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[1] Pesticides, which have been extensively used in agriculture, have become a major environmental issue, especially regarding surface and groundwater contamination. Of particular importance are vegetated farm drainage ditches, which can play an important role in the mitigation of pesticide contamination by adsorption onto ditch bed substrates. This role is, however, poorly understood, especially regarding the influence of hydrodynamic parameters, which make it difficult to promote best management practice of these systems. We have assessed the influence of three of these parameters (speed of the surface water flow, submergence, and geometrical characteristics of the bed forms) on the transfer and adsorption of selected pesticides (isoproturon, diuron, tebuconazole, and azoxystrobin) into the bed substrate by performing experiments with a tilted experimental flume, using hemp fibers as a standard of natural organic substrates that are found at the bottom of agricultural ditches. Results show the transfer of pesticides from surface water flow into bed substrate is favored, both regarding the amounts transferred into the bed substrate and the kinetics of the transfer, when the surface water speed and the submergence increase and when the bed forms are made of rectangular shapes. Extrapolation of flume data over a distance of several hundred meters suggests that an interesting possibility for improving the mitigation of pesticides in ditches would be to increase the submergence and to favor bed forms that tend to enhance perturbations and subsequent infiltration of the surface water flow.

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1. Introduction

[2] Contamination of the environment by pesticides extensively used in modern farming has become a major issue during recent decades [see, e.g., *Kolpin et al.*, 1996; *Poissant and Koprivnjak*, 1996; *Barbash et al.*, 2001; *Schulz*, 2004; *Bouvier et al.*, 2006; *Sahoo et al.*, 2006; *Yao et al.*, 2006; *Poissant et al.*, 2008; *Sadiki and Poissant*, 2008]. Various pesticides have especially been detected in shallow water tables, streams, and rivers [*Castillo et al.*, 2000; *Dabrowski et al.*, 2002; *Gerecke et al.*, 2002; *Gfrerer et al.*, 2002; *Neumann et al.*, 2002; *Jergentz et al.*, 2005; *Guo et al.*, 2007; *Zhou et al.*, 2008]. Once in water bodies, pesticides can reach nontargeted compartments, affect noncrop habitats, and enter water resources.

[3] When used in agricultural plots, pesticides can be transferred to water bodies by various pathways, especially by drift during application, runoff, drainage, leaching, and aerial deposition [*Edwards*, 1973; *Groenendijk et al.*, 1994; *Schiavon et al.*, 1995; *Schulz*, 2004]. In this context, various approaches have been proposed to reduce the amounts of pesticides used in agricultural plots, for instance, by shifting toward modified agricultural practices such as nonchemical farming or promoting a better use of pesticides (for example, pesticides with a better targeted impact). This may imply a significant revision of chemical plant protection strategies and even a change of agricultural systems. Even when limiting the amounts of applied pesticides, it is difficult to avoid any transfer to nontarget areas.

[4] This explains why great efforts have been devoted to the assessment of various complementary strategies that would favor pesticide mitigation before they reach water bodies. Strategies include the use of constructed wetlands, buffer strip settlements, and vegetated ditches. For instance, several studies indicated that constructed wetlands are a promising tool to mitigate pesticides [*Moore et al.*, 2000; *Sherrard et al.*, 2004; *Moore et al.*, 2006]. Other studies have shown the efficacy of using buffer strips to limit pesticide drift and runoff [*Van Dijk et al.*, 1996; *Patty et al.*, 1997; *Lacas et al.*, 2005; *Boivin et al.*, 2007]. However, the efficiency of such strips remains limited for agricultural plots with subsurface drainage or ditches.

[5] Available studies suggest that agricultural ditches can attenuate pesticide concentrations in surface water

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flows before they reach downstream rivers [*Crum et al.*, 1998; *Moore et al.*, 2001; *Margoum et al.*, 2003; *Cooper et al.*, 2004; *Leistra et al.*, 2004; *Schulz*, 2004; *Bennett et al.*, 2005; *Dabrowski et al.*, 2005; *Needelman et al.*, 2007; *Hunt et al.*, 2008; *Moore et al.*, 2008]. However, they often did not consider the influence of hydrodynamic parameters on the fate of pesticides in these systems, whereas the flow characteristics can greatly modify the chemical retention time and the pesticide accessibility to the retention surfaces [*Boutron et al.*, 2010]. One exception is the work by *Dabrowski et al.* [2005], who showed that the attenuation of pesticides in agricultural ditches was higher with low discharge conditions. However, the separate influences of surface water speed and water depth were not investigated.

[6] The purpose of this work was to study the influence of three hydrodynamic parameters on the transfer of pesticides in agricultural ditches: (1) the speed of the surface water flow, (2) the submergence, defined as the ratio of mean height of the bed forms to the mean water depth, and (3) the geometrical characteristics of the bed forms (shape of the forms and distance between the forms). Assessment of the influence of these parameters is important for improving the design and management of agricultural ditches for better pesticide mitigation. The influence of these parameters was assessed in well-controlled conditions by using laboratory studies. They were based on the use of a tilted experimental flume. In addition, when considering the large diversity of natural substrates that are found at the bottom of agricultural ditches, such as living and dead plants and leaves or sediments [*Lagacherie et al.*, 2006], we have decided to use a simplified organic standard substrate made of hemp fibers. The choice of hemp fibers was based on preliminary studies comparing various geotextile fibers with natural ditch bed substrates [*Boutron*, 2009; *Boutron et al.*, 2009]. We have selected four pesticides that have been extensively used in agricultural plots and are commonly found in surface waters: diuron, isoproturon, azoxystrobin, and tebuconazole.

2. Experiment

2.1. Experimental Flume

[7] The experimental tilting flume (Figure 1) was 7.3 m long and had a 0.4 m wide channel. The flume slope was 0.001. The flume and all the recirculation pipes were made of polyvinyl chloride. However, one lateral wall was made of Plexiglas to permit flow visualization. The hemp substrate (see section 2.2) was on the bottom of the channel and covered the entire bottom surface. The flume allows the control of the water speed and depth and recirculates the water to increase the contact time between the pesticides solution and the hemp substrate. A stabilization tank (see Figure 1) is required to prevent the occurrence of eddies at the entrance of the flume. The water depth in the channel is fixed using an impermeable end plate. Preliminary experiments showed that the impermeable ends did not provide satisfactory end conditions. A slim box was then installed at each end of the flume (see Figure 1). The two slim boxes were closed except for one vertical face of each box, which was covered by stainless steel mesh. Subsurface flow passed through the mesh and was recirculated from the end of the flume to the inlet by means of a peristaltic pump. Two vertical cross sections of the hemp substrate (mean thickness ranging from 8 to 10 cm, depending on the geometry of the forms; see section 2.2) were equipped with capillary tubes to determine the penetration depths of the four pesticides and potassium bromide (see Figure 1). The two cross sections were located 2 and 4 m downstream of the stabilization tank, respectively. Each section was equipped with three capillary tubes, located 20 cm from the lateral walls of the flume at depths of 2, 4.5, and 7 cm below the hemp upper surface, respectively. The position of the capillary tubes was based on preliminary experiments, which showed that there was a good lateral repartition of the pesticides in the substrate and that there were no interferences between the different capillary tubes when withdrawing the samples through the tubes.

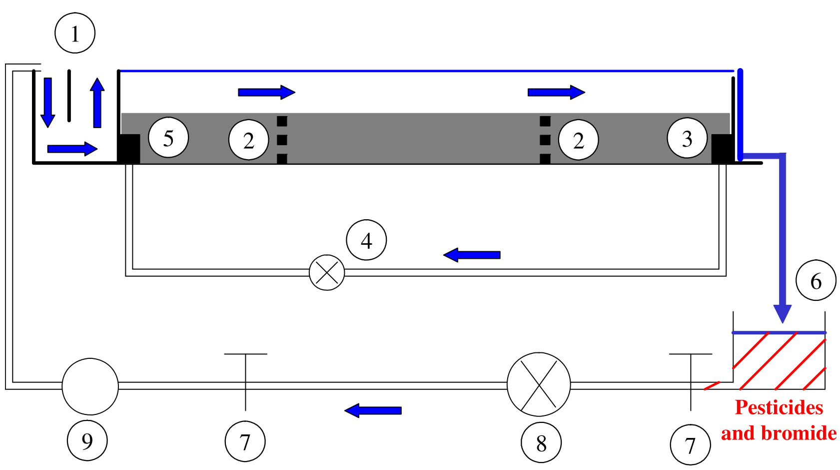

Figure 1. Schematic diagram of the flume: 1, upstream stabilization tank; 2, cross sections equipped with capillary tubes; 3, downstream subsurface flow discharge box; 4, peristaltic pump to recirculate subsurface flow; 5, upstream subsurface flow discharge box; 6, mixing tank for the preparation of the water solution containing simultaneously the four pesticides and potassium bromide; 7, valves; 8, centrifugal pump; 9, flowmeter.

2.2. Substrate

[8] The hemp substrate was obtained as rolls from Chanvre et Technique, Riec sur Belon, France (Technichanvre®). They are made of hemp fibers (85%), mixed with polyester fibers (15%) in order to provide adequate mechanical properties, especially regarding their geometry stability over long time periods. The porosity is 0.5, the vertical conductivity (i.e., through the thickness of the roll) is 3.4 cm s^{-1}, and the longitudinal conductivity (i.e., through the length of the roll) is 3.1 cm s^{-1}. The density is 25 kg m^{-3}, and the specific area is 1.07 m^2 g^{-1}. The mean elementary composition is as follows: C, 45.44%; H, 6.02%; N, 0.35%; O, 46.98% [*Boutron et al.*, 2010].

[9] Two bed surface configurations were used in the experiments, taking advantage of the good physical properties of hemp fibers. The first one was made of a succession of bumps (dunes), as illustrated in Figure 2a. The second was made of a succession of rectangular forms (crenels); see Figure 2b. Forms were made using adjustable rods attached to the lateral walls of the flume in order to obtain a constant wavelength (the mean distance between alternate crossings of the mean bed elevation) all along the flume (Figure 3). The wavelength was 0.2 m for the dunes, with a submergence (defined as the ratio of mean height of the bed forms to the mean water depth) of 0.6 (Figure 2a). The wavelength was 0.4 m for the crenels (Figure 3), with a submergence of 0.6 or 1.4. The location of the bed forms was such that one of the cross sections equipped with capillary tubes was located on top of a dune or a crenel, while the second was located in the hollow between two forms.

2.3. Pesticides

[10] Two herbicides, diuron (3-(3,4-dichlorophenyl)-l, l-dimethylurea) and isoproturon (3-(4-isopropylphenyl)-l, l-dimethylurea), and two fungicides, azoxystrobin (methyl (E)-2-{2-[6-(2-cyanophenoxy)pyrimidin-4-yloxy]phenyl}-3-methoxyacrylate) and tebuconazole ((*RS*)-l-p-chlorophenyl-4,4-dimethyl-3-(1*H*-l,2,4-triazol-l-ylmethyl)pentan-3-ol), were selected for study. These pesticides have been extensively used in agricultural plots in various countries and are commonly found in surface waters. In addition, they are characterized by a wide range of physicochemical properties (Table 1). The commercial formulations Seduron® (diuron), Folicur 250 EW® (tebuconazole), and Zodiac

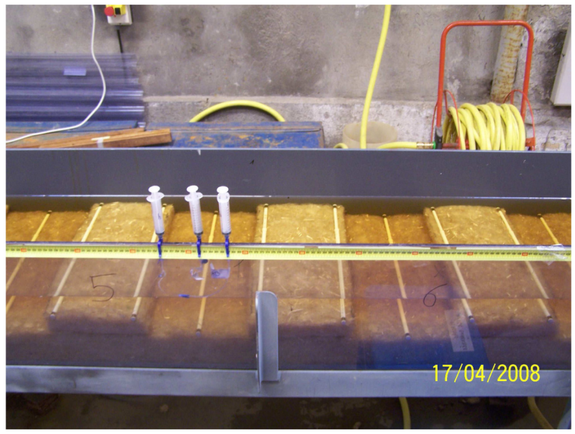

Figure 3. Photographs showing part of the rectangular-shaped bed forms (crenels) covering the bottom of the experimental flume with a wavelength of 0.4 m.

TX® (isoproturon) from Bayer Crop Science and Ortiva® (azoxystrobin) from Syngenta were used. In addition, potassium bromide was added as a tracer for water transport through the hemp substrate.

2.4. Pesticides and Bromide Determination

[11] Water samples were filtered using 0.2 µm filters (Chromafil filters PET 20/15 MS, Macherey Nagel), and a 990 µL aliquot was then transferred into an autosampler vial with 10 µL of deutered diuron D6 as an internal standard. The samples were then analyzed for diuron, isoproturon, azoxystrobin, and tebuconazole using a high-performance liquid chromatography instrument (Series 1100, Agilent Technologies) equipped with a 125-2 RP18e 5 µm LichroCART column (Merck), coupled to a triple quadrupole mass spectrometer (API 4000, LC/MS/MS system, Applied Biosystems) with an ESI source. Standard solutions from Cluzeau Info Labo, Cluzeau, France, and Sigma Aldrich were used for calibration. The injection volume was 100 µL (with triplicate determinations). The limit of detection was 0.02 µg L^{-1} for diuron, 0.05 µg L^{-1} for azoxystrobin, and 0.2 µg L^{-1} for tebuconazole and isoproturon.

[12] Bromide concentrations were determined by ion chromatography (Dionex DX-120 with an AS9-HC column)

(a) (b)

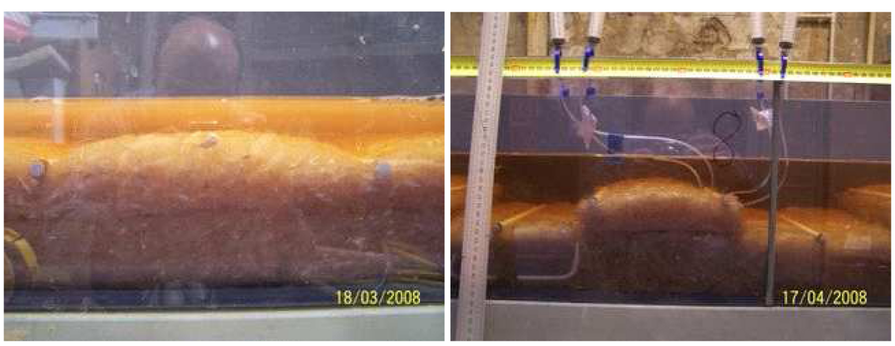

Figure 2. Photographs showing the two kinds of bed forms used in this work: (a) dunes and (b) crenels.

Table 1. Selected Properties of the Four Pesticides Considered in This Work[a]

	Solubility in Water (mg L^{-1}) (20°C)	K_{oc} (L kg^{-1}) (20°C)	log K_{ow}	Half Life (days)
Diuron	36	480	2.9	90–180
Isoproturon	70	120	2.5	6–28
Azoxystrobin	7	423	2.5	8.7–13.9
Tebuconazole	36	1554	3.7	30–62

[a]From *Tomlin* [2000], Afssa (unpublished data, 2008, available from http://www.dive.afssa.fr/agritox/php/fiches.php), and FOOTPRINT Pesticide Properties Database (unpublished data, 2008, available from http://www.eu-footprint.org/ppdb.html).

Table 2. Mean Surface Water Speed, Submergence, and Geometrical Characteristics of the Bed Forms (Bed Form Geometry and Wavelength) for the Five Experiments

Experiment	Mean Surface Water Speed (cm s^{-1})	Submergence	Bed Form Geometry	Wavelength of the Bed Forms (m)
1	2	0.6	dunes	0.2
2	2	1.4	crenels	0.4
3	7	0.6	dunes	0.2
4	7	1.4	crenels	0.4
5	2	0.6	crenels	0.4

using direct injections (limit of detection of 0.2 mg L^{-1}). Certified standard solutions from ACSD, France, were used for calibration.

[13] Uncertainties for the whole analytical procedure, determined as explained in detail by *Association Française de Normalisation* [2003], were smaller than 10%.

2.5. Experimental Protocols

[14] All experiments were performed with constant water discharge and uniform surface water flow conditions. The duration of each experiment was 7 h. The experimental protocol for each experiment was as follows:

[15] 1. A new hemp substrate is unrolled in the flume and attached to the flume with the desired bed forms. The flume is then filled with deionized water containing 5 m*M* of NaCl and 4 m*M* of $NaHCO_3$ to the desired water depth and is then allowed to stand for 24 h.

[16] 2. A water solution containing simultaneously the four pesticides and potassium bromide is then prepared using deionized water with 5 m*M* of NaCl and 4 m*M* of $NaHCO_3$ in a mixing tank (see point 6 in Figure 1). The pesticides and bromide concentrations in this water solution are chosen so that the concentrations in the surface water flow in the flume after dilution are about 20 μg L^{-1} for the pesticides and 100 mg L^{-1} for bromide.

[17] 3. The recirculation pumps for the surface and subsurface water flows (see points 4 and 8 in Figure 1) are then started simultaneously with predefined flow parameters, allowing the injection of the pesticides solution in the surface water flow at the upstream edge of the flume. The subsurface water speed is kept at 0.02 cm s^{-1}. This is a rather high, but not unrealistic, value compared to natural ones in vegetated ditches. This high value allows us to increase the kinetics of the transfer of the pesticides into the hemp substrate and then to compare the effect of the various parameters on this transfer. It allows us to obtain sufficiently discriminating conditions with moderate uncertainties on the results in a reasonable time to avoid interfering degradation processes (without that subsurface water flow, several days are needed to observe a consequent penetration [*Marion et al.*, 2002], with the associated problems of degradation of the pesticides studied).

[18] 4. Then 5 mL samples are collected from the surface water flow all along the flume at about 15 different times during the 7 h of each experiment. Samples are particularly collected in the surface water at the upstream edge of the flume, at the downstream edge of the flume, and above the two cross sections equipped with capillary tubes (2 and 4 m downstream of the stabilization tank). In addition, samples are also obtained using the capillary tubes at depths of 2, 4.5, and 7 cm below the hemp upper surface.

[19] 5. The water depth is determined every 20 cm all along the flume, while the speed of the surface water flow is determined at the upstream edge of the flume, at the downstream edge of the flume, and above the two cross sections equipped with capillary tubes (2 and 4 m downstream of the stabilization tank). These determinations are performed every hour during the experiment's duration.

[20] 6. The pH and the conductivity are monitored at the downstream edge of the flume during the entire experiment.

[21] 7. The bed surface topography is determined all along the flume.

[22] Five experiments were performed following this protocol. Experiment parameters are listed in Table 2. From each experiment, about 110 samples were obtained and analyzed for the four pesticides and bromide, taking considerable time and expense. This is the reason why it was not possible to perform more experiments.

2.6. Evaluation of Possible Losses and Reproducibility

[23] In order to make sure that no losses of pesticides occurred in the experimental system, we also performed experiments without hemp in the flume. Results show that there were no significant losses of pesticides in the whole experimental system (Figure 1) during the 7 h of the experiments (at the end of the experiments, losses of pesticides were found to be always smaller than 4% for tebuconazole and 2% for azoxystrobin and about 0% for diuron and isoproturon [*Boutron*, 2009]). This confirms that there was no adsorption of pesticides in the experimental system. In addition, it shows that there is no volatilization and degradation of the four investigated pesticides. This was further confirmed by the fact that the two main metabolites of diuron (3,4-dichloroaniline (DCA) and 3-(3,4-dichlorophenyl)-l-methyl urea (DCMU)) could not be detected during the 7 h of experiments [*Boutron*, 2009].

[24] In order to evaluate the reproducibility of the data, a few experiments were repeated. The results were found to be repeatable within the analytical uncertainties [*Boutron*, 2009].

3. Results and Discussion

3.1. Parameters Used for Comparison of the Results Obtained From the Different Experiments

[25] Two variables were considered for comparing the results of the experiments. The first one is the mass $M_{transferred}(t)$ of each pesticide transferred from the surface water

flow into the hemp substrate as a function of time t (expressed in hours) during the 7 h of the experiment:

$$M_{\text{transferred}}(t) = M_{\text{injected}} - C(t)V_{\text{dilution}}, \quad (1)$$

where M_{injected} represents the mass of pesticide or bromide introduced into the flume at the beginning of the experiment (expressed in μg), $C(t)$ represents the mean concentration of pesticide or bromide in the surface water flow (expressed in μg L^{-1} for the pesticides and in mg L^{-1} for bromide), and V_{dilution} is the volume of water in the flume system excluding interstitial water in the hemp substrate (expressed in L). It should be mentioned that at the beginning of the experiments, the concentration of pesticides or bromide was not the same at the entrance and at the exit of the flume. It was then necessary to wait until the pesticides or bromide became evenly distributed in the whole flume before $C(t)$ could be determined (typically 15 min). This was carefully checked for each experiment by comparing the concentrations measured at different locations and depths in the surface water flow (especially at the entrance of the flume, the exit of the flume, and the two cross sections equipped with capillary tubes) [*Boutron*, 2009].

[26] The second variable characterizes the total mass of each pesticide adsorbed onto the whole volume of hemp contained in the flume at the end of each experiment. As bromide is not adsorbed onto hemp and assuming that pesticides and bromide are submitted to the same physical processes, the mass of pesticides adsorbed at the end of the experiments was estimated from the difference between the mass of bromide and the mass of each pesticide remaining in the surface water after 7 h, as explained in detail by *Boutron* [2009]. This is a key parameter when assessing the potential of agricultural ditches to mitigate pesticide contamination since pesticides adsorbed onto the substrate will be less available for subsequent leaching than pesticides that are only physically trapped in the substrate.

3.2. Influence of the Surface Water Speed

[27] The influence of the surface water speed was investigated for the following two cases. For case 1, the bed forms were made of a succession of bumps (dunes; see Figure 2a), with a submergence of 0.6 and a wavelength of 0.2 m (experiments 1 and 3; see Table 2). For case 2, the bed forms were made of a succession of rectangular forms (crenels; see Figures 2b and 3), with a submergence of 1.4 and a wavelength of 0.4 m (experiments 2 and 4; see Table 2).

[28] Figure 4 shows changes in $M_{\text{transferred}}(t)$ during the 7 h for the four pesticides for experiments 1 and 3 (case 1 (dunes), Figure 4a) and 2 and 4 (case 2 (crenels), Figure 4b). $M_{\text{transferred}}(t)$ is expressed as a percentage of the initial mass of pesticides introduced into the flume at the beginning of the experiment.

[29] For all experiments, there is an initially rapid transfer of the pesticides, followed by a much slower transfer for about the last 5 h (Figures 4a and 4b). This is in agreement with published literature, which shows that adsorption of pesticides is often characterized by an initially rapid removal followed by a much slower removal [*Gaillardon*, 1996]. To determine if the active sites on the hemp become saturated, adsorption isotherms have also been realized (see *Boutron* [2009]; results are not shown here). They showed that adsorption capacity is linear (for initial concentrations ranging from 0.5 to 100 μg L^{-1}) and then confirmed that active sites are not saturated after 7 h of contact time.

[30] In all cases, an increase in the speed of surface water is found to lead to an increase in the mass of pesticides transferred into the hemp. This is further confirmed by the capillary tube data, which document the penetration of the pesticides into the hemp (the penetration has been shown to increase when the surface water speed increases from 2 to 7 cm s^{-1}). The results show, for instance, that in case 1 the amount of pesticides observed at a depth of 4.5 cm inside hemp at the end of the experiment is 1.7–2 times larger for a surface water speed of 7 cm s^{-1} than for a speed of 2 cm s^{-1}; see *Boutron* [2009]. This effect is very pronounced for case 1 (dunes; Figure 4a). It is much less important for case 2 (crenels; Figure 4b). In that case, the transfer is indeed already high for the speed of 2 cm s^{-1}.

[31] Table 3 shows the mass of each pesticide $M_{\text{transferred}}$(7 h) transferred from the surface water flow into the hemp substrate at the end of the experiments for experiments 1 and 3 (case 1 (dunes)) and 2 and 4 (case 2 (crenels)). $M_{\text{transferred}}$(7 h) is expressed as a percentage of the initial mass of pesticides introduced into the flume at the beginning of the experiment. It can be seen that for the experiments with dunes (case 1, experiments 1 and 3) the mass of pesticides transferred into hemp after 7 h is significantly larger for the highest speed (7 cm s^{-1}; experiment 3). This effect is especially pronounced for isoproturon and azoxystrobin (Table 3). The situation is different for the experiments with the crenels (case 2, experiments 2 and 4): the data suggest a limited influence of the water flow speed on the mass of pesticides transferred into hemp after 7 h. On average, the mass of pesticide transferred into hemp increases by about 25% for case 1 and by about 5% for case 2 when the speed of the water flow increases from 2 to 7 cm s^{-1}.

[32] The differences observed between case 1 (submergence of 0.6) and case 2 (submergence of 1.4) show that the value of the submergence and the geometrical characteristics of the bed forms have an impact on the influence of the speed of the surface water.

[33] In order to compare the transfer kinetics for the different pesticides, we have used a hyperbolic model previously described by *Jamet et al.* [1985]. In this model, the total mass of a given pesticide transferred into hemp as a function of time (expressed as percentage of the initial mass of pesticides introduced into the flume at the beginning of the experiment) is given by

$$M_{\text{transferred}}(t) = \frac{M_{\max} t}{k + t}, \quad (2)$$

where $M_{\max}$, t, and k represent the mass of pesticide transferred into the hemp after 7 h (expressed as a percentage of the initial mass of pesticides introduced into the flume at the beginning of the experiment), time (expressed in hours), and a constant, respectively. The k values are determined from the experimental data (without taking into account the data points obtained before the beginning of the transfer) using least squares fits. Table 4 shows the k values for experiments 1 and 3 (case 1, dunes with a submergence of 0.6 and a wavelength of 0.2 m) and 2 and 4

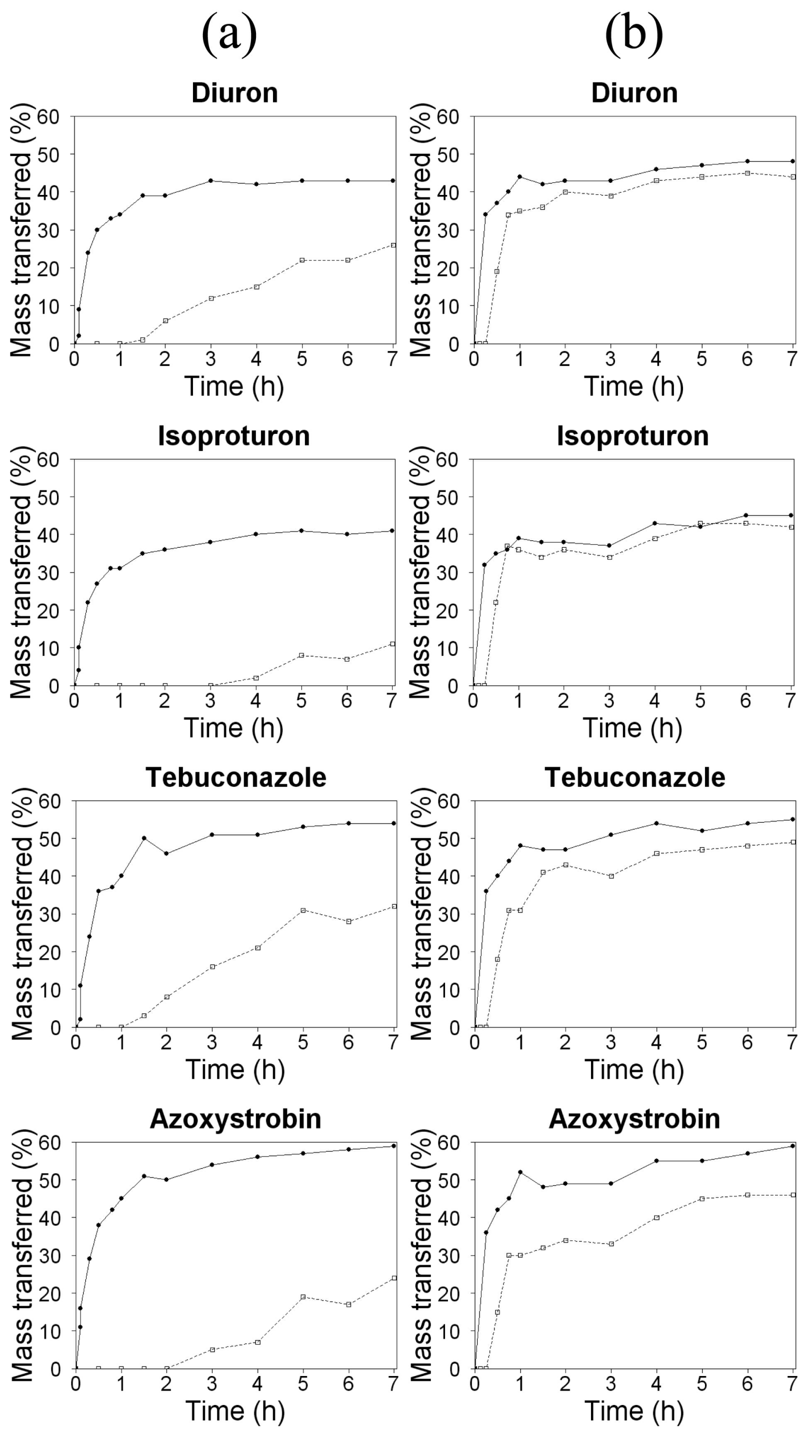

Figure 4. Changes in $M_{\mathrm{transferred}}(t)$ during the 7 h for the four pesticides. (a) Dunes with a submergence of 0.6 and a wavelength of 0.2 m and mean surface water speeds of 2 cm s^{-1} (dotted line with squares) and 7 cm s^{-1} (solid line with circles). (b) Crenels with a submergence of 1.4 and a wavelength of 0.4 m and mean surface water speeds of 2 cm s^{-1} (dotted line with squares) and 7 cm s^{-1} (solid line with circles). The mass is expressed as percentage (see text).

(case 2, crenels with a submergence of 1.4 and a wavelength of 0.4 m). The model fit for tebuconazole is illustrated in Figure 5 for experiment 3. Low k values indicate fast kinetics. It can be seen that for case 1, there is a strong increase of the kinetics when the water speed increases from 2 to 7 cm s^{-1} (k values decrease by factors ranging from 5 to 9, depending on the pesticide). For case 2, there is also a decrease in k values when the water speed increases from 2 to 7 cm s^{-1}, but the decrease is smaller than for case 1 (decrease by factors ranging from 2 to 3). The data then show that an increase of the speed of the surface water flow leads to faster transfer kinetics of pesticides

Table 3. Mass of Each Pesticide $M_{transferred}$(7 h) Transferred From the Surface Water Flow Into the Hemp Substrate at the End of the Five Experiments[a]

	Experiment				
Pesticide	1	2	3	4	5
Diuron	26	44	43	48	30
Isoproturon	11	42	41	45	31
Tebuconazole	32	49	54	55	36
Azoxystrobin	24	46	59	59	42

[a]Parameters of the experiments are given in Table 2. $M_{transferred}$(7 h) is expressed as a percentage of the initial mass of pesticides introduced into the flume at the beginning of the experiment.

into the hemp substrate. In addition, Table 4 suggests that the kinetics might be generally faster for isoproturon and slower for azoxystrobin, but this will need to be confirmed by further studies.

[34] Figure 6 shows the total mass of each pesticide adsorbed onto the whole volume of hemp after 7 h (expressed as a percentage of the initial mass of pesticides introduced into the flume at the beginning of the experiment). The observed percentages are generally in good agreement with the respective K_{oc} values listed in Table 1. For azoxystrobin, the data show a clear increase in the adsorbed mass in both cases when the speed increases from 2 to 7 cm s^{-1} (Figures 6a and 6b). The increase is especially pronounced in case 1, with an increase from 7% to 27%. Conversely, no clear increase is observed for diuron. The situation is less clear for the two other pesticides. For isoproturon, for instance, the increase observed for case 1 (Figure 6a) is not confirmed for case 2 (Figure 6b).

3.3. Influence of the Submergence

[35] The influence of the submergence was investigated for the bed form made of a succession of rectangular forms (crenels; see Figures 2b and 3), with a wavelength of 0.4 m and a surface water speed of 2 cm s^{-1}. Two values of the submergence were considered: 0.6 (experiment 5; see Table 2) and 1.4 (experiment 2; see Table 2).

[36] Figure 7 shows changes in $M_{transferred}(t)$ during the 7 h for the four pesticides and the two values of the submergence (experiments 2 and 5, Table 2). As before, $M_{transferred}(t)$ is expressed as percentage of the initial mass of pesticides introduced into the flume at the beginning of the experiment.

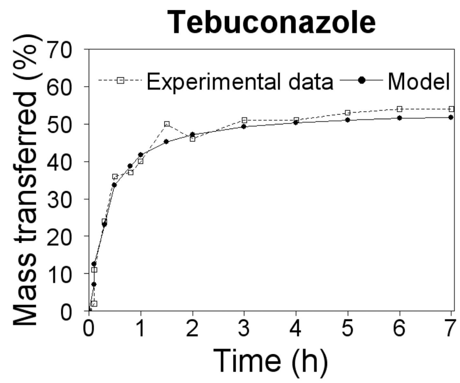

Figure 5. Hyperbolic model fit for tebuconazole for experiment 3 (dunes with a submergence of 0.6, a wavelength of 0.2 m, and a mean surface water speed of 7 cm s^{-1}).

[37] For diuron, isoproturon, and tebuconazole and, to a lesser extent, azoxystrobin, an increase in the mass transferred into hemp is observed when submergence increases from 0.6 to 1.4. This is again confirmed by the capillary tube data: the penetration of the pesticides into hemp is shown as increasing when the submergence is increasing [*Boutron*, 2009].

[38] Table 3 shows the total mass of each pesticide $M_{transferred}$(7 h) transferred from the surface water flow into the hemp substrate at the end of the experiments for the two submergences of 0.6 (experiment 5; see Table 2) and 1.4 (experiment 2; see Table 2). For all four pesticides, $M_{transferred}$(7 h) is found to be larger for the highest submergence (experiment 2 compared to experiment 5). The observed increase is more pronounced for diuron, isoproturon, and tebuconazole (from about 10% to 15%) than for azoxystrobin.

[39] In order to compare the transfer kinetics for the different pesticides, we have used the hyperbolic model previously described in section 3.2 (equation (2)). Table 5 shows the k values for the two submergences of 0.6 and 1.4. The k values are found to be smaller for the highest submergence (1.4), indicating that the kinetics is faster when the submergence is higher. On average, k values for the highest submergence (1.4) are about 2 times larger than for the smallest submergence (0.6).

[40] The total mass of each pesticide adsorbed onto the whole volume of hemp after 7 h was estimated for the two

Table 4. Hyperbolic Model for the Transfer Kinetics: Values of the Constant k and the Regression Coefficient r for the Four Pesticides for Experiments 1–4[a]

	Dunes[b]				Crenels[c]			
	$U = 2$ cm s^{-1} (Experiment 1)		$U = 7$ cm s^{-1} (Experiment 3)		$U = 2$ cm s^{-1} (Experiment 2)		$U = 7$ cm s^{-1} (Experiment 4)	
	k	r	k	r	k	r	k	r
Diuron	103	0.96	14	0.99	13	0.99	5	0.99
Isoproturon	83	0.89	14	0.99	10	0.97	6	0.97
Tebuconazole	87	0.95	17	0.99	20	0.99	7	0.98
Azoxystrobin	107	0.89	15	0.99	26	0.97	9	0.97

[a]U represents the mean surface water speed.
[b]With a submergence of 0.6 and a wavelength of 0.2 m.
[c]With a submergence of 1.4 and a wavelength of 0.4 m.

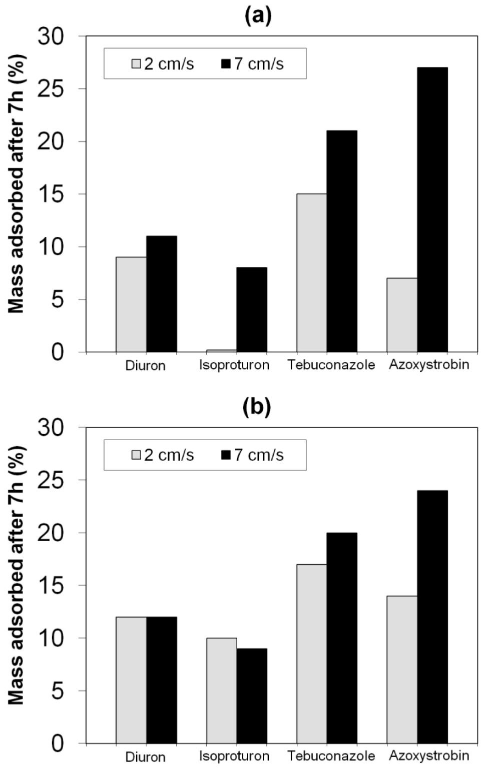

Figure 6. Total mass of each pesticide adsorbed onto the whole volume of hemp after 7 h for two different surface water speeds (2 and 7 cm s^{-1}). (a) Dunes with a submergence of 0.6 and a wavelength of 0.2 m and (b) crenels with a submergence of 1.4 and a wavelength of 0.4 m. The mass is expressed as percentage (see text).

submergences (0.6 and 1.4). The results suggest a limited increase in the total mass adsorbed onto hemp when the submergence is increasing, with the possible exception of azoxystrobin. Again, the data are in good agreement with the respective K_{oc} values listed in Table 1.

3.4. Influence of the Geometrical Characteristics of the Bed Forms

[41] The influence of the geometrical characteristics of the bed forms (shape of the forms and distance between the forms) was investigated for a surface water speed of 2 cm s^{-1} and a submergence of 1.4. Two bed forms were considered: one was made of a succession of dunes (Figure 2a), with a wavelength of 0.2 m (experiment 1; see Table 2), and the second was made of a succession of crenels (Figure 2b), with a wavelength of 0.4 m (experiment 5; see Table 2).

[42] Changes in $M_{\mathrm{transferred}}(t)$ during the 7 h for the two bed forms are illustrated in Figure 8. It can be seen that the mass of pesticides transferred into hemp is systematically larger for crenels than for dunes. This is again confirmed by the capillary tube data: the penetration of the pesticides into hemp is larger for crenels than for dunes [*Boutron*, 2009]. The effect is especially pronounced for isoproturon and azoxystrobin (Figure 8).

[43] It should, however, be mentioned that our experiments only allow a determination of the joint influence of the shape of the forms and the distance between the forms. It would have been interesting to test separately the influence of each of these parameters. This was unfortunately not possible because of practical constraints linked with the physical structure of the hemp rolls. The observed increase in pesticides transfer illustrated in Figure 8 does not imply

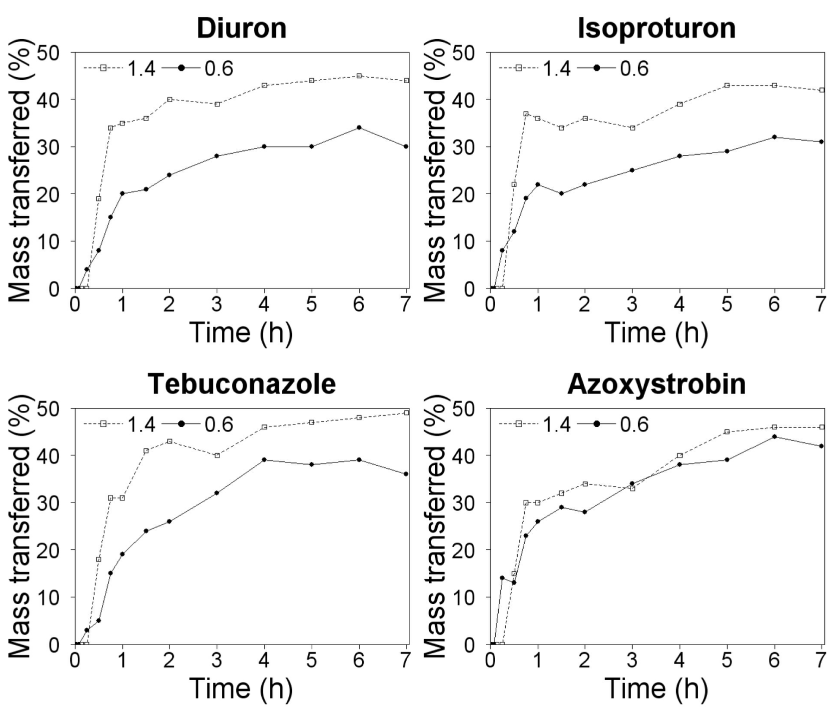

Figure 7. Changes in $M_{\mathrm{transferred}}(t)$ during the 7 h for the four pesticides for two submergences (0.6 and 1.4). The bed forms are made of crenels with a wavelength of 0.4 m, and the mean surface water speed is 2 cm s^{-1}. The mass is expressed as percentage (see text).

Table 5. Hyperbolic Model for the Transfer Kinetics: Values of the Constant k and the Regression Coefficient r for the Four Pesticides and Submergences of 0.6 and 1.4[a]

	Submergence			
	1.4 (Experiment 2)		0.6 (Experiment 5)	
	k	r	k	r
Diuron	13	0.99	34	0.98
Isoproturon	10	0.97	30	0.98
Tebuconazole	20	0.99	40	0.97
Azoxystrobin	26	0.97	33	0.97

[a]In both cases the bed forms are made of crenels with a wavelength of 0.4 m, and the surface water speed is 2 cm s^{-1}.

that both the shape of the forms and their distance are responsible for this increase.

[44] In order to better understand the relative influence of these two parameters, we have tentatively used a model described by *Elliott* [1990] and *Elliott and Brooks* [1997b]. The results show that an increase of the wavelength tends to decrease the mass transferred into the bed. This is in agreement with the findings by *Forman* [1998], who showed that at small times, the mass transfer into the bed is greater for the smaller wavelengths. In the case of our experiments, it suggests that if crenels increase the transfer, the increase in the wavelength rather decreases it. In our experiments, the influence of the shape of the forms appears then to be the dominant parameter. Further work is, however, needed to better assess the relative influence of the two parameters (shape and wavelength of the bed forms).

[45] Table 3 gives the total mass of pesticides $M_{\mathrm{transferred}}$(7 h) transferred from the surface water flow into the hemp substrate at the end of the experiments for the two cases (dunes, experiment 1; and crenels, experiment 5). For isoproturon and azoxystrobin, $M_{\mathrm{transferred}}$(7 h) is much larger for crenels than for dunes, with an increase by a factor of about 3 for isoproturon and 2 for azoxystrobin. The effect is much more limited for diuron and tebuconazole, with only a limited increase for crenels compared to dunes. Similar trends are observed for the total mass of pesticide adsorbed onto the whole volume of hemp after 7 h, with again a pronounced influence of the bed forms for isoproturon and azoxystrobin and virtually no influence for diuron and tebuconazole (see Figure 9).

[46] The kinetics parameter k of the hyperbolic model (equation (2)) is given in Table 6 for the two cases (dunes and crenels) and each pesticide. In all cases, the kinetics appear to be much faster for crenels, with k values 2–3 times lower than for dunes.

3.5. General Discussion of the Data and Applicability to Agricultural Ditches

[47] The experiments described in sections 3.1–3.4 have shown that the transfer of the four pesticides from the surface water flow into the bed substrate is favored when the surface water speed and the submergence increase and when the bed forms are made of crenels, both regarding the amounts transferred into the bed substrate and the kinetics of the transfer. Transfer of solutes between the surface water flow and the bed can occur mainly because of turbulent coupling of surface and pore water flows and bed form–induced advection [*Packman et al.*, 2004].

[48] Bed forms cause an increase in hydraulic roughness because they protrude into the flow, producing shear stress and turbulence. When flow is turbulent and viscous, the

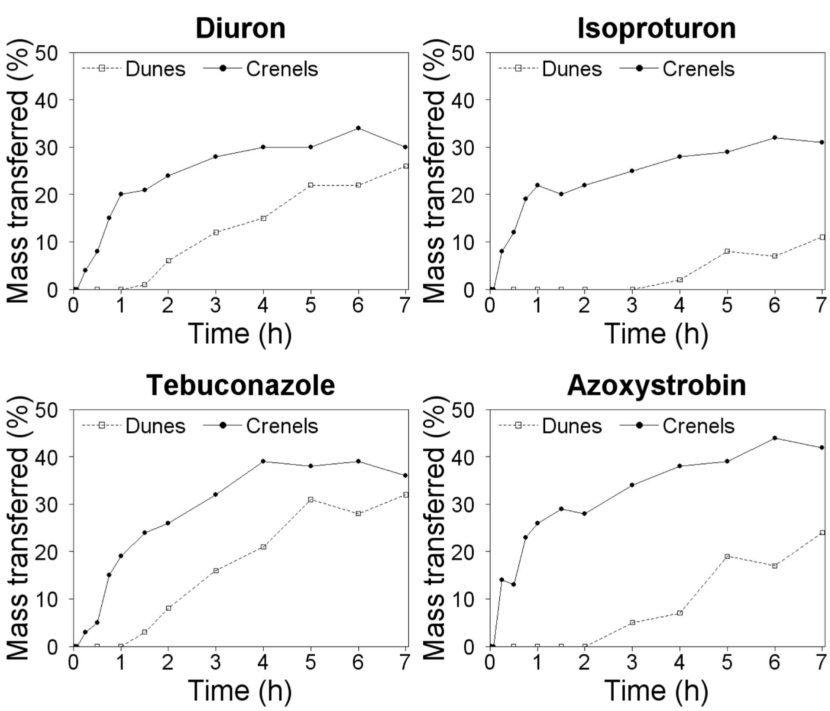

Figure 8. Changes in $M_{\mathrm{transferred}}(t)$ during the 7 h for the four pesticides for two different bed forms (dunes with a wavelength of 0.2 m and crenels with a wavelength of 0.4 m). The submergence is 0.6, and the mean surface water speed is 2 cm s^{-1} in both cases. The mass is expressed as percentage (see text).

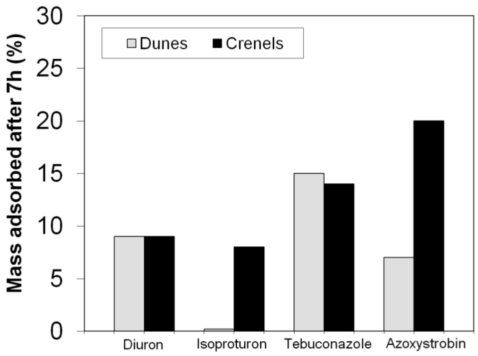

Figure 9. Total mass of each pesticide adsorbed onto the whole volume of hemp after 7 h for two different bed forms (dunes with a wavelength of 0.2 m and crenels with a wavelength of 0.4 m). The submergence is 0.6, and the mean surface water speed is 2 cm s^{-1} in both cases. The mass is expressed as percentage (see text).

flow can separate behind steep forms because of an increasing pressure gradient behind the form [*Chang*, 1970; *Buckles et al.*, 1984; *Best*, 2005]. There is a formation of a flow separation zone. The turbulence (eddies) generated in this flow separation zone slows the flow down. This implies a turbulent coupling of surface and pore water flows, which will also produce a turbulent transfer of solute across the "surface water–bed" interface. The amount of turbulence caused by flow over bed forms (and the associated turbulent transport of solute) is strongly related to the geometry of the forms, the general flow conditions, and the shape and size of the flow separation zone [*Vanoni and Hwang*, 1967]. In the case of our experiments, depending on flow velocity, there may or may not be a separation line coming off the top of the dunes underneath which is recirculation in the flow. For crenels, there will more likely be vortices at the base of each side of the crenel. Flow separation over the forms occurs at higher surface water speeds, and with higher surface water speeds the size of the vortex structures increases. This may explain why high surface water speeds and crenel geometry favor the transfer of pesticides into hemp.

[49] In addition, the transfer of solutes between the surface water flow and the bed can occur because of bed form–induced advection. The acceleration of the flow over the bed forms and the separation of the flow at the crest of the bed forms cause pressure variations over the bed surface. This pressure disturbance induces flow through the bed substrate. There is a transfer of solutes between the surface water flow and the bed resulting from this differential pressure gradient. *Elliott* [1990], *Eylers* [1994], *Elliott and Brooks* [1997a, 1997b], *Forman* [1998], and *Wörman et al.* [2002] showed that the exchange due to the bed form–induced advection increases with an increase in the speed of surface water and submergence. In addition, at small times, the mass transfer into the bed by advection is greater for the smaller wavelengths [*Forman*, 1998]. Our data appear to be in good agreement with these various studies, which were not dealing with pesticides.

Table 6. Hyperbolic Model for the Transfer Kinetics: Values of the Constant k and the Regression Coefficient r for the Four Pesticides and Two Different Geometrical Characteristics (Bed Form Geometry and Wavelength) of the Bed Forms[a]

	Dunes[b]		Crenels[c]	
	k	r	k	r
Diuron	103	0.96	34	0.98
Isoproturon	83	0.89	30	0.98
Tebuconazole	87	0.95	40	0.97
Azoxystrobin	107	0.89	33	0.97

[a]In both cases the submergence is 0.6, and the surface water speed is 2 cm s^{-1}.
[b]With a wavelength of 0.2 m (experiment 1).
[c]With a wavelength of 0.4 m (experiment 5).

[50] Although this study has represented considerable effort and time, our results give only a preliminary insight into the complex processes involved in agricultural ditches in real field conditions. A major difficulty is that there is an interplay between the different hydrodynamic parameters tested in our work. This is, for instance, illustrated in Figure 4, which indicates a link between the submergence and the influence of the surface water speed on the transfer of the pesticides into the bed substrate. Some general information that could be interesting for the mitigation of pesticides in real field conditions can be derived from our results. The first is that it is potentially useful to increase the surface water speed when there are bed forms in order to favor the transfer into the bed substrate. The second is that it is desirable to increase the submergence (the ratio of mean height of the bed forms to the mean water depth), either by increasing the height of the bed forms and/or decreasing the depth of the water flow. Also, it is better to favor bed forms with a geometry that tends to enhance perturbations on the surface water flow.

[51] An important point is to determine which parameter is the most relevant to improve the mitigation. Figure 10 shows the mass of diuron transferred into the bed substrate as a function of the corresponding cumulative channel length covered for the five experiments. It can be seen that the less favorable situation occurs when the surface water speed and the submergence are small and the bed forms are not pronounced (dunes) (experiment 1; see Table 2). In order to improve mitigation, the best possibility appears to be to increase the submergence and to favor bed forms such as crenels, which tend to enhance perturbations of the surface water flow and subsequent transfer into the substrate. In that case, indeed, the mass of pesticides transferred into the bed substrate is maximum, for surface water speeds of both 2 and 7 cm s^{-1} (experiments 2 and 4; see Figure 10 and Table 2). Similar conclusions are obtained for the three other pesticides. Intermediate situations are observed either when increasing only the surface water speed (experiment 3) or modifying only the shape of the bed forms (experiment 5).

[52] In spite of the scarce available data in the literature, an attempt has been made to compare our results in terms of pesticide transfer into the bed substrate to observed data in natural farm ditches for equivalent water flow and ditch lengths [*Margoum et al.*, 2001]. Our experimental results were similar to those observed by *Margoum et al.* [2001]. As an example, the mass transferred into the bed substrate (expressed as a percentage of the initial masses introduced into the ditch at the beginning of the experiment) was 36% for diuron and 34% for isoproturon in a 100 m long vegetated ditch (characterized by a deep layer of organic

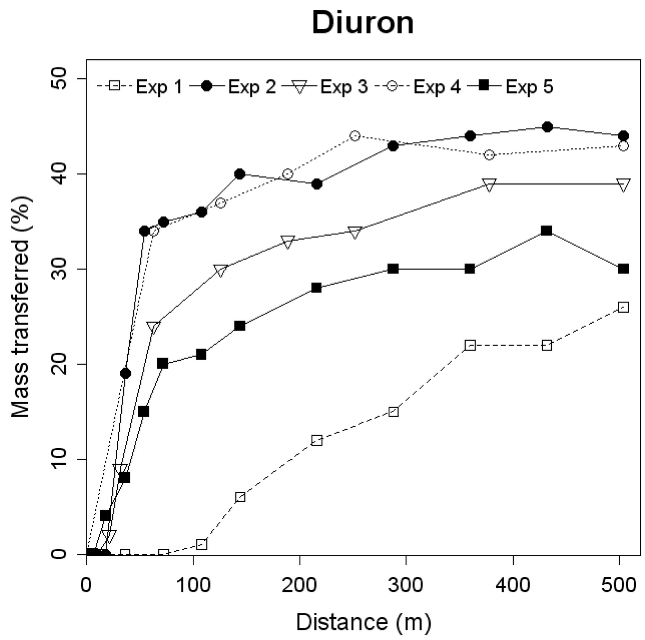

Figure 10. Mass of diuron transferred from the surface water flow into the hemp substrate over a distance of 500 m, obtained by extrapolation of the flume data for the five experiments. The mass is expressed as percentage (see text).

material (dead leaves) and a mean constant surface water speed of about 2 cm s^{-1}), compared to 36% and 35%, respectively, in our flume (experiment 2: crenels, submergence of 1.4 and surface water speed of 2 cm s^{-1}). Our results appear, then, to be relevant and useful to get some orders of magnitude.

4. Conclusions

[53] This work is one of the first attempts to assess the influence of some hydrodynamic parameters on the transfer of selected pesticides into natural substrates in agricultural ditches. It was based on the use of an experimental flume to overcome the difficulties encountered with field studies. An organic substrate made of hemp fibers was selected as a simplified standard of natural organic substrates that are found at the bottom of agricultural ditches. Our results provide a better understanding of the influence of these parameters, which should improve the mitigation of pesticides in agricultural ditches.

[54] Our work has underlined the complexity of the processes that are involved in the transfer and the interplay between the different parameters that were considered. In addition, our work suggests that the behavior of the different pesticides might be different. It will be important to expand this work in the future. In particular, it will be necessary to consider other pesticides and to relate their adsorption behavior to their individual properties. Also, it would be useful to consider other standards of substrates. In addition, it will be necessary to perform field experiments in agricultural ditches under realistic field conditions, particularly in order to investigate the impact of the varying cross sections and bed form geometry of natural ditches and the impact of the wide diversity and heterogeneity of the natural substrates on the influence of the hydrodynamic parameters considered in our work.

[55] It will also be necessary to perform additional experiments with larger variation ranges for the hydrodynamic parameters and perhaps additional parameters, such as the permeability of the substrate. Our experiments were, indeed, performed with relatively low surface water speeds (2 and 7 cm s^{-1}) and a bed substrate (hemp) with rather high permeability. It can therefore be expected that for larger surface water speeds and a less permeable substrate (which can be the case for natural ditches), there will be a "saturation" of the substrate, resulting in a limitation in water transfer into the substrate. It can be anticipated that above a certain surface water speed value, a further increase in surface water speed will no longer result in an increase in pesticide transfer into the bed substrate.

[56] Finally, a modeling approach will be required to better understand the interplay between the different parameters and also investigate the influence of the parameters over larger variation ranges.

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References

Association Française de Normalisation (2003), Qualité de l'eau—Protocole d'estimation de l'incertitude de mesure associée à un résultat d'analyse pour les méthodes physico-chimiques, *Rep. XP T 90-220*, 74 pp., La Plaine Saint-Denis, France.

Barbash, J. E., G. P. Thelin, D. W. Kolpin, and R. J. Gilliom (2001), Major herbicides in ground water: Results from the National Water-Quality Assessment, *J. Environ. Qual.*, *30*, 831–845.

Bennett, E. R., M. T. Moore, C. M. Cooper, S. Smith, F. D. Shields, K. G. Drouillard, and R. Schulz (2005), Vegetated agricultural drainage ditches for the mitigation of pyrethroid-associated runoff, *Environ. Toxicol. Chem.*, *24*, 2121–2127.

Best, J. (2005), The fluid dynamics of river dunes: A review and some future research directions, *J. Geophys. Res.*, *110*, F04S02, doi:10.1029/2004JF000218.

Boivin, A., C. Margoum, C. Guillemain, N. Ball, N. Carluer, J. J. Gril, and V. Gouy (2007), Water and pesticide transport dynamic in a grass buffer strip, paper presented at the International Conference on Water Pollution in Natural Porous Media at Different Scales (WAPO^2), Assessment of Fate, Impact and Indicators, Barcelona, Spain, Euro-Mediterranean Information System on know-how in the Water sector, 11–13 April.

Boutron, O. (2009), Etude de l'influence de l'hydrodynamique sur le transfert des produits phytosanitaires dans les fossés agricoles. Approches expérimentale et numérique, Ph.D. thesis, 256 pp., Univ. Claude Bernard, Lyon, France.

Boutron, O., V. Gouy, N. Touze-Foltz, P. Benoit, J. M. Chovelon, and C. Margoum (2009), Geotextile fibres retention properties to prevent surface water nonpoint contamination by pesticides in agricultural areas, *Geotextiles Geomembranes*, *27*, 254–261.

Boutron, O., C. Margoum, J. M. Chovelon, C. Guillemain, and V. Gouy (2010), Laboratory studies of the adsorption of two pesticides (diuron and tebuconazole) using a batch design and an experimental flume: Influence of contact conditions, *Int. J. Environ. Anal. Chem.*, *90*, 284–296.

Bouvier, G., O. Blanchard, I. Momas, and N. Seta (2006), Pesticide exposure of non-occupationally exposed subjects compared to some occupational exposure: A French pilot study, *Sci. Total Environ.*, *366*, 74–91.

Buckles, J., T. J. Hanratty, and R. J. Adrian (1984), Turbulent flow over large-amplitude wavy surfaces, *J. Fluid Mech.*, *140*, 27–44.

Castillo, L. E., C. Ruepert, and E. Solis (2000), Pesticide residues in the aquatic environment of banana plantation areas in the north Atlantic zone of Costa Rica, *Environ. Toxicol. Chem.*, *19*, 1942–1950.

Chang, P. K. (1970), *Separation of Flow*, Pergamon, Oxford, U. K.

Cooper, C. M., M. T. Moore, E. R. Bennett, S. Smith, J. L. Farris, C. D. Milam, and F. D. Shields (2004), Innovative uses of vegetated drainage ditches for reducing agricultural runoff, *Water Sci. Technol.*, *49*, 117–123.

Crum, S. J. H., G. H. Aalderink, and T. C. M. Brock (1998), Fate of the herbicide linuron in outdoor experimental ditches, *Chemosphere*, *36*, 2175–2190.

Dabrowski, J. M., S. K. C. Peall, A. J. Reinecke, M. Liess, and R. Schulz (2002), Runoff-related pesticide input into the Lourens River, South Africa: Basic data for exposure assessment and risk mitigation at the catchment scale, *Water Air Soil Poll.*, *135*, 265–283.

Dabrowski, J. M., E. R. Bennett, A. Bollen, and R. Schulz (2005), Mitigation of azinphos-methyl in a vegetated stream: Comparison of runoff- and spay-drift, *Chemosphere*, *62*, 204–212.

Edwards, C. A. (1973), Nature and origin of pollution of aquatic systems by pesticides, in *Environmental Pollution by Pesticides*, edited by C. A. Edwards, pp. 11–38, Plenum, London.

Elliott, A. H. (1990), Transfer of solutes into and out of streambeds, *Rep. KH-R-52*, 275 pp., Calif. Inst. of Technol., Pasadena.

Elliott, A. H., and N. H. Brooks (1997a), Transfer of nonsorbing solutes to a streambed with bed forms: Laboratory experiments, *Water Resour. Res.*, *33*, 137–151, doi:10.1029/96WR02783.

Elliott, A. H., and N. H. Brooks (1997b), Transfer of nonsorbing solutes to a streambed with bed forms: Theory, *Water Resour. Res.*, *33*, 123–136, doi:10.1029/96WR02784.

Eylers, H. (1994), Transport of adsorbing metal ions between stream water and sediment bed in a laboratory flume, *Rep. KH-R-56*, 174 pp., Calif. Inst. of Technol., Pasadena.

Forman, S. M. (1998), Transport of nonlinearly adsorbing compounds between stream water and sediment bed in a laboratory flume, *Rep. KH-R-58*, 324 pp., Calif. Inst. of Technol., Pasadena.

Gaillardon, P. (1996), Influence of soil moisture on long-term sorption of diuron and isoproturon by soil, *Pest. Sci.*, *47*, 347–354.

Gerecke, A. C., M. Scharer, H. P. Singer, S. R. Muller, R. P. Schwarzenbach, M. Sagesser, U. Ochsenbein, and G. Popow (2002), Sources of pesticides in surface waters in Switzerland: Pesticide load through waste water treatment plants-current situation and reduction potential, *Chemosphere*, *48*, 307–315.

Gfrerer, M., et al. (2002), Triazines in the aquatic systems of the eastern Chinese rivers Liao-He and Yangtse, *Chemosphere*, *47*, 455–466.

Groenendijk, P., J. W. H. Van der Kolk, and K. Z. Travis (1994), Prediction of exposure concentration in surface waters, in *Freshwater Field Tests for Hazard Assessment of Chemicals*, edited by I. R. Hill et al., pp. 105–125, Lewis, Boca Raton, Fla.

Guo, L., K. Kelley, and K. S. Goh (2007), Evaluation of sources and loading of pesticides to the Sacramento River, California, USA, during a storm event of winter, *Environ. Toxicol. Chem.*, *26*, 2274–2281.

Hunt, J., B. Anderson, B. Phillips, R. Tjeerdema, B. Largay, M. Beretti, and A. Bern (2008), Use of toxicity identification evaluations to determine the pesticide mitigation effectiveness of on-farm vegetated treatment systems, *Environ. Pollut.*, *156*, 348–358.

Jamet, P., J. C. Thoisy, and C. Laredo (1985), Etude et modélisation de la cinétique d'adsorption des pesticides dans le sol, in *Proceedings of the Colloquium Comportement et Effets Secondaires des Pesticides dans le Sol, 4–8 June 1984, Versailles, France, INRA Publ. 31*, pp. 135–146, Inst. Natl. de la Rech. Agron., Paris.

Jergentz, S., H. Mugni, C. Bonetto, and R. Schulz (2005), Assessment of insecticide contamination in runoff and stream water of small agricultural streams in the main soybean area of Argentina, *Chemosphere*, *61*, 817–826.

Kolpin, D. W., E. M. Thurman, and D. A. Goolsby (1996), Occurrence of selected pesticides and their metabolites in near-surface aquifers of the midwestern United States, *Environ. Sci. Technol.*, *30*, 335–350.

Lacas, J. G., M. Voltz, V. Gouy, N. Carluer, and J. J. Gril (2005), Using grassed strips to limit pesticide transfer to surface water: A review, *Agron. Sustainable Dev.*, *25*, 253–266.

Lagacherie, P., O. Diot, N. Domange, V. Gouy, C. Floure, C. Kao, R. Moussa, J. M. Robbez-Masson, and V. Szleper (2006), An indicator approach for describing the spatial variability of artificial stream networks with regard to herbicide pollution in cultivated watersheds, *Ecol. Indic.*, *6*, 265–279.

Leistra, M., A. J. Zweers, J. S. Warinton, S. J. H. Crum, L. H. Hand, W. H. J. Beltman, and S. J. Maund (2004), Fate of the insecticide lambda-cyhalothrin in ditch enclosures differing in vegetation density, *Pest Manage. Sci.*, *60*, 75–84.

Margoum, C., V. Gouy, R. Williams, and J. Smith (2001), Le rôle des fossés agricoles dans la dissipation des produits phytosanitaires, in *Ingénieries EAT, numéro spécial Phytosanitaires: transfert, diagnostic et solutions correctives*, edited by N. Carluer and V. Gouy, Cemagref, Antony, France, pp. 81–90.

Margoum, C., B. Laillet, G. Dramais, and V. Gouy (2003), Rétention des produits phytosanitaires dans les fossés de connexion parcelle-cours d'eau, *Rev. Sci. Eau*, *16*, 389–405.

Marion, A., M. Bellinello, I. Guymer, and A. Packman (2002), Effect of bed form geometry on the penetration of nonreactive solutes into a stream bed, *Water Resour. Res.*, *38*(10), 1209, doi:10.1029/2001WR000264.

Moore, M. T., J. H. Rodgers Jr., C. M. Cooper, and S. Smith Jr. (2000), Constructed wetlands for mitigation of atrazine-associated agricultural runoff, *Environ. Pollut.*, *110*, 393–399.

Moore, M. T., E. R. Bennett, C. M. Cooper, S. Smith Jr., F. D. Shields Jr., C. D. Milam, and J. L. Farris (2001), Transport and fate of atrazine and lambda-cyhalotrin in an agricultural drainage ditch in the Mississippi Delta, USA, *Agric. Ecosyst. Environ.*, *87*, 309–314.

Moore, M. T., E. R. Bennett, C. M. Cooper, S. Smith, J. L. Farris, K. G. Drouillard, and R. Schulz (2006), Influence of vegetation in mitigation of methyl parathion runoff, *Environ. Pollut.*, *142*, 288–294.

Moore, M. T., D. L. Denton, C. M. Cooper, J. Wrysinski, J. L. Miller, K. Reece, D. Crane, and P. Robins (2008), Mitigation assessment of vegetated drainage ditches for collecting irrigation runoff in California, *J. Environ. Qual.*, *37*, 486–493.

Needelman, B. A., P. J. A. Kleinman, J. S. Strock, and A. L. Allen (2007), Improved management of agricultural drainage ditches for water quality protection: An overview, *J. Soil Water Conserv.*, *62*, 171–178.

Neumann, M., R. Schutz, K. Schafer, W. Muller, W. Mannheller, and M. Liess (2002), The significance of entry routes as point and non-point sources of pesticides in small streams, *Water Res.*, *36*, 835–842.

Packman, A. I., M. Salehin, and M. Zaramella (2004), Hyporheic exchange with gravel beds: Basic hydrodynamic interactions and bedform-induced advective flows, *J. Hydraul. Eng.*, *130*, 647–656.

Patty, L., B. Real, and J. J. Gril (1997), The use of grassed buffer strips to remove pesticides, nitrate and soluble phosphorus compounds from runoff water, *Pest. Sci.*, *49*, 243–251.

Poissant, L., and J. F. Koprivnjak (1996), Fate and atmospheric concentrations of α and γ hexachlorocyclohexane in Quebec, Canada, *Environ. Sci. Technol.*, *30*, 845–851.

Poissant, L., C. Beauvais, P. Lafrance, and C. Deblois (2008), Pesticides in fluvial wetlands catchments under intensive agricultural activities, *Sci. Total Environ.*, *404*, 182–195.

Sadiki, M., and L. Poissant (2008), Atmospheric concentrations and gas-particle partitions of pesticides: Comparison between measured and gas-particle partitioning models from source and receptor sites, *Atmos. Environ.*, *42*, 8288–8299.

Sahoo, G. B., C. Ray, E. Mehnert, and D. A. Keefer (2006), Application of artificial neural networks to assess pesticide contamination in shallow groundwater, *Sci. Total Environ.*, *367*, 234–251.

Schiavon, M., C. Perrin-Ganier, and J. M. Portal (1995), The pollution of water by pesticides: State and origin, *Agronomie*, *15*, 157–170.

Schulz, R. (2004), Field studies on exposure, effects, and risk mitigation of aquatic nonpoint-source insecticide pollution: A review, *J. Environ. Qual.*, *33*, 419–448.

Sherrard, R. M., J. S. Bearr, C. L. Murray-Gulde, J. H. Rodgers, and Y. T. Shah (2004), Feasibility of constructed wetlands for removing chlorothalonil and chlorpyrifos from aqueous mixtures, *Environ. Pollut.*, *127*, 385–394.

Tomlin, C. D. S. (2000), *The Pesticide Manual*, Br. Crop Prot. Counc., Farnham, U. K.

Van Dijk, P. M., F. Kwaad, and M. Klapwijk (1996), Retention of water and sediment by grass strips, *Hydrol. Processes*, *10*, 1069–1080.

Vanoni, V. A., and L. S. Hwang (1967), Relation between bed forms and friction in streams, *J. Hydraul. Div. Am. Soc. Civ. Eng.*, *93*, 121–144.

Wörman, A., A. I. Packman, H. Johansson, and K. Jonsson (2002), Effect of flow-induced exchange in hyporheic zones on longitudinal transport of solutes in streams and rivers, *Water Resour. Res.*, *38*(1), 1001, doi:10.1029/2001WR000769.

Yao, Y., et al. (2006), Spatial and temporal distribution of pesticide air concentrations in Canadian agricultural regions, *Atmos. Environ.*, *40*, 4339–4351.

Zhou, R. B., L. Z. Zhu, and Y. Y. Chen (2008), Levels and source of organochlorine pesticides in surface waters of Qiantang River, China, *Environ. Monit. Assess.*, *136*, 277–287.

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