Factors Influencing the Adsorption of Fipronil on Soils

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A comparative study of the adsorption of fipronil, a phenylpyrazole acridicide, on two Sahelian soils (Saguia and Banizoumbou in Niger) and a Mediterranean soil (Montpellier) has shown that this phenomenon is dependent on the level of organic matter (OM): the adsorption coefficients (K_f) were, respectively, 4.3 (Saguia, 0.1% OM), 7.3 (Banizoumbou, 0.3% OM), and 45.5 (Montpellier, 6.5% OM). The partial destruction of the OM of the Montpellier soil sample by oxidation with hydrogen peroxide confirmed the fundamental role of this component: the values of log K_{OM} were practically constant (2.8−2.9) for OM levels ranging from 6.5 to 1.1%. Following the Giles classification, the adsorption isotherms of the two Sahelian soils seemed to be type S, characteristic of soils with low OM content. For natural Montpellier soil, the shape of the isotherm began close to type S but changed rapidly to type C. The temperature and the methanol cosolvent level were factors influencing the adsorption. For the Banizoumbou soil, increasing the temperature (from 22 to 35 °C) caused an increase in K_f (from 7.3 to 9.3) and modification of the mechanism of the fipronil−soil interaction. K_f decreased exponentially as the methanol fraction of the binary mixture increased. The quantitative study of the adsorption of fipronil on the soil demonstrated the influence of the soil/water ratio: K_f increased proportionately as the soil/water ratio decreased.

Keywords: *Fipronil; adsorption; soil; temperature; cosolvent; soil/water ratio*

INTRODUCTION

Fipronil, (±)-5-amino-1-(2,6-dichloro-α,α,α-trifluoro-*p*-tolyl)-4-[(trifluoromethyl)sulfinyl]pyrazole-3-carbonitrile (Figure 1), is a new phenylpyrazole insecticide discovered in 1987 by the French company Rhône-Poulenc Agro. Applied at low doses, it is active against a wide range of insect pests of crops, notably rice insects, thrips (citrus, cotton, mango, etc.), termites (sugarcane, corn), and click beetles (cereals, corn, sunflower, beets, etc.). It has also been recommended for use in locust control (Balança et al., 1997).

Few studies concerning the behavior of fipronil have been published, except those of Rhône-Poulenc Agro, on different soil types (loam, silt loam, clay loam, sand, etc.) under temperate conditions (United States, Europe). We could find no data on the behavior of fipronil under tropical conditions, in particular in the Sahelian region where locust invasions are a veritable menace to local crops. Therefore, in September 1995, we set up plain field trials in the Niamey region of Niger to study the fate of fipronil in the soil, i.e. the rate of degradation, formation of metabolites, and mobility. This study (Bobé et al., 1997) showed that fipronil did not migrate below the first 10 cm.

The objective of the present study was to complete the plain field trials with adsorption studies carried out in the laboratory. The behavior of a pesticide in the soil and its dissemination in the environment are strictly dependent on its adsorption, which in turn depends on the physical−chemical properties of the pesticide, the climate, and the nature of the soil.

We studied the adsorption of fipronil on two Sahelian soils (at Saguia and Banizoumbou, Niger), which were sandy and characterized by low levels of organic matter. A comparative study was carried out with a Mediterranean soil (from the region of Montpellier, France), which was richer in organic matter, to evaluate the influence of this parameter on the adsorption of fipronil. Given the high temperatures of the Sahelian region, adsorption was also examined at different temperatures (22, 30, and 35 °C). The low solubility of fipronil in water rendered necessary the addition of methanol to the working solutions. Following previous bibliographic references, the influence of the cosolvent was also evaluated. Finally, since the operating conditions of the various studies reported in the literature could be quite different, making comparison of results difficult or even impossible, we decided to study the influence of the soil/water ratio on the adsorption isotherms.

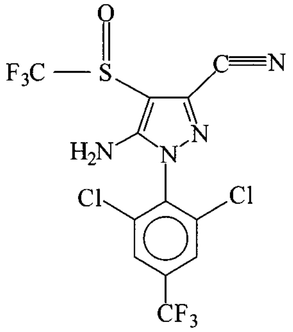

Figure 1. Chemical structure of fipronil.

MATERIALS AND METHODS

Materials. All solvents used were of pesticide residue analysis grade. Deionized water was redistilled. Reversed-phase octadecyl (Sep-Pak Classic, Short Body C_{18}) disposable cartridges for solid phase extraction (SPE) were obtained from Waters, France (ref. WAT051910). Analytical grade fipronil (purity 99.9%) was supplied by Rhône-Poulenc Agro, France. The solubility of fipronil at 20 °C was 1.9 mg L^{-1} in pure distilled water and 2.4 and 2.2 mg L^{-1} in distilled water at

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Table 1. Some Physical and Chemical Properties of the Three Soils

soil	pH (H_2O)	sand (%)	silt (%)	clay (%)	CEC (mequiv/100)	OM (%)
Ban	5.8	79.4	18.2	2.4	0.7	0.3
Sag	5.3	98	1.4	0.6	0.7	0.1
Mtp	8.3	54.4	23	22.6	23.5	6.5

pH 5 and 9, respectively. Two series of working solutions for the sorption studies were prepared at 0.01−1 and 2.5−20 mg L^{-1} in a methanol/water mixture. The methanol/water ratio, which was likely to influence the mechanism of adsorption, was set at between 0.2 and 2% for the lower fipronil concentrations and between 5 and 20% for the higher concentrations. A range of standard solutions (0.01−5 mg L^{-1} in toluene) were prepared for chromatographic analysis.

Three uncontaminated surface soils (0−10 cm depth) were collected under Sahelian or Mediterranean conditions: two from the Republic of Niger—to the south, Saguia (Sag), and the west, Banizoumbou (Ban), of Niamey in September 1995—and one from the region of Montpellier (Mtp) in the south of France. On the basis of U.S. Soil Taxonomy, Ban and Sag surface soils can be classified, respectively, as loamy sand and Entisols (*tropopsamments*), while Mtp soil belongs to the Inceptisols group (*eutrochrept*). Samples were air-dried, passed through a 2 mm sieve, and stored at 4 °C to minimize changes in their microbial populations. Their physical and chemical properties, determined by the Soil Laboratory, CIRAD, Montpellier, are summarized in Table 1. The organic matter (OM) content, pH, cation exchange capacity (CEC), and moisture content of the Sahelian soils were lower than those of the Mtp soil. The organic matter of the Mtp soil was removed by oxidation by heating with 30% hydrogen peroxide: 50 g of air-dried soil was kept in 50 mL of water and 100 mL of 30% hydrogen peroxide for 24 h at room temperature. The suspension was then heated on a hot plate at 100 °C to evaporate the water/hydrogen peroxide mixture. This treatment was repeated twice and the organic matter content determined after each oxidation.

Adsorption Study. Adsorption isotherms were obtained by analysis in duplicate using a batch equilibrium method (Mallawatantri et al., 1991; Pusino et al., 1992; Roy and Krapac, 1994). A known weight of soil sample (generally 2 g) was shaken (on a reciprocating shaker) with 5 mL of aqueous pesticide solution. The equilibrium time, determined in a prior kinetics study, was about 4 h. The temperature was carefully maintained constant (22 ± 1 °C). After centrifugation at 3000*g* for 20 min, the aqueous supernatant was separated and submitted to extraction and GC analysis. A control sample (without soil) was analyzed and did not show any adsorption of fipronil onto the glass of the tube. The amount of pesticide adsorbed was evaluated as the difference between that initially present in the solution and that remaining after equilibration with soil.

Several parameters might influence fipronil adsorption: organic cosolvent level in the solution, temperature, and soil/water ratio (S/W). Adsorption was studied, on the Ban soil, with solutions containing different levels of methanol in water: 0.2 and 2% of methanol for 0.01−1 mg L^{-1} fipronil solutions and 5, 10, and 20% methanol for 2.5−20 mg L^{-1} solutions. Another part of this study concerned evaluation of the possible influence of temperature on adsorption. A series of tests was carried out on the Ban soil at 22, 30, and 35 °C (±1 °C), using a water bath shaker and 2.5−20 mg L^{-1} aqueous solutions of fipronil (5% methanol in water). The effect of the S/W ratio was studied on the three soils by shaking in turn 0.5, 2, 5, 10, and 15 g of soil with 5 mL of pesticide solution (0.01−1 mg L^{-1}, 0.2% methanol in water).

The adsorption isotherms were obtained by plotting the equilibrium content of fipronil absorbed to soil (Qads in mg kg^{-1}) against the equilibrium concentration of fipronil in the liquid phase (Ce in mg L^{-1}). These isotherm data can be described by the Freundlich equation:

$$\mathrm{Qads} = K_f C_e^{\,n}$$

Values of the parameters of adsorption K_f (Freundlich coefficient) and n (Freundlich exponent) were estimated by linear regression after log−log transformation. K_f represents the amount adsorbed at unity equilibrium concentration, which is considered to be a measure of the relative adsorption capacity of soil, and n is the intensity factor of the adsorption (Hermosin and Cornejo, 1991). Due to the importance of OM content on pesticide adsorption (Calvet, 1989), the Freundlich coefficient can be corrected by the relationship

$$K_{\mathrm{OM}} = (K_f \times 100)/\%\ \mathrm{OM}$$

Analytical Procedure. Fipronil was extracted from the aqueous samples using SPE reversed−phase octadecyl (C_{18}) cartridges. The cartridge was first conditioned with 5 mL of methanol, followed by 5 mL of distilled water, before all of the aqueous solution (supernatant) was loaded. Elution of >90% of fipronil was obtained with 5 mL of toluene. If required, in particular for the lowest concentrations, the eluate could be concentrated under a gentle stream of nitrogen to <1 mL. It was then analyzed directly by gas chromatography, with an electron-capture and/or a mass detector, under the following operating conditions: GC Hewlett-Packard HP 5890 connected to a *mass spectrometric detector* HP MSD 5971A; electron impact mode, 70 eV; splitless injection mode (injection purge off = 0.75 min); injector temperature, 250 °C; transfer line temperature, 280 °C; column, SPB-17, 30 m, 0.25 mm i.d., 0.25 μm film thickness; initial oven temperature, 70 °C for 1 min raised at 50 °C min^{-1} to 240 °C, held for 16 min; solvent delay, 3 min; carrier gas, helium 5.5 at a flow rate of 1.2 mL min^{-1}. Analysis of fipronil was performed using the selected ion monitoring (SIM) method, with ions m/z 367 and 351 uma.

GC Hewlett-Packard HP 5890 equipped with a ^{63}Ni *electron-capture detector* (ECD); injector temperature, 280 °C; detector temperature, 300 °C; column, J&W Scientific DB-1701, 15 m, 0.32 mm i.d., 0.25 μm film thickness; initial oven temperature, 70 °C for 1 min raised at 50 °C min^{-1} to 240 °C, held for 16 min; carrier gas, helium 4.5 at a flow rate of 1.8 mL min^{-1} with argon/methane (90:10) as auxiliary gas (50 mL min^{-1}); data treatment software, Hewlett-Packard HP 3365 Series II Chemstation (DOS Series).

It should be noted that no degradation of fipronil was observed during the course of the adsorption experiments.

RESULTS AND DISCUSSION

Adsorption Studies on the Three Soils. In the first part of our study, adsorption isotherms were traced for each soil from data obtained with the two series of fipronil aqueous solutions: 0.01−1 mg L^{-1} (0.2% methanol in water) and 2.5−20 mg L^{-1} (5% methanol in water). Since the dose of fipronil applied in locust control does not exceed 8 g ha^{-1}, solutions of low concentration were studied to reproduce as closely as possible the field situation. However, to reduce errors caused by too-low concentrations (Fusi et al., 1976), the study was repeated using solutions of higher concentration, as are generally employed for this type of work. The addition of methanol was necessary because of the very low solubility of fipronil in water. Other parameters likely to influence the adsorption were set as follows: temperature, 22 ± 1 °C; S/W ratio, 0.4.

Figure 2 shows the adsorption isotherms of fipronil on three soils for the two series of concentrations. The two Sahelian soils (Ban and Sag) are oxidized soils of high mineral fraction and low levels of OM. According to the classification proposed by Giles et al. (1960), the adsorption isotherms for these two soils were type S (or perhaps type C for Saguia soil in Figure 2a). This isotherm type implies a low fipronil−soil affinity at low concentrations, with strong competition from the aqueous phase. Adsorption becomes easier as the concentration in the liquid phase increases (Calvet, 1989). The results appear to be in agreement with others found in

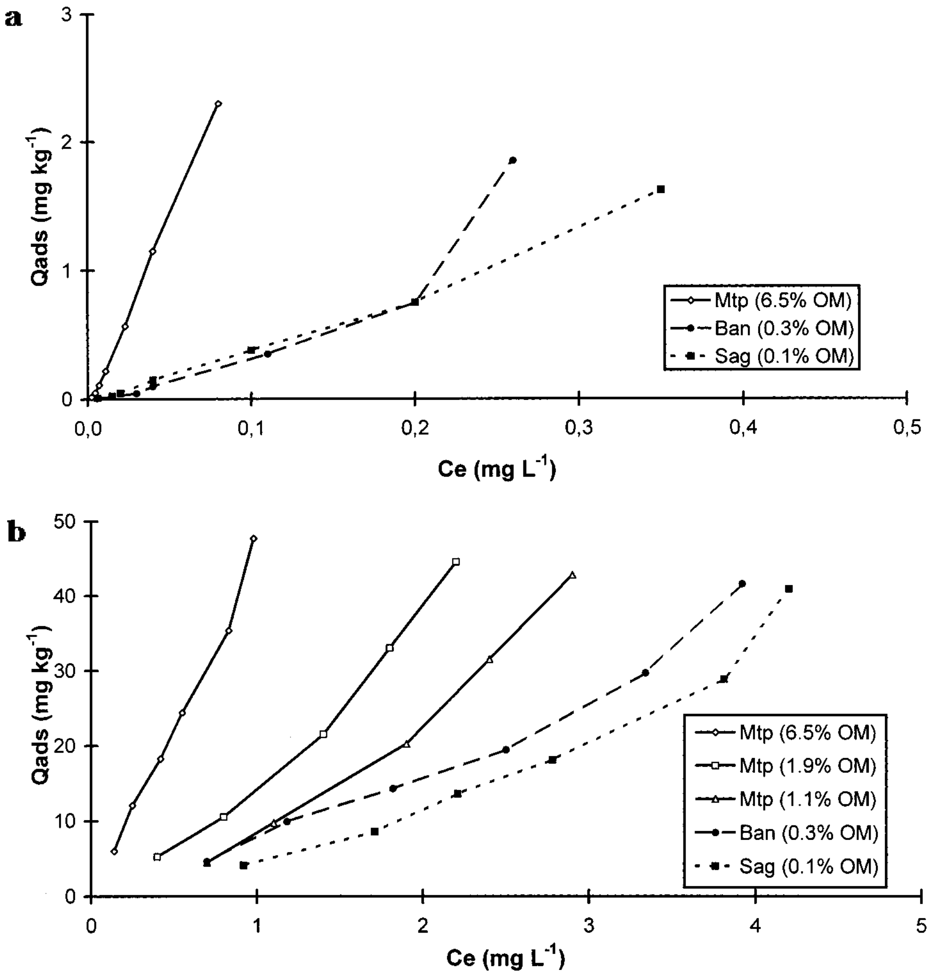

Figure 2. (a) Adsorption isotherms of fipronil by natural soils for the lowest insecticide concentrations (0.01 to 1 mg L^{-1}). (b) Adsorption isotherms of fipronil by natural and oxidized soils for the highest insecticide concentrations (2.5–20 mg L^{-1}).

Table 2. Parameters of the Freundlich Equation and K_{OM} Values for Fipronil in the Soils, at Different OM Contents

soil	OM (%)	K_f (mean ± SD)	n (mean ± SD)	r^2	log K_{OM}
Sag	0.1	4.3 ± 1.1	1.4 ± 0.1	0.987	3.6
Bani	0.3	7.3 ± 1.1	1.1 ± 0.1	0.987	3.4
Mtp	6.5	45.5 ± 1.0	1.0 ± 0.1	0.994	2.8
	1.9[a]	15.3 ± 1.0	1.2 ± 0.1	0.990	2.9
	1.1[b]	8.0 ± 1.0	1.5 ± 0.1	0.997	2.9

[a] After one treatment with hydrogen peroxide. [b] After two treatments with hydrogen peroxide.

the literature for soils with low OM content: Weber et al. (1986) working on fluridone; and Sánchez-Camazano et al. (1990), Sánchez-Martin and Sánchez-Camazano (1991), and Arienzo et al. (1994) studying several organophosphorus pesticides (mevinphos, diazinon, parathion, etc.). On the other hand, for the Mediterranean soil, the isotherm seemed to be type C, which is consistent with the low water solubility of the pesticide and the level of soil OM (6.5%). In fact, the shape of this isotherm could not be clearly defined: the initial curvature corresponded to type S but changed rapidly to type C.

The isotherms obtained fitted the Freundlich adsorption equation with a correlation coefficient of $r^2 \geq 0.98$. Values of K_f and n are presented in Table 2. K_f decreased as follows: Mtp ≫ Ban > Sag, which is also the order of decrease in OM and clay contents. The value of n, representing the degree of linearity between the solute concentration and the amount adsorbed, was >1 for the two Sahelian soils, which translates the concavity and S-type of the isotherm. For the Mtp soil, the value of n was close to 1, in accordance with the C-type.

As previously stated, K_f can often be corrected in terms of the OM content. The value of log K_{OM}, which is frequently used as a measure of the pesticide adsorption capacity of soils (Arienzo et al., 1994), ranged from 2.8 to 3.4 (Table 2). The largest values were found for the Sag and Ban soils, which had low OM contents. The log K_{OM} value for the Mtp soil, with OM content close to 6%, was 2.8. However, these values should be interpreted with care due to the very low OM content of the Sahelian soils. Reddy and Gambrell (1987), for 2,4-D and methyl parathion, and Calvet (1989), for triazine and substituted ureas, reported no correlation between adsorption and OM for OM contents below, respectively, 0.8 and 2%. To evaluate the influence of the OM on the adsorption of fipronil onto soil, we oxidized the Mtp soil (highest OM content) with hydrogen peroxide to obtain two samples of this soil with lower OM contents, respectively 1.9 and 1.1%. The adsorption isotherms of these samples are shown in Figure 2b. Data from Table 2 show that the destruction of OM in the Mtp soil leads to a decrease in the adsorption of fipronil (K_f falls sharply from 45.5 to 8.0) and a change in the isotherm generated for the Sahelian soils from type C to type S. However, the values of log K_{OM} remained practically constant with decreased OM content, thus demonstrating the major role of the organic matter in the adsorption of fipronil on Mtp soil.

Table 3. Freundlich Constant (K_f, n) for the Adsorption of Fipronil, in Banizoumbou Soil, in Methanol/Water Systems

MeOH (%)	K_f (mean ± SD)	n (mean ± SD)	r^2
	Scale of Concentration: 0.01−1 mg L^{-1}		
0.2	9.7 ± 1.3	1.5 ± 0.1	0.989
2	7.1 ± 1.2	1.3 ± 0.1	0.987
	Scale of Concentration: 2.5−20 mg L^{-1}		
5	7.3 ± 1.1	1.1 ± 0.1	0.993
10	5.9 ± 1.1	1.0 ± 0.1	0.991
20	5.1 ± 1.1	0.9 ± 0.1	0.990

Table 4. Parameters of the Freundlich Equation Describing the Adsorption Isotherms of Fipronil, in Banizoumbou Soil, at Different Temperatures

temp (°C)	K_f (mean ± SD)	n (mean ± SD)	r^2
22 ± 1	7.3 ± 1.1	1.1 ± 0.1	0.987
30 ± 1	8.2 ± 1.0	0.9 ± 0.1	0.990
35 ± 1	9.3 ± 1.1	0.7 ± 0.1	0.981

The role of mineral clay content, which might have become more important as a result of greater mineral surface made accessible by the destruction of the OM (Calvet et al., 1980; Sanchez-Martin and Sanchez-Camazano, 1991; Hermosin and Cornejo, 1991), remained relatively minor.

The effect of pH was also considered, notably given the difference in pH between the Sahelian soils (pH 5.5) and the Montpellier soil (pH 8.6), and potential protonation reactions of the molecule (on the pyrazole center or the amine function). Aqueous solutions of fipronil were prepared at pH 4.1 and 9.2 by addition of 0.1 M HCl and 0.1 M NaOH, respectively. The K_f values obtained on these solutions were very close to those obtained on neutral aqueous solutions ($K_f = 6.6$, 6.5, and 7.3 for Ban soil and 41.1, 42.6, and 45.5 for Mtp soil). These results, added to the fact that water solubility was not affected by pH, seem to suggest that fipronil sorption is not pH-dependent.

Effect of Organic Cosolvent on Adsorption. Table 3 summarizes the results obtained with different amounts of methanol in the aqueous fipronil solutions (0.01−1 and 2.5−20 mg L^{-1}). The Freundlich coefficient K_f decreased with increasing cosolvent content according to the equation

$$K_f = (8.2 \pm 0.3) - (0.9 \pm 0.1) \log(\%\ \mathrm{MeOH}) \qquad (r^2 = 0.94)$$

These results agree with those of several authors. Rao et al. (1985) reported that the sorption coefficient of hydrophobic organic chemicals from aqueous organic binary solvent mixtures decreased exponentially as the fraction of organic cosolvent increased. Since increasing the methanol fraction significantly increases the solubility of fipronil, a concomitant decrease in its adsorption seemed likely. However, several complementary hypotheses have been proposed to explain this phenomenon: direct competition between the pesticide and solvent for adsorption sites; pesticide−cosolvent interactions via hydrophobic bonds, as described by Arienzo et al. (1993) for diazinon which, like fipronil, has a pronounced hydrophobic character; and interactions of methanol with soil OM, resulting in shrinking or swelling of the OM and thereby influencing pesticide adsorption.

Effect of Temperature on Adsorption. This study was undertaken to evaluate the possible influence of temperature on adsorption under hot tropical conditions. Results obtained from the literature show that the effect of temperature on adsorption is highly variable. Valverde-Garcia et al. (1988) reported that elevation of the temperature favored adsorption of thiram and dimethoate on organic soils and attributed this to its increasing the number of active sites on humus. A similar interpretation was made by Khan et al. (1996) for lindane. However, Dios-Cancela et al. (1990) observed a decrease in the adsorption of cyanazine on different homoionic peats with increase in temperature. They attributed these results to either a reduction in the attractive forces between the pesticide and the peat or a change in the solubility of the pesticide. Fruhstorfer et al. (1993), in the study of the adsorption of atrazine on kaolin and montmorillon clays, postulated that since increasing the temperature causes an increase in the kinetic energy of the molecules (those already adsorbed and those approaching the matrix), with constant electrostatic attraction this leads to a decrease in adsorption. For the adsorption of fipronil onto Ban soil, increasing the temperature (from 22 to 35 °C) led to a significant increase in K_f (Table 4), which indicates that the fipronil adsorption process is endothermic. At the same time, we observed a change in the appearance of the isotherm (Figure 3), which changed from type S at 22 °C to type C (linear: adsorption proportional to concentration) at 30 °C and to type L at 35 °C. This result seems to indicate a change in the mechanism of bonding between the insecticide and the solid matrix of the soil as the temperature is increased, passing from mainly hydrophobic to mainly polar interactions.

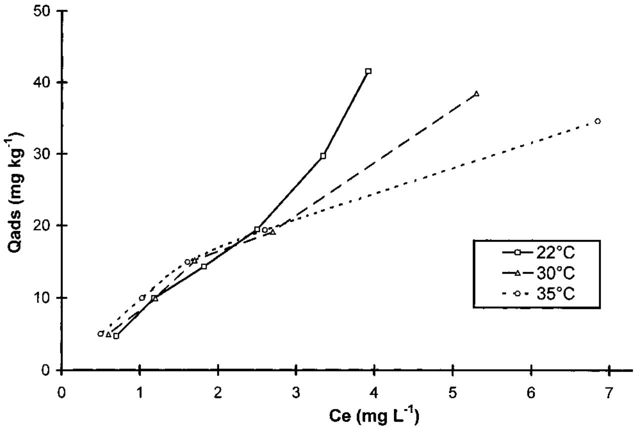

Figure 3. Adsorption isotherms of fipronil in the Bani soil, at different temperatures.

Effect of Ratio Soil/Water on Adsorption. For this type of study, the ratio soil/aqueous pesticide solution employed is usually <0.1. To investigate the influence of this ratio on the adsorption of fipronil, we repeated the adsorption experiment for ratios ranging from 0.1 to 3. Table 5 shows, for the three soils using the lower series of fipronil concentrations (0.01−1 mg L^{-1}), significant differences in K_f and n for different S/W ratios: the observed K_f increased as the S/W ratio was decreased. O'Connor and Connolly (1980) were the first to draw attention to this phenomenon. According to Jamet et al. (1988), adsorption (for isoxaben on a soil from Versailles, France) seems to be overestimated when the S/W ratio is too low. Grover and Hance (1970) and Cox et al. (1993) suggested that increase of K_f could be due mainly to desegregation of soil particles, favored by the high proportion of water, which would increase the adsorption surface.

Table 5. Influence of Ratio Soil/Water (S/W) on the Study of Freundlich Parameters (K_f, n) of Fipronil in the Three Soils

ratio S/W	K_f (mean ± SD)	n (mean ± SD)	r^2
Banizoumbou			
0.1	17.3 ± 1.3	1.3 ± 0.1	0.974
0.4	7.1 ± 1.2	1.3 ± 0.1	0.987
1	4.3 ± 1.5	1.3 ± 0.1	0.957
2	2.2 ± 1.2	1.1 ± 0.1	0.991
3	1.8 ± 1.3	1.0 ± 0.1	0.984
Saguia			
0.1	10.6 ± 1.3	1.4 ± 0.1	0.977
0.4	6.4 ± 1.2	1.3 ± 0.1	0.991
1	4.5 ± 1.5	1.6 ± 0.1	0.964
2	2.8 ± 1.2	1.4 ± 0.1	0.994
3	2.0 ± 1.3	1.2 ± 0.1	0.978
Montpellier			
0.1	197.5 ± 1.3	1.3 ± 0.1	0.989
0.4	57.8 ± 1.4	1.3 ± 0.1	0.983
1	28.7 ± 1.2	1.2 ± 0.1	0.993
2	14.1 ± 1.3	1.1 ± 0.1	0.993
3	6.6 ± 1.1	0.9 ± 0.1	0.998

Conclusion. The low OM content of the Sahelian soils (Saguia and Banizoumbou) makes it difficult to interpret its role in the adsorption of fipronil. However, the importance of this soil component in adsorption is confirmed by the fact that the decrease in the adsorption coefficient (K_f) was in line with the decrease in the OM content of the three soils; on the other hand, the values of log K_{OM} for Montpellier soil at different levels of oxidation were similar. The physical–chemical properties of fipronil, notably its low water solubility, also have a considerable influence on its adsorption. The hydrophobic character of this molecule could in addition explain the decrease in adsorption with increasing proportions of methanol in the binary water/organic solvent mixture. It has also been demonstrated that temperature influences adsorption: the mechanisms of soil–fipronil interaction seem to change when the temperature increases.

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