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Influence of the Formulation on the Sorption and the Mobility of Diuron in Soil

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Sorption of pesticides on soil determines in a large extent the fate of pesticide as well as the mobility (Boesten and van der Linden 1991) than the bioavailability towards micro-organisms (Ogram et al. 1985). The concentration of pesticide in the soil water solution also determines the exposition of organisms and micro-organisms present in soil. The solid liquid exchange in soil greatly affects the toxicity of pesticides in soil. The behaviour in soil of pure active matter has been extensively studied (Hance 1989, Weber et al. 1993). But studies about the influence of formulation on the fate of pesticides are rare. As surfactants are commonly used in the commercial formulations of pesticides, numerous studies have dealt with the influence of surfactants on the solubilization and sorption of poorly soluble contaminants in soil-water system. The effect of non ionic surfactants on the sorption of pesticides on soil has been investigated (Huggenberger et al 1973) together with the effect on the biodegradation of pollutants (Amonette and O'Connor 1980, Laha and Luthy 1992). The interaction of surfactants with organic contaminants in soil has been recently reviewed (Haigh 1996). Surfactants can also enhance the water solubility of pesticides (Nassetta et al. 1991, Jafvert et al. 1994). However surfactants are often used into a context of decontamination of soils (Edwards et al. 1992, Fountain et al. 1991). In such cases a high level of contamination was involved and required high concentrations of surfactant, specially greater than the critical micellar concentration, cmc, to enhance the solubility of pollutants.

More recently, the influence of low levels of non ionic and anionic surfactants on sorption of a fungicide on soil has been described (Beigel et al. 1998). In this paper we studied the role of formulations on the sorption and the mobility of diuron on a clay loam soil. The three experimental formulations used are non commercial they are aqueous concentrated suspensions, they differed by the size of grains, one of them also contains a small amount of oil. We have compared the behaviour of formulated diuron with the behaviour of dissolved active matter.

MATERIALS AND METHODS

A clay loam soil was collected at Dijon (France) The sand, silt and clay fractions were respectively %18, 49 and 33, the amount of organic matter was 1.36%. The

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soil was air dried then sieved through 2 mm, the soil moisture content was 5% (w/w).

The experimental formulations were concentrated flow suspensions furnished by Elf Atochem Agri and named respectively MD1, MD2 and MD3. The size of grains was 5 μm for MD1 and MD2 and 1 μm for MD3. In addition the MD1 formulation contained a small amount of oil. The concentration of diuron was respectively 24.6, 24.8 and 24.4 % w/w in each formulation.
A pure, 99.3%, diuron sample from Cluzeau Info Labo was used as a standard.

The diuron concentration was measured by HPLC analysis with a column TSK ODS-80 TM (250 x 4.6 mm ID). The mobile phase was 40% water 60% acetonitrile at 1 mL/min. UV absorbance was monitored at 243 nm. The injected volume was 20 μL using an automatic injector.

The extraction procedure proceed by shaking 10 g of dried soil with 4 ml of water and 30 ml of methanol during 36 h. Then 3 ml of the supernatant were passed through a 0.2 μm Whatman filter type and injected into the HPLC. The efficiency of this procedure was previously measured on the same soil and approached a yield of 100 % (Gaillardon and Dur 1995).

Three samples of 250 g each of dried soil were contaminated with the three formulations by using a spray tower. The soil was spread out onto a layer of 0.5 cm thick. Then 10 mL of a 5 g/L suspension of diuron were sprayed on soil sample. After a manual homogenisation step three aliquots of 10 g of treated soil were withdrawn to check up the degree of contamination. Then the three soil samples corresponding to each formulation were adjusted to the same concentration of 30 μg/g by addition of an appropriate quantity of non-treated dried soil.

The method to measure the adsorption of pesticides in soil in static conditions was previously described (Gaillardon and Dur 1995). It consisted to place 10 g of dried soil into a 5 cm diameter Petri dishes to give a 3-4 mm thick soil layer. Then 4 ml of water were applied on the soil surface bringing soil moisture to 40%. The diuron concentration in the soil solution was measured by using two superposed 42.5 mm diameter glass microfibre filters laid on the soil surface. After applying a slight pressure to improve the wetting of filters, the upper filter was recovered. The volume of the soil solution was determining by weighing. The concentration of diuron was measured by HPLC after a extraction with 2 mL of methanol. The diuron concentration was determined as a function of time after application of water in three replicates.
The mobility of diuron was studied using soil columns of 35 mm diameter and 9 cm height. Each columns contained 90 g of non treated soil. Then soil is brought to water saturation during 24 h. Then we added successively on the top of the column 10 g of contaminated soil and 10 g of sand to avoid perturbations at the soil surface. Percolation proceed according a semi-continuous regime: 10 mL of water were eluted each 15 min to bring a total volume of 240 mL. In these

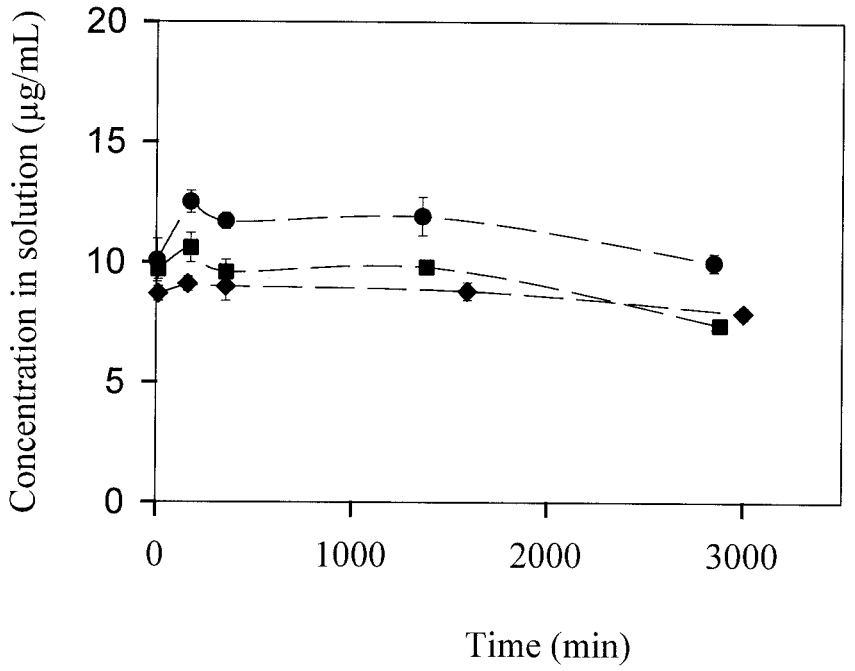

Figure 1. Variation with time of the concentration of diuron in water soil solution for formulation MD1 (•) MD2 (■) and MD3 (♦)

conditions the average flow rate was 0.7 mL/min. 6 fractions were collected during elution each corresponding about one poral volume of the column. The concentration of diuron in each fraction was then measured by HPLC analysis. For each formulation three columns were prepared giving a total of 9 columns.

RESULTS AND DISCUSSION

In a first step we studied the adsorption of diuron on undisturbed soil in static condition. The figure 1 shows the variation with time of the average diuron concentration in water soil solution. The formulation MD1 can be distinguished from two others because it lead to higher diuron concentrations specially at short time but the discrepancy observed at 48 h was still significant. The presence of oil into the formulation seems to slightly decrease the retention of diuron because the values of the partition coefficient K_{oc} were respectively 190 , 260 and 250 mL/g for the formulations MD1, MD2 and MD3. On the contrary the size of grains between 1 and 5 µm (corresponding to the formulations MD2 and MD3) did not affect the adsorption.

When formulated products were applied on the soil, there is a first step of dissolution of grains which lead to an increase of the aqueous concentration of diuron followed by an adsorption step leading to a decrease of the concentration of diuron in water soil solution. In order to evidence the limiting step in soil, we

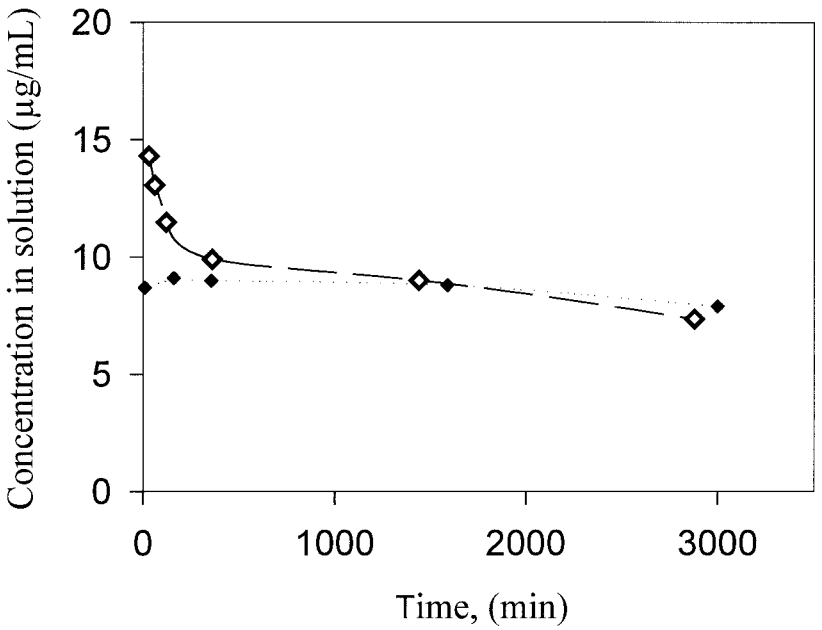

Figure 2. Temporal variation of the concentration of diuron in the soil water solution in the case of MD3 formulation empty symbol corresponded to dilute suspension, full symbols to concentrated suspension.

compared for each formulation, the temporal variation of the concentration of diuron when it was applied at the same dose, 30 µg/g, either as a concentrated suspension 5 g/L or diluted suspension 75 mg/L. The soil moisture was still 40 % in both cases. The concentration of diluted suspension was only twice fold the aqueous solubility of diuron, so the dissolution step was assumed to be very fast. The concentration of diuron measured with dilute suspensions continuously decreased with time due to the adsorption. The curves obtained with concentrated suspensions depended on the formulation. With the MD2 and MD3 formulations the concentration of diuron was almost constant. The two curves corresponding to the dilute and concentrated cases, having a crossing point at 2 hours for the MD2 formulation and 6 h. for the MD3 (see Figure 2). The dissolution was then the limiting step up to this time. The concentration of diuron measured in the case of the concentrated MD1 formulation exhibited a maximum. The crossing point occurred at one hour showing that the adsorption was the limiting step. The presence of oil into the formulation both increased the solubility of diuron but also the kinetic of dissolution. At the end we have shown that for each formulation the dissolution of grains occurred with several hours after application under our experimental conditions.

We have tested the influence of the dose applied on soil on the sorption of pure active matter of diuron measured after a contact time of 48 h.. The concentration of diuron did not vary linearly with the dose applied (Figure3). These non-

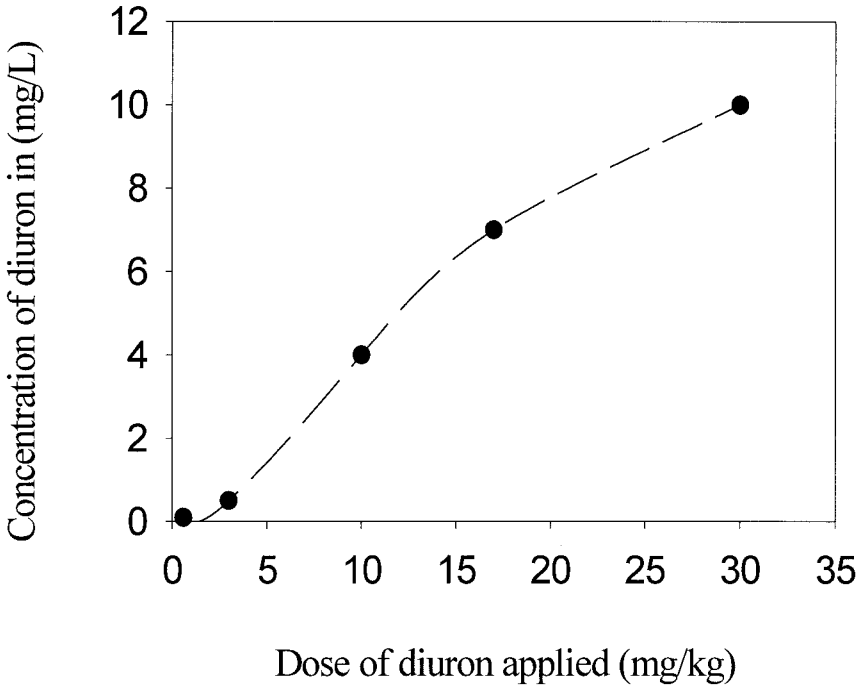

Figure 3. Influence of the dose of diuron applied on soil on the concentration of diuron in the water soil solution measured at 48 h

linearity could be explained by kinetic aspect because long term adsorption of diuron during several weeks has been evidenced (Gaillardon 1996). The dose applied was namely a key parameter and the discrepancies observed between formulations were low when compared to the importance of the dose effect. We now study the influence of formulation on the mobility of diuron. The concentrations of diuron in percolated samples were shown in Figure 4. Concentrations were very closed for each formulation at the beginning of elution up to 2.5 poral volume corresponding to 140 ml of water. Then greater values were measured with the MD1 formulation. The formulation MD1 containing a small amount of oil, slightly increased the mobility of diuron as 17 % ± 2.4 of the applied diuron were recovered compared to 14.2 ± 4.4 for MD2 and 13.5 ±1.3 for MD3. However the effect of oil was very small.

Results have shown a small effect of the oil in the diuron formulation both in static and dynamic conditions. The oil slightly enhanced the solubility of diuron and also the kinetic of dissolution of active matter grains.

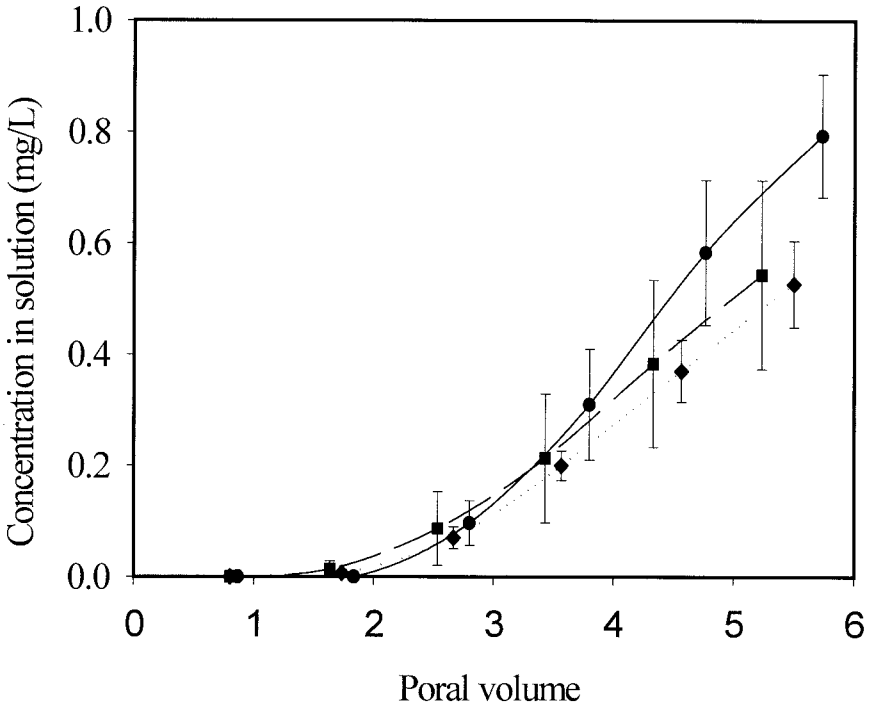

Figure 4 Variation of the concentration of diuron into the percolated water for the three formulations MD1 (•) MD2 (■) and MD3 (♦).

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