Picloram in Soil: Extraction and Mechanism of Adsorption[1]

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Quantitative extraction of pesticides has been a major obstacle in the analysis of pesticides from soils. A study has been designed to examine the various procedures used for extraction of weakly acidic herbicides from soils and to elucidate those factors and possible mechanisms of herbicide adsorption by soils which affect the extraction efficiency. The present report discusses observations on the extraction of picloram (4-amino-3,5,6-trichloropicolinic acid).

Weakly acidic herbicides are generally extracted by one of two procedures. Thus, picloram has been extracted either directly from the soil by an appropriate organic solvent under acid conditions (1, 2), or by a dilute aqueous alkali solution, followed by cleanup of the extract and partitioning of the extracted picloram to an organic solvent under acid conditions (3, 4). Recovery of added picloram from soils by these procedures is often incomplete. Moreover, extensive cleanup is sometimes required before the alkali-extracted picloram can be analyzed by gas chromatography.

Recently, Cheng (5) reported that picloram can be quantitatively extracted from soil under neutral conditions using a 2 N KCl solution. Such procedure has the added advantage of resulting in little organic matter dissolution in normal soils. This procedure has now been modified to permit analysis of the extracted picloram by gas chromatography.

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Materials and Methods

Ten soils having cation exchange capacities ranging from 8.2 to 26.6 me./100 g. of soil, pH values from 3.9 to 7.2, clay contents from 8 to 50%, and organic matter contents from 0.7 to 24.9% were used in this study. Detailed information on these soils was reported previously (5). Selected samples were treated with picloram and stored under refrigeration in moist condition for up to six months or subjected to alternate wetting and drying a number of times over the same interval. These samples were used in examining the effect of 'aging' on the extraction efficiency.

The general procedures used for extraction of picloram from soils and for determination of extracted picloram were as follows: Picloram was extracted from soils with a 2 N KCl solution at pH 7 using a 1:10 (w:v) soil:solution ratio. The KCl extract was adjusted to pH below 2 and partitioned twice with an equal volume of chloroform containing 5% ethanol. The chloroform extract was condensed under partial vacuum in a flash evaporator at 35°C until nearly dry. The condensate containing the extracted picloram was then transferred quantitatively with a small amount of methylene chloride to a test tube and methylated with diazomethane using a modified Schlenk and Gellerman procedure (6, 7). After completion of methylation, the solution was evaporated to complete dryness under an air stream at room temperature. The dried residue was dissolved in a measured amount of methylene chloride and the picloram methyl ester solution was stored in gas-tight vial ready for analysis.

The picloram methyl ester was determined using a gas chromatograph fitted with a 1.5 m. glass column packed with 5% SE 30 on Chromosorb W, and a tritium electron capture detector. The injection port temperature was maintained at 225°C, the oven at 175°C, and the detector at 210°C.

Results and Discussion

Extraction from soils

A basic assumption in all procedures used for extraction of weakly acidic herbicides from soils is that the undissociated molecular form of the herbicide has more affinity for organic solvents, whereas the ionic form prefers the aqueous media. By decreasing or increasing the pH of the system, one can make either the molecular or the ionic form predominant. Picloram has a pK_a of approximately 4.1 (8), thus at pH 2, over 99% of the herbicide is in the undissociated acid, whereas at pH greater than 6, it exists almost entirely as the dissociated anion.

Results obtained by extracting ten soils with 2 N KCl at pH 7 showed that recovery of added picloram ranged from 94 to 100%. The recovery efficiency was not affected by 'aging' the soil for as long as six months either under refrigeration in moist condition or through wetting and drying cycles a number of times. These results compare favorably with extraction efficiencies reported in the literature (Table I).

TABLE I

Comparison of the efficiency of various procedures for extracting picloram from soils

Extraction Solution	% Extraction Efficiency	Reference
Acetone - HCl	75	(1)
Acetone - H_3PO_4	83 - 92	(2)
NaOH	80 - 87	(3)
KOH - KCl	70 - 109	(4)
KCl (pH 7)	94 - 100	

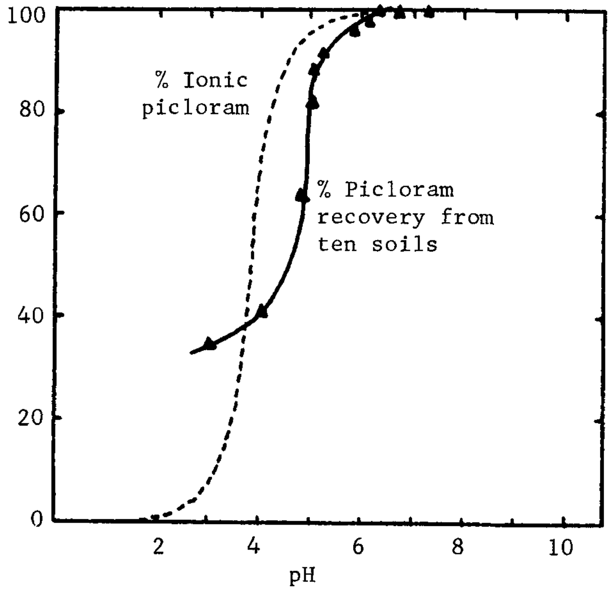
Mechanism of adsorption and extraction efficiency

The importance of adjusting soil pH to 7 before extraction is shown by comparing previous findings (5) with the data obtained for this study. It was shown previously that the percentage recovery of added picloram by extraction with 2 N KCl decreased as soil pH decreased in acid range. However, as shown in Table I, adjusting soil pH to 7 permitted quantitative recovery of added picloram for all soils tested. These findings indicate that the extraction efficiency is governed by the soil pH rather than by the amount of clay or organic matter present in the soil.

The decrease in extractable picloram with decreasing soil pH is also a reflection of an increase of picloram adsorbed by soil under these same conditions. The dependence on soil pH and the reversibility of the adsorption process indicate that picloram adsorption is a general surface phenomenon and does not necessarily involve any specific sites. The predominant mechanism involved is probably the physical adsorption of the undissociated molecules. Little or no adsorption of the anionic form of picloram was evident. The fact that picloram was equally extractable from freshly treated soil as from 'aged' soil provides further evidence for the physical adsorption mechanism.

The dependence of picloram recovery on the soil pH is illustrated graphically in Figure 1. The solid line represents percentage picloram recovery from ten soils which decreased as soil pH decreased. However, when the theoretical percentage of dissociated picloram present at each level (based on picloram $pK_a = 4.1$) was plotted on the same graph, it can be noted that a significant reduction of extraction efficiency occurred at measured soil pH levels at which little undissociated picloram should exist. This discrepancy between the experimental findings and the theoretical adsorption curve can be explained by the fact that the pH at soil particle surfaces, where adsorption takes place, is lower than that in the bulk solution, as reflected by the measured pH values. The displacement of the two curves merely reflects the difference in acidity of the bulk solution from that at soil particle surfaces. The crossing over of the two curves reflects the equilibrium between the adsorbed and the soluble picloram. Even when all the picloram is present in the undissociated form, considerable amount of the pesticide remains soluble.

Figure 1. Effect of soil pH on recovery of picloram from ten soils using 2 N KCl



The phenomenon of enhanced surface acidity has been discussed in the literature (e.g., 9, 10), and its importance in explaining herbicide adsorption by clay minerals has been demonstrated (11, 12, 13). However, previous studies have reported the effects of pH changes on herbicide adsorption for only one or a few clay minerals, and thus have not been able to distinguish between physical adsorption and the binding of herbicides at specific sites. The fitting of all data from the present study on a common curve and the lack of a relationship between adsorption and the clay or organic matter content of the soils further demonstrate that adsorption of picloram is almost entirely governed by soil pH and is not related to the presence of specific binding sites in the soil.

Partitioning into organic solvent

Following extraction of picloram from the soil with 2 N KCl at pH 7, the solution is customarily acidified and the extracted picloram is partitioned into an organic solvent before it is methylated and determined by gas chromatography. A number of solvents were tested for this purpose, using a 1:1 solvent:solution ratio for the partition. The amounts of picloram removed from the KCl solution by different solvents adjusted to various pH levels are shown in Table II. Picloram was found to have a very low affinity for benzene, hexane, and other nonpolar solvents, but a very high affinity for diethyl ether and ethanol at all pH levels. With methylene chloride and chloroform (which was freed of ethanol using basic alumina immediately before use), the undissociated picloram seemed to prefer the organic solvent, whereas the anionic picloram

TABLE II

Efficiency of organic solvents in removing picloram from 2 N KCl solution at various pH

	pH of 2 N KCl solution					
	1	2	3	4	5	6
Organic solvent	% picloram removed					
Benzene	2	--	.2	--	--	0
Methylene chloride	88	82	53	6	0	0
Chloroform (absolute)	90	86	69	21	9	8
Chloroform + 5% EtOH	100	--	100	--	--	95
Diethyl ether	100	--	100	--	--	97

preferred the aqueous medium. The chloroform-ethanol mixture was adopted for routine use because of the ease in handling this solvent.

The efficiency of various procedures for methylating picloram has been studied by Woolson and Harris (14), who reported that diazomethane converted picloram quantitatively to its methyl ester. The gas chromatography procedure used for determining picloram methyl ester is similar to the procedures described in the literature. A relatively low oven temperature was used so that any 2,4-D present in the samples could be determined simultaneously.

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