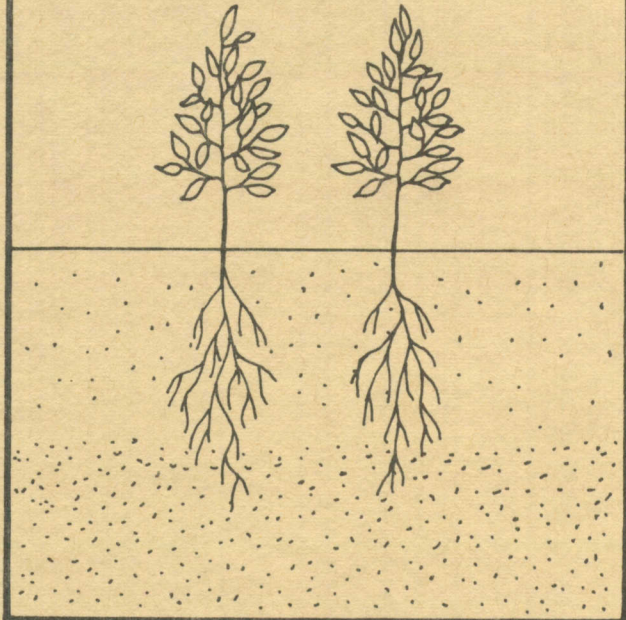
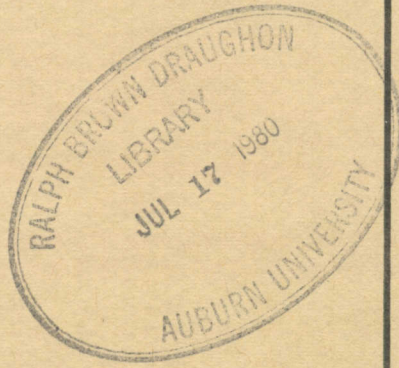


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LEACHING OF PICLORAM & NITRATE IN TWO ALABAMA SOILS



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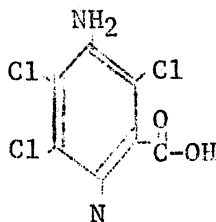
Leaching of Picloram and Nitrate in Two Alabama Soils^{1/}

A. E. Hiltbold, B. F. Hajek, G. A. Buchanan, and C. E. Scarsbrook^{2/}

INTRODUCTION

Picloram^{3/} (4-amino-3,5,6-trichloropicolinic acid) is an extremely potent herbicide used for control of perennial broadleaved plants in non-cropland areas. It is formulated as a water soluble potassium salt and is registered for application in foliage spray mixtures with 2,4-D or 2,4,5-T. The potassium salt is available also as a granular product for spot or broadcast treatment of soil over the roots of woody plants to be controlled. Liquid formulations are usually applied at 0.5 to 1.5 lb acid equivalent (ae)/A. The granular material is applied at 6 to 8 lb ae/A. While grasses are relatively tolerant of picloram, most broadleaved species are highly susceptible. Many legumes show injury symptoms at picloram concentrations as low as 1 ppb in soil.

Picloram has the following structural formula:



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^{3/} Tradenamed "Tordon" manufactured by Dow Chemical Co., Midland Michigan. Mention of a trademark does not signify its approval by Auburn University Agricultural Experiment Station.

The acid is soluble to the extent of 430 ppm in water at 25C, but the potassium salt will dissolve to the extent of 40 g/100 ml water. Picloram has a pK of 3.6 and, therefore, the proportion of ionized to non-ionized picloram decreases with decreasing soil pH. Minimum soil adsorption of picloram has been observed in neutral, light textured soils low in organic matter. Resistance to leaching is correlated with adsorption. The mobility of picloram decreases with decreasing pH, increasing organic matter, and increasing levels of hydrated iron and aluminum oxides (1). The low vapor pressure of picloram (6.1×10^{-7} mm at 35C) renders the herbicide essentially non-volatile. It has a low acute oral toxicity ($LD_{50} = 8,200$ mg/kg body weight of rats).

Picloram is degraded slowly by soil microorganisms. Its decomposition in soil is at rates similar to the urea and triazine herbicides. The percent decomposition of picloram decreases with increasing concentration according to half-order kinetics. Estimated half-order constants, $K_{1/2}$, range from about 0.2 in colder, drier areas to 1.0 in hotter, wetter areas. Starting with initial rates of 1 oz and 2 lb/A, the time required for the herbicide to decompose to a negligible level (0.01 oz/A) varies from 4.5 months to 4.6 years for a half-order constant of 0.2 and from 0.9 to 11 months for a half-order constant of 1.0 (1).

The persistence of picloram, its mobility in surface and percolating water, and its phytotoxicity at extremely low rates present an unusual situation as to potential environmental impact of a herbicide (3). Research reported here was undertaken with the objective of determining the leaching and dispersion characteristics of picloram in two Alabama soils. Since nitrate is a mobile anion of significance both in crop production and ground water quality it was selected as a comparison for picloram in field

experiments. The subject of nitrate in soil, water, and plants has recently been reviewed (4).

MATERIALS AND METHODS

Leaching of picloram was determined in field plots at Wiregrass and Sand Mountain substations on Dothan loamy sand and Hartsells fine sandy loam, respectively. The potassium salt of picloram was applied as broadcast spray at 10 pounds acid equivalent per acre on disked and smoothed soil. Two nitrate treatments (200 and 800 lb N/A from NaNO_3) and an unamended check were included in complete randomized blocks with 4 replications. Experimental sites were flat. Furrows were turned in borders and alleys between plots to prevent surface contamination. Plots were not planted. Picloram and nitrate applications were made on September 14, 1971 and April 12, 1972 at the Wiregrass Substation and on October 12, 1971 at Sand Mountain Substation. Daily rainfall was recorded at each location. Soil samples were collected at intervals over a 16-month period at Wiregrass and over 9 months at Sand Mountain for determination of picloram and nitrate. A hydraulic core sampler mounted on a truck provided a single core profile to 8 ft depth on each plot at each sampling date. Bulk density of each depth interval was measured, then the samples were screened and prepared for picloram and nitrate analysis. Nitrate values reported are measured values from treated plots minus nitrate measured in control plots.

Picloram was determined in a soil bioassay using Bragg soybeans. Weighed portions of each soil sample were diluted with 400 g of picloram-free soil to provide concentrations estimated to reduce the dry weight of soybeans 50 percent relative to controls. Seven seeds probably preferred, were planted in each soil sample. At 1 week the plants were

thinned to the best four and fertilized with a N-P-K solution. At 3 weeks the tops were cut at the level of the cotyledons and the plant material dried and weighed. Soybean yields in unknowns were compared to those in standards carried simultaneously to obtain picloram concentrations.

The standard response curve of soybeans grown at various concentrations of picloram in soil is shown in Figure 1. The sensitivity of soybeans to picloram (50 percent growth reduction with 1.1 ppb in soil) required considerable dilution of field samples to reduce picloram levels to this response range. For example, as little as 0.2 g of soil containing 2 ppm of picloram was sufficient in a 400-g soil blank to establish 1 ppb in the sample for bioassay. At the other extreme, a 40-g sample of field soil diluted to 400 g was capable of detecting 0.01 ppm picloram. In bioassaying unknowns, each sample was diluted 10-fold in a preliminary bioassay to aid in selecting more appropriate dilutions. On the basis of injury observed in the preliminary series, three dilutions were chosen to bracket the suspected concentration.

Nitrate concentration was determined by extraction of 50-g soil samples with water and distillation as NH_3 after reduction with Devarda's metal.

RESULTS AND DISCUSSION

Dothan loamy sand

Six samplings of field plots on Dothan loamy sand were made at the Wiregrass Substation after application of picloram. Percentage recovery of the applied picloram was generally low, ranging from about 20 percent to 103 percent among the profiles sampled. This may result from factors such as sampling variation within the plot, loss of picloram by degradation and error in bioassay.

While the amounts of picloram recovered within profiles varied considerably among replications, the vertical distribution was similar. Averaging across the replications at each sampling date provided a view of the progressive downward movement with time and cumulative rainfall (Figure 2).

Distribution of nitrate with depth in Dothan loamy sand for the 200 and 800 lb N/A rates is shown in Figure 3. The 6 sampling dates extended over a 16-month period. Comparison of cumulative rainfall and the depth at which the bulk of nitrate occurred in the profile shows that the zone of maximum nitrate moved downward about 1 inch for each 1 inch of rainfall received during the fall and winter following application in September, 1971. During the summer and fall 1972, however, nitrate movement slowed considerably despite accumulating rainfall. The penetration of nitrate from the 200 lb N application proceeded at about the same rate as that from the 800 lb N rate. Picloram movement was similar to that of nitrate, except for the tendency of picloram to be retained in the surface foot of soil while nitrate was thoroughly removed by leaching. This retention of picloram in the surface soil is probably associated with organic matter.

The movement of picloram and nitrate applied in the spring (April 12, 1972) to Dothan loamy sand was measured in duplicate soil profiles taken 2 ft apart on July 20, 1972. Picloram distribution on this date is shown in Figure 4 and nitrate in Figure 5 and Figure 6. The data show considerable variation in amounts of picloram and nitrate recovered in soil cores taken only 2 ft apart, however, the vertical zones of maximum concentration were similar. The penetration depth of nitrate averaged slightly greater than the cumulative inches of rainfall. Picloram leaching, on the other hand, was somewhat less than was nitrate. As observed

in samplings of the fall application, picloram remained in the surface soil after nitrate had been completely leached.

Hartsells fine sandy loam

Picloram concentration with depth in Hartsells fine sandy loam at Sand Mountain Substation is shown in Figure 7. The movement of picloram in Hartsells soil appears more rapid than in Dothan soil with comparable amounts of rainfall.

The average distribution of nitrate at each sampling date is plotted in Figure 8 for both 800 lb N and 200 lb N treatments. The penetration of nitrate into Hartsells soil was similar to Dothan, that is, at the rate of about 1 inch depth for each 1 inch of rainfall received.

Nitrate leaching model

In both Dothan and Hartsells soils nitrate distribution is essentially symmetrical around a peak concentration. This indicated that the equation

$$C/C_0 = \frac{1}{2} \left[\operatorname{erfc} \frac{x-vt}{2(Dt)^{1/2}} \right] \quad [1]$$

in which x = depth
 v = ion velocity
 t = time
 D = dispersion coefficient
 erfc = error function
 C/C_0 = relative concentrations

often used to predict anion distribution in laboratory soil columns (2), may be used to model nitrate depth distribution patterns in the field. The equation was modified to include factors for the presence of an initial residual nitrate content before application. In addition, a factor was included for incorporation of added nitrate into the surface soil layer at time zero. When these factors are added the equation takes the following form:

$$C = \left\{ \frac{C_0 - C_L}{2} \left[\operatorname{erfc} \frac{x - \frac{l_s + \frac{R}{\theta}}{b}}{2(Dt)^{\frac{1}{2}}} \right] + C_L \right\} - \left\{ \frac{C_0}{2} \left[\operatorname{erfc} \frac{x - \frac{R}{\theta b}}{2(Dt)^{\frac{1}{2}}} \right] \right\} \quad [2]$$

- C = concentration of NO₃-N in the soil solution
- C₀ = amount of NO₃-N added
- C_L = concentration of residual NO₃-N
- erfc = error function complement
- x = depth
- l_s = thickness of soil layer into which C₀ is incorporated
- R = inches (or cm) of rain that is effective in leaching
- θ = pore volume fraction
- b = adsorption factor equal to 1 if no adsorption occurs
- D = dispersion coefficient (.01 cm²/hr)
- t = time since leaching began after C₀ was applied

Figures 9 and 10 show the calculated distribution for the 800 lb N/A application rate on Dothan and Hartsells soils, respectively. The March and April, 1972 sampling dates were used to compare measured values to the calculated line. For these calculations the observed inch per inch relationship for effective rainfall leaching was used. It was assumed that the added nitrate was incorporated in the surface inch of soil. The initial residual nitrate and bulk density was taken as the average in check plots to 48 inches. The comparison of calculated values to concentrations observed at depths from four replications shows that the calculated line is within the variation from the field at most depths.

CONCLUSIONS

- (1.) Nitrate moved downward in Dothan loamy sand and in Hartsells fine sandy loam at the rate of about 1 inch per 1 inch of rainfall received.
- (2.) Some picloram was retained in surface soil whereas all nitrates were eventually leached below the surface soil.
- (3.) The picloram that was leached below the surface soil moved downward at about the same rate as nitrate.
- (4.) The rates of leaching 200- and 800-lb N/A applications are essentially equal.
- (5.) A mathematical model of nitrate leaching was developed that fit the observed leaching in these soils within the range of field sampling precision.

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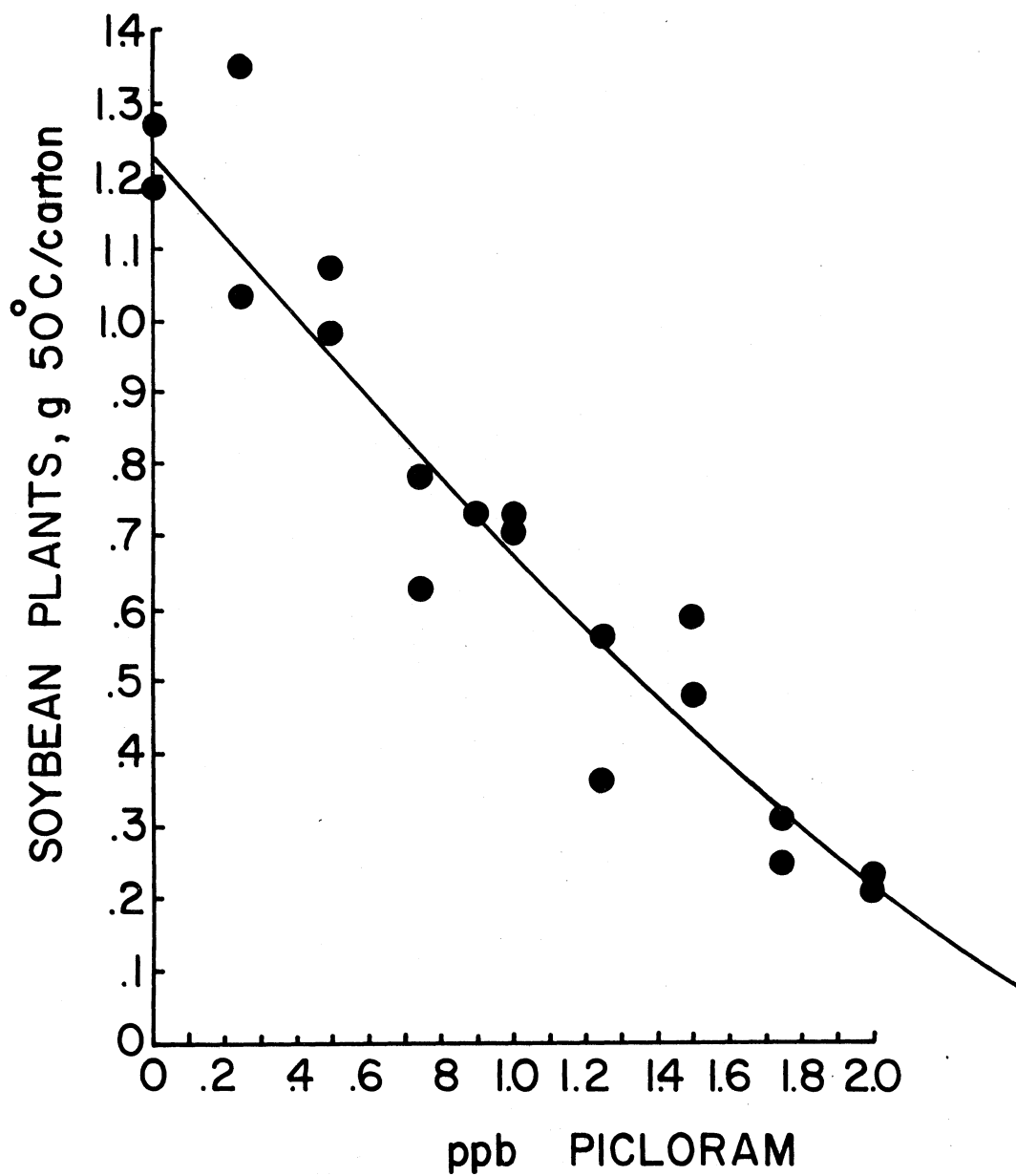


Fig. 1. Dry Weight Yield of Soybean Plants Grown for 3 Weeks in Soil Containing Picloram.

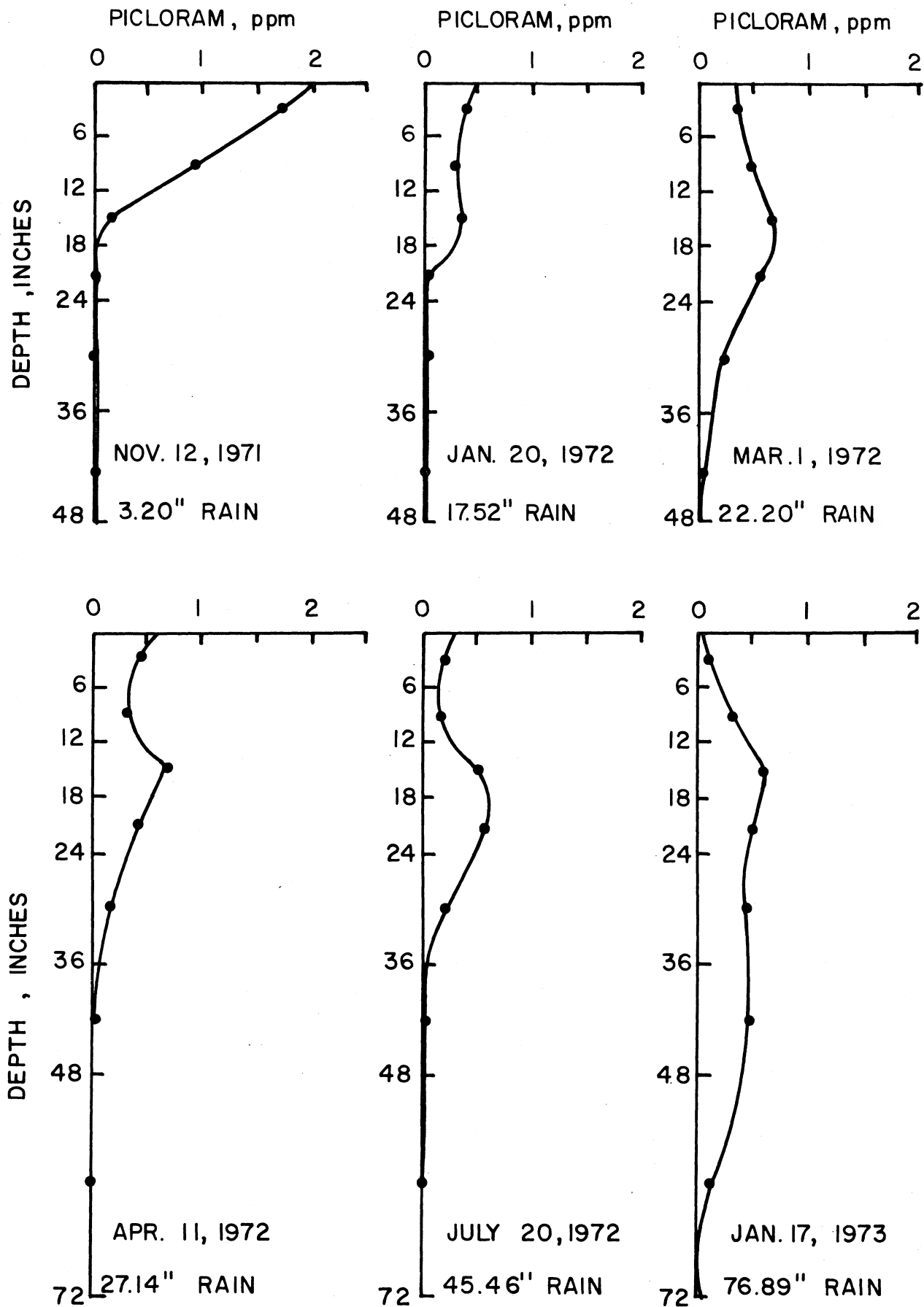


Fig. 2. Distribution of Picloram with Depth, Dothan l.s. after Application on September 14, 1971.

mean of 4 replications

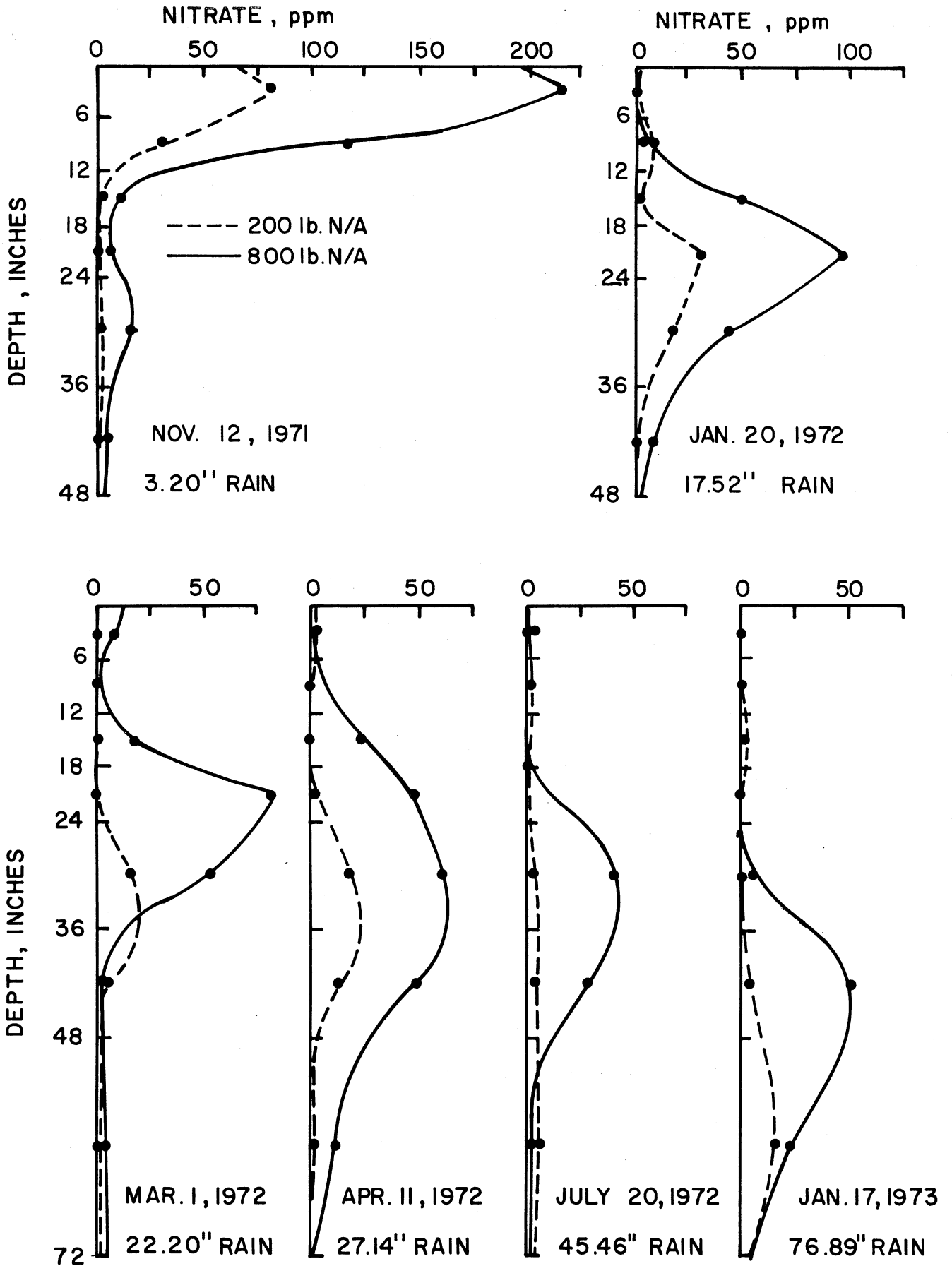


Fig. 3. Distribution of Nitrate with Depth, Dothan l.s. after Application of 200 and 800 lb N/A on September 14, 1971. mean of 4 replications

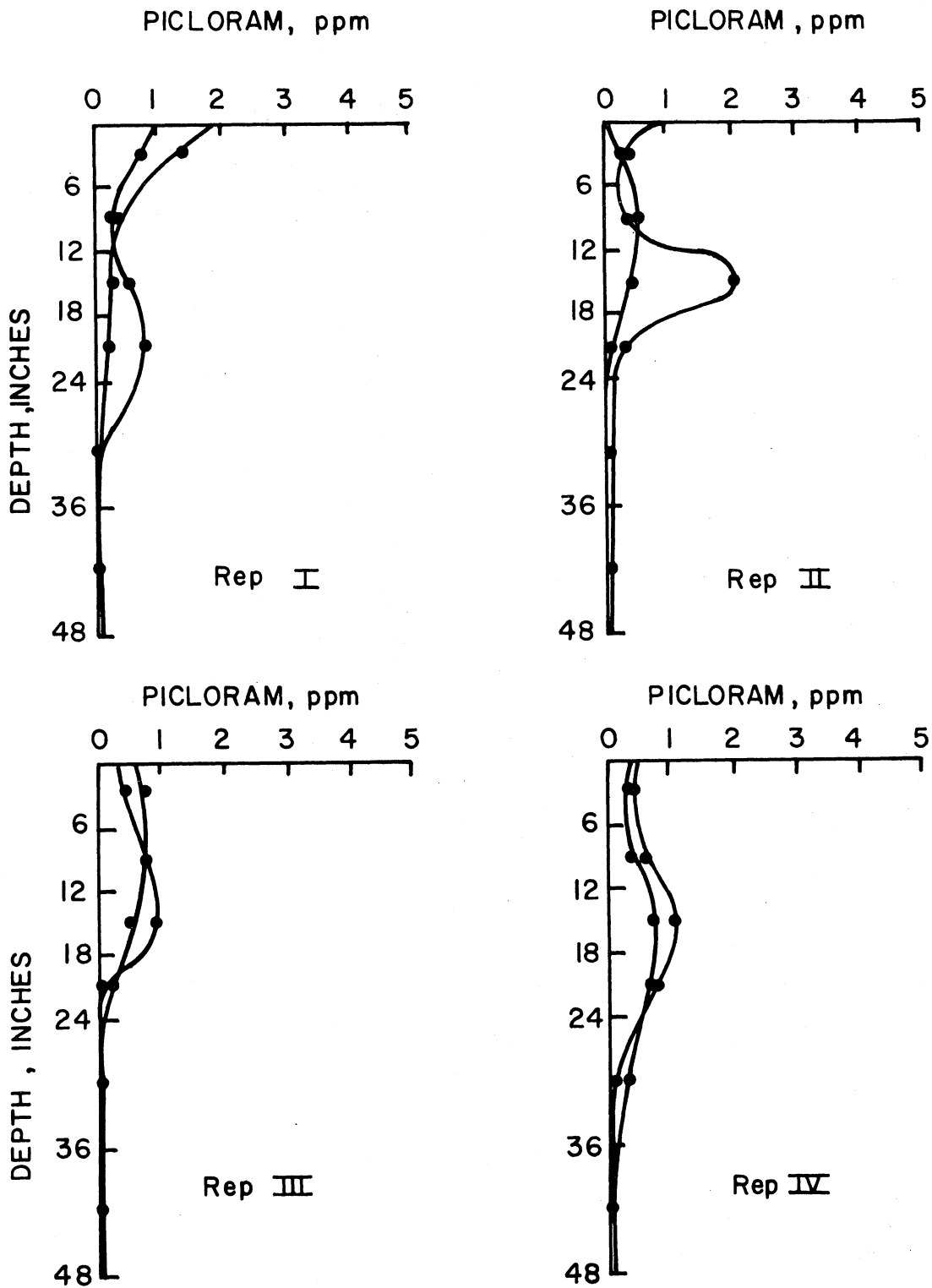


Fig. 4. Distribution of Picloram with Depth, Dothan l.s. 2 profiles per plot taken 2 ft. apart on July 20, 1972. 18.32" rainfall since application on April 12, 1972.

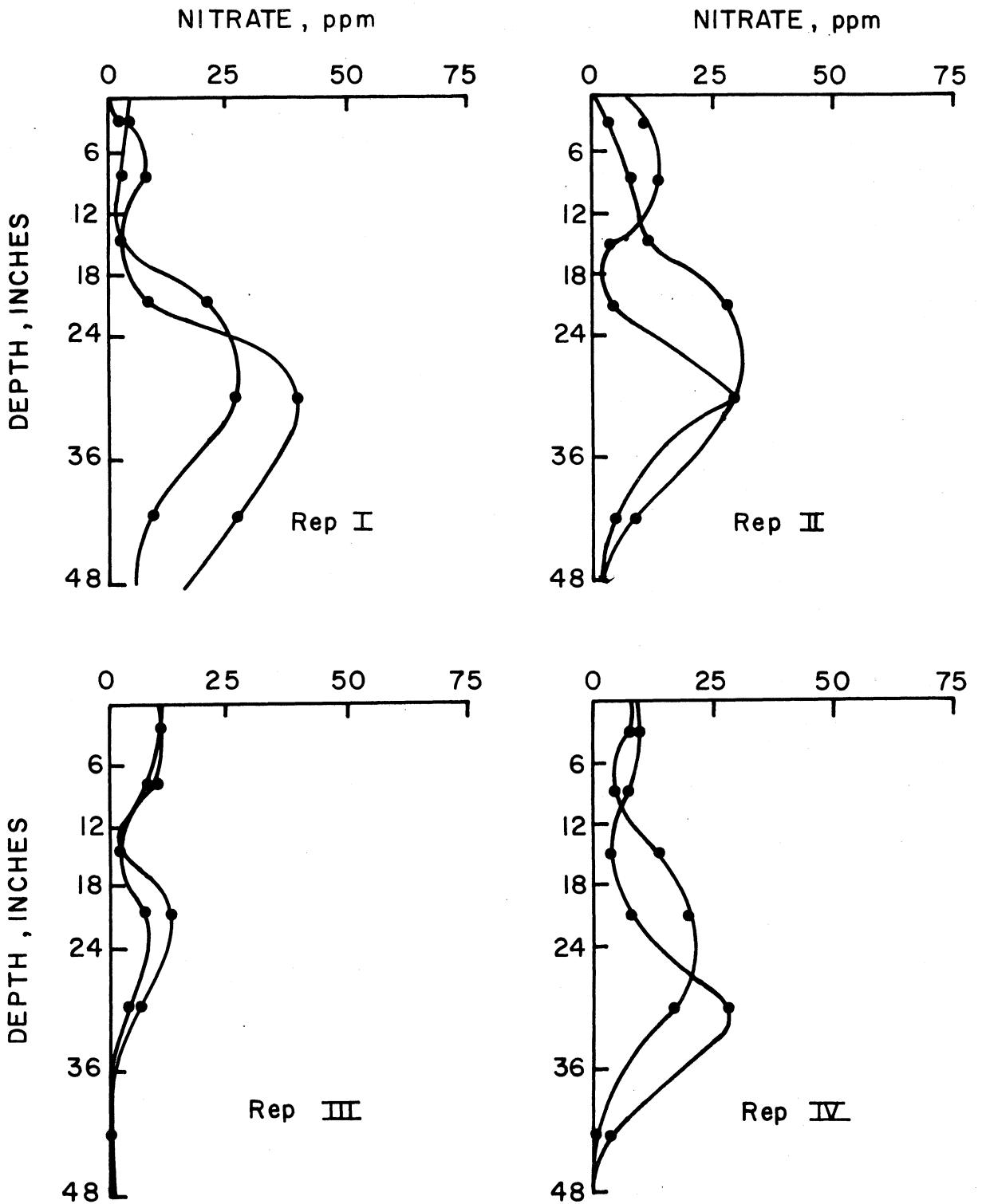


Fig. 5. Distribution of Nitrate with Depth, Dothan 1.s. 2 profiles per plot taken 2 ft. apart on July 20, 1972. 200 lb. N/A applied April 12, 1972. 18.32" rainfall.

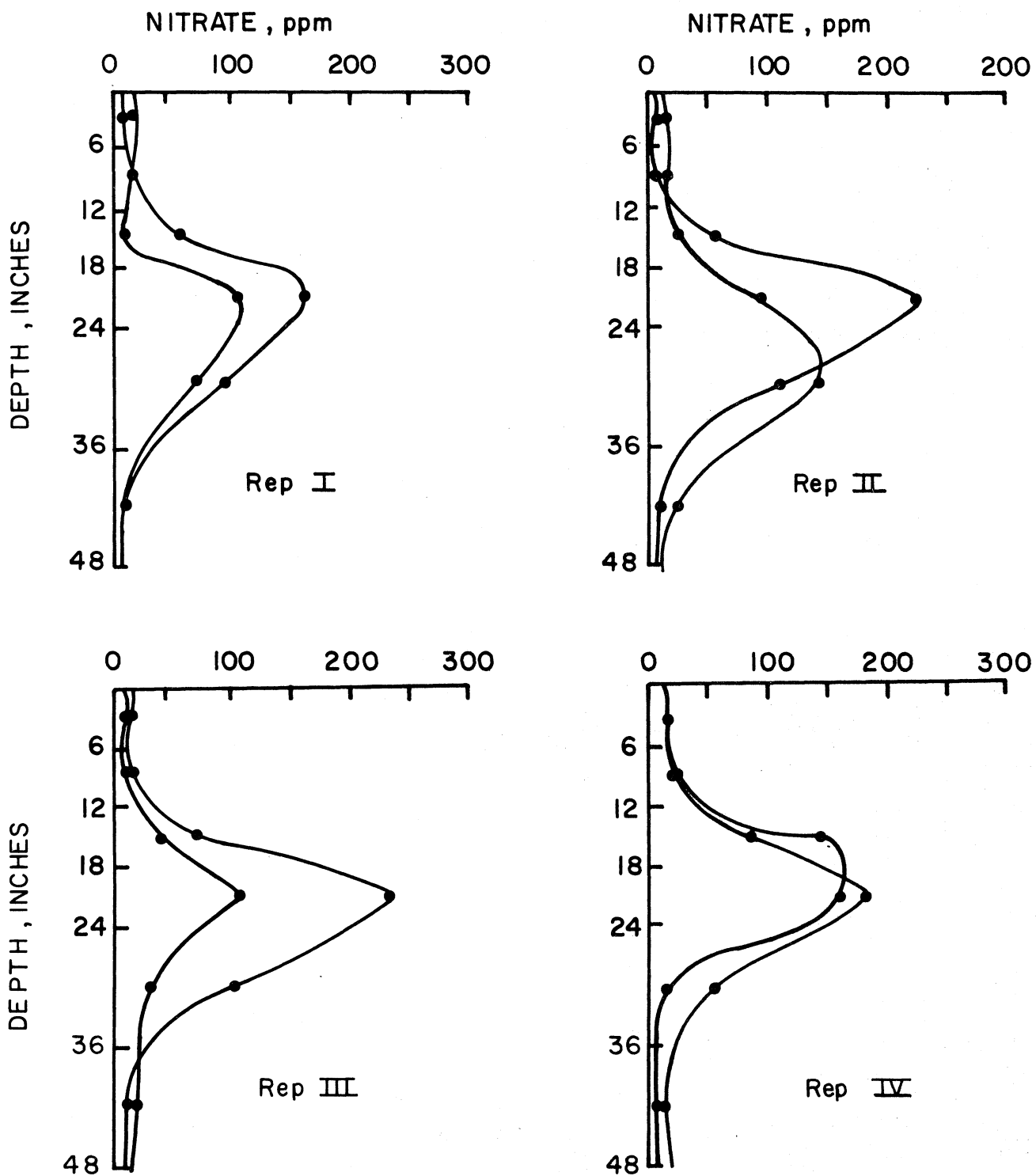


Fig. 6. Distribution of Nitrate with Depth, Dothan l.s. 2 profiles per plot taken 2 ft. apart on July 20, 1972. 800 lb. N/A applied April 12, 1972. 18.32" rainfall.

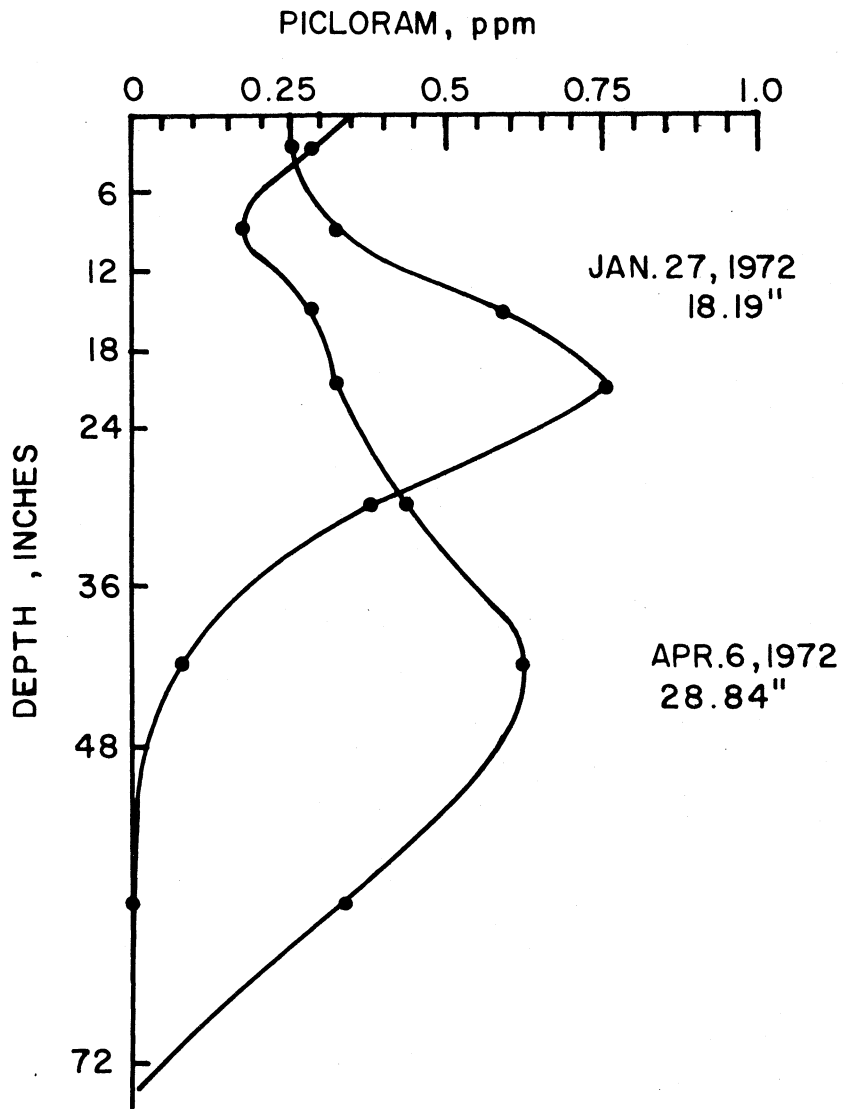


Fig. 7. Distribution of Picloram with Depth, Hartsells fsl. after application on October 12, 1971.
mean of 4 replications

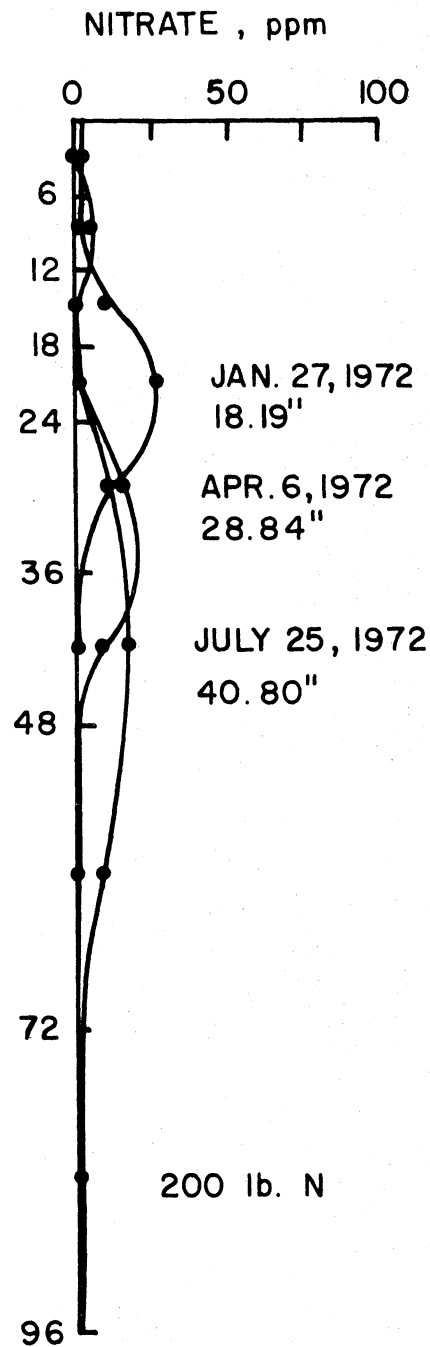
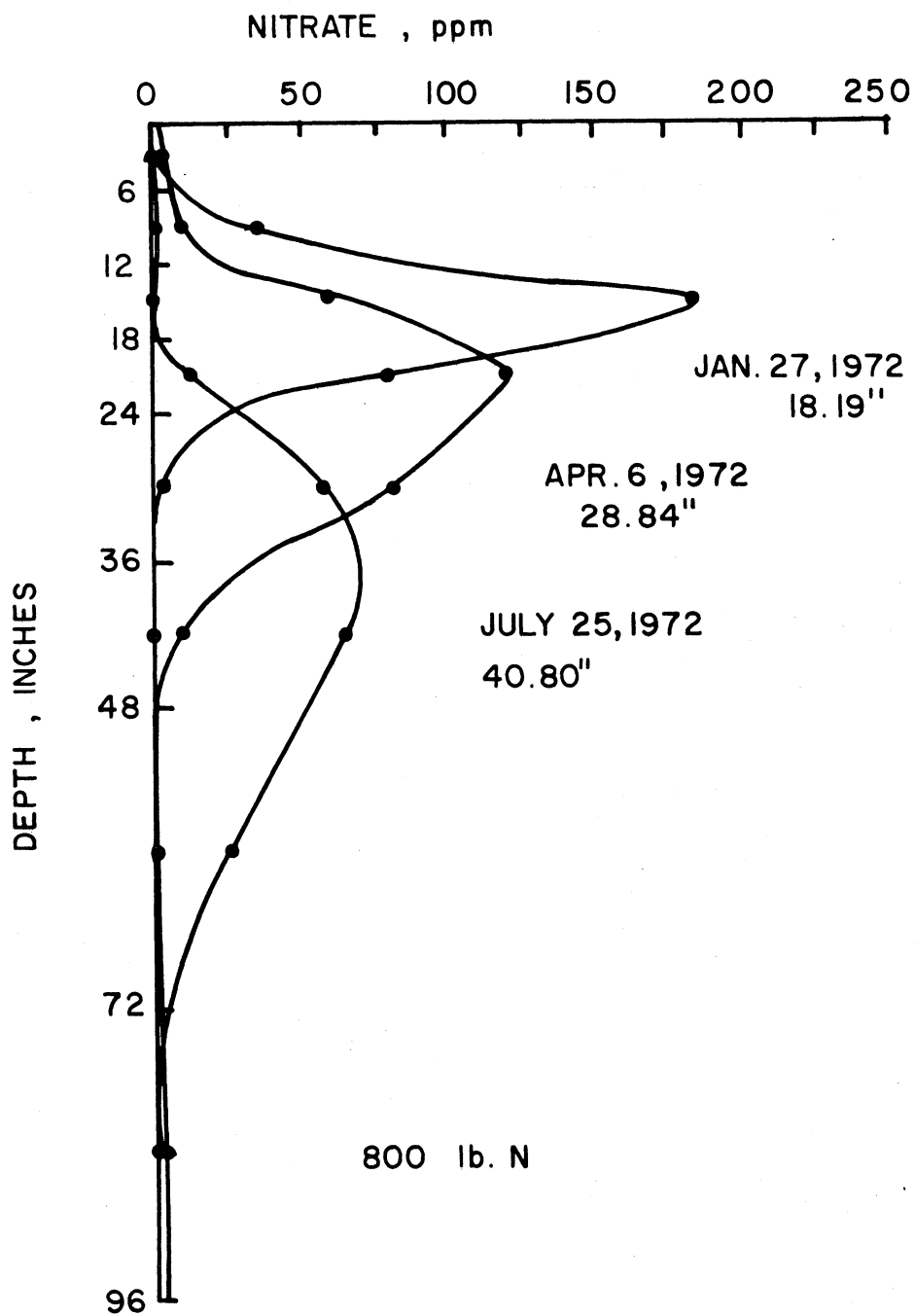


Fig. 8. Distribution of Nitrate with Depth, Hartsells fsl. after Application of 800 and 200 lb. N/A on October 12, 1971. mean of 4 replications

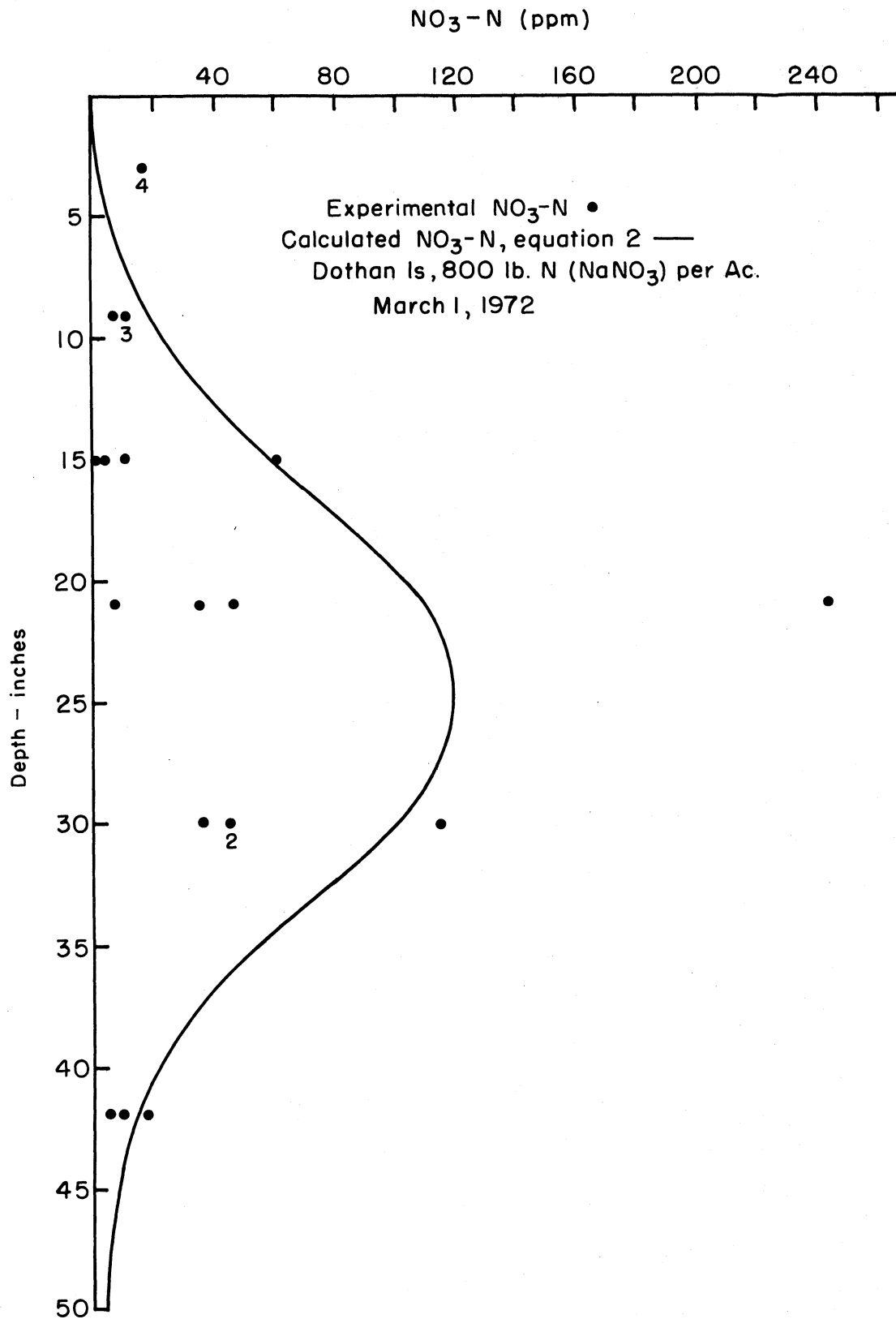


Fig. 9. Calculated Nitrate Distribution Using a Dispersion Model (line) Compared to Measured Concentrations in Dothan loamy sand on March 1, 1972 After Application of 800 lb N/A on September 14, 1971.

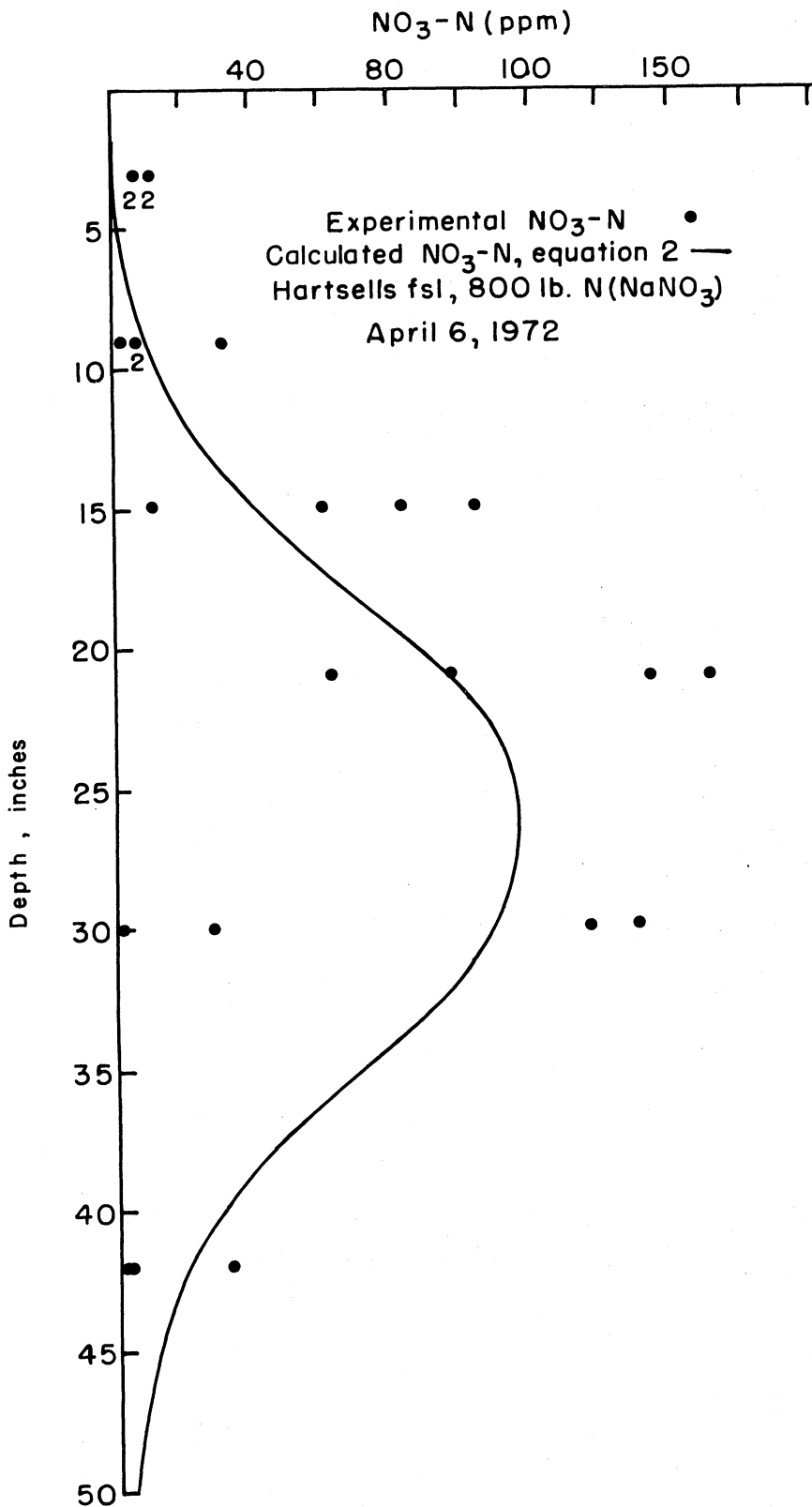


Fig. 10. Calculated Nitrate Distribution Using a Dispersion Model (line) Compared to Measured Concentrations in Hartsells fine sandy loam on April 6, 1972 After Application of 800 lb. N/A on October 12, 1971.

