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0045-6535(95)00109-3

Chemosphere, Vol. 30, No. 12, pp. 2375-2386, 1995
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0045-6535/95 $9.50+0.00

THE ROLE OF SOIL AND ACTIVE INGREDIENT PROPERTIES IN DEGRADATION OF PESTICIDES: A PRELIMINARY ASSESSMENT

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(Received in Germany 8 March 1995; accepted 10 April 1995)

Abstract
Pesticide disappearance from soils was observed in laboratory studies in which leaching and runoff were impeded, and volatilisation and degradation evaluated. Advection by volatilisation was negligible for the less volatile chemicals, and significant for the more volatile (Trifluralin and Heptachlor). Basic statistics applied to degradation DT50 data of 14 active ingredients in four different soils showed that the properties of pesticides play a major role in determining their degradability.

Introduction

Contamination of surface and ground water supplies by industrial solvents, agricultural fertilisers and pesticides has become a serious environmental and social problem in many developed and developing countries. As far as pesticides are concerned, agricultural uses are responsible for the main non-point sources of contamination. Many reports indicate that ground water supplies, particularly those of unconfined aquifers, may be reached by pesticides (Hutson and Roberts, 1990; Aharonson, 1987; Canter et al., 1987; Gustafson, 1993). The degree to which pesticides move from treated soils to water depends on the combination of environmental variables and the physicochemical properties of different active ingredients. Simulation models may be of great help in protecting the quality of aquifers. Among the variety of methods used to simulate pesticide behaviour in soils, evaluative and ranking models are the least complex. Based on simple deterministic approaches, they require very little information for their application, the basic assumption being that environmental variables do not significantly change the *relative* results of the simulation. Evaluative and ranking models are not suitable for environmental fate studies, but may be applied to group chemicals into relatively broad behavioural classes (Bacci et al., 1994).

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When released into the environment, pesticides move and react according to their "vocation" and according to environmental variables. If we assume that the relative behaviour will be similar under different environmental conditions, a ranking of the potential to reach water compartments, based essentially on the intrinsic properties of the chemical and on standardised environmental properties can be obtained. In order to produce these ranks, a *leaching index* must be calculated. Several leaching indices have been proposed (Wagenet and Rao, 1990; Trevisan et al., 1991; Jury et al, 1983; Jury et al., 1984; Rao et al., 1985; Laskowsky et al., 1982; Jury et al., 1987). Bacci and coworkers (1994) recently suggested a modification of the *surface soil model* by Mackay (1991), based on the calculation of the mass fraction (with respect to the quantity applied) leaching from a soil model in a fixed time interval (one year). The validity of this, as well as similar models, depends on the existence of homogeneous information on degradation kinetics in soil, currently expressed as half-life, ($t_{1/2}$ or DT50), which implies that, even if the degradation rate of a series of pesticides in different soils may change, in absolute terms, it should not modify the relative data. This may not be true in all possible cases, under actual field conditions. However, in the majority of current environmental conditions it is likely that a reactivity ranking could be maintained. To investigate on the role of soil and pesticide properties in determining pesticide reactivity, field data appears to be unsuitable, mainly because of uncontrolled variables and the fact that mass transfer phenomena, essentially by the mobile phases (water and air) and chemical transformation processes cannot be clearly separated. A possible alternative is the laboratory model (Laskowsky, 1982), in which selected components of real systems are included, with the aim of observing the behaviour of substances under simplified conditions.

In the present paper we applied a laboratory model to evaluate the role of soil and pesticide properties in determining degradation in contaminated soils.

Materials and Methods

Experimental Design

Pesticide degradation was observed into two cubic laboratory greenhouses, each with a volume of 200 litres (Bacci and Gaggi, 1985). Each greenhouse contained 36 50-ml glass vessels, in which 1.5 cm of four different soils was placed. The chemicals tested were divided into four groups, as follows:

Group 1	Group 2	Group 3	Group 4
Trifluralin	Endosulfan-α	Propoxur	Atrazine
Chlorpyriphos	Endosulfan-β	Carbaryl	Metribuzin
Heptachlor	Chlorpyriphos-methyl		Metalaxyl
Endosulfan-sulphate	Alachlor		Azinphos-methyl

A total of 9 replicates for each group of chemicals were constituted, for each of the four soils (36 vessels containing 0.2 mg of each chemical, corresponding to a load of 7.2 mg per chemical in each green-house). Soils fortified with groups 1 and 2 were in greenhouse A and groups 3 and 4 in greenhouse B, as shown in Figure 1.

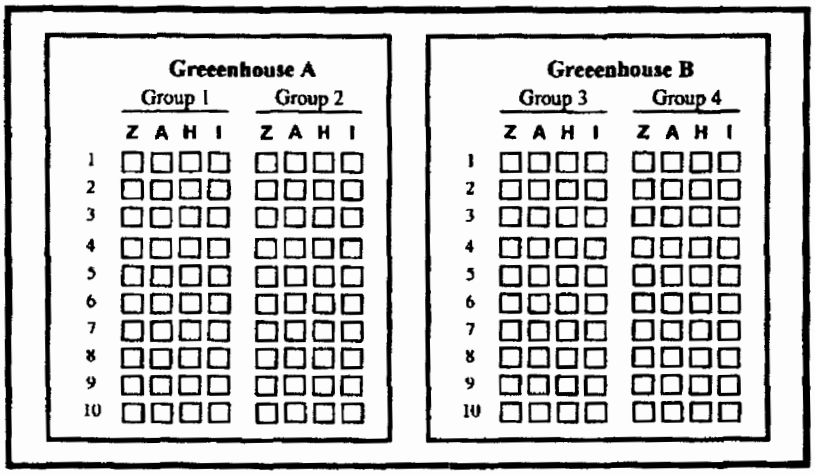

Figure 1.- Soil replicates in greenhouses.

Sampling times were 0, 39, 161, 185, 622, 861 and 1197 hours for greenhouse A, and 0, 24, 45, 75, 188, 288, 442 and 866 hours for greenhouse B. At each sampling time, four vessels (one for each soil and group were removed and analysed). Leaching and runoff were impeded, and volatilisation was strongly reduced with respect to field conditions due to slow air turnover (air turnover time was about 80 min). For the more volatile compounds, losses by volatilisation were calculated. The experimental conditions are reported in Table 1.

Table 1.- Experimental conditions for studying pesticide disappearance from soil.

Temperature	23 - 26 °C
Photo period	constant light
Illumination	1000 lx
Air turnover	2.5 ml/min

Soil fortification was carried out by adding 200 µg of active ingredient for each studied compound to each container. Four soils (a Pliocene sand: Z; an organic-rich orchard soil: A; an agricultural soil: H, and a soil from the volcanic area of Mount Amiata: I) differing in organic matter content, pH and texture were selected; their main properties are summarised in Table 2.

Table 2.- Soil properties.

Sample	pH	O.M. %	clay %	silt %	sand %
Z	7.7	0.07	12.8	8.7	76.8
A	7.41	8.8	17.3	22.7	61.2
H	7.38	3.7	18.8	23.4	60.8
I	4.86	4.1	21.2	28.3	52.2

The soil weights in each glass container varied according to the different soil type, with 35 g for soil Z, 30 for soil H and 18 for soils A and I. Properties of the chemicals are in Table 3.

Table 3.- Physicochemical and partition properties of selected substances. DT50 indicates the half-life, in days, of *disappearance* from soil (field data). Mm = molar mass; S = water solubility; P = vapour pressure, mp = melting point.

	Physicochemical Propierties							
Active ingredient	Mm	S (mg/l)	P (Pa)	Koc (f)	Kaw	Kow	DT50	mp °C
Alachlor	269.8a	240b	0.0029a	170b	1.32E-06	631c	15b	40.5a
Atrazine	215.7a	33b	0.00004a	100b	1.06E-07	251.2c	60b	174c
Azinphos-methyl	317.1a	29b	0.000027	1000b	1.19E-07	501.2c	10b	72.4a
Endosulfan-a	406.9a	0.32a	0.0011c	12400d	5.65E-04	3981c	50b	109a
Endosulfan-b	406.9a	0.33a	0.0011c	12400d	5.65E-04	3981c		213.3a
Endosulfan-sulphate								
Carbaryl	201.2a	120b	0.0053a	300b	3.59E-06	199.5c	10b	142a
Chlorpyriphos	350.6a	0.4b	0.0025a	6070b	8.84E-04	50000a	30b	43a
Chlorpyriphos-methyl	322.5a	4b	0.0056a	8181c	1.82E-04	19953c	7b	liquid
Heptachlor	373.3a	0.056g	0.053a	24000g	0.14	3630780d	250g	95.5a
Metalaxyl	279.3a	8400b	0.00029a	50b	3.89E-09	15.6d	70b	72a
Metribuzin	214.3a	1220b	0.000058	16.4e	4.11E-09	40a	40b	126a
Propoxur	209.2a	1800b	0.0013a	30b	6.10E-08	31.62c	30b	91.5c
Trifluralin	335.5a	0.3b	0.0137a	8000b	6.18E-03	118000a	60b	48.5a

a: Worthing & Hance, 1991
b: Wauchope et al. 1992
c: Suntio et al. 1988
d: Yalkowsky et al. 1985
e: Mackay, 1991
f: dimensionless (soil standard bulk density = 1.5 kg/L)
g: Augustijn-Beckers et al. 1994

Soil extraction procedure

A multiresidual extraction method was used. (Bacci et al., 1989), consisting in the following main steps:

1. Solid-liquid extraction: 20 - 40 g of soil sample was extracted with 100 ml of 2/1 vol/vol acetone/water solution by shaking 5 min and sonicating 25 min; extracts were centrifuged and evaporated to give an aqueous phase containing the residues of interest;
2. Liquid-liquid extraction: the aqueous phases were extracted again, twice, with 70 ml of chloroform;
3. Volume reduction and elimination of chlorinated solvent: the chloroform was evaporated and the residues redissolved in 5 ml n-hexane;
4. Florisil™ clean-up: hexane extracts (5 ml) were loaded on 1 cm ID glass columns filled with 2 g of Florisil™ (Merck, 60-100 mesh ASTM, art. No. 12518) and eluted with 50 ml n-hexane and 50 ml 4% acetone in hexane.

Air sampling & analysis

Air samples were collected by aspiration into 0.3-g Florisil™ traps prepared by partially filling Pasteur pipettes. The volume of air samples was 200 - 250 L, corrected for the vacuum (Bacci and Gaggi, 1985). Florisil™ was eluted with 50 ml of n-hexane and 50 ml of 4% acetone in n-hexane, and the final sample volume adjusted according the sensitivity of the analytical technique.

Regression and statistical analysis

All regressions were calculated with *TableCurve* software from *Jandel Scientific*. Statistics analysis was performed with *Microsoft Excel*.

Gas chromatographic analysis

The analytical conditions are summarised in Table 4.

Table 4.- Gas-chromatographic conditions

Organochlorines	
Gas-chromatograph:	Perkin Elmer Sigma 3B
Column:	SPB-5, 30 m, 0.25 mm ID, 0.25 µm film.
	Carrier: He, 100 kPa = 3 ml/min
Injector:	SP/SPL, 250 °C. Injection SPL 1 min, 2 µl
Detector:	ECD, 280 °C. scavenger CH_4 5% in Ar
Program:	100 °C hold 1min; then 3 °C/min to 280 °C, hold 5 min

Organophosphorus and Carbamates	
Gas-chromatograph:	Perkin Elmer Sigma 3B
Column:	CP-SIL5 CB, 10 m, 0.54 mm ID, 5 µm film.
	Carrier: N_2 18 ml/min
Injector:	On-column. 220 °C. Injection: 2 µl
Detector:	NPD 250°C. Air 180 kPa. H_2 100 kPa.
Program:	Isotherm 220°C

Results

Pesticide disappearance from soil is recognised to include four main processes: volatilisation, degradation, leaching and run-off. In our laboratory model, leaching and run-off were impeded. Although limited, volatilisation was evaluated, particularly for the more volatile chemicals, to obtain the degradation DT50. The disappearance from soil data was treated according to single-compartment first-order kinetics. Examples of experimental plots are given in Figures 2 and 3. Air concentrations of the chemicals are given in Table 5. The levels expected in green-house air were around 0.5-1 % saturation; the relatively high variability of the measured values may be due to the low loading (200 µg in each vessel) compared to similar previous volatilisation and bioconcentration studies (5-50 mg/100g soil; Bacci et al., 1992). Levels in air, jointly with air input (and output) rate and the mass of pesticide in the system (6.4 mg after 1st sampling) may be used to calculate the relative significance of volatilisation and degradation in the pesticide disappearance from soils.

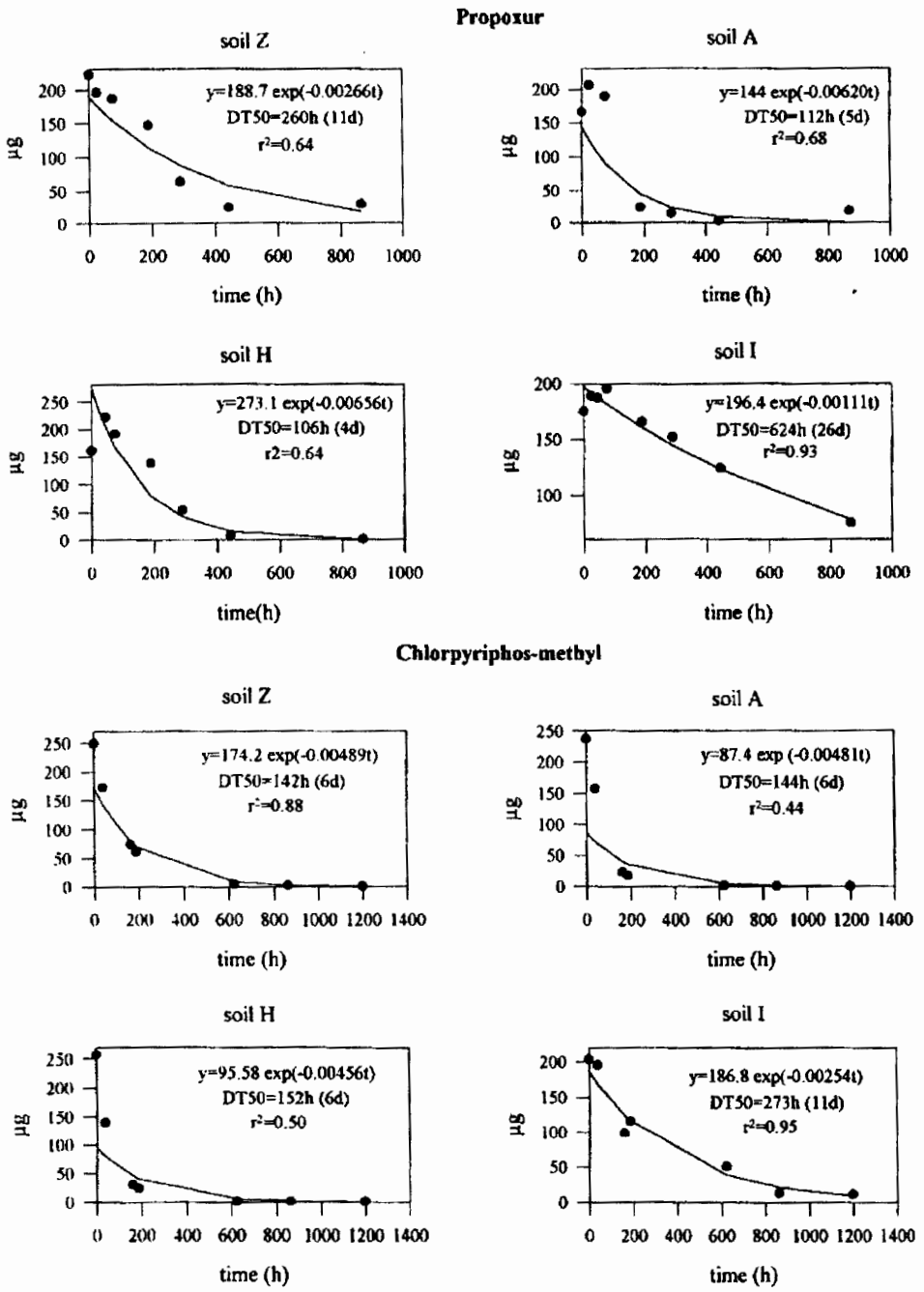

Figure 2.- Examples of plots on chemical disappearance from fortified soils

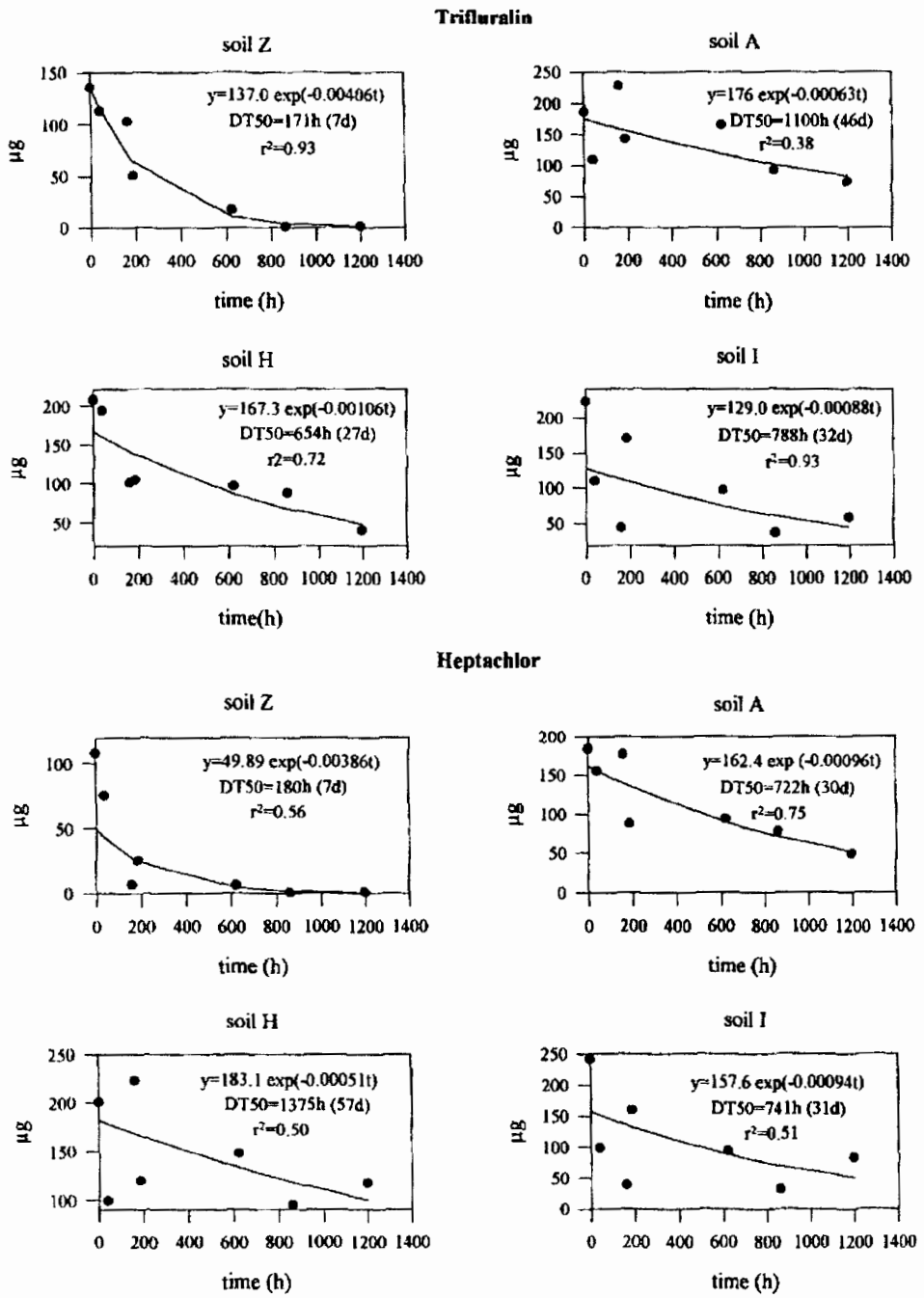

Figure 3.- Examples of plots on chemical disappearance from fortified soils

Table 5.- Concentration of pesticides in air samples from greenhouse A collected before 2nd soil sampling).

Active ingredient	ng/l	% sat
Chlorpyr.-methyl	4.3	1.2
Endosulfan-a	7.6	4.2
Endosulfan-b	2.3	1.3
Endosulfan-sulphate	0.6	—
Chlorpyriphos	<0.2	—
Carbaryl	<2	—
Alachlor	<0.2	—
Propoxur	<2	—
Heptachlor	16.1	0.2
Trifluralin	10.9	0.6

An advection rate constant, k_{adv}, can be obtained by dividing the quantity of chemical removed from the greenhouse per unit time, by the mass present in the soil. For Trifluralin, an air concentration of about 10 ng/L, with an air inflow of 2.5L/min, or 150 L/h, gave an elimination of 1500 ng/h by volatilisation. This corresponds to an advection rate constant of 1500/6400000= 0.00023 1/h. Analogously k_{adv} may be obtained for Heptachlor (0.00048 1/h), Chlorpyriphos Methyl (0.0001 1/h) and Endosulfan α (0.00017 1/h), β 0.00005 1/h) and sulphate (0.000014 1/h). A comparison of the disappearance and volatilisation rate constants is reported in Table 6. Advection by volatilisation appeared to be negligible for the less volatile chemicals (chlorpyriphos methyl, endosulfan sulphate and the others not included in Table 6).

The disappearance data was corrected, when necessary, and a summary of the degradation rate (and related parameters) in different chemicals and soils, expressed as degradation DT50, as shown in Table 7.

Discussion

Variations in degradation DT50 data, were analysed using basic statistical methods. The coefficient of variation, CV, defined as ratio of the mean to the standard deviation, was calculated for all DT50 data of each active ingredient in different soils, and for all DT50 data of each soil for the different active ingredients (Table 7). The first gave an estimate of the scattering due to soil properties for each active ingredient, and the second, the scattering due to pesticide properties for each soil. The mean CV for all active ingredients in each soil was higher than the CV of each active ingredient in all soils. Even with a relatively low air turnover, the volatility of pesticides from soil significantly affected disappearance, particularly in the case of compounds with higher vapour pressure values. Differences between the various soils were not considered, and this is a limitation of the approach used in this study. Further research is in progress to measure volatilisation rates in homogeneous soil systems, avoiding mixing soils with high retention potential (such as those rich in organic matter) with soils with little vapour retention (such as sand). Volatilisation is the resultant of interchange process between pesticides sorbed onto soil and the soil organic matter, dissolved in the pore water, and present in the soil atmosphere. (Racke, 1993).

Table 6.- Disappearance and volatilisation rate constants for the more volatile chemicals.
When advection by volatilisation is substantial, a $k_{deg} = k_{dis} - k_{adv}$ is indicated together with the corresponding DT50 for degradation.

Chemical	Soil	k_{dis} (1/h)	k_{adv} (1/h)	k_{deg} (1/h)	deg. DT50 h	d
Heptachlor	Z	0.00386	0.00037	0.00349	199	8.3
"	A	0.00050	0.00037	0.00013	5332	222
"	H	0.00092	0.00037	0.00055	1260	53
"	I	0.00067	0.00037	0.00030	2310	96
Trifluralin	Z	0.00395	0.00023	0.00372	186	7.7
"	A	0.00063	0.00023	0.00040	1733	72
"	H	0.00106	0.00023	0.00083	835	35
"	I	0.00087	0.00023	0.00064	1083	45
Chlorpy. Methyl	Z	0.00443	0.00010	no variation		
"	A	0.00481	0.00010			
"	H	0.00457	0.00010			
"	I	0.00254	0.00010			
Endosulfan α	Z	0.00242	0.00017	0.00225	308	13
"	A	0.00166	0.00017	0.00149	465	19
"	H	0.00105	0.00017	0.00088	788	33
"	I	0 .00057	0.00017	0.00040	1733	72
Endosulfan β	Z	0.00157	0.00005	0.00152	456	19
"	A	0.00026	0.00005	0.00021	3301	138
"	H	0.00019	0.00005	0.00014	4951	206
"	I	-----				
Endosulfan sulph.	Z	0.00018	0.000014	no variation		
"	A	0.00018	0.000014			
"	H	0.00019	0.000014			
"	I	0.00022	0.000014			

Factors that might be expected to influence loss of a pesticide by volatilisation from soil include the vapour pressure of the pesticide, its concentration, rate of transport to the soil surface, adsorption on soil, the soil temperature and moisture content, and the velocity and turbulence of the air above the soil surface (Plimmer, 1976). Volatilisation of soil incorporated compounds is controlled by their *effective pressure* within the soil (Voogt and Jansson, 1993). Apparent vapour pressures of pesticides are significantly reduced by interaction with soil, mainly as a result of adsorption (Kurtz, 1990). For non-ionic or weakly polar herbicides, soil organic matter is the most important factor controlling the adsorption (Chesters et al., 1989).

In soil Z, volatilisation was the main process implied in Trifluralin and Heptachlor disappearance. In this soil there is minimum adsorption, so that the apparent vapour pressure is practically the vapour pressure of the

active ingredient. Alachlor shows the opposite behaviour: its volatility is low, as shown by its relatively modest vapour pressure, but its degradation rate in soil Z, mainly a sand, was the lowest of the four soils. A reason for this may be the fact that the main route of degradation of Alachlor in soil is by micro-organisms (Chesters et al., 1989), which were probably less abundant in sand than in the other organic-rich soils.

Table 7.- Degradation DT50, in days, for different chemicals and in different soils.

	experiment time: 1197 h							
Active ingredient	**soil Z**	**soil A**	**soil H**	**soil I**	**mean**	**std.dev**	**std.err.**	**CV**
Alachlor	63	8	13	15	24.81	25.80	12.90	1.04
Atrazine	30	40	41	20	32.74	9.71	4.85	0.30
Azinphos-methyl	20	4	5	12	10.28	7.13	3.56	0.69
Carbaryl	4	4	4	20	7.89	7.87	3.94	1.00
Chlorpyriphos	7	12	9	15	10.78	3.38	1.69	0.31
Chlorpyriphos-methyl	7	6	6	11	7.55	2.55	1.28	0.34
Endosulfan-a	13	19	33	72	34.25	26.53	13.26	0.77
Endosulfan-b	19	138	206		121.00	94.65	47.33	0.78
Endosulfan-sulphate	164	157	150	134	151.10	13.01	6.50	0.09
Heptachlor	8	222	53	96	94.83	92.03	46.02	0.97
Metalaxyl	17		16	10	14.50	4.04	2.02	0.28
Metribuzin	31	19	30	15	23.67	8.11	4.05	0.34
Propoxur	11	4	5	27	11.72	10.53	5.27	0.90
Trifluralin	8	72	35	45	39.93	26.57	13.28	0.67
mean	28.73	54.24	43.27	37.81			**mean CV**	**0.61**
std.dev	41.87	72.18	60.08	39.03				
std.err.	13.24	22.82	19.00	12.34	**mean CV**			
CV	1.46	1.33	1.39	1.03	**1.30**			

It could be useful to compare the present results with published data. One of the main sources of information on pesticide DT50 is the SCS/ARS/CES Pesticide Properties Database (Wauchope et al., 1992; Augustijn-Beckers et al., 1994). The database gives figures on disappearance DT50 from the field, rather than degradation DT50, however to a first approximation (particularly in modelling) the half-life in the field is assumed to be equal to the degradation half-life. If so, pure degradation data should result in longer DT50 values than those from the field. A comparison is given in Table 8, together with the ratio between measured and literature values. The difference is roughly a factor of 2, with shorter DT50 values in the experimental series. This contrast may be due to the constant laboratory conditions, with high humidity, temperature and continuous light: all factors enhancing degradation. Another possible reason could be the relatively short experimental period, which would lead to an overestimation of the degradation rate due to the rapid disappearance of some chemicals in the initial phase.

Table 8.- Comparison between present (A) and literature database values (B) for disappearance DT50.

Active Ingredient	A DT50 obs	B DT50 bib	A/B ratio
Atrazine	32.7	60	0.55
Metribuzin	23.7	40	0.59
Azinphos-methyl	10.3	10	1.03
Chlorp.-methyl	7.6	7	1.08
Propoxur	11.7	30	0.39
Chlorpyriphos	10.8	30	0.36
Carbaryl	7.9	10	0.79
Alachlor	24.8	15	1.65
Endosulfan-a	34	50	0.68
Endosulfan-ß	95	250	0.38
Heptachlor	121	—	—
Trifluralin	40	60	0.66
Endosulfan sulph.	151	—	—

Despite the evident limitations of the approach, "mild" and "hard" chemicals could easily be identified in the database series and in our experimental results. For the purposes of simple modelling, the assumption that chemical properties are more significant in determining degradation than soil properties, seems acceptable, especially when extreme environmental conditions are excluded.

Conclusions

Degradation DT50 values obtained by laboratory studies were found to be related to published values. The properties of pesticides appears to play a major role in determining their degradability. Models based on standard soil properties may therefore be applied in predicting chemical behaviour.

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