Extraction of Picloram Residues from a Sandy Loam Soil

by

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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.
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°
- Column temperature: 180°
- Carrier gas: 80 ml/min oxygen-free N$_2$
- Detector temperature: 300°
- Detector voltage: pulse mode 150 usec.

<table>
<thead>
<tr>
<th>10% KCl containing KOH</th>
<th>pH of filtrate</th>
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<tbody>
<tr>
<td>nil</td>
<td>7.2</td>
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<tr>
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