SORPTION OF 2, 3- DICHLOROPROPIONANILIDE ON FIVE SOILS FROM THE DELTA OF THE SENEGAL RIVER IN MAURITANIA

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ABSTRACT

The 2,3-dichloropropionanilide is a position isomer of propanil, a weed-killer widely used nowadays in agriculture across the Sahellian countries. We report here the effect of 2,3-dichloropropionanilide on five soil samples collected in the Mauritanian delta of the Senegal River. Methodology: A bit of how soils were sampled and determined using the reactor must be provided to permit repeatability. The results obtained showed that the physical and chemical compositions of the five soils studied were different.

The adsorption in discontinuous reactor revealed a specific effect of 2, 3-dichloropropionanilide with respect to each of the five soils taken individually. The study of the synthetic product adsorption in dynamic reactor confirmed the affinity of the molecule for the organic matter and clay fraction as demonstrated by the effect of the product on a soil from Limoges (France) different from the five Mauritanian soils. The affinity of the 2, 3-dichloropropionanilide is physical for the organic matter and the clay fraction and chemical for the metal compounds such as Aluminium, Iron and Manganese.

Keywords: Adsorption, 2,3-dichloropropionanilide, discontinuous reactor, dynamic reactor, pesticide

INTRODUCTION

When a pesticide is scattered on a soil, it is distributed between the air, water and the soil itself through several mechanisms depending on the physicochemical nature of the molecule, its formulation, the climatic conditions, the pedology and the hydrogeology of the soil. In the soil, the pesticide is subject to various phenomena such as volatilisation, adsorption, solubilization, precipitation, biodegradation, oxidation and reduction. These processes affect the migration, the retention and the transformation of the pesticide.

Volatilisation and atmospheric transport are the major ways of pesticides spreading in the desert countries due to the very high temperatures and the frequent sand winds which remove most of the soil already weakened by a sustained evaporation (Ould Kankou, 2004). Volatilisation depends on the properties of the active substance in the pesticide, its formulation, the environment and the spreading techniques. Adsorption is the fixation of molecules or ions on the insoluble compounds of the soil. It constitutes the main process through which immobilisation of the composites occurs in the soil.

There are two types of adsorption:

- The physical adsorption which is a reversible process disrupted by a weak energy (50 KJ.mol^{-1}). It involves hydrogen or Van der Waals bonds.

- The chemical adsorption which requires a high energy (>80KJmol^{-1}). It involves mainly ionic and coordinations bonds and is irreversible (Piccoli et al., 1992).

In the adsorption process, interaction occurs between the pesticides and the soil components such as the organic matter (dissolved or solid), colloids and clays It has indeed been suggested (Abdoul-Karim and Simonet, 1995) that adsorption takes place both in the organic and mineral fractions of the soil depending on the nature of the pesticide. A non-specific adsorption could also be found.

The mineral composition of the soil includes metal oxides or hydroxides, gravel, sand, silt and clay. Metal oxides and metal hydroxides are responsible for the adsorption of anions on preferential sites of the soil. Iron, aluminium and manganese are the most cited for this type of adsorption (Konstantinu et al., 2000) as demonstrated by the adsorption of the 2, 4-dichlorophenoxy-acetic acid (2,4D) on iron oxides (Fusi, 1997). The clay minerals are silicates of aluminium arranged in layers maintained by electrostatic attractions between the ions. Besides, clay has a very important specific area (e.g.: 800 m^2.g^{-1} for montmorillonites) and therefore is likely to contain water molecules. Interactions between the humic components and clay lead to the formation of clay-humic complexes which adsorb better the organic pollutants (Saada et al., 2003). All these characteristics confer on clay the properties of a being a very good adsorbent for most pesticides.

The organic matter of the soils results from animal and vegetable residues and is located in various compartments of the soil. It plays an important part in the retention of pesticides (Landgraft et al., 1998) and is able to catalyse or inhibit biotic phenomena such as photo-decomposition (Minsour et al., 1999) and hydrolysis (Devitt and Weisner, 1998).

Understanding the mechanism of pesticides transport in the soil is therefore fundamental for the evaluation of the risks of contamination of the underground waters. Besides, most of the compounds contained in the soils are carried by the water through diffusion or convection. These mechanisms are very complex and involve various parameters related mainly to the nature of the soil itself.

The propanil (2, 3-dichloropropionanilide) is widely used in the agriculture of many African countries (Dardari and Mani, 2005). In Mauritania, the use of this pesticide is common especially in the delta of the river Senegal (Ould Kankou, 2004). In this paper, we present evidence on the adsorption of 2,3 DCPA on soils rich in organic matter and clay and the variation in soil content based on the affinity of the respective molecules.

MATERIALS AND METHODS

MATERIALS

Ultra Pure Water (UPW), prepared in the laboratory with a Millipore system, has a pH of 5.5, a resistivity of 18.2 M and a level of total organic carbon lower than10 mg.L^{-1}. Chemicals and soils: The 2,3-dichloropropionanilide (Figure 1) was purchased from Cluzeau Info Laboratory (CIP, Sainte- Foye la Grande, Toulouse, France). Stock solution at approximately 20 mg.L^{-1} was prepared by dissolving 20 mg of 2,3-dichloropropionanilide in 4 mL of HPLC grade methanol. The solution was placed 5 min in an ultrasound bath then diluted with ultra pure water in a graduated flask to 1L and left for 24 h under agitation. The prepared solution was kept in a dark place at 5°C. Use of a co-solvent such as methanol in negligible proportion (0.4%) does not affect the parameters of adsorption.
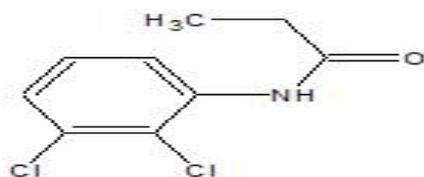

Figure 1: Structure of the 2,3-DCPA molecule

Standard solutions were obtained by dilution of the stock solution using ultra pure water. The five Mauritanian soils studied were all collected in the Trarza region and designated Rk, G, R, P, and T for the following locations : the lake of R' kiz, near the village of Garack, the irrigated perimeters of the town of Rosso, the opening of Aftout Sahéli and the peat near Tiguint respectively (Figure 2). The soils were left to dry at ambient temperature, homogenised and filtered to obtain a granulometry lower than 2 mm. They were then stored in fabric bags designed for this purpose (Ould Kankou, 2004). A sixth soil, known as soil of Douglas (D) from Limoges (France) (Devitt and Weisner, 1998) was added as a control in the study in dynamic reactor in order to confirm the data obtained on the Mauritanian soils in particular with regard to the adsorption of the 2,3-DCPA.
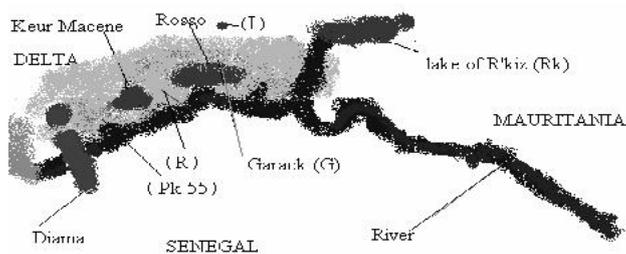

Figure 2: Locations of the Mauritanian soils on the delta
of the Senegal River

The physicochemical characteristics of all the soils used were determined in the "laboratory of the analysis of soils" of the departmental chamber of agriculture of Haute Vienne (France), using standardised methods for soil quality (Table 1).

Table 1: Main characteristics of the five Mauritanian soils and the Douglas French soil

	Soils	P	G	R	RK	T	D
depth	cm	0-50	0-50	0-50	0-50	0-100	0-60
pH	Waters	5.4	6.8	6.3	6.6	5.2	4.2
	KCl	5.1	6.0	5.8	5.5	5.1	3.3
	OM %	2.1	0.2	0.5	3.1	15.8	22.7
	Clay %	55.6	10.1	30.0	57.4	23.6	15.6
	CEC méq/100g	18.4	3.3	10.5	25.4	19.4	24.6
	SAT %	241.2	103.6	181.9	98.0	905.6	4.2
	Na$_2$O ppm (10^3)	7.4	0.47	12.3	0.121	31.3	--
	Cl ppm (10^3)	14.8	1.47	27.3	0.86	126	-

(**P**: Pk55; **R** : N'pourrié; **G** : Garack; **Rk** : R'kiz; **T** : peat and **D** : French (Douglas).
Clays; OM (organic matter); **CEC :**(Cationic Exchange Capacity) and **SAT** :(Saturation).

METHODS

Study in discontinuous reactor

The fixation experiments in batch were carried out at $20 \pm 2°C$ in 125 ml glass bottles. 50mL of a 2, 3 DCPA solution with a known concentration Co were added to 2,5g of soil to form a suspension at 50g.L^{-1}. The bottles were hermetically closed and placed under agitation at 248 rpm. The suspensions were filtered on PTFE (Polytétrafluoroéthylène) hydrophilic membrane (thickness 150 µm, porosity 0.45µm), membrane and analysed by HPLC. The residual concentration Cr thus obtained was used to measure the concentration of 2, 3 DCPA adsorbed on the soil (Cad): Cad = Co - Cr.

Kinetics of Adsorption

Kinetics of adsorption and fixation isotherms for the 2,3-DCPA were performed on the five Mauritanian soils using a soil suspension at 50 g.L^{-1} and a concentration of 2.3 DCPA at 9.498x10^{-3} mmol.L^{-1}. Adsorption was monitored in the time.

Isotherms of fixation

In these assays, a fixed soil concentration ($50g.L^{-1}$) and various 2,3-DCPA concentrations from 9.498×10^{-4} to 3.80×10^{-2} $mmol.L^{-1}$ were used. The agitation time was 3 h, determined according to the kinetics, to be higher than the equilibrium time.
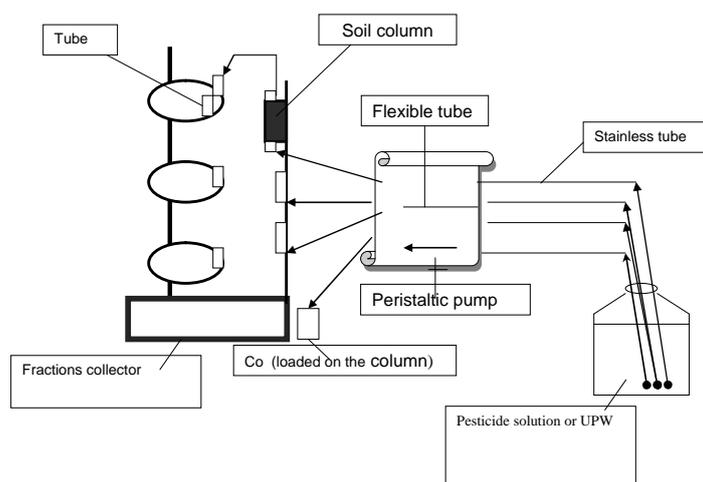
Dynamic study

Figure 3: Diagram of the dynamic reactor system

The study was carried out in a home made dynamic reactor (Figure 3). The column used consisted of a stainless tube (44 mm length; 14mm internal diameter) filled with the dried soil to be analysed. Each end of the column was fitted with a glass wool, a filter of glass fibre, a stainless grid and closed by a stopper connected to the tube carrying the solution. To avoid loss of pesticides by non specific adsorption, all the tubes were in stainless wire except those on the pump which were in tygon**.**

Experiments

During the adsorption phase, the pesticide solution of Co concentration was passed through the column against current using a peristaltic pump until the pesticide concentration, at the outlet of the column became constant and near Co (saturation phase). Desorption was performed by running ultrapure water through the column until obtaining a zero concentration in pesticide at the outlet of column. Both in the adsorption and desorption phases, the pesticide concentration was monitored at the outlet of the column on fractions collected hourly in a glass tube and analysed by HPLC (Ould Kankou, 2004)

Analysis methods

In order to obtain the maximum absorption wavelengths of the 2, 3-DCPA, UV spectra (from 200 nm to 800nm) were performed on different pesticide solutions at various pH using a spectrophotometer (Hewlett Packard, 8452A) with 1cm path length curve coupled to a computer (HP Vectra, 286/12). Although the pH affected the absorption spectrum of the 2, 3-DCPA it did not change the maximum wavelength which remained always at 205 nm. This value was therefore used for the HPLC analysis.

Residual concentrations of the pesticide (Cr) were measured by a Merck system HPLC-DAD (Lachrom Merck Hitachi D7000) using an injection loop of 100 µL, a reverse phase column (Lichrospher 100 RP18, 4x250 mm) and a detector (Lachrom Merck Hitachi L7455). Calibration curves were established with standard solutions using a correlation coefficient of about 0, 99. The eluting phases were prepared with a mixture of ultra pure water and HPLC grade methanol (20:80 respectively). The solutions were filtered and degassed before use. The pump (Lachrom Merck Hitachi 27100) flow rate used was 0.5 mL.min^{-1}. Under these conditions, the retention time of the 2,3-dichloropropionanilide was 11.73 min.

DATA PROCESSING

Discontinuous reactor (Adsorption isotherms)

The direct isotherm is expressed by the equation:

$$\frac{Cad}{m} = f(Cr) \tag{i}$$

Where Cad is the pesticide adsorbed concentration, Cr the residual concentration both in mmol.L^{-1} and m the concentration of the soil suspension in mg.L^{-1}. When the direct isotherm is linear, this results in the equation:

$$\frac{Cad}{m} = K_D.Cr \tag{ii}$$

Where the coefficient K_D represents the distribution of the pesticide between the solid and liquid phases. It is characteristic of the adsorption of a product on a soil considered entirely *as* adsorbent. The Freundlich modelling generally used in the representation of the adsorption equilibrium between a liquid phase and the surface of a solid is often used in the study of the adsorption of pesticides on the soil provided that the molecule concentrations used remains low.

The Freundlich modelling is represented by the relation:

$$\frac{Cad}{m} = K_F . Cr^{1/n} \tag{iii}$$

Which linearization leads to the equation:

$$Log(\frac{Cad}{m}) = Log(K_F) + \frac{1}{n}.Log(Cr) \tag{iv}$$

K_F (Freundlich constant) is the distribution coefficient between the two phases. $1/n$ gives the affinity between the soil and the pesticide ($0 < 1/n \quad 1$). If $1/n$ is equal to 1 then K_F is equal to K_D.

Dynamic reactor

The saturation curve [Co-Ce as function of V) allows, by integration, to obtain the amount of pesticide adsorbed on the soil (mad). The desorption curve, obtained using ultra pure water, results in the same way the amount of pesticide desorbed (md) from the column. Knowing the mass pesticide used or percolated mass (mp), the percentage of pesticide fixed (%fixed) is obtained using the relation:

$$\% fixed = \frac{mad.100}{mp} \tag{v}$$

The adsorption capacity of the soil is equal to:

$$capacity = \frac{mad}{m} \tag{vi}$$

Where m is the initial mass of the soil used weighed with a Sartorious precision balance.

RESULTS AND DISCUSSION
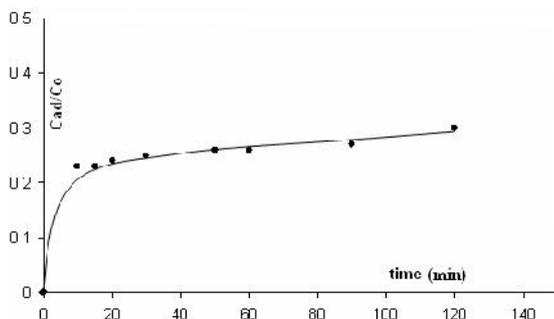
Adsorption in batch

Kinetic study:

Figure 4: Kinetic of adsorption of the 2,3-DCPA on the soil of R' kiz (Rk)

Figure 4 presents the kinetic of adsorption for R' kiz which is the richest of the Mauritania surface soils in organic matter and clay fraction. The curve showed a weak adsorption (30%) of the 2, 3-DCPA on this soil.

Isotherms of adsorption

The direct isotherms of adsorption for the 2, 3-DCPA on the five Mauritanian soils are depicted in Figure 5. Their shapes suggest that they are not linear. The use of Freundlich model enabled the determination of the two constants of Freundlich K_F and $1/n$ and the different correlation coefficients (Table 2).

Table 2: Constants of Freundlich and coefficients of correlation for the 2, 3-DCPA on the Mauritanian soils.

Soils	G	R	Rk	P	T
$K_F \pm 0.01.L\ mg^{-1}$	0.27	0.33	0.42	0.18	0.41
$K_F .10^{+3} \pm 0.01.L.\ mmol^{-1}$	1.24	1.51	1.93	0.83	1.88
$1/n \pm 0.01$	1.26	0.60	0.87	0.84	1.25
R^2	0.99	0.99	0.99	0.96	0.97

When $1/n$ is lower than 1, this means that the isotherm is convex (type L). In this case, the soil has a strong affinity for the pesticide and the number of the adsorption sites of the soil decreases if the concentration of the pesticide is increased. In this study, the values of $1/n$ for the different soils showed that the 2, 3-DCPA is weakly adsorbed on the soils G and T and better adsorbed on the three other soils. The apparent discrepancy in the values of K_F for the soils G

and P could be explained by the negative effect of the NaCl concentration. This has been demonstrated to reduce the adsorption capacity of the soils (Ould Kankou, 2004).The representation of the five direct isotherms on the same scale illustrates the difference of adsorption of the 2, 3-DCPA on these soils (Figure 5).
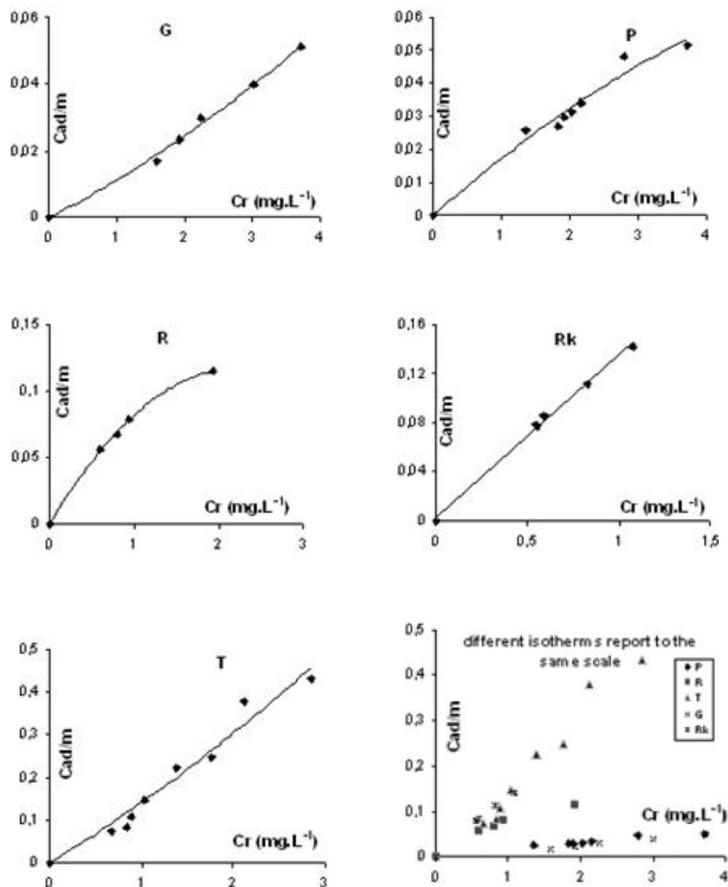

Figure 5: Direct isotherms of the 2,3-DCPA on the five Mauritanian soils

Adsorption in dynamic reactor:

Table 3 highlights the soils' characteristics in the dynamic reactor study.

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Table 3: Soils characteristics in the dynamic reactor study

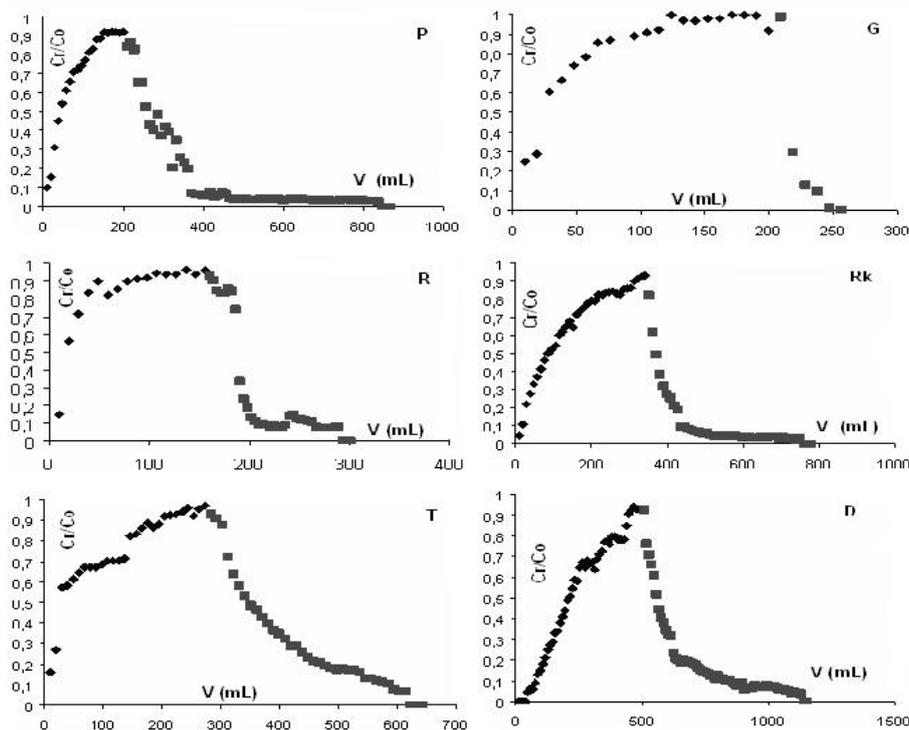|	soils	m	Co	mp	mad	Cap.	% Fixed
1.	**P**	6.08	6.075	1211.96	390.31	64.2	32
2.	**G**	10.60	6.200	1236.90	202.50	19.1	16
3.	**R**	10.30	4.697	732.70	124.90	12.1	17
4.	**Rk**	6.74	6.075	2077.70	714.30	106.0	34
5.	**T**	5.00	5.100	1392.30	345.40	69.1	25
6.	**D**	5.06	4.697	2335.60	1120.96	221.5	48

Figure 6: Adsorption and desorption curves of the 2,3-DCPA in the five Mauritanian soils and the Douglas soil of (D)

The desorption curves are different for the six soils studied in spite of an overall hysteresis similar among the five soils but more marked in the soils; D, P and Rk.

The volumes of UPW used during the desorption phase of the 2,3-DCPA fixed suggesting that the G soil contains components which may establish strong energy bonds with the molecule of the 2,3-DCPA while the bonds among the components of the five other soils and the 2,3-DCPA are of low energy.

Figure 7 shows the adsorption capacity of the different soils studied for the 2,3-DCPA (A), their organic matter content ratio to the different soil characteristics respectively (B) the clay percentage (C) the pH (D) the percentage of saturation (E) and the cation exchange capacity (F).
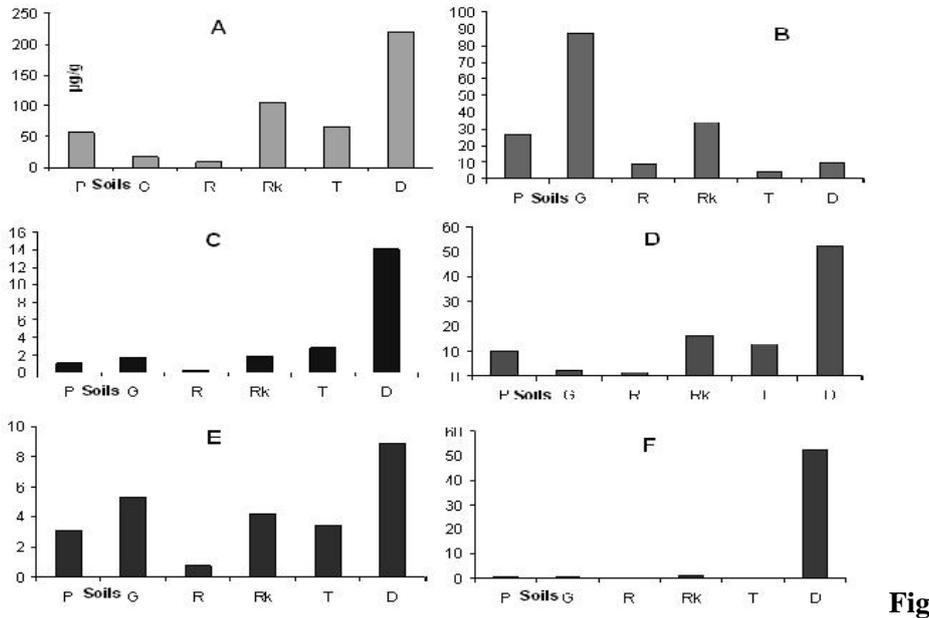

Figure 7: Adsorption capacities of the soils and the ratio of the capacity to the soil characteristics

Histogram A shows that the capacity of adsorption of the 2,3-DCPA on the Limoges soil was higher than those of the five Mauritanian soils. This could be explained by the characteristics of the Mauritanian soils, in particular that they all had lower levels of organic matter than the Limoges soil. Besides, in the Mauritanian surface soils, the absorption capacity increased with the organic matter and clay fraction. However, it was observed that although G had a lower content in organic matter, its adsorption capacity was higher than R. This could be explained by the fact that the amount of NaCl in R was higher than in G. Sodium chloride (NaCl) has indeed been reported to degrade the 2, 3-DCPA (Ould Kankou, 2004).
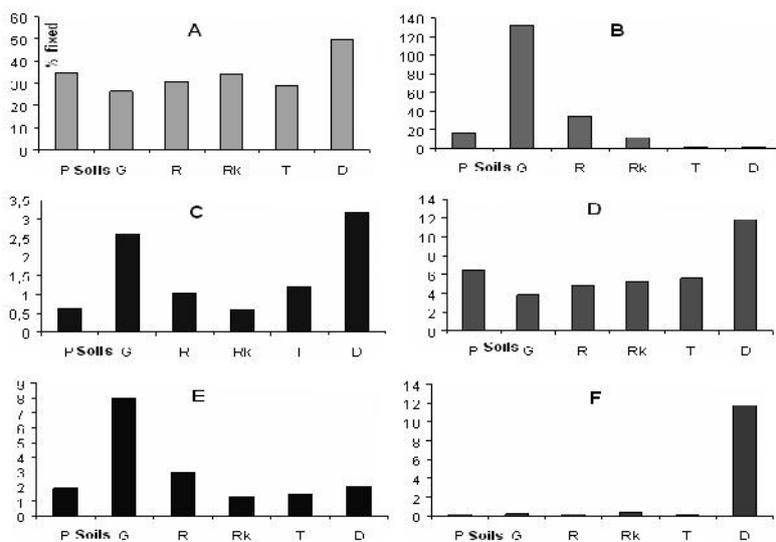
Figure 8: Percentage of pesticide fixed on soils and ratio of the % fixed to the soils

Characteristics: A: % of pesticide fixed on the five Mauritanian soils and the Limoges soil (D);

Histogram C indicates that the adsorption capacity was affected in the clay fraction as clearly demonstrated on the soils G and D. However, adsorption capacity was not affected by the soil pH (Histogram D) or the CCE (Histogram E).

Histogram A shows that the amounts of 2, 3-DCPA retained after desorption was higher in the Limoges soil than in the five Mauritanian soils. As indicated on Histograms B and C, the percentage of the 2, 3-DCPA fixed on the soil was affected by the organic matter content and the level of clay fraction in these soils. However this percentage was not affected by the pH (Histogram D) and the CEC (Histogram E).

Histogram F shows that the percentage of saturation affected the percentage of 2,3-DCPA fixed in the Mauritanian soils. It is important to indicate that the Mauritanian soils have comparatively higher percentage of saturation than the French soil. This may be explained in part, by the harsh climatic conditions to which the Mauritanian soils are exposed namely the high temperature, sand wind and wind transport (Figure 8).

CONCLUSION

In summary, the study in discontinuous reactor showed that the direct isotherms for the different soils studied were not linear and that the affinity of 2, 3-DCPA varied with the nature of the soil. However, adsorption increased with the concentration of the molecule. The adsorption of the 2, 3-DCPA was also a function of the organic matter content and the percentage of clay fraction of the soil. Adsorption was affected by the presence of NaCl in significant amounts (Ould Kankou, 2004) which was confirmed by the results obtained on soils T, R and P.

In dynamic reactor, the capacity of adsorption of the 2, 3-DCPA on the soils was closely related to their respective organic matter content. The clay fraction varied in the same way as the organic matter for the Mauritanian soils. The percentages of pesticide fixed for the five Mauritanian soils were not significantly different from each other but different from the soil.

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