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Measured and Simulated Persistence of Imazethapyr in Soil

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Imazethapyr, 2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1*H*-imidazol-2-yl]-5-ethyl-3-pyridinecarboxylic acid, is an herbicide used for the control of broadleaf weeds in soybean [*Glycine max* (L.) Merr.] (Hart et al. 1991). In previous reports this product has been found to have a long persistence in soil: Goetz et al. (1990) found half-lives varying from 192 to 318 days in a silty-clay soil and from 78 to 270 days in a silty-loam soil both incubated at different conditions of temperature and soil moisture. Loux et al. (1989) reported that imazethapyr dissipation in a silt-loam soil appeared to be a biphasic process with rapid dissipation during the first 60 days after application, followed by a period of slow dissipation. Since soybean in Italy is often in rotation with corn or wheat, the imazethapyr persistence could injure the subsequent crops. Furthermore, due to its low adsorption on soil colloids (Mangels 1991), the product could reach and pollute ground water. For a better understanding of the behaviour of imazethapyr in the field and its carryover potential to following crops, the factors that influence the persistence of this herbicide in soil need to be investigated. For this reason the persistence of imazethapyr at three initial concentrations was studied in a clay-loam soil under different incubation conditions.

In order to provide a picture of the differences between laboratory half life and time to 50% field loss, and thus a prevention tool against dangerous situations, the simulation of imazethapyr persistence was performed using the CALF model (Nicholls et al. 1982; Walker 1987) under typical pedo-climatic conditions of Central Italy.

MATERIALS AND METHODS

Imazethapyr (98% purity) was kindly supplied by Cyanamid Inc., Princeton, NY, USA. A clay-loam soil taken from the 0-20 cm horizon in Papiano-Perugia, (Central Italy) was used in the experiment. Some chemical and physico-chemical characteristics are reported in Table 1. One kg of air dried soil sieved at 2 mm was placed in each of nine polypropylene containers. An aqueous solution of the herbicide was incorporated into the soils to give the nominal initial concentrations of 0.1, 1.0, and 10.0 ppm, each for three containers. Water was added to adjust soil moisture content (% w/w) to 75% field capacity (fc) (6 containers) and 33% fc (3 containers). The samples were

Table 1. Some analytical characteristics of the Papiano soil

pH	8.1
$CaCO_3$ (%)	10
Organic matter (%)	2.09
CEC (meq/100 g)	18
Sand (%)	23.5
Silt (%)	47.5
Clay (%)	29.0
Field capacity (% w/w)	30.0
Wilting point (% w/w)	10.0

incubated at 20°C (3 containers at 75% fc and 3 containers at 33% fc) and 10°C (3 containers at 75% fc). Soil moisture was maintained by periodic additions of water.

Duplicate 25 g soil samples drawn from each container were extracted with 0.5 N NaOH (100 ml), shaken for 1 hour, centrifuged at 6000 g and filtered on extra-rapid paper. The pH was adjusted to 1.8-2.0 and the pesticide was partitioned twice in chloroform (2x40 ml). The organic extracts were collected, evaporated at 40°C and redissolved in methanol (1 ml). HPLC analysis was performed using a Perkin-Elmer Series 410 chromatograph equipped with a C8 DB Supelco column (4.6 mm i.d. x 15 cm length) and a UV detector Perkin-Elmer LC 95. The wavelength was set at 254 nm and the flow rate of the mobile phase (58% water, 38% methanol, 4% acetic acid) at 0.9 ml/min. Under these conditions the retention time of imazethapyr was 8.4 min and the sensitivity of the method was 0.005 ppm.

The CALF leaching model has been described in detail by Nicholls et al. (1982). It combines the soil nutrient mobility model of Addiscott (1977) modified to simulate soil drying and hence upward movement of solutes, with the herbicide persistence model of Walker and Barnes (1981). It divides the soil into a number of layers of equal depth and partitions the soil solution in each layer into mobile and non-mobile phases with the division between the two set at a soil water tension of -200 KPa (-2 bar). The degradation subroutine in the model was changed by Walker (1987) to include the sequence of equations used in the earlier persistence models of Walker (1974) and Walker and Barnes (1981) that account for moisture and temperature effects on degradation. In the model, moisture effects on degradation were characterized using the empirical equation:

$$H = A\,M^{-B}$$

(where H is the half-life at moisture content M, and A and B are constants). Temperature effects were characterized using the Arrhenius equation. Other data required were soil moisture contents at field capacity (-10 KPa) and at a soil water stress of -200 KPa, the average bulk density of the soil in the field, and the initial moisture content of each soil layer. Also required were weather data (daily rainfall, evaporation from an open water surface, and maximum and minimum air temperatures) for the period of the experiment.

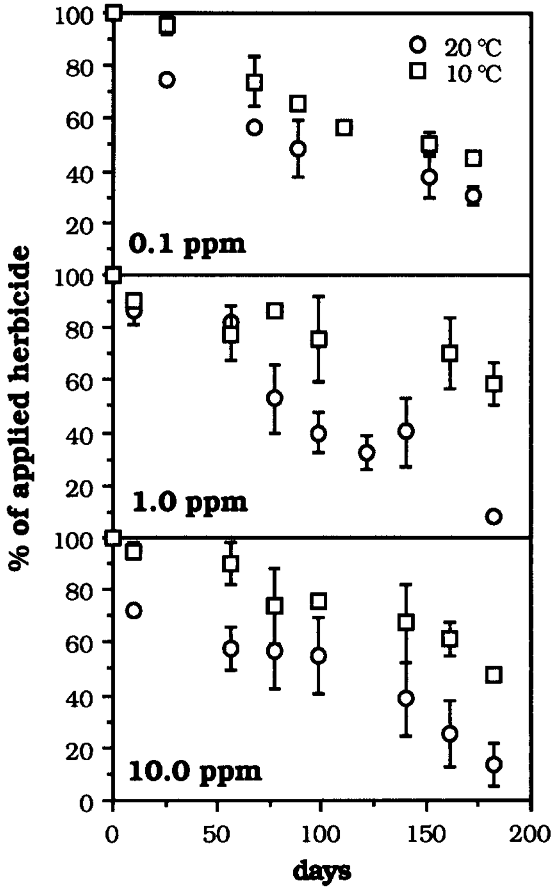

Figure 1. Degradation of imazethapyr in soil at 75% field capacity, at 20 and 10°C and at three different initial concentrations (I = deviation average of two measurements)

RESULTS AND DISCUSSION

In Figure 1 the comparison between imazethapyr degradation in soil at 20°C and 75% field capacity and 10°C and 75% field capacity at the three initial concentrations is reported. The data show that the temperature influenced imazethapyr persistence. As temperature decreased, the half-life [derived from the slopes of the best fit lines of the logarithms of the remaining concentrations against time of incubation ($P < 0.001$ for all tests)], increased in all tests. When temperatures varied from 20 to 10°C the half-life at the three initial concentrations increased by 55%, 250% and 140%, respectively (Table 2).

In Figure 2 the comparison between imazethapyr degradation in soil at 20°C and 75% field capacity and at 20°C and 33% field capacity at the three initial concentrations is reported. The data show that soil moisture also influenced imazethapyr persistence. When soil moisture varied from 75% to 33% of field capacity the half-life at the three initial concentrations increased by 20%, 60% and 105%, respectively (Table 2).

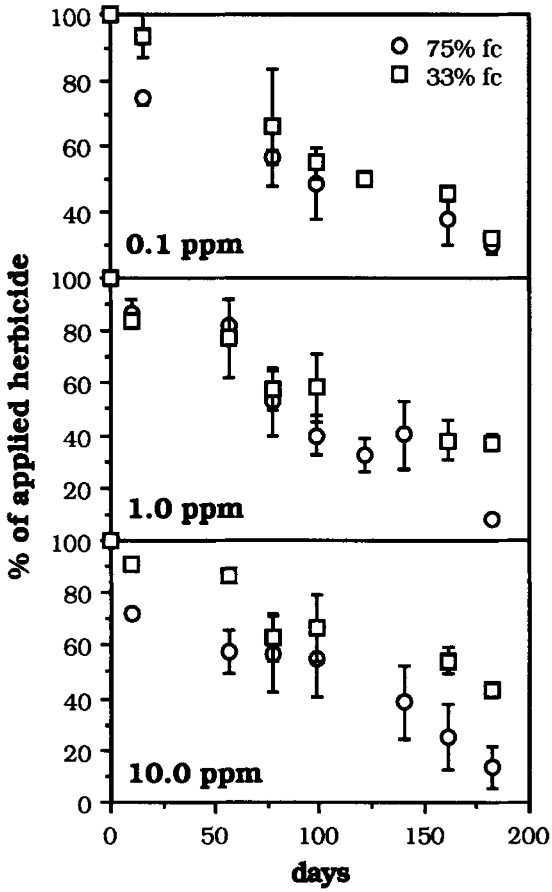

Figure 2. Degradation of imazethapyr in soil at 20°C, 75 and 33% of field capacity, and at three different initial concentrations (I = deviation average of two measurements)

Table 2. Half-lives (days) of imazethapyr in soil under different incubation conditions and at three different initial concentrations

Incubation conditions	*0.1 ppm*	*1.0 ppm*	*10.0 ppm*
20°C and 75% fc	95.38	72.94	76.38
20°C and 33% fc	114.43	116.51	156.57
10°C and 75% fc	147.78	257.28	184.03

fc = field capacity

The data in Figures 1 and 2 indicate that the initial dose also influenced herbicide persistence but with effects showing an irregular trend. At times the half-life increased with the initial concentration (e. g. at 20°C and 33% field capacity the half-life increased by 2% and 37% when the initial concentration varied from 0.1 to 1.0 and from 1.0 to 10.0 ppm, respectively), whereas other times it did not (e. g. at 10°C and 75% field capacity the half-life decreased by 40% when the initial concentration varied from 1.0 to 10.0 ppm)

(Table 2).

The data obtained from the laboratory experiment were used to calculate A, B and E constants which are required in the CALF model for simulating the herbicide persistence in field conditions. The A, B and E values for imazethapyr at the three initial concentrations are reported in Table 3. These values proved to be quite different, thus indicating that the initial dose significantly influences the herbicide degradation in soil.

Table 3. Values of constants A, B and E calculated at three initial concentrations for prediction of imazethapyr persistence with the CALF model

	0.1 ppm	*1.0 ppm*	*10.0 ppm*
A	210	552	1697
B	0.265	0.675	1.035
E (cal/mole)	7250	20850	14560

In Table 4 the simulation conditions, typical of the Central Italy scenario with intensive agriculture, are reported.

Table 4. Simulation conditions

Pesticide properties (imazethapyr)		
Application (kg/ha)		0.1
Water solubility (mg/l)		1400
K_d		0.11
Profile details and soil properties		
Depth (cm)		150
Segment thickness (cm)		50
Bulk density (kg/dm^3)		1.30
θ_{fc} (% w/w)		30
θ_{wp} (% w/w)		12
$\theta_{-200\,KPa}$ (% w/w)		18
Climate		
	Rain + irrigation (mm)	Mean mounthly temperature (°C)
May	102.6	16.85
June	154.0	18.41
July	80.0	24.95
Aug.	45.4	24.29
Sept.	9.2	19.06
Oct.	81.2	16.70
Nov.	62.8	7.14
Dec.	16.2	4.75
TOT.	551.4	

The simulation results are reported in Table 5. Under the simulated field conditions imazethapyr persistence was more than 200 days and the herbicide went below 1 m depth 50 days after treatment, due to its very low K_d value among other factors (Mangels 1991).

Table 5. Simulation with the CALF model of imazethapyr persistence (% of applied herbicide) in soil at three different depths and at three initial concentrations

	Days after	*0-50 cm*	*50-100 cm*	*100-150 cm*	*Total*
0.1 ppm	25	81.57	-	-	85.57
	67	53.57	0.73	0.10	54.40
	88	40.36	1.95	0.17	42.48
	151	19.14	1.35	0.14	20.33
	172	15.20	1.61	0.15	16.96
1.0 ppm	10	86.88	-	-	86.88
	56	36.71	0.42	0.08	37.21
	77	19.71	0.55	0.10	20.36
	98	7.83	0.38	0.09	8.30
	121	3.43	0.24	0.07	3.74
	141	1.81	0.13	0.01	1.95
	182	0.68	0.07	-	0.75
	205	0.54	0.09	-	0.63
10.0 ppm	10	92.71	-	-	92.71
	56	42.32	0.48	0.11	42.91
	77	24.88	0.68	0.13	25.69
	98	12.34	0.58	0.12	13.04
	140	3.81	0.26	0.09	4.16
	161	2.45	0.16	0.02	2.63
	182	1.58	0.16	-	1.74
	205	1.20	0.19	-	1.39

In Figure 3 the simulated persistence of imazethapyr in soil is depicted at the three initial concentrations in comparison with those measured in laboratory experiments at 20°C and 75% fc. The data are in agreement in the test performed at 0.1 ppm of initial concentration. Some significant discrepancies are found at 1.0 and 10.0 ppm of initial concentration, namely in the period between 50 and 150 days after treatment. During this intermediate period the model seems to underestimate the persistence. Previous validation experiments performed in field lysimeters on alachlor, metolachlor and linuron (Businelli et al. 1993) showed that this model generally tended to overestimate the persistence. This behaviour is also confirmed by the experiments of Walker (1976; 1978) in field plots. This could be explained by the fact that in real field conditions photodecomposition, volatilization and leaching occur, but are not considered in the CALF model. Indeed, the susceptibility of various herbicide compounds to the above mentioned phenomena could determine different degrees of overestimation of the persistence. The underestimation of imazethapyr persistence in the present experiment might be due to the higher temperatures and soil moisture in the simulated field conditions than in the laboratory experiment, thus the simulated degradation is faster.

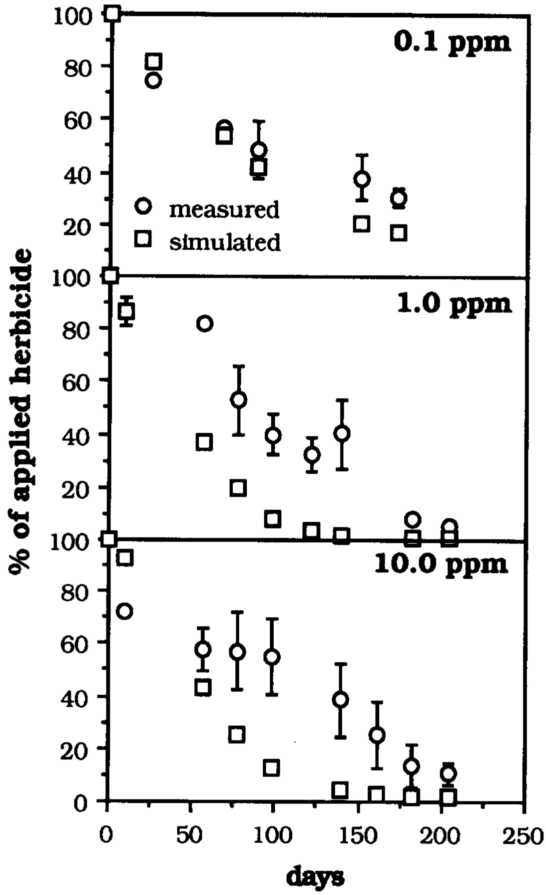

Figure 3. Persistence of imazethapyr in soil simulated and measured at 20°C and 75% fc (I = deviation average of two measurements)

Due to its high carryover potential to subsequent crops and to its high risk of ground water pollution further field studies on the fate of imazethapyr in soil need to be performed.

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