QUEENSLAND DEPARTMENT OF PRIMARY INDUSTRIES

DIVISION OF PLANT INDUSTRY BULLETIN No. 811

PERSISTENCE AND LEACHING OF PICLORAM APPLIED TO A CLAY SOIL ON THE DARLING DOWNS

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SUMMARY

Picloram (4-amino-3,5,6-trichloropicolinic acid) was applied at six rates (0, 23.3, 70, 210, 630 and 1890 g ha^{-1}) to a montmorillonitic clay soil. Rate of degradation of the herbicide and its vertical movement in the soil profile were determined by bioassays of field samples taken at four times (3.7, 7.4, 16.8 and 28.4 months) after application. Wheat, lucerne and soybeans were sown at various times following application to determine the effect of phytotoxic residues on the growth of these crops.

At all four sampling times the zone of highest concentration of picloram was in the surface 15 cm of soil. Picloram was not detected below 30 cm. At selective weed control rates of 23.3 g ha^{-1} and 70 g ha^{-1} less than 10% of the applied picloram was present in the soil 7.4 months after application.

At the latter rates, the growth of neither wheat nor lucerne was affected when planted 7.4 months after application.

I. INTRODUCTION

Picloram (4-amino-3, 5, 6-trichloropicolinic acid), as 'Tordon 50-D, (5% w/v picloram + 20% w/v 2,4-D) or 'Tordon M' (1·25% picloram + 20% w/v MCPA) is used for the selective control of certain weeds in a number of cereal crops and linseed on the Darling Downs (Rawson, Marley and Walsh 1976; Walsh and Marley 1977).

Rates of picloram application are 17·5 to 23·3 g ha^{-1} in winter cereals and linseed, and a maximum of 70 g ha^{-1} in maize and sorghum. Much higher rates of 2·2 kg ha^{-1} are used for spot treatment of small outbreaks of a number of perennial weeds in cultivation.

Many broadleaf crops are susceptible to damage from low concentrations of picloram in soil (Alley and Lee 1966; Bovey *et al.* 1975). Numerous field and laboratory studies (summarised by Bovey and Scifres 1971) have demonstrated that the persistence of picloram in soil may vary greatly.

The objectives of this study were to determine the persistence and movement of phytotoxic residues resulting from the application of picloram to a clay soil on the Darling Downs, and measure the effect of these residues on the establishment and growth of wheat, lucerne and soybeans when sown at intervals after application of the herbicide.

II. MATERIALS AND METHODS

The field experiment was conducted on the Hermitage Research Station near Warwick. The soil type was a black earth of montmorillonitic clay. Soil physical and chemical properties are listed in table 1.

TABLE 1

SOIL PHSYSICAL AND CHEMICAL PROPERTIES

Depth (cm)	Clay (%)	Silt (%)	Sand (%)	Organic Carbon (%)	Cation Exchange Capacity (m.e. %)	pH
0–15 ..	55·1	36·1	8·4	1·8	87	7·3
15–30 ..	53·6	37·4	9·6	1·7	73	7·7
30–60 ..	55·4	36·0	8·4	1·6	64	8·2
60–90 ..	53·1	37·9	8·8	1·4	60	8·5
90–120 ..	51·4	38·7	10·0	1·2	58	8·5

One week before application of the herbicide treatments the trial area, which was under a crop of wheat at the noding stage, was mown and raked. The area was then spray irrigated (38 mm) to close the soil cracks. Earthen banks were constructed between plots to prevent surface movement of herbicide from plot to plot. The slope of the trial area was less than 1%. Plots were 9 m by 22 m. Treatments were replicated four times in a randomised block design.

Picloram was applied to the plots, with an Oxford Precision Sprayer at 0, 23·3, 70, 210, 630 and 1890 g ha^{-1}. The commercial formulation 'Tordon 50-D' (5% picloram with 20% 2,4-D both present as the triisopropanolamine salt) was used. Treatments were applied on 29 October 1968. Soil surface was dry.

Little re-growth was made by the wheat crop. The plots were not harvested for grain and were chisel ploughed on 12 December 1968. Workings of the various sections of the plots from that date were those normally practised in the area for the production of the various crops subsequently sown.

Field-sown crops

WHEAT

Except for a strip retained for lucerne the bulk of each plot was sown to wheat cv. Timgalen on 13 June 1969 (7·4 months after application of picloram treatments). The wheat was harvested for grain yield on 3 December 1969. Dry conditions prevented sowing of wheat in the 1970 winter.

LUCERNE

Due to the coarse structure of the surface soil only two sowings (13 June 1969 and 22 July 1971) of the four sowings of lucerne cv. Hunter River established successfully. The lucerne was sown to a sub-plot of each plot at 8 kg ha^{-1} in ten rows, 22 m long, spaced 16 cm apart. Established plants

were counted in five quadrats each of 0·4 m² per sub-plot. Prior to each early-flowering harvest each sowing in the plots was sampled for dry-matter production. Five quadrats per plot were taken, bulked for each plot, oven-dried and weighed. Quadrat size was 0·4 m² for the 1969 sowing and 0·8 m² for the 1970 sowing.

Soybeans

Three-row sub-plots of soybeans were sown to the plots on three dates (27 January 1970, 23 February 1970, and 4 January 1971) following application of treatments. Rows were 22 m long at 53-cm spacing. Kent variety was used in the 1970 sowings and Hood variety in 1971. Marginal seed-bed moisture resulted in poor emergence of the first sowing which was cultivated out at the second trifoliate leaf stage after observations for growth abnormalities. Seedling establishment of the second sowing was determined by counting plants in six random lengths, each 0·91 m, in the centre row. Dry matter production at the early pod-filling stage was determined by cutting five random lengths of 1·52 m in the centre row, bulking for each plot, drying at 82°C and weighing. Frosting at that growth stage prevented grain formation. Damage by green vegetable bug (*Nezara viridula* L.) in 1971 resulted in seed yield figures which were not meaningful.

Bioassays

The plots were sampled four times after application of the herbicide treatments to determine levels of picloram residues in the soil profile. Sampling was carried out with a power-driven coring unit. Three cores per plot were extracted in the sub-section to be sown to wheat in each plot. The three cores were sectioned for depth levels indicated in table 2 and bulked for individual depth levels. The composite samples were dehydrated at 82°C for

TABLE 2

Details of Timings of Samplings for Bioassays, Cumulative Rainfall and Temperature Data, Depth Increments Bioassayed and Concentration Series Employed

Time from Picloram Application to Field Sampling (Months)	Cumulative Rainfall* (cm)	Cumulative Days Greater than 32·2°C max*	Depth Increments Sampled and Bioassayed (cm)	Concentration Series Employed (ppm x 10^5)
3·7	27·89 (30·89)	34 (22)	0–15, 15–30, 30–60 60–120, 120–180	15·625, 31·25, 62·5 125, 250, 500, 1000 2000
7·4	38·86 (49·89)	39 (25)	0–15, 15–30, 30–60 60–90, 90–120	25, 50, 100, 150, 200 300, 500, 1000
16·8	92·48 (111·20)	65 (52)	0–15, 15–30, 30–60 60–90	25, 50, 100, 150, 200 300, 500, 1000
28·4	170·56 (179·86)	91 (78)	0–15, 15–30, 30–60 60–90, 90–120	25, 50, 100, 150, 200 300, 500, 1000

* Figures in parentheses are long-term cumulative averages for those periods.

24 h and stored in the dark, prior to bioassay, in double-walled paper bags. The soil samples were crushed for potting by pulverising within the paper bags to avoid cross-contamination of samples.

Concentration of residual picloram in the field samples was determined by bioassay in a glasshouse. Soil samples were bioassayed using soybeans cv. Java as the indicator plant. Ten seeds, graded for uniform size, were planted in 700 ml waxed paper containers. Seedlings were thinned to five per container following emergence. Samples of expected high residual activity were diluted with control soil from the corresponding depth and replicate so that anticipated picloram concentration would be within the range of the prepared standard concentration series.

For each sampling a standard concentration series was prepared from control plot soil for each depth increment examined for each replicate. Picloram was added to the soil of the concentration series by supplementing the appropriate herbicide solution with sufficient water to wet the soil to field capacity. To wet the soil mass uniformly, the herbicide solution was added in three equal portions as three equal portions of soil were weighed into the container. Source of picloram for the concentration series was 'Tordon 22K' (240 g l^{-1} picloram as a potassium salt).

For concentrations greater than 0·002 ppm the index of measurement was the length of the two fully-expanded unifoliate leaves. For lower concentrations the more sensitive index of fully-expanded length of centre leaflet of the first trifoliate leaf was used. The lower limit of detection of the bioassay method varied between 50×10^{-5} and 100×10^{-5} ppm.

Details of times of field samplings after herbicide application, cumulative rainfall and temperature data, profile depth increments examined at each sampling and concentration series employed for bioassays are presented in table 2.

Following the initial sampling to 180 cm, subsequent sampling depths were reduced but on all occasions sampling depth was greater than the maximum downward extension of the wetting front.

For each sampling, the leaf measurement data from the field samples of unknown picloram concentration and from the standard concentration series for individual depth levels were subjected to analysis of variance. Where values for unknowns differed significantly from "nil herbicide" values at the 5% level of significance, estimated actual values and 90% confidence intervals were obtained for these unknowns from regression lines (linear or quadratic) of leaf length on picloram concentration (constructed from the standard concentration series data).

The percentages of applied picloram remaining after various time intervals following application were determined by converting estimated picloram concentrations to weight of picloram per hectare depth increment, totalling for the sampled profile, and expressing as a percentage of the applied rate. Bulk density of the soil was 1·2 g ml^{-1}.

Using the data for calculated loss of picloram activity for the various rates of application, the rate constants for various kinetic rate laws were calculated for each sampling date.

III. RESULTS

Field-sown crops

WHEAT

Yield and establishment data for wheat sown 7 months after application of treatments are shown in table 3. Both grain yield and establishment were significantly reduced at the highest rate of picloram application. Yield was not significantly affected at lower application rates, but establishment was also significantly reduced at the 630 g ha^{-1} rate of application.

TABLE 3

EFFECT OF PICLORAM APPLIED SEVEN MONTHS PREVIOUSLY ON ESTABLISHMENT AND YIELD OF TIMGALEN WHEAT

Picloram applied (g ha^{-1})	Seedling establishment (thousands ha^{-1})	Grain Yield (kg ha^{-1})
Nil	937·7	1369
23·3	927·5	1359
70	893·4	1401
210	905·4	1331
630	860·2	1382
1890	606·7	1017
L.S.D. 5%	75·6	82
1%	104·5	114

LUCERNE

Lucerne sown 7 months after picloram application (see table 4) failed to establish at rates of 630 and 1890 g ha^{-1}. Establishment was significantly reduced following 210 g ha^{-1}.

This latter reduction in establishment was reflected in a significantly reduced yield of the first harvest. Yields of later harvests and total yields of the 1969–70 harvests and 1970–71 harvests were not significantly reduced by that application rate.

Establishment of lucerne sown 33 months after picloram application (see table 5) was not significantly affected by treatments. The statistically significant yield differences in the first and third cuts of that sowing are considered fortuitous.

SOYBEANS

With soybeans sown 16 months after application of treatments, very slight distortion of trifoliate leaves was observed in a small percentage of plants at the 210 g ha^{-1} rate. Severe distortion of trifoliate leaflets was evident at the 630 g ha^{-1} rate. With the exception of the 1890 g ha^{-1} rate, where negligible establishment was obtained, plant establishment was not significantly affected by previous picloram application. Data for vegetative dry matter yield from this sowing were extremely variable and an apparently reduced yield at 630 g ha^{-1} did not attain significance. When soybeans were sown 26 months after application of treatments, establishment number was not significantly affected by treatments. Distortion of trifoliate leaflets was evident only at the 1890 g ha^{-1} rate of picloram application.

TABLE 4

EFFECT OF PICLORAM APPLIED SEVEN MONTHS PREVIOUSLY ON ESTABLISHMENT AND YIELD OF LUCERNE

Picloram Applied* (g ha^{-1})	Established Plant Number (per 2 m^2)		Dry Matter Yield of 1969–70 Harvests (kg ha^{-1})			Total Dry Matter Yields for 1969–70 Harvests (kg ha^{-1})	Dry Matter Yield of 1970–71 Harvests (kg ha^{-1})		Total Dry Matter Yields for 1970–71 Harvests (kg ha^{-1})
	Trans. Means ($\sqrt{x}$ trans.)	Equiv. Means	13 Nov 69	5 Feb 70	13 Mar 70		9 Nov 70	29 Dec 70	
Nil	9·2	85·3	1 850	1 229	1 441	4 520	1 983	2 773	4 756
23·3	9·2	85·3	1 606	1 024	1 478	4 108	1 888	2 852	4 740
70	8·4	71·3	1 627	993	1 691	4 311	2 244	2 994	5 238
210	5·2	27·2	670	955	1 579	3 204	1 982	2 255	4 237
Standard Error ..	0·9	..	243	170	203	519	209	305	427
L.S.D. 5% ..	3·0	..	778	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
1% ..	4·3	..	1 118	..	..	..	..	..	..

* At the picloram application rates of 630 and 1 890 g ha^{-1} lucerne did not establish. These treatments were not included in the statistical analysis of the results.

TABLE 5

EFFECT OF PICLORAM APPLIED 35 MONTHS PREVIOUSLY ON ESTABLISHMENT AND YIELD OF LUCERNE

Picloram Applied (g ha^{-1})	Established Plant Number (per 2 m^2)	Dry Matter Yield of 1971–72 Harvests (kg ha^{-1})					Total Dry Matter Yields for the 5 harvests (kg ha^{-1})
		10 Nov 71	20 Dec 71	2 Feb 72	16 Mar 72	9 May 72	
Nil	187·2	1 735	1 100	1 803	1 839	1 355	7 832
23·3	190·3	1 590	1 008	1 537	1 541	1 137	6 813
70	185·6	1 833	1 188	1 753	1 580	1 252	7 606
210	190·7	1 950	1 140	1 799	1 704	1 310	7 903
630	179·3	1 838	1 140	1 815	1 582	1 305	7 680
1 890	190·4	1 814	1 262	2 012	1 853	1 355	8 296
Standard Error ..	18·7	111	60	60	103	62	299
L.S.D. 5% ..	N.S.	335	N.S.	180	N.S.	N.S.	N.S.
1% ..	..	464	..	249	..	..	..

Bioassays

Picloram residues were not detected at depths greater than 30 cm at any sampling. At all times of sampling active picloram residues when detected were concentrated in the surface 15 cm of soil with much lower concentrations present at the 15 to 30-cm depth and then only at high application rates (table 6). The calculated data for percentage of applied picloram remaining with time (table 6) show that the rate of loss of picloram activity was greatest during the 0 to 3·7-month period following application. Also, following this initial period, loss of picloram activity was markedly slower at the highest application rate of 1890 g ha^{-1} than at lower levels of application.

In table 7 the results can be considered using the approach of Hamaker, Youngson and Goring (1968). Rate constants for various rate laws were calculated for each treatment at each sampling date. The constancy of such constants is a simple test as to which rate law the data appear to fit best. For no sampling are the zero-order and half-order functions even approximately constant. The first-order constants are reasonably similar for the 0 to 3·7-month period and with the exception of the highest application rate are closely concordant for the 0 to 7·4-month period. The first-order constants are markedly lower for the highest application rate at the final three samplings.

IV. DISCUSSION

Factors influencing the decomposition of picloram include phytolytic degradation (Merkle, Bovey and Davis 1967) the nature of the microbial population in the soil, organic matter content, soil moisture and temperature (Youngson *et al.* 1967). Adsorption, which influences the depth of leaching, is favoured by decreasing pH, increasing organic matter content and increasing levels of hydrated iron and aluminium oxides. Clays probably play only a minor role (Hamaker, Goring and Youngson 1966).

The initial 3·7-month period following picloram application was the period of greatest rate of loss of picloram activity and coincided with summer months of much higher mean temperatures and rainfall than for the longer periods. Hamaker, Youngson and Goring (1967) found picloram loss from soils collected from 18 states of U.S.A. to be positively correlated with the number of days over 32·2°C and annual rainfall. Also, significant losses from photodecomposition probably occurred during the 7 days between application and the first subsequent rainfall. Merkle, Bovey and Davis (1967) showed that 15% of picloram applied to a soil surface was degraded by a week's sunlight. Their study was conducted in a month when sunlight was near its minimum. Once in the soil picloram is protected from photodecomposition.

The considerably lower first-order constants for the longer sampling periods indicate the effects of much lower winter temperatures and rainfall in slowing decomposition.

The apparently lower rate of degradation of picloram at the highest rate of application indicated that the capacity of the soil to degrade picloram is lower at high concentrations, and could possibly be better described by Michaelis-Menton kinetics. This is consistent with the findings of Goring, Youngson and Hamaker (1965) and Herr, Stroube and Ray (1966). The Michaelis-Menton rate law functions between first and zero-order. The rate approaches first-order for very low concentrations and zero-order for very high concentrations.

TABLE 6

ESTIMATED PICLORAM CONCENTRATIONS AT VARIOUS DEPTH INCREMENTS IN THE SOIL PROFILE AND PERCENTAGE RECOVERY OF PICLORAM AT A NUMBER OF TIME INTERVALS FOLLOWING FIELD APPLICATION

Time (months)	Picloram Applied (g ha^{-1})	Depth Increments* and Residual Picloram				Percentage of Applied Picloram Remaining
		(0–15) cm		(15–30) cm		
		Picloram Concentration (ppm x 10^5)	90% Confidence Intervals (ppm x 10^5)	Picloram Concentration (ppm x 10^5)	90% Confidence Intervals (ppm x 10^5)	
3·7	23·3	200	155, 245	0	..	15·7
	70	255	175, 270	0	..	5·9
	210	1 805	1 525, 1 950	0	..	15·7
	630	3 400	2 400, 4 600	250	100, 400	10·6
	1 890	16 900	13 800, 23 300	375	225, 525	16·7
7·4	23·3	120	75, 180	0	..	9·4
	70	260	200, 350	0	..	6·8
	210	690	570, 860	0	..	6·0
	630	3 000	1 800, 4 400	0	..	8·7
	1 890	>20 000	Not obtainable	225	0, 450	>19·3
16·8	23·3	0	..	0	..	0·0
	70	0	..	0	..	0·0
	210	118	110, 127	0	..	1·0
	630	475	430, 525	0	..	1·4
	1 890	8 000	7 200, 9 000	112	103, 123	7·8
28·4	23·3	0	..	0	..	0·0
	70	0	..	0	..	0·0
	210	0	..	0	..	0·0
	630	161	111, 215	0	..	0·5
	1 890	930	820, uncertain	64	42, 85	1·0

* At no sampling was active picloram detected at depths greater than 30 cm.

TABLE 7

RATE REACTION CONSTANTS FOR THREE REACTION KINETICS EQUATIONS DESCRIBING THE DEGRADATION OF PICLORAM

Co (g ha^{-1})	Zero-order Constant $\left(k = \frac{Co - C}{t}\right)$†				First-order Constant $\left(k = \frac{\text{Log}\left(\frac{Co}{c}\right)}{t}\right)$†				Half-order Constant $\left(k = \frac{2(\sqrt{Co} - \sqrt{C})}{t}\right)$†			
	3·7 months	7·4 months	16·8 months	28·4 months	3·7 months	7·4 months	16·8 months	28·4 months	3·7 months	7·4 months	16·8 months	28·4 months
23·3 ..	5·3	2·9	*	*	0·50	0·32	*	*	1·56	0·90	*	*
70 ..	17·7	8·8	*	*	0·76	0·36	*	*	3·39	1·56	*	*
210 ..	47·6	26·7	12·4	*	0·50	0·38	0·27	*	4·68	2·94	1·55	*
630 ..	151·4	77·7	37·1	22·1	0·60	0·33	0·25	0·19	9·07	4·77	2·63	1·64
1 890 ..	423·2	<206·1	104·0	66·0	0·48	<0·22	0·15	0·16	13·80	<6·56	3·74	2·75

* Picloram no longer detectable.
† t = time (months); Co = initial concentration; C = concentration at time t.

The concentration of residues in the surface 15 cm of soil with no residues detected below 30 cm at any sampling indicates that contamination of ground-water is unlikely from applications of this type and rate.

It is concluded that on the heavy clay soils of the Darling Downs, picloram is degraded fairly rapidly and active residues are not leached rapidly through the soil profile. Also single or annual low-rate applications of picloram on this soil type do not present long-term hazards to following sensitive crops or to the ground-water.

V. ACKNOWLEDGEMENTS

The assistance and technical advice of Messrs N. Young and H. Ferguson of Dow Chemical in the development of the bioassay procedures used in this study are gratefully acknowledged. The Biometry Branch (in particular Dr A. Swain and Mr R. Mayer) provided assistance with statistical analysis of the results.

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(Received for publication 30 March 1978)

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