November 1997 Bulletin Number 863

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Effect of Application Frequency on the Fate of Azinphosmethyl[1] in a Sugarcane Field

H.M. Selim,[2] R.L. Bengtson,[3] L.M. Southwick,[4]
R.Ricaud,[2] and H.P. Schexnayder, Jr.[5]

Introduction

Reducing the amounts of dissolved substances in surface and ground water is of major concern nationally and within the agricultural community. Central to the issue of agricultural chemical management is the potential for contamination of surface and subsurface waters. A primary purpose of the Clean Water Act (Section 319) and the Coastal Zone Management Act (Section 6217) is to evaluate, demonstrate, and implement best management practices (BMPs) to improve the water quality in the 12 drainage basins of Louisiana (Louisiana Department of Environmental Quality (LDEQ), 1990). Because applied agricultural chemicals are potential contributors to nonpoint source contamination, there is a need to evaluate BMPs for potential improvement of water quality in surface waters. The primary focus of this study was to investigate the fate of azinphosmethyl (Guthion®) in sugarcane canopy, soil, and runoff water.

Over the last three decades, azinphosmethyl (O,O-dimethyl S-[4-oxo-1,2,3-benzotriazin-3(4H)-yl)methyl] phosphorodithioate) has been used extensively because of its effectiveness in controlling the sugarcane borer

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[1]This study was funded in part by the Louisiana Department of Environmental Quality contract number 24400-93-32, Jan Boydstun, project officer.

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Diatraea saccharalis (F). This insecticide is less harmful to beneficial arthropods, including borer parasites, and decomposes relatively fast in the plant canopy in subtropical regions such as south Louisiana (Southwick et al., 1995), Mississippi (Willis et al., 1994), and Florida (Thompson and Brooks, 1976). Following foliar application, the amount of azinphosmethyl within the plant canopy decreases with time depending on the rate of volatilization, degradation, and downward movement into the soil. Numerous studies indicate that rain and temperature have significant effect on azinphosmethyl disappearance from plant leaves. In a review by Chemagro (1974), azinphosmethyl disappearance from canopy leaves ranged from 12 to 30 days. Specifically, estimates for azinphosmethyl half-life on leaves are 50 days on citrus trees (Chemagro, 1974), 0.3 day on cotton (*Gossypium hirsutum* (L.)) (Willis et al., 1994), and 1 day on sugarcane (Southwick et al., 1995).

In order to estimate azinphosmethyl runoff losses, one needs to know its concentration in surface soil. However, azinphosmethyl disappearance from soil can be counteracted by its washoff from the sugarcane canopy, especially following a rainfall. An approach describing both disappearance and redistribution of azinphosmethyl was used by Goodman et al. (1983) for a Michigan apple orchard. They combined measurements of azinphosmethyl concentration on canopy leaves, grass, and in surface soil into a mass balance model. The model adequately predicted the rates of azinphosmethyl disappearance and redistribution between these orchard layers (leaves, grass, soil) as functions of time and rain conditions.

In this study, we quantified azinphosmethyl distributions on sugarcane leaves, surface soil, and runoff waters for three growing seasons in south Louisiana. The study was initiated in 1992 and was funded by the LDEQ (EPA, Section 319) to quantify the effect of azinphosmethyl application frequency on the quality of surface runoff water for a complete sugarcane cycle. Specifically, three different treatments were considered— high, medium, and low. These high, medium, and low treatments received three, two, and one azinphosmethyl applications during a growing season, respectively. Another objective of this study was to estimate the rates of azinphosmethyl disappearance from canopy leaves and surface soil. Prior to 1993, the application frequency of azinphosmethyl on sugarcane ranged from one to three per growing season. Currently, sugarcane integrated insect pest management systems (IPMS) in Louisiana are limited to one azinphosmethyl application per season (Louisiana Cooperative Extension Service, 1996).

Methods

The experimental site was 1.3 ha located at the St. Gabriel Research Station of the LSU Agricultural Center. The soil was a Commerce silt loam (fine-silty, mixed, nonacid, thermic, Aeric Fluvaquent) and was planted with sugarcane variety CP70-321 in September 1992. The site was divided into six 0.22-ha plots that received different numbers of azinphosmethyl applications for three growing seasons from 1993 to 1995. Three treatments were established: (1) a medium treatment receiving recommended levels of N, P, and K and number/method of herbicide and insecticide applications; (2) a high, and (3) a low treatment, receiving above and below the medium levels of chemical applications, respectively. Six 0.22-ha plots were selected (two plots for each treatment). Each plot consisted of 9 rows 150 meters long and 1.8 meter spacing. Two additional rows served as levees separating adjacent plots and providing drainage from areas outside the plots.

At the lowest part (north-east corner) of each plot, we installed sumps (corrugated, galvanized culverts, 90 cm in diameter and 2 meters in depth). A sheet metal plate was welded at the bottom of each sump. A hole was dug and was subsequently back filled following installation of the sumps and the remaining soil was used to close the levees surrounding each plot. Additional earth moving was carried out to insure that each plot was completely leveed and that runoff water was collected into each sump through a V-type opening. In each sump, a water pump connected to a flow meter was also installed. As a result, the only outlet for surface runoff water was through the pump and flow meter and exiting into the levees between plots. Adjacent to each sump, we placed an ISCO water sampler and connected the sampler tubing and sensors to each sump by placing the sampler cup and sensor at the bottom of each sump. Sample collection was triggered when runoff water was detected by a float in the water pump.

For each growing season, the high, medium, and low treatment plots received three, two, and one azinphosmethyl application, respectively. The amount of azinphosmethyl active ingredient applied was 0.82 kg/ha as a mixed emulsifiable concentrate with a water carrier for each application. The dates of applications in 1993 were July 28, August 19 and September 14. In 1994, azinphosmethyl was applied on July 16, August 10, and

September 8, and in 1995, the dates were July 8, August 10, and September 14. All applications were made with a high clearance ground sprayer, except for July 16, 1994, when a helicopter was used due to the impassability of the wet field. After each application, the leaf and soil samples were taken daily for the first 3-4 days and subsequently 2-7 days apart. On each sampling date, 15-20 canopy leaves and a composite sample of surface soil (25 mm depth) were taken along one of the five center rows of each of the six plots. The rows within each plot were alternated randomly between the sampling dates. In addition, subsurface soil samples were taken to a depth of 90-cm during the 1994 growing season.

Azinphosmethyl extraction from leaf surfaces was carried out by hand-shaking for 1 min in 250 mL of hexane, evaporation to 2.0 mL, and transfer into a gas chromatograph (GC) vial for analysis. Extraction of azinphosmethyl from the field (moist) soil was carried out using 0.01 M NaCl methanol/water solution (4:1 volume:volume), shaking for 24 hours, centrifuging, decanting, and removal of water using anhydrous sodium sulfate. The extracts were subsequently evaporated and transferred in hexane to 2.0-mL vials (Southwick et al., 1995). Runoff water samples (250 mL) were extracted using dichloromethane in a separatory funnel. The remaining steps were similar to that for soil extractions. Azinphosmethyl was measured using a Hewlett-Packard 5890A series II gas chromatograph nitrogen-phosphorus and electron-capture detectors (Gaston and Locke, 1995). For runoff water, the detection limit for azinphosmethyl was 0.2 ppb (or parts per billion).

RESULTS AND DISCUSSION

LEAVES AND SURFACE SOIL:

Figures 1-5 show azinphosmethyl concentrations on leaves and surface soil samples during the three growing seasons. For 1993, azinphosmethyl applications were followed by at least one rainfall event the following day. This caused wash-off of the insecticide from leaf surfaces and a sharp increase of concentration in the surface soil. For the application on August 19, 1993, azinphosmethyl concentration on leaf surfaces dropped after 2 days of rain to 0.03-0.08 $\mu g/cm^2$, and 2 days after application on September 14 the range was 0.01-0.07 $\mu g/cm^2$. Rainfall distributions during the growing seasons are shown in Figure 7.

As shown in figures 2-7, azinphosmethyl concentrations in the soil surface reflected that which remained on leaf canopy. Considerable azinphosmethyl was removed from the leaves and a large portion delivered onto the soil surface by rainfall events 1 or 2 days following application. Thus, one day after azinphosmethyl application, little residue was found on leaves (0.05 $\mu g/cm^2$), whereas considerably higher azinphosmethyl concentrations in the surface soil (200-700 $\mu g/cm^2$) were observed.

Based on results for three growing seasons (1993-1995) and for all treatments, concentrations on the leaves one day following azinphosmethyl application ranged from 0.5-2.5 $\mu g/cm^2$. Recently, a range of concentrations of 0.001-3 $\mu g/cm^2$ was reported by Southwick et al. (1995) for a similar investigation on sugarcane. Due to high intensity rainfall events (8 and 20 days following the third application), the average concentrations on leaves decreased gradually and reached levels below 0.05 $\mu g/cm^2$ by mid-October for each growing season. Although individual applications differed in the amounts of azinphosmethyl that reached the canopy leaves, the decrease in concentration both on leaves and in the surface soil was consistent for all three growing seasons.

Consistently during the growing seasons (1993-1995), only 1%-2% of applied azinphosmethyl remained on leaves and in surface soil 10-12 days after an application. To arrive at such estimates a leaf area index (LAI) was needed. Irvine (1974) provided an estimate of leaf area per unit leaf weight of 0.3 + 0.02 dm^2/g. The average stalk count on our plots was

68,200 per hectare with little variation among treatments and years, which produced an estimate of LAI of 1.9 + 0.2. A value of 2.0 was used in our study to convert concentration of azinphosmethyl on leaf surfaces (µg/cm^2) into an amount on a hectare basis (see Granovsky et al., 1996). Moreover, the total azinphosmethyl detected in both leaves and surface soil did not exceed 50% (350-400 g/ha) of the amount applied (820 g/ha).

Rates of azinphosmethyl disappearance on the leaves and in the surface soil were obtained from the results shown in figures 1-6. Using regression analyses, we calculated the rate of disappearance or half-life of azinphosmethyl as is widely reported in the literature for the soil surface (Wauchope et al., 1992). Estimated values for the half-life ranged from 2-8 days for the leaves and from 6-66 days for the surface soil (see Table 1). These values are best overall estimates since the assumption of a simple decay process cannot completely account for foliar washoff following rains and the influence of the time interval between chemical application and initial rainfall.

Table 1. Estimated degradation rates and corresponding half-lives for azinphosmethyl disappearance on sugarcane leaves and surface soil based on first-order decay

Date of application	Half-lives*	
	Leaves (d)	Soil (d)
08-19-93	2.70(2.19)	66.69(22.35)
09-14-93	7.75(1.57)	11.56(2.50)
07-16-94	2.50(0.26)	9.90(7.92)
08-10-94	2.77(0.34)	5.29(1.98)
09-08-94	6.99(0.64)	12.00(5.15)
07-08-95	1.83(0.40)	6.04(1.57)
08-10-95	3.13(0.65)	12.60(5.04)
09-14-95	7.38(4.55)	10.78(0.69)

* Values in parentheses are standard error.

Willis et al. (1994) used simulated rain applied to cotton plants at times ranging from 2 to 146 h after azinphosmethyl and fenvalerate application to determine the washoff characteristics of these insecticides. They found that the insecticides became increasingly resistant to washoff with increasing time interval between chemical application and initial rainfall. Goodman et al. (1983) developed a simple mass balance matrix approach to account for the effect of rain events on azinphosmethyl degradation and redistribution in three layers (or regions)—canopy, grass, and surface soil. Granovsky et al. (1996) successfully used the modeling approach of Goodman et al. (1983) to calculate rates of disappearance based on azinphosmethyl distributions shown in figures 1-6. Specifically, the approach used was to estimate the proportional daily losses/gains in an effort to arrive at rates of disappearance of azinphosmethyl that reflect the effect of rain as well as the contribution of foliar washoff on degradation rates. The values of half-lives obtained using the Goodman et al. (1983) model were as follows: on the leaves 1.55 and 0.62 d, and in the surface soil, 2.8 and 2.5 days for conditions of no rain and rain, respectively. The half-life values for the surface soil obtained using the Goodman et al. (1983) model, with or without rain, were much lower than the range of 10 to 30 days reported by others (Chemagro, 1974; Wauchope et al., 1992). Southwick et al. (1995) reported a value for half-life of 0.9-1.1 days for a Louisiana soil, which compares well with our values of 2.5-2.8 days.

RUNOFF:

Due to the unusually dry summer months of 1993 (see Figure 7), no surface water samples were collected during this period. There was no runoff water detected following periods of rainfall. Total amounts of rainfall during July, August, and September were 39, 68, and 38 mm, respectively. These amounts of rainfall water infiltrated into the soil with little if any amounts inundating the soil surface. As a result, no surface runoff from these events occurred.

As shown in figures 8-9, azinphosmethyl concentrations of 2 ppb in runoff waters were detected following the first application of July 16, 1994. The first runoff event occurred on July 27. While no rainfall event produced runoff following the second azinphosmethyl application of August 10, 1994, the third application of September 8, 1994, was followed by a series of small rains and one high intensity rainfall that generated two runoff events (September 15 and 16). Maximum azinphosmethyl concentrations in individual runoff samples reached 20-40 ppb. These peak concentrations in runoff waters decreased sharply to 2 ppb in the following runoff event (October 9). Moreover, concentrations of less than 1 ppb were observed in all runoff waters on October 22. This continued decrease was consistent where no azinphosmethyl was detected in runoff waters on December 5, 1994.

Because there were no large size storms after azinphosmethyl applications in 1995, no runoff resulted until 22 days after the first application and 11 days after the second application. Azinphosmethyl was only detected on August 1 (22 days after July application) and August 22 (11 days after August application) runoff events. Azinphosmethyl concentrations ranged from 0.4 to 1.9 ppb in the runoff water on August 1, and 1.0 to 10.5 ppb on August 22, 1995. Table 2 provides average azinphosmethyl concentrations in runoff water during 1994 and 1995 and the corresponding amounts of rain and runoff amounts. Concentration

Table 2. Azinphosmethyl losses in runoff water as related to water runoff, time elapsed after application

Runoff date	Elapsed time	Water runoff	Concentration in runoff water	Amount of azinphosmethyl loss in runoff
Losses	(d)	(mm)	(ppb)	(g/ha)
07-27-94	11	5.3	1.0 - 1.6	0.07
09-15-94	7	3.9	10.0 - 21.9	0.68
09-17-94	9	3.7	7.4 - 14.1	0.40
10-09-94	31	1.7	0.0 - 1.7	0.03
10-19-94	41	5.2	0.3 - 1.0	0.04
10-22-94	44	7.3	0.3 - 1.7	0.06
08-01-95	22	5.3	0.8 - 1.4	0.07
08-22-95	11	2.6	0.0 - 5.7	0.15
10-13-95	30	2.2	0.0 - 0.1	0.00

levels above the detection limit were not detected in runoff waters after October 26, 1995. In Table 2, we also present amount of azinphosmethyl losses per hectare due to runoff, which were calculated based on averaged concentrations and runoff water volume as determined from our flow meters for each plot. For all growing seasons, maximum losses per runoff event did not exceed 0.1% of that applied for all three treatments.

In contrast to 1994, significant rainfall events (50-60 mm) shortly after azinphosmethyl application (1-2 days) were not encountered in 1995. Such dry conditions are desirable and resulted in lower concentrations in the runoff due to corresponding lower amounts on leaves and the surface soil. Based on the data on leaves and surface soil, significant amounts of azinphosmethyl during these extended dry periods disappeared due to degradation and volatilization, which resulted in smaller amounts susceptible to losses in runoff water. Smith et al. (1983) reported a maximum azinphosmethyl concentration in runoff water of 420 + 140 ppb. For longer elapsed times (5-16 d), they observed concentrations in the runoff of 12-60 ppb. These concentrations were much higher than those observed in our study. In contrast, Southwick et al. (1995) reported, with only one exception (261 ppb), maximum runoff concentration of 26-32 ppb, which is consistent with our results. In the study of Southwick et al. (1995), three applications were made, and runoff from a single sugarcane row (7.8 m in length) was collected for only one growing season. In contrast, we report results for three consecutive years from three plots (150 m in length and 18 m in width) exceeding 0.2 ha (0.5 acre).

It is significant also to emphasize here that our observed runoff concentrations for three years were consistently below the toxicity levels (24 h LC_{50}) for bluegill (27.8 ppb) and other fish species (Chemagro, 1974, Southwick et al., 1995). Moreover, the frequency of application in a growing season did not affect the water quality in surface runoff for all treatments.

Summary and Conclusions

A field study was carried out to quantify the rate of disappearance of applied azinphosmethyl in sugarcane canopy and in surface soil and losses in runoff water. Azinphosmethyl was applied in July through September (1993-1995).

- We found only 1%-2% of applied azinphosmethyl remained within the canopy and the soil surface 10-12 d following application. Azinphosmethyl on leaf surfaces diminished sharply following rainfall events with subsequent increases in amounts in surface soil.
- Azinphosmethyl losses in runoff water decreased with time; the measured maximum concentration was 10-21.9 ppb.
- Azinphosmethyl concentrations were < 2 ppb in runoff waters 30 d after application for the entire sugarcane cycle.
- On a mass balance basis, maximum losses in runoff water during three years of the sugarcane cycle did not exceed 0.12 % of the amount applied.
- We further conclude that based on our results for an entire sugarcane growing cycle, the recommended rate of azinphosmethyl did not reach toxic concentration levels in runoff water.

Figures 1 - 9

Azinphosmethyl in Leaf Samples, 1993

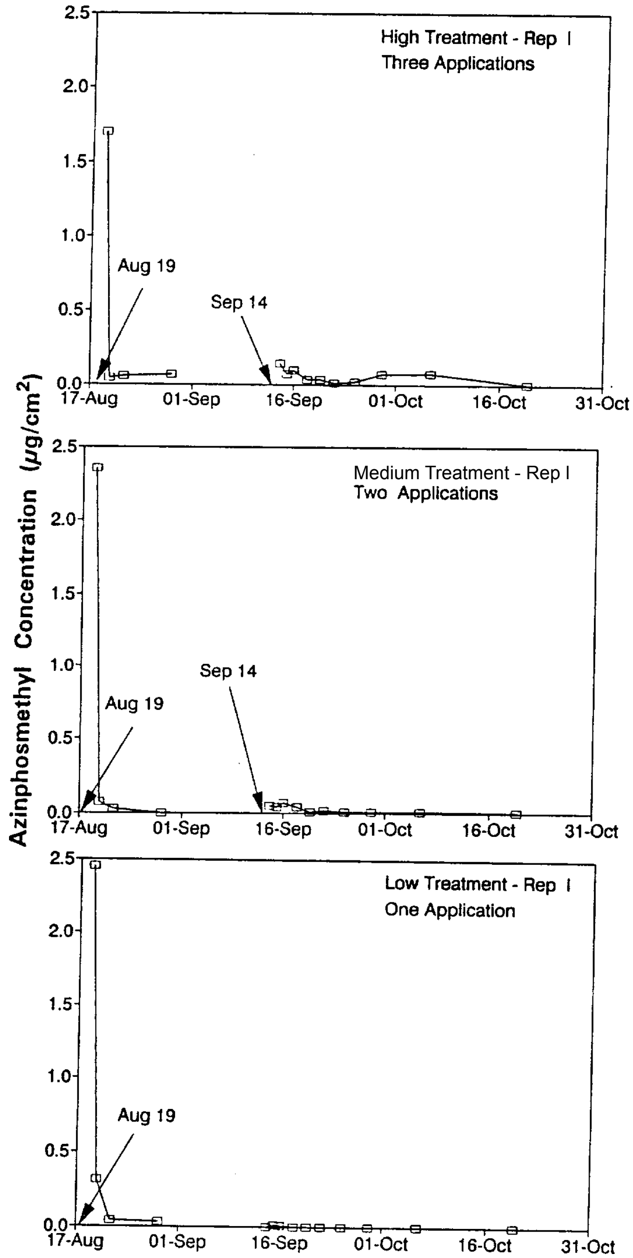

Figure 1a. Measured extractable azinphosmethyl amounts on sugarcane leaves following the second and third foliar application (replication # 1) in 1993.

Azinphosmethyl in Leaf Samples, 1993

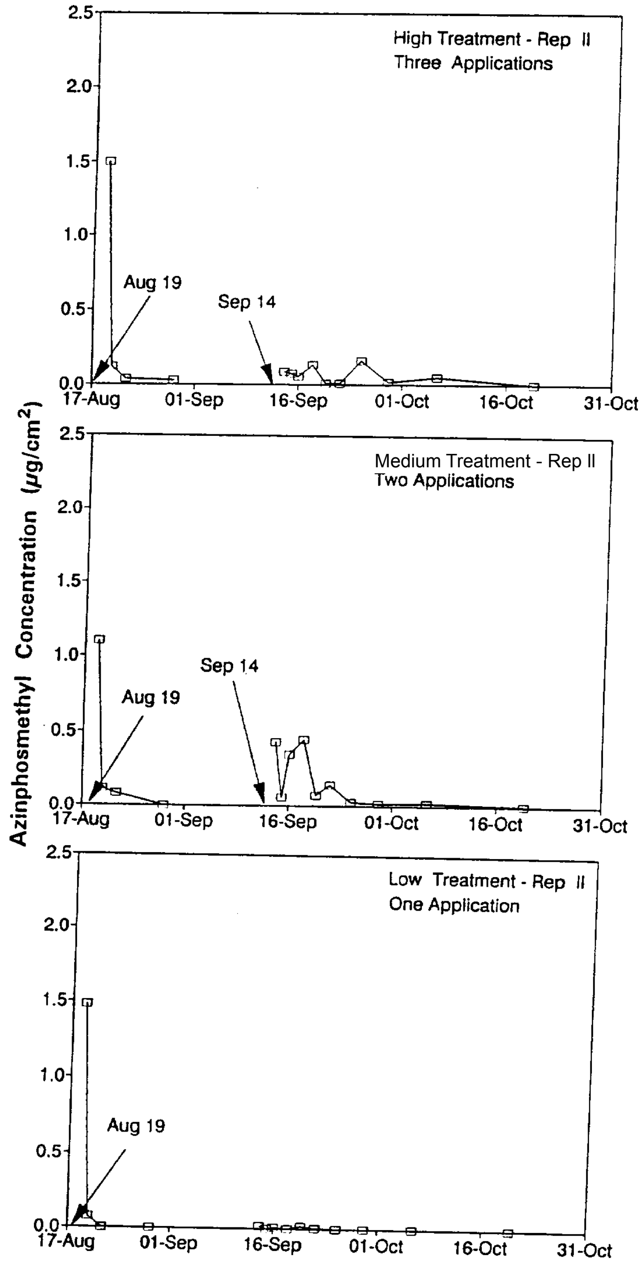

Figure 1b. Same as Figure 1a except for replication # 2.

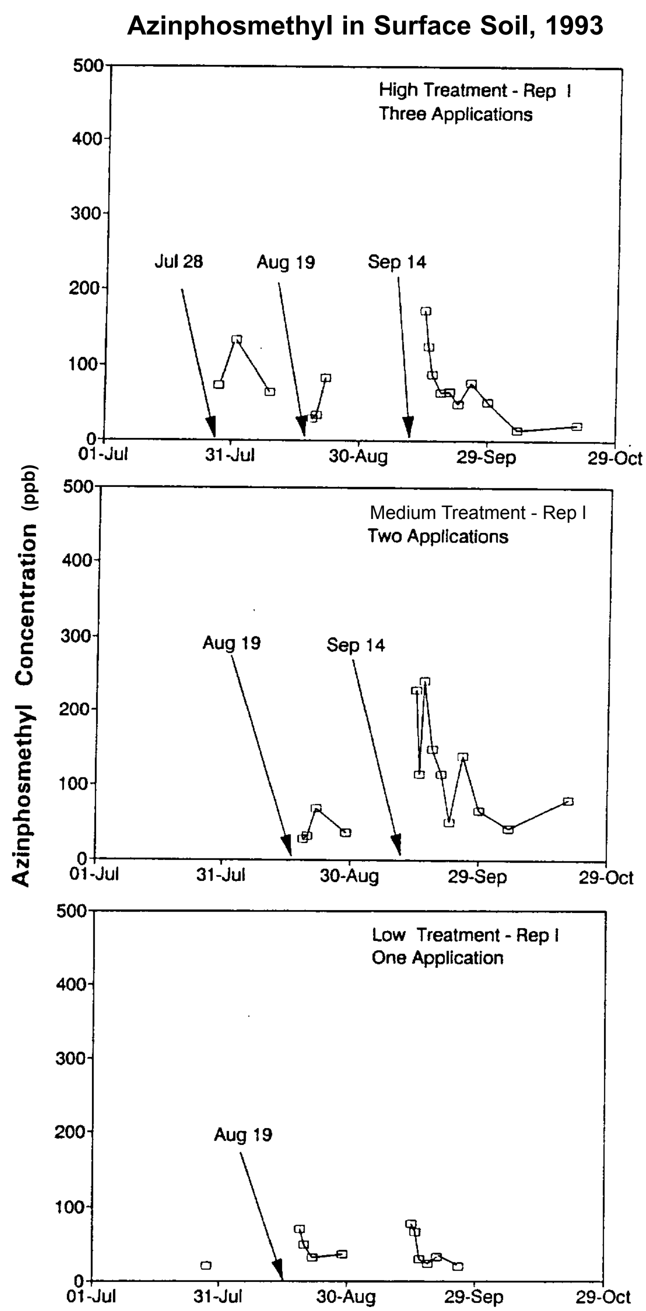

Figure 2a. Measured extractable azinphosmethyl concentration in surface soil following the second and third foliar application (replication # 1) in 1993.

Azinphosmethyl in Surface Soil, 1993

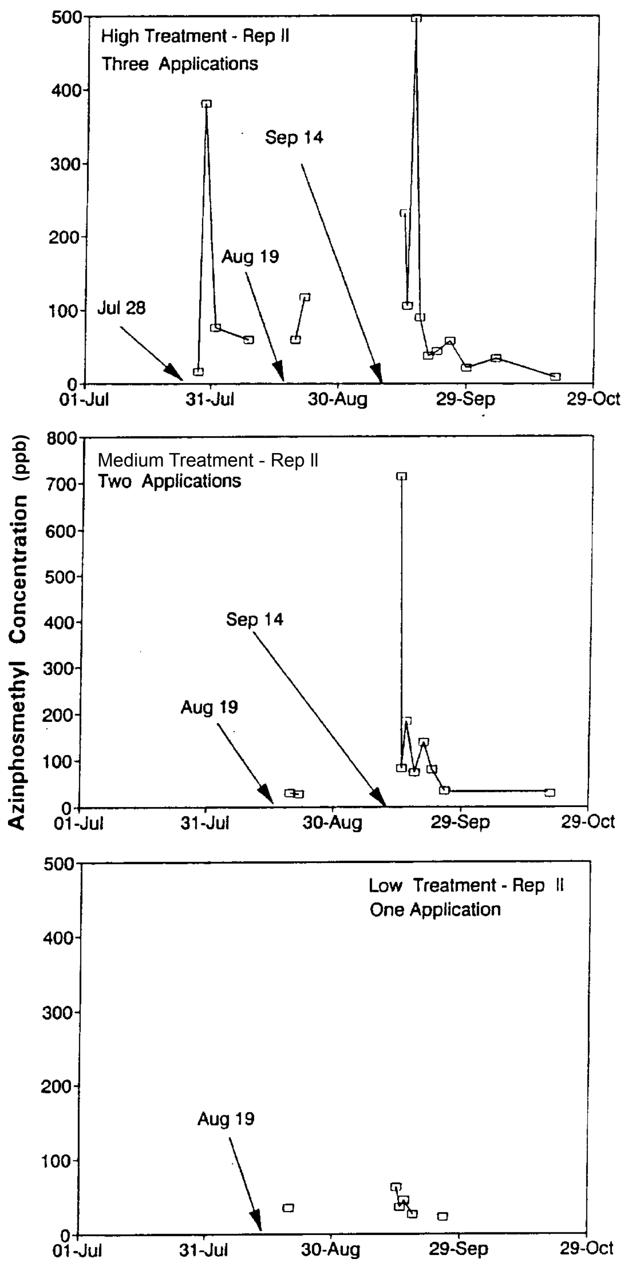

Figure 2b. Same as Figure 2a except for replication # 2.

Azinphosmethyl in Leaf Samples, 1994

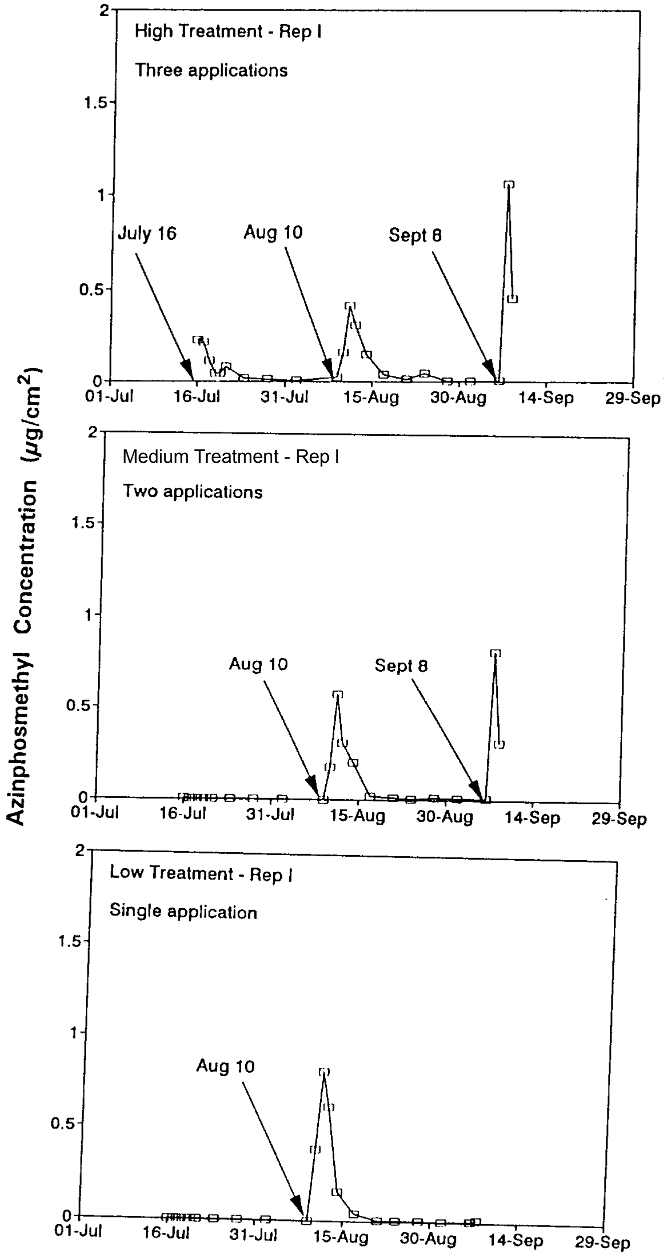

Figure 3a. Measured extractable azinphosmethyl amounts on sugarcane leaves following each foliar application (replication # 1) in 1994.

Azinphosmethyl in Leaf Samples, 1994

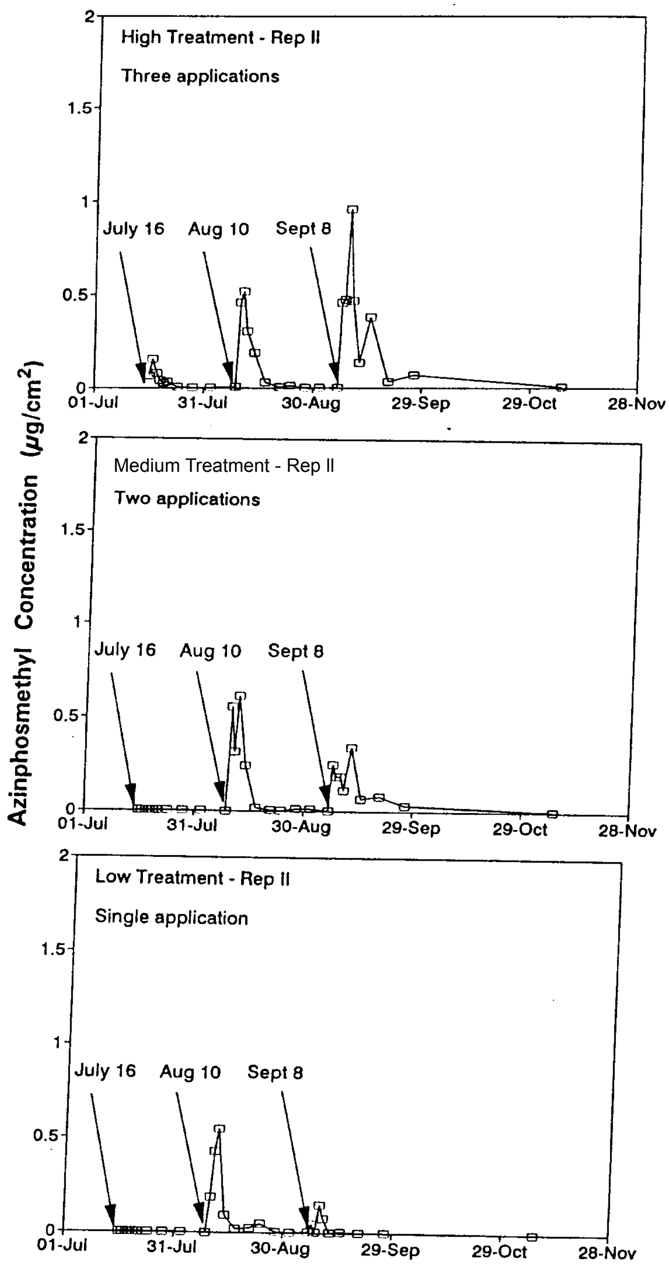

Figure 3b. Same as Figure 3a except for replication # 2.

Azinphosmethyl in Surface Soil, 1994

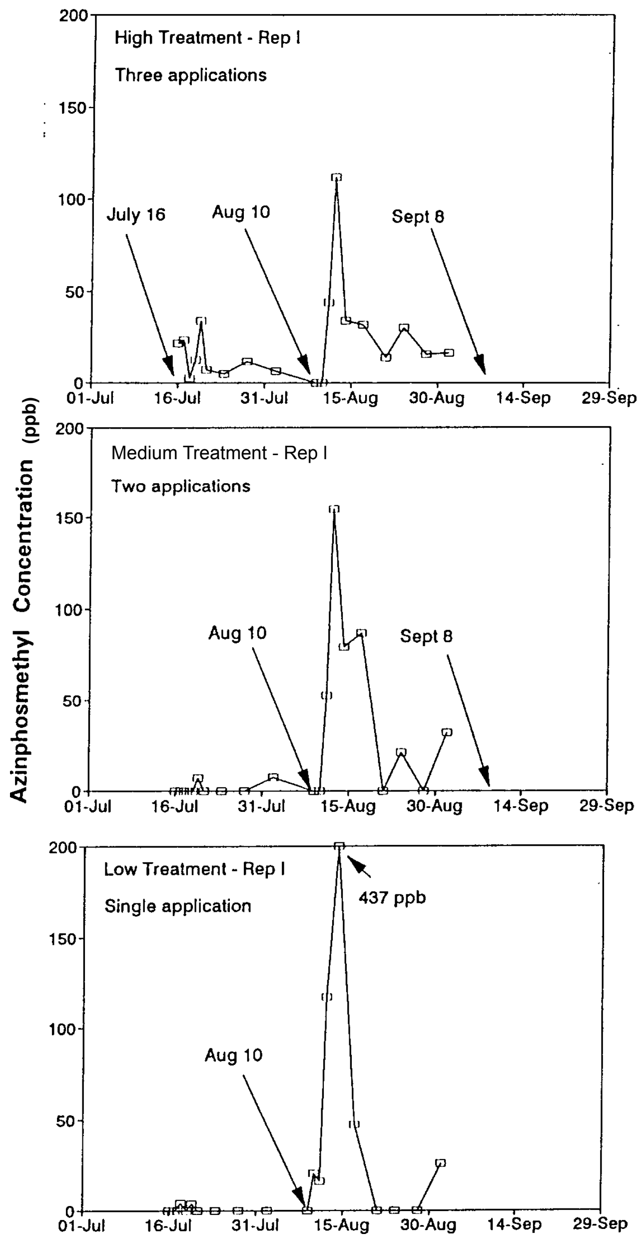

Figure 4a. Measured extractable azinphosmethyl concentration in surface soil following each foliar application (replication # 1) in 1994.

Azinphosmethyl in Surface Soil, 1994

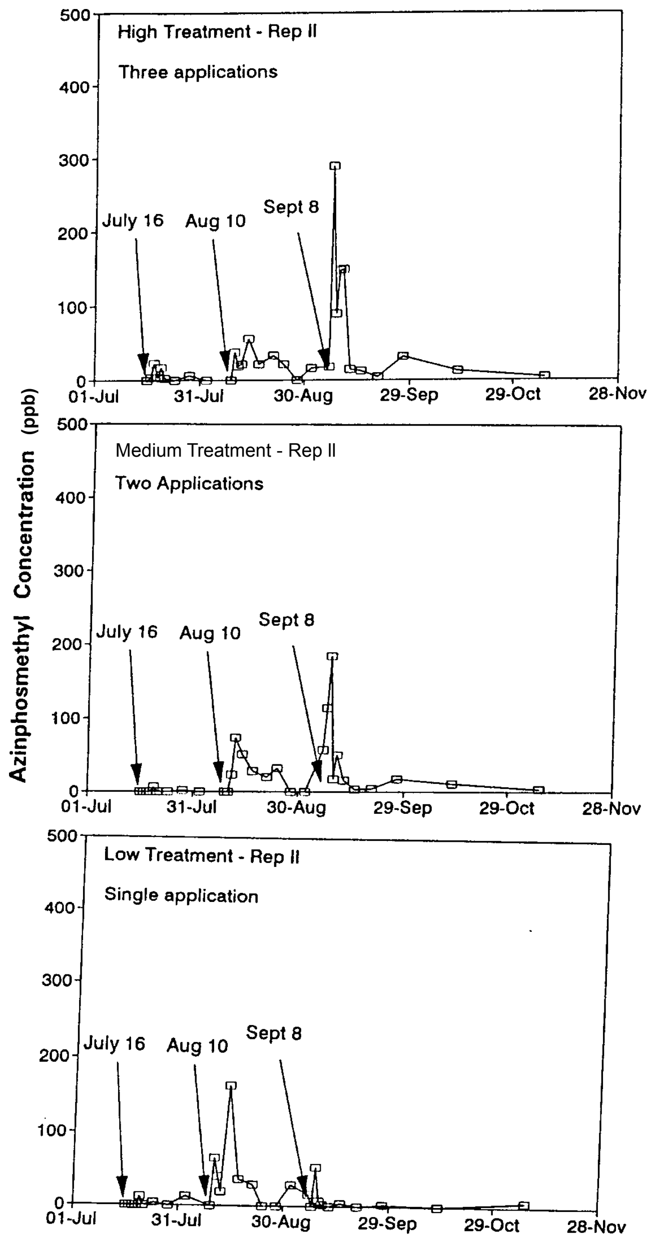

Figure 4b. Same as Figure 4a except for replication # 2.

Azinphosmethyl in Leaf Samples, 1995

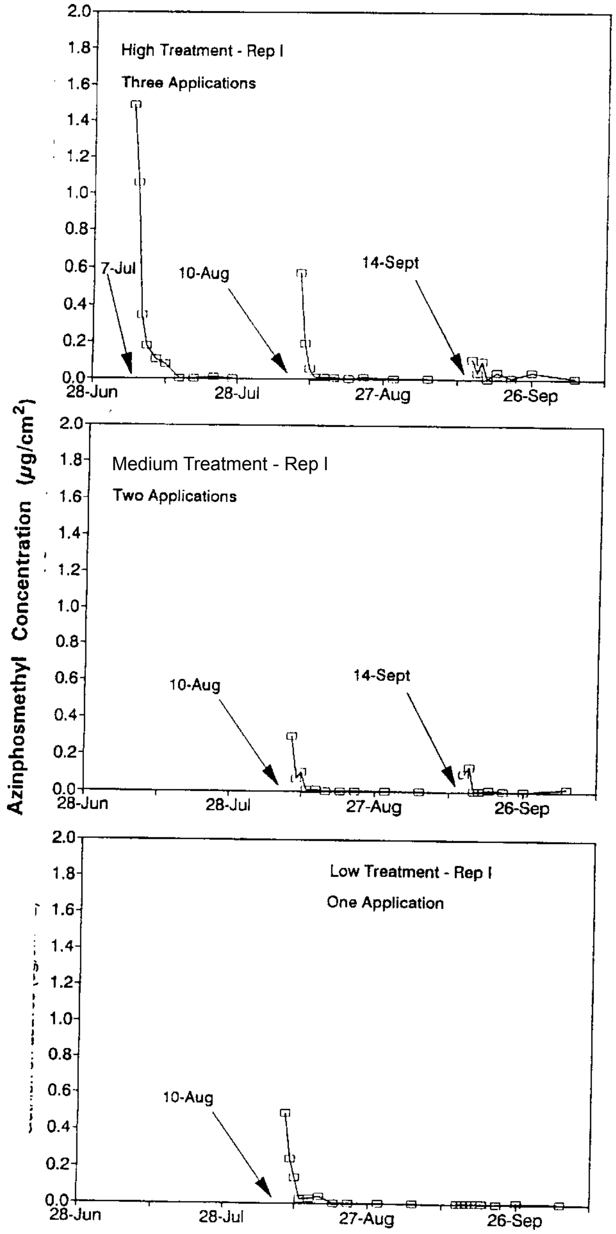

Figure 5a. Measured extractable azinphosmethyl amounts on sugarcane leaves following each foliar application (replication # 1) in 1995.

Azinphosmethyl in Leaf Samples, 1995

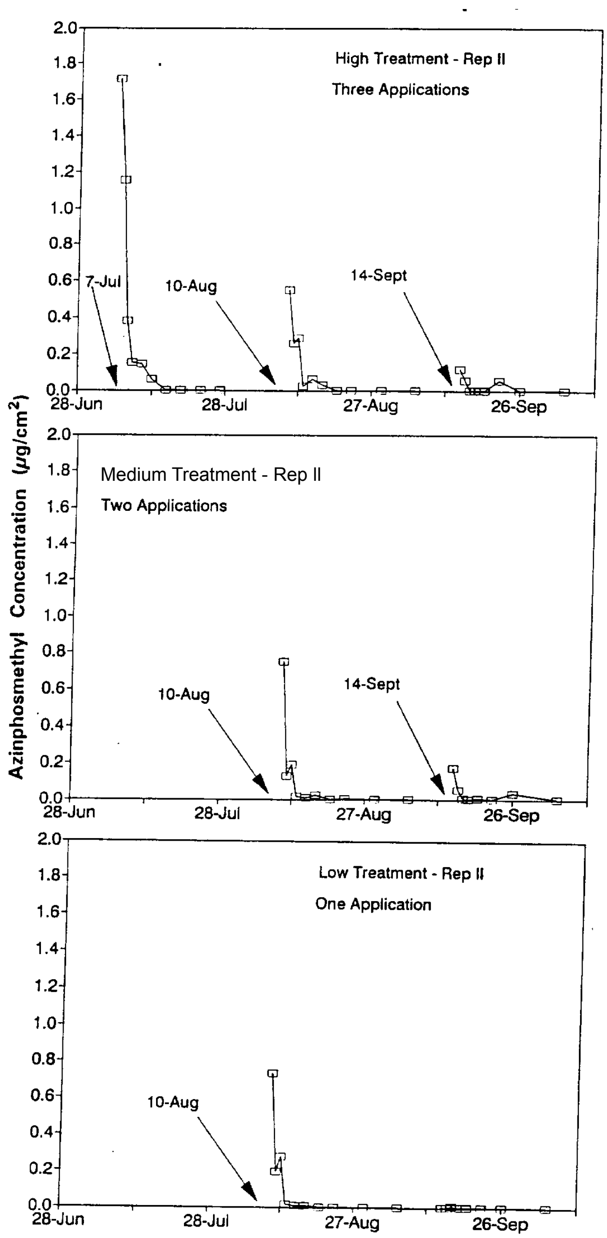

Figure 5b. Same as Figure 5a except for replication # 2.

Azinphosmethyl in Surface Soil, 1995

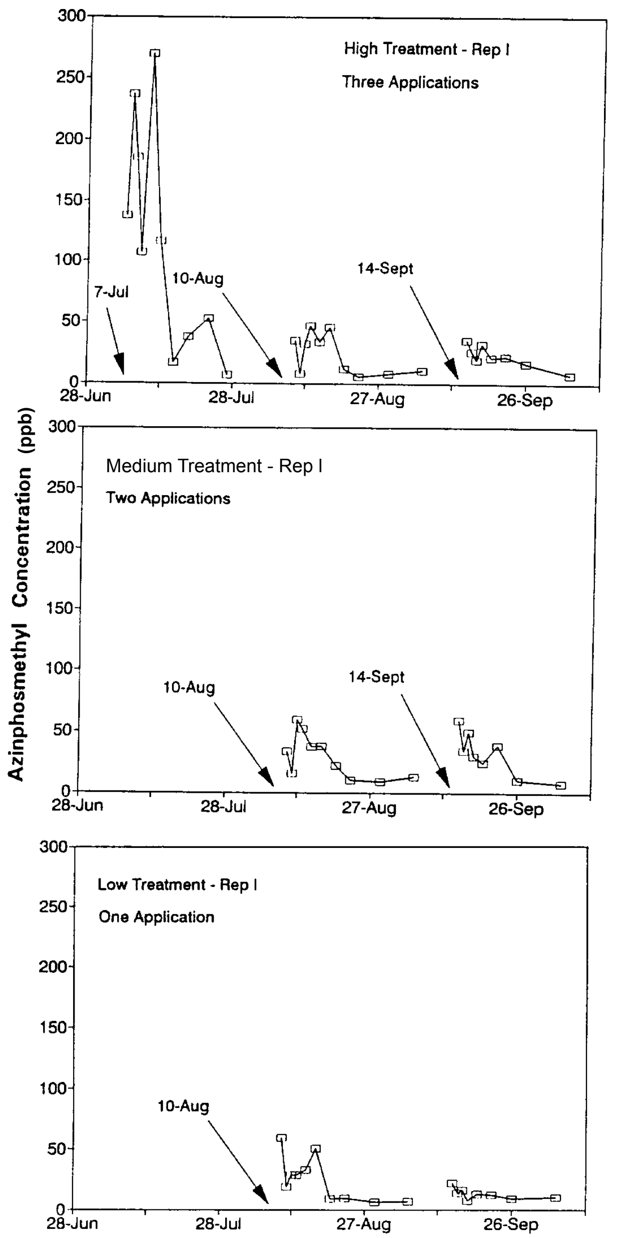

Figure 6a. Measured extractable azinphosmethyl concentration in surface soil following each foliar application (replication # 1) in 1995.

Azinphosmethyl in Surface Soil, 1995

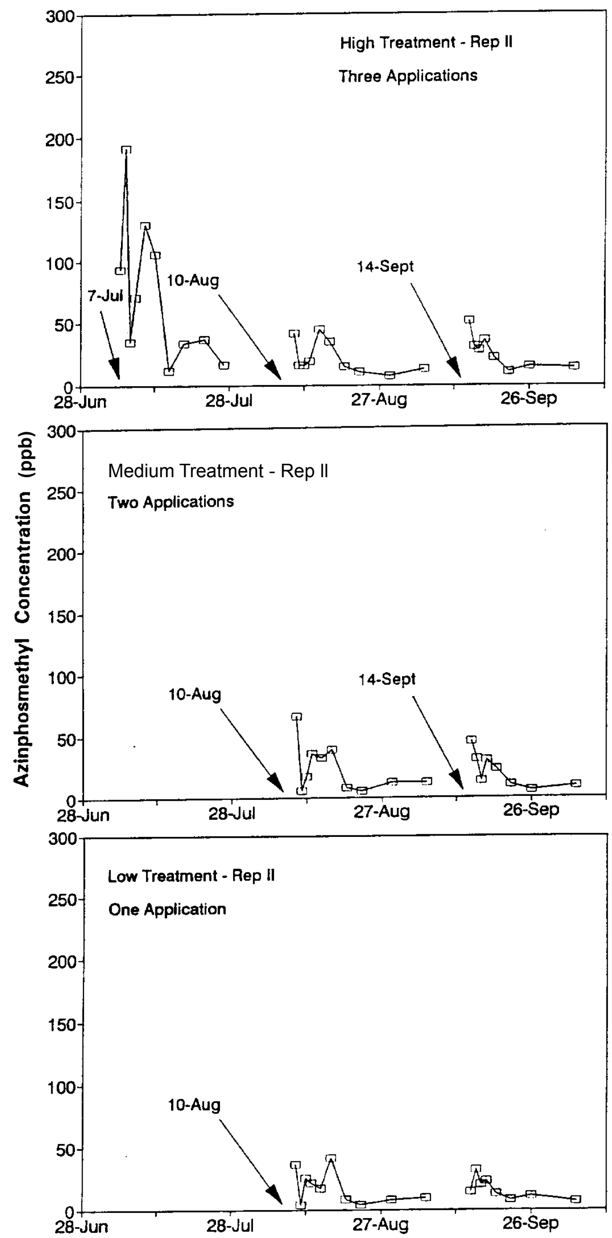

Figure 6b. Same as Figure 6a except for replication # 2.

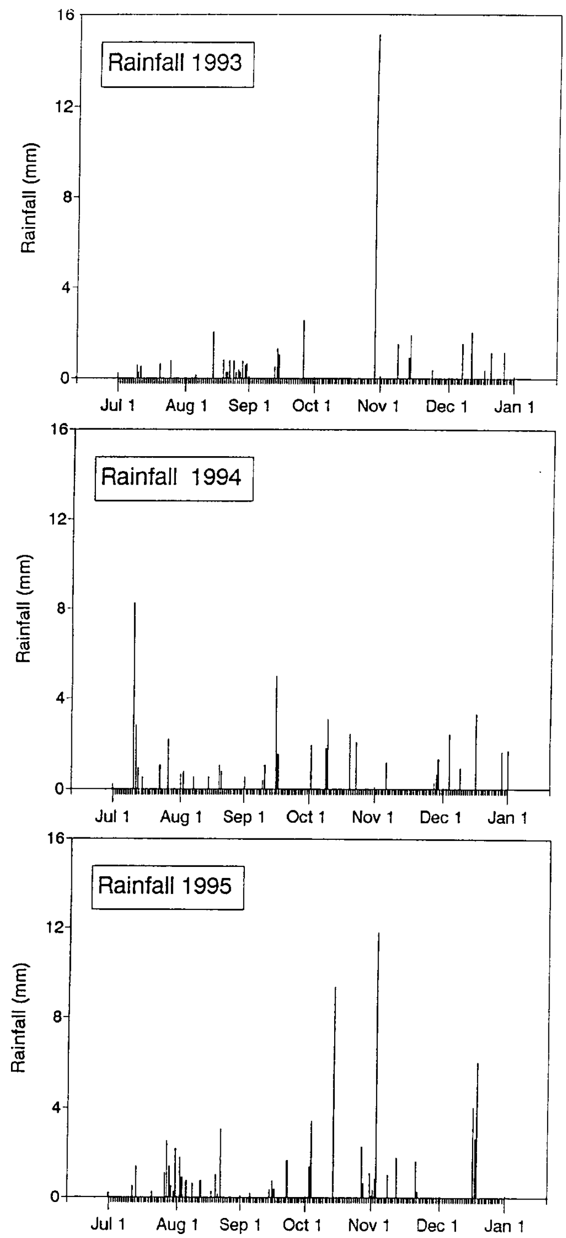

Figure 7. Rainfall distributions during 1993 to 1995 at the study site.

Azinphosmethyl in Runoff, 1994

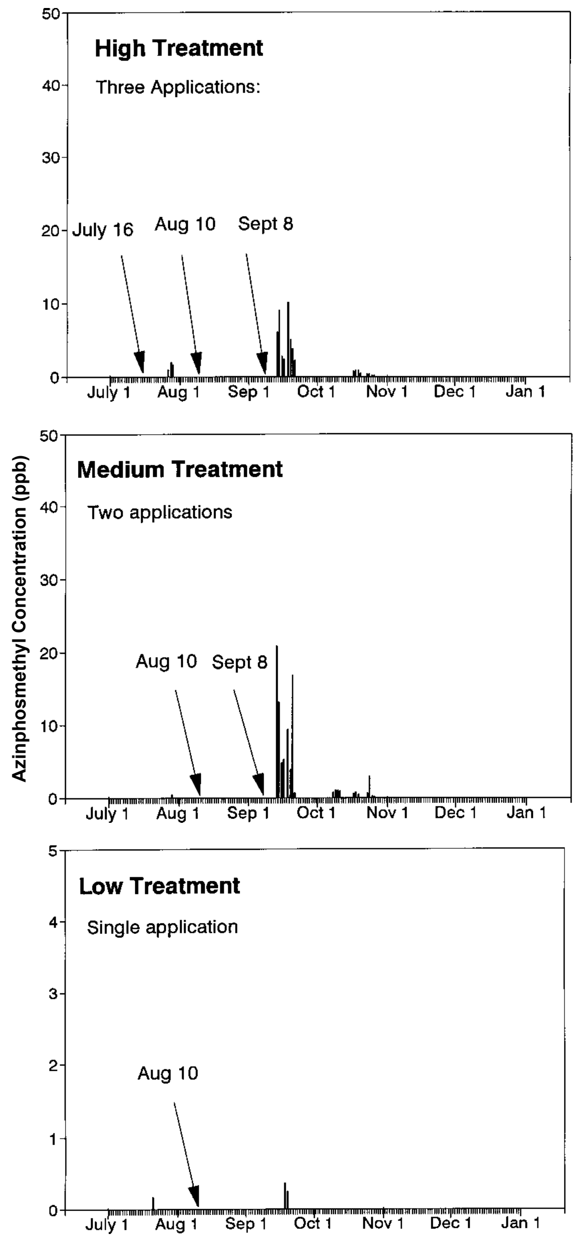

Figure 8. Measured azinphosmethyl concentrations in runoff water effluent during 1994. Results are average of two replications.

Azinphosmethyl in Runoff, 1995

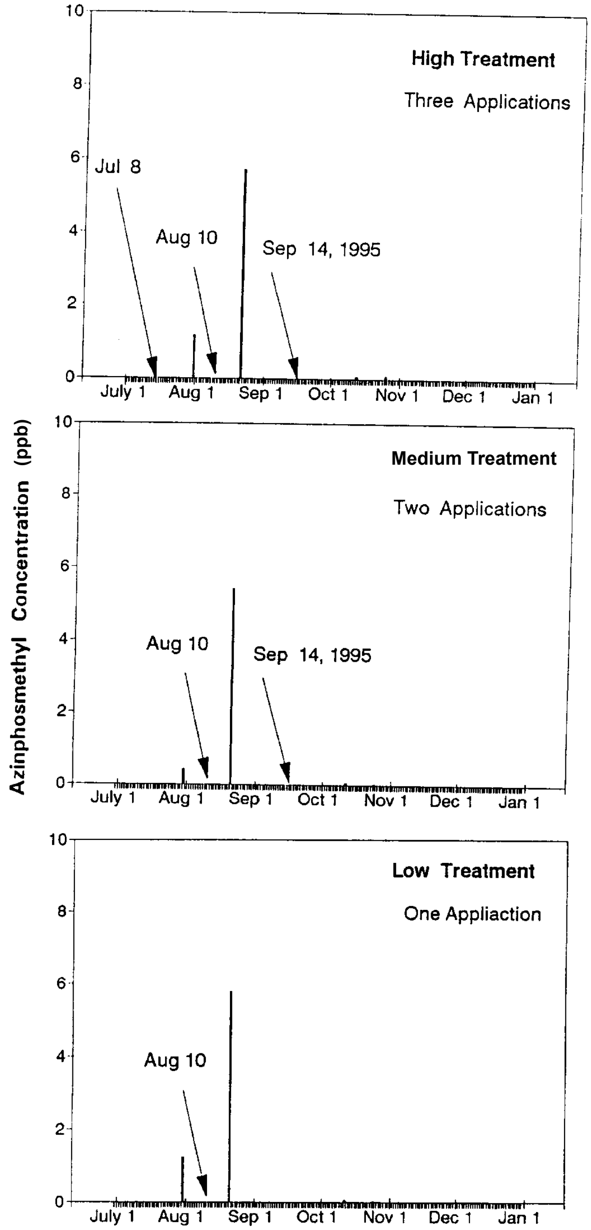

Figure 9. Measured azinphosmethyl concentrations in runoff water effluent during 1995. Results are average of two replications.

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Acknowledgments

The assistance of Harold Schexnayder, Sr., St. Gabriel Research Station; Claire W. Harmon, Department of Agricultural Chemistry; and L. Ma, S. K. Xue, and A. Granofsky, Department of Agronomy, LSU Agricultural Center, is also appreciated.

The support of Jan Boydstun of the Louisiana Department of Environmental Quality (LDEQ), who inspired this project, is gratefully acknowledged. To Gary Goay, also of LDEQ, who monitored the reporting of this project we also extend our thanks.

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