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Atrazine dissipation and off-plot movement in a Nebraska sandhills subirrigated meadow

J.J. BREJDA, P.J. SHEA, L.E. MOSER, AND S.S. WALLER

Abstract

Atrazine [6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine] can be used to modify species composition of naturally subirrigated Sandhills meadows. The potential for ground water contamination exists as the water table depth ranges from 0 to 3 m. Atrazine was applied at 2.2 and 3.4 kg ha⁻¹ in May 1984, August 1984, or May 1985 to a Gannett fine sandy loam (Typic Haplaquoll, coarse-loamy, mixed, mesic) in a Nebraska Sandhills subirrigated meadow. Residues of atrazine applied in 1984 and 1985 carried over into 1985 and 1986, respectively. Herbicide dissipation and off-plot movement were monitored in 1985 by sampling soil at 0 to 5 cm and 5 to 15 cm depths within and outside the experimental areas. Atrazine dissipation initially approached zero-order kinetics after May 1985 application, but generally followed first-order kinetics during the entire 320-day sampling period. Atrazine half-life in the entire 0 to 15 cm sampling zone was 46 ± 7 days. Herbicide concentrations at the 5 to 15 cm sampling depth did not exceed levels measured at 5 days after application. Low and highly variable atrazine concentrations detected in some of the untreated plots and in some off-plot soil samples indicated minimal lateral movement of the herbicide.

Key Words: triazine, ground water, runoff, leaching, contamination

Atrazine can be used in Nebraska Sandhills subirrigated meadows to manipulate the vegetation for haying and grazing (Brejda 1986). The Nebraska Sandhills overlay a major portion of the Ogallala aquifer and water levels are at or near the soil surface in naturally subirrigated meadows. In many meadows the water table rises above the soil surface in the spring, then recedes to a maximum depth of approximately 2 m during the summer. Soils are coarse-textured, composed primarily of fine sand, and the surface horizon is high in organic matter. Subirrigated meadows are primarily used for hay production and most have never been cultivated.

Atrazine has been identified as a contaminant in rivers, lakes, estuaries, and ground water (Richards et al. 1975, Junk et al. 1980, Spalding et al. 1980, Frank et al. 1982). Lateral movement of atrazine dissolved in surface runoff water and adsorbed on eroded sediment has been documented (White et al. 1967, Hall et al. 1972, Ritter et al. 1974, Wauchope 1978), and leaching through soil has been reported (Burnside et al. 1963, Rodgers 1968, Wehtje et al. 1984). Atrazine can be adsorbed on soil clay and organic colloids (McGlamery and Slife 1966, Weber et al. 1969, Weber 1970), but may leach in coarse-textured soils low in organic matter (Burnside et al. 1965, Rodgers 1968, Roeth et al. 1969). Atrazine persistence can increase with soil pH and depth (Roeth et al. 1969, Lavy et al. 1973) and degradation may be very slow under aquifer conditions (Goswami and Green 1971, Wehtje et al. 1983). The potential for ground water contamination is greatest where atrazine is applied to soils overlaying shallow water tables (Spalding et al. 1979).

Information is needed on the fate of atrazine in subirrigated meadows before widespread use occurs. The objective of this

research was to quantify herbicide residues in soil and determine off-plot movement following atrazine application to a naturally subirrigated meadow of the Nebraska Sandhills.

Materials and Methods

Research was conducted in 1984 and 1985 at the University of Nebraska Gudmundsen Sandhills Laboratory (GSL) located in Grant County, 12 km northeast of Whitman, Neb. (Brejda 1986). The GSL lies in a precipitation zone of 500 to 560 mm per year, of which 75 to 80% occurs between April and September. Precipitation during this period was average in 1984 and below average in 1985. The soil was a Gannett fine sandy loam (Typic Haplaquoll, coarse-loamy, mixed, mesic) (Table 1). The meadow had a slope of

Table 1. Soil properties of a Gannett fine sandy loam at two depths in a Sandhills subirrigated meadow at the Gudmundsen Sandhills Laboratory, Grant County, Nebraska.

Soil property	Depth	
	0-5 cm	5-15 cm
Organic carbon (g kg ⁻¹)	170 ¹	42
Total nitrogen (g kg ⁻¹)	12	5
Phosphorus (mg kg ⁻¹)	20	7
CEC (cmol p ⁺ kg ⁻¹)	51	32
pH (1:1 soil:water)	7.6	7.7
Sand, 0.05 to 2.0 mm (%)	57	65
Silt, 0.002 to 5.0 mm (%)	33	21
Clay, ≤0.002 mm (%)	10	14

¹Partially decomposed thatch was not removed.

<3% and surface drainage was from south to north. Subsurface water flow was from west to east.

The plant community of the experimental meadow prior to treatment consisted of predominantly cool-season grasses [Kentucky bluegrass (*Poa pratensis* L.), timothy (*Phleum pratense* L.), quackgrass (*Agropyron repens* L.), and redbud bentgrass (*Agrostis stolonifera* L.)], and red clover (*Trifolium pratense* L.). Small populations of native warm-season big bluestem (*Andropogon gerardii* Vitman), indiagrass [*Sorghastrum nutans* (L.) Nash], and switchgrass (*Panicum virgatum* L.) were also present.

Atrazine was applied to suppress the cool-season grasses and restore dominance of the more productive native warm-season grasses. Two separate experiments were conducted in which 0, 2.2, and 3.4 kg a.i. ha⁻¹ atrazine was applied in 200 L ha⁻¹ water to 6 × 12 m plots on 14 May or 23 August 1984, and on 15 May 1985 (Fig. 1). Wind speed was variable, but less than 16 km h⁻¹ at herbicide application. A tractor-mounted sprayer with shielded, flat fan nozzles was used to minimize herbicide drift during application. Water table depth ranged from 0.3 to 1.0 m at herbicide application. The 1984 field plot design was a split plot with season of application as whole plots and atrazine rate as sub-plots arranged in a randomized, complete block. A randomized, complete block design was used in 1985. The 1985 experimental site was approximately 185 m east of the 1984 site.

Soil was sampled from the center 3 × 9 m of each plot with a 10-cm diameter hand-held auger 5 days after atrazine application in May 1985, and at monthly intervals through 1 September 1985.

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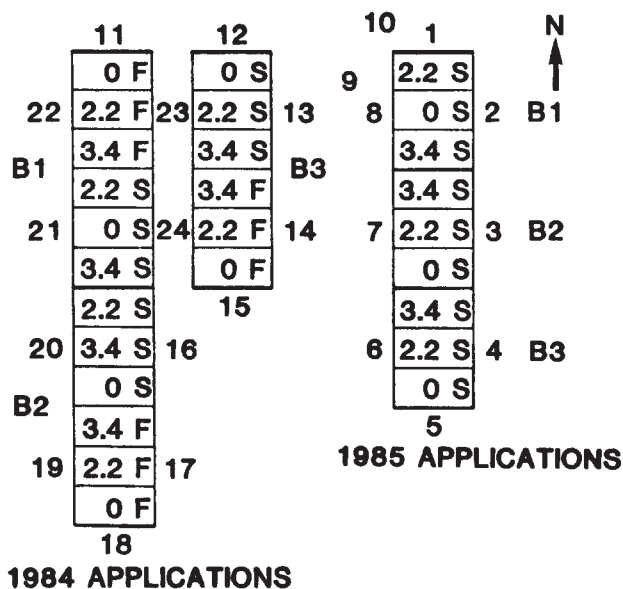


Fig. 1. Field treatment plan for experiments initiated in 1984 and 1985 at the Gundmundsen Sandhills Laboratory in Grant County, Nebraska. Atrazine was applied in May (S) or August (F) at 0, 2.2, or 3.4 kg a.i. ha⁻¹ in 3 blocks (B1, B2 and B3). The 1985 experimental site was approximately 185 m east of the 1984 site. Numbers outside treatment areas indicate locations of off-plot soil sampling.

Soil samples were also collected on 1 April 1986 to determine carry over of atrazine residues. Samples were similarly collected at monthly intervals between 1 June and 1 September 1985 from all 1984 experimental plots. Soil samples were concurrently collected 3 m north, south, east, and west of 1984 and 1985 experimental sites, and from 2 depressions northwest of the 1985 site (Fig. 1). At each sampling date 3 soil cores were removed from random locations within each plot and off-plot locations at 0 to 5 and 5 to 15 cm depths, composited, and frozen at -20° C until atrazine analysis.

Samples were thawed; thatch and plant material were removed and discarded. Soil was screened through a 1-mm sieve and air-dried at 25° C prior to atrazine analysis. Atrazine was Soxhlet-extracted from 30 to 40 g of soil with 125 ml methanol for 1.75 hours. The extract was reduced to 5 ml by rotary evaporation, transferred to a test tube, and taken to near dryness under a stream of nitrogen gas in a water bath at 45° C. Three ml of toluene were added to the tube and thoroughly mixed using a vortex stirrer. Atrazine concentration was determined with a Perkin-Elmer Sigma 2000 gas chromatograph equipped with a thermionic nitro-

gen-phosphorus specific detector. A spiral glass column (91 cm long, 2 mm i.d.) packed with 1.5% OV-17 + 1.95% OV-202 on 100/120 mesh Chromosorb W HP was used for the separation. Carrier gas was nitrogen at 30 ml min⁻¹, and detector gases were hydrogen at 3 ml min⁻¹ and air at 160 ml min⁻¹. Peak area for each sample was integrated by a dedicated microprocessor. Minimum atrazine detection was 1 µg kg⁻¹ and the limit of quantitative determination was 10 µg kg⁻¹. Extraction efficiency was greater than 90% and atrazine recovery following field application was calculated using a soil bulk density of 1.33 g cm⁻³.

Data from the 1984 and 1985 experimental sites were analyzed using analysis of variance for split-plot and randomized, complete block designs, respectively (Steele and Torrie 1980, SAS Institute 1982). Soil depths and sampling dates were treated as repeated measures in both experiments. Treatment means were compared using preplanned orthogonal contrasts. Exponential regression equations for atrazine dissipation over time were computed using the least squares method (James et al. 1985) with best fit based on lowest root mean square error (RMSE) values (Willmott 1982).

Results and Discussion

Dissipation

Atrazine recovery from the 0 to 5 cm soil depth at 5 days after the May 1985 application was 27 ± 2% of that applied and only 2 ± 1% was detected at the 5 to 15 cm depth (Table 2). No rainfall was received during this period. Atrazine detection in some untreated plots indicated low level contamination during application, after application, or during soil sampling. The vapor pressure of atrazine is relatively low, 0.04 kPa at 20° C (Weed Science Society of America 1983), and air temperatures did not exceed 25° C during the 5-day period after application. However, some vapor drift may have occurred, as surface temperatures may be significantly higher than air temperatures under high light intensity (Parr and Papendick 1978). Some atrazine photolysis may also have occurred through secondary sensitization and catalysis from exposure to ultraviolet light (Jordan 1970). Thatch was not analyzed for atrazine, but previous research indicated significant atrazine interception and retention by crop residues (Ghadiri et al. 1984a).

Atrazine dissipation in soil initially approached zero-order kinetics following the May 1985 application, but generally followed first-order kinetics over the entire 320-day sampling period (Fig. 2). The initial deviation from first-order may be partially due to atrazine wash-off from the sod and thatch onto soil during rainfall, as previously observed (Ghadiri et al. 1984b). The 45 µg kg⁻¹ atrazine detected at the 5 to 15 cm depth at 5 days after application may be due to contamination during sampling, as no rainfall was received during this period. Atrazine concentration did not exceed this level at any of the later sampling dates. The lack

Table 2. Atrazine concentrations¹ in soil at 0-5 cm and 5-15 cm depths in 1985 and April 1986 following applications at 0, 2.2 and 3.4 kg ha⁻¹ in May 1985. Atrazine treatment and soil depth comparisons were made using orthogonal contrasts and preplanned tests of hypotheses.

Sampling date	Time after application (days)	Cumulative rainfall (mm)	Untreated		2.2 kg ha ⁻¹		3.4 kg ha ⁻¹	
			0-5 cm	5-15 cm	0-5 cm	5-15 cm	0-5 cm	5-15 cm
			(µg kg ⁻¹ ± S.D.)					
20 May 1985	5	0	11 ± 11	T	749 ± 34	33 ± 7	1432 ± 215	45 ± 19
1 June	17	12	T	ND	795 ± 151	11 ± 5	1394 ± 34	T
1 July	47	29	10 ± 10	T	283 ± 110	22 ± 11	623 ± 21	15 ± 5
1 Aug.	78	65	11 ± 11	T	405 ± 5	14 ± 13	589 ± 109	T
1 Sept.	109	116	ND	T	241 ± 62	12 ± 6	159 ± 37	ND
1 Apr. 1986	320	289	T	ND	21 ± 11	T	47 ± 28	T
Comparison			PR > F					
Untreated vs. Treated			<0.001					
2.2 kg ha ⁻¹ vs. 3.4 kg ha ⁻¹			0.002					
0-5 cm vs. 5-15 cm Soil Depth			<0.001					

¹'T' indicates atrazine detected was below the 10 µg kg⁻¹ limit of quantification. 'ND' indicates no atrazine was detected.

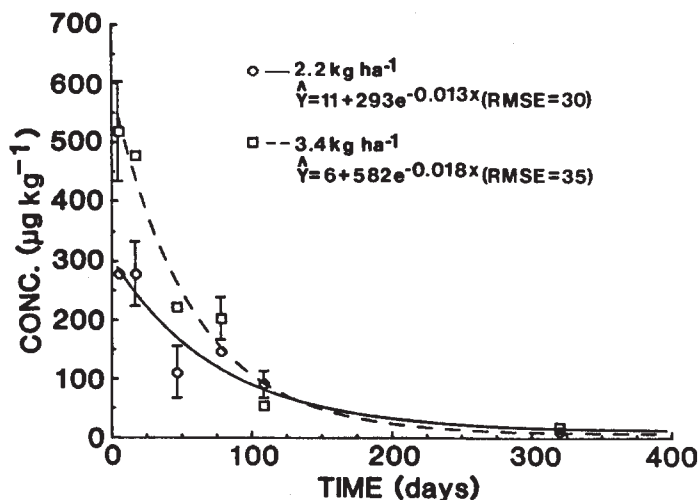


Fig. 2. Best-fit exponential regression for atrazine dissipation over time at the 0 to 15 cm soil depth following application at 2.2 kg ha⁻¹ or 3.4 kg a.i. ha⁻¹ on 15 May 1985 to a subirrigated meadow at the Gudmundsen Sandhills Laboratory in Grant County, Nebraska. Vertical bars indicate standard deviations of the means. No bar indicates a standard deviation $\leq 13 \mu \text{kg}^{-1}$.

of change may be due to herbicide retention in thatch, degradation, and the minimal precipitation received during spring and summer 1985. Atrazine half-life in the entire 0 to 15-cm sampling zone was estimated to be 46 ± 7 days.

Atrazine applied in August 1984 carried over and residues were detected in the 0 to 15-cm sampling zone within the treated area in June 1985 (Table 3). Atrazine concentrations at the 5 to 15 cm depth appeared to be higher in plots that had received the higher herbicide application rate, but variability was also greater in those samples. Less than 2% of the atrazine applied in August was recovered from the 0 to 15-cm sampling zone at 375 days after application.

Low concentrations of residual atrazine from May 1984 and

May 1985 applications were detected at the 0 to 5 cm depth in June 1985 and April 1986, respectively, and trace concentrations were detected at the 5 to 15 cm depth (Tables 2 and 3). Residual atrazine concentrations in plots treated in May 1984 were not significantly different from that detected in untreated plots (Table 3). Soil was not sampled at depths greater than 15 cm, but data from the 0 to 15 cm depths did not substantiate atrazine leaching.

Atrazine mobility increases as soils become more coarse in texture (Helling 1970, 1971), but organic matter can adsorb the herbicide and reduce leaching (Rodgers 1968, Weber et al. 1969). Although the meadow soil was high in sand and low in clay content, the soil was covered by dense thatch and organic matter content was very high near the surface. Experimental data did not indicate mass displacement of atrazine, as concentrations at the 5 to 15 cm depth did not exceed initial levels at any later sampling date. Less residual atrazine was detected at both sampling depths at 320 days after the May 1985 application than after a similar interval following August 1984 application. However, no differences in atrazine residues after comparable intervals following August or May 1984 applications were apparent in 1985. Although experimental data were inconclusive, slower, degradation during the winter months (Talbert and Fletchall 1964, Burnside et al. 1965, Roeth et al. 1969) could increase the contamination risk from late-season atrazine application.

Off-Plot Movement

Low and variable atrazine concentrations detected in some untreated plots (Tables 2 and 3) and soil samples collected outside the experimental area (Tables 4 and 5) did not support lateral herbicide movement, with the possible exception of off-plot depressions where water accumulated. Elevated atrazine concentrations in the depressions on 1 June were not likely caused by runoff, as only 12 mm of precipitation was received (4 mm was the largest event) between herbicide application and soil sampling. The higher atrazine application found in 1 depression (site 10) on 1 July could have resulted from runoff, as 15 mm of precipitation was received in 1 event. Atrazine concentration did not increase in the other depression (site 9), and differences between the depressions may be due to variations in topography.

Atrazine concentrations were significantly higher in soil sampled

Table 3. Atrazine concentrations¹ in soil at 0–5 cm and 5–15 cm depths in 1985 following application at 0, 2.2 or 3.4 kg ha⁻¹ in May and August 1984. Atrazine treatment and soil depth comparisons were made using orthogonal contrasts and preplanned tests of hypotheses.

Sampling date	Time after application (days)	Cumulative rainfall (mm)	Untreated		2.2 kg ha ⁻¹		3.4 kg ha ⁻¹	
			0–5 cm	5–15 cm	0–5 cm	5–15 cm	0–5 cm	5–15 cm
			($\mu\text{g kg}^{-1} \pm \text{S.D.}$)					
			May 1984 Application					
1 June 1985	384	468	T	T	44 ± 17	ND	43 ± 10	ND
1 July	414	485	19 ± 17	T	T	T	33 ± 4	T
1 Aug.	445	521	31 ± 14	T	10 ± 4	ND	34 ± 12	T
1 Sept.	476	572	T	T	T	T	19 ± 17	ND
Comparison		PR > F						
Untreated vs. Treated		0.721						
2.2 kg ha ⁻¹ vs. 3.4 kg ha ⁻¹		0.293						
0–5 cm vs. 5–15 cm Soil Depth		0.002						
			August 1984 Application					
1 June 1985	283	163	T	ND	274 ± 39	41 ± 17	1091 ± 722	342 ± 294
1 July	313	180	T	T	175 ± 21	44 ± 22	403 ± 91	39 ± 17
1 Aug.	344	216	18 ± 12	T	82 ± 47	37 ± 29	312 ± 146	23 ± 7
1 Sept.	375	267	T	T	19 ± 5	14 ± 7	47 ± 19	T
Comparison		PR > F						
Untreated vs. Treated		0.047						
2.2 kg ha ⁻¹ vs. 3.4 kg ha ⁻¹		0.062						
0.5 vs. 5–15 cm Soil Depth		0.034						

¹T indicates atrazine detected was below the 10 $\mu\text{g kg}^{-1}$ limit of quantification. 'ND' indicates no atrazine detected.

Table 4. Atrazine concentrations¹ measured in 1985 and April 1986 in soil at 0–5 cm and 5–15 cm depths at sampling sites 3 m north (N), south (S), east (E), west (W) of the experimental area treated with the herbicide on 15 May 1985. Depressions (sites 9 and 10) were located northwest (NW) of the experimental area. Sampling date, depth and east-west comparisons were made using preplanned tests of hypothesis.

Site number	Direction	1 June 1985		1 July		1 Aug.		1 Sept.		1 April 1986	
		0–5 cm	5–15 cm	0–5cm	5–15 cm	0–5 cm	5–15 cm	0–5 cm	5–15 cm	0–5 cm	5–15 cm
($\mu\text{g kg}^{-1}$)											
1	N	T	T	T	T	T	ND	ND	ND	T	ND
2	E	ND	T	T	ND	T	T	ND	ND	T	ND
3	E	106	11	10	T	11	37	ND	T	T	ND
4	E	T	ND	T	T	—	T	10	T	ND	ND
5	S	T	ND	T	T	ND	T	ND	T	16	26
6	W	ND	ND	T	T	T	T	45	ND	T	18
7	W	T	40	152	ND	54	ND	T	T	T	ND
8	W	T	T	11	T	T	T	20	T	16	T
9	NW	581	315	97	34	121	T	12	T	—	—
10	NW	293	20	944	454	55	65	98	418	—	—
Comparison		PR > F									
Sampling Date		0.761									
Sampling Depth		0.111									
East vs. West		0.021									

¹T indicates atrazine detected was below the 10 $\mu\text{g kg}^{-1}$ limit of quantification.
¹ND indicates no atrazine detected.

Table 5. Atrazine concentrations¹ measured in 1985 in soil at 0–5 cm and 5–15 cm depths at sampling sites 3 m north (N), south (S), east (E), west (W) and between (B) blocks at the experimental area treated with the herbicide on 14 May or 23 August 1984. Sampling date, depth and east-west comparisons were made using preplanned tests of hypotheses.

Site number	Direction	1 June 1985		1 July		1 Aug.		1 Sept.			
		0–5 cm	5–15 cm	0–5 cm	5–15 cm	0–5 cm	5–15 cm	0–5 cm	5–15 cm		
($\mu\text{g kg}^{-1}$)											
11	N	ND	T	T	28	14	T	16	ND		
12	N	ND	12	T	44	T	24	ND	ND		
13	E	ND	ND	12	T	10	T	11	ND		
14	E	15	T	T	T	29	T	25	12		
15	S-E	ND	T	14	T	ND	ND	10	ND		
16	E	T	T	T	T	10	—	T	ND		
17	E	98	ND	16	ND	ND	ND	ND	ND		
18	S	ND	13	T	T	10	32	ND	ND		
19	W	ND	ND	33	T	18	T	ND	ND		
20	W	T	ND	T	T	22	T	T	ND		
21	W	ND \	ND	10	T	11	T	ND	10		
22	W	10	ND	41	54	13	T	15	T		
23	B	11	ND	33	ND	20	ND	113	ND		
24	B	43	ND	12	ND	T	ND	70	ND		
Comparison		PR > F									
Sampling Date		0.319									
Sampling Depth		0.002									
East vs. West		0.533									

¹T indicates atrazine detected was below the 10 $\mu\text{g kg}^{-1}$ limit of quantification.
¹ND indicates no atrazine detected.

west than east of the experimental area in May 1985. As the direction was opposite ground water flow, these data did not support significant subsurface movement of atrazine in 1985. Atrazine concentrations were not consistently higher in any particular direction outside of the experimental area at the later sampling dates. Atrazine runoff has been observed to be greater when rainfall occurs shortly after herbicide application (Ritter et al. 1974), and little rainfall was received during the first several weeks after herbicide application in 1985 (Table 2).

A dense grass sod was present in the meadow and a 1.5 to 2.5 cm thick layer of roots, rhizomes and thatch had accumulated on the soil surface. As thatch accumulation would prevent sediment movement off treated areas, atrazine displacement would be limited to transport in water. Variable and irregular distribution of atrazine residues in off-plot soil samples did not indicate significant runoff or subsurface movement of atrazine at the Sandhills

meadow during the experimental period.

Conclusions

The hydrology of subirrigated meadows, in which the water table periodically rises to the soil surface, may increase the potential for ground water contamination. Herbicide movement from treated areas could contaminate streams and ponds that drain the meadows. Observations following atrazine application to a subirrigated Nebraska Sandhills meadow did not indicate significant herbicide movement. However, late-season atrazine applications may have greater potential for contamination than spring applications due to slower degradation in cooler soils, and the fact that the water table rises to the soil surface in the fall and winter. Additional studies are needed to adequately characterize atrazine dissipation in naturally subirrigated meadows.

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