

Leaching of Atrazine from Sugarcane in Southern Louisiana[†]

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Atrazine was applied to sugarcane at 4.48 (earlier, 1989-1990, study) or 2.24 kg/ha (later, 1990-1991, investigation), and leaching into subsurface drains 1 m deep was measured for 3 months. Atrazine flow into the drains was characterized by maximum concentrations in the earlier study of 82-403 $\mu\text{g/L}$ within 11 days after application; the concentrations averaged below 3 $\mu\text{g/L}$ (the lifetime health advisory for drinking water) after day 20. The later study produced highs of 82-165 $\mu\text{g/L}$ within 7 days of application; after day 30, concentrations averaged less than 3 $\mu\text{g/L}$. Total losses were 1.6-2.6% of the application in the earlier study and 0.6-1.8% of the application for the later investigation. Essentially all (97-98%) of the losses into the drains for 1989-1990 occurred within the first 21 days during a period of 203 mm of rainfall. In the 1990-1991 study a similar proportion of total leaching (91-95%) did not occur until 48 days after application; in this study 42 days passed before 209 mm of rain had fallen on the plots.

INTRODUCTION

Atrazine, one of the most commonly used herbicides in the United States, is one of the most routinely observed pesticides in groundwater samples from agricultural areas (Garner et al., 1986). Consequently, atrazine is one of the most commonly studied chemicals in investigations of pesticide movement into groundwater. Several research groups have studied movement of atrazine from the soil surface to shallow groundwater or to subsurface drains. These studies have shown a wide variation in the time between application and the appearance of the herbicide in leachate samples. In addition, a broad range in time and magnitude of maximum atrazine concentration in these samples has been reported.

Muir and Baker (1976) applied atrazine (2.80 kg/ha) to Courval sandy loam in Quebec, Canada, and detected the herbicide and its dealkylated metabolites in drains 1.2 m deep 8 days later. Six weeks after application these investigators observed in drain water the herbicide at its highest concentration (10.8 $\mu\text{g/L}$) in the 9-month study. Over this period atrazine and its metabolites in the drain water amounted to 0.16% of the application.

Gold and Loudon (1982) studied the leaching of atrazine into tile drains through a fine loamy, mixed mesic soil of east central Michigan. The drains were about 0.5 m deep at the lower end of the plots. A storm 4 days after herbicide application (1.4 kg/ha) provided atrazine in the drains at 80-170 $\mu\text{g/L}$. Leaching for about 6 weeks after application amounted to 1.0 (conventional tillage) or 2.2% (conservation tillage) of the application.

In a study on Evesboro loamy sand in coastal plain Delaware (Ritter et al., 1987), atrazine leaching was monitored by wells 3.1 m deep. In 1984, after 24 days and 67 mm of rain, atrazine was present in the well water at a maximum concentration of 2 $\mu\text{g/L}$ from a 4.48 kg/ha application. After 59 days and 227 mm of rainfall, the herbicide was observed at its highest well concentration,

54 $\mu\text{g/L}$. In 1985 the herbicide was not observed until day 183, when it was present in the well at 1 $\mu\text{g/L}$ after 1025 mm of rain plus irrigation water. At day 240 atrazine occurred at its maximum concentration of 9 $\mu\text{g/L}$ after 1152 mm of rain plus irrigation water.

Brinsfield et al. (1988) applied atrazine (1.68 kg/ha) to silty soils of the Maryland coastal plain. They observed the herbicide (1-6 $\mu\text{g/L}$) in groundwater (3-5 m deep) samples 4-5 months after application.

In a study of atrazine movement through Lakeland sand to shallow (about 3 m deep) groundwater in southern Georgia, Smith et al. (1990) detected 350 $\mu\text{g/L}$ atrazine in soil water 0.61 m deep 12 days after an application of 4.5 kg/ha. They did not observe the herbicide in groundwater until 2 months after application after the cumulative fall of 450 mm of rain and irrigation water. The highest atrazine concentration (90 $\mu\text{g/L}$) in groundwater was measured 6 months after application and 8 days after an application of 240 mm of irrigation water.

In a study in southern Louisiana, we (Southwick et al., 1990) applied 1.63 kg/ha atrazine to shallow water table Mississippi River alluvial soil (Commerce clay loam) and observed the herbicide in subsurface drains 1 m deep 12 days later. This first observation occurred during a 45-mm rain event over a 24-h period. This first leaching event contained atrazine in its highest concentration for the season, 3.53 $\mu\text{g/L}$. Total loss over the 243-day season was 0.04% of the application.

Gish et al. (1991) applied atrazine to Codorus loam in a tillage study and observed the chemical in its maximum concentrations for the season in 1.0 m deep soil water 6 days later. These concentration highs occurred after 48 mm of rainfall over a 2-day period. The highs from the conventional tillage plots averaged 59 $\mu\text{g/L}$; the no-till plots afforded the herbicide at an average maximum of 243 $\mu\text{g/L}$.

The above studies indicate the potential of leaching into shallow groundwater exhibited by atrazine. In Louisiana, this chemical and metribuzin, another triazine herbicide, are applied to about half of the 115 800 ha (Gianessi and Puffer, 1991) planted to sugarcane in 19 parishes in the south central section of the state. This region is one of abundant rainfall and high water tables, where leaching of soil-applied chemicals into groundwater could be a

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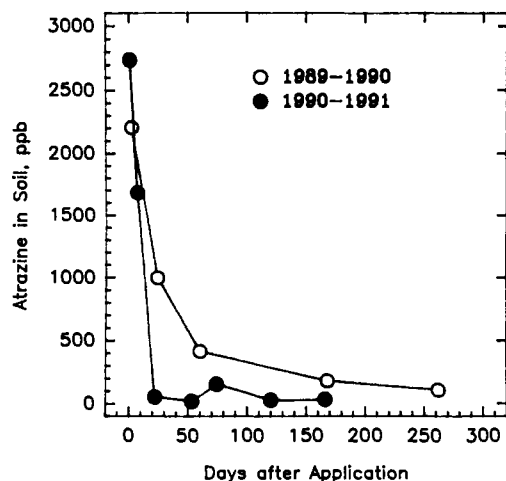


Figure 1. Atrazine in top 2.5 cm of soil, St. Gabriel, LA, 1989-1990, 1990-1991.

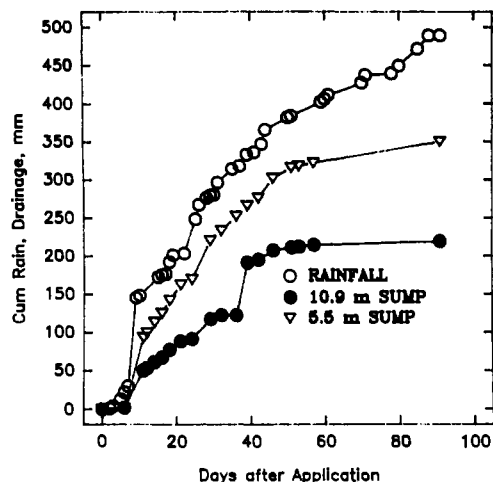


Figure 2. Cumulative rainfall and drainage, St. Gabriel, LA, 1989-1990.

problem. Virtually nothing is known about the presence of atrazine in shallow water tables in the cane-growing area of Louisiana. Both summer and winter applications of atrazine are routinely made by sugarcane growers. We report here results of a field study of the leaching potential of atrazine in sugarcane culture conducted in each of these seasons.

MATERIALS AND METHODS

The field work was carried out on the St. Gabriel Research Station (St. Gabriel, LA, Iberville Parish) of the Louisiana Agricultural Experiment Station, Louisiana State University. The study was conducted on Mississippi River alluvial soil (Sharkey clay: vertic haplaquepts; very fine, montmorillonitic, nonacid, thermic) on which sugarcane was being grown. In 1978 subsurface drains (10 cm diameter corrugated and perforated polyethylene tubes) were installed 1 m deep and the land was graded to about 0.2% slope. The study area consisted of two subsurface drained plots and one plot without such drains. One subsurface drained plot was 16.4 × 197.6 m (0.32 ha) and contained three drains 5.5 m apart running the length of the plot. The distance between the two outside drains and the plot border was nominally 2.7 m (50% of the drain spacing). The other plot containing subsurface drains was 32.8 × 197.6 m (0.65 ha); the three drains of this plot were 10.9 m apart, and the distance between the outside drains and the plot edge was 5.5 m. The plot without subsurface drains was positioned between the two subsurface-drained plots and was 13.7 × 197.6 m (0.27 ha).

The subsurface drains of each plot directed leachate into a single sump. The sumps were made of 6-mm sheet steel with the

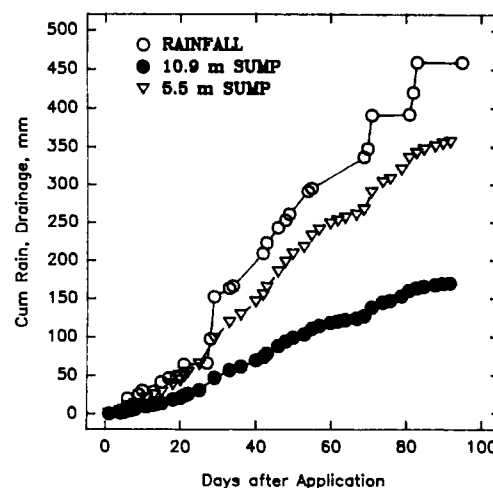


Figure 3. Cumulative rainfall and drainage, St. Gabriel, LA, 1990-1991.

dimensions 1.2 × 1.2 × 3.0 m; two-thirds of the length was below ground level. Water was pumped from the sumps through a water meter so that cumulative flow from the drains was recorded.

Drain water and soil (top 2.5 cm) samples were periodically collected and brought to the laboratory for analysis. Water samples were stored at 4 °C until extraction; the interval between collection and extraction did not exceed 1 week. Water samples (250 mL) were extracted for their atrazine content by stirring (magnetic) with ethyl acetate (100 mL) for 1 h after addition of 2 g of sodium chloride to improve (by salting out) extraction efficiency. The organic fraction was dried by passing through anhydrous sodium sulfate, a keeper (2 mL of 0.1% Nujol in hexane) was added, the ethyl acetate was evaporated just to dryness (air stream), and the residue was taken up in hexane for analysis by gas chromatography. This procedure provided 95% recovery of atrazine from water samples.

Immediately after soil samples were brought to the laboratory, they were spread out to dry at ambient temperature, ground to pass a 2-mm screen, and frozen (-5 °C) until extraction. Soil (20 g) was extracted for atrazine by Soxhlet with ethyl acetate (200 mL) for 4 h, affording the herbicide in 80% recovery. The extract was worked up for GC analysis in a manner identical to that for water extracts.

Gas chromatographic conditions were the following: Tracor 540 gas chromatograph; injector temperature, 220 °C; oven temperature, 160 °C; detector, Tracor Hall 1000 electrolytic conductivity detector with base temperature at 320 °C and reactor temperature at 920 °C; J&W Scientific megabore (0.53 mm i.d.) DB-1 column.

Atrazine 4L (Ciba-Geigy) at 4.48 kg of ai/ha was applied by ground rig on June 19, 1989. The second study season was begun on December 13, 1990, by application of 2.24 kg/ha atrazine.

RESULTS AND DISCUSSION

In both seasons atrazine disappeared rapidly from the surface (2.5 cm) layer of soil (Figure 1). In addition to leaching into subsurface drains discussed below, runoff (Wauchope, 1978), degradation (Erickson and Lee, 1989), irreversible binding to the soil (Hamaker and Goring, 1976), and volatilization (Kearney et al., 1964) are the expected disappearance pathways of the herbicide in our work. In an earlier study of atrazine movement from subsurface-drained corn plots on Mississippi River alluvial soil, Southwick et al. (1990) measured runoff losses of 1.4% of the application.

The soil disappearance data of the three plots for each study season were combined to develop Figure 1 and to generate (using Table Curve 2.1, Jandel Scientific) regression equations for the disappearance. The data of neither season could be satisfactorily fit ($r^2 < 0.66$) to a single (pseudo) first-order equation, but the 1989-1990

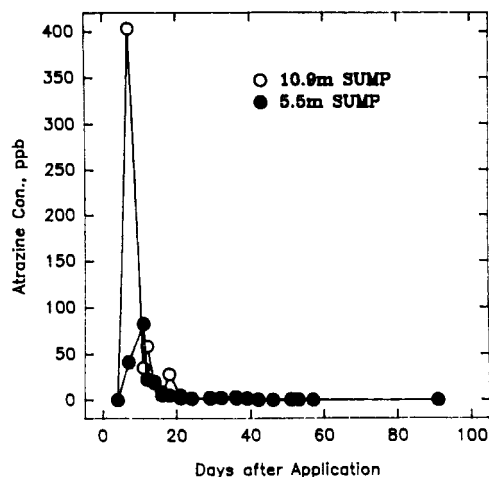


Figure 4. Atrazine concentration in drain water, St. Gabriel, LA, 1989-1990.

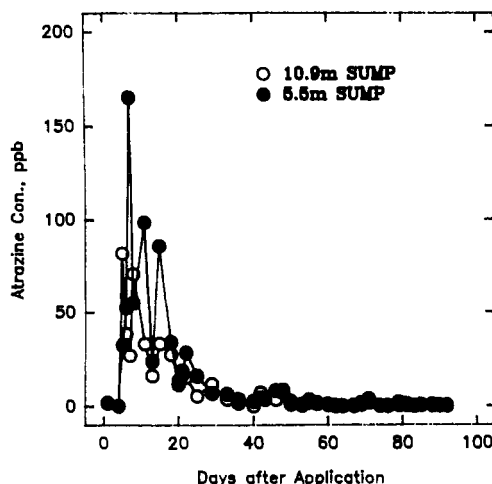


Figure 5. Atrazine concentration in drain water, St. Gabriel, LA, 1990-1991.

data did fit a two-phase first-order equation ($n = 9$ for each equation):

atrazine in soil, days 0-60

$$\ln C = 7.68 - 0.029t \quad (1)$$

$$r^2 = 0.90, t_{1/2} = 24 \text{ days}$$

atrazine in soil, days 60-262

$$\ln C = 5.96 - 0.0068t \quad (2)$$

$$r^2 = 0.78, t_{1/2} = 102 \text{ days}$$

The 1990-1991 season soil disappearance data did not fit a first-order equation. Study of Figure 1 affords a DT_{50} (time to 50% disappearance) of about 9 days for the latter season. We cannot explain the faster, compared to the 1989-1990 study, disappearance of atrazine here; for the first 30 days of the 1990-1991 season temperatures averaged 14 °C lower and rainfall was 124 mm less than that for the comparable period of the 1989-1990 season.

Sirons et al. (1973) showed in a figure a biphasic disappearance (first DT_{50} about 52 days, second DT_{50} about 165 days) of atrazine from the top 6 cm of a Perth clay loam in Ontario, Canada. Our study of atrazine leaching from plots planted to corn (Southwick et al., 1990)

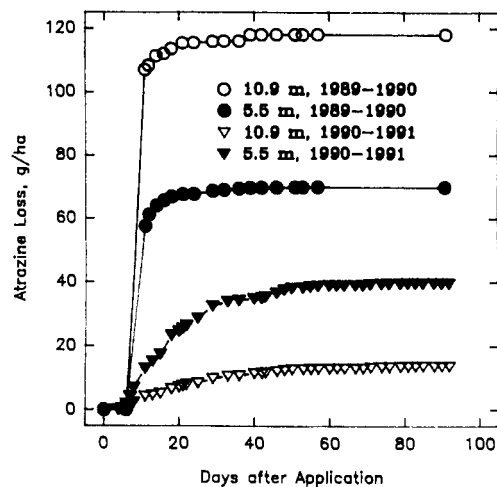


Figure 6. Cumulative atrazine leaching into drains, St. Gabriel, LA, 1989-1990, 1990-1991.

generated first-order data ($r^2 = 0.88-0.92$) with $t_{1/2} = 35-36$ days. In a series of field investigations on Dalhousie clay loam in Ontario, Canada, Frank et al. (1991) have obtained pseudo-first-order soil disappearance data for atrazine in the top 15 cm with regression coefficients (r^2) in the range 0.68-0.99 and $t_{1/2}$ values in the range 37-198 days. Hiltbold and Buchanan (1977) reported atrazine DT_{50} values in Alabama soils (Decatur silt loam, McLaurin sandy loam, and Hartsells fine sandy loam); their values at pH 6-7 and application rates of 1.12-3.36 kg/ha were in the range 27-41 days for the silt loam, 8-14 days for the sandy loam, and 12-28 days for the fine sandy loam.

Figures 2 and 3 show cumulative rainfall and subsurface drainage for the two seasons of the study for 3 months after application. In the 1989-1990 season 489 mm of rain occurred in the first 91 days (June 19-September 18) after application. During this period drainage for the 5.5-m spacing was 350 mm, while drainage for the 10.9-m spacing was 219 mm. Through day 315 (data not shown), drainage into the more narrowly spaced drains was 1226 mm and into the more widely spaced drains was 524 mm. During the 1990-1991 season 459 mm of rain fell on the plots in the first 95 days (December 14, 1990-March 18, 1991) after application. In this time cumulative drainages were 356 mm for the 5.5-m spacing and 170 mm for the 10.9-m spacing. Flow into sumps with smaller drain spacing is routinely greater for subsurface-drained plots.

Figures 4 and 5 present atrazine concentrations in the drain water for the two seasons. For the 1989-1990 study (Figure 4) high concentrations occurred on days 11 (82 $\mu\text{g/L}$, 5.5-m spacing, 148 mm of rainfall) and 7 (403 $\mu\text{g/L}$, 10.9-m spacing, 30 mm of rain). No other peaks were observed in this season except for highs for the 10.9-m spacing on days 12 (58 $\mu\text{g/L}$) and 18 (28 $\mu\text{g/L}$). Concentrations for days 21-91 averaged $1.13 \pm 0.96 \mu\text{g/L}$ (12 measurements) for the 5.5-m spacing and $1.53 \pm 1.57 \mu\text{g/L}$ (12 samples) for the 10.9-m spacing. From day 108 to day 315 (data not shown in Figure 4) atrazine concentrations in the drain water averaged $0.30 \pm 0.28 \mu\text{g/L}$ ($n = 81$). In the 1990-1991 season (Figure 5) maxima were observed on days 7 (165 $\mu\text{g/L}$, 5.5-m spacing, 20 mm of rainfall) and 5 (82 $\mu\text{g/L}$, 10.9-m spacing, 4 mm of rain). Other peaks were measured for the 5.5-m spacing at days 11 (98 $\mu\text{g/L}$), 15 (85 $\mu\text{g/L}$), and 22 (28 $\mu\text{g/L}$); the average atrazine concentration for the 26 measurements from days 30 to 92 was $2.0 \pm 2.3 \mu\text{g/L}$ with a high of 8.2 $\mu\text{g/L}$ at day 46. For the 10.9-m spacing additional highs were found on days 8 (70 $\mu\text{g/L}$), 15 (33 $\mu\text{g/L}$), 21 (19 $\mu\text{g/L}$), and 29 (12 $\mu\text{g/L}$); from days 30 to 92 atrazine in the sump averaged

Table I. Movement of Atrazine into Subsurface Drains or into Shallow Groundwater or Soil Water

study	soil	depth, m	highest concn, $\mu\text{g/L}$	days after application	rainfall (irrigation), mm
Muir and Baker (1976)	Courval sandy loam	1.2	11	42	
Gold and Loudon (1982)	fine loamy	0.5	80-170	4	
Ritter et al. (1987)	Evesboro loamy sand	3.1	54	59	227
		3.1	9	240	1152
Brinsfield et al. (1988)	silty	3-5	6	120-150	
Smith et al. (1990)	Lakeland sand	0.6	350	12	
		3	90	180	
Southwick et al. (1990)	Commerce clay loam	1.0	4	12	47
Gish et al. (1991)	Codorus loam	1.0	243 (NT)	6	48
		1.0	59 (CT)	6	48
		1.0	82-403	7-11	30-148
Southwick et al. (present study)	Sharkey clay	1.0	82-165	5-7	4-20
		1.0			

(26 measurements) $1.8 \pm 2.3 \mu\text{g/L}$ with a high of $8.7 \mu\text{g/L}$ on day 48. Atrazine concentrations in drain water after the first 3 weeks of the earlier season and after the first 4 weeks of the later season were below the lifetime health advisory for drinking water of $3 \mu\text{g/L}$ for atrazine (U.S. EPA, 1988).

Cumulative losses of atrazine into the subsurface drains are given in Figure 6. For the earlier season these losses at 91 days after the application amounted to 69.8 g/ha (1.6% of the 4.48 kg/ha application) for the 5.5-m spacing and 118.1 g/ha (2.6% of the application) for the 10.9-m spacing. Through day 315 (data not shown), losses were 72.2 g/ha for the narrower spacing and 119.1 g/ha for the wider spacing. In this early season, loss of atrazine into the drains did not follow the drainage trend; the maximum herbicide concentration in the drains with the 10.9-m spacing was 4.9 times the highest concentration in the drains with 5.5-m spacing (Figure 4), thus counteracting the higher flow into the more closely spaced drains, which for the first 91 days was 1.6 times the drainage for the 10.9-m spacing. For the later season (Figure 6) atrazine losses into the drains were 39.5 (5.5-m spacing) and 13.6 g/ha (10.9-m spacing), amounting to 1.8 (more closely spaced drains) and 0.6% (more widely spaced drains) of the application (2.24 kg/ha). In the later study, herbicide losses and drain flows were in the same direction. Gold and Loudon (1982), Smith et al. (1990), and Frank et al. (1991) have reported atrazine losses into subsurface drains or into shallow groundwater in the range 1-5% of the application.

Figures 4 and 6 reveal that for the first 91 days drain water samples were collected in the 1989-1990 study, essentially all, 97-98%, of the atrazine losses into the drains occurred before day 21. By this day 67.5 g/ha atrazine had leached into the drains with 5.5-m spacing and 115.4 g/ha had flowed through the drains with the 10.9-m spacing. In the 1990-1991 season (Figures 5 and 6) it was not until day 48 that similar percentages of total losses were measured: 95%, 37.5 g/ha, for the 5.5-m spacing and 91%, 12.4 g/ha, for the 10.9-m spacing. This delay of 3-4 weeks in atrazine leaching percentage of total losses in the second season corresponds to a similar delay in rainfall for this season. In the 1989-1990 study 203 mm of rain had occurred by day 22, whereas in the later season a similar quantity (209 mm) of rain had not fallen until day 42.

In addition to the present investigation, a number of studies of atrazine leaching into subsurface drains or into shallow groundwater have collected evidence of rapid appearance after application of this herbicide in subsurface water samples. Muir and Baker (1976), Gold and Loudon (1982), Ritter et al. (1987), Smith et al. (1990), Gish et al. (1991), and Kladvik et al. (1991) have all reported early leaching of atrazine into subsurface water. In our earlier atrazine study (Southwick et al., 1990), we measured atrazine in its highest concentration in the first leachate sample

of the season 12 days after application. These studies may be evidence of preferential flow of this herbicide. With dye and bromide tracer work Steenhuis et al. (1990) collected evidence of preferential flow of atrazine through a sandy clay loam and a variant clay loam in northeastern New York. Smith et al. (1990) observed in Lakeland sand in southern Georgia a high concentration ($350 \mu\text{g/L}$) of atrazine at 0.61 m in soil water 12 days after application. Bromide work of these investigators allowed them to calculate that 2.4 times as much water was required to move the atrazine peak concentration to the 0.61-m depth as was needed to move the bromide and to calculate a retardation factor of 6 for atrazine in Lakeland sand. Therefore, Smith et al. (1990) observed rapid leaching of atrazine but demonstrated retardation of the chemical. In our present study, we cannot report direct evidence (i.e., tracer work) for or against preferential flow of atrazine into the drains. However, in contrast to our earlier investigation (Southwick et al., 1990), highest atrazine concentrations in the drains did not occur until the second (Figure 4, 10.9-m spacing) or third (Figure 5, 10.9-m spacing) sample of the season.

In this study of leaching losses of atrazine in sugarcane culture, a rapid appearance (5-11 days after application) of the herbicide in its highest concentrations ($82-403 \mu\text{g/L}$) occurred in the drain water. Table I allows a comparison of the results of this paper with those of others who have reported leaching of atrazine into subsurface drains or into shallow groundwater or soil water. As in the present study, others (Gold and Loudon, 1982; Smith et al., 1990; Gish et al., 1991) have reported rapid (within 2 weeks) leaching of the herbicide at concentrations greatly in excess (more than 10 times) of the lifetime health advisory ($3 \mu\text{g/L}$) for atrazine in drinking water. In our present work, these highs were 27-134 times the lifetime health advisory for atrazine in drinking water, but within 3-4 weeks after application drain water concentrations averaged less than this advisory. Total leaching losses for the 3-month studies were 0.6-2.6% of the application.

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