A REVIEW OF THE DEGRADATION AND MOVEMENT OF PICLORAM IN SOIL AND WATER

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Picloram (4-amino-3,5,6-trichloropicolinic acid) is a widely used herbicide and plant growth regulator low in toxicity to mammals, fish, and birds, aquatic chain organisms, and soil microorganisms.

PATTERN OF DEGRADATION

Picloram is degraded in plants soils, and microorganism cultures, and in water by sunlight. It is not a readily available energy source for microorganisms but is co-metabolized with other energy sources. Slow chemical degradation in soil at high temperatures has also been reported.

Metabolites that are transitory and low in concentration relative to picloram include 4-amino-3,5-dichloro-6-hydroxypicolinic acid in wheat and soil, 4-amino-3,5,6-trichloropyridine in wheat, and a *Trichoderma* culture, and conjugates hydrolyzable to picloram in wheat and cotton.

RATES OF DEGRADATION IN SOIL

Rates decrease with increasing concentration and fit Michaelis-Menten or half-order kinetics. Rates increase in the presence of plant roots and with increasing organic matter, temperature and moisture until soil approaches saturation. Decomposition occurs in saturated soil. There is some evidence that decomposition is most rapid between pH 5.5 and 6.5.

SORPTION AND LEACHING

Picloram has a pK of 3.6. Minimum sorption occurs in neutral or alkaline, sandy loam soils low in organic matter and increases with decreasing pH increasing organic matter, and increasing hydrated iron and aluminium oxides. Resistance to leaching is correlated with sorption. Picloram is sorbed at least as strongly as atrazine or monuron in some soils.

MOVEMENT UNDER FIELD CONDITIONS

Picloram has a vapour pressure of 6.1×10^{-7} mm at $35^{\circ}C$ and, therefore, losses by volatilization are negligible.

Small amounts of picloram (<6%) may be removed from the site of application in run-off water. Percent loss is about the same for varying rates of application, increases with increased slope, decreases with time, and is greater for sod than for fallow soil. Loss of picloram in run-off water also increases with intensity of rainfall. The percentage in run-off water decreases when the water passes over untreated sod.

Leaching of picloram through soil at the same time that it is degrading resembles a spreading and subsiding wave. Since rate of decomposition decreases with increasing depth, the average depth of leaching of picloram is above the zone of highest concentration. For annual precipitation up to 40-50 in. (101.6-127.00 cm) maximum concentrations of picloram usually occur throughout the season in the top 1-2 ft (30.5-61.0 cm) of soil except for sandier soil receiving 30-50 in. (76.2-127.0 cm) where maximum concentrations may occur at 2-4 ft (61.0-12.2 cm). Above 50 in. (127.0 cm), most of the picloram is still not leached out of the top 4 ft for heavy soils, but substantial leaching through sandy soils might occur. Picloram resists leaching to at least as great an extent as fenac or prometone in some soils.

PERSISTENCE UNDER FIELD CONDITIONS

Picloram decomposes in soil at rates similar to the urea and triazine herbicides. Estimated half-order constants in the United States vary from about 0.2 in the colder, drier areas to 1.0 in the hotter, wetter areas. The time required for the herbicide to decompose to a negligible level (0.01 oz per acre) starting with initial rates of 1 oz and 2 lb per acre (0.07 and 2 kg per hectare) varies from 4.5 months to 4.6 years for a half-order constant of 0.2 and, for a half-order constant of 1.0, from 0.9 to 11 months.

Observed half-order constants for published data on the disappearance of picloram from soil profiles estimated to be under non-leaching conditions and predicted half-order constants from climatological data were similar (Table 2). The correlation coefficient between the observed and predicted half-order constants was 0.88.

At equivalent rates, picloram may be more persistent in its phytotoxic action than urea and triazine herbicides when crops highly sensitive to picloram are planted after its application. Included among the more sensitive crops are legumes, tomato, cucumber, potato, cotton, safflower, sunflower, lettuce, buckwheat, and sugar beet. Picloram may be less persistent in its phytotoxic action than urea and triazine herbicides when lower rates are used or when crops tolerant to picloram are planted after application.

TABLE 1

Leaching and Decomposition Pattern of Picloram in Soils*

Picloram oz/ac	Sample Depth inches	Recovery of Picloram†					
		Toledo Silty Clay			Brookston Silt Loam		
		101 days	280 days	476 days	90 days	270 days	463 days
4	0-6	55.2	25.6	2.4	62.4	4.0	0
	6-12	4.8	6.4	0	3.2	1.6	0
	12-18	0.8	1.6	0	0	0.8	0
	18-24	0	1.6	0	0	0.8	0
	24-30	0.8	0.8	0	0	0.8	0
	30-36	0	1.6	0	0	0.8	0
	0-36	61.6	37.6	2.4	65.6	8.8	0
8	0-6	59.6	30.8	0.8	84.0	8.4	0
	6-12	8.0	6.4	0.4	3.6	9.6	0
	12-18	1.6	1.6	0	1.2	0.4	0
	18-24	0.8	0.4	0	0.4	0	0
	24-30	0	0.4	0	0	0	0
	30-36	2.0	0.4	0.4	0	0.4	0
	0-36	72.0	40.0	1.6	89.2	18.8	0
32	0-6	-	31.8	2.7	54.0	11.0	1.4
	6-12	-	32.2	1.1	3.0	8.8	1.6
	12-18	-	5.1	1.9	1.5	5.6	1.6
	18-24	-	1.3	0.3	0.6	8.2	2.2
	24-30	-	0.5	0.3	0.2	3.9	0.7
	30-36	-	0.6	0.2	0	0.6	1.3
	0-36	-	71.5	6.5	59.3	38.1	8.8

* Calculated from the data of Herr, D.F., *et al.*

† Original data converted from parts per billion by weight to oz per acre, and percent recovery calculated on the assumption that 1 ppm in 6 in. of profile is equivalent to 32 oz per acre.

TABLE 2

Observed and Predicted Half-Order Constants for the Degradation of Picloram in Soils at Various Locations in the United States and Canada

State or Province and Reference	Location	Soil Type	Time Interval after application (months)	Application rates (oz/ac)
Saskatchewan	Rockhaven	Oxbow Clay Loam	11.5 to 35	4-48
	Scott	Scott Loam	2.5 to 27.5	0.5-8
Alberta	Lacombe	Navarre Loam	11 to 28	8 and 16
	Lacombe	Malmo Loam	14.5	2 and 4
Ohio	Castalia	Toledo Silty Clay	3.4-15.9	2-64
	Columbus	Brookston Silt loam	3.2-15.4	2-64
Nebraska	Lincoln	Pawnee Silty Clay loam	26	16 and 32
	Bennet	Sharpsburg Silty Clay loam	10	1-16
	Concord	Moody Silty Clay loam	10	8-32
Texas	Bryan	Erving Clay loam	3-18	16-144

*U.S.A. Climatological Data, National Summary, U.S. Department D.M. Brown, University of Guelph, Ontario, Canada

†1 p.p.m. in 6 in. of profile assumed equivalent to 32 oz per ac; and t = interval between application and soil analysis

$k_{1/2} = \frac{2\left[\sqrt{C_o} - \sqrt{C}\right]}{t}$. Where C_o = Rate of application of

††$k_{1/2}$ predicted from estimated annual precipitation in in. (X_4)

$k_{1/2} = -0.049 + 0.0119\ X_4 + 0.0056\ X_5$.

TABLE 2

Observed and Predicted Half-Order Constants for the Degradation of Picloram in Soils at Various Locations in the United States and Canada

Profiles sampled (number)	Annual* Precipitation (inches)	Days per* year ≥ 90°F (number)	Observed $k_{1/2}$†		Predicted†† $k_{1/2}$
			Average	Standard Deviation of Average	
30	13.9	5	0.226	0.017	0.144
18	13.9	5	0.145	0.019	0.144
6	18.6	1	0.219	0.030	0.178
2	18.6	1	0.118	0.024	0.178
13	20.4	33	0.288	0.047	0.379
11	36.2	30	0.417	0.078	0.549
4	27.9	24	0.300	0.043	0.418
5	27.4	21	0.291	0.086	0.395
3	23.6	35	0.646	0.131	0.428
8	26.7	107	1.84	0.42	0.868

of Commerce; Canadian Climatological Data, private communication,

acre and total oz per acre in each profile calculated.

picloram in oz per acre; C = picloram in soil profile in oz per

in months.

and days per year ≥ 90°F (X_5) by the equation,

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STIMULATING SOIL MICROORGANISMS TO DECOMPOSE PYRIDINE HERBICIDE RESIDUES

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INTRODUCTION

Picloram, or Tordon, and Daxtron are two persistent herbicides that are lethal to many plants at a concentration of 0.1 p.p.m. but are non-toxic to many soil bacteria, actinomycetes, and fungi, even at concentrations up to 100 p.p.m. Yet in most soils, their decomposition is extremely slow, and months or years may pass before it is safe to sow new crops.

REVIEW OF THE LITERATURE

Meikle, Williams, and Redemann (1966) found that 4% of picloram, labelled with ^{14}C in the carboxyl position, was decarboxylated by plant roots and rhizosphere microorganisms in 15 days at 25-28° C. Redemann *et al.* (1968) using 0.9 p.p.m. of picloram, totally labelled with ^{14}C, in pots of wheat, detected traces of radioactive oxalic acid, 4-amino-3,5-dicholoro-6-hydroxy-picolinic acid, and 4-amino-2,3,5-trichloropyridine after 98 days. Rieck (1969) added organisms to glucose media containing 0.1 p.p.m. of picloram (carboxyl-^{14}C labelled) and found that *Rhodotorula glutinis* decomposed 24%, *Trichoderma* spp. 11% and *Aspergillus tamarii* 6% in 30 days.

RESULTS

Varying the moisture content, pH, temperature, or levels of organic substrates in soils had little effect on microbial degradation of picloram or Daxtron, but sterilization stopped decomposition. Numerous microorganisms isolated as pure cultures