenced pesticide adsorption (e.g., De Wilde et al., 2009). The anisotropic cellular and molecular structure of the plant matrices allowed for a larger internal surface area, faster and easier diffusion into organic matrices and more sorption sites than for sediment (Rose et al., 2006; Rampoldi et al., 2011).

Concerning the sediment, sorption equilibrium was reached in 96 h in unit 2 for all of the molecules, while in unit 3, FLX and ORY reached equilibrium in 72 h, and CYA and FLP did not reach equilibrium in 120 h

(Table 3; Figure S1a, b). These equilibrium time values are on the same order of magnitude as those previously obtained by Gaullier et al. (2018) on sediments. The more humified MO in unit 3 could speed up the adsorption of hydrophobic molecules such as FLX and ORY, whereas the moderately hydrophobic (CYA) or poorly hydrophobic (FLP) molecules would be less reactive as previously shown by De Wilde et al. (2009) and Passeport et al. (2011). According to the HRT calculated in the two units, equilibrium could be reached *in situ* in 85% of cases for all of the molecules in unit 2 and for FLX and ORY in unit 3. Equilibrium could be reached in only 42% of cases in unit 3 for CYA and FLP.

The  $K_d$  (and  $P_{ads}$ ) values of the four pesticides (Tables 3 and 4; Figure 3a, c, e) from both units were not significantly different, which could be explained by similar physico-chemical characteristics of the sediments in both units (Table 2).

Equilibrium was reached faster in *M. aquatica* and *P. australis* roots (24 h) than in *I. pseudacorus* (48 h) and *T. latifolia* (72 h and >96 h) for FLP and CYA (Table 3; Figure S1c–f). This was also the case for Cu (24 h and >48 h in *M. aquatica* and *P. australis*; 72 h in *I. pseudacorus* and



**Figure 3.** Adsorbed concentration ( $C_{ads}$ ;  $\text{mg kg}^{-1}$ ) as a function of the equilibrium concentration ( $C_{eq}$ ;  $\text{mg L}^{-1}$ ) of cyazofamid (a), fludioxonil (b) and fluopicolide (c) in sediments (on the left) and plant roots (on the right). Experimental values (full symbols) were modeled by linear regression (dotted line). Oryzalin was almost always adsorbed at 100% ( $C_{eq} < 0.01\text{ mg L}^{-1}$ ); thus, the modeling of the experimental values was not feasible. Data are, however, available in Table 4.

*T. latifolia*). The opposite tendency was observed for ORY (48 h in *T. latifolia* and *I. pseudacorus*; > 48 h in *M. aquatica* and *P. australis*). FLX never reached equilibrium in plant roots under the experimental conditions. Therefore, equilibrium would be reached *in situ* in 85% of cases or more in plant roots, apart from CYA and FLX in *T. latifolia* and FLX in *I. pseudacorus* (only 60%).

*T. latifolia* and *I. pseudacorus* roots presented higher  $K_d$  and  $K_{oc}$  values for CYA, FLX and, to a lesser extent, FLP ( $K_d = 54.1\text{--}819\text{ L kg}^{-1}$ ;  $K_{oc} = 133\text{--}2018\text{ L kg}^{-1}$ ) than *M. aquatica* and *P. australis* roots ( $K_d = 14.1\text{--}55.6\text{ L kg}^{-1}$ ;  $K_{oc} = 32.8\text{--}167\text{ L kg}^{-1}$ ; Table 4; Figure 3b, d, f). Despite the small number of points available for  $K_d$  calculation due to its strong adsorption, ORY seemed to better adsorb in *P. australis*, followed by *T. latifolia*, *I. pseudacorus* and *M. aquatica* (Table 4).

The differences observed between the plant species could be related to root morphology, molecular composition and specific surface area or total cross-sectional perimeter (Rogers and Stringfellow, 2009). The adsorption capacity of lignin was reported to be higher than that of cellulose due to its greater specific surface area, many potentially reactive functional groups and abundant free radical sites (Ahmad et al., 2006; Cassigneul et al., 2016). Hemicellulose can act by opening the pores of the lignocellulose matrix structure and increasing the exposed area and polar interactions with organic molecules (Rampoldi et al., 2011). However, its influence could be different from one plant to another according to the size and distribution of pores (Rampoldi et al., 2011; Guo et al., 2014; Cassigneul et al., 2016). While the lignin and cellulose contents were not greatly different between the four plants, the hemicellulose content in *P. australis* was 2 and 4 times higher than that in *T. latifolia* and *I. pseudacorus*, respectively. A high hemicellulose content in *P. australis* could reduce its adsorption capacity for CYA, FLX and FLP, while the influence was negligible for ORY. The particularity of *M. aquatica* was its low OC content and C/N ratio compared to the other plant roots, but in the absence of data on the hemicellulose content in *M. aquatica*, one could conclude that its characteristics did not affect the kinetic parameters but led to the low adsorption capacity of the four pesticides.

### 3.3. Molecule behaviour

In sediments, according to the  $T_{eq}$  (and  $P_{ads}$ ; Table 3) and  $K_d$  values (Table 4; Figure 3a, c, e), the more hydrophobic pesticides FLX and ORY were more rapidly and quantitatively adsorbed than CYA (moderately hydrophobic) and FLP (poorly hydrophobic; Rose et al., 2006; Pose-Juan et al., 2011). Contrary to Arias et al. (2005), the results did not show a clear relationship between the affinity of pesticides for solid substrates and their solubility. De Wilde et al. (2009) suggested that there is competition between pesticides for adsorption sites according to their molecular weight. In our study, pesticides with lower molecular weights (i.e., FLX, ORY and, to a lesser extent, CYA; Table 1) seemed to be favoured for adsorption in sediments. The  $T_{eq}$  of Cu was less than that of the pesticides, and its  $P_{ads}$  was close to the  $P_{ads}$  of FLX and ORY during the kinetic experiments (Table 3), reflecting the strong affinity of Cu for sediments. Copper and some pesticides can form complexes, which reduces or enhances adsorption of pesticide depending on the soil type and pH (Dousset et al., 2007). Huguenot et al. (2010) showed that sorption of glyphosate on low cost sorbents was enhanced when mixed with Cu. Competition between Cu and pesticides and/or Cu-pesticide complexation increasing sorption of pesticides on sediment and plant roots cannot be evidenced in this study.

The  $K_d$  values of the four selected pesticides in sediments are scarce in the literature. Nevertheless, the  $K_d$  values of FLX (111 and 116  $\text{L kg}^{-1}$ ) were close to or slightly lower than earlier values reported in soils (65–123  $\text{L kg}^{-1}$ , Pose-Juan et al., 2011; 161–208  $\text{L kg}^{-1}$ , Rodriguez-Liébaná et al., 2016; 62–213  $\text{L kg}^{-1}$ , Arias et al., 2005) and were much lower than the  $K_f$  values found in PPBD (290–7300  $\text{L kg}^{-1}$ ,  $1/n = 0.81\text{--}1.19$ ; Lewis et al., 2016). The  $K_d$  values obtained for CYA and FLP in sediments (approximately 28 and 6.0  $\text{L kg}^{-1}$ , respectively) were close to

the  $K_f$  values given by PPBD (23 and 4.2  $\text{L kg}^{-1}$ ,  $1/n = 0.83\text{--}1.19$ ; Lewis et al., 2016) or the  $K_f$  values supplied by Tang et al. (2019; 17  $\text{L kg}^{-1}$ ;  $n = 0.76$ ). The  $K_d$  values of ORY obtained in sediments in our study (108 and 163  $\text{L kg}^{-1}$ ) were higher than those reported by Landry et al. (2004; 10.5–38.4  $\text{L kg}^{-1}$ ) in Burgundy vineyard soils after leaching experiments. After C normalization, the  $K_{oc}$  values of FLX (1,100 and 1,289  $\text{L kg}^{-1}$ ) were on the same order as those of Arias et al. (2005; 1,671 and 5785  $\text{L kg}^{-1}$ ) and Rodriguez-Liébaná et al. (2016; approximately 4000  $\text{L kg}^{-1}$ ). The  $K_{oc}$  values of ORY (1150 and 1622  $\text{L kg}^{-1}$ ) were close to the values of 700 to 1000  $\text{L kg}^{-1}$  given by Landry et al. (2004). The differences between our study and previous works might be mainly related to the experimental conditions, especially the agitation method used (slow horizontal versus end-over-end agitation; Kah and Brown 2007).

In plant roots, the ranking based on  $T_{eq}$  was  $\text{ORY} \geq \text{FLP} \geq \text{CYA} \geq \text{FLX}$  for *T. latifolia* and *I. pseudacorus* but differed for *M. aquatica* and *P. australis* ( $\text{FLP} \approx \text{CYA} > \text{ORY} \approx \text{FLX}$ ; Table 3). The results obtained for Cu during the kinetic experiments ( $T_{eq}$ ) were close to those of FLP and CYA. According to their  $K_d$  values in roots, the rank of pesticides again differed from one plant to another:  $\text{ORY} \gg \text{FLX} > \text{CYA} > \text{FLP}$  in *T. latifolia* and *I. pseudacorus*;  $\text{ORY} > \text{CYA} > \text{FLX} \approx \text{FLP}$  in *M. aquatica*; and  $\text{ORY} > \text{FLP} > \text{CYA} \approx \text{FLX}$  in *P. australis* (Figure 3b, d, f). ORY seemed to be the most adsorbed pesticide in plant roots because of its strong affinity for OM (like numerous hydrophobic pesticides; De Wilde et al., 2009). Afterwards, the patterns in *T. latifolia* and *I. pseudacorus* were the same than as those in sediments and related to the decreasing  $K_{ow}$  and  $K_{oc}$  from FLX to CYA and FLP. The exceptions of these general trends (adsorption of CYA and FLP was faster than that of FLX in *P. australis* and *M. aquatica*; adsorption of CYA and FLP was greater than that of FLX in *P. australis* and CYA in *M. aquatica*) were probably due to the favoured lower  $K_{ow}$  of CYA and FLP compared to that of FLX when adsorbed in plants (Stottmeister et al., 2003; Imfeld et al., 2009; Guo et al., 2014; Liu et al., 2019) and maybe to the more favourable influence of the hemicellulose content on CYA and FLP adsorption compared to that of FLX. To our knowledge, there are no data in the literature on the  $K_d$  and  $K_{oc}$  of these pesticides in plant roots, making comparisons with earlier works difficult.

### 3.4. Rough assessment of adsorbed pesticide amounts in the DP

Thanks to the laboratory experiments, we roughly estimated the adsorbed quantities of pesticides in sediments (units 2 and 3) and plant roots (unit 3) over one year (November 2016–November 2017) at the scale of the two units considering the sediment weight and plant biomass (Eqs. (6), (7), and (8)). The calculations hypothesized that (i) the equilibrium time is usually reached when the HRT is higher than the equilibrium time in 85% of runoff events or more during the thirteen months and (ii) pesticides are spatially uniformly adsorbed in sediments, which is likely to be inaccurate, as previously shown by Gaullier et al. (2019).

The weight of sediments was approximately 30 tons in units 2 and 3 (Table 5) and was slightly higher in unit 2 because of the flow direction of the water and suspended particles (from north to south; Figure 2). The weight of plant roots in unit 3 varied from 66 kg (*I. pseudacorus*; Table 5) to approximately 400 kg (*T. latifolia* and *P. australis*) in relation to the growth rate and density of *T. latifolia* and *P. australis*.

In general, the estimated adsorbed quantities of pesticides were largely higher in sediments than in plant roots (including *T. latifolia* and *I. pseudacorus*, despite their high adsorption capacity) because of the higher quantities of sediment substrates. For the same reason, the adsorbed quantities of pesticides in sediments were slightly more important in unit 2 than in unit 3, but the values were on the same order of magnitude. In unit 3, *T. latifolia* presented high adsorbed quantities of pesticides (2.7–154 mg; Table 5) due to the dense root system and high  $K_d$  and  $K_{oc}$  values. Even if the density and total weight of *P. australis* roots were higher than those of *T. latifolia*, the adsorbed quantities were significant only for FLP (11.3 mg) and ORY (215 mg) because of the low  $K_d$  of CYA and FLX. Despite the well-developed root system and/or high  $K_d$ , *M. aquatica* and *I. pseudacorus* showed small adsorption capacities based

**Table 5.** Area (m<sup>2</sup>), sediment height (m), volume of wet sediments (m<sup>3</sup>), number of plants per m<sup>2</sup> (unit 3), total dry weight of sediments and roots (kg; calculated using Eqs. (6) and (7)) and adsorbed quantities (mg; mean, minimum and maximum, calculated using Eq. (8) with the mean, minimum (LOQ) and maximum concentrations measured in the water entering the units; Table 1) of CYA, FLX, FLP and ORY and the sum of the four pesticides in the six substrates (sediments of units 2 and 3, roots of *T. latifolia*, *I. pseudacorus*, *M. aquatica* and *P. australis*) from November 2016 to November 2017. The total quantities adsorbed in the plant roots in unit 3 and in sediments plus plant roots in unit 3 and the percent of adsorbed quantities in plant roots relative to total adsorbed quantity in unit 3 (sediments plus plant roots) are also presented.

	Area (m <sup>2</sup> )	Sediment height (m)	Wet sediment volume (m <sup>3</sup> )	Number of plants per m <sup>2</sup>	Total dry weight (kg)	CYA (mg)	FLX (mg)	FLP (mg)	ORY (mg)	TOTAL (mg)
Unit 2	1764	6.5 × 10 <sup>-2</sup>	53.9	–	32.9 × 10 <sup>3</sup>	18.3	76	140	311	1236
						9.1–146	38.1–7307	1.0–1596	35.4–3288	83.6–12338
Unit 3	2310	2.0 × 10 <sup>-2</sup>	29.6	–	28.4 × 10 <sup>3</sup>	14.2	617	93.8	334	1058
						7.9–94.5	31.5–4763	0.8–608	46.4–2180	86.5–7645
<i>Typha latifolia</i>	293	–	–	37	380	2.7	61.1	11.9	154	229
						1.5–17.8	3.1–472	0.1–77.2	21.4–1004	26.1–1571
<i>Iris pseudacorus</i>	36	–	–	26	66	0.3	10.4	3.3	14.7	28.7
						0.2–2.3	0.5–80.0	0.03–21.3	2.0–96	2.8–200
<i>Mentha aquatica</i>	80	–	–	2480	166	0.2	0.5	1.4	22.4	24.4
						0.1–1.1	0.02–3.8	0.01–8.8	3.1–146	3.2–160
<i>Phragmites australis</i>	258	–	–	128	444	0.1	1.3	11.3	215	228
						0.1–0.8	0.1–9.9	0.1–73.1	29.9–1406	30.1–1490
Total adsorbed on plant roots in unit 3 (mg)	–	–	–	–	–	3.3	73.2	27.8	406	511
Total adsorbed in unit 3 (sediments + plants; mg)	–	–	–	–	–	17.5	690	122	740	1569
% adsorbed on plant roots relative to total adsorbed in unit 3						18.9	10.6	22.9	54.9	32.5

on their low quantities compared to *T. latifolia* and *P. australis*. However, the adsorbed quantities of FLX in *I. pseudacorus* (10.4 mg) and ORY in *I. pseudacorus* (14.7 mg) and *M. aquatica* (22.4 mg) were not negligible. FLX was the most adsorbed pesticide in sediments (617 and 766 mg). ORY was greatly adsorbed in sediments (almost 300 mg) but was also greatly adsorbed in plant roots (up to 215 mg). FLP was mainly adsorbed in sediments (94 and 140 mg). The low adsorbed quantities of CYA in sediments and plant roots were attributed to its low concentrations in the water (0.02 µg L<sup>-1</sup>; Table 1).

The total adsorbed quantities in unit 2 (in the absence of plants) and unit 3 (in the presence of plants) were 1236 mg and 1569 mg, respectively (Table 5). The quantities adsorbed by plant roots relative to the total adsorbed quantities in unit 3 were 32.5%. These two estimates highlight the potential role of plant roots in the removal of the four pesticides and in the performance of the DP studied, as reported elsewhere (Rose et al., 2006; Guo et al., 2014; Lyu et al., 2018). The relative contribution of plant roots reached approximately 11% (FLX), 19% (CYA), 23% (FLP) and 55% (ORY) of the total annual adsorbed quantities in unit 3 (Table 5). These values were close to or higher than those reported in studies conducted *in situ* by Maillard and Imfeld (2014; from 0.2 to 26.4% according to the season and the vegetative stage and considering pesticide degradation) and Liu et al. (2019; from 1 to 14% according to the hydrophobicity and solubility of pesticides). The adsorption of the four studied pesticides was especially ensured by *T. latifolia* and *P. australis*, the most used and dense species in DPs.

#### 4. Conclusion

Without minimizing the mineralization processes leading to organic pollutant elimination in DPs, adsorption on substrates such as sediments and plant roots is an important process to remove pesticides such as cyazofamid, fludioxonil, flupicolid, oryzalin and copper from water. The measured average HRT in both DP units allows the adsorption process to reach equilibrium for pesticides and copper after most of the runoff events, both in sediments and plant roots. Pesticide adsorption on the studied substrates was mainly linked to their hydrophobicity. The adsorption capacity of plant roots was higher (up to 8 to 62 times) than

that of sediments because plant roots had higher OC content and a porous molecular structure that increased the specific surface area and favoured diffusion in root matrices. In addition, at the laboratory scale, *T. latifolia* and *I. pseudacorus* were more effective in adsorption removal than *P. australis* and *M. aquatica*.

At the DP scale, due to their greater weight, sediments would likely adsorb more pesticides than plant roots. However, given the better adsorption capacity of plant roots (covering approximately 29% of the entire surface of the phytoremediation unit), their presence contributed to more than 30% of the mitigation of contaminants in the green unit. This contribution will likely be higher during subsequent years when plants colonize the entire surface of the unit. Thus, the establishment of suitable and effective plants should be systematically promoted to optimize mitigation processes in DPs and reduce water pollution.

#### Declarations

##### Author contribution statement

Beatrice MARIN, Pr: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

Sylvie DOUSSET, Pr: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

Beatrice MARIN; Sylvie DOUSSET: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

Anne CANER-CHABRAN, Dr: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data.

Alexandra GUILLANEUF; David BILLET: Contributed reagents, materials, analysis tools or data.

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None.

##### Data availability statement

Data included in article/supp. material/referenced in article.

### Declaration of interest's statement

The authors declare no conflict of interest.

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