Tricyclazol retention by soils

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Adsorption of tricyclazol on 18 different soils from the marshes surrounding the Doñana National Park was studied. Adsorption isotherms were of S-type in all cases. Regression analysis of Freundlich K_f values and several soil properties showed poor correlation when all 18 soils were taken into account. When 13 soils were considered, correlation improved greatly. Clay content, CEC, illite and montmorillonite contents were chosen as significant independent variables. Although organic matter content has been reported to be a major factor in pesticide adsorption, it did not show a good correlation with the different K_f values calculated for tricyclazol.

Key words: adsorption; tricyclazol; pesticide; clay materials; soil

INTRODUCTION

The soil is the ultimate sink for many of the pesticides used, and at the same time it can act as a source from which pesticide residues can move into living organisms, ground and surface waters and the atmosphere (Gerstl and Mägelgrin, 1984). Pesticides can reach the soil either by direct applications or indirectly, for example, from spray fallout, runoff or inflowing water, rain and dust and from crop and mineral remains incorporated into the soil (Edwards, 1974). Two major processes affecting pesticides in soils are degradation and adsorption. The relative persistence of a pesticide in soils under given environmental conditions is often determined by its chemical structure and by soil properties (Meikle, 1972; Mercado and Kahanowitz, 1977). Adsorption of a pesticide, on the other hand, can vary greatly between soils as adsorption is frequently related to the soil organic matter and clay content (Bailey and White, 1964; Kerpen and Schlessner, 1980; Moreale and Van Bladel, 1980a).

The processes affecting pesticide behaviour in soil are some of the items more repeatedly studied in the current literature, because of the increase in concern of environmental quality. Actually, there is a high number of models that attempt to describe the behaviour of pesticide in soils (Walker, 1978;

Boesten et al., 1989) but all these models invariably include an adsorption coefficient as one of the most important parameters. Repeatedly books and reviews (Khan, 1988; Calderbank, 1989; Rao, 1990) on pesticide behaviour pointed out the adsorption of these xenobiotics on soil surfaces as a fundamental process determining the ultimate fate of these compounds in the environment.

It is of great interest to relate the adsorption parameter of a pesticide with the soil variables in order to be able to predict these values for other soils. Numerous papers have shown that soil variables related to pesticide adsorption depended on the nature of the pesticide considered (Sanchez Martín and Sanchez Camazano, 1989; Hermosín and Cornejo, 1989, 1990) and the soil variables allowed for (Hermosín et al., 1987; Hermosín and Cornejo, 1989). Although organic matter has been shown to be the soil variable most related to pesticide adsorption (Karickhoff, 1979) however, in many other cases the important role of other soil variables has been pointed out, such as clay components (Weber et al., 1986; Hermosín and Cornejo, 1990) and pH (Moreale and Van Bladel, 1980b).

Tricyclazol is a relatively new fungicide used in rice which is cultivated intensively in the marshy soil surrounding the Doñana National Park (SW Spain). Albaiges et al. (1987) have shown the impact of agricultural and urban-industrial organic pollutants in water and sediment of the Doñana National Park. Thus it is of great interest to study the soil factors related to tricyclazol adsorption by soils corresponding to this important zone of Europe. The objective of this work was to establish the soil variables that determine the tricyclazol adsorption by soils.

MATERIALS AND METHODS

The soils used in this study were selected on the basis of previous work done in our Institute. These studies allowed us to select sampling points representing the diverse soil present in the intensive cultivation zone surrounding Doñana National Park as shown in Fig. 1. These samples were air-dried and ground to 2 mm. Physical and chemical properties were determined in the Soil Analysis Laboratories of our Institute. Free iron content and clay mineral composition of these soils were determined according to the methods of Holmgren (1967), Olsen and Ellis (1982) and X-ray diffraction on oriented specimen on glass slide, respectively.

Tricyclazol (Fig. 2), pure active compound, was kindly supplied by Elli Lilly and Co. Although the solubility in water of this compound found in the *Handbook of Pesticides* (1980) and the Elli Lilly characteristics brochure was high, we found the solubility to be much lower and thus we needed to prepare a methanol solution of tricyclazol, and from the latter we prepared

Fig. 1. The studied area with indication of sampling sites.

Fig. 2. Tricyclazol.

the aqueous (2% in methanol) solution to perform the soil adsorption isotherms.

The soil adsorption isotherms were carried out by weighing duplicate samples of 2 g of the soils in 50-ml polypropylene centrifuge tubes with screw caps and adding 20 ml of tricyclazol aqueous solution (0.1, 0.2, 0.4, 0.6, 0.8, 1 and 1.2 mM) in 2% (v/v) methanol, 0.01 M CaCl₂. The tubes were shaken for 24 h; previously this time had been checked to be sufficient to reach the adsorption equilibrium. The tubes were then centrifuged at 15 000 rev./min and the supernatant analysed by UV spectroscopy at 268 nm. The differences between the initial and final concentrations were assumed to be adsorbed.

The adsorption isotherms were obtained by plotting the amount of tricyclazol adsorbed, C_s ($\mu\text{mol/g}$), versus the equilibrium concentration, C_e (mmol/10 ml) (Bowman, 1981, 1982; Hermosín and Cornejo, 1987).

RESULTS

The soil properties more directly involved in pesticide adsorption are shown in Table 1.

The adsorption isotherms shown in Fig. 3 are of S type, where the initial part of the curves is convex implying (Giles et al., 1960) that as more solute is adsorbed, additional amounts can become fixed. The isotherm curves in Fig. 3 correspond to different S subtypes: S₁, S₂, S₃ and d is of S type initially but after that it transforms to C type. Figure 3 summarizes the different type of curves and the soils showing the same type of curve.

The adsorption data were fitted to the Freundlich equation:

$$C_s = K_f C_e^n$$

where C_s is the amount adsorbed ($\mu\text{mol/g}$) and C_e is the solute concentration at equilibrium ($\mu\text{mol/10 ml}$). The units of C_e were chosen in order to

TABLE 1

Properties of the soils

Soil profile	Depth cm	% Clay	% OM	CEC	% Silt	pH	% Fe ₂ O ₃	% Illite	% Mont.	% Kaol.
1 P-10	0-20	68.0	2.17	24.1	31.7	7.5	1.07	37.4	11.5	17.0
2 P-10	120-160	63.9	1.38	18.4	33.6	7.5	1.00	35.1	11.5	10.9
3 P-3	0-20	57.8	1.59	19.6	35.1	7.6	1.11	32.4	14.4	11.0
4 P-3	50-80	33.1	0.67	18.8	47.6	7.6	0.94	16.5	5.0	11.2
5 P-1	5-20	45.4	2.31	19.2	42.6	7.7	1.17	30.0	8.2	7.3
6 P-1	70-90	2.4	1.84	10.1	48.2	7.9	0.57	7.1	3.2	2.1
7 P-1	90-110	12.8	0.33	7.6	22.6	8.0	0.51	7.3	3.2	2.2
8 P-2	5-20	20.1	1.48	9.0	11.1	7.9	1.04	12.3	3.4	4.4
9 P-2	30-	38.7	0.60	19.6	9.5	7.5	2.37	15.5	15.5	5.7
10 P-9	50-100	27.3	0.29	5.7	6.2	5.3	1.75	21.6	0.0	5.7
11 P-9	0-30	9.0	1.75	4.2	8.1	6.2	1.63	1.9	0.0	7.1
12 P-9	115-250	15.4	0.24	3.6	7.7	5.1	1.07	3.1	0.0	12.3
13 P-4	0-30	14.4	0.83	8.5	26.5	8.1	1.00	8.6	2.2	3.6
14 P-5	0-30	48.4	1.79	21.5	23.3	7.7	1.60	14.0	24.2	9.7
15 P-7	0-25	51.5	3.31	28.5	36.3	7.6	0.71	18.5	17.5	15.4
16 P-8	0-25	23.6	2.48	11.9	22.4	7.8	0.58	18.9	1.2	3.5
17 P-11	0-20	22.3	0.98	11.9	17.4	7.0	0.87	11.2	7.8	3.3
18 P-11	40-70	15.5	0.40	11.1	13.8	6.8	1.06	7.8	5.4	2.3

Fig. 3. Adsorption isotherm types found for soils studied: S₁ (1, 2, 4, 5, 9, 14, 15, 17, 18); S₂ (3, 6, 10, 11, 12, 13); S₃ (7, 8); S → C (16).

have $C_e = 1$ within the range of experimental concentrations (Hermosín and Cornejo, 1987). At this concentration, $C_e = 1 \mu\text{mol}/10 \text{ ml}$, the amount adsorbed is K_f , which is a constant of the solute/sorbent systems and is used as a measure of the relative adsorption capacity of soils, and n is a measure of the adsorption intensity (Moreale and Van Bladel, 1980). The values of K_f and n for all soils studied, besides the correlation coefficient found for the application of the linearized (logarithmic) form of Eqn 1, are summarized in Table 2. The K_f values for tricyclazol varied from $16.52 \mu\text{mol/g}$ to $0.24 \mu\text{mol/g}$ and n varied from 1.18 to 3.12.

The K_f values are difficult to compare with literature data because its measurement units are confusing (Bowman, 1982; Hermosín and Cornejo, 1987). However, these tricyclazol values can be considered as indicating medium retention (Hermosín and Cornejo, 1989, 1990) as compared with other polar molecules.

The adsorption coefficients K_f for these 18 soils were plotted against the soil properties. Some of them are shown in Fig. 4. The correlation coefficients obtained by linear regression analysis are shown in Table 3. This Table shows two correlation coefficients (r_1 and r_2): r_1 values were obtained considering all soils studied and r_2 considering only 13 soils (omitting soils No.

TABLE 2

K_f and n , values from Freundlich equation isotherms for adsorption of tricyclazol by soils and their correlation coefficients (r)

Soil profile	Depth (cm)	K_f ($\mu\text{mol g}^{-1}$)	n	r
1 P-10	0-20	5.00	2.39	0.99
2 P-10	120-160	12.35	2.13	0.98
3 P-3	0-20	9.32	2.13	0.98
4 P-3	50-80	5.58	1.93	0.99
5 P-1	5-20	2.36	2.28	0.99
6 P-1	70-90	1.17	2.37	0.99
7 P-1	90-110	1.02	1.69	0.98
8 P-2	5-20	0.67	2.17	0.97
9 P-2	30-	4.60	1.83	0.98
10 P-9	50-100	1.16	1.18	0.98
11 P-9	0-30	0.24	1.23	0.96
12 P-9	115-250	2.18	1.36	0.97
13 P-4	0-30	0.59	1.40	0.97
14 P-5	0-30	1.82	2.17	0.99
15 P-7	0-25	1.18	2.27	0.99
16 P-8	0-25	1.30	1.31	0.99
17 P-11	0-20	3.84	3.12	0.99
18 P-11	40-70	16.52	2.65	0.94

1, 5, 14, 15 and 18). When all soils were considered K_f -values correlated poorly with all soil variables. However when these 13 soils were considered K_f appeared better correlated with important soil variables such as clay content, CEC, illite and montmorillonite content. These variables have been studied by other authors (Sanchez Camazano and Sanchez Martn, 1988; Weber et al., 1989; Hermosn et al., 1987; Hermosn and Cornejo, 1987, 1989) since these mineral components of the colloidal fraction have the most important part of the soil surfaces associated to them (Bailey and White, 1973; Calderbank, 1989).

DISCUSSION

The shape of the isotherm curves of tricyclazol on the soils studied were of S or C type as shown in Fig. 3. According to Giles et al. (1960) the S curves appeared when the solute molecule is monofunctional, has moderate intermolecular attraction and meets strong competition for the substrate sites from the solvent molecules. The tricyclazol molecule seems to fulfill the three

Fig. 4. Relationships between K_f values and soil variables. (a) All soils considered; (b) after neglecting the soils 1, 5, 14, 15 and 18.

TABLE 3

Correlation coefficient of K_f versus different soil properties for 18 soils (r_1) and 13 soils (r_2)

	% Clay	% OM	C.E.C.	% Silt	pH
r_1	0.33	-0.22	0.24	0.12	-0.01
r_2	0.95	0.07	0.79	0.45	0.15
	% Clay + OM	% Fe_2O_3	% Illite	% Mont.	% Kaolin.
r_1	0.32	0.02	0.34	0.22	0.09
r_2	0.91	0.05	0.82	0.77	0.64

conditions: it has only one polar group in the third ring of the molecule, its solubility in water is low which would suggest that it meets strong competition for the substrate sites from the solvent molecules, and it would have moderate intermolecular attraction, because of its high molecular weight. This type of isotherm indicates a tendency for large adsorbed molecules to associate in clusters rather than remain isolated and, thus, as the first part of the molecules has been adsorbed the second part of the curve, that is, the amount of fungicide adsorbed, increases rapidly. The S type curves also indicated a medium to low affinity of the solute by the sorbent.

The adsorption coefficients obtained from the Freundlich equation indicated also a medium affinity of tricyclazol for the soil surfaces. The adsorption capacity values are medium as compared with other polar molecules studied by us (Hermosín and Cornejo, 1990), but the comparison with other literature values is difficult because in the majority of cases K_f is reported without units (Hermosín and Cornejo, 1987).

The K_f values, used as a measure of the relative adsorption capacity, were assayed by linear correlation with soil properties shown in Table 1. As shown in Table 3, when all soils were considered no correlation was found with any soil variable. This is really surprising because the organic chemicals with low solubility and low to medium adsorption usually correlates their sorption capacity with the organic matter (Chiou, 1989). Recently, several workers proposed that the adsorption of a pesticide by soil can be determined accurately if its aqueous solubility or 1-octanol/water partition coefficient (K_{ow}) are known (Chiou et al., 1977; Felsot and Dahm, 1979; Karickhoff et al. 1979; Briggs, 1981). From these values the distribution coefficient of the pesticide between soil organic matter and water (K_{om}) is determined so that the only soil parameter necessary for describing sorption is the soil organic matter content. This method assumes a constant value for the K_{om} of a com-

pound in all soils. Unfortunately, several drawbacks exist with this approach. The aqueous solubility of many pesticides, as reported by their manufacturers, differs significantly from that reported in the literature (Bowman and Sans, 1979; Felsot and Dahm, 1979). For very large or very small K_{ow} values, sufficient accuracy is difficult to achieve and the results published often differ greatly (Chiou et al., 1977; Felsot and Dahm, 1979; Karickhoff et al., 1979). A good fit between K_{om} and either K_{ow} or solubility often does not exist for soils with low (1%) organic matter content, and even for soils with higher organic matter content numerous deviations occur (Mingelgrin and Gerstl, 1983). Furthermore, a close look at the correlations published by several workers reveals significant differences between their regression equations (Chiou et al., 1977; Felsot and Dahm, 1979; Karickhoff et al., 1979; Briggs, 1981). Despite the limitations of this method it can supply a first approximation of the sorption of some pesticide by certain soils. However, the organic matter content of soils studied here showed a very low and negative correlation coefficient and hence that approach should not be applied. After five of the 18 soils were neglected the linear correlation improved for clay and illite content, CEC and montmorillonite content (Table 3). Figure 4 shows the relationships between K_f values and soil variables. Figure 4a correspond to all soils considered and Fig. 4b corresponds to thirteen soils (after neglecting Nos. 1, 5, 14, 15 and 18).

According to these last results K_f values for tricyclazol seemed to be determined by the clay content of soils and this is confirmed by the good correlation found for the sorption capacity with CEC. Actually, the CEC of soil is determined by the colloidal fraction, especially their mineral components which are more abundant (Bailey and White, 1970). The correlation corresponding to clay fraction plus organic matter content did not improve that found with only the first variable.

Thus, K_f can be obtained according to these four variables: clay content, illite content, CEC and montmorillonite content by the following equations:

$$\begin{array}{lll} K_f = -2.13 + 0.20 \text{ clay} & (R^2 = 0.90) \\ K_f = -2.38 + 0.50 \text{ CEC} & (R^2 = 0.62) \\ K_f = -1.03 + 3.30 \text{ illite} & (R^2 = 0.67) \\ K_f = 0.62 + 0.53 \text{ mont.} & (R^2 = 0.59) \end{array}$$

The determination coefficients (R^2) indicate the percentage of K_f variability justified by the respective equation. Taking into account the high correlation coefficient obtained for clay and illite soil content initially this fungicide would be highly retained by the marshy soil surrounding the Doñana National Park because these soils are rich in both clay and illite components.

CONCLUSIONS

Adsorption capacity values K_f for tricyclazol considering 18 soils did not correlate with any soil variable. When the soils were reduced to 13, adsorption capacity for tricyclazol was related to clay content, CEC, illite and montmorillonite content.

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REFERENCES

- Albaiges, J., J. Algaba, P. Arambarri, F. Cabrera, G. Baluja, L.M. Hernandez and J. Castroviejo, 1987. Budget of organic and inorganic pollutants in the Doñana National Park (Spain). *Sci. Total Environ.*, 63: 13–28.
- Bailey, G.W. and J.L. White, 1964. Review of adsorption and desorption of organic pesticides by soil colloids, with implications concerning pesticide bioactivity. *J. Agric. Food Chem.*, 12: 324–332.
- Bailey, G.W. and J.L. White, 1973. Factors influencing the adsorption, desorption and movement of pesticides in soils. *Residue Rev.*, 32: 29–92.
- Boesten, J.J.T.I., L.J.T. Van der Pas and J.H. Smeit, 1989. Field test of a mathematical model for non-equilibrium transport of pesticides in soil. *Pestic. Sci.*, 25: 187–203.
- Bowman, B.T. 1981. Anomalies in the log Freundlich equation resulting deviations in adsorption K_f values of pesticides and other organic compounds when the system of units is changed. *J. Environ. Sci. Health.*, B 16: 113–123.
- Bowman, B.T. 1982. Conversion of Freundlich adsorption K values to the mole fraction format and the use of Sy values to express relative adsorption of pesticides. *Soil Sci. Soc. Am. J.*, 46: 740–743.
- Briggs, G.G. 1981. Theoretical and experimental relationships between soil adsorption octanol/water partition coefficients, water solubilities, bioconcentration factors and the parachor. *J. Agric. Food Chem.*, 29: 1050–1059.
- Calderbank, A. 1989. The occurrence and significance of bound pesticide residues in soil. *Rev. Environ. Contam. Toxicol.*, 108: 71–103.
- Chiou, C.T., V.H. Freed, D.W. Schemedding and R.L. Rohmert, 1977. Partition coefficient and bioaccumulation of selected organic chemicals. *Environ. Sci. Technol.*, 11: 475–478.
- Chiou, C.T. 1989. Theoretical considerations of the partition uptake of nonionic organic compounds by soil organic matter. In: *Reactions and Movement of Organic Chemicals in Soils*, SSSA Special Publication No. 22, pp. 1–29.
- Edwards, C.A. 1974. Pesticides residues in soil and water. In: C.A. Edwards (Ed.), *Environmental Pollution by Pesticides*, Plenum Press, London, pp. 409–458.
- Felsot, A. and Dahm, P.A. 1979. Sorption of organophosphorus and carbonate insecticides by soil. *J. Agric. Food Chem.*, 27: 557–563.
- Gersts, Z. and Mingelgrin, 1984. Sorption of organic substances by soils and sediments. *J. Environ. Sci. Health*, B 19 (3): 297–312.

- Giles, G.H., T.H. MacEwan, S.N. Nakhwa, and D. Smith, 1960. Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms and its use in diagnosis of adsorption mechanism and in measurement of specific surface areas of solids. *J. Chem. Soc.*, 3973–3993.
- Hermosin, M.C., J. Cornejo, and J.L. Perez-Rodriguez, 1987. Adsorption and desorption of maleic hydrazide as a function of soil properties. *Soil Sci.*, 144: 253–256.
- Hermosin, M.C. and J. Cornejo, 1987. Maleic hydrazide adsorption by soils and the use of the mole fraction form of the Freundlich equation. *Soil Sci.*, 144, 453–456.
- Hermosin, M.C., J. Cornejo, and J.L. Perez-Rodriguez, 1989. Mineralogy of the soil clay fraction as affecting pesticide adsorption-soil properties relationships. In: P. Jamet (Ed.), *Methodological Aspects of the Study of Pesticides Behaviour in Soil*, INRA, Paris, pp. 21–26.
- Hermosin, M.C. and J. Cornejo, 1989. Assessing factors related to pesticide adsorption by soils. *Toxicol. Environ. Chem.*, 25: 45–55.
- Hermosin, M.C. and J. Cornejo, 1990. Soil adsorption of 2,4-D as affected by the clay mineralogy. *Toxicol. Environ. Chem.*, 31–32, 69–77.
- Holmgren, G.G.S. 1967. A rapid citrate-dithionite extractable iron procedure. *Soil Sci. Soc. Am. Proc.*, 31: 210–211.
- Karickhoff, S.W., D.S. Brown, and T.A. Scott, 1979. Sorption of hydrophobic pollutants on natural sediments. *Water Res.*, 13: 241–248.
- Kerpen, W. and G. Schlessler, 1980. Adsorption and desorption of methabenzthiazaron, metamitron and metribuzin in soils. In: A. Banin and U. Kafafi (Eds.), *Agrochemicals in soils*, Pergamon Press, Oxford, pp. 141–148.
- Khan, S.V. 1980. *Pesticides in the Soil Environment*, Elsevier Scientific Publishers, New York.
- Meikle, R.W. 1972. Descomposition: qualitative relationships. In: Goring and J.W. Hamaker (Eds.), *Organic Chemicals in the Soil Environment*, Vol. I, Marcel Dekker, NY, pp. 145–252.
- Mercado, A. and Y. Kahanovitz, 1977. Groundwater pollution from pesticides in the coastal plain: hazard evaluation. In: M. Horowitz (Ed.), *Behaviour of Pesticides in Soil*, ARO, Bet Dagan, Special Publication 82.
- Mingelgrin, U. and Z. Gerstl, 1983. Reevaluation of partitioning as a mechanism of nonionic chemicals adsorption in soils. *J. Environ. Qual.*, 12: 1–11.
- Moreale, A. and R. Van Bladel, 1980a. Sorption behaviour of *p*-chloroaniline residues in soils. In: A. Banin and U. Kafafi (Eds.), *Agrochemicals in Soils*, Pergamon Press, Oxford, pp. 131–140.
- Moreale, A. and R. Van Bladel, 1980b. Fate of 2,4-D in Belgium soils. *J. Environ. Qual.*, 9: 627–630.
- Olsen, R.V. and R. Ellis, Jr., 1982. Iron. In: A.L. Page (Ed.), *Methods of Soil Analysis*, Part. 2. Chemical and Microbiological Properties, Monograph No. 9, Am. Soc. Agr., Madison, pp. 301–312.
- Rao, P.S.C. 1990. Sorption of organic contaminants. *Water Sci. Tech.*, 22: 1–2.
- Sanchez-Camazano, M.J. and M.J. Sanchez-Martín, 1988. Influence of soil characteristics on the adsorption of pirimicarb. *Environ. Toxicol. Chem.*, 7: 559–574.
- Sanchez-Martín, M.J. and M.J. Sanchez-Camazano, 1989. Influence of organic matter and clay fraction in pesticide adsorption by soils. Importance of pesticide structure. In: P. Jamet (Ed.), *Methodological Aspects of the Study of Pesticide Behaviour in Soils*, INRA, Paris, pp. 175–177.
- Walker, A. 1978. Simulation of the persistence of eight soil-applied herbicides. *Weed Res.*, 18: 305–313.
- Weber, J.B., D.H. Shea and S.B. Weed, 1986. Fluoridone retention and release in soils. *Soil Sci. Soc. Am. J.*, 50: 582–588.
- Worthing, C.R. and S.B. Walker, 1980. *The Pesticide Manual*. British Crop Protection Council, Croydon, UK.