Extraction of Picloram Residues from a Sandy Loam Soil

by
C. E. McKone and E. G. Cotterill
Agricultural Research Council, Weed Research Organization, Begbroke Hill, Yarnton, Oxford OX5 1PF, Great Britain

The herbicide picloram (4-amino-3,5,6-trichloropicolinic acid) is used in the U.K. and elsewhere for control of perennial weeds in non-agricultural grassland and in some countries for control of broadleaved weeds in cereals. Because of its high activity on some plant species, small residues (<0.1 ppm) which may remain in the soil for a considerable period may be highly phytotoxic. It is therefore necessary to be able to measure these residues after periods of 1 year or more following field application.

It is generally acknowledged that the recovery of picloram residues from soil is dependent on the pH of the slurry during extraction. The pH ranges used for laboratory extraction quoted in the literature vary from pH 7 (Cheng 1969, 1971), pH 10 (Baur et al. 1971), approximately pH 11 (Leahy and Taylor 1967) and $>$pH 13 (Moseman and Aue 1969). In addition earlier workers have used acidified acetone for extraction (Saha and Gadallah 1967; Merkle et al. 1966). In some of these publications details of the picloram concentration in the soil were omitted and sometimes the efficiency of extraction methods were not checked on weathered field residues. The work described here was undertaken to examine the recovery of low levels of picloram (0.01 to 0.10 ppm) at pH levels above 7 from soil fortified in the laboratory and from the same soil containing residues from a field application.

MATERIALS AND METHODS

Soil

A sandy loam soil (organic carbon 1.93%, pH 7.1) was taken from experimental plots that had received 24 oz/ac picloram 67 weeks prior to sampling. Soil from control plots was used for fortification experiments in the laboratory.

Extractants

1. A series of potassium hydroxide concentrations was prepared in 10% potassium chloride. Fifty millilitre aliquots when shaken with 25 g of the soil gave filtrates with the following pH.

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10% KCl containing KOH	pH of filtrate 25 g soil/50 ml
nil	7.2
0.01M	7.5
0.025	8.0
0.050	9.35
0.075	10.35
0.100	11.6

2. Fifty millilitres of distilled water with 2 g of calcium hydroxide was used to extract 25 g portions of soil.

Soil extraction and herbicide measurement

Air dried soil (25 g) ground to pass a 2.5 mm sieve was shaken for 1 hour on a wrist-action shaker with 50 ml of extractant. After shaking, the soil slurry was allowed to settle and the supernatant liquid was filtered through a fluted Whatman No. 42 filter paper. A 25-ml aliquot of the filtrate was transferred by pipette to a 100-ml separating funnel and sufficient 2M sulphuric acid was added to adjust the pH to <2. The acidified extract was shaken twice with 25 ml of chloroform containing 5% ethanol (Cheng 1971). The chloroform extracts were combined and transferred to a stoppered 100-ml conical flask. A glass still head was fitted and the solution was evaporated to about 0.5 ml under reduced pressure on a water bath at 55°. The remaining solvent was removed with a gentle stream of air. The residue was dissolved in 10 ml of diethyl ether (dried) and methylated with diazomethane (Schlenk and Gellerman 1960). Following methylation the ether and diazomethane were removed with a gentle stream of air and the residue was dissolved in hexane. Aliquots of this solution were injected into the gas chromatograph and measured against a series of standards containing pure picloram methyl ester dissolved in hexane.

A Pye 104 gas chromatograph was used fitted with a ^{63}Ni electron capture detector. The operating conditions were as follows:

Column 1.5 m x 4 mm i.d. glass, packed with 1.5% XE 60 on 80/100 mesh Chromosorb W. High Performance.

Injector temperature:	215°	Attenuation:	10×10^2
Column temperature:	180°	Carrier gas:	80 ml/min oxygen-free N_2
Detector temperature:	300°	Detector voltage:	pulse mode 150 usec.

RESULTS

Figure 1a shows the quantities of picloram extracted with the KOH solutions from the field treated soil. Below pH 8 the residue was below the limit of detection (0.001 ppm). Above pH 8, extractable picloram increased almost linearly to 0.038 ppm at pH 11.6 which was the highest pH in this experiment. Higher concentrations of potassium hydroxide to give a greater pH were not practical because of large increases in the background responses from coextracted material. Figure 1b shows the amounts of picloram recovered when soil taken from untreated control plots was fortified with 0.05 ppm picloram in the laboratory prior to extraction with the KOH solutions.

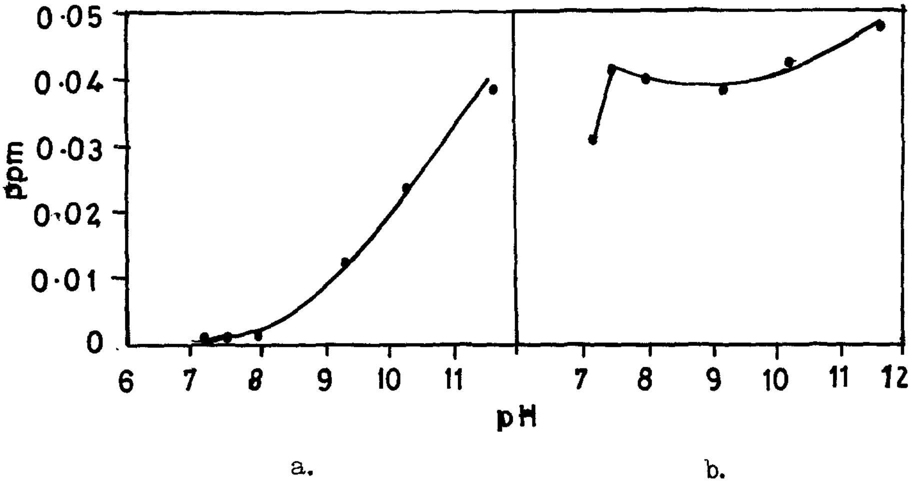

Fig. 1. a) picloram extracted (ppm) with KOH solution from field treated soil,
b) picloram extracted (ppm) with KOH solutions from control soil fortified in the laboratory with 0.05 ppm picloram.

At all pH levels a recovery was obtained from the fortified soil which ranged from 60% at pH 7.2 to 96% at pH 11.6.

Having demonstrated the importance of maintaining a high pH during the extraction of low levels of picloram from weathered field samples, a further experiment using the calcium hydroxide extraction was carried out. This extractant was selected in a preliminary experiment because it conveniently buffered 12 different soils of varying pH to pH 12.4. Table 1 shows the recovery of picloram added to the untreated soil in the laboratory prior to extraction with calcium hydroxide solution.

TABLE 1

The mean percentage recovery of picloram from soil fortified in the laboratory and extracted with calcium hydroxide solution

ppm	wt. soil g	µg added	mean µg found	No. of Determinations	Mean % Recovery	S.D.
-	nil	1.25	1.24	3	99.2	5.7
0.01	25	0.25	0.26	6	104.0	5.9
0.05	25	1.25	1.28	6	102.4	3.5
0.10	25	2.5	2.64	5	105.6	2.3
1.00	25	25	25.70	3	103.0	1.1

The method recovered the picloram quantitatively at the levels tested. The reproducibility of the method improved with increasing concentration as shown by the standard deviations. The recovery from the soil slightly exceeded 100%. Table 2 shows the residue obtained from a number of samples taken from a Weed Research Organization field trial on picloram and illustrates the increase in residue obtained at the higher pH.

TABLE 2

The amount of picloram extracted from field treated samples at two pH levels

	ppm	
Sample No.	pH 9.35 (KOH)	pH 12.4 ($Ca(OH)_2$)
1	0.010	0.033
2	0.010	0.033
3	0.007	0.037
4	0.002	0.007
5	0.008	0.044
6	0.002	0.006

A considerable increase in extractable picloram is obtained at the higher pH. Six replicate analyses of sample 5, Table 2 gave a mean of 0.044 ppm with a standard deviation of 0.001 ppm using the calcium hydroxide extraction.

DISCUSSION

The limit of detection of picloram with this soil was 0.001 ppm at all pH levels. It can therefore be assumed that changes in background are not responsible for the increased residues at the higher pH extractions. It would have been useful and interesting to have extended this work to other soils containing higher organic matter contents treated with picloram in the field but these were not available. Apparently the low residual amount of picloram remaining in this soil is tightly bound, hence its existence, and it requires a more stringent extraction procedure than that required for a sample fortified in the laboratory at a similar level. This work illustrates the importance of using a soil containing a field applied, weathered residue for developing methods for the analysis of persistent soil herbicides.

CONCLUSIONS

The efficiency of extraction of low levels of picloram from field treated soil using aqueous systems is dependent on the pH during extraction. Data from laboratory experiments and residue analyses on soil from a field experiment have been used to demonstrate this effect. Saturated calcium hydroxide solutions (pH 12.4) were effective for the extraction of field weathered residues of picloram.

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References

BAUR, J.R., BAKER, R.D., BOVEY, R.W. and SMITH, J.D. Weed Sci., 20, 305 (1972)

CHENG, H.H. J. Agr. Food Chem., 17, 1174 (1969)

CHENG, H.H. Bull. Envir. Contam. Toxicol., 6, 28 (1971)

LEAHY, J.S. and TAYLOR, T. Analyst, 92, 371 (1967)

MERKLE, M.G., BOVEY, R.W. and HALL, R. Weeds, 14, 161 (1966)

MOSEMAN, R.F. and AUE, W.A. Paper presented at the 5th Midwest Regional ACS Conference in Kansas City, Missouri, October 1969

SAHA, J.G. and GADALLAH, L.A. J. Assoc. Offic. Anal. Chem., 50, 637 (1967)

SCHLENK, H. and GELLERMAN, J.L. Anal. Chem., 32, 1412 (1960)