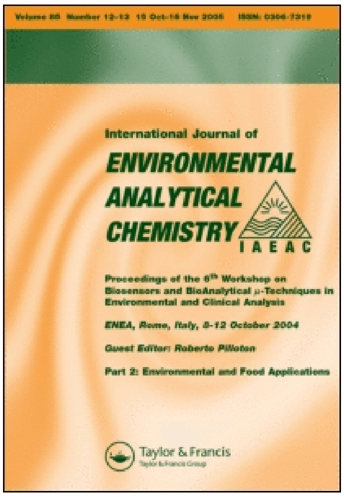

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Laboratory studies of the adsorption of two pesticides (diuron and tebuconazole) using a batch design and an experimental flume: influence of contact conditions

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Laboratory studies of the adsorption of two pesticides (diuron and tebuconazole) using a batch design and an experimental flume: influence of contact conditions

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The adsorption of two commonly used pesticides, diuron and tebuconazole, on an organic substrate (hemp), which was chosen as an analogue for natural substrates often found in agricultural ditches, has been studied using three different contact schemes: (1) contact in a beaker using a modified batch method; (2) contact in an experimental flume, with a dry start substrate; and (3) same as (2) but with the substrate initially saturated with water. Changes in pesticides concentrations as a function of time as well as adsorption after seven hours have been determined for each case. The highest adsorption is observed for the experiments with a flume initially containing dry hemp. In that case, both the initial condition (hemp initially without water) and the contact conditions between the pesticide solution and the substrate appear to favour adsorption. The lowest adsorption is obtained for the flume containing hemp initially saturated with water. In that case, samples that were obtained at different depths inside the hemp using capillary tubes showed that only the superficial part of the hemp was in equilibrium with the surface water. The presence of an initial water table appears to be a limiting factor for pesticides penetration and further adsorption onto hemp. An intermediate adsorption is obtained for the modified batch method. These results highlight the pronounced influence on adsorption of both the initial hemp wetness conditions and the contact conditions between the pesticides solution and the substrate. This influence should be studied further to assess the potential of agricultural ditches to mitigate pesticides contamination in surface water.

Keywords: pesticides; diuron; tebuconazole; adsorption; contact conditions; agricultural ditches; experimental flume; hemp

1. Introduction

The intensification of agriculture has led to a diffuse contamination source for surface and ground waters by various pesticides [1–4]. Once pesticides are applied to a plot, they can be transferred through the soil and different landscape components before reaching the water courses. Of particular importance are farm ditches, which play a major role in the collection and transfer of water from agricultural plots. The fluxes of pesticides through

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ditches can be modified by a number of physical, chemical or biological processes which can contribute to the reduction of the amount of pesticides reaching the rivers [5–9]. Pesticides in the surface water flow can be transferred into the ditch bed substrate by molecular diffusion and advection. Molecular diffusion is due to the gradient of pesticide concentration, while advection is due to the mean velocity of the flow. Once inside the substrate, pesticides can be transported by molecular diffusion, advection and kinematic dispersion (kinematic dispersion is due to the structure of the bed substrate) and can be adsorbed onto the substrate. Pesticides adsorption onto ditch substrates is a very interesting process for the mitigation of surface water contamination, the efficiency of which is poorly understood. The pesticides adsorption that occurs during water flows in natural ditches is not easy to predict, as it depends upon the adsorption capacities of the substrates which are present at the bottom of the ditches and the capacity of the pesticides to reach the reactive sites of the substrate, mainly by hydraulic transport.

This study is aimed at evaluating the influence of various contact conditions on the adsorption of two pesticides onto a standard of ditch substrate under controlled conditions. Special attention was given to the influence of the initial conditions (dry or water saturated substrate) and water dynamics. We studied the adsorption kinetics and the adsorption at equilibrium which are observed for three different contact schemes: (1) contact in a glass beaker using a modified batch method; (2) contact in a recirculating experimental flume, in which the substrate covers the bottom part of the flume and is initially without water; (3) same as (2) but with a substrate initially saturated with pesticide free water. The comparison of the data obtained with Scheme 1, where the transfer of the pesticides onto and inside the substrate is assisted by orbital shaking of the beaker, and Scheme 2, where the transfer of the pesticides is linked to the flow in the flume, allowed us to evaluate the influence of the water dynamics on the transfer and adsorption of the pesticides onto and inside the substrate. The comparison of the data obtained by Schemes 2 and 3 allowed us to test the influence of the presence of water inside the substrate at the start of the experiment on the transfer and adsorption of the pesticides onto and inside the substrate. Schemes 2 and 3 were designed to mimic the contact conditions that are commonly encountered in ephemeral ditches, those in which the substrate dries out between successive water flow events, and those with a permanent water flow.

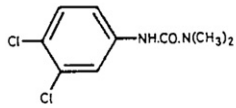
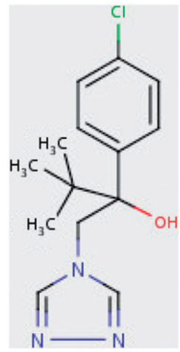
The use of an experimental flume was selected to overcome the difficulties encountered with field studies, which make it difficult to establish quantitative balances. In addition, when considering the wide diversity of substrates that are found at the bottom of agricultural ditches [10] (typically living and/or dead plants, with various decomposition levels, or sediments), and any possible changes in their characteristics over time, we have decided to use a simplified organic substrate made of hemp fibres, as discussed in detail by Boutron and Boutron *et al.* [11–12].

2. Experimental

2.1 *Pesticides*

Two pesticides, diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) and tebuconazole ((*RS*)-1-p-chlorophenyl-4,4-dimethyl-3-(1*H*-1,2,4-triazol-1-ylmethyl)pentan-3-ol) were selected because they have been extensively used in agricultural plots and are commonly found in surface waters. They are characterised by a wide range of physico-chemical properties as shown in Table 1, so that various behaviours can be expected for their adsorption onto

Table 1. Selected properties of the two pesticides considered in this work [22–24].

	Diuron	Tebuconazole
Chemical structure		
Solubility in water ($mg\,L^{-1}$) (20°C)	36	36
K_{oc} ($L\,kg^{-1}$) (20°C)	480	1554
log K_{ow} (20°C)	2.9	3.7
Half-life (day)	90–180	30–62

the substrate. The commercial formulations Zodiac TX (diuron) and Folicur 250 EW (Tebuconazole) from Bayer Crop Science were used. In addition, potassium bromide was added as a tracer for water transport through the substrate.

2.2 *Substrate*

We have used hemp fibres as a standard for the natural vegetation based substrates that can be found in agricultural ditches. They were obtained as rolls (with a thickness of 10 cm) from Chanvre et Technique, Riec sur Belon, France (Technichanvre trade mark), see Figure 1. They are made of 85% of hemp fibres, mixed with 15% of polyester fibres in order to obtain adequate mechanical properties, especially regarding their geometry stability over long time periods. A number of relevant physical and chemical parameters for this substrate have been determined, in collaboration with Nathalie Touze-Foltz and Rolland Gallo from Cemagref Antony. These fibres have the following physical characteristics: a porosity of 0.5, a vertical conductivity (i.e. through the thickness of the roll) of $3.4\,cm\,s^{-1}$ and a longitudinal conductivity (i.e. through the length of the roll) of $3.1\,cm\,s^{-1}$. 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%.

2.3 *Modified batch adsorption experiments*

Adsorption experiments were performed using the modified batch technique as described by Margoum *et al.* [13]. A piece of hemp roll (8 g) was placed in a glass beaker with 250 mL of an aqueous solution containing the two pesticides at a concentration of $20\,\mu g\,L^{-1}$ and bromide at a concentration of $100\,mg\,L^{-1}$. The solution was prepared using deionised water containing NaCl (5 mM) and $NaHCO_3$ (4 mM). The pH was typically 7.5 [11].

Figure 1. The rolls of hemp used in this study.

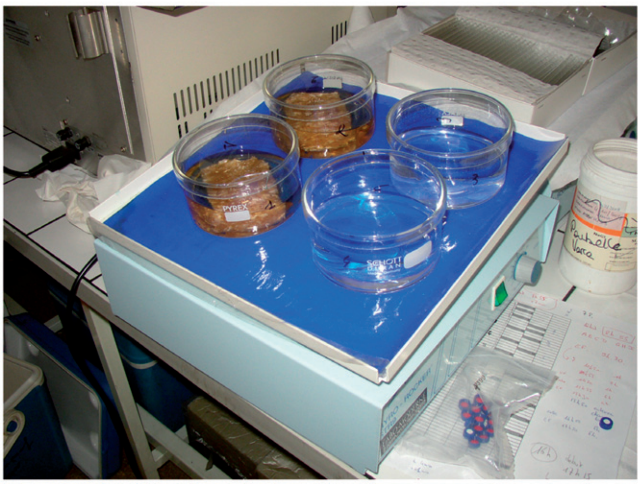


Figure 2. Modified batch adsorption experiment.

The beaker was covered with a Petri dish to avoid evaporation and was gently shaken for 7 hours (50 rpm – orbital mixer STR, Stuart Scientific) at room temperature (Figure 2). Water samples were taken at different intervals during the 7 hour period, in order to determine the adsorption kinetics. Each experiment was repeated three times, giving mean values used for the discussion. Control samples without substrate, and pesticide free blanks were also analysed. No pesticide degradation or sorption onto the glass beaker walls were observed. The initial concentration of $20\,\mu g\,L^{-1}$ for the two pesticides was chosen as a good compromise between the typical concentrations found at the edge of agricultural plots (see e.g. [14]) and the minimisation of analytical uncertainties. We have assessed changes in the C/C_0 ratio as a function of time during the 7 hours, where C represents the concentration of diuron, tebuconazole or bromide in the water at a given time, and C_0 the concentration of diuron, tebuconazole or bromide in the water at the beginning of the experiment. As bromide is not adsorbed onto hemp, the mass of pesticides adsorbed at the end of the experiments has also been estimated from the difference

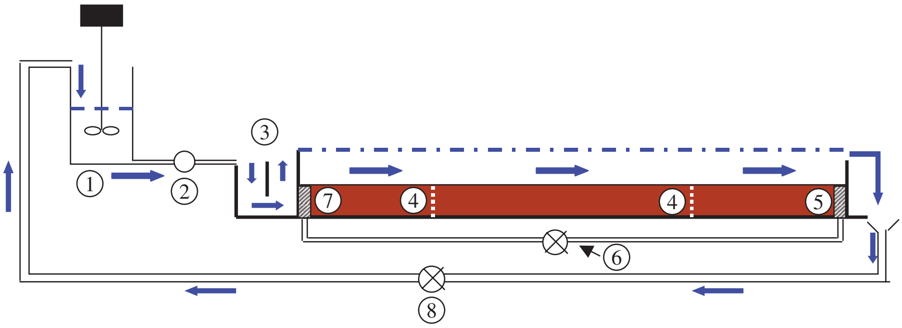


Figure 3. Schematic diagram of the flume. 1: mixing tank; 2: flowmeter; 3: upstream stabilisation tank; 4: cross sections equipped with capillary tubes; 5: downstream sub-surface flow discharge box; 6: peristaltic pump to recirculate sub-surface flow; 7: upstream sub-surface flow discharge box; 8: centrifugal pump. Hemp is shown with a brown colour. Depending upon the experimental scheme, it is initially with water or without water.

between the mass of bromide and the mass of diuron or tebuconazole remaining in the aqueous solution after 7 hours, as explained in detail by Boutron [11].

2.4 *Experimental flume*

The experimental flume (Figure 3) was 730 cm long and had a 40 cm wide channel. The flume and all the recirculation pipes were made of PVC. However, one lateral wall was made of Plexiglas to permit flow visualisation. The hemp rolls were on the bottom of the flume, 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. As shown in Figure 3, a mixing tank was added to homogenise the concentration of the pesticides in the water solution. A flowmeter and a stabilisation tank are necessary to prevent the occurrence of eddies at the entrance of the flume, and are placed upstream of the flume itself. The water depth in the flume is fixed using an impermeable end-plate. Preliminary experiments showed that the impermeable ends did not provide very good end conditions. A slim box was then installed at each end of the flume (see Figure 3). The boxes were closed except one vertical face of each box which was covered by a stainless steel mesh. The 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 were equipped with capillary tubes to determine the penetration depths of the pesticides, see Figure 3. They were located 2 and 4 m downstream of the stabilisation tank, respectively. Each section was equipped with 3 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 experimental duration was 7 hours. For experiments with the hemp initially saturated in water, the flume was filled at the beginning of the experiment with the deionised water in which 5 mM of NaCl and 4 mM of $NaHCO_3$ had been added. For the experiments with hemp initially without water, the flume was left dry. In both cases, a solution containing the two pesticides and bromide was prepared in the mixing tank using deionised water with 5 mM of NaCl and 4 mM of $NaHCO_3$ as a diluent, to obtain concentrations of 20 $\mu g\ L^{-1}$ for the two pesticides and 100 $mg\ L^{-1}$ for bromide in the surface water flow in the flume (after dilution in the case of the substrate initially saturated with water). Water samples were collected during the whole experiment at different time intervals downstream of the flume, at various points in the surface flow, and from each capillary tube to determine the pesticides and bromide concentrations. From each flume experiment, an extremely large number of samples were obtained and analysed for the two pesticides and bromide, taking considerable time and costs. This is the reason why it was not possible to repeat the experiments, as was done for the modified batch adsorption experiments. The water depth above the hemp surface and the speed of the surface water flow were also monitored. During the experiments, the surface water speed was kept to $2\,cm\,s^{-1}$, while the sub-surface water speed was $0.02\,cm\,s^{-1}$ [11] and the water depth was kept at 3 cm [11]. These three parameters were kept constant during the experiments. Additional detailed information about the experiments can be found in Boutron's work [11]. We have assessed changes in the C/C_0 ratio as a function of time during the 7 hours, where C represents the concentration of diuron, tebuconazole or bromide in the surface water flow at the downstream end of the flume at a given time. For the flume experiments with initially dry hemp, C_0 represents the diuron, tebuconazole or bromide concentration in the water at the beginning of the experiment. For the flume experiments with hemp initially saturated with water, C_0 represents the concentration after dilution in the surface water flow. The mass of pesticides adsorbed at the end of the flume experiments has also been estimated from the difference between the mass of bromide and the mass of diuron or tebuconazole remaining in the aqueous solution after 7 hours, as explained in detail by Boutron [11].

2.5 *Pesticides and bromide determination*

Bromide concentrations were determined by Ion Chromatography (Dionex DX-120 with a AS9-HC column) using direct injections (limit of detection: $0.2\,mg\,L^{-1}$). For diuron and tebuconazole, the 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 analysed 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. The injection volume was 100 µL (with triplicate determinations). The limit of detection was $0.02\,\mu g\,L^{-1}$ for diuron and $0.2\,\mu g\,L^{-1}$ for tebuconazole. The analytical uncertainties were about 10%.

3. Results and discussion

3.1 *Comparison of the adsorption kinetics for Schemes 1 and 2*

The comparison of the experiments with Schemes 1 (modified batch method) and 2 (dry hemp) allowed an investigation of the influence of the water dynamics on the adsorption of the pesticides. In both cases, the solution of pesticides is in contact with the whole hemp volume at the beginning of the experiment (at introduction of the pesticides solution into the beaker or into the flume, which were initially dry). In addition, the mass of hemp/volume of water ratio was kept the same for both experiments.

Figure 4 shows changes in diuron, tebuconazole and bromide concentrations in water as a function of time for the batch experiments (contact Scheme 1). It is interesting to

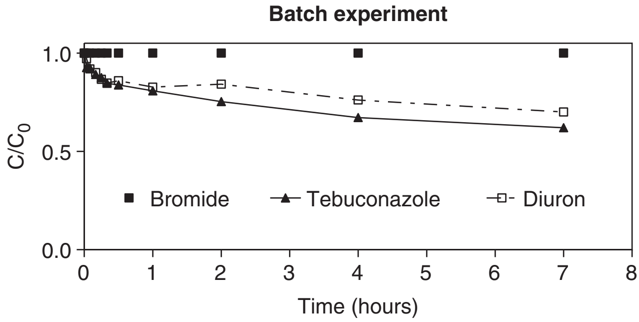


Figure 4. Diuron, tebuconazole and bromide concentrations in water as a function of time for the batch experiments. The results are expressed as C/C_0, where C represents the concentration of diuron, tebuconazole or bromide in the water at a given time, and C_0 the concentration of diuron, tebuconazole or bromide in the water at the beginning of the experiment.

compare these data with those obtained for the flume with dry hemp (Figure 5(a)). For the flume experiments, equilibrium was reached after 7 hours. Conversely, equilibrium for the batch experiments was not reached after 7 hours (additional experiments over 48 hours showed that it was reached after about 24 hours).

For the two schemes, the transfer of the pesticide molecules into the whole volume of hemp was relatively easy at the start of the experiments, as the hemp was initially dry (see steps 1 and 2 in Figures 6 and 7), leading to the adsorption of a fraction of the pesticide molecules (see steps 2 and 3 in Figures 6 and 7). The pesticide molecules that remained outside the hemp were then transferred into the hemp via various mechanisms.

Tentatively, it can be assumed that this transfer is mainly linked to turbulent diffusion in the batch experiments (see step 4 in Figure 6), and to advection for the flume experiments [15–21] (see step 4 in Figure 7). Turbulent diffusion, which returns to a combination of molecular diffusion coupled with turbulence, is a process which is slower and less efficient than advection for the transfer of contaminants; this is in good agreement with the observed differences for the two experiments (see Figures 4 and 5(a)). It should, however, be kept in mind that for the batch experiments, turbulent diffusion is not homogeneous in the whole hemp volume because of orbital shaking, leading to stronger diffusion in the outer parts of the hemp and much weaker diffusion in the centre (see step 4 in Figure 6). For the flume experiments, the situation is different, there is a rather homogeneous advection due to the use of two pumps (see step 4 in Figure 7).

Our experiments indicate that it is necessary to take into account the water dynamics when assessing the adsorption kinetics of the pesticides. So when investigating the adsorption kinetics of pesticides in agricultural ditches, it will then be necessary to design experiments which reproduce the water dynamics in agricultural ditches for realistic field conditions, as example obtained with flume experiments.

3.2 *Influence on the kinetics of adsorption of the presence of water in the hemp at the beginning of the experiments*

The comparison of the data obtained with the experimental flume for Schemes 2 (dry hemp) and 3 (saturated hemp) allows an evaluation of the influence on the adsorption

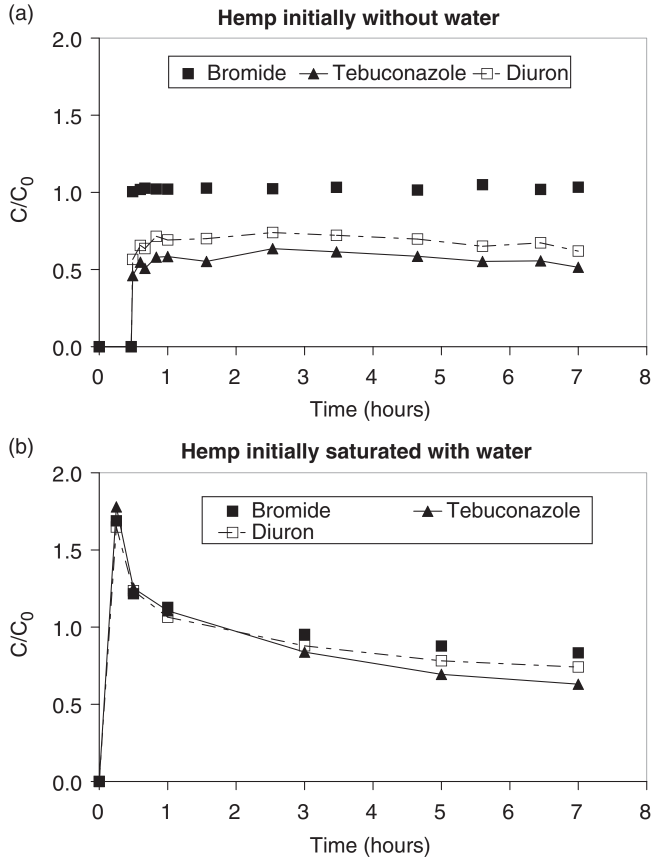


Figure 5. Diuron, tebuconazole and bromide concentrations in water as a function of time for two contact schemes using an experimental flume. (a) initially dry hemp and (b) initially saturated hemp (same mass of hemp/water volume ratio for the two schemes). The results are expressed as C/C_0, where C represents the concentration of diuron, tebuconazole or bromide in the surface water flow at the downstream end of the flume at a given time. For the flume experiments with initially dry hemp, C_0 represents the diuron, tebuconazole or bromide concentration in the water of the mixing tank at the beginning of the experiment. For the flume experiments with hemp initially saturated with water, C_0 represents the concentration after dilution in the surface water flow.

kinetics of the presence of water at the beginning of the experiments. Figure 5 shows the changes in diuron, tebuconazole and bromide concentrations in water as a function of time for the contact Schemes 2 (Figure 5(a)) and 3 (Figure 5(b)). It indicates that the adsorption kinetics is faster with initially dry hemp than for hemp initially saturated with water. For initially dry hemp, as soon as the water overflows above the downstream impermeable end-plate (after about 30 minutes), the C/C_0 ratio is very close to the equilibrium ratio value for the two pesticides. The whole hemp cross section is rapidly involved in the adsorption of the two pesticides since no water was present in the hemp at the beginning of the experiment (see steps 1 and 2 in Figure 7). The situation is different for hemp initially saturated with water, with equilibrium still not reached even after 7 hours. In this case, the penetration of the pesticides and bromide into the hemp is determined by the capillary

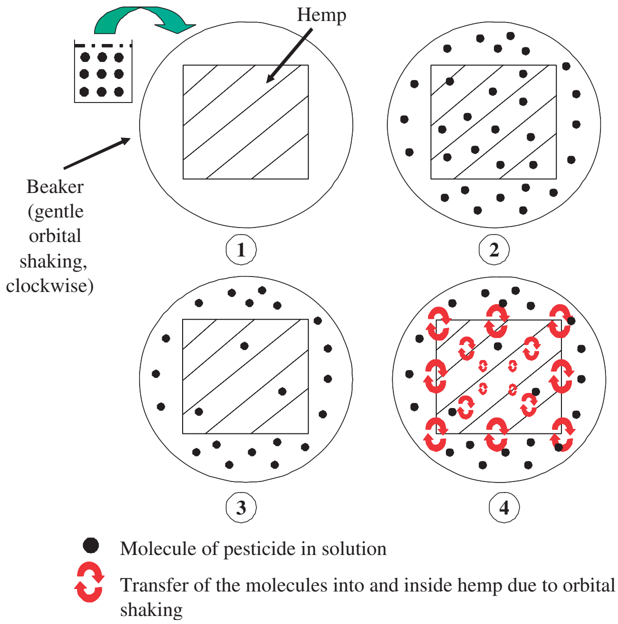


Figure 6. Batch experiment. The diagrams show a top view of the beaker and the piece of hemp. 1: Introduction of the pesticides solution into the beaker (initially dry hemp). 2: Some of the pesticides molecules have already penetrated inside hemp. 3: Adsorption of some of the pesticides molecules onto hemp (illustrated by the disappearance of some of the black dots). 4: The clockwise shaking of the beaker creates a water motion in the beaker, which results in a transfer of the molecules of pesticides from the outside water to the bulk hemp mainly by turbulent diffusion. Because of the orbital shaking, turbulent diffusion is small in the centre of hemp and greater in the outer parts of the hemp. Vertical motions of the water and molecules are not represented in the diagrams.

tubes data, and is shown as increasing over time as illustrated by the observed changes in the penetration of diuron, tebuconazole and bromide into the hemp (Figure 8). It can be seen that diuron, tebuconazole and bromide have not penetrated uniformly into hemp after 7 hours since they are mainly present in the upper layer of the hemp. Similar observations have already been made by Elliott and Brooks [17] for two sand beds ('Ottawa 30' medium sand and 'Oklahoma 90' fine sand) and two fluorescent dye tracers (Amino G Acid and Lissamine FF). These data suggest that pesticides penetration into the lowest part of the hemp would probably continue to increase slowly after seven hours, but this would need to be confirmed by performing longer experiments.

3.3 *Comparison of the adsorption after 7 hours for the different experiment schemes*

Table 2 shows the percentages of the mass of diuron and tebuconazole adsorbed onto hemp after 7 hours for the three experimental schemes (the results are expressed as percentages of the initial mass of pesticide in water at the beginning of the adsorption experiment), with the same hemp/volume of water ratio for the three schemes. The adsorption for tebuconazole is larger than for diuron in all cases, which is in good agreement with their respective Koc values (see Table 1).

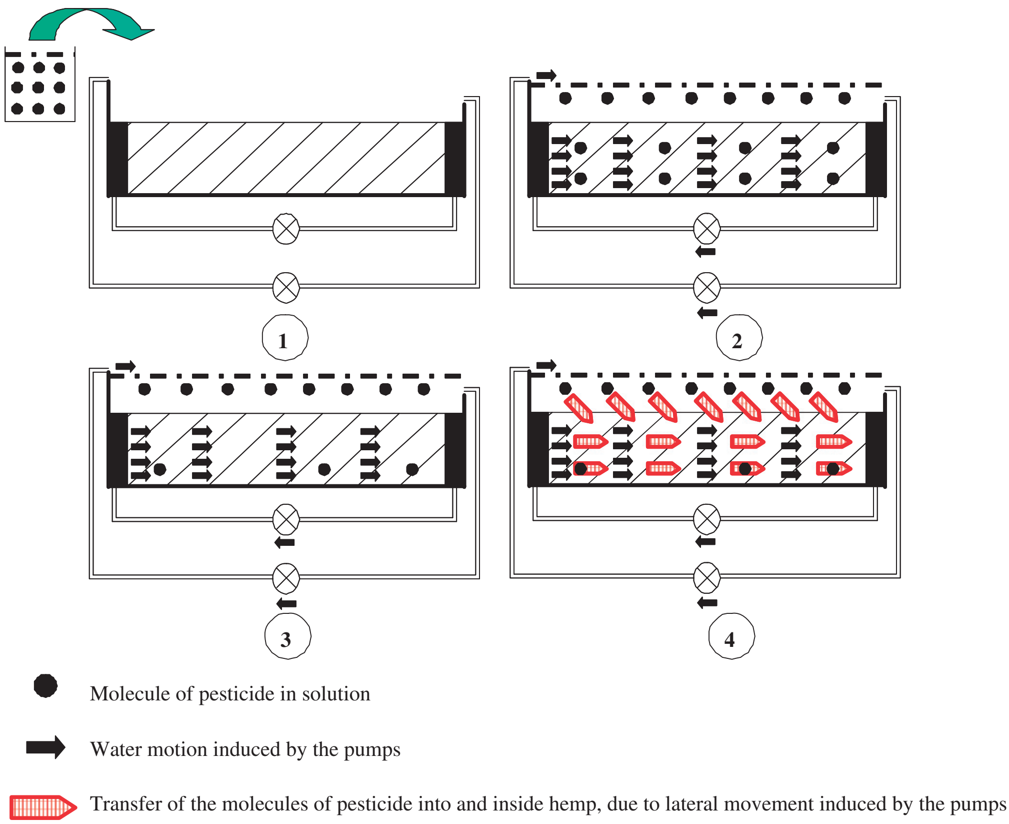


Figure 7. Flume experiment with the initially dry hemp. 1: Introduction of the pesticides solution into the flume. 2: Some of the pesticides molecules have already penetrated inside hemp. 3: Adsorption of some of the pesticides molecules onto the hemp (illustrated by the disappearance of some of the black dots). 4: Because of the high surface water flow and the weaker lateral water flow inside the hemp, the molecules of pesticides that are present in the surface water flow penetrate into hemp mainly by advection. Inside the hemp, the transfer of these molecules is mainly by advection.

Table 2 shows that after 7 hours, contact Scheme 2 (flume with dry hemp) gives the highest adsorption both for diuron and tebuconazole. These high adsorption values can be explained by the lack of water in the hemp at the beginning of the experiment and a rapid transfer of the pesticides into hemp, probably mainly by advection. Intermediate adsorption values are observed after 7 hours for the batch experiments, which also allow full contact of the pesticides solution with hemp, but with a transfer of the pesticides into hemp probably mainly by turbulent diffusion.

When comparing the adsorption at equilibrium for Schemes 1 (equilibrium reached after 24 hours) and 2 (equilibrium reached after 7 hours), it appears that total adsorption is similar for the two schemes for tebuconazole while adsorption is lower for diuron with the batch experiment (Table 2). For diuron, this suggests that advection could favour both the adsorption kinetics and the adsorption at equilibrium, compared to turbulent diffusion, while it may only favour the adsorption kinetics for tebuconazole. It would be interesting to perform similar experiments for other pesticides to better assess the effect of these two processes on their adsorption at equilibrium.

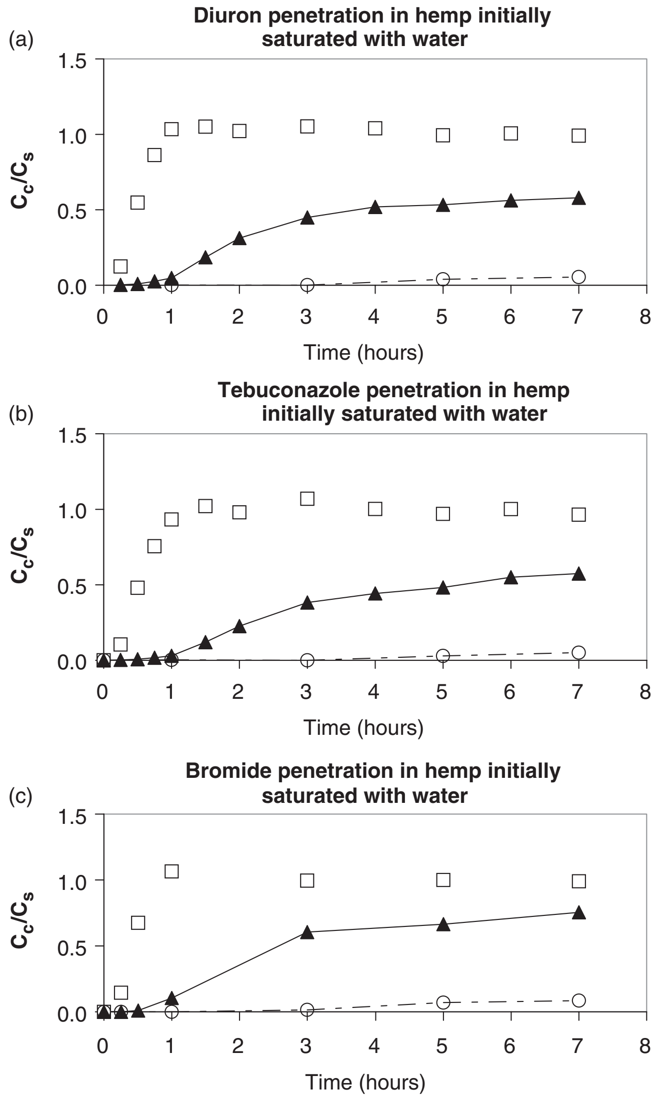


Figure 8. Penetration of diuron (a), tebuconazole (b) and bromide (c) into hemp initially saturated with water as a function of time. The results are expressed as C_C/C_S, where C_C represents the concentration of diuron, tebuconazole or bromide in the water sample collected with a capillary tube for a given depth while C_S represents the concentration of diuron, tebuconazole or bromide measured in the surface water flow. Open squares: surface down to 3.3 cm; black triangles: 3.3 to 6.6 cm; open circles: 6.6 to 10 cm. The values shown on the figure are averages of the different C_C/C_S values measured at the two sections equipped with capillary tubes.

Finally, the least favourable situation appears to be that for Scheme 3 (flume initially saturated hemp), see Table 2. In this case, equilibrium is still not reached after 7 hours, and adsorption is linked to the penetration of pesticides into the hemp. It will be necessary to perform additional studies to investigate the influence of the water flow parameters on their penetration (especially the water depth and speed), the characteristics of the substrate

Table 2. Percentages of the mass of diuron and tebuconazole adsorbed onto hemp for the three experimental schemes after 7 or 24 hours (the results are expressed as percentages of the initial mass of pesticide in water at the beginning of the adsorption experiment).

Pesticide	Batch experiment after 7 hours	Batch experiment after 24 hours (at equilibrium)	Flume with initially dry hemp after 7 hours (at equilibrium)	Flume with initially saturated hemp after 7 hours
Diuron	29	35	44	9
Tebuconazole	34	47	48	20

(conductivity, porosity) and the shape of the interface between the substrate and the surface water flow. Similar studies have already been performed for other compounds (metals, cationic surfactants) and substrates (sand beds), by Elliott, Brooks, Eylers, and Forman [15–17,20,21].

4. Conclusion

The aims of this study were to compare the adsorption of two pesticides onto a standard (hemp) for agricultural ditch substrate with different contact conditions, using three different experimental schemes. The first was adapted from a standard batch method (Scheme 1). For this first scheme the hemp was initially dry and the transfer of the pesticides into hemp was tentatively attributed to turbulent diffusion. The second and third schemes, based on an experimental flume, were designed to approach the field conditions as encountered for dry (Scheme 2) or wet agricultural ditches (Scheme 3). In these last two schemes, the transfer of the pesticides into hemp was tentatively attributed to advection.

The highest adsorption was observed for Schemes 1 and 2 with initially dry hemp, especially for Scheme 2 which corresponds to the conditions typically encountered in the field in dry agricultural ditches. The highest adsorption observed for Scheme 2 could tentatively be explained by the prevalence of advective transfer of the pesticides, compared to the predominance of turbulent diffusive transfer for Scheme 1. Conversely, adsorption by hemp initially saturated with water was much less and is mainly linked to the limited penetration of the pesticides into the hemp during the experiments.

To improve the mitigation of pesticides in agricultural ditches, it seems important to favour ephemeral ditches in which the substrate remains dry between successive water flow events, and to favour the advective transfer of the pesticides into the bed substrate.

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References

[1] L. Guo, K. Kelley, and K.S. Goh, Environ. Toxicol. Chem. **26**, 2274 (2007).
[2] IFEN, French Institute of Environment, Orléans, France, http://ifen.fr/ (accessed 15 September 2008).
[3] S. Jergentz, H. Mugni, C. Bonetto, and R. Schulz, Chemosphere **61**, 817 (2005).
[4] R.B. Zhou, L.Z. Zhu, and Y.Y. Chen, Environ. Monit. Assess. **136**, 277 (2008).
[5] E.R. Bennett, M.T. Moore, C.M. Cooper, S. Smith, F.D. Shields, K.G. Drouillard, and R. Schulz, Environ. Toxicol. Chem. **24**, 2121 (2005).
[6] C.M. Cooper, M.T. Moore, E.R. Bennett, S. Smith, J.L. Farris, C.D. Milam, and F.D. Shields, Water Sci. Technol. **49**, 117 (2004).
[7] M.T. Moore, E.R. Bennett, C.M. Cooper, S. Smith, F.D. Shields, C.D. Milam, and J.L. Farris, Agric. Ecosyst. Environ. **87**, 309 (2001).
[8] M.T. Moore, D.L. Denton, C.M. Cooper, J. Wrysinski, J.L. Miller, K. Reece, D. Crane, and P. Robins, J. Environ. Qual. **37**, 486 (2008).
[9] R. Schulz, J. Environ. Qual. **33**, 419 (2004).
[10] P. Lagacherie, O. Diot, N. Domange, V. Gouy, C. Floure, C. Kao, R. Moussa, J.M. Robbez-Masson, and V. Szleper, Ecol. Indic. **6**, 265 (2006).
[11] O. Boutron, Ph.D. thesis (University Claude Bernard of Lyon, France, 2009).
[12] O. Boutron, V. Gouy, N. Touze-Foltz, P. Benoit, J.M. Chovelon, and C. Margoum, Geotextiles and Geomembranes **27**, 254 (2009).
[13] C. Margoum, C. Malessard, and V. Gouy, Chemosphere **63**, 1835 (2006).
[14] X. Louchart, M. Voltz, P. Andrieux, and R. Moussa, J. Environ. Qual. **30**, 982 (2001).
[15] A.H. Elliott, Ph.D. thesis (California Institute of Technology, Pasadena, USA, 1990).
[16] A.H. Elliott and N.H. Brooks, Water Resour. Res. **33**, 123 (1997).
[17] A.H. Elliott and N.H. Brooks, Water Resour. Res. **33**, 137 (1997).
[18] S.A. Savant, D.D. Reible, and L.J. Thibodeaux, Water Resour. Res. **23**, 1763 (1987).
[19] L.J. Thibodeaux and J.D. Boyle, Nature **325**, 341 (1987).
[20] H. Eylers, Ph.D. thesis (California Institute of Technology, Pasadena, USA, 1994).
[21] S.M. Forman, Ph.D. thesis (California Institute of Technology, Pasadena, USA, 1998).
[22] INRA, available from: http://dive.afssa.fr/agritox/index.php (accessed 20 May 2007).
[23] C.D.S. Tomlin, *The Pesticide Manual* (British Crop Protection Council, Farnham, UK, 2000).
[24] FOOTPRINT Pesticide Properties Database, available from: http://eu-footprint.org/ppdb.html (accessed 10 October 2008).