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K. Wechsler^a; M. Rombourg^b; F. Bindler^a; A. Exinger^a; C. Breuzin^c

^a Centre d'Analyses et de Recherches, Illkirch-Graffenstaden, France ^b IUT Louis Pasteur, Schiltigheim, France ^c Agence de l'Eau Rhin-Meuse, Moulins-Lès, Metz, France

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POLLUTION POTENTIAL OF SOME TRIAZOLE PESTICIDES

K. WECHSLER¹, M. ROMBOURG², F. BINDLER^{1*}, A. EXINGER¹ and
C. BREUZIN³

¹*Centre d'Analyses et de Recherches, 76 route du Rhin, 67400 Illkirch-Graffenstaden, France;* ²*IUT Louis Pasteur, 3 rue St-Paul, 67300 Schiltigheim, France;* ³*Agence de l'Eau Rhin-Meuse, B.P. 19, 57161 Moulins-Lès-Metz, France*

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The widespread occurrence of pesticides, especially in the groundwater has stimulated research into the behavior of these agrochemicals in the environment. In this work a simple model to describe the fate of the two triazole fungicides Flutriafol and Flusilazol in a silt soil is presented. For this purpose we constructed mini-columns of soil, on which we applied the two fungicides, the percolation waters and the soils were collected at different times and the pesticides quantified in these samples. In the first part, these experiments were carried out outdoors during a period of 6 months on the silt soil and in a second part, we did similar indoor experiments with the same soil and with two others. To complete our work, we studied the adsorption of these two compounds on these three types of soil with batch equilibrium experiments. The results demonstrate that the fungicide Flusilazol is an immobile compound in soil, being strongly adsorbed whatever the nature of the soil. The Flutriafol is slightly to moderately mobile in the different soils, being less adsorbed.

KEY WORDS: Flusilazol, Flutriafol, groundwater, soil, adsorption, mobility.

INTRODUCTION

Pesticides are widely used in agriculture for controlling weeds, insects and fungi, but when these xenobiotic substances have accomplished their intended effects, their residues are left in the ecosystem, particularly in the soil, where they can be leached to the underlying water table¹. Thus, the widespread occurrence of pesticides, especially in the groundwater has stimulated research on the behavior of these agrochemicals in the environment. Different methods, such as soil columns²⁻⁵, lysimeters^{6,7}, soil thin-layer chromatography^{8,9} have been employed to assess the mobility of these xenobiotics in soil. In this work, a simple model to describe the fate of the two triazole fungicides Flutriafol and Flusilazol, using soil mini-columns is presented¹⁰. Besides the mobility of pesticides in soil, the adsorption is an important process also involved in the environmental behavior of these agrochemicals. Therefore, to complete our study, we evaluated the adsorption of these two fungicides using laboratory batch experiments¹¹⁻¹³.

* To whom correspondence should be addressed.

EXPERIMENTAL

Soil column experiments

In order to study the mobility of Flutriafol and Flusilazol, whose structures are presented in Figure 1, we used small columns filled with the equivalent of a height of 5 cm of soil, because the main part of the adsorption and degradation processes take place in the first centimeters of the soil^{14,15}. Therefore we slightly modified the experimental model used by Perrin-Ganier¹⁰ and constructed the columns with PVC tubes, about 7 cm high and 7 cm diameter. A plan of these soil columns is presented in Figure 2. Previous tests, performed with water spiked with different concentrations of the two fungicides, have shown no adsorption of these compounds on PVC; the recovery being the same in the absence or in the presence of PVC. So, we concluded that the problem of adsorption on PVC is negligible for these pesticides.

The soil samples were collected on the top 5 cm, the soil was then air-dried and passed through a 2 mm-sieve, the physicochemical characteristics of the French soils used are given in Table 1.

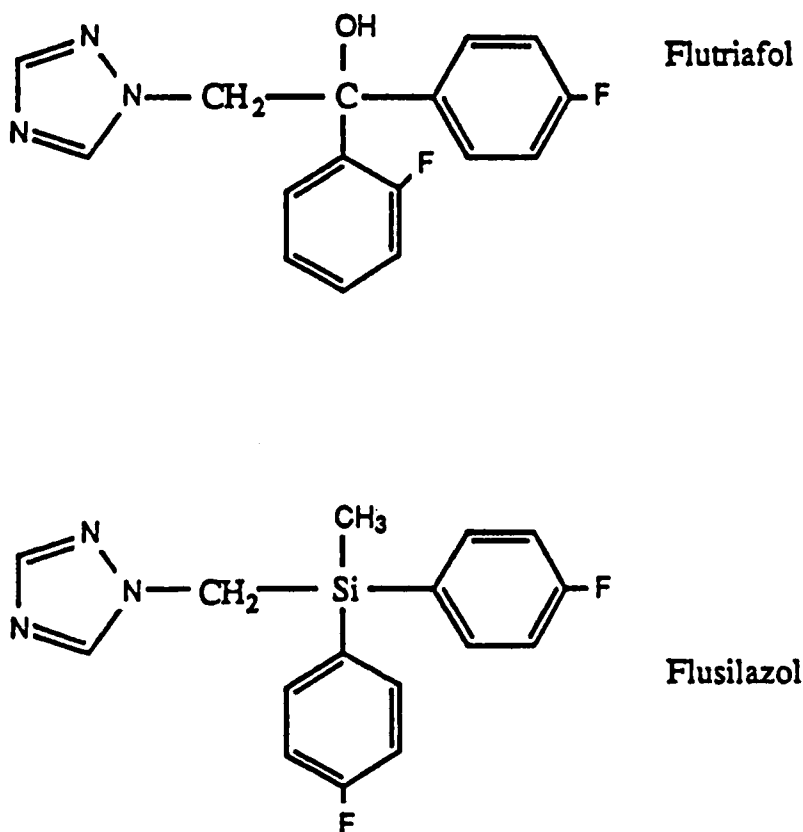


Figure 1 Structures of Flusilazol and Flutriafol.

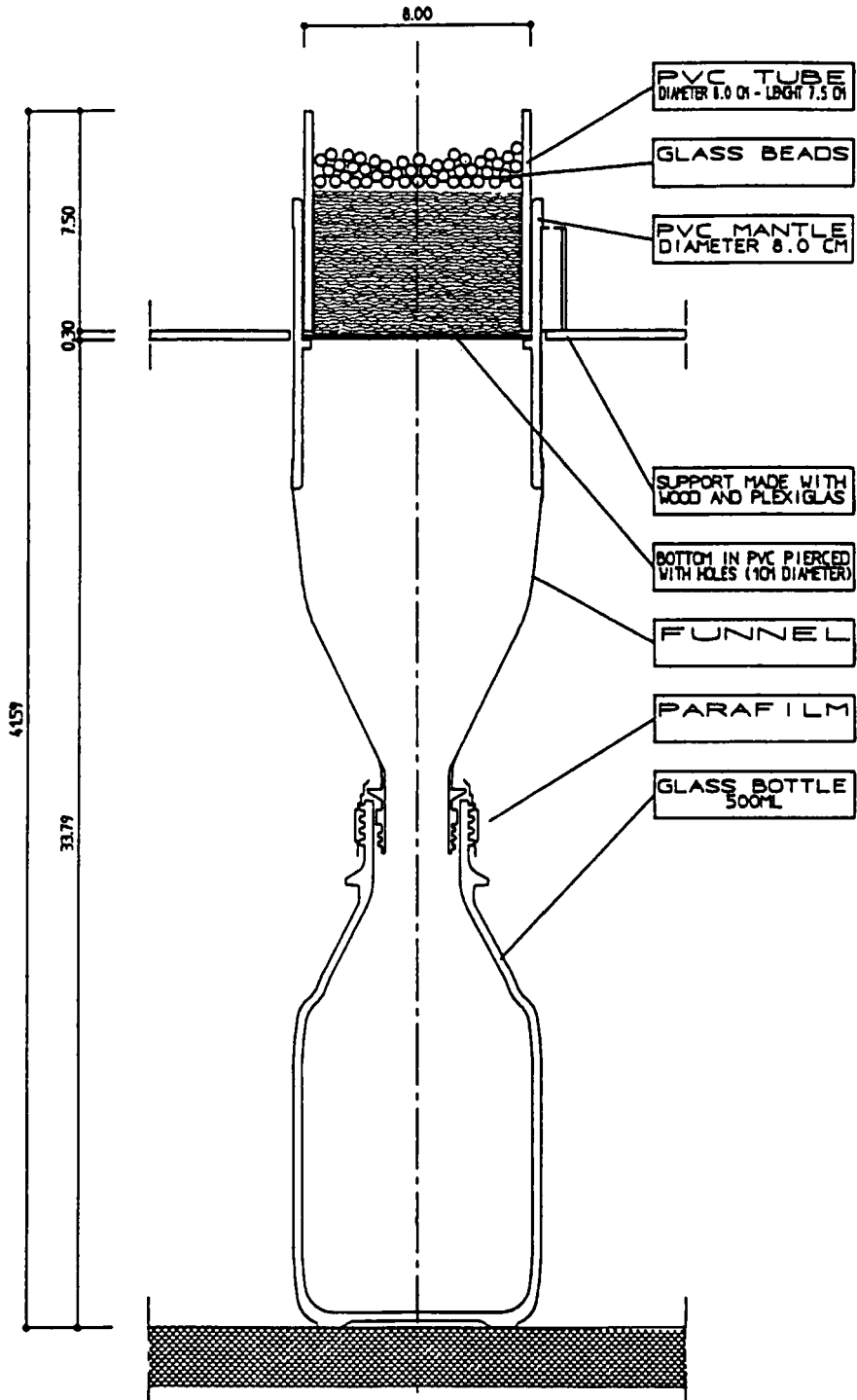


Figure 2 Plan of the experimental model.

Table 1 Physicochemical characteristics of the different soils.

Soil	Parcel	pH	Sand %	Silt %	Clay %	Organic Matter %	C/N
1	Illkirch	8,1	34,8	35,9	27,0	1,82	7,7
2	Haguenau	4,1	82,3	6,0	4,8	1,77	14,7
3	Vosges	5,5	44,1	29,6	11,4	14,0	18,9

Outdoor experiments. These experiments were conducted on the silt soil (soil 1). 5 µg of each fungicide (Flutriafol and Flusilazol, Promochem) were applied in aqueous solution, on the top of twelve columns, filled with 240 grams of soil. As a control, six other columns were prepared without any application of pesticides. The treatment was carried out on the first of November 1994, and the columns were placed outdoors during a period of 1 to 6 months. At regular intervals the percolation waters and the soils were collected and analysed.

The pluviometry, registered automatically during these 6 months, is given in Tables 2 and 3.

Indoor experiments. The same type of experiments were conducted indoor in an accelerated speed, first with the same silt soil, and then with the two other soils. 240 g were used for the soil 2 and 120 g only for the soil 3.

We reproduced the annual pluviometry of the site (640 mm) over 12 days of experimentation, adding every day 200 mL of distilled water, beginning one day after the application of the pesticides. The percolation waters were collected and analysed every two days. At the end of the experiment the soil was analysed as well. Three columns were prepared for each soil, two as replicate assays (5 µg of each pesticide) and the third as a control.

Adsorption studies

These experiments were conducted on the three types of soils. Two grams of each soil were mixed with 10 mL of a fungicide-0,01 M CaCl₂ solution in glass tubes stoppered with screw caps. These experiments were done separately for the two fungicides over a range of concentrations (Flusilazol: 0,2–0,4–1,0–2,0 mg/L and Flutriafol: 0,04–0,1–0,2–0,4 mg/L). The suspensions were shaken on a test tube agitator (Breda Scientific) during 24 hours, and then centrifuged (Centrifuger Prolabo). The supernatants were filtered and 5 mL of the filtrate were extracted twice with 10 mL of dichloromethane. The extract was passed through anhydrous sodium sulphate, concentrated and analysed by gas chromatography.

EXTRACTION PROCEDURES

The extraction procedure of the two fungicides from water was adapted from methods already available in the literature^{16–18}, the other one, from the soil, was developed in our laboratory.

Reagents

Dichloromethane (for pesticides analysis), ethyl acetate (for pesticides analysis) and sodium sulphate (analytical grade) were obtained from SDS. The water was purified

using a MilliQ Water Purification System (Millipore). Sample of triazole fungicide were obtained from Promochem. The standard stock solutions of Flusilazol or Flutriafol (100 mg/l) were prepared in ethyl acetate. The standard working solutions, used for gas chromatography, were obtained from the stock solutions diluted in ethyl acetate (1 mg/L).

Apparatus

Chromatographic separation of the fungicides were achieved with a Gas Chromatograph Varian 3300, equipped with a thermoionic specific detector and a capillary column DB17 (30 m × 0,320 mm × 0,25 μm JW Scientific). An split-splitless injector and helium carrier gas (2 mL/min) were used. The injection system was splitless (1 μL). The temperature program was: 50°C (2 min) to 260°C (25 min), at 20°C/min.

The extraction of the fungicides from water was done with an mechanical agitator Luckham LTD. The extraction of the fungicides from soils was done in a Soxtherm automatic Gerhardt, equipped with a Variostat Gerhardt. The evaporation steps were performed with a TurboVap Zymark (0,8 psi at 30°C).

Methods

Extraction procedure from water samples

The fungicides were extracted three times from water samples (0,2–1 l) with 50, 25 and 25 mL of dichloromethane respectively and filtered through anhydrous sodium sulphate. The extract was evaporated first in the TurboVap to 1 mL, and then to dryness under a stream of air. A purification step is not necessary. The sample was redissolved in 1 mL of ethyl acetate before analysis by gas chromatography.

Extraction procedure from soil samples

40 grams of soil were extracted in a cellulose thimble with 150 mL of dichloromethane during 2 hours in the Soxtherm apparatus. The extract was evaporated first to 1 mL in the TurboVap and then to dryness under a stream of air. A purification step is not necessary. The sample was redissolved in 1 mL of ethyl acetate before analysis by gas chromatography.

RESULTS AND DISCUSSION

Soil column experiments

Outdoor experiments. Tables 2 and 3 show the recovery of Flusilazol and Flutriafol respectively in the percolation waters and the soil analysed during the experimentation. One month after the application of the pesticides, 2 columns were removed. The residues of the two substances still remaining in these soils were determined and the percolation waters of these two columns were analysed. The same manipulations were done every month. The percolation waters of the columns kept until the end of the experimentation (column 1 and 2, see in Tables 2 and 3), were analysed every month, in order to follow

Table 2 Recovery of Flusilazol in the different percolates (P) and soils (S) after 1 to 6 months during the outdoor experiments (%) and corresponding pluviometry.

No column	November 94	December 94	January 95	February 95	March 95	April 95	Total (P)	Soil (S)	Total (P+S)
<i>Percolates</i>									
1	nd						nd	45,6	45,6
2	nd						nd	34,4	34,4
3		nd	EXPERIMENTATION END				nd	40,3	40,3
4		nd					nd	33,9	33,9
5			nd				nd	35,6	35,6
6			nd				nd	40,0	40,0
7		nd		nd			nd	40,8	40,8
8		nd		nd			nd	43,1	43,1
9		nd	nd		nd		nd	38,8	38,8
10		nd		nd			nd	34,1	34,1
11	nd	nd	nd	nd	nd	nd	nd	27,9	27,9
12	nd	nd	nd	nd	nd	nd	nd	24,1	24,1
Pluvio. in mm	9,2	18,1	51,1	43,8	52,7	14,6			

nd: not detected.

Table 3 Recovery of Flutriafol in the different percolates (P) and soils (S) after 1 to 6 months during the outdoor experiments (%) and corresponding pluviometry.

No column	November 94	December 94	January 95	February 95	March 95	April 95	Total (P)	Soil (S)	Total (P+S)
<i>Percolates</i>									
1	nd						nd	39,9	39,9
2	nd						nd	32,2	32,2
3		3,1	EXPERIMENTATION END				3,1	34,9	38,0
4		1,5					1,5	32,7	34,2
5			6,1				6,1	35,2	41,3
6			5,0				5,0	35,0	40,0
7		4,4		7,8			12,2	30,3	42,5
8		3,6		7,6			11,2	28,8	40,0
9		4,8	7,1		6,6		18,5	22,6	41,1
10		3,4		7,0	3,7		14,1	26,3	40,4
11	nd	1,6	4,0	2,5	2,9	2,3	13,3	19,4	32,7
12	nd	2,1	4,7	3,7	4,5	2,7	17,7	20,1	37,8
Pluvio. in mm	9,2	18,1	51,1	43,8	52,7	14,6			

nd: not detected.

the kinetic of the leaching of the fungicides. In addition, during the experiments, when a bottle was full, the content was analysed, and the bottle replaced under the soil column.

The fungicide Flusilazol was never detected in the percolation waters during these 6 months, this indicates that this pesticide seems to be quite immobile in such a soil.

The determination of the Flusilazol in the soil gave an average recovery of $37 \pm 6\%$ of the quantity of Flusilazol applied on the top of the columns, which means that an important part of the fungicide disappeared, probably adsorbed or degraded.

The Flutriafol seems to leach down to 5 cm continuously, but only in small amounts. We didn't find any residues in the first percolation waters, because the pluviometry was very low in November 1994, only 9 mm. The total average recovery of the Flutriafol was about $38 \pm 3\%$, so we can conclude that the Flutriafol disappears as well as the Flusilazol.

On the other hand, we could still observe the presence of these fungicides in the soil after 6 months, these compounds can thus be considered as persistent. Patil¹⁹ could do the same observation for the Flutriafol, he determined a half-life in soil of about 580 days for this fungicide.

Our results confirm also the work of Jamet⁸, who assessed the movement of some triazole fungicides by soil thin-layer chromatography, since he listed the Flusilazol among the immobile substances and the Flutriafol among the slightly to moderately mobile compounds. The differences in mobility could probably be explained by the different solubility of these compounds in water. The most soluble fungicide, Flutriafol (130 mg/L) is more mobile than the Flusilazol (50 mg/L).

Indoor experiments. Tables 4 and 5 show the recovery in the different percolates and the soil of the Flusilazol and the Flutriafol respectively, applied on the 3 different types of soil.

We will first compare the results obtained indoors for the silt soil with the outdoor ones. The indoor experiments confirm that the Flutriafol is more mobile than the Flusilazol in this soil, and that a part of the two pesticides applied dissipated even in 13 days. We observed that the respective quantities of the two pesticides leached during the indoor experiments are slightly higher than those obtained outside, particularly at the beginning. We assumed that it was due to the short delay between the application of the two fungicides and the first addition of water (24 hours), this time being probably not long enough for some reactions (adsorption, degradation or diffusion) to take place.

Considering these results on the silt soil we can conclude that the indoor experiments give a good approximation of the behavior of the fungicides, and of course have the great advantage to be easier to perform and to give more rapidly a description of the fate of the pesticides in soils. Thus, we compared the mobility of these fungicides on two

Table 4 Recovery of Flusilazol in the percolation waters (P) and soils (S) during the indoor experiments (%).

Soil	Type 1		Type 2		Type 3	
	Y	Z	A	B	G	H
Column						
Percolate 1	1,2	4,9	0,6	0,7	5,3	15,6
Percolate 2	1,0	0,8	nd	nd	nd	1,3
Percolate 3	1,3	0,6	nd	nd	nd	0,9
Percolate 4	1,8	0,6	nd	nd	nd	1,2
Percolate 5	1,6	0,6	nd	nd	0,6	0,8
Percolate 6	2,0	0,8	nd	nd	0,6	1,1
Total P	8,9	8,3	0,6	0,7	6,5	20,9
Soil	37,9	37,9	14,9	13,8	13,7	13,2
Total P+S	46,8	46,2	15,5	14,5	20,2	34,1

nd: not detected.

Table 5 Recovery of Flutriafol in the percolation waters (P) and soils (S) during the indoor experiments (%).

Soil	Type 1		Type 2		Type 3	
	Y	Z	A	B	G	H
Column						
Percolate 1	14,3	4,9	6,7	4,8	15,3	40
Percolate 2	13	10,4	2,9	3,2	5	6,2
Percolate 3	10,8	11,6	3,1	2,9	2,2	3,4
Percolate 4	7,5	8,0	3,3	2,9	3,0	3,0
Percolate 5	5,2	6,0	3,0	4,0	2,3	1,5
Percolate 6	3,8	5,3	4,4	4,1	2,3	2,0
Total P	54,6	46,2	23,4	21,9	30,1	56,1
Soil	14,0	15,9	18,3	18,3	10,9	9,0
Total P+S	68,6	62,1	41,7	40,2	41	65,1

other types of soil, using indoor experiments. We observed that whatever the nature of the soil, we found only small amounts of Flusilazol or any residue at all in the percolation waters. There was only the first percolate of the column H (soil 3), in which the quantity of Flusilazol (and Flutriafol as well) was higher, we assumed it was due to the nature of the soil, less dense than the other soils. For this reason, the leaching could become more important at the beginning, the soil not being packed down enough before wetting. So we conclude that Flusilazol is actually an almost immobile pesticide. The behavior of Flusilazol is not the same in the different soils, its dissipation seems to be more important in the soil 2 and 3.

The comparison of the results in the case of Flutriafol confirm that this fungicide is a moderate leacher, and we can also observe that its behavior is not the same in the different soils. Its leaching is more important in soil 1, than in the two others. The quantities of Flutriafol still remaining in the soil after the 13 days are not significantly different, but the dissipation of the Flutriafol seems to be more important in soil 2 and 3. The influence of the nature of the soil on the leachability of these fungicides will be discussed later.

It is well known that the sorption and degradation are key processes controlling pesticide dissipation²⁰ in soil, and thus the potential for contamination of the groundwater. There is little information, in the literature, about degradation products of these fungicides in the ecosystem. Guinivan et Gagnon¹⁸ mentioned a phenyl metabolite of the Flusilazol, but only obtained *in vivo*, after injection of the parent product on a rat. Other authors¹⁹ observed that several compounds containing the triazole groups are very persistent. They showed that the Flutriafol was degraded very slowly in the soil, its half-life is 578 days. In this work, we only investigated the adsorption, involved in the dissipation of pesticides.

Adsorption studies

In order to have an idea of the behavior of Flusilazol and Flutriafol in soil, to compare them and to evaluate the influence of the nature of the soil on the adsorption phenomenon, we tried to apply a simple and rapid method of adsorption study. We plotted the adsorption isotherms for Flusilazol and Flutriafol from the batch equilibrium experiments, presented in Figures 3 and 4 respectively. We choose the most currently used model, described numerically by the Freundlich's equation:

$$Q = K_f C_e^n$$

where Q is the adsorbed amount per unit mass of adsorbent (mg/kg), C_e is the equilibrium concentration (mg/L), and K_f and n are 2 constants for a given herbicide-soil system^{11-13,21}.

The values of these constants are obtained after linearization of the equation and subsequent regression, reported in Tables 6 and 7. The constants r are near 1 and n is in the range accepted by Brouwer *et al.*²¹ (0,7-1,1). These results show that the model of Freundlich can be applied for the adsorption study of Flusilazol and Flutriafol.

The adsorption isotherm of Flusilazol clearly demonstrate that the adsorption of this fungicide decreased in the following sequence of soils:

$$\text{soil 3} > \text{soil 2} > \text{soil 1}$$

These observations are confirmed by the calculated constants K_f .

The adsorption isotherms of Flutriafol demonstrate as well that the adsorption process is more important in the soils of the Vosges, though the sequence is the same. These observations are also supported by the calculated constants K_f . These values confirm that Flusilazol is much more adsorbed than Flutriafol, whatever the nature of the soil.

Organic matter generally is assumed to be the primary factor correlated to the adsorption of pesticides on soil²²⁻²⁴. In our study, soil 3, which contains the most organic matter (14%), actually presents the highest adsorption capacity for the two

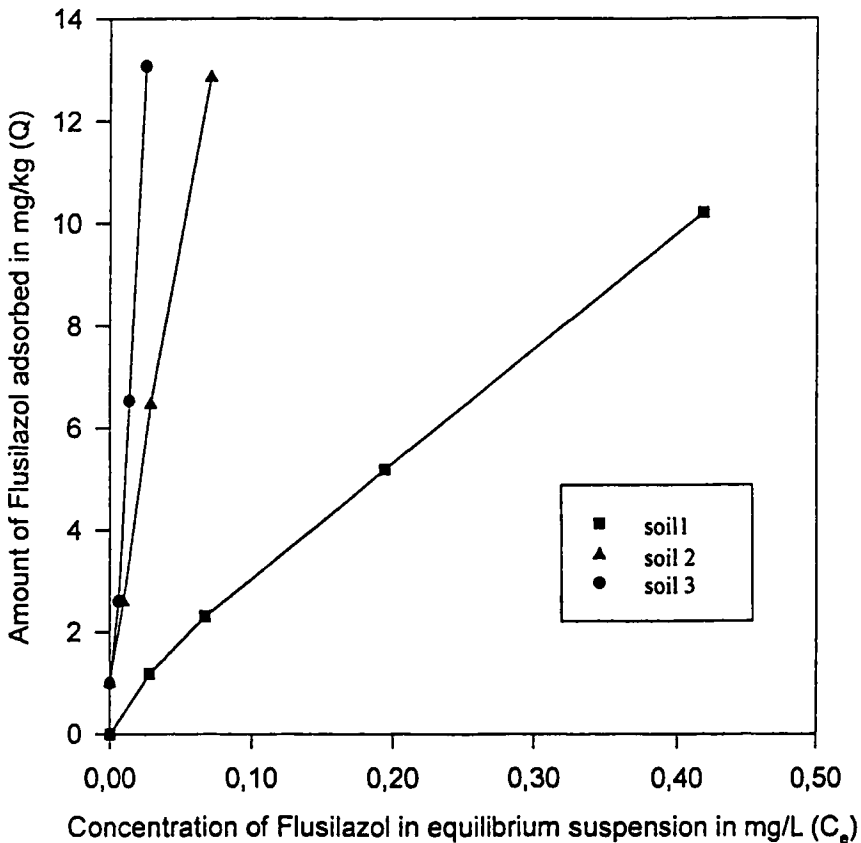


Figure 3 Freundlich isotherms for adsorption of Flusilazol on different soils.

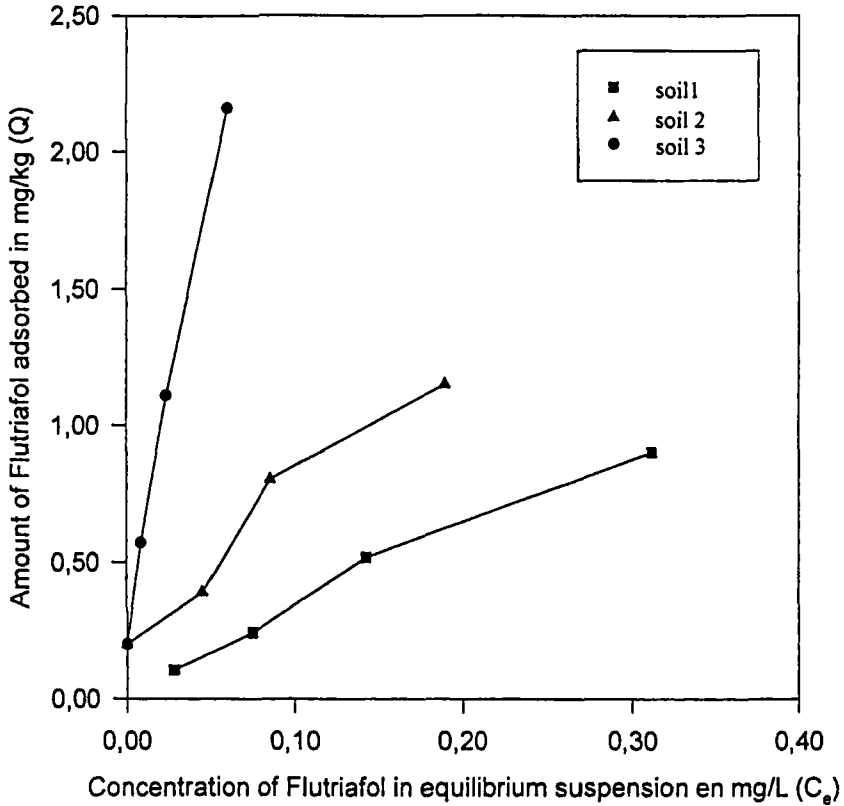


Figure 4 Freundlich isotherms for adsorption of Flutriafol on different soils.

Table 6 Values of the Freundlich constants for the Flusilazol on the different soils.

Soil	K_f	n	r
1	19,9	0,798	0,9996
2	110,1	0,810	0,9997
3	816,2	1,131	0,9999

Table 7 Values of the Freundlich constants for the Flutriafol on the different soils.

Soil	K_f	n	r
1	2,76	0,916	0,9966
2	7,46	0,937	0,9947
3	14,7	0,684	0,9995

fungicides, the most water-soluble pesticide (Flutriafol) being less adsorbed on this soil. The percentage of organic matter is almost the same in the soil 1 and 2, but the adsorption rate is higher in the second one. Often, when the organic matter content is low (< 2%), the significance of other soil properties on pesticide adsorption is revealed²². We assume that the difference in the value of the pH of the soil solution could explain this phenomenon. Bailey and White²⁰ indicated that in case of triazine, adsorption began when the pH approached the pK_a for a particular compound, and increased gradually when the pH decreased. The pK_a of Flusilazol and Flutriafol are: 2,4 and 2,3 respectively, and the pH of the first soil is high (8,1), compared to the second one (4,1). When the pH decreases, the concentration of ionic acidic forms of the pesticides increases, these forms could interact with other ionic sites of the soil or cause ionic exchange reactions. Thus, when the pH decreases, new ionic interactions between soil and fungicides are created, and the two compounds are more strongly adsorbed in the second soil (the more acidic one). We also observe that the nature of the organic matter has an influence on the intensity of adsorption. The fresher the organic matter (ratio C/N high), the more important the adsorption.

CONCLUSION

These studies demonstrated, that Flusilazol is an almost immobile, strongly adsorbed and persistent pesticide, its pollution potential of the soil solution thus seems to be negligible. Concerning the Flutriafol, we observed that this fungicide is adsorbed too, but less than the Flusilazol, it is persistent and moderately mobile. Thus the risk of contamination of the soil solution by this compound could not be excluded.

This work also showed that the adsorption process is different from one soil to another, the organic matter content and its nature, as well as the pH of the soil, seem to be the most important parameters in this case.

Finally, the adsorption studies added to the indoor experiments with mini-columns of soils give interesting informations about the behavior and thus the pollution potential of the soil solution by a pesticide.

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