Determination of Linuron Residue in Soil

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Pre - or postemergence treatment of soil with linuron [3-(3, 4-dichlorophenyl) -1-methoxy-1-methylurea] is used for the control of weeds in vegetables, cotton, corn and other crops. Application at the rate of 2-3 lb/acre may result in its persistence in some soils for more than one year (FRYER and EVANS 1969).

Most methods for the analysis of linuron involve gas chromatography of either the unchanged herbicide (McKONE and HANCE 1968, McKONE 1969, KATZ and STRUSZ 1969, LASKI and WATTS 1973) or its halogenated herivatives (THIER 1972) or derivatised hydrolysis products (GUTENMANN and LISK 1964, BAUNOK and GEISS-BUEHLER 1968, COHEN and WHEALS 1969). A major problem encountered in the gas chromatographic analysis of linuron has been its on column decomposition (SPENGLER and HAMROLL 1970, COCHRANE and PURKAYASTHA 1973). Although some workers report the analysis of intact linuron using various columns (McKONE and HANCE 1968, McKONE 1969), others observed that some thermal decomposition of the herbicide always occurred on the column (SPENGLER and HAMROLL 1970). KATZ and STRUSZ (1969) used short column (41 cm x 0.6 cm) to reduce thermal decomposition. In view of the conflicting reports in literature, it was thought necessary to further examine thermal decomposition of linuron and to develop a reliable and sensitive gas chromatographic procedure for the analysis of intact linuron. Since a quantitative extraction of herbicide is essential to studies of the persistence of linuron in soil, the factors influencing the extraction of linuron from soil were also studied.

Materials and Methods

Chemicals. Solvents used were reagent or pesticide grade. Recrystallized linuron reference standard was supplied by Du Pont, Wilmington, Del.

Soils. the soils studied were surface samples selected to provide a range of texture and organic matter content (Table 1). They were obtained from the experimental plots which had known

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history of linuron treatment. The samples were air-dried at room temperature, ground to pass through a 2 mm sieve and mixed thoroughly.

TABLE 1

Composition and pH of Soils

Soil Type	Composition %				pH
	Organic Matter	Clay	Silt	Sand	
Fox Sandy Loam	1.1	5.1	6.5	88.4	6.0
Regina Heavy Clay	4.2	69.4	25.3	5.3	7.7
Organic	76.0	--	--	--	6.4

Extraction methods. (a) Mechanical shaker: Ten g of soil was shaken for 1 hour on a mechanical shaker with 50 ml of the solvent or solvent mixture. The supernatant liquid was filtered, the residue washed with the same solvent (15 ml x 3) and filtered. The combined filtrate was concentrated to about 40 ml in a rotary evaporator and diluted to 50 ml in a volumetric flask with the solvent.

(b) Blender: Ten g of soil was blended at high speed for 5 min with 50 ml methanol. The mixture was filtered and the residue and container were washed with methanol (15 ml x 3). The filtrates were combined, concentrated to about 40 ml in a rotary evaporator and diluted to 50 ml in a volumetric flask with methanol.

(c) Soxhlet: Ten g of soil was extracted with 80 ml methanol in a Soxhlet extractor for 6 hours. The extract was concentrated to about 40 ml in a rotary evaporator and diluted to 50 ml in a volumetric flask with methanol.

(d) Extraction of soil in presence of water: To study the effect of water on the recovery of linuron residue, appropriate amounts of water were added to ten g of soil and mixed thoroughly. The mixture was allowed to stand at room temperature for 1 hour in stoppered flask and then extracted with 50 ml methanol using the mechanical shaker method. To determine the effect of time of contact with water on the recovery of linuron residue, an appropriate amount of water was added to 10 g of soil, mixed thoroughly and allowed to stand at room temperature in stoppered flasks. At the end of the specified contact time the mixture was extracted with 50 ml methanol using the mechanical shaker method.

Cleanup of soil extract. A 10 ml aliquot of the soil extract was transferred with a pipette to a round bottom flask and was evaporated to dryness in a rotary evaporator at about 35°C. The residue was dissolved in 6% diethyl ether in hexane

(5 ml) and quantitatively transferred to a Florisil column (2.5 cm diameter, 20 g Florisil 60/100 PR grade, prewashed with 100 ml hexane) topped with 2.4 cm of anhydrous sodium sulfate. The column was first eluted with 200 ml of 6% diethyl ether in hexane and the elute discarded. The column was then eluted with 400 ml of 20% diethyl ether in hexane. During the cleanup procedure the flow rate was maintained at about 5 ml/min. The eluate was evaporated just to dryness and taken up in 10 ml hexane. An aliquot of this solution was injected into the gas chromatograph. The solution was diluted or concentrated where necessary so that the injected volume contained an amount of linuron within the linear range of the detector.

Recovery of linuron from fortified soil. The soil sample (10 g) was fortified with linuron at 0.1 ppm level. The solvent (hexane) was allowed to evaporate and the soil was mixed thoroughly. Linuron was then extracted with 50 ml methanol using the mechanical shaker method.

All extraction and recovery experiments were conducted in duplicate and average of duplicate analyses are reported.

Gas chromatography. The gas chromatograph was a Pye series 104, model 74 fitted with a ^{63}Ni electron capture detector. The column was a 38 cm x 0.6 cm glass tube packed with 1.5% XE-60 coated on 80-100 mesh chromosorb WHP. The operating conditions were: injector port temperature control turned off; column and detector temperatures, 160°C and 270°C, respectively; detector operated in the pulse mode at 500 μ sec and at an amplifier attenuation of 5×10^{-10} A; carrier gas (nitrogen) flow rate 50 ml/min. The column was conditioned at 225°C for 2 days and treated with silyl 8 before connecting to the detector.

In preliminary experiments, injections were made with a Hamilton Syringe so that either the tip of the needle just extended only into the glass wool prepacking (5 cm), or it just touched the surface of the packing (7 cm). The injector block temperature control was varied from off position (150°C) to 220°C.

The concentration of linuron in the soil extract was determined by comparing the peak height with that of a reference standard. The identity of the desired peak was proved by comparing its mass spectrum with those of pure linuron and by co-chromatography with the latter. For the mass spectrum, an aliquot of the above solution containing approximately 1-2 μg of linuron was injected into a Pye gas chromatograph interfaced with a Du Pont Model 490 mass spectrometer by a jet separator.

Thermogravimetric analysis. The pure linuron standard was pyrolyzed in a platinum crucible in stagnant air or in nitrogen (flow rate-100 ml/min) on a Stanton Recording Thermobalance. The rate of heating was constant at 5°C per min. Thermogravi-

metric curves were obtained by plotting the weight loss vs temperature.

Results and Discussion

In the preliminary experiments a number of gas chromatographic columns including 3% OV-101 (92 cm and 38 cm), 3% OV-17 (1.5 m), 3% Silar 5 CP (1.5 m), and 1.5% XE-60 (1.5 m and 38 cm) were examined in terms of peak elution pattern, effect on EC detector sensitivity and retention time. The shorter columns (38 cm) packed with 1.5% XE-60 or 3% OV-101 were better in performance to the other columns that were tried. In the case of longer columns the chromatograms showed tailing of the parent major peak, the appearance of subsidiary peaks, or low response of linuron. The 1.5% XE-60 column was preferred to that of 3% OV-101 due to the higher sensitivity. For a 50% full scale deflection, samples of 0.3 ng and 0.8 ng, respectively, were required for the two columns. Under the GC conditions described and using 1.5% XE-60 column (38 cm), only one peak was observed on the gas chromatogram with a retention time of 3.5 min. This compound was shown to be intact linuron by its mass spectrum which had a strong parent ion peak at m/e 249. The response of the electron capture detector was linear in the range of 0.05 ng to 0.4 ng and the least detectable amount of linuron (2 x noise level) was of the order 0.28×10^{-12} g/sec. The thermogravimetric analysis, based on the loss of weight on heating, revealed that decomposition of linuron started at 122°C in air and 116°C in nitrogen, and increased rapidly after about 170°C and 165°C, respectively (Fig. 1). The decomposition of linuron was complete by about 220°C.

It was found that injection onto the silonized glass wool prepacking (5 cm needle) resulted in poor peak shape and longer retention time as compared with direct on-column injection (7 cm needle). This is shown in Figure 2a. It was also found that the temperature of the injection port played an important role in the decomposition of linuron. No decomposition was observed with the injector heater control turned off and on-column injection (Fig. 2a). In agreement with the thermogravimetric analysis, temperatures above 165°C resulted in decreased response and appearance of secondary peaks (Fig. 2a and b), indicating decomposition. Eventually with an injector block temperature of 220°C virtually no linuron could be detected. Thus the use of short GC column, on-column injection and injection temperature 165°C eliminated or kept to a minimum the decomposition of linuron. The results of McKONE (1969) and McKONE and HANCE (1968) where injector temperature of 265°C was used are difficult to rationalize in terms of no decomposition of linuron.

Recoveries of linuron residues from the fortified untreated soil samples (10 g) at 0.1 ppm levels ranged from 80-97% (Table 2) While this is not a true indication of extraction efficiency as applied to field treated soil, it does show that little loss of

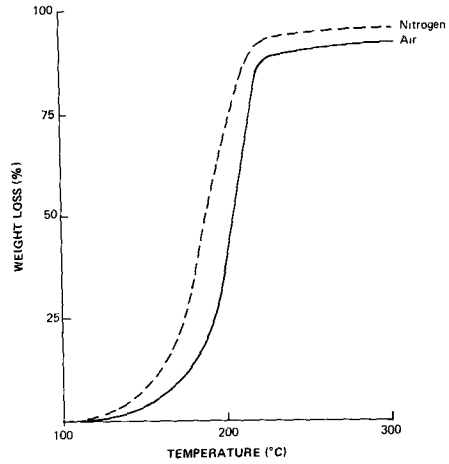

Figure 1. Thermogravimetric curves for linuron.

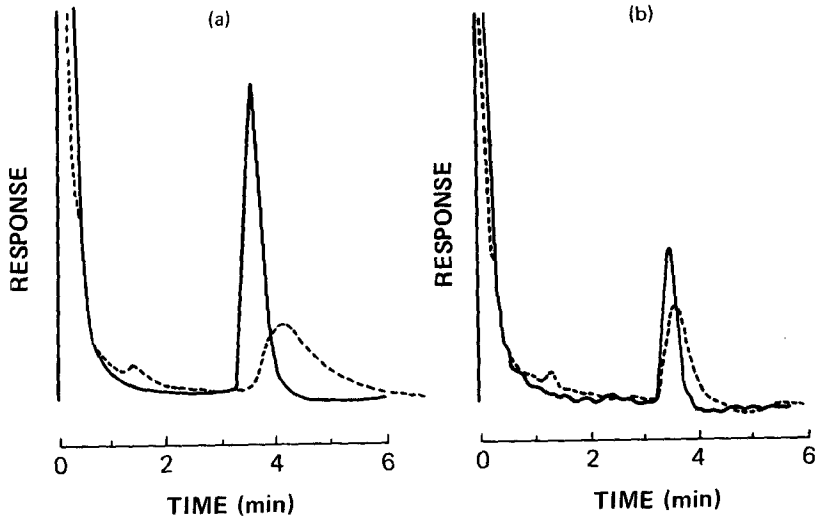

Figure 2. Gas chromatograms of linuron. (a) injector heater off; (b) injector heater at 190°C; ———— on-column injection (7 cm needle); ---------injection onto the glass wool packing (5 cm needle). Other conditions: glass column - 38 cm x 0.6 cm packed with 1.5% XE-60 on chromosorb WHP; column temperature 160°C; ^{63}Ni electron capture detector temperature 270°C; carrier gas (nitrogen) flow rate 60 ml/min; pulse period 500 μ sec; attenuation 5 x 10^{-10}A.

TABLE 2
Recovery of linuron from soils fortified at 0.1 ppm level

Soil Type	% Recovery
Fox Sandy Loam	97
Regina Heavy Clay	92
Organic	80

linuron was experienced during the working procedures subsequent to extraction. The blank samples of the two mineral soils showed no co-extractive peaks interferring with linuron. The background interference for the organic soil was 0.03 µg per g sample (i.e. 0.03 ppm). The recovery value of 110% was corrected to 80% by subtracting the interference level observed in the blank sample of organic soil. The limit of detection of the method is about 0.1 ppm. However, if required this detectability may be increased by concentrating the final solution (10 ml) to some smaller volumes.

The chromatographic tracings of the check and linuron treated soil samples obtained from the experimental plots are shown in Figure 3. Several unknown peaks appeared in the chromatograms but they did not interfere with linuron peak (retention time - 3.5 min). The latter gave a mass spectral parent peak at m/e 249 and was shown to be intact linuron.

The relative extraction efficiency of various solvent systems is compared in Table 3. Methanol gave higher recovery of linuron residues from air-dried field treated soils than any other solvent or mixture of solvents. McKONE (1969) also obtained highest recovery of linuron when the soil was extracted with methanol. The extraction efficiency increased with increase in dielectric constant (ε) of the solvent. For example, the solvent order for increasing extraction efficiency of linuron residues from three soils was: methanol ($\varepsilon = 33.6$) $>$ ethanol ($\varepsilon = 24.3$) $>$ acetone ($\varepsilon = 20.7$) $>$ methylene chloride ($\varepsilon = 9.1$). However, the variation in the extraction efficiencies of these solvents was not related to the solubility of linuron. Linuron is more soluble in acetone than methanol but the latter extracted more linuron from the soil than the former. The method of extraction influenced the recovery of linuron residue from a given soil (Table 4). Extraction of the air-dried soil by mechanical shaking gave the highest recovery of linuron residue. Blending for 5 min extracted more herbicide than Soxhlet extraction. The latter also extracts appreciable co-extractive from soils.

Table 5 shows the effect of moisture on the recovery of linuron residues from the three field treated soils. It would appear that certain amount of moisture in mineral soils does

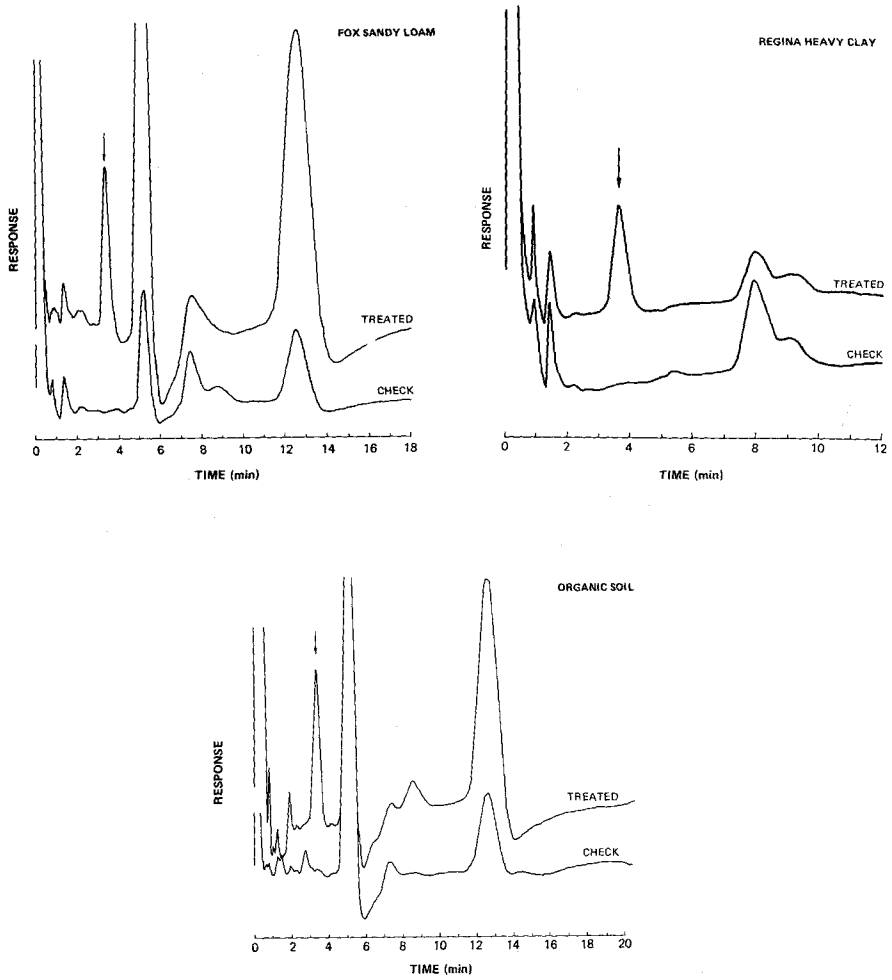

Figure 3. Gas chromatograms from determination of linuron in soils. GC conditions as in Fig. 2a (on column injection).

facilitate extraction. Thus addition of 20% and 30% water to the air-dried Fox Sandy Loam and Regina Heavy Clay soils increased recovery by about 25% and 41%, respectively. However, further addition of water reduced the residue recovery. Thus a total moisture content of between 20-30% for mineral soils would appear satisfactory for good extraction. The residue recovery was not affected by the addition of water to organic soil. The presence of 75% of water in this soil gave only a 2% increase in the residue recovery. Furthermore, increasing the time of contact with water from 1 hour to 3 hours increased the residue recovery by about 3.4% from this

TABLE 3

Effect of solvent on the recovery of linuron residues from the air-dried soil (mechanical shaker method)

Solvent	Linuron (ppm)		
	Fox Sandy Loam	Regina Heavy Clay	Organic
Acetone	0.52	0.49	1.03
Acetone/hexane (1:1)	0.50	0.58	1.00
Hexane/2-Propanol (1:1)	0.26	0.18	0.46
Hexane/2-Propanol (2:1)	0.28	0.27	0.29
Methylene Chloride	0.49	0.17	0.79
Ethanol	0.83	0.51	2.68
Methanol	1.10	0.68	3.21

TABLE 4

Effect of extraction method on the recovery of linuron residues from the air-dried soil by methanol

Description of Method	Linuron (ppm)		
	Fox Sandy Loam	Regina Heavy Clay	Organic
Mechanical shaker, 1 hr.	1.10	0.68	3.21
Soxhlet, 6 hr	0.48	0.49	1.50
Blending, 5 min	0.90	0.60	1.80

TABLE 5

Effect of the amount of water added to the air-dried soil on the recovery of linuron residues by methanol (mechanical shaker method)

Water Added %	Linuron (ppm)		
	Fox Sandy Loam (0.5)[a]	Regina Heavy Clay (7.6)[a]	Organic (14.3)[a]
5	1.21	--	--
10	1.22	--	--
15	1.31	--	--
20	1.36	0.81	--
25	1.28	--	3.03
30	1.21	0.96	--
40	1.16	0.85	3.16
50	1.13	0.82	3.24
75	--	0.72	3.27
100	--	0.68	3.01
150	--	--	2.80

[a]Figures in parentheses are % moisture in the air-dried soil.

soil (Table 6). The time interval between the addition of water to the air-dried mineral soils and extraction by methanol had little affect on the recovery of linuron residue (Table 6).

TABLE 6

Effect of time of contact with water on the recovery of linuron residues from the moist soil by methanol (mechanical shaker method)

Time of contact (hr)	Linuron (ppm)		
	Fox Sandy Loam (20% Water)	Regina Heavy Clay (30% Water)	Organic (75% Water)
1	1.36	0.96	3.27
3	1.14	0.90	3.38
6	1.11	0.90	3.09
12	1.10	0.92	3.02
24	1.10	0.90	3.17

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