

Sorption of atrazine, terbutryn and 2,4-D herbicides in two Brazilian Oxisols

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(Received February 21, 1991; accepted after revision October 9, 1991)

ABSTRACT

Barriuso, E., Feller, Ch., Calvet, R. and Cerri, C., 1992. Sorption of atrazine, terbutryn and 2,4-D herbicides in two Brazilian Oxisols. *Geoderma*, 53: 155–167.

The adsorption by Oxisols of 3 herbicides: atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine), terbutryn (2-(ter-butylamino)-4-(ethylamino)-6-(methyltio)-s-triazine), and 2,4-D (2,4-dichlorophenoxy acetic acid) was studied in two sites (MPR and MSP sites) with plots under natural vegetations and plots cropped for up to 56 years after clearing. The main mineralogical difference between the soils from the two sites was the higher content of gibbsite and hematite of the MPR than of the MSP site. In both locations, the soil organic matter (SOM) content decreased after clearing and cropping.

The adsorption of atrazine and terbutryn (models of neutral and weakly basic herbicides, respectively) decreased with years of cultivation because of their significant correlation with decreasing SOM content. While the atrazine K_{oc} values were relatively constant (average $K_{oc} = 54 \pm 22 \text{ l}\cdot\text{kg}^{-1}$), the terbutryn K_{oc} varied greatly with different soils (average $K_{oc} = 308 \pm 184 \text{ l}\cdot\text{kg}^{-1}$). The terbutryn adsorption depended on soil pH: it was maximum between pH=4.5 and 5.0, and between 5.0 and 5.5 for soils from the MSP and MPR sites, respectively. The adsorption of 2,4-D (model of acidic herbicides) was always higher in soils from the MPR than from the MSP plots. In soils from the MPR site, 2,4-D adsorption decreased with years of cultivation. An opposite tendency was observed with soils from the MSP site. The adsorption of 2,4-D increased strongly with decreasing soil pH. Soils from the MPR plots were more sensitive to pH modifications than those from the MSP plots. In order to compare adsorption of polar herbicides on soils with different pH, we proposed to calculate the K_d and K_{oc} coefficients for a controlled pH.

INTRODUCTION

The purpose of this paper is to study the relationship between the sorption of herbicides and changes in soil properties due to the clearing and cultivation

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of Oxisols. Large areas of Brazil, under natural vegetation (tropical forest and grassland), are deforested and cleared every year for crop production. As in other intertropical regions, the deforestation followed by intensive cultivation induces chemical and biological degradations of soil properties. Results found by Sanchez et al. (1983) and Cerri et al. (1991) in Peru and Brazil, confirm these tendencies which have often been observed on African Oxisols (Fauck et al., 1969; Siband, 1974; Moreau, 1983).

Soil organic matter (SOM) is the most important factor in the retention of non-polar pesticides (Hamaker and Thompson, 1972; Hassett et al., 1983; Calvet, 1989). However, other soil properties, such as pH, can have a great influence on pesticide adsorption (Weber, 1970; Yamane and Green, 1972; Calvet et al., 1980; Nicholls, 1988). The soil pH regulates the electrostatic charge of soil colloids (organic matter and oxides) and the chemical dissociation or protonation of herbicide molecules. Charges modification of either the adsorbent or the chemical influences adsorption involving electrical interactions (Hingston et al., 1972).

For this study, three herbicides representative of a large spectrum of herbicide chemical properties, mostly related to their polarity, were chosen: atrazine, terbutryn and 2,4-D. For the soil pH range used in this study (pH = 4 to 5.5), atrazine can be considered as a neutral molecule. Terbutryn is a weakly basic molecule which can sometimes exist in cationic form. And, 2,4-D is an anionic molecule. Two Oxisols were chosen on the basis of their natural vegetation (forest and grassland) and on the duration of continuous cultivation after clearing.

MATERIALS AND METHODS

Sites description

Two sites were selected: the "MPR" site, at the Agronomy Station of Ponta Grossa (Parana State) and the "MSP" site, located near Piracicaba City (Sao Paulo State) and previously described by Cerri et al. (1985). Soil samples were taken from 3 plots (T0, T11 and T45) and 5 plots (T0, T12, T18, T50 and T56) from the MPR and MSP sites, respectively. The T0 samples were under natural cover (grassland for MPR site or forest for MSP site) and plots were distinguished by the number of years maintained under cultivation (Table 1). Oxisols (Dark Red Latosol or Typic Haplorthox, according to the Brazilian Soil Classification or "Soil Taxonomy", respectively) were found in all plots with properties described in Tables 1 and 2. X-ray analysis of the clay fraction showed that both MSP and MPR samples contained kaolinite, hematite, goethite and gibbsite. However, gibbsite and hematite contents were higher and kaolinite content lower for the MPR than for the MSP site. The zero points of charge (ZPC) were 4.7 and 4.0 in MSP-T0 (0-6 cm) and MPR-

TABLE 1

Soil properties at the MPR and MSP sites

Plot	Crop (No. of years)	Depth (cm)	C content (%)	pH(H ₂ O)	pH(CaCl ₂) ^a	0-20 μ m (%)	CEC (meq/100g)
MPR-T0	Natural cover (Grassland)	0-10	4.09	5.1	4.3	69	3.4
		10-20	3.55	4.7	4.1	74	2.6
		20-40	2.59	4.8	4.2	75	1.9
MPR-T11	Wheat-soja (11 yr)	0-10	3.48	5.5	5.1	73	8.4
		10-20	3.18	5.1	4.6		5.3
		20-40	2.11	4.7	4.3		2.1
MPR-T45	Wheat-soja (45 yr)	0-10	2.84	4.8	4.5	86	4.8
		10-20	2.84	5.0	4.5		4.4
MSP-T0	Natural cover (forest)	0-6	4.71	5.8	5.5	60	12.6
		6-12	2.31	5.5	5.3	63	6.8
		12-20	1.35	5.0	4.6	68	3.9
MSP-T12	Cane (12 yr)	0-10	1.36	5.3	4.8	68	2.7
MSP-T18	Cane (18 yr)	0-10	1.68	4.7	4.4		
		10-20	1.28	4.9	4.5		
MSP-T50	Cane (50 yr)	0-10	1.34	4.8	4.5	67	2.6
MSP-T56 (56 yr)	Cane 10-20	0-10 1.18	1.40 4.9	4.8 4.3	4.5		

^aAverage pH of soil suspensions during herbicide adsorption.

T0 (0-10 cm), respectively. Cropped fields were fertilized with NPK every year. Soils from the cultivated MPR plots were limed.

Adsorption studies

For each soil adsorption experiment, 10.0 ± 0.5 mg herbicide per liter of a $0.01 \text{ mol} \cdot \text{l}^{-1}$ CaCl₂ solution were used. Atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine), terbutryn (2-(ter-butylamino)-4-(ethylamino)-6-(methyltio)-s-triazine) and 2,4-D (2,4-dichlorophenoxy acetic acid) (Chem Service, Interchim) were used. A 10 ml aliquot of each solution was added to 5 g of soil in a polycarbonate centrifuge tube, and was shaken in an end-over-head agitator for 24 h at $25 \pm 1^\circ\text{C}$. The suspensions were centri-

TABLE 2

Total Fe, and extractable Fe, Al, and Si by the citrate-bicarbonate-dithionite (CBD) and the oxalate methods

Plot	Depth (cm)	Total Fe (mg/g)	Oxalate method (mg/g of soil)			CBD method (mg/g of soil)		
			Fe	Al	Si	Fe	Al	Si
MPR-T0	0-10	125	2.6	3.6	0.1	92	17.0	0.8
MPR-T45	0-10	118	2.0	3.2	0.1	88	16.0	0.8
MSP-T0	0- 6	83	1.9	1.1	0.1	66	6.4	1.2
MSP-T50	0-10	90	1.0	1.6	0.1	74	8.4	0.8

fused for 15 min at 48,000g, and the supernatant filtered through a 0.45 μm filter (HV Millipore). The amount of herbicide in supernatant was determined by HPLC analysis (NovaPak C18, 15 cm \times 3.9 mm column, and Waters appliance with UV detector). The mobile phase was methanol/water for all 3 herbicides: 70/30 (v/v) for atrazine; 80/20 (v/v) for terbutryn; and 70/30 plus 0.01 mol \cdot l $^{-1}$ tetrabutyl-ammonium chloride for 2,4-D. Detection was performed at 222, 224 and 228 nm for atrazine, terbutryn, and 2,4-D, respectively.

Herbicide adsorption at equilibrium was calculated as the difference in herbicide concentration between the initial solution and the solution at equilibrium with soil. The distribution coefficient, K_d , was calculated as follows:

$$K_d = (x/m)/C_e$$

where x is the mass of adsorbed herbicide (μg), m the mass of soil (g), and C_e the herbicide concentration ($\text{mg}\cdot\text{l}^{-1}$) of the supernatant solution at equilibrium. The distribution coefficient (K_{oc}) was related to the soil organic carbon content (%C), by expressing the concentration of the adsorbed herbicide per unit of organic carbon:

$$K_{oc} = (x/m)_C/C_e = K_d \cdot 100/\%C$$

where $(x/m)_C$ is the mass of adsorbed herbicide (μg) per gram of soil organic carbon (Hamaker and Thompson, 1972).

Variations in pesticide adsorption with pH were studied by modifying the soil suspension pH with $\text{Ca}(\text{OH})_2$ and HCl.

RESULTS AND DISCUSSION

Effects of the duration of cultivation and soil organic matter content on herbicide adsorption

Soil adsorption was greater with terbutryn than atrazine for all soils samples and soil depths (Table 3). Soil adsorption of these two herbicides also

TABLE 3

Distribution coefficients (K_d and K_{oc}) of atrazine, terbutryn and 2,4-D adsorption for soils of the MPR and MSP sites

Plot	Depth (cm)	K_d ($l \cdot kg^{-1}$)			K_{oc} ($l \cdot kg^{-1}$)		
		Atrazine	Terbutryn	2,4-D	Atrazine	Terbutryn	2,4-D
MPR-T0	0-10	2.78	18.2	11.5	68	445	281
	10-20	1.74	8.3	15.0	49	235	422
	20-40	1.08	4.6	17.7	42	179	685
MPR-T11	0-10	2.50	16.1	3.8	72	462	110
	10-20	2.04	11.9	6.3	64	376	199
	20-40	0.94	4.2	9.6	45	199	456
MPR-T45	0-10	1.28	6.5	4.9	45	231	173
	10-20	1.14	5.8	5.5	40	206	195
MSP-T0	0-6	2.66	13.9	1.1	57	294	24
	6-12	1.06	8.6	0.7	46	374	32
	12-20	0.60	6.3	1.3	45	468	96
MSP-T12	0-10	0.68	4.6	1.6	50	336	116
MSP-T18	0-10	0.98	4.3	3.0	59	258	181
	10-20	0.68	3.5	2.5	53	278	194
MSP-T50	0-10	0.74	3.5	2.6	55	264	196
MSP-T56	0-10	0.85	5.0	2.8	61	358	202
	10-20	0.66	3.2	3.3	56	267	278

decreased with years of cultivation, and since this was also true for SOM (Fig. 1, Table 3). The adsorption coefficients (K_d) of these two herbicides appeared to be linearly correlated with the soil organic carbon content (Fig. 2). The corresponding linear regressions are:

$$K_d = -0.15 + 59(\%C/100) \quad (r=0.93) \text{ for the atrazine}$$

$$K_d = -0.38 + 314(\%C/100) \quad (r=0.80) \text{ for the terbutryn}$$

Extrapolation of the regression line to zero organic carbon content gives small K_d values thus underlining the preponderant role of organic matter in herbicide sorption. The variation of K_d with SOM was larger for terbutryn than for atrazine. The high linear correlation coefficient (0.93) between atrazine sorption and SOM content confirmed that atrazine retention in soil was mostly due to organic matter (Weber et al., 1969; Hayes, 1970). The lower correlation coefficient for terbutryn sorption (0.80) indicated that, besides

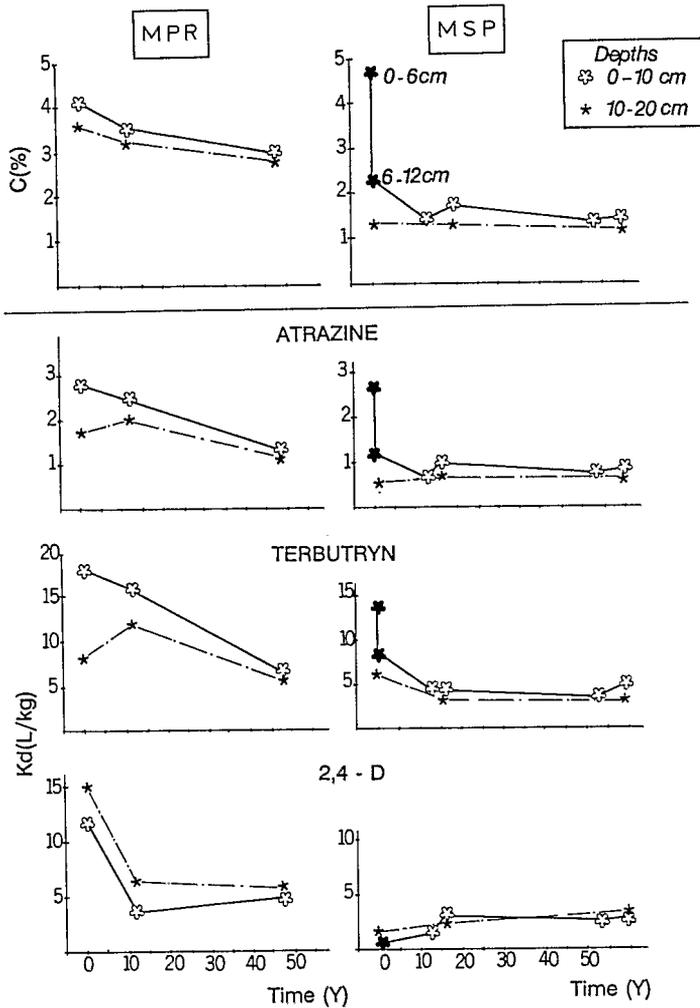


Fig. 1. Influence of years of cropping on soil organic carbon, and the adsorption coefficient (K_d) of atrazine, terbutryn and 2,4-D. Data obtained for soils under natural cover were plotted at time origin (Time=0).

the SOM content, other factors were involved in terbutryn sorption. During cultivation, modifications of the organic matter composition did occur as the SOM content decreased. For the MSP site, the most labile organic compounds under forest were replaced by organic matter of sugarcane origin. Cerri et al. (1985) have estimated, using $\delta^{13}C$ measurements, that, after 50 years of cultivation, 45% of soil organic carbon came from organic residues of the initial forest and 55% from the sugarcane residues in the MSP plots.

Linear correlations between soil organic carbon content and adsorption

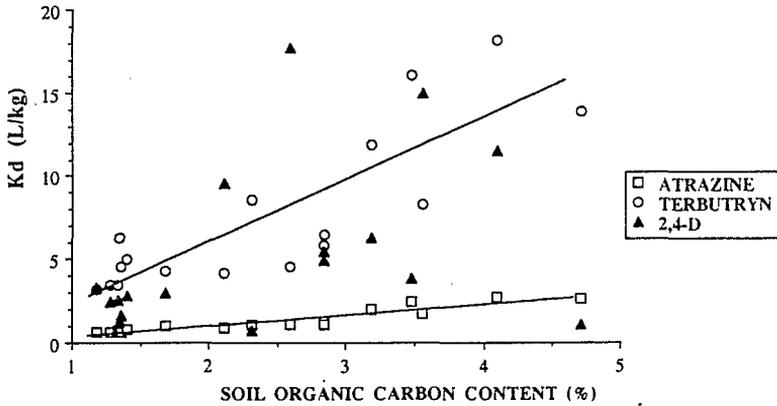


Fig. 2. Relationships between the adsorption coefficient of the herbicides and the soil organic content. The lines correspond to the linear correlations for atrazine and terbutryn.

coefficients (K_d) have often been reported for many non-ionized compounds (Hassett et al., 1983; Calvet, 1989). This positive correlation has justified the use of adsorption coefficients related to the organic carbon content, or K_{oc} parameters, which are more stable than the corresponding K_d (Hamaker and Thompson, 1972). The slope of the linear correlations gives the average values of the corresponding K_{oc} for all soil samples. Thus the average K_{oc} value from Table 3 was 54 ± 22 for atrazine and 308 ± 184 for terbutryn.

Variations in K_{oc} values are probably due to different affinities of SOM for the pesticide during pesticide adsorption (Hamaker and Thompson, 1972), other soil factors being assumed to be constant. While the atrazine K_{oc} values were relatively constant (Table 3), the terbutryn K_{oc} values varied greatly with the different soils, especially in the MPR plots, without any observed relationship between the terbutryn K_{oc} values and years of cultivation. This is an indication of modifications in the nature of organic compounds involved in the terbutryn adsorption, or variations of other physico-chemical soil characteristics.

The greatest adsorption of 2,4-D was found in soils from the MPR-T0 soil (Table 3, Fig. 1). In soils from the MPR site, 2,4-D retention decreased with years of cultivation. On the other hand, an opposite tendency was observed with soils from the MSP site: the K_d was 3 times greater with soils from the oldest cultivated field (MSP-T56) than from the original forest soil (MSP-T0). In any case, 2,4-D adsorption was always higher in soils from the MPR than the MSP plots. We did not find any relation between the K_d value for 2,4-D and the soil organic carbon content (Fig. 2).

The 2,4-D molecule was anionic under the soil conditions found in this study. Its adsorption involved ionic interactions with positive charges in soil and also the less energetic van der Waals forces and charge transfer (Steven-

son, 1982). In these soils, positive charges are generated by the iron and aluminum oxides. Their fundamental role in the anion adsorption is well-known (Hingston et al., 1972). Particularly, the specific 2,4-D adsorption on iron oxides was well studied by Watson et al. (1973). Iron and aluminum oxides concentration are greater in soils from the MPR than from MSP plots (Table 2). This difference could partially explain the higher adsorption of 2,4-D for soils from the MPR site.

The SOM can adsorb some 2,4-D through weak interactions, but more often its overall negative charge causes charge repulsion (Stevenson, 1982) and neutralizes the positive charges of the metal oxides. This could explain an increase of 2,4-D adsorption in soils from the MSP plots resulting from organic matter losses with cultivation and, on the other hand, an adsorption increase with depth associated to organic matter decrease. The highest 2,4-D adsorption observed in soils from the MPR-T0 plot, in spite of its high organic matter content, is probably related to its high oxide content, and its high acidity.

Effect of soil pH on herbicide adsorption

Cultivation modified the soil pH: At the MSP site, the acidity increased after cultivation (Table 1); and the pH at the MPR site increased during the first 11 years of cultivation because of liming, but afterwards the pH decreased again.

Figure 3 shows the variation of atrazine, terbutryn and 2,4-D K_d adsorption with pH for all the samples. The K_d of atrazine appeared to be independent of the soil pH, while the K_d of 2,4-D increased strongly when pH decreased.

The K_d value of terbutryn varied greatly but was not correlated with pH.

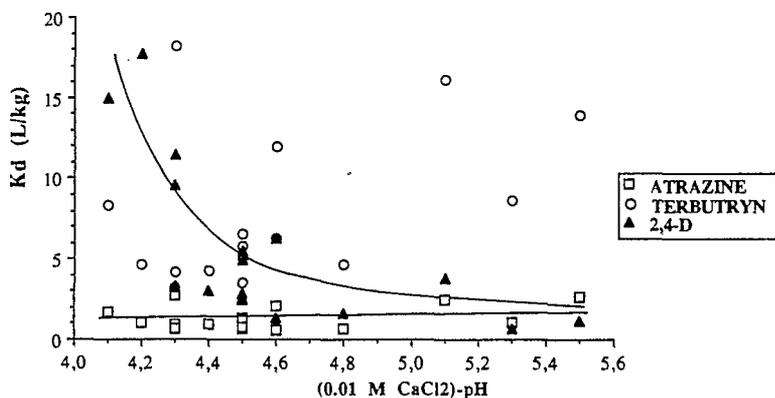


Fig. 3. Variations of atrazine, terbutryn and 2,4-D K_d values with the natural soil pH (0.01M CaCl_2) in all MPR and MSP samples. The lines show the atrazine and 2,4-D variations.

For a better understanding of the pH effect in the case of terbutryn and 2,4-D, adsorption studies were performed in the laboratory with artificially stabilized pH conditions on MSP and MPR soil samples. Results are presented for terbutryn and 2,4-D in Fig. 4. The terbutryn K_d was maximum between pH=4.5 and 5.5, depending on the sample. The behavior of soils from MSP-T0 was different as compared to those from MPR-T0, in spite of their similar organic matter contents. The greatest adsorption was observed between pH=4.5 and 5.0, and between 5.0 and 5.5 for soils from the MSP-T0 and MPR-T0, respectively. Such adsorption-pH variations have often been found for the terbutryn and generally for weak bases (Weber, 1970; Calvet et al., 1980; Tercé, 1985); however, this phenomenon has not yet been explained completely. Two phenomena seemed to interfere: the protonation of terbutryn molecules, and the soil charge modification. Decrease of terbutryn adsorption with pH below pH=5 could be explained by its protonation

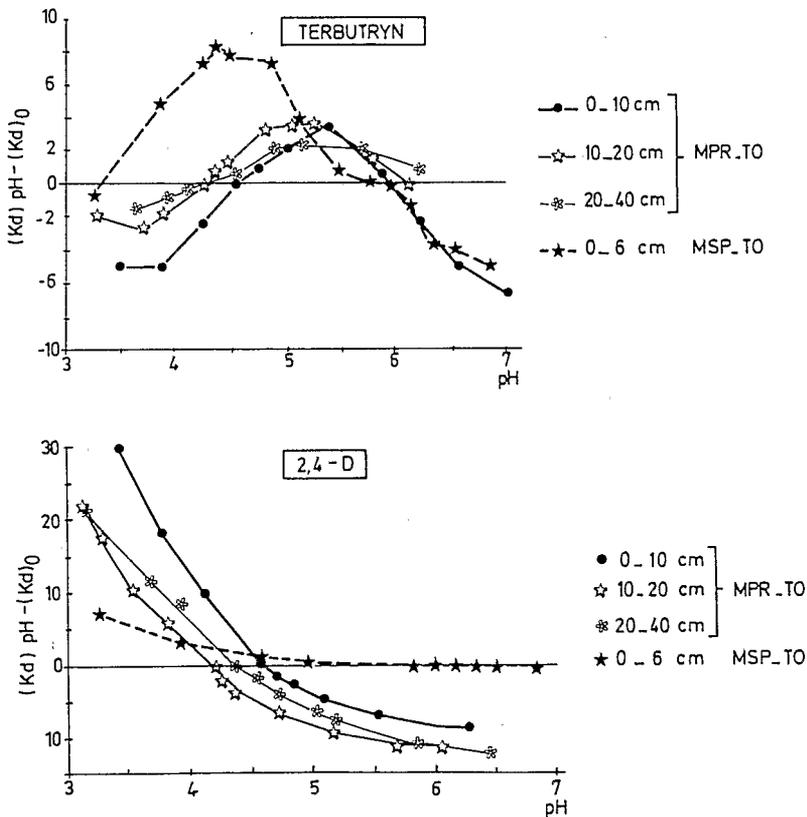


Fig. 4. Influence of laboratory modified soil pH on K_d of (a) terbutryn and (b) 2,4-D. Results are expressed as the difference between the K_d values at the modified pH, $(K_d)_{pH}$, and the natural soil pH, $(K_d)_0$.

($pK_a=4.3$) as the soil colloids become positively charged ($ZPC=4.0-4.7$). Generally, it has been assumed that the greatest adsorption occurs at pH around the molecule pK_a (Weber, 1970; Hingston et al., 1972). Such result was found for soils from the MSP-T0, but not for the MPR-T0 samples. Moreover, there was no relation between the maximum adsorption pH and the ZPC values.

The 2,4-D K_d value decreased when the pH increased for all the samples (Fig. 3). A similar behavior was found in the laboratory studies (Fig. 4). Adsorption has been shown to vary similarly with pH for 2,4-D and other anionic chemicals in presence of Oxisols or iron and aluminum oxides (Hingston et al., 1972; Watson et al., 1973; Nicholls, 1988; Charlet and Sposito, 1989). Samples from the MPR plots were more sensitive to laboratory pH modifications than those from the MSP plots, probably because of the difference in oxide composition of these two soils (Table 2).

Variation of 2,4-D K_d values with pH could be explained by the decrease of negative charge of the organic matter and the increase of positive charge on iron and aluminum oxides, as the pH decreased. As for the weakly basic chemicals, anion adsorption greatly increased when the pH decreased until a pH around the molecule's pK_a (Hingston et al., 1972): the pK_a of 2,4-D is 2.6.

To sum up, for a given soil sample, both SOM content and pH were necessary to explain K_d variations of polar herbicides. SOM effect had to be studied at a standardized pH. Thus, the K_d and K_{oc} values of terbutryn and 2,4-D estimated at the same pH ($pH=5$) are reported in Table 4. The variations shown in Fig. 4 were used to make these estimations.

The K_d values of 2,4-D at $pH=5$ for MSP samples were not modified by cultivation (between 0.7 and 1.9), but for the MPR samples, K_d values at $pH=5$ decreased with cultivation and were often higher than those observed on the MSP site. However, after 45 years of cultivation the K_d of 2,4-D in soils from MPR and MSP samples became similar. No significant correlation appeared between the K_d values at $pH=5$ and the SOM content for either the MSP or MPR samples. So, 2,4-D adsorption seemed to be essentially pH and mineral type-dependent but independent of the SOM content.

The K_d values of terbutryn at $pH=5$ were close to those found with the natural soil pH (Table 3) but the correlation between K_d values at $pH=5$ and organic carbon content was improved ($r=0.95$ instead of 0.80 for soils at the natural soil pH). Therefore, terbutryn adsorption is pH and SOM-dependent.

SUMMARY AND CONCLUSION

The three herbicides used, atrazine, terbutryn and 2,4-D, can be considered as models of neutral, weakly basic and acid chemicals respectively. It is possible to forecast the adsorption decrease of atrazine and terbutryn with years

TABLE 4

K_d and K_{oc} at pH=5 of terbutryn and 2,4-D adsorption for all MPR and MSP soil samples (the K_d variation with pH shown in Fig. 4 was used to estimate K_d at pH=5)

Plot	Depth (cm)	$(K_d) - pH5 (l \cdot kg^{-1})$		$(K_{oc}) - pH5 (l \cdot kg^{-1})$	
		Terbutryn	2,4-D	Terbutryn	2,4-D
MPR-T0	0-10	20.2	7.5	494	183
	10-20	11.8	6.5	332	183
	20-40	6.6	11.7	255	452
MPR-T11	0-10	16.1	4.8	463	138
	10-20	12.9	3.3	406	104
	20-40	7.2	4.1	341	194
MPR-T45	0-10	8.5	1.1	299	39
	10-20	7.8	0.7	275	25
MSP-T0	0-6	18.9	1.7	401	36
	6-12	10.8	1.0	468	43
	12-20	4.3	0.7	319	52
MSP-T12	0-10	3.1	1.4	228	103
MSP-T18	0-10	1.8	1.8	107	107
	10-20	1.0	1.5	78	117
MSP-T50	0-10	1.5	1.6	112	119
MSP-T56	0-10	2.5	1.8	179	129
	10-20	1.2	1.9	102	161

of cultivation because of their significant correlation with the decreasing organic matter level. Consequently, any kinetic models describing organic matter variations with years of cultivation (see Jenkinson et al., 1987) will allow the evolution of K_d values to be estimated. However, for terbutryn (model of weakly basic herbicides), these estimations can be improved if the pH effect on adsorption is also considered. Decreasing soil pH generally increases herbicide adsorption. Variations to this rule are related to the chemical nature of the pesticide (Weber, 1970; Hamaker and Thompson, 1972; Calvet et al., 1980; Stevenson, 1982). Adsorption modifications with pH are moderate for the neutral molecules, but they are very important for the charged molecules, especially for the anionic ones. For terbutryn, adsorption goes through a maximum for pH values around the pK_a of the molecule, but this maximum also depends on other soil characteristics. This is a general rule for the weakly basic and acidic molecules (Hingston et al., 1972). The best way to compare

the adsorption of polar chemicals on soils of different pH is to calculate the K_d after adjustment of the pH to a controlled value.

In this way, we found that years of cultivation, in relation with the decrease of SOM, is the most important factor controlling the adsorption of neutral herbicides (as atrazine) on Oxisols. In contrast, the adsorption of anionic chemicals (as 2,4-D) depends on soil mineralogy and physico-chemical factors, particularly the soil pH. Soil pH is related to cultivation practices and can be easily modified by soil management. When cultivated, the upper soil layers are acidified in absence of liming. This acidification can provoke an adsorption increase of anionic herbicides as 2,4-D. The adsorption of weakly basic chemicals, as terbutryn, mainly depends on SOM content. They are more sensitive than neutral chemicals to the organic matter nature and to soil pH conditions, thus their adsorption on soils is influenced by years of cultivation and management practices.

ACKNOWLEDGEMENTS

We would like to thank J. Rouiller and E. Jeanroy of Centre de Pédologie Biologique, CNRS, Vandoeuvre for metal and X-ray analysis, and Dr. J. Molina of Soil Science Department, University of Minnesota for improvements of the manuscript.

REFERENCES

- Calvet, R., Tercé, M. and Arvieu, J.C., 1980. Adsorption des pesticides par les sols et leurs constituants. II. Les facteurs de l'adsorption. *Ann. Agron.*, 31: 125-162.
- Calvet, R., 1989. Adsorption of organic chemicals in soils. *Environ. Health Persp.*, 83: 145-177.
- Cerri, C., Balesdent, J., Feller, C., Victoria, R. and Plenecassagne, A., 1985. Application du traçage isotopique naturel en ^{13}C à l'étude de la dynamique de la matière organique dans les sols. *C. R. Acad. Sci. Paris Ser. II*, 9: 423-426.
- Cerri, C., Feller, C. and Chauvel, A., 1991. Avaliação das principais propriedades de um latossolo vermelho escuro após desmatamento e cultivo por 12 e 50 anos com cana-de-açúcar. *Cah. ORSTOM Ser. Pedol.*, 26: 37-51.
- Charlet, L. and Sposito, G., 1989. Bivalent ion adsorption by an Oxisol. *Soil Sci. Soc. Am. J.*, 53: 691-695.
- Fauck, R., Moureaux, C. and Thomann, Ch., 1969. Bilan de l'évolution des sols de Séfa (Casamance, Sénégal) après 15 années de cultures continues. *Agron. Trop.*, 24: 263-301.
- Hamaker, J.W. and Thompson, J.M., 1972. Adsorption. In: C.A.J. Goring and J.W. Hamaker (Editors), *Organic Chemicals in the Soil Environment*, 1. Marcel Dekker, New York, pp. 49-143.
- Hassett, J.J., Banwart, W.L. and Griffin, R.A., 1983. Correlation of compound properties with sorption characteristics of non-polar compounds by soils and sediments: concepts and limitations. In: C.W. Francis and S.I. Auerbach (Editors), *Environment and Solid Wastes*. Butterworths, Boston, pp. 161-178.

- Hayes, M.H.B., 1970. Adsorption of triazine herbicides on soil organic matter, including a short review on soil organic matter chemistry. *Residues Rev.*, 32: 131-174.
- Hingston, F.J., Posner, A.M. and Quirk, J.P., 1972. Anion adsorption by goethite and gibbsite I. The role of the proton in determining adsorption envelopes. *J. Soil Sci.*, 23: 177-192.
- Jenkinson, D.S., Hart, P.B.S., Rayner, J.H. and Parry, L.C., 1987. Modeling the turnover of organic matter in long-term experiments at Rothamsted. *INTECOL Bull.*, 15: 1-8.
- Moreau, R., 1983. Evolution des sols sous différents modes de mise en culture en Côte d'Ivoire forestière et préforestière. *Cah. ORSTOM Ser. Pedol.*, 20: 311-325.
- Nicholls, P.H., 1988. Factors influencing entry of pesticides into soil water. *Pestic. Sci.*, 22: 123-137.
- Sanchez, P.A., Villachica, J.H. and Bandy, D.E., 1983. Soil fertility diagnosis after clearing a tropical rainforest in Peru. *Soil Sci. Soc. Am. J.*, 47: 1171-1178.
- Siband, P., 1974. Evolution des caractères et de la fertilité d'un sol rouge de Casamance. *Agron. Trop.*, 29: 1228-1248.
- Stevenson, F.J., 1982. Organic matter reactions involving pesticides in soil. In: F.J. Stevenson (Editor), *Humus Chemistry*. Wiley, New York, pp. 403-419.
- Tercé, M., 1985. Etude des propriétés d'adsorption de constituants minéraux modèles de ceux existant dans les sols vis-à-vis de molécules organiques à caractère herbicide. Doctor Thesis, Univ. Paris.
- Watson, J.R., Posner, A.M. and Quirk, H.M., 1973. Adsorption of the herbicide 2,4-D on goethite. *J. Soil Sci.*, 24: 503-511.
- Weber, J.B., 1970. Adsorption of s-triazines by montmorillonite as a function of pH and molecular structure. *Soil Sci. Soc. Am. Proc.*, 34: 401-404.
- Weber, J.B., Weed, S.B. and Ward, T.M., 1969. Adsorption of s-triazines by soil organic matter. *Weed Sci.*, 17: 417-421.
- Yamane, V.K. and Green, R.E., 1972. Adsorption of ametryne and atrazine on an Oxisol, montmorillonite, and charcoal in relation to pH and solubility effects. *Soil Sci. Soc. Am. Proc.*, 36: 58-63.